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Search for new Zintl phases for thermoelectricity

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Abstract

In order to find promising candidates for materials with a high thermoelectric (TE) figure of merit, various Zintl phases were designed or chosen from literature and synthesised by melting elements together. These included Yb_2SnGe_2 , Yb_2InGe_2 , Sr_2PbGe_2 , $\text{Sm}_4\text{Bi}_2\text{Te}$, $\text{Yb}_4\text{Sb}_2\text{S}$ and $\text{SmGa}_6\text{Te}_{10}$. Depending on the composition, they were synthesised either directly in an open cold boat or in a sealed tantalum crucible. For the latter, an induction furnace was specifically designed.

The synthesised polycrystals were analysed at room temperature (RT), using X-ray powder diffraction (XRD) and, in some cases, SEM/EDX analysis. From these data, phase relations were analysed. If the sample's quality was deemed good enough, the TE properties were measured. This involved measurements of the electrical resistivity (2 K - 870 K), as well as high temperature measurements of the Seebeck coefficient (RT - 870 K) and the thermal conductivity (420 K - 820 K). Additionally, the Hall coefficient was measured at low temperatures (2 K - RT), with a magnetic field of 9 T.

Both Yb_2SnGe_2 and Yb_2InGe_2 display typical metallic behaviour, with a linearly rising electrical resistivity, a high charge carrier concentration and small Seebeck coefficient values. Together with a high thermal conductivity, these TE properties suggest that neither of these two compounds is a promising thermoelectric material and the chances of improving them through doping are very small.

The other materials could not be obtained in a single-phase form. Sr_2PbGe_2 samples, synthesised both in the cold boat and in a sealed Ta crucible at 1200 °C, always contained free Pb, which did not disappear after annealing. The synthesis of the charge compensated $\text{Sm}_4\text{Bi}_2\text{Te}$ in a sealed Ta crucible at 1500 °C resulted

in a sample that contained both $\text{Sm}_4\text{Bi}_2\text{Te}$ and SmTe . Annealing could not eliminate the foreign SmTe phase. An attempt to synthesise the charge compensated $\text{Yb}_4\text{Sb}_2\text{S}$ in a sealed Ta crucible at 1600 °C resulted in a $\text{Yb}_4\text{Sb}_{2.6}\text{S}_{0.4}$ matrix with YbS inclusions. Annealing did not improve the quality of the sample. The results indicate a limited incorporation of the chalcogens Te and S into anti- Th_3P_4 structure-type pnictogen phases. Finally, the attempt of synthesising $\text{SmGa}_6\text{Te}_{10}$ in a sealed Ta crucible at 1500 °C produced mainly a mixture of GaTe and Ga_2Te_3 . These materials do not seem to be obtainable easily by simple melt synthesis. For this reason, and because some of them contain toxic components, they were not investigated in the framework of the current master's thesis..

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1. Introduction

Humanity has a constant need for energy. It is used in all aspects of our lives, ranging from the industrial sector to housing and transportation. Meanwhile, the issue of global warming is more relevant than ever. By signing the Paris Agreement in 2016, 195 countries pledged to work towards limiting the global temperature rise to less than 2 °C above pre-industrial levels. This can only be achieved by drastically reducing greenhouse gas emissions and instead promoting alternative energy sources. In fact, a scenario from the World Energy Outlook 2016 predicts that by 2040 60% of the generated power will come from renewables [1]. Therefore, the development of efficient and cheap alternative energy sources is indispensable. A very active field of research is devoted to thermoelectric (TE) devices. They are based on the Seebeck effect and the Peltier effect, which describe a material's ability to convert a temperature gradient $\vec{\nabla}T$ into an electric field and vice versa. By combining an n-type and a p-type thermoelectric semiconductor one can build a thermoelectric module, which generates electric current, if one junction is at a higher temperature than the other (Figure 1.1a). A similar set-up can be used as a heat pump, if voltage is applied (Figure 1.1b).

Thermoelectric devices consist of several thermoelectric modules, connected electrically in series and thermally in parallel. However, they have no moving parts. This feature allows them to operate without noise and ensures a long life time. TE heat pumps find use in a wide array of fields, e. g. in microelectronics, in portable refrigerators and as automotive climate systems, while TE generators are

