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Synthesis, characterization and crystal structures of novel alkaline earth oxotellurates

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Kurzfassung

Oxotellurate(IV) und (VI) besitzen interessante kristallchemische und physikalische Eigenschaften. Viele Oxotellurate(IV) sind aufgrund des stereochemisch aktiven freien Elektronenpaares E der Te^{IV} -Atome und der hohen Polarisierbarkeit der $[\text{Te}^{\text{IV}}\text{O}_x]$ -Einheiten ausgeprägte Ferroelektrika oder besitzen nicht-lineare optische (NLO) Eigenschaften. In Oxotelluraten(VI) hingegen sind die Te^{VI} -Atome in der Regel durch sechs O-Atome in der Form praktisch regulärer Oktaeder koordiniert. Viele dieser Verbindungen kristallisieren im Perowskit- oder einem davon abgewandelten Strukturtyp. Perowskite sind ebenfalls für ihre ferroelektrischen und NLO Eigenschaften bekannt.

Da nur spärliche Information über die Strukturchemie von Erdalkalioxotelluraten vorliegt, wurde der Schwerpunkt dieser Arbeit auf die Synthese und strukturelle Charakterisierung der entsprechenden Phasen im System $M/\text{Te}/\text{O}/X$ ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{K}, \text{Tl}$; $X = \text{Cl}, \text{Br}, \text{OH}^-, \text{NO}_3^-$) gelegt. Eine überraschend große Anzahl der während dieser Arbeit gezüchteten Kristalle war polytyp und konnte mittels Order/Disorder (OD) Theorie beschrieben werden. Weiters kristallisierten viele Verbindungen in ausgeprägten Überstrukturen. Daher wurde das Hauptaugenmerk bei den strukturellen Beschreibungen auf diese zwei Aspekte gelegt.

Einkristalle und mikrokristalline Pulver der Calciumtellurat(IV) Phasen α -, β -, β' - und γ - CaTeO_3 wurden synthetisiert und mittels Röntgenbeugung (XRD), thermischer Analyse und Schwingungsspektroskopie charakterisiert. Die bis dato unbekannten Strukturen sind aus $[\text{Te}^{\text{IV}}\text{O}_3]$ -Einheiten und $[\text{CaO}_x]$ -Polyedern ($x = 6-8$) aufgebaut. Die Strukturen aller Polymorphe besitzen Kanäle, in die die freien Elektronenpaare der Te^{IV} -Atome hineinragen. Die Tieftemperaturphase α - CaTeO_3 ist bis 1168 K thermodynamisch stabil. Sie besitzt fast zylindrische Kanäle (Durchmesser ≈ 4 Å) und unterscheidet sich strukturell grundlegend von den Hochtemperaturphasen, die eng miteinander verwandt sind und ovale Kanäle (kurzer und langer Durchmesser ≈ 2 und 8 Å) besitzen. γ - CaTeO_3 kann als OD-Struktur, bestehend aus zwei Arten apolarer Schichten mit Symmetrie $p12_1/m(1)$ und $p12_1(1)$ beschrieben werden. Die untersuchten γ - CaTeO_3 -Kristalle bestanden aus zwei Polytypen mit maximalem Ordnungsgrad (MDO). β - CaTeO_3 besitzt einen Phasenübergang bei ≈ 293 K. Die Tieftemperaturmodifikation β' - CaTeO_3 sowie die Hochtemperaturmodifikation β - CaTeO_3 , können als dreifache Überstruktur, basierend auf dem MDO_1 Polytyp von γ - CaTeO_3 , angesehen werden.

Einkristalle und einphasige mikrokristalline Proben von festen Lösungen mit Zusammensetzung $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ wurden synthetisiert und mittels XRD charakterisiert. Abhängig vom eingesetzten Ca:Sr Verhältnis kristallisieren die Phasen $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ im α - CaTeO_3 , γ - CaTeO_3 (MDO_1 und MDO_2), γ - CaTeO_3 (MDO_1), β'' - CaTeO_3 oder β - SrTeO_3 Strukturtyp. Der β'' - CaTeO_3 Strukturtyp ist eng mit den Strukturen der β - und β' - CaTeO_3 Polymorphen verwandt.

Ditellurate(IV) $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ wurden in Form von Einkristallen und als einphasige Pulver hergestellt. Im Rahmen dieser Arbeit wurden drei verschiedene Kristallstrukturen in diesem System aufgeklärt. Alle drei Strukturen sind Überstrukturen, deren Basisstrukturen der gleichen hexagonalen OD-Familie angehören. Die Basisstrukturen bestehen aus zwei Arten von hexagonalen Schichten mit Symmetrie $pmmm(\bar{3})111$ und $pmmm(6)mmm$. Die Hauptpolytypen der isotypen Verbindungen CaTe_2O_5 und $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ sind 28-fache Überstrukturen mit Symmetrie $A12/a1$. Der Hauptpolytyp von $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ ist eine achtfache Überstruktur mit Symmetrie $P2_1/c$ und jener von SrTe_2O_5 eine zehnfache Überstruktur mit Symmetrie $P\bar{1}$.

Bei systematischen Untersuchungen der Bildungsbedingungen von Telluraten(IV) unter hydrothermalen Bedingungen wurden zahlreiche neue Verbindungen im System $M/\text{Te}^{\text{IV}}/\text{O}/X$ ($M = \text{K}, \text{Ca}, \text{Sr}, \text{Ba}$; $X = \text{Cl}, \text{Br}, \text{NO}_3, \text{H}_2\text{O}, \text{OH}$) erhalten und deren Kristallstrukturen aufgeklärt. $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$, $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$, $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ und $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$

bestehen aus kristallchemischen Schichten und sind polytyp. Die eng verwandten Strukturen von $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ ($P2_1/n$) und $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ ($P2_1/n$) können mittels einer erweiterten OD-Theorie als bestehend aus Stäben und als vierfache Überstrukturen beschrieben werden. $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ ($P2_1/c$) besitzt ein verwandtes Ca/Te/O-Netzwerk, welches allerdings verzerrt ist. Die Struktur wurde daher als OD-Struktur bestehend aus zwei Arten von Schichten mit Symmetrie $p12_1(1)$ und $p11(2)$ beschrieben. $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ist die einzige nicht-OD polytype Verbindung, welche in dieser Arbeit vorgestellt wird. Sie besteht aus drei Arten von Schichten mit Symmetrie $p(m)cb$ und $p(1)c1$ ($2\times$). Eine Phase im System K/Ca/Te/O/Cl wurde zu einer vorläufigen Zusammensetzung von $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ verfeinert. Die zugrunde liegende Kristallstruktur kann als OD-Struktur bestehend aus drei Arten von Schichten mit Symmetrie $pmm(m)$ ($2\times$) und $pma(2)$ beschrieben werden. Die das Te/O-Netzwerk enthaltenden Schichten können als zwölfache Überstrukturen mit Besetzungsmodulation der $[\text{TeO}_x]$ -Gruppen aufgefasst werden.

Das strukturelle Hauptmotiv der Kristallstrukturen von $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$ ($P21/c$), $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ ($Aea2$) und $\text{Ba}_3\text{Te}_3\text{O}_8\text{Br}_2$ ($Pnma$) sind dreidimensionale Te/O/ M -Netzwerke, die von Kanälen durchdrungen werden, in die die freien Elektronenpaare der Te^{IV} -Atome hineinragen und in denen sich die Anionen befinden. $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ kristallisiert in einer vierfachen Überstruktur.

Einkristalle von Verbindungen mit einer Zusammensetzung $M_3\text{Te}_2\text{O}_6X_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$; $X = \text{Cl}, \text{Br}, \text{OH}$) wurden unter hydrothermalen Bedingungen und im Erdalkalihalogenuidfluss gezüchtet. Die kubischen Strukturen (Symmetrie $Fd\bar{3}m$ und $F\bar{4}3m$) bestehen aus homeotypen Te/O/ M -Netzwerken und unterscheiden sich in der Lage und der Besetzung der Halogenidatome und der Wassermoleküle. Die unter hydrothermalen Bedingungen erhaltenen Phasen wurden mittels Schwingungsspektroskopie untersucht.

Die Orthotellurate(VI) des Strontium und Barium wurden bei 1373 K durch Luftoxidation von TeO_2 in einer Schmelze aus SrBr_2 und BaBr_2 hergestellt, und ihre Strukturen wurden mittels XRD bestimmt. Sr_3TeO_6 ($F\bar{1}$, $Z = 32$) und Ba_3TeO_6 ($I4_1/a$, $Z = 80$) sind acht und 40-fache Überstrukturen, die als pseudo-kubische dichte Packung von $[\text{TeO}_6]$ -Oktaedern mit M -Atomen ($M = \text{Ba}, \text{Sr}$) in den Tetraeder- und Oktaederlücken beschrieben werden können. Sr_3TeO_6 und Ba_3TeO_6 sind Hettotypen eines kubischen Aristotyp mit Doppelperowskitstruktur (Symmetrie $Fm\bar{3}m$).

Kristalle der polytypen Te^{VI} -Verbindung MgTeO_8H_8 wurden mittels Geldiffusion gezüchtet. Ihre Strukturen bestehen aus einer Art von kristallchemischen Schichten, die durch $\text{O}-\text{H}\cdots\text{O}$ Wasserstoffbrückenbindungen verbunden sind. Um eine OD-Beschreibung zu erhalten, wurde die Struktur in zwei Arten von Schichten mit Symmetrie $cm\bar{m}(4/e)mm$ und $p11(4/m)11$ zerlegt. Vier MDO-Polytype wurden im untersuchten Kristall nachgewiesen.

Die thermochrome gemischtvalente $\text{Te}^{\text{IV}/\text{VI}}$ -Verbindung $\text{Tl}_2\text{Te}_2\text{O}_6$ wurde in der Form von Einkristallen unter hydrothermalen Bedingungen und als einphasiges Pulver durch Festkörperreaktion bei 723 K hergestellt. Die Kristallstruktur ist Mitglied einer Kategorie IV OD Familie und besteht aus anionischen Te/O- und kationischen Tl-Schichten mit Symmetrie $p(1)2_1/c1$ und $p(b)cm$. Sie ist eng mit der Struktur von $\text{Ag}_2\text{Te}_2\text{O}_6$ -III verwandt, die aus isotypen Te/O aber deutlich verschiedenen kationischen Schichten besteht. Die thermische Analyse ergab einen Zersetzungspunkt von 775 K.

Abstract

Oxotellurates(IV) and (VI) of alkaline earth metals bear interesting crystal-chemical and physico-chemical properties. Due to the stereochemically active electron lone pair E of the Te^{IV} atoms and the high polarisability of the $[\text{Te}^{\text{IV}}\text{O}_x]$ groups many oxotellurates(IV) possess ferroelectric or non-linear optical (NLO) properties. In oxotellurates(VI), on the other hand, the Te^{VI} atoms are usually coordinated by six O atoms forming close to regular $[\text{TeO}_6]$ octahedra. Many of these compounds crystallize in perovskite or perovskite-derived structures, which are likewise well known for their ferroelectric and NLO properties.

Since the structural information on alkaline earth oxotellurates are scarce, the main focus of the present was subjected to synthesis and structure determination of respective phases in the systems $M/\text{Te}/\text{O}/X$ ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{K}, \text{Tl}$; $X = \text{Cl}, \text{Br}, \text{OH}, \text{NO}_3$). A strikingly large fraction of the crystals grown during this work are polytypic and their structures can be described according to order/disorder (OD) theory. Furthermore, many structures can be considered as superstructures. Therefore special attention will be paid to these two aspect during structure description.

Single crystals and microcrystalline samples of the calcium tellurate(IV) phases α -, β -, β' - and γ - CaTeO_3 have been synthesized and characterized by X-ray diffraction (XRD), thermal analysis, and vibrational spectroscopy. The main building units of the hitherto unknown structures are isolated $[\text{Te}^{\text{IV}}\text{O}_3]$ units and $[\text{CaO}_x]$ ($x = 6 - 8$) polyhedra. The crystal structures of all polymorphs exhibit channels in which the Te^{IV} electron lone pairs protrude. The low-temperature phase α - CaTeO_3 is the thermodynamically stable phase up to 1168 K. It exhibits nearly cylindrical channels (diameter ≈ 4 Å) and differs structurally from the β -, β' - and γ -phases, whereas the metastable high-temperature phases are closely related to each other. They feature oval channels (shortest and longest diameter ≈ 2 and 8 Å). γ - CaTeO_3 can be described as an OD structure of two non-polar layers with layer groups $p12_1/m(1)$ and $p12_1(1)$. The γ - CaTeO_3 crystals under investigation consist of two polytypes with a maximum degree of order (MDO). β - CaTeO_3 shows a distinct reversible phase transition at ≈ 293 K. The low-temperature modification β' - CaTeO_3 as well as its high-temperature modification β - CaTeO_3 can be considered as threefold superstructures based on the MDO_1 polytype of γ - CaTeO_3 .

Single crystals and single phase microcrystalline materials of solid solutions with composition $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ have been synthesized and characterized by XRD. Depending on the employed Ca:Sr ratio, $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ crystallizes in the α - CaTeO_3 , γ - CaTeO_3 (MDO_1 and MDO_2), γ - CaTeO_3 (MDO_1), β'' - CaTeO_3 or β - SrTeO_3 structure types. The β'' - CaTeO_3 structure type is closely related to structures of the β - and β' - CaTeO_3 polymorphs.

The ditellurates(IV) $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ were obtained as single crystals and single-phase microcrystalline materials and characterized by XRD. During this work, three unique crystal structures were identified in this system. They are all superstructures with basic structures which belong to the same hexagonal OD family. The basic structures are composed of hexagonal layers of two kinds with symmetry $pm\bar{m}m(3)111$ and $pm\bar{m}m(6)mmm$. The major polytypes of the isotypic CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ are 28-fold superstructures with overall symmetry $A12/a1$. The major polytype of $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ is an eightfold superstructure with symmetry $P2_1/c$ and of SrTe_2O_5 a tenfold superstructure with symmetry $P\bar{1}$ is observed.

Systematic investigations of the building conditions of tellurate(IV) compounds under hydrothermal conditions resulted in the elucidation of numerous crystal structures in the system $M/\text{Te}^{\text{IV}}/\text{O}/X$ with ($M = \text{K}, \text{Ca}, \text{Sr}, \text{Ba}$; $X = \text{Cl}, \text{Br}, \text{NO}_3, \text{H}_2\text{O}, \text{OH}$). The structures of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$, $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$, $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ and $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ contain distinct crystallo-chemical layers and can be considered polytypic. The closely related

structures $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ ($P2_1/n$) and $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ ($P2_1/n$) can be described according to an extended OD theory of rods and as fourfold superstructures. $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ ($P2_1/c$) contains a related Ca/Te/O network, yet is, due to distortion, more favourably described as an OD structure composed of layers of two kinds with symmetry $p12_1(1)$ and $p11(2)$. $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ ($P2_1/c$) is an OD structure composed of layers of three kinds with symmetry $p(4/m)mm$, $p(2)mb$ and $p(m)cb$. $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is the only non-OD polytypic structure presented in this work. It can be decomposed into layers of three kinds with symmetry $p(m)cb$ and $p(1)c1$ (twice). A phase in the system K/Ca/Te/O/Cl has been refined to a preliminary composition of $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$. The underlying crystal structure can be described as being composed of OD-layers of three kinds with symmetry $pmm(m)$ (twice) and $pma(2)$. The layer containing Te/O groups can be considered a twelvefold superstructure with occupational modulation of the $[\text{TeO}_x]$ groups.

The main structural motifs of the crystal structures of $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$ ($P21/c$), $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ ($Aea2$) and $\text{Ba}_3\text{Te}_3\text{O}_8\text{Br}_2$ ($Pnma$) are three-dimensional Te/O/ M networks which are perforated by channels in which the electron lone pairs of the Te^{IV} atoms protrude and the anions are located. $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ crystallizes in a fourfold superstructure.

Single crystals of phases with general formula $M_3\text{Te}_2\text{O}_6X_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$; $X = \text{Cl}, \text{Br}, \text{OH}$) were grown under hydrothermal conditions and in alkaline earth halide fluxes. The cubic structures (symmetry $Fd\bar{3}m$ or $F\bar{4}3m$) contain homeotypic Te/O/ M networks and differ in the location and distribution of the anions and water molecules. Vibrational spectroscopy has been performed on the phases obtained under hydrothermal conditions.

The orthotellurates(VI) of strontium and barium were synthesized at 1373 K in air by oxidation of TeO_2 in a melt of SrBr_2 and BaBr_2 , respectively. Their structures were determined by XRD. Sr_3TeO_6 ($F\bar{4}3m$, $Z = 32$) and Ba_3TeO_6 ($I4_1/a$, $Z = 80$) are eight- and 40-fold superstructures which can be described as a pseudo-cubic close-packing of $[\text{TeO}_6]$ octahedra with M ($M = \text{Ba}, \text{Sr}$) atoms located in the tetrahedral and octahedral voids. Sr_3TeO_6 and Ba_3TeO_6 are hettotypes of the cubic aristotype with the double perovskite structure crystallizing in space group $Fm\bar{3}m$.

Crystals of the polytypic Te^{VI} compound MgTeO_8H_8 were grown using gel diffusion techniques. Their structures are composed of crystallochemical layers of one kind which are connected by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. To obtain an OD description, the structure was decomposed into layers of two kinds with symmetry $cm\bar{m}(4/e)mm$ and $p11(4/m)11$, respectively. Four MDO polytypes were identified in the crystal under investigation.

The mixed valent $\text{Te}^{\text{IV}/\text{VI}}$ thermochromic compound $\text{Tl}_2\text{Te}_2\text{O}_6$ was obtained in the form of single crystals under hydrothermal conditions and as single phase microcrystalline material by solid state reaction. The crystal structure belongs to a category IV OD family composed of anionic Te/O and cationic Tl layers with symmetry $p(1)2_1/c1$ and $p(b)cm$. It is closely related to the structure of $\text{Ag}_2\text{Te}_2\text{O}_6$ -III which is composed of isotypic Te/O, but unrelated cationic layers. Thermal analysis revealed a point of decomposition at 775 K.

Parts of this work have been published

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- B. Stöger, M. Weil, and E. Zobetz. Sr_3TeO_6 and Ba_3TeO_6 : double perovskites with pronounced superstructures. *Z. Kristallogr.*, 225:125–138, 2010.

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Acronyms and abbreviations

ADP	atomic displacement parameter
ATR	attenuated total reflection
CCD	charge-coupled device
DSC	differential scanning calorimetry
EDX	energy-dispersive X-ray spectroscopy
TG	thermogravimetry
a.u.	arbitrary units
BVS	bond valence sum
<i>c.c.p.</i>	cubic close packing
<i>c.n.</i>	coordination number
HT	high temperature
ICSD	Inorganic Crystal Structure Database
IR	infrared
LT	low temperature
MDO	maximum degree of order
MIR	mid-infrared
NLO	non-linear optical
OD	order/disorder
PO	partial (symmetry) operation
RT	room temperature
occ.	occupation
s.u.	standard uncertainty
VC	vicinity condition
v.u.	valence units

VSEPR valence shell electron-pair repulsion

XRD X-ray diffraction

XRPD X-ray powder diffraction

Symbols

$\leftrightarrow$	Continuation between two layers/modules
$\times$	Composition of operations and partial operations
${}_{i,j}a$	Partial operation transforming layer/module i into layer/module j
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	Basis vectors in direct space
a, b, c	Length of the basis vectors in direct space
$\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0$	Vectors connecting two equivalent layers/rods in a polytypic structure
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	Basis vectors in reciprocal space
α, β, γ	Angles between lattice basis vectors ($\alpha = \widehat{\mathbf{b}, \mathbf{c}}, \beta = \widehat{\mathbf{c}, \mathbf{a}}, \gamma = \widehat{\mathbf{a}, \mathbf{b}}$)
α, β, γ	Coordinates of the modulation wave vector
$\text{\AA}$	Ångström (10^{-10} m)
d	Dimensionality
d	Distance
D	Density
δ	Tilt angle
e	Elementary charge ($1.602 \cdot 10^{-19}$ C)
e	Identity function of euclidean space
${}_{i,i}e$	Identity partial operation
E	Electron lone pair
F	Structure factor
(hkl)	Miller indices describing a plane
$\{hkl\}$	Miller indices describing a family of planes related by symmetry
$[hkl]$	Miller indices describing a direction
$\langle hkl \rangle$	Miller indices describing a family of directions related by symmetry
i, j, k, l	Index describing a module in a polytypic structure
i, j, k, l	Integers
K	Kelvin (SI unit of temperature)
$\mathbf{l}$	Lattice vector
${}_{i,j}\lambda$	A partial operation transforming a layer (module) into itself
m	Metre (SI unit of length)
mm	10^{-3} m
M	Number of equivalence classes in a polytype
M_r	Relative molecular mass
μ	Absorption coefficient
$\mathbb{N}$	Set of natural numbers
$\mathbb{N}^+$	Set of natural numbers without 0
$\mathbf{o}$	Origin of a coordinate system
$\mathbb{R}$	Set of real numbers
π	Circumference of a circle with diameter 1

π	A polytype
r	Distance between atoms
r, s	Relative translational components
r_M	Ionic radius of atom M
R, R_ω, R_{int}	Reliability factors (Residuals on $ F $, on F^2 and on equivalent reflections)
R_o, R_i	Bond lengths
ρ	Electron density
$_{i,j}\rho$	A partial operation turning a side of a layer facing upwards into a side facing upwards
s	Second (SI unit of time)
S	Surface
$_{i,j}\sigma$	Standard uncertainty
σ_i	Component of the modulation wave vector parallel to $\mathbf{a}_i$
$_{i,j}\sigma$	A partial operation transforming a layer (module) into an adjacent layer (module)
T	Translational group
T	Transmission coefficient
t	Time
t	Translation
t	Tolerance factor
$\mathbf{t}$	Translation vector
θ	Angle of a rotation
θ	Angle of diffraction
$_{i,j}\tau$	A partial operation turning a side of a layer facing upwards into a side facing downwards
w	Weighting factor
U	Displacement parameter
U_{eq}	Equivalent isotropic displacement parameter
V	Unit cell volume
Z	Number of formula units per unit cell
$\mathbb{Z}$	Set of integral numbers
ψ^1	Coordination polyhedron with one electron lone pair considered a ligand

Part I

Main

Chapter 1

Introduction

1.1 Motivation

Materials that exhibit ferroelectric or nonlinear optical properties have extensive technical applications in the fields of capacitors, lasers, frequency doubling and other electric and optical devices. The basic prerequisite for such a class of compounds is the existence of a polar direction without symmetrically equivalent directions (which occur in the crystal classes 1, m , 2, $mm2$, 3, $3m$, 4, 6, $4mm$, $6mm$ (Hahn, 1983)) and the existence of a high polarisability and a strong preference for a particular stereochemistry. Possible building blocks for crystal engineering of these materials are oxoanions of the type XEO_3^{n-} ($X = As^{III}, S^{IV}, Te^{IV}, Se^{IV}$), exhibiting a stereochemically active electron lone pair E . For various technological applications the desired materials must have both chemical and thermal stability over a wide temperature range, ruling out most of the arsenates(III), sulfates(IV) and selenates(IV) due to easy hydrolysis, oxidation or thermal decomposition of these compounds. The most promising behaviour in respect of the desired stability ranges applies for oxotellurate(IV) compounds, in particular the heavier homologues $MTeO_3$ of the alkaline earth elements, where $M = Ca, Sr, Ba$.

Indeed, the tellurates(IV) $CaTeO_3$ (Rai et al., 2002) and $SrTeO_3$ (Yamada and Iwasaki, 1972; Yamada, 1975) as well as the ditellurates(IV) $CaTe_2O_5$ (Redman et al., 1970; Tripathi et al., 2001) and $SrTe_2O_5$ (Redman et al., 1970; Mishra et al., 1998a) show ferroelectric properties and many research efforts have been devoted to measurements and physico-chemical characterisation of these materials, including reports on thermally induced phase transitions. The structures of four known $SrTeO_3$ polymorphs have been determined in the meantime (Elerman, 1993; Dityatiev et al., 2006; Zavodnik et al., 2007a,b,c, 2008), whereas it has not been possible up to now to determine reliably the crystal structure of one of the reported $CaTeO_3$ polymorphs (Mishra et al., 1998b; Tripathi et al., 2001) or the ditellurates MTe_2O_5 .

Many compounds exhibiting ferroelectric properties belong to the vast class of perovskites. Interesting physical properties are caused by slight distortions of the cubic perovskite aristotype. Thus, double perovskites of general formula $M_2M'M''X_6$ allow for fine-tuning of properties by adjustment of the cations M , M' and M'' . Due to their octahedral coordination, oxotellurates(VI) are prime candidates for the crystal engineering of these compounds. Indeed, many oxotellurates(VI) have been synthesized and their structural properties well characterized. For example the structures of the bivalent orthotellurates M_3TeO_6 have been determined for $M = Mg$ (Schulz and Bayer, 1971), Ca (Hottentot and Loopstra, 1981), Mn (Weil, 2006a), Co (Becker et al., 2006), Ni (Becker and Berger, 2006), Zn (Weil, 2006b), Cu (Falck et al., 2008), Cd (Burckhardt et al., 1982) and Hg (Weil, 2003a). Yet, of the alkaline earth orthotellurates(VI) only the structures of the Mg and Ca homologues have been reliably determined.

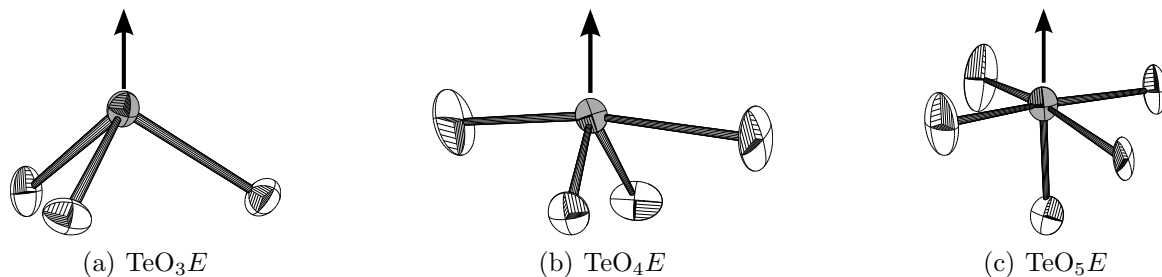


Figure 1.1: Ellipsoid plots of (a) $[\text{TeO}_3E]$, (b) $[\text{TeO}_4E]$ and (c) $[\text{TeO}_5E]$ units representative for the corresponding polyhedra as observed in $\alpha\text{-CaTeO}_3$ (sec. 3.3.4), $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ (sec. 4.2.5) and SrTe_2O_5 (sec. 3.5). Te and O atoms are represented by gray and white ellipsoids drawn at 75% probability levels. The assumed position of the electron lone pair E is indicated by arrows.

Combining Te^{IV} and Te^{VI} building blocks in one crystal structure can even lead to interesting properties. For example, electric conductivity has recently been reported for mixed-valent $\text{Te}(\text{IV},\text{VI})$ oxo-compounds (Siritanon et al., 2009).

In this work, the synthesis and properties of alkaline earth oxotellurates(IV) and (VI) will be (re)investigated with an emphasis on crystal structure determination and crystal chemistry. It is hoped that the gained insight will lead to the development of novel materials with interesting physical properties.

1.2 Crystal chemistry of oxotellurates

1.2.1 Crystal chemistry of tellurates(IV)

Reviews on the crystal chemistry of tellurates(IV) have already been given by Zemmann (1971), Loub (1993), Trömel (1980) and Dolgikh (1991). The shape of the $[\text{Te}^{\text{IV}}\text{O}_x]$ groups is characterized by the stereochemically active electron lone pair E of the Te atom, a variable coordination number (*c.n.*) of 3–5 and a broad range of bond-lengths ($\approx 1.8\text{--}2.6\text{ \AA}$) (Dolgikh, 1991). The most common oxo-coordination of Te^{IV} atoms are ψ^1 -tetrahedral $[\text{Te}^{\text{IV}}\text{O}_3E]$ (Fig. 1.1(a)) and ψ^1 -trigonal-bipyramidal $[\text{Te}^{\text{IV}}\text{O}_4E]$ groups (Fig. 1.1(b)), where E denotes the electron-lone pair (Dolgikh, 1991). Furthermore, few examples of ψ^1 -octahedral $[\text{Te}^{\text{IV}}\text{O}_5E]$ groups (Fig. 1.1(c)) have been published (*e.g.* $\text{NH}_4[\text{Te}^{\text{IV}}\text{Te}^{\text{VI}}\text{O}_5(\text{OH})]$ (Philippot et al., 1979), $\text{Te}_3\text{O}_3(\text{PO}_4)_2$ (Mayer and Weil, 2003) and SrTe_3O_8 (Barrier et al., 2006; Weil and Stöger, 2007)). $[\text{Te}^{\text{IV}}\text{O}_6]$ coordination was observed for two pyrochlore-type structures, *viz.* $\text{Cs}_2\text{Te}_4\text{O}_{12}$ (Loopstra and Goubitz, 1986) and $\text{Pr}_2\text{Te}_2\text{O}_7$ (Weber and Schleid, 2000), though the assignment to Te^{IV} is uncertain. Often, instead of using the ψ -notation, $[\text{Te}^{\text{IV}}\text{O}_x]$ polyhedra are described disregarding the electron lone pair as trigonal-pyramidal ($[\text{Te}^{\text{IV}}\text{O}_3]$), seesaw ($[\text{Te}^{\text{IV}}\text{O}_4]$) and square pyramidal ($[\text{Te}^{\text{IV}}\text{O}_5]$). The $[\text{Te}^{\text{IV}}\text{O}_x]$ units typically obey the rules of the valence shell electron-pair repulsion (VSEPR) model, which states that electron lone pairs are sterically more demanding than O atoms. Indeed, O–Te–O angles in $[\text{TeO}_3]$ units are often distinctly smaller than the ideal tetrahedral angle of $\cos^{-1}(-\frac{1}{3}) \approx 109.5^\circ$. *Trans*-O–Te–O angles in $[\text{Te}^{\text{IV}}\text{O}_4]$ and $[\text{Te}^{\text{IV}}\text{O}_5]$ units often deviate significantly from 180° (Trömel, 1980). It has to be noted that the VSEPR theory is used to predict the shapes of molecules and cannot generally be applied to inorganic crystal structures.

In ternary tellurates(IV) the $[\text{Te}^{\text{IV}}\text{O}_x]$ units are usually either isolated or connected *via* corners. In higher condensed phases like the ditellurates $M\text{Te}_2\text{O}_5$ (sec. 3.5) or the binary

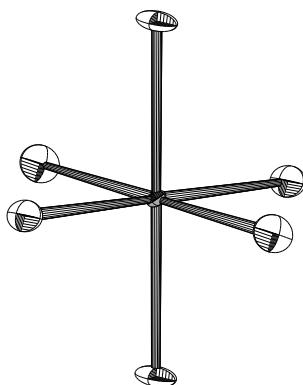


Figure 1.2: Ellipsoid plot of a characteristic $[\text{Te}^{\text{VI}}\text{O}_6]$ unit observed in Sr_3TeO_6 (sec. 5.1), Colour codes as in Fig. 1.1.

tellurates(IV) $\alpha\text{-TeO}_2$ and $\beta\text{-TeO}_2$ (Loub, 1993), edge-sharing $[\text{Te}^{\text{IV}}\text{O}_x]$ groups are observed.

1.2.2 Crystal chemistry of tellurates(VI)

Reviews on the crystal chemistry of tellurates(VI) have already been given by Kratotochvíl and Jenšovský (1986), Levason (1997) and Loub (1993). Contrary to tellurates(IV), the crystal chemistry of tellurates(VI) is generally simple. Practically all tellurates(VI) exhibit octahedral $[\text{Te}^{\text{VI}}\text{O}_6]$ coordination (Fig. 1.2) with a narrow bond-length distribution (Loub, 1993). Very few tellurates(VI) with a *c.n.* less than six have been reported in compounds with large cations. For example $\text{Cs}_2\text{K}_2\text{TeO}_5$ (Untenecker and Hoppe, 1986) contains trigonal-bipyramidal $[\text{Te}^{\text{VI}}\text{O}_5]$ units, Cs_2TeO_4 Weller et al. (1999) tetrahedral $[\text{Te}^{\text{VI}}\text{O}_4]$ units and $\text{Rb}_6\text{Te}_2\text{O}_9$ both, trigonal-bipyramidal $[\text{Te}^{\text{VI}}\text{O}_5]$ and tetrahedral $[\text{Te}^{\text{VI}}\text{O}_4]$ units.

Octahedral $[\text{Te}^{\text{VI}}\text{O}_6]$ units were observed as isolated, connected *via* corners or *via* edges (Levason, 1997). Isolated oligomers, one dimensional rods, or two and three dimensional networks were reported as well (Kratotochvíl and Jenšovský, 1986).

1.2.3 Survey of tellurates(IV) and (VI) compiled in the Inorganic Crystal Structure Database (ICSD)

The ICSD (Belsky et al., 2002) is a comprehensive database of published crystal structures. A survey of the coordination chemistry of Te^{IV} and Te^{VI} compounds was performed on the 2010-1 version which contains 132526 entries. Data of all 3985 crystal structures containing Te atoms were exported using the search interface. Heuristics were used to exclude unreliable datasets. In a first pass, all datasets containing Te atoms which were refined without anisotropic atomic displacement parameter (ADP) (2605), containing Te in oxidation states other than +IV and +VI (2946), containing oxygen atoms with oxidation state other than -II (9) and Te atoms with occupation different from 1 (515) were excluded. It has to be noted that some well-determined structures were removed because the oxidation state of the Te or O atoms was erroneously reported as 0, though not all rejected structures were checked in detail. In a second pass, the Te-O coordination polyhedra in the remaining 550 structures were examined. For atoms S, F, Cl, Br, I, O, Se, N, P, As and H bond valences using the parameters in Tab. 1.1 were computed. If the bond valence exceeded 0.2 valence units (v.u.) (5% of the expected total bond valence sum (BVS) of a Te^{IV} atom), the structure was excluded, since it cannot be considered a pure oxotellurate. The 175 affected structures contain for example $[\text{Te}^{\text{IV}}\text{F}_3]^+$ or $[\text{Te}^{\text{VI}}\text{OF}_5]^-$ units.

Table 1.1: Bond valence parameters used for the calculation of Te- X bond valences.

Atom 1	Atom 2	R_o [Å]	b [Å]	reference
Te ^{IV}	O	1.977	0.37	†
Te ^{IV}	S	2.44	0.37	*
Te ^{IV}	F	1.87	0.37	‡
Te ^{IV}	Cl	2.37	0.37	‡
Te ^{IV}	Br	2.55	0.37	*
Te ^{IV}	I	2.787	0.37	*
Te ^{VI}	O	1.917	0.37	†
Te ^{VI}	F	1.82	0.37	‡
Te ^{VI}	Cl	2.30	0.37	‡
Te ^{VI}	Br	2.53	0.37	‡
Te ^{VI}	I	2.76	0.37	‡
Te ^{VI}	S	2.45	0.37	‡
Te ^{IV} and Te ^{VI}	Se	2.53	0.37	‡
Te ^{IV} and Te ^{VI}	Te	2.76	0.37	‡
Te ^{IV} and Te ^{VI}	N	2.12	0.37	‡
Te ^{IV} and Te ^{VI}	P	2.52	0.37	‡
Te ^{IV} and Te ^{VI}	As	2.60	0.37	‡
Te ^{IV} and Te ^{VI}	H	1.83	0.37	‡

† Altermatt and Brown (1985)

‡ Brese and O’Keeffe (1991)

* Brown (2007)

For atoms X not in the given list the distance to Te atoms were computed. Structures in which the Te- X distance is less than 1.33 times the sum of the ionic radii of Te and the X atom (Shannon, 1976) were likewise excluded. One structure (ICSD entry 81346) was affected with a Te-K distance of 2.21 Å, caused by an erroneous dataset. Structures with disordered O atoms (occupation < 1) closer than 3.3 Å to a Te atom (19), with Te-O distances less than 1.6 Å (2) or with O-O distances less than 1.6 Å (13) were excluded. The latter contained structures in which the O atoms are disordered. Short Te-O distances were observed for two structures (ICSD entries 51417 and 153123) which are probably erroneous. Finally, those structures for which the total BVS of all Te-O bonds of a Te atom deviate by more than 1.5 v.u. from the expected values (4 v.u. for Te^{IV} and 6 v.u. for Te^{VI}) were excluded. Besides the erroneous entry 51417, these were ICSD entry 240377, for which the cell parameters a and b were wrongly reported and entry 260284 for which a Te-II atom was reported as Te^{VI}.

For the remaining 361 structures, Te-O distances < 2.6 Å are compiled in Fig. 1.3. Te-O contacts with a distance ≥ 2.6 Å were considered non-bonding, since the corresponding bond valence contribution amounts to less than 0.2 v.u., *viz.* 5% of the expected total BVS of a Te^{IV} atom. The highest density for Te^{IV} atoms is observed for the $1.8 < d(\text{Te}^{\text{IV}}\text{-O}) \leq 1.9$ Å class. Only few bond distances shorter than 1.8 Å have been reported. The number of reported bond lengths decreases sharply from 1.9–2.2 Å and stays practically constant up to 2.6 Å. As expected, the bond length distribution is much narrower for Te^{VI} atoms. Bond lengths were only observed in the 1.7–2.1 Å range, with a distinct maximum at the $1.9 < d(\text{Te}^{\text{IV}}\text{-O}) \leq 2.0$ Å class. Thus, as expected for higher coordination numbers, typical Te^{VI}-O bonds are slightly longer than Te^{IV}-O bonds.

O-Te-O angles of ψ^1 -tetrahedral [Te^{IV}O₃ E] units are compiled in Fig. 1.4(a). As predicted by the VSEPR model, angles are distinctly smaller than the ideal angle of $\approx 109.47^\circ$. Only one analysed structure contained an O-Te-O angle > 109.47°. Closer inspection of Cd₂Te₂O₇

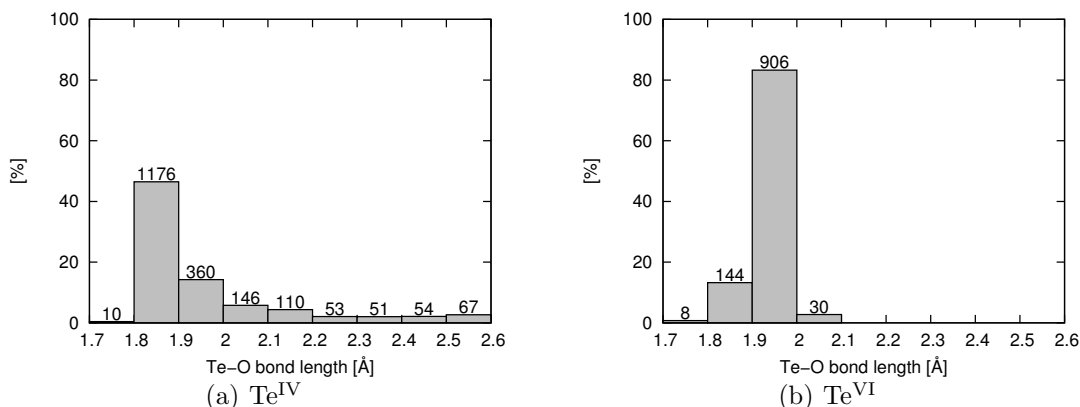


Figure 1.3: Histograms of (a) Te^{IV}-O and (b) Te^{VI}-O distances reported for 361 structures in the ICSD. Class size is 0.1 Å. Values on the ordinate indicate the percentage of the total number of bonds. Absolute numbers are indicated on top of the bars.

(Weil, 2004) revealed that the affected Te^{IV} atom is coordinated to two more O atoms with Te-O distances ≈ 2.7 Å and may therefore be described as [3+2]- instead of [3]-coordinated. Most reported angles are located in the region 92–102°. In few structures, highly distorted angles $< 84^\circ$ are reported. *cis*-O-Te-O and *trans*-O-Te-O bonds of octahedral [Te^{VI}O₆] units are compiled in Fig. 1.4(b) and (c). The highest density is observed close to the ideal angles 90° and 180°. Of the 324 reported angles in the $178^\circ < \text{O-Te-O} \leq 180^\circ$ class, 219 are exactly 180° caused by [Te^{VI}O₆] units symmetric by inversion or $\bar{3}$ -rotoinversion.

Fig. 1.5 gives an overview of the BVS of all Te-O bonds with distances less than 2.6 Å. The distributions adopt bell shaped curves for Te^{IV} and Te^{VI} atoms. As expected, the maximum densities are close to the ideal values of 4 and 6, since bond-valence parameters are obtained from empirical data (Brown, 2002).

Tab. 1.2 lists the observed O-coordination of Te^{IV} and Te^{VI} atoms. Bonds with a length of less than 2.2 Å are considered short, those between 2.2–2.6 Å long. Te^{IV} atoms exhibit a large variety of coordination polyhedra. The most common coordination is [3+0] (293 units), followed by fourfold coordination (229 units). In most [Te^{IV}O₄] units one Te-O bond is distinctly longer ([3+1]-coordination). Fivefold coordination is distinctly less common (6 units), and sixfold coordination was only observed in two structures. The coordination polyhedra of Te^{VI} atoms are less varied. Practically all Te^{VI} atoms are coordinated by 6 O atoms (192) with few exceptions of fivefold (2 units) and fourfold coordination (1 unit).

The connectivity of [TeO_x] units was analyzed by determining all O atoms which are closer than 2.6 Å to two or more Te atoms. Connectivity is compiled in Tab. 1.3 itemized by charge and coordination numbers of the central Te atom. A group can connect to more other groups *via* corners than it has ligands, since an O atom may be part of more than two [TeO_x] units. An extreme example is given by the highly condensed structure of K(UO₂(Te₂O₅OH)) (Wisser and Hoppe, 1990), in which a [Te^{IV}O₄] unit is connected *via* corners to eight other units. Most [Te^{IV}O₃] units are isolated (199 units) or connected *via* one corner (67 units) to other groups. Only few are connected *via* corners to two (22 units), three (4 units) or even four (1 unit) other groups. [Te^{IV}O₄] units show a large range of connectivities. They are isolated, connected *via* corners to one to eight other groups or *via* one or two edges or a combination thereof. The most common connectivity is *via* two corners. [Te^{IV}O₅] units possess a likewise large diversity of connectivities, the most common being *via* one edge and three corners. [Te^{VI}O₆] units are

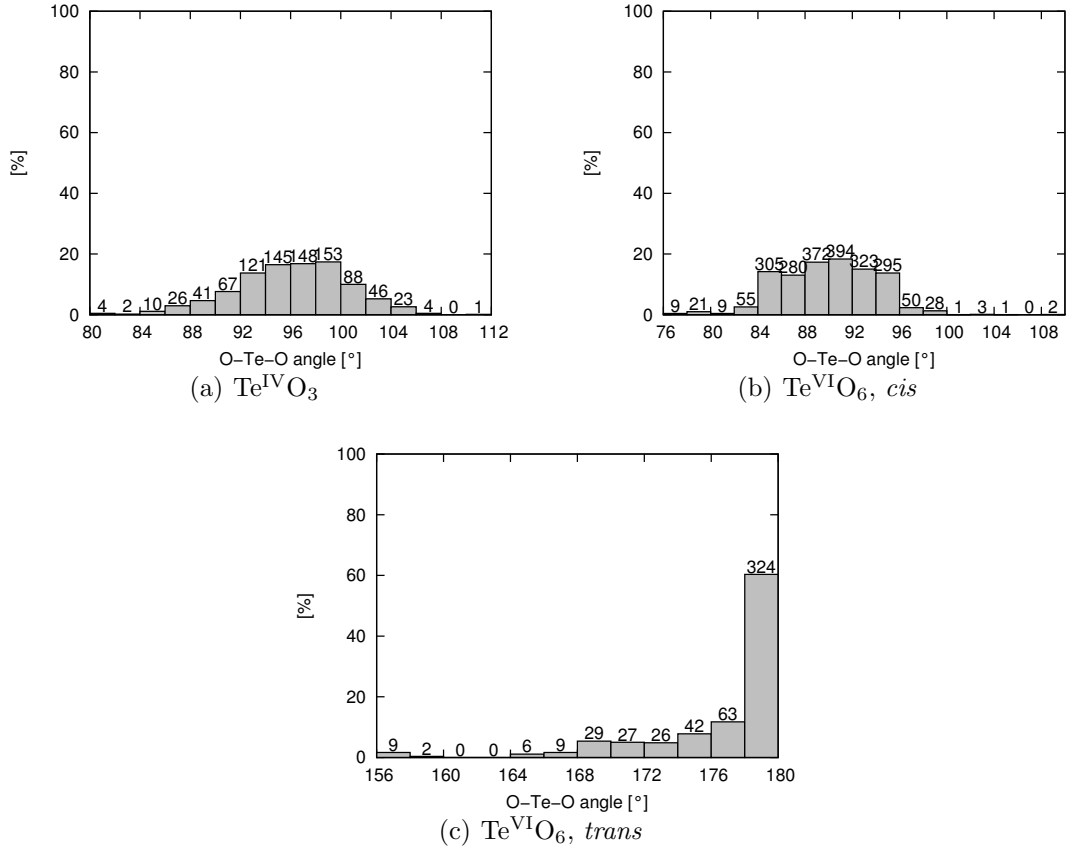


Figure 1.4: Histograms of O-Te-O angles (a) in $[\text{Te}^{\text{IV}}\text{O}_3E]$ units, (b) of *cis*-standing and (c) *trans*-standing O atoms in $[\text{Te}^{\text{VI}}\text{O}_6]$ units. Class size is 2° . Values on the ordinate indicate the percentage of the total number of angles. Absolute numbers are indicated on top of the bars.

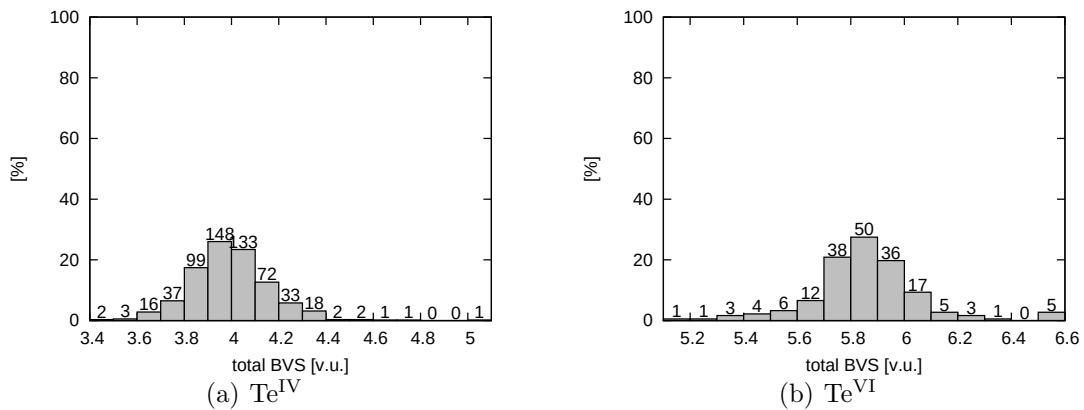


Figure 1.5: Histograms of the BVS of all Te-O bonds with distances less than $2.6 \text{ \AA}$ for (a) Te^{IV} and (b) Te^{VI} atoms. Class size is 0.1 v.u. . Values on the ordinate indicate the percentage of the total number of bonds. Absolute numbers are indicated on top of the bars.

Table 1.2: Reported coordination types of Te^{IV} and Te^{VI} atoms. Te–O bonds with a length of less than 2.2 Å are considered short, those between 2.2–2.6 Å long.

Atom	Coordination type	count	Atom	Coordination type	count
Te^{IV}	[2 + 2]	1	Te^{VI}	[4 + 0]	1
Te^{IV}	[3 + 0]	293	Te^{VI}	[5 + 0]	2
Te^{IV}	[3 + 1]	161	Te^{VI}	[6 + 0]	192
Te^{IV}	[3 + 2]	24			
Te^{IV}	[4 + 0]	67			
Te^{IV}	[4 + 1]	14			
Te^{IV}	[5 + 0]	6			
Te^{IV}	[6 + 0]	2			

most commonly observed as isolated (120 units), followed by connections *via* all six corners (23 units). Connections *via* edges are less common, connections *via* faces were not found in the analyzed structures.

1.3 Polytypism and order disorder (OD) theory

A large fraction of the crystal structures presented in this work can be considered as polytypic. Therefore in this chapter notations, conventions and results of the theory of polytypic structures that will be used in subsequent chapters will be introduced. So far, most work has been performed on the prevalent case of structures composed of layers and many authors use the term *polytypic* only in the context of structures composed of layers. These well-worked out aspects will be presented in sec. 1.3.2–1.3.15. Since two structures in this work ($\text{Sr}_4\text{Te}_4\text{O}_{11}\text{X}_2$ ($\text{X} = \text{Br}, \text{NO}_3$), sec. 4.2) can be described as being composed of rods, more general definitions will be given in sec. 1.3.20.

1.3.1 Polytypes

A polytypic structure is composed of modules (layers, rods or blocks) which can be arranged in different ways (Zvyagin, 1993). A concrete arrangement of modules is called a „polytype”. In a polytypic structure, the modules are practically identical in all possible polytypes. Structures which are composed of modules which show significant „chemical stress” (*i.e.* distortion) for different arrangements of polytypes are not considered as polytypic and are called „chemical twins” (Nespolo et al., 2004) instead.

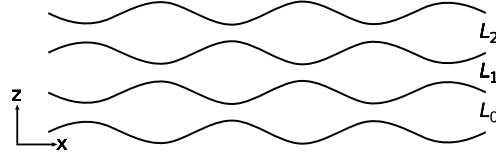
1.3.2 Layers

In a polytypic structure composed of layers every point of Euclidean space $\mathbb{R}^3$ is part of either one layer or of two adjacent layers. A layer is a continuous subset of $\mathbb{R}^3$ infinite and periodic in two dimensions. Each layer connects *via* both sides to two other layers forming a layer sequence. Thus, the interface between two layers is a two-dimensional infinite surface, which is not necessarily a plane (Fig. 1.6). The interface is considered part of both connecting layers.

A pivotal point of the theory of polytypic structures is the similarity of different parts of a structure. Layers which are congruent or enantiomorphic are said to be equivalent or to be of the same kind (Dornberger-Schiff and Grell-Niemann, 1961). Layers in a polytypic structure are of a finite number $M \geq 1$ of kinds. The structure is said to be composed of layers of M kinds.

Table 1.3: Connections of $[\text{TeO}_x]$ units by charge and *c.n.* for Te–O distances $< 2.6 \text{ \AA}$.

Atom	<i>c.n.</i>	connected <i>via</i>	count	Atom	<i>c.n.</i>	connected <i>via</i>	count
Te ^{IV}	3	isolated	199	Te ^{VI}	4	isolated	1
Te ^{IV}	3	corner (1×)	67	Te ^{VI}	5	isolated	2
Te ^{IV}	3	corners (2×)	22	Te ^{VI}	6	isolated	120
Te ^{IV}	3	corners (3×)	4	Te ^{VI}	6	corner (1×)	2
Te ^{IV}	3	corners (4×)	1	Te ^{VI}	6	corners (2×)	6
Te ^{IV}	4	isolated	27	Te ^{VI}	6	corners (3×)	2
Te ^{IV}	4	corner (1×)	24	Te ^{VI}	6	corners (4×)	11
Te ^{IV}	4	corners (2×)	87	Te ^{VI}	6	corners (6×)	23
Te ^{IV}	4	corners (3×)	37	Te ^{VI}	6	edge (1×)	9
Te ^{IV}	4	corners (4×)	10	Te ^{VI}	6	edge (1×) and corner (1×)	6
Te ^{IV}	4	corners (8×)	1	Te ^{VI}	6	edge (1×) and corners (3×)	3
Te ^{IV}	4	edge (1×)	6	Te ^{VI}	6	edge (1×) and corners (4×)	1
Te ^{IV}	4	edge (1×) and corner (1×)	19	Te ^{VI}	6	edges (2×)	9
Te ^{IV}	4	edge (1×) and corners (2×)	12				
Te ^{IV}	4	edge (1×) and corners (3×)	5				
Te ^{IV}	4	edges (2×) and corners (2×)	1				
Te ^{IV}	5	isolated	3				
Te ^{IV}	5	corner (1×)	1				
Te ^{IV}	5	corners (2×)	5				
Te ^{IV}	5	corners (3×)	5				
Te ^{IV}	5	corners (4×)	7				
Te ^{IV}	5	corners (5×)	5				
Te ^{IV}	5	corners (6×)	1				
Te ^{IV}	5	edge (1×)	1				
Te ^{IV}	5	edge (1×) and corners (2×)	5				
Te ^{IV}	5	edge (1×) and corners (3×)	10				
Te ^{IV}	5	edges (2×)	1				
Te ^{IV}	6	corners (6×)	2				

**Figure 1.6:** Schematic representation of a triple of consecutive layers (L_0, L_1, L_2) stacked along $[001]$ viewed down $[010]$. The interfaces between adjacent layer pairs are represented by black lines.

A particular layer in a polytype composed of layers of M kinds is designated L_i^m , where the superscript $1 \leq m \leq M$ indicates the kind of the layer. For structures being composed of only one kind of layer or when specifying a layer of an arbitrary kind, the superscript is left out. The subscript i is an integer designating a sequence number. Thus a layer L_i connects on one side to layer L_{i-1} and on the other side to layer L_{i+1} .

1.3.3 Symbols used for the description of layer symmetry

For the description of layer symmetry, symbols according to Dornberger-Schiff (1956) will be used. In these symbols the directions of missing translational symmetry are indicated by parentheses. The symbol $pm(2)$, for example, describes a layer which is periodic in direction $[100]$

and [010], is symmetric by a twofold rotation axis normal to the layer plane and two mirror planes which are both orthogonal to the layer plane.

For the description of the wide range of polytypic compounds these symbols are advantageous in comparison with the symbols normed in the *International Tables of Crystallography, Vol. E*, since for the latter it is not obvious how to express layers with non-standard stacking directions (*e.g.* a tetragonal layer with a stacking direction other than [001]) and the stacking direction might not be immediately clear to the reader.

Instead of the standard Bravais symbols used by Dornberger-Schiff (1956) (capital italic letters *P, A, B, C, I, F*), the symbols of the *International Tables of Crystallography, Vol. E* will be used for subperiodic groups, *viz.* lower case italic letters (*p, a, b, c*) to designate layer groups and lower case script letters (*ℓ*) to designate rod groups.

In the context of polytypic structures, the symmetry of tetragonal layers will be indicated using five instead of three placed symbols (Dornberger-Schiff and Grell-Niemann, 1961), where the places stand for the directions [100], [010], [001], [110] and $[\bar{1}10]$ ¹ so that tetragonal and non-tetragonal layer groups use the same places.

For order/disorder (OD) structures composed of hexagonal layers, layer symmetry is expressed by seven instead of three placed symbols (Dornberger-Schiff and Grell-Niemann, 1961). The symmetry operations are given in succession for the directions [100], [010], $[\bar{1}\bar{1}0]$, [001], $[\frac{1}{\sqrt{3}}\frac{2}{\sqrt{3}}0]$, $[\frac{2}{\sqrt{3}}\frac{1}{\sqrt{3}}0]$ and $[\frac{2}{\sqrt{3}}\frac{1}{\sqrt{3}}0]$ (*c.f.* App. A.2). The corresponding vectors are called **a**₁, **a**₂, **a**₃, **c**, **b**₁, **b**₂, **b**₃ (Dornberger-Schiff and Grell-Niemann, 1961).

1.3.4 Order disorder (OD) structures

Most polytypic compounds can be described according to order/disorder (OD) theory. The term OD structure was introduced by Dornberger-Schiff (1956). On one hand, OD theory is a geometrical approach to describe the symmetry of polytypic compounds, on the other hand, it redefines the notion of crystalline matter with emphasis on local symmetry (Dornberger-Schiff, 1979).

Indeed, many chemical compounds can be adequately modelled using atomistic or force field approaches (Pertsin and Kitaigorodskii, 1987). According to these, the total energy of a system can be expressed as the sum of energy contributions of electronic interactions between atoms. In a stable structure, the total energy of the system is at a (local) minimum. The atom-atom interactions are typically dependent on atom distances, angles of atom triples and dihedral angles of atom quadruples. The amplitude of the energy contribution of atom-atom interactions quickly decreases with the distance between interacting atoms. For example, the amplitude of the electrostatic potential is inversely proportional to the distance *r* from the generating atom, and the widely-used Lennard-Jones-(exp,6)-potential is composed of terms in e^{-r} and r^{-6} (Pertsin and Kitaigorodskii, 1987). Therefore, the position of an atom in a crystal will mainly depend on atoms in a close vicinity. It should be noted that this is not necessarily true for all compounds: Due to quantum effects, charges may be delocalized over a whole crystal resulting in for example charge-density-waves (van Smaalen, 2005).

In consequence, the layout of a layer of a structure will be influenced only by nearby layers and, if the layers are thick enough, only by adjacent layers. Furthermore, it can be assumed that there is only one way of achieving a minimum energy configuration for adjacent layers. These two assumption are expressed by the vicinity condition (VC) of OD theory (Dornberger-Schiff and Grell-Niemann, 1961) which can be formulated for structures composed of layers as

¹ The fifth direction $[\bar{1}10]$ follows the recommendation of Fichtner (1979a). It is used instead of $[1\bar{1}0]$ according to Dornberger-Schiff and Grell-Niemann (1961) since **a** + **b**, **b** − **a**, **c** forms a right handed coordinate system.

(paraphrased from Dornberger-Schiff (1979)):

- (VC α) The structure can be described by a stacking of distinct layers of a finite number of kinds.
- (VC β) The layers are periodic in two dimensions. The translational groups of adjacent layers are subgroups of a common supergroup².
- (VC γ) Equivalent sides of equivalent layers are faced by adjacent layers in such a way that the pairs thus formed are equivalent.

During the last 50 years, numerous slightly different formulations of the VC have been given (Dornberger-Schiff and Grell-Niemann, 1961; Dornberger-Schiff and Fichtner, 1972; Fichtner, 1977a; Dornberger-Schiff, 1979), often for the special case of structures consisting of layers of only one kind. A more concise formulation of VC γ will be given in sec. 1.3.9, after introduction of the necessary notations. A central statement of OD theory is that structures fulfilling the VC are infinite, but not necessarily periodic in three dimensions (Dornberger-Schiff, 1979). Indeed, those structures for which VC necessarily results in a periodic structure in three dimensions are called „fully ordered”, whereas those for which this is not the case are called OD structures (Dornberger-Schiff and Grell-Niemann, 1961).

Some polytypic compounds do not fulfill VC γ , and therefore are not considered OD structures. These are called non-OD polytypic (Ferraris et al., 2004). For some of them (*e.g.* MgTeO₈H₈, sec. 5.2), whether they are described as OD or non-OD polytypic depends on the choice of layers. Typically for this type of structure, layer choices according to crystallochemical considerations result in non-OD descriptions, which can then be transformed into an OD description, by „slicing” them into sublayers. Ferraris et al. (2004) argue against such slicing if purely anionic or cationic layers are obtained and information on coordination polyhedra is thus lost. According to Zvyagin (1993), it may be useful to give both, *i.e.* non-OD and OD, descriptions to achieve a more complete understanding of the structures. For other non-OD polytypic compounds, no sensible layer choice can be achieved which results in an OD structure. In these compounds (*e.g.* Ca₅Te₄O₁₂(NO₃)₂·2H₂O, sec. 4.5), non-equivalent pairs of adjacent layers with similar energy are observed.

1.3.5 Polytypes with a maximum degree of order (MDO)

The concept of polytypes with a maximum degree of order (MDO) was introduced following the observation that in many ordered polytypes not only pairs of adjacent layers, but arbitrary n -tuples of adjacent layers are equivalent. Indeed it seems reasonable that under given experimental conditions and little stacking faults, not only adjacent layers have influence on the orientation of a layer but also layers farther apart, even when the influence is small. For example for structures composed of non-polar layers of one kind, from the equivalence of layer triples the equivalence of arbitrary n -tuples follows (Dornberger-Schiff, 1982).

According to the definition of Dornberger-Schiff (1982), which also accounts for structures composed of layers of $M > 1$ kinds and/or for polar layers, an OD polytype π_0 is an MDO polytype if:

Amongst the whole family of polytypes, there is no polytype π_1 in which the kinds of n -tuples of consecutive layers for some numbers n constitute only a selection of the kinds of n -tuples contained in π_0 .

² Dornberger-Schiff (1979) requires that the translational groups of *all* layers are subgroups of a common supergroup. As will be shown in an example in sec. 1.3.12, this is not necessarily the case.

The amount of different MDO polytypes for a given OD family is small for structures composed of one kind of layer, but can become large for structures composed of $M > 1$ kinds of layers (Dornberger-Schiff and Grell, 1982), especially if the translational group of one kind of layers is of significantly higher order than the translational group of adjacent layers. This is, for example, the case in $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ (sec. 4.4). A large number of MDO polytypes is also possible for structures composed of layers of $M \gg 1$ kinds. A systematic procedure for obtaining all possible MDO polytypes of structures composed of OD layers is described by Dornberger-Schiff (1982); Dornberger-Schiff and Grell (1982). Over the years it has been found that the vast majority of actual polytypes are MDO polytypes.

1.3.6 Symmetry groupoids

An operation transforming a layer into an equivalent layer has not to be valid for the whole polytype and is therefore called partial (symmetry) operation (PO) (Dornberger-Schiff and Grell-Niemann, 1961). Per definition, two equivalent layers are related by at least one PO. A PO transforming layer L_i^m into an equivalent layer L_j^m is written ${}_{i,j}a$. L_i^m and L_j^m are called source and target layers of the PO. In the general case, a PO is not a symmetry operation, since it does not transform an object into itself. A PO ${}_{i,j}a$ is a partial, distance preserving function on $\mathbb{R}^3$ with domain of definition $s(i)$ and range $s(j)$, where $s(i) \subseteq \mathbb{R}^3$ is the subset of three-dimensional Euclidean space occupied by layer L_i . A PO ${}_{i,j}a$ can be extended to exactly one isometry on $\mathbb{R}^3$ which will be written a :

$${}_{i,j}a := a|_{s(i)}$$

The isometry a will be called „the isometry characterizing ${}_{i,j}a$ ”.

The composition $\times$ of two POs is a partial function defined for pairs of POs in which the target layer of the first evaluated PO is the source layer of the second evaluated PO:

$${}_{j,k}a_2 \times {}_{i,j}a_1 = {}_{i,k}(a_2 \times a_1)$$

with the usual semantics for the composition of affine transformations. The composition of POs

- is not closed: ${}_{k,l}a_1 \times {}_{i,j}a_2$ is not defined for $j \neq k$.
- is associative: $({}_{k,l}a_3 \times {}_{j,k}a_2) \times {}_{i,j}a_1 = {}_{k,l}a_3 \times ({}_{j,k}a_2 \times {}_{i,j}a_1)$
- possesses identity elements ${}_{i,i}e$ for every layer L_i which are characterized by the identity operation e : ${}_{j,j}e \times {}_{i,j}a = {}_{i,j}a \times {}_{i,i}e = {}_{i,j}a$.
- possesses an inverse PO ${}_{j,i}a^{-1}$ for every PO ${}_{i,j}a$: ${}_{j,i}a^{-1} \times {}_{i,j}a = {}_{i,i}e$. The isometry a^{-1} characterizing ${}_{j,i}a^{-1}$ is the inverse of the isometry a characterizing ${}_{i,j}a$.

The POs of a polytype combined with the composition $\times$ form an algebraic structure called „symmetry groupoid” (Fichtner, 1977a). If a polytype consists of layers of only one kind (*i.e.* if for every pair of layers (L_i, L_j) there exists a PO ${}_{i,j}a$), the corresponding groupoid is called Brandt groupoid, if it consists of more than one kind of layers, it is called Ehresmann groupoid (Fichtner, 1977a) in honour of the seminal works on groupoids by Brandt (1926) and Ehresmann (1957). More recently, the terms „connected” or „transitive” are used to describe Brandt groupoids (Brown, 1987).

The groupoid of all POs of a polytype fulfilling the VC is called OD groupoid. The term OD groupoid is not used consistently in the literature: According to Fichtner (1977a), any groupoid fulfilling the VC is called OD groupoid, whereas according to Dornberger-Schiff and Fichtner (1972) OD groupoids are abstracted from all metric properties (like lattice parameters

or translational components between layers) and thus play a similar role for the description of a given polytype as do space groups for the description of a fully ordered crystal. A concise mathematical formulation of the conditions leading to an OD groupoid for a polytype composed of layers is given in Fichtner (1977a).

1.3.7 Continuations

If two POs $_{i,j}a_1$ and $_{k,l}a_2$ are characterized by the same isometry ($a_1 = a_2$) but affect different layers ($i \neq k$ and $j \neq l$), $_{k,l}a_2$ is said to be the continuation of $_{i,j}a_1$ and *vice versa* (Dornberger-Schiff and Grell-Niemann, 1961). In symbols this reads as:

$$_{i,j}a_1 \leftrightarrow _{k,l}a_2$$

Often the same letter is used for both POs to emphasize that they are characterized by the same isometry:

$$_{i,j}a \leftrightarrow _{k,l}a$$

If an isometry transforms a layer L_i into a layer L_j and *vice versa*, the corresponding POs are said to be reverse continuations of each other:

$$_{i,j}a \leftrightarrow _{j,i}a$$

The isometry characterizing a reverse continuation is a symmetry operation of the affected layer pair. For example a centre of inversion or a twofold screw with translational component $\frac{1}{2}\mathbf{a}$ ($\mathbf{a}$ is a lattice basis vector of the affected layer) possess reverse continuations, whereas a twofold screw with translational component $r\mathbf{a}$, $r \neq \frac{1}{2}n$, $n \in \mathbb{Z}$ or a screw whose translational component cannot be expressed with lattice basis vectors of the layer possess no reverse continuation.

If a PO $_{i,j}a$ possesses a continuation for every layer in the polytype, *i.e.* for every layer L_k there exists a continuation of $_{i,j}a$:

$$_{i,j}a \leftrightarrow _{k,l}a$$

then the isometry a characterizing $_{i,j}a$ is a symmetry operation of the whole polytype. $_{i,j}a$ is then called a total operation, otherwise a proper PO. Thus, a polytypic structure is a structure for which proper POs exist.

1.3.8 λ - and σ -POs

POs $_{i,i}a$ transforming a layer into itself are called λ -POs (Dornberger-Schiff and Grell-Niemann, 1961). All λ -POs of a given layer form a group isomorphous to the symmetry group of the respective layer.

The term σ -POs has been introduced to describe POs transforming a layer into the next layer of the same kind (Grell and Dornberger-Schiff, 1982). In other words, a PO $_{i,j}a$ is called σ -PO if $i \neq j$ and there exists no layer of the same kind between the layers designated by i and j . In OD structures every layer has exactly two next layers of the same kind³. For structures composed of layers of only one kind, these correspond to the adjacent layers.

³ In non-OD structures or OD structures composed of layers of $M = \infty$ of kinds, a layer may not have two next layers. The case of $M = \infty$ will not be treated in this work.

1.3.9 Polarity and orientation of layers

For OD structures composed of layers, the notion of polarity and orientation of layers has been proven an important and useful tool for the classification of OD groupoids and will therefore be introduced in the following paragraphs.

An important distinction of POs is whether they transform a side of a layer facing upwards into a side facing upwards or downwards (Dornberger-Schiff and Grell-Niemann, 1961). The former (*viz.* identity, translation, mirror or glide plane perpendicular to the layers, and rotation or screw axis normal to the layer planes) are called τ -POs, the latter (*viz.* centre of inversion, rotoinversion normal to the layer stacking direction, mirror or glide plane normal to the layer stacking direction, and rotation or screw axis normal to the layer stacking direction) are called ρ -POs. Whether a PO is a τ - or a ρ -PO can be deduced from the matrix describing the rotational component of the corresponding isometry: For layers normal to [001] the rotational component of a PO can be expressed as a regular matrix

$$\begin{pmatrix} x_{11} & x_{12} & 0 \\ x_{21} & x_{22} & 0 \\ 0 & 0 & x_{33} \end{pmatrix}.$$

The PO is a τ -PO if $x_{33} = 1$ and a ρ -PO if $x_{33} = -1$. Unspecified τ - and ρ -POs that transform a layer i into a layer j will simply be written $_{i,j}\tau$ and $_{i,j}\rho$.

With the introduced notations, $VC\gamma$ (sec. 1.3.4) for structures composed of layers can thus be reformulated as:

- (VC γ) If there exists a τ -PO which transforms layer L_i into a layer L_j , then there exists a pair of τ -POs

$$_{i,j}\tau' \leftrightarrow _{i+1,j+1}\tau'$$

and there exists a pair of τ -POs

$$_{i,j}\tau' \leftrightarrow _{i-1,j-1}\tau'$$

If there exists a ρ -PO which transforms layer L_i into a layer L_j , then there exists a pair of ρ -POs

$$_{i,j}\rho' \leftrightarrow _{i+1,j-1}\rho'$$

and there exists a pair of ρ -POs

$$_{i,j}\rho' \leftrightarrow _{i-1,j+1}\rho'$$

Layers for which only λ - τ -POs exist, are polar, whereas layers for which λ - ρ -POs exist, are non-polar. Two polar layers of the same kind are said to be of the same orientation if they are related by τ -POs and of different orientation if they are related by ρ -POs. Non-polar layers of the same kind are always related by τ - and ρ -POs.

Dornberger-Schiff and Grell-Niemann (1961) introduced a layer nomenclature taking into account the orientation of layers. Non-polar layers are designated by the letter A . The letters d and b stand for the two different orientations of a polar layer. The kind of layer and the layer sequence are indicated by super- and subscripts, as described in sec. 1.3.2.

1.3.10 Type of OD groupoids of polytypes composed of layers

The polarity and orientation of layers are used to associate a type to OD groupoids of polytypes composed of layers (Fichtner, 1977a). In order to deduce the type of an OD groupoid the notion of absolute orientation of a layer is introduced. Polar layers can appear in one out of two

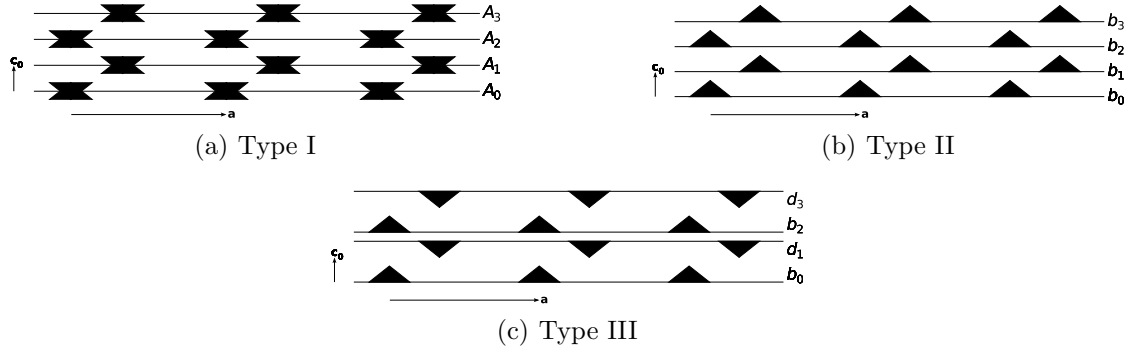


Figure 1.7: Schema of OD polytypes composed of layers of one kind with OD groupoids of type (a) I, (b) II and (c) III.

orientations („facing up” and „facing down”), which will be represented by arrows facing up ($\uparrow$) or down ($\downarrow$). Non-polar layers can only appear in one orientation, which will be designated by a double arrow ($\updownarrow$). In a polytype composed of layers of M kinds, the polar layers of an arbitrary layer tuple $L_n \dots L_{n+M-1}$, which contains each kind of layer exactly once, are considered facing up. Other polar layers are considered facing up if they are of the same orientation or facing down if they are of a different orientation.

Two groupoids are said to be of the same type if the corresponding polytypes consist of the same amount M of kinds of layers and if they can be represented by the same sequence of layers being non-polar, facing up or facing down. A concise mathematical definition of the concept is given in Fichtner (1977a).

It can be shown that OD groupoids of polytypes composed of layers of one kind can be of one out of three types and OD groupoids of polytypes composed of layers of $M > 1$ kinds can be of one out of four types⁴ (Fichtner, 1977a). The possible types of OD groupoids have been assigned roman numbers (Fichtner, 1977a). For OD groupoids of polytypes composed of layers of one kind they are given as:

- Type I: one kind of non-polar layers: $\dots \updownarrow \updownarrow \updownarrow \dots$
- Type II: one kind of polar layers with same orientation: $\dots \uparrow \uparrow \uparrow \dots$
- Type III: one kind of polar layers with alternating orientation: $\dots \uparrow \downarrow \uparrow \downarrow \dots$

Examples of polytypes with OD groupoids of all three type are schematized in Fig. 1.7. For OD groupoids of polytypes composed of layers of $M > 1$ kinds the types are given as:

- Type I: one kind of non-polar and $M - 1$ kinds of polar layers:

$$\dots \underbrace{\uparrow \dots \uparrow}_{(M-1) \times} \underbrace{\updownarrow \dots \updownarrow}_{(M-1) \times} \underbrace{\uparrow \dots \uparrow}_{(M-1) \times} \underbrace{\updownarrow \dots \updownarrow}_{(M-1) \times} \dots$$
- Type II: M kinds of polar layers with same orientation:

$$\dots \underbrace{\uparrow \dots \uparrow}_{M \times} \underbrace{\uparrow \dots \uparrow}_{M \times} \dots$$
- Type III: M kinds of polar layers with alternating orientation of layer packets:

$$\dots \underbrace{\uparrow \dots \uparrow}_{M \times} \underbrace{\downarrow \dots \downarrow}_{M \times} \underbrace{\uparrow \dots \uparrow}_{M \times} \underbrace{\downarrow \dots \downarrow}_{M \times} \dots$$

⁴ The groupoids of polytypes composed of layers of an infinity of kinds ($M = \infty$) fulfilling $VC\beta$ and $VC\gamma$ can be of one out of three types (Fichtner, 1977a), but this case violates $VC\alpha$ and therefore will not be treated here.

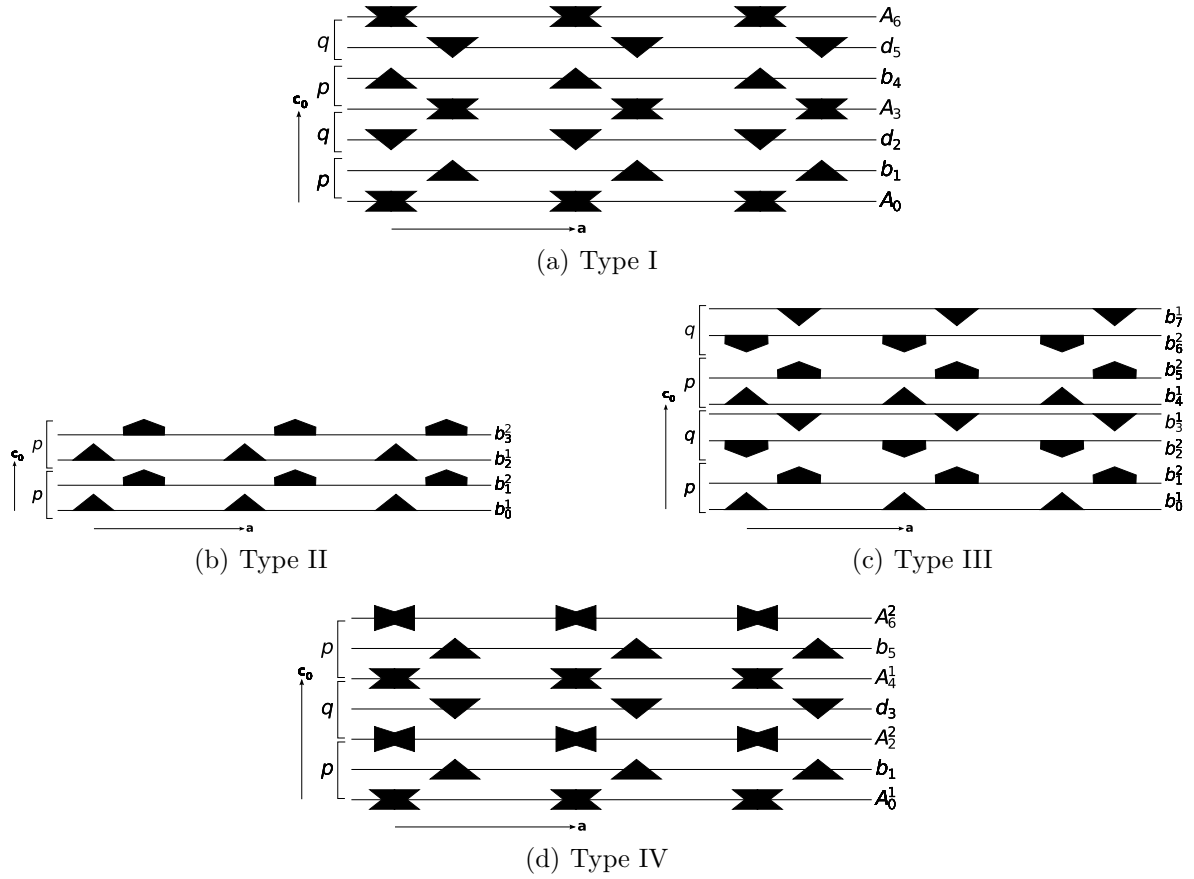


Figure 1.8: Schema of OD polytypes composed of layers of $M > 1$ kinds with OD groupoids of types I–IV. (a) Type I, one kind of non-polar and one kind of polar layers. (b) Type II, two kinds of polar layers. (c) Type III, two kinds of polar layers. (d) Type IV, non-polar layers of two and polar layers of one kind. To the left of the layers, layer packets according to Āurovič (1974) are indicated.

- Type IV: two kinds of non-polar layers and $M - 2$ kinds of polar layers:

$$\dots \underbrace{\uparrow \dots \uparrow}_{(M-2) \times} \underbrace{\downarrow \dots \downarrow}_{(M-2) \times} \underbrace{\uparrow \dots \uparrow}_{(M-2) \times} \underbrace{\downarrow \dots \downarrow}_{M-2 \times} \dots$$

Examples of polytypes with OD groupoids of all four types are schematized in Fig. 1.8

1.3.11 Layer n -tuples and layer packets

According to the VC, an equivalent side of a layer adjoins always to the same kind of layer on the same side. Thus an OD polytype composed of layers of M kinds is composed of (possibly overlapping) n -tuples of adjacent layers $L_n^1 \dots L_{n+M-1}^M$ or $L_n^M \dots L_{n+M-1}^1$ containing each kind of layer exactly once. In this work, n -tuples of layers always designates adjacent layers. Layer n -tuples consisting of the same sequence of layer kinds are said to be of the same class (Dornberger-Schiff and Grell, 1982). Layer n -tuples of the same class need not be equivalent, *i.e.* of the same kind.

For structures composed of layers of $M > 1$ kinds, Āurovič (1974) introduced the notion of OD packets, which is defined as

the smallest continuous part of an OD structure, which is periodical in two dimen-

Table 1.4: Possible combinations of superposition and point group of an OD groupoid.

No.	Crystallographic superposition group	Crystallographic point group
1	yes	yes
2	no	yes
3	no	no

sions and which represents completely its composition. The OD packets are equal or smaller to the n -tuples of layers containing each kind of layer exactly once, as they may contain half layers obtained by slicing polar layers into two equivalent non-polar layers. The choice of layer packet is unique for OD groupoid types with the exception of type II. In type I and type IV OD groupoids the polar layers are sliced into non-polar layers.

Layer packets for polytypes composed of layers of $M > 1$ kinds with OD groupoids of type I-IV are indicated in Fig. 1.8. Only in polytypes of type II and III the layer packets correspond to layer n -tuples. In analogy to the notation of layers, layer packets are designated p and q , depending on orientation with respect to the stacking direction. Polytypes of type I, III and IV consist of an alternative stacking of layer packets $\dots pqpq \dots$. In polytypes of type II all layer packets are of the same orientation $\dots pp \dots$. Layer packets play a pivotal role in the determination of MDO polytypes (Dornberger-Schiff and Grell, 1982).

1.3.12 Superposition group and point group of an OD groupoid

The superposition group of an OD groupoid is the group generated by the isometries characterizing all POs (Fichtner, 1977a). The point group of an OD groupoid is the group generated by the rotational components of the isometries characterizing all POs (Fichtner, 1977a).

Neither is the superposition group of an OD groupoid necessarily a crystallographic space group, nor is the point group of an OD groupoid necessarily a crystallographic point group. If the superposition group is a crystallographic space group, the point group is a crystallographic point group corresponding to the point group of the superposition group. If the point group of an OD groupoid is not a crystallographic point group, then the superposition group cannot be a crystallographic space group (Fichtner, 1977a). There are therefore three possible combinations of crystallographic and non-crystallographic superposition and point group which are listed in Tab. 1.4. The exact conditions for a crystallographic superposition group in the case of polytypes composed of layers are given in Fichtner (1977a).

An example of an OD groupoid with a crystallographic superposition group is given by the symmetry of a polytype composed of layers of one kind parallel to (001), as depicted in Fig. 1.9(a). Each layer is symmetric by mirroring at (100), as schematized by black triangles which are not symmetry by mirroring at (010). Two adjacent layers L_n and L_{n+1} are related by a glide parallel to (100) with a translational component $\mathbf{c}_0$, located at $x = \frac{1}{6}$, relative to the origin of layer L_0 . It is an OD polytype, since all pairs of adjacent layers are equivalent, and the mirror planes of the layers are proper POs. Since the glides are total operations, the space group of the polytype is $Pc11$ (with basis vectors $\mathbf{a}$, $\mathbf{b}$, $2\mathbf{c}_0$). The generating elements of the superposition group are the mirror plane of layer L_0 located at $x = 0$, the glide plane relating L_0 and L_1 located at $x = \frac{1}{6}$ and the translations along the lattice basis vectors $\mathbf{a}$ and $\mathbf{b}$ of layer L_0 . All other POs of the polytype can be expressed using these four operations. The resulting

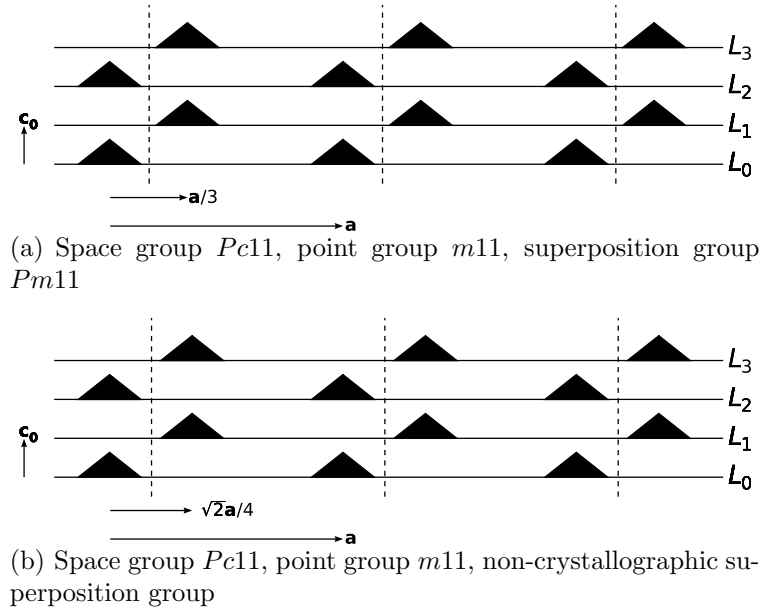


Figure 1.9: Schema of layers $L_0 \dots L_3$ of two similar OD polytypes, characterized by layers symmetric by mirroring at a plane parallel to (100). Two adjacent layers are related by glides parallel to (100) located at $x = \frac{1}{6}$ (a) or $x = \frac{\sqrt{2}}{8}$ (b) resulting in a polytype with (a) a crystallographic and (b) an non-crystallographic superposition group.

superposition group has symmetry $Pm11$ with basis vectors $(\frac{1}{3}\mathbf{a}, \mathbf{b}, \mathbf{c}_0)$. Since all POs of the polytype are characterized by mirror planes or glides parallel to (100), the point group of the OD groupoid is $m11$.

A similar polytype, in which all layers are related by a glide located at an incommensurate position (e.g. $x = \frac{\sqrt{2}}{8} \approx 0.178$, Fig. 1.9(b)) has the same space group $Pc11$ and point group $m11$. Yet the superposition group cannot be a crystallographic space group since by the action of the glide and the mirror plane (or the glide and the translation along $\mathbf{a}_0$), symmetry operations with non zero but arbitrarily small translational components are obtained. Thus two very similar polytypes can either have a crystallographic or a non-crystallographic space group.

An example of an OD groupoid with non-crystallographic point group (adapted from Fichtner (1977a) and Grimmer and Nespolo (2006)) is a polytype composed of square layers of one kind parallel to (001) as schematized in Fig. 1.10. Two adjacent layers L_i and L_{i+1} are related by a screw with screw axis located at $(0, 0, z)$, with angle $\theta = 2 \tan^{-1} \frac{1}{3} \approx 36.87^\circ$ and a translational component $\mathbf{c}_0$ along [001]. Both layers share a common translational subgroup and thus fulfill VC β . The point group of the OD groupoid of the polytypes contains a rotation of $\theta \approx 36.87^\circ$ and can therefore not be a crystallographic point group. Indeed, since θ is incommensurate relative to a full rotation by 360° ⁵, the point group contains rotations around [001] with an arbitrary small magnitude > 0 . Furthermore, for every translation $t \neq e$ of the translational group T_0 of layer L_0 there is a layer L_n , for which t is not part of the translational group T_n . Thus the common translational group of all layers of the polytype contains only the identity operation: $\bigcup_i T_i = \{e\}$.

The point and superposition groups provide an alternative classification schemes for OD groupoids to OD groupoid types. In this work the superposition group will be indicated if it exists. Instead of the point group, the corresponding crystal system will be given. In the case

⁵ θ expressed in $^\circ$ is irrational and also transcendental

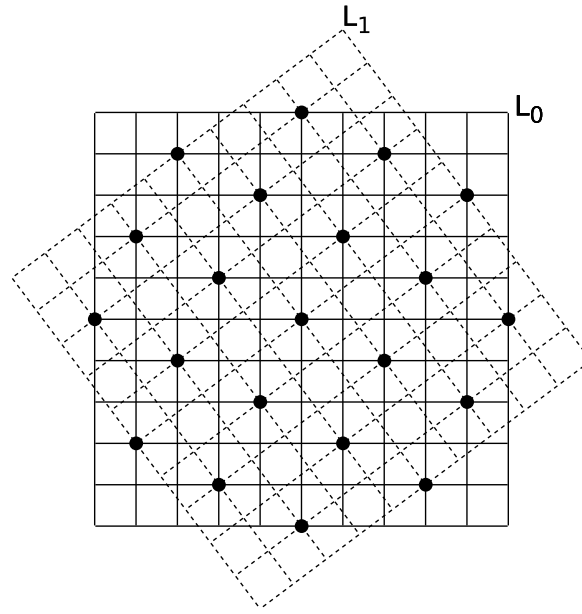


Figure 1.10: The lattices of two adjacent equivalent square layers (L_0, L_1) parallel to (001) viewed down [001]. The lattices of L_0 and L_1 are represented by continuous and dashed lines, respectively. Layer L_1 is related to layer L_0 by a screw parallel to [001] passing through the origin with rotation angle $\theta = 2 \tan^{-1} \frac{1}{3}$. The lattice elements generated by the common translational group of both layers are indicated by black dots.

of monoclinic point groups those with twofold axes normal and those with twofold axes parallel to the layer planes will be discerned and called according to the *International Tables of Crystallography Vol. E* (Kopsky and Litvin, 2002) monoclinic/oblique and monoclinic/rectangular⁶, respectively.

1.3.13 OD families

As has been mentioned in sec. 1.3.6, the symmetry of a polytype of an OD structure is described by an OD groupoid. Since OD structures allow for a varying degree of disorder, it will in the typical case neither be possible, nor desirable to determine the exact stacking sequence of a polytypic compound. Therefore the concept of „symmetry principle” (Fichtner, 1979a) has been introduced, which classifies polytypes according to the symmetry of the layers and the relationship between adjacent layers. Thus two structures are built according to the same symmetry principle if they fulfill the VC „in the same way”.

The corresponding algebraic concept are OD groupoid families. All OD groupoids which are of the same type and characterized by the same λ -POs and the same σ -POs (disregarding differences in the translational components) relating adjacent layers are said to be of the same OD groupoid family. A concise mathematical formulation of the concept is given in Fichtner (1977a). Polytypes which crystallize with OD groupoids of the same OD groupoid family are said to belong to the same OD family or follow the same „symmetry principle” (Fichtner, 1979a). The OD family is associated with a category, corresponding to the type of the OD groupoids (Fichtner, 1977a). All OD groupoids of an OD family possess the same point group, which is said to be the point group of the OD groupoid family.

⁶ In the wording of Dornberger-Schiff and Grell-Niemann (1961), they are called monoclinic I and II, respectively.

There is a finite number (400) of OD groupoid families of structures composed of layers of one kind which were deduced by Fichtner (1977b). For OD structures composed of layers of $M > 1$ kinds, there are an infinity of OD groupoid families. Consider for example an OD structure composed of two kinds of layers L^1 and L^2 normal to $[001]$. Layer L^1 has lattice basis vectors $\mathbf{a}, \mathbf{b}$, L^2 lattice basis vectors $n\mathbf{a}, \mathbf{b}$, $n > 1$. For different n , the structure is part of a different OD family. Therefore an infinity of OD families of structures composed of two layers is possible.

OD families are a valuable tool for the classification of polytypic substances. Different structures belonging to an OD family can be either of the same or similar chemical composition, obtained under varying experimental conditions or by slight variation of the composition (*e.g.* the $M\text{TeO}_3$ class of compounds, sec. 3.3.5) or of entirely different composition (*e.g.* cubic Cu and hexagonal Mg). In the latter case, a description according to OD theory provides a convincing classification scheme, which is not possible using traditional group-subgroup relationships. Indeed, the space groups of the cubic and hexagonal close packings ($Fm\bar{3}m$ and $P6_3/mmc$) do not stand in a direct group-subgroup relationship, nor are subgroups of a common supergroup despite them being both close sphere packings. Even if only one kind of polytype is known, the description as a polytypic compound serves as a description of additional symmetry, which would be missed by simply stating traditional space-group symmetry.

1.3.14 Coordinate system

In the most common case, all layers in an OD structure composed of layers possess a common translational group. Two of the basis vectors are then chosen according to the crystal system of the common translational group. The layer stacking direction is called $\mathbf{a}_0$, $\mathbf{b}_0$ or $\mathbf{c}_0$. Thus in structures composed of layers parallel to (001) , the vector $\mathbf{c}_0$ designates the direction of possible disorder. $\mathbf{c}_0$ connects two equivalent layers between which each other kind of layer is located exactly once. Generally $\mathbf{c}_0$ is chosen normal to the layer planes, only in the case of OD groupoids with a monoclinic/rectangular point group, $\mathbf{c}_0$ is chosen with an angle $\beta = \widehat{\mathbf{c}_0, \mathbf{a}}$, reflecting the monoclinic angle of the point group (Fichtner, 1979b). In most cases the length of the basis vectors and the angles between basis vectors are specified implicitly by the lattice parameters of a given polytype.

The relative positions of layers is given as components parallel to $\mathbf{c}_0$ and parallel to the layer planes. Usually the relative distance of layers along $\mathbf{c}_0$ are given implicitly by the atomic coordinates of a given polytype. The translational components between origins of layers parallel to the layer planes are given as the translational components of the σ -POs relating two equivalent layers or as the components $r\mathbf{a} + s\mathbf{b}$ of the projection along $\mathbf{c}_0$ of the vector connecting the origins of two adjacent non-equivalent layers on the layer plane.

1.3.15 Symbols used in the description of OD families

Since translational components of screws and glides relating different layers need not necessarily be of crystallographic nature, the notation for screws and glides had to be generalized (Dornberger-Schiff and Grell-Niemann, 1961). Thus 2_2 and 2_r represent screws with translational component of one and $\frac{r}{2}$ parts of a lattice vector. In analogy, $n_{2,r}$ represents a glide with a translational component of one and $\frac{r}{2}$ parts of two lattice vectors, *etc.*

Two line symbols describing OD groupoid families have been devised for structures composed of layers of one kind (Dornberger-Schiff and Grell-Niemann, 1961). The first line describes the λ -POs, the second line the σ -POs. Thus for example the symbol (adapted from Dornberger-Schiff and Fichtner (1972))

$$\begin{array}{cccc} p & m & 1 & (1) \\ & \{1 & n_{2,r'} & (2_2)\} \end{array}$$

stands for an OD groupoid family of polytypes consisting of layers of one kind normal to $[001]$ which are symmetric by a mirror plane normal to $[100]$. Two adjacent layers are related by a twofold screw perpendicular to the layers with translational component of $\mathbf{c}_0$, a glide normal to $[010]$ with a translational component of $\mathbf{c}_0 + \frac{r}{2}\mathbf{a}$ or any operation leading to an equivalent layer pair. For certain OD groupoid families (*e.g.* those of category III), more than one set of σ -POs has to be specified. In this case three lines (Dornberger-Schiff and Grell-Niemann, 1961) or two lines (Fichtner, 1979a) can be used.

OD groupoid families of polytypes consisting of layers of $M > 1$ kinds are described using three line symbols devised by Grell and Dornberger-Schiff (1982). The first line indicates the layer names according to the convention given in sec. 1.3.9. The second line gives the λ -POs as in the symbols for $M = 1$. The third line lists the σ -POs for adjacent layers of the same type as in the symbols for polytypes consisting of layers of one kind. For adjacent layers of different kinds, one possible origin shift between both layers is instead given (the other possible origin shifts can be deduced from the λ -POs of the affected layers). For this purpose the vector leading from the origin of one layer to the origin of an adjacent layer is projected on the layer plane and the components relative to the lattice basis vectors are indicated. Grell and Dornberger-Schiff (1982) do not explicitly specify whether the projection is to be perpendicular or along $\mathbf{c}_0$ in the case of monoclinic/rectangular point groups, but the latter seems more sensible and will be used in the present work. Thus for example the symbol

$$\begin{array}{ccc} A^1 & & A^2 \\ p11(2/m) & & p\bar{1}\bar{1}(\bar{1}) \\ & [r, s] & \end{array}$$

describes an OD groupoid family of polytypes consisting of two kinds of non-polar layers with layer groups $p11(2/m)$ and $p\bar{1}\bar{1}$, respectively. The origin of the layer A^2 is related to the origin of an adjacent layer A^1 by a translation along $r\mathbf{a} + s\mathbf{b} + x\mathbf{c}_0$.

In structures composed of layers of $M > 1$ kinds the translational groups of individual layers may be supergroups of the common translational group of all layers. Additional translational symmetry of a layer has therefore to be reflected by the OD groupoid family symbol. According to Grell and Dornberger-Schiff (1982) it is indicated by custom Bravais lattice symbols, which are introduced *ad-hoc* in each case. In the present work the following conventions will be used: Lattices with one lattice basis vector halved compared to the corresponding basis vector of the common translational group will be indicated by a „ d ” Bravais symbol with the direction of doubled translational symmetry given in the subscript. Thus d_x indicates a halving of the lattice basis vector $\mathbf{a}$. For more complicated cases, the lattice basis vectors of the corresponding layer will be given as a list of general expressions of the lattice basis vectors of the common translational group in the subscript of the Bravais symbol. An example is given by the layer group symbol $p_{\mathbf{a}'=\frac{1}{2}\mathbf{a}-\frac{1}{2}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{b}}mm(m)$. If the common translational group of all layers is the trivial subgroup $\{e\}$, it is sufficient to use the common translational group of one layer n -tuple containing a layer of every kind exactly once.

Symmetry elements will be described using a notation devised by Ferraris et al. (2004). The symbols consist of 3–7 places according to the notation given for layer and rod groups above placed in square brackets. The symmetry element is indicated at the position corresponding to its direction, the other positions are marked by a „–” sign. Thus $[- - m]$ indicates a mirror plane normal to direction $[001]$ and $[2 - -]$ indicates a twofold rotation parallel to $[100]$. The notation is not unambiguous in all cases and may have to be adapted to the case at hand.

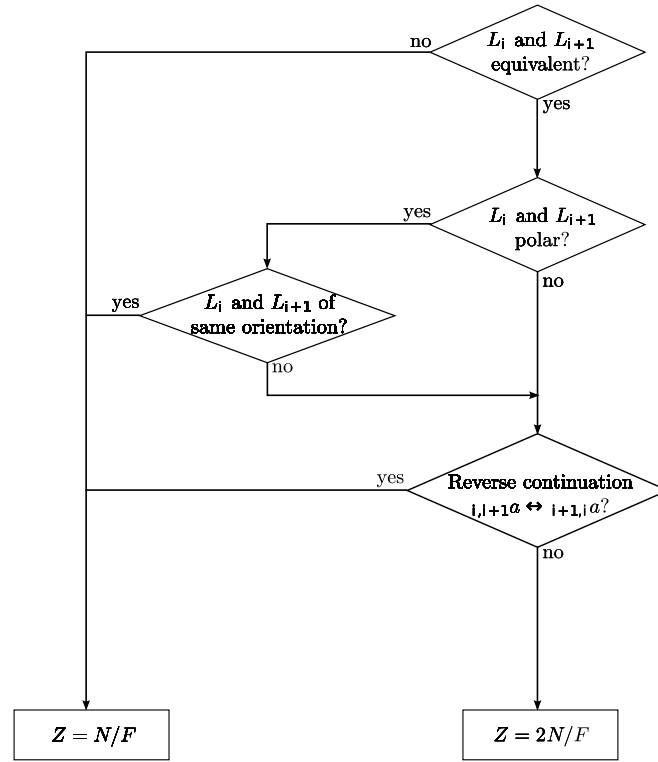


Figure 1.11: Flowchart describing the applicability of both forms of the NFZ relationship $Z = N/F$ and $Z = 2N/F$ on a pair of adjacent layers L_i and L_{i+1} .

1.3.16 NFZ relationship

Given the position of a layer L_i , the NFZ relationship (Đurovič, 1997) describes how many different non-overlapping positions an adjacent layer L_{i+1} may adopt while satisfying the VC. It is fundamental in determining the stacking possibilities of a given OD family. In the NFZ relationship N stands for the order of the group G of λ - τ -POs of layer L_i , F for the order of the group F of those elements in G which are also valid for layer L_{i+1} (*i.e.* those elements $_{i,i}a \in G$ which possess continuations $_{i,i}a \leftrightarrow _{i+1,i+1}a$) and Z is the number of different positions a layer L_{i+1} may adopt given the position of layer L_i . Since a layer group possesses an infinity of symmetry operations, the orders $|G|$ and $|F|$ have to be expressed relative to a common translational group. Thus, if the common translational group of layers L_i and L_{i+1} is $T = T_i \cap T_{i+1}$, N and F may more concisely be expressed as the orders of the quotient groups G/T and F/T .

The NFZ relationship reads as $Z = N/F$ if there exists no σ - ρ -PO or if there exists a reverse continuation between both layers L_i and L_{i+1} . It reads $Z = 2N/F$ if there exists a σ - ρ -PO but no reverse continuation between both layers L_i and L_{i+1} . For non-equivalent layers or non-polar layers with same orientation, no σ - ρ -POs exists and therefore the ZNF relationship reads as $Z = N/F$. The flowchart in Fig. 1.11 gives an overview when to apply which formula.

The NFZ relationship can be illustrated using the following plausibility arguments: If $_{i,i}a$ is a λ -PO of layer L_i , which does not possess a continuation $_{i+1,i+1}a$ in layer L_i , then by applying the isometry characterizing $_{i,i}a$ on the layer pair $L_i L_{i+1}$, an equivalent layer pair $L_i L_{i+1}^a$ is obtained. An example is given in Fig. 1.12(a): Layer L_0 is symmetric by mirroring at a plane parallel to (100) which does not apply to layer L_1 . There are therefore two ways of obtaining an equivalent layer pair $L_i L_{i+1}$. Thus all possible orientations of layer L_{i+1} are related by the isometries

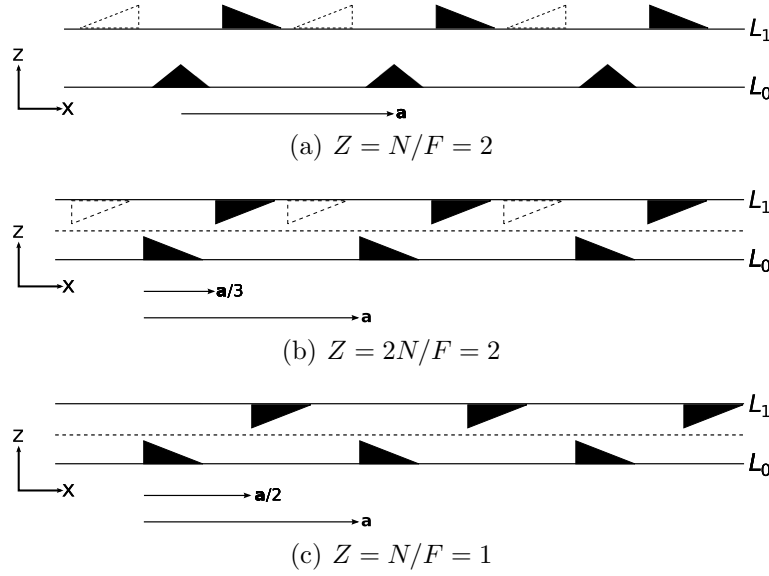


Figure 1.12: Layer pairs exemplifying the NFZ relationship. Layers are stacked along $[001]$. Layers L_0 are fixed, one possible arrangement of layers L_1 is represented by black polygons, an alternative arrangement leading to an equivalent layer pair by polygons with a dashed outline. (a) Two non equivalent layers with same orientation and mirror planes only valid for layer L_0 . (b) Two equivalent non-polar layers with different orientations related by a glide with translational component $\frac{1}{3}\mathbf{a}$. (c) As (b) with a glide along $\frac{1}{2}\mathbf{a}$

characterizing the factor group G/F . The order of the factor group $|G/F| = |G|/|F| = N/F = Z$ corresponds to the amount of different orientations.

If layer L_i is related to layer L_{i+1} by a σ - ρ -PO $_{i,i+1}a$, and no reverse continuation exists, then there is a second σ - ρ -PO $_{i,i+1}a^{-1}$ ⁽⁷⁾ characterized by the inverse isometry of $_{i,i+1}a$ which results in an equivalent layer pair. An example is schematized in Fig. 1.12(b): Layer L_0 is related to layer L_1 by a glide normal to the layer stacking direction $[001]$ with translational component $\frac{1}{3}\mathbf{a}$. By applying the inverse screw with translational component $-\frac{1}{3}\mathbf{a}$ an equivalent layer pair is obtained. If the glide has translational component $\frac{1}{2}\mathbf{a}$ instead of $\frac{1}{3}\mathbf{a}$ as schematized in Fig. 1.12(c), the corresponding PO possesses a reverse continuation. Only one way to obtain layer L_1 is possible, since the glide along $\frac{1}{2}\mathbf{a}$ and $-\frac{1}{2}\mathbf{a}$ result in the same location of layer L_1 . Thus if no reverse continuation exists the equation $Z = 2N/F$ has to be applied.

For a pair of layers with $Z = 1$, the structure is a fully ordered structure and both layers should be combined to a single layer. In a few cases, a description with $Z = 1$ may be useful, for example to compare closely related structures, where one structure is an OD structure, whereas the other is fully ordered, for example due to a variation in the translational components relating different layers.

1.3.17 Desymmetrization and increased apparent symmetry

A characteristic phenomenon in polytypic structures is the desymmetrization of layers in actual ordered polytypes compared to the idealized description according to the space groupoid of the polytype (Đurovič, 1979). This is explained by layers being located in an environment with lowered symmetry compared to the symmetry of the layers. In polytypes composed of layers of $M > 1$ kinds, often only some of the layers are affected by desymmetrization (*e.g.* the polytypes

⁷ Note that $_{i,i+1}a^{-1}$ is not the inverse PO of $_{i,i+1}a$. The inverse PO of $_{i,i+1}a$ is $_{i+1,i}a^{-1}$.

of γ -CaTeO₃, sec. 3.3.5). In rare cases the symmetry of all layers remains. For example, in cubic close packings the layers still have hexagonal symmetry despite sixfold rotational symmetry not being total operations of the polytype. All polytypic compounds presented in this work show desymmetrization. A direct consequence of desymmetrization is that a certain amount of idealization is necessary in the description of polytypic compounds. In consequence, the obtained OD description depends on the amount of idealization and therefore should be based either on different actual measured polytypes or sound crystallochemical considerations. A small deviation from the idealized structure is an indication of the validity of the OD description.

In what seems to be a contradictory matter of fact, desymmetrization is larger, with increasing order of the polytypes. In reverse, the diffraction patterns of disordered polytypes appear to have increased symmetry compared to the idealized description (Ferraris et al., 2004). Due to high disorder, layers appear as a superposition of multiple orientations. The POs of other layers are „multiplied” into the layer group, resulting in superposition structures. The superposition structure with the highest possible symmetry, obtained by superimposing all possible polytypes of a polytype family, is called family structure.

The family structure plays an important role in OD theory. On one hand, its symmetry corresponds to the symmetry of the superposition group and therefore its point group serves as a classification system for OD structures (sec. 1.3.12), on the other hand in many cases the family structure can be deduced from the diffraction pattern and it therefore plays a key role in the determination of OD structures. Not all OD families possess a family structure with a discrete three dimensional lattice. Indeed, as pointed out in sec. 1.3.12, OD families with σ -POs with an incommensurate (relative to the lattice basic vectors of the layers) translational component possess no crystallographic superposition group and thus no family structure.

1.3.18 Ordered *vs.* disordered polytypes

As has been mentioned, in the general case it will not be possible to determine the precise stacking sequence of a polytype. The stacking sequence will therefore be described as valid for „large” regions of the polytype with qualitative statements on the amount of disorder. A given polytype may possess a varying degree of disorder.

In the ideal case it contains only one stacking sequence. A real polytypic compound will have at least a few stacking faults, resulting in a crystal composed of different individuals. If these individuals can be related by translational symmetry, this can typically not be determined by single crystal diffraction. If the individuals are related by symmetry operations containing non-translational parts, the stacking faults may interfere with structure determination. Depending on whether the purely rotational part of the operation is part of the point group of the individuals, merohedric or non-merohedric twins are obtained (Grimmer and Nespolo, 2006).

A high stacking fault probability typically interferes with structure solution. It becomes noticeable by diffuse scattering (*c.f.* sec. 1.3.19). If structure solution is possible, the resulting structure is an overlap of the different stacking sequences. In extreme cases, only the family structure can be determined.

The most complicated case for structure elucidation are crystals which contain large regions of different stacking sequences. These result in multi-phase crystals with overlapping reflections. This case is uncommon and supported only by few software packages for structure refinement. Electron diffraction and transmission electron microscopy might be necessary for a satisfactory structure solution and refinement.

1.3.19 Diffraction features of polytypic structures

Many polytypic compounds possess peculiar diffraction patterns. One important result of OD theory states that the reflections corresponding to the family structure (called family reflections) are always sharp. The reflections corresponding only to certain polytypes (called characteristic reflections) are sharp if the polytype is ordered or show varying levels of diffuseness (streaking in the stacking direction) if the polytype is disordered (Ferraris et al., 2004).

Another characteristic feature of the diffraction patterns of OD structures is the existence of non-spacegroup absences. An example in this work showing distinct non-spacegroup absences is MgTeO_8H_8 for which the diffraction pattern will be explained in app. B. Both effects are known since the early fifties of the last century for the mineral wollastonite (Jeffery, 1953) and were seminal in the development of OD theory.

1.3.20 Generalisation to rods and blocks

So far, little theoretical work has been performed on a generalized theory of polytypic structures composed of aperiodic (blocks) and periodic in one dimension (rods) modules. The crystal structure of $\text{Na}_2\text{H}_2\text{P}_4\text{O}_{12}$ (Dornberger-Schiff, 1964) has been described as a two dimensionally disordered OD structure composed of rods. An extended OD approach using layers, blocks and rods has fruitfully been applied to the analysis of the crystal chemistry of various borates (Belokoneva, 2005)

Modules

In a generalized theory of polytypic structures, layers are replaced by modules. In the literature the nature of modules is usually defined implicitly by their properties. In the following text modules are three-dimensional (with a non zero volume), closed⁸, continuous subsets of Euclidean space $\mathbb{R}^3$ which are finite and aperiodic (blocks) or infinite and periodic in one (rods) or two (layers) dimensions.

As for layers, modules which are congruent or enantiomorphic are said to be equivalent or to be of the same kind (Dornberger-Schiff and Grell-Niemann, 1961). The modules in a polytypic structure are of a finite number $M \geq 1$ of kinds. The polytype is said to be composed of modules (layers, rods, blocks) of M kinds. A concrete stacking sequence or arrangement of modules is called a „polytype”.