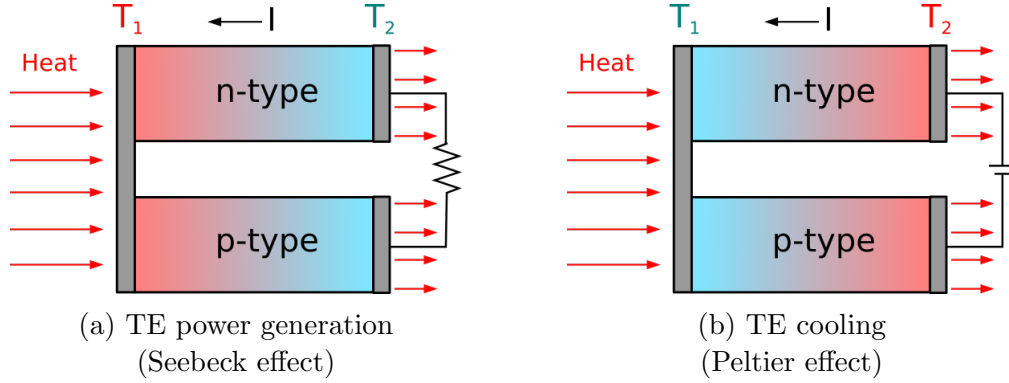


Figure 1.1.: Working principle of thermoelectric modules.

mainly used to recover energy from waste heat. Unfortunately, due to their low power conversion efficiency, many of the possible applications are still restricted to specialized fields, where efficiency and low costs are not the main requirement. [2, 3, 4, 5]

The conversion efficiency of TE generators can be defined as

$$\eta = \frac{\Delta T}{T_{\text{hot}}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_{\text{cold}}}{T_{\text{hot}}}} \quad (1.1)$$

with the first term being the Carnot efficiency η_c and ZT being the figure of merit [2].

ZT is dimensionless and dependent on the average temperature T and the material, more precisely, the material's Seebeck coefficient S , its electrical conductivity σ and its thermal conductivity κ :

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1.2)$$

(1.1) shows that the conversion efficiency is better, the bigger the temperature difference is and the larger ZT . Therefore, achieving a high figure of merit is the main goal in TE material development. According to (1.2), this can be accom-

plished, if both S and σ are high, while κ remains low. Unfortunately, the reality is more complicated, since these quantities are interrelated. Altering one leads to a change in another, making it an important task to find an optimum between these quantities. In the last couple of years, values of $ZT > 2$ have been reported [4]. However, it is still a long way to successful commercialisation.

The material classes researched for TE material development are manifold. They involve skutterudites, clathrates, half-Heusler alloys, rare-earth chalcogenides and pnictides, just to name a few. Furthermore, nano-structured materials, thin films and superlattices are being studied, all with the goal of improving the performance of thermoelectrics.[4]

Materials, which have received a lot of interest recently, are so-called Zintl phases [6]. These intermetallics consist of moderately electronegative elements and very electropositive elements and are formed through both covalent and ionic bonding. A set of electron counting rules, the Zintl-Klemm concept, helps to understand the electronic structure and the crystal structure. It provides a useful tool for the search for new TE materials, since it gives an estimation of what physical properties might be expected.

In this master's thesis, potential TE materials were chosen based on the Zintl-Klemm concept and synthesised from melt, in order to determine their usefulness for further research. For this, the composition of the synthesised polycrystals was determined via XRD and SEM/EDX, and the single-phase samples were prepared for measurements of the electrical resistivity, Seebeck coefficient, thermal conductivity and Hall coefficient.

2. Transport theory

Transport phenomena usually occur due to a gradient or external field and are a means of achieving equilibrium. Viewed macroscopically, each gradient gives rise to a flux, which appears to be proportional to the gradient:

$$\vec{j}_e = \sigma \vec{\nabla} \Phi = \sigma \vec{E} \quad (2.1)$$

$$\vec{j}_q = -\kappa \vec{\nabla} T \quad (2.2)$$

with the electric current density $\vec{j}_e$, the heat flux $\vec{j}_q$, the electric field $\vec{E}$, the temperature gradient $\vec{\nabla} T$ and the electrical and thermal conductivities σ and κ . Furthermore, the temperature gradient causes charge carriers to diffuse to the warmer/colder side, which induces an electric field:

$$\vec{E} = S \vec{\nabla} T \quad (2.3)$$

with S being the thermopower.

This chapter is meant to give a better understanding of the transport properties from a microscopic point of view. For that, a few concepts from solid state physics are introduced. For more detailed explanations, see [7] and [8], which serve as the main sources for this chapter.

2.1. Semi-classical model

The semi-classical model describes the behaviour of electrons under the influence of external forces, while also retaining the knowledge of the band structure. This is achieved by superposing the quantum-mechanical Bloch waves $\psi_{j,\vec{k}}(\vec{r})$ with wave vectors in the interval $[k - \Delta k/2, k + \Delta k/2]$ to form wave packages, which then can be treated as classical particles.

Assuming that the band index j is constant, this approach leads to the following equations of motion:

$$\frac{d\vec{r}}{dt} = \vec{v}_j(\vec{k}) = \frac{1}{\hbar} \frac{\partial E_j(\vec{k})}{\partial \vec{k}} \quad (2.4)$$

$$\hbar \frac{d\vec{k}}{dt} = \vec{F}(\vec{r}, t) \quad (2.5)$$

with $E_j(\vec{k})$ being the energy of the crystal electrons and $\vec{F}(\vec{r}, t)$ being an external force.