The intersection between modules is called the interface between modules. Modules with a common interface are said to be adjacent. As opposed to layers, which always form a stacking sequence, determination of adjacency is more complicated. A rod may connect to only one other rod (rod *A* in Fig. 1.13(a)), to a larger, but finite number of other rods (rod *B* in Fig. 1.13(a)) or up to an infinity of rods (Fig. 1.13(b)). The interface between two rods may possess an infinite (Fig. 1.13(a)) or a finite (Fig. 1.13(b)) surface. Other authors did not consider the kind of rod connectivity depicted in Fig. 1.13(b), possibly because the corresponding structures can be thought of as being composed of blocks. For example Fichtner (1977a) writes in his final remarks: „Über allgemeinere Möglichkeiten der Anordnung der Stäbe gibt die Theorie der homogenen Mosaik (Krötenheerdt, 1969) Auskunft.” One can conclude that the author had only arrangements of parallel rods with interfaces with an infinite surface in mind. Similar considerations apply to blocks, with the main difference that blocks can only connect to a finite number of other blocks and the surface of the interfaces between blocks must be finite.

⁸A module contains its boundary

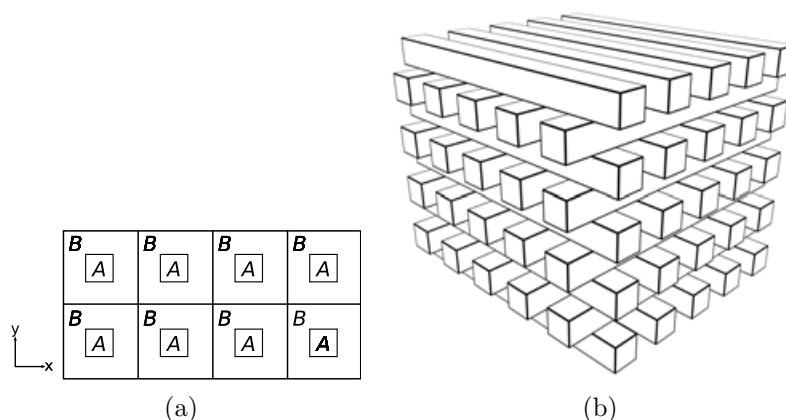


Figure 1.13: (a) Arrangement of two kinds of rods A and B running along $[001]$ viewed down $[001]$. Rods A are completely encompassed by rods B . (b) Perspective projection of an arrangement of rods, in which each rod connects to an infinity of other rods and the interface between rods has a finite surface. Parts of space are not part of any rod.

Furthermore, in the case of rods and blocks, points of space may have to be considered not being part of a module if the distance between modules is too large for interaction between atoms located in different modules (Fig. 1.13(b)) or can be parts of more than two modules (corners of rods B in Fig. 1.13(a)). Thus, derivation of rod and block connectivity is significantly more complicated than in the case of layers and may include crystallochemical considerations or be based on observed stacking possibilities (Dornberger-Schiff, 1964).

It seems that the concept of interface will play a much more central role in a fully elaborated theory on polytypic structures composed of rods and blocks than it does for layers.

Designation of rods and blocks

To designate a given rod or block, it will be useful to use pairs and triples of integers. As for layers, the location of the module will be indicated in the subscript and the kind of the module will be indicated in the superscript. Thus $M_{i,j}^k$ designates a rod of type k at position (i, j) . Due to the large variety of stacking possibilities, the exact meaning of (i, j) will be defined *ad-hoc*. Accordingly, a POs transforming a rod (i, j) into rod (k, l) is written $_{(i,j),(k,l)}a$

Vicinity condition

The vicinity condition of OD theory can be directly adapted to rods and blocks. It reads for example:

- (VC α) The structure can be described by an arrangement of distinct modules of a finite number of kinds.
- (VC β) The translational groups of adjacent periodic modules are subgroups of a common supergroup.
- (VC γ) Equivalent interfaces of equivalent modules are faced by adjacent modules in such a way that the pairs thus formed are equivalent.

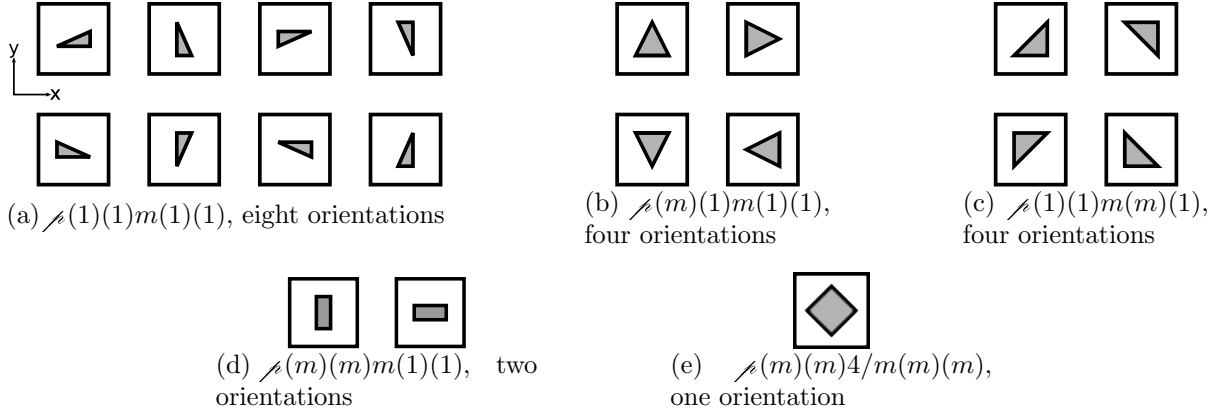


Figure 1.14: Rods with a square cross section running along $[001]$ with different symmetries. For each rod all possible orientation are schematized. The symmetry group of one representative is given using the symbolism for tetragonal symmetry groups explained in sec. 1.3.15. Grey triangles, rectangles and squares are symmetric by mirroring at (001) .

λ - and σ -POs

The definition of λ -POs can be directly adapted from the definition for layers: A λ -POs transforms a module into itself. The set of λ -POs of a module forms the symmetry group of the module.

For structures composed of rods and blocks the notion of „next module of the same kind” is not immediately obvious. Therefore, in this work the term σ -POs will only be used in the context of adjacent modules (also in the case of layers).

Polarity and orientation

The notions of polarity and orientation of layers can not be trivially generalized to rods and blocks, as these typically possess more than two interfaces. As an example, consider rods with a square cross section as depicted in Fig. 1.14, connecting *via* all four faces to another rod. Depending on the symmetry of the rod, all four interfaces may be mutually non-equivalent (Fig. 1.14(a)), two interfaces may be equivalent and the two other non-equivalent (Fig. 1.14(b)), two interfaces may be pairwise equivalent (Fig. 1.14(c), 1.14(d)) or all four interfaces may be equivalent (Fig. 1.14(e)). The respective rods may appear in eight (Fig. 1.14(a)), four (Fig. 1.14(b), 1.14(c)), two (Fig. 1.14(d)) or one (Fig. 1.14(e)) orientations. In the case of rods it seems therefore prudent to define polarity *ad-hoc*, depending on the form of the rods and their interfaces.

To the best of my knowledge, a generalization of the OD groupoid type to polytypes composed of rods and blocks and a deduction of the possible types has not been performed up to know.

NFZ relationship and τ -POs

Since the concept of polarity and orientation is not trivially applied to rods and blocks, the meaning of τ - and ρ -POs is not immediately obvious and the NFZ relationship has to be rephrased. In order to determine the number of possible arrangements of two adjacent modules, the interface between both modules has to be taken into consideration. It will be useful to define τ -POs not for a module in general but for each interface of a module. Thus a λ - τ -PO of an

interface of module will be a λ -PO which transforms an interface into itself. τ -POs which are not λ -POs and ρ -POs will not be used in the context of rods and blocks. The new definition of λ - τ -PO is a generalization of the λ - τ -POs of layers, since in the case of layers a λ - τ -PO of one interface is always a λ - τ -PO of the other interface. Using this definition of λ - τ -PO the concept of continuations and the *NFZ* relationship can be applied as in the case of layers.

OD groupoids and families

The definition of OD groupoids and OD groupoid families of polytypes composed of rods or blocks directly follows the definition for layers (sec. 1.3.6). The number of OD groupoid families for structures composed of rods or blocks of one kind has not been worked out so far. For $M > 1$ kinds of rods or blocks, an argument similar to the one applied to $M > 1$ layers can be applied. The definition of superposition, point group and family structure is analogous to the definition of OD groupoids of structures composed of layers.

Coordinate system

As opposed to structures composed of layers, in structures composed of rods, the directions of missing periodicity need not be the same for all rods (Fig. 1.13(b)), therefore the coordinate system will be defined *ad-hoc*. If all rods are parallel, the basis vectors will be chosen in analogy to the basis vectors of structures composed of layers. For examples for structures composed of rods running along [001] the vectors $\mathbf{a}_0$, $\mathbf{b}_0$ and $\mathbf{c}$ will be used.

MDO polytypes

The concept of MDO polytypes has also been applied to structures composed of rods (Dornberger-Schiff, 1964) and can easily be adapted to structures composed of blocks. For structures composed of rods of $M > 1$ kinds, the amount of possible MDO polytypes can become very large (*e.g.* $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{X}_2$ ($\text{X} = \text{Br}, \text{NO}_3$), sec. 4.2) A systematic procedure for deriving all possible MDO polytypes of structures composed of rods or blocks has not been devised up to now.

Diffraction pattern

As opposed to structures composed of layers, which can be disordered only with respect to the layer direction, structures composed of rods and blocks can be disordered in no or up to two (rods) or three (blocks) directions. Accordingly, characteristic reflections can take the form of sharp spots, streaks, disks or spheres (Dornberger-Schiff, 1964).

1.3.21 Overview of polytypic structures

Tab. 1.5 gives an overview of the structures investigated in this work which will be described as polytypic. The second column from left indicates the type of basic building blocks. With the exception of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ and $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$, which are described as being composed of rods, all structures are composed of layers. The third column indicates whether the structures can be considered OD polytypic, *i.e.* whether all polytypes fulfill the VC. Only in one compound ($\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) the VC is not fulfilled.

In columns four and five the number of crystallochemical and OD layers are listed. Column six indicates whether crystallochemical and OD layers are identical. Only in two structures which can be considered OD polytypic ($\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}$ and $\text{Tl}_2\text{Te}_2\text{O}_6$) crystallochemical and OD layers correspond. Often the boundaries between crystallochemical layers is only one out

Table 1.5: Oxotellurates(IV) presented in this work which can be considered polytypic

Structure	Module type	OD polytypic	Kinds of crystallochemical layers	Kinds of OD layers	OD layers and crystallochemical layers correspond	OD groupoid type	MDO polytype
γ -(CaSr)TeO ₃	layers	yes	-	2	-	IV	mixture of two MDO polytypes
MTe ₂ O ₅	layers	yes	1	2	no	III	yes
Ca ₁₀ Te ₈ O ₂₃ Cl	layers	yes	2	2	yes	III	yes
Ca ₅ Te ₄ O ₁₂ (NO ₃) ₂ ·2H ₂ O	layers	no	2	-	-	-	-
Sr ₄ Te ₄ O ₁₁ Br ₂	rods	yes	2	2	no	IV	yes
Sr ₄ Te ₄ O ₁₁ (NO ₃) ₂	rods	yes	2	2	no	IV	yes
Ca ₃ Te ₃ O ₈ Cl ₂ ·H ₂ O	layers	yes	2	2	no	I	yes
Ca ₇ Te ₁₀ O ₂₄ Cl ₆	layers	yes	2	3	no	IV	yes
KCa ₃ Te ₅ O ₁₂ Cl ₃	layers	yes	2	3	no	IV	yes
MgTeO ₈ H ₈	layers	yes	1	2	no	IV	disordered
Tl ₂ Te ₂ O ₆	layers	yes	2	2	yes	IV	yes

of multiple interfaces of OD layers. The γ -MTeO₃ phases are not composed of layers in the crystallochemical sense.

All of the described structures contain OD layers of two or more kinds (even the structures composed of OD rods can be considered being composed of OD layers, *c.f.* sec. 4.2). This is in stark contrast to the remark by Grell and Dornberger-Schiff (1982), stating that symbols for OD structures composed of one kind of layers have been more useful so far than symbols for OD structures composed of $M > 1$ kinds of layers.

Column seven lists the OD family category, if applicable. The structures composed of rods can be described as a family of OD structures composed of layers of the same category. All structures belong to either a category I, III or IV OD family, and therefore possess at least one kind of non-polar layer. So far no structure belonging to a category II OD family has been described (Ferraris et al., 2004). Column eight indicates whether the structure crystallizes in MDO polytypes. With the exception of the disordered MgTeO₈H₈, all structures are composed either of one or a mixture of two MDO polytypes.

1.4 Superstructures

1.4.1 Introduction

In the 70ies of the last century the superspace approach was developed as a convenient way to describe incommensurately modulated structures and other aperiodic crystals (Wolff, 1974).

Superstructures can be described as a special case of modulated structures and the superspace approach has been fruitfully applied to this case. For example structures in the system $M_2P_2O_7$ ($M = \text{Cr, Zn, Co, Mg, Ni, Cu}$) with different spacegroup symmetry have been described using the same superspace group symmetry (Palatinus et al., 2006). Numerous structures in this work can be described as superstructures and therefore in this chapter the concept of the superspace approach and the notations used to describe superspace symmetry will be introduced.

1.4.2 Modulated structures

The atoms in a crystal structures are characterized by their type, position, ADPs and occupational parameters. For the sake of simplicity, atoms in this chapter will be considered fixed point charges with an occupation of 1. All arguments below can be applied in analogy to the modulation of ADPs and occupational parameters.

A modulated crystal structure is derived from a basic structure, which is periodic in three dimensions. The basic structure is, like ordinary crystal structures, fully characterized by the lattice basis vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and the position of all atoms in the unit cell. Let

$$\mathbf{x}^0(\mu) = x_1^0(\mu)\mathbf{a}_1 + x_2^0(\mu)\mathbf{a}_2 + x_3^0(\mu)\mathbf{a}_3$$

be the position of atom μ in the basic structure relative to the origin of the unit cell with

$$x_1^0(\mu), x_2^0(\mu), x_3^0(\mu) \in [0, 1)$$

(notation according to van Smaalen (2007)). The position of any atom in the basic structure is given by

$$\bar{\mathbf{x}}(\mu) = \mathbf{x}^0(\mu) + \mathbf{l}$$

where $\mathbf{l}$ is a lattice vector

$$\mathbf{l} \in \{n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 | n_1, n_2, n_3 \in \mathbb{Z}\}$$

$\bar{\mathbf{x}}$ is usually expressed using the lattice basis vectors in direct space:

$$\bar{\mathbf{x}}(\mu) = \bar{x}_1\mathbf{a}_1 + \bar{x}_2\mathbf{a}_2 + \bar{x}_3\mathbf{a}_3 \quad (1.1)$$

In a d -dimensionally modulated structure, atoms are displaced from their position in the basic structure by one or more vectors $\mathbf{u}_m^\mu$, $1 \leq m \leq d$. In the case of one-dimensionally modulated structures the subscript m is left out. $\mathbf{u}_m^\mu: \mathbb{R} \rightarrow \mathbb{R}^3$ are plane waves, *i.e.* periodic functions ($\mathbf{u}_m^\mu(x+1) = \mathbf{u}_m^\mu(x)$) with argument $\bar{\mathbf{x}}(\mu) \cdot \mathbf{q}_m + t_m^\mu$. $\mathbf{q}_m$ is called the m th modulation wave vector. It is independent from the atom. The position of an atom in the modulated structure becomes

$$\mathbf{x} = \bar{\mathbf{x}}(\mu) + \mathbf{u}_1^\mu(\bar{\mathbf{x}}(\mu) \cdot \mathbf{q}_1 + t_1^\mu) + \mathbf{u}_2^\mu(\bar{\mathbf{x}}(\mu) \cdot \mathbf{q}_2 + t_2^\mu) + \dots \quad (1.2)$$

In Fig. 1.15 the cases of a one-dimensionally modulated structure with a modulation wave normal to $[100]$ is schematized with purely longitudinal (Fig. 1.15(a)) and transversal (Fig. 1.15(b)) modulation.

Modulation wave vectors $\mathbf{q}$ are expressed using the reciprocal basis vectors of the basic structure:

$$\mathbf{q} = \sigma_1\mathbf{a}_1^* + \sigma_2\mathbf{a}_2^* + \sigma_3\mathbf{a}_3^*$$

The vector is then written in coordinate representation as $\mathbf{q} = (\sigma_1, \sigma_2, \sigma_3)$. If the components σ_1 , σ_2 , and σ_3 are rational one speaks of a commensurate modulation, or if any of the components is irrational of incommensurate modulation.

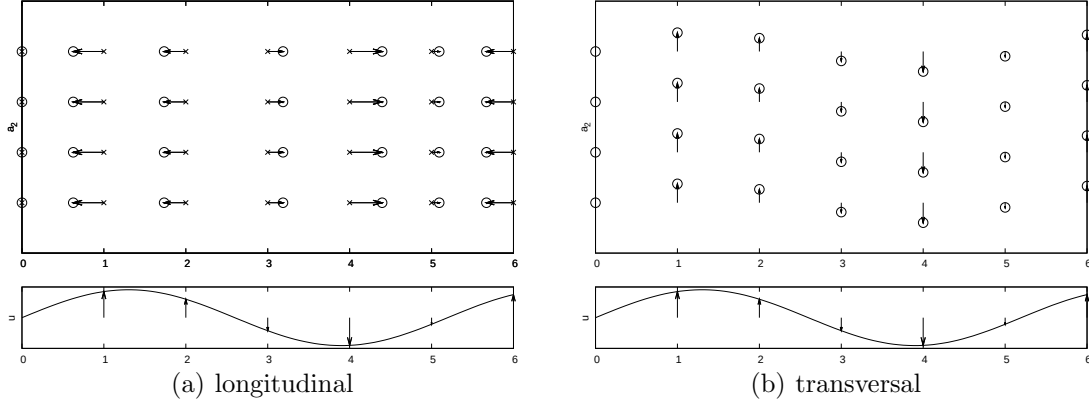


Figure 1.15: Schematic representations of incommensurately modulated crystal structures containing one atom in the unit cell with (a) purely longitudinal ($\mathbf{u}(x) = -0.4 \sin(2\pi x) \mathbf{a}_1$) and (b) purely transversal ($\mathbf{u}(x) = -0.4 \sin(2\pi x) \mathbf{a}_2$) modulations with a modulation wave vector $\mathbf{q} = \frac{1}{\sqrt{27}} \mathbf{a}_1$. Positions of atoms in the basic structure are represented by crosses, of atoms in the modulated structures by circles. The amplitude $u = |\mathbf{u}|$ of the modulation function is plotted at the bottom.

1.4.3 The superspace approach

Incommensurately modulated structures are not periodic in three dimensions, but many results of crystallography are based on the periodicity of crystals. To achieve a periodic description of modulated structures, they are embedded in a $(3+d)$ -dimensional superspace (d being the dimensionality of the modulation). To differentiate between superspace and actual three-dimensional space, the latter will be called physical space.

For a one-dimensionally modulated structure, euclidean (physical) space $\mathbb{R}^3$ is extended by a fourth dimension with a basis vector $\mathbf{b}$ normal to $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. Atoms in superspace are one-dimensional strings perpendicular to the $x_4 = 0$ plane satisfying the equation:

$$\mathbf{x} = \bar{\mathbf{x}}(\mu) + \mathbf{u}^\mu(\bar{\mathbf{x}}(\mu) \cdot \mathbf{q} + t^\mu + x_4) + x_4 \mathbf{b} \quad (1.3)$$

Thus, every atom is its modulation function „rotated” into the fourth dimension (van Smaalen, 2007). For $x_4 = 0$, the equation becomes eq. 1.2. Since the modulation functions $\mathbf{u}^\mu$ are periodic with a period of 1, translation along $\mathbf{b}$ results in a superposition of all atoms and therefore is a symmetry operation of the structure. By substitution with the coordinate representations of $\bar{\mathbf{x}}(\mu)$ (eq. 1.1) and the modulation wave vector $\mathbf{q}$ (eq. 1.4.2), the argument $\bar{\mathbf{x}}(\mu) \cdot \mathbf{q} + t^\mu + x_4$ of the modulation function in equation 1.3 becomes (since $\mathbf{a}_i \cdot \mathbf{a}_i^* = a_i$ and $\mathbf{a}_i \cdot \mathbf{a}_j^* = 0$ for $i \neq j$):

$$\bar{\mathbf{x}}(\mu) \cdot \mathbf{q} + t^\mu + x_4 = \bar{x}_1 \sigma_1 a_1 + \bar{x}_2 \sigma_2 a_2 + \bar{x}_3 \sigma_3 a_3 + t^\mu + x_4$$

Therefore the structure is symmetric by translation along $\mathbf{a}_i + \sigma_i \mathbf{b}$ ($i = 1, 2, 3$). The vectors $\mathbf{a}_i + \sigma_i \mathbf{b}$ ($i = 1, 2, 3$) and $\mathbf{b}$ form a basis in $(3+1)$ -dimensional superspace. They are designated $\mathbf{a}_{si}$:

$$\mathbf{a}_{s1} = \mathbf{a}_1 + \sigma_1 \mathbf{b}$$

$$\mathbf{a}_{s2} = \mathbf{a}_2 + \sigma_2 \mathbf{b}$$

$$\mathbf{a}_{s3} = \mathbf{a}_3 + \sigma_3 \mathbf{b}$$

$$\mathbf{a}_{s4} = \mathbf{b}$$

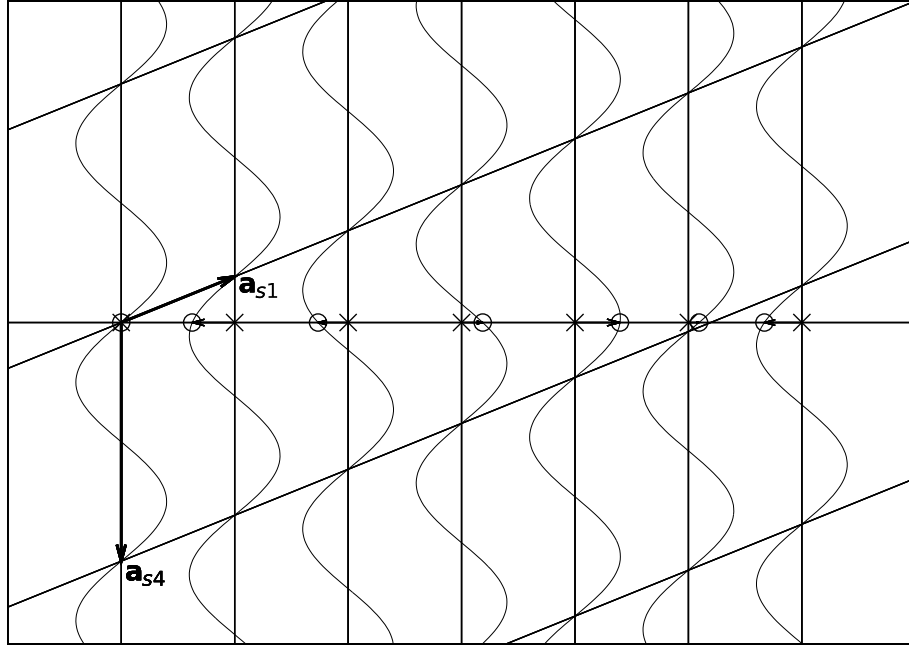


Figure 1.16: Section through the $(\mathbf{a}_{s1}, \mathbf{a}_{s4})$ plane of super space of a modulated crystal structure with longitudinal modulation as in Fig. 1.15(a).

An incommensurately modulated structure is fully characterized by the lattice generated by the vectors $\mathbf{a}_{si}$ and one corresponding unit-cell content in superspace (Fig. 1.16). Every point in physical space exists exactly once per unit cell in superspace and *vice-versa*. To relate superspace and physical space, a distance t from real space is introduced per modulation dimension. It is defined in the one dimensional case as

$$t = x_{s4} - \mathbf{q} \cdot \mathbf{x}.$$

Every cut through superspace with $t = \text{const}$ is equivalent (by translation) to the whole modulated structure in physical space.

The construction of superspace for d -dimensionally modulated structures with $d > 1$ is analogous to the description for $d = 1$ given above. Thus, in two-dimensionally modulated structures atoms are surfaces in $(3 + 2)$ -dimensional superspace, *etc.*

1.4.4 Symmetry in superspace

Superspace must follow the symmetry of the basic structure. Thus, in a one-dimensionally modulated monoclinic structure with unique axis b , the modulation wave vector $\mathbf{q}$ must either have the coordinate representation $(\alpha, 0, \gamma)$ or $(0, \beta, 0)$. In the general case $\mathbf{q} = (\alpha, \beta, \gamma)$, the structure must be two-dimensionally modulated by a second modulation wave vector $\mathbf{q}_2 = (-\alpha, \beta, -\gamma)$. In consequence no cubic structure with (incommensurate) one-dimensional modulation can exist.

Superspace symmetry is a subset of general symmetry in euclidean n -dimensional space. Modulation functions can only be transformed into themselves or on symmetry-equivalent modulation directions. Therefore in the case of a one-dimensionally modulated structure, the matrix

expressing the rotational part of symmetry operations has the form:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} & 0 \\ a_{21} & a_{22} & a_{23} & 0 \\ a_{31} & a_{32} & a_{33} & 0 \\ 0 & 0 & 0 & \pm 1 \end{pmatrix}$$

Symmetry operations may have translational components in direction of the modulation dimension with translation vector $\pm \frac{1}{2}\mathbf{a}_{si}$, $\pm \frac{1}{3}\mathbf{a}_{si}$, $\pm \frac{1}{4}\mathbf{a}_{si}$ or $\pm \frac{1}{6}\mathbf{a}_{si}$ ($i > 3$) (Wolff et al., 1981).

The set of all superspace symmetry operations of a modulated structure and the composition form a group called superspace group. Wolff et al. (1981) introduced two-lined symbols for the description of $(3 + 1)$ -dimensional space groups. In the present work the one-lined notation normed in the *International Tables for Crystallography Vol. C* (Prince, 2004) will be used (e.g. $C2/m(\alpha 0 \beta)0s$). The first part of the symbol describes the symmetry of the basic structure and is identical to the spacegroup symbols according to the *International Tables for Crystallography Vol. A* (Hahn, 1983). In the second part of the symbol the modulation wave vector is indicated using coordinate notation. Incommensurate components are designated by α , β and γ and actual values given in the text. Finally, if symmetry operations with translations along the modulation direction are present, the translational component in modulation direction is indicated for each generating element. The generating elements and their sequence is chosen arbitrarily for each superspace group. Translational components are indicated by the letters s , t , q , h which stand for translations along $\pm \frac{1}{2}a_4$, $\pm \frac{1}{3}a_4$, $\pm \frac{1}{4}a_4$ or $\pm \frac{1}{6}a_4$, respectively.

Superspace group symbols for the case of modulation in $d \geq 2$ dimensions have been used (Yamamoto, 1996) but are not normed so far. van Smaalen (2007) recommends *ad-hoc* definitions. In this work only symbols for the one-dimensional case will be used.

1.4.5 Diffraction pattern

The diffraction pattern of a modulated structure can be constructed from the superspace description introduced in sec. 1.4.6. The Fourier transform of a structure periodic in n -dimensional superspace is a discrete pattern in n -dimensional reciprocal superspace. The lattice is generated by the basis vectors $(\mathbf{a}_{s1}^*, \dots, \mathbf{a}_{sn}^*)$. For $i = 1 \dots 3$, $\mathbf{a}_{si}^*$ is identical to the reciprocal lattice vectors of the basic structure $\mathbf{a}_i^*$. For $i > 3$, $\mathbf{a}_{si}^* = \mathbf{q}_{(i-3)} + \mathbf{b}_{(i-3)}^*$ where $\mathbf{q}$ are the modulation wave vectors and $\mathbf{b}_i^*$ are vectors parallel to the vectors $\mathbf{b}_i$ defined in sec. 1.4.6 with $\mathbf{b}_i \mathbf{b}_i^* = 1$. Every peak or reflection can be indexed with n integers. In the $(3 + 1)$ -dimensional case they are often designated h , k , l and m or more generally and in the higher-dimensional cases $h_1, h_2, h_3, \dots, h_n$. Reflections with all h_i , $i > 3$ zero are called basic structure reflections. They correspond to the Fourier transform of the basic structure. Reflections with any $h_i > 0$, $i > 3$ are called satellite reflections. $\sum_{i>3} h_i$ is the order of the reflection⁹. In modulated structures the intensity of the reflections decreases rapidly with the order of the reflections. Thus often only satellites of first or second order can be determined. Only in very rare case reflections up to the order nine were observed (Marmeggi et al., 1990). In Fig. 1.17 two common cases are depicted: a twinned one-dimensionally modulated structure (Fig. 1.17(a)) and a two-dimensionally modulated structure (Fig. 1.17(b)). They can be differentiated by the occurrence or absence of second order reflections which can only be indexed using two modulation wave vectors.

The diffraction pattern obtained by single crystal X-ray diffraction (XRD) corresponds to the projection of the diffraction pattern in superspace along the vectors $\mathbf{b}_i$. In the general case

⁹ In the case of hexagonal lattices with d -dimensional modulation ($d \geq 3$), the expression for the satellite-order can be more complex (van Smaalen, 2007).

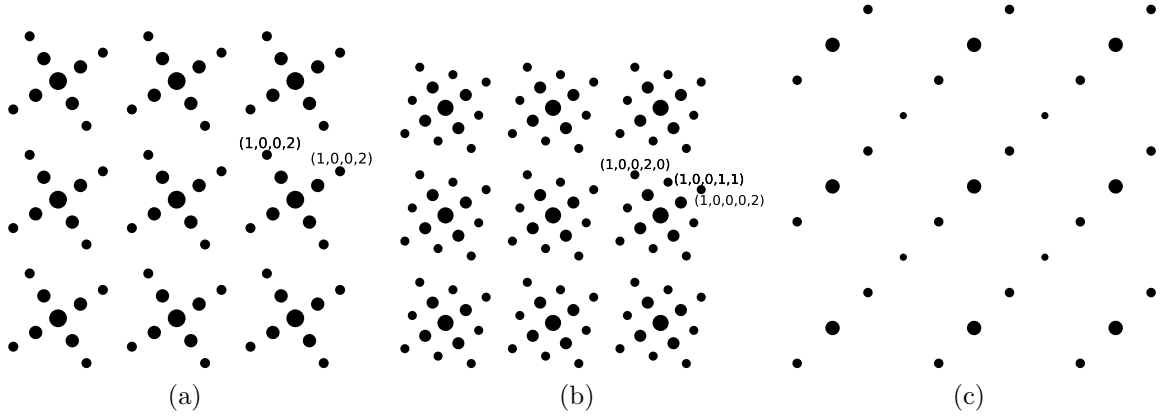


Figure 1.17: Schematic representation of the $hk0$ plane in reciprocal space of (a) a one dimensionally modulated structure with a pseudo-tetragonal basic structure with a modulation wave vector $\mathbf{q} \approx (\sigma_1, \sigma_2, 0)$ twinned by a fourfold axis normal to (001) and (b) a two dimensionally modulated tetragonal structure with modulation wave vectors $\mathbf{q}_1 = (\sigma_1, \sigma_2, 0)$ and $\mathbf{q}_2 = (\sigma_2, \sigma_1, 0)$ and (c) a fourfold superstructure of a basic structure with pseudo-tetragonal metrics. The basic structure reflections are represented by large disks, satellite reflections of order one and two by succinctly smaller disks.

of incommensurately modulated structures and satellites of arbitrary order, arbitrarily close and therefore overlapping reflections would be observed. Yet, in realistic cases, due to the rapid decline of intensities with increasing order, no or only few reflections are overlapping. As in the case of non-modulated structures, symmetry operations with translational components cause systematic extinctions in the diffraction pattern. For example structures crystallizing in superspace group $C2/m(\alpha 0 \gamma)0s$ reflections $h0km$ with $m = 2n + 1$, $n \in \mathbb{Z}$ are extinct, as opposed to the case of $C2/m(\alpha 0 \gamma)$ Orlov et al. (2008).

1.4.6 Superstructure

A superstructure can be considered a commensurately modulated structure, *i.e.* all components of the modulation wave vectors are rational. It can therefore be described using the superspace approach. Whereas in the case of incommensurately modulated structures every point in the unit cell in superspace is found in the physical structure, in commensurately modulated structures only a finite amount of sections through superspace have a physical meaning. For a superstructure with multiplicity m , these are cuts at $t = \frac{n}{m} + t_0$, $m \in \mathbb{Z}$. The remaining part of superspace, and accordingly the modulation functions, is undefined. In Fig. 1.18, two commensurate modulation functions resulting in the same superstructures are depicted. The modulation function can be decomposed into harmonic waves. $\frac{m}{2}$ harmonic waves are needed and sufficient to describe the modulation of an atom, thus the same amount of parameters is needed in the superspace description and the traditional approach using m atoms in physical space.

As opposed to an incommensurately modulated structure, a superstructure is periodic in physical space, with reduced translational group compared to the basic structure. The symmetry of the actual structure on the superspace group, the modulation wave vector and t_0 . For example superstructures with superspace group $P2/m(\frac{1}{3} \frac{1}{3} \frac{1}{2})$ have symmetry $A2/m$ for $t_0 = \frac{n}{12}$ or Am in the general case (Orlov et al., 2008). In the latter case, it seems favourable to use a superspace group of lower symmetry which more adequately reflects the symmetry requirements of the

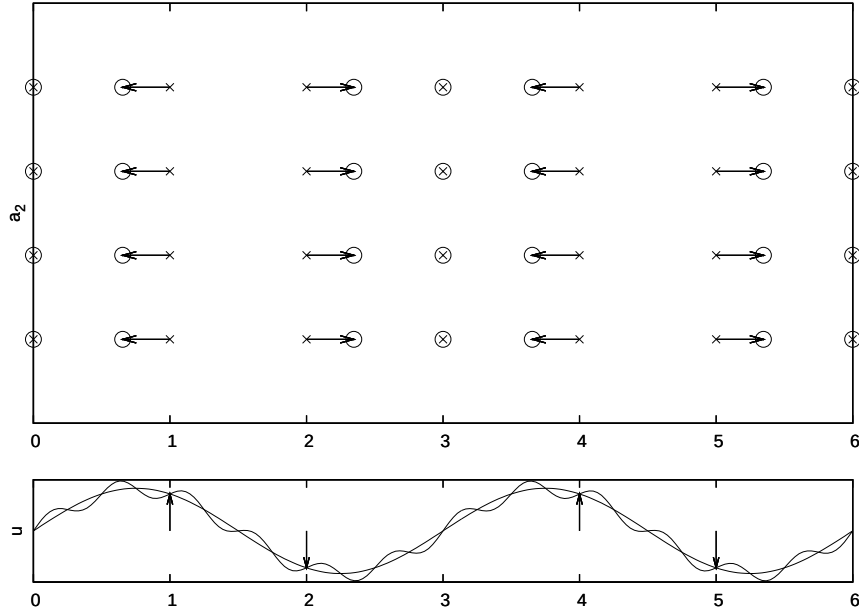


Figure 1.18: Schematic representation of a threefold superstructure with longitudinal modulation. Two modulation functions resulting in the same superstructure are depicted. Symbols as in Fig. 1.15.

superstructure.

Using the superspace approach, satellite reflections of an m -fold superstructure with order $i > \frac{m}{2}$ are projected on the same position as either a basic structure reflection or a satellite reflection of order $i < \frac{m}{2}$ (Fig. 1.17(c)).

Chapter 2

Used methods

2.1 Preparative Methods

2.1.1 Reaction containers

High temperature reactions with reactants that are prone to oxidation or evaporation were performed in evacuated fused silica ampoules. Fused silica tubes of *c.a.* 1 m length and 1 cm diameter were sealed on one end using an oxyhydrogen flame. The remaining open end was attached to a ground fused silica joint. The sample was introduced into the tube either as-is or, in the case of reactants that react with silica, placed in Au or corundum crucibles. The tube was then thinned to a capillary using a oxyhydrogen flame. Finally, the tube was evacuated using a rotary oil pump and the capillary closed. Thus ampoules of with varying length between 4–10 cm were obtained.

For high temperature reactions with reactants that are not sensitive to atmospheric conditions, corundum or porcelain crucibles were used. Reactions under hydrothermal conditions were performed in steel autoclaves with teflon inlays. The teflon inlays had 5–10 ml sample volume.

2.1.2 Furnaces

High temperature reactions were usually performed in muffle furnaces. Tab. 2.1 lists the used furnaces and their nominal maximum temperatures. All furnaces were equipped with programmable temperature controllers. For reactions under hydrothermal conditions, autoclaves were placed in a Heraeus UT6060 drying oven operated at a constant temperature ≤ 513 K.

Table 2.1: Used muffle furnaces and nominal maximum temperatures T_{max} .

Furnace	T_{max} [K]
Carbolite RHF 1600	1873
Heraeus KM 170	1423
Nabertherm N 11	1373
Nabertherm LHT 04/16	1873
Nabertherm C 30	1373

Table 2.2: Source and quality of used chemicals

Chemical	Supplier	Quality
<i>Solids</i>		
BaBr ₂ ·2H ₂ O	Riedel-de Haën	<i>p.a.</i>
BaCl ₂ ·2H ₂ O	Sigma-Aldrich	ACS > 99%
CaCl ₂ ·2H ₂ O	Merck	<i>p.a.</i> > 99.5%
Ca(NO ₃) ₂ · 4H ₂ O	Merck	<i>p.a.</i> > 98.5%
CaCO ₃	Merck	<i>p.a.</i>
Gelatin	Dr. Oetker	Food grade
H ₆ TeO ₆	Aldrich	97.5%–102.5%
MgCl ₂ ·6H ₂ O	Fluka	puriss > 99%
NaOH	Riedel-de Haën	> 98%
NH ₄ Cl	Merck	<i>p.a.</i> > 98.5%
KOH	Merck	<i>p.a.</i> > 85%
SrCO ₃	Merck	puriss
SrNO ₃	Merck	<i>p.a.</i> > 99%
SrBr ₂ ·2H ₂ O	<i>unknown</i>	<i>unknown</i>
SrCl ₂ ·6H ₂ O	Aldrich	ACS > 99%
TeO ₂	Sigma-Aldrich	> 99%
TeO ₂	Merck	puriss
Tl	Aldrich	> 99.5%
Tl ₂ CO ₃	Fluka	puriss
Tl ₂ O ₃	<i>unknown</i>	<i>unknown</i>
<i>Liquids</i>		
aq. NH ₃ solution (25% _{wt})	Merck	<i>p.a.</i>
acetone	Merck	<i>p.a.</i> > 99.5%

2.1.3 Chemicals

Unless noted otherwise, chemicals were obtained commercially and used without purification. Tab. 2.2 lists the quality and the supplier of the used chemicals.

2.2 Analytical Methods

2.2.1 Single crystal diffraction

Single crystals were separated under a polarizing microscope and fixed on glass fibres using a cyanoacrylate based glue. Three different single crystal diffractometers were used to collect reflection intensities. All data were obtained using $MoK\alpha$ radiation, $\lambda = 0.71073$ Å.

A Bruker AXS SMART APEX three-circle diffractometer equipped with a charge-coupled device (CCD) camera was used to collect data at room temperature (RT) and at cryogenic temperatures in a dry N₂ stream using a Oxford Cryosystems Series 700 instrument. Typically three independent sets of 600 frames were measured with 55 mm detector distance in the ω -scan technique with 0.3° frame width, thus scanning the whole reciprocal sphere with high redundancy.

RT data was collected on a Bruker AXS SMART APEX II four-circle diffractometer with κ -geometry. The orientation matrix of the crystal was determined in a preliminary measurement

with three runs over 6° using the ω -scan technique. The detector distance and measurement program were then optimized from the lattice parameters, the orientation matrix, the crystal mosaicity and intensities of reflections to obtain full completeness and high redundancy, while avoiding overlapping reflections. Data were collected in the ϕ - and ω -scan techniques using 0.5° frame width.

Measurements above RT were performed on a NONIUS Kappa-CCD four circle diffractometer using the ω -scan technique. 414 frames with 2° rotation width were collected in 9 runs. Heating and cooling was performed by a stream of dry N_2 .

Frames were integrated using the SAINT PLUS software (Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2007). Absorption correction was applied using the multi-scan approach implemented by SADABS (Sheldrick, 2001) or by numerical methods implemented by HABITUS (W. Herrendorf, 1997). Crystal structures were solved and refined using the SHELX software package (Sheldrick, 2008). Coordinates of a first refinement cycle were obtained by direct methods or from known closely related structures. Drawings of structural details were produced using the software ATOMS (Dowty, 2006).

2.2.2 X-ray powder diffraction (XRPD)

Microcrystalline or bulk samples were characterized using X-ray powder diffraction (XRPD). Samples with low volume were placed on silicon single-crystal sample holders, samples with large volume on steel sample holders with a cut-out. To avoid texture or preferred orientation effects, samples were ground in an agate mortar under acetone. Measurements were performed on a Philips X'Pert Pro diffractometer with Bragg-Brentano geometry equipped with an X'Celerator multi-channel detector with 2.546° scan length with $Cu\ K\alpha_{1,2}$ radiation ($1.54060\ \text{\AA}$, $1.54439\ \text{\AA}$) in the 2θ range $5\text{--}70^\circ$ with 24.8 s exposure time per scan length. The scans were finally converted into 0.02° step-size bins.

2.2.3 Thermal analysis

Simultaneous thermogravimetry (TG)/differential scanning calorimetry (DSC) experiments were performed on a NETZSCH 409 PC *Luxx* Thermobalance in a Pt crucibles equipped with Ar and synthetic air. TG measurements were conducted on a NETZSCH 209 *F3* Thermobalance in Al_2O_3 crucibles under Ar and synthetic air atmosphere. Low temperature (233–273 K) DSC measurements were performed on a NETZSCH DSC 204 *F1 Phoenix* and a NETZSCH 200 *F3* Differential Scanning Calorimeter.

2.2.4 Vibrational spectroscopy

Raman spectra were recorded on a Jobin Yvon LabRAM HR Raman microscope and on a Renishaw RM1000 Mikro-Raman Spectrometer. In both cases the 632.8 nm line of a He/Ne laser was used. Spectra in the mid-infrared (MIR) range were recorded on a Bruker Tensor 27 FTIR spectrometer equipped with an attenuated total reflection (ATR) cell. Samples were either placed on the ATR cell or measured in transmission. In the latter case a small amount of sample was dispersed in dry KBr and pressed into pellets of *ca.* 1 mm thickness.

Chapter 3

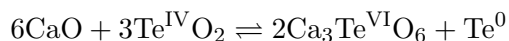
Oxotellurates(IV) of calcium and strontium

3.1 Introduction

3.1.1 Known phases in the system $\text{Ca}/\text{Te}^{\text{IV}}/\text{O}$

First systematic investigations of phases with composition CaTeO_3 date back to the mid-sixties of the last century. Independent studies reported preparation and thermal behaviour of calcium tellurate(IV) starting from the hydrous phase $\text{CaTeO}_3 \cdot \text{H}_2\text{O}$ (Ivankova et al., 1966), from solid state reaction of $\text{CaCO}_3/\text{TeO}_2$ mixtures (Malyutin et al., 1969), or from thermal decomposition of CaH_4TeO_6 , which also revealed a high-temperature modification above 1123 K (Knyaceva and Gushchina, 1968). In subsequent studies, Trömel and Ziethen-Reichenach (1970) reported two CaTeO_3 modifications stable at room temperature. However, none of the XRPD data reported in these publications were indexed. Some years later, dimorphism of CaTeO_3 at room temperature was also observed (Wroblewska et al., 1979), but (unindexed) prominent reflections in the XRPD pattern deviated significantly from the previous investigation by Trömel and Ziethen-Reichenach (1970). The most recent experiments employing thermal analysis and XRPD methods (Mishra et al., 1998b; Tripathi et al., 2001) revealed only one stable room temperature modification (α) and two high-temperature polymorphs (β - and γ - CaTeO_3). The phase transition temperatures from α - to β - and from β - to γ - CaTeO_3 were reported as 1155 and 1167 K, respectively (Tripathi et al., 2001). Corresponding XRPD patterns were indexed (Tripathi et al., 2001) on the basis of triclinic (α), monoclinic (β) and hexagonal cells (γ). However, all derived cells are dubious because prominent reflections of the compound $\text{Ca}_4\text{Te}_5\text{O}_{14}$ with a very similar composition (ratio $\text{CaO}:\text{TeO}_2 = 4:5$ instead of 1:1) were used for indexation of the three CaTeO_3 polymorphs. The crystal structure of $\text{Ca}_4\text{Te}_5\text{O}_{14}$ was unknown at that time but has been fully characterized in the meantime by single crystal structure analysis (Weil, 2004). Therefore it is most likely that a phase mixture consisting of various CaTeO_3 polymorphs and $\text{Ca}_4\text{Te}_5\text{O}_{14}$ instead of single CaTeO_3 phases were used for the indexing procedure (Tripathi et al., 2001). A ferroelectric phase transition in CaTeO_3 at 293 K was reported by Rai et al. (2002).

Experiments in evacuated silica ampoules performed for the present work have shown that three thermodynamically stable crystalline phases with composition $(\text{CaO})_x \cdot (\text{TeO}_2)_y$ exist at 973 K: CaTe_2O_5 , $\text{Ca}_4\text{Te}_5\text{O}_{14}$ and α - CaTeO_3 . Attempts to obtain phases with a $\text{CaO}:\text{TeO}_2$ ratio > 1 always resulted in disproportionation of Te^{IV} according to



as was already noted by Trömel and Ziethen-Reichenach (1970). Even repeating the reaction with a large excess of Te in order to shift the equilibrium to the left side did not produce a measurable amount of any $(\text{CaO})_x \cdot (\text{TeO}_2)_y$ phase containing more than one equivalent of Ca. On the other hand, using more than two parts of TeO_2 per part CaO resulted in formation of CaTe_2O_5 (Wroblewska et al., 1979) and unreacted TeO_2 .

Of these three $(\text{CaO})_x \cdot (\text{TeO}_2)_y$ phases only the crystal structure $\text{Ca}_4\text{Te}_5\text{O}_{14}$ (Weil, 2004) was determined up to now. The ditellurate(IV) CaTe_2O_5 was investigated by Redman et al. (1970); Sadovskaya et al. (1983, 1987); Tripathi et al. (2001); Barrier (2010). Four different polymorphs were identified by XRPD (Tripathi et al., 2001). The XRPD pattern of the RT phase $\alpha\text{-CaTe}_2\text{O}_5$ is complex. It has distinct main reflections which were indexed by Redman et al. (1970) in a monoclinic crystal system. The lattice parameters were confirmed and the basic structure solved by Barrier (2010) using electron diffraction and XRPD experiments. Structure elucidation of the actual structure was unsuccessful so far since CaTe_2O_5 crystallizes in mica-like platelets with high stacking-fault probability as do the Sr and Cd analogues (Redman et al., 1970). An unrelated non-twinned CaTe_2O_5 phase was recently obtained by hydrothermal synthesis (Weil and Stöger, 2008; Barrier et al., 2009). Structures of hydrous phases in the system Ca/Te/O have not been characterized up to now.

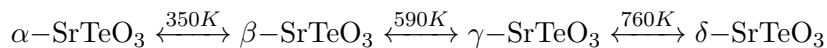
At temperatures above 1173 K compounds with a CaO:TeO₂ ratio < 1 are unstable. Thermogravimetry (TG) experiments performed during the present work showed that $\text{Ca}_4\text{Te}_5\text{O}_{14}$ slowly decomposes under loss of TeO_2 in order to give CaTeO_3 . This fact can be used to obtain single phase CaTeO_3 samples by using a small excess of TeO_2 . At elevated temperatures, the formed $\text{Ca}_4\text{Te}_5\text{O}_{14}$ will thereby slowly transform into CaTeO_3 .

None of the three CaTeO_3 polymorphs indexed by Mishra et al. (1998b) correspond to any of the α , β , β' or γ - CaTeO_3 phases reported here. The major reflections in the XRPD pattern of „ $\alpha\text{-CaTeO}_3$ ” obtained by Mishra et al. (1998b) can be assigned to a mixture of the Te-rich phase $\text{Ca}_4\text{Te}_5\text{O}_{14}$ and $\alpha\text{-CaTeO}_3$, whereas the origin of the reflections of „ β -” and „ $\gamma\text{-CaTeO}_3$ ” remains unclear.

3.1.2 Known phases in the system Sr/Te^{IV}/O

The ferroelectric properties of SrTeO_3 were discovered 35 years ago (Yamada, 1975; Simon et al., 1979; Ismailzade et al., 1979). It has interesting physical and optical properties setting it aside from other ferroelectrics. For this reason its polymorphism has been intensely studied (Bergman et al., 1969; Yamada and Iwasaki, 1972, 1973; Burckhardt et al., 1984; Mishra et al., 1998a). The symmetry of the crystal structures of the various polymorphs has been subject to intense debate. Early results indicating a centrosymmetric space group $C2/c$ for the RT phase (Yamada, 1975; Ismailzade et al., 1979; Elerman, 1993) have been challenged by second harmonic generation methods suggesting a non-centrosymmetric space group (Ivanov, 2001).

Only recently the structures of all four thermodynamically stable SrTeO_3 polymorphs have been reliably determined by single crystal XRD (Dityatiev et al., 2006; Zavodnik et al., 2007a,c,b, 2008). Four thermodynamical stable phases have been structurally identified (Zavodnik et al., 2007a), with the following transition temperatures:



Their thermal behaviour is highly unusual because the stability ranges of the practically identical (same symmetry and very similar atomic coordinates) phases α - and γ - SrTeO_3 are intermitted by a temperature range in which the β - SrTeO_3 phase with different symmetry is stable. A more detailed description of the relationship of the four polymorphs will be given in sec. 3.3.7. The

experiments performed during this work suggest that under varying conditions, both the non-centrosymmetric α - and the centrosymmetric β -polymorphs may be obtained at RT, leading to the contradicting earlier results.

A fifth polymorph, *viz.* ϵ -SrTeO₃ was obtained recently by thermal dehydration of the monohydrate SrTeO₃·H₂O and the structure elucidated from XRPD data (Weil et al., 2010). The structure forms topochemically from the monohydrate and thus is closely related to SrTeO₃·H₂O. The latter crystallizes isotypically with BaTeO₃·H₂O (Nielsen et al., 1971).

A mica-like ditellurate SrTe₂O₅ has been described by Redman et al. (1970). Like for the Ca homologue, structure determination was unsuccessful so far due to high stacking fault probability. A high temperature SrTe₂O₅ polymorph was described by Klc et al. (1984); Mishra et al. (1998a). Other phases in the system Sr/Te^{IV}/O include Sr₃Te₄O₁₁ (Dityatiev and Dolgikh, 1999), the mixed valent SrTe₃O₈ (Barrier et al., 2006; Weil and Stger, 2007) and the metastable tellurium rich phase SrTe₅O₁₁ (Burckhardt and Trmel, 1983). The structure parameters of the latter were obtained from XRPD data and are problematic due to excessively large temperature factors and can not be considered reliable. The only hydrous phase in the system Sr/Te^{IV}/O that has been described so far is the mono-hydrate SrTeO₃·H₂O (Weil et al., 2010).

3.2 Preparation of precursor compounds

Employed CaO was prepared by heating CaCO₃ in porcelain crucibles at 1123 K for 10 h under atmospheric conditions. CaO/SrO mixtures were prepared by heating the corresponding CaCO₃/SrCO₃ mixtures in porcelain crucibles at 1573 K for 12 h.

3.3 Single crystals in the system MTeO₃

3.3.1 Preparation

All experiments were performed in evacuated silica-ampoules. At temperatures above 1000 K and when employing precursors containing Sr, the samples were put into gold or alumina crucibles in order to prevent reaction with the wall of the ampoule. Quenching of reaction mixtures from different temperatures was performed in a cold-water bath.

Single crystals of α -CaTeO₃ were obtained by heating a CaO:TeO₂ mixture with a 10% excess of TeO₂ at 1273 K and slowly cooling to 1000 K over the course of 70 h.

A mixture of single crystals of β -CaTeO₃ and γ -CaTeO₃ was obtained by heating the same mixture to 1273 K over the course of 70 h and by quenching the reaction container. When small gold crucibles (6 mm diameter, 1 mm height) and little sample weight (less than 10 mg) were used, the sample contained only γ -CaTeO₃. With alumina crucibles (20 mm × 3 mm, 2 mm wall thickness) single-phase β -CaTeO₃ was obtained.

Single crystals of the composition Ca_xSr_{1-x}TeO₃ ($x = 0.80, 0.77, 0.55, 0.14, 0.07$) were obtained in the same way by replacing CaO with the corresponding CaO:SrO mixtures with employed ratios of 3:1, 2:1, 1:1, 1:8 and 1:16 respectively. The reaction conditions of different batches are summarized in Tab. 3.1. The β - to γ -ratio obtained in different batches from melts varied notably. Up to now all the factors that come into play, like heating program, sample size and crucible material for synthesis, for preparation of single phase material are not fully understood.

Table 3.1: Details of the crystal growth experiments in the system M/TeO_3 . Mass percentages according to Rietveld refinement (FULLPROF (Rodríguez-Carvajal, 1993)) of XRPD measurements.

Sample weight	Crucible	T [K]	t [h]	Remarks	Result
60.0 mg CaO, 175.6 mg TeO ₂	Au	1273	70	molten, quenched	91% γ -CaTeO ₃ (single crystals), 9% β -CaTeO ₃ (single crystals)
60.0 mg CaO, 175.6 mg TeO ₂	Au	1273	70	molten, quenched, small crucible, 10 mg sample weight [†]	γ -CaTeO ₃ (single crystals)
60.0 mg CaO, 175.6 mg TeO ₂	Al ₂ O ₃	1273	70	molten, quenched	β -CaTeO ₃ (single crystals)
60.0 mg CaO, 175.6 mg TeO ₂	Al ₂ O ₃	1273 $\rightarrow$ 1000	70 h	molten	α -CaTeO ₃ (single crystals), unknown phase
65.6 mg Ca _{0.80} Sr _{0.20} O, 180 mg TeO	Al ₂ O ₃	1223 $\rightarrow$ 1170	70	molten, quenched	Ca _{<i>x</i>} Sr _{1-<i>x</i>} TeO ₃ (γ -Ca) [†] (single crystals), unknown phase
77.0 mg Ca _{0.67} Sr _{0.33} O, 190 mg TeO ₂	Al ₂ O ₃	1223 $\rightarrow$ 1170	70	molten, quenched	Ca _{0.77} Sr _{0.23} TeO ₃ (γ -Ca) (single crystals), unknown phase
85.5 mg Ca _{0.5} Sr _{0.5} O, 190 mg TeO ₂	Al ₂ O ₃	1223 $\rightarrow$ 1170	70	molten, quenched	Ca _{0.55} Sr _{0.45} TeO ₃ (γ -Ca) (single crystals), unknown phase
98.3 mg Ca _{0.11} Sr _{0.89} O, 180 mg TeO	Al ₂ O ₃	1223 $\rightarrow$ 1170	70	molten, quenched	Ca _{0.14} Sr _{0.86} TeO ₃ (β -Ca) (single crystals), unknown phase
100.8 mg Ca _{0.07} Sr _{0.93} O, 180 mg TeO	Al ₂ O ₃	1223 $\rightarrow$ 1170	70	molten, quenched	Ca _{0.07} Sr _{0.93} TeO ₃ (β -Sr)(single crystals), unknown phase

[†] Only 10 mg of the reactant mixture were used.

[‡] Composition could not be determined reliably.

3.3.2 Single crystal diffraction

Data of single crystals of $\alpha\text{-CaTeO}_3$, $\gamma\text{-CaTeO}_3$ and $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ ($x = 0.55$ and $x = 0.77$) were collected at RT. Three independent sets of 600 frames with 0.3° rotation width were measured thus scanning the whole reciprocal sphere with high redundancy.

Diffraction intensities of single crystals of $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ ($x = 0.07, 0.14, 0.80$) were collected at RT in multiple sets in ω - and ϕ -scan techniques, optimized for completeness and redundancy. In total 2291 ($x = 0.07$), 3906 ($x = 0.14$) and 2677 ($x = 0.80$) frames with 0.5° rotation width were recorded.

Data of β - and β' - CaTeO_3 crystals were collected at 200, 250, 275, 295, 325, and 350 K using the ω -scan technique with 2.0° rotation width on 414 frames in 9 runs. Cooling and heating was performed by a stream of nitrogen.

More details of the various data collections are summarized in Tab. 3.2–3.5. Relative atomic coordinates and isotropic ADP are listed in Tab. C.1–C.13.

3.3.3 Overview

All structures described to this section belong to one of the novel α -, β -, β' -, β'' -, γ - CaTeO_3 structure types or are isotypic to the known β - SrTeO_3 (Zavodnik et al., 2007b) structure type. The structure type of solid solutions $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ will be indicated in parentheses. For example $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TeO}_3$ (β -Ca) designates the β - CaTeO_3 structure type, $\text{Ca}_{0.04}\text{Sr}_{0.96}\text{TeO}_3$ (β -Sr) the β - SrTeO_3 structure type, etc... γ - CaTeO_3 will be discussed before β - CaTeO_3 , because the structure of the latter can be described as a superstructure based on the former.

3.3.4 The α - CaTeO_3 structure type

α - CaTeO_3 features two crystallographically different nearly cylindrical channels (diameter ≈ 4 Å) with rod group ∞_3 running along $0, 0, z$ and $\frac{1}{2}, \frac{1}{2}, z$, respectively (Fig. 3.1). Each channel is delimited by two crystallographically different $[\text{Te}^{\text{IV}}\text{O}_3]$ units (Te1, Te5 and Te2, Te4, respectively) with the electron lone pair E of the Te atoms oriented towards the centre of the channel (Fig. 3.2). A fifth $[\text{Te}^{\text{IV}}\text{O}_3]$ unit (Te3) is located between the channels with the electron lone pair oriented into an enclosed cavity. These units are connected by two Ca atoms (Ca3 and Ca5) forming infinite chains along $[001]$ with rod group ∞_2 (Fig. 3.3). The different $[\text{Te}^{\text{IV}}\text{O}_3]$ units share corners and edges with five different irregular $[\text{CaO}_x]$ ($x = 6 - 8$) polyhedra, that fill the space between the channels, establishing a framework structure. The trigonal-pyramidal shape of the $[\text{Te}^{\text{IV}}\text{O}_3]$ units is characteristic for three-coordinated Te^{IV} atoms (Zemann, 1971). All Te–O distances (Tab. 3.6) are in good agreement with the data given in a review on the crystal chemistry of oxotellurium(IV) compounds (Dolgikh, 1991). The lone pair electrons of the Te^{IV} atoms are stereochemically active and are located in the channels (Te1, Te2, Te4 and Te5) and in enclosed cavities (Te3). The Ca–O distances range from 2.262(4) to 3.033(5) Å, which compares well with those observed for other structures in the $\text{Ca}/\text{Te}^{\text{IV}}/\text{O}$ system, *viz.* $\text{Ca}_4\text{Te}_5\text{O}_{14}$ (Weil, 2004) and CaTe_2O_5 (Weil and Stöger, 2008). Moreover, the average Ca–O distance of 2.46 Å is in good agreement with the value of 2.42 Å calculated from the sum of the ionic radii of O^{2-} and seven coordinate Ca^{2+} given by Shannon (1976).

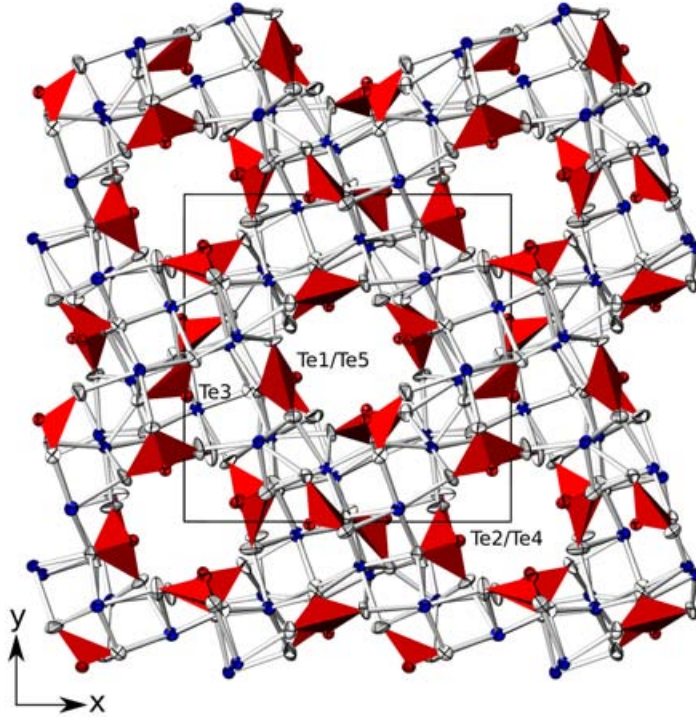


Figure 3.1: The crystal structure of α -CaTeO₃ viewed down [001]. [Te^{IV}O₃] units and Te atoms are given in red, Ca atoms are dark blue and O atoms white. Displacement ellipsoids represent 90% probability levels.

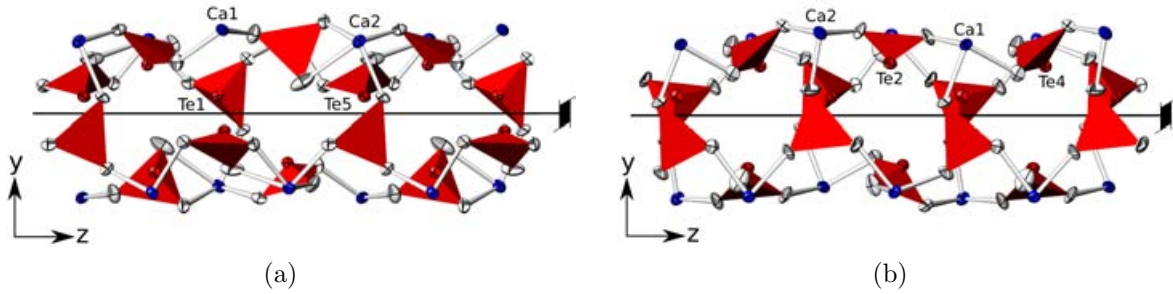


Figure 3.2: The two different channels in α -CaTeO₃, delimited by (a) Te1 & Te5 and (b) Te2 & Te4, respectively, viewed down [100]. Colour codes and displacement ellipsoids as in Fig. 3.1. Graphical symmetry element symbols according to the *International Tables* (Hahn, 1983).

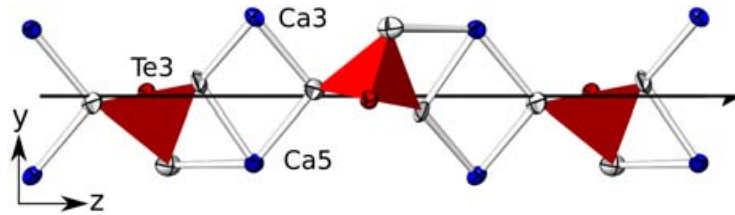


Figure 3.3: α -CaTeO₃: $\frac{1}{\infty}[\text{TeCa}_2\text{O}_3]^{2+}$ chain built of [Te₃O₃] units connected by Ca3 and Ca5 atoms with symmetry 2₁ running along [001], as viewed down [100]. Colour codes, displacement ellipsoids and symbols as in Fig. 3.2.

Table 3.2: Crystal data and details of the refinements of $\alpha\text{-CaTeO}_3$, and the mixed Ca/Sr phase $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ ($\beta\text{-Sr}$)

	$\alpha\text{-CaTeO}_3$	$\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ ($\beta\text{-Sr}$)
Crystal data		
Chemical formula	CaTeO_3	$\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$
M_r	215.68	236.91
Symmetry	Tetragonal, $P4_3$	Monoclinic, $C2/c$
Temperature [K]	295(2)	295(2)
a, b, c [Å]	12.1070(10), 12.1070(10), 11.0911(18)	27.9800(3), 5.89650(10), 28.3527(3)
α, β, γ [°]	90, 90, 90	90, 114.280(10) , 90
V [Å ³]	1625.7(3)	4263.98(10)
Z	20	48
D_x [Mg·m ⁻³]	4.406	4.855
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	10.515	22.043
Crystal form, colour	Fragment, colourless	Fragment, colourless
Crystal size [mm]	$0.06 \times 0.06 \times 0.02$	$0.12 \times 0.05 \times 0.04$
Data collection		
Diffractometer	SMART APEX	SMART APEX II
Data collection method	ω scans	ω and ϕ scans
Absorption correction	<i>SADABS</i>	<i>SADABS</i>
T_{min}, T_{max}	0.571, 0.817	0.178, 0.473
No. of measured, independent and observed reflections	18973, 4932, 4591	64744, 13135, 10073
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.030	0.042
θ_{max} [°]	30.5	30.5
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.030, 0.058, 1.03	0.032, 0.078, 1.05
No. of reflections	4932	13135
No. of parameters	226	284
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0238P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_0^2) + (0.0278P)^2 + 35.9344P]$ where $P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.003
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	1.60, -0.91	6.23, -5.67
Absolute structure	Flack (1983)	-
Flack parameter	0.05(3)	-
Extinction method	-	SHELXL
Extinction coefficient	-	0.000209(9)

3.3.5 The $\gamma\text{-CaTeO}_3$ structure type

Refinement

During refinement of $\gamma\text{-CaTeO}_3$ in spacegroup $P2_1/c$ excessive residual electron density in the difference Fourier map was observed and could not be explained by a simple structure model. The three highest residual peaks were on positions $x' = x$, $y' = \frac{1}{2} - y$, $z' = z$ relative to a Te and two Ca atoms, respectively, suggesting a mirror plane normal to the y -axis. Closer

Table 3.3: Crystal data and details of the refinements of γ -CaTeO₃, and the mixed Ca/Sr phases Ca_{*x*}Sr_{1-*x*}TeO₃ ($x = 0.77, 0.55$)

	γ -CaTeO ₃ , MDO ₁ (MDO ₂)	Ca _{0.77} Sr _{0.23} TeO ₃	Ca _{0.55} Sr _{0.45} TeO ₃
Crystal data			
Chemical formula	CaTeO ₃	Ca _{0.77} Sr _{0.23} TeO ₃	Ca _{0.55} Sr _{0.45} TeO ₃
M_r	215.68	215.68	226.61
Symmetry	Monoclinic, $P2_1$ ($P2_1/c$)	Monoclinic, $P2_1$	Monoclinic, $P2_1$
Temperature [K]	295(2)	295(2)	295(2)
a, b, c [Å]	8.4010(17), 5.6913(11), 11.340(3) (22.680(5))	8.4941(6), 5.7368(4), 11.4562(8)	8.5689(17), 5.7805(11), 11.553(2)
α, β, γ [°]	90, 110.82(3), 90	90, 110.0810(10), 90	90, 109.975(3), 90
V [Å ³]	506.8(2) (1013.6(3))	524.31(6)	537.83(18)
Z	6 (12)	6	6
D_x [Mg·m ⁻³]	4.240	4.306	4.389
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	10.120	12.92	15.47
Crystal form, colour	Fragment, colourless	Fragment, colourless	Fragment, colourless
Crystal size [mm]	0.10 × 0.08 × 0.05	0.18 × 0.12 × 0.07	0.30 × 0.06 × 0.03
Data collection			
Diffractionmeter	SMART APEX	SMART APEX	SMART APEX
Data collection method	ω scans	ω scans	ω scans
Absorption correction	<i>SADABS</i>	<i>SADABS</i>	<i>SADABS</i>
T_{min}, T_{max}	0.431, 0.632	0.205, 0.465	0.090, 0.654
No. of measured, independent and observed reflections	11577, 5987, 5480	5866, 2996, 2958	6223, 3266, 3222
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.035	0.023	0.021
θ_{max} [°]	30.5	31.0	31.0
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.044, 0.099, 1.20	0.019, 0.045, 1.07	0.019, 0.045, 1.06
No. of reflections	5987	2996	3266
No. of parameters	187	141	141
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 6.4447P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0172P)^2 + 0.2737P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 0.3278P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.080	0.001	0.014
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.00, -1.74	0.65, -0.86	0.71, -0.84
Extinction method	-	SHELXL	SHELXL
Extinction coefficient	-	0.0101(4)	0.0082(3)
Twin (polymorph) volume fractions	(19.8 : 80.2(2))	49 : 51(2)	49.8 : 50.2(9)

Table 3.4: Crystal data and details of the refinements of β -CaTeO₃

	β -CaTeO ₃	β -CaTeO ₃	β -CaTeO ₃
Crystal data			
Chemical formula	CaTeO ₃	CaTeO ₃	CaTeO ₃
M_r	215.68	215.68	215.68
Symmetry	Triclinic, $P1$	Triclinic, $P1$	Triclinic, $P\bar{1}$
Temperature [K]	275(2)	295(2)	350(2)
a, b, c [Å]	25.6201(4), 11.3279(2)	10.2408(2), 25.6220(4), 11.3327(2)	10.2467(2), 25.6225(9), 11.3482(4)
α, β, γ [°]	107.2180(10), 110.245(2)	110.245(2), 107.2180(10), 110.245(2)	107.2380(10), 110.255(2), 110.260(2)
V [Å ³]	33.0160(10)	33.0190(10)	33.0220(10)
Z	18	18	18
D_x [Mg·m ⁻³]	4.243	4.240	4.232
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	10.127	10.119	10.099
Crystal form, colour	Fragment, colourless	Fragment, colourless	Fragment, colourless
Crystal size [mm]	0.12 × 0.08 × 0.03	0.12 × 0.08 × 0.03	0.12 × 0.08 × 0.03
Data collection			
Diffractometer	NONIUS Kappa CCD	NONIUS Kappa CCD	NONIUS Kappa CCD
Data collection method	ω scans	ω scans	ω scans
Absorption correction	partial multi-scan	partial multi-scan	partial multi-scan
T_{min}, T_{max}	0.376, 0.786	0.376, 0.786	0.377, 0.786
No. of measured, independent and observed reflections	25813, 25813, 19328	25930, 25930, 19234	25949, 13856, 9563
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0	0	0.052
θ_{max} [°]	36.28	36.28	36.28
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F)], wR(F^2), S$	0.052, 0.113, 1.04	0.051, 0.105, 1.05	0.043, 0.083, 1.02
No. of reflections	25813	25930	13856
No. of parameters	543	813	417
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 7.5688P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 2.6344P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2 + 2.5354P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.026	0.007	0.002
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	3.70, -3.89	2.98, -3.53	2.06, -2.07
Extinction method	SHELXL	SHELXL	SHELXL
Extinction coefficient	0.00100(4)	0.00096(3)	0.00110(3)
Twin volume fractions	46:54(4)	45:55(6)	-
occupation (occ.), O32a:O32b	-	-	38:62(1)

Table 3.5: Crystal data and details of the refinements of β' -CaTeO₃ and Ca_{0.14}Sr_{0.23}TeO₃ (β'' -Ca)

	β' -CaTeO ₃	β' -CaTeO ₃	β' -CaTeO ₃	Ca _{0.14} Sr _{0.89} TeO ₃ (β'' -Ca)
Crystal data				
Chemical formula	CaTeO ₃	CaTeO ₃	CaTeO ₃	Ca _{0.14} Sr _{0.23} TeO ₃
M_r	215.68	215.68	215.68	256.38
Symmetry	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature [K]	200(2)	250(2)	275(2)	295(2)
a, b, c [Å]	25.5990(5), 11.2384(3) 108.620(1), 32.307(2)	25.6149(4), 11.2440(2) 108.608(1), 32.313(1)	25.6215(5), 11.2481(2) 108.604(9), 32.3190(10)	26.493(11), 11.791(4) 107.415(8), 33.016(15)
α, β, γ [°]	10.3871(2), 112.398(2), 1476.60(6)	10.3921(2), 112.394(2), 1479.25(5)	10.3933(2), 112.393(13), 1480.59(5)	10.627(4), 110.378(16), 1695.4(11)
V [Å ³]	18	18	18	18
D_x [Mg·m ⁻³]	4.366	4.358	4.354	4.520
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	10.420	10.401	10.391	19.900
Crystal form, colour	Fragment, colourless	Fragment, colourless	Fragment, colourless	Fragment, colourless
Crystal size [mm]	$0.12 \times 0.08 \times 0.03$	$0.12 \times 0.08 \times 0.03$	$0.12 \times 0.08 \times 0.03$	$0.12 \times 0.08 \times 0.03$
Data collection				
Diffractionmeter	NONIUS Kappa CCD	NONIUS Kappa CCD	NONIUS Kappa CCD	SMART APEX2
Data collection method	ω scans	ω scans	ω scans	ω and ϕ scans
Absorption correction	partial multi-scan	partial multi-scan	partial multi-scan	multi-scan
T_{min}, T_{max}	0.3678, 0.7451	0.3683, 0.7455	0.3686, 0.7812	0.1987, 0.6361
No. of measured, independent and observed reflections	17367, 12498, 9708	25122, 13422, 10123	25213, 13485, 10052	48585, 17488, 13574
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.041	0.047	0.047	0.033
θ_{max} [°]	36.23	36.24	36.24	37.49
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F)], wR(F^2), S$	0.039, 0.086, 1.01	0.034, 0.066, 1.01	0.034, 0.068, 1.01	0.037, 0.086, 1.02
No. of reflections	12498	13422	13485	17488
No. of parameters	407	407	407	416
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0210P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 2.2490P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.003	0.005	0.004	0.008
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.96, -2.40	2.06, -2.32	2.40, -2.12	4.80, -3.20
Extinction method	SHELXL	SHELXL	SHELXL	SHELX
Extinction coefficient	0.00066(4)	0.00087(3)	0.00085(3)	0.00014(2)

Table 3.6: Selected interatomic distances d and angles in $\alpha\text{-CaTeO}_3$

Atoms	d [Å]	Atoms	d [Å]	Atoms	d [Å]
Te1–O9	1.839 (4)	Ca1–O6	2.262 (4)	Ca3–O15	2.449 (5)
Te1–O7	1.860 (5)	Ca1–O8	2.370 (5)	Ca3–O3	2.491 (5)
Te1–O8	1.871 (5)	Ca1–O4	2.380 (5)	Ca3–O4	2.643 (5)
Te2–O4	1.834 (4)	Ca1–O15	2.394 (5)	Ca4–O7	2.368 (5)
Te2–O5	1.844 (5)	Ca1–O11	2.395 (5)	Ca4–O1	2.415 (5)
Te2–O3	1.850 (4)	Ca1–O12	2.407 (5)	Ca4–O12	2.437 (5)
Te3–O6	1.880 (4)	Ca2–O3	2.317 (5)	Ca4–O3	2.448 (5)
Te3–O1	1.883 (4)	Ca2–O5	2.325 (5)	Ca4–O10	2.449 (5)
Te3–O2	1.890 (4)	Ca2–O7	2.354 (5)	Ca4–O2	2.516 (5)
Te4–O11	1.858 (4)	Ca2–O13	2.390 (5)	Ca4–O5	2.796 (5)
Te4–O10	1.879 (4)	Ca2–O14	2.409 (4)	Ca4–O8	3.033 (5)
Te4–O12	1.883 (4)	Ca2–O10	2.432 (5)	Ca5–O9	2.391 (4)
Te5–O13	1.861 (5)	Ca2–O9	2.855 (6)	Ca5–O6	2.399 (4)
Te5–O15	1.873 (4)	Ca3–O2	2.296 (5)	Ca5–O7	2.428 (5)
Te5–O14	1.874 (4)	Ca3–O8	2.421 (5)	Ca5–O13	2.429 (4)
Ca1–O6	2.262 (4)	Ca3–O1	2.430 (5)	Ca5–O1	2.440 (5)
Ca1–O8	2.370 (5)	Ca3–O14	2.439 (4)	Ca5–O10	2.441 (5)
				Ca5–O2	2.461 (5)
Atoms	angle [°]	Atoms	angle [°]	Atoms	angle [°]
O9–Te1–O7	93.7 (2)	O6–Te3–O1	97.1 (2)	O13–Te5–O15	97.50 (19)
O9–Te1–O8	103.2 (2)	O6–Te3–O2	89.1 (2)	O13–Te5–O14	100.3 (2)
O7–Te1–O8	98.1 (2)	O1–Te3–O2	92.39 (19)	O15–Te5–O14	101.45 (19)
O4–Te2–O5	100.2 (2)	O11–Te4–O10	96.2 (2)		
O4–Te2–O3	93.7 (2)	O11–Te4–O12	103.5 (2)		
O5–Te2–O3	92.9 (2)	O10–Te4–O12	101.0 (2)		

inspection revealed that $\gamma\text{-CaTeO}_3$ can be described as an OD structure and the residual electron density corresponds to a minor polytype in space group $P2_1$ and the basis vector $\mathbf{c}$ halved when compared to the major polytype.

In order to refine $\gamma\text{-CaTeO}_3$ with both polytype fractions, the lattice parameters of the polytype with the doubled cell volume ($P2_1/c$) and space group $P2_1$, which is the greatest common subgroup of $P2_1$ and $P2_1/c$, were used. In a first step, the $P2_1/c$ polytype was refined by pairs of atoms constrained to positions (x, y, z) and $(-x, -y, -z)$, thus obtaining the inversion symmetry missing in the overall structure. Moreover, the ADPs of the corresponding atoms were constrained to be equivalent. Then, for parts of the structure where both polytypes do not overlap (layers B in the description below), for the $P2_1$ polytype pairs of atoms constrained to positions (x, y, z) and $(x, y, \frac{1}{2} + z)$ and equivalent ADPs were added, thus taking into account the halved unit cell. Of the atoms in the minor polytype only the Ca atoms were refined anisotropically since some of the Te and O atoms gave physically meaningless values. The sum of the occupation of atoms in both polytypes was constrained to unity. In the final difference Fourier map no remarkable additional electron density was found.

On CCD frames collected from a $\gamma\text{-CaTeO}_3$ crystal, pseudo-precession photographs computed from those frame sets, and likewise in line scans performed with a point detector, the reflections with $l = 2n$, corresponding to family reflections of the OD structure, are sharp, whereas those with $l = 2n + 1$ (characteristic reflections) show distinct broadening in $[001]$ (Fig. 3.3.5), indicating disorder in the layer stacking direction (Ferraris et al., 2004).

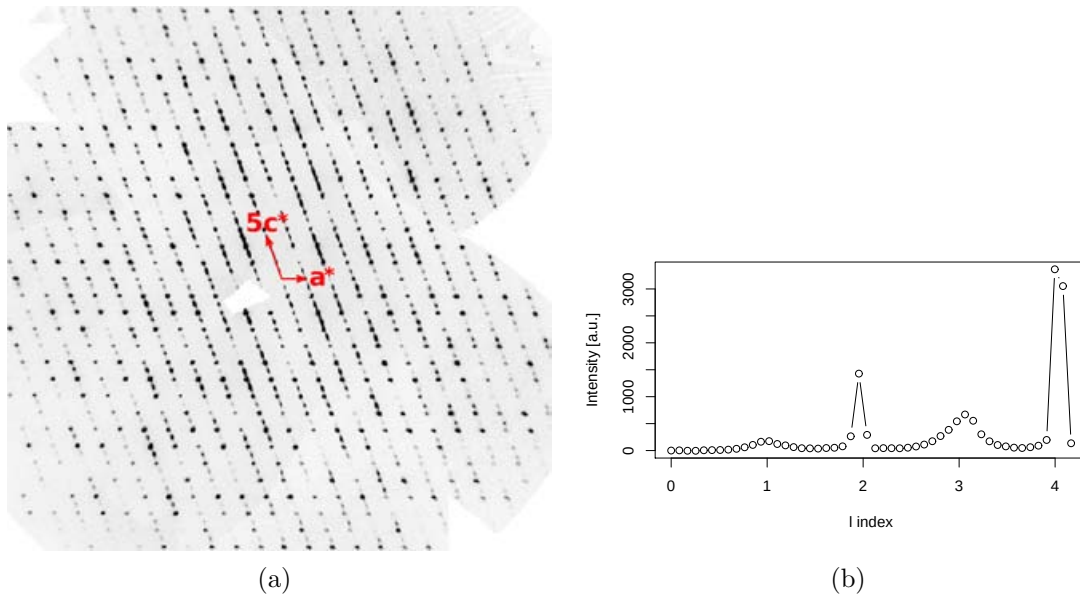


Figure 3.4: (a) $h3l$ plane of reciprocal space reconstructed from CCD frames obtained from a $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ (γ -Ca) crystal. (b) Line scan of the segment $[230, 234]$ in reciprocal space of a γ - CaTeO_3 crystal (indexed with the MDO_2 polytype), performed on a NONIUS CAD4 diffractometer with a point detector with $\psi = 0^\circ$ showing distinct broadening of reflections with $l = 2n + 1$ in direction c^* . Measurements with $\psi = 2.5, 5, 7, 10, 15^\circ$ resulted in practically the same values.

Calculations have shown that polytypes with more complex stacking orders would produce pronounced reflections on the line segments $[020, 022]$, $[040, 042]$, $[122, 126]$, $[142, 146]$, $[230, 234]$, $[334, 338]$, $[334, 338]$, $[420, 424]$, $[440, 444]$, $[524, 5210]$ and $[544, 5410]$ in reciprocal space (indexed with the $P2_1/c$ cell setting of the major polytype). However, no reflections with non-integer hkl -values could be detected on these segments.

A crystal isolated from an experiment with a Ca:Sr ratio of 4:1 had the lattice parameters similar to those of γ - CaTeO_3 . The M positions which are not overlapping in both polytypes were refined with free occupation due to limitations in the SHELX (Sheldrick, 2008) software package. Two polytypes corresponding to those in γ - CaTeO_3 could be determined, but the reliability factors of the final refinement cycles were not satisfactory ($R = 0.12$, $R_w = 0.30$), possibly because the crystal is composed of multiple domains. Refinements with the program JANA2006 (Petříček et al., 2006) which supports multi-domain crystals were not successful so far.

The closely related non-centrosymmetric structures of composition $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ (γ -Ca, $x = 0.55$ and $x = 0.77$, $P2_1$) were refined as inversion-twins with a twin-ratio close to 1. The occupational disorder of the Ca and Sr atom was refined with the occupation constrained to be equal to 1 for each metal site and common ADPs were used. The cell origin was chosen so that the y -coordinates of the atoms are comparable to those in γ - CaTeO_3 .

Structure

γ - CaTeO_3 and $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ (γ -Ca) belong to a monoclinic/rectangular category IV OD family with two kinds of non-polar layers A and B parallel to (001) (Fig. 3.5, left). The OD groupoid family symbol reads as

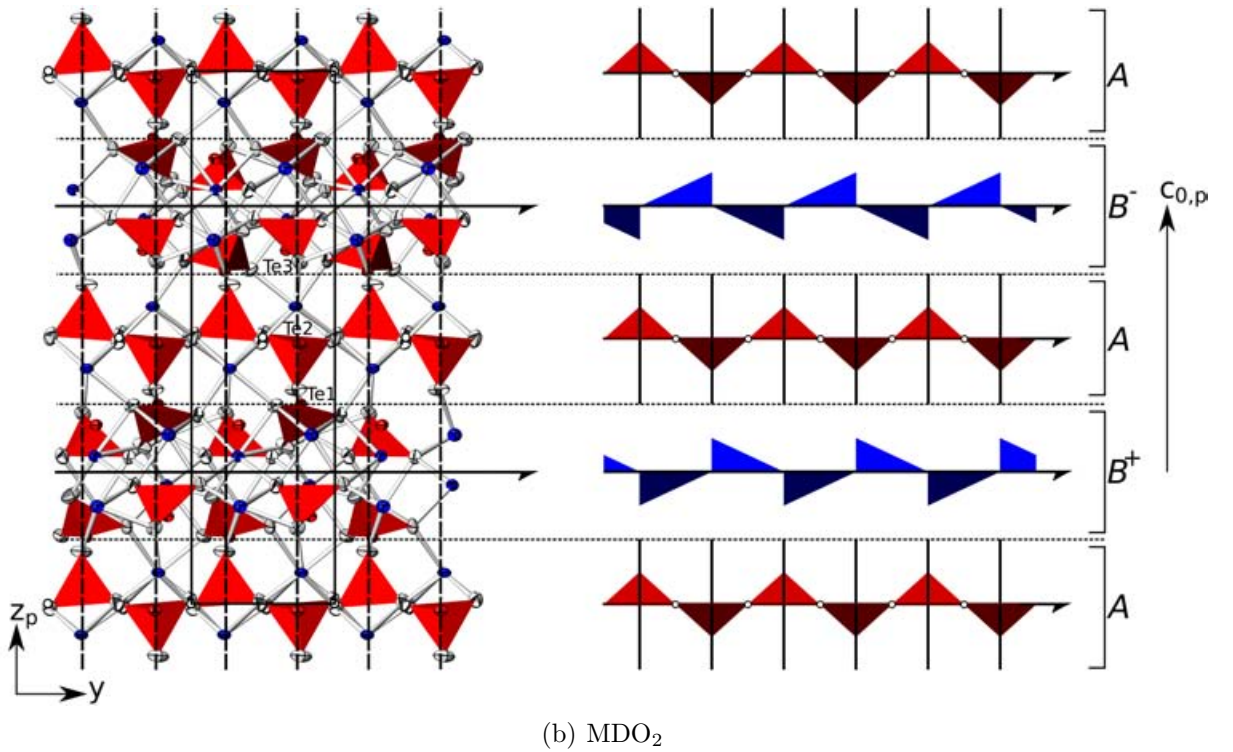
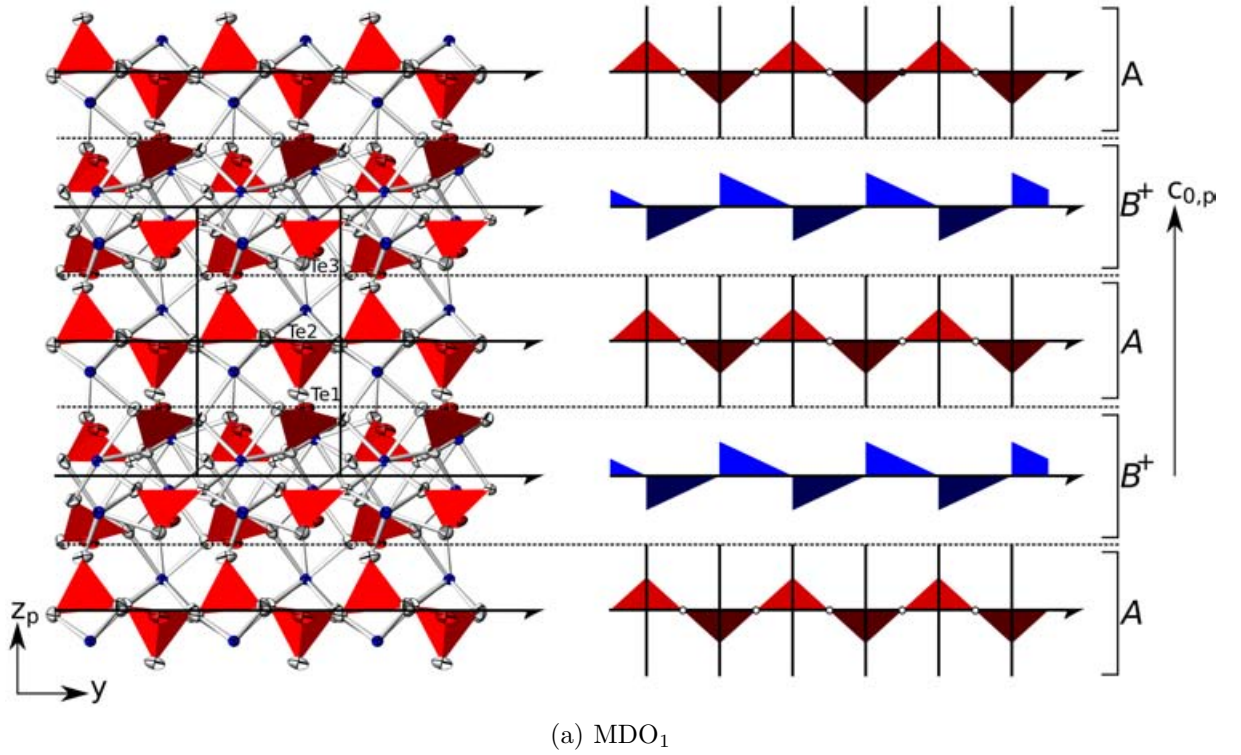


Figure 3.5: (a) MDO_1 and (b) MDO_2 polytypes of $\gamma\text{-CaTeO}_3$ and $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$, respectively, viewed down $[100]$. To the right the schematized OD structure is represented by red triangles with a mirror plane normal to $[010]$ and blue triangles. Bright and dark colours symbolize the front and the back side of the triangles. Letters to the right describe the layer type. Colour codes, displacement ellipsoids and symbols as in Fig. 3.2. A subscript „p” designates a coordinate axis which does not lie in the drawing plane (Hahn, 1983).

$$\begin{array}{cc} A & B \\ p12_1/m(1) & p12_1(1) \\ [0, 0] & \end{array}$$

according to the notation devised by Grell and Dornberger-Schiff (1982). Layer names¹ deviating from the layer notation used by Grell and Dornberger-Schiff (1982) have been chosen for clarity. Te1 marks the boundary between both layers. Layers *A* (Te1, Te2, Ca2, O4–O6) and *B* (Te3, Ca1, Ca3, O1–O3, O7–O9) have layer symmetry $p12_1/m(1)$ and $p12_1(1)$, respectively.

Given the position of a layer *A*, adjacent layers of type *B* can appear in two enantiomorphic orientations with respect to $[010]$, which will be denoted by B^+ and B^- . This is expressed by the NFZ relationship, which is given for layers of different kind as $Z = N/F$ (Đurovič, 1997). $Z = 2$ is the number of distinct positions of layers *B* given a fixed position of a layer *A*, $N = 2$ is the order of the group of λ - τ -POs of layers *A* ($G = p1m1$) and $F = 1$ the order of the group of those operations in G which are also valid for adjacent layers *B* ($p1$). For layers of type *B*, on the other hand, $G = p1$, and hence $Z = N = F = 1$.

Consequently, two kinds of BAB layer triples (*viz.* B^+AB^+ and B^+AB^-) but only one kind of ABA triples exist. These give rise to two possible MDO stacking orders (Dornberger-Schiff and Grell, 1982), $MDO_1 (\dots AB^+AB^+ \dots, P2_1, \mathbf{c} = \mathbf{c}_0)$ and $MDO_2 (\dots AB^+AB^- \dots, P2_1/c, \mathbf{c} = 2\mathbf{c}_0)$. The schematized structures and local symmetry of the MDO_1 and MDO_2 polytypes are illustrated in Fig. 3.5 (right) by two kinds of triangles: red ones possessing a mirror plane normal to $[010]$, blue ones exhibiting no mirror plane. The triangles are double-sided, the different sides being represented by bright and dark colours, respectively. For different γ - CaTeO_3 crystals an $MDO_1:MDO_2$ ratio of $\approx 2 : 8$ was determined in each case. In the $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ (γ -Ca) structures with $x = 0.67$ and $x = 0.33$ only MDO_2 exists. For $x = 0.74$, no reliable $MDO_1:MDO_2$ ratio could be determined due to problems during structure refinement.

The generating operation of MDO_1 is a translation along $\mathbf{c}_0$. The $[-2_1-]$ screw rotations of layers *A* and *B* are total operations of the complete structure. MDO_2 is generated by continuous application of a $[-c-]$ glide. The glide plane coincides with the $[-m-]$ plane of layers *A* at $y = \frac{1}{4}$. The $[-2_1-]$ screw rotations of layers *B* and the inversion symmetry of layers *A* are total operations of the MDO_2 polytype.

In both MDO polytypes the mirror symmetry of layers *A* is lost. Additionally, in MDO_1 their inversion centre is lost, resulting in actual $p12_1(1)$ symmetry for layers *A*, whereas in MDO_2 the $[-2_1-]$ screw axis is missing, resulting in $p\bar{1}$ symmetry. Layers of type *B*, on the other hand, retain their $[-2_1-]$ screw axis in both MDO polytypes and have the same symmetry in the real MDO structures as well as in the OD interpretation.

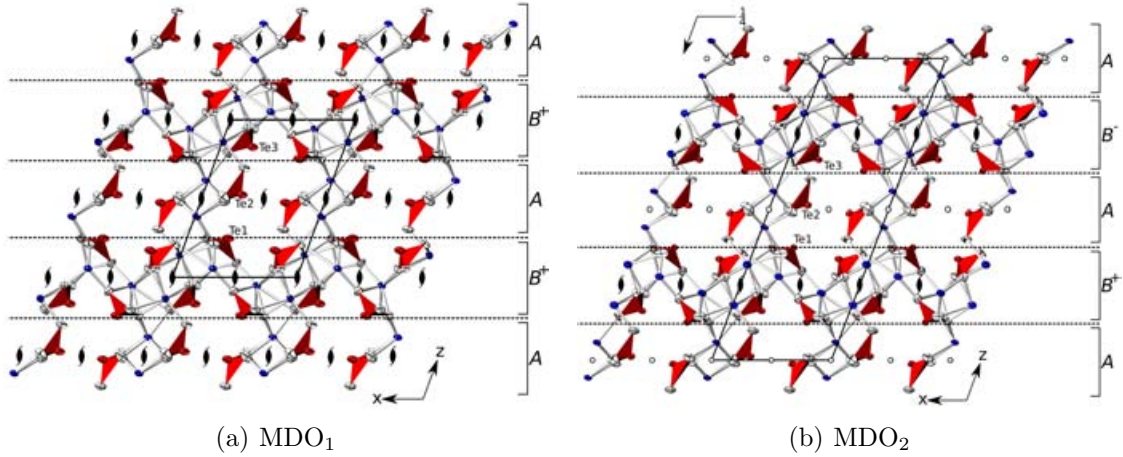
Since layers *A* in the OD approach have a higher symmetry than in the real structure, they have to be idealized. The idealized positions of atoms in layer *A* were constructed by moving atoms that are located close to the mirror plane (with $y \approx \frac{1}{4}$ or $y \approx \frac{3}{4}$, *viz.* Ca2, Te1, Te2 and O4) onto the plane. For the two remaining atoms (O5 and O6), which are related by (pseudo-)mirror symmetry, an averaged atom has been constructed. Coordinates of the idealized structure are listed in Tab. C.14 and C.15. The distances of the atomic positions calculated on the basis of single crystal diffraction data from the atoms in the idealized structure are given in Tab. 3.7 for γ - CaTeO_3 and for $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ (γ -Ca), respectively. The maximum deviation of only 0.108 Å for heavy atoms (Te or Ca/Sr) is a clear indication of the higher local symmetry of layer *A* and therefore of the validity of the OD interpretation.

All polytypes exhibit oval channels (smallest and largest diameter ≈ 2 Å and 8 Å, respectively) running along $[010]$, delimited by six $[\text{Te}^{IV}\text{O}_3]$ units (Fig. 3.6). The long and the

¹ According to Grell and Dornberger-Schiff (1982), layers *A* and *B* would be called A^1 and A^2 , respectively.

Table 3.7: Deviations [$\text{\AA}$] of the real structure atoms in layer A in $\gamma\text{-CaTeO}_3$ and $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ to the corresponding atoms in the idealized structure.

Atom	$\gamma\text{-CaTeO}_3$	$\text{Ca}_{0.77}\text{Sr}_{0.23}\text{TeO}_3$	$\text{Ca}_{0.55}\text{Sr}_{0.45}\text{TeO}_3$
Te1	0.102	0.012	0.019
Te2	0.032	0.067	0.074
Ca2	0.108	0.054	0.055
O4	0.098	0.241	0.267
O5, O6	0.123	0.169	0.183

**Figure 3.6:** Representations of the (a) MDO₁ and the (a) MDO₂ polytype of $\gamma\text{-CaTeO}_3$ and $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$, respectively, viewed down $[010]$. MDO₁ is represented by the crystal structure of $\text{Ca}_{0.77}\text{Sr}_{0.23}\text{TeO}_3$, MDO₂ by the major polytype of $\gamma\text{-CaTeO}_3$. Letters to the right describe the layer type. A superscript „+” or „-” next to the symbol „B” indicates its orientation with respect to $[010]$. Colour codes, displacement ellipsoids and symbols as in Fig. 3.2.

short diameter of the channels are parallel to $[001]$ and $[100]$, respectively. $[\text{MO}]_x$ polyhedra ($M = \text{Ca}, \text{Sr}$; $x = 7 - 8$) are located around the channels and connect the $[\text{Te}^{\text{IV}}\text{O}_3]$ units via corners and edges. The lone pair electrons of the Te^{IV} atoms are directed towards the channels (Fig. 3.6). The Te–O distances in all polytypes (Tab. 3.8) are in good agreement with the data given in a review on the crystal chemistry of oxotellurium(IV) compounds (Dolgikh, 1991).

Occupational disorder in $\text{Ca}_x\text{Sr}_{1-x}\text{O}_3$ ($\gamma\text{-Ca}$)

There is considerably more substitution by Sr in one of the 3 different Ca positions (Ca1) (Tab. 3.9). As expected, the Ca–O distances increase with the amount of substitution (Tab. 3.8). Even in unsubstituted $\gamma\text{-CaTeO}_3$, the Ca–O distances are slightly larger for Ca1 than for Ca2 and Ca3, indicating more space at the Ca1 position required for larger atoms when substituted.

3.3.6 The β -, β' -, β'' - CaTeO_3 structure types

In the following sections β -, β' - CaTeO_3 and $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ (β'' -Ca) will be called „the β -polymorphs” when general aspects concerning all three structures are discussed.

Table 3.8: Selected interatomic distances [Å] and angles [°] in γ -CaTeO₃ (MDO₁ and MDO₂), Ca_xSr_{1-x}TeO₃ (γ -Ca). For MDO₂ only atoms in layer *B* are considered, since atoms in layer *A* were not refined separately for both polytypes.

	γ -CaTeO ₃ , MDO ₁	γ -CaTeO ₃ , MDO ₂	Ca _{0.77} Sr _{0.23} TeO ₃	Ca _{0.55} Sr _{0.45} TeO ₃
Te1-O3	1.859 (6)	1.87 (4)	1.866 (3)	1.866 (3)
Te1-O1	1.868 (5)	1.88 (4)	1.862 (3)	1.862 (3)
Te1-O2	1.872 (5)	1.86 (4)	1.870 (3)	1.867 (3)
Te2-O6	1.834 (4)		1.833 (4)	1.831 (4)
Te2-O4	1.840 (4)		1.841 (3)	1.836 (3)
Te2-O5	1.852 (4)		1.858 (4)	1.857 (4)
Te3-O7	1.838 (5)	1.90 (3)	1.859 (3)	1.858 (3)
Te3-O9	1.841 (12)	1.94 (5)	1.853 (3)	1.858 (3)
Te3-O8	1.875 (5)	1.78 (4)	1.864 (3)	1.865 (3)
Ca1-O4	2.340 (4)	-	2.389 (3)	2.433 (4)
Ca1-O8	2.392 (5)	2.41 (4)	2.455 (3)	2.495 (3)
Ca1-O8	2.419 (5)	2.44 (4)	2.498 (3)	2.547 (3)
Ca1-O9	2.429 (6)	2.48 (5)	2.528 (3)	2.585 (4)
Ca1-O1	2.538 (5)	2.54 (4)	2.600 (3)	2.643 (3)
Ca1-O7	2.669 (6)	2.56 (4)	2.708 (3)	2.733 (3)
Ca1-O7	2.702 (6)	2.72 (3)	2.712 (3)	2.741 (3)
Ca1-O2	2.785 (6)	2.72 (4)	2.750 (4)	2.767 (4)
Ca2-O6	2.322 (4)		2.337 (4)	2.358 (4)
Ca2-O9	2.339 (12)		2.350 (3)	2.387 (3)
Ca2-O5	2.339 (4)		2.344 (4)	2.368 (4)
Ca2-O1	2.393 (5)		2.387 (3)	2.405 (3)
Ca2-O6			2.337 (4)	2.575 (4)
Ca2-O5			2.344 (4)	2.636 (4)
Ca2-O2	2.517 (6)		2.638 (4)	2.676 (4)
Ca3-O7	2.220 (5)	2.21 (3)	2.251 (3)	2.285 (3)
Ca3-O3	2.292 (6)	2.35 (4)	2.305 (3)	2.323 (3)
Ca3-O2	2.297 (5)	2.24 (4)	2.322 (3)	2.347 (3)
Ca3-O8	2.467 (5)	2.53 (4)	2.480 (3)	2.488 (3)
Ca3-O3	2.521 (6)	2.45 (4)	2.532 (3)	2.561 (3)
Ca3-O1	2.550 (6)	2.58 (4)	2.572 (3)	2.608 (4)
Ca3-O9	3.019 (14)	3.12 (6)	3.068 (3)	3.069 (3)
O1-Te1-O2	93.4 (2)	93.0 (17)	93.73 (16)	94.11 (16)
O1-Te1-O3	92.2 (2)	89.0 (18)	91.95 (14)	91.87 (15)
O2-Te1-O3	103.5 (3)	99.4 (18)	102.45 (15)	101.89 (16)
O4-Te2-O5	103.27 (18)	-	93.47 (16)	103.40 (18)
O4-Te2-O6	103.43 (18)	-	102.99 (17)	103.04 (19)
O5-Te2-O6	93.10 (18)	-	103.36 (17)	93.18 (17)
O7-Te3-O8	94.1 (2)	91.3 (16)	93.94 (13)	94.60 (14)
O7-Te3-O9	90.2 (3)	94.2 (17)	91.44 (14)	91.94 (14)
O8-Te3-O9	99.4 (4)	104 (2)	99.53 (15)	99.10 (15)

Data collection

Multiple heating/cooling cycles of a β -CaTeO₃ crystal mounted on a single crystal diffractometer have shown that β -CaTeO₃ slowly transforms into a low temperature (LT) phase β' -CaTeO₃ at temperatures below ≈ 270 K with distinctly different lattice parameters. To obtain a single crystal of β' -CaTeO₃, the crystal had to be cooled for a few hours at 200 K. When the measure-

Table 3.9: Ca substitution in the phases $\text{Ca}_x\text{Sr}_{1-x}\text{O}_3$ (γ -Ca)

Ca:Sr ratio used in synthesis	1:1	2:1
Single Crystal Data		
Sum Formula	$\text{Ca}_{0.55}\text{Sr}_{0.45}\text{TeO}_3$	$\text{Ca}_{0.77}\text{Sr}_{0.23}\text{TeO}_3$
a [Å]	8.5689(17)	8.4941(6)
b [Å]	5.7805(11)	5.7368(4)
c [Å]	11.553(2)	11.4562(8)
β [°]	109.975(3)	110.0810(10)
Ca1:Sr1	31.1:68.9(4)	60.0:40.0(5)
Ca2:Sr2	63.7:36.3(4)	83.8:16.2(4)
Ca3:Sr3	71.3:28.6(4)	87.5:12.5(4)

ments were started shortly after cooling, the reflections showed considerable splitting, which can be attributed to simultaneous existence of β - as well as β' - CaTeO_3 .

The reverse transition β' - $\text{CaTeO}_3 \rightarrow \beta$ - CaTeO_3 occurred instantly when heating the crystal at ≈ 300 K. Due to this large hysteresis it was possible to avoid a spontaneous phase transition and collect data for both β - and β' - CaTeO_3 phases using the same crystal for measurement at 275 K, by cooling from 300 K and by heating from 200 K, respectively. Data of the related solid solution $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ (β'' -Ca) was collected at RT.

The lattice parameters of the β -polymorphs clearly indicate triclinic crystal system. While β' - CaTeO_3 and $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ (β'' -Ca) crystallize without doubt in $P\bar{1}$, the situation for β - CaTeO_3 is not so clear. Refinements of β - CaTeO_3 always resulted in satisfactory and comparable R -values for both structure models in $P1$ as well as in $P\bar{1}$. The structure models obtained by refinements in $P1$ and in $P\bar{1}$ are practically equivalent with the exception of one O atom, which is disordered around a centre of inversion when refined in $P\bar{1}$. For measurements at 275 and 295 K, refinements in $P1$ gave distinctly better reliability factors than in $P\bar{1}$. For data sets collected at 325 and 350 K, the situation was reversed: refinements in $P\bar{1}$ gave better reliability values than refinements in $P1$. The refined structures were practically identical to those obtained at lower temperatures. Fig. 3.12 gives a survey of the lattice parameters and space groups of β -, β' - CaTeO_3 at different temperatures.

For the dataset of the β - CaTeO_3 phase collected at 275 K, the O atoms were refined with isotropic temperature factors since the ADPs were highly anisotropic, one O atom even giving a physically meaningless U_{eq} . This can be attributed to the kinetically inhibited phase transition β - $\text{CaTeO}_3 \rightarrow \beta'$ - CaTeO_3 in this temperature range.

Analysis of the diffraction intensities revealed distinct superstructure reflections. Indeed, reflections corresponding to a cell with similar metrics as γ - CaTeO_3 (MDO_1) are considerably stronger than the remaining reflections (Tab. 3.10). The ratio of the average intensities of basic to super structure reflections is distinctly larger for β - CaTeO_3 (≈ 3.33) and $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ (β'' -Ca) (≈ 3.82) than for β' - CaTeO_3 (1.69). Thus, in the latter structure the subcells deviate more from the averaged structure.

The super structure reflections can be indexed with a fourth basis vector $\mathbf{q} = (\frac{1}{3}, \frac{1}{3}, 0)$ in reciprocal space. Therefore the β -polymorphs can be described as threefold superstructures with superspace symmetry $P1(\frac{1}{3}, \frac{1}{3}, 0)$ (β) and $P\bar{1}(\frac{1}{3}, \frac{1}{3}, 0)$ (β' , β''). The volume of the unit cell of β -polymorphs is approximately three times that of MDO_1 of γ - CaTeO_3 . In Fig. 3.7 a lattice of γ - CaTeO_3 is represented with x_4 -values indicated for every lattice node. Three possible unit cells for the superstructures without additional centring conditions have been indicated (with

Table 3.10: Average and maximum intensities in a.u. of basic ($h = 3n$) and super structure ($h \neq 3n$) reflections in different measurements of the β -polymorphs and ratio Δ of intensities of super to basic structure reflections. Only reflections with $\theta \leq 30^\circ$ were considered.

Structure	T [K]	$h = 3n$		$h \neq 3n$		Δ	
		I_{avg} [a.u.]	I_{max} [a.u.]	I_{avg} [a.u.]	I_{max} [a.u.]	I_{avg} [a.u.]	I_{max} [a.u.]
β' -CaTeO ₃	275	19.6	1000.0	11.6	213.6	1.69	4.68
β -CaTeO ₃	275	23.3	1000.0	7.0	133.6	3.33	7.49
β -CaTeO ₃	295	23.4	1000.0	7.0	128.5	3.34	7.78
Ca _{0.11} Sr _{0.89} TeO ₃	295	17.2	1000.0	4.5	73.5	3.82	13.60

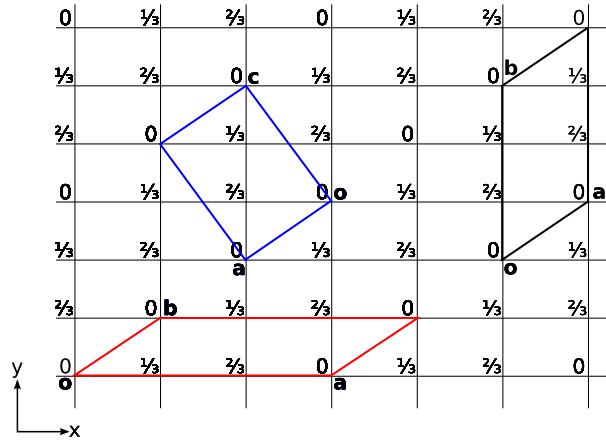


Figure 3.7: Lattice of the basic structure of the β -polymorphs projected along [001]. The γ angle of the basic structure has been idealized to 90° . Numbers next to lattice nodes indicate x_4 -values (modulo the period 1 of the modulation function). Three equivalent unit cells of the super structures have been indicated. Blue lines represent the reduced cell. Black and red lined cells emphasize the super structure aspect. Red lines represent the unit cell chosen for the description of the β -polymorphs in this work.

different origins for the sake of clarity). The reduced cell of the superstructure, which is related to the basis vectors $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$ of γ -CaTeO₃ (MDO₁) by the transformation

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}) \approx (\mathbf{a}', \mathbf{b}', \mathbf{c}') \begin{pmatrix} \bar{1} & 0 & \bar{1} \\ \bar{1} & 0 & 2 \\ 0 & 1 & 0 \end{pmatrix},$$

is represented by blue lines. The unit cells which are represented by red and black lines and which are related to the cell of γ -CaTeO₃ (MDO₁) by

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}) \approx \begin{pmatrix} 3 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ and } \begin{pmatrix} 1 & 0 & 0 \\ 1 & 3 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

emphasize the relationship to γ -CaTeO₃ (MDO₁). The former cell setting has been chosen in this work since the representation of the unit cell contents is more clear than in the other cases. The relationship between the chosen unit cells of β -, β' - and β'' -CaTeO₃ and both γ -CaTeO₃ polytypes is represented in Fig. 3.8.