Inserting (2.4) and (2.5) into Newton's second law of motion yields the **effective mass**

$$m^*(\vec{k}) = \frac{\hbar^2}{d^2 E_j(\vec{k}) / dk^2} \quad (2.6)$$

which describes the effect of the lattice-periodic potential on the electron's movement.

2.2. Boltzmann equation

In thermal equilibrium, the average number of electrons with a certain energy $E(\vec{k})$ is given by the **Fermi-Dirac distribution**

$$f_0(E(\vec{k})) = \frac{1}{\exp\left[\frac{E(\vec{k}) - \eta}{k_B T}\right] - 1} \quad (2.7)$$

where η is the chemical potential, k_B the Boltzmann constant and T the temperature.

Electrical and thermal transport phenomena cause the distribution function to change with time, due to an interplay between a driving force and the inhibiting effect of particle interactions. The latter makes the mathematical description very difficult. Therefore, one simplifies the situation by considering solely two-body interactions, which are summed up in a collision term. This leads to the **Boltzmann equation**, which describes the temporal evolution of the distribution function:

$$\frac{df(\vec{r}, \vec{k}, t)}{dt} = \frac{\partial f}{\partial t} + \dot{\vec{r}} \frac{\partial f}{\partial \vec{r}} + \dot{\vec{p}} \frac{\partial f}{\partial \vec{p}} = \left. \frac{\partial f}{\partial t} \right|_{\text{coll}} \quad (2.8)$$

or, generally written

$$\frac{\partial f}{\partial t} = \left. \frac{\partial f}{\partial t} \right|_{\text{diff}} + \left. \frac{\partial f}{\partial t} \right|_{\text{force}} + \left. \frac{\partial f}{\partial t} \right|_{\text{coll}} \quad (2.9)$$

Relaxation-time approximation

The relaxation-time approximation linearises the Boltzmann equation by assuming that the collisions are causing the system to relax into thermal equilibrium with the time constant τ . Therefore the collision term can be approximated by

$$\left. \frac{\partial f}{\partial t} \right|_{\text{coll}} = -\frac{f - f_0}{\tau} \quad (2.10)$$

The time constant τ is dependent on the different scattering mechanisms in the solid. Each type of scattering centre causes a different relaxation time, which can be combined into the general time constant

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} \quad (2.11)$$

General transport coefficients

Using the relaxation-time approximation and considering a stationary state $\frac{\partial f}{\partial t} = 0$, the distribution function under the influence of a temperature gradient and an electric field can be written as

$$f = f_0 + \left(-\frac{\partial f_0}{\partial E} \right) \tau \vec{v} \left[e\vec{E} - \frac{E(\vec{k})}{T} \frac{\partial T}{\partial \vec{r}} \right] \quad (2.12)$$

This distribution function can be inserted into the current density $\vec{j}_e$ and the heat flux $\vec{j}_q$

$$\vec{j}_e = \frac{1}{4\pi^3} \int e\vec{v}(\vec{k}) f(\vec{k}) d^3k \quad (2.13)$$

$$\vec{j}_h = \frac{1}{4\pi^3} \int E(\vec{k}) \vec{v}(\vec{k}) f(\vec{k}) d^3k \quad (2.14)$$

which leads to

$$\vec{j}_e = L^{11} \vec{E} + L^{12} (-\vec{\nabla} T / T) \quad (2.15)$$

$$\vec{j}_h = L^{21} \vec{E} + L^{22} (-\vec{\nabla} T / T) \quad (2.16)$$

with the general transport coefficients L^{ij} . $\vec{j}_e$ and $\vec{j}_h$ are dependent on both tem-

perature and electric field. This extends equations (2.1) and (2.2) and shows that a temperature gradient also gives rise to a current density and an electric field also causes a heat flux.

Comparing (2.15) without the temperature gradient with (2.1) leads to following conclusion:

$$\vec{j}_e = L^{11} \vec{E} = \hat{\sigma} \vec{E} \quad (2.17)$$

with $\hat{\sigma}$ being the electrical conductivity. Based on the previous equations, it can be written as

$$\hat{\sigma}(E) = \frac{1}{4\pi^3} \frac{e^2}{\hbar} \int_{E=E_F} dS_E \frac{\tau(\vec{k}) \vec{v}(\vec{k}) \vec{v}(\vec{k})}{v(k)} \quad (2.18)$$

and therefore can be used to define the other general transport coefficients:

$$L^{11} = \hat{\sigma}(E_F) \quad (2.19)$$

$$L^{12} = L^{21} = \frac{\pi^2}{3} \frac{(k_B T)^2}{e} \left. \frac{\partial \hat{\sigma}(E)}{\partial E} \right|_{E=E_F} \quad (2.20)$$

$$L^{22} = \frac{\pi^2}{3} \frac{(k_B T)^2}{e^2} \hat{\sigma}(E_F) \quad (2.21)$$