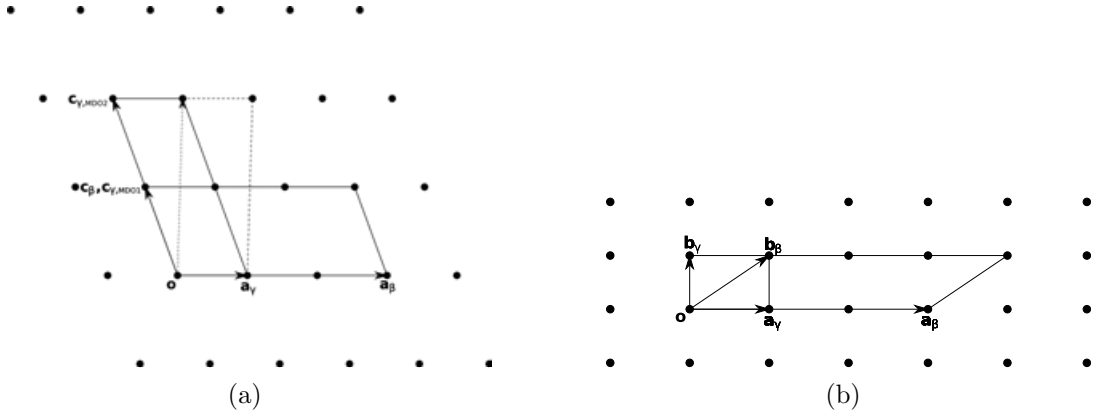


Figure 3.8: Relationship of the unit cells of $\beta\text{-CaTeO}_3$ and the $\gamma\text{-CaTeO}_3$ polytypes MDO₁ and MDO₂ in projection on (a) (010) and (b) (001). The dots represent the crystal lattice of the MDO₁ polytype in $\gamma\text{-CaTeO}_3$. a_β is tripled when compared to a_γ owing to the threefold superstructure of $\beta\text{-CaTeO}_3$ along [100]. c_{γ, MDO_1} is doubled when compared to c_{γ, MDO_2} . The dotted lines in the left part represent the reduced setting of the unit cell of $\gamma\text{-CaTeO}_3$ MDO₂ with pseudo-orthorhombic metrics.

The labelling of the atoms has been assigned consistently with the $\gamma\text{-CaTeO}_3$ polymorphs: The numbers of the Te and Ca atoms in β -polymorphs consist of two digits, the first digit being the same as of the corresponding atom in $\gamma\text{-CaTeO}_3$. In the following discussion, Te1*x* will be written for all or a subset of the atoms corresponding to atom Te1 in $\gamma\text{-CaTeO}_3$, *etc.*...

The O atoms have been labelled according to the connectivity to the Te atoms: The first digit was chosen so that the first digit of all atoms in the $[\text{Te}^{\text{IV}}\text{O}_3]$ units relate to those of the corresponding unit in $\gamma\text{-CaTeO}_3$. Thus, since Te1 connects to O1-O3 in $\gamma\text{-CaTeO}_3$, Te1*x* connects to O1*x*, O2*x* and O3*x* in β - and $\beta'\text{-CaTeO}_3$, *etc.*

Structure

The β -polymorphs are threefold superstructures along [100] based on the MDO₁ polytype description of $\gamma\text{-CaTeO}_3$.

Although the symmetry conditions given for layers *A* and *B* in the description of $\gamma\text{-CaTeO}_3$ do not hold anymore, it is still useful to distinguish between those layers for comparison with $\gamma\text{-CaTeO}_3$ (Fig. 3.9).

Due to the superstructure, the β -polymorphs can be described as being composed of three different translationally non-equivalent rods with pseudo-monoclinic metrics (Tab. 3.11), running along [001] (Fig. 3.10).

Each rod consists of a stacking of distorted $\gamma\text{-CaTeO}_3$ (MDO₁) unit cells. Two types of rods can be differentiated, which will be denoted by *C* and *D*. Rods of type *D* are very similar in all three β -polymorphs. They are non-centrosymmetric (symmetry $\neq 1$) and can appear in two enantiomorphic orientations (D^+ and D^-). Adjacent rods *D* are related by inversion symmetry ($\beta'\text{-CaTeO}_3$, $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ ($\beta''\text{-Ca}$)) or pseudo-inversion symmetry ($\beta\text{-CaTeO}_3$).

Rods *C*, on the other hand, are different in the three β -polymorphs. They are centrosymmetric ($\neq \bar{1}$) in $\beta'\text{-CaTeO}_3$ and $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ ($\beta''\text{-Ca}$) and will be called C' and C'' , respectively. In $\beta\text{-CaTeO}_3$ rods *C* are only symmetric by pseudo-inversion symmetry ($\neq 1$) and can appear in two enantiomorphic orientations which will be designated C^+ and C^- .

The rods expand along [100] (and $[\bar{1}30]_\beta \hat{=} [010]_\gamma$) according to: $\dots D^+ C D^- D^+ C D^- \dots$ (Fig. 3.10). The resulting structures of $\beta'\text{-CaTeO}_3$ and $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ with rod arrange-

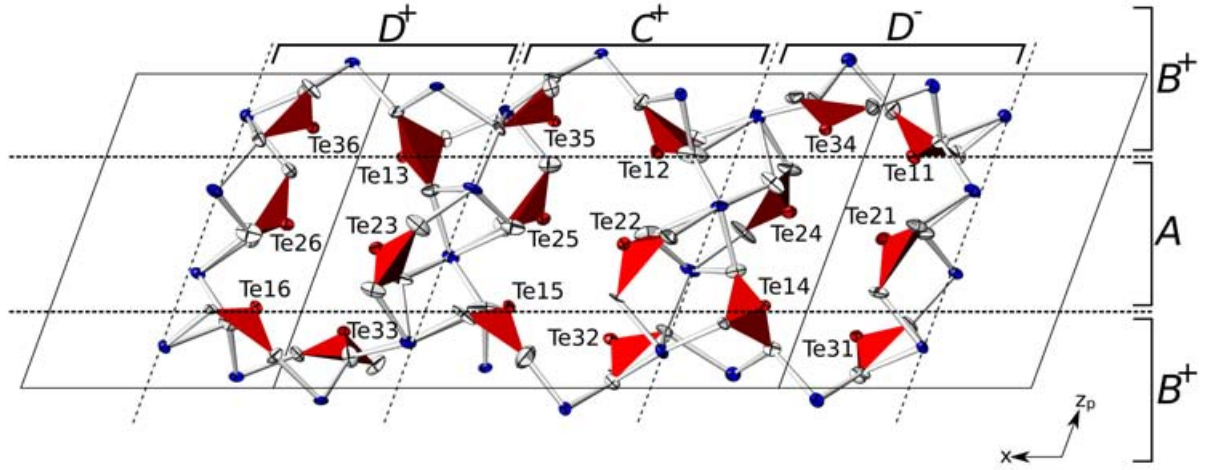
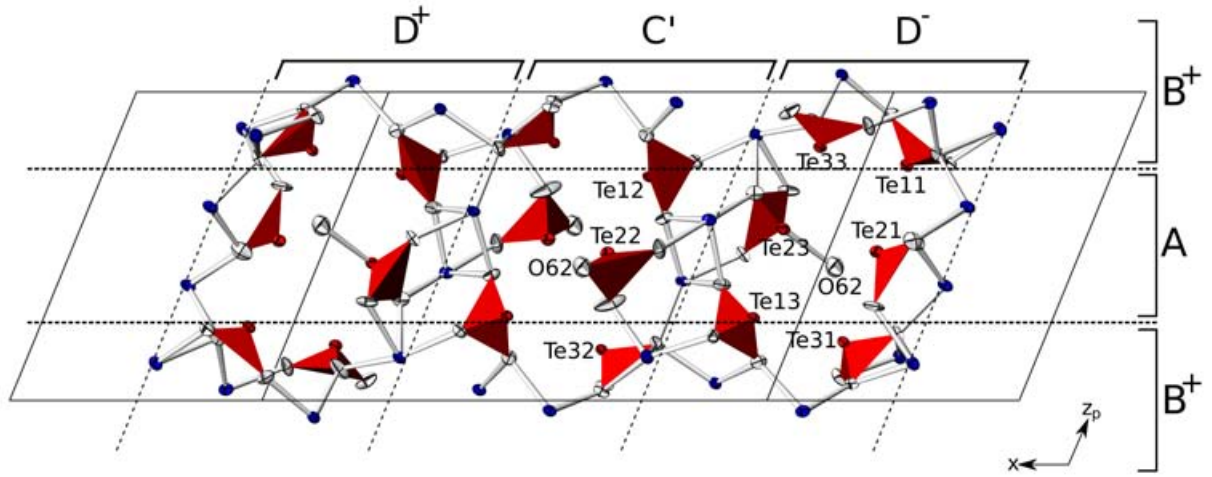
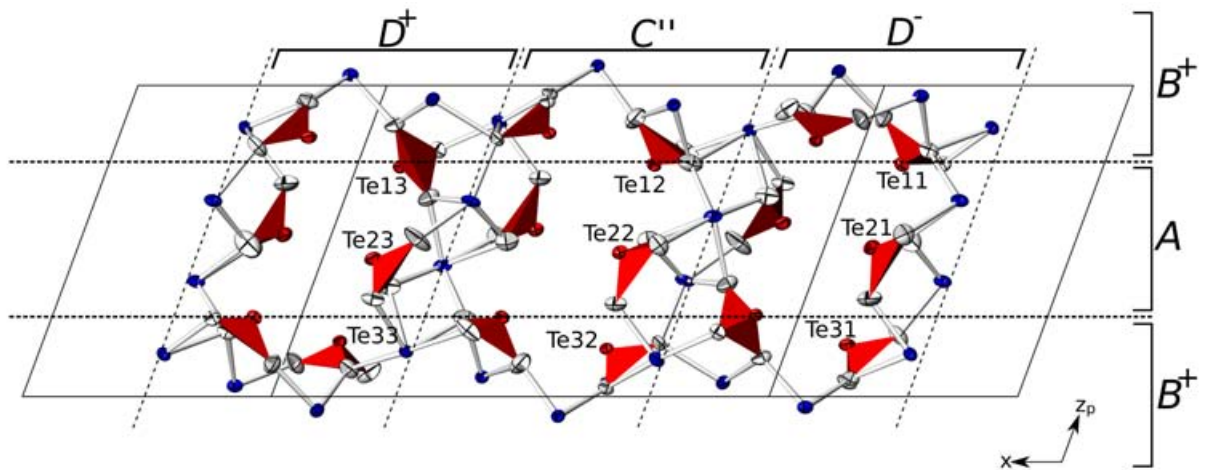
(a) β -CaTeO₃(b) β' -CaTeO₃(c) β'' -CaTeO₃

Figure 3.9: Unit-cell contents of the crystal structures of (a) β - ($P1$), (b) β' -CaTeO₃ ($P\bar{1}$) and (c) Ca_{0.11}Sr_{0.89}TeO₃ (β'' -Ca) ($P\bar{1}$), measured at 295 and at 200 K, respectively, projected along $[130]$ exemplifying the threefold superstructure along $[100]$. Colour codes, displacement ellipsoids and symbols as in Fig. 3.2. The layer type according to the OD description of γ -CaTeO₃ is denoted by letters to the right. Letters at the top denote the rod type.

Table 3.11: Comparison of the pseudo-monoclinic metrics of the subcells in β - and β' - CaTeO_3 measured at different temperatures with the cell parameters of MDO_1 of γ - CaTeO_3

Compound	β' - CaTeO_3	β' - CaTeO_3	β' - CaTeO_3	γ - CaTeO_3 (MDO_1)
T [K]	200(2)	250(2)	275(2)	295(2)
a [Å]	8.5330(2)	8.5383(1)	8.5405(1)	8.4010(17)
b [Å]	5.5568(2)	5.5604(1)	5.5619(1)	5.6913(11)
c [Å]	11.2384(3)	11.2440(2)	11.2481(1)	11.340(3)
α [°]	90.671(2)	90.652(2)	90.639(5)	90
β [°]	112.398(1)	112.394(2)	112.393(7)	110.82(3)
γ [°]	87.461(1)	87.480(1)	87.499(1)	90
V [Å ³]	492.20(2)	493.08(2)	493.53(2)	506.8(2)
Compound	β - CaTeO_3	β - CaTeO_3	β - CaTeO_3	β - CaTeO_3
T [K]	275(2)	295(2)	325(2)	350(2)
a [Å]	8.5400(1)	8.5407(3)	8.5410(1)	8.5408(3)
b [Å]	5.5801(1)	5.5816(2)	5.5839(1)	5.5856(2)
c [Å]	11.3279(2)	11.3327(4)	11.3413(2)	11.3482(4)
α [°]	90.783(1)	90.786(1)	90.807(1)	90.814(1)
β [°]	110.245(1)	110.245(1)	110.255(1)	110.260(1)
γ [°]	89.517(1)	89.511(1)	89.480(1)	89.460(1)
V [Å ³]	506.43(2)	506.81(3)	507.40(2)	507.82(3)

ments $\dots D^+ C' D^- D^+ C' D^- \dots$ and $\dots D^+ C'' D^- D^+ C'' D^- \dots$ are centro-symmetric (Fig. 3.10). In β - CaTeO_3 rods C appear either only in one orientation ($\dots D^+ C^+ D^- D^+ C^+ D^- \dots$) resulting in a structure with symmetry $P1$ or in a disordered manner, corresponding to refinements in space group $P\bar{1}$.

When compared to MDO_1 of γ - CaTeO_3 , one of two $[\text{Te}2x\text{O}_3]$ units of rods D is rotated by about 45° removing the mirror plane of layer A . One $[\text{Te}1x\text{O}_3]$ unit, which lies entirely in layer B in γ - CaTeO_3 , is rotated so that one O atom moves from layer B to layer A (Fig. 3.11).

The centrosymmetric subcell C' in β' - CaTeO_3 shows even more deviation from MDO_1 . Both $[\text{Te}1x\text{O}_3]$ units are moved partly into layer A . The $[\text{Te}2x\text{O}_3]$ units of layer A are tilted so that one O atom (O62) is not connected to a Ca atom anymore, but is instead located in the channel. O62 is located 2.47 Å from Te23 in the next subcell in $[\bar{1}30]$ -direction on the opposite side of the channel, giving the only $[3+1]$ oxygen coordination of any Te atom and the only corner sharing between two $[\text{Te}^{IV}\text{O}_x]$ units of all $M\text{TeO}_3$ structures presented in this work.

Rods of type $C^{+/-}$ in β - CaTeO_3 are closely related to the unit cell of the MDO_1 polytype in γ - CaTeO_3 . The atoms in layer A show only slight deviation from those in γ - CaTeO_3 . In layer B , one of the $[\text{Te}3x\text{O}_3]$ units is rotated, so that the two $[\text{Te}3x\text{O}_3]$ units are related by (pseudo-)inversion symmetry, but break the 2_1 symmetry of γ - CaTeO_3 . The $[\text{Te}1x\text{O}_3]$ units, on the other hand, retain the position from MDO_1 , fulfilling 2_1 symmetry, but breaking inversion symmetry. In Fig. 3.10 the units that correspond to those of layers B in γ - CaTeO_3 are shown projected along $[001]$, the O atoms breaking inversion symmetry being highlighted. Rod C can therefore be seen as an intermediate step in a $P\bar{1} \rightarrow P2_1$ transition from β' - CaTeO_3 to γ - CaTeO_3 , which is not yet confirmed.

Rods of type C'' in $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ (β'' -Ca) can be considered a mixture of rods of type $C^{+/-}$ and C' . The atoms in layer A are arranged close to those in rods $C^{+/-}$ in β - CaTeO_3 . In layer B , on the other hand, the $[\text{Te}^{IV}\text{O}_3]$ groups exhibit the centrosymmetric configuration of rods C' in β' - CaTeO_3 . This arrangement is probably possible due to the larger ionic radii of the

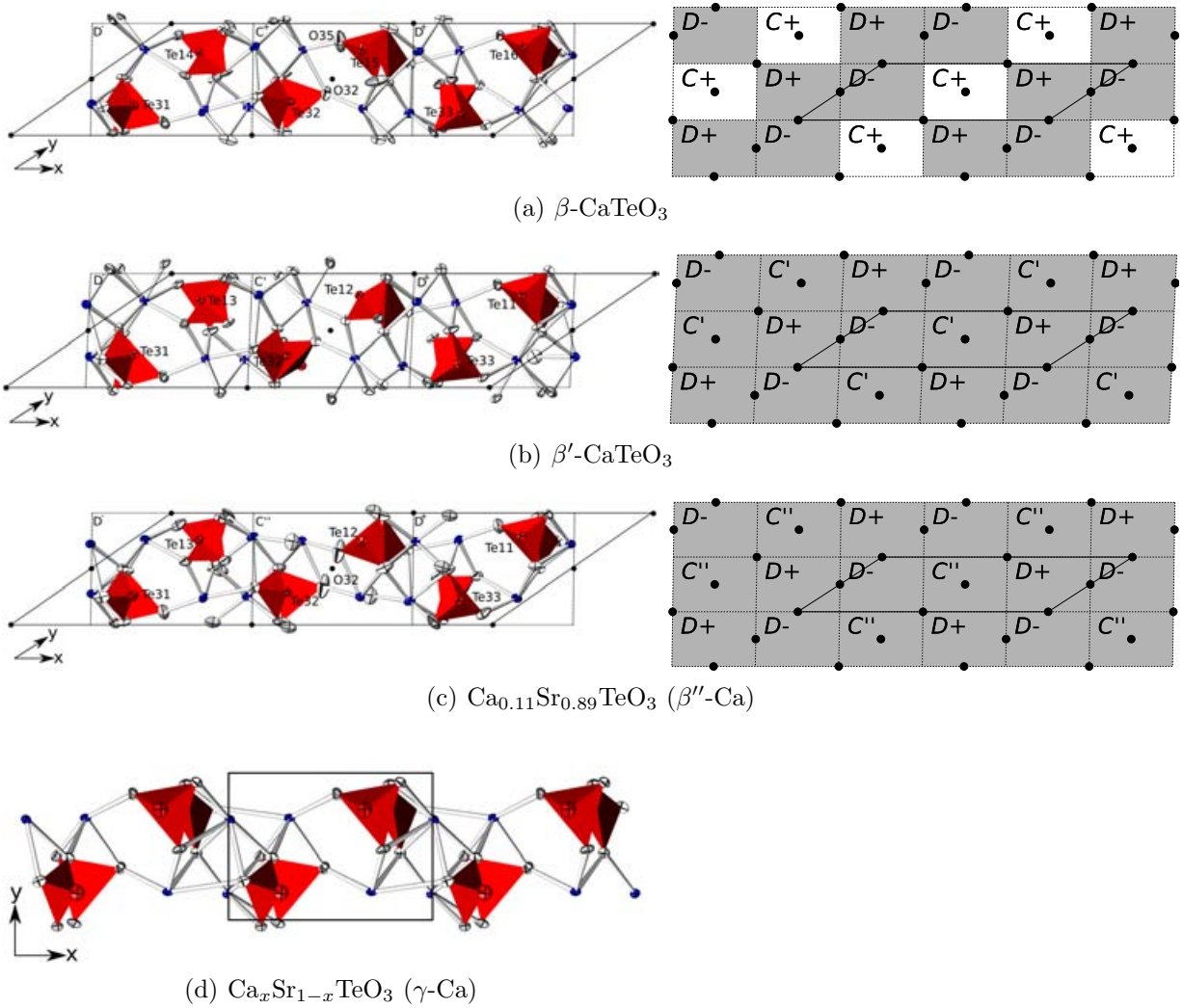


Figure 3.10: Layer *B* of the β -polymorphs and Ca_{*x*}Sr_{1-*x*}TeO₃ (γ -Ca) viewed down [001]. Colour codes and displacement ellipsoids as in Fig. 3.2. Dots symbolize centres of (pseudo-)inversion symmetry. (a) β -CaTeO₃: The pair of oxygen atoms breaking inversion symmetry (O32/O35) is labelled. (b) β' -CaTeO₃. (c) Ca_{0.11}Sr_{0.89}TeO₃ (β'' -Ca) ($P\bar{1}$). (d) Ca_{*x*}Sr_{1-*x*}TeO₃ (γ -Ca). Right: Symbolic arrangement of different types of rods. Rods with a grey background belong to the centrosymmetric parts of the structures.

Sr atoms compared to the Ca positions in the β and β' polymorphs.

In all β -polymorphs, the trigonal-pyramidal shape of the [Te^{IV}O₃] units is characteristic for three-coordinated Te^{IV} atoms (Zemann, 1971). All Te–O distances (Tab. 3.12) are in good agreement with the data given in a review on the crystal chemistry of oxotellurium(IV) compounds (Dolgikh, 1991). The Te–O-distances in the [Te^{IV}O₃₊₁] polyhedron in β' -CaTeO₃ is typical for this kind of coordination, which is, for example, also found in the structures Zn₂Te₃O₈, Te₂MoO₇, CuTeO₃ and CuTe₂O₅ (Arnaudov et al., 1982).

Table 3.12: Selected interatomic distances [$\text{\AA}$] and angles [$^\circ$] in β^- , β' - CaTeO_3 and $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{TeO}_3$ (β'' - Ca) calculated from datasets measured at 350 K, 200 K and 295 K, respectively. Ca/Sr -O distances and data for β^- , and β' - CaTeO_3 measured at other temperatures are given in the supplementary materials.

	β			β'			β''		
	$x = 1$	$x = 2$	$x = 3$	$x = 1$	$x = 2$	$x = 3$	$x = 1$	$x = 2$	$x = 3$
$\text{Te1}x\text{-O}3x$	1.857(3)	-	1.859(3)	1.855(3)	1.884(3)	1.861(3)	1.859(3)	1.845(4)	1.852(3)
$\text{Te1}x\text{-O}3xB$	-	1.805(9)	-	-	-	-	-	-	-
$\text{Te1}x\text{-O}1x$	1.873(3)	1.852(4)	1.888(3)	1.887(3)	1.888(3)	1.891(3)	1.877(3)	1.855(3)	1.884(3)
$\text{Te1}x\text{-O}2x$	1.877(3)	1.827(4)	1.882(3)	1.875(3)	1.865(3)	1.887(3)	1.877(3)	1.869(3)	1.873(3)
$\text{Te1}x\text{-O}3xA$	-	1.915(6)	-	-	-	-	-	-	-
$\text{Te2}x\text{-O}4x$	1.835(3)	1.837(3)	1.858(3)	1.847(3)	1.846(4)	1.867(3)	1.820(4)	1.837(3)	1.861(3)
$\text{Te2}x\text{-O}5x$	1.852(4)	1.839(4)	1.843(4)	1.842(3)	1.859(3)	1.909(3)	1.851(4)	1.863(4)	1.846(4)
$\text{Te2}x\text{-O}6x$	1.857(3)	1.837(3)	1.825(4)	1.857(3)	1.850(4)	1.858(3)	1.855(3)	1.846(3)	1.834(4)
$\text{Te3}x\text{-O}8x$	1.853(3)	1.859(3)	1.848(3)	1.882(3)	1.859(3)	1.864(4)	1.855(3)	1.863(3)	1.865(4)
$\text{Te3}x\text{-O}9x$	1.859(3)	1.889(3)	1.855(3)	1.860(3)	1.887(3)	1.874(3)	1.855(3)	1.885(3)	1.857(3)
$\text{Te3}x\text{-O}7x$	1.862(3)	1.896(3)	1.851(3)	1.883(3)	1.898(3)	1.846(3)	1.862(3)	1.885(3)	1.854(3)
$\text{O}3x\text{-Te1}x\text{-O}1x$	93.37(14)	-	98.61(14)	91.79(15)	97.19(14)	96.73(14)	95.42(14)	102.0(2)	98.21(15)
$\text{O}3x\text{-Te1}x\text{-O}2x$	101.34(15)	-	101.21(14)	101.10(15)	99.74(14)	100.83(14)	100.45(16)	90.70(19)	100.72(14)
$\text{O}1x\text{-Te1}x\text{-O}2x$	93.87(14)	95.8(2)	99.31(14)	95.11(14)	104.20(14)	99.45(14)	95.42(14)	94.25(17)	99.19(14)
$\text{O}32B\text{-Te12-O}22$	-	112.9(4)	-	-	-	-	-	-	-
$\text{O}32B\text{-Te12-O}12$	-	80.5(4)	-	-	-	-	-	-	-
$\text{O}22\text{-Te12-O}32A$	-	84.1(2)	-	-	-	-	-	-	-
$\text{O}12\text{-Te12-O}32A$	-	103.4(2)	-	-	-	-	-	-	-
$\text{O}4x\text{-Te2}x\text{-O}5x$	103.04(17)	104.96(17)	94.51(17)	103.59(17)	99.82(17)	91.63(15)	102.8(2)	104.37(17)	96.50(15)
$\text{O}4x\text{-Te2}x\text{-O}6x$	104.71(16)	101.87(16)	93.43(17)	102.23(16)	98.61(19)	91.61(15)	104.5(2)	102.25(17)	93.95(16)
$\text{O}5x\text{-Te2}x\text{-O}6x$	92.45(17)	94.86(17)	103.4(2)	92.03(16)	99.17(16)	102.89(15)	93.11(18)	94.71(16)	102.5(2)
$\text{O}8x\text{-Te3}x\text{-O}9x$	94.10(15)	98.08(14)	93.04(16)	90.99(15)	96.32(15)	94.69(16)	94.92(15)	96.80(13)	92.50(19)
$\text{O}8x\text{-Te3}x\text{-O}7x$	92.66(14)	92.71(13)	95.97(16)	93.45(15)	92.17(14)	98.76(16)	94.92(13)	94.35(12)	95.18(16)
$\text{O}9x\text{-Te3}x\text{-O}7x$	93.87(14)	89.01(14)	101.90(15)	94.31(14)	89.57(14)	99.65(15)	94.89(14)	91.02(12)	101.61(15)

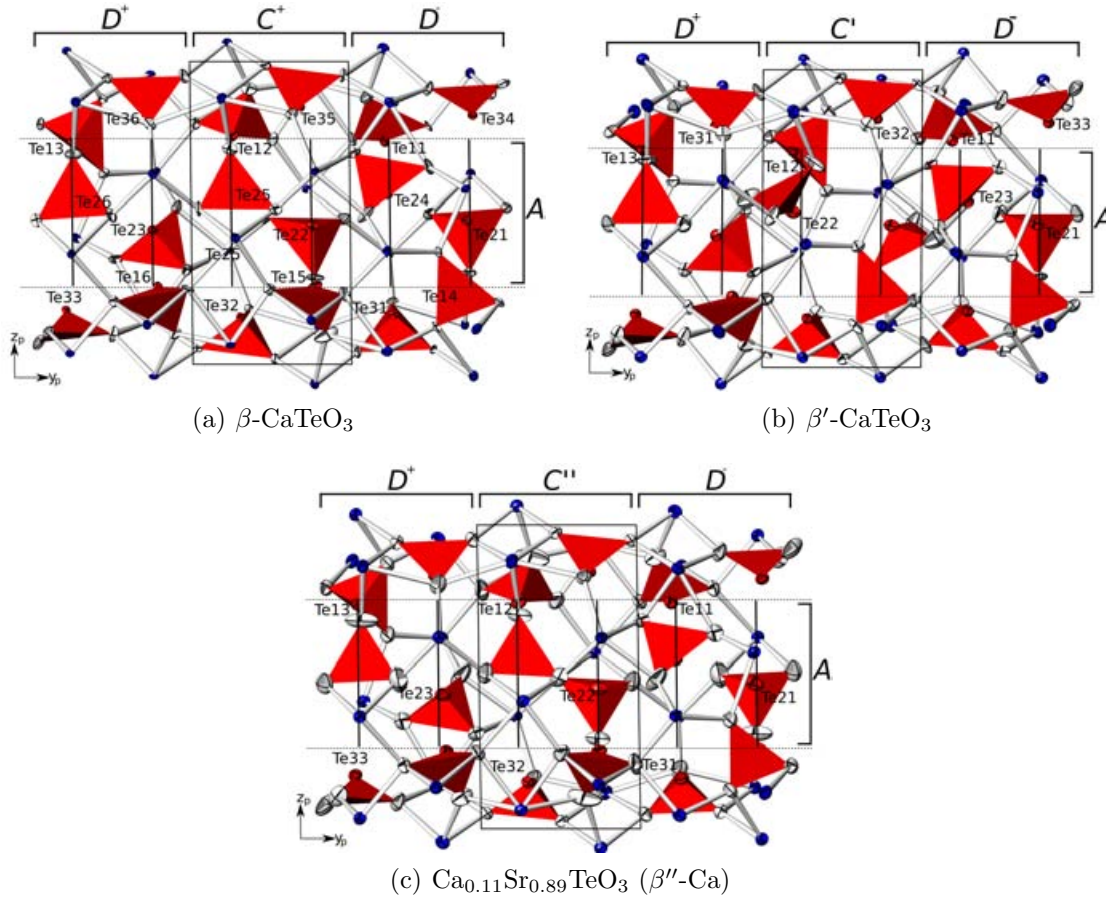


Figure 3.11: Slabs of (a) β -, (b) β' -CaTeO₃ and (c) Ca_{0.11}Sr_{0.89}TeO₃ (β'' -Ca) viewed down [100]. Colour codes and displacement ellipsoids as in Fig. 3.2. The middle part corresponds to layer A of γ -CaTeO₃. Black, nearly vertical lines represent the mirror planes of the idealized structure of layer A.

Lattice parameters of the β -polymorphs *vs.* temperature and composition

Due to the superstructure of the β -polymorphs, their lattice parameters and those of the subcells corresponding to the lattice parameters of γ -CaTeO₃ ($b' = |\mathbf{b}'| = |\frac{1}{3}\mathbf{a} - \mathbf{b}|$, $\alpha' = \mathbf{b}', \mathbf{c}$ and $\gamma' = \mathbf{a}, \mathbf{b}'$) and their relation to those of γ -CaTeO₃ were analyzed.

The cell volume of β - and β' -CaTeO₃ increases linearly with temperature (Fig. 3.12(a)) as do the lattice parameters b , b' and c . a , on the other hand, increases linearly only in β' -CaTeO₃, whereas in β -CaTeO₃ the increase is less marked and a even reaches a maximum at 325 K (Fig. 3.12(b)). The angles of the subcell α' , β and γ' all show opposite behaviour in β - and β' -CaTeO₃: α' and β decrease with temperature in β' - and increase in β -CaTeO₃, γ' increases in β' - and decreases in β -CaTeO₃ (Fig. 3.12(b)).

The phase transition β' -CaTeO₃ $\rightarrow$ β -CaTeO₃ is marked by a distinct jump in lattice parameters as can be seen by comparison of the lattice parameters of both phases measured at 275 K: The cell volume increases from 1480.59(5) to 1519.28(5) Å³, c increases from 5.5619(1) to 5.5801(1) Å, whereas b decreases from 10.3933(2) to 10.2408(2) Å. This can be associated with an increase of γ' by over 2° from 87.499(1)° to 89.517(1)°, resulting in a pseudo-monoclinic metrics of the subcell, and thus a shortening of the diagonal of the basis of the subcell. a does practically not change for β - and β' -CaTeO₃ at 275 K. b' jumps significantly from 5.5619(1) to

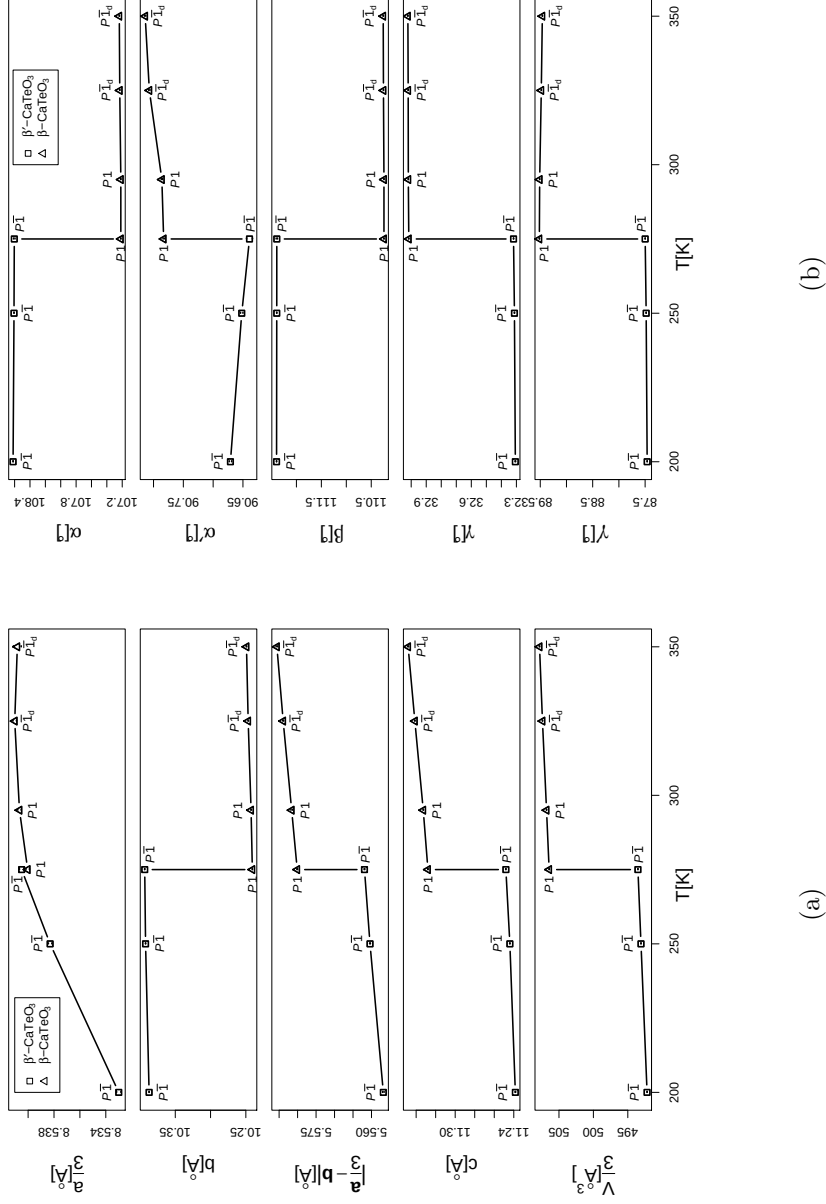


Figure 3.12: Variation of (a) the lattice parameters a , b , c , $b' = \left| \frac{1}{3} \mathbf{a} - \mathbf{b} \right|$ and cell volume and (b) the angles α , $\alpha' = \widehat{\mathbf{b}'\mathbf{c}}$, β , γ , $\gamma' = \widehat{\mathbf{a}\mathbf{b}'}$ (b) of β -, β' -CaTeO₃ with temperature. Measurements of β - and β' -CaTeO₃ are indicated by triangles and squares, respectively. The text next to the symbol indicates the spacegroup, a subscript „d” meaning a disordered structure. Error bars have been omitted since they are smaller than the symbol sizes.

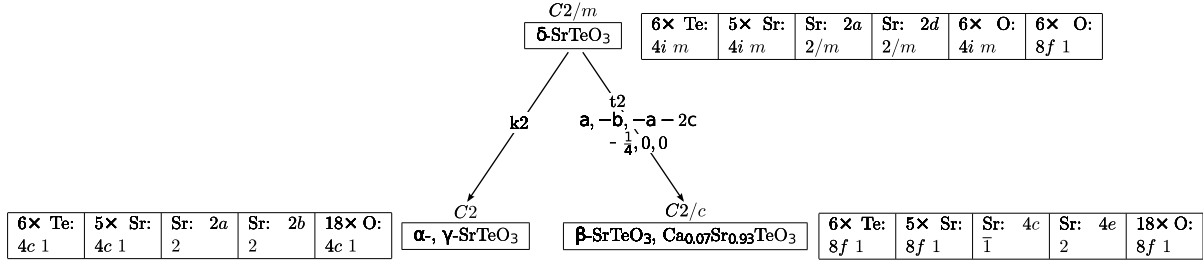


Figure 3.13: Bärnighausen family tree illustrating the group-subgroup relationship of the phases α -, β -, γ -, δ -SrTeO₃ and Ca_{0.07}Sr_{0.93}TeO₃ (β -Sr).

5.5801(1) Å showing stretching of the structure in direction of the channels. α' slightly increases from 90.639(5)° to 90.783(5)°. β decreases from 112.392(7)° to 110.245(1)°, the latter being closer to the corresponding angle in γ -CaTeO₃ (110.82(3)°). Finally, γ' jumps by over 2° from 87.499(1)° to 89.517(1)°.

As expected, the cell volume of the Ca/Sr phase Ca_{0.11}Sr_{0.89}TeO₃ (β'' -Ca) is considerably larger than of the unsubstituted β -CaTeO₃ phase measured at the same temperature (1520.42 vs. 1695.42 Å³). The length of the basis vectors of the basic structure increase by approximately equivalent factors (a' increases by 3.2% from 8.5407 to 8.8309 Å, b' by 3.6% from 5.5816 to 5.7911 Å, and c' by 3.9% from 11.3327 to 11.7908 Å). The angles $\alpha' = 91.0455^\circ$ and $\gamma' = 89.2045^\circ$ of the basic cell Ca_{0.11}Sr_{0.89}TeO₃ (β'' -Ca) are close to ideal monoclinic metric. α' is slightly more obtuse than the corresponding angles in β - and β' -CaTeO₃. γ' deviates slightly more from monoclinic metric than γ' in β -CaTeO₃, but is distinctly closer to monoclinic metric than in β' -CaTeO₃.

3.3.7 Crystal structure of Ca_{0.07}Sr_{0.93}TeO₃ (β -Sr)

Refinement

The lattice parameters, symmetry and systematic extinctions of Ca_{0.07}Sr_{0.93}TeO₃ clearly indicated a close relationship to β -SrTeO₃ (Zavodnik et al., 2007b). A first refinement cycle was therefore started with the atomic coordinates published for β -SrTeO₃. Subsequently occupational disorder of the Sr positions was introduced. Each M site was refined as partially occupied by Ca and Sr. The total occupation of every site was then constrained to unity. The atomic coordinates and ADPs of atoms on the same site were constrained to the same values. For three sites (Sr3, Sr5, Sr7), the Ca:Sr ratio was refined to less than the standard uncertainty (s.u.) of the parameter and they were therefore modelled as containing only Sr atoms.

Structure

The Ca_{0.07}Sr_{0.93}TeO₃ (β -Sr) crystals under investigation are solid solutions with a minor Ca content relative to β -SrTeO₃ (Zavodnik et al., 2007b) and crystallize in space group $C2/c$. β -SrTeO₃ is closely related to the α -, γ - and δ -SrTeO₃ polymorphs (Zavodnik et al., 2007a,c, 2008). So far, no detailed overview on the relationship of the (α - δ)-SrTeO₃ polymorphs has been published. All four polymorphs crystallize in monoclinic C -centred space groups. From a group-theoretical point of view, δ -SrTeO₃ (symmetry $C2/m$), the modification stable at the highest temperature, is the aristotype of the structure family. An overview of the group-subgroup relationship of the symmetry groups of the polymorphs is illustrated in a Bärnighausen family tree (Bärnighausen, 1980) in Fig. 3.13. Compared to δ -SrTeO₃, the structures of α - and γ -

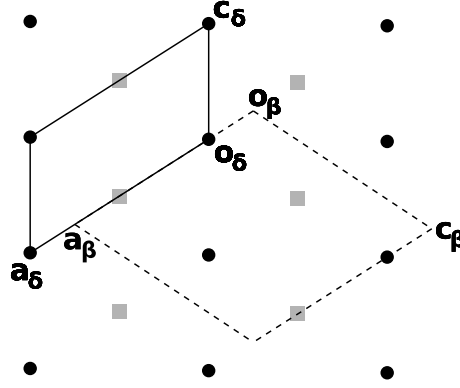


Figure 3.14: The lattice of $\delta\text{-SrTeO}_3$ viewed down $[010]$, represented by circles (located on the drawing plane) and squares (translated by $\frac{1}{2}\mathbf{b}$). The unit cells of $\delta\text{-SrTeO}_3$ and $\beta\text{-SrTeO}_3$ are represented by continuous and dashed lines, respectively.

Table 3.13: Parameters of the monoclinic cells of α -, γ -, $\delta\text{-SrTeO}_3$ (Zavodnik et al., 2007a,c, 2008) and the cells of the basic structures of $\beta\text{-SrTeO}_3$ (Zavodnik et al., 2007b) and $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ ($\beta\text{-Sr}$). The temperature during data collection is indicated.

Structure	Rem.	T [K]	a [Å]	b [Å]	c [Å]	β [Å]	V [Å ³]
$\alpha\text{-SrTeO}_3$		295	28.151(6)	5.8970(10)	15.261(3)	122.09(3)	2146.3(8)
$\beta\text{-SrTeO}_3$	†	473	28.206(6)	5.9210(10)	15.417(7)	122.42(2)	2173.5(12)
$\gamma\text{-SrTeO}_3$		583	28.262(6)	5.9350(10)	15.434(3)	122.21(3)	2190.4(8)
$\delta\text{-SrTeO}_3$		780	28.438(6)	5.9500(10)	15.550(3)	122.45(3)	2220.3(8)
$\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ ($\beta\text{-Sr}$)	†	295	27.9800(3)	5.8965(10)	15.2835(10)	122.2730(10)	2131.99(5)

† Lattice parameters of the basic structure are given.

SrTeO_3 ($C2$), which belong to the same structure type, lack mirror symmetry normal to $[010]$ corresponding to a *klassengleiche* symmetry reduction by a factor two. In $\beta\text{-SrTeO}_3$ translational symmetry of $\delta\text{-SrTeO}_3$ parallel to $[001]$ is lost, resulting in a structure with symmetry $C2/c$ and doubled lattice vector $\mathbf{c}$. Instead of the cell setting $\mathbf{c}' = 2\mathbf{c}$ Zavodnik et al. (2007b) chose the reduced cell

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c}) = \begin{pmatrix} 1 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ 0 & 1 & \bar{2} \end{pmatrix}.$$

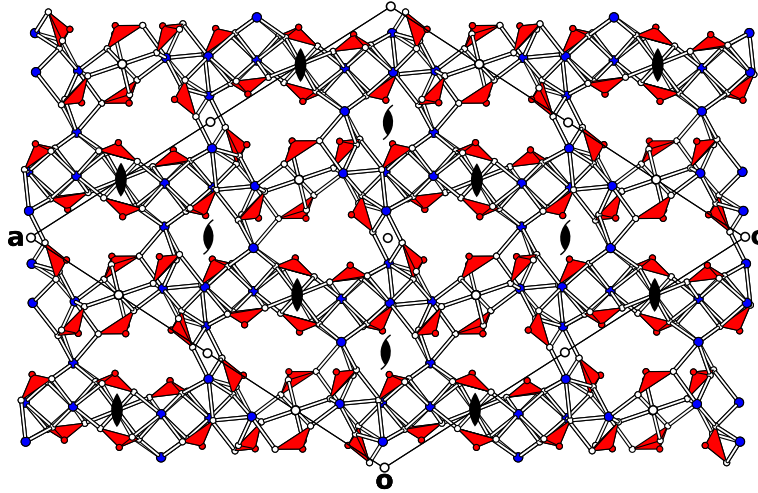
The same setting will be used for the description of $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ ($\beta\text{-Sr}$) for the sake of comparability. The origin of $\beta\text{-SrTeO}_3$ is located at $(-\frac{1}{4}, 0, 0)$ indexed with the basis of $\delta\text{-SrTeO}_3$ ². In Fig. 3.14 a comparison of the cells of $\beta\text{-SrTeO}_3$ and $\delta\text{-SrTeO}_3$, is given. In Tab. 3.13 the cell parameters of α -, γ -, $\delta\text{-SrTeO}_3$ and the basic structures of $\beta\text{-SrTeO}_3$ and $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ ($\beta\text{-Sr}$) are listed. As expected the length of the axes increases with temperature. The volume of the unit cell of $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ ($\beta\text{-Sr}$) is smaller than the volume of $\alpha\text{-SrTeO}_3$ measured at the same temperature, due to partial substitution of Sr by smaller Ca atoms.

The symmetry reduction from $\delta\text{-SrTeO}_3$ to $\beta\text{-SrTeO}_3$ can be described according to the theory of modulated structures. $\beta\text{-SrTeO}_3$ is a twofold a superstructure with a basic structure isotypic to $\delta\text{-SrTeO}_3$. The superspace group symbol reads as $C2/m(00\frac{1}{2})0s$. Reflections

² The origin shift between the α - and $\beta\text{-SrTeO}_3$ polymorphs could have been avoided by using the non-reduced setting $\mathbf{c}' = 2\mathbf{c}$.

Table 3.14: Average and maximum intensities of different reflection classes in $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr).

Reflection class	Avg. [a.u.]	Max. [a.u.]
$h + l = 2n, k + l = 2n$	17.1	1000.0
$h + l = 2n + 1, k + l = 2n + 1$	1.8	47.0

**Figure 3.15:** Crystal structure of $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr) viewed down $[100]$. Atoms are represented by spheres, colour codes as in Fig. 3.1. Rotation axes, screw axes and centres of inversion are indicated using graphical symmetry element symbols according to the *International Tables* (Hahn, 1983).

of $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr) corresponding to the cell of δ - SrTeO_3 ($h + l = 2n$ and $k + l = 2n^3$) are on average 9.4 times more intense than reflection with $h + l = 2n + 1$ and $h + l = 2n + 1$ (Tab. 3.14). These reflection conditions indicate an F -centred cell. Indeed, the additional translational symmetry of δ - SrTeO_3 compared to β - SrTeO_3 corresponds to an F -centring (Fig. 3.14).

Like in the CaTeO_3 structures, the α - δ - SrTeO_3 and $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr) polymorphs contain MO_x ($x = 7 - 8$) polyhedra and isolated trigonal-prismatic $[\text{Te}^{\text{IV}}\text{O}_3]$ polyhedra, linked together to form channels that run down $[010]$. However, the connection of the MO_x and $[\text{Te}^{\text{IV}}\text{O}_3]$ polyhedra differs significantly between the Ca and Sr phases, leading to entirely different structures. The asymmetric unit of $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr) contains six Te, seven M and 18 O atoms. Ca6/Sr6 and Sr7 are located on a centre of inversion and a twofold rotational axis, the remaining atoms on general positions. The structure is composed of layers parallel to (101) with a layer group $p12/c(1)^4$ (Fig. 3.15). The layers consist of a central sheet containing M atoms which is sandwiched on both sides by isolated $[\text{Te}^{\text{IV}}\text{O}_3]$ units. Two further M atoms ($M5$ and $M1$) are located on the surface of the layers and between the layers, respectively.

Two adjacent layers are related by inversions and twofold screws. They are connected *via* the Ca1/Sr1 atoms and the $[\text{Te}5\text{O}_3]$ groups. Thus channels running along $[010]$ are formed. Like in the CaTeO_3 structures, the channels provide space that is required for the electron lone pairs of the $[\text{Te}^{\text{IV}}\text{O}_3]$ units.

³ $h + l = 2n$ and $k + l = 2n$ are equivalent, since $h + k = 2n$ due to the C -centring.

⁴ The basis vectors $\mathbf{a}'$, $\mathbf{c}'$ of the layer are related to the basis vectors of $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ by $\mathbf{a}' = \mathbf{a} - \mathbf{c}$, $\mathbf{c}' = (\mathbf{a} + \mathbf{c})/4$

Table 3.15: Ca substitution in $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{O}_3\text{TeO}_3$ (β -Sr)

Atoms	Ratio
Ca1:Sr1	0.031(5):0.969(5)
Ca2:Sr2	0.226(5):0.774(5)
Ca3:Sr3	0:1
Ca4:Sr4	0.017(5):0.983(5)
Ca5:Sr5	0:1
Ca6:Sr6	0.320(7):0.680(7)
Ca7:Sr7	0:1

Occupational disorder

Only two out of seven M positions (Ca2/Sr2, Ca6/Sr6) in $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr) contain a significant amount of Ca (23% and 32%). The remaining positions contain less than 4% Ca, three of them less than the s.u.. In Tab. 3.16 a comparison of the Te–O and M –O distances of $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{O}_3\text{TeO}_3$ (β -Sr) and β -SrTeO₃ (Zavodnik et al., 2007b) is given. In general the atomic distances are shorter in the Ca/Sr phase, since the data was collected at RT as opposed to 473 K. As expected the decrease of the M –O distances is more pronounced for positions with significant substitution of Sr by Ca (Ca2/Sr2, Ca6/Sr6).

3.4 Microcrystalline materials in the system $M\text{TeO}_3$

3.4.1 Preparation

$M\text{TeO}_3$ phases were obtained as microcrystalline materials by heating samples below the melting point of the used mixtures. All experiments were performed in evacuated silica-ampoules. At temperatures above 1000 K and when employing precursors containing Sr, the samples were put into gold or alumina crucibles in order to prevent reaction with the wall of the ampoule. Quenching of reaction mixtures from different temperatures was performed in a cold-water bath. The absence of impurities was controlled by XRPD of the ground bulk products.

Microcrystalline α -CaTeO₃ was obtained by heating a stoichiometric mixture of CaO and TeO₂ at 973 K for 70 h. Since the hygroscopic CaO had absorbed small amounts of water, multiple experiments were necessary to optimize the amount of CaO in order to obtain single-phase material.

Microcrystalline β -CaTeO₃ was obtained by quenching a mixture of CaO and TeO₂ which was heated in either a gold or an alumina crucible at 1273 K for 70 h.

Microcrystalline $\text{Ca}_x\text{Sr}_{1-x}\text{O}_3$ phases were obtained by replacing CaO with the corresponding CaO:SrO mixtures and heating at 1123 K for 70 h. The ampoules were slowly cooled to room temperature over several hours in order to obtain the thermodynamically stable phases. The reaction conditions of different batches are summarized in Tab. 3.17.

Rietveld refinement

The thermodynamically stable solid solutions $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ with $0.03 \leq x \leq 1$ as described in 3.4.1 were analyzed with XRPD. The phases were identified and the relative weight percentages quantified using Rietveld refinement (FULLPROF (Rodriguez-Carvajal, 1993)). The atomic coordinates and ADPs were taken from single crystal data with the closest composition to

Table 3.16: Selected interatomic distances [$\text{\AA}$] in $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr) and β -SrTeO₃ (Zavodnik et al., 2007b), and relative differences Δ in % of the atomic distances in both structures (β -Sr).

Atoms	$\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$	β -SrTeO ₃	Δ [%]	Avg. Δ [%]	Atoms	$\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$	β -SrTeO ₃	Δ [%]	Avg. Δ [%]
Te1-O12	1.815(5)	1.813(12)	0.11		Sr3-O62	2.540(3)	2.571(8)	-1.21	
Te1-O11	1.845(3)	1.855(9)	-0.54	-0.09	Sr3-O51	2.565(3)	2.555(8)	0.39	
Te1-O13	1.849(3)	1.846(9)	0.16		Sr3-O41	2.622(3)	2.657(11)	-1.32	
Te2-O22	1.837(3)	1.850(10)	-0.70		Sr3-O61	2.657(3)	2.673(9)	-0.60	
Te2-O23	1.867(3)	1.850(10)	0.92	-0.27	Sr3-O63	2.856(3)	2.907(9)	-1.75	-0.49
Te2-O21	1.870(3)	1.859(9)	0.59		Sr3-O43	2.880(3)	2.887(10)	-0.24	
Te3-O33	1.845(3)	1.821(10)	1.32		Sr3-O33	2.982(4)	3.047(11)	-2.13	
Te3-O31	1.846(3)	1.843(8)	0.16	0.31	Sr3-O32	3.065(4)	3.023(11)	1.39	
Te3-O32	1.856(3)	1.866(10)	-0.54		Sr3-O52	3.070(4)	3.045(9)	0.82	
Te4-O42	1.816(4)	1.783(11)	1.85		Sr3-O61	3.267(3)	3.274(9)	-0.21	
Te4-O43	1.844(3)	1.848(9)	-0.22	0.56	Sr4-O22	2.429(3)	2.425(10)	0.16	
Te4-O41	1.845(3)	1.844(10)	0.05		Sr4-O43	2.563(3)	2.563(9)	0.00	
Te5-O52	1.841(4)	1.844(9)	-0.16		Sr4-O63	2.571(3)	2.594(10)	-0.89	
Te5-O53	1.849(5)	1.878(13)	-1.54	-1.07	Sr4-O21	2.636(3)	2.640(9)	-0.15	-0.28
Te5-O51	1.853(3)	1.881(8)	1.49		Sr4-O42	2.667(4)	2.658(13)	0.34	
Te6-O61	1.868(3)	1.869(6)	-0.05		Sr4-O41	2.733(3)	2.761(9)	-1.01	
Te6-O62	1.870(3)	1.856(8)	0.75	0.41	Sr4-O23	2.782(4)	2.829(10)	-1.66	
Te6-O63	1.877(3)	1.867(9)	0.54		Sr4-O62	2.883(3)	2.856(9)	0.95	
Sr1-O63	2.454(3)	2.460(9)	-0.24		Sr5-O13	2.571(3)	2.597(9)	-1.00	
Sr1-O21	2.500(3)	2.525(10)	-0.99		Sr5-O61	2.575(3)	2.596(6)	-0.81	
Sr1-O62	2.510(3)	2.534(8)	-0.95		Sr5-O32	2.584(3)	2.584(10)	0.00	
Sr1-O11	2.582(4)	2.621(8)	-1.49	-1.22	Sr5-O51	2.614(3)	2.603(9)	0.42	-0.28
Sr1-O33	2.667(4)	2.678(10)	-0.41		Sr5-O52	2.637(4)	2.626(9)	0.42	
Sr1-O32	2.781(4)	2.879(11)	-3.40		Sr5-O11	2.676(4)	2.671(9)	0.19	
Sr1-O23	2.791(3)	2.820(11)	-1.03		Sr5-O31	2.712(4)	2.733(9)	-0.77	
Sr2-O53	2.358(5)	2.381(13)	-0.97		Sr5-O33	3.000(4)	3.020(10)	-0.66	
Sr2-O41	2.407(3)	2.428(9)	-0.86		Sr6-O12	2.400(5)	2.440(12)	-1.64	
Sr2-O52	2.444(4)	2.506(9)	-2.47		Sr6-O31	2.430(3)	2.476(8)	-1.86	-1.83
Sr2-O43	2.474(3)	2.505(9)	-1.24	-1.24	Sr6-O13	2.501(4)	2.552(10)	-2.00	
Sr2-O51	2.481(3)	2.510(8)	-1.16		Sr7-O42	2.433(4)	2.479(12)	-1.86	
Sr2-O61	2.778(3)	2.832(7)	-1.91		Sr7-O22	2.684(4)	2.728(10)	-1.61	
Sr2-O53	2.930(6)	2.932(14)	-0.07		Sr7-O23	2.686(3)	2.709(11)	-0.85	-1.19
					Sr7-O21	2.775(3)	2.787(9)	-0.43	

Table 3.17: Details of experiments in the system $\text{Ca}/\text{Sr}/\text{Te}/\text{O}$ below the melting point of the used mixtures. Weight percentages of the elucidated structure types according to Rietveld refinement (FULLPROF (Rodríguez-Carvajal, 1993)). The values may differ from actual weight percentages, since the exact composition of the solid solutions is not known. Structural models close to the expected ones were used in the refinements.

Sample weight	Crucible	T [K]	t [h]	Remarks	Structure types
117.8 mg CaO , 319.2 mg TeO_2	-	973	70	-	97% α - CaTeO_3 , 3% $\text{Ca}_4\text{Te}_5\text{O}_{14}$
123.4 mg CaO , 319.2 mg TeO_2	-	973	70	-	95% α - CaTeO_3 , 5% Ca_3TeO_6
120.0 mg CaO , 319.2 mg TeO_2	-	973	70	-	α - CaTeO_3
120.0 mg CaO , 319.2 mg TeO_2	Au	1273	70	quenched	β - CaTeO_3
61.4 mg $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% α - CaTeO_3 , Minor amounts of unidentified phases
65.6 mg $\text{Ca}_{0.80}\text{Sr}_{0.20}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	35% α - CaTeO_3 65% γ - CaTeO_3 MDO ₁ and MDO ₂
71.9 mg $\text{Ca}_{0.67}\text{Sr}_{0.33}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% γ - CaTeO_3 , MDO ₁
79.8 mg $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% γ - CaTeO_3 , MDO ₁
87.8 mg $\text{Ca}_{0.33}\text{Sr}_{0.67}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% γ - CaTeO_3 , MDO ₁
94.1 mg $\text{Ca}_{0.20}\text{Sr}_{0.80}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% γ - CaTeO_3 , MDO ₁
97.0 mg $\text{Ca}_{0.14}\text{Sr}_{0.86}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% β'' - CaTeO_3
98.3 mg $\text{Ca}_{0.11}\text{Sr}_{0.89}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	83% β'' - CaTeO_3 , 17% β - SrTeO_3
100.8 mg $\text{Ca}_{0.06}\text{Sr}_{0.94}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% β - SrTeO_3
103.6 mg $\text{Ca}_{0.03}\text{Sr}_{0.97}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1123	70	slow cooling	100% β - SrTeO_3

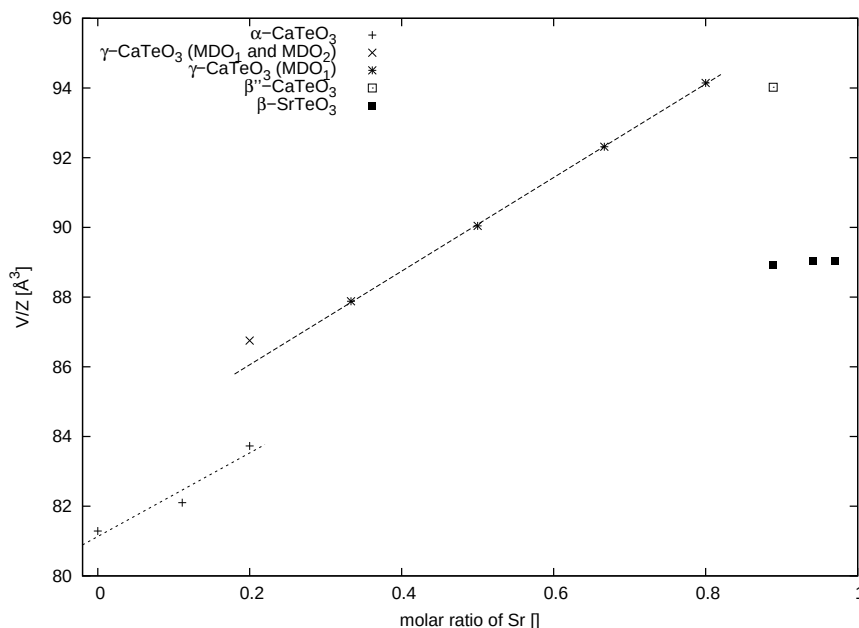


Figure 3.16: V/Z of $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ phases obtained at 1120 K plotted against the molar Sr content of the used $\text{Ca}_x\text{Sr}_{1-x}\text{O}$ precursor. Phases crystallizing in the α - CaTeO_3 structure type are represented by plus-signs (+), γ - CaTeO_3 (MDO_1 and MDO_2) by a cross ($\times$), γ - CaTeO_3 (MDO_1) by stars (*), β'' - CaTeO_3 by a square ($\square$) and β - SrTeO_3 by filled squares ($\blacksquare$). Error bars have been omitted since they are smaller than the symbol size.

the expected phases. After initial refinement runs to identify the phases, lattice parameters were carefully refined. Attempts to refine the Ca:Sr ratio of individual atomic positions or the overall Ca:Sr ratio were unsuccessful. In all cases they resulted in unreasonable, and some times physically meaningless values. Finally crystallite sizes were refined in order to obtain a better match of calculated and measured peak shapes.

Lattice parameters *vs.* composition

In Fig. 3.16, the unit cell volume per formula unit of the microcrystalline phases are plotted against Ca:Sr ratio of the MO reagent. In experiments resulting in more than one phases, the different phases need not necessarily contain the same Ca:Sr ratio. For Ca:Sr ratios $\geq 4 : 1$ the α - CaTeO_3 structure type is obtained. The unit cell volume shows a nearly linear dependence on the Ca:Sr ratio as is indicated by a regression line ($V/Z = 12(3)(1 - x) + 81.1(4) \text{ \AA}^3$) in Fig. 3.16 (symbol +). The sample with a Ca:Sr ratio of 4 : 1 consists of a mixture of the α and γ ($\text{MDO}_1 + \text{MDO}_2$) structure types. The latter has a significantly larger unit cell volume per formula unit which correlates with the reduced density of the unsubstituted γ - CaTeO_3 phase compared to the unsubstituted α - CaTeO_3 phase (4.240 *vs.* $4.406 \text{ g}\cdot\text{ml}^{-1}$). Samples with a ratio of $2 : 1 \geq \text{Ca:Sr} \geq 1 : 4$ crystallize in the γ - CaTeO_3 (MDO_1) structure type. The unit cell volume shows practically a linear dependence on the Sr content as is indicated by a regression line ($V/Z = 13.4(1)(1 - x) + 83.37(7) \text{ \AA}^3$, symbol *) in Fig. 3.16. The unit cell volume of the γ - CaTeO_3 ($\text{MDO}_1 + \text{MDO}_2$) phase with a Ca:Sr ratio of 4 : 1 is larger than expected from this linear dependence. The sample with a Ca:Sr ratio = 1 : 8 contained a mixture of the β'' - CaTeO_3 and β - SrTeO_3 structure types. The transition from the γ - to the β - CaTeO_3 structure type is marked by a decrease of the unit cell volume compared to the interpolated volume of the

γ - CaTeO_3 structure types. This is in contrast to the unsubstituted β - and γ - CaTeO_3 phases, which possess practically the same density at 293 K. At Ca:Sr ratios $\geq 1 : 8$, phases with a β - SrTeO_3 structure type are obtained. Their unit cell volume per formula unit is distinctly smaller than the values interpolated from the phases with α - γ - CaTeO_3 structure types and is practically independent from the Ca:Sr ratio.

3.4.2 Thermal behaviour of α -, β - and γ - CaTeO_3

α -, β - and γ - CaTeO_3 were subjected to simultaneous TG/DSC experiments in a Pt crucible under Ar atmosphere. The samples were heated with a heating rate of 10 K/min from room temperature to 1423 K and subsequently cooled down to room temperature with the same rate. In Fig. 3.17(a) the results of a representative TG/DSC experiment of α - CaTeO_3 are depicted. On heating, a first endothermic effect was determined at 1161(5) K. This corresponds well with the fact that samples that were heated beyond 1170 K and quenched, consisted of β - or γ - CaTeO_3 . So far it was not possible to reveal the nature of this high temperature (HT)- CaTeO_3 phase with temperature-dependent XRPD experiments of single phase CaTeO_3 , since slightly below the phase transition point CaTeO_3 either reacts with the used silica capillaries or is oxidized by atmospheric oxygen to tellurates(VI). A phase transition of „ β ”- to „ γ ”- CaTeO_3 was reported by Tripathi et al. (2001) at a similar temperature of 1167 K. The origin of the „ α ”- to „ β ”- CaTeO_3 transition reported by Tripathi et al. (2001) at 1155 K remains unclear.

The melting point of CaTeO_3 was determined as 1379(5) K. The reverse exothermic effects (crystallization and phase transition $\text{HT-CaTeO}_3 \rightarrow \alpha\text{-CaTeO}_3$) were determined at 1361 and 1045 K, respectively. Total mass loss during the experiment was 2% probably due to minor amounts of evaporated TeO_2 . The residue was identified as single phase α - CaTeO_3 using XRPD.

α -, β and γ - CaTeO_3 were subjected to low temperature (233–273 K) DSC measurements. A representative measurement of β - CaTeO_3 is depicted in Fig. 3.17(b). The endothermic phase transition $\beta' \rightarrow \beta$ is relatively sharp and occurs at ≈ 280 K, whereas the reverse phase transition $\beta \rightarrow \beta'$ is relatively slow, ranging from 273 K to 233 K when cooling with 5 K/s. This corresponds well with the observations made during low temperature single crystal XRD experiments on β - CaTeO_3 (sec. 3.3.6). Since no other CaTeO_3 polymorph investigated during this work showed any phase transition in this temperature range, the ferroelectric phase transition in this temperature range reported by Rai et al. (2002) seems to originate from the β - CaTeO_3 polymorph.

3.5 Single crystals of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$

3.5.1 Preparation

Single crystals of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ were grown by slow cooling of melts which resulted from using excess TeO_2 and were isolated by gentle crushing of chunks between two glass slides. In a typical run a mixture of TeO_2 and MO with molar ratio $\approx 2.1 : 1$ was introduced into an Au or Al_2O_3 crucible which was placed in an evacuated silica ampoule. The reaction container was heated to 1220 K and slowly cooled to 973 K over a period of 72 h. Reaction conditions of several batches are summarized in Tab. 3.18.

3.5.2 Data collection

In all experiments heavily intergrown mica-like crystals were obtained as was already observed by Redman et al. (1970). Isolating crystals suitable for single crystal diffraction proved difficult

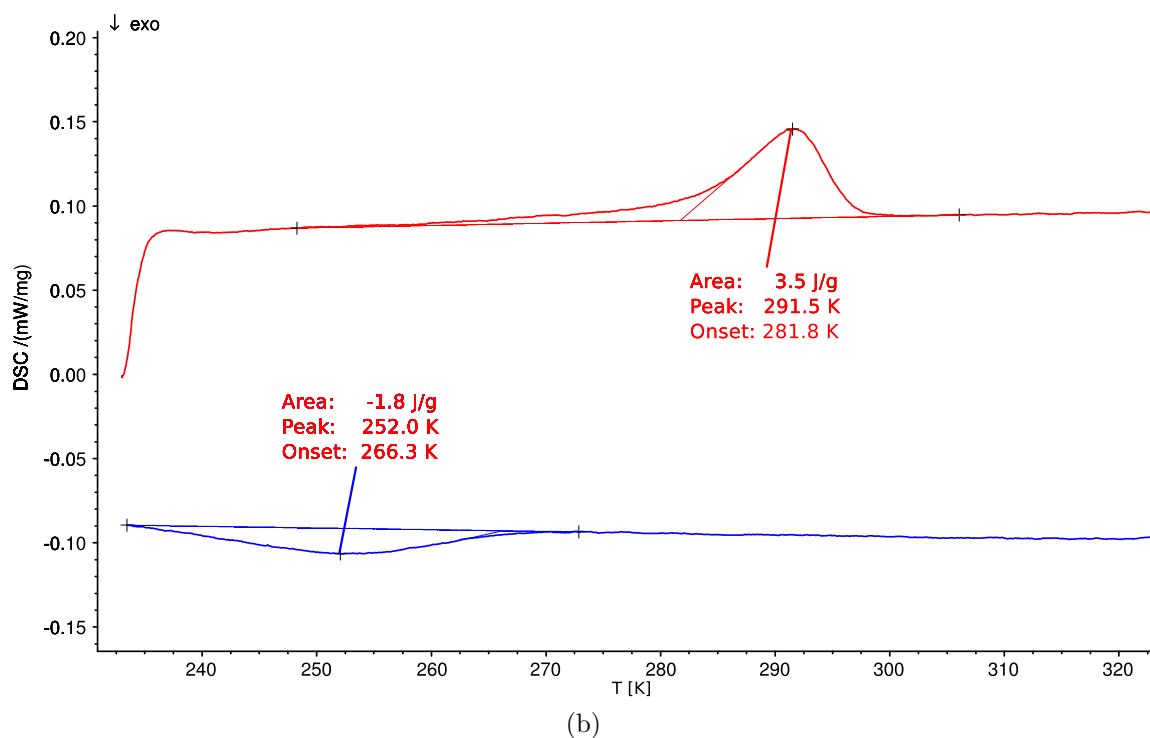
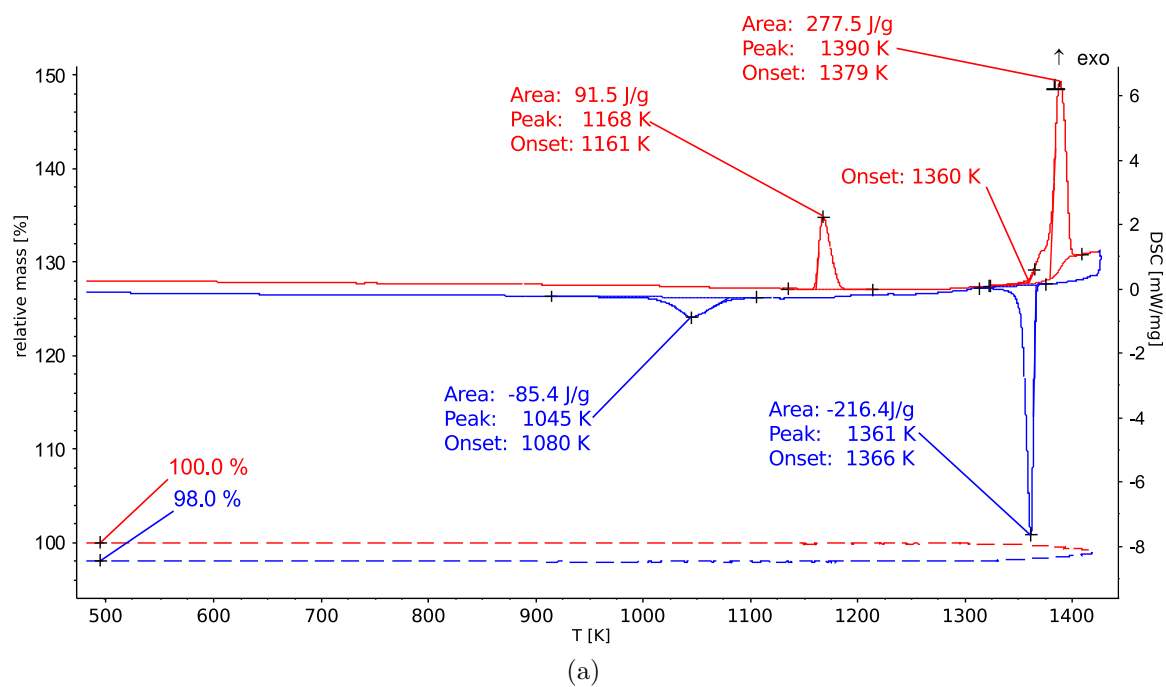


Figure 3.17: (a) Simultaneous TG/DSC experiments on α -CaTeO₃ and (b) DSC experiment on β -CaTeO₃. Both experiments were conducted with heating/cooling rates of 10 K/min under Ar atmosphere. The TG and DSC curves are indicated by dashed and continuous lines. The heating and cooling curves are red and blue, respectively.

Table 3.18: Details of single crystal growth experiments in the system $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$.

Sample weight	Crucible	T [K]	t [h]	Remarks	Phases
56 CaO, 340 mg TeO_2	Au	1220→973	72	molten	Single crystals of unknown phase
65.6 mg $\text{Ca}_{0.80}\text{Sr}_{0.20}\text{O}$, 340 mg TeO_2	Au	1220→973	72	molten	Single crystals of $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$
79.8 mg $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{O}$, 340 mg TeO_2	Al_2O_3	1220→973	72	molten	Single crystals of $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$
103.6 mg SrO , 340 mg TeO_2	Au	1220→973	72	molten	Single crystals of SrTeO_3

as diffraction intensities were either too weak due to small crystal volume or reflections were too diffuse for reliable unit cell determination. Usable crystals were obtained by lifting off a thin plate of a larger conglomerate using a scalpel. A small part of a plate which showed no obvious signs of multiple domains crystal was then cut and mounted on a single crystal sample holder.

Diffraction intensities of single crystals of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ ($x = 1, 0.89, 0.60, 0$) were acquired in multiple sets in ω - and ϕ -scan techniques with 0.5° rotation width, optimized for completeness and redundancy. In total 2626 ($x = 1$), 1136 ($x = 0.89$), 5859 ($x = 0.60$) and 2626 ($x = 0$) frames were recorded.

The direction normal to the main plane of the plate corresponds to direction $\mathbf{c}^*$ in the description below. The diffraction patterns of all crystals showed streaking in $\mathbf{c}^*$ direction, indicating disorder in the stacking direction, and arcing to a varying degree. The arcs are asymmetric, extending from a strong reflection in a single direction by up to $\approx 8^\circ$ and getting continuously weaker. Similar arcing has been described for diffraction patterns obtained from polytypic HgI_2 (Hostettler et al., 2002) and CdS crystals (Trigunayat and Verma, 1962), yet up to now the phenomenon is not fully understood. Only data obtained from crystals without excess arcing lead to satisfying structure refinements. In Fig. 3.5.2 the $h\bar{5}l$ plane in reciprocal space of two SrTe_2O_5 crystals is depicted. Refinements with data of the crystal in Fig. 3.18(a) did not lead to a reasonable model, whereas the structure presented in this work is based on the crystal of Fig. 3.18(b). Despite diffuseness of reflections, the reflections could be indexed in all cases. Analysis of the measured intensities revealed distinct super structure reflections for all $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ phases (Tab. 3.19). For $x = 1$ and $x = 0.89$ reflections with $h + \frac{2}{7}k = 4n$ and $k = 7n$ are on average 47.7 and 61.9 times more intense than of the remaining reflections, corresponding to a monoclinic C -centred basic structure with lattice basis vectors

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c}) \begin{pmatrix} \bar{1} & 0 & \frac{1}{4} \\ 0 & \frac{1}{7} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$$

For $x = 0.60$ reflections with $h + \frac{1}{4}k = 2n$ and $k = 4n$ are on average 8.5 times more intense than remaining reflections, indicating a C -centred basic structure with lattice basis vectors

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c}) \begin{pmatrix} \bar{1} & 0 & \frac{1}{2} \\ 0 & \frac{1}{4} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$$

For SrTe_2O_5 ($x = 0$), reflections with $5h + k = 2n$ are on average 6.4 times more intense than

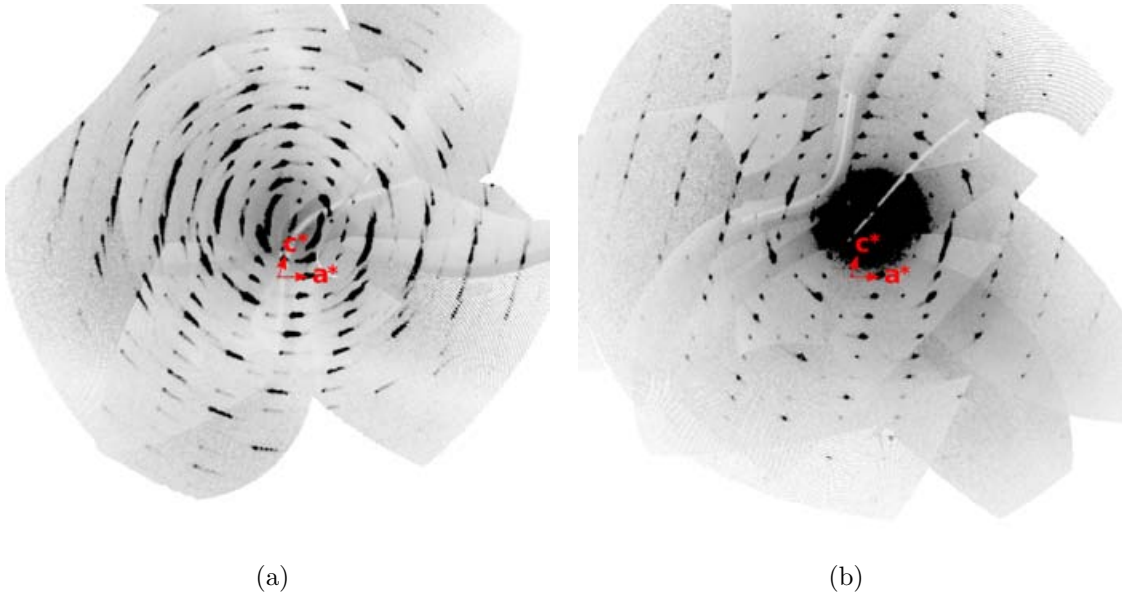


Figure 3.18: $h\bar{5}l$ plane of reciprocal space reconstructed from CCD frames obtained of two different SrTe_2O_5 crystals.

Table 3.19: Average and maximum intensities in a.u. of basic and super structure reflections in different $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ phases.

Structure	Basic structure		Superstructure		$I_{\text{basic}}/I_{\text{super}}$	
	I_{avg} [a.u.]	I_{max} [a.u.]	I_{avg} [a.u.]	I_{max} [a.u.]	I_{avg} [a.u.]	I_{max} [a.u.]
CaTe_2O_5	54.5	1000.0	1.1	78.2	47.7	12.8
$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$	92.4	1000.0	1.5	75.9	61.9	13.2
$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$	21.1	1000.0	2.4	51.4	8.5	19.5
SrTe_2O_5	54.4	1000.0	4.4	106.4	6.4	9.4

remaining reflections, indicating a C -centred basic structure with lattice basis vectors

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c}) \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \frac{1}{5} & \frac{3}{5} \\ 0 & 0 & 1 \end{pmatrix}$$

A comparison of the cell parameters of the basic structures of the $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ phases is given in Tab. 3.20. The values for CaTe_2O_5 compare well with those determined by Redman et al. (1970); Barrier (2010) using XRPD. The unit cell parameters of the α - δ - CaTe_2O_5 polymorphs reported by Tripathi et al. (2001) could not be related to this basic structure.

More details of the various data collections are summarized in Tab. 3.21. Relative atomic coordinates and isotropic ADPs are listed in tables C.16–C.18

3.5.3 Refinement

Since all $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ structures described in this section are composed of closely related layers, the basis vectors have been chosen consistently across the structures. $\mathbf{a}$ and $\mathbf{b}$ are lattice

Table 3.20: Comparison of the cell parameters of the basic structures of the $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ phases and the values for CaTe_2O_5 obtained by Redman et al. (1970); Barrier (2010).

Compound	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å ³]
CaTe_2O_5	6.90	3.89	9.32	90	106.1	90	239.9
$\text{CaTe}_2\text{O}_5^\dagger$	6.90	3.86	9.94	90	115.9	90	238.2
$\text{CaTe}_2\text{O}_5^\ddagger$	6.90	3.89	9.32	90	106.1	90	239.9
$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$	6.91	3.90	9.33	90	106.0	90	241.7
$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$	6.87	4.04	9.33	90	104.6	90	250.5
SrTe_2O_5	7.00	4.09	9.44	87.5	105.9	89.7	259.5

[†] Values determined by Redman et al. (1970)[‡] Values determined by Barrier (2010)

basis vectors of the layers along equivalent directions. This results in non-standard setting for the structures with $x = 1, 0.89$ (symmetry $A12/a1$) and $x = 0$ ($\alpha \approx 38.5^\circ$).

Most heavy atoms were located using direct methods implemented by the SHELX program package (Sheldrick, 2008). The remaining heavy atoms and O atoms were located subsequently from difference Fourier maps. M and Te atoms were refined anisotropically, whereas O atoms were refined using isotropic ADP for $x = 0.89$ and $x = 0.60$, since refinements of the ADPs resulted in unreasonable values. In the structure with $x = 0.60$, the displacement ellipsoids of the M and Te atoms are systematically enlarged parallel to the $\mathbf{c}^*$ and systematic residual electron density is located ≈ 0.60 Å from every Te atom in $\mathbf{c}^*$ and $-\mathbf{c}^*$ direction. This is probably caused by unsatisfactory absorption correction of the very thin plate.

The M positions were refined with occupationally disordered Ca and Sr atoms for the structures with $x = 0.89$ and $x = 0.60$. Atoms on the same site were constrained to the same coordinates and ADPs. The sum of the occupation of each site was constrained to unity. In one position ($M(A)$) in $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ the Sr content was refined to less than its s.u.; it was therefore modelled as containing only Ca in the final refinement cycles.

In order to determine averaged atomic positions and origin shifts between layers, the coordinates of all atoms located in the unit cell ($0 \leq x < 1$, $0 \leq y < 1$, $0 \leq z < 1$) were expressed in a coordinate system with basis vector $\mathbf{c}$ normal to $\mathbf{a}$ and $\mathbf{b}$. The coordinates were then transformed into a pseudo-hexagonal cell of the basic structure. The metrics of the basic cell were idealized to $a_{id} = b_{id} = \sqrt{(ab \sin \gamma)/\sqrt{3}}$, $\gamma_{id} = 120^\circ$. Average structures and origins of the layers were computed by averaging the positions of heavy atoms (Te, M) which are equivalent by the symmetry operations of the idealized basic structure (*c.f.* sec. 3.5.4).

3.5.4 Crystal structure

$\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ are superstructures composed of distinct crystallochemical layers L parallel to (001) (Fig. 3.19). They can be considered as polytypic structures according to OD theory. This explains the high stacking fault probability which interfered during structure determination. Two aspects of the structures are polytypic: On one hand the central parts of the crystallochemical layers have different symmetry than the parts close to the interface between layers. The layers can therefore be „sliced” into sublayers which allow for different orientations according to OD theory. On the other hand, the crystallochemical layers L are connected *via* weak non-bonding interactions which allow for multiple stacking possibilities. For the sake of

Table 3.21: Crystal data and details of the refinements of the ditellurate(IV) phases CaTe_2O_5 , $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$, $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ and SrTe_2O_5 .

	CaTe_2O_5	$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$	$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$	SrTe_2O_5
Crystal data				
Chemical formula	CaTe_2O_5	$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$	$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$	SrTe_2O_5
M_r	375.28	380.63	394.41	422.82
Symmetry	Monoclinic, $A12/a1$	Monoclinic, $A12/a1$	Monoclinic, $P2_1/C$	Triclinic, $P\bar{1}$
Temperature [K]	295(2)	295(2)	295(2)	295(2)
a, b, c [Å]	13.7942(4), 17.9881(5)	13.8201(5), 18.0223(7)	6.874(5), 18.181(11)	6.9952(2), 20.440(6), 15.1538(5)
α, β, γ [°]	90, 95.5550(10), 90	90, 95.615(2), 90	90, 96.83(2), 90	38.518(2), 79.880(2), 89.663(2)
V [Å ³]	6718.2(3)	6766.5(4)	2004(2)	1297.42(7)
Z	56	56	16	10
D_x [Mg·m ⁻³]	5.194	5.231	5.229	5.412
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	13.147	14.162	16.419	21.337
Crystal form, colour	Platelet, colourless	Fragment, colourless	Platelet, colourless	Fragment, colourless
Crystal size [mm]	$0.20 \times 0.08 \times 0.02$	$0.18 \times 0.12 \times 0.07$	$0.20 \times 0.09 \times 0.02$	$0.30 \times 0.20 \times 0.03$
Data collection				
Diffractionmeter	SMART APEX II	SMART APEX II	SMART APEX II	SMART APEX II
Data collection method ω and ϕ scans	ω and ϕ scans	ω and ϕ scans	ω and ϕ scans	
Absorption correction	<i>SADABS</i>	<i>SADABS</i>	<i>SADABS</i>	<i>SADABS</i>
T_{min}, T_{max}	0.301, 0.880	0.164, 0.765	0.1378, 0.7908	0.060, 0.567
No. of measured, independent and observed reflections	75323, 9800, 7510	26378, 8407, 6044	40912, 8774, 6585	27849, 9325, 5957
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.056	0.051	0.071	0.066
θ_{max} [°]	30.0	31.0	35.1	32.7
Refinement				
Refinement on $R[F^2 > 2\sigma(F^2)], wR(F^2), S$	F^2 0.035, 0.052, 1.03	F^2 0.056, 0.168, 1.03	F^2 0.088, 0.240, 1.15	F^2 0.061, 0.187, 1.03
No. of reflections	9800	8407	8774	9325
No. of parameters	510	347	193	361
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 80.6842P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0760P)^2 + 209.2202P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 294.8232P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1029P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001	0.014
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	4.048, -2.961	6.647, -3.73	9.731, -5.13	6.41, -3.53

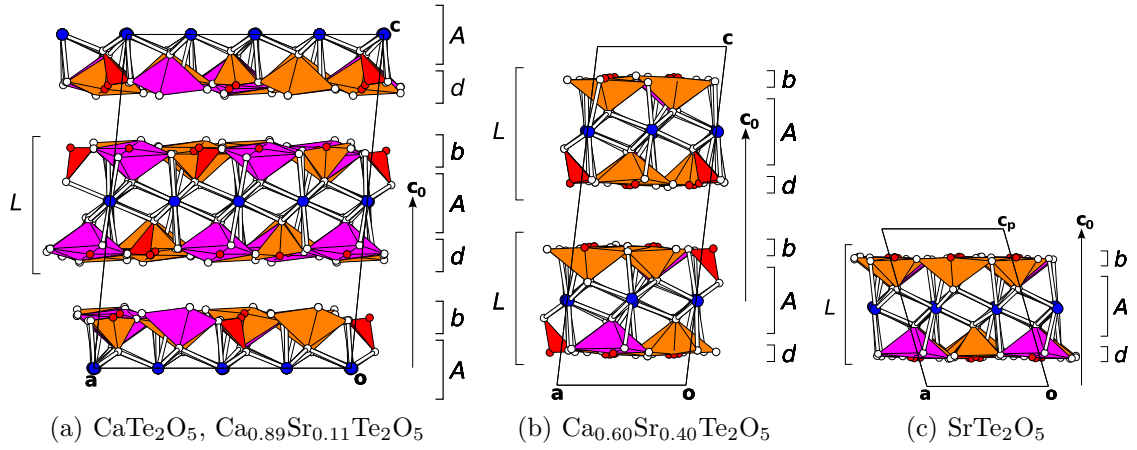


Figure 3.19: The major polytypes in the actual structures of (a) CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ ($A2/a$), (b) $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ ($P21/c$) (c) SrTe_2O_5 ($P\bar{1}$) viewed down $[010]$. $[\text{TeO}_4]$ and $[\text{TeO}_5]$ polyhedra are orange and pink, other atom colour codes as in Fig. 3.1.

simplicity, the OD character will be described on the idealized basic structure. Since the basic structures belong to the same OD family, the parameters of the OD groupoid family provide a convenient way of describing translational components between layers. The super structures of CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ are isotypic, but $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ and SrTe_2O_5 crystallize in unique structure types.

Basic structure

The idealized basic structure of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ belongs to a hexagonal category III OD family with one kind of non-polar layers A and one kind of polar layers b . The OD groupoid family symbol reads as

$$\begin{array}{cc} A & b \\ pmmm(\bar{3})111 & pmmm(6)mmm \\ [r, s] & \{2_{r'}2_{r''}2_{r'''} \left(\begin{array}{c} 6 \\ 3 \end{array} \right) 2_{s'}2_{s''}2_{s'''}\} \end{array}.$$

according to the notation of Grell and Dornberger-Schiff (1982). The translational parameters of the σ -POs relating adjacent layers b and d are expressed in terms of the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{c}$, $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ (Dornberger-Schiff and Grell-Niemann, 1961), the relative translational components between layers A and b in terms of $\mathbf{a}_1$ and $\mathbf{a}_2$.

Layers A (Fig. 3.20(a)) with composition $\infty[\text{MO}_2]^{2-}$ ($M = \text{Ca}, \text{Sr}$) have symmetry $pmmm(\bar{3})111$ ($\hat{=} p(\bar{3})m1$). One crystallographically different M atom is located on a site with symmetry $pmmm(\bar{3})...$, one O atom on a site with symmetry $mmm(3)...$. From a geometrical point of view layers A can be subdivided into OD layers containing only the M and O atoms, respectively. Since layers A are practically identical in all polymorphs, they will be considered only one layer for the sake of simplicity. Layers b (Fig. 3.21(a)) have symmetry $pmmm(6)mmm$ ($\hat{=} p(6)mm$) and contain one crystallographically different Te atom on a site with symmetry $mmm(6)mmm$ and one O atom on a site with symmetry $mmm(3)...$ with an occupation of $\frac{3}{4}$. The Te and O atoms are practically coplanar. The layers are stacked along $[001]$ direction according to $\dots dAbdAb \dots$. A layer triple dAb corresponds to a layer L in the crystallochemical sense.

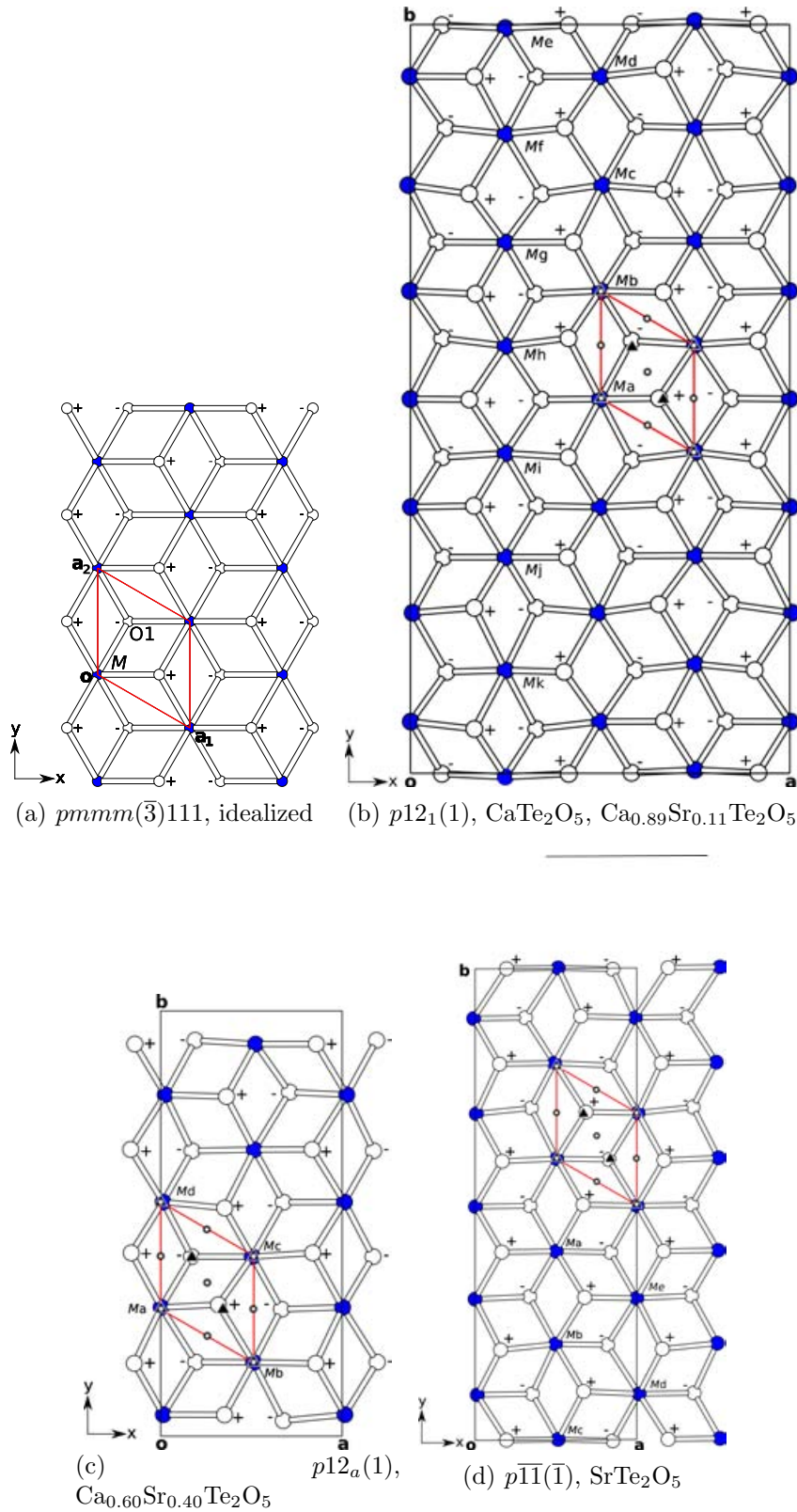


Figure 3.20: OD layers A in (a) the idealized basic structure and the actual structures of $Ca_xSr_{1-x}Te_2O_5$ with (b) $x = 1, 0.89$, (c) $x = 0.60$ and (d) $x = 0$ projected on (001). The unit cells of the layers in the actual structures and the idealized basic structures are indicated by black and red lines, respectively. (Pseudo-)threefold rotation axes and centres of inversion are indicated using graphical symmetry element symbols according to the *International Tables* (Hahn, 1983). The layer symmetries are indicated using the hexagonal cell setting for the idealized basic structure and using the monoclinic cell setting for the actual structure. „+” and „-” signs indicate O atoms above and below the drawing plane, respectively. Atom colour codes as in Fig. 3.19.

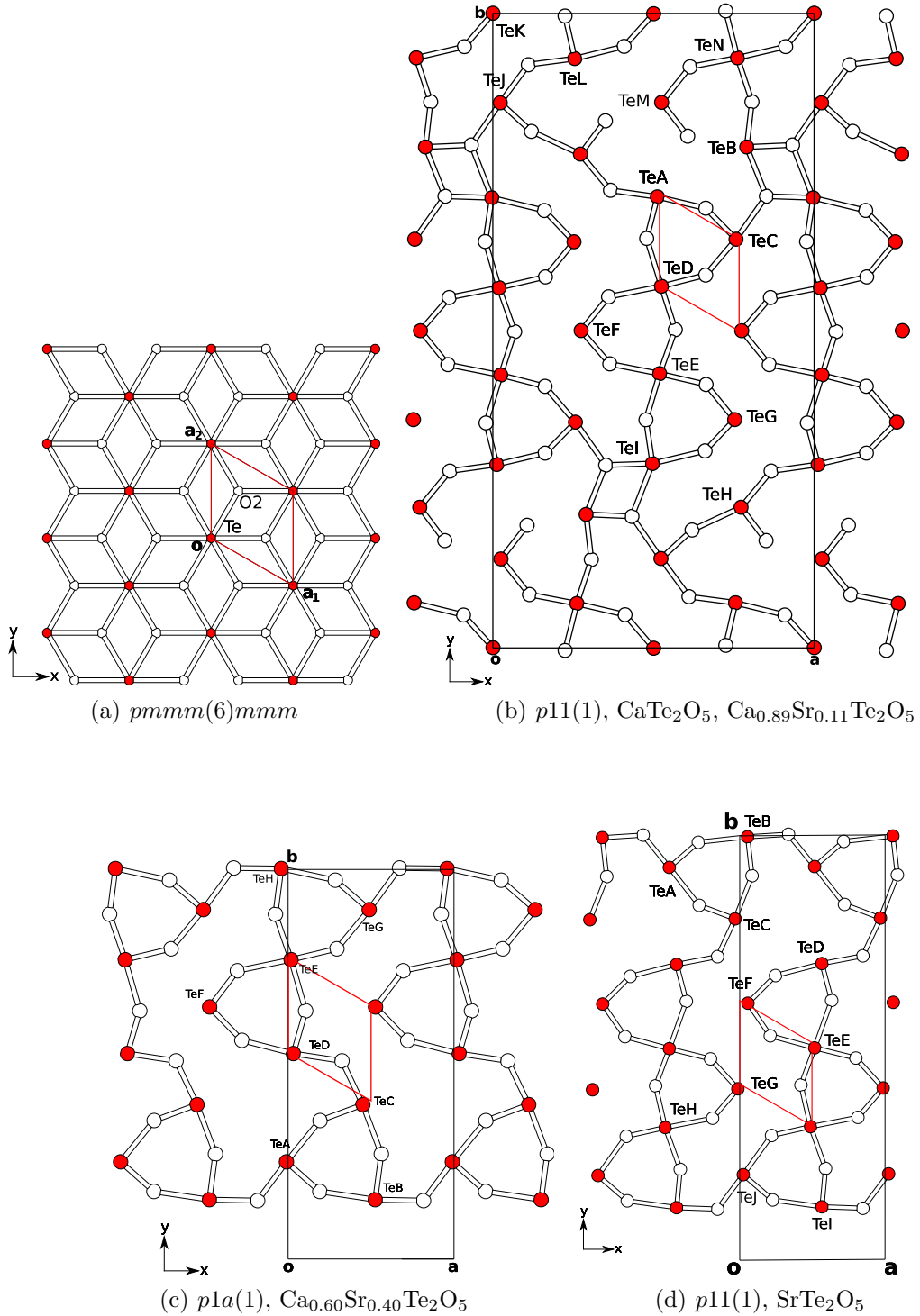


Figure 3.21: OD layers b in (a) the idealized basic structure and the actual structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ with (b) $x = 1, 0.89$, (c) $x = 0.60$ and (d) $x = 0$ projected on (001) . Symbols and colour codes as in Fig. 3.20. Atom colour codes as in Fig. 3.19.

Table 3.22: Dependency of the parameters r' , r'' , r''' , s' , s'' , s''' of the σ -POs between layers b and d on the coordinates (x, y) of the vector leading from the origin of a layer b to the origin of an adjacent layer d projected on the layer plane and values of the parameters and length of the translation vectors $\mathbf{t}$ of the corresponding screws. The origin shifts (x, y) are $(-0.59, -0.30)$, $(0.41, 0.70)$ (CaTe_2O_5), $(-0.60, -0.30)$ or $(0.40, 0.70)$ ($\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$), $(0.33, 0.45)$ ($\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$), $(-0.63, -0.33)$ or $(0.37, 0.67)$ (SrTe_2O_5)

Parameter	Dependency on (x, y)	CaTe_2O_5		$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$		$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$		SrTe_2O_5	
		value	$ \mathbf{t} $ [Å]	value	$ \mathbf{t} $ [Å]	value	$ \mathbf{t} $ [Å]	value	$ \mathbf{t} $ [Å]
r'	$\frac{1}{2}x - \frac{1}{4}y$	0.03	0.22	0.04	0.21	0.05	0.43	0.01	0.14
r''	$-\frac{1}{4}x + \frac{1}{2}y$	0	0	0	0	0.14	1.13	-0.01	0.06
r'''	$\frac{1}{4}x - \frac{1}{4}y$	0.22	1.74	0.22	1.75	-0.20	1.56	0.24	1.96
s'	$\frac{\sqrt{3}}{4}y$	-0.13	1.00	-0.13	1.01	0.19	1.55	-0.14	-1.16
s''	$-\frac{\sqrt{3}}{4}x$	-0.18	1.39	-0.18	1.38	-0.14	1.15	-0.16	-1.29
s'''	$-\frac{\sqrt{3}}{4}x - \frac{\sqrt{3}}{4}y$	-0.13	1.00	-0.13	1.01	-0.05	0.40	-0.13	-1.06

The origins of two adjacent layers A and b projected on the layer plane are related by a translation along $r\mathbf{a}_1 + s\mathbf{a}_2$. For CaTe_2O_5 ($\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$) and SrTe_2O_5 , the origin shifts are similar with $(r, s) = (0.67, 0.34)$ and $(r, s) = (0.68, 0.32)$, respectively, whereas in $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ they are substantially different with $(r, s) = (0.68, 0.46)$

Two adjacent layers b and d are related by twofold screws parallel to the layer planes with translational components $2r'\mathbf{a}_1$, $2r''\mathbf{a}_2$, $2r'''\mathbf{a}_3$, $2s'\mathbf{b}_1$, $2s''\mathbf{b}_2$ and $2s'''\mathbf{b}_3$. The parameters r' , r'' , r''' , s' , s'' and s''' are not independent. They can be expressed in terms of the coordinates x and y (in the coordinate system $(\mathbf{a}_1, \mathbf{a}_2)$) of the vector leading from the origin of a layer b to the origin of an adjacent layer d projected on the layer plane. A derivation of the dependencies is given in app. A.3. The origin shift (x, y) is ambiguous⁵ and has been chosen to result in small absolute values of the parameters. An overview of the actual values and the corresponding length of the translation vectors are listed in Tab. 3.22. A graphical overview of the translational components of the screws is given in Fig. 3.22. Similar to the translation vectors connecting layer pairs Ab , the translational parameters connecting layer pairs bd are similar in CaTe_2O_5 , $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ and SrTe_2O_5 but differ significantly from the parameters in $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$. While r'' is 0 in CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ for reasons of symmetry, it is close to 0 in SrTe_2O_5 .

NFZ relationship

According to the OD description, the idealized basic structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ contain two non-equivalent intralayer contacts, *viz.* Ab , bd . For both the NFZ relationship in the form $Z = N/F$ (Đurovič, 1997) can be applied: Layer pairs bd are symmetric by inversion and therefore possess reverse continuations. Layer pairs Ab consist of layers of different kinds and therefore no σ - τ -PO relating both layers exists.

The group of λ - τ -POs of layers A is $pmmm(3)111$. Layers b are polar, therefore all λ -POs are λ - τ -POs and the group of λ - τ -POs is $pmmm(6)111$. The number of possible layer stackings depends on the the allowed amount of idealization. Symmetry elements which are closer than 0.1 Å will be considered overlapping. The distance of the symmetry elements in a layers A and in adjacent layers b can be calculated from the origin shift $r\mathbf{a}_1 + s\mathbf{a}_2$ (app. A.3). Values for the

⁵ Arbitrary integers can be added to x and y .

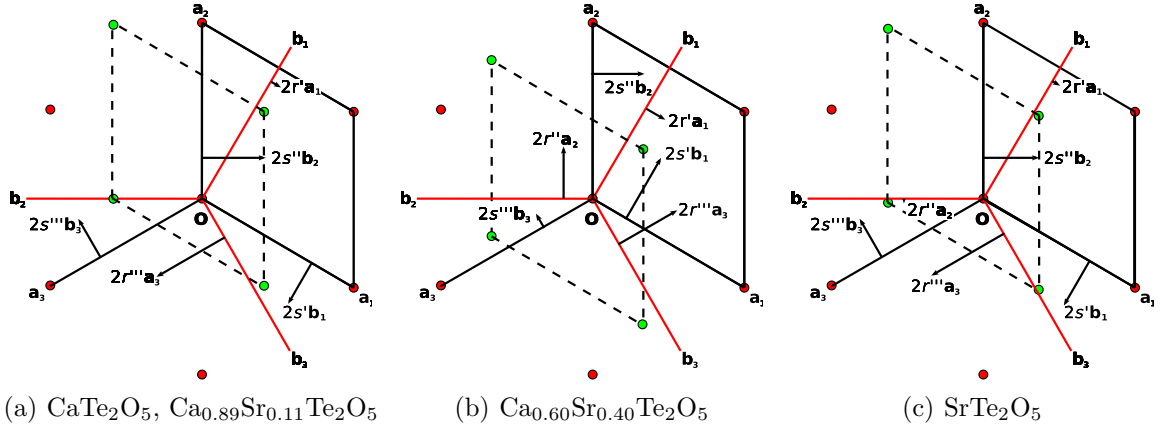


Figure 3.22: Two adjacent layers b and d in the idealized basic structures of (a) CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$, (b) $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ and (c) SrTe_2O_5 projected on (001). Only Te atoms are indicated for reasons of clarity. Te atoms in layers b and d are red and green, respectively. The unit cells of the layers b and d are represented by continuous and dashed lines. The translational components of the screws relating both layers are indicated by arrows. The vector $2r''$ has been left out for $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$, since it is of zero length.

Table 3.23: Distance of symmetry elements in adjacent layers A ($pmmm(3)111$) and b ($pmmm(6)111$) in the idealized basic structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$.

Symm. A	Symm. b	Direction	CaTe_2O_5 d [Å]	$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ d [Å]	$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ d [Å]	SrTe_2O_5 d [Å]
3	6	$\mathbf{c}_1$	0.01	0.02	0.48	0.08
m	m	$\mathbf{a}_1$	0.01	0.01	0.44	0.04
m	m	$\mathbf{a}_2$	0.01	0.02	0.06	0.04
m	m	$\mathbf{a}_3$	0.01	0.01	0.39	0.08

idealized basic structures are listed in Tab. 3.23. In CaTe_2O_5 , $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ and SrTe_2O_5 all λ - τ -POs of layers A also apply for layers b and therefore $F = G = |pmmm(3)111| = 6$. Thus, given the position of a layer A , an adjacent layer b can appear in $Z = N/F = 6/6 = 1$ orientations and given the position of a layer b an adjacent layer A can appear in $Z = N/F = 12/6 = 2$ orientations. In $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$, the mirror planes normal to $\mathbf{a}_2$ of adjacent layers A and b are only separated by 0.06 Å and can therefore be considered as overlapping. The remaining symmetry elements are separated by 0.39 Å or more. The group of λ - τ -POs which apply to a layer pair Ab is therefore $p1m1(1)111$ and $F = |p1m1(1)111| = 2$. Thus, given the position of a layer A , an adjacent layer b can appear in $Z = N/F = 6/2 = 3$ orientations and given the position of a layer b an adjacent layer A can appear in $Z = N/F = 12/2 = 6$ orientations.

For a layer pair bd , the distances between symmetry elements are directly obtained from the parameters r' , r'' , r''' , s' , s'' , and s''' (Tab. 3.22). The group of λ - τ -POs which apply to a layer pair bd is $p1m1(1)111$ for CaTe_2O_5 , $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ and SrTe_2O_5 and $p111(1)111$ for $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$. Given a layer b , an adjacent layer d can appear in $Z = N/F = 12/2 = 6$ and $Z = N/F = 12/1 = 12$ orientations, respectively. In Tab. 3.24 and 3.25 an overview on the NFZ relationship applied to layer pairs Ab and bd is given.

Table 3.24: Overview of the different layer stacking possibilities according to the NFZ relationship in the basic structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ with $x = 1, 0.89, 0$.

L	CaTe_2O_5 , $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ and SrTe_2O_5				
	G	N	F	F	$Z = N/F$
A	$pmmm(3)111$	6			2
			$pmmm(3)111$	6	
b	$pmmm(6)mmm$	12			1
b	$pmmm(6)mmm$	12			6
			$p1m1(1)111$	2	
d	$pmmm(6)mmm$	12			6

Table 3.25: Overview of the different layer stacking possibilities according to the NFZ relationship in the basic structures of $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$.

L	CaTe_2O_5				
	G	N	F	F	$Z = N/F$
A	$pmmm(3)111$	6			6
			$p1m1(1)111$	2	
b	$pmmm(6)mmm$	12			3
b	$pmmm(6)mmm$	12			12
			$p111(1)111$	1	
d	$pmmm(6)mmm$	12			12

Major polytypes of the basic structure

In all $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ crystals under investigation, the basic structure of the major polytype consists of only one kind of layer triple (for $x = 1, 0.89, 0$ only one kind of layer triple can exist according to the NFZ relationship (sec. 3.5.4)). The major polytype of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ ($x = 1, 0.89, 0$) has symmetry $C2/m$ with lattice vectors

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{c}_0) \begin{pmatrix} 2 & 0 & 1+r \\ 1 & 1 & s \\ 0 & 0 & 1 \end{pmatrix}$$

Superstructure

Apart from desymmetrization, layers A in the actual structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ are identical to the description of the basic structure given above. Layers b , on the other hand, can be described as 28-fold ($x = 1, 0.89$), eightfold ($x = 0.60$) and tenfold ($x = 0$) superstructures of the corresponding layer in the basic structure. Since the superstructures are not (pseudo-)trigonal or (pseudo-)hexagonal, their lattice basis vectors will be called $\mathbf{a}$ and $\mathbf{b}$. They are

related to the lattice basis vectors of the basic structure by $(\mathbf{a}, \mathbf{b}) = (\mathbf{a}_1, \mathbf{b}_2) \begin{pmatrix} 4 & 7 \\ 2 & 0 \end{pmatrix}$ ($x = 0.89$),

$(\mathbf{a}, \mathbf{b}) = (\mathbf{a}_1, \mathbf{b}_2) \begin{pmatrix} 1 & 4 \\ 2 & 0 \end{pmatrix}$ ($x = 0.60$) and $(\mathbf{a}, \mathbf{b}) = (\mathbf{a}_1, \mathbf{b}_2) \begin{pmatrix} 1 & 5 \\ 2 & 0 \end{pmatrix}$ ($x = 0$). In each case, three out of four O positions in the superstructure are occupied. As expected, atoms are moved towards non-occupied O positions (Fig. 3.21).

Table 3.26: Selected inter-atomic distances in the actual structures of CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$.

CaTe_2O_5				$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$			
Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
TeA–O1F	1.854(4)	TeH–O2A	1.852(4)	TeA–O1F	1.848(6)	TeH–O2A	1.797(8)
TeA–O2R	1.881(4)	TeH–O1J	1.855(4)	TeA–O2R	1.878(7)	TeH–O1J	1.851(6)
TeA–O2Q	2.097(4)	TeH–O2Q	2.008(4)	TeA–O2Q	2.081(7)	TeH–O2Q	2.031(7)
TeA–O2C	2.134(4)	TeH–O2T	2.299(4)	TeA–O2C	2.145(7)	TeH–O2T	2.332(8)
TeB–O1M	1.845(4)	TeI–O1B	1.857(4)	TeB–O1M	1.846(7)	TeI–O1B	1.855(7)
TeB–O2U	1.958(4)	TeI–O2K	1.919(4)	TeB–O2U	1.974(8)	TeI–O2K	1.918(7)
TeB–O2S	1.982(4)	TeI–O2D	2.011(4)	TeB–O2S	1.995(7)	TeI–O2D	2.024(7)
TeB–O2D	2.306(4)	TeI–O2J	2.334(4)	TeB–O2D	2.281(7)	TeI–O2J	2.324(7)
TeC–O1N	1.867(4)	TeI–O2U	2.421(4)	TeC–O1N	1.863(6)	TeI–O2U	2.454(8)
TeC–O2C	1.881(4)	TeJ–O2T	1.845(4)	TeC–O2C	1.879(7)	TeJ–O2T	1.823(7)
TeC–O2E	2.036(4)	TeJ–O1C	1.861(4)	TeC–O2E	2.023(6)	TeJ–O1C	1.865(6)
TeC–O2D	2.236(4)	TeJ–O2P	2.055(4)	TeC–O2D	2.272(7)	TeJ–O2P	2.042(6)
TeD–O1G	1.845(4)	TeJ–O2U	2.202(4)	TeD–O1G	1.843(6)	TeJ–O2U	2.204(8)
TeD–O2E	1.955(4)	TeK–O1D	1.854(4)	TeD–O2E	1.963(6)	TeK–O1D	1.863(6)
TeD–O2F	2.028(4)	TeK–O2N	1.893(4)	TeD–O2F	2.018(6)	TeK–O2M	1.891(6)
TeD–O2R	2.185(4)	TeK–O2M	1.901(4)	TeD–O2R	2.200(7)	TeK–O2N	1.893(7)
TeD–O2H	2.347(4)	TeL–O1K	1.850(4)	TeD–O2H	2.340(6)	TeL–O1K	1.841(6)
TeE–O1A	1.844(4)	TeL–O2L	1.898(4)	TeE–O1A	1.844(6)	TeL–O2L	1.916(6)
TeE–O2F	2.060(3)	TeL–O2P	2.040(4)	TeE–O2F	2.066(6)	TeL–O2P	2.047(6)
TeE–O2I	2.062(4)	TeL–O2N	2.189(4)	TeE–O2I	2.048(7)	TeL–O2N	2.185(7)
TeE–O2K	2.091(4)	TeM–O2B	1.856(4)	TeE–O2K	2.100(7)	TeM–O2B	1.838(7)
TeE–O2G	2.188(4)	TeM–O1E	1.857(4)	TeE–O2G	2.207(6)	TeM–O1E	1.861(7)
TeF–O1H	1.861(4)	TeM–O2O	1.959(4)	TeF–O1H	1.862(6)	TeM–O2O	1.969(6)
TeF–O2H	1.884(4)	TeN–O1L	1.850(4)	TeF–O2H	1.881(6)	TeN–O1L	1.845(6)
TeF–O2G	1.906(4)	TeN–O2S	2.052(4)	TeF–O2G	1.894(6)	TeN–O2S	2.062(7)
TeG–O1I	1.853(4)	TeN–O2M	2.115(4)	TeG–O1I	1.848(6)	TeN–O2O	2.110(6)
TeG–O2J	1.861(4)	TeN–O2O	2.122(4)	TeG–O2J	1.858(8)	TeN–O2L	2.117(6)
TeG–O2I	1.934(4)	TeN–O2L	2.134(4)	TeG–O2I	1.949(7)	TeN–O2M	2.128(6)

The symmetry of layers b is reduced to $p1$ ($x = 0.60$ and $x = 0$) and $p1a(1)$ ($x = 0.89$). In both cases an OD interpretation as given in sec. 3.5.4 would result in only $Z = 1$ different possible orientations of a layer d , given an adjacent layer b . This appears unlikely, given the large distance between the atoms of layers b and d . Instead, layers b can be split into two layers, *viz.* layers b^1 containing the O atoms and layers b^2 containing the Te atoms resulting in a stacking sequence of $\dots d^2 d^1 A b^1 b^2 d^2 d^1 A b^1 b^2 \dots$. According to this model, contact between crystallochemical layers L is based mainly on the interaction of Te atoms, *i.e.* their lone pairs which protrude towards the layers. Thus, an OD description equivalent to the one given in sec. 3.5.4 is obtained with additional stacking possibilities of the O atoms in layers b^1 . Since layers b^1 have different lattices in the three structures, they belong to different OD families.

Every Te atom in the superstructures is connected to one O atom in layer A and to two to four O atoms in layer b , resulting in $[\text{Te}^{\text{IV}}\text{O}_x]$ polyhedra with $3 \leq x \leq 5$ (Tab. 3.26 and 3.27). Most Te atoms coordinate to three close (1.797(14)–2.081(7) Å) and up to three more remote (2.100(7)–2.454(8) Å) O atoms. The $[3+x]$ coordination with the given distances is characteristic for oxotellurates(IV). The $[\text{Te}^{\text{IV}}\text{O}_x]$ units are connected *via* corners forming networks infinite in three (CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$) and two ($\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ and SrTe_2O_5) dimensions

Table 3.27: Selected inter-atomic distances in the actual structures of $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ and SrTe_2O_5 .

$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$				SrTe_2O_5			
Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
TeA–O1D	1.855(14)	TeE–O1C	1.880(13)	TeA–O1F	1.845(9)	TeE–O2F	2.439(8)
TeA–O2B	1.866(13)	TeE–O2I	1.955(16)	TeA–O2B	1.860(8)	TeF–O1D	1.844(9)
TeA–O2A	2.006(14)	TeE–O2K	2.000(18)	TeA–O2A	2.003(9)	TeF–O2H	1.882(8)
TeA–O2C	2.208(17)	TeE–O2F	2.221(15)	TeA–O2C	2.324(9)	TeF–O2G	1.904(8)
TeB–O1F	1.867(13)	TeE–O2G	2.283(13)	TeB–O1A	1.859(10)	TeG–O1C	1.860(10)
TeB–O2D	1.913(14)	TeF–O1A	1.867(14)	TeB–O2D	1.884(8)	TeG–O2J	1.866(8)
TeB–O2A	2.001(13)	TeF–O2G	1.899(13)	TeB–O2A	1.971(9)	TeG–O2I	1.949(9)
TeB–O2B	2.333(13)	TeF–O2H	1.924(15)	TeB–O2B	2.396(8)	TeH–O1I	1.853(9)
TeC–O1E	1.866(14)	TeG–O2J	1.866(16)	TeC–O1E	1.844(9)	TeH–O2L	1.935(8)
TeC–O2C	1.891(17)	TeG–O1B	1.881(13)	TeC–O2C	1.850(9)	TeH–O2K	2.061(9)
TeC–O2E	2.009(14)	TeG–O2I	2.108(16)	TeC–O2E	2.005(8)	TeH–O2M	2.153(8)
TeC–O2D	2.187(14)	TeG–O2L	2.145(12)	TeC–O2D	2.233(8)	TeH–O2J	2.323(9)
TeD–O1G	1.864(14)	TeH–O1H	1.856(14)	TeD–O2F	1.842(7)	TeI–O1J	1.855(9)
TeD–O2F	1.866(15)	TeH–O2K	1.915(18)	TeD–O1G	1.847(9)	TeI–O2M	1.871(8)
TeD–O2E	2.039(14)	TeH–O2L	1.984(12)	TeD–O2E	2.006(9)	TeI–O2O	1.971(9)
TeD–O2H	2.205(15)	TeH–O2J	2.291(16)	TeD–O2H	2.308(8)	TeI–O2N	2.402(9)
				TeE–O1H	1.826(9)	TeJ–O1B	1.858(9)
				TeE–O2K	1.909(8)	TeJ–O2N	1.866(9)
				TeE–O2I	2.041(10)	TeJ–O2O	2.071(8)
				TeE–O2G	2.221(9)	TeJ–O2L	2.336(8)

(Fig. 3.23). In $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ the $[\text{Te}(\text{B})\text{O}_4]$ and $[\text{Te}(\text{I})\text{O}_5]$ units are connected *via* an edge.

Major polytypes

The major polytype of CaTe_2O_5 and the isotypic $\text{Ca}_{0.98}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ has symmetry $A12/a1$. The crystallochemical layers L have symmetry $p12/a(1)$. Seven M atoms are located on the twofold axis, one on a centre of inversion, the remaining are located on general positions. Adjacent layers L are related by inversion symmetry and 2_1 screws. The major polytype of $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ has symmetry $P2_1/c$. Layers L have symmetry $p12_1(1)$ and are related by centres of inversion. The major polytype of SrTe_2O_5 has symmetry $P\bar{1}$. Layers L have symmetry $p\bar{1}$ and are related by centres of inversion.

Desymmetrization with respect to the idealized basic structure results in deviation from the idealized metrics of the basic cells and a deviation of the atomic coordinates from the idealized position. A comparison of the idealized and actual metrics of the basic cells is given in Tab. 3.28. In all cases the axis lengths deviate by less than 1.2% and the angles by less than 0.6% from the idealized hexagonal metric. As expected, the length of the basis vectors increase with substitution of Ca by Sr due to more space required by the heavier homologue. The deviation of atoms in the actual structure to those in the idealized basic structure is given in Tab. 3.29 and 3.30. The positions of atoms in layers A are practically identical to those in the idealized basic structure with maximum deviations of 0.12 Å for M and 0.24 Å for O atoms (Fig. 3.20, top). Due to the occupational modulation of O atoms in layers b , the atoms show distinctly larger deviations from the idealized basic structure with up to 0.37 Å for Te and up to 0.83 Å for O atoms.

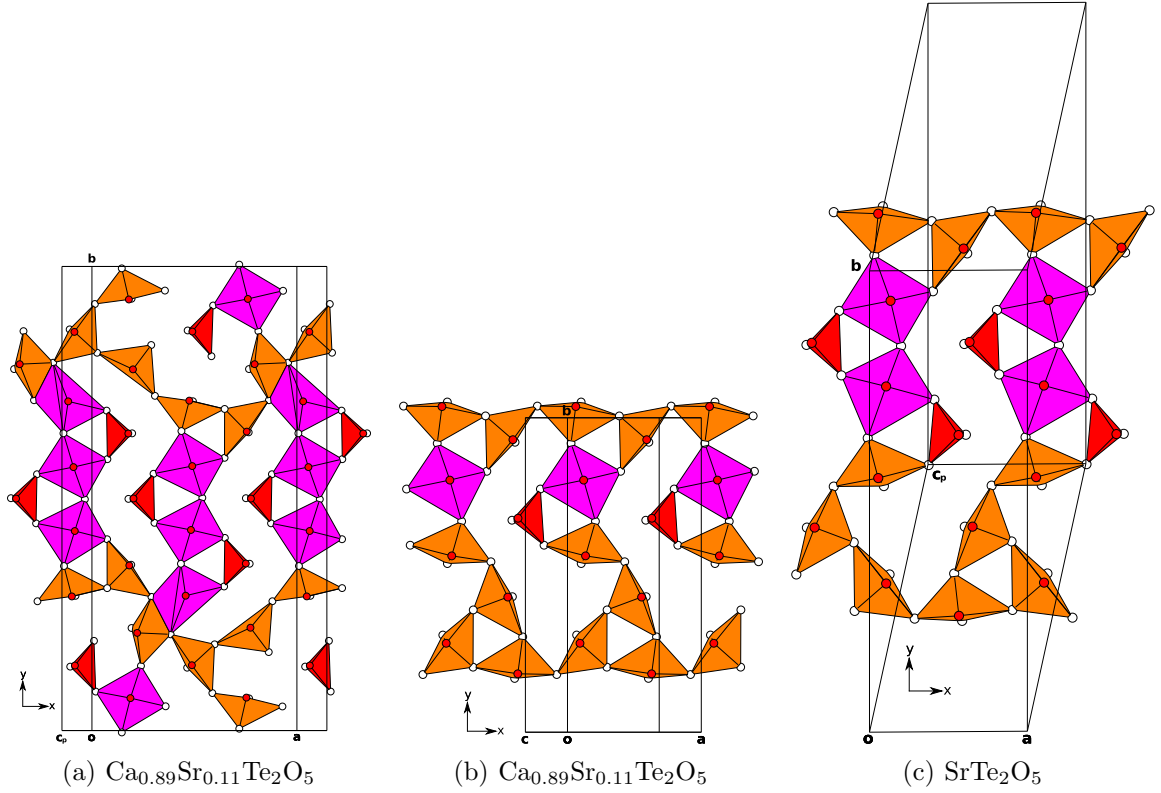


Figure 3.23: Te/O network in the actual structures of (a) CaTe_2O_5 and $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$, (b) $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ and (c) SrTe_2O_5 . Atom colour codes as in Fig. 3.19.

Table 3.28: Metrics of the layers in the idealized basic structures of the $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ with $x = 1, 0.89, 0.60, 0$. Only the lengths a_1 , a_2 of the lattice basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and the angle $\gamma = \widehat{\mathbf{a}_1, \mathbf{a}_2}$ are listed.

	Actual			Idealized		
	a_1 [Å]	a_2 [Å]	γ [°]	a_1 [Å]	a_2 [Å]	γ [°]
CaTe_2O_5	3.958	3.886	119.4	3.934	3.934	120
$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$	3.967	3.900	119.4	3.944	3.944	120
$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$	3.986	4.038	120.4	4.003	4.003	120
SrTe_2O_5	4.041	4.088	120.1	4.063	4.063	120

3.5.5 Occupational disorder

In $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$, all M positions possess the same Ca:Sr ratio of 40:60(2) within the s.u. (Tab. 3.31, right) due to the M positions being located in a very similar chemical vicinity. Surprisingly, in $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$ the Ca:Sr ratio varies distinctly between positions from 1:0 (CaA:SrA) to 0.695:0.305 (CaC:SrC).

Table 3.29: Distance of atoms in layers A of the actual structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ with $x = 1, 0.89, 0.60, 0$ to the idealized basic structures. Site symmetry is indicated for the idealized and actual layer groups, respectively.

Basic Structure			Actual structure									
			CaTeO ₅ , Ca _{0.89} Sr _{0.11} Te ₂ O ₅				Ca _{0.60} Sr _{0.40} Te ₂ O ₅				SrTe ₂ O ₅	
Layer	Atom	Site	Atom	Site	Distance[Å]	Distance†[Å]	Atom	Site	Distance [Å]	Atom	Site	Distance [Å]
A	M	mmm(3̄)...	MA	1̄	0.017	0.017	MA	1	0.076	MA	1	0.090
A	M	mmm(3̄)...	MB	1	0.085	0.082	MB	1	0.106	MB	1	0.156
A	M	mmm(3̄)...	MC	1	0.086	0.077	MC	1	0.103	MC	1	0.109
A	M	mmm(3̄)...	MD	1	0.080	0.085	MD	1	0.052	MD	1	0.187
A	M	mmm(3̄)...	ME	2	0.126	0.112				ME	1	0.041
A	M	mmm(3̄)...	MF	2	0.080	0.069						
A	M	mmm(3̄)...	MG	2	0.130	0.127						
A	M	mmm(3̄)...	MH	2	0.009	0.004						
A	M	mmm(3̄)...	MI	2	0.051	0.046						
A	M	mmm(3̄)...	MJ	2	0.058	0.064						
A	M	mmm(3̄)...	MK	2	0.184	0.160						
A	O1	mmm(3̄)...	O1A	1	0.178	0.163	O1A	1	0.089	O1A	1	0.144
A	O1	mmm(3̄)...	O1B	1	0.107	0.108	O1B	1	0.113	O1B	1	0.177
A	O1	mmm(3̄)...	O1C	1	0.267	0.270	O1C	1	0.150	O1C	1	0.065
A	O1	mmm(3̄)...	O1D	1	0.077	0.056	O1D	1	0.238	O1D	1	0.054
A	O1	mmm(3̄)...	O1E	1	0.233	0.238	O1E	1	0.109	O1E	1	0.072
A	O1	mmm(3̄)...	O1F	1	0.287	0.236	O1F	1	0.099	O1F	1	0.153
A	O1	mmm(3̄)...	O1G	1	0.304	0.282	O1G	1	0.222	O1G	1	0.210
A	O1	mmm(3̄)...	O1H	1	0.208	0.207	O1H	1	0.075	O1H	1	0.081
A	O1	mmm(3̄)...	O1I	1	0.099	0.088				O1I	1	0.192
A	O1	mmm(3̄)...	O1J	1	0.419	0.368				O1J	1	0.165
A	O1	mmm(3̄)...	O1K	1	0.064	0.073						
A	O1	mmm(3̄)...	O1L	1	0.386	0.358						
A	O1	mmm(3̄)...	O1M	1	0.164	0.173						
A	O1	mmm(3̄)...	O1N	1	0.079	0.071						

† CaTe₂O₅
‡ Ca_{0.89}Sr_{0.11}Te₂O₅

[†] CaTe_2O_5

[‡] $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$

Table 3.30: Distance of atoms in layers b of the actual structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ with $x = 1, 0.89, 0.60, 0$ to the idealized basic structures. Site symmetry is indicated for the idealized and actual layer groups, respectively.

Basic Structure			Actual structure			
Layer	Atom	Site	CaTe_2O_5 , $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$		$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$	
			Atom	Site	Distance [†] [Å]	Distance [‡] [Å]
b	Te	$mmm(6)mmm$	TeA	1	0.137	0.141
b	Te	$mmm(6)mmm$	TeB	1	0.362	0.366
b	Te	$mmm(6)mmm$	TeC	1	0.153	0.159
b	Te	$mmm(6)mmm$	TeD	1	0.078	0.084
b	Te	$mmm(6)mmm$	TeE	1	0.122	0.130
b	Te	$mmm(6)mmm$	TeF	1	0.181	0.180
b	Te	$mmm(6)mmm$	TeG	1	0.190	0.188
b	Te	$mmm(6)mmm$	TeH	1	0.266	0.246
b	Te	$mmm(6)mmm$	TeI	1	0.293	0.291
b	Te	$mmm(6)mmm$	TeJ	1	0.129	0.138
b	Te	$mmm(6)mmm$	TeK	1	0.212	0.216
b	Te	$mmm(6)mmm$	TeL	1	0.156	0.151
b	Te	$mmm(6)mmm$	TeM	1	0.199	0.200
b	Te	$mmm(6)mmm$	TeN	1	0.098	0.100
b	O2	$mmm(3)...$	O2A	1	0.683	0.637
b	O2	$mmm(3)...$	O2B	1	0.595	0.622
b	O2	$mmm(3)...$	O2C	1	0.770	0.741
b	O2	$mmm(3)...$	O2D	1	0.087	0.070
b	O2	$mmm(3)...$	O2E	1	0.538	0.544
b	O2	$mmm(3)...$	O2F	1	0.576	0.578
b	O2	$mmm(3)...$	O2G	1	0.606	0.614
b	O2	$mmm(3)...$	O2H	1	0.531	0.543
b	O2	$mmm(3)...$	O2I	1	0.452	0.465
b	O2	$mmm(3)...$	O2J	1	0.717	0.720
b	O2	$mmm(3)...$	O2K	1	0.740	0.745
b	O2	$mmm(3)...$	O2L	1	0.797	0.792
b	O2	$mmm(3)...$	O2M	1	0.636	0.643
b	O2	$mmm(3)...$	O2N	1	0.627	0.630
b	O2	$mmm(3)...$	O2O	1	0.454	0.447
b	O2	$mmm(3)...$	O2P	1	0.369	0.520
b	O2	$mmm(3)...$	O2Q	1	0.429	0.376
b	O2	$mmm(3)...$	O2R	1	0.848	0.834
b	O2	$mmm(3)...$	O2S	1	0.702	0.699
b	O2	$mmm(3)...$	O2T	1	0.674	0.646
b	O2	$mmm(3)...$	O2U	1	0.210	0.230
			Atom	Site	Distance [Å]	Distance [Å]
			TeA	1	0.300	0.393
			TeB	1	0.245	0.295
			TeC	1	0.344	0.399
			TeD	1	0.281	0.354
			TeE	1	0.133	0.183
			TeF	1	0.222	0.235
			TeG	1	0.101	0.282
			TeH	1	0.373	0.293
			TeA	1		0.463
			TeA	1		0.147
			Atom	Site	Distance [Å]	Distance [Å]
			O2A	1	0.164	0.186
			O2B	1	0.539	0.508
			O2C	1	0.644	0.659
			O2D	1	0.723	0.760
			O2E	1	0.182	0.220
			O2F	1	0.464	0.449
			O2G	1	0.506	0.449
			O2H	1	0.772	0.856
			O2I	1	0.535	0.827
			O2J	1	0.830	0.680
			O2K	1	0.650	0.458
			O2L	1	0.234	0.404
			O2A	1		0.785
			O2A	1		0.749
			O2A	1		0.283

[†] CaTe_2O_5
[‡] $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$

Table 3.31: Ca substitution in $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ for $x = 0.89$ and $x = 0.60$.

$\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$		$\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$	
Atoms	Ratio	Atoms	Ratio
CaA:SrA	1:0	CaA:SrA	0.40:0.60(2)
CaB:SrB	0.909:0.091(11)	CaB:SrB	0.40:0.60(2)
CaC:SrC	0.695:0.305(10)	CaC:SrC	0.41:0.59(2)
CaD:SrD	0.975:0.025(10)	CaD:SrD	0.41:0.59(2)
CaE:SrE	0.928:0.072(14)		
CaF:SrF	0.852:0.148(12)		
CaG:SrG	0.943:0.057(13)		
CaH:SrH	0.870:0.130(12)		
CaI:SrI	0.868:0.132(12)		
CaJ:SrJ	0.960:0.040(12)		
CaK:SrK	0.845:0.155(12)		

Table 3.32: Details of experiments in the system $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ below the melting point of the used mixtures.

Sample weight	Crucible	T [K]	t [h]	Structure types
56.0 mg CaO , 159.6 mg TeO_2	Al_2O_3	1120	72	CaTe_2O_5
65.6 mg $\text{Ca}_{0.80}\text{Sr}_{0.20}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1120	72	CaTe_2O_5
71.9 mg $\text{Ca}_{0.67}\text{Sr}_{0.33}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1120	72	CaTe_2O_5
79.8 mg $\text{Ca}_{0.50}\text{Sr}_{0.50}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1120	72	CaTe_2O_5
87.8 mg $\text{Ca}_{0.33}\text{Sr}_{0.67}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1120	72	42.9% $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$, 57.1% Sr_2TeO_5
94.1 mg $\text{Ca}_{0.20}\text{Sr}_{0.80}\text{O}$, 159.6 mg TeO_2	Al_2O_3	1120	72	Sr_2TeO_5

3.6 Microcrystalline solid solutions $M\text{Te}_2\text{O}_5$

Microcrystalline samples of phases in the system $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ were prepared in order to relate their structure to the structure of single crystalline $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ phases described in sec. 3.5. Since it is not yet certain that all thermodynamically stable phases in the system $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ have been elucidated the structure types will be named according to the compositions determined in sec. 3.5.

3.6.1 Preparation

Microcrystalline powders were obtained by reacting a mixture of TeO_2 and MO with molar ratio 2:1 in Al_2O_3 crucibles placed in evacuated silica ampoules. The mixtures were heated below their melting points at 1120 K for 72 h. Reaction conditions of several batches are summarized in Tab. 3.32. In all cases microcrystalline white powders were obtained.

3.6.2 Rietveld refinement

The microcrystalline powders were measured using XRPD and refined using the Rietveld method implemented by the program TOPAS (Coelho, 2002). The basis of each refinement were the

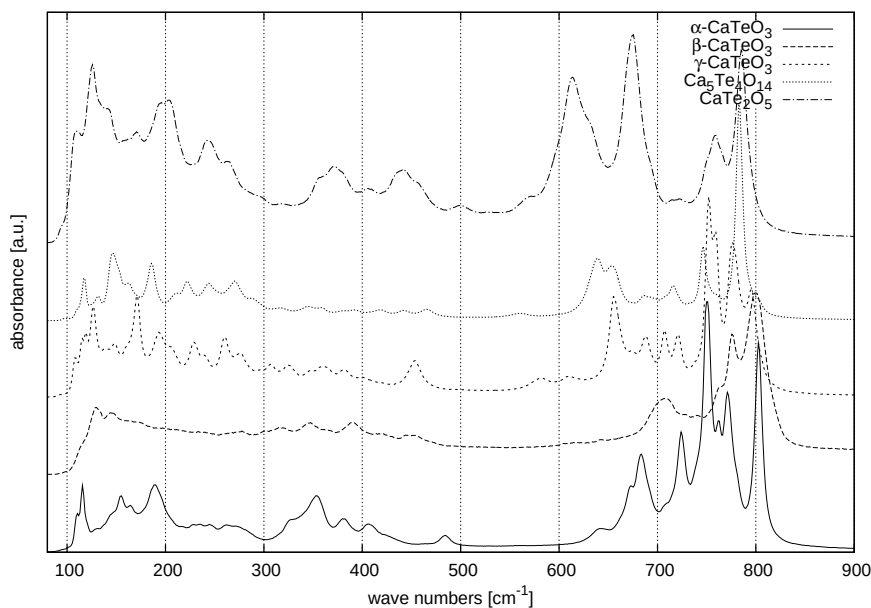


Figure 3.24: Raman spectra of compounds in the system $(\text{CaO})_x \cdot (\text{TeO}_2)_y$ in the region 900–75 cm^{-1} . The curves from bottom to top represent the Raman spectra of α -, β -, γ - CaTeO_3 , $\text{Ca}_4\text{Te}_5\text{O}_{14}$ and CaTe_2O_5 .

crystal structures of $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$. A first refinement step was used to assign the phases on hand. In subsequent refinement steps the lattice parameters and crystallite sizes were refined. In order to obtain reasonable matching of calculated with measured intensities, preferred orientations of crystallites in (001) direction using a March-Dollase function had to be refined. This is in accordance with the plate-like habit of the crystals noted during single crystal diffraction experiments. In all cases good agreement of calculated and measured diffraction patterns were obtained. A few reflections showed slight discrepancies in intensities and one diffuse reflection at $\approx 43.6^\circ$ in the sample with Ca:Sr ratio of 1:0 could not be explained by CaO , TeO_2 any of the $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ or CaTeO_3 structure types.

In experiments employing a Ca:Sr ratio $\geq 1 : 1$ practically single phase samples with CaTe_2O_5 structure types were obtained (Tab. 3.32). For Ca : Sr = 2 : 3 a mixture of the $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{Te}_2\text{O}_5$ and Sr_2TeO_5 structure types was obtained. Therefore the $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ phase diagram probably has no phases between $3 : 2 \geq \text{Ca} : \text{Sr} \geq 0$ with structure types differing from the ones described in sec. 3.5. Additional experiments will have to be performed with ratios $1 : 1 \geq \text{Ca} : \text{Sr} \geq 1 : 2$ to determine the presence or absence of additional structure types in this region.

3.7 Raman spectroscopy of phases in the system $(\text{CaO})_x \cdot (\text{TeO}_2)_y$

Single phase materials of α -, β -, γ - CaTeO_3 , $\text{Ca}_4\text{Te}_5\text{O}_{14}$ and CaTe_2O_5 obtained as described in sec. 3.3.1, 3.4.1 and 3.5.1 were subjected to Raman spectroscopy in the spectral range 3000–50 cm^{-1} . Representative Raman spectra are depicted in Fig. 3.24. All compounds under investigation show intense Raman active modes in the 800–500 cm^{-1} region which are characteristic for oxotellurium compounds and can be attributed to Te–O stretching vibrations (Mirgorodsky et al., 2002). While the spectra of α -, γ - CaTeO_3 and $\text{Ca}_4\text{Te}_5\text{O}_{14}$ in this region possess sharp peaks, the spectra of β - CaTeO_3 and CaTe_2O_5 are more diffuse. The most prominent Te–O peaks

in CaTe_2O_5 are located at smaller wave numbers than in the other compounds, possibly due to the existence of bridging Te–O–Te bonds and higher coordination numbers of the Te atoms, resulting in a weakening of Te–O bonds. Raman peaks in the region $350\text{--}220\text{ cm}^{-1}$ can be attributed to O–Te–O bending vibrations. These are of low intensity and diffuse in all compounds under investigation. Finally the bands in the region $220\text{--}100\text{ cm}^{-1}$ correspond to the motion of the heavy atoms (Ca and Te).

Chapter 4

Anionic derived alkaline earth metal tellurates(IV)

4.1 Introduction

During systematic studies of the formation conditions of alkaline earth metal tellurates under hydrothermal conditions starting from halides or other soluble salts, numerous anionic modified oxotellurates(IV) with general formula $(MO)_x(\text{TeO}_2)_y(MX)_z(\text{H}_2\text{O})_t$ with $M = \text{Ca}, \text{Sr}, \text{Ba}$ and $X = \text{Cl}, \text{Br}, \text{NO}_3^-, \text{OH}^-$ were obtained. Up to now the structures of only two representatives of this system have been published. $\text{Sr}_4\text{Te}_3\text{O}_8\text{Cl}_4$ (Jiang and Mao, 2008) is composed of one-dimensional Sr/Te/O frameworks, which are encompassed by the Cl atoms. $\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$ (Hottentot and Loopstra, 1983) crystallizes in a cubic structure type with isolated $[\text{TeO}_3]$ units.

The crystal structures described in this chapter will be divided into three categories: In sec. 4.2–4.6 structures composed of distinct crystallochemical layers will be presented. They are composed of an alternation of cationic Te/ M /O layers and anionic layers containing the halide or nitrate ions and water molecules in the case of hydrates. The lone pairs E of the Te^{IV} atoms are directed towards space between the layers. In the structures described in sec. 4.7–4.9 the $[\text{TeO}_x]$ units are connected by M atoms forming a three dimensional network around channels in which the lone pairs E of the Te^{IV} atoms protrude and the halide ions are located. Finally, in sec. 4.10 a family of structures which is closely related to the cubic structure of $\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$ (Hottentot and Loopstra, 1983) will be presented. An overview of the structures described in this chapter is given in Tab. 4.1.

4.2 $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$, $X = \text{Br}, \text{NO}_3$

4.2.1 Introduction

The phases $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$ ($X = \text{Br}, \text{NO}_3$) are composed of structures that can be described as super structures and as OD structures composed of rods. Using the basic structures of $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$ it will be shown that some results of OD theory of structures composed of layers can be applied to structures composed of rods and that in this special case an OD structure composed of rods can be considered a family of OD structures composed of layers.

It will be shown that the deviation of possible arrangements of rods is complex for structures composed of rods of $M > 1$ kinds and many MDO polytypes are possible, in contrast to structures composed of layers, where the amount of MDO polytypes is typically small. For structure composed of rods no systematic derivation of the MDO polytypes has been worked

Table 4.1: Anionic derived oxotellurates(IV) and the values of x , y and z in the general formula $(MO)_x(\text{TeO}_2)_y(MX_2)_z(\text{H}_2\text{O})_t$.

Formula unit	x	y	z	t	type	section
$\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$	3	4	2	0	layered	4.2
$\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$	3	4	2	0	layered	4.2
$\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2\cdot\text{H}_2\text{O}$	2	3	2	2	layered	4.3
$\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$	7	8	6	0	layered	4.4
$\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$	2	5	1.5 [†]	0	layered	4.6
$\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$	5	5	2	0	channel framework	4.7
$\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$	5	10	2	0	channel framework	4.8
$\text{Ba}_3\text{Te}_3\text{O}_8\text{Br}_2$	2	3	2	0	channel framework	4.9
$M_3\text{Te}_2\text{O}_6(\text{OH})_zX_{2-z}(\text{H}_2\text{O})_t$	2	2	z	t	cubic framework	4.10
$M_3\text{Te}_2\text{O}_6X_2$	2	2	1	0	cubic framework	4.10

[†] KCl counted as $\frac{1}{2}(MX_2)$

out as it has solely been done for layered structures (Dornberger-Schiff, 1982; Dornberger-Schiff and Grell, 1982). The MDO polytypes must be derived in an error prone process *ab initio* in each case. Therefore the derivation of the possible OD polytypes will only be performed for the simpler case of the basic structures as opposed to the super structures.

4.2.2 Preparation

160 mg TeO_2 and 247 mg $\text{SrBr}_2\cdot\text{H}_2\text{O}$ were placed in a teflon inlay with approximately 6 ml volume, that was filled with a hydrous NH_4OH solution (20%_{wt}) to two thirds of its volume. The inlay was placed in a steel autoclave and heated at 493 K for 14 d. The aqueous phase was decanted and the residue subsequently washed in with water and acetone. It contained octahedral colourless crystals of a cubic phase $\text{Sr}_3\text{Te}_2\text{O}_6(\text{OH})_x\text{Br}_{2-x}$ (sec. 4.10) and colourless plates of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$. In an analogous experiment, employing 212 mg $\text{Sr}(\text{NO}_3)_2$ instead of SrBr_2 , small crystals of SrCO_3 , $\text{SrTeO}_3\cdot\text{H}_2\text{O}$ and colourless plates of $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ were obtained.

4.2.3 Structure determination

Absorption correction for the intensity data of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ was performed using a multi-scan approach with SADABS (Sheldrick, 2001). For $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ a numerical absorption correction was applied with HABITUS (W. Herrendorf, 1997).

The structures were solved using direct methods using the SHELX program package (Sheldrick, 2008). Most of the heavy atoms (Te, Sr, Br) could be assigned to electron density peaks found by direct methods, the remaining atoms were located in the difference Fourier maps in subsequent refinement steps. The ADPs of the atoms of the NO_3 groups were highly anisotropic and the corresponding atoms were therefore refined with isotropic ADPs. O atoms of NO_3 groups located on a centre of inversion were refined as disordered over two positions with an occupation of $\frac{1}{2}$. All other atoms were refined with anisotropic temperature factors. No unusual remaining electron density was detected in the final difference Fourier maps. The cell setting $P2_1/n$ was chosen over the conventional setting $P2_1/c$ since in the former the basis vector $\mathbf{c}$ is parallel to the lattice basis vector of the rods in the description below. More details on data collection and refinement are summarized in Tab. 4.2, atomic coordinates and isotropic displacement parameters are listed in Tab. C.20 and C.21.

Table 4.2: Crystal data and details of the refinements of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ and $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$.

	$\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$	$\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$
Crystal data		
Chemical formula	$\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$	$\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$
M_r	1196.70	1160.90
Cell setting, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature [K]	295(2)	295(2)
a, b, c [Å]	7.0994(9), 16.869(2), 16.6525(16)	7.1123(6), 18.1839(15), 16.4817(11)
β [°]	125.563(4)	125.204(3)
V [Å ³]	1622.3(3)	1741.7(2)
Z	4	4
D_x [Mg·m ⁻³]	4.900	4.427
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	25.099	18.839
Crystal form, colour	plate, colourless	plate, colourless
Crystal size [mm]	$0.15 \times 0.08 \times 0.01$	$0.18 \times 0.08 \times 0.01$
Data collection		
Diffractometer	SMART APEX	SMART APEX
Data collection method	ω scans	ω scans
Absorption correction	<i>SADABS</i>	<i>HABITUS</i>
T_{min}, T_{max}	0.117, 0.787	0.105, 0.231
No. of measured, independent and observed reflections	17625, 4723, 2986	18920, 5051, 2665
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.071	0.082
θ_{max} [°]	30.0	30.0
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.044, 0.105, 0.95	0.038, 0.081, 0.81
No. of reflections	4723	5051
No. of parameters	190	214
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0348P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_0^2) + (0.0205P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.44, -1.68	2.00, -1.51
Extinction method	-	-

4.2.4 Structures

In the following sections the layer notation according to Grell and Dornberger-Schiff (1982) will be used: A_m^n denotes a non-polar layer, where n indicates the layer type and m the sequence number of the layer. In analogy, rods which are non-polar in both directions missing translational symmetry will be called H , whereas rods which are non-polar in only one direction will be called M .

All rods in the description below possess translational symmetry in $[001]$ direction. $\mathbf{c}$ designates the lattice basis vector of the rod with the largest cell parameter c (*i.e* the lowest translational symmetry group) used in the description below. The lattice generated by $\mathbf{c}$ is a sublattice of all rods that will be used.

Idealized structures and rods were computed by transforming the atom coordinates into a conventional coordinate system of the symmetry group of the idealized structure or rod. The origin was determined from the position of symmetry equivalent (in the idealized structure or

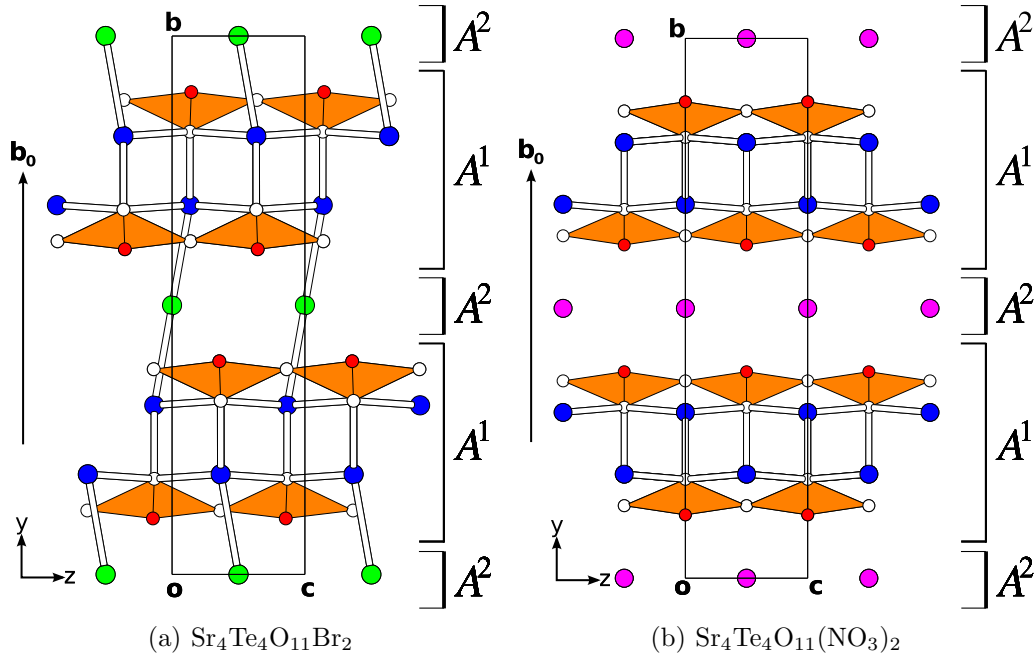


Figure 4.1: The idealized basic structures of (a) $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ and (b) $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ viewed down [100]. Te, Sr, O, Br and N atoms are represented by red, blue, white, green and pink spheres, $[\text{TeO}_4]$ units by orange polyhedra. The O atoms of the NO_3 groups have been omitted. Layer names according to the OD description have been indicated to the right.

rod) heavy atoms (Te, Sr, Br). Atoms of the same type equivalent by symmetry were grouped and their positions averaged. If such an averaged atom was located close ($< 1 \text{ \AA}$) to a symmetry element without translational component, it was moved onto the element. Finally, the obtained structures and rods were checked for correct composition and reasonable inter-atomic distances.

4.2.5 $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$

Idealized basic structure

$\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ is a fourfold superstructure. Its idealized basic structure (Fig. 4.1(a)) can be described as an OD structure composed of two kinds of rods M and H running along [001] arranged as schematized in Fig. 4.2.

Rods M are non-polar with respect to the [100] and polar with respect to the [010] direction. They have symmetry $\mathcal{M}(m)(2)m$, lattice basis vector $\mathbf{c}' = \frac{1}{4}\mathbf{c}$ and composition $\frac{1}{\infty}[\text{Sr}_4\text{Te}_4\text{O}_{11}]^{2-}$. One crystallographically different Te and one Sr atom are located on the same Wyckoff position with symmetry $m(2)m$ with the same x and z and differing y coordinates. There are two kinds of O atoms: One, with an occupation of $\frac{3}{4}$, is located on a site with symmetry $m(2)m$ and connects two Te atoms, the other, fully occupied, on a site with symmetry $\dots m$ is coordinated to only one Te atom. Thus infinite chains of corner sharing $[\text{TeO}_4]^{4-}$ polyhedra running along [001] are formed (Fig. 4.3).

Rods M are arranged along [100], spaced by $\mathbf{a}_0$ forming cationic layers A^1 parallel to (010) (Fig. 4.3).

Rods H are non-polar in [100] and [010] direction. They have composition $\frac{1}{\infty}[\text{Br}]^-$, symmetry group $\mathcal{H}(m)(m)m$ and the same lattice basis vector as rods M ($\mathbf{c}' = \frac{1}{4}\mathbf{c}$). Each unit cell contains one Br atom on a site with symmetry mmm resulting in chains of colinear Br atoms running

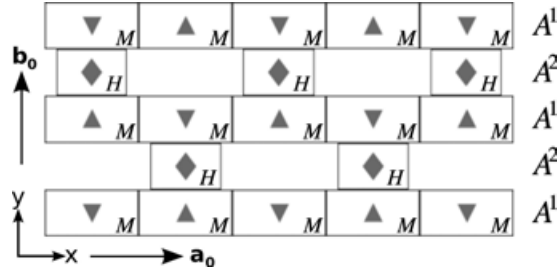


Figure 4.2: Schematic representation of the rods M and H in $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ and $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ viewed down $[001]$. Rods M are represented by grey triangles, rods H by grey rhombi. Both are symmetric by mirroring at (100) and (001) , only rods H also by mirroring at (010) . The different origins of rods in $[001]$ direction, which is responsible for the OD character of the structure, is not indicated. Rods H are represented non-touching. To the right layer names used in the description of the basic structure are given.

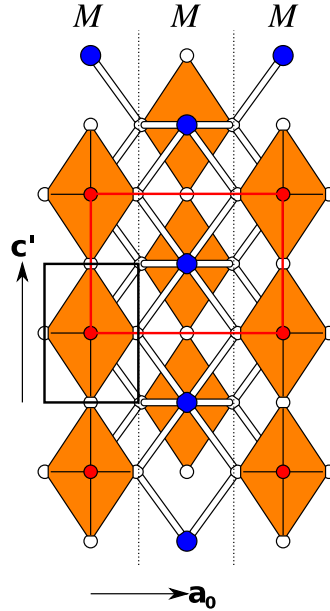


Figure 4.3: Rods M ($\sqrt{2}m$)(2) m) in the idealized basic structure of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ arranged along $[100]$ forming layers A^1 ($pm(n)m$). The unit cell of the layer A^1 is indicated in red, the unit cell of rods M in black. The interface between two adjacent rods M is represented by dotted lines. Atom colour codes as in Fig. 4.1.

along $[001]$ (Fig. 4.4)

Rods H are arranged along $[100]$ forming anionic layers A^2 parallel to (010) . They are spaced by $2a_0$ (Fig. 4.2). Due to the large distance ($> 5.7 \text{ \AA}$) between Br atoms in adjacent rods H , adjacent rods H have to be considered non-touching (Dornberger-Schiff, 1964).

With respect to the $[010]$ direction, rods M connect only *via* one side to rods H (Fig. 4.2). Rods H , on the other hand connect *via* both sides to rods M . The origin of two adjacent rods M and H is translated by $\pm sc$ along $[001]$ with $s = 0.018$. s is given relative to the quadrupled basis vector $\mathbf{c}$ of the superstructure and therefore, when giving operations relative to the coordinate system of the basic structure, the corresponding translational component is $4s$.

The NFZ relationship (Đurovič, 1997) which is used to determine the number of possible stacking possibilities in a polytype family of structures composed of layers can be applied in

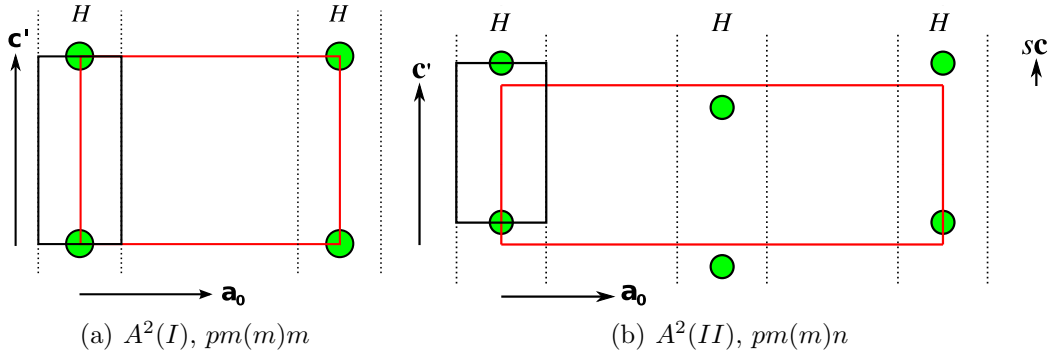


Figure 4.4: Rods H ($\nearrow(m)(m)m$) in the idealized basic structure of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ arranged along $[100]$ forming layers (a) $A^2(I)$ or (b) $A^2(II)$. The border of rods H is represented by dotted lines. Atom colour codes as in Fig. 4.1.

analogy to structures composed of rods. Since all pairs of adjacent rods in this structure are either composed of different kinds of rods or possess a reverse continuation in the form of a centre of symmetry, it reads as $Z = N/F$, where N is the order of the group G of λ - τ -POs of a given rod and N the order of the subgroup of those POs which are also valid for adjacent rods. The meaning of G , N and F are dependent on the stacking direction. For the M, M -contact in $[100]$ direction, $G = \nearrow(1)(1)2$. G is also valid for the adjacent rod. Therefore, $Z = N/N = 1$ and layers A^1 are fully ordered with symmetry $pm(n)m$ as schematized in Fig. 4.5(a). For the M, H -contact in $[010]$ direction, $G = \nearrow(m)(2)m$ for both kinds of rods. Due to the origin shift sc , only the subgroup $\nearrow(m)(1)1$ is also valid for adjacent rods. Therefore, given a rod M , an adjacent rod H can appear in $Z = 4/2 = 2$ orientations, related by a $[- - m]$ operation and *vice-versa*.

Given a layer A_n^1 , all rods H in an adjacent layer A_{n+1}^2 can appear in at most two positions, with an origin located at $+sc + \mathbf{b}_0$ and $-sc + \mathbf{b}_0$ relative to the origin of adjacent rods in layer A_n^1 . Thus, layers A^2 can appear in two non-equivalent configurations where all n -tuples of consecutive rods H are equivalent¹:

- Type *I* (Fig. 4.4(a)), $pm(m)m$, $\mathbf{a} = 2\mathbf{a}_0$, all rods H with the same origin shift along $[001]$.
- Type *II* (Fig. 4.4(b)), $pm(m)n$, $\mathbf{a} = 4\mathbf{a}_0$, rods H have alternating origin shift $+sc$ and $-sc$ along $[001]$.

These two kinds of layers will be called $A^2(I)$ and $A^2(II)$ in the following discussion. Any other arrangement of rods H will be called $A^2(III)$.

Two consecutive layers A_n^1 and A_{n+2}^1 can be related by a $[- - 2]$ PO, independent of the intermediate layer A_{n+1}^2 , or by a $[- - 2_{\pm 16s}]$ operation (corresponding to a translational component of $\pm 2sc$), only if the intermediate layer A_{n+1}^2 is of type $A^2(I)$.

In polytypes of the basic structure with a maximum degree of order (MDO) (Dornberger-Schiff, 1982) all layers A^2 must be of the same type *I* or *II* (type *III* cannot result in MDO polytypes).

If all layers A^2 are of type *I*, the resulting structure belongs to a category IV OD family composed of two kinds of non-polar layers. The OD groupoid family symbol reads as

¹ The term maximum degree of order (MDO) is not used here, since layers A^2 are not decomposed into rods fulfilling vicinity condition (Dornberger-Schiff and Grell-Niemann, 1961).

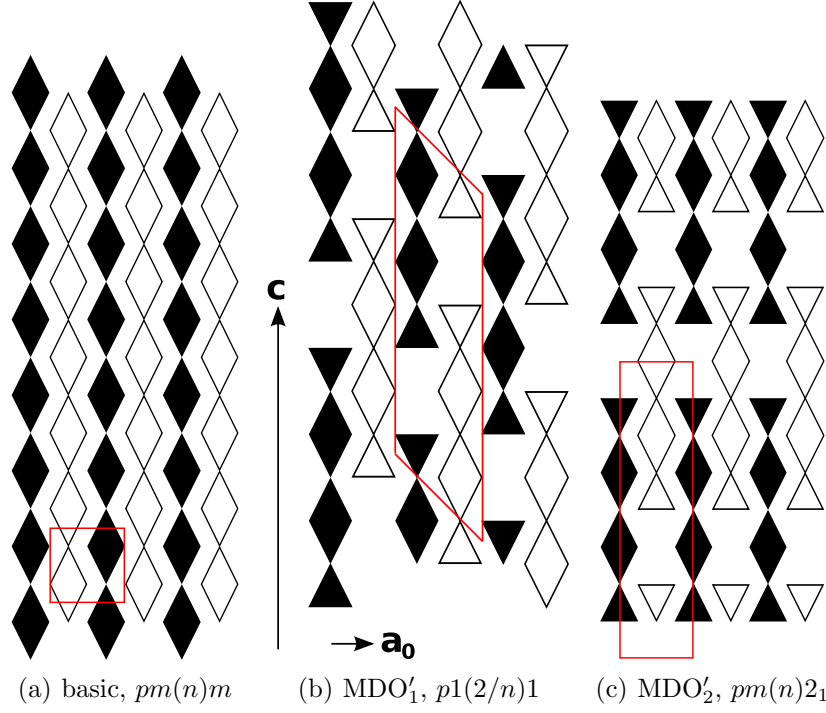


Figure 4.5: Schematic representation of the symmetry of layers A^1 in $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ in (a) the idealized basic structure and the (b) MDO'_1 and (c) MDO'_2 polytypes viewed down $[001]$. Triangles are black on one and white on the other side. The unit cells of the layers are indicated by red polyhedra.

$$\begin{array}{cc} A^1 & A^2(I) \\ pm(n)m & pm(m)m \\ & [0, 4s] \end{array}$$

according to the symbolism devised by Grell and Dornberger-Schiff (1982). In polytypes of this OD family a layer A^1_n is related to the next layer A^1_{n+2} by a $[- - 2]$ or a $[- - 2_{\pm 16s}]$ PO. A layer $A^2_n(I)$ is related to the next layer $A^2_{n+2}(I)$ by a $[- - 2_1]$ or a $[- - 2_{1\pm 16s}]$ PO. These POs give rise to four non equivalent MDO polytypes which are schematized in Fig. 4.6:

- MDO_1 (Fig. 4.6(a)), $I2/m11$, $\mathbf{a} = 2\mathbf{a}_0$, $\mathbf{b} = 2\mathbf{b}_0 + 4s\mathbf{c}$: All layer pairs $A^1_n A^1_{n+2}$ are related by $[- - 2_{+16s}]$, all layer pairs $A^2_n A^2_{n+2}$ by $[- - 2_{1+16s}]$ POs.
- MDO_2 (Fig. 4.6(b)), $Pmnn$, $\mathbf{a} = 2\mathbf{a}_0$, $\mathbf{b} = 2\mathbf{b}_0$: All layer pairs $A^1_n A^1_{n+2}$ are related by $[- - 2]$, layer pairs $A^2_n A^2_{n+2}$ alternately by $[- - 2_{1+16s}]$ and $[- - 2_{1-16s}]$ POs.
- MDO_3 (Fig. 4.6(c)), $Pmnn$, $\mathbf{a} = 2\mathbf{a}_0$, $\mathbf{b} = 2\mathbf{b}_0$: Layer pairs $A^1_n A^1_{n+2}$ are related alternately by $[- - 2_{+16s}]$ and $[- - 2_{-16s}]$, all layer pairs $A^2_n A^2_{n+2}$ by $[- - 2_1]$ POs.
- MDO_4 (Fig. 4.6(d)), $Imm2$, $\mathbf{a} = 2\mathbf{a}_0$, $\mathbf{b} = 2\mathbf{b}_0$: All layer pairs $A^1_n A^1_{n+2}$ by $[- - 2]$, all layer pairs $A^2_n A^2_{n+2}$ by $[- - 2_1]$ POs.

If all layers A^2 are of type II , the resulting structure belongs to a category IV OD family composed of two kinds of non-polar layers. The OD groupoid family symbol reads as:

$$\begin{array}{cc} A^1 & A^2(II) \\ d_x m(n)m & pm(m)n \\ & [0, 4s] \end{array}$$

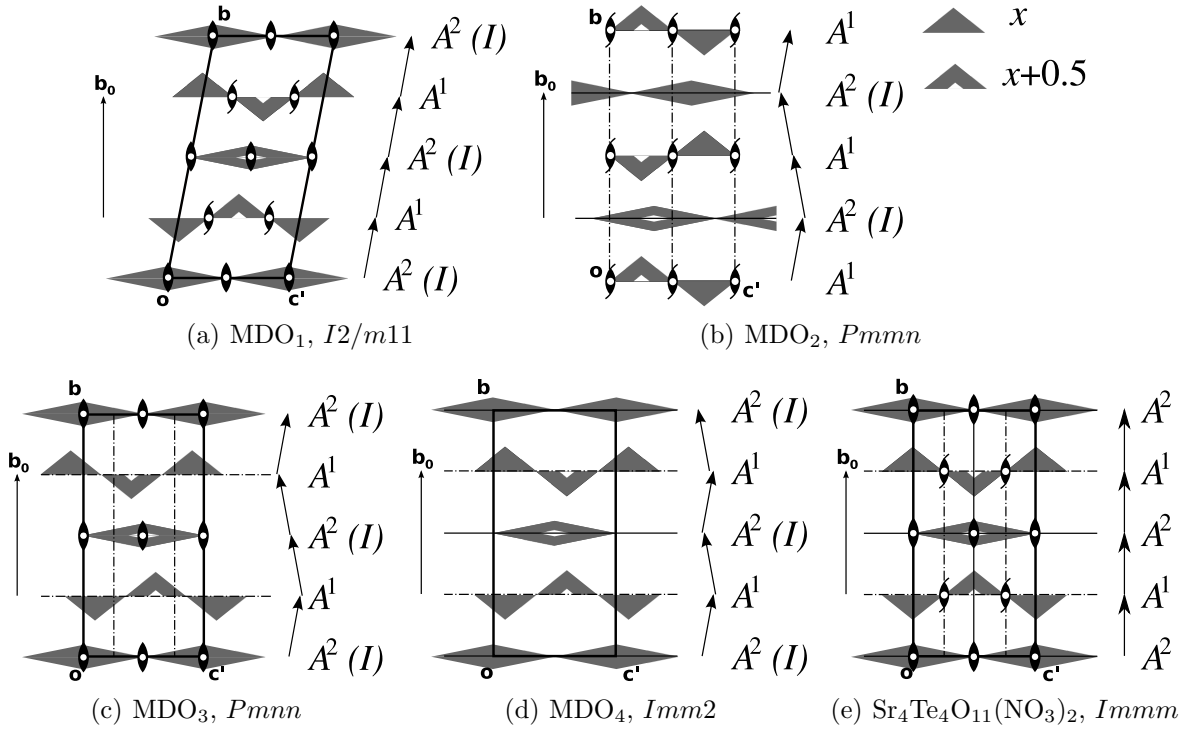


Figure 4.6: Schematic representations of the symmetry of the (a)–(d) MDO₁–MDO₄ polytypes of the basic structure of $Sr_4Te_4O_{11}Br_2$ and of (e) the fully ordered basic structure of $Sr_4Te_4O_{11}(NO_3)_2$, viewed down [100]. Grey triangles are symmetric by mirroring at a plane parallel to (100). A small white triangle indicates translation along $\frac{1}{2}\mathbf{a}_0$. The kind of layer is indicated to the right. Arrows to the right indicate the shift of the origin from one layer to the adjacent layer. Symmetry elements parallel to [100] have been indicated by the symbols according to the *International Tables for Crystallography* (Hahn, 1983).

according to the notation devised by Dornberger-Schiff and Grell-Niemann (1961). The Bravais centring symbol „ d_x ” designates doubled translational symmetry in direction [001]. In this case, the position of all layers A^1 is fixed, whereas a layer $A^2_n(II)$ is related to the next layer $A^2_{n+2}(II)$ by either of a $[2_{\pm\frac{1}{2}} - -]$ PO. Thus, two further non equivalent MDO polytypes are obtained which have a doubled lattice vector $\mathbf{a}$, when compared to MDO₁–MDO₄ and which are schematized in Fig. 4.7:

- MDO₅ (Fig. 4.7(a)), $A112/a$, $\mathbf{a} = 4\mathbf{a}_0$, $\mathbf{b} = 2\mathbf{b}_0 + 2\mathbf{a}$: All layer pairs (A^2_n, A^2_{n+2}) are related by $[2_{\pm\frac{1}{2}} - -]$ POs.
- MDO₆ (Fig. 4.7(b)), $Pnma$, $\mathbf{a} = 4\mathbf{a}_0$, $\mathbf{b} = 2\mathbf{b}_0$: Layer pairs (A^2_n, A^2_{n+2}) are alternately related by $[2_{+\frac{1}{2}} - -]$ and $[2_{-\frac{1}{2}} - -]$ POs.

While the idealized OD description is based on the equivalence of adjacent layer (rod) pairs, in actual structures also interaction between layers (rods) farther apart have to be considered, especially when layers are narrow, like in the case of layers A^2 . In $Sr_4Te_4O_{11}Br_2$, the translation sc between the origins of adjacent layers might be explained by the lone pairs of two opposite Te^{IV} atoms in two layers A^1_n and A^1_{n+2} coming too close for $s \approx 0$. Also, when two layers A^1_n and A^1_{n+2} possess the same origin shift in relation to the intermediate layer A^2_{n+1} , the coordination sphere of the Br atoms in those intermediate layers are unusual and might not be realizable. If

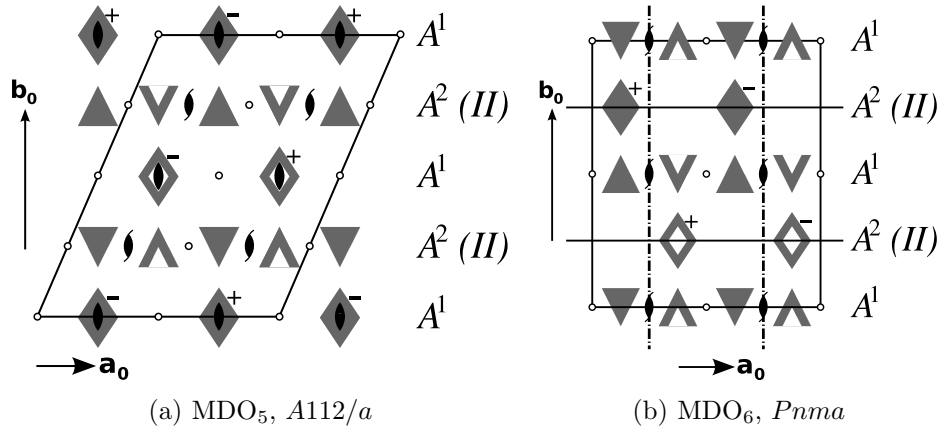


Figure 4.7: Schematic representations of the symmetry of the (a) MDO_5 and (b) MDO_6 polytypes of the basic structure of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ viewed down $[001]$. Grey triangles and rhombi are symmetric by mirroring at a plane parallel to (001) . A small white triangle indicates translation by $\frac{1}{2}\mathbf{c}'_0$. „+” and a „-” signs next to a rhombus indicate further translation by $+\mathbf{sc}$ and $-\mathbf{sc}$, respectively. The kind of layer is indicated to the right. Symmetry elements parallel to $[001]$ have been indicated by the symbols according to the *International Tables for Crystallography* (Hahn, 1983).

either of these objections is true, only polytypes where two consecutive layers A^1_n and A^1_{n+2} are related by $[- - 2_{\pm 16s}]$ but not by $[- - 2]$ POs might be possible (of the MDO polytypes only MDO_1 and MDO_3).

Idealized superstructure

The superstructure can be described as an OD structure composed of rods of two different kinds, which can be derived from the rods of the basic structure. Rods H and therefore also layers A^2 are unchanged from the description of the basic structure. Rods M have the same composition (${}^1_\infty[\text{Sr}_4\text{Te}_4\text{O}_{11}]^{2-}$) as in the basic structure and an isomorphous space group $\mathcal{A}(m)(2)m$ with a quadrupled lattice vector $\mathbf{c}$. In the superstructure the bridging O atoms are occupationally modulated with every fourth position being unoccupied resulting in isolated $[\text{Te}_4\text{O}_{11}]$ units (Fig. 4.8(a)). The remaining bridging O atoms have occupancy 1 (in comparison with $\frac{3}{4}$ in the basic structure). Two adjacent rods M in $[100]$ direction are related by a $[- - 2_{\pm \frac{3}{4}}]$ screw rotation or, equivalently, by a $[-n_{2, \pm \frac{3}{4}} -]$ glide plane.

Thus, layers A^1 are described by an orthorhombic² OD structure composed of one kind of rods. The OD groupoid symbol, in analogy to the symbols for OD structures composed of one kind of layers (Dornberger-Schiff and Grell-Niemann, 1961)³, reads as

$$\mathcal{A} \begin{pmatrix} (m) & (2) & m \\ \{(22) & (n_{2,s'}) & 2_{s'}\} \end{pmatrix}$$

with $s' = \frac{3}{4}$.

The λ - τ -POs, in analogy to the definition for layers, are $G = \mathcal{A}(1)(1)m$. Only the identity e is also valid for adjacent rods. Therefore, according to the NFZ relationship (Đurović, 1997),

² Rod crystal system.

³ The notation for OD structures composed of one kind of rods (Dornberger-Schiff, 1964) is not used here, since layer A^1 is more akin to an OD structure composed of layers with translational symmetry missing in one direction than a three dimensional OD structure composed of rods.

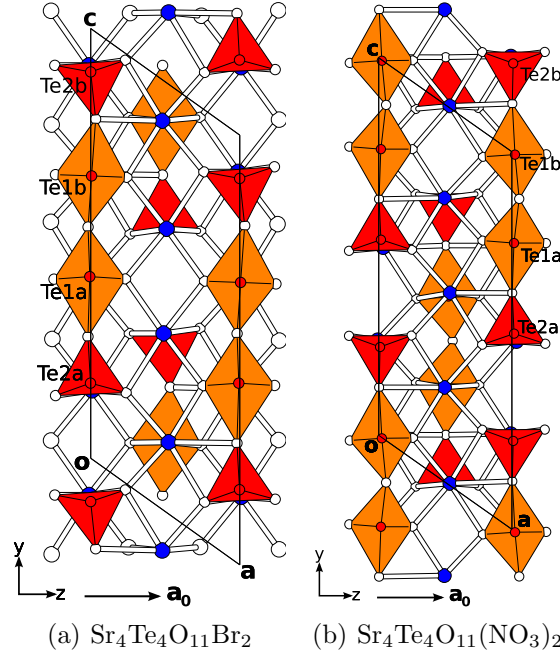


Figure 4.8: Layer A^1 in the actual structures of (a) $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ and (b) $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$. $[\text{TeO}_3]$ groups are represented by red lines, other colour codes as in Fig. 4.3.

given a fixed rod, an adjacent rod can appear in $Z = 2$ orientations which are related by $[- - m]$. All possible arrangements of rods result in layers which practically differ only in the location of the unoccupied O positions.

There are two possible non-equivalent MDO layers A^1 , which are obtained by continuous application of $[- - 2_{+\frac{3}{4}}]$ (MDO'_1 , $\mathbf{a} = 2\mathbf{a}_0 - \frac{1}{4}\mathbf{c}_0$, $p1(2/n)1$) or by alternating application of $[- - 2_{+\frac{3}{4}}]$ and $[- - 2_{-\frac{3}{4}}]$ (MDO'_2 , $\mathbf{a} = 2\mathbf{a}_0$, $pm(n)2_1$). In MDO'_1 mirror symmetry parallel to (100) and (001) is lost. In MDO'_2 twofold rotation parallel to [010] is lost. The MDO layers are schematized in Fig. 4.5 (b) and (c), respectively.

Due to the additional translational symmetry of rods H compared to rods M , given a rod H , an adjacent rod M can appear in eight different positions (origin shift along [001] by $\frac{n}{4} \pm \mathbf{sc}$, $n = 0, 1, 2, 3$), which result in different possible arrangements of rods and accordingly to a large number of different MDO polytypes. They can be related to the MDO polytypes of the basic structure by group/subgroup relationships. A full derivation of the possible MDO polytypes has not been performed up to now.

Actual structure

Despite the numerous possibilities for polytypic arrangement, only one polytype could be detected in the crystals under investigation. It is an MDO polytype with symmetry $P2_1/n$ and lattice vectors

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ \frac{1}{4} & 0 & 1 \end{pmatrix}$$

which can be derived from the MDO_3 polytype of the basic structure (sec. 4.2.5).

The arrangement of rods M in the actual structure corresponds to the MDO'_1 layer-polytype

Table 4.3: Distances of atoms in the actual structure $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ to the idealized positions in rod $M \nearrow(m)(2)m$ and $H \nearrow(m)(m)m$ of the superstructure and the basic structure (Pmn).

Rod Atom	Actual structure			Idealized superstructure				Basic structure			
	mult.	site	Atom	mult.	site	d[Å]	Atom	mult.	site	d[Å]	
M	Te1a	4	1	Te1	2	$m..$	0.065	Te	4	$m..$	0.292
M	Te1b	4	1	Te1	2	$m..$	0.062	Te	4	$m..$	0.205
M	Te2a	4	1	Te2	2	$m..$	0.071	Te	4	$m..$	0.295
M	Te2b	4	1	Te2	2	$m..$	0.071	Te	4	$m..$	0.327
M	Sr1a	4	1	Sr1	2	$m..$	0.129	Sr	4	$m..$	0.328
M	Sr1b	4	1	Sr1	2	$m..$	0.142	Sr	4	$m..$	0.074
M	Sr2a	4	1	Sr2	2	$m..$	0.102	Sr	4	$m..$	0.175
M	Sr2b	4	1	Sr2	2	$m..$	0.108	Sr	4	$m..$	0.281
M	O1a	4	1	O1	4	1	0.043	O1	8	1	0.274
M	O1b	4	1	O1	4	1	0.052	O1	8	1	0.261
M	O1c	4	1	O1	4	1	0.054	O1	8	1	0.198
M	O1d	4	1	O1	4	1	0.080	O1	8	1	0.229
M	O4a	4	1	O4	4	1	0.132	O1	8	1	0.334
M	O4b	4	1	O4	4	1	0.084	O1	8	1	0.270
M	O4c	4	1	O4	4	1	0.175	O1	8	1	0.249
M	O4d	4	1	O4	4	1	0.096	O1	8	1	0.357
M	O2	4	1	O2	1	$m2m$	0.106	O2	4	$m..$	0.407
M	O3a	4	1	O3	2	$m..$	0.113	O2	4	$m..$	0.338
M	O3b	4	1	O3	2	$m..$	0.193	O2	4	$m..$	0.164
H	Bra	4	1	Br	1	mmm	0.022	Br	4	$m..$	0.022
H	Brb	4	1	Br	1	mmm	0.022	Br	4	$m..$	0.022

of A^1 . Two consecutive layers A_n^1 and A_{n+2}^1 are related by a pseudo- $[- - 2_{\pm 4s}]$ operation. All atoms are located on general positions.

Symmetry reduction from the idealized structure proceeds in two steps: from the basic structure to the idealized OD rods in the superstructure and finally to the $P2_1/n$ structure. Symmetry reduction is noticeable by deviation of the lattice parameters from the idealized metrics and by deviation of atom positions from idealized positions. According to the OD description, the lattice vector of the main polytype $\mathbf{a}$ can be expressed as $\mathbf{a} = \mathbf{a}_0 + \frac{1}{4}\mathbf{c}$ with $\mathbf{a}_0$ normal to $\mathbf{c}$. Therefore in the idealized polytype, the value of the lattice parameter β is $\beta = \cos^{-1}(\frac{-c}{4a}) = 125.90^\circ$. The actual value of $\beta = 125.563(4)^\circ$ is very close to the idealized one.

The distances of the atoms in layer A^1 to the idealized positions according to the OD description of the superstructure are listed in Tab. 4.3, column 7. The deviations are small (< 0.2 Å for all atoms and < 0.1 Å for Te atoms), thus convincingly confirming the OD description. Tab. 4.3, column 12, gives the distance of the atoms in the actual to the basic structure. Distances are likewise small, being < 0.33 Å for heavy atoms (Te and Sr) and < 0.41 Å for O atoms. The deviations can be explained by the different coordination spheres of the Te atoms in the basic and the actual structures. While in the former all Te atoms exhibit $[\text{TeO}_4]$ coordination, in the latter two Te atoms are $[3]$ - and two other $[3 + 1]$ -coordinated. The largest deviation affects atom O2, the central bridging atom of the $[\text{Te}_4\text{O}_{11}]$ units, which is distinctly displaced in $[010]$ direction, compared with the other bridging O atoms (O3a, O3b) (Fig. 4.9(a)).

The Te–O distances compare well with those given in reviews on Te–O coordination chemistry

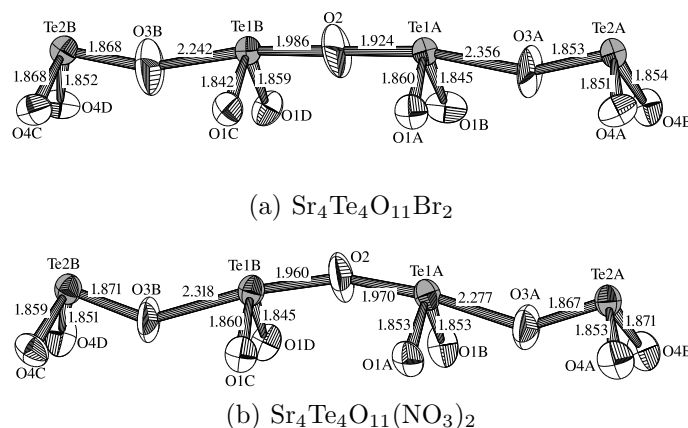


Figure 4.9: Ellipsoid plots of the $[\text{Te}_4\text{O}_{11}]$ units in (a) $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ and (b) $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$. Te atoms are represented by grey and O atoms by white ellipsoids. Ellipsoids represent 90% probability levels. Numbers next to bonds indicate bond distances in Å.

(Zemann, 1971) for $[\text{TeO}_3]$ and $[\text{TeO}_{3+1}]$ coordination with 1.842(6)–1.987(6) Å for the three close and 2.242(6)–2.356(6) for the more remote O atom. The average Sr–O distance of 2.69 Å is smaller than the value of 2.81 Å calculated from the sum of the ionic radii of O^{2-} and seven coordinate Sr^{2+} given by Shannon (1976), due to additional bonding to Br atoms. Indeed, bond valence calculations with $v_i = \exp(\frac{R_o - R_i}{b})$ (Brown, 2002) with the parameters $R_o = 2.680$ Å, $b = 0.37$ for Sr–Br result in significant bond valences of 0.24 s.u. for all Sr–Br bonds. The total BVS obtained with parameters $R_o = 2.680$ Å, $b = 0.37$ for the Sr–O bonds (2.00 for Sr1A, 2.02 for Sr1B, 1.99 for Sr2A and 1.93 for Sr2B) are very close to the expected value of 2.

4.2.6 $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$

$\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ is closely related to $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ and hence the same notations as in sec. 4.2.5 will be used. The NO_3 groups will be considered as single atoms in the OD description. In the following discussion only the differences to $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ will be highlighted, for a closer description of the structure *c.f.* sec. 4.2.5.

Idealized basic structure

Compared to the basic structure of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$, the Br atoms are replaced by NO_3 groups and the origin shift between adjacent rods H and M and therefore between layers A^1 and A^2 is negligible ($s = 0$), possibly because the anionic layers A^2 are considerably thicker and thus the electron lone pairs of two opposite Te^{IV} atoms do not interact with each other (Fig. 4.1(b)). Due to the negligible translational component s , the basic structure is fully ordered with symmetry $Immm$ as schematized in Fig. 4.6(e).

Idealized superstructure

The superstructure is composed of rods M and H as in $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$. But since $s = 0$, given a rod H , an adjacent rod M can only appear in four instead of eight positions (origin shift by $\frac{n}{4}\mathbf{c}$, $n = 0, 1, 2, 3$), resulting in distinctly less possible arrangements and consequently MDO polytypes. Notably, only one kind of layers A^2 ($A^2(I)$ according to the description given in sec. 4.2.5) is possible.

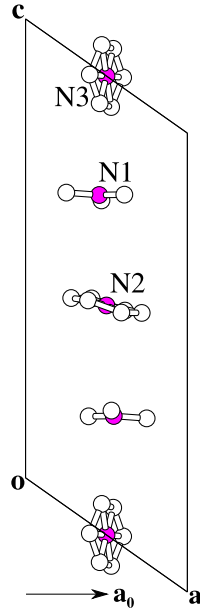


Figure 4.10: Layer A^2 in the actual structure of $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ viewed down $[010]$. N atoms are represented by pink spheres, other colour codes as in Fig. 4.3.

Actual structure

Despite the different symmetries of the basic structure, the actual structure has the same symmetry $P2_1/n$ and comparable lattice vectors

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ \frac{1}{4} & 0 & 1 \end{pmatrix}$$

as $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$.

Layers A^1 are isotypic to the corresponding layers in $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$. Whereas in the actual structure of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ two consecutive layers A_n^1 and A_{n+2}^1 are related by pseudo- $[- - 2_{\pm 4s}]$ operations in $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ they are related by pseudo- $[- - 2_{\pm \frac{1}{2}}]$ operations.

While in both $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{X}_2$ compounds layers A^2 are of type II , in $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$, two out of three crystallographically different NO_3 groups are located on a centre of inversion with disordered O atoms, whereas in $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ all atoms are located on general positions.

In all NO_3 groups the temperature factors of the O atoms are large, owing to disorder effects. This is not unusual for weakly coordinating anions like NO_3^- , PF_6^- or BF_4^- (Krossing and Raabe, 2004). While two NO_3 groups (N1, N2) are oriented nearly parallel to (001) , the third (N3) is nearly parallel to (100) (Fig. 4.10).

The distance of the atoms in the actual structure to the atoms of the idealized OD structure and of the basic structure (disregarding O atoms of the NO_3 groups) is small as is the case of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ (Tab. 4.4). The only exception is O2 with a deviation of 0.68 Å from the basic structure, which is caused by a higher difference of the y coordinates of the central bridging O atom (O2) and the other bridging atoms (O3a, O3b) (Fig. 4.9(b)).

Table 4.4: Distance of the atoms in the basic structure of $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$ ($Immm$) to the idealized positions in rod M ($\nearrow(m)(2)m$) and H ($\nearrow(m)(m)m$) of the superstructure and to the idealized basic structure ($Immm$). O atoms of the NO_3 groups have been left out.

Rod	Actual structure			Idealized rod				Basic structure			
	Atom	mult.	site	Atom	mult.	site	d[Å]	Atom	mult.	site	d[Å]
M	Te1a	4	1	Te1	2	$m..$	0.093	Te	4	$m2m$	0.083
M	Te1b	4	1	Te1	2	$m..$	0.136	Te	4	$m2m$	0.188
M	Te2a	4	1	Te2	2	$m..$	0.106	Te	4	$m2m$	0.261
M	Te2b	4	1	Te2	2	$m..$	0.072	Te	4	$m2m$	0.315
M	Sr1a	4	1	Sr1	2	$m..$	0.045	Sr	4	$m2m$	0.139
M	Sr1b	4	1	Sr1	2	$m..$	0.213	Sr	4	$m2m$	0.142
M	Sr2a	4	1	Sr2	2	$m..$	0.213	Sr	4	$m2m$	0.188
M	Sr2b	4	1	Sr2	2	$m..$	0.091	Sr	4	$m2m$	0.175
M	O1a	4	1	O1	4	1	0.082	O1	8	$..m$	0.194
M	O1b	4	1	O1	4	1	0.084	O1	8	$..m$	0.088
M	O1c	4	1	O1	4	1	0.103	O1	8	$..m$	0.275
M	O1d	4	1	O1	4	1	0.097	O1	8	$..m$	0.165
M	O4a	4	1	O4	4	1	0.072	O1	8	$..m$	0.234
M	O4b	4	1	O4	4	1	0.098	O1	8	$..m$	0.206
M	O4c	4	1	O4	4	1	0.079	O1	8	$..m$	0.182
M	O4d	4	1	O4	4	1	0.130	O1	8	$..m$	0.205
M	O2	4	1	O2	1	$m2m$	0.319	O2	4	$m2m$	0.680
M	O3a	4	1	O3	2	$m..$	0.028	O2	4	$m2m$	0.349
M	O3b	4	1	O3	2	$m..$	0.030	O2	4	$m2m$	0.306
H	N1	4	1	N	1	mmm	0.215	N	2	mmm	0.215
H	N2	2	$\bar{1}$	N	1	mmm	0.107	N	2	mmm	0.107
H	N3	2	$\bar{1}$	N	1	mmm	0.107	N	2	mmm	0.107

4.3 $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$

4.3.1 Preparation

160 mg TeO_2 , 1 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 40 mg NaOH were introduced into a teflon inlay with approximately 6 ml volume, which was filled to two thirds thirds with H_2O . The inlay was placed in a steel autoclave and heated at 493 K for 7 d. The aqueous phase was decanted and the residue washed subsequently with water and acetone. It contained colourless plates of $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and an off white powder of unknown composition.

4.3.2 Data collection

Crystals suitable for single crystal XRD were separated under acetone using a polarizing microscope. Reflection intensities were collected at 295 K using the ω - and ϕ -scan techniques. Eight independent sets totalling at 2942 frames were collected thus scanning the whole reciprocal sphere with high redundancy. More details on data collection and refinement are summarized in Tab. 4.5, atomic coordinates and isotropic displacement parameters are listed in Tab. C.22.

Table 4.5: Crystal data and details of the refinements of $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$.

$\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$	
Crystal data	
Chemical formula	$\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$
M_r	719.96
Cell setting, space group	Monoclinic, $P2_1/c$
Temperature [K]	295(2)
a, b, c [Å]	9.7466(8), 6.8764(6), 21.0441(15)
β [°]	117.856(4)
V [Å ³]	1247.86(9)
Z	4
D_x [Mg·m ⁻³]	3.835
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	8.661
Crystal form, colour	plate, colourless
Crystal size [mm]	0.15 × 0.10 × 0.04
Data collection	
Diffractometer	SMART APEX II
Data collection method	ω and ϕ scans
Absorption correction	SADABS
T_{min}, T_{max}	0.357, 0.723
No. of measured, independent and observed reflections	38026, 5476, 5303
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.031
θ_{max} [°]	35.0
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.020, 0.045, 1.31
No. of reflections	5476
No. of parameters	161
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0133P)^2 + 1.3566P]$ where $P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.003
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	0.84, -1.57

4.3.3 Structure determination

The standard setting ($\beta = 117.856(4)^\circ$, space group $P2_1/c$) was chosen over the reduced setting with pseudo-orthorhombic metrics ($\beta = 90.265(3)^\circ$, space group $P2_1/n$) in order to emphasize the OD character of the structure.

Absorption correction was performed using a multi-scan approach with SADABS (Sheldrick, 2001). The structure was solved using direct methods using the SHELX program package (Sheldrick, 2008). Most heavy atoms (Te, Ca, Cl) could be assigned to electron density peaks found by direct methods, the remaining atoms were located in the difference Fourier maps in subsequent refinement steps. All non-H atoms were refined with harmonic anisotropic temperature factors. The O–H bond lengths and the H–H distances of the water molecule were restrained to reasonable values of 0.86(5) and 1.50(10) Å. No excess electron density was detected in the final difference Fourier maps.

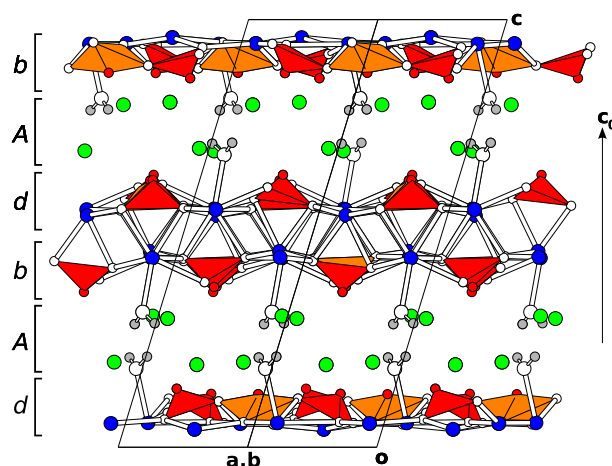


Figure 4.11: Crystal structure of $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ viewed down $[\bar{1}10]$. Te, Ca, O, Cl and H atoms are represented by red, blue, white, green and grey spheres, $[\text{TeO}_3]$ and $[\text{TeO}_4]$ units by red and orange polyhedra, respectively. The O atoms of the NO_3 groups have been omitted. Layer names according to the OD description have been indicated to the right.

4.3.4 Structure

Overview

$\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ is composed of an alternating stacking of anionic (symmetry $p12_1(1)$, composition ${}^2_\infty[\text{Cl}_2 \cdot \text{H}_2\text{O}]^{2-}$) and cationic (symmetry $p\bar{1}\bar{1}(\bar{1})$, composition ${}^2_\infty[\text{Ca}_3\text{Te}_3\text{O}_8]^{2+}$) layers parallel to (001) (Fig. 4.11). The cationic layers are closely related to the cationic layers of the structures of $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$ ($X = \text{Br}, \text{NO}_3$) (sec. 4.2). They can be considered superstructure layers with commensurate occupational modulation of one O atom (O2) and can be derived from the same basic layer with symmetry $pm\bar{m}(n)$ as the corresponding layers of $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$ (Fig. 4.12(a))⁴. The main building block of the idealized basic layers are $[\text{TeO}_4]$ units located on a site with symmetry $mm2$ which are connected via corners forming infinite chains running along a $\langle 110 \rangle$ direction with symmetry $\mu(m)(2)m$. The chains are arranged in the (001) plane, alternatingly facing up or down. They are connected by Ca atoms which are located on the same Wyckoff position with symmetry $mm2$ as the Te atoms.

In the superstructure, every third (as opposed to every fourth in the structures of $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$) bridging oxygen position is unoccupied (Fig. 4.12(b)). Additionally, as opposed to the structures of $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$, the resulting $[\text{TeO}_3]$ units are rotated significantly around the c^* direction (Fig. 4.12(b)). Due to this rotation, the layers can not reasonably be described as an OD structure being composed of rods as in the case of $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$. Instead, they can be decomposed into OD layers, as detailed in the next section.

OD description

In order to describe $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ according to OD theory, the cationic layers are „sliced” into two equivalent polar layers d and b . The anionic layers are considered a single non-polar layer A . Thus, the structure belongs to a category I OD groupoid family consisting of layers of two kinds whose OD groupoid family symbol reads as

⁴ Other coordinates than in the description of $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$ will be used for the sake of simplicity.

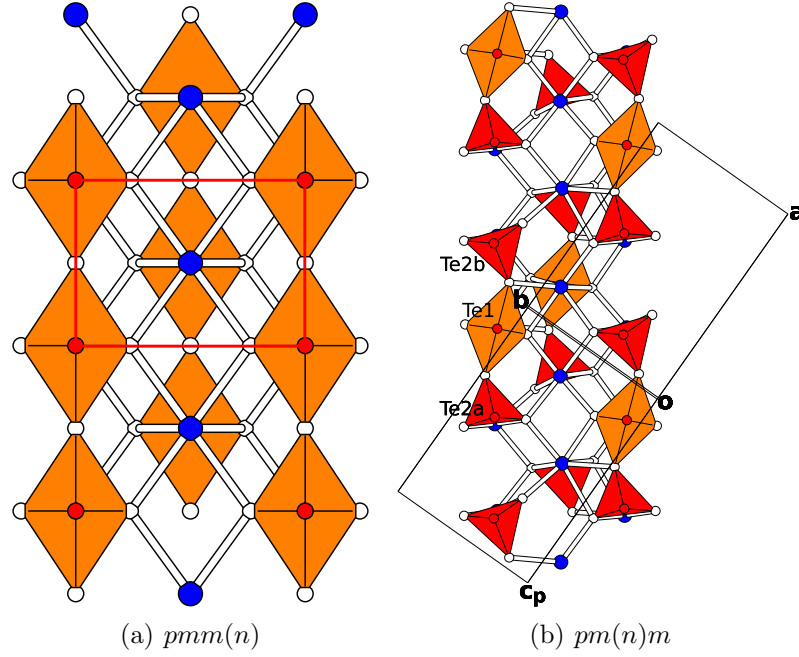


Figure 4.12: Cationic layers in the (a) idealized basic structure and (b) the actual structure of $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ projected on (001). The unit cell of the layer in the idealized basic structure is indicated by red, the unit cell of the actual structure by black lines.

$$\begin{array}{cc}
 A & b \\
 p12_1(1) & p11(2) \\
 [r, 0] & \{11(n_{r'}, s')\}
 \end{array}$$

according to the notation devised by Grell and Dornberger-Schiff (1982) with $r = -0.082$, $r' = -0.170$ and $s' = -0.084$. The symbol describes an unusual OD groupoid family, since layers A are monoclinic/rectangular and layers b are monoclinic/oblique and therefore pose different requirements on the common lattice. The layers are stacked along $[001]$ according to $\dots AbdAbd \dots$. The point group of the OD groupoid family belongs to the orthorhombic crystal system. Therefore the vector $\mathbf{c}_0$ connecting a layer and the next equivalent layers is chosen normal to the layer planes. Accordingly, the origin shift $r\mathbf{a}$ between adjacent layers A and b corresponds to the orthogonal projection of the vector connecting the origins of layers A and b on the layer plane.

The group of λ - τ -POs of a layer b is $G = p11(2)$. Of these operations only the identity e is valid for adjacent layers A or d . Therefore, according to the NFZ -relationship (Đurovič, 1997), given the position of a layer b and adjacent layer d or A can appear in $Z = N/F = |p11(2)|/|p1| = 2$ orientations, related by the $[-2]$ operation of layer b . The λ - τ -POs of a layer A , on the other hand, is $p1$ and therefore given the position of a layer A , the positions of adjacent layers d and b are fixed. Thus only one kind of layer triples dAb exists, in which the layers d and b are related by the $[-2_1-]$ operation of the intermediate layer A . Therefore layer pairs db occur alternately in two orientations, related by a $[-2_1-]$ screw.

To compute an idealized layer b , atom coordinates were transformed into an orthogonal coordinate system ($a' = a$, $b' = b$, $c' = c \sin \beta$, $\alpha' = \beta' = \gamma' = 90^\circ$). The origin of layer b was set to the centre of gravity of the heavy atoms (Ca, Te). The positions of atoms related by symmetry in the idealized layer were averaged and the resulting atoms close to the $[-2]$ axis were moved on the axis.

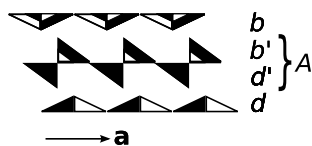


Figure 4.13: Schematic representation of the symmetry of the only possible layer packet pair qp , corresponding to a layer quadruple $dd'b'b$ in $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2\cdot\text{H}_2\text{O}$ viewed down $[010]$. Triangles are polar with respect to the $[010]$ direction. They are black on one and white on the opposite side. Triangles translated by $\frac{1}{2}\mathbf{b}$ are marked by small triangles of the opposite colour. The length of the translation vectors along $\mathbf{a}$ are not true to scale.

MDO polytypes

Dornberger-Schiff and Grell (1982) described a way to systematically derive all possible MDO polytypes of an OD family composed of layers of $M > 1$ kinds, which will be exemplified with the structure at hand. In a first step, the polar layers A are split into half-layers d' and b' in order to obtain a layer stacking belonging to a category III OD family. The half-layers d' and b' have symmetry $p1$. The obtained layer stacking $\dots dd'b'bdd'b' \dots$ corresponds to an OD groupoid family whose symbol reads as:

$$\begin{array}{ccc} b' & & b \\ p11(1) & & p11(2) \\ \{12_1(1)\} & [r, 0] & \{11n_{r',s'}\}. \end{array}$$

The newly obtained layers are then grouped into layer packets as defined by Āurovič (1974). In the case of the title compounds, these packets are dd' and $b'b$, which will henceforth be called q and p . In an MDO polytype, all layer packets are equivalent. For packets consisting of pairs of layers (as opposed to n -tuples with $n > 2$), this requirement is always fulfilled due to the vicinity condition of OD theory (Dornberger-Schiff and Grell-Niemann, 1961). In a subsequent step, all packet pairs qp and pq have to be determined and checked for violation of the MDO conditions (Dornberger-Schiff and Grell, 1982). Only one kind of packet pair qp (corresponding to a layer quadruple $dd'b'b$) can exist as schematized in Fig. 4.13. $d'b'$ corresponds to a layer A of which only one kind exists and given the position of a layer A , the positions of adjacent layers d and b are fixed, as elaborated in sec. 4.3.4. This packet pair qp has symmetry $p12_1(1)$ and is therefore non-polar. In consequence it is a „not violating” packet pair (Dornberger-Schiff and Grell, 1982).

Packet pairs pq (corresponding to a stacking $b'bdd'$) can appear in four non-equivalent kinds as schematized in Fig. 4.14. Given a layer b' the position of an adjacent layer b is fixed. The following two layer contacts bd and dd' allow for two different layer stackings each, as described above.

The central bd part of packet pairs pq is in all cases non-polar since layers b and d are related by a $[-(n)]$ glide. Of the four kinds of packet pairs pq two are non-polar (symmetry $p\bar{1}\bar{1}(\bar{1})$) (Fig. 4.14(a) and 4.14(b)) and therefore not violating. The other two (Fig. 4.14(c), 4.14(d)) are polar with symmetry $p1$. They violate the MDO condition because the only PO transforming b into d does not apply for the whole layer packet. Therefore these layer packet pairs cannot appear in an MDO polytype.

In order to deduce all MDO polytypes, the two non-equivalent and non violating packet pairs pq are combined with the only kind of packet pair qp . Thus, there are two possible MDO polytypes MDO_1 and MDO_2 as schematized in Fig. 4.15 with a symmetry belonging to space group $P2_1/c$ and lattice vector $\mathbf{c} = 2\mathbf{c}_0 + (4r + 4r')\mathbf{a}$ (MDO_1 , Fig. 4.15(a)) and

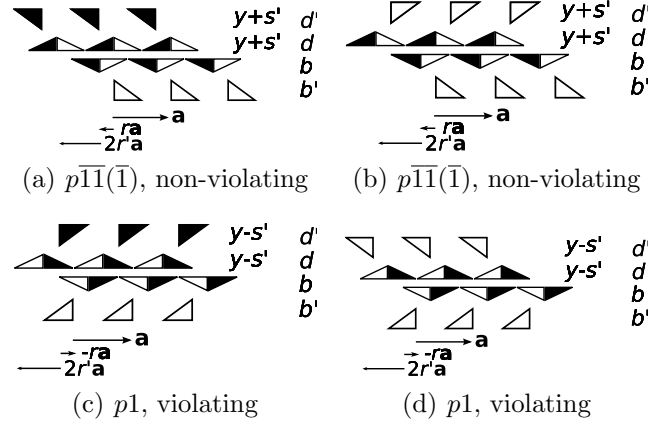


Figure 4.14: Schematic representation of the four possible layer packet pairs pq , corresponding to layer quadruples $b'bdd'$ in $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ viewed down $[010]$. Symbols as in Fig. 4.13, additional translation of layers along $\pm s'\mathbf{b}$ is indicated by $y \pm s'$. The length of the translation vectors along $\mathbf{a}$ are not true to scale.

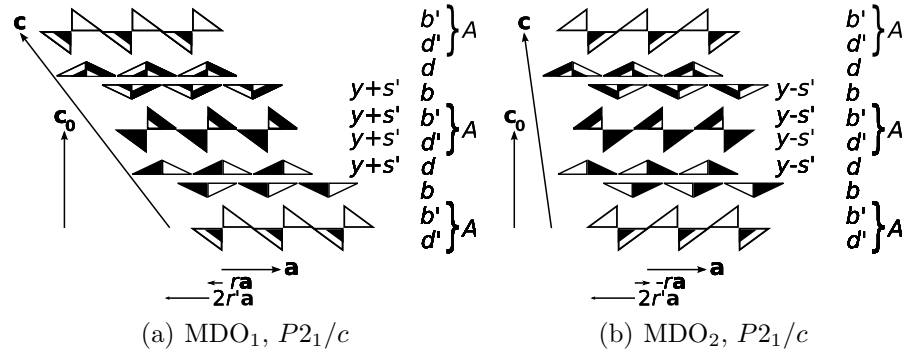


Figure 4.15: Schematic representation of the four possible layer packet pairs pq , corresponding to layer quadruples $b'bdd'$ in $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ viewed down $[010]$. Symbols as in Fig. 4.13, additional translation of layers along $\pm s'\mathbf{b}$ is indicated by $y \pm s'$. The length of the translation vectors along $\mathbf{a}$ are not true to scale.

$\mathbf{c} = 2\mathbf{c}_0 + (-4r + 4r')\mathbf{a}$ (MDO_2 , Fig. 4.15(b)). As is characteristic for ordered polytypes, the MDO polytypes are desymmetrized compared to the idealized OD description (Đurovič, 1979). In both MDO polytypes the symmetry of layers b is reduced from $p11(2)$ to $p1$. Of the operations relating two adjacent layers b and d ($[-(n_{r',s'})]$ and $\bar{1}$), only the centre of symmetry $\bar{1}$ is retained.

4.3.5 Actual structure

The crystal under investigation corresponds to the MDO_1 polytype of the description above. The distances of the idealized atomic positions to those in the actual structure are listed in Tab. 4.6. The largest deviation of only 0.31 Å (O3) convincingly confirms the validity of the OD description. Since for the actual values of r and r' , $4r + 4r' \approx -1$, the lattice vector $\mathbf{c} = 2\mathbf{c}_0 + (4r + 4r')\mathbf{a}$ is very close to $2\mathbf{c}_0 - \mathbf{a}$, explaining the β angle close to 90° in the reduced setting.

The Te–O distances compare well with those given in reviews on Te–O coordination chemistry

Table 4.6: Distances of the atoms of layer *b* in the actual structure of $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2\cdot\text{H}_2\text{O}$ to the idealized positions according to the OD description.

Actual structure				Basic structure				d[Å]
Atom	mult.	Wyckoff	site	Atom	mult.	Wyckoff	site	
Te1	4	<i>e</i>	1	Te1	1	<i>a</i>	2	0.075
Te2A, Te2B	4	<i>e</i>	1	Te2	2	<i>e</i>	2	0.133
Ca1A, Ca1B	4	<i>e</i>	1	Ca1	2	<i>e</i>	2	0.050
Ca2	4	<i>e</i>	1	Ca2	2	<i>b</i>	2	0.029
O1A, O1B	4	<i>e</i>	1	O1	2	<i>e</i>	2	0.057
O2A, O2B	4	<i>e</i>	1	O2	2	<i>e</i>	2	0.092
O3A, O3B	4	<i>e</i>	1	O3	2	<i>e</i>	2	0.308
O4A, O4B	4	<i>e</i>	1	O4	2	<i>e</i>	2	0.084

(Zemann, 1971) with 1.8455(17)–1.8586(14) Å in the case of $[\text{TeO}_3]$ and 1.8535(14)–2.0990(15) Å in the case of $[\text{TeO}_4]$ coordination.

4.4 $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$

4.4.1 Preparation

147 mg $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ and 160 mg TeO_2 were introduced in a 5 ml teflon inlay which was filled to two thirds of its volume with a 20%_{wt} hydrous NH_4OH solution. The inlay was placed in a steel autoclave and heated at 493 K for 10 d. The residue was washed with water and acetone and dried at room temperature. It consisted mainly of plates of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ and a yellowish micro-crystalline powder of unknown composition.

4.4.2 Data collection

Crystals suitable for single crystal XRD were separated under acetone using a polarizing microscope. Diffraction intensities were collected at 295 K using the ω -scan technique with 0.3° rotation width. Three independent sets of 600 frames were collected, thus scanning the whole reciprocal sphere with high redundancy. Data was reduced to F^2 values using the SAINT software (Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2007). Absorption correction was performed using a multi-scan approach with SADABS (Sheldrick, 2001).

4.4.3 Structure determination

The structures of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ was solved using direct methods using the SHELX program package (Sheldrick, 2008). Most of the heavy atoms (Te, Ca, Cl) could be assigned to electron density peaks found by direct methods, the remaining atoms were located in the difference Fourier maps in subsequent refinement steps. All atoms were refined with anisotropic ADP.

More details on data collection and refinement are summarized in Tab. 4.7, atomic coordinates and isotropic displacement parameters are listed in Tab. C.23.

Table 4.7: Crystal data and details of the refinements of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$

$\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$	
Crystal data	
Chemical formula	$\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$
M_r	2002.30
Cell setting, space group	Monoclinic, $P2_1/c$
Temperature [K]	295(2)
a, b, c [Å]	11.9721(6), 30.6264(15), 24.0406(11)
β [°]	131.4120(10)
V [Å ³]	6610.8(6)
Z	8
D_x [Mg·m ⁻³]	4.024
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	9.075
Crystal form, colour	plate, colourless
Crystal size [mm]	0.16 × 0.10 × 0.01
Data collection	
Diffractometer	SMART APEX
Data collection method	ω scans
Absorption correction	SADABS
T_{min}, T_{max}	0.325, 0.915
No. of measured, independent and observed reflections	72786, 19195, 12478
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.057
θ_{max} [°]	30.0
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.042, 0.092, 0.98
No. of reflections	19195
No. of parameters	847
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0322P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.56, -1.25

4.4.4 Idealized structures

Idealized structures and layers were computed by transforming the atom coordinates into a standard coordinate system of the symmetry group of the idealized structure or layer. The origin of the coordinate system was optimized from the position of symmetry equivalent (in the idealized structure) heavy atoms (Te, Ca, Cl). Symmetry equivalent atoms of the same type were grouped and their positions averaged. If an averaged atom was located close (< 1 Å) to a symmetry element without translational component, it was moved onto this element. Finally, the obtained structures were checked for correct composition and reasonable interatomic distances.

4.4.5 Structure

OD Description

The structure of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ belongs to a tetragonal category IV OD family composed of two kinds of non-polar layers A^1 and A^2 and one kind of polar layers b parallel to (100) with a

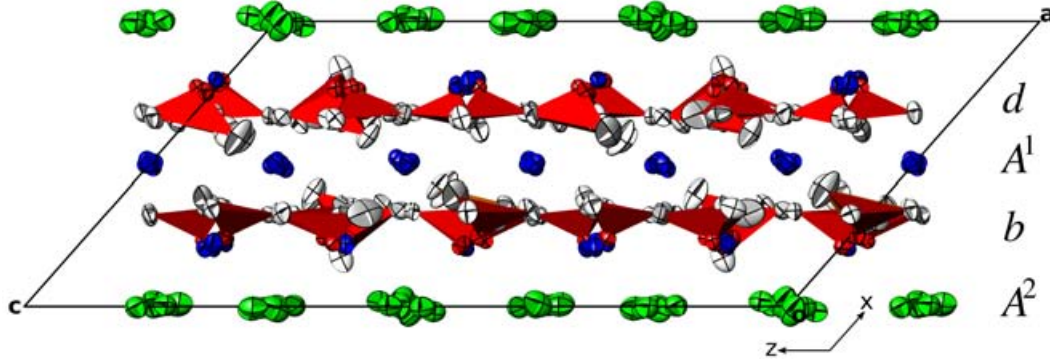


Figure 4.16: Unit cell content of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ viewed down $[010]$. Layer names are indicated to the right. Te, Ca, Cl and O atoms are represented by red, blue, green and white ellipsoids. $[\text{TeO}_3]$ groups are red. Ellipsoids represent 90% probability levels.

Table 4.8: Overview of the different layer stacking possibilities according to the NFZ relationship in $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$.

$L1 \leftrightarrow L2$	L	G	$N = G $	$G_{L1} \cap G_{L2}$	F	$Z = N/F$
$A^1 \leftrightarrow b$	A^1	$p_{\mathbf{b}'=\frac{1}{8}\mathbf{b}, \mathbf{c}'=\frac{1}{6}\mathbf{c}}(4)mmmm$	384	$p_{\mathbf{c}'=\frac{1}{2}\mathbf{c}}(2)mb$	8	1
	b	$p_{\mathbf{c}'=\frac{1}{2}\mathbf{c}}(2)mb$	8			48
$A^2 \leftrightarrow d$	A^2	$p(2)cb$	4	$p(2)cb$	4	2
	d^2	$p_{\mathbf{c}'=\frac{1}{2}\mathbf{c}}(2)mb$	8			1

stacking sequence of $\dots dA^1bA^2 \dots$ (Fig. 4.16). The OD-groupoid family symbol reads as

$$\begin{array}{ccc}
 A^1 & b & A^2 \\
 p_{\mathbf{b}'=\frac{1}{8}\mathbf{b}, \mathbf{c}'=\frac{1}{6}\mathbf{c}}(4/m)mmmm & p_{\mathbf{c}'=\frac{1}{2}\mathbf{c}}(2)mb & p(m)cb \\
 [\frac{1}{16}, 0] & [0, 0] &
 \end{array}$$

according to the notation of Grell and Dornberger-Schiff (1982). The symbol designates an unusual OD-groupoid family since it contains two layers with rectangular lattices and one layer with a square lattice, which are not compatible in the general case. To describe the symmetry of layers with square lattice, Dornberger-Schiff and Grell-Niemann (1961) devised layer group symbols with five instead of three places, designating symmetry elements in directions $[100]$, $[010]$, $[001]$, $[110]$ and $[\bar{1}10]$. Since the fourfold axes of layers A^1 are parallel to $[100]$, symmetry elements are instead given in $[100]$, $[010]$, $[001]$, $[011]$, $[0\bar{1}1]$ directions. For non-tetragonal layer groups the directions $[011]$ and $[0\bar{1}1]$ are left out.

Layers A^1 (Ca1) have high idealized symmetry $p_{\mathbf{b}'=\frac{1}{8}\mathbf{b}, \mathbf{c}'=\frac{1}{6}\mathbf{c}}(4/m)mmmm$. Layers b (Ca2–Ca4, Te1–Te5, O1–O7) have symmetry $p_{\mathbf{c}'=\frac{1}{2}\mathbf{c}}(2)mb$. Layers A^2 (Cl1–Cl12) have symmetry $p(m)cb$. An overview of the NFZ relationship (Đurović, 1997) as applied to all layer contacts is given in Tab. 4.8. The group of λ - τ -POs of layers A^1 is $G = p_{\mathbf{b}'=\frac{1}{8}\mathbf{b}, \mathbf{c}'=\frac{1}{6}\mathbf{c}}(4)mmmm$. The operations valid for adjacent layers b form the subgroup $F = p_{\mathbf{c}'=\frac{1}{2}\mathbf{c}}(2)mb$. Therefore, from a geometric point of view, given a layer A^1 , an adjacent layer b can appear in 48 different positions.

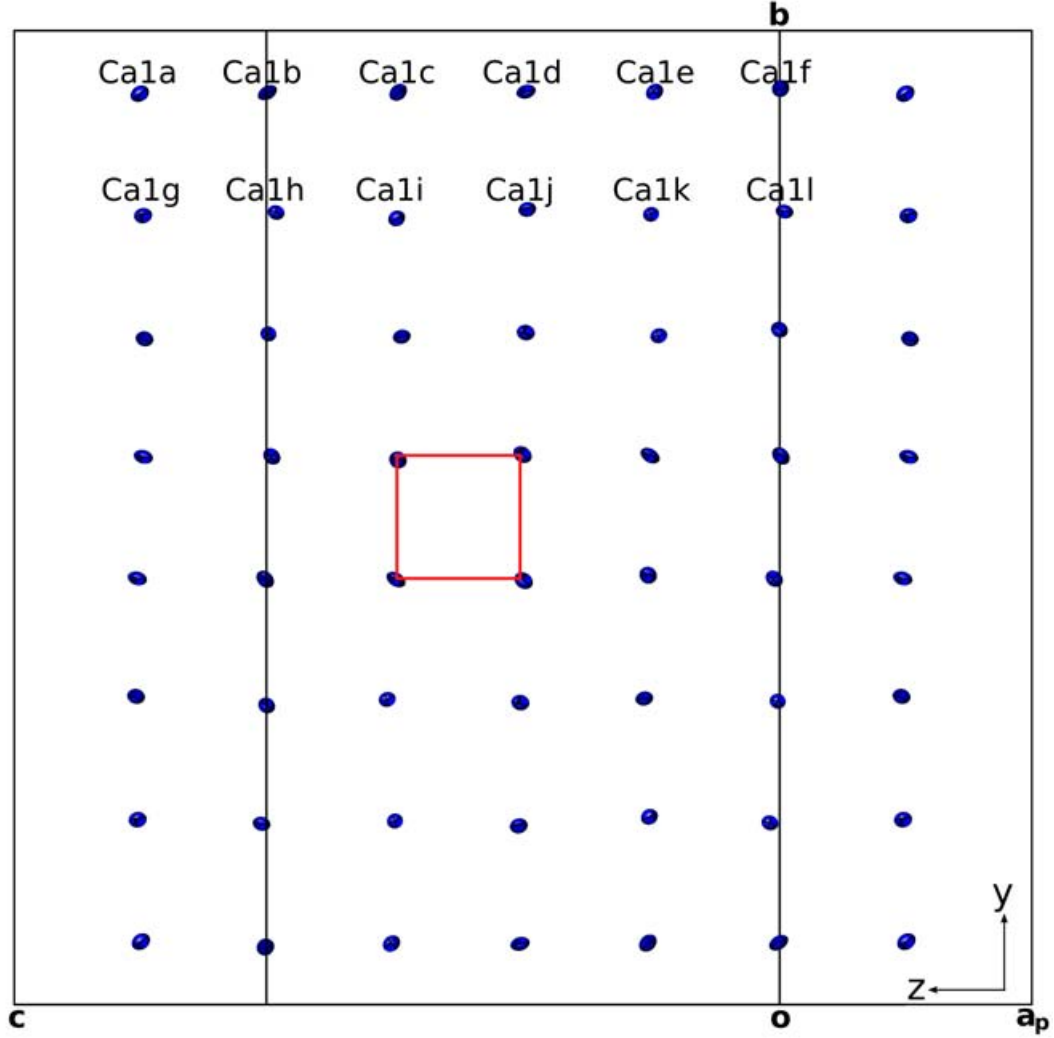


Figure 4.17: Layer A^1 in the actual structure of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ projected on (100). The unit cells of the actual structure and of the idealized layer with symmetry $p_{\mathbf{b}'=\frac{1}{8}\mathbf{b}, \mathbf{c}'=\frac{1}{6}\mathbf{c}}(4/m)mm$ are indicated by red and black lines, respectively.

All λ - τ -POs of layers A^2 ($G = p(2)cb$) are also valid for adjacent layers b and therefore depending on the position of the former, the position of the latter is fixed. Two layers b which are connected by a layer A^2 are related by the $[m - -]$ operation of the intermediate layer A^2 .

Since layers b are polar, the layer group of the layer $p_{\mathbf{c}'=\frac{1}{2}\mathbf{c}}(2)mb$ is identical to the group of λ - τ -POs. Of these POs only those of the subgroup $F = p(2)cb$ are also valid for adjacent A^2 layers which can therefore appear in two orientations related by a $[-m -]$ operation.

Due to the high symmetry of the layers A^1 , numerous different stacking orders and consequently MDO polytypes are possible from a geometrical point of view. The exact number of MDO polytypes has not been worked out so far.