2.2.1. Electrical resistivity

Integrating (2.18) leads, after some calculation, to the expression known from the **Drude model**

$$\sigma = \frac{1}{\rho} = \frac{e^2 \tau(E_F)}{m^*} n \quad (2.22)$$

with the effective mass m^* and the electron density n . The inverse of σ is called **electrical resistivity** ρ and describes how much a material hinders the flow of

electric current. Seeing that ρ is indirectly proportional to τ , one can use (2.11) to break down the resistivity into the contributions from the different scattering mechanisms:

$$\rho(T) = \rho_0 + \rho_{\text{ph}}(T) + \rho_{\text{el-el}}(T) + \rho_{\text{mag}}(T) + \dots \quad (2.23)$$

This is known as the **Matthiessen rule**. The residual resistivity ρ_0 is temperature independent and appears due to scattering on defects and impurities, while $\rho_{\text{ph}}(T)$ is caused by electron-phonon scattering, $\rho_{\text{el-el}}(T)$ by electron-electron scattering and $\rho_{\text{mag}}(T)$ by scattering on magnetic moments.

The resistivity in most metals, however, can be simply treated as $\rho \approx \rho_0 + \rho_{\text{ph}}(T)$, since these contributions outweigh the others. The contribution due to scattering on phonons can be described by the **Bloch-Grüneisen law**

$$\rho_{\text{ph}}(T) \propto \left(\frac{T}{\Theta_{\text{D}}} \right)^5 \int_0^{\Theta_{\text{D}}/T} \frac{4x^5}{(e^x - 1)(1 - e^x)} dx \quad (2.24)$$

with $x = \frac{\hbar\omega_{\text{q}}}{k_{\text{B}}T}$, the Debye temperature Θ_{D} and the phonon frequency ω_{q} . At low temperatures, this leads to a T^5 dependency of the resistivity, while the behaviour at high temperatures appears to be linear:

$$\rho_{\text{ph}}(T) \propto \left(\frac{T}{\Theta_{\text{D}}} \right)^5 \quad T \ll \Theta_{\text{D}} \quad (2.25)$$

$$\rho_{\text{ph}}(T) \propto \left(\frac{T}{\Theta_{\text{D}}} \right) \quad T \gg \Theta_{\text{D}} \quad (2.26)$$

2.2.2. Thermal conductivity

The thermal conductivity $\hat{\kappa}$ connects a temperature gradient to the resulting heat flux, if there is no electric current ($\vec{j}_e = 0$). Combining this constraint with (2.15)

and (2.16) leads to

$$\vec{j}_h = [L^{22} - L^{21}(L^{11})^{-1}L^{12}] (-\vec{\nabla}T/T) = \hat{\kappa}(-\vec{\nabla}T) \quad (2.27)$$

In a metal, the second term is much smaller than the first and can be disregarded. With (2.21) the thermal conductivity can be written as

$$\hat{\kappa}_{\text{el}} = \frac{L^{22}}{T} = \frac{\pi^2}{3} \frac{k_{\text{B}}^2 T}{e^2} \hat{\sigma} \quad (2.28)$$

This relation is called **Wiedemann-Franz law**. The proportionality constant between the thermal and the electrical conductivity is known as the **Lorenz number**:

$$L = \frac{\pi^2}{3} \frac{k_{\text{B}}^2}{e^2} = 2.44 \times 10^{-8} \text{W}\Omega\text{K}^{-2} \quad (2.29)$$

The Wiedemann-Franz law only describes the heat transfer due to electrons. Considering that electrical insulators nevertheless conduct heat, there must be another mechanism at play, namely heat transfer through phonons. Therefore, the total thermal conductivity is a combination of electronic and phononic contributions:

$$\kappa = \kappa_{\text{ph}} + \kappa_{\text{el}} \quad (2.30)$$

The phononic contribution to κ is determined by the material's specific heat c_V , the phonons' group velocity v and their mean free path λ

$$\kappa_{\text{ph}} = \frac{1}{3} c_V v \lambda \quad (2.31)$$

The specific heat can be approximated with the Debye model and yields

$$c_V = \frac{12\pi^4}{5} \frac{R}{M} \left(\frac{T}{\Theta_D} \right)^3 \quad T \ll \Theta_D \quad (2.32)$$

$$c_V = \frac{3R}{M} \quad T \gg \Theta_D \quad (2.33)$$

with R being the universal gas constant $R = N_A k_B \approx 8.31$ J/mol K, M being the molecular mass and Θ_D the Debye temperature.