Crystal chemistry

Layers A^1 have composition $\frac{2}{\infty}[\text{Ca}]^{2+}$ with one Ca per unit cell located on a site with symmetry $4/mmm$. (Fig. 4.17). Layers b have composition $\frac{2}{\infty}[\text{Ca}_4\text{Te}_8\text{O}_{23}]^{6-}$. They are composed of $[\text{TeO}_3]$

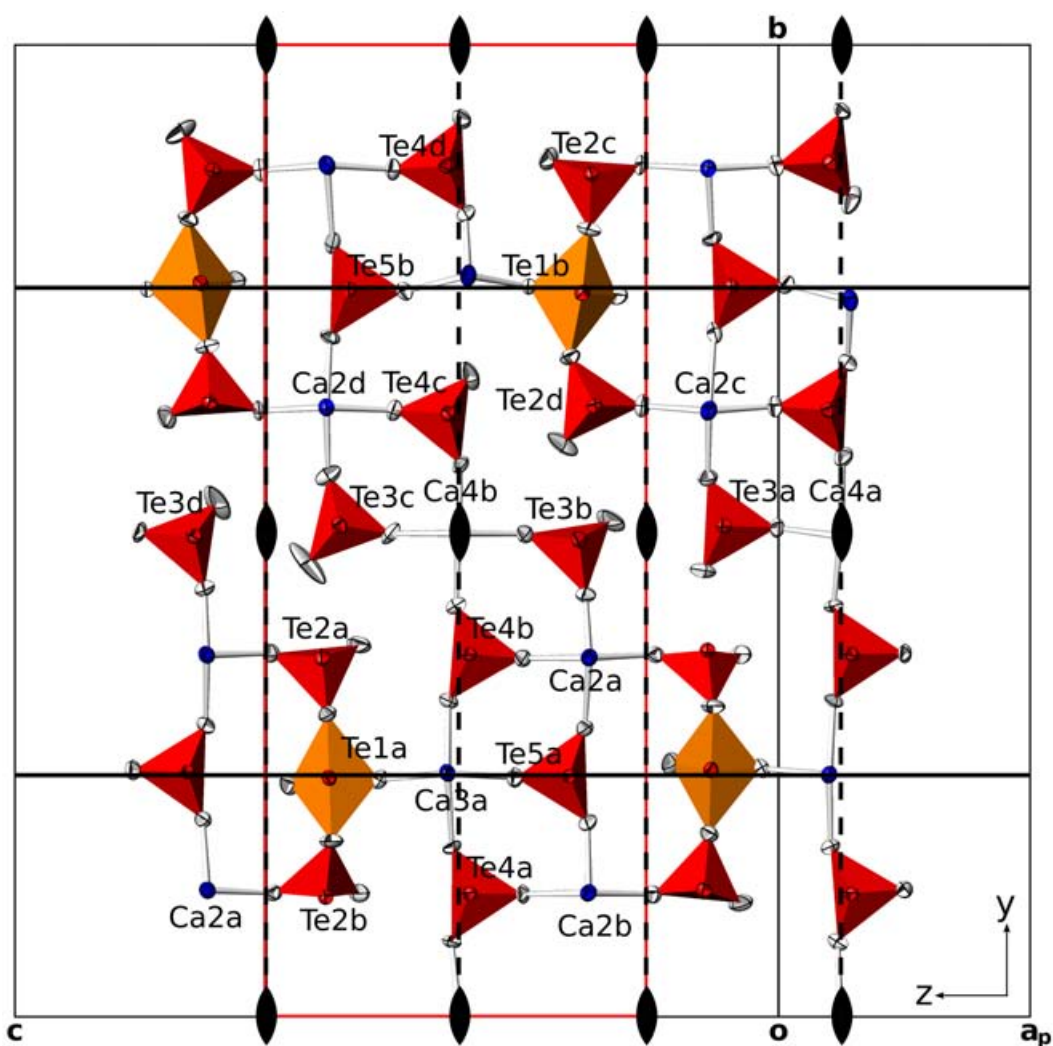


Figure 4.18: Layer b^1 in the actual structure of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ projected on (100). The unit cells of the actual structure and of the idealized layer with symmetry $p_{c'= \frac{1}{2}c}(2)mb$ are indicated by black and red lines, respectively. Pseudo-symmetry elements of the idealized layer are indicated by symbols according to the *International Tables for crystallography Vol. A* (Hahn, 1983).

and $[\text{TeO}_4]$ units and Ca atoms (Fig. 4.18). The trigonal-pyramidal shape of the $[\text{TeO}_3]$ units and the Te–O distances 1.808(5)–1.9025 Å as well as the shape of the $[\text{TeO}_4]$ units with two close (1.8462–1.8890 Å) and two farther (2.0279–2.1537 Å) O atoms are frequently found for Te^{IV} -oxo compounds (Zemann, 1971). Each $[\text{TeO}_4]$ unit is connected via corners to two $[\text{TeO}_3]$ units, forming a $[\text{Te}_3\text{O}_8]$ group. Two further isolated $[\text{TeO}_3]$ groups are located on a mirror plane parallel to (010) and on a general position, respectively. One Ca atom is located on a general position, two more on a mirror plane.

Layers A^2 have composition ${}_{\infty}^2[\text{Cl}]^-$ and symmetry $p(m)cb$ (Fig. 4.19). All Cl atoms are located at a site with symmetry m in the idealized structure. Layers b connect to layers A^2 layers *via* Ca–Cl bonds, the electron lone pairs of the Te^{IV} atoms are directed towards voids of layers A^2 (Fig. 4.16). Layers b connect to the A^1 layers *via* Ca–O bonds.

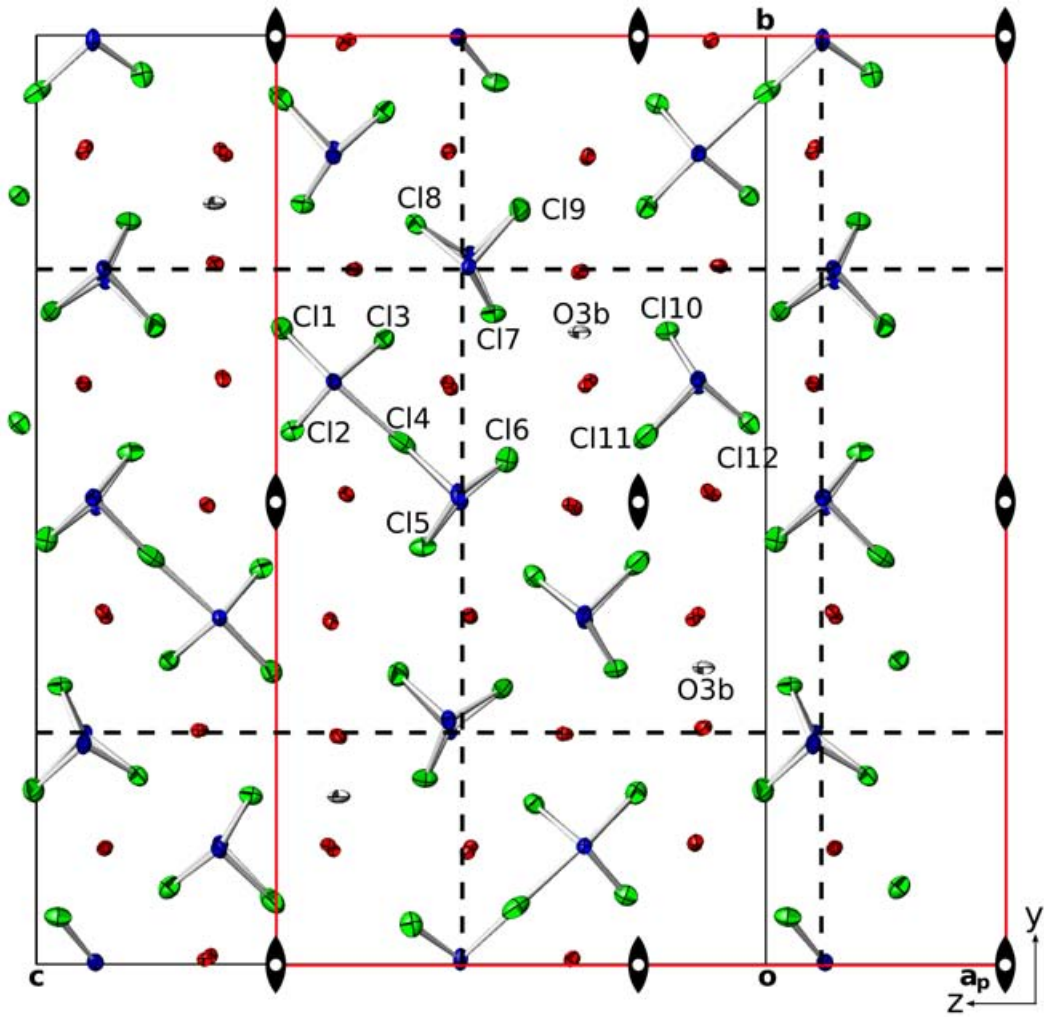


Figure 4.19: Layer A^2 in the actual structure of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ projected on (100) with closest atoms from the adjacent layers. The unit cells of the actual structure and of the idealized layer with symmetry $p(m)cb$ are indicated by black and red lines, respectively. Pseudo-symmetry elements of the idealized layer are indicated by symbols according to the *International Tables for crystallography Vol. A* (Hahn, 1983).

Actual structure

Only one polytype could be directly detected in the actual structure. Indeed, many of the geometrically possible dA^1b layer triples lead to unreasonable $[\text{CaO}_x]$ polyhedra and are therefore not realizable. Many kinds of stackings deviating from the major polytype, which are possible according to the OD description, result in a twinned crystal with twin domains related by translation and thus can not be detected if they occur infrequently. No unusual streaking has been detected in the direction normal to the layer planes. In the determined polytype, two layers b which are connected by a layer A^1 are related by a $[- - 2\frac{1}{6}]$ pseudo-screw, which is thus responsible for the β -angle deviating from 90° . The symmetry of layers A^1 is reduced by a factor 196 from $p_{b'= \frac{1}{8}b, c'= \frac{1}{6}c}(4/m)mm$ to $p(1)2_1/c1$. The Ca atom on site symmetry $4/mmm$ is split into 12 atoms on general positions. They are distanced less than $0.44 \text{ \AA}$ from their idealized positions (Tab. 4.9). The symmetry of layers A^2 is reduced by a factor 2 from $p(m)cb$

Table 4.9: Distance of the atoms in the actual structure of $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ to the atoms in the idealized structure. The layer and site symmetry of the atoms in the idealized layers are indicated. Site symmetry of all atoms in the actual structure is 1.

Atoms	Layer	Site symm.	d [Å]	Atoms	Layer	Site symm.	d [Å]
Te1A	<i>b</i>	<i>.m.</i>	0.230	O8A	<i>b</i>	1	0.183
Te1B	<i>b</i>	<i>.m.</i>	0.243	O8B	<i>b</i>	1	0.218
Te2A	<i>b</i>	1	0.107	O8C	<i>b</i>	1	0.072
Te2B	<i>b</i>	1	0.224	O8D	<i>b</i>	1	0.013
Te2C	<i>b</i>	1	0.166	O9A	<i>b</i>	1	0.049
Te2D	<i>b</i>	1	0.142	O9B	<i>b</i>	1	0.119
Te3A	<i>b</i>	1	0.107	O9C	<i>b</i>	1	0.110
Te3B	<i>b</i>	1	0.170	O9D	<i>b</i>	1	0.052
Te3C	<i>b</i>	1	0.136	O10A	<i>b</i>	1	0.123
Te3D	<i>b</i>	1	0.063	O10B	<i>b</i>	1	0.102
Te4A	<i>b</i>	1	0.087	O10C	<i>b</i>	1	0.208
Te4B	<i>b</i>	1	0.088	O10D	<i>b</i>	1	0.112
Te4C	<i>b</i>	1	0.146	O11A	<i>b</i>	1	0.171
Te4D	<i>b</i>	1	0.040	O11B	<i>b</i>	1	0.194
Te5A	<i>b</i>	<i>.m.</i>	0.091	O11C	<i>b</i>	1	0.428
Te5B	<i>b</i>	<i>.m.</i>	0.085	O11D	<i>b</i>	1	0.091
Ca2A	<i>b</i>	1	0.113	O12A	<i>b</i>	<i>.m.</i>	0.137
Ca2B	<i>b</i>	1	0.066	O12B	<i>b</i>	<i>.m.</i>	0.125
Ca2C	<i>b</i>	1	0.136	O13A	<i>b</i>	1	0.107
Ca2D	<i>b</i>	1	0.038	O13B	<i>b</i>	1	0.057
Ca3A	<i>b</i>	<i>.m.</i>	0.102	O13C	<i>b</i>	1	0.132
Ca3B	<i>b</i>	<i>.m.</i>	0.400	O13D	<i>b</i>	1	0.067
Ca4A	<i>b</i>	2..	0.181	Ca1A	A^1	4/ <i>mmm</i>	0.349
Ca4B	<i>b</i>	2..	0.099	Ca1B	A^1	4/ <i>mmm</i>	0.438
O1A	<i>b</i>	<i>.m.</i>	0.224	Ca1C	A^1	4/ <i>mmm</i>	0.256
O1B	<i>b</i>	<i>.m.</i>	0.140	Ca1D	A^1	4/ <i>mmm</i>	0.161
O2A	<i>b</i>	<i>.m.</i>	0.441	Ca1E	A^1	4/ <i>mmm</i>	0.096
O2B	<i>b</i>	<i>.m.</i>	0.385	Ca1F	A^1	4/ <i>mmm</i>	0.253
O3A	<i>b</i>	1	0.329	Ca1G	A^1	4/ <i>mmm</i>	0.423
O3B	<i>b</i>	1	0.864	Ca1H	A^1	4/ <i>mmm</i>	0.209
O3C	<i>b</i>	1	0.517	Ca1I	A^1	4/ <i>mmm</i>	0.327
O3D	<i>b</i>	1	0.401	Ca1J	A^1	4/ <i>mmm</i>	0.158
O4A	<i>b</i>	1	0.263	Ca1K	A^1	4/ <i>mmm</i>	0.417
O4B	<i>b</i>	1	0.578	Ca1L	A^1	4/ <i>mmm</i>	0.145
O4C	<i>b</i>	1	0.885	Cl1	A^2	<i>m.</i> ..	0.032
O4D	<i>b</i>	1	0.291	Cl2	A^2	<i>m.</i> ..	0.023
O5A	<i>b</i>	1	0.074	Cl3	A^2	<i>m.</i> ..	0.031
O5B	<i>b</i>	1	0.034	Cl4	A^2	<i>m.</i> ..	0.088
O5C	<i>b</i>	1	0.070	Cl5	A^2	<i>m.</i> ..	0.008
O5D	<i>b</i>	1	0.105	Cl6	A^2	<i>m.</i> ..	0.038
O6A	<i>b</i>	1	0.115	Cl7	A^2	<i>m.</i> ..	0.107
O6B	<i>b</i>	1	0.117	Cl8	A^2	<i>m.</i> ..	0.050
O6C	<i>b</i>	1	0.137	Cl9	A^2	<i>m.</i> ..	0.036
O6D	<i>b</i>	1	0.036	Cl10	A^2	<i>m.</i> ..	0.164
O7A	<i>b</i>	1	0.518	Cl11	A^2	<i>m.</i> ..	0.146
O7B	<i>b</i>	1	0.710	Cl12	A^2	<i>m.</i> ..	0.025
O7C	<i>b</i>	1	0.418				
O7D	<i>b</i>	1	0.224				

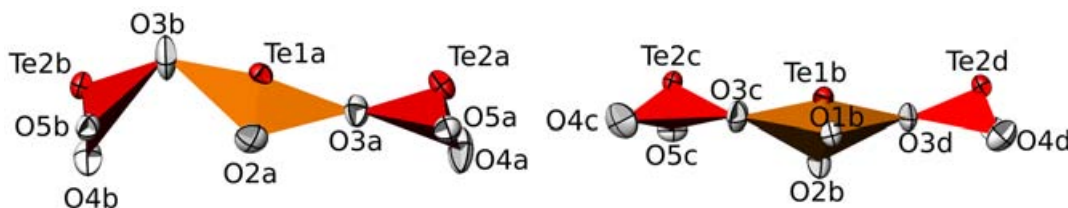


Figure 4.20: The two crystallographically different $[\text{Te}_3\text{O}_8]$ groups in $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$ which are related by pseudo-symmetry viewed down $[001]$. Atom O3b which is moved towards layer A^2 and thus breaks pseudo-symmetry.

to $p(1)2_1/c1$. The Cl atoms are located close ($< 0.17 \text{ \AA}$) to their idealized positions on the mirror plane $x = 0$ (Tab. 4.9).

The symmetry of layers d is reduced by a factor 4 from $p_{c'=\frac{1}{2}c}(2)mb$ to $p(1)c1$. The twofold rotation axis parallel to $[100]$ and the b -glide planes parallel to (001) of the idealized structure are lost and the mirror planes parallel to (010) remain as c -glide planes. The $[\text{Te}_3\text{O}_8]$ groups of the idealized layers are split into two crystallographically different groups. Atoms in layers d show the highest deviation from the idealized positions (Tab. 4.9). While the heavy atoms (Ca, Te) are close to their idealized positions ($0.4 \text{ \AA}$ for Ca3B, which is moved away from the mirror plane parallel to (010) ; $< 0.25 \text{ \AA}$ for all others), the O atoms show distinctly larger deviations with up to $0.85 \text{ \AA}$ for O4C. The atoms with large deviations are located in a part of the layer located in the vicinity of a pseudo- $[2 -]$ operation, relating two $[\text{Te}_3\text{O}_8]$ and two $[\text{TeO}_3]$ groups. Indeed, in one of the former the bridging O3b atom is moved towards the adjacent layer A^2 (Fig. 4.20). O3b is the only O atom in the structure having an x -coordinate similar to those of the other Te atoms (Fig. 4.19). The atoms in this region show highly anisotropic displacement parameters, hinting towards disorder in the structure. The most extreme cases being O7b, O7c and O7d (Fig. 4.18).

4.5 $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

4.5.1 Preparation

1 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 160 mg TeO_2 were introduced in a 5 ml teflon inlay which was filled to two thirds of its volume with a hydrous NH_4OH solution ($20\%_{wt}$). The inlay was placed in a steel autoclave and heated at 493 K for 10 d. The residue was washed with water and acetone. It contained thin plates of $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, plates of a second calcium nitrate tellurate with composition $\text{Ca}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$, for which no satisfactory structure refinement was possible so far, and a yellowish micro-crystalline powder of unknown composition.

4.5.2 Data collection

Crystals suitable for single crystal XRD were separated under acetone using a polarizing microscope. Reflection intensities were collected at 295 K using the ω -scan technique with 0.3° rotation width. Three independent sets of 600 frames were collected, thus scanning the whole reciprocal sphere with high redundancy. Data was reduced to F^2 values using the SAINT software (Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2007). Absorption correction was performed using a multi-scan approach with SADABS (Sheldrick, 2001).

4.5.3 Structure determination

Reflection condition $h + k = 2n$ for reflections $hk0$ indicated possible space groups $C2/c$ and Cc . Both space groups result in practically equivalent R_{int} values of 0.042. Structure solution and refinement in the centrosymmetric space group $C2/c$ gave acceptable reliability factors, but disordered NO_3 groups. Refinement in the corresponding non-centro symmetric spacegroup Cc as inversion twin resolved the disorder of the NO_3 group and resulted in distinctly better reliability factors. The origin was chosen to coincide with a centre of inversion of the refinement in $C2/c$.

The structure of $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was solved using direct methods implemented by the SHELX program package (Sheldrick, 2008). Most heavy atoms (Te, Ca) could be assigned to electron density peaks found by direct methods, the remaining atoms were located in the difference Fourier maps in subsequent refinement steps. All atoms were refined with anisotropic temperature factors. The H atoms of the water molecules could not be reliably located and were omitted from refinement.

More details on data collection and refinement are summarized in Tab. 4.10, atomic coordinates and isotropic displacement parameters are listed in Tab. C.24.

4.5.4 Structure

Idealized symmetry

$\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is a non-OD polytypic structure (Ferraris et al., 2004) composed of non-polar layers A and two kinds of polar layers b^1 and b^2 parallel to (100) (Fig. 4.21). The non-OD groupoid family of the structure is described by a symbol based on the symbols for OD groupoid families according to Grell and Dornberger-Schiff (1982) which reads:

$$\begin{array}{cc} A & b^1 \\ p(m)cb & p(1)c1 \\ [0, 0] & \end{array} \left\{ \begin{array}{l} b^2 \\ p(1)c1 \\ [0, s] \\ \{-2-\} \\ d^2 \\ p(1)c1 \\ [0, s] \end{array} \right. .$$

In this symbol, if a layer can adjoin to other layers in non equivalent ways, these are written aligned vertically and indicated by a brace. If these alternatives concern the same kind of layer in different orientations, the operations relating those different orientations (*i.e.* transforming the layers and their origins into each other) are indicated in braces between these layers in the notation used to indicate σ -POs. Each line is then continued to the right as in traditional OD symbols until a known layer is reached or all possible layer connections have been described. If necessary, multiple splittings are introduced. This notation cannot unambiguously describe all possible non-OD groupoid families, nor is it as concise as possible, but it is suitable for most realistic non-OD polytypic structures and is easily understood by those accustomed to OD groupoid family symbols devised by Dornberger-Schiff and Grell (1982).

As for OD families the non-OD family can be associated with a point group which is generated by all possible σ -POs. In the case of a non-OD family, the point group of members of the family may be a subgroup of the point group of the family, since a polytypes may contain different sets

Table 4.10: Crystal data and details of the refinements of $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

$\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	
Crystal data	
Chemical formula	$\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
M_r	1058.82
Cell setting, space group	Monoclinic, Cc
Temperature [K]	295(2)
a, b, c [Å]	25.258(3), 5.7289(7), 17.0066(19)
β [°]	124.377(2)
V [Å ³]	2031.0(4)
Z	4
D_x [Mg·m ⁻³]	3.463
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	7.047
Crystal form, colour	plate, colourless
Crystal size [mm]	$0.12 \times 0.08 \times 0.01$
Data collection	
Diffractometer	SMART APEX
Data collection method	ω scans
Absorption correction	SADABS
T_{min}, T_{max}	0.485, 0.933
No. of measured, independent and observed reflections	10731, 5210, 4083
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.047
θ_{max} [°]	30.0
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.043, 0.087, 0.97
No. of reflections	5210
No. of parameters	281
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0355)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	1.60, -1.22
Twin operation	$\bar{1}$
Twin volume fraction	56:44(5)

of σ -POs. The point group of the non-OD groupoid family at hand as well as of the groupoids of all possible polytypes belong to the orthorhombic crystal system.

Layers A (Ca1, Ca3) have orthorhombic symmetry $p(m)cb$ and layers b^1 (Te1, Te2, Ca2, O1–O6) and b^2 (N1, N2, ON1–ON6, OW1, OW2) monoclinic symmetry $p(1)c1$. They are arranged along (100) according to $\dots L^2 d^1 A b^1 L^2 d^1 A b^1 \dots$ where layers L^2 can appear in orientation b^2 or d^2 . This stacking order does not correspond to an OD-structure, since it can contain pairs of equivalent layers $b^2 d^1$ and $b^1 b^2$, which are not equivalent by symmetry⁵.

An overview of the NFZ relationship as applied to all layer contacts is given in Tab. 4.11. Layers A connect on both sides to layers b^1 , forming layer triples $d^1 A b^1$. Of the λ - τ -POs of layers A ($G = p(2)cb$) only the subgroup $p(1)c1$ is also valid for the adjacent layers b^1 . Therefore, given a layer A , adjacent layers b^1 can appear in two orientations, related by a $[2 - -]$ PO. This leads to

⁵ For OD structures layer symbols have to be chosen so that adjacent polar layers of different kinds are represented by the same character „ b ” or „ d ” (Grell and Dornberger-Schiff, 1982), therefore layer pair $b^2 d^1$ cannot exist in an OD structure.

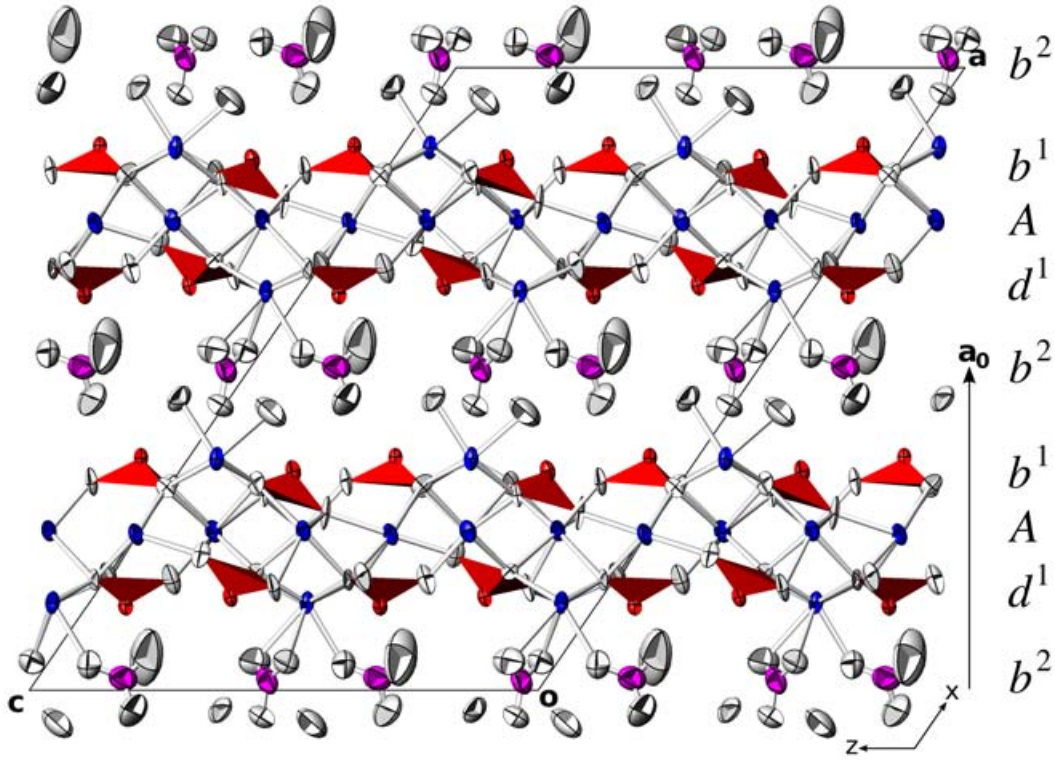


Figure 4.21: Unit cell content of the actual structure $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, viewed down $[010]$. Layer names are indicated to the right. Te, Ca, O and N atoms are represented by red, blue, white and pink ellipsoids, $[\text{TeO}_3]$ units by red polyhedra. Ellipsoids represent 90% probability levels.

Table 4.11: Overview of the different layer stacking possibilities according to the NFZ relationship in $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

$L1 \leftrightarrow L2$	L	G	$N = G $	$G_{L1} \cap G_{L2}$	F	$Z = N/F$
$A \leftrightarrow b^1$	A	$p(2)cb$	4	$p(1)c1$	2	1
	b^1	$p(1)c1$	2			2
$b^1 \leftrightarrow b^2$	b^1	$p(1)c1$	2	$p(1)c1$	2	1
	b^2	$p(1)c1$	2			1
$b^1 \leftrightarrow d^2$	b^1	$p(1)c1$	2	$p(1)c1$	2	1
	d^2	$p(1)c1$	2			1

two different possible layer triples $b^1 A d^1$ with layer groups $p(1)2_1/c1$ and $p(m)c2_1$ as schematized in Fig. 4.22 (a) and (b).

The side of layers $b^1 = d^1$ not connected to layers A can adjoin to layers b^2 in two non-equivalent ways ($d^1 b^2$ and $d^1 d^2$). In both cases, the origin of adjacent layers projected on the layer plane are related by sc . The NFZ relationship can be used to analyse both contacts $d^1 b^2$ and $d^1 d^2$: Both layers possess the same group of λ - τ -POs ($G = p(1)c1$) with overlapping

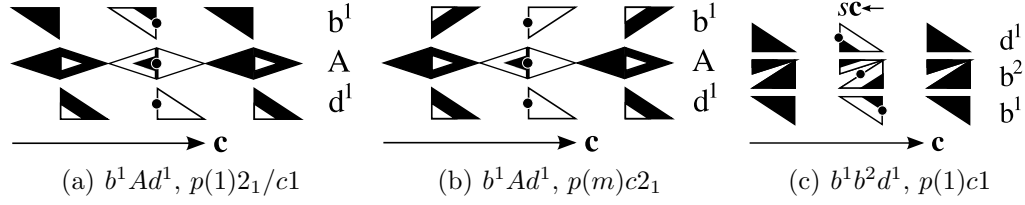


Figure 4.22: Schematic representation of the two geometrically possible kinds of layer triples b^1Ad^1 in (a) $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ with layer group $p(1)2_1/c1$ and (b) $p(m)c2_1$ and (c) of the layer triple $b^1b^2d^1$, equivalent to $b^1d^2d^1$, with symmetry $p(1)c1$ viewed down $[010]$. Polygons are black on one and white on the other side. Layer origins are indicated by a black dot.

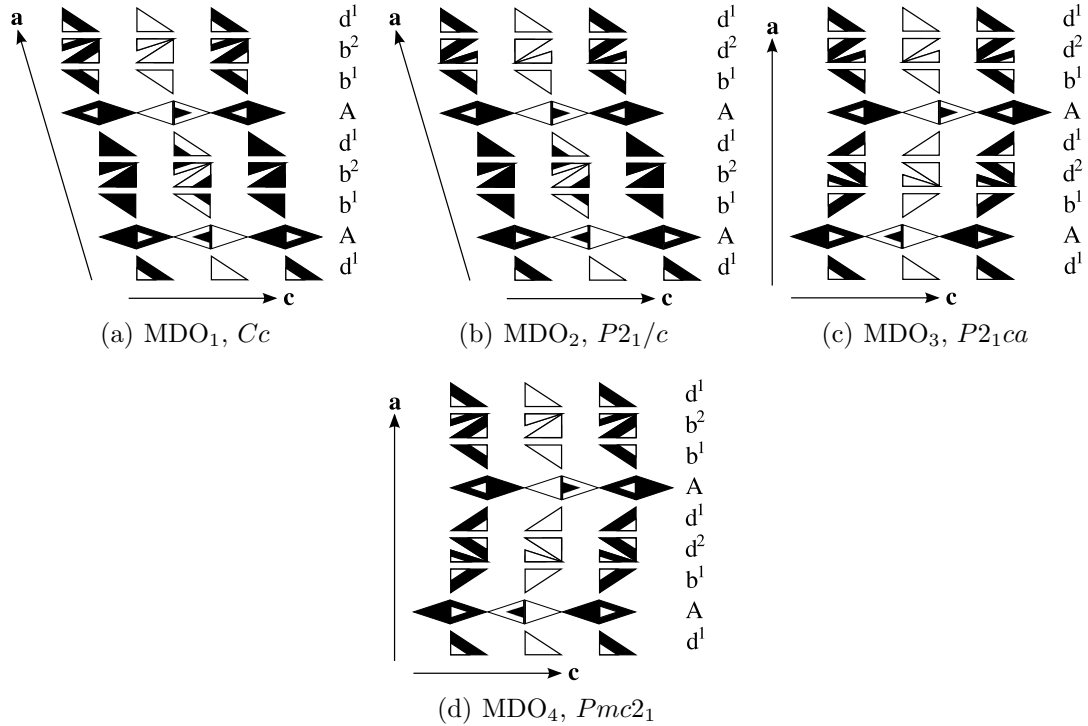


Figure 4.23: Scheme of the four MDO polytypes in the non-OD polytypic structure $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Symbols as in Fig. 4.22.

symmetry elements and therefore, according to the NFZ -relationship, only one way to realize each stacking is possible, resulting in layer pairs d^1b^2 and d^1d^2 , each with symmetry $p(1)c1$.

The only way to combine these pairs to triples is $d^1d^2b^1$ and $d^1b^2b^1$, both equivalent with symmetry $p(1)c1$. To understand how layers d^1 are related to the next equivalent layers b^1 in these triples, which is necessary to determine the symmetry of possible layer stackings, the symmetry operations relating the alternative orientations of layers b^2 have to be considered. Thus a layer d^1 is related to the next layer b^1 by a $[2 - -]$ PO and the origin is translated by $2rc$ as schematized in Fig. 4.22(c).

Despite not being an OD structure, in this case the concept of polytypes with a maximum degree of order (MDO) (Dornberger-Schiff, 1982) can still be applied. Thus four kinds of non-equivalent polytypes where all n -tuples of the same kind of adjacent layers are equivalent are possible which are schematized in Fig. 4.23:

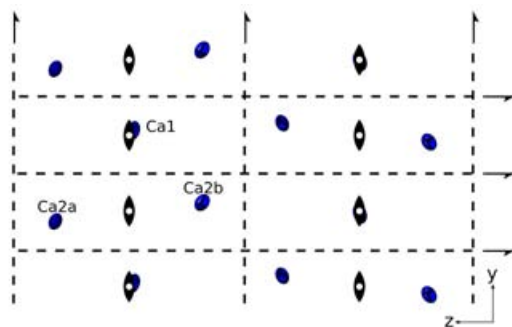


Figure 4.24: Layer A in the actual structure of $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, projected on (100) . Atom colour codes as in Fig. 4.21. Symmetry elements of the idealized layer are indicated by symbols according to the *International Tables for crystallography Vol. A* (Hahn, 1983).

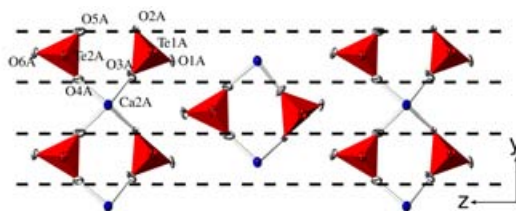


Figure 4.25: One out of two layers b^1 in the actual structure of $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, projected on (100) . Atom colour codes as in Fig. 4.21. Symmetry elements of the layer are indicated by symbols according to the *International Tables for crystallography Vol. A* (Hahn, 1983).

- MDO₁: d^1Ab^1 symmetry $p(1)2_1/c1$, only $d^1d^2b^1$ triples, $\mathbf{a} = 2\mathbf{a}_0 + 4\mathbf{sc}$, Cc .
- MDO₂: d^1Ab^1 symmetry $p(1)2_1/c1$, alternately $d^1d^2b^1$ and $d^1b^2b^1$ triples, $\mathbf{a} = 2\mathbf{a}_0 + 4\mathbf{sc}$, $P2_1/c$.
- MDO₃: d^1Ab^1 symmetry $p(m)c2_1$, only $d^1d^2b^1$ triples: $\mathbf{a} = 2\mathbf{a}_0$, $P2_1ca$.
- MDO₄: d^1Ab^1 symmetry $p(m)c2_1$, alternately $d^1d^2b^1$ and $d^1b^2b^1$ triples, $\mathbf{a} = 2\mathbf{a}_0$, $Pmc2_1$.

Crystal chemistry

Layer A has composition ${}^\infty_2[\text{Ca}]^{2+}$. It contains two crystallographically different Ca atoms, located on sites with symmetry m and $2/m$, respectively (Fig. 4.24).

Layer b^1 has composition ${}^\infty_2[\text{CaTe}_2\text{O}_6]^{2-}$ (Fig. 4.25). Two kinds of isolated $[\text{TeO}_3]$ units are connected *via* Ca^{2+} ions to form infinite chains running along $[010]$. One $[\text{TeO}_3]$ unit (Te1) is approximately symmetric by mirroring at (010) (approximate symmetry m), whereas the other (Te2) has symmetry 1. Te and Ca atoms are located on the side of the layer connecting layer b^2 (d^2), whereas the O atoms are located on the side connecting to layer A . The lone pairs of the Te atoms are directed towards layers b^2 (d^2).

Layer b^2 has composition ${}^\infty_2[\text{NO}_3 \cdot \text{H}_2\text{O}]^-$ (Fig. 4.26). It contains two crystallographically different NO_3^- ions and two water molecules. The N atoms are located in the middle of the layer, whereas the O atoms are located on both sides.

Layers A connect on both sides to layers b^1 *via* Ca–O bonds. As mentioned above, layers b^1 and b^2 can connect in two non-equivalent ways (d^1b^2 and d^1d^2). In the d^1b^2 stacking, atom Ca2 in layers b^1 connects to the water molecules, whereas in the d^1d^2 stacking Ca2 connects to both NO_3^- ions. One NO_3^- ion (N2) connects *via* one, the other (N1) *via* two O atoms (Fig. 4.21).

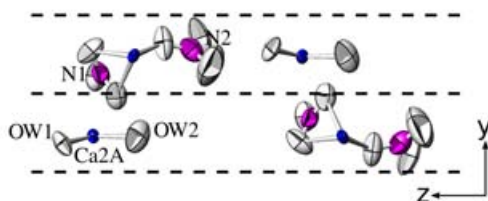


Figure 4.26: Layer b^2 in the actual structure of $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, projected on (100), including Ca atoms of the adjacent layers b^1 and d^1 . Atom colour codes as in Fig. 4.21. Symmetry elements of the layer are indicated by symbols according to the *International Tables for crystallography Vol. A* (Hahn, 1983).

The atoms of the NO_3^- ions and the water molecules possess large displacement parameters, as is characteristic of weakly bonding ions (Krossing and Raabe, 2004).

Actual structure

In the actual structure only the polytype MDO_1 where all layers b^2 occur in the same orientation ($\dots b^2 d^1 A b^1 b^2 d^1 A b^1 \dots$) and where the layer triples $d^1 A b^1$ have symmetry $p(1)2_1/c1$ has been directly observed. The other kind of layer triples $d^1 A b^1$ would result in non-merohedral twinning with a twin plane of (001), which however was not observed. Indeed, in layer triples $d^1 A b^1$ with symmetry $p(m)c2_1$ atoms O1 of layers d^1 and b^1 may come too close and the layer triple may therefore not be realizable. Different orientations of layers b^2 would result in twinning by inversion which was indeed detected but is no definite proof of this alternative layer stacking, as other reasons for twinning are conceivable. Such inversion twins are frequently found for non-centrosymmetric space groups.

As in OD structures, ordered non-OD polytypes are desymmetrized. The symmetry of layers A is reduced from $p(1)2_1/c1$ to $p(1)c1$. Layers d^1 retain symmetry $p(1)c1$, but appear in two instead of one crystallographically different forms which are related by $[-2-]$, the symmetry element relating both alternative orientations of layers b^2 . Accordingly, the symmetry of the $b^1 A d^1$ layer triples is reduced from $p(1)2_1/c1$ to $p(1)c1$. Layers d^2 retain $p(1)c1$ symmetry.

The positions of the atoms in layer triples $d^1 A b^1$ in the actual structure deviate only slightly from the idealized symmetry $p(1)2_1/c1$ (Tab. 4.12), thus convincingly confirming the description as non-OD polytypic structure. The largest deviations affect atoms O3A/O3B (0.205 Å), O6A/O6B (0.187 Å) and Ca1 (0.162 Å), which are moved slightly off the pseudo-centre of inversion.

4.6 $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$

4.6.1 Preparation

160 mg TeO_2 , 1 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 66 mg KOH were placed in a teflon inlay with approximately 6 ml volume that was filled with water to two thirds of its volume. The inlay was placed in a steel autoclave and heated at 493 K for 7 d. The aqueous phase was decanted and the residue subsequently washed in with water and acetone. It contained thin plates of $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$.

Table 4.12: Distance of the atoms in layer triples d^1Ab^1 in the actual structure ($p(1)c1$) of $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ to the atoms in the idealized structure ($p(1)2_1/c1$) and site symmetry in the idealized structure. Site symmetry of all atoms in the actual structure is 1. Atoms related by symmetry in the idealized structure have been grouped.

Atoms	Layer	Site symm.	d [$\text{\AA}$]
Te1A, Te1B	b^1, d^1	1	0.065
Te2A, Te2B	b^1, d^1	1	0.065
Ca2A, Ca2B	b^1, d^1	1	0.107
O1A, O1B	b^1, d^1	1	0.129
O2A, O2B	b^1, d^1	1	0.096
O3A, O3B	b^1, d^1	1	0.205
O4A, O4B	b^1, d^1	1	0.127
O5A, O5B	b^1, d^1	1	0.112
O6A, O6B	b^1, d^1	1	0.187
Ca1	A	$\bar{1}$	0.162
Ca3A, Ca3B	A	$\bar{1}$	0.060

4.6.2 Data collection

Crystals suitable for single crystal XRD were separated under acetone using a polarizing microscope. Reflection intensities were collected at 295 K using the ω - and ϕ -scan techniques. Five independent sets totalling at 2969 frames were collected thus scanning the whole reciprocal sphere with high redundancy. Due to diffuse reflections, the anisotropic crystal habit and small crystal size, the internal reliability factors of the dataset are not satisfactory ($R_{int} \approx 10\%$). More details on data collection and refinement are summarized in Tab. 4.13, atomic coordinates and isotropic displacement parameters are listed in Tab. C.25.

4.6.3 Structure determination

Absorption correction was performed using a multi-scan approach with SADABS (Sheldrick, 2001). Due to the problems during data collection no satisfactory structure refinement was possible so far and the composition $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ is not entirely certain. The metrics of the crystal is pseudo-orthorhombic with one angle ($\beta = 89.907(5)$) deviating slightly from 90° . Attempts to solve the structure in the orthorhombic crystal system were unsuccessful, therefore solution and refinement was performed in a monoclinic space group. Instead of the standard C -centred setting, an unusual I -centred setting was used, which reflects the pseudo-orthorhombic metrics and in which the c axis is perpendicular to the layers given in the description below. Most heavy atoms (Te and Ca) were located by direct methods implemented by the SHELX program package (Sheldrick, 2008). The remaining atoms were located in difference Fourier maps in subsequent refinement steps. The structure was refined as a pseudo-merohedral twin of two components related by mirroring at (100). The thus obtained model had reasonable inter-atomic distances, but excess electron density was observed in the difference Fourier maps. These peaks could be assigned to Te atoms of a minor polytype. Therefore, with the exception of one Te atom for which both polytypes overlap, the Te atoms were refined as pairs of disordered atoms. The occupational ratio of all pairs was constrained to the same value. To obtain a model of an electronically neutral compound two residual peaks in the difference Fourier map were assigned to a K atom and the corresponding atom in the minor polytype. The refined ADP of

Table 4.13: Crystal data and details of the refinements of $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$

$\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$	
Crystal data	
Chemical formula	$\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$
M_r	1095.69
Cell setting, space group	Monoclinic, $I2/a$
Temperature [K]	295(2)
a, b, c [Å]	24.8910(10), 7.5750(3), 17.9289(9)
β [°]	89.907(5)
V [Å ³]	3380.5(3)
Z	8
D_x [Mg·m ⁻³]	4.306
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	10.210
Crystal form, colour	plate, colourless
Crystal size [mm]	0.12 × 0.06 × 0.01
Data collection	
Diffractometer	SMART APEX II
Data collection method	ω and ϕ scans
Absorption correction	<i>SADABS</i>
T_{min}, T_{max}	0.374, 0.951
No. of measured, independent and observed reflections	34413, 5677, 4067
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.1041
θ_{max} [°]	35.0
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.055, 0.159, 1.02
No. of reflections	5677
No. of parameters	195
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0944P)^2 + 1.3566P]$ where $P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.77, -5.06
Twin operation	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
Twin domain volume fraction	44.9:55.1(2)

the K atom in the major polytype is very large, casting some doubt on this assignment. Indeed, the interatomic distances indicate an NH_4^+ group, but electron density refines to an atom with the atomic number of K or higher. It is close to a „phantom atom” of the minor polytype, which could explain the difficulties during refinement. Only the Te atoms were refined using anisotropic ADPs. Attempts to refine the remaining atoms with anisotropic ADPs resulted in highly anisotropic and physically meaningless values, possibly due to the imprecise integration caused by diffuse reflections and the plate-like habit.

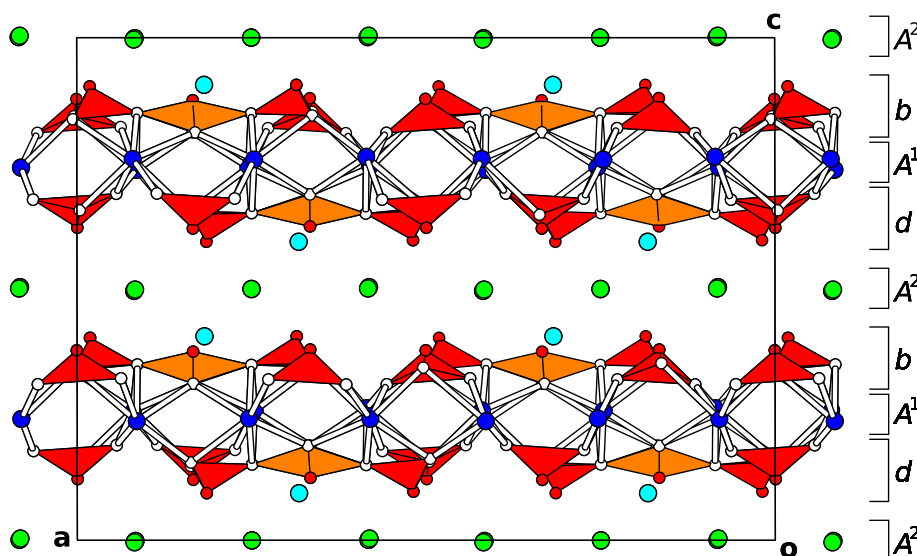


Figure 4.27: The major polytype of $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ viewed down $[010]$. Te, Ca, K, Cl and O atoms are represented by red, blue, light blue, green and white spheres. Layer names according to the OD description are indicated to the right. .

4.6.4 Structure

OD description

$\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ belongs to an orthorhombic category IV OD family composed of two non-polar layers A^1 and A^2 and one polar layer b . The OD groupoid family symbol reads as

$$\begin{array}{ccc}
 A^1 & b & A^2 \\
 p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(m) & pma(2) & p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(m) \\
 [0, 0] & [0, 0] &
 \end{array}$$

according to the notation devised by Grell and Dornberger-Schiff (1982). Layers A^1 (Ca), b (Te1–Te3, O1–O7) and A^2 (Cl) are orthorhombic with symmetry $p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(m)$, $pma(2)$ and $p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(m)$, respectively. The higher translational symmetry of layers A^1 and A^2 is indicated in the subscript of the Bravais symbol by the expression of the lattice vectors relative to the common lattice of all layers. The layers are stacked along $[001]$ according to $\dots dA^1bA^2dA^1bA^2\dots$ (Fig. 4.27).

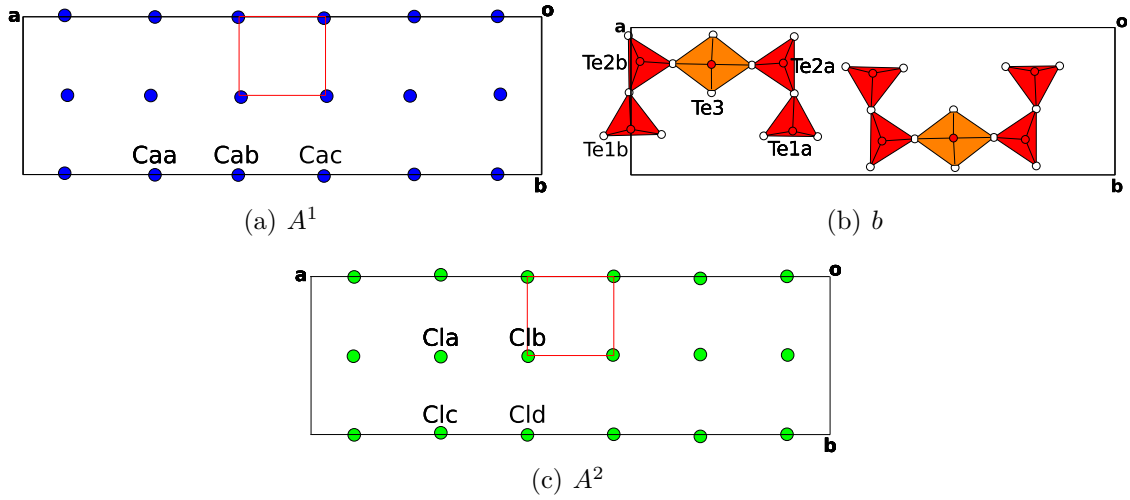
An overview of the NFZ relationship applied to all layer contacts is given in Tab. 4.14. The group of λ - τ -POs of layers A^1 is $p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(2)$. Since layers b are polar the group of λ - τ -POs corresponds to the symmetry group of the layer, *viz.* $pma(2)$. All POs of layers b apply also to adjacent layers A^1 , therefore given the orientation of a layer b , the orientation of an adjacent layer A^1 is fixed. On the other hand, given a layer A^1 , an adjacent layer b can appear in $Z = N/F = |p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(2)|/|pma(2)| = 12$ orientations, which are related by translation. The same considerations apply to the layer contact $A^2 \leftrightarrow b$, since A^1 and A^2 have the same symmetry and origin shifts relative to layers b .

Crystal chemistry

Layers A^1 contain one crystallographically unique Ca atom located on a site with symmetry mmm (Fig. 4.28(a)). Layers b consist of two crystallographically different $[\text{TeO}_3]$ units located

Table 4.14: Overview of the different layer stacking possibilities according to the NFZ relationship in $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$.

$L1 \leftrightarrow L2$	L	G	$N = G $	$G_{L1} \cap G_{L2}$	F	$Z = N/F$
$A^1 \leftrightarrow b$	A^1	$p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(2)$	48			12
	b	$pma(2)$	4	$pma(2)$	4	1
$A^2 \leftrightarrow d$	A^2	$p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(2)$	48			12
	b	$pma(2)$	4	$pma(2)$	4	1

**Figure 4.28:** Layers (a) A^1 , (b) b and (c) A^2 in the major polytype of $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$. Atom colour codes as in Fig. 4.27. In (a) and (c), the unit cells of the layers according to the OD description are indicated by red lines, the unit cell of the major polytype by black lines.

on general positions and one $[\text{TeO}_4]$ unit located on a site with symmetry $m..$ (Fig. 4.28(b)). The $[\text{TeO}_x]$ units are connected *via* corners forming a $[\text{Te}_5\text{O}_{12}]$ unit with symmetry m . Layers A^2 are isotypic to layers A^1 . They contain one Cl atom located on a site with symmetry mmm (Fig. 4.28(c)).

The trigonal pyramidal shapes of the $[\text{TeO}_3]$ units and ψ^1 -trigonal bipyramidal shapes of the $[\text{TeO}_4]$ units are characteristic for three- and four-coordinated Te^{IV} atoms (Zemann, 1971). All Te–O distances (Tab. 4.15) are in good agreement with the data given in a review on the crystal chemistry of oxotellurium(IV) compounds (Dolgikh, 1991). The Ca atoms are coordinated by eight oxygen atoms forming distorted cubes. The Ca–O distances range from 2.278(10) to 3.034(12) Å, which is in good agreement with the Ca–O bond length distribution given in a survey by Blatov et al. (1999). Moreover, bond valence calculations with $v_i = \exp(\frac{R_o - R_i}{b})$ (Brown, 2002) for these bonds with the parameters $R_o = 1.967$ Å and $b = 0.370$ (Brese and O’Keeffe, 1991) result in total BVS of 1.96 v.u. (CaA) and 1.97 v.u. (CaB, CaC), which is close to the expected value of 2 v.u..

The K atom is coordinated by four O, two close Cl and two more remote Cl atoms forming a slightly distorted square anti-prism. The close Cl atoms (ClC, ClA) are located 2.98(3) Å and 3.03(3) Å from the K atom, the more remote (ClD, ClB) 3.53(2) Å and 3.52(2) Å and

Table 4.15: Selected atomic distances [$\text{\AA}$] and angles [$^\circ$] in the major polytype of $\text{KC}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$

Atoms	d [$\text{\AA}$]	Atoms	d [$\text{\AA}$]	Atoms	d [$\text{\AA}$]
Te1A–O1A	1.810(12)	CaA–O2A	2.349(10)	CaC–O1B	2.294(10)
Te1A–O2A	1.854(10)	CaA–O2A	2.366(10)	CaC–O1A	2.312(12)
Te1A–O3A	1.993(8)	CaA–O7	2.355(13)	CaC–O2B	2.360(11)
Te1B–O1B	1.867(11)	CaA–O6	2.389(13)	CaC–O7	2.453(13)
Te1B–O2B	1.881(11)	CaA–O5A	2.520(12)	CaC–O5B	2.526(11)
Te1B–O3B	1.988(10)	CaA–O4A	2.657(12)	CaC–O4B	2.605(12)
Te2A–O4A	1.833(9)	CaA–O4A	2.638(12)	CaC–O3B	2.668(12)
Te2A–O5A	1.920(12)	CaA–O3A	3.034(12)	CaC–O3A	2.893(12)
Te2A–O3A	1.926(9)	CaB–O1B	2.278(10)	K–O6	2.88(3)
Te2B–O4B	1.861(10)	CaB–O1A	2.288(12)	K–O7	2.87(3)
Te2B–O5B	1.936(11)	CaB–O2B	2.377(11)	K–O2A	2.76(3)
Te2B–O3B	1.992(10)	CaB–O4B	2.441(12)	K–ClC	2.98(3)
Te3–O6	1.844(8)	CaB–O6	2.452(13)	K–ClA	3.03(3)
Te3–O7	1.899(8)	CaB–O4	2.465(12)	K–O2B	3.35(3)
Te3–O5B	2.037(11)	CaB–O5B	2.780(12)	K–ClD	3.53(3)
Te3–O5A	2.137(12)	CaB–O3B	2.961(12)	K–ClB	3.52(3)
Atoms	angle [$^\circ$]	Atoms	angle [$^\circ$]	Atoms	angle [$^\circ$]
O1A–Te1A–O2A	98.7(4)	O4A–Te2A–O5A	89.0(5)	O6–Te3–O7	104.7(4)
O1A–Te1A–O3A	87.3(5)	O4A–Te2A–O3A	102.4(4)	O6–Te3–O5B	82.9(5)
O2A–Te1A–O3A	91.2(4)	O5A–Te2A–O3A	86.2(5)	O7–Te3–O5B	83.7(5)
O1B–Te1B–O2B	104.2(5)	O4B–Te2B–O5B	90.9(5)	O6–Te3–O5A	81.2(5)
O1B–Te1B–O3B	86.8(4)	O4B–Te2B–O3B	98.6(4)	O7–Te3–O5A	80.5(5)
O2B–Te1B–O3B	90.5(5)	O5B–Te2B–O3B	86.5(4)	O5B–Te3–O5A	153.9(4)

therefore interact only slightly. Bond valence calculations for all K–O and K–Cl bonds with the parameters $R_o = 2.132 \text{ \AA}$ and $b = 0.370$ (K–O) and $R_o = 2.519 \text{ \AA}$ and $b = 0.370$ (K–Cl) (Brese and O’Keeffe, 1991) result in a total BVS of 1.07 for the K atom, which is close to the expected value of 1. Yet, due to the poor determination of the K atom, this determined value may differ significantly from the actual value.

Actual structure

The major polytype in the actual structure is an MDO polytype with $\mathbf{c} = 2\mathbf{c}_0$ and overall symmetry $I2/a$. In layer triples dA^1b , layers d and b are related by $[-2_1-]$ operations (the symbol of the screw axis is given using the lattice common to all layers). In bA^2d triples, layers b and d are related by $[-2-]$ operations. The metrics of the actual structure deviates only slightly from the idealized polytype ($\beta = 89.907(5)^\circ$ vs. 90°). The symmetry of layers A^1 is reduced by a factor of 24 from $p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(m)$ to $p12_1/a(1)$. The Ca atom is split into three positions located on a general position.

The $[m-]$ and $[-2]$ operations of layers b are lost, resulting in a symmetry reduction by a factor of 2 from $pma(2)$ to $p1a(1)$. The symmetry of layers A^2 is reduced by a factor of 24 from $p_{\mathbf{a}'=\frac{1}{6}\mathbf{b}, \mathbf{b}'=\frac{1}{2}\mathbf{c}}mm(m)$ to $p12/a(1)$. The Cl atom is split into four crystallographically different atoms, two of which are located on a twofold axis and two on a general position.

The positions of the atoms in the actual structure deviate only slightly from the idealized positions according to the OD description (Tab. 4.16). The Ca atoms of layers A^1 are distanced

Table 4.16: Distance d in Å of the real structure atoms in $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ to the atoms in the idealized structure according to the OD description.

Layer	Actual structure				Idealized structure				d [Å]
	Atom	mult.	Wyck.	Site symmetry	Atom	mult.	Wyck.	Site symmetry	
A^1	Ca	1	a	mmm	Caa	8	f	1	0.149
A^1	Ca	1	a	mmm	Cab	8	f	1	0.231
A^1	Ca	1	a	mmm	Cac	8	f	1	0.157
b	Te1	4	d	1	Te1a	4	e	2	0.050
b	Te1	4	d	1	Te1b	4	e	2	0.050
b	Te2	4	d	1	Te2a	4	e	2	0.049
b	Te2	4	d	1	Te2b	4	e	2	0.049
b	Te3	2	c	$m..$	Te3	4	e	2	0.013
b	K	2	c	$m..$	K	4	e	2	0.391
b	O1	4	d	1	O1a	4	e	2	0.054
b	O1	4	d	1	O1b	4	e	2	0.054
b	O2	4	d	1	O2a	4	e	2	0.056
b	O2	4	d	1	O2b	4	e	2	0.056
b	O3	4	d	1	O3a	4	e	2	0.078
b	O3	4	d	1	O3b	4	e	2	0.078
b	O4	4	d	1	O4a	4	e	2	0.068
b	O4	4	d	1	O4b	4	e	2	0.068
b	O5	4	d	1	O5a	4	e	2	0.053
b	O5	4	d	1	O5b	4	e	2	0.053
b	O6	2	c	$m..$	O6	4	e	2	0.016
b	O7	2	c	$m..$	O7	4	e	2	0.064
A^2	Cl	1	a	mmm	Cl a	4	e	2	0.009
A^2	Cl	1	a	mmm	Cl b	8	f	1	0.069
A^2	Cl	1	a	mmm	Cl c	4	e	2	0.015
A^2	Cl	1	a	mmm	Cl d	8	f	1	0.020

by less than 0.24 Å from the idealized positions. The largest deviation of all atoms (0.39 Å) is observed for the K atom in layer b , which is removed from the mirror plane of layer b normal to $[100]$. Indeed, the ADP of the affected atom is very large, hinting towards disorder of the atom around the mirror plane. The remaining atoms in layers b are close to the idealized positions with distances smaller than 0.08 Å as are the Cl atoms in layers A^2 with distances being less than 0.07 Å. These small deviations are clear indication of the higher local symmetry of the OD layers and therefore of the validity of the OD interpretation.

Intense diffuse scattering in direction of the layer stacking was observed for reflections hkl with $h \neq 3n$, $n \in \mathbb{N}$, indicating disorder in this direction (Fig. 4.29). The twinning by mirroring at (100) can likewise be explained by stacking faults.

A second minor polytype is apparent by „phantom” atoms in the refinement of the actual structure. Layers b have been refined as an overlap of two orientations, related by a $[- - 2]$ (or equivalently a $[m - -]$) operation (Fig. 4.6.4). Atom Te1 is located on the mirror plane relating both orientations and therefore is located at the same position as the corresponding phantom atom. The ratio of major to minor polytype is 80.7:19.3(2).

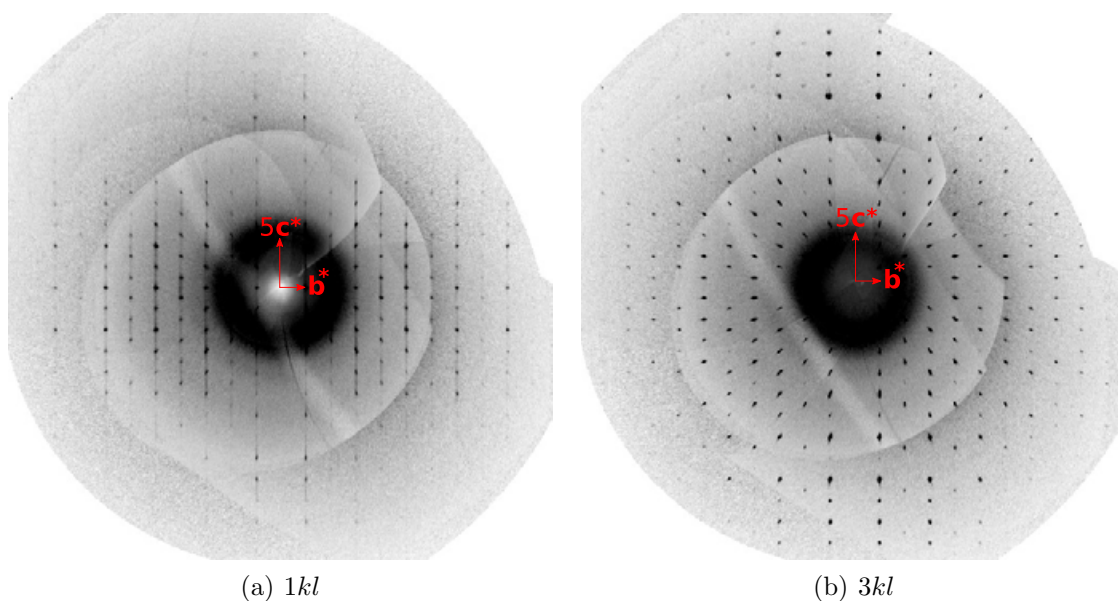


Figure 4.29: (a) 1kl and (b) 3kl plane of reciprocal space reconstructed from CCD frames of a $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ crystal.

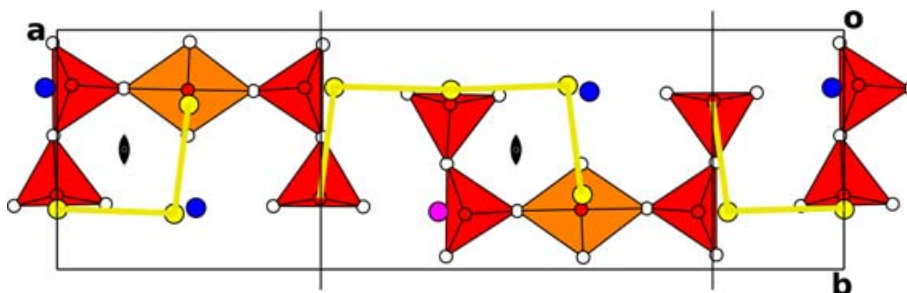


Figure 4.30: Layer *b* in the major polytype of $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$ with „phantom” atoms. The Te atoms corresponding to the minor polytype are represented by yellow spheres. They are connected by yellow lines to accentuate the structural motif. The K atom of the major and minor polytype are represented by light blue and pink spheres. Other colour codes as in Fig. 4.27. The two-fold rotation axis and mirror planes relating both orientations are indicated by symbols according to the *International Tables* (Hahn, 1983).

4.7 $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$

4.7.1 Preparation

159.6 mg TeO_2 , 1 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 40 mg NaOH were introduced in a 6 ml teflon inlay with which was filled to approximately two thirds of its volume with deionized water. The inlay was placed in a steel autoclave and heated at 493 K for 7 d. The solid reaction product was washed with water and acetone. It consisted of a yellowish microcrystalline powder and small rods of $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$. XRPD of the ground bulk product revealed $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$ ($\approx 91\%$, according to Rietveld refinement using Topas (Coelho, 2002)), unreacted TeO_2 ($\approx 9\%$) and minor amounts of unidentified phases.

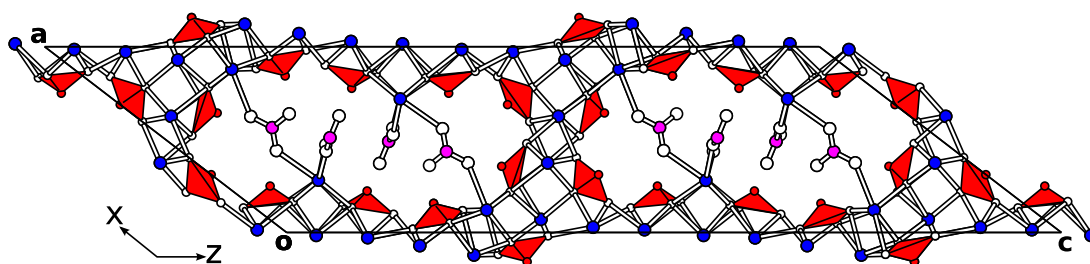


Figure 4.31: Unit cell content of $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$ viewed down $[010]$. Te, Ca, O and N atoms are represented by red, blue, white, and pink spheres, $[\text{TeO}_3]$ units by red polyhedra.

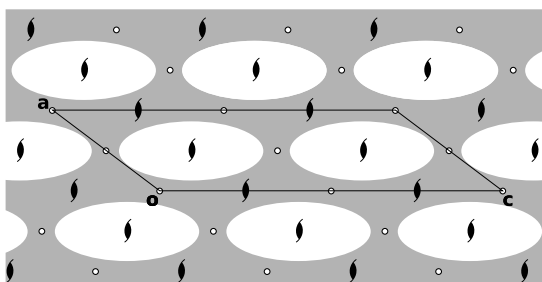


Figure 4.32: Schematic representation of the symmetry in $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$ viewed down $[010]$. The Ca/Te/O network and the channels are represented by grey and white surfaces. The unit cell is indicated by black lines, centres of inversion and two-fold screw axes by the symbols according to the *International Tables for Crystallography, Vol. A* (Hahn, 1983).

4.7.2 Structure determination

An absorption correction was applied using the multi-scan approach with the program SADABS (Sheldrick, 2001). The crystal structure of $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$ was solved and refined using the SHELX program package (Sheldrick, 2008). An unusual cell setting in $P2_1/c$ with a β angle of $142.480(5)^\circ$ was used over the reduced setting in the same space group with a β angle of $90.508(2)^\circ$ so that the unit cell encompasses exactly two main structural motifs. Both, the used and the The lattice vector $\mathbf{c}$ of the chosen setting is related to the vectors $\mathbf{a}'$ and $\mathbf{c}'$ in the reduced setting by $\mathbf{c} = -2\mathbf{a}' + \mathbf{c}'$. The heavy atoms (Te and Ca) were located using direct methods, the other atoms were assigned to peaks in difference Fourier syntheses in subsequent refinement steps. The difference Fourier maps of the final refinements showed no significant residual electron density.

Further details of the data collections and the crystal data are summarized in Tab. 4.17, atomic coordinates and isotropic displacement parameters are listed in Tab. C.29. Selected interatomic distances and angles are listed in Tab. 4.18.

4.7.3 Structure

$\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$ crystallizes in space group $P2_1/c$. The asymmetric unit contains five $[\text{TeO}_3]$ groups, six Ca atoms and two NO_3^- ions, all located on general positions. The Ca atoms connect the $[\text{TeO}_3]$ groups forming an infinite three dimensional network which is perforated by oval channels running along $[010]$ with long and short diameter of *ca.* Å and *ca.* ≈ 5 Å, respectively (Fig. 4.31). The channels are located around a 2_1 screw axis. Channels adjacent in $[001]$ direction are related by inversion, channel adjacent in $[100]$ direction are either related by 2_1 screws or inversions (Fig. 4.32). The electron lone pairs E of the Te^{IV} atoms and the NO_3^-

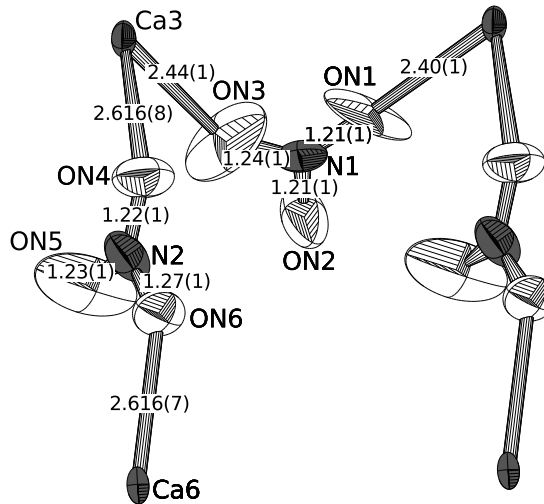
Table 4.17: Crystal data and details of the refinements of $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$

$\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$	
Crystal data	
Chemical formula	$\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$
M_r	1242.50
Cell setting, space group	monoclinic, $P21/c$
Temperature [K]	295(2)
a, b, c [Å]	15.494(2), 5.6145(7), 39.338(4)
β [°]	142.480(5)
V [Å ³]	2084.2(4)
Z	4
D_x [Mg·m ⁻³]	3.960
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	8.495
Crystal form, colour	Rod, colourless
Crystal size [mm]	$0.07 \times 0.02 \times 0.01$
Data collection	
Diffractometer	SMART APEX
Data collection method	ω scans
Absorption correction	SADABS
T_{min}, T_{max}	0.5878, 0.9199
No. of measured, independent and observed reflections	21816, 6049, 3026
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.111
θ_{max} [°]	30
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.043, 0.070, 0.71
No. of reflections	6049
No. of parameters	307
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0037P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	1.75, -1.88

ions are located inside the channels. One group (N1) bridges two Ca3 atoms arranged along the channel direction. The ADPs of the atoms of this group are very large, hinting toward unresolved disorder (Fig. 4.33). The other group (N2) bridges Ca3 and Ca6, located on opposite sides of the channel. In this group only the O atom which does not connect to Ca atoms has large ADPs as is characteristic for weakly bonding anions. The trigonal-pyramidal shape of the $[\text{Te}^{IV}\text{O}_3]$ units is characteristic for three-coordinated Te^{IV} atoms (Zemann, 1971). All Te–O distances (Tab. 3.6) are in good agreement with the data given in a review on the crystal chemistry of oxotellurium(IV) compounds (Dolgikh, 1991).

Table 4.18: Selected distances in Å and angles in Ca₆Te₅O₁₅(NO₃)₂

Atoms	<i>d</i> [Å]	Atoms	angle [°]
Te1–O1	1.841(6)	O1–Te1–O2	103.1(3)
Te1–O2	1.867(6)	O1–Te1–O3	92.0(3)
Te1–O3	1.870(6)	O2–Te1–O3	93.0(3)
Te2–O4	1.859(6)	O4–Te2–O5	98.2(3)
Te2–O5	1.860(6)	O4–Te2–O6	100.6(3)
Te2–O6	1.886(6)	O5–Te2–O6	98.6(3)
Te3–O7	1.840(6)	O7–Te3–O8	102.8(3)
Te3–O8	1.857(6)	O7–Te3–O9	90.3(3)
Te3–O9	1.861(6)	O8–Te3–O9	93.8(3)
Te4–O10	1.847(6)	O10–Te4–O11	102.5(3)
Te4–O11	1.856(6)	O10–Te4–O12	93.9(3)
Te4–O12	1.882(6)	O11–Te4–O12	93.3(3)
Te5–O13	1.848(6)	O13–Te5–O14	93.9(3)
Te5–O14	1.871(6)	O13–Te5–O15	99.7(3)
Te5–O15	1.885(6)	O14–Te5–O15	88.4(3)

**Figure 4.33:** Ellipsoid plot of the NO₃[−] ions and the connected Ca atoms in Ca₆Te₅O₁₅(NO₃)₂ viewed down approximately [001]. Ca, O and N atoms are represented by light grey, white and dark grey ellipsoids, respectively. Ellipsoids represent 90% probability levels. Bond lengths in Å are indicated by numbers next to the bonds.

4.8 Ba₆Te₁₀O₂₅Br₂

4.8.1 Preparation

159.6 mg TeO₂ and 333 mg BaBr₂·2H₂O were introduced into a 5 ml teflon inlay which was filled with 3 ml of a hydrous NH₄OH solution (20%_{wt}). The inlay was placed in a steel autoclave and heated at 493 K for 15 days. The residue was washed consecutively with water and acetone. Besides major amounts of a dark grey microcrystalline powder it contained colourless rods of Ba₆Te₁₀O₂₅Br₂ and thin colourless plates whose structure could not be determined due to intense streaking which can be attributed to a high stacking fault probability. The XRPD pattern of the

Table 4.19: Analysis of the intensity data for different reflection classes in $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$.

Class	Averaged intensity / a.u.	Maximum intensity / a.u. (reflection)
$h, k, \text{ or } l = 2n + 1$	19.2	276.1 (1 $\overline{22}$ $\overline{6}$)
$h, k, \text{ and } l \neq 2n + 1$	375.3	9986.2 (4 0 0)
$hk0, h + k = 4n + 2$	12.9	80.7 (0 $\overline{14}$ 0)
$hk0, h + k \neq 4n + 2$	324.1	9986.2 (4 0 0)

ground bulk product could not be attributed to known phases. Crystals of the title compounds were separated under acetone and broken in order to obtain fragments suitable for single crystal diffraction.

4.8.2 Structure determination

An absorption correction was applied using the multi-scan approach with the program SADABS (Sheldrick, 2001). In the diffraction pattern of the crystal under investigation distinct superstructure reflections were apparent. Reflections with $h, k, \text{ or } l = 2n$ have on average a 19.5 times higher intensity than reflections with $h, k, \text{ and } l = 2n + 1$ (Tab. 4.19), which corresponds to a basic structure with the length of all axes halved in comparison to the superstructure. Of the basic structure reflections $hk0$, those with $h + k = 4n + 2$ have on average a 25 times lower intensity than reflections $hk0$ with $h + k \neq 4n + 2$, thus indicating a pseudo-glide plane parallel to (001) and therefore pseudo- $Pm\overline{m}n$ symmetry of the basic structure.

Even though the unit cell volume of the actual structure (V) is eight times the volume of the basic structure (V_b), the multiplicity of the super structure is only four, because the Bravais lattice of the super structure is A -centred whereas the basic structure has a primitive cell. For the basic structure origin choice 1 of space group $Pm\overline{m}n$ was chosen. The origin of the super structure, which can be moved freely along the c -axis, was chosen so that it is located on the n -glide plane of the $Pm\overline{m}n$ basic structure. Thus super and basic structure have the same origin.

The diffraction spots of the superstructure could be indexed with an orthorhombic base-centred lattice. The extinction conditions indicated spacegroup $Cmca$ or the corresponding non-centrosymmetric spacegroup $Aba2$. The crystal structure of $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ was solved and refined using the SHELX program package (Sheldrick, 2008). Attempts to refine the model in the centrosymmetric spacegroup $Cmca$ were unsuccessful, therefore the non-centrosymmetric spacegroup $Aba2$ was used. The heavy atoms (Ba, Te) were located using direct methods, the remaining atoms were located by difference Fourier syntheses in subsequent refinement steps. $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ was refined as an inversion twin with twin volume ratio of 56:44(2). All atoms were refined anisotropically. The ADPs of some O atoms are highly anisotropic, hinting towards disorder in the structure or insufficient absorption correction. The difference Fourier maps of the final refinement contains no significant residual electron density. The highest peaks are close to Ba, Br and Te atoms.

The atoms in the super structure were named according to their relationship to the atoms in the basic structure: The first digit of the atom number is equal to the atom number in the basic structure (with the exception of $\text{Br}x$, since all Br atoms are equivalent in the basic structure). In order to determine the second (first for $\text{Br}x$) digit, the atoms were moved into the asymmetric unit of the super structure, which corresponds to exactly one unit cell of the basic structure. To each atom was then assigned a number in the range $[1 \dots 8]$, depending on the asymmetric unit of the $Pm\overline{m}n$ basic structure in which the atom is located. In Tab. 4.20 the coordinates of the

Table 4.20: Second (first in the case Br x) digit in the naming of atoms in Ba₆Te₁₀O₂₅Br₂ depending on the relative coordinates x , y and z of the atom.

	$0 \leq y \leq \frac{1}{2}$		$\frac{1}{2} < y \leq 1$	
	$0 \leq x \leq \frac{1}{2}$	$\frac{1}{2} < x \leq 1$	$0 \leq x \leq \frac{1}{2}$	$\frac{1}{2} < x \leq 1$
$0 \leq z \leq \frac{1}{2}$	1	2	3	4
$\frac{1}{2} < z \leq 1$	5	6	7	8

atoms in the superstructure and the assigned numbers are listed.

Further details of the data collections and the crystal data are summarized in Tab. 4.21, atomic coordinates and isotropic displacement parameters are listed in Tab. C.26. Selected interatomic distances and angles are listed in Tab. 4.22.

4.8.3 Structure

Idealized basic structure

In order to compute the idealized basic structure, all atoms were translated into the unit cell of the basic structure with $0 \leq x < \frac{1}{2}$, $0 \leq y < \frac{1}{2}$, and $0 \leq z < \frac{1}{2}$. Atoms of the same type which were closer to each other than 1.2 Å (using the symmetry operations of space group $Pmmn$) were grouped and their positions averaged. Resulting atoms which were located closer than 1 Å to a symmetry element of space group $Pmmn$ were moved onto the element. Atom coordinates of the basic structure are listed in Tab. C.27.

The distance of the atoms in the actual structure to the corresponding atoms in the idealized basic structure is given in Tab. 4.23. The heavy atoms (Ba, Te, Br) in the superstructure deviate only slightly from the positions in the idealized basic structure. For Br and Ba atoms the maximum deviation is 0.03 Å and 0.13 Å, respectively. For the Te atoms, deviation is larger, with atoms Te1 x (*i.e.* those atoms corresponding to atom Te1 in the basic structure) showing the largest deviation: 0.35 Å for Te15 and 0.12–0.18 Å for the other Te1 x atoms. Atoms Te3 x deviate by 0.21 and 0.14 Å from the idealized symmetry because the averaged atom is not located exactly on the site with symmetry $mm2$ in the basic structure. Atoms Te2 x are close to their idealized positions with deviations of 0.04–0.10 Å. As expected O atoms possess the highest deviations. Atoms O4 x deviate by up to 1.13 Å (O43) from their idealized positions, other O atoms by up to 0.43 Å.

Since $V = 8V_b$ the occupancy $o(A)$ of an atom A in the idealized basic structure can be derived from the multiplicity $m(A)$ of the atom by:

$$o(A) = \frac{\sum_x o(Ax) \cdot m(Ax)}{8 \cdot m(A)}$$

The expected occupancy of 1 is obtained for all atoms with the exception of O5. For atom O5 a occupancy of $\frac{3}{4}$ is obtained (Tab. 4.23). Indeed, one O5 x atom is missing in every fourth subcell of the super structure and thus O5 has to be considered as occupationally modulated. The central atom of the [TeO $_x$] unit affected by the missing O5 atom (Te15) is the Te atom with the highest deviation from the basic structure.

Idealized basic structure

The idealized basic structure of Ba₆Te₁₀O₂₅Br₂ consists of three crystallographically distinguishable [TeO $_x$] groups, which are connected by corners to form two-dimensional corrugated layers

Table 4.21: Crystal data and details of the refinements of Ba₆Te₁₀O₂₅Br₂.

Ba ₆ Te ₁₀ O ₂₅ Br ₂	
Crystal data	
Chemical formula	Ba ₆ Te ₁₀ O ₂₅ Br ₂
M_r	2659.86
Cell setting, space group	Orthorhombic, <i>Aea</i> 2
Temperature [K]	295(2)
a, b, c [Å]	11.4707(9), 31.140(2), 18.3216(14)
V [Å ³]	6544.4(9)
Z	8
D_x [Mg·m ⁻³]	5.399
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	18.374
Crystal form, colour	Fragment, colourless
Crystal size [mm]	0.06 × 0.05 × 0.02
Data collection	
Diffractometer	SMART APEX
Data collection method	ω scans
Absorption correction	<i>SADABS</i>
T_{min}, T_{max}	0.4052, 0.7101
No. of measured, independent and observed reflections	35328, 9331, 7155
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.050
θ_{max} [°]	30.0
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)], wR(F^2), S$	0.038, 0.082, 0.986
No. of reflections	7155
No. of parameters	392
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0281P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	1.45, -1.47
Twin operation	$\bar{1}$
Twin volume fractions	56:44(2)

(Fig. 4.34(a)). The layers are connected by two crystallographically different Ba atoms. They are perforated by oval channels running along [100] in which the electron lone pairs of the Te^{IV} atoms protrude and in which the crystallographically unique Br atom is located on a site with symmetry *mm*2.

Te1 is located at the base of a square pyramid (symmetry *m*), formed by five coordinating O atoms. Te2 is coordinated by four O atoms (symmetry *m*), forming a TeO₄*E* ψ^1 -trigonal bipyramid (symmetry *m*) with the electron lone pair *E* as a fifth ligand. Te3 is coordinated by four O atoms which are related by symmetry and form a slightly distorted square. The Te3 atom is located out of the plane resulting in a square pyramidal [TeO₄] group (symmetry *mm*2,

Table 4.22: Selected distances [Å] in the idealized basic structure and the actual structure of Ba₆Te₁₀O₂₅Br₂.

Idealized		Actual			
Atoms	<i>d</i> [Å]	Atoms	<i>d</i> [Å]	Atoms	<i>d</i> [Å]
Te1–O3(2×)	1.798	Te13–O57	1.860(8)	Te15–O52	1.842(8)
Te1–O5(2×)	2.009	Te13–O33	1.870(9)	Te15–O36	1.842(8)
Te1–O4	2.413	Te13–O43	2.009(7)	Te15–O55	1.952(8)
		Te13–O52	2.417(7)	Te17–O47	1.833(7)
		Te14–O34	1.838(9)	Te17–O38	1.837(8)
		Te14–O41	1.860(8)	Te17–O48	1.929(7)
		Te14–O55	2.059(8)	Te17–O57	2.442(7)
		Te14–O44	2.346(7)		
Te2–O1(2×)	1.844	Te23–O12	1.840(8)	Te26–O16	1.838(8)
Te2–O2	1.960	Te23–O13	1.846(7)	Te26–O15	1.860(8)
Te2–O3	2.416	Te23–O23	1.943(8)	Te26–O27	1.941(7)
		Te23–O33	2.514(8)	Te26–O36	2.465(8)
		Te24–O14	1.846(8)	Te27–O17	1.847(8)
		Te24–O11	1.850(8)	Te27–O18	1.848(8)
		Te24–O23	1.960(8)	Te27–O27	2.002(7)
		Te24–O34	2.429(8)	Te27–O38	2.318(8)
Te3–O4(4×)	1.933	Te34–O42	1.838(8)	Te38–O46	1.840(8)
		Te34–O44	1.892(8)	Te38–O45	1.846(7)
		Te34–O43	1.993(7)	Te38–O48	2.021(7)
		Te34–O41	2.441(8)	Te38–O47	2.430(7)
Ba–Br	3.424	Br4–Ba15	3.503(2)	Br6–Ba11	3.435(3)
		Br5–Ba13	3.334(2)		

the Te3 atom located at a vertex). This kind of coordination is not found for tellurates, and only calculated in the idealized basic structure. The [Te1O₅] pyramids are connected by corners forming infinite zig-zag chains running along [100] (Fig. 4.35(a)). The chains are connected by the [Te3O₄] pyramids and [Te₂O₇] groups (symmetry *mm*2) formed by two corner sharing [Te2O₄] groups.

Actual structure

In the actual structure the channels running along [100] are split into two crystallographically different kinds. One of them is bisected by a twofold rotation axis parallel to [001], where two different Br atoms (Br5, Br6) are bisected. The other has symmetry 1 and contains one crystallographically distinguishable Br atom (Br4) (Fig. 4.34(b)).

Due to the occupational modulation of atom O5 in the actual structure, the morphology of some [TeO_{*x*}] units differs strongly from those in the idealized basic structure. The [Te1O₅] pyramids change to three [Te1*x*O₃₊₁] units and one [Te1*x*O₃] unit. Instead of infinite chains, they form segments consisting of four units (Fig. 4.35(b)). The shapes of the [Te₂O₇] units differ only slightly from those in the idealized structure, but their symmetry is reduced from *mm*2 to 1. The [Te3O₄] pyramids which link by all four O atoms to other [TeO_{*x*}] units in the idealized basic structure become two [TeO₃₊₁*E*] units with typical trigonal bipyramidal geometry, which

Table 4.23: Deviation d of the position of the atoms in actual structure of $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ ($Aea2$) from the positions in the idealized basic structure ($Pmmn$). Symmetry and multiplicity of the site is given in brackets.

Ideal	Actual	d [Å]	Ideal	Actual	d [Å]
O1(1,8)	O15(1,8)	0.055	O5($\bar{1}$,4)	O52(1,8)	0.783
	O18(1,8)	0.073		O57(1,8)	0.866
	O16(1,8)	0.085		O55(1,8)	0.574
	O14(1,8)	0.085	Ba1($mm2$,2)	Ba13(..2,4)	0.116
	O13(1,8)	0.116		Ba15(1,8)	0.124
	O12(1,8)	0.050		Ba11(..2,4)	0.041
	O17(1,8)	0.092	Ba2(m .,4)	Ba24(1,8)	0.107
	O11(1,8)	0.156		Ba26(1,8)	0.080
	O27(1,8)	0.098		Ba25(1,8)	0.090
	O23(1,8)	0.051		Ba22(1,8)	0.125
O2($mm2$,2)	O33(1,8)	0.292	Br($mm2$,2)	Br5(..2,4)	0.026
	O36(1,8)	0.208		Br4(1,8)	0.028
	O38(1,8)	0.319		Br6(..2,4)	0.029
O3(m .,4)	O34(1,8)	0.425	Te1(m .,4)	Te15(1,8)	0.350
	O45(1,8)	0.539		Te17(1,8)	0.141
	O44(1,8)	0.282		Te13(1,8)	0.119
O4(1,8)	O46(1,8)	0.671		Te14(1,8)	0.183
	O48(1,8)	0.672	Te2(m .,4)	Te27(1,8)	0.056
	O42(1,8)	1.012		Te26(1,8)	0.096
	O47(1,8)	0.513		Te24(1,8)	0.043
	O43(1,8)	1.129		Te23(1,8)	0.082
	O41(1,8)	0.514	Te3($mm2$,2)	Te34(1,8)	0.208
				Te38(1,8)	0.135

link only by two O atoms.

In the actual structure the shape of the $[\text{TeO}_{3+1}]$ units and the Te–O distances (1.833(7)–2.058(7) Å for the three near neighbours and 2.318(8)–2.514(8) Å for the more distant O atom) are characteristic of $[3+1]$ coordinate Te atoms (Zemann, 1971). Other Te^{IV} compounds with comparable $[\text{TeO}_{3+1}]$ units are $\text{Zn}_2\text{Te}_3\text{O}_8$, Te_2MoO_7 , CuTeO_3 , and CuTe_2O_5 as discussed by Arnaudov et al. (1982).

The Ba atoms are located at the centre of irregular $[\text{BaO}_x]$ and $[\text{BaBrO}_x]$ ($x = 8 - 9$) polyhedra, connected by corners and edges. The Br atoms are connected to Ba atoms, the Ba–Br distance ranging from 3.334(4)–3.348(3) Å, which is close to 3.43 Å, the sum of the effective ionic radii for nine coordinate Ba^{2+} (1.47 Å) and Br^- (1.96 Å) according to Shannon (1976). The smallest Br–Te distance is 3.330(2) Å. A bond valence calculation for this bond with $S = \exp(\frac{R_o - R}{B})$ ($R_o = 2.55$ Å, $B = 0.37$ Å (Brese and O’Keeffe, 1991)) gives a BVS of 0.12 v.u. and therefore only weak bonding interaction.

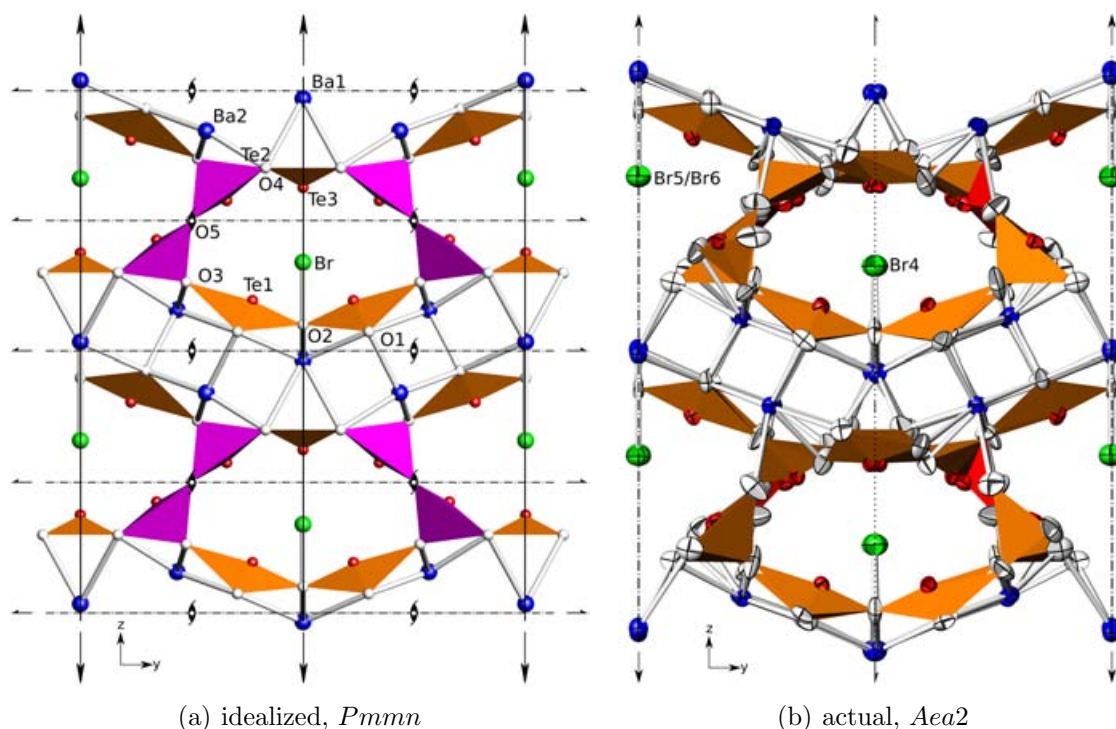


Figure 4.34: Main structural motif of Ba₆Te₁₀O₂₅Br₂ in the idealized (a) and actual (b) structures viewed down [100]. Ba atoms are represented by blue, O atoms by white and Br atoms by green ellipsoids. Te atoms and [TeO₃] polyhedra are red, [TeO₃₊₁] and [TeO₄] polyhedra orange and [TeO₅] polyhedra pink. Ellipsoids represent 90% probability levels. Two unit cells of the idealized structure and half of the unit cell (corresponding to two asymmetric units) of the actual structure are represented.

4.9 Ba₃Te₃O₈Br₂

4.9.1 Preparation

In an experiment using the same conditions as for the preparation of Ba₆Te₁₀O₂₅Br₂ (sec. 4.8), the solvent was fully evaporated and colourless rods of Ba₃Te₃O₈Br₂ were obtained. According to XRPD the reaction product was nearly of single phase Ba₃Te₃O₈Br₂ with minor impurities of unknown composition. Crystals of Ba₃Te₃O₈Br₂ were separated under acetone and cut using a scalpel in order to obtain crystals with a size suitable for single crystal diffraction.

4.9.2 Structure determination

Absorption correction was applied using the multi-scan approach with the program SADABS (Sheldrick, 2001). The crystal structure of Ba₃Te₃O₈Br₂ was solved with direct methods and refined using the SHELX program package (Sheldrick, 2008). The heavy atoms Ba and Te were located by direct methods, the other atoms were assigned to peaks in difference Fourier syntheses. The difference Fourier maps of the final refinements showed no significant residual electron density. The highest peaks are close to Ba, Br and Te atoms.

Further details of the data collections and the crystal data are summarized in Tab. 4.24, atomic coordinates and isotropic displacement parameters are listed in Tab. C.28. selected interatomic distances and angles are listed in Tab. 4.25.

Table 4.24: Crystal data and details of the refinements of Ba₃Te₃O₈Br₂.

Ba ₃ Te ₃ O ₈ Br ₂	
Crystal data	
Chemical formula	Ba ₃ Te ₃ O ₈ Br ₂
M_r	2659.86
Cell setting, space group	Orthorhombic, $Pnma$
Temperature [K]	295(2)
a, b, c [Å]	12.6226(8), 5.9663(4), 18.1112(12)
V [Å ³]	1363.96(15)
Z	4
D_x [Mg·m ⁻³]	5.272
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	20.731
Crystal form, colour	Rod, colourless
Crystal size [mm]	0.06 × 0.05 × 0.02
Data collection	
Diffractometer	SMART APEX II
Data collection method	ω and ϕ scans
Absorption correction	<i>SADABS</i>
T_{min}, T_{max}	0.0921, 0.5751
No. of measured, independent and observed reflections	34523, 5897, 4672
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.051
θ_{max} [°]	45.2
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.026, 0.051, 1.033
No. of reflections	4672
No. of parameters	88
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0154P)^2 + 0.4891P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.003
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.11, -2.34

Table 4.25: Selected distances in Å and angles in Ba₃Te₃O₈Br₂

Atoms	d [Å]	Atoms	angle [°]
Te1–O1	1.846(3)	O1–Te1–O2 (2×)	98.45(8)
Te1–O2 (2×)	1.8669(16)	O2–Te1–O2	95.85(10)
Te2–O3 (2×)	1.8436(16)	O3–Te2–O3	96.27(11)
Te2–O4	1.8436(16)	O3–Te2–O4 (2×)	90.92(7)
Te3–O4	1.943(2)	O5–Te3–O5	100.24(13)
Te3–O5 (2×)	1.8339(18)	O5–Te3–O4 (2×)	91.33(7)

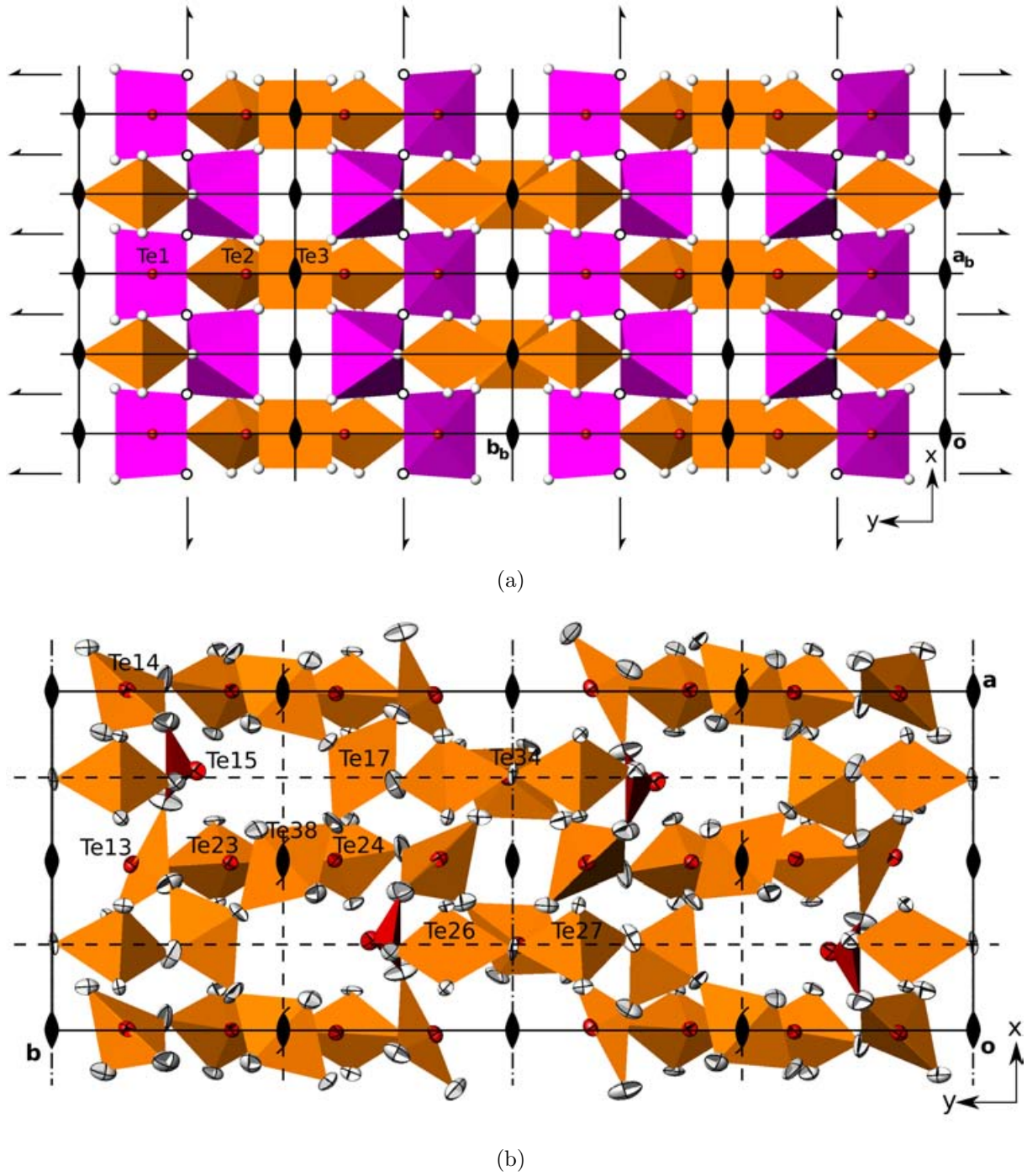


Figure 4.35: Comparison of the Te/O network in the idealized basic structure of $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ (a) and the actual structure (b) viewed down [001]. Colour codes as in Fig. 4.34.

4.9.3 Structure

The asymmetric unit of $\text{Ba}_3\text{Te}_3\text{O}_8\text{Br}_2$ contains one formula unit. Every Te atom is coordinated by three O atoms. The Ba and Br atoms and the $[\text{TeO}_3]$ groups are located on a mirror plane parallel to (010). Two $[\text{TeO}_3]$ units (Te2 and Te3) are connected *via* a corner, forming a $[\text{Te}_2\text{O}_5]$ unit. The $[\text{Te}_2\text{O}_5]$ units and the remaining isolated $[\text{TeO}_3]$ unit (Te1) are connected

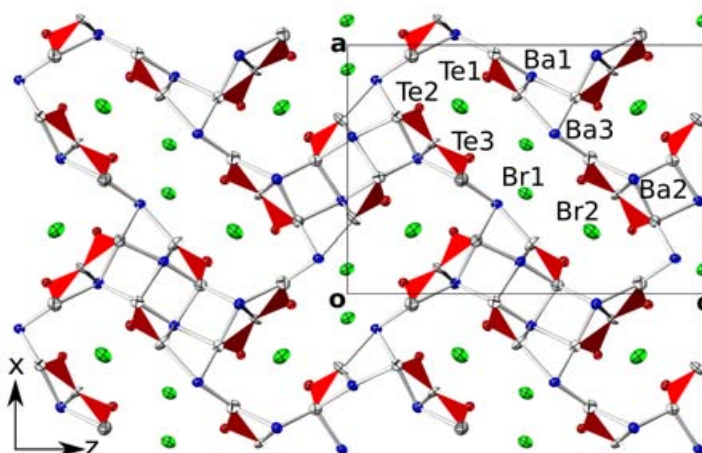


Figure 4.36: Crystal structure of $\text{Ba}_3\text{Te}_3\text{O}_8\text{Br}_2$ viewed down $[010]$. Colour codes as in Fig. 4.34.

via the Ba atoms forming an infinite three dimensional network through which oval channels (long and short diameter ≈ 16.6 and ≈ 5.5 Å) propagate along $[010]$ arranged in a herringbone pattern (Fig. 4.36). The channels are bisected by a twofold rotation axis and contain two crystallographically distinguishable Br atoms and the electron lone pairs E of the Te^{IV} atoms. All Te–O distances (Tab. 4.25) are in good agreement with the data given in a review on the crystal chemistry of oxotellurium(IV) compounds (Dolgikh, 1991). The Ba atoms are located at the centre of highly irregular coordination polyhedra formed by O and Br atoms. Ba1 is coordinated by eight O and one Br, Ba2 by eight O and two Br and Ba3 by 5 O and three Br atoms. The Ba–O bond lengths vary from 2.6607 to 3.1928 Å, the Ba–Br bond lengths from 3.3611 to 3.6563 Å. Bond valence calculations with $v_i = \exp(\frac{R_o - R_i}{b})$ (Brown, 2002) for these bonds with the parameters $R_o = 2.285$ Å and $b = 0.370$ for Ba–O and $R_o = 2.880$ Å and $b = 0.370$ for Ba–Br (Brese and O’Keeffe, 1991) result in BVS of 1.99 v.u. (Ba1), 2.01 v.u. (Ba2) and 2.51 v.u. (Ba3). The BVS for Ba1 and Ba2 thus are very close to the expected value of 2, whereas it differs significantly in the case of Ba3. Comparable high values of ≈ 2.5 v.u. are for example observed in Ba_3TeO_6 (sec. 5.1).

4.10 Cubic structures with a ${}^3_\infty[\text{M}_3\text{Te}_2\text{O}_6]^{2+}$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) framework

4.10.1 Introduction

Single crystals of the orthotellurate Ca_3TeO_6 have been grown by air oxidation of TeO_2 in a melt of CaCl_2 (Hottentot and Loopstra, 1981). In an attempt to adapt the method to Ba_3TeO_6 , Hottentot and Loopstra (1983) obtained single crystals of the oxotellurate(IV) $\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$ from a melt of BaCl_2 at 1275 K. The compound is remarkable since Te^{IV} compounds usually are not stable in air at temperatures $T > 1000$ K.

In this work, the crystal structure of $\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$ was redetermined and crystals of the homologues $\text{Ba}_3\text{Te}_2\text{O}_6\text{Br}_2$ and $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_2$ were obtained by replacing BaCl_2 with BaBr_2 and SrCl_2 , respectively. Furthermore, during systematic studies of the building conditions of alkaline earth metal tellurates(IV) under hydrothermal conditions using halides as precursor compounds, closely related phases with partial substitution of halide ions by hydroxyl anions were obtained.

Table 4.26: Details of the $M_3\text{Te}_2\text{O}_6X_2$ crystal growth experiments from halide fluxes. Relative mass percentages of the identified phases according to Rietveld refinement using TOPAS (Coelho, 2002).

Reactants	crucible	T [K]	t [h]	Result
100 mg TeO_2 , 500 mg SrCl_2	Pt	1273	30	35% Sr_3TeO_6 , 65% $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_2$
100 mg TeO_2 , 500 mg BaCl_2	Al_2O_3	1273	30	16% Ba_3TeO_6 , 84% $\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$, minor amounts of unidentified phase(s)
100 mg TeO_2 , 500 mg SrCl_2	Al_2O_3	1373	70	46% Sr_3TeO_6 , 54% $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_2$
100 mg TeO_2 , 500 mg BaBr_2	Al_2O_3	1373	70	73% Ba_3TeO_6 , 27% $\text{Ba}_3\text{Te}_2\text{O}_6\text{Br}_2$

Table 4.27: Details of the hydrothermal experiments leading to single crystalline $M_3\text{Te}_2\text{O}_6\text{Cl}_{1+x}(\text{OH})_{1-x}(\text{H}_2\text{O})_y$ phases.

Reactants	T [K]	t [d]	Single crystals
159.6 mg TeO_2 , 2000 mg $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	493	18	$\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$
159.6 mg TeO_2 , 1500 mg CaBr_2	493	14	$\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$
159.6 mg TeO_2 , 266.6 mg $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	493	4	$\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$
159.6 mg TeO_2 , 247.4 mg SrBr_2	493	4	$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.11}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$

4.10.2 Preparation

From halide fluxes

In a modification of the procedure described by Hottentot and Loopstra (1983), TeO_2 and $MX_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Sr}, \text{Ba}$, $X = \text{Cl}, \text{Br}$) were heated in a Pt or Al_2O_3 crucible at 1273 K. After cooling to room temperature the reaction product was leached out with water to remove excess fluxing agent and subsequently washed with acetone. Dependent on the reaction batch, the reaction products consisted of a white to yellowish microcrystalline powder, small nearly isometric colourless crystals of the orthotellurates $M_3\text{TeO}_6$ and colourless larger crystals of $M_3\text{Te}_2\text{O}_6X_2$ in the form of octahedra and truncated octahedra. Experimental details and composition of the reaction products according to XRPD are given in Tab. 4.26. Attempts to grow crystals with composition $\text{SrTe}_2\text{O}_6\text{Br}_2$ from SrBr_2 melts were unsuccessful. Performing the experiments in evacuated silica ampoules resulted in birefringent crystals with composition $\text{Sr}_4\text{Te}_3\text{O}_8\text{Br}_4$, for which no satisfactory structure refinement was possible so far.

Under hydrothermal conditions

CaBr_2 was obtained by reaction of 1.50 g $\text{Ca}(\text{OH})_2$ and 3.92 g NH_4Br in 50 ml H_2O . The water was evaporated, the residue washed with ethanol, taken up in a small amount of H_2O , filtered and the filtrate dried at 200°. The white powder was single phase CaBr_2 according to XRPD. All other reactants were obtained commercially and used without further purification.

Single crystals of composition $M_3\text{Te}_2\text{O}_6X_{1+x}(\text{OH})_{1-x}(\text{H}_2\text{O})_y$ ($M = \text{Ca}, \text{Sr}$ and $X = \text{Cl}, \text{Br}$) were prepared by reaction of TeO_2 and the corresponding alkaline earth metal halides (CaCl_2 , CaBr_2 , SrCl_2 and SrBr_2) under hydrothermal conditions. The reactants were introduced in a 5 ml teflon inlay which was filled to two thirds of its volume with a hydrous NH_4OH solution (20%_{wt}). The inlay was placed in a steel autoclave and heated at 493 K. Reaction time and details of the used mixtures are listed in Tab. 4.27. The residue was washed in succession with water, ethanol and acetone.

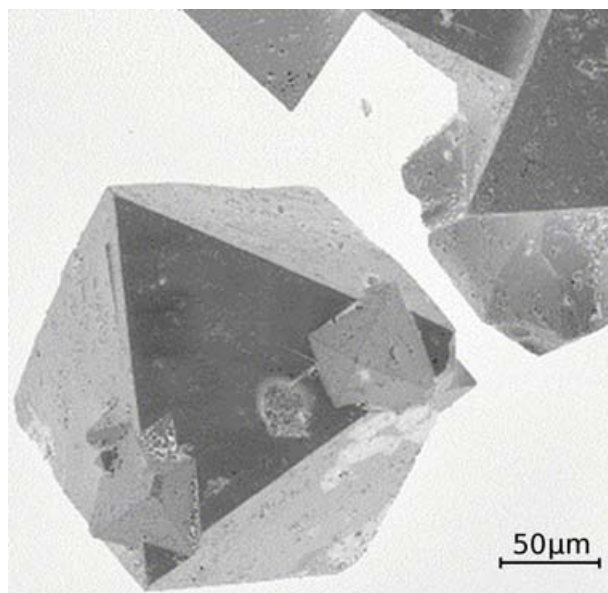


Figure 4.37: Scanning electron micrograph of a conglomerate of $\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1+x}(\text{OH})_{1-x}(\text{H}_2\text{O})_y$ crystals with characteristic octahedral shape.

In all experiments microcrystalline powders (grey for $M = \text{Ca}/X = \text{Br}$), colourless otherwise) and crystals with a octahedral habit (Fig. 4.37) were found. The crystals were separated under acetone and suitable individuals were subjected to single crystal XRD, Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDX) analysis. In the experiment employing SrCl_2 , additionally platelets of $\text{SrTeO}_3 \cdot \text{H}_2\text{O}$ and needles of unknown composition were obtained. When using SrBr_2 , additionally thin plates of $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$ (sec. 4.2) were obtained.

4.10.3 Single crystal diffraction

Data of crystals with composition $M_3\text{Te}_2\text{O}_6\text{X}_2$ obtained in halide fluxes and with composition $\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$ and $\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.11}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$ obtained under hydrothermal conditions were collected using combined ω - and ϕ -scan techniques with 0.5° rotation width. Multiple independent sets optimized for completeness and redundancy were measured totalling at 3907 ($\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_2$), 4394 ($\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$), 3906 ($\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$), 2487 ($\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$) and 3288 ($\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.11}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$) frames. The faces of the octahedra are normal to a $\langle 111 \rangle$ direction.

Reflection intensities of single crystals with composition $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$ and $\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$ obtained under hydrothermal conditions were collected at 295 K and 100 K using the ω -scan technique with 0.3° rotation width. Three independent sets of 600 frames were measured thus scanning the whole reciprocal sphere with high redundancy.

Data were collected at RT and under a dry stream of N_2 cooled to 100 K. Data obtained at 100 K resulted in practically the same refinements compared with data obtained at ambient conditions and will therefore not be described in the following sections. More details of the various data collections are summarized in Tab. 4.28 and 4.29. Atomic coordinates and isotropic displacement parameters are listed in Tab. C.30–C.36.

Table 4.28: Crystal data and details of the refinements of cubic phases with composition $M_3\text{Te}_2\text{O}_6\text{Cl}_{1+x}(\text{OH})_{1-x}(\text{H}_2\text{O})_y$ obtained under hydrothermal conditions.

	$M = \text{Ca}, X = \text{Cl}$	$M = \text{Sr}, X = \text{Cl}$	$M = \text{Ca}, X = \text{Br}$	$M = \text{Sr}, X = \text{Br}$
Crystal data				
Chemical formula	$\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$	$\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$	$\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}$	$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.11}(\text{OH})_{0.88}$
M_r	528.83	671.13	$(\text{H}_2\text{O})_{0.42}$ 584.69	$(\text{H}_2\text{O})_{0.40}$ 725.60
Symmetry	Cubic, $F\bar{d}3m$	Cubic, $F\bar{4}3m$	Cubic, $F\bar{d}3m$	Cubic, $F\bar{d}3m$
Temperature [K]	295(2)	295(2)	295(2)	295(2)
a [Å]	15.2943(18)	15.9231(6)	15.3679(11)	15.9829(2)
V [Å ³]	3577.6(7)	4037.2(3)	3629.5(4)	4082.88(9)
Z	16	16	16	16
D_x [Mg·m ⁻³]	3.927	4.240	4.280	4.722
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	8.618	21.792	13.138	25.603
Crystal form, colour	octahedron, colourless	truncated octahedron, colourless	truncated octahedron, colourless	octahedron, colourless
Crystal size [mm]	$0.05 \times 0.05 \times 0.05$	$0.09 \times 0.09 \times 0.08$	$0.11 \times 0.11 \times 0.10$	$0.13 \times 0.13 \times 0.13$
Data collection				
Diffractometer	SMART APEX II	SMART APEX	SMART APEX	SMART APEX II
Data collection method	ϕ and ω scans	ω scans	ω scans	ϕ and ω scans
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
T_{min}, T_{max}	0.6725, 0.6725	0.2445, 0.2745	0.3259, 0.3533	0.1356, 0.1356
No. of measured, independent and observed reflections	28031, 684, 594	8307, 699, 640	9972, 317, 312	49997, 664, 602
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.062	0.042	0.028	0.051
θ_{max} [°]	43.2	31.0	30.9	40.2
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.037, 0.082, 1.05	0.028, 0.066, 1.13	0.051, 0.094, 1.12	0.019, 0.043, 1.30
No. of reflections	684	699	317	664
No. of parameters	21	35	22	24
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 135.7442P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 94.4577P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0109P)^2 + 42.0767P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0083P)^2 + 52.8965P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.000	0.000	0.000
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.93, -3.87	1.41, -1.66	0.50, -0.53	1.05, -1.01
Extinction method	-	-	-	SHELXL
Extinction coefficient	-	-	-	0.000184(8)
Twin volume fractions	-	47:53(3)	-	-

Table 4.29: Crystal data and details of the refinements of cubic phases with composition $M_3\text{Te}_2\text{O}_6\text{Cl}_2$ obtained from halide fluxes.

	$M = \text{Sr}, X = \text{Cl}$	$M = \text{Ba}, X = \text{Cl}$	$M = \text{Ba}, X = \text{Br}$
Crystal data			
Chemical formula	$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_2$	$\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$	$\text{Ba}_3\text{Te}_2\text{O}_6\text{Br}_2$
M_r	684.96	834.12	923.04
Symmetry	Cubic, $F\bar{d}3m$	Cubic, $F\bar{d}3m$	Cubic, $F\bar{d}3m$
Temperature [K]	295(2)	295(2)	295(2)
a [Å]	15.9351(4)	16.688(2)	16.8072(3)
V [Å ³]	4046.36(18)	4647.3(12)	4747.73(15)
Z	16	16	16
D_x [Mg·m ⁻³]	4.497	4.769	5.165
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	21.934	15.431	21.388
Crystal form, colour	truncated colourless	truncated colourless	truncated colourless
Crystal size [mm]	$0.23 \times 0.13 \times 0.09$		
Data collection			
Diffractionmeter	SMART APEX II	SMART APEX II	SMART APEX II
Data collection method	ϕ and ω scans	ϕ and ω scans	ϕ and ω scans
Absorption correction	multi-scan	multi-scan	multi-scan
T_{min}, T_{max}	0.0812, 0.2429	0.3716, 0.3716	0.1834, 0.2491
No. of measured, independent and observed reflections	25525, 647, 595	62298, 736, 702	44318, 753, 711
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.072	0.040	0.051
θ_{max} [°]	39.9	39.9	40.0
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F)], wR(F^2), S$	0.027, 0.053, 1.13	0.025, 0.070, 1.12	0.034, 0.085, 2.72
No. of reflections	647	736	753
No. of parameters	23	24	23
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (81.0877P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_0^2) + (0.0271P)^2 + 138.1456P]$ where $P = (F_0^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_0^2) + (0.0102P)^2 + 48.1135P]$ where $P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.001	0.000
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.00, -2.38	5.07, -3.23	1.44, -8.56
Extinction method	SHELX	SHELX	SHELXL
Extinction coefficient	0.00027(2)	0.000026(7)	0.000156(17)

Table 4.30: Comparison of R_{obs} and wR_{all} of the refinements of the cubic structures in space groups $Fd\bar{3}m$ and $F\bar{4}3m$ of data collected at $T = 100$ and $T = 295$ K.

Composition	$Fd\bar{3}m$			$F\bar{4}3m$		
	R_{obs}	wR_{all}	Rem.	R_{obs}	wR_{all}	Rem.
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$	0.037	0.082		0.036	0.086	
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$	0.036	0.084	†	0.028	0.066	
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$	0.016	0.036		0.014	0.035	‡,§
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.11}(\text{OH})_{0.89}(\text{H}_2\text{O})_{0.51}$	0.030	0.076		0.030	0.068	‡,†
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.12}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$	0.019	0.043		0.017	0.037	‡,†
$\text{Sr}_3\text{Te}_2\text{Cl}_2\text{O}_6$	0.027	0.053		0.028	0.057	
$\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$	0.025	0.070		0.025	0.060	
$\text{Ba}_3\text{Te}_2\text{Br}_2\text{O}_6$	0.017	0.036		0.017	0.037	

† ADP of atom OW, OWA or OWB non positive definite

‡ Composition differs slightly from composition of refinement in $Fd\bar{3}m$ § U_{eq} of atom OHB very large

4.10.4 Refinement

Automatic space group determination using systematic absences and correlation of symmetry equivalent reflections suggested the cubic space group $Fd\bar{3}m$ for all crystals under investigation. Closer inspection of reflection intensities revealed that numerous reflections $0kl$ with $k+l = 4n+2$ were of weak intensity but not absent ($I > 5\sigma(I)$) as would be expected for a crystal with a d glide plane parallel to (100). Analogous results were obtained for the the equivalent directions (010) and (001). Possible causes for the reflections include the Renninger effect (Renninger, 1936), reflections caused by $\frac{\lambda}{2}$ -radiation (Dudka, 2010), or a lower symmetry than $Fd\bar{3}m$ in parts of the crystal or the whole crystal. The two maximum subgroups of $Fd\bar{3}m$ with same metrics and lacking a d glide are $F\bar{4}3m$ and $F4_132$. Refinements in space group $F4_132$ are practically identical to those in $Fd\bar{3}m$, and therefore can be excluded. To determine the correct space group, refinements were performed in centrosymmetric space group $Fd\bar{3}m$ and the non-centro symmetric space group $F\bar{4}3m$. Refinements of structures of crystals obtained under hydrothermal conditions containing Sr and Cl atoms resulted in better reliability factors in $F\bar{4}3m$ than in $Fd\bar{3}m$. A position with occupational disorder in the $Fd\bar{3}m$ refinement was split in two positions without occupational disorder.

Refinements of the structure of crystals obtained under hydrothermal conditions containing Br atoms in spacegroup $F\bar{4}3m$ resulted in atoms with unreasonable ADPs. Final refinements were therefore performed in space group $Fd\bar{3}m$.

For crystals obtained under hydrothermal conditions containing Ca and Cl atoms and crystals obtained from halide fluxes, reliability factors of refinements in space groups $F\bar{4}3m$ and $Fd\bar{3}m$ are nearly identical and both refinements in both space groups provide similar ADPs and coordinates. Therefore the higher symmetric space group $Fd\bar{3}m$ was chosen for the final structure model. An overview of the reliability factors obtained for different data sets is listed in Tab. 4.30.

The structures were refined using the SHELX (Sheldrick, 2008) software package. Initial coordinates and atom names were obtained from the published data of $\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$ (Hottentot and Loopstra, 1983). According to Hottentot and Loopstra (1983), atom Cl3 in $\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$ is disordered around a position with symmetry $3/m$. Similar refinements of the corresponding

atom X3 resulted distinctly better reliability factors and smaller ADPs in the structures obtained from halide fluxes. For structures obtained under hydrothermal conditions, on the other hand, attempts to model X3 as disordered did not lead to improved reliability factors and often resulted in unstable refinements.

$M_3\text{Te}_2\text{O}_6X_{1+x}(\text{OH})_{1-x}(\text{H}_2\text{O})_y$ phases

In the phases obtained under hydrothermal conditions, one peak of excessive electron density in the difference Fourier maps was assigned to hydroxyl ions and water molecules. The corresponding O atom was named OW. The H atoms could not be located.

In $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$ OW was refined with an occupancy of $\frac{3}{4}$, resulting in an electronically neutral structure if all atoms OW are part of hydroxyl ions and not of water molecules. In $\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$ the sum of the site occupation factors of Cl1 and OW were constrained so that the resulting structure is electronically neutral under the assumption that all atoms OW are part of a hydroxyl group.

In the phases containing Br atoms, refinements with the same constraints led to unreasonable ADPs of the affected Br and O atoms. Therefore the occupancies of the Br atoms and O atoms of the hydroxyl groups were independently refined. The resulting structures contain more Br and O atoms than expected from a compound with composition $M_3\text{Te}_2\text{O}_6\text{Cl}_{1+x}(\text{OH})_{1-x}$. The excessive atoms OW were modelled as H_2O molecules.

$M_3\text{Te}_2\text{O}_6X_2$ phases

In $\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$, Cl2 and Cl3 were refined as occupationally disordered. The sum of the site occupation factors of Cl2 and Cl3 were constrained to result in an electronically neutral structure. In $\text{Sr}_3\text{Te}_2\text{Cl}_2\text{O}_6$, Cl2 was refined with an occupation of $\frac{1}{2}$. Refinement of the Cl2:Cl3 ratio did not result in better reliability factors as was the case for $\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$. In $\text{Ba}_3\text{Te}_2\text{Br}_2\text{O}_6$, the occupation of the Br2 position refines to only ≈ 0.29 as opposed to $\frac{1}{2}$ needed for an electronically neutral structure. Repeating of the synthesis with freshly prepared halide to exclude the possibility of contamination with Cl did not improve the situation. All other halide atoms are fully occupied.

4.10.5 Structure

Cationic network

All crystal structures described in this section can be derived from the same cationic ${}^3_\infty[M_3\text{Te}_2\text{O}_6]^{2+}$ network with $Fd\bar{3}m$ symmetry, and differ in the location of the OH^- and X anions and water molecules. The network consists of one crystallographically unique M , one Te and one O atom (Fig. 4.38). The M atom is located on a site with symmetry $2mm$, forming regular M_6 octahedra (symmetry $\bar{4}3m$) with faces normal to $\langle 111 \rangle$. The M - M edge length varies from 4.2187(15) Å ($M = \text{Ca}$, $X = \text{Cl}$) to 4.7907(4) Å ($M = \text{Ba}$, $X = \text{Br}$). The M_6 octahedra are connected by trigonal pyramidal $[\text{TeO}_3]$ (symmetry $3m$) groups which are located above every second face of the M_6 octahedra (Fig. 4.39). The $M/\text{Te}/\text{O}$ network is perforated by channels running along $\langle 110 \rangle$ in which the electron lone pairs E of the Te^{IV} atoms are located.

Anions

Halogenide ion X1 (Cl1 or Br1) is located at the centre of the M_6 octahedra. In the structures of crystals obtained using halide fluxes, the position is fully occupied (Tab. 4.31). In the struc-

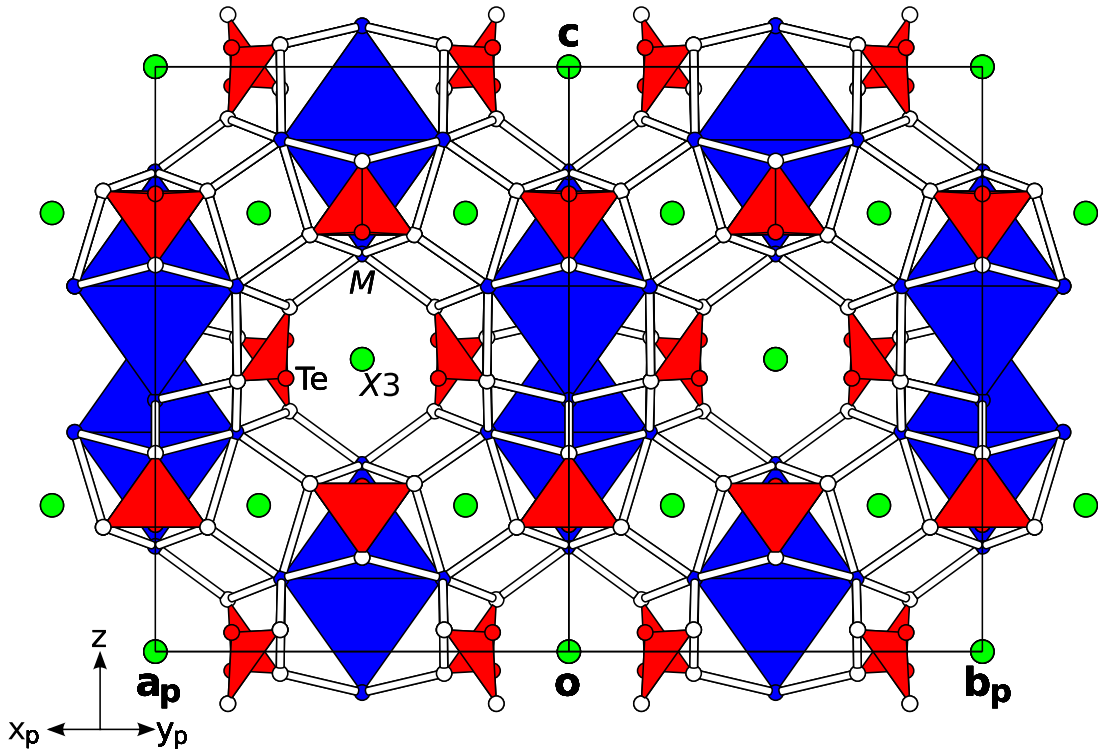


Figure 4.38: $\frac{3}{\infty}[M_3\text{Te}_2\text{O}_6]^{2+}$ network with $Fd\bar{3}m$ symmetry in the cubic phases with halide ions X located in channel running along $\langle 111 \rangle$. Te, M and X atoms are represented by red, blue and green spheres, $[\text{TeO}_3]$ units and M_6 octahedra by red and blue polyhedra.

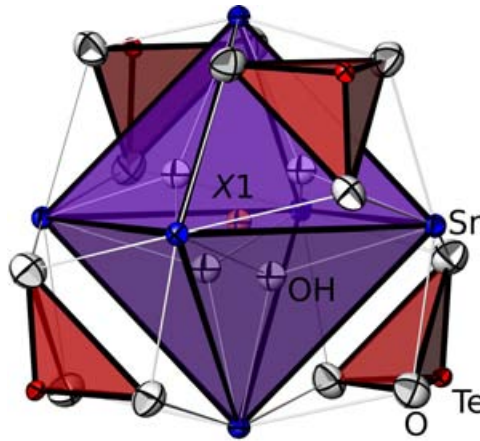


Figure 4.39: M_6 octahedron in the cubic phases with $[\text{TeO}_3]$ units located above each second faces. Inside the octahedron are located occupationally disordered OH groups, water molecules and X anions. M , Te and O atoms are represented blue, red and white ellipsoids. Ellipsoids represent 50% probability levels.

tures of crystals obtained by hydrothermal synthesis, only some M_6 octahedra contain halide ions. Inside the remaining octahedra, hydroxyl ions and water molecules are located on three-fold rotation axes, capping those M_3 faces which are not capped by $[\text{TeO}_3]$ units (Fig. 4.39). In $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$, M_6 octahedra are alternately filled with Cl and OH ions, causing a symmetry reduction from $Fd\bar{3}m$ to $F43m$. In $\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$ in slightly more than

Table 4.31: Occupation of atoms $X1$, $X2$, $X3$ ($X = \text{Cl}, \text{Br}$) and OW in the cubic structures. The occupation of disordered $M3$ atoms is given relative to the non-disordered position.

Composition	space group	$X1$		$X2$		$X3$		OW	
		site	occ.	site	occ.	site	occ.	site	occ.
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$	$Fd\bar{3}m$	$\bar{4}3m$	0.54(2)	-	-	$\bar{3}m$	1	$.3m$	0.37(2)
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$	$F\bar{4}3m$	$\bar{4}3m$	1	-	-	$.3m$	1	$.3m$	$\frac{3}{4}$
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}$	$Fd\bar{3}m$	$\bar{4}3m$	0.275(6)	-	-	$\bar{3}m$	1	$.3m$	0.65(6)
$(\text{H}_2\text{O})_{0.42}$									
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.12}(\text{OH})_{0.88}$	$Fd\bar{3}m$	$\bar{4}3m$	0.228(12)	-	-	$\bar{3}m$	1	$.3m$	0.70(3)
$(\text{H}_2\text{O})_{0.40}$									
$\text{Sr}_3\text{Te}_2\text{Cl}_2\text{O}_6$	$Fd\bar{3}m$	$\bar{4}3m$	1	$\bar{3}m$	$\frac{1}{2}$	$\bar{3}m^\dagger$	1	-	-
$\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6^\ddagger$	$Fd\bar{3}m$	$\bar{4}3m$	1	$\bar{3}m$	1	$\bar{3}m^\dagger$	$\frac{1}{2}$	-	-
$\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$	$Fd\bar{3}m$	$\bar{4}3m$	1	$\bar{3}m$	.58(1)	$\bar{3}m^\dagger$	.92(1)	-	-
$\text{Ba}_3\text{Te}_2\text{Br}_2\text{O}_6$	$Fd\bar{3}m$	$\bar{4}3m$	1	$\bar{3}m$	$\frac{1}{2}^*$	$\bar{3}m^\dagger$	1	-	-

[†] Atom disordered around this site.

[‡] According to Hottentot and Loopstra (1983)

* Refines to less than given value.

Table 4.32: O–O distances d between OH^- ions and water molecules in the cubic phases obtained under hydrothermal conditions.

Composition	d [Å]
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$	2.28(2)
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$	2.25(2)
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$	2.192(12)
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.12}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$	2.177(10)

every second M_6 octahedron a Cl ion is located in a disordered manner. In the phases obtained under hydrothermal conditions containing Br, only 14.7% ($\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$) and 11.7% ($\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.12}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$) of the M_6 octahedra are occupied with Br ions. The O–O distance between OH groups (Tab. 4.32) with ≈ 2.2 Å are $\approx 10\%$ shorter than the shortest known O–O distances between OH groups (Libowitzky, 1999). The short O–O distances are probably an artifact caused by unsatisfactory approximation of the ADPs by harmonic probability density functions. Indeed, refinement of atom OW in the phase $\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$ with anharmonic tensors using JANA2006 Petříček et al. (2006) results in distinctly better reliability factors ($R_{\text{obs}} = 3.1$ vs. $R_{\text{obs}} = 3.4$) and an increase in bond length from ≈ 2.3 Å to ≈ 2.5 Å. Refinement of anharmonic ADPs of the OW atoms in other phases did not have a significant effect on the OW–OW distance or reliability factors.

In the phases obtained from halide fluxes, $\text{Sr}_3\text{Te}_2\text{Cl}_2\text{O}_6$, $\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$ and $\text{Ba}_3\text{Te}_2\text{Br}_2\text{O}_6$ atoms $X2$ are located on sites with symmetry $\bar{3}m$. They connect two M_6 octahedra *via* faces that are not capped by $[\text{TeO}_3]$ units. The $X2$ position is unoccupied in crystals obtained by hydrothermal synthesis.

Halogenide ions $X3$ ($\text{Cl}3$ or $\text{Br}3$) are located in channels running along $\langle 110 \rangle$. In the phases obtained from halide fluxes, $X3$ is disordered around a site with symmetry $3/m$. In the structures of the crystals obtained by hydrothermal synthesis $X3$ was refined as not disordered. In the

Table 4.33: Principal mean square atomic displacements U of atoms X3 in the cubic phases parallel to $\langle 111 \rangle$ and $\{111\}$. For the disordered X3 atoms, the principal mean square atomic displacements approximately parallel to $\langle 111 \rangle$ and $\{111\}$ are given.

Composition	atom	refined as disordered	$U_{\langle 111 \rangle} [\text{\AA}^2]$	$U_{\{111\}} [\text{\AA}^2]$
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$	Cl3	no	0.0330	0.0982
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$	Cl3	no	0.0346	0.1286
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$	Br3	no	0.0206	0.0352
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.12}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$	Br3	no	0.0251	0.0406
$\text{Sr}_3\text{Te}_2\text{Cl}_2\text{O}_6$	Cl3	yes	0.0354	0.0481, 0.0528
$\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$	Cl3	yes	0.0532	0.0835, 0.0561
$\text{Ba}_3\text{Te}_2\text{Br}_2\text{O}_6$	Br3	yes	0.0405	0.0457, 0.0415

Table 4.34: Lattice parameter a of the crystal structures of cubic phases at 293 K.

Composition	$a [\text{\AA}]$
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$	15.2943(18)
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$	15.9231(6)
$\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$	15.3679(11)
$\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.12}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$	15.9733(16)
$\text{Sr}_3\text{Te}_2\text{Cl}_2\text{O}_6$	15.9351(4)
$\text{Ba}_3\text{Te}_2\text{Cl}_2\text{O}_6$	16.689(2)
$\text{Ba}_3\text{Te}_2\text{Br}_2\text{O}_6$	16.8072(3)

phases containing Cl obtained by hydrothermal synthesis ($\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.30}(\text{OH})_{0.70}(\text{H}_2\text{O})_{0.25}$ and $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$) Cl3 has very large ADP (Tab. 4.33), hinting towards disorder which could not be resolved.

Lattice parameter a

The lattice parameter a of the crystal structures of the cubic phases at 293 K are listed in Tab. 4.34. The influence of the alkaline earth metal on the lattice parameter a is significantly larger than the influence of the halide ions. Replacement of Ca by Sr in the phases obtained under hydrothermal conditions results in a $\approx 4\%$ increase of a , replacement of Sr by Ba in the phases obtained in halide fluxes in a $\approx 5\%$ increase. The lattice parameter a of the phases with $M = \text{Sr}$ and $M = \text{Cl}$ obtained under hydrothermal conditions and fluxes are very similar (15.9231(6) and 15.9351(4) $\text{\AA}$). The increase of a when replacing Cl by Br is in all cases less than 1%. The halide ions, which are located in the channels of the structures and the M_6 octahedra, have no influence on the size of the metal-oxo framework.

4.10.6 Element distribution

The phases obtained under hydrothermal conditions were subjected to EDX analysis. Element distribution for all compounds obtained by EDX differ only slightly from those calculated from single crystal XRD data with two exceptions: For $M = \text{Ca}$, $X = \text{Cl}$ the measured Te:Ca ratio differs from the theoretical, whereas for $M = \text{Ca}$, $X = \text{Br}$ the halide ion content significantly exceeds the value determined by XRD.

Table 4.35: Comparison of element composition (in atomic %) of the compounds obtained under hydrothermal conditions measured by EDX and computed from single crystal XRD data.

Composition	EDX				XRD			
	Te	<i>M</i>	<i>X</i>	O	Te	<i>M</i>	<i>X</i>	O
<i>M</i> =Ca/ <i>X</i> =Cl	20.74	19.17	9.97	50.12	15.38	23.08	9.62	51.92
<i>M</i> =Sr/ <i>X</i> =Cl	15.76	25.56	8.62	50.06	15.38	23.08	9.62	51.92
<i>M</i> =Ca/ <i>X</i> =Br	16.43	20.86	11.44	51.27	14.90	22.35	8.49	54.25
<i>M</i> =Sr/ <i>X</i> =Br	13.57	22.81	7.94	55.68	14.93	22.39	8.35	54.33

Table 4.36: Characteristic bands in cm^{-1} in the Raman spectra of the cubic phases obtained under hydrothermal conditions.

	OH bending		<i>M</i> -OH bending		Te-O stretching			Te-O- <i>M</i>		<i>M</i> /Te motion		
<i>M</i> =Ca/ <i>X</i> =Cl	3643	3622	1092	1077	813	776	-	695	433	392	127	65
<i>M</i> =Sr/ <i>X</i> =Cl	3643	3627	1080	1075	803	780	764	693	418	383	115	50
<i>M</i> =Ca/ <i>X</i> =Br	-	-	1091	1075	790	-	-	688	433	383	122	71
<i>M</i> =Sr/ <i>X</i> =Br	-	-	1082	1073	780	-	-	686	418	370	114	59

No elements other than the expected (*M*, *X*, Te and O) were found. In particular, no measurable amount nitrogen could be detected, therefore the existence of NH_4^+ -ions in the crystal structure can be excluded.

4.11 Raman spectroscopy

The cubic phases obtained under hydrothermal conditions were subjected to Raman spectroscopy. The 632.8 nm line of a He/Ne laser was focused on the {111} faces of the single crystals. Multiple spectra with varying angle of incidence in the spectral range of 3500 cm^{-1} to 50 cm^{-1} were recorded.

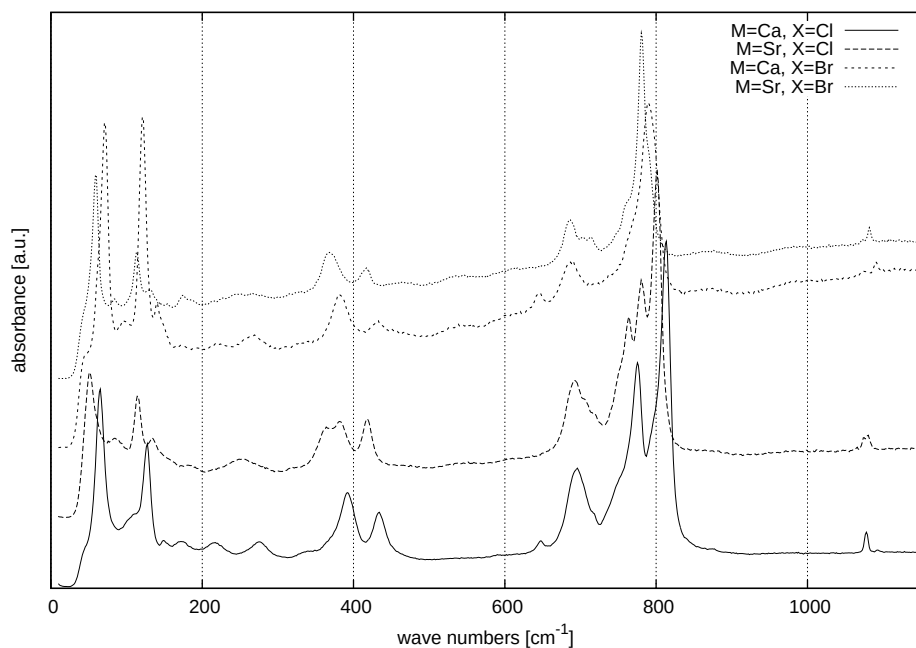
As expected for cubic crystals, the degree of incidence has practically no influence on the recorded spectra. Representative spectra of the regions $1200\text{--}0\text{ cm}^{-1}$ and $3700\text{--}3500\text{ cm}^{-1}$ are depicted in Fig. 4.40. The spectral regions $3500\text{--}1200\text{ cm}^{-1}$ contain no peaks in all crystals. The wave numbers of characteristic bands are listed in Tab. 4.36. The spectra of crystals containing Cl atoms show two small sharp Raman active modes at $\approx 3643\text{ cm}^{-1}$, which correspond to OH stretching vibrations (Kloprogge and Frost, 1999). The spectra of crystals containing Br contain no bands in this region. Small and non-existing Raman active OH stretching vibrations in this region are well-known for phases with very short (*i.e.* strong) hydrogen bonds (Mihajlović et al., 2004). The difference between compounds containing Cl and Br correlates well with the different anion distribution determined by single crystal XRD.

The spectra obtained from all four phases show two small bands at ≈ 1085 and $\approx 1075\text{ cm}^{-1}$, which are probably caused by *M*-O-H bending vibrations or by stretching vibrations of OH groups with very short hydrogen bonds (Libowitzky, 1999). They are practically identical in phases containing the same cation *M* and differ slightly in phases containing different cations *M*.

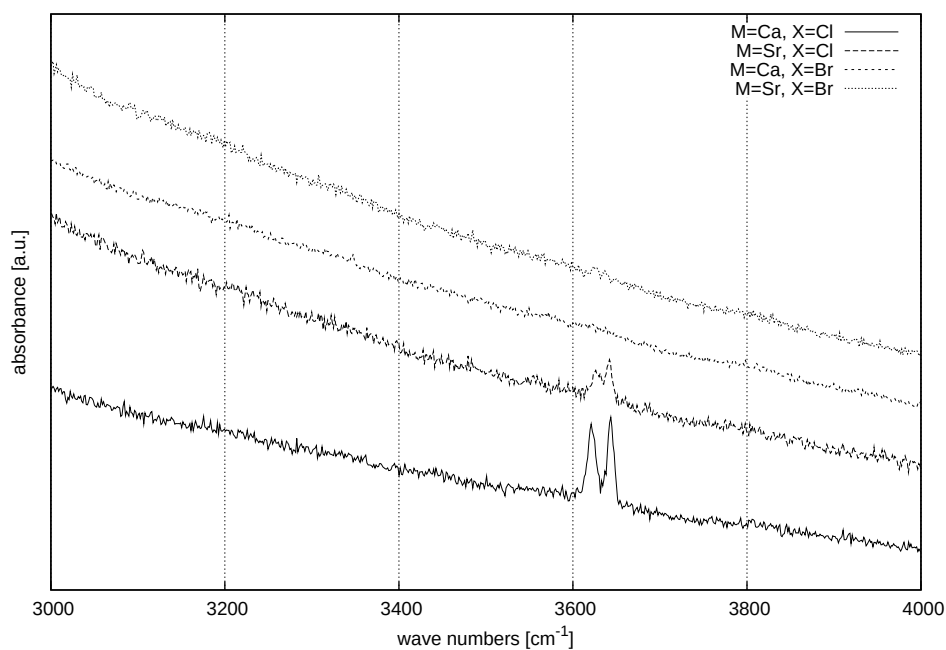
Crystals of all four phases possess intense Raman active modes in the $850\text{--}600\text{ cm}^{-1}$ region

which are characteristic for oxotellurates and can be attributed to Te–O stretching vibrations (Mirgorodsky et al., 2002). The peaks are shifted towards lower wave numbers (*i.e.* lower energy) with increasing atomic number of the alkaline earth metals and the halide ions. The phases containing Br ions show one major peak in the region $\approx 800\text{ cm}^{-1}$. The corresponding peak is split in the phases containing Cl ions, possibly due to lower (local) symmetry of these phases.

The bands at ≈ 380 and $\approx 430\text{ cm}^{-1}$ probably originate from Te–O– M vibrations (Jiang and Mao, 2008). The bands in the region $220\text{--}100\text{ cm}^{-1}$ correspond to the motion of the heavy atoms (Ca, Sr and Te). Indeed, these bands are practically identical in those phases containing the same alkaline earth metal M . In the case of the heavier Sr, they are shifted towards lower wave numbers compared to Ca.



(a)



(b)

Figure 4.40: Raman spectra of the cubic phases obtained under hydrothermal conditions in the region (a) $1200\text{--}0\text{ cm}^{-1}$ and (b) $3700\text{--}3500\text{ cm}^{-1}$.

Chapter 5

Oxotellurates(VI)

5.1 The orthotellurates Sr_3TeO_6 and Ba_3TeO_6

5.1.1 Introduction

Orthotellurates(VI) of alkaline earth metals with general formula $M_2M'\text{Te}^{VI}\text{O}_6$ bear interesting crystal-chemical and physico-chemical aspects and a number of these phases and their solid solutions are structurally well-characterized (Prior et al., 2005; Fu et al., 2008). So far, for alkaline earth metal tellurates(VI) with a single M cation and general formula $M_3\text{Te}^{VI}\text{O}_6$ only two reliable structure determinations have been published, *viz.* Ca_3TeO_6 (Hottentot and Loopstra, 1981) and Mg_3TeO_6 (Schulz and Bayer, 1971), both on the basis of single crystal XRD data. The higher homologues Sr_3TeO_6 and Ba_3TeO_6 have originally been prepared (Külcü and Trömel, 1984) as microcrystalline powders and their room temperature XRD patterns were indexed with small unit cells in the tetragonal and orthorhombic crystal systems, respectively: Sr_3TeO_6 : $a = 8.358 \text{ \AA}$, $c = 8.242 \text{ \AA}$; Ba_3TeO_6 : $a = 8.806 \text{ \AA}$, $b = 8.688 \text{ \AA}$, $c = 8.578 \text{ \AA}$. From the diffraction patterns and unit cell volumes cryolite-related structures were derived, but a complete structure determination has not been reported up to now.

XRPD measurements of the $\text{Sr}_3\text{Te}^{VI}\text{O}_6$ and $\text{Ba}_3\text{Te}^{VI}\text{O}_6$ phases performed during this work showed identical main reflections as published by Külcü and Trömel (1984), but additional superstructure reflections were observed for both orthotellurates. Since it was not possible to find a reliable cell considering all superstructure reflections, single crystals were grown using a flux of the respective alkaline earth halides under atmospheric conditions for detailed structure analyses. This approach was already successfully applied by Hottentot and Loopstra (1981) for obtaining single crystals of the related phase $\text{Ca}_3\text{Te}^{VI}\text{O}_6$ in a CaCl_2 melt at 1033 K which led to an oxidation of Te^{IV} to Te^{VI} . It should be noted that the same authors likewise tried to apply this method for crystal growth of Ba_3TeO_6 under similar conditions in a BaCl_2 flux, but yielded a the Te^{IV} phase $\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$ described in sec. 4.10 instead (Hottentot and Loopstra, 1983). The latter preparation conditions were modified by using MX_2 fluxes ($M = \text{Sr}, \text{Ba}$; $X = \text{Cl}, \text{Br}$) and mixtures containing single crystals of $M_3\text{Te}_2\text{O}_6X_2$ and $M_3\text{TeO}_6$ were obtained. Prolongation of reaction times, variation of the MX_2 fluxes and working at higher temperatures gradually increased the yield of the $M_3\text{TeO}_6$ phases, and allowed eventually to obtain single-phase material. Although the grown crystals were relatively small and in all cases twinned, a complete structure analysis was possible for both compounds. The Sr_3TeO_6 and Ba_3TeO_6 structures have much larger unit cells than assumed by Külcü and Trömel (1984) and are pronounced superstructures that can be derived from the cubic elpasolite structure (K_2NaAlF_6 , $Fm\bar{3}m$). Since in the literature regarding to $M_3\text{TeO}_6$ or related $M_2M'\text{Te}^{VI}\text{O}_6$ structures, the description as

Table 5.1: Experimental details. Relative mass percentages of the identified phases according to Rietveld refinement using TOPAS (Coelho, 2002).

Flux medium	crucible	T [K]	t [h]	Rem.	Result
SrCl ₂	Pt	1273	30		35% Sr ₃ TeO ₆ , 65% Sr ₃ Te ₂ O ₆ Cl ₂
BaCl ₂	Al ₂ O ₃	1273	30	†	16% Ba ₃ TeO ₆ , 84% Ba ₃ Te ₂ O ₆ Cl ₂
SrCl ₂	Al ₂ O ₃	1373	70		46% Sr ₃ TeO ₆ , 54% Sr ₃ Te ₂ O ₆ Cl ₂
SrBr ₂	Al ₂ O ₃	1373	70		100% Sr ₃ TeO ₆
BaCl ₂	Al ₂ O ₃	1373	70		100% Ba ₃ TeO ₆
BaBr ₂	Al ₂ O ₃	1373	70		73% Ba ₃ TeO ₆ , 27% Ba ₃ Te ₂ O ₆ Br ₂

† Minor amounts of unidentified phase(s)

a „double perovskite” (which is basically the same structure as elpasolite) is found much more frequently (Anderson et al., 1993), the two novel $M_3\text{TeO}_6$ ($M = \text{Sr}, \text{Ba}$) structures will likewise be described as derivatives of the double perovskite structure.

Other phases in the system $\text{Ca}/\text{Te}^{VI}/\text{O}$ include the mixed-valent $\text{Te}^{IV}/\text{Te}^{VI}$ mineral carlriesite, CaTe_3O_8 (Effenberger et al., 1978), and the Te^{VI} compounds CaTeO_4 (Hottentot and Loopstra, 1979) and Ca_3TeO_6 (Hottentot and Loopstra, 1981; Burckhardt et al., 1982). A phase with composition $\text{Ca}_5\text{Te}_3\text{O}_{14}$, corresponding to a $\text{Te}:\text{O}$ ratio of 5:3 was obtained by Fu and IJdo (2008) at 973 K using an open system.

5.1.2 Preparation

In a variation of the procedure given by Hottentot and Loopstra (1983), 100 mg TeO_2 and 500 mg $MX_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Ba}, \text{Sr}; X = \text{Cl}, \text{Br}$) were heated in a platinum or corundum crucible at $T = 1273, 1373$ K for a period of $t = 30, 70$ h. After cooling to RT, the reaction product was leached out with water to remove excess fluxing agent and subsequently washed with acetone. Dependent on the reaction batch, the reaction products consisted of a white to yellowish microcrystalline powder (composition according to powder diffraction phase analysis given in Tab. 5.1), small nearly isometric colourless crystals of $M_3\text{TeO}_6$ and colourless larger cubic crystals of $M_3\text{Te}_2\text{O}_6X_2$ in the form of truncated octahedra.

5.1.3 Structure determination and refinement

Sr_3TeO_6

Intensity data were recorded in ten batches (ϕ - and ω -scan modes) with 0.5° frame width and 14 s exposure time, leading to a high redundancy of the data set. A numerical absorption correction using the program HABITUS (W. Herrendorf, 1997) was applied. The lattice parameters of the reduced triclinic cell of $a = 11.7113(2)$ Å, $b = 11.7392(2)$ Å, $c = 11.7503(2)$ Å, $\alpha = 119.7745(7)^\circ$, $\beta = 119.6593(7)^\circ$, $\gamma = 90.3348(8)^\circ$, as well as the elements of the Niggli matrix with $\mathbf{a} \cdot \mathbf{a} = 137.155$ Å², $\mathbf{b} \cdot \mathbf{b} = 137.809$ Å², $\mathbf{c} \cdot \mathbf{c} = 137.070$ Å², $\mathbf{b} \cdot \mathbf{c} = -68.500$ Å², $\mathbf{a} \cdot \mathbf{c} = -68.096$ Å², $\mathbf{a} \cdot \mathbf{b} = -0.803$ Å², made it seem appropriate to consider higher symmetries. The lattice of this cell can be transformed into monoclinic, orthorhombic, tetragonal and rhombohedral lattices, in each case with different slight deviations from the ideal metrics. Transformation with the matrix

$$\begin{pmatrix} 1 & 1 & \bar{1} \\ 1 & \bar{1} & \bar{1} \\ 0 & 0 & 2 \end{pmatrix}$$

leads to a nearly cubic F -centred cell with $a = 16.5338(2)$ Å, $b = 16.6308(2)$ Å, $c = 16.7112(3)$ Å, $\alpha = 90.031(2)^\circ$, $\beta = 90.035(2)^\circ$, $\gamma = 90.1370(10)^\circ$. The point group of the corresponding lattice, $m\bar{3}m$, includes all symmetry operations that are present in the point groups of all the above mentioned lattices with lower symmetry. However, a closer inspection of the diffraction pattern showed no evidence for diffraction symmetry higher than $\bar{1}$ ($R_{int} = 0.071$). Symmetry-equivalent reflections according to the other symmetry operations of $m\bar{3}m$ gave only $R_{int} > 0.25$. Hence the structure was solved in space group $P\bar{1}$ (reduced cell) by direct methods and subsequent Fourier maps, but the refinement converged at unsatisfactory reliability factors, with the final $R[F^2 > 2\sigma(F^2)]$ value being 0.07. Such unsatisfactory results indicate, for instance, twinning, and since no non-crystallographic extinctions nor splitting of the reflections was observed, twinning by pseudo-merohedry was considered. For that purpose the method introduced by Britton (1972) and further developed by Fisher and Sweet (1980) for the detection of twinning by (pseudo-)merohedry, the determination of twin operations, and the estimation of the volume fractions of the twin domains, was used. In a twin by (pseudo-)merohedry, or strictly speaking (pseudo-)hemihedry, the observed intensities I_1 and I_2 , related by the twin operation, are combinations of the intensities J_1 and J_2 from an untwinned crystal: $I_1 = (1 - \alpha)J_1 + \alpha J_2$, $I_2 = (1 - \alpha)J_2 + \alpha J_1$ where $0 \leq \alpha \leq 0.5$ is the volume fraction of the smaller twin mate. This system can be solved to obtain

$$J_1 = \frac{I_1 - \alpha(I_1 + I_2)}{1 - 2\alpha},$$

and

$$J_2 = \frac{I_2 - \alpha(I_1 + I_2)}{1 - 2\alpha}.$$

For $I_1 < I_2$ the term $I_1 - \alpha(I_1 + I_2)$ and consequently J_1 can become negative for values of α greater than the actual volume fraction; for values of α smaller than the actual volume fraction $I_1 - \alpha(I_1 + I_2)$ and hence J_1 is always positive. For those symmetry operation of the pseudo-cubic lattice with order two, intensities related by twinning were compared and the number of negative values of J as a function of α was plotted. Fig. 5.1 shows the graphical treatment of the data for twin operation $(100/010/00\bar{1})$, twin mirror plane (001) , or twin operation $(\bar{1}00/0\bar{1}0/001)$, twofold twin axis $[001]$ (twin obliquity $w = 0.047^\circ$). The curve does not show a sharp break, as expected for ideal intensities. This may be due to the absorption-induced low accuracy of weak intensities on which the estimate of α strongly depends. But the regression line for the range $0.16 \leq \alpha \leq 0.40$ yields $\alpha = 0.0979(3)$ which is in excellent agreement with the twin fraction $\alpha = 0.0965(4)$ obtained in the course of the subsequent structure refinement.

Ba_3TeO_6

Several tiny Ba_3TeO_6 crystals were measured. Intensity data were recorded in four batches (ϕ - and ω -scan modes) with 0.3° frame width and 20 s exposure time. Due to the small crystal size and an undefined habit, absorption correction using the multi-scan approach implemented by the SADABS program (Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2007) was applied. All investigated crystals consisted at least of two twin fractions related by non-merohedry preventing a straightforward unit cell determination. Merely in one crystal the second twin domain was so small that a reasonable I -centred cell was found and integration could be performed disregarding reflections from the second twin component. The orientation matrix relating the two twin domains was determined using the CELLNOW program (Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2007). The twin domains are typically related by a rotation of 120° around $[4, 12, 5]$ or an equivalent axis in direct space which corresponds to a space diagonal of the cubic aristotype.

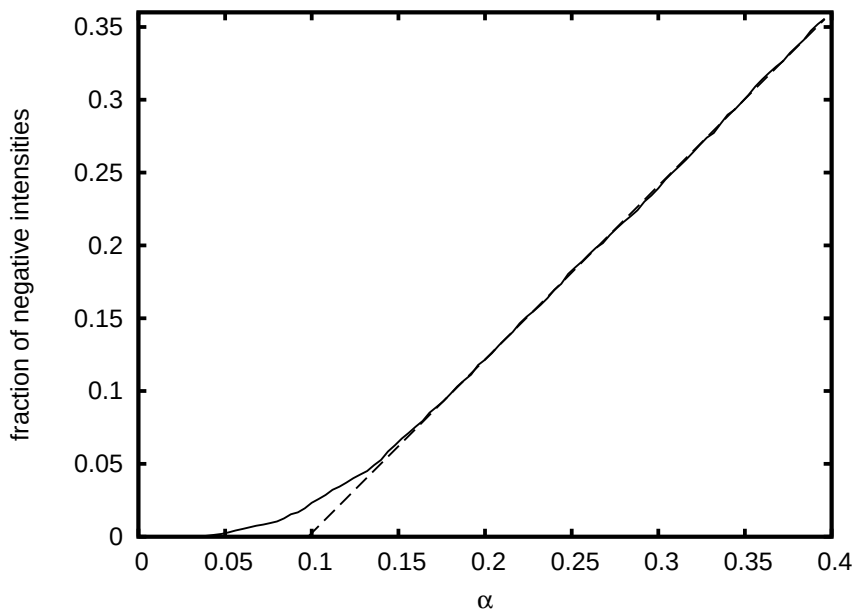


Figure 5.1: Sr_3TeO_6 : Fraction of negative intensities J plotted against the twin volume fraction α (continuous line) and regression line for the range $0.16 \leq \alpha \leq 0.40$ (dashed line).

Sr_3TeO_6 and Ba_3TeO_6

In the final refinement cycles all atoms were refined with anisotropic displacement parameters. No significant residual electron density peaks were observed in the difference Fourier maps for the finally chosen models. Details of the single crystal data collections and refinements are summarized in Tab. 5.2, atomic coordinates and isotropic displacement parameters are listed in Tab. C.37 and Tab. C.38.

5.1.4 Structures

Sr_3TeO_6 (triclinic, $F\bar{1}$, $Z = 32$) and Ba_3TeO_6 (tetragonal, $I4_1/a$, $Z = 80$) are hettotypes of their common cubic aristotype with the double perovskite structure $M_2M'\text{Te}^{\text{VI}}\text{O}_6$, or in a more general formula $M_2^{[12c]}M'^{[6o]}M''^{[6o]}X_6$, in space group $Fm\bar{3}m$ and $Z = 4$. The cubic aristotype contains four atoms in the asymmetric unit with Wyckoff positions $8c$ for the M site, $4b$ for the M' site, $8a$ for the M'' site and $24c$ for the X site. In the following discussion Miller indices with respect to the unit cell of the aristotype will be marked by a subscript „ a ”.

5.1.5 Description of the structures as cubic close packing (*c.c.p.*) arrangements

Sr_3TeO_6 and Ba_3TeO_6 crystallize with eight- and 40-fold superstructures. They contain rigid, isolated and close to regular $[\text{TeO}_6]$ octahedra. The arrangement of the octahedra can be described as a cubic close packing (*c.c.p.*). This arrangement leads to two different positions for the remaining metal cations. The M -type atoms are in cuboctahedral voids and the M' -type atoms (like the Te or M'' -type atoms) are in octahedral voids (Fig. 5.2). Hence there are one octahedrally and two cuboctahedrally coordinated M positions in the cubic $M_3\text{TeO}_6$ aristotype. In terms of layer packing, the two structures can be considered as a stacking of pseudo-hexagonal

Table 5.2: Crystal data and details of the refinements of Sr_3TeO_6 and Ba_3TeO_6

	Sr_3TeO_6	Ba_3TeO_6
Crystal data		
Chemical formula	Sr_3TeO_6	Ba_3TeO_6
M_r	486.46	635.62
Symmetry	Triclinic, $F\bar{1}$	Tetragonal, $I4_1/a$
Temperature [K]	295(2)	295(2)
a, b, c [Å]	16.5338(2), 16.6308(2), 16.7112(3)	19.3878(10), 19.3878(10), 34.909(2)
α, β, γ [°]	90.031(2), 90.035(2), 90.1370(10)	90, 90, 90
V [Å ³]	4595.07(11)	13121.9(12)
Z	32	80
D_x [Mg·m ⁻³]	5.625	6.435
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ [mm ⁻¹]	32.699	22.134
Crystal form, colour	Fragment, colourless	Undefined habit, colourless
Crystal size [mm]	$0.13 \times 0.12 \times 0.10$	$0.05 \times 0.05 \times 0.05$
Data collection		
Diffractometer	SMART APEX II	SMART APEX II
Data collection method	ω and ϕ scans	ω and ϕ scans
Absorption correction	<i>HABITUS</i>	<i>SADABS</i>
T_{min}, T_{max}	0.0390, 0.1677	0.3502, 0.4713
No. of measured, independent and observed reflections	72318, 19195, 14608	146437, 19576, 13414
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.071	0.058
θ_{max} [°]	45.31	40.52
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.035, 0.076, 0.937	0.034, 0.060, 0.996
No. of reflections	19195	19576
No. of parameters	375	453
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0336P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_0^2) + (0.0221P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.003
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	3.87, -2.34	3.46, -2.53
Twin operation	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$	-
Twin domain volume fraction	90.3:9.7	-
Extinction method	SHELXL	SHELXL
Extinction coefficient	0.000250(5)	0.0000038(2)

layers of $[\text{TeO}_6]$ units along $\langle 111 \rangle_a$ with stacking sequence $ABCA'B'C'$ for Sr_3TeO_6 and with a stacking period of 20 varying layer triplets $(ABC, A'B'C', \dots)$ for Ba_3TeO_6 (Fig. 5.3).

The description of the Sr_3TeO_6 and Ba_3TeO_6 structures as a *c.c.p.* arrangement becomes beneficial for comparison with the structures of other orthotellurates(VI) of the same formula type $M_3\text{TeO}_6$, where $M = \text{Mg}$ (Schulz and Bayer, 1971), Ca (Hottentot and Loopstra, 1981), Mn (Weil, 2006a), Co (Becker et al., 2006), Ni (Becker and Berger, 2006), Zn (Weil, 2006b), Cu (Falck et al., 2008), Cd (Burckhardt et al., 1982) and Hg (Weil, 2003a). All these structures

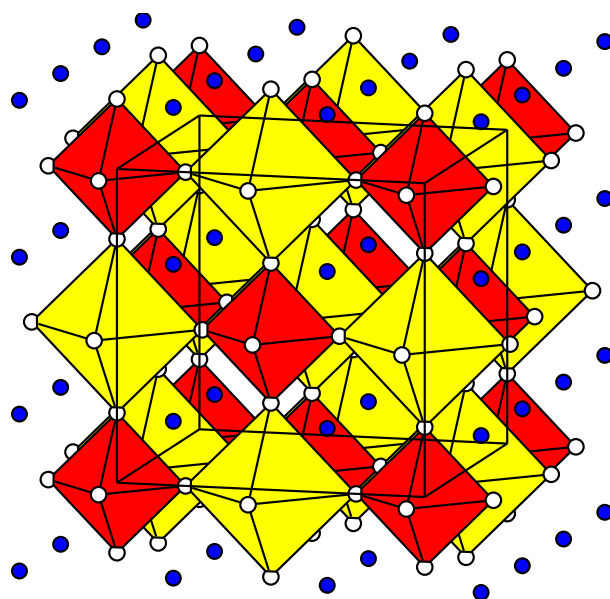


Figure 5.2: The cubic double perovskite aristotype of the $M_3\text{TeO}_6$ ($M = \text{Sr}, \text{Ba}$) structures. Red octahedra represent $[\text{TeO}_6]$ and yellow octahedra represent $[\text{MO}_6]$ units. O atoms are given as white spheres. The remaining M^{2+} ions in the cuboctahedral voids are represented by blue spheres.

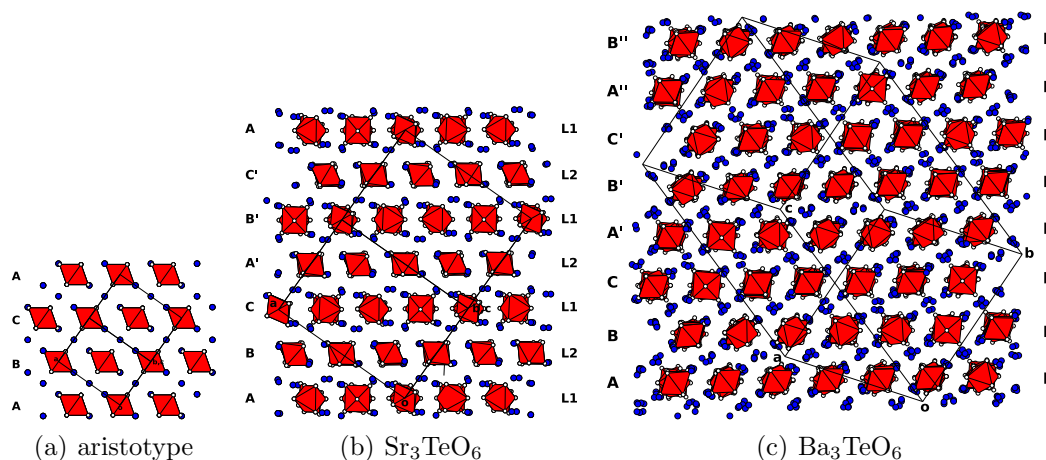


Figure 5.3: Stacking of trigonal layers parallel to $(111)_a$ in (a) the cubic aristotype of the $M_3\text{TeO}_6$ ($M = \text{Sr}, \text{Ba}$) structures and (b) of pseudo-trigonal layers in the actual structure of Sr_3TeO_6 parallel to $(111)_a \equiv (111)$ projected on $(00\bar{1})$ (middle) and of (c) Ba_3TeO_6 parallel to $(111)_a \equiv (134)$ projected on $(21\bar{4})$ (right). Colour code as in Fig. 5.2. To the left of the figures: traditional layer notation according to the *c.c.p.* (...ABC...) arrangement. To the right of the actual structures: layer names used in the text.

can likewise be described as more or less distorted *c.c.p.* arrangements built up of layers of isolated $[\text{TeO}_6]$ octahedra. The primitive cells of the structures with $M = \text{Mg}, \text{Mn}, \text{Ca}, \text{Cd}$ contain two formula units, whilst for $M = \text{Cu}$ Z is 4, for $M = \text{Co}, \text{Zn}$ Z is 6, and for $M = \text{Hg}$ Z is 8. Ca_3TeO_6 and Cd_3TeO_6 are isotypic and crystallize with the α -cryolite structure type in space group $P2_1/n$. They are pseudo-tetragonal with a layer stacking sequence of ABC along $[021]$. In the isotypic compounds Mg_3TeO_6 and Mn_3TeO_6 ($R\bar{3}$) the $[\text{TeO}_6]$ units are rotated

around $[111]_a$ with a stacking sequence of the layers of $ABCA'B'C'$ along $[001]$. Cu_3TeO_6 and Hg_3TeO_6 both crystallize in space group $Ia\bar{3}$. While the former is a bixbyite derivative with an ABC layer stacking along $[111]$, the latter has a unique structure type with a more complex stacking sequence of $ABCA'B'C'$ along the same direction. Co_3TeO_6 and Zn_3TeO_6 ($C2/c$) crystallize in the $\beta\text{-Li}_3\text{VF}_6$ structure type where the $ABCA'B'C'$ arrangement along $[001]$ of the close packed $[\text{TeO}_6]$ units is heavily distorted. Finally, Ni_3TeO_6 ($R3$) can be described as a derivative of the corundum structure with an ABC stacking sequence along $[001]$

5.1.6 Description of the structures as derivatives of the double perovskite structure

Despite the usefulness to derive the various $M_3\text{TeO}_6$ structures from a simple *c.c.p.* arrangement of $[\text{TeO}_6]$ units, this approach remains at a general and qualitative level. Moreover, for some of the $M_3\text{TeO}_6$ phases detailed structural similarities are hard to find. For example, only the Ca_3TeO_6 , Cd_3TeO_6 , Sr_3TeO_6 and Ba_3TeO_6 structures are closely related and are derivatives from the double perovskite structure. The latter structure family will be the main aspect in the following discussion. More detailed group-subgroup relationships and the formalism devised by Bärnighausen (1980) will be used for this purpose.

The symmetry reduction from the double perovskite aristotype to Sr_3TeO_6 and Ba_3TeO_6 is illustrated in a Bärnighausen family tree (Bärnighausen, 1980) in Fig. 5.4. This family tree can be considered as a supplement of already published group-subgroup relations that were derived for numerous perovskite and double perovskite structures (Bärnighausen, 1975; Bock and Müller, 2002; Müller, 2004).

The symmetry reduction from $Fm\bar{3}m$ can be split into five and six maximal group-subgroup relations for Sr_3TeO_6 and Ba_3TeO_6 , respectively. In order to ensure correctness of the described symmetry reductions, it is essential to follow the development of the site symmetries of all atomic positions. Therefore, for each listed space group site symmetries and coordinates are given. For those space groups which have no published representative yet, an averaged structure has been calculated from a lower symmetry structure, only considering atoms which do not deviate too far from the position of the higher symmetry structures. For reasons of brevity, the coordinates of the O atoms in lower symmetry structures have not been listed. It should be noted that the sequences of the respective symmetry reductions are arbitrarily chosen whereas each single symmetry reduction is clearly determined by its group-subgroup relation. The first two symmetry reductions were chosen in order to reflect symmetry reductions of known double perovskite structures. For the further steps, no published representatives are known.

In the case of group subgroup relations for Sr_3TeO_6 , the first two steps correspond to the symmetry reduction of the known compounds $\text{Ba}_2\text{SrIrO}_6$ (Jung et al., 1993) and $\text{Ba}_2\text{SrTeO}_6$ (Fu et al., 2008). In the slightly distorted double perovskite $\text{Ba}_2\text{SrIrO}_6$ all fourfold rotation axes of the cubic aristotype are lost. In $\text{Ba}_2\text{SrTeO}_6$ additionally the mirror planes are lost. In order to emphasize the similarity with the cubic aristotype, an *F*-centred cell with metrics comparable to the cell of the aristotype was chosen for these intermediate structures as opposed to standard *R*-centred cells. The next two steps correspond to a doubling of all basis vectors of the *F*-centred cell. The intermediate step proceeds *via* an *R*-centred cell to ensure pseudo-cubic metrics and easy comparability of the coordinates (an intermediate step *via* an *F*-centred cell would result in a cell with lattice parameters α , β and $\gamma \approx 60^\circ$). In the final step trigonal symmetry is reduced to triclinic symmetry. It was chosen as the last step, because the structure of Sr_3TeO_6 is pseudo-trigonal.

For group-subgroup relations for Ba_3TeO_6 , the first two steps represent loss of threefold rotation axes for Ba_2CuWO_6 (Bock and Müller, 2002) and loss of the mirror planes parallel to

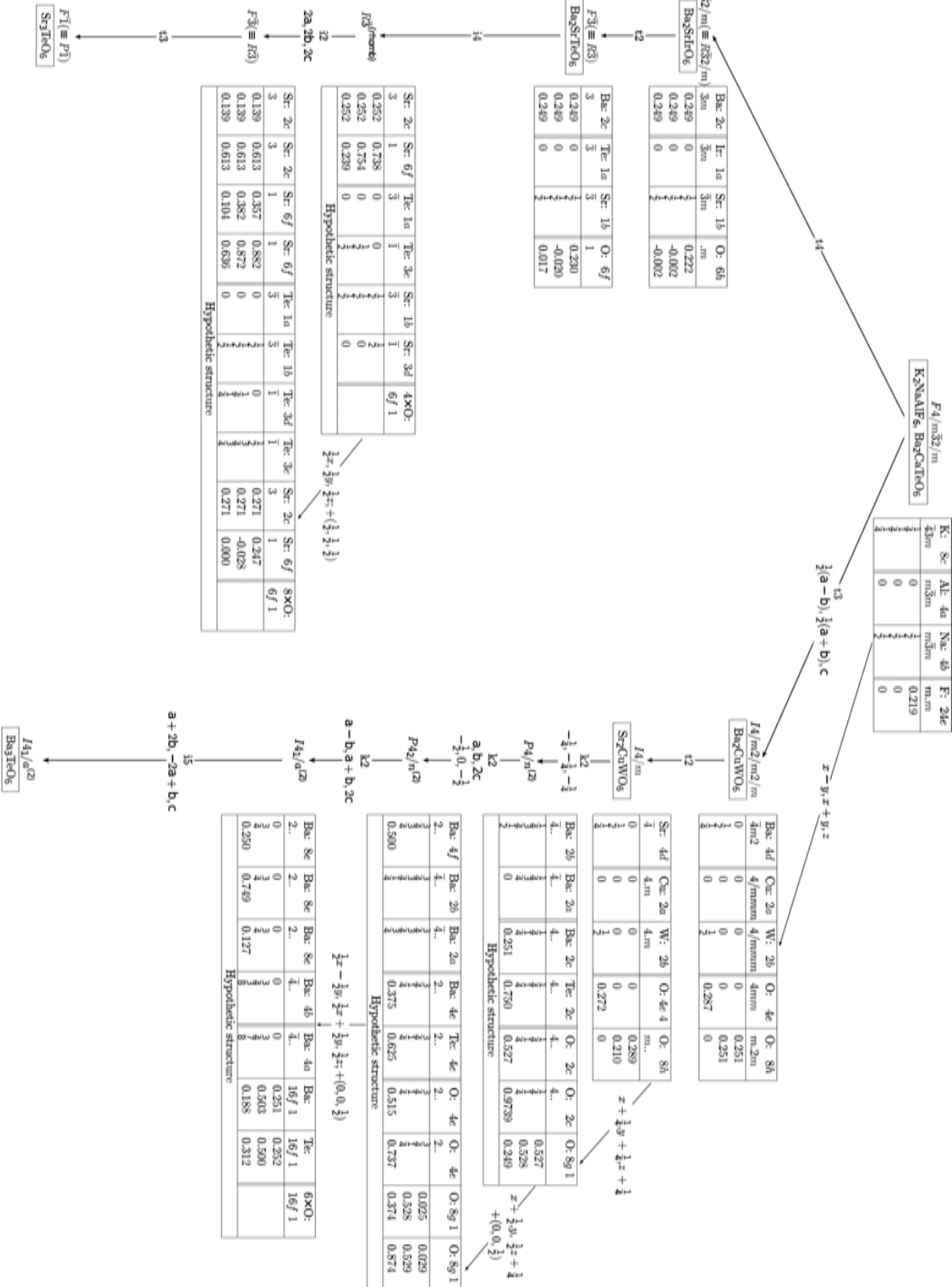


Figure 5.4: Group-subgroup relationship of Sr_3TeO_6 and Ba_3TeO_6 with their common cubic aristotype. Coordinates for K_2NaAlF_6 , Ba_2CuWO_6 and Sr_2CuWO_6 taken from Bock and Müller (2002), coordinates for $\text{Ba}_2\text{SrIrO}_6$ and $\text{Ba}_2\text{SrTeO}_6$ from Jung et al. (1993) and Fu et al. (2008), respectively.

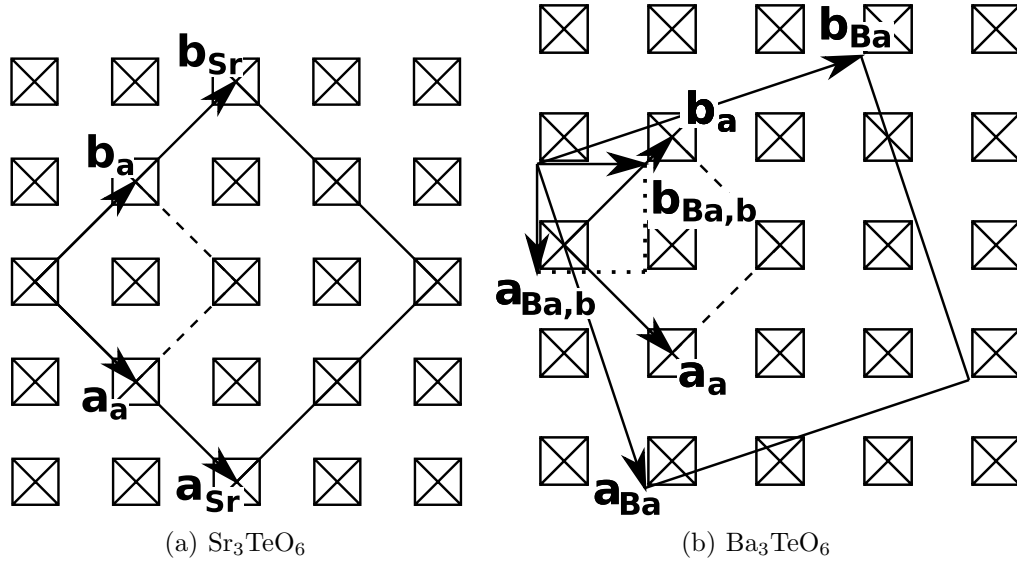


Figure 5.5: Relation between the basis vectors $\mathbf{a}$ and $\mathbf{b}$ of the actual structure, basic structure and the cubic aristotype of (a) Sr_3TeO_6 and (b) Ba_3TeO_6 disregarding deviations of the lattice angles from 90° . $[\text{TeO}_6]$ groups are represented by squares and crosses (only one square layer is shown). The unit cell of the actual structure, basic structure and aristotype are represented by continuous, dashed and dotted lines, respectively. In Sr_3TeO_6 the basic structure and the aristotype have identical unit cells.

$\{100\}$ and $\{110\}$ of the resulting tetragonal structure for Sr_2CuWO_6 (Bock and Müller, 2002). In the next three steps, translational symmetry along the remaining tetragonal axis $[001]$ is removed, resulting in a quadrupling of the lattice vector $\mathbf{c}$ and symmetry reduction of the 4 axis to 4_1 , 4_3 and $\bar{4}$ axes. The fivefold isomorphic symmetry reduction ($\mathbf{a}' = \mathbf{a} + 2\mathbf{b}$, $\mathbf{b}' = -2\mathbf{a} + \mathbf{b}$) has been chosen as a last step.

In the vast literature on perovskite structures, indication of the octahedral tilt systems devised by Glazer (1972) and extended by Woodward (1997) is common. Because of the pronounced superstructures, the strong distortions of the $[\text{MO}_x]$ polyhedra and the tilting of the $[\text{TeO}_6]$ polyhedra by up to $\approx 45^\circ$ in the Sr_3TeO_6 and Ba_3TeO_6 structures, the use of the Glazer notation is limited, as was also pointed out by Bock and Müller (2002). Therefore this symbolism will not be used for the structure descriptions and the tilting of the octahedra. In the following discussion „basic structure” denotes the basic structure according to the theory of modulated structures (van Smaalen, 2007), *viz.* the averaged structure obtained by only considering the main reflections (*i.e.* the strong reflections, corresponding to reflections (hkl) with $h = 2n$, $k = 2n$, $l = 2n$ for Sr_3TeO_6 and $l = 4n$, $8h + 4k + 5l = 40n$ for Ba_3TeO_6). When it comes to the description of basic structures this will be marked by a subscript „b”. The basic structures of Sr_3TeO_6 and Ba_3TeO_6 have triclinic and tetragonal symmetry, respectively. „Actual structure” and „actual cell” in the following discussion signify the structure and cells of Sr_3TeO_6 and Ba_3TeO_6 as determined by single crystal diffraction (*viz.* the superstructure and supercell). An overview of the relationships of the unit cells of the actual and basic structures of Sr_3TeO_6 and Ba_3TeO_6 and their common aristotype is given in Fig. 5.5.

In order to highlight the relationship to its aristotype and to be able to express the twin law in a simple manner, the non-standard setting $F\bar{1}$ has been chosen for Sr_3TeO_6 . With this setting the basis vectors of the basic structure ($\mathbf{a}_{\text{Sr,b}}$, $\mathbf{b}_{\text{Sr,b}}$, $\mathbf{c}_{\text{Sr,b}}$) and of the aristotype ($\mathbf{a}_a$, $\mathbf{b}_a$, $\mathbf{c}_a$) are identical (disregarding the deviation from the cubic metrics) and can be obtained by halving

Table 5.3: Te–O distances in Å of the [TeO₆] units in Sr₃TeO₆ (top) and Ba₃TeO₆ (bottom).

Atom	d [Å]	d [Å]	d [Å]	d [Å]	d [Å]	d [Å]
Te1	1.917(2) (2×)	1.938(3) (2×)	1.949(2) (2×)			
Te2	1.925(3) (2×)	1.932(3) (2×)	1.953(3) (2×)			
Te3	1.920(3) (2×)	1.922(2) (2×)	1.953(3) (2×)			
Te4	1.902(2) (2×)	1.938(3) (2×)	1.951(3) (2×)			
Te5	1.881(3) (2×)	1.938(2) (2×)	1.951(3) (2×)			
Te6	1.896(3) (2×)	1.944(3) (2×)	1.951(2) (2×)			
Te7	1.919(3) (2×)	1.919(3) (2×)	1.921(2) (2×)			
Te8	1.913(3) (2×)	1.916(3) (2×)	1.922(3) (2×)			
Te1	1.927(3)	1.931(3)	1.933(3)	1.947(3)	1.951(3)	1.974(3)
Te2	1.925(3)	1.935(3)	1.937(3)	1.956(3)	1.959(3)	1.962(3)
Te3	1.912(3)	1.925(3)	1.927(3)	1.940(3)	1.944(3)	1.953(3)
Te4	1.920(3)	1.932(3)	1.934(3)	1.935(3)	1.941(3)	1.943(3)
Te5	1.892(3)	1.916(3)	1.937(3)	1.944(3)	1.948(3)	1.959(3)

the basis vectors of the actual cell ($\mathbf{a}_{\text{Sr}}, \mathbf{b}_{\text{Sr}}, \mathbf{c}_{\text{Sr}}$):

$$(\mathbf{a}_{\text{Sr}}, \mathbf{b}_{\text{Sr}}, \mathbf{c}_{\text{Sr}}) = 2(\mathbf{a}_{\text{Sr,b}}, \mathbf{b}_{\text{Sr,b}}, \mathbf{c}_{\text{Sr,b}}) = 2(\mathbf{a}_a, \mathbf{b}_a, \mathbf{c}_a)$$

Sr₃TeO₆ possesses a pseudo-threefold rotation axis parallel to $[111]_a \equiv [111]$ and is twinned by mirroring at $(001)_a \equiv (001)$.

In Ba₃TeO₆ ($I4_1/a$) the unit cell of the basic structure and of the aristotype are not identical. Since the aristotype is F -centred and the basic structure is I -centred, the former has twice the cell volume. The relationship of the basis vectors of the Ba₃TeO₆ basic and actual structures to the aristotype is given as

$$(\mathbf{a}_{\text{Ba}}, \mathbf{b}_{\text{Ba}}, \mathbf{c}_{\text{Ba}}) = (\mathbf{a}_{\text{Ba,b}}, \mathbf{b}_{\text{Ba,b}}, \mathbf{c}_{\text{Ba,b}}) \begin{pmatrix} 3 & \bar{1} & 0 \\ 1 & 3 & 0 \\ 0 & 0 & 4 \end{pmatrix} =$$

$$(\mathbf{a}_a, \mathbf{b}_a, \mathbf{c}_a) \begin{pmatrix} 2 & 1 & 0 \\ \bar{1} & 2 & 0 \\ 0 & 0 & 4 \end{pmatrix}.$$

The origin $\mathbf{o}_a$ of the aristotype is located at $(1/4, 0, 1/16)$, with respect to the coordinate system of the actual structure of Ba₃TeO₆. The latter has fourfold rotation axes parallel to $[001]_a$ and crystals are twinned by non-merohedry by rotation around an axis parallel to $\langle 111 \rangle_a$.

In order to compute structures of the idealized cubic aristotypes, unit cells with $a = \sqrt[3]{V/8}$ (Sr₃TeO₆) and $a = \sqrt[3]{V/20}$ (Ba₃TeO₆), respectively, were used. The oxygen atom was placed as to reflect the average Te–O distance of the actual structures (1.928(20) Å in Sr₃TeO₆ and 1.938(17) Å in Ba₃TeO₆). Individual Te–O distances of the actual structures are gathered in Tab. 5.3.

The coordinates of the idealized structures are given in Tab. 5.4. The unit cell parameters of the actual cells compare favourably to those of the idealized cells (Tab. 5.5). The coordinates of the M and Te atoms in the coordinate system of the aristotype and the distance to the idealized positions $((x', y', z') = (\frac{1}{2}n_x, \frac{1}{2}n_y, \frac{1}{2}n_z), n_x + n_y + n_z = 2n$ for Te and $(x', y', z') = (\frac{1}{2}n_x, \frac{1}{2}n_y, \frac{1}{2}n_z), n_x + n_y + n_z = 2n + 1$ and $(x', y', z') = (\frac{1}{4}n_x, \frac{1}{4}n_y, \frac{1}{4}n_z)$ for Ba) are given in

Table 5.4: Coordinates of the atoms in the cubic aristotype ($Fm\bar{3}m$) of Sr_3TeO_6 and Ba_3TeO_6 .

Atom	Multiplicity	Wyckoff letter	Site symmetry	Sr_3TeO_6			Ba_3TeO_6		
				x	y	z	x	y	z
Te	4	a	$m\bar{3}m$	0	0	0	0	0	0
$M1$	4	b	$m\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$M2$	8	c	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
O	24	e	$4m.m$	0.2319	0	0	0.2230	0	0

Tab. 5.6. In the Sr_3TeO_6 structure the Te atoms are located at centres of inversion and therefore match exactly with those calculated for the idealized positions, whereas in the Ba_3TeO_6 structure the Te atoms deviate slightly by 0.013–0.113 Å from their idealized values. With up to 0.556 Å (Sr) and 0.454 Å (Ba), deviations of the M atoms from their idealized positions are significantly larger. The deviations of the O atoms are even larger. Indeed, two types of $[\text{TeO}_6]$ units can be distinguished: Those oriented similarly to the corresponding octahedra in the aristotype (Te4–Te8 in Sr_3TeO_6 and Te3–Te5 in Ba_3TeO_6) and those rotated by $\approx 45^\circ$ around a direction of $\langle 100 \rangle_a$ (Te1–Te3 in Sr_3TeO_6 and Te1–Te2 in Ba_3TeO_6).

Six octahedra in Sr_3TeO_6 (Te1–Te6) are tilted moderately from the idealized positions with a tilt of $4.2^\circ < \delta < 8.7^\circ$ and two further octahedra (Te7 and Te8) are tilted considerably by $\delta = 16.5^\circ$ and 19.9° , respectively. In Ba_3TeO_6 , on the other hand, the octahedra are oriented close to ideal and deviate only by $1.9^\circ < \delta < 5.0^\circ$.

The distances and angles of the individual $[\text{TeO}_6]$ units exhibit only slight variations (Tab. 5.3: Te–O: 1.882–1.953 Å in Sr_3TeO_6 ; Te–O: 1.893–1.974 Å in Ba_3TeO_6). The rigid conformation of the octahedral $[\text{TeO}_6]$ anion and the average Te–O distances are characteristic (sec. 1.2.2).

As opposed to the $[\text{TeO}_6]$ octahedra, the $[\text{MO}_x]$ polyhedra are highly irregular and their shapes differ distinctly from the aristotype. As explained before, the aristotype contains octahedral and cuboctahedral voids. The space provided by the aristotype does not match properly the requirements of the corresponding M atoms. Whereas the octahedral voids are too small, the cuboctahedral voids are too big for a convenient filling of the $M_3\text{TeO}_6$ structures. In the idealized Sr_3TeO_6 aristotype the M –O distances are 2.943 Å and 2.228 Å for cuboctahedrally and octahedrally coordinated atoms, respectively. The corresponding distances in cubic Ba_3TeO_6 are 3.081 Å and 2.407 Å. Bond valence calculations with $v_i = \exp(\frac{R_o - R_i}{b})$ (Brown, 2002) for these bonds with the parameters $R_o = 2.212$ Å and $b = 0.370$ for Sr and $R_o = 2.285$ Å and $b = 0.370$ for Ba (Brese and O’Keeffe, 1991) result in BVS of 1.29 v.u. (Sr) and 1.42 v.u. (Ba) for cuboctahedrally coordinated and 4.40 v.u. (Sr) and 4.46 v.u. (Ba) for octahedrally coordinated sites, differing extremely from the expected value of 2 v.u.. For comparison, bond valence calculations for all Sr–O and Ba–O bonds in the actual structures are compiled in Tab. 5.6. The calculated valence sums for the M atoms still deviate from the expected value, but they are much closer to the expected value with an average of 2.37 v.u. (Sr) and 2.50 v.u. (Ba) for the (pseudo-)octahedrally coordinated sites and 1.89 v.u. (Sr) and 1.83 v.u. (Ba) for the other sites. Either increasing or decreasing the lattice parameters would have a positive effect on one, but a negative effect on the other coordination sphere. Therefore tilting of the $[\text{TeO}_6]$ units seems to be the only way to achieve a stable structure, resulting in a pronounced formation of superstructures accompanied by a change of the coordination numbers for the M sites. In general, the coordination number for the originally six-coordinate M site in the aristotype is increased (to 7–9 in Sr_3TeO_6 and Ba_3TeO_6) and those of the 12-coordinate site is decreased (to 9–10 in Sr_3TeO_6 and 9–12 in Ba_3TeO_6) (Tab. 5.6).

Table 5.5: Comparison of the cell parameters of the actual structure, the basic structure, the pseudo-cubic structure and the idealized cubic double perovskite structure of Sr_3TeO_6 and Ba_3TeO_6 .

	Bravais lattice	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å ³]
Sr_3TeO_6								
Actual structure	triclinic F	16.5338(2)	16.6308(2)	16.7112(3)	90.031(2)	90.035(2)	90.1370(10)	4595.07(11)
Basic structure	triclinic F	8.2669	8.3154	8.3556	90.031	90.035	90.137	574.38
Pseudo-cubic structure	triclinic F	8.2669	8.3154	8.3556	90.031	90.035	90.137	574.38
Idealized cubic packing	cubic F	8.3125	8.3125	8.3125	90	90	90	574.38
Ba_3TeO_6								
Actual structure	tetragonal I	19.3878(10)	19.3878(10)	34.909(2)	90	90	90	13121.9(12)
Basic structure	tetragonal I	6.1310	6.1310	8.7273	90	90	90	328.0
Pseudo-cubic structure	tetragonal F	8.6705	8.6705	8.7273	90	90	90	656.1
Idealized cubic packing	cubic F	8.6894	8.6894	8.6894	90	90	90	656.1

Table 5.6: Positions of the Te, Sr and Ba atoms in Sr_3TeO_6 (top) and Ba_3TeO_6 (bottom) given in the coordinate system of the cubic aristotype and distances of idealized to actual atoms under idealization of the metrics of the actual structure ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$). For the Sr and Ba atoms the total BVS in the actual structure and *c.n.* in the cubic aristotype and the actual structure are listed.

Atom	x	y	z	d [Å]	BVS [v.u.]	<i>c.n.</i> (aristo- type)	<i>c.n.</i> (actual)
Te1	$\frac{1}{2}$	1	$\frac{1}{2}$	0	5.72	6	6
Te2	1	$\frac{1}{2}$	$\frac{1}{2}$	0	5.69	6	6
Te3	$\frac{1}{2}$	$\frac{1}{2}$	1	0	5.77	6	6
Te4	$\frac{1}{2}$	$\frac{1}{2}$	0	0	5.79	6	6
Te5	$\frac{1}{2}$	0	$\frac{1}{2}$	0	5.91	6	6
Te6	0	$\frac{1}{2}$	$\frac{1}{2}$	0	5.81	6	6
Te7	1	0	0	0	5.96	6	6
Te8	0	0	0	0	6.01	6	6
Sr1	0.059	0.998	0.502	0.4853	2.63	6	7
Sr2	1.002	0.503	0.055	0.4600	2.56	6	7
Sr3	0.515	0.053	0.997	0.4585	2.43	6	7
Sr4	0.542	0.540	0.534	0.5561	1.85	6	9
Sr5	0.716	0.765	0.206	0.4811	2.01	12	9
Sr6	1.232	0.226	0.224	0.3320	2.09	12	9
Sr7	0.768	0.206	0.715	0.4973	2.02	12	9
Sr8	0.730	0.235	0.258	0.2194	1.76	12	9
Sr9	0.210	0.709	0.757	0.4777	2.06	12	8
Sr10	0.257	0.728	0.232	0.2463	1.75	12	9
Sr11	0.279	0.273	0.275	0.3678	1.71	12	10
Sr12	0.243	0.253	0.727	0.2025	1.71	12	10
Te1	1.000	1.999	-0.001	0.0132	5.59	6	6
Te2	2.002	1.003	-0.003	0.0336	5.56	6	6
Te3	1.503	-0.499	0.011	0.1009	5.74	6	6
Te4	0.513	0.510	0.002	0.1020	5.73	6	6
Te5	1.005	1.012	-0.009	0.1125	5.76	6	6
Ba1	1.049	0.502	0.038	0.4451	2.25	6	8
Ba2	1.999	1.438	0.002	0.3803	2.84	6	7
Ba3	1.497	0.044	-0.036	0.4154	2.30	6	8
Ba4	1.504	0.938	-0.002	0.3793	2.83	6	7
Ba5	0.541	1.943	-0.004	0.4329	2.27	6	8
Ba6	$\frac{5}{4}$	$\frac{5}{4}$	$\frac{1}{4}$	0	1.57	12	12
Ba7	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{4}$	0	1.56	12	12
Ba8	$\frac{5}{4}$	$\frac{5}{4}$	-0.250	0.0006	1.57	12	12
Ba9	$\frac{1}{4}$	$\frac{3}{4}$	-0.221	0.2505	1.86	12	10
Ba10	$\frac{3}{4}$	$\frac{1}{4}$	0.229	0.1800	1.88	12	10
Ba11	1.233	-0.268	-0.201	0.4540	2.00	12	9
Ba12	2.299	1.233	0.239	0.3325	1.96	12	9
Ba13	0.739	0.770	0.210	0.3750	2.04	12	9
Ba14	2.294	1.236	-0.236	0.3087	2.06	12	9
Ba15	1.254	-0.250	0.243	0.0654	1.70	12	9
Ba16	1.706	1.230	0.231	0.3419	2.00	12	9
Ba17	0.763	0.747	-0.232	0.1730	1.70	12	11
Ba18	1.711	1.238	-0.243	0.2592	1.89	12	9

Nevertheless, for orthotellurates(VI) $M_2M'\text{TeO}_6$ the cubic aristotype can be stabilized by replacing the octahedrally coordinated M' sites (that in case of Sr_3TeO_6 and Ba_3TeO_6 are of the same chemical type as the cuboctahedrally coordinated M sites) by atoms with a smaller ionic radius. In fact, $\text{Ba}_2\text{CaTeO}_6$ ($Fm\bar{3}m$) crystallizes in the most highly symmetrical aristotype. As pointed out by Fu et al. (2008), the cubic symmetry is expected for double perovskites of the type $M_2M'X\text{O}_6$ when the tolerance factor

$$t = \frac{r_M + r_O}{\sqrt{2}(r_{M',X} + r_O)},$$

where r designates the ionic radius and $r_{M',X}$ is the averaged ionic radius of the M' and X cations, is close to unity. The more the tolerance factors deviate from this value, the more symmetry is typically reduced. As a rough guideline, cubic symmetry is expected for t greater than 0.98 ($\text{Ba}_2\text{CaTeO}_6$: $t = 0.98$), trigonal symmetry for t between 0.98 and 0.96, and for double perovskites with t lower than 0.96 monoclinic symmetry is most frequently found. This explains also the symmetry reduction observed for $\text{Ba}_2\text{SrTeO}_6$ ($R\bar{3}$; see also Fig. 5.4) when the Ca atoms are replaced by the bigger Sr atoms, resulting in a trigonal distortion with the $[\text{TeO}_6]$ units slightly tilted around $[111]_a$ (Fu et al., 2008). Although the tolerance factor for this structure ($t = 0.94$) suggests a still lower symmetry according to the above classification, the trigonal symmetry is retained. This behaviour has been explained by the more covalent nature of the $\text{Te}^{VI}\text{--O}$ bonds in comparison with other $[\text{XO}_6]$ octahedra, where $X = \text{Nb}^V, \text{Bi}^V$, and the different Coulomb interaction between the M cations and the $[\text{XO}_6]$ octahedra (Fu et al., 2008). According to this assumption, a different ionic contribution is apparently present in the structures of the orthotellurates(VI) Sr_3TeO_6 and Ba_3TeO_6 . Their tolerance factors, calculated with the tabulated Shannon radii (Shannon, 1976), are similar ($t = 0.89$ for the Sr and $t = 0.90$ for the Ba structure), but their symmetries are notably different although their $[\text{XO}_6]$ octahedra are of the same chemical type.

5.1.7 Special features of the structures and description with a different layer stacking

Sr_3TeO_6

Sr_3TeO_6 ($F\bar{1}$) has pseudo-trigonal symmetry (idealized space group $R\bar{3}$). In the hexagonal setting the basis vectors are related to the basis vectors of the actual structure by

$$(\mathbf{a}_H, \mathbf{b}_H, \mathbf{c}_H) = (\mathbf{a}_{\text{Sr}}, \mathbf{b}_{\text{Sr}}, \mathbf{c}_{\text{Sr}}) \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ 0 & \frac{1}{2} & 1 \\ \frac{1}{2} & 0 & 1 \end{pmatrix}.$$

The threefold rotation axes of the aristotype parallel to any of the $\langle 111 \rangle_a$ directions are only retained as pseudo- $\bar{3}$, pseudo- 3_1 and pseudo- 3_2 axes along $[111]$. With the exception of the oxygen atoms that are part of the $[\text{TeO}_6]$ octahedron (O81–O83, deviation of 1.01 Å), the average deviation from the idealized trigonal symmetry is below 0.3 Å. This explains convincingly why a rhombohedral cell was suggested from the APEX2 program during cell determination of Sr_3TeO_6 crystals.

Due to the pseudo- $\bar{3}$ rotation axis parallel to $[111]$ it can be useful to describe Sr_3TeO_6 as a stacking of layers parallel to (111) . Using this description, the aristotype contains one kind of trigonal layers (layer group $p\bar{3}m1$, Fig. 5.6, left). The actual structure, on the other hand, consists of an alternate stacking of two crystallographically different layers, $L1$ and $L2$ (Fig. 5.6,

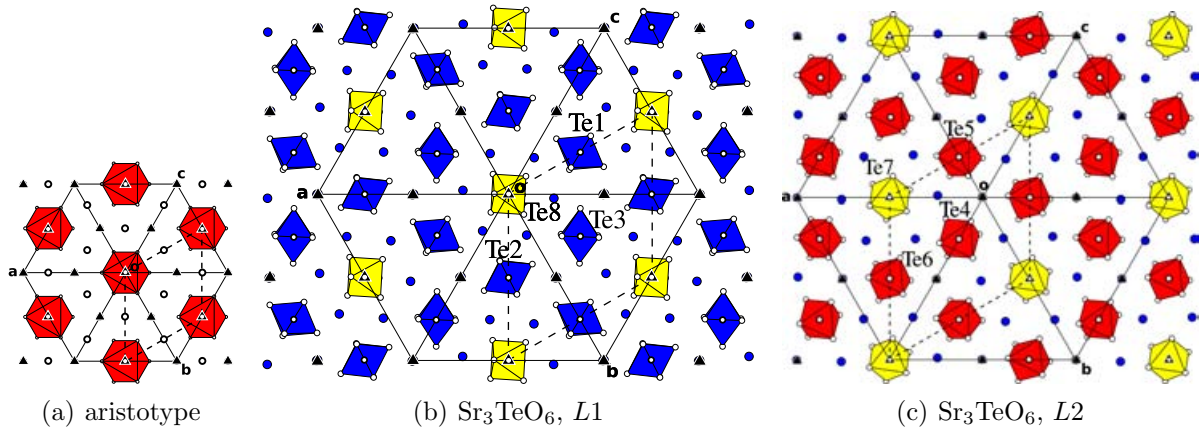


Figure 5.6: (Pseudo-)trigonal layers in (a) the aristotype ($p\bar{3}m1$) and layers (b) $L1$ and (c) $L2$ in the actual structure of Sr_3TeO_6 (idealized symmetry $p\bar{3}$) parallel to $(111)_a$ projected along $[111]_a$. Sr atoms are represented by blue, O atoms by white spheres. $[\text{TeO}_6]$ octahedra oriented similarly to the corresponding octahedra in the aristotype are red, rotated by $\approx 45^\circ$ around a direction of $\langle 111 \rangle_a$ blue and those deviating by more than 10° from such a position yellow. Actual and pseudo-3 ($\bar{3}$) axes and centres of symmetry are represented by symbols of the International Tables (Hahn, 1983). Mirror planes were omitted for reasons of clarity. The unit cell of Sr_3TeO_6 and its aristotype is represented by continuous, the unit cells of the respective layers by dashed lines.

middle and right) with pseudo-trigonal symmetry (idealized symmetry $p\bar{3}$, actual symmetry $p\bar{1}$) and doubled lattice basis vectors relative to the corresponding layer of the aristotype (Fig. 5.3).

Each of the two layers contains four crystallographically different $[\text{TeO}_6]$ octahedra. One of them is close to the pseudo- $\bar{3}$ axis (*viz.* Te8 in $L1$ and Te7 in $L2$) the other three are related by the pseudo- $\bar{3}$ symmetry (*viz.* Te1–Te3 in $L1$ and Te5–Te7 in $L2$).

In comparison with the layer of the aristotype, the $[\text{Te8O}_6]$ octahedron close to the pseudo- $\bar{3}$ axis in $L1$ is tilted by $\approx 20^\circ$ away from this axis and thus breaks the trigonal symmetry of the layer and in consequence the trigonal symmetry of the overall structure. The three $[\text{TeO}_6]$ octahedra related by the pseudo- $\bar{3}$ symmetry in $L1$ (Te1, Te2, Te3) are tilted by *ca.* 45° in a cyclic manner around the $\bar{3}$ axis. The corresponding octahedra in $L2$ (Te4, Te5, Te6) almost retain their orientation from the aristotype.

While the octahedrally coordinated Sr atoms in the aristotype are located halfway between two layers (Fig. 5.3, left), the corresponding atoms in the actual structure (Sr1–Sr4) are shifted along $[111]$ towards layer $L1$ (Fig. 5.3, middle). The Sr atom with the highest deviation from its idealized position is Sr4. It is located on a pseudo- $\bar{3}$ axis, which is located between the three flipped $[\text{TeO}_6]$ octahedra in layer $L1$. It has an unusual high coordination number of 9 and an unusual low bond valence sum of 1.8 v.u. compared to the other Sr atoms corresponding to the octahedrally coordinated Sr atoms in the aristotype (Sr1–Sr3: coordination number 7, 2.6–2.4 v.u., Tab. 5.6).

Twining in Sr_3TeO_6

Since crystals of Sr_3TeO_6 are pseudo-merohedrally twinned by a mirror plane parallel to (001) , it is likewise useful to consider the structure as a stacking of two alternating layers parallel to (001) consisting of a pseudo-square packing of $[\text{TeO}_6]$ octahedra (Fig. 5.7). While one layer (A^1) has a pseudo-mirror plane parallel to (001) and therefore idealized symmetry $p112/m$, the

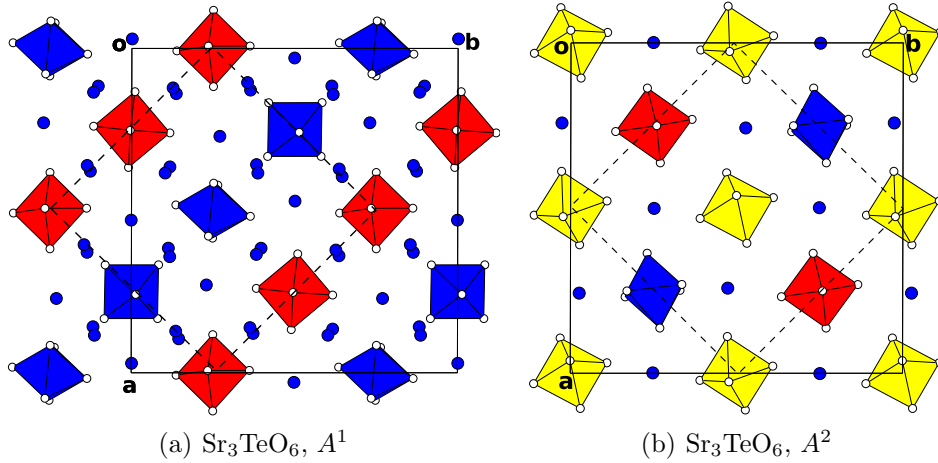


Figure 5.7: Two kinds of pseudo-square packed layers in the actual structure of Sr_3TeO_6 parallel to (001) projected along $[001]$. (a) A^1 , $\frac{1}{8} < z \leq \frac{3}{8}$, idealized symmetry $p112/m$, actual symmetry $p\bar{1}$. (b) A^2 , $-\frac{1}{8} < z \leq \frac{1}{8}$, $p\bar{1}$. The projection of the unit cell of Sr_3TeO_6 is represented by continuous, the unit cell of the layers by dashed lines. Colours and symbols as in Fig. 5.6. Symmetry element symbols have been omitted for clarity.

other (A^2) has no mirror plane and symmetry $p\bar{1}$. The deviations of the actual structure atoms in layer A^1 from the idealized positions are less than 0.3 Å. In consequence, Sr_3TeO_6 can be alternatively described as a category IV order/disorder(OD)-structure with more than one kind of layer, whose OD groupoid symbol reads as

$$\begin{array}{cc} A^1 & A^2 \\ p112/m & p\bar{1} \\ [\frac{1}{4}, \frac{1}{4}] & \end{array}$$

according to the notation devised by Dornberger-Schiff and Grell (1982). No streaking of reflections in pseudo-precession images reconstructed from CCD data was observed, therefore no disorder in the stacking direction could be detected. Yet the OD description is a plausible explanation of the observed twinning.

Ba_3TeO_6

Ba_3TeO_6 has tetragonal symmetry ($I4_1/a$). The threefold rotation axes of the cubic aristotype are lost and fourfold rotation axes only remain in the $[001]_a$ direction. The mirror planes parallel to directions $\{100\}_a$ and $\{110\}_a$ are lost as well, therefore the actual structure can be derived from Sr_2CuWO_6 ($I4/m$) (Fig. 5.4, right) (Bock and Müller, 2002).

Due to the unique direction $[001]_a$, it is reasonable to describe Ba_3TeO_6 as a stacking of equivalent layers composed of two-dimensional pseudo-square packings of $[\text{TeO}_6]$ units parallel to $(001)_a$ (Fig. 5.8). The layers have symmetry $p112$ and contain five crystallographically different $[\text{TeO}_6]$ units of which three are oriented as in the aristotype (Te3–Te5), whereas the other two are rotated by $\approx 45^\circ$ around $[001]_a$ (Te1) and $[100]_a$ or $[010]_a$ (Te2). Since the Ba atoms are close to their position in the aristotype and the $[\text{TeO}_6]$ octahedra are pseudo-symmetric by mirroring at $(001)_a$, the layers can be idealized as having symmetry $p112/m$. Only the O atoms which are part of the $[\text{Te1O}_6]$ unit show significant deviations from this idealized symmetry with a distance of up to 0.25 Å from the idealized positions. All other atoms deviate by less than 0.13 Å. Two consecutive layers are related alternately by inversion and $\bar{4}$ symmetry (Fig. 5.9).

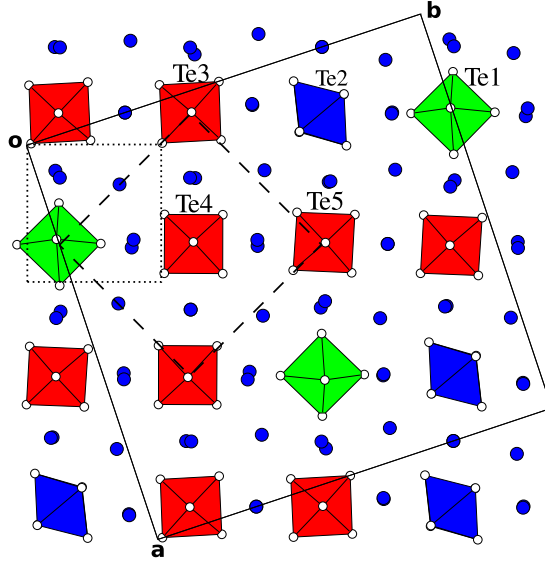


Figure 5.8: Layer of $[\text{TeO}_6]$ octahedra and Ba^{2+} ions in Ba_3TeO_6 parallel to (100) with $-0.02 \leq x \leq 0.14$. For better visibility the $[\text{TeO}_6]$ octahedra are coloured according to orientation: Octahedra oriented similarly to the corresponding octahedra in the aristotype (Te3–Te5) are red, Te1 and Te2 are green and blue, respectively. Other atom colour codes as in Fig. 5.2. Unit cells as in Fig. 5.5. The continuous, dashed and dotted lines correspond to the unit cells stated in Fig. 5.5.

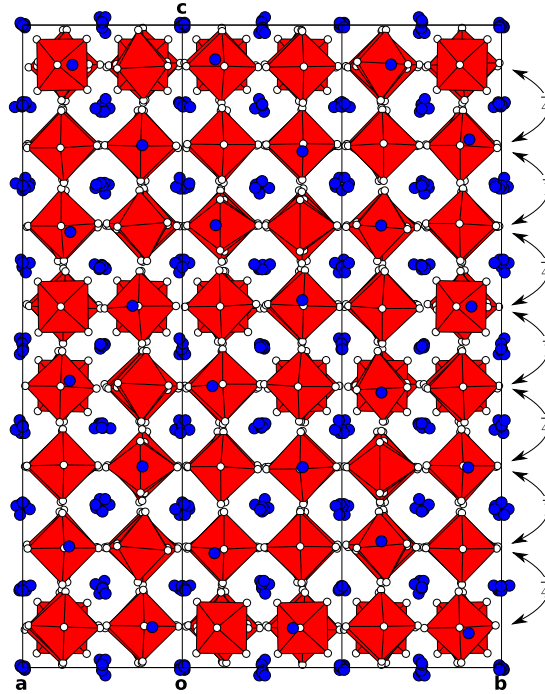


Figure 5.9: Stacking of pseudo-square packed layers of $[\text{TeO}_6]$ octahedra parallel to (001) in Ba_3TeO_6 projected along $[210] \equiv [100]_a$. Arrows on the right indicate the symmetry operation which relates two adjacent layers. Colour codes as in Fig. 5.2.

5.1.8 Sr_3TeO_6 and Ba_3TeO_6 obtained by solid-state reaction

Sr_3TeO_6 and Ba_3TeO_6 were obtained by reaction of equimolar stoichiometric amounts of MCO_3 and TeO_2 under varying conditions as microcrystalline materials and subjected to XRPD analysis. The XRPD patterns of both compounds are complex. The major reflections correspond well to those of the corresponding compounds obtained from halide fluxes (Fig. 5.10). The basic structure can therefore likewise be assumed to be a double perovskite derivative. The minor reflections, on the other hand, differ distinctly from those of the compounds obtained from fluxes. The superstructures of compounds obtained by solid-state reaction and from fluxes therefore are different.

5.2 MgTeO_8H_8

5.2.1 Preparation

Crystals of the MgTeO_8H_8 were grown using a gel diffusion technique in gelatin. Three gelatin sheets (*ca.* 4.5 g) were dissolved in a solution of 4.34 g 85% KOH and 7.89 g H_6TeO_6 in 300 ml water. 25 ml of the solution were introduced into a large test tube. After solidification, the gel was covered with 10 ml of a neutral gelatin solution, prepared by dissolving one gelatin sheet (*ca.* 1.5 g) in 100 ml water. After solidification of the second gelatin layer, it was covered with 10 ml of a 0.5% Mg^{2+} solution, obtained by dissolving 4.16 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 ml water. The test tube was sealed with plastic film and kept at 295 K for one month. Crystals of the MgTeO_8H_8 had formed at the interface of both gelatin layers. The gel was cut with a scalpel and crystals with an adequate size for single crystal diffraction were isolated under a polarizing microscope (Fig. 5.11).

5.2.2 Data collection

The diffraction images showed diffuseness of reflections in one direction, but distinct maxima could be located which were indexed using a tetragonal *I*-centred lattice. Data were reduced using the SAINT software (Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2007). Absorption correction was performed using a multi-scan approach with SADABS (Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2007). Details of the single crystal data collection and the refinement are summarized in Tab. 5.7.

5.2.3 Structure refinement

The structure of MgTeO_8H_8 was solved and refined using the SHELX software package (Sheldrick, 2008). The *M* (*M* = Mg, Te) atoms were located using direct methods. The O atoms were located in subsequent difference Fourier maps. The H atoms could not be located from the diffraction data since the parent O atoms are disordered. All atoms were refined using anisotropic ADPs.

One O atom (O3) was refined as disordered around a mirror plane with occupation $\frac{1}{2}$. By introducing occupational disorder of the *M* positions (each position was refined as containing atoms of the other type), the reliability factors could be improved significantly from $R[I > 2\sigma(I)] = 0.035$ to 0.022. The total occupation of each *M* position and the total Te:Mg ratio were constrained to 1. Atoms located on the same position were constrained to the same ADP.

No unusual electron density was apparent in the difference Fourier map of the last refinement cycle. Atomic coordinates and isotropic ADPs are listed in Tab. C.39.

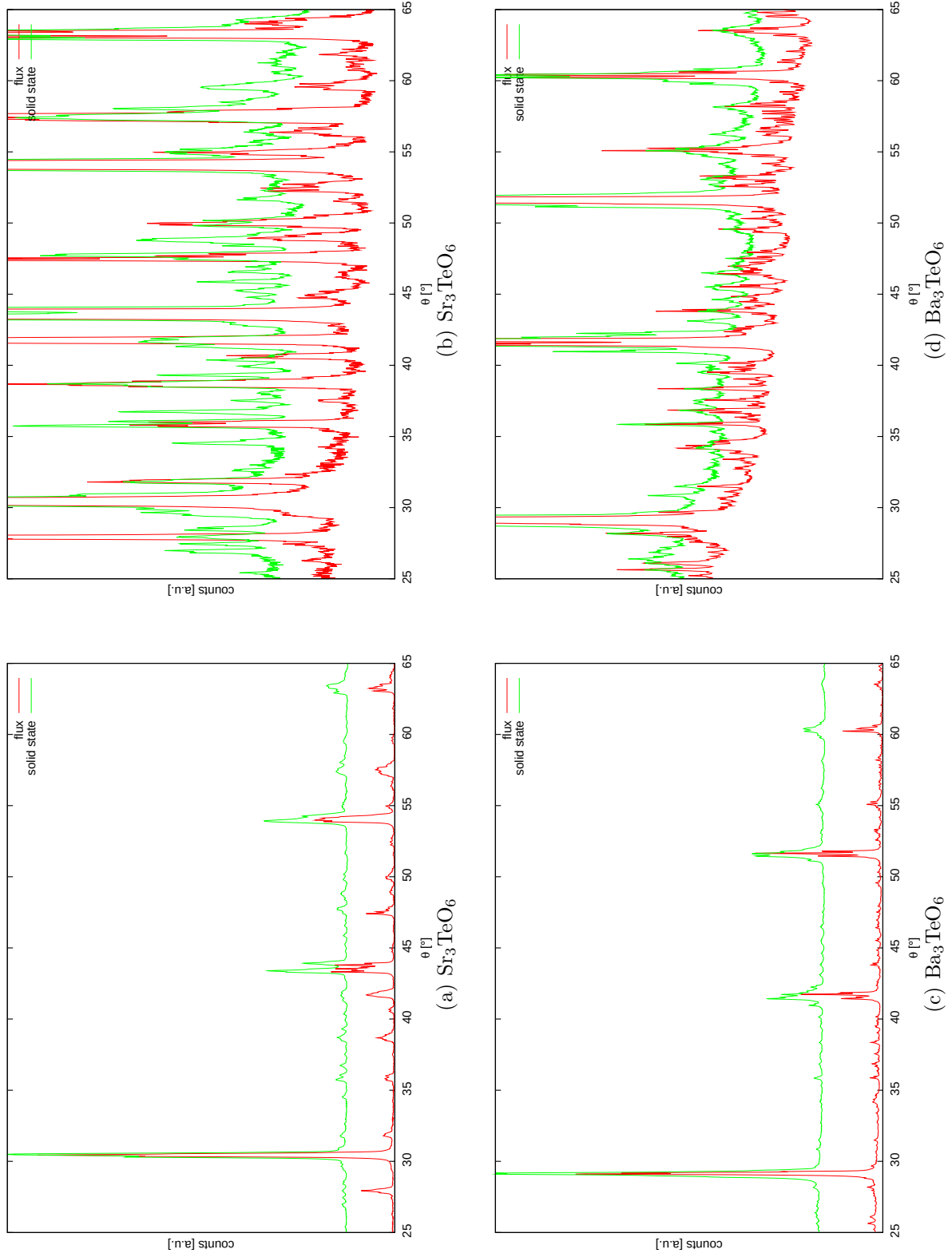


Figure 5.10: Comparison of the XRPD patterns in the range $25^\circ < 2\theta < 65^\circ$ of (a,b) Sr_3TeO_6 and (c,d) Ba_3TeO_6 samples obtained from fluxes (red lines) and solid state reactions (green lines). In (a) and (c) an overview is given showing similarity of the basic structure reflections for samples obtained by both methods. In (b) and (d) the distinctly different satellite reflections are enlarged.

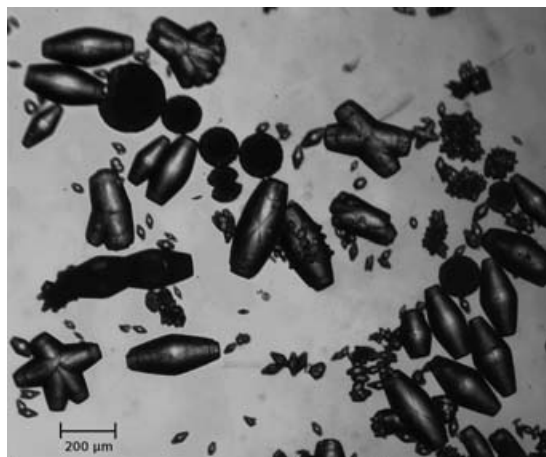


Figure 5.11: Micrograph of MgTeO_8H_8 crystals with characteristic shape.

Table 5.7: Crystal data and details of the refinements of MgTeO_8H_8 .

MgTeO_8H_8	
Crystal data	
Chemical formula	MgTeO_8H_8
M_r	486.46
Cell setting, space group	Tetragonal, $I4_1/amd^{(2)}$
Temperature [K]	295(2)
a, c [Å]	5.32910(10), 20.6765(4)
V [Å ³]	587.198(19)
Z	4
D_x [Mg·m ⁻³]	3.166
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	5.167
Crystal form, colour	square bipyramid, clear colourless
Crystal size [mm]	$0.22 \times 0.15 \times 0.15$
Data collection	
Diffractometer	SMART APEX II
Data collection method	ω and ϕ scans
Absorption correction	<i>SADABS</i>
T_{min}, T_{max}	0.3961, 0.5112
No. of measured, independent and observed reflections	7344, 467, 422
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.036
θ_{max} [°]	39.1
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.022, 0.063, 1.48
No. of reflections	467
No. of parameters	23
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 0.9527P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.003
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	0.96, -1.76

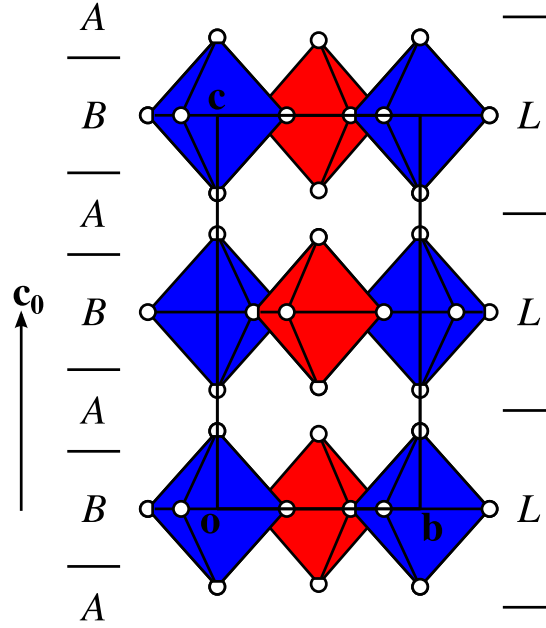


Figure 5.12: The MDO_2 polytype of MgTeO_8H_8 ($Pcnn$) viewed down $[100]$. $[\text{MgO}_6]$ and $[\text{TeO}_6]$ octahedra are red and blue, O atoms are white. Layer names according to the non-OD and the OD description are indicated to the right and left, respectively.

5.2.4 Crystal structure

Overview

MgTeO_8H_8 is a polytypic structure composed of distinct crystallochemical layers. The crystallochemical layers do not fulfill the vicinity condition of OD theory (Dornberger-Schiff and Grell-Niemann, 1961), since pairs of layers can appear in non-equivalent ways. This kind of compound has been called non-OD polytypic by Ferraris et al. (2004). An alternative choice of layers, disregarding crystallochemical considerations, leads to a description of MgTeO_8H_8 following OD theory. Ferraris et al. (2004) argue against such artificial „slicing” of crystallochemical layers to obtain OD layers, especially if one type of OD layers obtained is purely anionic or cationic and information on coordination polyhedra is lost.

In the case of MgTeO_8H_8 , both approaches are useful and will be described in the following sections. In Fig. 5.12 both layer choices are illustrated for one possible polytype: crystallochemical layers, which will henceforth be called L , are non-OD layers. These layers will be used to describe the chemical coordination of the structure units. In order to obtain an OD model, the structure is described as being composed of two layers A and B , which make up the central parts of the crystallochemical layers L and the interface between two adjacent layers L , respectively. The OD approach emphasizes the similarity of the interface between the crystallochemical (non-OD) layers in any polytype and thus plausibly explains the high stacking fault probability. Furthermore, it permits application of OD theory for the determination of stacking possibilities, determination of MDO polytypes and the explanation of features in the diffraction pattern, as these have not been fully worked out for non-OD structures yet.

In the following discussion, layer group symbols will be given using five placed symbols as devised by Dornberger-Schiff and Grell-Niemann (1961). Symmetry elements are given subsequently in $[100]$, $[010]$, $[001]$, $[110]$ and $[1\bar{1}0]$ directions. The direction of missing translational symmetry is indicated by parentheses. For reasons of brevity, symmetry elements will be given

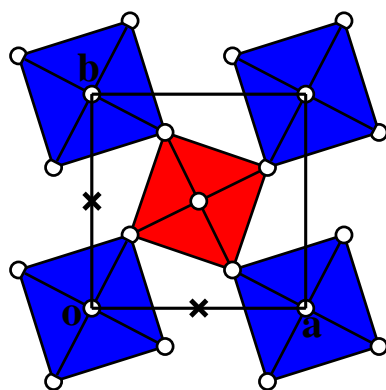


Figure 5.13: Crystallochemical layer L in MgTeO_8H_8 with symmetry $p11(4/m)11$ viewed down $[001]$. Atom colour codes as in Fig. 5.12. Crosses indicate the possible origins of adjacent layers.

Table 5.8: Selected atomic distances d and angles in the actual structure of MgTeO_8H_8 .