(2.33) is also known as the **Dulong-Petit law** and states that the molar specific heat capacity of many solid elements has a constant value of 24.9 J/mol K. This is valid for high temperatures, but at low temperatures quantum mechanical effects have to be considered. Therefore, the Debye model gives a more appropriate description of the specific heat, which shows a T^3 dependency at low temperatures. Apart from the specific heat, κ_{ph} also depends on the mean free path of the phonons, which is defined by scattering processes. Here, scattering on defects plays an import role, as well as phonon-phonon scattering. While normal 3-phonon processes $\vec{q}_1 + \vec{q}_2 = \vec{q}_3$ preserve the total momentum and are therefore irrelevant to the heat transfer, so-called **Umklapp processes** $\vec{q}_1 + \vec{q}_2 = \vec{q}_3 + \vec{G}$ have to lose the momentum $\vec{G}$, in order to stay inside their Brillouin zone. This opposes the heat flux and therefore influences the thermal conductivity. Since the sum of $\vec{q}_1$ and $\vec{q}_2$ only lies outside of the Brillouin zone, if their energy is sufficiently high, the number of Umklapp processes decreases with decreasing temperature. Therefore, at low temperatures κ_{ph} is mainly determined by scattering on defects.

2.2.3. Seebeck coefficient

With no electric current, the Seebeck coefficient defines the relation between electric field and temperature gradient. Therefore, one can rearrange (2.15) into

$$\vec{E} = (L^{11})^{-1} L^{12} (\vec{\nabla} T / T) = S \vec{\nabla} T \quad (2.34)$$

With (2.19) and (2.20) this results in the **Mott formula**

$$S = \frac{(L^{11})^{-1} L^{12}}{T} = \frac{\pi^2 k_B^2 T}{3 e} \left[\frac{1}{\hat{\sigma}} \frac{\partial \hat{\sigma}(E)}{\partial E} \right]_{E=E_F} \quad (2.35)$$

According to (2.22), $\hat{\sigma}$ is proportional to n , which is proportional to the electronic density of states $D(E_F)$ at the Fermi level. With this approximations, one can write

$$S \propto \frac{1}{n} \left. \frac{\partial D(E)}{\partial E} \right|_{E=E_F} \quad (2.36)$$

This means that the Seebeck coefficient is bigger, the steeper the function $D(E)|_{E=E_F}$ is. On the other hand, a very high charge carrier concentration lowers the thermopower.

2.3. Hall effect

If a magnetic field is applied perpendicular to a current-carrying conductor, the deflection of charge carriers due to the **Lorentz force** leads to an additional voltage U_H , which can be detected perpendicular to both current and magnetic field. This is called **Hall effect**.

To understand the Hall effect, we consider a metallic conductor, where the only charge carriers are electrons. The Lorentz force is

$$\vec{F} = q \left[\vec{E} + (\vec{v} \times \vec{B}) \right] \quad (2.37)$$

with the electron charge q , the electric field $\vec{E}$, the electron velocity $\vec{v}$ and the

magnetic field $\vec{B}$. Choosing $\vec{v} = v_x$ and $\vec{B} = B_z$ in order to simplify the equation and considering the steady-state $\vec{F} = 0$, one gets

$$E_y = v_x B_z \quad (2.38)$$

Introducing the Hall coefficient $R_H = \frac{1}{nq}$, this can be written as

$$E_y = \frac{1}{nq} j_x B_z = R_H j_x B_z \quad (2.39)$$

which, with the sample thickness d and its width b , leads to

$$U_H = R_H \frac{I B_z}{d} \quad (2.40)$$

Here, the relations $U = Eb$ and $j_x = \frac{I}{bd}$ were used.

In case that both positive and negative charge carriers give rise to the current, the resulting Hall coefficient is also determined by both contributions:

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{|e| (p\mu_h + n\mu_e)^2} \quad (2.41)$$

with n being the electron concentration, p being the hole concentration and μ_h and μ_e being the respective mobilities.

3. Thermoelectric design concepts

As mentioned before, the key to obtaining efficient TE devices is to use materials with a high figure of merit ZT . Considering (1.2), an ideal thermoelectric would exhibit a high thermopower S , a high electrical conductivity σ and a low thermal conductivity κ . While the optimisation of these quantities varies for each material, there are some general design concepts that have proven to enhance the figure of merit for various material classes.

3.1. Tuning the charge carrier concentration

In order to obtain a high ZT , both S and σ ought to be as high as possible. This task is more difficult than it seems at first sight, due to the interrelated nature of the mentioned quantities. For instance, the Seebeck coefficient of a metal or degenerate semiconductor can be written as

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (3.1)$$

with the Boltzmann constant k_B , the electron charge e , the Planck constant h and the effective mass m^* [2].

According to (3.1), S gets smaller with an increasing charge carrier concentration

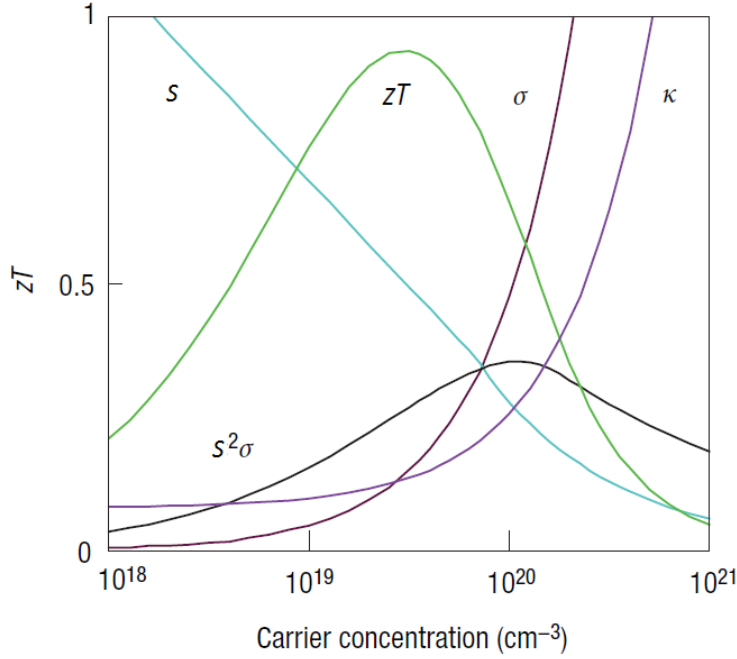


Figure 3.1.: Typical dependency of S , σ and κ on the charge carrier concentration, as well as the resulting power factor $S^2\sigma$ and figure of merit ZT . [2]

n . On the other hand, (2.22) states that σ increases with increasing n . A similar problem occurs for the effective mass m^* . Here, the thermopower increases, while the electrical conductivity decreases with rising values of m^* .

Figure 3.1 illustrates how the dependency of S , σ and κ on the charge carrier concentration influences the figure of merit. Typically, the maximum of ZT lies between 10^{19} cm^{-3} (10^{25} m^{-3}) and 10^{21} cm^{-3} (10^{27} m^{-3}). These charge carrier concentrations can be found in heavily doped semiconductors. [2]

Since the exact maximum of ZT is different for each material, the ability to vary the charge carrier concentration is an important tool in TE material development. This is, e.g. done by doping the material with elements, which have slightly more or less electrons than the substituted ones.

3.2. Strongly correlated electron systems

A promising route to efficient TE materials is the modification of the electronic band structure near the Fermi level. According to (2.36), the Seebeck coefficient is proportional to the derivative of the electronic density of states (DOS) at the Fermi level. Therefore, a sharp peak in the DOS at the Fermi level can lead to high S values.

While simple metals and semiconductors have a rather smooth DOS, sharp features in the DOS near the Fermi level often occur in so-called **strongly correlated electron systems** (SCESs). Generally speaking, electrons are strongly correlated, if the energy of their mutual Coulomb repulsion is bigger than their kinetic energy, i.e. if it becomes impossible to view an electron as independent of the others. This behaviour can be observed in Kondo systems, high temperature superconductors, transition metal oxides, strontium ruthenates, and many other material classes. [9]

Especially **Kondo systems** are of great interest for TE applications. Here, elements with partially filled $4f$, $5f$, or sometimes $3d$ shells give rise to magnetic impurities. The f (or d) levels of these impurities lie close to the Fermi level, so that the localised electrons can strongly interact with the itinerant electrons. They do so by being virtually excited into the conduction band, which causes a sharp resonance in their DOS, called **Kondo resonance**. This leads to a large thermopower. [9, 10]

3.3. Phonon glass - electron crystal

In order to achieve a high ZT , a material ought to have a high electrical conductivity σ and a low thermal conductivity κ . However, according to the Wiedemann-Franz law (2.28), the electronic contribution to the thermal conductivity κ_{el} is

proportional to the electrical conductivity σ . Therefore, the only way to reduce the thermal conductivity κ , while keeping a high σ , is to minimise the lattice thermal conductivity κ_{ph} . This gives rise to the concept of a **phonon glass - electron crystal** (PGEC), which behaves like a glass for phonons and therefore conducts heat poorly, while at the same time acting like a crystal for electrons. There are several ways of achieving this, for instance reducing one dimension, so that it is smaller than the mean free path of the phonons, but bigger than the mean free path of the electrons, or using materials with complex crystal structures. Very promising materials are so-called **cage compounds**, which consist of large polyhedra, in which heavy atoms can be incorporated. These guest atoms "rattle" inside their cages, thus obstructing the phonons. [10]

3.4. The Zintl-Klemm concept

Zintl phases are a group of intermetallics, which consists of very electropositive alkali or alkaline-earth metals and rather electronegative elements from group 13 to 15. The electronegative elements form polyanionic units through covalent bonding, while also receiving electrons from the electropositive cations. The resulting phase is therefore formed through both ionic and covalent bonding. While Zintl phases can display rather complex crystal structures, they can also be understood using electron counting rules, due to a well defined relation between the electronic structure and the crystal structure. This is known as the **Zintl-Klemm concept** and it has been successfully used to prepare novel compounds with interesting properties. [11]