Atoms	d [Å]	Atoms	angle [°]
Te1–O1	1.973(3) (2×)	O1–Te1–O1	180
Te1–O3	1.906(3) (4×)	O1–Te1–O3	89.03(9)
Mg2–O2	2.047(3) (2×)	O3–Te1–O3	90.017(3)
Mg2–O3	2.062(3) (4×)	O3–Te1–O3	178.05(17)
O1–O1	2.932(3) (2×)	O2–Mg2–O2	180
O1–O2	2.902(2) (2×)	O2–Mg2–O3	89.10(8)
O2–O2	2.874(3) (2×)	O3–Mg3–O3	90.014(3)
O3–O3	2.532(7)	O3–Mg3–O3	178.20(16)

using only three placed symbols, as introduced by Ferraris et al. (2004). Thus $[m - -]$ and $[- - m]$ represent mirror planes normal to $[100]$ and $[001]$, respectively. Space groups will be given using their usual three placed symbols as defined in the *International Tables vol. A* (Hahn, 1983).

Description according to crystallochemical layers

MgTeO_8H_8 is composed of a stacking of distinct crystallochemical layers L normal to $[001]$ with symmetry $p11(4/m)11$, lattice basis vectors $\mathbf{a}$ and $\mathbf{b}$ and third basis vector $\mathbf{c}_0$. Layers L are composed of corner sharing, close to regular $[MO_6]$ ($M = \text{Mg}, \text{Te}$) octahedra forming an infinite two dimensional network (Fig. 5.13). The octahedra are located on sites with symmetry $4/m$ and rotated in opposite direction around $[001]$, thus leaving rhomboidal voids with long and short diameter of ≈ 5.0 and ≈ 2.5 Å. The M positions are alternately occupied with Mg and Te^{IV} atoms. The $[\text{MgO}_6]$ octahedra are slightly larger than the $[\text{TeO}_6]$ octahedra with an average Mg–O distance of 2.057 Å compared to the average Te–O distance of 1.953 Å. Selected distances and angles in the actual structure are compiled in Tab. 5.8.

The rigid conformation of the octahedral $[\text{Te}^{\text{IV}}\text{O}_6]$ anion and the determined Te–O distances are characteristic and have been observed for numerous oxotellurates(VI). Reviews on the crystal chemistry of these compounds were given by Kratochvíl and Jenšovský (1986); Loub (1993); Levason (1997). Octahedral coordination is the most common coordination of Mg atoms and the average Mg–O distance of 2.057 Å compares well to the maximum of the distribution of Mg–O distances of 2.1 Å given in a survey on Mg–O coordination polyhedra (Blatov et al., 1999).

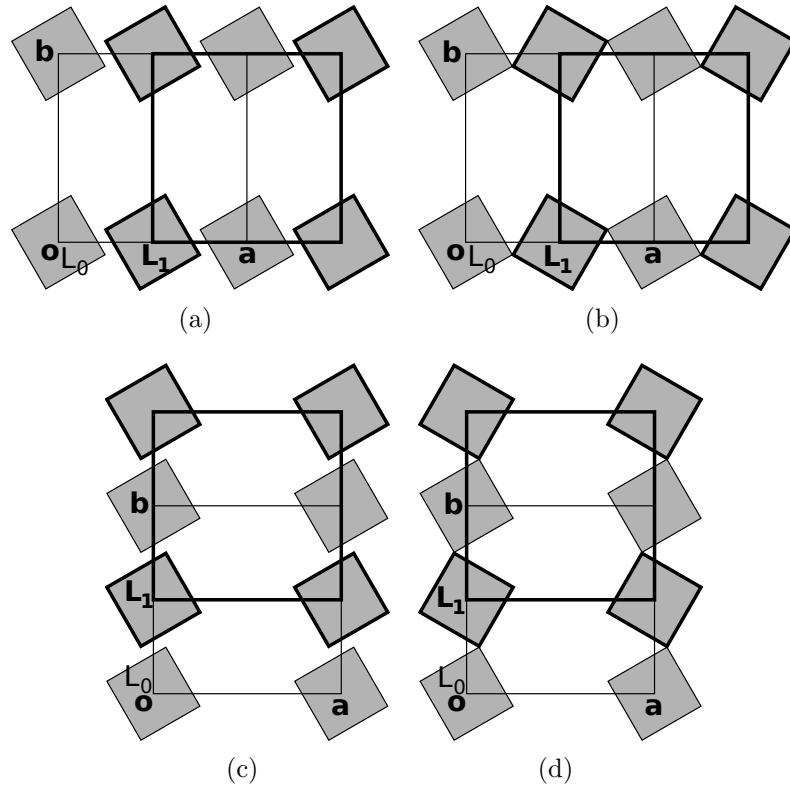


Figure 5.14: Schematic representation of the stacking possibilities of two adjacent layers L_0 and L_1 in MgTeO_8H_8 . Grey squares are symmetric by mirroring at (001) . Thin lines represent layer L_0 , thick lines layer L_1 . In (a) and (b) the origins of layers L_0 and L_1 are related by a translation along $\frac{1}{2}\mathbf{a} + \mathbf{c}_0$, in (c) and (d) by a translation along $\frac{1}{2}\mathbf{b} + \mathbf{c}_0$. In (a) and (c) layers L_0 and L_1 have the same orientation with respect to $[100]$, in (b) and (d) they have different orientation.

The origin of layer L_{n+1} is related to the origin of an adjacent layer L_n by a translation of $\frac{\mathbf{a}}{2} + \mathbf{c}_0$ or $\frac{\mathbf{b}}{2} + \mathbf{c}_0$ as indicated in Fig. 5.13. Additionally, each layer L can appear in two orientations related by a mirror plane normal to $[100]$ (or equivalently $[010]$). All four stacking possibilities are schematized in Fig. 5.14. The described structure is non-OD polytypic, since pairs of adjacent layers in which layers have the same orientation with respect to $[100]$ (Fig. 5.14 (a,c)) and layer pairs in which both layers are oriented differently (Fig. 5.14 (b,d)) are not equivalent.

BVS are a useful tool to estimate the position of H atoms which cannot be located unambiguously using XRD (Donnay and Allmann, 1970). In the ideal case, the oxygen atoms of H_2O molecules, OH^- ions and O^{2-} ions have total BVS of 0, 1 and 2 v.u., respectively. Deviations from these ideal BVS give information on hydrogen bonding. Bond valence calculations with $v_i = \exp(\frac{R_o - R_i}{b})$ (Brown, 2002) with the parameters $R_o = 1.693 \text{ \AA}$, $b = 0.37$ for Mg-O , $R_o = 1.917 \text{ \AA}$, $b = 0.37$ for Te-O , and $R_o = 1.500 \text{ \AA}$, $b = 0.35$ for O-O (Brese and O’Keeffe, 1991) result in BVS of 0.91 v.u. (O1), 0.48 v.u. (O2) and 1.44 v.u. (O3). These values have been obtained by considering that O1 is connected to $(1-x)$ Te atoms and x Mg atoms and *vice versa* for atom O2 with $x = 0.06$. Thus, a small error is introduced, since the $M\text{-O}$ distance is a weighted arithmetic average of the Mg-O and Te-O distances, but bond valences depend exponentially on interatomic distance.

These BVS strongly suggest that the Mg atoms are connected to two water molecules and

the Te atoms to two hydroxyl (OH^-) anions with the H atoms directed towards the adjacent layers. The remaining two H atoms per formula unit are connected to one out of two O3 atoms, amounting to one per rhomboidal void. Thus the composition of the compound can be written as $(\text{MgTeO}_2(\text{OH})_4(\text{H}_2\text{O})_2)$. This is in agreement with crystallochemical considerations and corresponds to an electronically neutral structure.

The large bond valence sum of 0.44 for the H_2O atom compared to the expected value of 0 can be explained by the protons of the water molecules being involved in hydrogen bonds. Indeed, the distances between close O atoms (O1–O1: 2.932(3) Å, O1–O2: 2.902(2) Å, O2–O2: 2.874(3) Å, O3–O3: 2.532(7) Å) strongly suggest formation of intra- and interlayer $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Gilli and Gilli, 2009).

OD structure of two kinds of layers

By „slicing” MgTeO_8H_8 into cationic and purely anionic layers, it can be described as a tetragonal category IV OD-structure of two types of apolar layers *A* and *B* (Fig. 5.12) with the same lattice basis vectors **a** and **b** as the crystallochemical layers *L*.

The OD-groupoid family symbol reads as

$$\begin{array}{cc} A & B \\ cmm(4/e)mm & p11(4/m)11 \\ [0,0] \end{array}$$

according to the notation of Grell and Dornberger-Schiff (1982). Layer names¹ deviating from the layer notation used by Grell and Dornberger-Schiff (1982) have been chosen for clarity. The unusual setting $cmm(4/e)mm$ for layer *A* was chosen over the standard setting $pmm(4/n)mm$ so that layers *A* and *B* share the same lattice basis vectors (Grell and Dornberger-Schiff, 1982).

The order of the group of λ - τ -POs of a layer *A* is $N = |G| = |cmm(4)mm| = 16$. The order of the group of those POs, which are also valid for an adjacent layer *B* is $F = |p11(4)11| = 4$. Therefore, according to the NFZ relationship (Đurovič, 1997) given a layer *A*, an adjacent layer of type *B* can appear in $Z = N/F = 4$ orientations. Every λ - τ -PO of a layer *B*, on the other hand, is also a PO of an adjacent layer *A* and therefore given a layer *B*, the position of the adjacent layers *A* is fixed.

A layer *A* is related to the next layer *A* by the $[- - m]$ PO of the intermediate layer *B*. A layer *B* is related to the next layer *B* by either one of the four POs: $[2 - -]$, $[-2 -]$, $[n_{1,2} - -]$ or $[-n_{2,1} -]$ of the intermediate layer *A*. Continuous application of these operations can generate four non-equivalent polytypes with a maximum degree of order (Dornberger-Schiff and Grell, 1982):

- MDO₁: ... $[n_{1,2} - -]$..., $B112/m$, **c** = $2\mathbf{c}_0$
- MDO₂: ... $[2 - -]$..., $Pcnm$, **c** = $2\mathbf{c}_0$
- MDO₃: ... $[n_{1,2} - -]$ $[-n_{2,1} -]$, $I4_1/a$, **c** = $4\mathbf{c}_0$
- MDO₄: ... $[2 - -]$ $[-2 -]$..., $I\bar{4}2d$, **c** = $4\mathbf{c}_0$

Atom coordinates of the MDO polytypes are listed in Tab. 5.9.

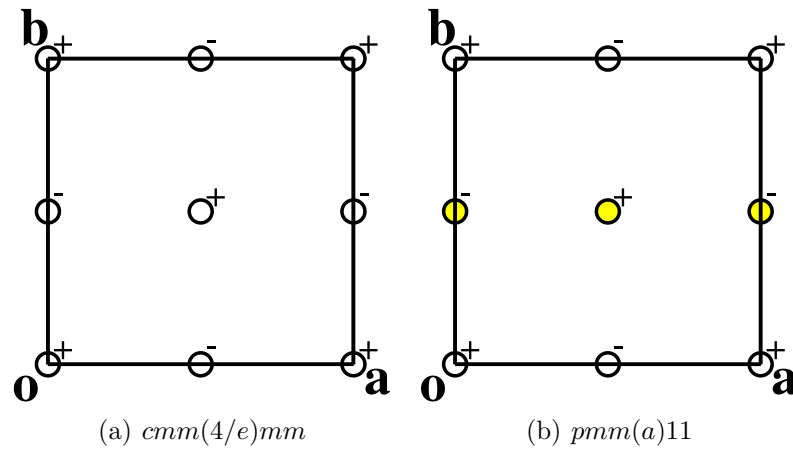
Layers *A* contain one crystallographically unique O atom located at the fourfold axes at $(0, 0, z)$ and $(\frac{1}{2}, \frac{1}{2}, z)$ (Fig. 5.15(a)).

Layers *B* consist of one crystallographically unique Mg and one Te atom located at the $4/m$ sites at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively and one O atom located on the mirror plane at $z = 0$, thus forming MgO_4 and TeO_4 squares (Fig. 5.16(a)).

¹ According to Grell and Dornberger-Schiff (1982), layers *A* and *B* would be called A^1 and A^2 , respectively.

Table 5.9: Site symmetry and fractional coordinates in the MDO polytypes of MgTeO_8O_6 .

Atom	Site symmetry,	x	y	z
MDO ₁ ($B112/m$, $\mathbf{c} = 2\mathbf{c}_0$)				
Te	$\frac{1}{2}$	$\frac{1}{2}$	0	
Mg	0	0	0	
O1	$\frac{1}{2}$	$\frac{1}{2}$	0.1908	
O2	0	0	0.1978	
O3a	0.3424	0.1787	0	
O3b	0.1787	0.6576	0	
MDO ₂ ($Pcnm$, $\mathbf{c} = 2\mathbf{c}_0$)				
Te	$\frac{1}{2}$	$\frac{1}{2}$	0	
Mg	0	0	0	
O1	$\frac{1}{2}$	$\frac{1}{2}$	0.1908	
O2	0	0	0.1978	
O3a	0.3424	0.1787	0	
O3b	0.1787	0.6576	0	
MDO ₃ ($I4_1/a^{(2)}$, $\mathbf{c} = 4\mathbf{c}_0$)				
Te	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{1}{8}$	
Mg	0	$\frac{1}{4}$	$\frac{1}{8}$	
O1	$\frac{1}{2}$	$\frac{3}{4}$	0.2204	
O2	0	$\frac{1}{4}$	0.2239	
O3	0.1787	0.5924	$\frac{1}{8}$	
MDO ₄ ($I\bar{4}2d$, $\mathbf{c} = 4\mathbf{c}_0$)				
Te	$\frac{1}{2}$	$\frac{1}{2}$	0	
Mg	0	0	0	
O1	$\frac{1}{2}$	$\frac{1}{2}$	0.0954	
O2	0	0	0.0989	
O3	0.1787	0.3424	0	

**Figure 5.15:** OD layer A in MgTeO_8H_8 (a) without and (b) with differentiation of OH^- and H_2O groups. O atoms are represented by white spheres or yellow spheres if being part of a water molecule. „+” and „-” symbols mark atoms located above and below the drawing plane, respectively.

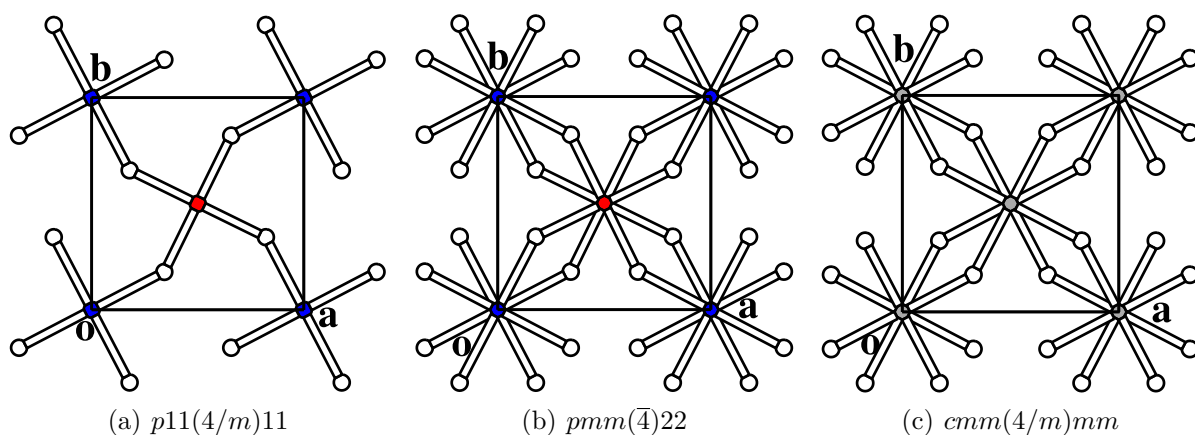


Figure 5.16: (a) OD layer B in MgTeO_8H_8 with symmetry $p11(4/m)11$ and superpositions of layer B as found (b) in the actual structure, symmetry $pmm(\bar{4})22$ and (c) in the family structure, symmetry $cmm(4/m)mm$. Te, Mg and O atoms are represented by red, blue and white spheres. 1:1 overlaps of Mg and Te atoms are represented by grey spheres. In (c) the coordinates of the O atom have been idealized to fulfill the equation $x + y = 0.5$.

Alternative OD-description considering H atoms

The OD groupoid family given in sec. 5.2.4 was obtained under the assumption that the O atoms in layer A are equivalent. In sec. 5.2.4 it has been shown that Mg most probably connects to water and Te to OH^- ions. By differentiating between both kinds of O atoms the symmetry of layers A is reduced from $cmm(4/e)mm$ to $pmm(a)11$ or $pmm(b)11$ (Fig. 5.15(b)). The corresponding OD groupoid family symbol therefore reads as

$$\begin{array}{cc} A & B \\ pmm(a)11 & p11(4/m)11 \\ [0, 0] & \end{array} .$$

As opposed to the description of sec. 5.2.4, given a layer B , and adjacent layer A can appear in two orientations, related by a $[- - 4]$ operation. The polytypes of both descriptions differ only in the location of the H atoms in layers B . Since the H atoms could not be located using XRD, both descriptions are equivalent from a crystallographical point of view and the simpler description given in sec. 5.2.4 seems favourable.

Family structure

The family structure of MgTeO_8H_8 has symmetry $F4/mmm$ with $\mathbf{c} = 2\mathbf{c}_0$. Layers A in the family structure are unchanged compared to the idealized description, since all POs of layers B are valid for the whole structure (*i.e.* are full operations). The symmetry of layers B , on the other hand, is complemented by mirror planes of layer A normal to $\langle 100 \rangle$ and $\langle 110 \rangle$, resulting in symmetry $cmm(4/m)mm$ (Fig. 5.16(c)).

Actual structure

The crystal under investigation has been refined as a superposition of MDO_1 , MDO_2 , MDO_3 and MDO_4 with approximate ratio 3:3:47:47 resulting in a structure with averaged symmetry $I4_1/amd$ and basis vector $\mathbf{c} = 4\mathbf{c}_0$.

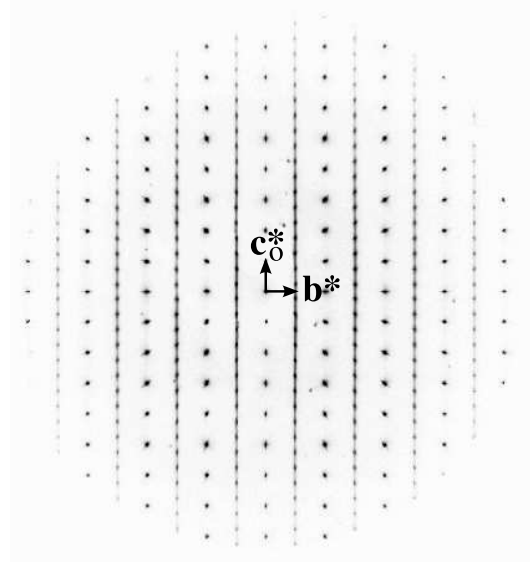


Figure 5.17: $(2kl)^*$ plane in reciprocal space of MgTeO_8H_8 reconstructed from CCD data showing intense streaking of reflections with $h + k = 2n + 1$, $n \in \mathbb{Z}$ along $\mathbf{c}_0^*$.

The symmetry of layers A is reduced from $cm\bar{m}(4/e)mm$ in the idealized description to $pmm(a)11$ or $pmm(b)11$ in the actual structure. Fourfold rotational symmetry as well as mirror symmetry parallel to $\{110\}$ and translational symmetry is lost.

Layers B show at the same time increased symmetry and desymmetrization. They have been refined as a superposition of two idealized layers B related by $[m - -]$. Such a superposition has increased symmetry $pmm(4/m)mm$ compared to symmetry $p11(4/m)11$ of a single layer. Due to desymmetrization, in the actual structure the fourfold rotation of this layer group is only retained as $\bar{4}$ rotoinversion and mirror symmetry parallel to $\{110\}$ is lost. The remaining symmetry of layers B in the actual structure is $pmm(\bar{4})22$.

The existence of 3% MDO_1 and 3% MDO_2 is evidenced by Mg positions containing $\approx 6\%$ of Te and *vice versa*. It has to be noted that this feature in the refinement could also be explained by occupational disorder of the M positions or by stacking faults of rods in layers B . Yet the explanation in terms of the OD theory given above seems to be the most plausible one, given the high stacking fault probability.

Features of the diffraction patterns

An important result of OD theory states that the family reflections (*i.e.* those reflections common to all polytypes) are always sharp, whereas the characteristic reflections (*i.e.* which are only generated by certain polytypes), are either sharp if the polytypes are ordered or diffuse if they show disorder (Ferraris et al., 2004).

Indeed, in pseudo-precession images reconstructed from CCD data, the family structure reflections, corresponding to the reflections (hkl) (indexed with $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}_0^*$) with $h + k = 2n$, $n \in \mathbb{Z}$ and $l = \frac{1}{2}h + n_l$, $n_l \in \mathbb{Z}$, are sharp. For rows in reciprocal space with $h + k = 2n + 1$, $n \in \mathbb{Z}$, on the other hand, pronounced streaking in $\mathbf{c}^*$ direction is observed, indicating strong disorder in the layer stacking normal to (001) (Fig. 5.17).

The diffraction pattern shows a second phenomenon common in OD-structures, *viz.* the occurrence of systematic non-crystallographic absences: Reflections (hkl) with $h + k = 2n$, $n \in \mathbb{Z}$ are extinct with the exception of the family reflections. Calculations (sec. B.2) show that this

Table 5.10: Average and maximum intensities in a.u. of non-extinct ($h + l = 4n$) and extinct ($h + l \neq 4n$) reflections in a simulated diffraction pattern of the MDO₃ polytype of MgTeO₈H₈.

Reflections	I_{avg} [a.u.]	I_{max} [a.u.]
$h + l = 4n$	35.01	1000.00
$h + l \neq 4n$	0.01	1.19

extinction condition is valid in the general case for the planes $0kl$ and $h0l$ of reciprocal space. It becomes valid for whole reciprocal space if atom O3 is located at a position $x + y = \frac{1}{2}$ in the coordinate system of layer B (sec. B.3). Indeed, atom O3 is located close to such a position with $(x, y) = (0.1787, 0.3424)$. Constraining the coordinates of O3 to $x + y = \frac{1}{2}$ during refinement led to a sharp deterioration of reliability factors. The diffraction pattern of the MDO₃ polytype with the O3 position from the actual structure was simulated using the JANA2006 software package (Petříček et al., 2006) to determine the effect of the small deviation of atom O3 from the idealized position. Tab. 5.10 lists the maximum and average intensities of reflections (hkl) with $h + k = 2n, n \in \mathbb{Z}$ for the non-extinct ($k + l = 4n$) and the extinct ($k + l \neq 4n$) cases. The intensity of the extinct reflections are small, but distinctly non-zero. The extinction condition also becomes valid if the layers B in the OD-description (sec. 5.2.4) are considered as disordered by mirroring at (100) as is the case in the crystals under investigation (sec. B.4).

5.3 Tl₂Te₂O₆

5.3.1 Introduction

During investigations of hydrothermal formation conditions in the $M/\text{Te}/\text{O}$ system, single crystals of the hitherto unknown mixed valent oxotellurate(IV/VI) Tl₂Te₂O₆ were obtained. Attempts to obtain microcrystalline single-phase material by solid state reaction from oxides and carbonates were successful and allowed to obtain data on vibrational spectra and thermal behaviour.

Structurally characterized oxotellurates(IV/VI)

Tl₂Te₂O₆ and the isoformular, isopointal and closely related Ag₂Te₂O₆-III (Weil, 2007) ($P2_1/c$) crystallize with distinct anionic [Te₂O₆]²⁻ and cationic [Ag₂]²⁺ layers. Other isoformular mixed valent Te^{IV/VI} oxo-compounds with a Te^{IV}:Te^{VI} ratio of 1 are Ag₂Te₂O₆-I and -II (Klein et al., 2005). They are both likewise composed of alternating anionic [Te₂O₆]²⁻ and cationic [Ag₂]²⁺ layers. In Tl₂Te₂O₆ and Ag₂Te₂O₆-I and -III [Te^{VI}O₆]-octahedra are condensed to [Te^{VI}O₁₀]-units, in Ag₂Te₂O₆-II they are connected by corners, forming infinite chains. Compounds possessing an anionic layer with the same connectivity as Ag₂Te₂O₆-II are BaTe₂O₆ (Koçak et al., 1979) and (NH₄)HTe₂O₆ (Philippot et al., 1979). In H₂Te₂O₆ (Lindqvist and Moret, 1973a), infinite chains of corner sharing [Te^{IV}O₄]-units are connected by [Te^{VI}O₆]-octahedra *via* corners.

Of the structures with a Te^{IV}:Te^{VI} ratio of 1, but a Te:O ratio $< 1 : 3$, BaCuTe₂O₇ (Sedello and Müller-Buschbaum, 1996) and α - and β -Hg₂Te₂O₇ (Weil, 2003b) have anionic layers, whereas Ag₂Te₄O₁₁ (Klein et al., 2005) and Bi₂Te₂O₈ (Thomas et al., 1996) (disordered), form three dimensional anionic Te–O frameworks perforated by channels in which the cations are located. The only compound with a Te^{IV}:Te^{VI} ratio of 1 and a Te:O ratio $> 1 : 3$ for which a structure has been published is Te₂O₅ (Lindqvist and Moret, 1973b). Its crystal structure can be described as a condensation of the layers of H₂Te₂O₆ to a three dimensional network.

5.3.2 Preparation

Single crystals

130 mg elemental Tl and 172 mg H_6TeO_6 were placed in a 5 ml teflon inlay filled to two thirds with water. The teflon inlay was placed in a steel autoclave and heated for five days at 493 K. After cooling to room temperature the residue was washed with water and acetone. It contained a grey microcrystalline powder, major amounts of single crystalline of $\text{Tl}_2\text{Te}_2\text{O}_6$ and fewer paratellurite single crystals. A suitable $\text{Tl}_2\text{Te}_2\text{O}_6$ crystal was separated under acetone and subjected to single-crystal diffraction.

Microcrystalline material

A ground mixture of 234.4 mg (0.5 mmol) Tl_2CO_3 , 228.4 mg (0.5 mmol) Tl_2O_3 and 319.2 (2 mmol) TeO_2 in an evacuated fused silica ampoule was heated for one week at 723 K. The obtained thermochromic yellow powder was single phase $\text{Tl}_2\text{Te}_2\text{O}_6$, as evidenced by XRPD.

5.3.3 Single crystal diffraction

Intensity data of a $\text{Tl}_2\text{Te}_2\text{O}_6$ crystal was collected in ω -scan mode in three sets of 600 frames with 0.3° scan width. Numerical absorption correction was performed with HABITUS (W. Herrendorf, 1997). Structure solution and refinement was performed with the SHELX (Sheldrick, 2008) program package. The heavy atoms Tl and Te were located using direct methods. The O atoms were found in the difference Fourier maps in subsequent refinement steps. All atoms were refined anisotropically. The highest residual electron peaks in the final Fourier map are close ($\approx 0.8 \text{ \AA}$) to heavy atoms. The conventional setting of the spacegroup $P2_1/c$ was chosen over the reduced cell setting $P2_1/n$ in order to highlight the layered structure and for better comparability of the atom coordinates to the closely related compound $\text{Ag}_2\text{Te}_2\text{O}_6$ -III (Weil, 2007). Relative atomic coordinates and isotropic ADP are listed in Tab. C.40. More details on data collection and refinement are summarized in Tab. 5.11.

5.3.4 Crystal structure

OD interpretation

The structure of $\text{Tl}_2\text{Te}_2\text{O}_6$ ($P2_1/c$, $Z = 4$) belongs to an orthorhombic category IV OD groupoid family composed of an alternative stacking of two non-polar layers *A* and *B* (Fig. 5.18). The OD groupoid family symbol reads as

$$\begin{array}{cc} A & B \\ p(1)2_1/c1 & p(b)cm \\ & [0, s] \end{array}$$

with $s = -0.24$ according to the notation devised by Grell and Dornberger-Schiff (1982). Layer names² deviating from the layer notation used by Grell and Dornberger-Schiff (1982) have been chosen for clarity. Layers *A* (Te1, Te2, O1–O6) and *B* (Tl) have symmetry $p(1)2_1/c1$ and $p(b)cm$, respectively. Atom O6 marks the boundary between both layers.

The group of G of λ - τ -POs of layers *A* and *B* are $p(1)c1$ and $p(2)cm$, respectively. Tab. 5.12 gives an overview of the *NFZ* relationship (Đurovič, 1997) applied to both layers. The *c* glide planes of both layers overlap and therefore, according to the *NFZ* relationship, given a layer

² According to Grell and Dornberger-Schiff (1982) layers *A* and *B* are named A^1 and A^2 , respectively.

Table 5.11: Crystal data and details of the refinements of $\text{Tl}_2\text{Te}_2\text{O}_6$.

$\text{Tl}_2\text{Te}_2\text{O}_6$	
Crystal data	
Chemical formula	$\text{Tl}_2\text{Te}_2\text{O}_6$
M_r	759.94
Cell setting, space group	Monoclinic, $P2_1/c$
Temperature [K]	295(2)
a, b, c [Å]	7.6071(15), 7.1018(14), 13.458(2)
β [°]	114.926(9)
V [Å ³]	659.3(2)
Z	4
D_x [Mg·m ⁻³]	7.656
Radiation type	Mo $K\alpha$
μ [mm ⁻¹]	57.461
Crystal form, colour	block, colourless
Crystal size [mm]	$0.14 \times 0.06 \times 0.02$
Data collection	
Diffractometer	SMART APEX
Data collection method	ω scans
Absorption correction	HABITUS
T_{min}, T_{max}	0.055, 0.376
No. of measured, independent and observed reflections	7032, 1920, 1671
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.056
θ_{max} [°]	30.1
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F)]$, $wR(F^2)$, S	0.028, 0.057, 0.978
No. of reflections	1920
No. of parameters	92
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0230P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ [eÅ ⁻³]	2.089, -2.092
Extinction method	-

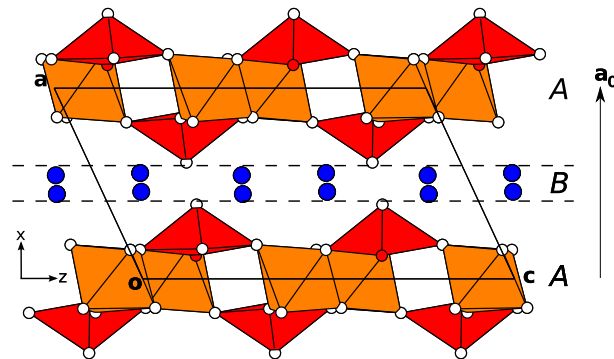


Figure 5.18: Unit cell contents of $\text{Tl}_2\text{Te}_2\text{O}_6$ projected along $[010]$. Tl atoms are represented by blue, Te atoms by red and O atoms by white spheres. $[\text{Te}^{\text{VI}}\text{O}_6]$ octahedra and $[\text{Te}^{\text{IV}}\text{O}_{3+1}]$ units are represented by orange and red polyhedra, respectively. Layer names according to the OD description are indicated to the right. The interface between layers is marked by dashed lines.

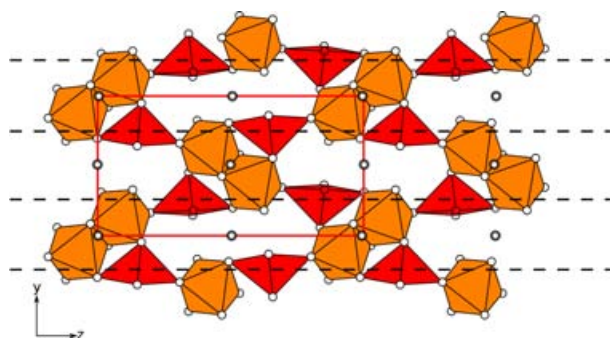


Figure 5.20: Layer *A* in $\text{Tl}_2\text{Te}_2\text{O}_6$ projected on (100). Atom colour codes as in Fig. 5.18.

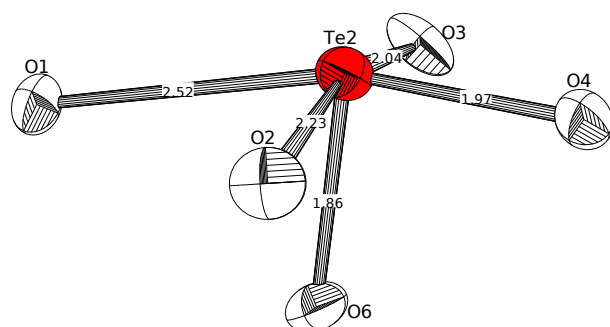


Figure 5.21: Ellipsoid plot of the coordination sphere of Te_2 . Ellipsoids represent 74% probability levels. Bond distances are given in Å, atom colour codes as in Fig. 5.18.

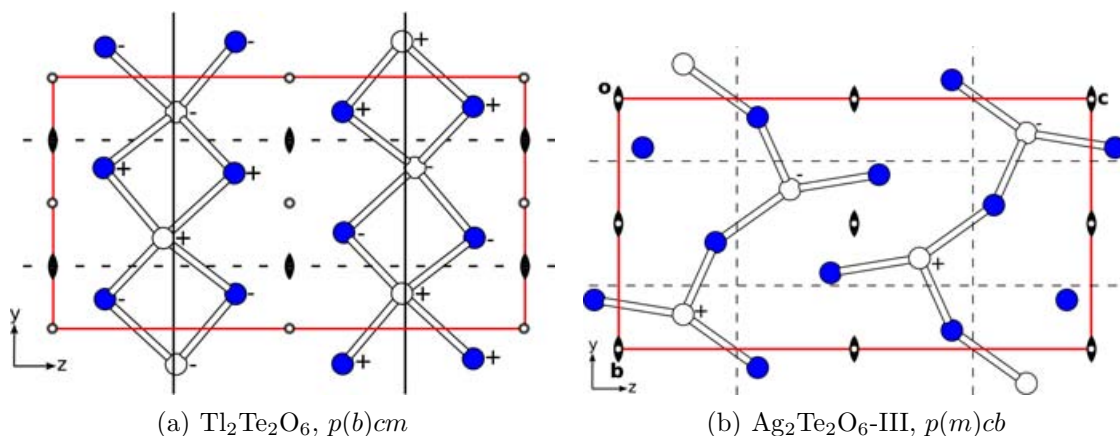


Figure 5.22: Layer *B* in the actual structures of (a) $\text{Tl}_2\text{Te}_2\text{O}_6$ and (b) $\text{Ag}_2\text{Te}_2\text{O}_6\text{-III}$ projected on (100), including oxygen atoms from adjacent layers *A*. Atom colour codes as in Fig. 5.18. Atoms marked with a „+”- and „-”-signs are located above and below the drawing plane, respectively.

2002) for these bonds with the parameters $R_o = 1.977$ Å and $b = 0.370$ result in total BVS of 3.96 v.u. for the Te atom, which is close to the expected value of 4. The fifth O atom contributes 0.23 v.u. or 5.7% to the total BVS.

Layers *B* (Fig. 5.22(a)) with composition $\frac{2}{\infty}[\text{Tl}_2]^{2+}$ contain one crystallographically different Tl atom, which is connected to atom O6 (O6 can be considered being part of layers *A* and *B*), forming infinite chains running along [010] with symmetry $\not\sim(b)2_1(m)$. The electron lone pairs *E* of the Tl^{I} atoms pertrude in the space between the chains.

Actual structure

In the actual structure of $\text{Tl}_2\text{Te}_2\text{O}_6$ only the MDO_1 polytype was observed. Other stacking sequences would result in non-merohedral twinning by mirroring at (001), which could not be detected in precession images reconstructed from CCD-frames.

The symmetry of layers *A* according to the OD description ($p(1)2_1/c1$) is retained in the actual structure. The symmetry of layers *B*, on the other hand, is reduced by a factor of 4 from $p(b)cm$ to $p(1)2_1/c1$. The Tl position in the idealized layers *B* is split into two crystallographic different position Tla and Tlb. The distance of the actual Tl atoms to the idealized position is 0.17 Å.

Comparison with $\text{Ag}_2\text{Te}_2\text{O}_6$ -III

$\text{Ag}_2\text{Te}_2\text{O}_6$ -III (Weil, 2007) ($P2_1/c$) is isopointal and closely related to $\text{Tl}_2\text{Te}_2\text{O}_6$. Using the OD description given above, $\text{Ag}_2\text{Te}_2\text{O}_6$ -III is composed of two non-polar layers *A* and *B* with composition $\frac{2}{\infty}[\text{Te}_2\text{O}_6]^{2-}$ and $\frac{2}{\infty}[\text{Ag}_2]^{2+}$, respectively. Layers *A* are isotypic to the corresponding layers in $\text{Tl}_2\text{Te}_2\text{O}_6$. Due to the significantly different coordination chemistry of Ag^+ and Tl^+ layers *B* are different in both structures (Fig. 5.22(b)). Layer *B* in $\text{Ag}_2\text{Te}_2\text{O}_6$ -III has symmetry $p(m)cb$, the OD groupoid symbol accordingly reads as

$$\begin{array}{cc} A & B \\ p(1)2_1/c1 & p(m)cb \\ & [0, s] \end{array}$$

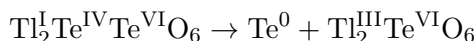
with $s \approx 0$. In the actual structure of $\text{Ag}_2\text{Te}_2\text{O}_6$ -III, the symmetry of layers *B* is reduced to $p(1)2_1/c1$ as in the case of $\text{Tl}_2\text{Te}_2\text{O}_6$. Therefore layers *B* in the actual structures of both compounds are isopointal, but not isotypic. Due to the parameter s being practically 0, the angle β of the actual structure is close to 90° as opposed to 114° in $\text{Tl}_2\text{Te}_2\text{O}_6$.

5.3.5 Vibrational spectroscopy

MIR and Raman spectra of microcrystalline single phase $\text{Tl}_2\text{Te}_2\text{O}_6$ samples were recorded in the spectral region $3000\text{--}550\text{ cm}^{-1}$ and $3000\text{--}50\text{ cm}^{-1}$, respectively. Representative spectra are depicted in Fig. 5.23. Vibrational spectra of compounds in the system Tl/Te/O have been intensely studied (Mirgorodsky et al., 2002; Rieger and Mudring, 2007) (and references therein). The Te–O stretching vibrations of $\text{Tl}_2\text{Te}_2\text{O}_6$ are located in the region of $800\text{--}500\text{ cm}^{-1}$. In the MIR spectrum, they are located at $746, 720, 669$ and 621 cm^{-1} . The corresponding raman active modes are located at $752, 696, 675, 616$ and 586 cm^{-1} . Bands in the region $350\text{--}220\text{ cm}^{-1}$ can be attributed to O–Te–O bending vibrations. In the raman spectrum they can be located at $327, 319, 303$ and 291 cm^{-1} . The bands in the region $220\text{--}120\text{ cm}^{-1}$ correspond to the motion of the heavy atoms (Te and Tl). Lattice dynamic calculations are necessary for a more concise assignement of vibrational modes to the measured spectra.

5.3.6 Thermal behaviour

$\text{Tl}_2\text{Te}_2\text{O}_6$ was subjected to DSC and TG analysis in synthetic air and N_2 atmosphere (Fig. 5.24). At 775 K an irreversible highly exothermic effect takes place. The diffraction pattern of a sample heated for 1 h at 825 K in an evacuated fused silica ampoule showed presence of crystalline Tl^{III} orthotellurate (Tl_2TeO_6) and a broad peak hinting at amorphous components. Therefore the exothermic effect probably corresponds to an internal redox reaction



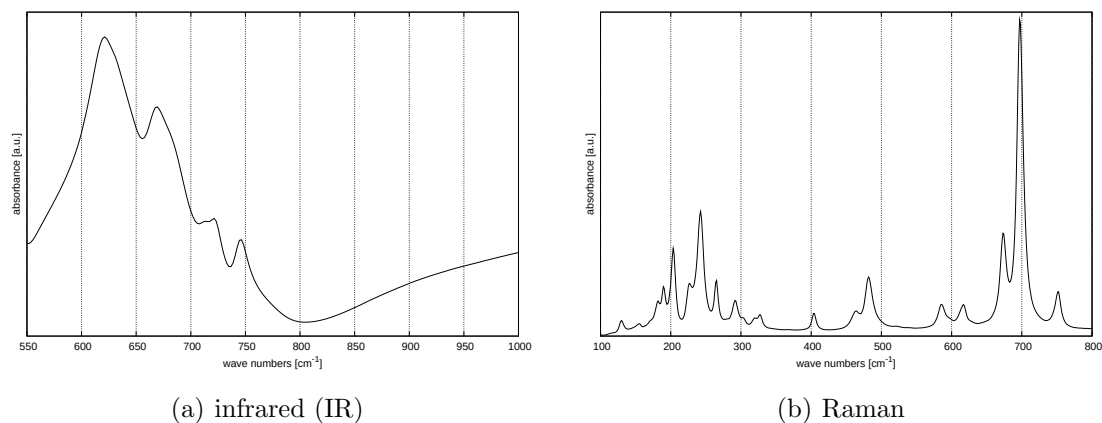


Figure 5.23: (a) IR and (b) Raman spectra of $\text{Tl}_2\text{Te}_2\text{O}_6$ in the spectral range $1000\text{--}550\text{ cm}^{-1}$ and $800\text{--}50\text{ cm}^{-1}$, respectively. The spectra contain no peaks in the non-depicted regions of $3000\text{--}1000$ and $3000\text{--}800\text{ cm}^{-1}$, respectively.

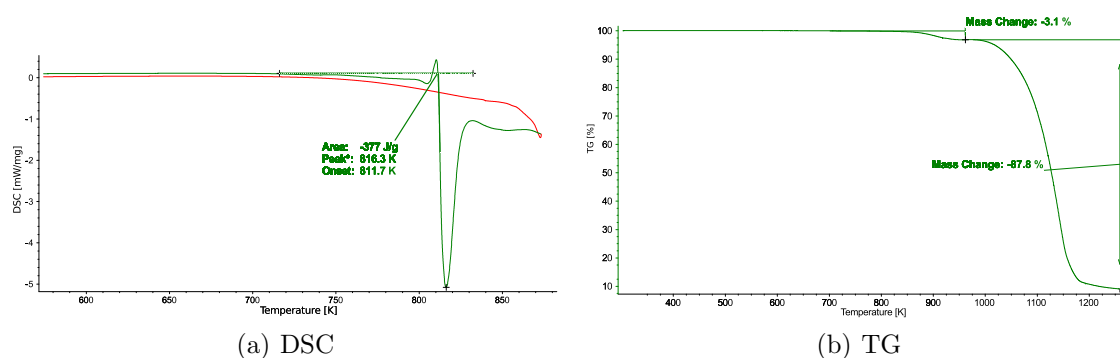


Figure 5.24: (a) DSC and (b) TG measurements of microcrystalline $\text{Tl}_2\text{Te}_2\text{O}_6$ samples under N_2 atmosphere. The heating and cooling curves are represented by red and green lines, respectively.

where both resulting compounds are obtained in amorphous form. On heating beyond the decomposition point, the sample loses mass in two steps ($\approx 3\%$ in the $850\text{--}950\text{ K}$ range and $\approx 88\%$ in the $1000\text{--}1230\text{ K}$ range), most likely due to sublimation of first elemental Te and later TeO_2 .

Chapter 6

Conclusion and outlook

In the course of the present work the hitherto unknown structures of several alkaline earth tellurates(IV) and (VI) were determined. The stable phases in the CaO/TeO_2 and $\text{Ca}_x\text{Sr}_{1-x}\text{TeO}_3$ systems are now well understood (sec. 3). The structures of two metastable polymorphs of CaTeO_3 were elucidated (β - and γ - CaTeO_3 , sec. 3.3.5). So far it is not clear which of these structures, if any, corresponds to the high temperature polymorph of CaTeO_3 as evidenced by thermal analysis. Structure elucidation was unsuccessful due to the high reactivity of these compounds at elevated temperatures. Furthermore, more work will be needed to identify and structurally characterize polymorphs in the CaO/TeO system which are stable under high-temperature and high-pressure conditions. Likewise, the existence and properties of phases in the more general system $\text{CaO}/\text{SrO}/\text{TeO}_2$ with a $\text{Ca}:\text{Sr}$ ration $\neq 1$ have not been established up to now. Preliminary structural investigations on the ditellurates $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ have been performed during this work (sec. 3.5). It has been shown that all stable $\text{Ca}_x\text{Sr}_{1-x}\text{Te}_2\text{O}_5$ phases are superstructures which can be derived from very similar basic structures which can be related by OD theory. It will be interesting to substitute Ca and Sr by Cd in these phases as CdTe_2O_5 belongs to the same class of compounds (Redman et al., 1970).

During the work on anionic modified alkaline earth oxotellurates(IV) the structures of several phases in the $M/\text{Te}/\text{O}/X$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$; $X = \text{Cl}, \text{Br}, \text{OH}^-, \text{NO}_3^-$) system have been determined, although it seems that only a minor amount of phases has been prepared and structurally characterized and thus numerous phases with novel composition and structures are expected in this system. A more thorough investigation will be needed to deepen the understanding of this complex system. The structures of some of the obtained polymorphs are not yet fully elucidated ($\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$, sec. 4.6 and $\text{Ba}_3\text{Te}_2\text{O}_6\text{Br}_2$, sec. 4.10) and complementary methods like chemical analysis, spectroscopic methods, or electron diffraction may be necessary for that purpose. As an alternative to crystal growth under hydrothermal conditions, it has been shown that gel diffusion is a viable technique. It might be used for the synthesis of anionic modified tellurates that are unstable under hydrothermal conditions, like fluorides, cyanides, fluoroborates, *etc.*

The structures of the orthotellurates Sr_3TeO_6 and Ba_3TeO_6 were described as complex heterotypes of the double perovskite aristotype (sec. 5.1). Additional XRPD diffraction experiments showed that at least a second polymorph of each phase exists which can likewise be derived from the double perovskite structure type. Indeed, in preliminary experiments eightfold twinned crystals with a composition of Sr_3TeO_6 were obtained which crystallize in a sixfold superstructure which could not be solved satisfactorily up to now.

A striking observation in the course of this work has been that numerous crystal structures of oxotellurate(IV) phases can be described as OD structures and/or as superstructures. In some cases (*e.g.* $M\text{Te}_2\text{O}_5$, sec. 3.5 or $\text{Sr}_4\text{Te}_4\text{O}_{11}X_2$, sec. 4.2) both descriptions are interdependent, yet

so far no unifying description of both phenomena has been worked out. It seems that additional work on the OD theory of superstructures is warranted. Moreover, due to the difficult and error-prone task of determining OD groupoid families, possible stacking sequences and MDO polytypes, the development of a software routines for the automation of these tasks would be most useful.

Part II

Appendix

Appendix A

Directions in hexagonal OD groupoids

A.1 Introduction

In symbols describing hexagonal OD groupoid families symmetry elements and translational components are indicated with respect to seven directions: $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{c}$, $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ (*c.f.* sec. 1.3.15). In App. A.2 the directions will be expressed in the standard coordinate system for hexagonal layers. In App. A.3 the relationship between relative translational components and the coordinates of a translation vector will be derived.

A.2 Directions

The vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ are coplanar and of length $|\mathbf{a}_n| = |\mathbf{b}_n| = a$. $\mathbf{c}$ is perpendicular to these vectors and of length $|\mathbf{c}| = c$. $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ correspond to the $[100]$, $[010]$ and $[\bar{1}\bar{1}0]$ directions of the standard hexagonal setting. Thus $\widehat{\mathbf{a}_1, \mathbf{a}_2} = \widehat{\mathbf{a}_2, \mathbf{a}_3} = \widehat{\mathbf{a}_3, \mathbf{a}_1} = \frac{2\pi}{3}$. $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are normal to $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$, respectively: $\widehat{\mathbf{a}_1, \mathbf{b}_1} = \widehat{\mathbf{a}_2, \mathbf{b}_2} = \widehat{\mathbf{a}_3, \mathbf{b}_3} = \frac{\pi}{2}$. An overview of the directions is given in Fig. A.1(a).

The coplanar vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ can be expressed using the orthogonal coordinate system $(\mathbf{a}_1, \mathbf{b}_1)$:

$$\mathbf{a}_1 = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (\text{A.1})$$

$$\mathbf{a}_2 = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} \cos \frac{2\pi}{3} \\ \sin \frac{2\pi}{3} \end{pmatrix} = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} -\frac{1}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix} \quad (\text{A.2})$$

$$\mathbf{a}_3 = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} \cos \frac{4\pi}{3} \\ \sin \frac{4\pi}{3} \end{pmatrix} = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} -\frac{1}{2} \\ -\frac{\sqrt{3}}{2} \end{pmatrix} \quad (\text{A.3})$$

$$\mathbf{b}_1 = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (\text{A.4})$$

$$\mathbf{b}_2 = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} \cos \frac{7\pi}{6} \\ \sin \frac{7\pi}{6} \end{pmatrix} = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} -\frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} \quad (\text{A.5})$$

$$\mathbf{b}_3 = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} \cos \frac{11\pi}{6} \\ \sin \frac{11\pi}{6} \end{pmatrix} = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} \quad (\text{A.6})$$

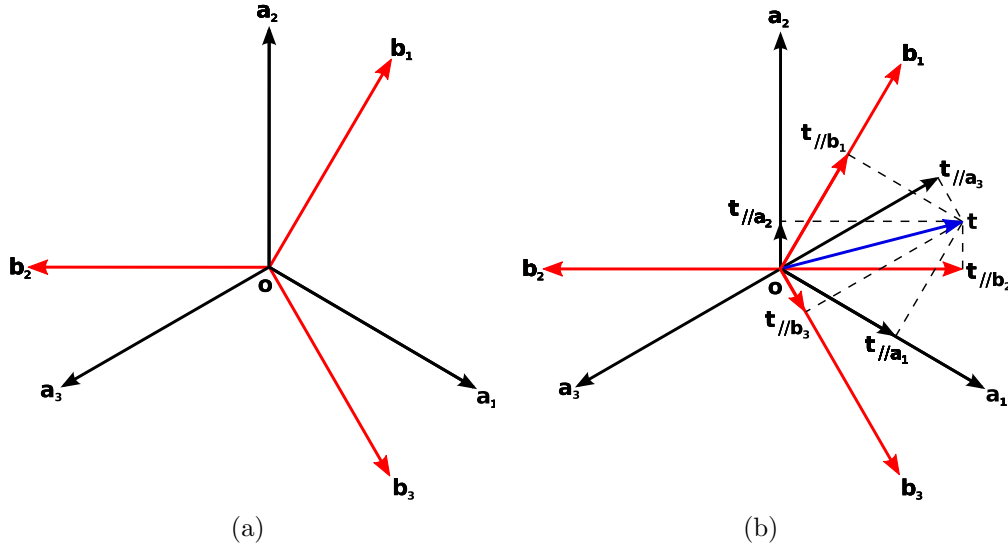


Figure A.1: (a) The coplanar directions $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ used in the notation for hexagonal OD groupoid families. (b) Components parallel to $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ of a translation vector $\mathbf{t}$.

Thus, the standard basis vectors $(\mathbf{a}_1, \mathbf{a}_2)$ used for hexagonal layers are related to the orthogonal basis vectors $(\mathbf{a}_1, \mathbf{b}_1)$ by

$$(\mathbf{a}_1, \mathbf{a}_2) = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix} \quad (\text{A.7})$$

and consequently $(\mathbf{a}_1, \mathbf{b}_1)$ is related to $(\mathbf{a}_1, \mathbf{a}_2)$ by

$$(\mathbf{a}_1, \mathbf{b}_1) = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix}^{-1} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} \end{pmatrix}$$

Substitution of $(\mathbf{a}_1, \mathbf{b}_1)$ by this term in the equations A.1–A.6 above results in:

$$\begin{aligned} \mathbf{a}_1 &= (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \mathbf{a}_2 &= (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ \mathbf{a}_3 &= (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} \\ -\frac{\sqrt{3}}{2} \end{pmatrix} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} -1 \\ -1 \end{pmatrix} \\ \mathbf{b}_1 &= (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{3}} \end{pmatrix} \\ \mathbf{b}_2 &= (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} -\frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} -\frac{2}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \end{pmatrix} \end{aligned}$$

$$\mathbf{b}_3 = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} 1 & \frac{1}{\sqrt{3}} \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix} \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \end{pmatrix}$$

In consequence, the directions of the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{c}, \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are described by the Miller indices $[100], [010], [\bar{1}\bar{1}0], [001], [\frac{1}{\sqrt{3}} \frac{2}{\sqrt{3}} 0], [\frac{2}{\sqrt{3}} \frac{1}{\sqrt{3}} 0]$ and $[\frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} 0]$.

A.3 Translational components of symmetry operations

For the description of screws and glides in hexagonal OD groupoid families the translational component is indicated by the relative lengths of $\mathbf{t}_{//\mathbf{a}_1}, \mathbf{t}_{//\mathbf{a}_2}, \mathbf{t}_{//\mathbf{a}_3}, \mathbf{t}_{//\mathbf{b}_1}, \mathbf{t}_{//\mathbf{b}_2}, \mathbf{t}_{//\mathbf{b}_3}$, the orthogonal projections of the translation vector $\mathbf{t}$ on the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{b}_1, \mathbf{b}_2$ and $\mathbf{b}_3$ (Fig. A.1(b)).

The translational components normal to the stacking direction of screws and glides in hexagonal OD groupoid families are usually obtained as coordinates x and y in a standard coordinate system of hexagonal layers:

$$\mathbf{t} = (\mathbf{a}_1, \mathbf{a}_2) \begin{pmatrix} x \\ y \end{pmatrix}$$

Equation A.7 is used to transform the coordinates into an orthogonal coordinate system:

$$\mathbf{t} = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} 1 & -\frac{1}{2} \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} x - \frac{1}{2}y \\ \frac{\sqrt{3}}{2}y \end{pmatrix}$$

The translational component of $\mathbf{t}$ projected on an arbitrary vector $\mathbf{v}$ can be expressed as

$$\mathbf{t}_{//\mathbf{v}} = \frac{\mathbf{t} \cdot \mathbf{v}}{\mathbf{v} \cdot \mathbf{v}} \mathbf{v}$$

If $\mathbf{v}$ is coplanar to the vectors $\mathbf{a}_n$ and $\mathbf{b}_n$, it can be expressed in the orthogonal coordinate system $(\mathbf{a}_1, \mathbf{b}_1)$:

$$\mathbf{v} = (\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} x' \\ y' \end{pmatrix}$$

Since $\mathbf{a}_1 \cdot \mathbf{b}_1 = \mathbf{b}_1 \cdot \mathbf{a}_1 = 0$ and $\mathbf{a}_1 \cdot \mathbf{a}_1 = \mathbf{b}_1 \cdot \mathbf{b}_1$, the scalar product $\mathbf{t} \cdot \mathbf{v}$ is:

$$\mathbf{t} \cdot \mathbf{v} = ((\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} x - \frac{1}{2}y \\ \frac{\sqrt{3}}{2}y \end{pmatrix}) \cdot ((\mathbf{a}_1, \mathbf{b}_1) \begin{pmatrix} x' \\ y' \end{pmatrix}) = ((x - \frac{1}{2}y)x' + \frac{\sqrt{3}}{2}yy') \mathbf{a}_1 \cdot \mathbf{a}_1$$

Thus, if $|\mathbf{v}| = |\mathbf{a}_1|$:

$$\mathbf{t}_{//\mathbf{v}} = ((x - \frac{1}{2}y)x' + \frac{\sqrt{3}}{2}yy') \mathbf{v}$$

Using equations A.1–A.6, one obtains:

$$\begin{aligned} \mathbf{t}_{//\mathbf{a}_1} &= (((x - \frac{1}{2}y)1) + \frac{\sqrt{3}}{2}0) \mathbf{a}_1 = (x - \frac{1}{2}y) \mathbf{a}_1 \\ \mathbf{t}_{//\mathbf{a}_2} &= ((x - \frac{1}{2}y)(-\frac{1}{2}) + \frac{\sqrt{3}}{2}y \frac{\sqrt{3}}{2}) \mathbf{a}_2 = (-\frac{1}{2}x + y) \mathbf{a}_2 \\ \mathbf{t}_{//\mathbf{a}_3} &= ((x - \frac{1}{2}y)(-\frac{1}{2}) + \frac{\sqrt{3}}{2}y(-\frac{\sqrt{3}}{2})) \mathbf{a}_3 = (-\frac{1}{2}x - \frac{1}{2}y) \mathbf{a}_3 \\ \mathbf{t}_{//\mathbf{b}_1} &= ((x - \frac{1}{2}y)(0) + \frac{\sqrt{3}}{2}y(1)) \mathbf{b}_1 = \frac{\sqrt{3}}{2}y \mathbf{b}_1 \end{aligned}$$

$$\begin{aligned}\mathbf{t}_{//\mathbf{b}_2} &= ((x - \frac{1}{2}y)(-\frac{\sqrt{3}}{2}) + \frac{\sqrt{3}}{2}y(-\frac{1}{2}))\mathbf{b}_2 = (-\frac{\sqrt{3}}{2}x)\mathbf{b}_2 \\ \mathbf{t}_{//\mathbf{b}_3} &= ((x - \frac{1}{2}y)(\frac{\sqrt{3}}{2}) + \frac{\sqrt{3}}{2}y(-\frac{1}{2}))\mathbf{b}_3 = (\frac{\sqrt{3}}{2}x - \frac{\sqrt{3}}{2}y)\mathbf{b}_3\end{aligned}$$

Appendix B

Structure factor calculations

B.1 Overview

In this chapter the structure factors of MgTeO_8H_8 as described in sec. 5.2 will be derived. $\mathbf{a}$, $\mathbf{b}$ are the lattice basis vectors and $\mathbf{c}_0$ the non-lattice basis vector of layers L . $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}_0^*$ are the corresponding basis vectors in reciprocal space.

$F(hk\nu)$ is the Fourier transform of the entire structure with $M + 1$ layers $L_p, p \leq M$ at $(h\mathbf{a}^*, k\mathbf{b}^*, \nu\mathbf{c}_0^*)$. Under the assumption of infinite layers which are symmetric by translation along $\mathbf{a}$ and $\mathbf{b}$, $F(hk\nu)$ can only be non-zero for $h, k \in \mathbb{Z}$. $F(hk\nu)$ is the sum of the Fourier transform of all layers L_p :

$$F(hk\nu) = \sum_{p=0}^M F_p(hk\nu)$$

According to the description in sec. 5.2.4, the origin of layer L_p is related to the origin of layer L_{p-1} by a translation along

$$\mathbf{t}_p = \alpha_p \frac{\mathbf{a}}{2} + \beta_p \frac{\mathbf{b}}{2} + \mathbf{c}_0, 1 \leq p \leq M$$

with

$$(\alpha_p, \beta_p) \in \{(0, 1), (1, 0)\}$$

The origin of layer L_p is related to the origin of layer L_0 by a translation along

$$\sum_{q=1}^p \mathbf{t}_q = \left(\sum_{q=1}^p \frac{\alpha_q}{2} \right) \mathbf{a} + \left(\sum_{q=1}^p \frac{\beta_q}{2} \right) \mathbf{b} + p\mathbf{c}_0$$

Each layer can appear in two orientations with respect to (100). γ_p is 0 if layer L_p has the same orientation as layer L_0 and 1 if layer L_p is mirrored by $[m - -]$ compared to layer L_0 .

Thus the Fourier transform of layer L_p is related to the Fourier transform of layer L_0 by:

$$F_p(hk\nu) = F_0((-1^{\gamma_p}h)k\nu) \exp\left[2\pi i \left(\frac{1}{2} \sum_{q=1}^p (h\alpha_q + k\beta_q) + \nu p\right)\right] \quad (\text{B.1})$$

(N.B.: $\sum_{q=1}^0 (h\alpha_q + k\beta_q) = 0$ and therefore the equation is also valid for $p = 0$.)

B.2 Non-space group extinctions for all polytypes

For $h = 0$ eq. B.1 simplifies to:

$$F_p(0k\nu) = F_0(0k\nu) \exp[2\pi i(\frac{1}{2} \sum_{q=1}^p k\beta_q + \nu p)]$$

Thus the Fourier transform of the whole crystal can be written as:

$$F(0k\nu) = S(0k\nu)F_0(0k\nu)$$

with

$$S(0k\nu) = \sum_{p=0}^M \exp[2\pi i(\frac{1}{2} \sum_{q=1}^p k\beta_q + \nu p)]$$

For $k = 2n_k, n_k \in \mathbb{Z}$: $k\beta_q$ is even and therefore $\sum_{q=1}^p k\beta_q = 2n_p, n_p \in \mathbb{Z}$ which gives:

$$S(0k\nu) = \sum_{p=0}^M \exp[2\pi i\nu p]$$

For a large number of layers:

$$\lim_{M \rightarrow \infty} S(0k\nu) = \sum_{l \in \mathbb{Z}} \delta(\nu - l)$$

Therefore for $h = 0$ and k even, only sharp reflections are obtained, located at $\nu = l \in \mathbb{Z}$.

An analogous result is obtained for $k = 0$ since, due to tetragonal symmetry, layers related by $[m - -]$ are also related by $[-m -]$. The same result does not hold for $h \neq 0$ and $k \neq 0$.

B.3 Non-space group extinctions in structures with O3 located at $x + y = \frac{1}{2}$

The Fourier transform $F_p(hk\nu)$ of layer p can be split into contributions of atoms O3 ($F_p^O(hk\nu)$) and the remaining atoms Te, Mg, O1 and O2 ($F_p^M(hk\nu)$):

$$F_p(hk\nu) = F_p^O(hk\nu) + F_p^M(hk\nu)$$

If atom O3 is located at coordinates $(x, \frac{1}{2} - y, z)$, application of a mirror plane at $x = 0$, a fourfold rotation axis at $(0, 0, z)$ and translation by a vector $(\frac{1}{2}, \frac{1}{2}, 0)$ results in the original atom. Thus, the atoms O3 of a layer and the same layer mirrored at $x = 0$ are related by a translation along $(\frac{1}{2}, \frac{1}{2}, 0)$:

$$F_p^O((-h)k\nu) = F_p^O(hk\nu) \exp[2\pi i(\frac{1}{2}(h + k) + \nu p)] \quad (\text{B.2})$$

For $h + k = 2n, n \in \mathbb{Z}$, this expression simplifies to:

$$F_p^O((-h)k\nu) = F_p^O(hk\nu)$$

Te, Mg, O1 and O2 are located at $(\frac{n_x}{2}, \frac{n_y}{2}, z)$, $n_x, n_y \in \mathbb{Z}$ therefore mirroring at a plane $x = 0$ results in atoms with the same positions and thus:

$$F_p^M((-1)^{\gamma_p} h)k\nu) = F_p^M(hk\nu) \quad (\text{B.3})$$

Using eq. B.2 and B.3, eq. B.1 simplifies for $h + k = 2n$ to:

$$F_p(hk\nu) = F_0(hk\nu) \exp[2\pi i(\frac{1}{2} \sum_{q=1}^p (h\alpha_q + k\beta_q) + \nu p)]$$

The Fourier transform of the whole structure consequently is:

$$F(hk\nu) = S(hk\nu)F_0(hk\nu)$$

with

$$S(hk\nu) = \sum_{p=0}^M \exp[2\pi i(\frac{1}{2} \sum_{q=1}^p (h\alpha_q + k\beta_q) + \nu p)] \quad (\text{B.4})$$

Two cases can be differentiated: h and k both even or h and k both odd. For $h = 2n_h, n_h \in \mathbb{Z}$ and $k = 2n_k, n_k \in \mathbb{Z}$: $(h\alpha_q + k\beta_q)$ is even and therefore $\sum_{q=1}^p (h\alpha_q + k\beta_q) = 2n, n \in \mathbb{Z}$ which gives:

$$S(hk\nu) = \sum_{p=0}^M \exp[2\pi i\nu p]$$

For a large number of layers:

$$\lim_{M \rightarrow \infty} S(hk\nu) = \sum_{l \in \mathbb{Z}} \delta(\nu - l)$$

Therefore for h and k even, only sharp reflections are observed, located at $\nu = l \in \mathbb{Z}$.

For $h = 2n_h + 1, n_h \in \mathbb{Z}$ and $k = 2n_k + 1, n_k \in \mathbb{Z}$: Since $\alpha_q + \beta_q = \pm 1$, $h\alpha_q + k\beta_q$ is odd and therefore $\sum_{q=1}^p (h\alpha_q + k\beta_q)$ is even if and only if p is even or:

$$\sum_{q=1}^p (h\alpha_q + k\beta_q) = 2m_p + p, m_p \in \mathbb{Z}$$

One obtains:

$$S(hk\nu) = \sum_{p=0}^M \exp[2\pi i(\frac{1}{2}(2m_p + p) + \nu p)]$$

$$S(hk\nu) = \sum_{p=0}^M \exp[2\pi i(\frac{1}{2} + \nu)p]$$

For a large number of layers:

$$\lim_{M \rightarrow \infty} S(hk\nu) = \sum_{l \in \mathbb{Z}} \delta(\nu + \frac{1}{2} - l)$$

Therefore for h and k odd, only sharp reflections are observed, located at $\nu = l - \frac{1}{2}, l \in \mathbb{Z}$. Combined with the reflection conditions for h and k even, the general reflection condition for reflections with $h + k = 2n$ is $\nu = l + (h\frac{1}{2}), l \in \mathbb{Z}$. Thus, for all $h + k = 2n, 2n \in \mathbb{N}$ only sharp reflections are observed.

B.4 Non-space group extinctions in structures with disordered layers B

For polytypes where layers B are disordered by mirroring at $[m - -]$, layers B have only one possible orientation with respect to (100) . In this case, γ_p is 0 for every layer L_p and eq. B.1 becomes:

$$F_p(hk\nu) = F_0(hk\nu) \exp[2\pi i(\frac{1}{2} \sum_{q=1}^p (h\alpha_q + k\beta_q) + \nu p)]$$

Thus, following the reasoning of sec. B.3, for all $h + k = 2n$, $2n \in \mathbb{N}$ only sharp reflections are observed.

Appendix C

Atomic coordinates

C.1 System $M/\text{Te}/\text{O}$ with $M = \text{Ca}, \text{Sr}$

Table C.1: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in $\alpha\text{-CaTeO}_3$

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Ca1	4 a 1	0.24339(10)	0.22740(10)	0.27425(13)	0.0100(2)
Ca2	4 a 1	0.26510(10)	0.74143(10)	0.03616(13)	0.0109(3)
Ca3	4 a 1	0.56630(10)	0.16230(10)	0.26708(13)	0.0097(2)
Ca4	4 a 1	0.34495(10)	0.03956(10)	0.01503(14)	0.0120(3)
Ca5	4 a 1	0.13681(10)	0.46137(9)	0.01819(15)	0.0096(2)
Te1	4 a 1	0.44460(3)	0.31234(3)	0.01768(4)	0.01004(8)
Te2	4 a 1	0.06250(4)	0.16813(3)	0.54077(4)	0.01098(9)
Te3	4 a 1	-0.00800(3)	0.38405(3)	0.25959(4)	0.00880(8)
Te4	4 a 1	0.05797(3)	0.15718(3)	-0.00413(4)	0.00873(8)
Te5	4 a 1	0.44166(3)	0.34168(3)	0.54110(4)	0.00872(9)
O1	4 a 1	0.0139(4)	0.4891(4)	0.3826(4)	0.0115(10)
O2	4 a 1	-0.0288(4)	0.4947(4)	0.1416(4)	0.0121(9)
O3	4 a 1	0.1156(4)	0.2728(4)	0.6475(4)	0.0143(10)
O4	4 a 1	0.0916(4)	0.2531(4)	0.4076(4)	0.0154(10)
O5	4 a 1	-0.0826(4)	0.2066(4)	0.5687(4)	0.0229(12)
O6	4 a 1	0.1403(4)	0.3722(4)	0.2113(4)	0.0134(9)
O7	4 a 1	0.4016(4)	0.2011(4)	-0.0881(4)	0.0125(10)
O8	4 a 1	0.4095(4)	0.2407(4)	0.1621(4)	0.0161(10)
O9	4 a 1	0.3215(4)	0.3972(4)	-0.0120(5)	0.0230(11)
O10	4 a 1	0.0975(4)	0.2877(4)	-0.0851(4)	0.0119(10)
O11	4 a 1	-0.0433(4)	0.2222(4)	0.0999(4)	0.0175(10)
O12	4 a 1	0.1831(4)	0.1351(4)	0.0937(4)	0.0145(10)
O13	4 a 1	0.4007(4)	0.2264(4)	0.6427(4)	0.0121(10)
O14	4 a 1	0.5525(3)	0.2724(4)	0.4507(4)	0.0133(9)
O15	4 a 1	0.3212(4)	0.3333(4)	0.4355(4)	0.0137(9)

Table C.2: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in β -CaTeO₃, measured at 275 K

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te11	1 <i>a</i> 1	0.19456(6)	0.22060(13)	-0.26545(8)	0.01377(16)
Te12	1 <i>a</i> 1	0.52108(6)	0.26272(15)	-0.24839(8)	0.01821(17)
Te13	1 <i>a</i> 1	-0.14100(5)	0.24898(13)	0.73516(7)	0.00966(15)
Te14	1 <i>a</i> 1	0.14412(5)	-0.25928(12)	0.26327(7)	0.00950(15)
Te15	1 <i>a</i> 1	0.47043(6)	-0.22541(15)	0.25933(8)	0.01787(17)
Te16	1 <i>a</i> 1	-0.19992(6)	-0.21440(13)	0.25637(8)	0.01333(15)
Te21	1 <i>a</i> 1	0.02402(6)	-0.26797(14)	0.47512(7)	0.01490(16)
Te22	1 <i>a</i> 1	0.35186(6)	-0.23200(16)	0.45933(8)	0.01757(18)
Te23	1 <i>a</i> 1	-0.32036(6)	0.75628(14)	0.44475(8)	0.01504(17)
Te24	1 <i>a</i> 1	0.32617(6)	0.23612(13)	-0.43965(8)	0.01532(17)
Te25	1 <i>a</i> 1	-0.36180(6)	0.26271(16)	0.53810(9)	0.01765(18)
Te26	1 <i>a</i> 1	-0.02787(6)	0.26934(14)	0.52031(7)	0.01552(17)
Te31	1 <i>a</i> 1	0.16691(6)	0.26742(14)	0.16499(7)	0.01255(15)
Te32	1 <i>a</i> 1	0.47748(6)	-0.69622(12)	0.15611(7)	0.01294(15)
Te33	1 <i>a</i> 1	-0.13385(6)	0.20567(13)	0.17986(7)	0.01126(15)
Te34	1 <i>a</i> 1	0.13830(6)	-0.22286(13)	0.82285(7)	0.01270(16)
Te35	1 <i>a</i> 1	-0.47281(6)	0.69647(12)	0.84944(7)	0.01172(14)
Te36	1 <i>a</i> 1	-0.16613(6)	-0.27778(13)	-0.17126(7)	0.01266(15)
Ca11	1 <i>a</i> 1	-0.07336(18)	-0.2885(4)	0.1300(2)	0.0124(5)
Ca12	1 <i>a</i> 1	0.24215(19)	-0.2105(4)	0.1174(3)	0.0152(5)
Ca13	1 <i>a</i> 1	0.59507(18)	-0.2513(4)	0.1450(2)	0.0147(5)
Ca14	1 <i>a</i> 1	0.4081(2)	0.2551(5)	-0.1362(3)	0.0136(5)
Ca15	1 <i>a</i> 1	-0.23999(18)	0.1991(4)	0.8786(2)	0.0145(5)
Ca16	1 <i>a</i> 1	0.07423(18)	0.2806(4)	0.8653(2)	0.0126(5)
Ca21	1 <i>a</i> 1	-0.07958(19)	-0.2404(4)	0.6272(2)	0.0139(5)
Ca22	1 <i>a</i> 1	0.25671(19)	-0.2699(4)	0.5791(2)	0.0148(5)
Ca23	1 <i>a</i> 1	-0.4266(2)	0.7818(4)	0.6345(2)	0.0175(5)
Ca24	1 <i>a</i> 1	-0.56882(19)	1.2301(4)	0.3748(2)	0.0190(5)
Ca25	1 <i>a</i> 1	-0.2625(2)	0.2765(4)	0.4184(2)	0.0161(5)
Ca26	1 <i>a</i> 1	0.07507(18)	0.2413(4)	0.3640(2)	0.0128(5)
Ca31	1 <i>a</i> 1	0.02235(19)	-0.2353(4)	-0.0383(2)	0.0138(5)
Ca32	1 <i>a</i> 1	0.35047(18)	-0.2362(4)	-0.0660(2)	0.0119(5)
Ca33	1 <i>a</i> 1	0.67986(18)	-0.2461(4)	-0.0405(2)	0.0130(4)
Ca34	1 <i>a</i> 1	0.32641(18)	0.2203(5)	0.0431(3)	0.0170(5)
Ca35	1 <i>a</i> 1	-0.34874(19)	0.2372(4)	0.0646(2)	0.0120(5)
Ca36	1 <i>a</i> 1	-0.02092(19)	0.2265(4)	0.0361(3)	0.0145(5)
O11	1 <i>a</i> 1	0.2018(6)	0.0261(14)	-0.2568(8)	0.0190(18)
O12	1 <i>a</i> 1	0.5562(5)	-1.9667(12)	-0.2035(7)	0.0179(14)

O13	1 a 1	-0.1263(6)	0.0637(13)	0.7925(7)	0.0116(15)
O14	1 a 1	0.1249(6)	-0.0644(13)	0.2037(8)	0.0143(16)
O15	1 a 1	0.4646(5)	-0.0405(12)	0.2323(7)	0.0183(14)
O16	1 a 1	-0.2053(6)	-0.0215(13)	0.2513(7)	0.0120(15)
O21	1 a 1	0.0737(7)	-0.5034(15)	-0.2133(8)	0.0222(19)
O22	1 a 1	0.3878(6)	-0.4868(14)	-0.2564(8)	0.0281(18)
O23	1 a 1	-0.1768(5)	0.4464(12)	0.8794(7)	0.0123(14)
O24	1 a 1	0.1834(6)	-0.4664(14)	0.1253(8)	0.0190(17)
O25	1 a 1	0.5967(6)	-0.5222(14)	0.2477(8)	0.0288(18)
O26	1 a 1	-0.0781(6)	-0.4937(13)	0.2095(7)	0.0134(15)
O31	1 a 1	0.2797(6)	-0.8831(15)	-0.1159(8)	0.0262(19)
O32	1 a 1	0.5298(5)	-0.6246(12)	-0.0888(6)	0.0216(14)
O33	1 a 1	-0.2605(6)	0.4507(14)	0.6280(8)	0.0184(17)
O34	1 a 1	0.2644(6)	-0.4513(14)	0.3713(7)	0.0163(16)
O35	1 a 1	0.4028(6)	-0.1568(16)	0.0995(8)	0.041(2)
O36	1 a 1	-0.2832(6)	-0.1072(13)	0.1012(7)	0.0156(15)
O41	1 a 1	-0.0026(6)	-0.2494(14)	0.3040(8)	0.0197(17)
O42	1 a 1	0.3335(7)	-0.2261(15)	0.2861(8)	0.0256(19)
O43	1 a 1	-0.4058(5)	0.9719(13)	0.3142(7)	0.0181(15)
O44	1 a 1	0.4176(6)	0.0296(13)	-0.3021(7)	0.0204(16)
O45	1 a 1	-0.3377(7)	0.2460(15)	0.7108(8)	0.0240(18)
O46	1 a 1	-0.0050(7)	0.2671(15)	0.6925(9)	0.026(2)
O51	1 a 1	0.0502(6)	-0.4938(15)	0.4971(8)	0.0230(18)
O52	1 a 1	0.4186(6)	-0.5146(15)	0.4880(8)	0.0300(19)
O53	1 a 1	-0.2916(6)	0.5258(13)	0.3448(7)	0.0207(16)
O54	1 a 1	0.2727(6)	-0.4997(14)	-0.3504(7)	0.0228(17)
O55	1 a 1	-0.4120(6)	0.5303(14)	0.5144(7)	0.0230(16)
O56	1 a 1	-0.0600(6)	0.5007(15)	0.4940(8)	0.0258(19)
O61	1 a 1	-0.0986(6)	-0.0184(14)	0.5172(8)	0.0195(17)
O62	1 a 1	0.2337(6)	-0.0416(15)	0.4826(8)	0.0203(18)
O63	1 a 1	-0.4159(5)	0.9180(12)	0.5207(6)	0.0170(13)
O64	1 a 1	0.4203(6)	0.1142(14)	-0.4997(7)	0.0259(17)
O65	1 a 1	-0.2388(6)	0.0460(15)	0.5140(8)	0.0211(18)
O66	1 a 1	0.0938(6)	0.0204(14)	0.4774(8)	0.0187(17)
O71	1 a 1	0.0584(6)	-0.4847(14)	0.0490(8)	0.0168(17)
O72	1 a 1	0.3822(6)	-0.4807(13)	0.0176(7)	0.0142(16)
O73	1 a 1	-0.2516(6)	0.4984(14)	0.1032(7)	0.0196(16)
O74	1 a 1	0.2576(6)	-0.4998(14)	0.9160(7)	0.0194(16)
O75	1 a 1	-0.3792(5)	0.4841(13)	-0.0148(7)	0.0123(15)
O76	1 a 1	-0.0578(6)	-0.5188(13)	-0.0538(7)	0.0108(15)
O81	1 a 1	0.2219(6)	0.0337(14)	0.0376(7)	0.0171(16)
O82	1 a 1	0.5437(6)	0.0369(13)	0.0505(7)	0.0110(15)
O83	1 a 1	-0.1349(6)	0.0338(15)	0.0720(8)	0.0205(18)
O84	1 a 1	0.1290(7)	-0.0268(15)	-0.0748(8)	0.0224(19)
O85	1 a 1	-0.5412(6)	0.9637(14)	-0.0464(8)	0.0172(17)
O86	1 a 1	-0.2259(6)	-0.0390(14)	-0.0511(8)	0.0194(17)
O91	1 a 1	0.1051(6)	-0.7429(14)	0.2028(8)	0.0191(17)
O92	1 a 1	0.3919(5)	-1.6403(12)	0.1836(7)	0.0152(15)

O93	1 <i>a</i> 1	-0.0445(6)	0.0913(13)	0.1070(7)	0.0151(16)
O94	1 <i>a</i> 1	0.0487(6)	-0.1061(14)	0.8937(8)	0.0166(16)
O95	1 <i>a</i> 1	-0.3838(5)	0.6375(13)	0.8269(7)	0.0162(15)
O96	1 <i>a</i> 1	-0.1086(6)	-0.2540(14)	-0.2066(7)	0.0178(17)

Table C.3: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in β -CaTeO₃, measured at 295 K

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te11	1 <i>a</i> 1	0.19487(6)	0.22004(13)	-0.26521(7)	0.01439(16)
Te12	1 <i>a</i> 1	0.52120(6)	0.26161(14)	-0.24889(7)	0.01896(17)
Te13	1 <i>a</i> 1	-0.14117(5)	0.24957(12)	0.73532(7)	0.01046(15)
Te14	1 <i>a</i> 1	0.14402(5)	-0.25884(12)	0.26328(6)	0.00988(15)
Te15	1 <i>a</i> 1	0.47094(6)	-0.22737(15)	0.25904(7)	0.01879(17)
Te16	1 <i>a</i> 1	-0.19993(6)	-0.21432(13)	0.25621(7)	0.01373(15)
Te21	1 <i>a</i> 1	0.02418(6)	-0.26831(13)	0.47506(7)	0.01576(17)
Te22	1 <i>a</i> 1	0.35222(6)	-0.23313(15)	0.45956(8)	0.01822(18)
Te23	1 <i>a</i> 1	-0.32047(6)	0.75683(14)	0.44481(7)	0.01618(18)
Te24	1 <i>a</i> 1	0.32607(6)	0.23619(13)	-0.43982(7)	0.01618(18)
Te25	1 <i>a</i> 1	-0.36138(6)	0.26169(16)	0.53847(8)	0.01864(18)
Te26	1 <i>a</i> 1	-0.02792(6)	0.26960(13)	0.52049(7)	0.01620(17)
Te31	1 <i>a</i> 1	0.16689(6)	0.26772(14)	0.16495(7)	0.01330(15)
Te32	1 <i>a</i> 1	0.47736(6)	-0.69634(12)	0.15612(7)	0.01337(15)
Te33	1 <i>a</i> 1	-0.13416(6)	0.20662(12)	0.17973(6)	0.01197(15)
Te34	1 <i>a</i> 1	0.13796(6)	-0.22179(12)	0.82260(7)	0.01338(16)
Te35	1 <i>a</i> 1	-0.47289(5)	0.69673(12)	0.84952(7)	0.01258(14)
Te36	1 <i>a</i> 1	-0.16616(6)	-0.27729(13)	-0.17110(7)	0.01344(15)
Ca11	1 <i>a</i> 1	-0.07335(18)	-0.2881(4)	0.1302(2)	0.0127(5)
Ca12	1 <i>a</i> 1	0.24225(19)	-0.2108(4)	0.1176(2)	0.0161(5)
Ca13	1 <i>a</i> 1	0.59529(19)	-0.2523(4)	0.1449(2)	0.0153(5)
Ca14	1 <i>a</i> 1	0.4079(2)	0.2555(5)	-0.1363(3)	0.0153(5)
Ca15	1 <i>a</i> 1	-0.23990(18)	0.1991(4)	0.8786(2)	0.0154(5)
Ca16	1 <i>a</i> 1	0.07436(18)	0.2802(4)	0.8655(2)	0.0132(5)
Ca21	1 <i>a</i> 1	-0.07990(19)	-0.2395(4)	0.6274(2)	0.0153(5)
Ca22	1 <i>a</i> 1	0.25643(19)	-0.2691(4)	0.5788(2)	0.0158(5)
Ca23	1 <i>a</i> 1	-0.42666(19)	0.7815(4)	0.6351(2)	0.0179(5)
Ca24	1 <i>a</i> 1	-0.56908(19)	1.2299(4)	0.3748(2)	0.0195(5)
Ca25	1 <i>a</i> 1	-0.26207(19)	0.2762(4)	0.4180(2)	0.0171(5)
Ca26	1 <i>a</i> 1	0.07488(18)	0.2420(4)	0.3640(2)	0.0143(5)
Ca31	1 <i>a</i> 1	0.02214(19)	-0.2346(4)	-0.0380(2)	0.0142(5)
Ca32	1 <i>a</i> 1	0.35033(19)	-0.2357(4)	-0.0658(2)	0.0132(5)
Ca33	1 <i>a</i> 1	0.67943(18)	-0.2452(4)	-0.0404(2)	0.0137(4)
Ca34	1 <i>a</i> 1	0.32575(18)	0.2226(4)	0.0431(3)	0.0185(5)

Ca35	1 a 1	-0.34924(19)	0.2383(4)	0.0645(2)	0.0126(5)
Ca36	1 a 1	-0.02145(19)	0.2279(4)	0.0366(3)	0.0160(5)
O11	1 a 1	0.2022(6)	0.0231(14)	-0.2579(8)	0.0180(18)
O12	1 a 1	0.5550(7)	-1.9671(14)	-0.2044(8)	0.026(2)
O13	1 a 1	-0.1261(6)	0.0615(13)	0.7931(7)	0.0132(16)
O14	1 a 1	0.1256(6)	-0.0668(13)	0.2048(8)	0.0144(17)
O15	1 a 1	0.4632(7)	-0.0393(14)	0.2300(8)	0.027(2)
O16	1 a 1	-0.2048(6)	-0.0248(13)	0.2497(7)	0.0126(15)
O21	1 a 1	0.0744(6)	-0.5025(13)	-0.2135(7)	0.0162(17)
O22	1 a 1	0.3889(7)	-0.4816(16)	-0.2561(8)	0.041(3)
O23	1 a 1	-0.1769(6)	0.4484(13)	0.8783(7)	0.0163(17)
O24	1 a 1	0.1830(6)	-0.4641(13)	0.1239(7)	0.0164(16)
O25	1 a 1	0.5977(7)	-0.5152(15)	0.2472(9)	0.051(3)
O26	1 a 1	-0.0779(6)	-0.4941(14)	0.2071(7)	0.0201(19)
O31	1 a 1	0.2796(7)	-0.8855(15)	-0.1159(8)	0.029(2)
O32	1 a 1	0.5285(4)	-0.6216(11)	-0.0904(6)	0.0235(14)
O33	1 a 1	-0.2615(6)	0.4501(13)	0.6278(8)	0.0214(18)
O34	1 a 1	0.2632(5)	-0.4509(13)	0.3708(7)	0.0170(17)
O35	1 a 1	0.4050(7)	-0.166(2)	0.0986(8)	0.060(3)
O36	1 a 1	-0.2837(6)	-0.1075(13)	0.1011(7)	0.0162(15)
O41	1 a 1	-0.0019(7)	-0.2520(15)	0.3028(7)	0.024(2)
O42	1 a 1	0.3329(7)	-0.2277(16)	0.2872(7)	0.0248(19)
O43	1 a 1	-0.4059(7)	0.9681(15)	0.3116(8)	0.027(2)
O44	1 a 1	0.4156(6)	0.0302(14)	-0.3048(8)	0.0231(18)
O45	1 a 1	-0.3386(7)	0.2453(16)	0.7115(8)	0.027(2)
O46	1 a 1	-0.0041(7)	0.2639(16)	0.6919(8)	0.027(2)
O51	1 a 1	0.0530(8)	-0.4977(15)	0.4980(9)	0.032(2)
O52	1 a 1	0.4172(7)	-0.5157(16)	0.4883(8)	0.039(3)
O53	1 a 1	-0.2877(7)	0.5202(16)	0.3463(8)	0.031(2)
O54	1 a 1	0.2766(7)	-0.5046(14)	-0.3495(8)	0.028(2)
O55	1 a 1	-0.4152(7)	0.5332(15)	0.5141(8)	0.028(2)
O56	1 a 1	-0.0584(7)	0.4985(15)	0.4940(9)	0.030(2)
O61	1 a 1	-0.0973(6)	-0.0188(14)	0.5182(8)	0.0221(19)
O62	1 a 1	0.2336(6)	-0.0439(13)	0.4817(8)	0.0225(19)
O63	1 a 1	-0.4169(7)	0.9172(14)	0.5197(8)	0.031(2)
O64	1 a 1	0.4201(6)	0.1111(15)	-0.5011(8)	0.033(2)
O65	1 a 1	-0.2396(6)	0.0471(14)	0.5125(8)	0.0215(18)
O66	1 a 1	0.0938(6)	0.0220(14)	0.4778(8)	0.022(2)
O71	1 a 1	0.0587(6)	-0.4848(14)	0.0480(8)	0.0153(17)
O72	1 a 1	0.3828(6)	-0.4820(13)	0.0178(8)	0.0154(17)
O73	1 a 1	-0.2526(6)	0.4986(14)	0.1011(8)	0.0233(19)
O74	1 a 1	0.2558(6)	-0.4990(14)	0.9129(8)	0.0192(17)
O75	1 a 1	-0.3794(6)	0.4849(14)	-0.0134(7)	0.0157(17)
O76	1 a 1	-0.0580(6)	-0.5192(13)	-0.0551(7)	0.0140(17)
O81	1 a 1	0.2223(6)	0.0334(13)	0.0385(8)	0.0187(18)
O82	1 a 1	0.5441(6)	0.0367(13)	0.0520(8)	0.0168(18)
O83	1 a 1	-0.1339(7)	0.0298(14)	0.0715(8)	0.022(2)
O84	1 a 1	0.1303(7)	-0.0312(15)	-0.0750(8)	0.026(2)

O85	1 a 1	-0.5418(5)	0.9650(13)	-0.0460(7)	0.0124(16)
O86	1 a 1	-0.2248(6)	-0.0388(13)	-0.0492(8)	0.0205(19)
O91	1 a 1	0.1062(6)	-0.7452(14)	0.2047(7)	0.0208(18)
O92	1 a 1	0.3921(6)	-1.6412(14)	0.1843(7)	0.0203(17)
O93	1 a 1	-0.0455(6)	0.0929(14)	0.1073(8)	0.0185(17)
O94	1 a 1	0.0490(6)	-0.1057(13)	0.8950(8)	0.0192(17)
O95	1 a 1	-0.3847(5)	0.6376(12)	0.8265(7)	0.0148(15)
O96	1 a 1	-0.1073(6)	-0.2563(14)	-0.2045(7)	0.0191(17)

Table C.4: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in β -CaTeO₃, measured at 325 K

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te11	2 <i>i</i> 1	1	0.19786(3)	0.21613(7)	-0.26017(4)	0.01565(8)
Te12	2 <i>i</i> 1	1	0.52442(3)	0.24573(9)	-0.25437(4)	0.02323(10)
Te13	2 <i>i</i> 1	1	-0.14239(3)	0.25374(6)	0.73635(3)	0.01100(7)
Te21	2 <i>i</i> 1	1	0.02644(3)	-0.26979(7)	0.47731(4)	0.01733(8)
Te22	2 <i>i</i> 1	1	0.35658(3)	-0.24706(8)	0.46042(4)	0.02153(9)
Te23	2 <i>i</i> 1	1	-0.32320(3)	0.76088(7)	0.44243(4)	0.01830(8)
Te31	2 <i>i</i> 1	1	0.16666(3)	0.27210(7)	0.16801(4)	0.01494(8)
Te32	2 <i>i</i> 1	1	0.47506(3)	-0.69675(7)	0.15328(4)	0.01427(8)
Te33	2 <i>i</i> 1	1	-0.13590(3)	0.21381(7)	0.17871(4)	0.01402(8)
Ca11	2 <i>i</i> 1	1	-0.07405(8)	-0.2837(2)	0.13198(11)	0.0148(2)
Ca12	2 <i>i</i> 1	1	0.24092(9)	-0.2050(2)	0.11912(12)	0.0174(2)
Ca13	2 <i>i</i> 1	1	0.59367(9)	-0.2543(2)	0.14112(12)	0.0168(2)
Ca21	2 <i>i</i> 1	1	-0.07717(9)	-0.2413(2)	0.63206(12)	0.0165(2)
Ca22	2 <i>i</i> 1	1	0.25854(9)	-0.2718(2)	0.58015(12)	0.0181(2)
Ca23	2 <i>i</i> 1	1	-0.42841(9)	0.7754(2)	0.63034(12)	0.0225(3)
Ca31	2 <i>i</i> 1	1	0.02201(9)	-0.2321(2)	-0.03729(11)	0.0162(2)
Ca32	2 <i>i</i> 1	1	0.35046(9)	-0.2388(2)	-0.06516(11)	0.0143(2)
Ca33	2 <i>i</i> 1	1	0.67683(9)	-0.2349(2)	-0.04154(12)	0.0184(2)
O11	2 <i>i</i> 1	1	0.2034(3)	0.0244(8)	-0.2530(4)	0.0171(8)
O12	2 <i>i</i> 1	1	0.5469(4)	-1.9647(9)	-0.2166(6)	0.0417(16)
O13	2 <i>i</i> 1	1	-0.1251(3)	0.0625(7)	0.7948(4)	0.0155(8)
O21	2 <i>i</i> 1	1	0.0760(3)	-0.5049(8)	-0.2111(4)	0.0194(9)
O22	2 <i>i</i> 1	1	0.3941(4)	-0.4846(10)	-0.2533(6)	0.056(2)
O23	2 <i>i</i> 1	1	-0.1798(3)	0.4554(8)	0.8773(4)	0.0192(9)
O31	2 <i>i</i> 1	1	0.2828(3)	-0.8919(9)	-0.1076(5)	0.0256(10)
O32A	2 <i>i</i> 1	0.615(14)	0.5311(6)	-0.6326(16)	-0.0930(8)	0.027(2)
O32B	2 <i>i</i> 1	0.385(14)	0.5987(10)	-0.845(3)	-0.0994(11)	0.029(4)
O33	2 <i>i</i> 1	1	-0.2616(3)	0.4493(7)	0.6295(4)	0.0199(9)
O41	2 <i>i</i> 1	1	0.0005(4)	-0.2562(10)	0.3055(4)	0.0285(11)
O42	2 <i>i</i> 1	1	0.3356(4)	-0.2371(10)	0.2883(5)	0.0289(11)

O43	2 <i>i</i> 1	1	-0.4117(4)	0.9714(8)	0.3088(4)	0.0289(12)
O51	2 <i>i</i> 1	1	0.0559(4)	-0.4989(9)	0.5019(5)	0.0349(13)
O52	2 <i>i</i> 1	1	0.4159(4)	-0.5236(9)	0.4869(5)	0.0381(14)
O53	2 <i>i</i> 1	1	-0.2803(4)	0.5096(9)	0.3486(5)	0.0326(12)
O61	2 <i>i</i> 1	1	-0.0956(3)	-0.0202(8)	0.5204(5)	0.0243(10)
O62	2 <i>i</i> 1	1	0.2361(3)	-0.0446(8)	0.4841(4)	0.0256(10)
O63	2 <i>i</i> 1	1	-0.4178(4)	0.9015(9)	0.5100(6)	0.0439(17)
O71	2 <i>i</i> 1	1	0.0587(3)	-0.4833(7)	0.0525(4)	0.0144(8)
O72	2 <i>i</i> 1	1	0.3812(3)	-0.4837(7)	0.0166(4)	0.0157(8)
O73	2 <i>i</i> 1	1	-0.2541(3)	0.4993(8)	0.0946(5)	0.0260(11)
O81	2 <i>i</i> 1	1	0.2242(3)	0.0345(8)	0.0445(4)	0.0229(10)
O82	2 <i>i</i> 1	1	0.5429(3)	0.0357(7)	0.0486(4)	0.0161(8)
O83	2 <i>i</i> 1	1	-0.1325(4)	0.0312(9)	0.0732(5)	0.0278(11)
O91	2 <i>i</i> 1	1	0.1069(3)	-0.7447(8)	0.2045(4)	0.0221(10)
O92	2 <i>i</i> 1	1	0.3881(3)	-1.6394(8)	0.1783(4)	0.0209(9)
O93	2 <i>i</i> 1	1	-0.0470(3)	0.0992(8)	0.1064(4)	0.0210(9)

Table C.5: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\beta\text{-CaTeO}_3$, measured at 350 K

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te11	2 <i>i</i> 1	1	0.19814(2)	0.21568(5)	-0.25974(3)	0.01651(7)
Te12	2 <i>i</i> 1	1	0.52404(2)	0.24635(6)	-0.25461(3)	0.02260(7)
Te13	2 <i>i</i> 1	1	-0.14233(2)	0.25352(5)	0.73650(3)	0.01202(6)
Te21	2 <i>i</i> 1	1	0.02665(2)	-0.27037(6)	0.47723(3)	0.01871(7)
Te22	2 <i>i</i> 1	1	0.35645(2)	-0.24719(6)	0.46030(3)	0.02131(7)
Te23	2 <i>i</i> 1	1	-0.32326(2)	0.76155(6)	0.44262(3)	0.01959(7)
Te31	2 <i>i</i> 1	1	0.16667(2)	0.27193(5)	0.16784(3)	0.01583(6)
Te32	2 <i>i</i> 1	1	0.47505(2)	-0.69697(5)	0.15328(3)	0.01507(6)
Te33	2 <i>i</i> 1	1	-0.13579(2)	0.21363(5)	0.17879(3)	0.01481(6)
Ca11	2 <i>i</i> 1	1	-0.07409(6)	-0.28359(16)	0.13209(9)	0.01549(18)
Ca12	2 <i>i</i> 1	1	0.24089(6)	-0.20489(16)	0.11899(9)	0.01814(19)
Ca13	2 <i>i</i> 1	1	0.59385(7)	-0.25490(16)	0.14131(9)	0.01799(19)
Ca21	2 <i>i</i> 1	1	-0.07724(7)	-0.24121(16)	0.63234(9)	0.01698(18)
Ca22	2 <i>i</i> 1	1	0.25818(7)	-0.27152(16)	0.57999(9)	0.0195(2)
Ca23	2 <i>i</i> 1	1	-0.42836(7)	0.77541(16)	0.63041(9)	0.0222(2)
Ca31	2 <i>i</i> 1	1	0.02228(7)	-0.23262(16)	-0.03750(9)	0.01735(18)
Ca32	2 <i>i</i> 1	1	0.35090(7)	-0.24013(16)	-0.06504(9)	0.01521(17)
Ca33	2 <i>i</i> 1	1	0.67699(7)	-0.23582(17)	-0.04154(9)	0.01918(19)
O11	2 <i>i</i> 1	1	0.2042(2)	0.0226(6)	-0.2531(3)	0.0197(7)
O12	2 <i>i</i> 1	1	0.5478(3)	-1.9647(6)	-0.2151(4)	0.0403(11)
O13	2 <i>i</i> 1	1	-0.1252(2)	0.0632(5)	0.7949(3)	0.0176(7)
O21	2 <i>i</i> 1	1	0.0765(2)	-0.5054(6)	-0.2103(3)	0.0211(7)

O22	2 <i>i</i> 1	1	0.3934(3)	-0.4856(7)	-0.2538(4)	0.0559(15)
O23	2 <i>i</i> 1	1	-0.1803(2)	0.4565(6)	0.8773(3)	0.0198(7)
O31	2 <i>i</i> 1	1	0.2825(3)	-0.8911(6)	-0.1066(3)	0.0270(8)
O32A	2 <i>i</i> 1	0.621(11)	0.5319(5)	-0.6361(13)	-0.0940(6)	0.030(2)
O32B	2 <i>i</i> 1	0.379(11)	0.5972(9)	-0.839(2)	-0.0994(9)	0.033(4)
O33	2 <i>i</i> 1	1	-0.2621(2)	0.4499(6)	0.6295(3)	0.0212(7)
O41	2 <i>i</i> 1	1	0.0005(3)	-0.2566(7)	0.3055(3)	0.0305(9)
O42	2 <i>i</i> 1	1	0.3350(3)	-0.2354(7)	0.2878(3)	0.0298(8)
O43	2 <i>i</i> 1	1	-0.4116(3)	0.9702(6)	0.3081(3)	0.0315(9)
O51	2 <i>i</i> 1	1	0.0559(3)	-0.4990(6)	0.5019(4)	0.0372(10)
O52	2 <i>i</i> 1	1	0.4160(3)	-0.5234(6)	0.4871(4)	0.0381(10)
O53	2 <i>i</i> 1	1	-0.2794(3)	0.5093(6)	0.3495(4)	0.0357(10)
O61	2 <i>i</i> 1	1	-0.0947(2)	-0.0214(6)	0.5215(3)	0.0259(8)
O62	2 <i>i</i> 1	1	0.2368(2)	-0.0465(6)	0.4842(3)	0.0263(8)
O63	2 <i>i</i> 1	1	-0.4179(3)	0.9013(7)	0.5102(4)	0.0434(12)
O71	2 <i>i</i> 1	1	0.0588(2)	-0.4838(5)	0.0519(3)	0.0166(6)
O72	2 <i>i</i> 1	1	0.3811(2)	-0.4832(5)	0.0163(3)	0.0176(7)
O73	2 <i>i</i> 1	1	-0.2539(2)	0.4991(6)	0.0953(4)	0.0275(8)
O81	2 <i>i</i> 1	1	0.2240(2)	0.0357(6)	0.0444(3)	0.0223(7)
O82	2 <i>i</i> 1	1	0.5431(2)	0.0354(5)	0.0487(3)	0.0170(6)
O83	2 <i>i</i> 1	1	-0.1325(3)	0.0311(6)	0.0735(3)	0.0271(8)
O91	2 <i>i</i> 1	1	0.1069(2)	-0.7443(6)	0.2043(3)	0.0230(7)
O92	2 <i>i</i> 1	1	0.3876(2)	-1.6396(6)	0.1778(3)	0.0201(7)
O93	2 <i>i</i> 1	1	-0.0475(2)	0.0995(6)	0.1065(3)	0.0220(7)

Table C.6: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in β' -CaTeO₃, measured at 200 K

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te11	2 <i>i</i> 1	0.21366(2)	0.18711(5)	-0.23828(3)	0.00770(6)
Te12	2 <i>i</i> 1	0.54787(2)	0.18894(5)	-0.27507(3)	0.00665(6)
Te13	2 <i>i</i> 1	-0.14168(2)	0.23824(5)	0.73139(3)	0.00636(6)
Te21	2 <i>i</i> 1	0.02903(2)	-0.27990(6)	0.48255(3)	0.00954(6)
Te22	2 <i>i</i> 1	0.35367(2)	-0.18971(6)	0.47748(3)	0.00988(6)
Te23	2 <i>i</i> 1	-0.30743(2)	0.70895(5)	0.44460(3)	0.00778(6)
Te31	2 <i>i</i> 1	0.16591(2)	0.29312(5)	0.18864(3)	0.00707(6)
Te32	2 <i>i</i> 1	0.48424(2)	-0.71540(5)	0.16415(3)	0.00642(6)
Te33	2 <i>i</i> 1	-0.13538(2)	0.20468(5)	0.17876(3)	0.00705(6)
Ca11	2 <i>i</i> 1	-0.08191(7)	-0.27243(16)	0.11981(9)	0.00873(17)
Ca12	2 <i>i</i> 1	0.24491(7)	-0.18945(16)	0.14145(9)	0.00906(17)
Ca13	2 <i>i</i> 1	0.59105(7)	-0.24742(16)	0.13900(9)	0.00785(17)
Ca21	2 <i>i</i> 1	-0.07686(7)	-0.24963(16)	0.62739(9)	0.00844(17)
Ca22	2 <i>i</i> 1	0.26468(7)	-0.27132(16)	0.58561(9)	0.00801(17)

Ca23	2 <i>i</i> 1	-0.43729(7)	0.78212(16)	0.61323(9)	0.00790(17)
Ca31	2 <i>i</i> 1	0.02681(7)	-0.24072(16)	-0.03523(9)	0.00858(17)
Ca32	2 <i>i</i> 1	0.36616(7)	-0.25500(16)	-0.03372(9)	0.00715(16)
Ca33	2 <i>i</i> 1	0.67459(7)	-0.25628(16)	-0.05540(9)	0.00716(16)
O11	2 <i>i</i> 1	0.2300(2)	-0.0248(6)	-0.2307(3)	0.0109(7)
O12	2 <i>i</i> 1	0.5409(2)	0.0468(6)	-0.2255(3)	0.0094(6)
O13	2 <i>i</i> 1	-0.1204(2)	0.0438(6)	0.7920(3)	0.0086(6)
O21	2 <i>i</i> 1	0.0854(2)	0.4648(6)	-0.2026(3)	0.0095(6)
O22	2 <i>i</i> 1	0.4353(2)	0.3993(6)	-0.4083(3)	0.0106(6)
O23	2 <i>i</i> 1	-0.1783(2)	0.4402(6)	0.8753(3)	0.0102(6)
O31	2 <i>i</i> 1	0.2932(3)	0.0980(6)	-0.0744(3)	0.0126(7)
O32	2 <i>i</i> 1	0.5001(2)	0.4094(6)	-0.1385(3)	0.0106(6)
O33	2 <i>i</i> 1	-0.2671(2)	0.4350(6)	0.6244(3)	0.0104(7)
O41	2 <i>i</i> 1	0.0006(3)	-0.2719(7)	0.3051(3)	0.0155(7)
O42	2 <i>i</i> 1	0.3695(3)	-0.3273(7)	0.3165(4)	0.0273(10)
O43	2 <i>i</i> 1	-0.4006(3)	0.9474(6)	0.3194(3)	0.0127(7)
O51	2 <i>i</i> 1	0.0606(3)	-0.5053(6)	0.5151(4)	0.0159(7)
O52	2 <i>i</i> 1	0.2448(2)	-0.0606(6)	0.4904(3)	0.0123(7)
O53	2 <i>i</i> 1	-0.2995(2)	0.5147(6)	0.3283(3)	0.0117(7)
O61	2 <i>i</i> 1	-0.0973(2)	-0.0267(6)	0.5168(3)	0.0138(7)
O62	2 <i>i</i> 1	0.2876(3)	0.0867(7)	0.4327(4)	0.0202(8)
O63	2 <i>i</i> 1	-0.4070(2)	0.8891(6)	0.5259(3)	0.0095(6)
O71	2 <i>i</i> 1	0.0572(2)	0.5185(6)	0.0543(3)	0.0088(6)
O72	2 <i>i</i> 1	0.3851(2)	-0.4856(6)	0.0283(3)	0.0090(6)
O73	2 <i>i</i> 1	-0.2538(2)	0.5060(6)	0.1029(4)	0.0152(7)
O81	2 <i>i</i> 1	0.2400(3)	0.0290(6)	0.0761(3)	0.0117(7)
O82	2 <i>i</i> 1	0.5455(2)	-0.9699(6)	0.0498(3)	0.0092(6)
O83	2 <i>i</i> 1	-0.1402(3)	0.0394(6)	0.0625(3)	0.0155(7)
O91	2 <i>i</i> 1	0.1143(2)	0.2486(6)	0.2145(3)	0.0110(7)
O92	2 <i>i</i> 1	0.3948(2)	-0.6556(6)	0.1835(3)	0.0098(6)
O93	2 <i>i</i> 1	-0.0454(2)	0.0921(6)	0.1095(3)	0.0115(7)

Table C.7: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in β' -CaTeO₃, measured at 250 K

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te11	2 <i>i</i> 1	0.213549(17)	0.18718(4)	-0.23816(2)	0.00955(5)
Te12	2 <i>i</i> 1	0.547554(17)	0.18975(4)	-0.27497(2)	0.00823(5)
Te13	2 <i>i</i> 1	-0.141696(17)	0.23835(4)	0.73149(2)	0.00786(5)
Te21	2 <i>i</i> 1	0.028898(18)	-0.27956(4)	0.48246(2)	0.01179(5)
Te22	2 <i>i</i> 1	0.353524(18)	-0.19004(4)	0.47736(2)	0.01221(5)
Te23	2 <i>i</i> 1	-0.307513(17)	0.70931(4)	0.44464(2)	0.00969(5)
Te31	2 <i>i</i> 1	0.166095(17)	0.29255(4)	0.18868(2)	0.00891(5)

Te32	2 i 1	0.484313(17)	-0.71572(4)	0.16411(2)	0.00811(5)
Te33	2 i 1	-0.135498(17)	0.20477(4)	0.17834(2)	0.00875(5)
Ca11	2 i 1	-0.08161(5)	-0.27293(13)	0.12004(7)	0.01070(14)
Ca12	2 i 1	0.24491(5)	-0.18978(13)	0.14148(7)	0.01094(14)
Ca13	2 i 1	0.59101(5)	-0.24736(13)	0.13903(7)	0.01002(14)
Ca21	2 i 1	-0.07701(5)	-0.24965(13)	0.62740(7)	0.01054(14)
Ca22	2 i 1	0.26444(5)	-0.27104(13)	0.58564(7)	0.00989(14)
Ca23	2 i 1	-0.43690(5)	0.78116(13)	0.61322(7)	0.01025(14)
Ca31	2 i 1	0.02698(5)	-0.24109(13)	-0.03518(7)	0.01056(14)
Ca32	2 i 1	0.36621(5)	-0.25524(12)	-0.03349(7)	0.00917(14)
Ca33	2 i 1	0.67455(5)	-0.25599(12)	-0.05513(7)	0.00899(14)
O11	2 i 1	0.22964(19)	-0.0252(5)	-0.2316(2)	0.0128(5)
O12	2 i 1	0.54083(19)	0.0475(4)	-0.2250(2)	0.0111(5)
O13	2 i 1	-0.12029(18)	0.0435(4)	0.7918(2)	0.0109(5)
O21	2 i 1	0.08590(19)	0.4643(4)	-0.2020(3)	0.0127(5)
O22	2 i 1	0.43498(18)	0.3999(4)	-0.4078(2)	0.0114(5)
O23	2 i 1	-0.17825(18)	0.4392(4)	0.8748(2)	0.0121(5)
O31	2 i 1	0.2936(2)	0.0969(5)	-0.0743(3)	0.0151(6)
O32	2 i 1	0.49962(19)	0.4104(4)	-0.1385(2)	0.0132(5)
O33	2 i 1	-0.26642(18)	0.4331(4)	0.6245(2)	0.0133(5)
O41	2 i 1	0.0004(2)	-0.2705(5)	0.3059(3)	0.0196(6)
O42	2 i 1	0.3688(2)	-0.3272(6)	0.3166(3)	0.0315(8)
O43	2 i 1	-0.4004(2)	0.9473(5)	0.3194(3)	0.0156(6)
O51	2 i 1	0.0606(2)	-0.5054(5)	0.5151(3)	0.0185(6)
O52	2 i 1	0.24478(19)	-0.0610(5)	0.4906(3)	0.0157(6)
O53	2 i 1	-0.29943(19)	0.5153(4)	0.3288(2)	0.0120(5)
O61	2 i 1	-0.09756(19)	-0.0266(5)	0.5169(3)	0.0163(6)
O62	2 i 1	0.2873(2)	0.0859(6)	0.4317(3)	0.0263(7)
O63	2 i 1	-0.40718(19)	0.8892(4)	0.5252(3)	0.0133(5)
O71	2 i 1	0.05750(18)	0.5180(4)	0.0542(2)	0.0100(5)
O72	2 i 1	0.38503(18)	-0.4860(4)	0.0284(2)	0.0105(5)
O73	2 i 1	-0.25417(19)	0.5049(5)	0.1020(3)	0.0176(6)
O81	2 i 1	0.2399(2)	0.0286(5)	0.0773(3)	0.0159(6)
O82	2 i 1	0.54539(18)	-0.9705(4)	0.0499(2)	0.0108(5)
O83	2 i 1	-0.1402(2)	0.0403(5)	0.0628(3)	0.0179(6)
O91	2 i 1	0.1138(2)	0.2489(5)	0.2142(3)	0.0141(5)
O92	2 i 1	0.39494(19)	-0.6565(5)	0.1837(2)	0.0115(5)
O93	2 i 1	-0.04583(19)	0.0926(5)	0.1091(3)	0.0130(5)

Table C.8: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in β' -CaTeO₃, measured at 275 K

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
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Te11	2 i 1	0.213527(18)	0.18719(4)	-0.23810(2)	0.01029(5)
Te12	2 i 1	0.547381(17)	0.19010(4)	-0.27497(2)	0.00894(5)
Te13	2 i 1	-0.141718(17)	0.23844(4)	0.73150(2)	0.00851(5)
Te21	2 i 1	0.028790(19)	-0.27924(5)	0.48238(2)	0.01276(5)
Te22	2 i 1	0.353446(19)	-0.19023(5)	0.47736(2)	0.01321(5)
Te23	2 i 1	-0.307515(18)	0.70945(4)	0.44468(2)	0.01047(5)
Te31	2 i 1	0.166203(18)	0.29231(4)	0.18874(2)	0.00961(5)
Te32	2 i 1	0.484374(17)	-0.71586(4)	0.16415(2)	0.00881(5)
Te33	2 i 1	-0.135518(18)	0.20484(4)	0.17816(2)	0.00954(5)
Ca11	2 i 1	-0.08144(6)	-0.27329(13)	0.12007(7)	0.01162(15)
Ca12	2 i 1	0.24491(6)	-0.19030(13)	0.14120(8)	0.01207(15)
Ca13	2 i 1	0.59098(5)	-0.24723(13)	0.13901(7)	0.01082(14)
Ca21	2 i 1	-0.07698(6)	-0.24974(13)	0.62743(7)	0.01154(15)
Ca22	2 i 1	0.26423(6)	-0.27067(13)	0.58572(7)	0.01073(14)
Ca23	2 i 1	-0.43682(6)	0.78092(13)	0.61312(7)	0.01119(14)
Ca31	2 i 1	0.02706(6)	-0.24119(13)	-0.03523(7)	0.01114(14)
Ca32	2 i 1	0.36619(5)	-0.25521(13)	-0.03338(7)	0.00980(14)
Ca33	2 i 1	0.67453(5)	-0.25576(13)	-0.05517(7)	0.00966(14)
O11	2 i 1	0.2297(2)	-0.0248(5)	-0.2313(3)	0.0135(5)
O12	2 i 1	0.54063(19)	0.0478(5)	-0.2250(3)	0.0131(5)
O13	2 i 1	-0.12039(19)	0.0438(4)	0.7921(2)	0.0113(5)
O21	2 i 1	0.08570(19)	0.4643(4)	-0.2025(3)	0.0146(6)
O22	2 i 1	0.43455(19)	0.4004(4)	-0.4075(2)	0.0125(5)
O23	2 i 1	-0.17838(19)	0.4393(5)	0.8751(3)	0.0137(6)
O31	2 i 1	0.2929(2)	0.0980(5)	-0.0742(3)	0.0165(6)
O32	2 i 1	0.49999(19)	0.4094(4)	-0.1384(2)	0.0137(6)
O33	2 i 1	-0.26654(19)	0.4335(5)	0.6247(3)	0.0148(6)
O41	2 i 1	0.0002(2)	-0.2699(5)	0.3061(3)	0.0215(7)
O42	2 i 1	0.3685(2)	-0.3277(6)	0.3173(3)	0.0347(9)
O43	2 i 1	-0.4000(2)	0.9470(5)	0.3196(3)	0.0164(6)
O51	2 i 1	0.0606(2)	-0.5055(5)	0.5146(3)	0.0195(6)
O52	2 i 1	0.2451(2)	-0.0619(5)	0.4909(3)	0.0160(6)
O53	2 i 1	-0.29918(19)	0.5144(5)	0.3289(3)	0.0136(6)
O61	2 i 1	-0.0974(2)	-0.0269(5)	0.5168(3)	0.0185(6)
O62	2 i 1	0.2871(2)	0.0857(6)	0.4312(3)	0.0271(7)
O63	2 i 1	-0.40732(19)	0.8901(4)	0.5253(3)	0.0124(5)
O71	2 i 1	0.05739(18)	0.5182(4)	0.0545(2)	0.0103(5)
O72	2 i 1	0.38515(19)	-0.4856(4)	0.0285(2)	0.0118(5)
O73	2 i 1	-0.2543(2)	0.5052(5)	0.1022(3)	0.0192(6)
O81	2 i 1	0.2401(2)	0.0279(5)	0.0771(3)	0.0164(6)
O82	2 i 1	0.54538(18)	-0.9706(4)	0.0497(2)	0.0110(5)
O83	2 i 1	-0.1403(2)	0.0404(5)	0.0630(3)	0.0199(6)
O91	2 i 1	0.1139(2)	0.2488(5)	0.2142(3)	0.0140(6)
O92	2 i 1	0.3953(2)	-0.6575(5)	0.1835(3)	0.0139(6)
O93	2 i 1	-0.04552(19)	0.0924(5)	0.1091(3)	0.0145(6)

Table C.9: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\text{Ca}_{0.14}\text{Sr}_{0.86}\text{TeO}_3$ (β'' -Ca).