In recent years, the interest in Zintl phases as thermoelectrics has increased, due to their many properties that enable a high figure of merit. First off, they are valence balanced compounds, which is a characteristic of most good thermoelectric ma-

terials, and their often complex structures cause low lattice thermal conductivity. Furthermore, the covalent bonding of the anions provides the wanted electron-crystal structure and the phase can be alloyed or doped without disrupting it. That means, that one can minimise phonon transport through alloy scattering or control the charge carrier concentration without losing the good electrical conductivity. This way, the thermoelectric properties can be optimised. [2, 6]

4. Experimental set-up

4.1. Synthesis

All samples were synthesised at high temperatures $T > 1000^{\circ}\text{C}$, but depending on their chemical properties the procedures varied. Air-sensitive metals (Sm, Yb, Sr) were stored, handled and weighed in a glove box with Ar atmosphere and an oxygen and water vapour level < 0.6 ppm. In some cases, stoichiometric amounts of the needed elements were simply melted via high-frequency induction in a Cu crucible in Ar atmosphere. For others, a synthesis in a sealed crucible was necessary. To seal the crucible, a tetra-arc was used.

4.1.1. Direct high-frequency induction melting

There are various set-ups for induction melting. One rather simple design is the so-called cold boat (Figure 4.1).

This set-up is suitable for conductive material, which is placed in an indentation of a water-cooled Cu rod. The rod is surrounded by an Ar filled quartz tube and an induction coil. A high-frequency (HF) alternating current (AC) is sent through the coil and induces an HF magnetic field, which in turn induces eddy currents in the material. That way, the material gets heated until it melts. By cooling it down, one obtains a polycrystalline sample. For purposes of homogeneity, the sample is broken in half, put into the cold boat with the outer ends turned inwards

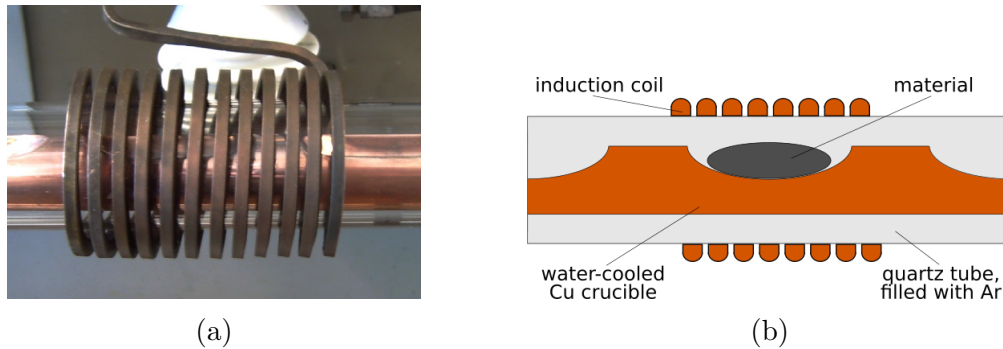


Figure 4.1.: a) Picture [12] and b) schematic view of a Cu cold boat.

and then melted again. This process is repeated 2-3 times.

4.1.2. Indirect high-frequency induction melting

As the name suggests, in indirect HF induction melting the eddy currents are not induced directly in the material, but rather in a surrounding susceptor. For this reason, it is also possible to melt non-conductive material, as well as material inside a sealed Ta crucible. The latter is very useful for volatile elements and is described in detail in Chapter 8.

The schematic set-up of the HF induction furnace is shown in Figure 4.2. A cylindrical tube made of Ta foil with a thickness of 0.1 mm serves as the susceptor of the HF electromagnetic field energy. Due to the high melting point of Ta ($\sim 3020^\circ\text{C}$), one can achieve temperatures high enough, so that the radiated heat melts the sample. To minimise energy loss, the susceptor is surrounded by a radiation shield, which is a slightly larger cylinder made of Ta foil. A lengthwise gap suppresses eddy currents in the shield.

A crucible, filled with material, is placed within the susceptor and radiation shield. This assembly is inserted into the induction coil, where it is held in place with two water-cooled steel rods and centring discs made of BN. Since the crucible reaches very high temperatures, a Ta tube with $\varnothing$ 1 cm, containing a thermocouple, is