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te11	2 <i>i</i> 1	1	0.200863(18)	0.21073(4)	-0.25496(2)	0.01721(5)
Te12	2 <i>i</i> 1	1	0.517944(18)	0.25473(5)	-0.25546(2)	0.01802(5)
Te13	2 <i>i</i> 1	1	-0.138466(16)	0.24232(4)	0.73719(2)	0.01364(5)
Te21	2 <i>i</i> 1	1	0.02767(2)	-0.27374(5)	0.47952(3)	0.02377(6)
Te22	2 <i>i</i> 1	1	0.35482(2)	-0.25033(5)	0.46366(2)	0.02141(5)
Te23	2 <i>i</i> 1	1	-0.325130(18)	0.77260(5)	0.44326(2)	0.02080(5)
Te31	2 <i>i</i> 1	1	0.167271(18)	0.26130(5)	0.16635(2)	0.01892(5)
Te32	2 <i>i</i> 1	1	0.476499(16)	-0.70550(4)	0.15361(2)	0.01362(5)
Te33	2 <i>i</i> 1	1	-0.136032(16)	0.21485(4)	0.17681(2)	0.01565(5)
Sr11	2 <i>i</i> 1	0.964(4)	-0.07491(2)	-0.27989(6)	0.13615(3)	0.01507(10)
Sr12	2 <i>i</i> 1	0.962(4)	0.24032(2)	-0.21410(6)	0.11920(3)	0.01777(11)
Sr13	2 <i>i</i> 1	0.973(4)	0.59420(2)	-0.25730(6)	0.14472(3)	0.01488(10)
Sr21	2 <i>i</i> 1	0.831(4)	-0.07529(3)	-0.24805(7)	0.63000(4)	0.01805(12)
Sr22	2 <i>i</i> 1	0.821(4)	0.25562(3)	-0.27313(7)	0.57941(4)	0.01893(12)
Sr23	2 <i>i</i> 1	0.826(4)	-0.42717(3)	0.77079(7)	0.62760(4)	0.01902(12)
Sr31	2 <i>i</i> 1	0.765(4)	0.02611(3)	-0.24033(7)	-0.03433(4)	0.01655(12)
Sr32	2 <i>i</i> 1	0.774(4)	0.35652(3)	-0.25157(7)	-0.06294(4)	0.01505(11)
Sr33	2 <i>i</i> 1	0.786(4)	0.67984(3)	-0.24443(7)	-0.04485(4)	0.01682(12)
Ca11	2 <i>i</i> 1	0.036(4)	-0.07491(2)	-0.27989(6)	0.13615(3)	0.01507(10)
Ca12	2 <i>i</i> 1	0.038(4)	0.24032(2)	-0.21410(6)	0.11920(3)	0.01777(11)
Ca13	2 <i>i</i> 1	0.027(4)	0.59420(2)	-0.25730(6)	0.14472(3)	0.01488(10)
Ca21	2 <i>i</i> 1	0.169(4)	-0.07529(3)	-0.24805(7)	0.63000(4)	0.01805(12)
Ca22	2 <i>i</i> 1	0.179(4)	0.25562(3)	-0.27313(7)	0.57941(4)	0.01893(12)
Ca23	2 <i>i</i> 1	0.174(4)	-0.42717(3)	0.77079(7)	0.62760(4)	0.01902(12)
Ca31	2 <i>i</i> 1	0.235(4)	0.02611(3)	-0.24033(7)	-0.03433(4)	0.01655(12)
Ca32	2 <i>i</i> 1	0.226(4)	0.35652(3)	-0.25157(7)	-0.06294(4)	0.01505(11)
Ca33	2 <i>i</i> 1	0.214(4)	0.67984(3)	-0.24443(7)	-0.04485(4)	0.01682(12)
O11	2 <i>i</i> 1	1	0.2114(2)	0.0136(5)	-0.2521(3)	0.0202(5)
O12	2 <i>i</i> 1	1	0.5560(3)	-1.9748(6)	-0.2144(3)	0.0349(9)
O13	2 <i>i</i> 1	1	-0.1171(2)	0.0494(5)	0.7927(3)	0.0202(5)
O21	2 <i>i</i> 1	1	0.0823(2)	-0.5221(5)	-0.2094(3)	0.0230(6)
O22	2 <i>i</i> 1	1	0.3914(2)	-0.5092(6)	-0.2492(3)	0.0332(8)
O23	2 <i>i</i> 1	1	-0.1743(2)	0.4337(5)	0.8741(3)	0.0235(6)
O31	2 <i>i</i> 1	1	0.2793(3)	-0.8830(6)	-0.1052(3)	0.0316(7)
O32	2 <i>i</i> 1	1	0.5355(3)	0.3451(9)	-0.1062(4)	0.0567(13)
O33	2 <i>i</i> 1	1	-0.2552(2)	0.4298(5)	0.6389(3)	0.0273(7)
O41	2 <i>i</i> 1	1	0.0039(4)	-0.2695(9)	0.3151(4)	0.0554(12)
O42	2 <i>i</i> 1	1	0.3383(3)	-0.2606(7)	0.2980(3)	0.0372(8)
O43	2 <i>i</i> 1	1	-0.4128(2)	0.9760(5)	0.3144(3)	0.0273(7)
O51	2 <i>i</i> 1	1	0.0563(3)	-0.4924(7)	0.5081(4)	0.0471(11)

O52	2 <i>i</i> 1	1	0.4067(2)	-0.5056(6)	0.5002(3)	0.0329(8)
O53	2 <i>i</i> 1	1	-0.2742(3)	0.5171(6)	0.3557(3)	0.0330(8)
O61	2 <i>i</i> 1	1	-0.0904(2)	-0.0292(6)	0.5205(3)	0.0336(8)
O62	2 <i>i</i> 1	1	0.2359(2)	-0.0385(6)	0.4871(3)	0.0306(7)
O63	2 <i>i</i> 1	1	-0.4130(2)	0.8866(7)	0.5059(4)	0.0465(11)
O71	2 <i>i</i> 1	1	0.0646(2)	-0.4968(5)	0.0576(3)	0.0191(5)
O72	2 <i>i</i> 1	1	0.38682(19)	-0.4930(5)	0.0260(2)	0.0166(5)
O73	2 <i>i</i> 1	1	-0.2503(2)	0.4806(5)	0.0892(3)	0.0266(7)
O81	2 <i>i</i> 1	1	0.2259(2)	0.0306(5)	0.0482(3)	0.0230(6)
O82	2 <i>i</i> 1	1	0.54456(18)	0.0359(5)	0.0516(2)	0.0158(5)
O83	2 <i>i</i> 1	1	-0.1271(3)	0.0248(7)	0.0778(4)	0.0411(10)
O91	2 <i>i</i> 1	1	0.1074(2)	-0.7515(5)	0.1962(3)	0.0290(7)
O92	2 <i>i</i> 1	1	0.39528(19)	-1.6645(5)	0.1715(3)	0.0189(5)
O93	2 <i>i</i> 1	1	-0.0506(2)	0.1062(6)	0.1079(3)	0.0323(8)

Table C.10: Multiplicity, polytype, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\gamma\text{-CaTeO}_3$. Wyckoff letters for atoms in polytype MDO_1 are given for symmetry group $P2_1$, for atoms both polytypes or in polytype MDO_2 according to symmetry group $P2_1/c$. Atoms of MDO_1 obtained by translation along $\frac{1}{2}\mathbf{c}$ are not indicated.

Atom	Polytype	Multiplicity, occ. Wyckoff letter, site symmetry		x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te1	MDO ₁	2 a 1	0.198(2)	0.3264(10)	0.2728(8)	0.1237(4)	0.0112(11)
Te1	MDO ₂	4 e 1	0.802(2)	0.3299(2)	0.26796(10)	0.12545(8)	0.0098(2)
Te2	MDO _{1,2}	4 e 1	1	0.68594(4)	0.25569(5)	0.012147(15)	0.01428(9)
Te3	MDO ₁	2 a 1	0.198(2)	0.7438(5)	0.8345(6)	0.16505(18)	0.0275(9)
Te3	MDO ₂	4 e 1	0.802(2)	0.74146(6)	0.83509(7)	0.16394(2)	0.00783(14)
Ca1	MDO ₁	2 a 1	0.198(2)	0.9934(13)	0.338(2)	0.1827(5)	0.028(2)
Ca1	MDO ₂	4 e 1	0.802(2)	0.99250(18)	0.3423(2)	0.18261(7)	0.0107(3)
Ca2	MDO _{1,2}	4 e 1	1	0.01884(13)	-0.23104(16)	0.05842(5)	0.01376(18)
Ca3	MDO ₁	2 a 1	0.198(2)	0.2981(13)	-0.176(2)	0.2228(5)	0.025(2)
Ca3	MDO ₂	4 e 1	0.802(2)	0.29504(19)	-0.1733(3)	0.22271(7)	0.0093(3)
O1	MDO ₁	2 a 1	0.198(2)	0.144(5)	0.086(7)	0.126(2)	0.029(8)
O1	MDO ₂	4 e 1	0.802(2)	0.1462(7)	0.0884(9)	0.1278(2)	0.0121(10)
O2	MDO ₁	2 a 1	0.198(2)	0.242(5)	0.541(7)	0.1495(19)	0.025(8)
O2	MDO ₂	4 e 1	0.802(2)	0.2419(8)	0.5475(9)	0.1449(3)	0.0174(11)
O3	MDO ₁	2 a 1	0.198(2)	0.460(5)	0.154(7)	0.202(2)	0.030(9)
O3	MDO ₂	4 e 1	0.802(2)	0.4707(7)	0.1572(10)	0.2037(3)	0.0152(11)
O4	MDO _{1,2}	4 e 1	1	0.7478(5)	0.2327(7)	0.09833(18)	0.0235(8)
O5	MDO _{1,2}	4 e 1	1	0.8051(5)	0.0127(7)	-0.00745(19)	0.0232(8)
O6	MDO _{1,2}	4 e 1	1	0.8303(5)	0.4809(7)	0.00209(19)	0.0241(8)
O7	MDO ₁	2 a 1	0.198(2)	0.793(4)	0.601(5)	0.2285(16)	0.016(6)

O7	MDO ₂	4 <i>e</i> 1	0.802(2)	0.7825(8)	0.5963(9)	0.2221(3)	0.0178(11)
O8	MDO ₁	2 <i>a</i> 1	0.198(2)	0.844(5)	1.054(7)	0.2221(19)	0.029(8)
O8	MDO ₂	4 <i>e</i> 1	0.802(2)	0.8466(6)	1.0650(9)	0.2245(2)	0.0099(9)
O9	MDO ₁	2 <i>a</i> 1	0.198(2)	0.922(7)	0.734(8)	0.135(2)	0.010(9)
O9	MDO ₂	4 <i>e</i> 1	0.802(2)	0.9257(18)	0.7416(8)	0.1439(6)	0.017(2)

Table C.11: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\text{Ca}_{0.77}\text{Sr}_{0.23}\text{TeO}_3$ (γ -Ca).

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}[\text{\AA}^2]$
Te1	2 <i>a</i> 1	1	0.66550(3)	0.25202(4)	0.24724(2)	0.01599(6)
Te2	2 <i>a</i> 1	1	0.68797(3)	0.73826(5)	0.52610(2)	0.01977(6)
Te3	2 <i>a</i> 1	1	0.74426(3)	0.31542(5)	-0.169342(19)	0.01550(6)
Ca1	2 <i>a</i> 1	0.600(5)	1.00619(6)	0.31917(11)	0.13784(4)	0.01672(18)
Sr1	2 <i>a</i> 1	0.400(5)	1.00619(6)	0.31917(11)	0.13784(4)	0.01672(18)
Ca2	2 <i>a</i> 1	0.838(4)	0.98321(8)	0.75942(13)	0.38510(5)	0.0167(2)
Sr2	2 <i>a</i> 1	0.162(4)	0.98321(8)	0.75942(13)	0.38510(5)	0.0167(2)
Ca3	2 <i>a</i> 1	0.875(4)	0.29843(8)	0.30785(13)	-0.05469(5)	0.0157(2)
Sr3	2 <i>a</i> 1	0.125(4)	0.29843(8)	0.30785(13)	-0.05469(5)	0.0157(2)
O1	2 <i>a</i> 1	1	0.8437(4)	0.0642(6)	0.2462(3)	0.0236(7)
O2	2 <i>a</i> 1	1	0.7589(5)	0.5226(6)	0.2074(3)	0.0257(7)
O3	2 <i>a</i> 1	1	0.5307(4)	0.1435(6)	0.0914(3)	0.0251(6)
O4	2 <i>a</i> 1	1	0.7464(4)	0.7079(7)	0.6957(3)	0.0335(8)
O5	2 <i>a</i> 1	1	0.8082(5)	0.5019(6)	0.4841(3)	0.0291(7)
O6	2 <i>a</i> 1	1	0.8295(5)	0.9677(7)	0.5101(4)	0.0338(8)
O7	2 <i>a</i> 1	1	0.7886(4)	0.0766(6)	-0.0529(3)	0.0248(7)
O8	2 <i>a</i> 1	1	0.8414(4)	0.5446(5)	-0.0512(3)	0.0186(6)
O9	2 <i>a</i> 1	1	0.9285(4)	0.2347(6)	-0.2123(3)	0.0245(6)

Table C.12: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\text{Ca}_{0.55}\text{Sr}_{0.45}\text{TeO}_3$ (γ -Ca).

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}[\text{\AA}^2]$
Te1	2 <i>a</i> 1	1	0.66448(3)	0.24676(4)	0.24718(2)	0.01831(6)
Te2	2 <i>a</i> 1	1	0.31229(3)	0.26279(5)	0.47355(2)	0.02255(7)
Te3	2 <i>a</i> 1	1	0.74562(3)	0.18758(5)	0.83152(2)	0.01725(6)
Ca1	2 <i>a</i> 1	0.311(4)	0.00594(4)	0.18468(9)	0.13873(4)	0.01737(14)
Sr1	2 <i>a</i> 1	0.689(4)	0.00594(4)	0.18468(9)	0.13873(4)	0.01737(14)

Ca2	2 <i>a</i> 1	0.637(4)	0.01550(7)	0.24044(11)	0.61401(5)	0.01933(18)
Sr2	2 <i>a</i> 1	0.363(4)	0.01550(7)	0.24044(11)	0.61401(5)	0.01933(18)
Ca3	2 <i>a</i> 1	0.713(4)	0.70041(7)	0.69450(11)	0.05488(5)	0.01715(18)
Sr3	2 <i>a</i> 1	0.287(4)	0.70041(7)	0.69450(11)	0.05488(5)	0.01715(18)
O1	2 <i>a</i> 1	1	0.8401(4)	0.4375(6)	0.2482(3)	0.0270(7)
O2	2 <i>a</i> 1	1	0.7594(4)	-0.0195(6)	0.2081(3)	0.0272(7)
O3	2 <i>a</i> 1	1	0.5333(4)	0.3523(6)	0.0918(3)	0.0307(7)
O4	2 <i>a</i> 1	1	0.2561(4)	0.2962(7)	0.3062(3)	0.0371(9)
O5	2 <i>a</i> 1	1	0.1928(5)	0.4961(7)	0.5160(4)	0.0358(9)
O6	2 <i>a</i> 1	1	0.1708(5)	0.0358(7)	0.4877(4)	0.0422(10)
O7	2 <i>a</i> 1	1	0.7891(4)	0.4256(6)	0.9462(3)	0.0251(7)
O8	2 <i>a</i> 1	1	0.8372(4)	-0.0425(5)	0.9482(3)	0.0194(6)
O9	2 <i>a</i> 1	1	0.9317(4)	0.2599(6)	0.7907(3)	0.0295(6)

Table C.13: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\text{Ca}_{0.07}\text{Sr}_{0.93}\text{TeO}_3$ (β -Sr).

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Te1	8 <i>f</i> 1	1	0.155713(10)	0.25003(5)	0.426568(10)	0.01606(6)
Te2	8 <i>f</i> 1	1	0.416037(10)	0.27206(5)	0.173415(10)	0.01315(6)
Te3	8 <i>f</i> 1	1	0.277151(10)	0.26147(4)	0.139240(10)	0.01313(6)
Te4	8 <i>f</i> 1	1	0.008932(11)	0.26916(5)	0.112203(12)	0.01861(7)
Te5	8 <i>f</i> 1	1	0.400031(13)	0.25218(5)	0.002008(11)	0.02085(7)
Te6	8 <i>f</i> 1	1	0.302497(9)	0.26980(4)	0.292168(9)	0.01050(6)
Ca1	8 <i>f</i> 1	0.031(5)	0.164333(15)	0.25567(6)	0.289469(14)	0.01125(13)
Sr1	8 <i>f</i> 1	0.969(5)	0.164333(15)	0.25567(6)	0.289469(14)	0.01125(13)
Sr2	8 <i>f</i> 1	0.774(5)	0.440377(17)	0.28427(8)	0.445193(18)	0.01523(15)
Ca2	8 <i>f</i> 1	0.226(5)	0.440377(17)	0.28427(8)	0.445193(18)	0.01523(15)
Sr3	8 <i>f</i> 1	1	0.146477(16)	0.27847(7)	0.137445(15)	0.01673(8)
Sr4	8 <i>f</i> 1	0.983(5)	0.429891(15)	0.23835(7)	0.303482(15)	0.01334(13)
Ca4	8 <i>f</i> 1	0.017(5)	0.429891(15)	0.23835(7)	0.303482(15)	0.01334(13)
Sr5	8 <i>f</i> 1	1	0.297628(15)	0.25449(7)	0.424651(15)	0.01430(8)
Sr6	4 <i>c</i> $\bar{1}$	0.680(7)	$\frac{1}{4}$	$\frac{1}{4}$	0	0.0182(2)
Ca6	4 <i>f</i> $\bar{1}$	0.320(7)	$\frac{1}{4}$	$\frac{1}{4}$	0	0.0182(2)
Sr7	4 <i>e</i> 2	1	0	0.21849(9)	$\frac{1}{4}$	0.01457(11)
O11	8 <i>f</i> 1	1	0.19370(15)	0.1974(9)	0.38769(14)	0.0389(10)
O12	8 <i>f</i> 1	1	0.1734(2)	0.5430(8)	0.4452(2)	0.0552(14)
O13	8 <i>f</i> 1	1	0.19502(14)	0.0981(6)	0.48729(13)	0.0260(7)
O21	8 <i>f</i> 1	1	0.40651(12)	0.4800(5)	0.21863(12)	0.0172(6)
O22	8 <i>f</i> 1	1	0.48368(12)	0.3579(6)	0.18749(14)	0.0248(7)
O23	8 <i>f</i> 1	1	0.42025(13)	0.0155(6)	0.21353(14)	0.0229(7)
O31	8 <i>f</i> 1	1	0.22723(13)	0.3114(7)	0.07298(13)	0.0270(7)
O32	8 <i>f</i> 1	1	0.24650(14)	0.0114(6)	0.15550(13)	0.0263(7)

O33	8 <i>f</i> 1	1	0.25357(14)	0.4766(6)	0.17186(14)	0.0256(7)
O41	8 <i>f</i> 1	1	0.05617(13)	0.4852(6)	0.11109(13)	0.0211(6)
O42	8 <i>f</i> 1	1	0.0171(2)	0.3486(8)	0.1770(2)	0.0572(16)
O43	8 <i>f</i> 1	1	0.05360(13)	0.0254(5)	0.12357(12)	0.0201(6)
O51	8 <i>f</i> 1	1	0.37253(14)	0.4463(6)	-0.05421(13)	0.0229(7)
O52	8 <i>f</i> 1	1	0.38532(15)	-0.0198(6)	-0.03298(15)	0.0303(8)
O53	8 <i>f</i> 1	1	0.46777(19)	0.3050(12)	0.0090(2)	0.0678(17)
O61	8 <i>f</i> 1	1	0.34356(12)	0.2265(6)	0.36264(11)	0.0180(6)
O62	8 <i>f</i> 1	1	0.34027(12)	0.5217(5)	0.28623(12)	0.0185(6)
O63	8 <i>f</i> 1	1	0.33969(12)	0.0465(6)	0.27397(12)	0.0189(6)

Table C.14: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates of the idealized MDO₁ polytype derived from atoms in Ca_{0.77}Sr_{0.23}TeO₃ (γ -Ca) and Ca_{0.45}Sr_{0.55}TeO₃ (γ -Ca).

Atom	Multiplicity, Wyckoff letter, site symmetry	Ca _{0.77} Sr _{0.23} TeO ₃ (γ -Ca)			Ca _{0.45} Sr _{0.55} TeO ₃ (γ -Ca)		
		<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Te1	2 <i>a</i> 1	0.6655	0.2500	0.2472	0.6645	0.2500	0.2472
Te2	2 <i>a</i> 1	0.6880	0.7500	0.5261	0.3123	0.2500	0.4736
Te3	2 <i>a</i> 1	0.7443	0.3154	0.8307	0.7456	0.1876	0.8315
Ca1	2 <i>a</i> 1	0.0062	0.3192	0.1378	0.0059	0.1847	0.1387
Ca2	2 <i>a</i> 1	0.9832	0.7500	0.3851	0.0155	0.2500	0.6140
Ca3	2 <i>a</i> 1	0.2984	0.3078	0.9453	0.7004	0.6945	0.0549
O1	2 <i>a</i> 1	0.8437	0.0642	0.2462	0.8401	0.4375	0.2482
O2	2 <i>a</i> 1	0.7589	0.5226	0.2074	0.7594	0.9805	0.2081
O3	2 <i>a</i> 1	0.5307	0.1435	0.0914	0.5333	0.3523	0.0918
O4	2 <i>a</i> 1	0.7464	0.7500	0.6957	0.2561	0.2500	0.3062
O5	2 <i>a</i> 1	0.8189	0.5171	0.4971	0.1818	0.4801	0.5018
O6	2 <i>a</i> 1	0.8189	-0.0171	0.4971	0.1818	0.0199	0.5018
O7	2 <i>a</i> 1	0.7886	0.0766	0.9471	0.7891	0.4256	0.9462
O8	2 <i>a</i> 1	0.8414	0.5446	0.9488	0.8372	0.9575	0.9482
O9	2 <i>a</i> 1	0.9285	0.2347	0.7877	0.9317	0.2599	0.7907

Table C.15: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates of the idealized MDO₂ polytype derived from atoms in CaTeO₃.

Atom	Multiplicity, Wyckoff letter, site symmetry	<i>x</i>	<i>y</i>	<i>z</i>
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Te1	2 a 1	0.6655	0.2500	0.2472
Te3	2 a 1	0.7443	0.3154	0.8307
Te2	2 a 1	0.6880	0.7500	0.5261
Ca1	2 a 1	0.0062	0.3192	0.1378
Ca2	2 a 1	0.9832	0.7500	0.3851
Ca3	2 a 1	0.2984	0.3078	0.9453
O1	2 a 1	0.8437	0.0642	0.2462
O2	2 a 1	0.7589	0.5226	0.2074
O3	2 a 1	0.5307	0.1435	0.0914
O4	2 a 1	0.7464	0.7500	0.6957
O5	2 a 1	0.8189	0.5171	0.4971
O6	2 a 1	0.8189	-0.0171	0.4971
O7	2 a 1	0.7886	0.0766	0.9471
O8	2 a 1	0.8414	0.5446	0.9488
O9	2 a 1	0.9285	0.2347	0.7877

Table C.16: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in CaTe_2O_5 . Wyckoff letters correspond to those of space group $C2/c$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
TeA	8 f 1	-0.06280(2)	0.288521(11)	0.16450(2)	0.00961(7)
TeB	8 f 1	0.21115(3)	0.210010(12)	0.15333(2)	0.01336(8)
TeC	8 f 1	0.18099(2)	0.355620(11)	0.16379(2)	0.00896(7)
TeD	8 f 1	-0.05334(2)	0.429484(11)	0.158708(19)	0.01004(7)
TeE	8 f 1	-0.05943(2)	0.567699(11)	0.158699(19)	0.00961(7)
TeF	8 f 1	-0.30455(2)	0.499943(10)	0.150455(19)	0.00804(7)
TeG	8 f 1	0.67513(2)	0.360242(11)	0.16066(2)	0.00968(7)
TeH	8 f 1	-0.30811(2)	0.222284(13)	0.14950(2)	0.01109(8)
TeI	8 f 1	0.41873(2)	0.290082(12)	0.162801(19)	0.01045(8)
TeJ	8 f 1	-0.05682(2)	-0.141429(11)	0.151770(19)	0.00947(8)
TeK	8 f 1	0.42311(2)	-0.000701(11)	0.161778(19)	0.00900(7)
TeL	8 f 1	0.17711(2)	-0.071708(11)	0.161153(19)	0.01045(7)
TeM	8 f 1	-0.05404(2)	0.140433(11)	0.150517(19)	0.00948(8)
TeN	8 f 1	0.18433(2)	0.069713(11)	0.161408(19)	0.00972(7)
CaA	4 a $\bar{1}$	0	0	0	0.0138(3)
CaB	8 f 1	0.50136(7)	0.14436(4)	0.49685(6)	0.0140(2)
CaC	8 f 1	0.00648(7)	0.21475(4)	0.00158(6)	0.0122(2)
CaD	8 f 1	0.49892(7)	0.06918(4)	0.00036(6)	0.0105(2)
CaE	4 e 2	$\frac{1}{4}$	0.99478(5)	0	0.0151(3)
CaF	4 e 2	$\frac{1}{4}$	0.85360(5)	0	0.0127(3)
CaG	4 e 2	$\frac{1}{4}$	0.70890(5)	0	0.0148(3)
CaH	4 e 2	$\frac{1}{4}$	0.57094(5)	0	0.0099(3)
CaI	4 e 2	$\frac{1}{4}$	0.42732(5)	0	0.0101(3)

CaJ	4 <i>e</i> 2	$\frac{1}{4}$	0.28845(5)	0	0.0098(3)
CaK	4 <i>e</i> 2	$\frac{1}{4}$	0.13672(6)	0	0.0150(3)
O1A	8 <i>f</i> 1	-0.0763(3)	0.57847(14)	0.0571(2)	0.0145(7)
O1B	8 <i>f</i> 1	0.4211(3)	0.28841(13)	0.0598(2)	0.0132(7)
O1C	8 <i>f</i> 1	-0.0893(3)	-0.13582(13)	0.0493(2)	0.0127(7)
O1D	8 <i>f</i> 1	0.4257(3)	-0.00095(13)	0.0589(2)	0.0151(8)
O1E	8 <i>f</i> 1	-0.0861(3)	0.13817(14)	0.0479(2)	0.0147(8)
O1F	8 <i>f</i> 1	-0.0575(3)	0.28998(13)	0.0619(2)	0.0163(8)
O1G	8 <i>f</i> 1	-0.0769(3)	0.41811(14)	0.0575(2)	0.0141(7)
O1H	8 <i>f</i> 1	-0.3385(3)	0.50101(13)	0.0478(2)	0.0128(7)
O1I	8 <i>f</i> 1	0.6790(3)	0.35990(12)	0.0580(2)	0.0139(8)
O1J	8 <i>f</i> 1	-0.3419(3)	0.22725(14)	0.0474(2)	0.0158(8)
O1K	8 <i>f</i> 1	0.1772(3)	-0.07064(13)	0.0583(2)	0.0153(8)
O1L	8 <i>f</i> 1	0.1759(3)	0.05813(13)	0.0596(2)	0.0128(7)
O1M	8 <i>f</i> 1	0.1751(3)	0.22070(13)	0.0532(2)	0.0134(7)
O1N	8 <i>f</i> 1	0.1744(3)	0.35689(12)	0.0597(2)	0.0128(7)
O2A	8 <i>f</i> 1	-0.2303(3)	0.16791(16)	0.1376(3)	0.0296(10)
O2B	8 <i>f</i> 1	0.0265(3)	0.19440(14)	0.1421(2)	0.0223(9)
O2C	8 <i>f</i> 1	0.0883(3)	0.30679(14)	0.1786(3)	0.0216(9)
O2D	8 <i>f</i> 1	0.2723(3)	0.28881(14)	0.1511(2)	0.0206(9)
O2E	8 <i>f</i> 1	0.0843(3)	0.41233(14)	0.1585(3)	0.0226(9)
O2F	8 <i>f</i> 1	-0.0140(3)	0.49847(12)	0.1311(2)	0.0164(8)
O2G	8 <i>f</i> 1	-0.2158(3)	0.55269(13)	0.1406(2)	0.0165(8)
O2H	8 <i>f</i> 1	-0.2209(3)	0.44604(13)	0.1409(2)	0.0164(8)
O2I	8 <i>f</i> 1	0.5860(3)	0.41530(14)	0.1572(3)	0.0234(9)
O2J	8 <i>f</i> 1	0.5829(3)	0.31033(15)	0.1609(3)	0.0297(11)
O2K	8 <i>f</i> 1	0.4008(3)	0.35935(14)	0.1764(3)	0.0258(10)
O2L	8 <i>f</i> 1	0.1496(3)	-0.00513(13)	0.1825(2)	0.0187(8)
O2M	8 <i>f</i> 1	0.3343(3)	0.05253(14)	0.1650(3)	0.0218(9)
O2N	8 <i>f</i> 1	0.3314(3)	-0.05236(14)	0.1631(3)	0.0240(9)
O2O	8 <i>f</i> 1	0.0331(3)	0.08443(14)	0.1406(2)	0.0166(8)
O2P	8 <i>f</i> 1	0.0300(3)	-0.08089(14)	0.1418(2)	0.0167(8)
O2Q	8 <i>f</i> 1	-0.2127(3)	0.27706(14)	0.1394(3)	0.0219(9)
O2R	8 <i>f</i> 1	-0.0953(3)	0.35420(14)	0.1834(3)	0.0206(9)
O2S	8 <i>f</i> 1	0.2244(3)	0.13905(13)	0.1315(3)	0.0208(9)
O2T	8 <i>f</i> 1	0.0399(3)	-0.18681(16)	0.1400(3)	0.0271(10)
O2U	8 <i>f</i> 1	0.3520(3)	0.20801(15)	0.1470(3)	0.0244(9)

Table C.17: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$. Wyckoff letters correspond to those of space group $C2/c$.

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
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TeA	8 <i>f</i> 1	1	-0.06468(4)	0.28907(2)	0.16424(3)	0.00902(14)
TeB	8 <i>f</i> 1	1	0.21208(5)	0.21047(2)	0.15379(3)	0.01486(16)
TeC	8 <i>f</i> 1	1	0.17993(4)	0.355849(19)	0.16343(3)	0.00758(14)
TeD	8 <i>f</i> 1	1	-0.05293(4)	0.430034(19)	0.15874(3)	0.00803(14)
TeE	8 <i>f</i> 1	1	-0.05838(4)	0.56774(2)	0.15868(3)	0.00784(14)
TeF	8 <i>f</i> 1	1	-0.30384(4)	0.499896(17)	0.15095(3)	0.00525(14)
TeG	8 <i>f</i> 1	1	0.67531(4)	0.35989(2)	0.16077(3)	0.00791(14)
TeH	8 <i>f</i> 1	1	-0.30610(4)	0.22160(2)	0.15066(3)	0.01260(15)
TeI	8 <i>f</i> 1	1	0.41971(4)	0.29058(2)	0.16290(3)	0.00940(15)
TeJ	8 <i>f</i> 1	1	-0.05530(4)	-0.140842(19)	0.15218(3)	0.00800(14)
TeK	8 <i>f</i> 1	1	0.42306(4)	-0.000404(18)	0.16158(3)	0.00638(14)
TeL	8 <i>f</i> 1	1	0.17788(4)	-0.071085(19)	0.16132(3)	0.00865(14)
TeM	8 <i>f</i> 1	1	-0.05329(4)	0.140189(19)	0.15136(3)	0.00756(14)
TeN	8 <i>f</i> 1	1	0.18429(4)	0.069934(19)	0.16147(3)	0.00786(14)
CaA	4 <i>a</i> $\bar{1}$	1	0.0000	0.0000	0.0000	0.0099(5)
CaB	8 <i>f</i> 1	0.909(11)	0.50078(11)	0.14433(6)	0.49688(9)	0.0124(7)
SrB	8 <i>f</i> 1	0.091(11)	0.50078(11)	0.14433(6)	0.49688(9)	0.0124(7)
CaC	8 <i>f</i> 1	0.695(10)	0.00588(9)	0.21440(5)	0.00097(7)	0.0105(5)
SrC	8 <i>f</i> 1	0.305(10)	0.00588(9)	0.21440(5)	0.00097(7)	0.0105(5)
CaD	8 <i>f</i> 1	0.975(10)	0.49902(11)	0.06898(6)	0.00014(9)	0.0073(6)
SrD	8 <i>f</i> 1	0.025(10)	0.49902(11)	0.06898(6)	0.00014(9)	0.0073(6)
CaE	4 <i>e</i> 2	0.928(14)	$\frac{1}{4}$	0.99533(9)	0	0.0144(9)
SrE	4 <i>e</i> 2	0.072(14)	$\frac{1}{4}$	0.99533(9)	0	0.0144(9)
CaF	4 <i>e</i> 2	0.852(12)	$\frac{1}{4}$	0.85407(8)	0	0.0127(8)
SrF	4 <i>e</i> 2	0.148(12)	$\frac{1}{4}$	0.85407(8)	0	0.0127(8)
CaG	4 <i>e</i> 2	0.943(13)	$\frac{1}{4}$	0.70904(8)	0	0.0115(8)
SrG	4 <i>e</i> 2	0.057(13)	$\frac{1}{4}$	0.70904(8)	0	0.0115(8)
CaH	4 <i>e</i> 2	0.870(12)	$\frac{1}{4}$	0.57085(7)	0	0.0091(7)
SrH	4 <i>e</i> 2	0.130(12)	$\frac{1}{4}$	0.57085(7)	0	0.0091(7)
CaI	4 <i>e</i> 2	0.868(12)	$\frac{1}{4}$	0.42749(7)	0	0.0083(7)
SrI	4 <i>e</i> 2	0.132(12)	$\frac{1}{4}$	0.42749(7)	0	0.0083(7)
CaJ	4 <i>e</i> 2	0.960(12)	$\frac{1}{4}$	0.28865(8)	0	0.0081(8)
SrJ	4 <i>e</i> 2	0.040(12)	$\frac{1}{4}$	0.28865(8)	0	0.0081(8)
CaK	4 <i>e</i> 2	0.845(13)	$\frac{1}{4}$	0.13759(9)	0	0.0158(8)
SrK	4 <i>e</i> 2	0.155(13)	$\frac{1}{4}$	0.13759(9)	0	0.0158(8)
O1A	8 <i>f</i> 1	1	-0.0761(4)	0.5779(2)	0.0571(3)	0.0105(12)
O1B	8 <i>f</i> 1	1	0.4215(5)	0.2885(2)	0.0602(4)	0.0149(13)
O1C	8 <i>f</i> 1	1	-0.0885(4)	-0.1355(2)	0.0497(3)	0.0111(12)
O1D	8 <i>f</i> 1	1	0.4247(5)	-0.0007(2)	0.0583(4)	0.0102(13)
O1E	8 <i>f</i> 1	1	-0.0863(5)	0.1378(2)	0.0488(4)	0.0136(13)
O1F	8 <i>f</i> 1	1	-0.0624(5)	0.2904(2)	0.0619(4)	0.0141(13)
O1G	8 <i>f</i> 1	1	-0.0762(4)	0.4189(2)	0.0577(3)	0.0114(12)
O1H	8 <i>f</i> 1	1	-0.3386(5)	0.50075(19)	0.0485(3)	0.0101(12)
O1I	8 <i>f</i> 1	1	0.6786(5)	0.3595(2)	0.0585(4)	0.0118(13)
O1J	8 <i>f</i> 1	1	-0.3390(5)	0.2259(2)	0.0488(4)	0.0146(13)
O1K	8 <i>f</i> 1	1	0.1762(5)	-0.0694(2)	0.0591(4)	0.0141(13)
O1L	8 <i>f</i> 1	1	0.1759(4)	0.0592(2)	0.0600(3)	0.0121(12)
O1M	8 <i>f</i> 1	1	0.1754(5)	0.2210(2)	0.0538(4)	0.0140(13)

O1N	8 <i>f</i> 1	1	0.1748(5)	0.3573(2)	0.0598(3)	0.0101(12)
O2A	8 <i>f</i> 1	1	-0.2297(6)	0.1692(3)	0.1410(5)	0.039(2)
O2B	8 <i>f</i> 1	1	0.0269(5)	0.1933(2)	0.1438(4)	0.0214(14)
O2C	8 <i>f</i> 1	1	0.0872(5)	0.3070(2)	0.1756(4)	0.0222(15)
O2D	8 <i>f</i> 1	1	0.2726(5)	0.2881(2)	0.1512(4)	0.0230(15)
O2E	8 <i>f</i> 1	1	0.0846(5)	0.4123(2)	0.1581(4)	0.0195(14)
O2F	8 <i>f</i> 1	1	-0.0134(5)	0.4984(2)	0.1315(4)	0.0151(13)
O2G	8 <i>f</i> 1	1	-0.2158(5)	0.5523(2)	0.1420(4)	0.0170(13)
O2H	8 <i>f</i> 1	1	-0.2197(4)	0.4466(2)	0.1415(3)	0.0144(13)
O2I	8 <i>f</i> 1	1	0.5857(5)	0.4152(2)	0.1570(4)	0.0228(15)
O2J	8 <i>f</i> 1	1	0.5829(5)	0.3105(3)	0.1606(4)	0.0302(17)
O2K	8 <i>f</i> 1	1	0.4013(5)	0.3595(3)	0.1774(4)	0.0268(17)
O2L	8 <i>f</i> 1	1	0.1503(5)	-0.0040(2)	0.1826(4)	0.0157(13)
O2M	8 <i>f</i> 1	1	0.3346(5)	0.0523(2)	0.1646(4)	0.0169(13)
O2N	8 <i>f</i> 1	1	0.3315(5)	-0.0519(2)	0.1625(4)	0.0212(14)
O2O	8 <i>f</i> 1	1	0.0340(4)	0.0841(2)	0.1410(3)	0.0141(12)
O2P	8 <i>f</i> 1	1	0.0306(4)	-0.0808(2)	0.1426(3)	0.0152(13)
O2Q	8 <i>f</i> 1	1	-0.2138(5)	0.2787(2)	0.1416(4)	0.0235(15)
O2R	8 <i>f</i> 1	1	-0.0957(5)	0.3546(2)	0.1831(4)	0.0211(15)
O2S	8 <i>f</i> 1	1	0.2254(5)	0.1393(3)	0.1319(4)	0.0276(17)
O2T	8 <i>f</i> 1	1	0.0401(6)	-0.1858(3)	0.1419(4)	0.0311(17)
O2U	8 <i>f</i> 1	1	0.3538(6)	0.2073(3)	0.1478(4)	0.0322(18)

Table C.18: Multiplicity, Wyckoff letter, site symmetry, occupation, fractional coordinates and U_{eq} of atoms in $\text{Ca}_{0.89}\text{Sr}_{0.11}\text{Te}_2\text{O}_5$.

Atom	Multiplicity, Wyckoff letter, site symmetry	occ.	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
TeA	4 <i>e</i> 1	1	0.37941(13)	0.21707(6)	0.40922(6)	0.01207(18)
TeB	4 <i>e</i> 1	1	0.91383(13)	0.31419(6)	0.40660(6)	0.01184(18)
TeC	4 <i>e</i> 1	1	0.83985(13)	0.07018(6)	0.40934(6)	0.01208(18)
TeD	4 <i>e</i> 1	1	0.42005(14)	0.93910(6)	0.40640(6)	0.01222(18)
TeE	4 <i>e</i> 1	1	0.40576(13)	0.69816(5)	0.40599(6)	0.01110(18)
TeF	4 <i>e</i> 1	1	-0.08552(13)	0.81946(6)	0.40345(6)	0.01176(18)
TeG	4 <i>e</i> 1	1	0.87784(14)	0.56960(6)	0.40836(6)	0.01285(18)
TeH	4 <i>e</i> 1	1	0.34762(14)	0.46421(6)	0.40817(6)	0.01219(18)
CaA	4 <i>e</i> 1	0.598(19)	0.9882(3)	0.19701(12)	0.24837(13)	0.0130(6)
SrA	4 <i>e</i> 1	0.402(19)	0.9882(3)	0.19701(12)	0.24837(13)	0.0130(6)
CaB	4 <i>e</i> 1	0.601(19)	-0.4995(3)	0.82644(13)	0.24482(13)	0.0136(6)
SrB	4 <i>e</i> 1	0.399(19)	-0.4995(3)	0.82644(13)	0.24482(13)	0.0136(6)
CaC	4 <i>e</i> 1	0.595(19)	0.4893(3)	0.07786(13)	0.24518(14)	0.0155(7)
SrC	4 <i>e</i> 1	0.405(19)	0.4893(3)	0.07786(13)	0.24518(14)	0.0155(7)
CaD	4 <i>e</i> 1	0.594(19)	0.0005(3)	0.44933(12)	0.24816(13)	0.0136(6)
SrD	4 <i>e</i> 1	0.406(19)	0.0005(3)	0.44933(12)	0.24816(13)	0.0136(6)

O1A	4 <i>e</i> 1	1	-0.163(2)	0.8257(8)	0.3016(7)	0.021(2)
O1B	4 <i>e</i> 1	1	0.861(2)	0.5777(8)	0.3046(7)	0.021(2)
O1C	4 <i>e</i> 1	1	0.3650(19)	0.7014(8)	0.3019(7)	0.018(2)
O1D	4 <i>e</i> 1	1	0.323(2)	0.1909(9)	0.3096(8)	0.024(3)
O1E	4 <i>e</i> 1	1	0.842(2)	0.0690(9)	0.3068(8)	0.022(2)
O1F	4 <i>e</i> 1	1	0.858(2)	0.3288(8)	0.3044(7)	0.021(2)
O1G	4 <i>e</i> 1	1	0.356(2)	0.9635(9)	0.3062(8)	0.023(2)
O1H	4 <i>e</i> 1	1	0.356(2)	0.4498(8)	0.3073(8)	0.021(2)
O2A	4 <i>e</i> 1	1	0.2031(19)	0.3165(8)	0.4017(7)	0.021(2)
O2B	4 <i>e</i> 1	1	0.5757(19)	0.2930(8)	0.3947(7)	0.018(2)
O2C	4 <i>e</i> 1	1	0.582(2)	0.1110(10)	0.4101(9)	0.031(3)
O2D	4 <i>e</i> 1	1	0.949(2)	0.1968(8)	0.4024(8)	0.021(2)
O2E	4 <i>e</i> 1	1	0.713(2)	0.9579(8)	0.4066(7)	0.021(2)
O2F	4 <i>e</i> 1	1	0.489(2)	0.8293(9)	0.3907(8)	0.026(3)
O2G	4 <i>e</i> 1	1	0.0782(19)	0.7265(8)	0.3929(7)	0.020(2)
O2H	4 <i>e</i> 1	1	0.108(2)	0.9052(9)	0.4011(8)	0.025(3)
O2I	4 <i>e</i> 1	1	0.681(2)	0.6701(10)	0.4023(9)	0.029(3)
O2J	4 <i>e</i> 1	1	0.675(2)	0.4940(10)	0.4140(9)	0.030(3)
O2K	4 <i>e</i> 1	1	0.309(3)	0.5813(11)	0.3977(9)	0.034(3)
O2L	4 <i>e</i> 1	1	0.0570(17)	0.4627(7)	0.3970(7)	0.015(2)

Table C.19: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in SrTe_2O_5 .

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
TeA	2 <i>i</i> 1	0.03784(11)	0.21667(6)	0.18201(9)	0.01423(17)
TeB	2 <i>i</i> 1	0.49920(12)	0.14601(6)	0.18152(9)	0.01416(17)
TeC	2 <i>i</i> 1	-0.41441(11)	0.34017(6)	0.17974(9)	0.01360(17)
TeD	2 <i>i</i> 1	-0.01235(12)	0.44555(7)	0.18170(9)	0.01423(17)
TeE	2 <i>i</i> 1	0.03853(12)	0.64581(6)	0.17869(9)	0.01456(17)
TeF	2 <i>i</i> 1	0.49701(11)	0.53854(6)	0.18052(9)	0.01339(16)
TeG	2 <i>i</i> 1	-0.43188(12)	0.74232(7)	0.17673(9)	0.01667(18)
TeH	2 <i>i</i> 1	0.06456(12)	0.82769(7)	0.18499(9)	0.01503(17)
TeI	2 <i>i</i> 1	-0.01393(13)	1.01627(7)	0.18561(9)	0.01781(18)
TeJ	2 <i>i</i> 1	0.52647(13)	0.93857(7)	0.18738(10)	0.02113(19)
SrA	2 <i>i</i> 1	0.25168(17)	0.45560(10)	0.49419(14)	0.0165(2)
SrB	2 <i>i</i> 1	0.24820(16)	0.26038(9)	0.49123(13)	0.0147(2)
SrC	2 <i>i</i> 1	0.25928(17)	0.04985(10)	0.50586(14)	0.0169(2)
SrD	2 <i>i</i> 1	0.75719(17)	0.14234(10)	0.51088(14)	0.0172(2)
SrE	2 <i>i</i> 1	0.74766(16)	0.35196(9)	0.49937(13)	0.0144(2)
O1A	2 <i>i</i> 1	0.4440(13)	0.0175(7)	0.3843(10)	0.0176(18)
O1B	2 <i>i</i> 1	0.4741(13)	0.8107(7)	0.3901(10)	0.0184(18)
O1C	2 <i>i</i> 1	-0.5404(14)	0.6203(8)	0.3798(11)	0.0213(19)
O1D	2 <i>i</i> 1	0.4691(13)	0.4231(7)	0.3806(10)	0.0183(18)

O1E	2 <i>i</i> 1	-0.5372(14)	0.2245(7)	0.3794(10)	0.022(2)
O1F	2 <i>i</i> 1	-0.0138(13)	0.1218(8)	0.3798(10)	0.0191(18)
O1G	2 <i>i</i> 1	-0.0500(14)	0.3134(7)	0.3796(10)	0.0197(19)
O1H	2 <i>i</i> 1	-0.0420(12)	0.5212(7)	0.3789(10)	0.0162(17)
O1I	2 <i>i</i> 1	-0.0429(12)	0.7088(7)	0.3877(10)	0.0180(18)
O1J	2 <i>i</i> 1	-0.0587(13)	0.9163(7)	0.3856(10)	0.0171(18)
O2A	2 <i>i</i> 1	0.2147(13)	0.1349(8)	0.1913(11)	0.025(2)
O2B	2 <i>i</i> 1	-0.1699(12)	0.1451(8)	0.2039(11)	0.023(2)
O2C	2 <i>i</i> 1	-0.1676(13)	0.3067(9)	0.1814(13)	0.035(3)
O2D	2 <i>i</i> 1	0.4670(14)	0.2346(9)	0.1868(12)	0.031(3)
O2E	2 <i>i</i> 1	-0.2951(13)	0.4259(8)	0.1848(11)	0.023(2)
O2F	2 <i>i</i> 1	-0.0869(13)	0.5198(7)	0.2033(10)	0.021(2)
O2G	2 <i>i</i> 1	0.3387(13)	0.6080(8)	0.1936(11)	0.023(2)
O2H	2 <i>i</i> 1	0.3039(13)	0.4682(7)	0.1901(10)	0.0214(19)
O2I	2 <i>i</i> 1	-0.2436(14)	0.6720(9)	0.1759(13)	0.036(3)
O2J	2 <i>i</i> 1	-0.2587(14)	0.8105(9)	0.1780(13)	0.034(3)
O2K	2 <i>i</i> 1	0.1289(15)	0.7258(9)	0.1912(13)	0.034(3)
O2L	2 <i>i</i> 1	0.3248(12)	0.8350(7)	0.2072(10)	0.022(2)
O2M	2 <i>i</i> 1	-0.0488(14)	0.9102(8)	0.2130(12)	0.030(2)
O2N	2 <i>i</i> 1	0.3199(13)	0.9905(7)	0.2011(10)	0.023(2)
O2O	2 <i>i</i> 1	0.7015(14)	1.0151(8)	0.1945(12)	0.026(2)

C.2 Ionic modified alkaline earth tellurates(IV)

Table C.20: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Sr}_4\text{Te}_4\text{O}_{11}\text{Br}_2$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$
Te1A	4 <i>e</i> 1	0.49337(9)	0.39525(3)	-0.07892(4)	0.01155(13)
Te1B	4 <i>e</i> 1	0.50560(9)	0.39231(3)	0.15855(4)	0.01124(13)
Te2A	4 <i>e</i> 1	0.49823(9)	0.39719(3)	-0.32559(4)	0.01231(13)
Te2B	4 <i>e</i> 1	0.49927(9)	0.38886(3)	0.39903(4)	0.01279(13)
Sr1A	4 <i>e</i> 1	0.97923(13)	0.31234(5)	0.40435(6)	0.01281(18)
Sr1B	4 <i>e</i> 1	0.52322(13)	0.18326(5)	0.16714(6)	0.01278(18)
Sr2A	4 <i>e</i> 1	0.00912(14)	0.30864(6)	0.16033(6)	0.01507(18)
Sr2B	4 <i>e</i> 1	0.48880(14)	0.18120(5)	0.41175(6)	0.01497(19)
BrA	4 <i>e</i> 1	0.0362(2)	0.49844(7)	0.38662(10)	0.0453(3)
BrB	4 <i>e</i> 1	0.0356(2)	0.49643(7)	0.13803(10)	0.0458(3)
O1A	4 <i>e</i> 1	0.2533(10)	0.3220(4)	-0.1443(4)	0.0171(13)
O1B	4 <i>e</i> 1	0.7335(9)	0.3233(4)	-0.0247(4)	0.0179(13)
O1C	4 <i>e</i> 1	0.2634(10)	0.3213(4)	0.1014(4)	0.0169(13)
O1D	4 <i>e</i> 1	0.7425(10)	0.3178(4)	0.2139(4)	0.0164(13)
O2	4 <i>e</i> 1	0.4819(15)	0.3941(5)	0.0337(5)	0.043(2)
O3A	4 <i>e</i> 1	0.4812(12)	0.3726(4)	-0.2215(5)	0.0310(18)

O3B	4 e 1	0.5330(13)	0.3693(5)	0.2976(5)	0.0362(19)
O4A	4 e 1	0.2638(10)	0.3280(4)	-0.4126(4)	0.0183(13)
O4B	4 e 1	0.7375(10)	0.3273(4)	-0.2885(4)	0.0170(13)
O4C	4 e 1	0.2588(10)	0.3163(4)	0.3546(4)	0.0181(13)
O4D	4 e 1	0.7325(10)	0.3184(4)	0.4840(4)	0.0162(13)

Table C.21: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Sr}_4\text{Te}_4\text{O}_{11}(\text{NO}_3)_2$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	U_{eq} [$\text{\AA}^2$]	
Te1A	4 e 1	0.51577(9)	0.38507(4)	0.26202(4)	0.01443(14)	1
Te1B	4 e 1	0.52314(9)	0.38668(4)	0.49806(4)	0.01431(14)	1
Te2A	4 e 1	0.51646(9)	0.38097(4)	0.02246(4)	0.01467(13)	1
Te2B	4 e 1	0.50963(9)	0.38587(4)	0.73650(4)	0.01465(14)	1
Sr1A	4 e 1	0.49403(13)	0.19145(6)	0.25000(6)	0.0160(2)	1
Sr2A	4 e 1	0.53399(15)	0.18839(6)	0.00567(6)	0.0175(2)	1
Sr1B	4 e 1	0.03626(14)	0.30575(6)	0.01097(6)	0.0157(2)	1
Sr2B	4 e 1	0.99225(14)	0.30296(6)	0.25128(6)	0.0157(2)	1
O1A	4 e 1	0.2790(10)	0.3171(4)	0.2097(4)	0.0188(15)	1
O1B	4 e 1	0.7549(9)	0.3177(4)	0.3215(4)	0.0197(15)	1
O1C	4 e 1	0.2823(9)	0.3195(4)	0.4324(4)	0.0176(14)	1
O1D	4 e 1	0.7573(9)	0.3182(4)	0.5573(4)	0.0178(14)	1
O2	4 e 1	0.5549(12)	0.4027(4)	0.3889(5)	0.0340(18)	1
O3A	4 e 1	0.5025(11)	0.3490(4)	0.1265(5)	0.0286(16)	1
O3B	4 e 1	0.5031(11)	0.3513(4)	0.6280(4)	0.0277(16)	1
O4A	4 e 1	0.2766(10)	0.3194(4)	-0.0667(4)	0.0220(15)	1
O4B	4 e 1	0.7504(9)	0.3146(4)	0.0538(4)	0.0199(15)	1
O4C	4 e 1	0.2766(10)	0.3212(3)	0.7082(4)	0.0191(15)	1
O4D	4 e 1	0.7466(10)	0.3236(4)	0.8256(4)	0.0212(15)	1
N1	4 e 1	0.5449(17)	0.0060(5)	0.2704(7)	0.032(2)	1
ON12	4 e 1	0.3897(17)	0.0486(6)	0.2310(7)	0.071(3)	1
ON13	4 e 1	0.7483(17)	0.0303(6)	0.3158(7)	0.069(3)	1
ON14	4 e 1	0.5309(17)	-0.0589(7)	0.2787(8)	0.089(3)	1
N2	2 c $\bar{1}$	$\frac{1}{2}$	0	$\frac{1}{2}$	0.056(5)	1
ON21	4 e 1	0.386(3)	-0.0551(10)	0.4827(11)	0.047(4)	$\frac{1}{2}$
ON22	4 e 1	0.408(5)	0.0583(15)	0.4925(17)	0.099(8)	$\frac{1}{2}$
ON23	4 e 1	0.282(7)	0.009(2)	0.462(3)	0.175(14)	$\frac{1}{2}$
N3	2 d $\bar{1}$	$\frac{1}{2}$	0	0	0.037(3)	1
ON31	4 e 1	0.029(3)	0.4607(10)	0.4396(11)	0.047(4)	$\frac{1}{2}$
ON32	4 e 1	0.103(3)	0.4470(10)	0.5224(13)	0.050(4)	$\frac{1}{2}$
ON33	4 e 1	0.958(3)	0.5416(9)	0.4302(11)	0.046(4)	$\frac{1}{2}$

Table C.22: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Ca}_3\text{Te}_3\text{O}_8\text{Cl}_2\cdot\text{H}_2\text{O}$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$
Te1	4 e 1	0.962295(14)	0.080412(16)	0.124249(6)	0.01105(3)
Te2A	4 e 1	1.277073(13)	0.408707(17)	0.136995(6)	0.01143(3)
Te2B	4 e 1	0.635109(14)	-0.227980(17)	0.125008(6)	0.01107(3)
Cl1	4 e 1	0.59483(7)	0.32730(11)	0.30094(3)	0.02930(12)
Cl2	4 e 1	0.02201(9)	0.56452(14)	0.19302(4)	0.04290(19)
Ca1A	4 e 1	0.20823(4)	0.90422(5)	0.05574(2)	0.01244(6)
Ca1B	4 e 1	0.57253(4)	0.25435(5)	0.05726(2)	0.01228(6)
Ca2	4 e 1	0.86919(4)	0.58344(5)	0.04205(2)	0.01139(6)
O1A	4 e 1	0.83008(17)	0.26079(19)	0.05886(8)	0.0135(2)
O1B	4 e 1	0.94764(17)	-0.09388(19)	0.05352(8)	0.0136(2)
O2A	4 e 1	1.14436(18)	0.1865(2)	0.10717(9)	0.0196(3)
O2B	4 e 1	0.75152(18)	-0.0263(2)	0.11399(10)	0.0216(3)
O3A	4 e 1	1.3667(2)	0.3330(3)	0.08069(10)	0.0278(4)
O3B	4 e 1	0.45475(17)	-0.1040(2)	0.05894(8)	0.0167(3)
O4A	4 e 1	1.13758(16)	0.57118(19)	0.06487(8)	0.0131(2)
O4B	4 e 1	0.63766(17)	-0.3971(2)	0.05668(8)	0.0142(2)
OW	4 e 1	0.7084(3)	0.3382(4)	0.18387(11)	0.0369(5)
HW1	4 e 1	0.663(6)	0.285(8)	0.208(3)	0.107(15)
HW2	4 e 1	0.803(5)	0.313(9)	0.206(3)	0.107(15)

Table C.23: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Ca}_{10}\text{Te}_8\text{O}_{23}\text{Cl}_6$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$
Te1A	4 e 1	0.78743(5)	0.254158(13)	0.34796(2)	0.01031(8)
Te1B	4 e 1	0.25333(5)	0.245101(13)	-0.00295(2)	0.01129(9)
Te2A	4 e 1	0.76398(5)	0.129893(13)	0.34948(3)	0.01278(10)
Te2B	4 e 1	0.76288(5)	0.377442(12)	0.34434(3)	0.01051(9)
Te2C	4 e 1	0.20963(5)	0.128701(13)	-0.00134(2)	0.01061(9)
Te2D	4 e 1	0.21986(5)	0.367339(13)	-0.00258(2)	0.01013(9)
Te3A	4 e 1	0.23165(5)	0.005240(13)	0.17523(2)	0.01031(9)
Te3B	4 e 1	0.74968(5)	0.491297(13)	0.50857(2)	0.01276(10)
Te3C	4 e 1	0.22181(5)	0.005884(13)	0.66870(2)	0.01164(9)
Te3D	4 e 1	0.75656(5)	0.005795(13)	0.51473(2)	0.01153(9)
Te4A	4 e 1	0.76760(5)	0.126878(12)	0.65746(2)	0.00957(9)

Te4B	4 e 1	0.76934(5)	0.126804(12)	0.15854(2)	0.00968(9)
Te4C	4 e 1	0.24090(5)	0.379504(13)	0.31772(3)	0.01105(9)
Te4D	4 e 1	0.24020(5)	0.124182(13)	0.31522(3)	0.01067(9)
Te5A	4 e 1	0.76949(5)	0.252088(13)	0.02762(2)	0.00963(8)
Te5B	4 e 1	0.23906(5)	0.251786(13)	0.18686(2)	0.00967(8)
Cl1	4 e 1	0.0036(2)	0.31526(6)	0.00840(11)	0.0251(4)
Cl2	4 e 1	0.0025(2)	0.07396(5)	0.52212(10)	0.0212(4)
Cl3	4 e 1	0.0034(2)	0.32711(5)	0.14835(10)	0.0188(4)
Cl4	4 e 1	0.9902(2)	0.06105(6)	0.66893(12)	0.0290(5)
Cl5	4 e 1	0.0009(2)	0.05100(5)	0.29997(11)	0.0227(4)
Cl6	4 e 1	0.0042(2)	0.45719(6)	0.31685(11)	0.0239(4)
Cl7	4 e 1	0.0120(2)	0.29967(5)	0.30088(10)	0.0215(4)
Cl8	4 e 1	0.9944(2)	0.20310(5)	0.18868(10)	0.0196(4)
Cl9	4 e 1	0.0040(2)	0.18769(6)	0.33460(11)	0.0252(4)
Cl10	4 e 1	0.0183(2)	0.18182(5)	0.04142(10)	0.0199(4)
Cl11	4 e 1	0.0162(3)	0.06812(6)	0.01135(11)	0.0323(5)
Cl12	4 e 1	0.0028(2)	0.08258(6)	0.14793(10)	0.0221(4)
Ca1A	4 e 1	0.50004(17)	0.43531(4)	0.49927(8)	0.0133(3)
Ca1B	4 e 1	0.50383(17)	0.06357(4)	0.16725(8)	0.0139(3)
Ca1C	4 e 1	0.50104(16)	0.06326(4)	0.33722(8)	0.0127(3)
Ca1D	4 e 1	0.49816(16)	0.06243(4)	0.50334(8)	0.0123(3)
Ca1E	4 e 1	0.50278(17)	0.06277(4)	0.67274(8)	0.0126(3)
Ca1F	4 e 1	0.49959(16)	0.44084(4)	0.33640(8)	0.0122(3)
Ca1G	4 e 1	0.51132(16)	0.18992(4)	0.00727(8)	0.0124(3)
Ca1H	4 e 1	0.51889(16)	0.18664(4)	0.18363(8)	0.0110(3)
Ca1I	4 e 1	0.50987(16)	0.19286(4)	0.33821(8)	0.0118(3)
Ca1J	4 e 1	0.49935(16)	0.18353(4)	0.50533(8)	0.0118(3)
Ca1K	4 e 1	0.49300(16)	0.31146(4)	0.16503(8)	0.0110(3)
Ca1L	4 e 1	0.49419(16)	0.31429(4)	0.33967(8)	0.0112(3)
Ca2A	4 e 1	0.79405(16)	0.13018(4)	0.00947(8)	0.0122(3)
Ca2B	4 e 1	0.79477(16)	0.12746(4)	0.51073(8)	0.0119(3)
Ca2C	4 e 1	0.22202(17)	0.12371(4)	0.15235(8)	0.0144(3)
Ca2D	4 e 1	0.21668(17)	0.37295(4)	0.14987(8)	0.0130(3)
Ca3A	4 e 1	0.77583(15)	0.24910(4)	0.18925(7)	0.0130(3)
Ca3B	4 e 1	0.20248(16)	0.23733(4)	0.33107(8)	0.0144(3)
Ca4A	4 e 1	0.79122(17)	0.00533(5)	0.67930(8)	0.0168(3)
Ca4B	4 e 1	0.77672(17)	0.00226(4)	0.17515(8)	0.0148(3)
O1A	4 e 1	0.6735(5)	0.25589(13)	0.2443(2)	0.0121(9)
O1B	4 e 1	0.3464(5)	0.25142(13)	-0.0421(2)	0.0106(8)
O2A	4 e 1	0.6388(5)	0.26060(14)	0.3514(3)	0.0179(11)
O2B	4 e 1	0.4198(6)	0.24196(14)	0.0976(2)	0.0186(11)
O3A	4 e 1	0.7030(5)	0.18838(13)	0.3225(3)	0.0154(10)
O3B	4 e 1	0.8276(6)	0.31927(14)	0.3581(3)	0.0228(12)
O3C	4 e 1	0.3000(6)	0.17892(14)	-0.0037(3)	0.0175(10)
O3D	4 e 1	0.3021(5)	0.31041(13)	0.0219(3)	0.0171(11)
O4A	4 e 1	0.6107(6)	0.11702(15)	0.2508(3)	0.0251(13)
O4B	4 e 1	0.5946(6)	0.37284(14)	0.2450(3)	0.0196(11)
O4C	4 e 1	0.3111(6)	0.08946(16)	-0.0095(3)	0.0303(13)

O4D	4 e 1	0.3507(6)	0.38281(15)	-0.0151(3)	0.0197(11)
O5A	4 e 1	0.6608(5)	0.12597(13)	0.3826(3)	0.0127(10)
O5B	4 e 1	0.6646(5)	0.37268(13)	0.3804(3)	0.0122(10)
O5C	4 e 1	0.3359(5)	0.12870(14)	0.1028(3)	0.0139(10)
O5D	4 e 1	0.3326(5)	0.37632(13)	0.0991(2)	0.0112(9)
O6A	4 e 1	0.3261(5)	0.00320(14)	0.2759(2)	0.0138(10)
O6B	4 e 1	0.6611(6)	0.49681(14)	0.5499(3)	0.0154(10)
O6C	4 e 1	0.3268(6)	-0.00268(14)	0.7704(3)	0.0187(11)
O6D	4 e 1	0.6680(5)	0.00145(14)	0.5567(3)	0.0145(10)
O7A	4 e 1	0.3452(6)	-0.04099(14)	0.1854(3)	0.0179(11)
O7B	4 e 1	0.5909(7)	0.51048(16)	0.4145(3)	0.0353(15)
O7C	4 e 1	0.3276(7)	-0.0335(2)	0.6620(4)	0.053(2)
O7D	4 e 1	0.6109(7)	-0.02885(19)	0.4363(3)	0.0386(16)
O8A	4 e 1	0.3422(5)	0.05447(13)	0.1908(3)	0.0148(10)
O8B	4 e 1	0.6767(5)	0.43428(13)	0.4754(3)	0.0144(10)
O8C	4 e 1	0.3279(5)	0.05699(14)	0.6889(3)	0.0186(11)
O8D	4 e 1	0.6683(6)	0.05929(14)	0.4716(3)	0.0169(11)
O9A	4 e 1	0.6757(5)	0.12612(13)	0.5571(3)	0.0119(10)
O9B	4 e 1	0.6779(6)	0.13096(14)	0.0583(3)	0.0156(10)
O9C	4 e 1	0.3253(5)	0.37602(13)	0.2743(3)	0.0141(10)
O9D	4 e 1	0.3306(5)	0.12810(14)	0.2747(3)	0.0147(10)
O10A	4 e 1	0.6615(6)	0.07727(13)	0.6460(3)	0.0153(10)
O10B	4 e 1	0.6599(5)	0.17496(13)	0.1493(3)	0.0143(10)
O10C	4 e 1	0.3420(5)	0.43203(14)	0.3668(3)	0.0141(10)
O10D	4 e 1	0.3502(5)	0.17305(13)	0.3764(2)	0.0145(10)
O11A	4 e 1	0.6502(5)	0.17465(13)	0.6418(2)	0.0120(9)
O11B	4 e 1	0.6556(5)	0.07707(13)	0.1384(2)	0.0133(10)
O11C	4 e 1	0.3810(6)	0.34064(16)	0.3915(3)	0.0263(13)
O11D	4 e 1	0.3564(6)	0.07615(14)	0.3730(3)	0.0179(11)
O12A	4 e 1	0.6785(5)	0.25388(14)	0.0688(2)	0.0148(9)
O12B	4 e 1	0.3224(5)	0.25340(14)	0.2868(2)	0.0124(9)
O13A	4 e 1	0.6549(5)	0.29996(14)	-0.0343(2)	0.0145(10)
O13B	4 e 1	0.6552(5)	0.20310(13)	-0.0304(2)	0.0139(10)
O13C	4 e 1	0.3573(5)	0.20394(14)	0.2043(2)	0.0145(10)
O13D	4 e 1	0.3482(5)	0.30051(14)	0.1982(3)	0.0148(10)

Table C.24: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Ca}_5\text{Te}_4\text{O}_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	U_{eq} [$\text{\AA}^2$]
Te1A	4 e 1	0.35223(3)	0.1936(2)	0.27681(5)	0.0146(2)
Te1B	4 e 1	0.14952(3)	0.6901(2)	0.23079(5)	0.0132(2)
Te2A	4 e 1	0.37375(3)	-0.7746(2)	0.59397(5)	0.0125(2)

Te2B	4 e 1	0.13478(4)	-0.2683(2)	-0.07606(5)	0.0130(2)
Ca1	4 e 1	0.2500(2)	0.2710(9)	0.0000(3)	0.0179(6)
Ca2A	4 e 1	0.25578(15)	0.6778(6)	0.1761(2)	0.0152(7)
Ca2B	4 e 1	0.25485(16)	0.1984(7)	0.3517(2)	0.0173(7)
Ca3A	4 e 1	0.37159(17)	-0.2810(6)	0.4434(2)	0.0162(7)
Ca3B	4 e 1	0.14048(19)	0.2132(7)	0.0723(3)	0.0153(6)
O1A	4 e 1	0.2845(6)	0.280(2)	0.1563(7)	0.024(3)
O1B	4 e 1	0.2174(5)	0.810(2)	0.3452(7)	0.021(2)
O2A	4 e 1	0.3131(5)	-0.0413(19)	0.3044(7)	0.012(2)
O2B	4 e 1	0.1903(5)	0.4399(19)	0.2155(7)	0.013(2)
O3A	4 e 1	0.3324(5)	0.4243(18)	0.3328(6)	0.018(2)
O3B	4 e 1	0.1647(5)	0.8868(19)	0.1578(7)	0.021(2)
O4A	4 e 1	0.3253(5)	-0.5370(19)	0.5048(7)	0.015(2)
O4B	4 e 1	0.1816(6)	-0.013(2)	-0.0024(8)	0.025(3)
O5A	4 e 1	0.3307(5)	-1.0124(19)	0.5048(7)	0.017(2)
O5B	4 e 1	0.1772(5)	-0.4883(18)	0.0214(7)	0.014(2)
O6B	4 e 1	0.1777(5)	-0.353(2)	-0.1303(7)	0.027(3)
O6A	4 e 1	0.3351(5)	-0.7967(19)	0.6587(7)	0.019(2)
ON11	4 e 1	0.0464(6)	0.178(2)	0.0962(10)	0.041(3)
ON12	4 e 1	-0.0429(4)	0.3590(18)	0.0077(7)	0.037(2)
ON13	4 e 1	0.0457(4)	0.4963(17)	0.0337(6)	0.036(2)
ON21	4 e 1	0.0410(6)	0.124(3)	-0.0831(9)	0.047(4)
ON22	4 e 1	-0.0327(5)	0.080(2)	-0.2310(7)	0.060(3)
ON23	4 e 1	0.0528(8)	0.282(2)	-0.1855(10)	0.101(6)
N1	4 e 1	0.0151(5)	0.3413(18)	0.0455(7)	0.028(2)
N2	4 e 1	0.0191(5)	0.172(2)	-0.1679(8)	0.035(3)
OW1	4 e 1	0.4680(5)	-0.334(2)	0.5982(7)	0.032(3)
OW2	4 e 1	0.4470(6)	-0.284(3)	0.4007(10)	0.051(4)

Table C.25: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{KCa}_3\text{Te}_5\text{O}_{12}\text{Cl}_3$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	U_{eq} [$\text{\AA}^2$]	
Te1A	8 f 1	0.16601(6)	0.29769(9)	0.37952(4)	0.01258(19)	1
Te1B	8 f 1	-0.00053(10)	0.18970(19)	0.12200(16)	0.0106(3)	0.802(3)
Te2A	8 f 1	0.18531(5)	-0.24056(14)	0.40582(7)	0.0077(2)	0.802(3)
Te2B	8 f 1	0.01878(6)	0.72974(13)	0.09713(8)	0.0091(2)	0.802(3)
Te3	8 f 1	0.33384(8)	-0.24996(14)	0.37538(11)	0.0073(2)	0.802(3)
Te1D	8 f 1	0.3321(4)	-0.3095(8)	0.3772(5)	0.0190(13)	0.198(3)
Te2C	8 f 1	0.1474(3)	-0.2402(10)	0.4082(7)	0.0412(19)	0.198(3)
Te3C	8 f 1	0.0007(4)	0.2461(11)	0.1236(7)	0.0186(17)	0.198(3)
Te2D	8 f 1	0.34812(18)	0.2352(6)	0.4050(4)	0.0151(10)	0.198(3)
K	8 f 1	0.3176(9)	0.252(3)	0.406(2)	0.357(16)	0.802(3)

KB	8 <i>f</i> 1	-0.0129(10)	0.741(3)	0.0953(11)	0.027(4)	0.198(3)
CaA	8 <i>f</i> 1	0.2459(3)	-0.0005(4)	0.25773(17)	0.0154(7)	1
CaB	8 <i>f</i> 1	0.0851(3)	-0.0034(5)	0.26285(14)	0.0142(5)	1
CaC	8 <i>f</i> 1	-0.0801(3)	-0.0080(5)	0.25849(15)	0.0155(6)	1
ClA	4 <i>e</i> 2	$\frac{1}{4}$	0.0049(11)	$\frac{1}{2}$	0.0267(14)	1
ClB	8 <i>f</i> 1	0.0816(3)	0.4943(12)	0.0037(2)	0.0312(10)	1
ClC	4 <i>e</i> 2	$\frac{1}{4}$	-0.5108(10)	$\frac{1}{2}$	0.0198(12)	1
ClD	8 <i>f</i> 1	0.0830(2)	0.9986(11)	0.00109(17)	0.0237(7)	1
O1A	8 <i>f</i> 1	0.1146(5)	0.2599(14)	0.3101(7)	0.027(2)	1
O1B	8 <i>f</i> 1	-0.0561(4)	0.2346(12)	0.1894(6)	0.019(2)	1
O2A	8 <i>f</i> 1	0.2261(4)	0.2649(12)	0.3198(5)	0.0133(18)	1
O2B	8 <i>f</i> 1	0.0624(4)	0.2256(13)	0.1779(6)	0.025(2)	1
O3A	8 <i>f</i> 1	0.1626(5)	-0.4476(11)	0.3520(5)	0.0216(19)	1
O3B	8 <i>f</i> 1	-0.0038(5)	0.9401(12)	0.1560(6)	0.023(2)	1
O4A	8 <i>f</i> 1	0.1625(5)	-0.0612(11)	0.3450(5)	0.0213(18)	1
O4B	8 <i>f</i> 1	-0.0053(4)	0.5547(13)	0.1619(6)	0.023(2)	1
O5A	8 <i>f</i> 1	0.2503(5)	-0.2546(14)	0.3482(7)	0.026(2)	1
O5B	8 <i>f</i> 1	0.0864(4)	0.7448(13)	0.1500(7)	0.025(2)	1
O6	8 <i>f</i> 1	0.3340(5)	-0.4414(11)	0.3118(5)	0.0237(17)	1
O7	8 <i>f</i> 1	0.3308(5)	-0.0504(11)	0.3115(5)	0.0214(17)	1

Table C.26: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	U_{eq} [$\text{\AA}^2$]
Ba11	2 <i>a</i> ..2	0	0	0.01937(6)	0.0166(2)
Ba13	2 <i>a</i> ..2	0	$\frac{1}{2}$	0.01084(6)	0.0131(2)
Ba15	1 <i>b</i> 1	0.24537(6)	0.247304(18)	0.47876(5)	0.01601(17)
Ba22	1 <i>b</i> 1	0.25893(5)	0.10649(2)	0.08032(4)	0.01428(15)
Ba24	1 <i>b</i> 1	0.25053(5)	0.38974(2)	0.07365(4)	0.01269(14)
Ba25	1 <i>b</i> 1	0.00158(5)	0.13892(2)	0.41886(4)	0.01249(14)
Ba26	1 <i>b</i> 1	0.49605(5)	0.14336(2)	0.42002(4)	0.01302(14)
Br4	1 <i>b</i> 1	0.25243(11)	0.25016(4)	0.16990(10)	0.0268(3)
Br5	2 <i>a</i> ..2	0	0	0.0250(4)	
Br6	2 <i>a</i> ..2	$\frac{1}{2}$	0	0.0243(4)	
Te13	1 <i>b</i> 1	0.01007(6)	0.41465(2)	0.21396(4)	0.01330(16)
Te14	1 <i>b</i> 1	0.49464(5)	0.41957(2)	0.20911(4)	0.01336(16)
Te15	1 <i>b</i> 1	0.23374(6)	0.15552(2)	0.28170(5)	0.01574(15)
Te17	1 <i>b</i> 1	0.24516(5)	0.33217(2)	0.29156(4)	0.01235(15)
Te23	1 <i>b</i> 1	0.00534(5)	0.30758(2)	0.09392(4)	0.01204(17)
Te24	1 <i>b</i> 1	0.49744(5)	0.30604(2)	0.09786(4)	0.01160(17)
Te26	1 <i>b</i> 1	0.25764(6)	0.05588(2)	0.40499(4)	0.01211(15)
Te27	1 <i>b</i> 1	0.24914(6)	0.44267(2)	0.40069(4)	0.01166(16)

Te34	1 <i>b</i> 1	0.25293(6)	0.49379(2)	0.19116(5)	0.01339(17)
Te38	1 <i>b</i> 1	0.49915(6)	0.25372(2)	0.31631(5)	0.01393(18)
O11	1 <i>b</i> 1	0.1217(6)	0.1735(3)	0.0437(4)	0.0148(17)
O12	1 <i>b</i> 1	0.3821(6)	0.1751(3)	0.0368(4)	0.0163(19)
O13	1 <i>b</i> 1	0.1226(6)	0.3235(3)	0.0304(4)	0.0141(18)
O14	1 <i>b</i> 1	0.3798(7)	0.3214(3)	0.0342(4)	0.0185(19)
O15	1 <i>b</i> 1	0.1307(6)	0.0724(2)	0.4615(5)	0.0147(17)
O16	1 <i>b</i> 1	0.3736(6)	0.0733(2)	0.4676(5)	0.0146(17)
O17	1 <i>b</i> 1	0.1302(6)	0.4239(3)	0.4606(5)	0.0175(18)
O18	1 <i>b</i> 1	0.3708(6)	0.4286(2)	0.4623(5)	0.0141(17)
O23	1 <i>b</i> 1	0.0039(8)	0.2505(2)	0.0511(6)	0.021(2)
O27	1 <i>b</i> 1	0.2416(6)	0.49971(18)	0.4509(6)	0.015(2)
O33	1 <i>b</i> 1	0.0183(6)	0.3862(3)	0.1242(5)	0.0218(18)
O34	1 <i>b</i> 1	0.4647(7)	0.3794(3)	0.1380(5)	0.034(2)
O36	1 <i>b</i> 1	0.2669(6)	0.1325(2)	0.3720(4)	0.0163(16)
O38	1 <i>b</i> 1	0.2745(7)	0.3723(3)	0.3628(5)	0.028(2)
O41	1 <i>b</i> 1	0.1197(6)	0.0543(3)	0.1623(5)	0.0243(19)
O42	1 <i>b</i> 1	0.3364(6)	0.0168(3)	0.1177(5)	0.0235(18)
O43	1 <i>b</i> 1	0.1717(7)	0.4373(2)	0.1968(5)	0.0254(19)
O44	1 <i>b</i> 1	0.3702(6)	0.4634(3)	0.1401(4)	0.0195(17)
O45	1 <i>b</i> 1	0.0949(6)	0.2144(3)	0.3765(4)	0.0201(17)
O46	1 <i>b</i> 1	0.4081(6)	0.2211(3)	0.3777(5)	0.0247(19)
O47	1 <i>b</i> 1	0.1488(6)	0.2984(2)	0.3470(4)	0.0201(17)
O48	1 <i>b</i> 1	0.3879(7)	0.3040(2)	0.3200(5)	0.0244(19)
O52	1 <i>b</i> 1	0.3246(6)	0.1219(3)	0.2217(5)	0.030(2)
O55	1 <i>b</i> 1	0.0900(6)	0.1225(3)	0.2720(5)	0.029(2)
O57	1 <i>b</i> 1	0.0654(6)	0.3735(3)	0.2789(5)	0.0261(18)

Table C.27: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and occupation of the atoms in the idealized basic structure of $\text{Ba}_6\text{Te}_{10}\text{O}_{25}\text{Br}_2$ with symmetry $Pmmn$ (origin choice 1).

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	occ.
Ba1	2 <i>a</i> $mm2$	0	0	0.03430	1
Ba2	4 <i>e</i> $m..$	$\frac{1}{2}$	0.21724	0.15754	1
Te1	4 <i>e</i> $m..$	0	0.82879	0.42490	1
Te2	4 <i>e</i> $m..$	0	0.61342	0.19305	1
Te3	2 <i>b</i> $mm2$	$\frac{1}{2}$	0	0.37485	1
Br	2 <i>a</i> $mm2$	$\frac{1}{2}$	$\frac{1}{2}$	0.33942	1
O1	8 <i>g</i> 1	0.24150	0.35260	0.07330	1
O2	2 <i>b</i> $mm2$	0	$\frac{1}{2}$	0.10019	1
O3	4 <i>e</i> $m..$	0	0.76293	0.26371	1
O4	8 <i>g</i> 1	0.28428	0.08429	0.29889	1

O5	4 $c \bar{1}$	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$
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Table C.28: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Ba}_3\text{Te}_3\text{O}_8\text{Br}_2$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$
Ba1	4 $c .m.$	-0.128883(13)	$\frac{1}{4}$	0.515303(10)	0.01252(3)
Ba2	4 $c .m.$	0.041619(14)	$\frac{1}{4}$	0.302640(9)	0.01221(3)
Ba3	4 $c .m.$	0.357984(12)	$\frac{1}{4}$	0.418939(9)	0.01055(3)
Te1	4 $c .m.$	-0.129368(14)	$-\frac{1}{4}$	0.392459(10)	0.01121(3)
Te2	4 $c .m.$	0.246920(13)	$-\frac{1}{4}$	0.298216(10)	0.00988(3)
Te3	4 $c .m.$	0.544213(14)	$-\frac{1}{4}$	0.342562(10)	0.01071(3)
Br1	4 $c .m.$	0.59845(3)	$\frac{1}{4}$	0.50113(2)	0.01775(6)
Br2	4 $c .m.$	-0.24745(3)	$\frac{1}{4}$	0.31560(3)	0.02765(8)
O1	4 $c .m.$	-0.1992(2)	$-\frac{1}{4}$	0.48200(17)	0.0269(6)
O2	1 $d 1$	-0.03402(12)	-0.0177(3)	0.41132(9)	0.0144(3)
O3	1 $d 1$	0.21175(13)	-0.0199(3)	0.36157(9)	0.0139(2)
O4	4 $c .m.$	0.60295(19)	$-\frac{1}{4}$	0.24340(14)	0.0192(5)
O5	1 $d 1$	0.45688(15)	-0.0141(3)	0.31997(10)	0.0192(3)

Table C.29: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of the atoms in $\text{Ca}_6\text{Te}_5\text{O}_{15}(\text{NO}_3)_2$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$
Te1	4 $e 1$	0.64351(7)	0.29413(11)	0.11120(3)	0.01250(15)
Te2	4 $e 1$	0.68846(7)	0.31090(11)	0.00018(3)	0.01349(15)
Te3	4 $e 1$	0.25041(7)	0.26838(11)	0.05678(3)	0.01370(15)
Te4	4 $e 1$	0.22359(7)	0.24273(10)	0.17361(3)	0.01295(14)
Te5	4 $e 1$	0.84306(7)	0.35318(11)	0.26134(3)	0.01288(15)
Ca1	4 $e 1$	0.6253(2)	0.7622(3)	0.04611(8)	0.0122(4)
Ca2	4 $e 1$	0.9847(2)	0.2346(3)	0.53335(8)	0.0146(4)
Ca3	4 $e 1$	0.2813(2)	0.7630(3)	0.12879(8)	0.0158(4)
Ca4	4 $e 1$	0.9716(2)	0.7894(3)	0.09571(8)	0.0139(4)
Ca5	4 $e 1$	0.9291(2)	0.3345(3)	0.14966(8)	0.0148(4)
Ca6	4 $e 1$	0.8788(2)	0.8259(3)	0.20390(8)	0.0139(4)
O1	4 $e 1$	0.5212(7)	0.4102(10)	0.0405(3)	0.0160(15)
O2	4 $e 1$	0.7380(7)	0.0494(10)	0.1179(2)	0.0120(15)
O3	4 $e 1$	0.7818(7)	0.5195(9)	0.1433(3)	0.0142(16)
O4	4 $e 1$	0.5970(7)	0.0965(10)	0.0001(3)	0.0191(16)

O5	4 e 1	0.8400(7)	0.1185(11)	0.0349(3)	0.0220(17)
O6	4 e 1	0.7826(6)	0.5031(11)	0.0618(3)	0.0140(15)
O7	4 e 1	0.1326(7)	0.3686(11)	-0.0144(3)	0.0217(17)
O8	4 e 1	0.1537(7)	0.0092(10)	0.0445(3)	0.0133(15)
O9	4 e 1	0.1669(7)	0.4852(10)	0.0603(3)	0.0160(16)
O10	4 e 1	0.0986(7)	0.1607(11)	0.1687(3)	0.0214(16)
O11	4 e 1	0.1346(7)	0.5016(10)	0.1257(3)	0.0174(16)
O12	4 e 1	0.1470(7)	0.0241(10)	0.1184(3)	0.0131(15)
O13	4 e 1	0.9821(7)	0.2183(11)	0.3317(3)	0.0242(16)
O14	4 e 1	0.8825(7)	0.1579(11)	0.2363(3)	0.0255(17)
O15	4 e 1	0.9498(7)	0.5956(10)	0.2736(3)	0.0126(15)
N1	4 e 1	0.5094(11)	0.269(2)	0.2150(5)	0.032(2)
ON1	4 e 1	0.4376(11)	0.095(2)	0.1877(5)	0.112(5)
ON2	4 e 1	0.6273(9)	0.2515(14)	0.2637(4)	0.059(3)
ON3	4 e 1	0.4728(12)	0.478(2)	0.1981(5)	0.089(4)
N2	4 e 1	0.5648(11)	0.8079(17)	0.1578(4)	0.035(3)
ON4	4 e 1	0.4412(8)	0.7597(15)	0.1244(3)	0.043(2)
ON5	4 e 1	0.6389(11)	0.900(2)	0.2029(5)	0.098(4)
ON6	4 e 1	0.6248(8)	0.7477(13)	0.1488(3)	0.039(2)

Table C.30: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, U_{eq} and occupation of the atoms in $\text{Ca}_3\text{Te}_2\text{O}_6\text{Cl}_{1.27}(\text{OH})_{0.73}$

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$	occ.
Te	32 e .3m	0.217298(19)	0.217298(19)	0.217298(19)	0.01835(10)	1
Ca	48 f 2.mm	0.42996(6)	$\frac{1}{8}$	$\frac{1}{8}$	0.01536(15)	1
Cl3	16 c . $\bar{3}$ m	0	0	0	0.0685(15)	1
O	96 g ..m	0.21280(16)	0.21280(16)	0.3393(2)	0.0261(6)	1
Cl1	8 b $\bar{4}3m$	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	0.0183(14)	0.537(19)
OW	32 e .3m	0.4277(5)	0.4277(5)	0.4277(5)	0.0160(19)	0.366(5)

Table C.31: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and occupation of the atoms in $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_{1.25}(\text{OH})_{0.75}$

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$	occ.
TeA	16 e .3m	0.09539(4)	0.09539(4)	0.09539(4)	0.0155(3)	1
TeB	16 e .3m	-0.34210(4)	-0.34210(4)	-0.34210(4)	0.0156(3)	1
SrA	24 f 2.mm	0.30307(10)	0	0	0.0135(3)	1

SrB	24 g $2.mm$	-0.55211(9)	$-\frac{1}{4}$	$-\frac{1}{4}$	0.0134(3)	1
Cl3	16 e $.3m$	-0.1241(4)	-0.1241(4)	-0.1241(4)	0.096(2)	1
OA	48 h $..m$	0.0899(4)	0.0899(4)	0.2120(5)	0.023(2)	1
OB	48 h $..m$	-0.3373(3)	-0.3373(3)	-0.4585(4)	0.0214(17)	1
Cl1A	4 b $\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.0176(13)	1
OWB	16 e $.3m$	-0.5501(4)	-0.5501(4)	-0.5501(4)	0.017(3)	$\frac{3}{4}$

Table C.32: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, U_{eq} and occupation of the atoms in $\text{Ca}_3\text{Te}_2\text{O}_6\text{Br}_{1.14}(\text{OH})_{0.86}(\text{H}_2\text{O})_{0.42}$

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$	occ.
Te	32 e $.3m$	0.218029(13)	0.218029(13)	0.218029(13)	0.01517(10)	1
Ca	48 f $2.mm$	0.42945(6)	$\frac{1}{8}$	$\frac{1}{8}$	0.01891(17)	1
Br3	16 c $\bar{3}m$	0	0	0	0.0303(2)	1
O	96 g $..m$	0.21257(11)	0.21257(11)	0.33879(15)	0.0248(5)	1
Br1	8 b $\bar{4}3m$	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	0.0258(14)	0.275(6)
OW	32 e $.3m$	0.4254(3)	0.4254(3)	0.4254(3)	0.030(2)	0.644(15)

Table C.33: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, U_{eq} and occupation of the atoms in $\text{Sr}_3\text{Te}_2\text{O}_6\text{Br}_{1.11}(\text{OH})_{0.88}(\text{H}_2\text{O})_{0.40}$

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$	occ.
Te	32 e $.3m$	0.219623(11)	0.219623(11)	0.219623(11)	0.01210(7)	1
Sr	48 f $2.mm$	0.42760(2)	$\frac{1}{8}$	$\frac{1}{8}$	0.01381(8)	1
Br3	16 c $\bar{3}m$	0	0	0	0.0364(2)	1
O	96 g $..m$	0.21378(11)	0.21378(11)	0.33578(13)	0.0189(4)	1
Br1	8 b $\bar{4}3m$	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	0.0255(15)	0.235(7)
OW	32 e $.3m$	0.4231(2)	0.4231(2)	0.4231(2)	0.0183(14)	0.642(16)

Table C.34: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, U_{eq} and occupation of the atoms in $\text{Sr}_3\text{Te}_2\text{O}_6\text{Cl}_2$

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$	occ.
Te	32 e $.3m$	0.217204(16)	0.217204(16)	0.217204(16)	0.02123(10)	1
Sr	48 f $2.mm$	0.42737(2)	$\frac{1}{8}$	$\frac{1}{8}$	0.01313(9)	1
Cl1	8 b $\bar{4}3m$	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.0179(4)	1
Cl2	16 d $\bar{4}3m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0152(5)	$\frac{1}{2}$
Cl3	16 h $..2$	-0.0202(5)	0	0.0202(5)	0.045(4)	$\frac{1}{6}$
O	96 g $..m$	0.21378(11)	0.21378(11)	0.33578(13)	0.0301(6)	1

Table C.35: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, U_{eq} and occupation of the atoms in $\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$	occ.
Te	32 e $.3m$	0.217755(19)	0.217755(19)	0.217755(19)	0.02253(11)	1
Ba	48 f $2.mm$	0.426078(19)	$\frac{1}{8}$	$\frac{1}{8}$	0.01720(9)	1
Cl1	8 b $\bar{4}3m$	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.0228(6)	1
Cl2	16 d $\bar{4}3m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0160(8)	0.576(11)
Cl3	16 h $..2$	-0.0217(14)	0	0.0217(14)	0.064(12)	0.1540(18)
O	96 g $..m$	0.21215(17)	0.21215(17)	0.3288(2)	0.0305(7)	1

Table C.36: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, U_{eq} and occupation of the atoms in $\text{Ba}_3\text{Te}_2\text{O}_6\text{Br}_2$

Atom	Multiplicity, Wyckoff letter, Site symmetry	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$	occ.
Te	32 e $.3m$	0.21980(2)	0.21980(2)	0.21980(2)	0.01837(14)	1
Ba	48 f $2.mm$	0.42343(3)	$\frac{1}{8}$	$\frac{1}{8}$	0.01375(12)	1
Br1	8 b $\bar{4}3m$	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.0202(4)	1
Br2	16 d $\bar{4}3m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0340(8)	$\frac{1}{2}$
Br3	16 h $..2$	$\frac{1}{4}$	0.2644(10)	0.0144(10)	0.044(5)	$\frac{1}{6}$
O	96 g $..m$	0.2139(2)	0.2139(2)	0.3301(3)	0.0242(9)	1

C.3 Tellurates(VI) and tellurates(IV/VI)

Table C.37: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, and U_{eq} of atoms in Sr_3TeO_6 . Wyckoff letters correspond to the positions in the reduced cell in $P\bar{1}$.

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Sr1	8 i 1	0.029318(16)	0.498931(17)	0.250937(18)	0.00822(4)
Sr2	8 i 1	0.501059(16)	0.251373(18)	0.027476(18)	0.00876(5)
Sr3	8 i 1	0.257548(16)	0.026512(18)	0.498678(18)	0.00911(5)
Sr4	8 i 1	0.270817(17)	0.270120(18)	0.266878(19)	0.01093(5)
Sr5	8 i 1	0.357984(16)	0.382695(18)	0.102942(18)	0.00901(5)
Sr6	8 i 1	0.615786(17)	0.113012(18)	0.111956(19)	0.00939(5)
Sr7	8 i 1	0.384065(16)	0.102769(18)	0.357250(18)	0.00888(5)
Sr8	8 i 1	0.365054(17)	0.11727(2)	0.12908(2)	0.01166(5)
Sr9	8 i 1	0.104918(17)	0.354643(18)	0.378711(18)	0.00893(5)
Sr10	8 i 1	0.128471(17)	0.363867(19)	0.11591(2)	0.01125(5)
Sr11	8 i 1	0.139282(17)	0.136257(19)	0.137666(19)	0.01052(5)
Sr12	8 i 1	0.121506(19)	0.126448(19)	0.363473(19)	0.01139(5)
Te1	4 h $\bar{1}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	0.00577(4)
Te2	4 f $\bar{1}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	0.00589(4)
Te3	4 c $\bar{1}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	0.00593(4)
Te4	4 d $\bar{1}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0.00592(4)
Te5	4 b $\bar{1}$	$\frac{1}{4}$	0	$\frac{1}{4}$	0.00580(4)
Te6	4 g $\bar{1}$	0	$\frac{1}{4}$	$\frac{1}{4}$	0.00602(4)
Te7	4 e $\bar{1}$	$\frac{1}{2}$	0	0	0.00561(4)
Te8	4 a $\bar{1}$	0	0	0	0.00578(4)
O11	8 i 1	0.24139(14)	0.48673(15)	0.13510(14)	0.0119(4)
O12	8 i 1	0.16729(13)	0.41947(14)	0.25851(15)	0.0108(4)
O13	8 i 1	0.33314(13)	0.41681(13)	0.25126(15)	0.0097(3)
O21	8 i 1	0.48245(14)	0.13549(13)	0.23796(15)	0.0109(4)
O22	8 i 1	0.42130(14)	0.26422(15)	0.16610(15)	0.0123(4)
O23	8 i 1	0.41525(13)	0.25131(14)	0.33131(15)	0.0103(4)
O31	8 i 1	0.13694(12)	0.23075(15)	0.48180(15)	0.0107(4)
O32	8 i 1	0.23130(14)	0.33529(14)	0.57548(16)	0.0123(4)
O33	8 i 1	0.24908(13)	0.32988(14)	0.41421(15)	0.0115(4)
O41	8 i 1	0.23157(14)	0.36463(14)	-0.00618(16)	0.0116(4)
O42	8 i 1	0.36310(12)	0.26972(15)	-0.00784(15)	0.0115(4)
O43	8 i 1	0.25086(14)	0.25862(15)	0.11638(15)	0.0119(4)
O51	8 i 1	0.36668(13)	-0.00965(15)	0.24716(16)	0.0121(4)
O52	8 i 1	0.24772(16)	0.00466(16)	0.13758(15)	0.0138(4)
O53	8 i 1	0.26036(14)	0.11710(14)	0.25013(16)	0.0109(4)
O61	8 i 1	-0.00707(15)	0.23426(16)	0.36484(15)	0.0138(4)
O62	8 i 1	-0.00738(14)	0.36222(14)	0.26851(16)	0.0126(4)
O63	8 i 1	0.11771(13)	0.25020(14)	0.25952(16)	0.0112(4)
O71	8 i 1	0.61124(13)	0.02738(15)	-0.01960(15)	0.0112(4)

O72	8 <i>i</i> 1	0.47844(14)	0.10930(14)	0.02880(15)	0.0110(4)
O73	8 <i>i</i> 1	0.52616(14)	-0.02265(15)	0.10956(14)	0.0118(4)
O81	8 <i>i</i> 1	0.53152(16)	0.38990(14)	0.01119(17)	0.0151(4)
O82	8 <i>i</i> 1	0.39359(14)	0.46941(16)	-0.03448(17)	0.0143(4)
O83	8 <i>i</i> 1	0.46190(16)	0.49933(16)	0.10813(15)	0.0150(4)

Table C.38: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, and U_{eq} of atoms in Ba_3TeO_6 .

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}}[\text{\AA}^2]$
Ba1	16 <i>f</i> 1	0.569070(12)	0.410654(12)	0.071933(7)	0.00949(4)
Ba2	16 <i>f</i> 1	0.762171(11)	0.975106(11)	0.063023(7)	0.00805(4)
Ba3	16 <i>f</i> 1	0.839948(12)	0.317177(12)	0.053527(7)	0.00994(4)
Ba4	16 <i>f</i> 1	0.663914(11)	0.676123(11)	0.061981(7)	0.00742(4)
Ba5	16 <i>f</i> 1	0.077754(12)	0.885203(13)	0.061412(7)	0.01075(4)
Ba6	4 <i>b</i> $\bar{4}$	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{1}{8}$	0.01170(9)
Ba7	4 <i>a</i> $\bar{4}$	0	$\frac{1}{4}$	$\frac{1}{8}$	0.01030(8)
Ba8	8 <i>e</i> 2..	$\frac{1}{2}$	$\frac{3}{4}$	0.000017(9)	0.00997(6)
Ba9	8 <i>e</i> 2..	0	$\frac{1}{4}$	0.007175(11)	0.01039(6)
Ba10	8 <i>e</i> 2..	$\frac{1}{2}$	$\frac{1}{4}$	0.119844(10)	0.01008(6)
Ba11	16 <i>f</i> 1	0.796912(12)	0.139481(12)	0.012273(7)	0.00856(4)
Ba12	16 <i>f</i> 1	0.923093(12)	0.953102(12)	0.122354(7)	0.00880(4)
Ba13	16 <i>f</i> 1	0.391490(12)	0.455483(12)	0.115022(7)	0.00814(4)
Ba14	16 <i>f</i> 1	0.920361(12)	0.953315(12)	0.003542(7)	0.00912(4)
Ba15	16 <i>f</i> 1	0.801621(12)	0.150891(12)	0.123274(7)	0.00965(4)
Ba16	16 <i>f</i> 1	0.686515(12)	0.833032(12)	0.120157(7)	0.00849(4)
Ba17	16 <i>f</i> 1	0.405598(13)	0.451362(12)	0.004408(7)	0.00970(4)
Ba18	16 <i>f</i> 1	0.686725(12)	0.837259(13)	0.001711(7)	0.00891(4)
Te1	16 <i>f</i> 1	0.250222(11)	0.999419(11)	0.062212(11)	0.00457(4)
Te2	16 <i>f</i> 1	0.850215(11)	0.801491(11)	0.061742(7)	0.00461(4)
Te3	16 <i>f</i> 1	0.950878(11)	0.100872(11)	0.065350(7)	0.00433(4)
Te4	16 <i>f</i> 1	0.353015(11)	0.306721(11)	0.062906(7)	0.00421(4)
Te5	16 <i>f</i> 1	0.449365(11)	0.605871(11)	0.060263(7)	0.00420(4)
O11	16 <i>f</i> 1	0.26265(18)	0.99294(16)	0.00745(10)	0.0151(6)
O12	16 <i>f</i> 1	0.15609(14)	0.02992(17)	0.05703(9)	0.0140(6)
O13	16 <i>f</i> 1	0.21906(15)	0.90251(14)	0.06123(9)	0.0109(5)
O14	16 <i>f</i> 1	0.28080(15)	0.09507(14)	0.06353(10)	0.0127(5)
O15	16 <i>f</i> 1	0.34569(14)	0.96904(15)	0.06753(9)	0.0111(5)
O16	16 <i>f</i> 1	0.23695(18)	0.99652(15)	0.11706(10)	0.0145(6)
O21	16 <i>f</i> 1	0.87482(15)	0.73744(15)	0.02150(9)	0.0136(6)
O22	16 <i>f</i> 1	0.82217(15)	0.86751(14)	0.02223(8)	0.0106(5)
O23	16 <i>f</i> 1	0.94356(14)	0.84057(15)	0.06172(10)	0.0140(5)
O24	16 <i>f</i> 1	0.75553(14)	0.76967(14)	0.06203(10)	0.0110(5)
O25	16 <i>f</i> 1	0.87546(16)	0.73545(15)	0.10047(9)	0.0139(6)
O26	16 <i>f</i> 1	0.82377(15)	0.86637(14)	0.10204(8)	0.0107(5)

O31	16 <i>f</i> 1	0.94951(16)	0.09908(16)	0.00967(8)	0.0124(6)
O32	16 <i>f</i> 1	0.03635(14)	0.14996(15)	0.06412(10)	0.0137(6)
O33	16 <i>f</i> 1	0.99930(14)	0.01255(14)	0.06410(9)	0.0100(5)
O34	16 <i>f</i> 1	0.86460(14)	0.05173(15)	0.06442(9)	0.0132(5)
O35	16 <i>f</i> 1	0.90202(14)	0.18744(14)	0.06561(9)	0.0107(5)
O36	16 <i>f</i> 1	0.95046(16)	0.09765(16)	0.12090(8)	0.0127(6)
O41	16 <i>f</i> 1	0.35409(17)	0.30386(17)	0.00793(8)	0.0134(6)
O42	16 <i>f</i> 1	0.30879(14)	0.39660(14)	0.06148(9)	0.0111(5)
O43	16 <i>f</i> 1	0.26329(14)	0.26310(14)	0.06172(10)	0.0116(5)
O44	16 <i>f</i> 1	0.44199(14)	0.35156(14)	0.06327(9)	0.0112(5)
O45	16 <i>f</i> 1	0.39727(14)	0.21704(14)	0.06541(9)	0.0121(5)
O46	16 <i>f</i> 1	0.34708(16)	0.30842(16)	0.11819(8)	0.0125(6)
O51	16 <i>f</i> 1	0.44571(17)	0.59994(17)	0.00460(8)	0.0138(6)
O52	16 <i>f</i> 1	0.53852(15)	0.64554(16)	0.05895(10)	0.0161(6)
O53	16 <i>f</i> 1	0.40838(15)	0.69736(14)	0.05929(9)	0.0118(5)
O54	16 <i>f</i> 1	0.35855(14)	0.56714(15)	0.06285(10)	0.0125(5)
O55	16 <i>f</i> 1	0.48794(15)	0.51384(14)	0.06277(10)	0.0125(5)
O56	16 <i>f</i> 1	0.44974(16)	0.60905(17)	0.11634(8)	0.0142(6)

Table C.39: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates, occupation and U_{eq} of atoms in the actual structure of MgTeO_8H_8 .

Atom	Multiplicity, Wyckoff letter, site symmetry,	x	y	z	occ.	$U_{\text{eq}} / \text{\AA}^2$
Te1	4 <i>b</i> $\bar{4}m2$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	0.941(3)	0.00943(10)
Mg1	4 <i>b</i> $\bar{4}m2$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	0.059(3)	0.00943(10)
Mg2	4 <i>a</i> $\bar{4}m2$	0	$\frac{1}{4}$	$\frac{1}{8}$	0.941(3)	0.0101(5)
Te2	4 <i>a</i> $\bar{4}m2$	0	$\frac{1}{4}$	$\frac{1}{8}$	0.059(3)	0.0101(5)
O1	8 <i>e</i> $2mm.$	$\frac{1}{2}$	$\frac{1}{4}$	0.22042(16)	1	0.0240(7)
O2	8 <i>e</i> $2mm.$	0	$\frac{1}{4}$	0.22398(17)	1	0.0225(6)
O3	32 <i>i</i> 1	0.8215(6)	0.0933(6)	0.12657(14)	1	0.0173(6)

Table C.40: Multiplicity, Wyckoff letter, site symmetry, fractional coordinates and U_{eq} of atoms in the actual structure of $\text{Tl}_2\text{Te}_2\text{O}_6$

Atom	Multiplicity, Wyckoff letter, site symmetry	x	y	z	$U_{\text{eq}} / \text{\AA}^2$
Tla	4 <i>e</i> 1	0.45672(5)	0.88214(4)	0.10452(3)	0.02351(10)
Tlb	4 <i>e</i> 1	0.44470(5)	0.86138(4)	0.37483(3)	0.02541(10)

Te1	4 e 1	0.00080(7)	0.63845(6)	0.08973(4)	0.00970(10)
Te2	4 e 1	0.12181(7)	1.17431(6)	0.17182(4)	0.01249(11)
O1	4 e 1	0.1767(7)	0.8241(6)	0.1693(4)	0.0138(10)
O2	4 e 1	-0.1786(8)	0.6584(7)	0.1516(4)	0.0165(11)
O3	4 e 1	-0.1519(8)	0.8066(7)	-0.0287(4)	0.0160(11)
O4	4 e 1	0.1570(7)	0.4478(7)	0.1975(4)	0.0163(11)
O5	4 e 1	-0.1518(7)	0.4218(7)	-0.0027(4)	0.0130(10)
O6	4 e 1	0.3893(8)	1.1402(6)	0.2372(4)	0.0141(10)

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