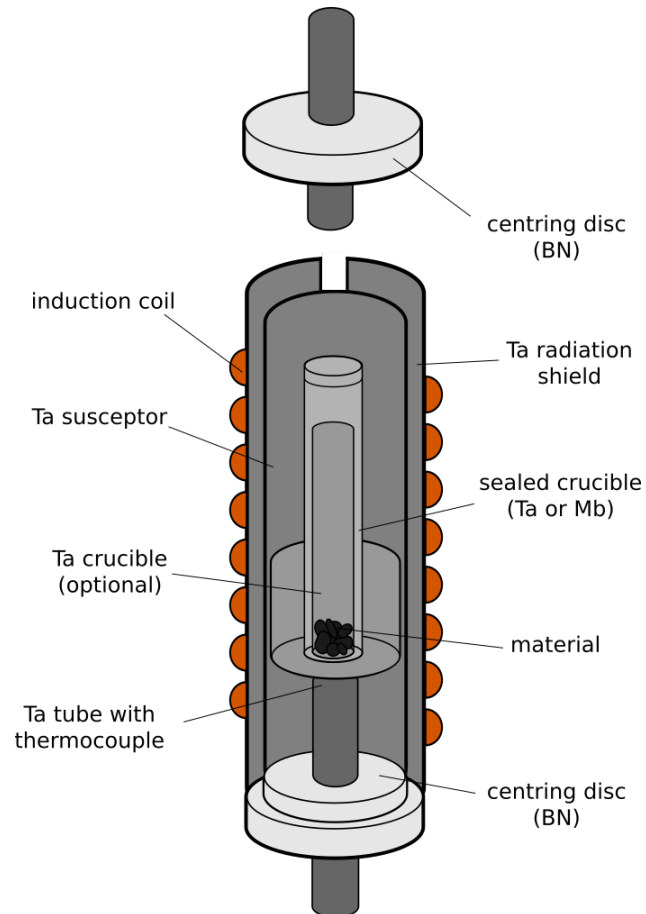


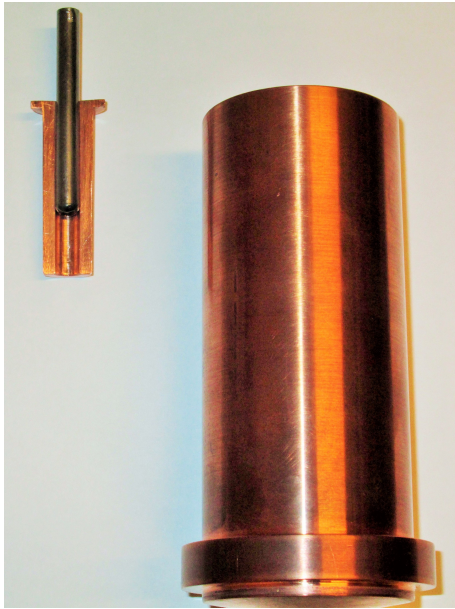
Figure 4.2.: Schematic of set-up for indirect HF induction melting, where the Ta susceptor is heated up by the HF electromagnetic field. The resulting heat radiation melts the material inside the susceptor, while a radiation shield prevents excessive heat radiation to the outside.

attached to the lower steel rod and serves as the crucible holder. The steel rods can be moved up or down, making it possible to choose the sample's position inside the induction coil. Lastly, the chamber with the set-up, which is cooled by water, is evacuated to a pressure of $\sim 10^{-5}$ mbar, to prevent dielectric-barrier discharge at higher frequencies.

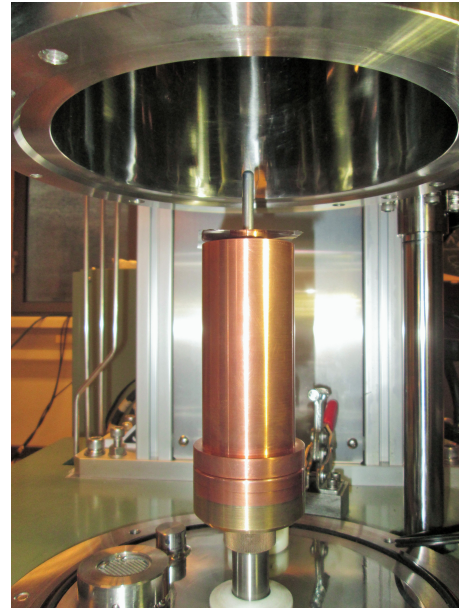
The thermocouple, which is secured inside the Ta tube, provides information about the temperature at the bottom of the crucible. To prevent contact between the two arms, they are clamped to opposite sides by two springs. The input voltage for the induction coil can be controlled manually or with a computer program. The latter allows for running temperature ramps, if the voltage dependence of the temperature is known (Figure 8.4). The program can be also used to move the crucible relatively to the inductor with a predefined speed, thus enabling the growth of single crystals via the **Bridgeman technique**.

4.1.3. Arc welding

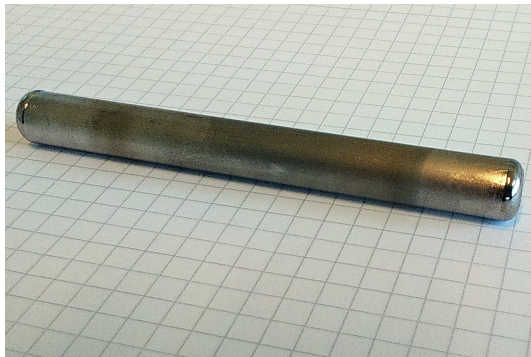
Some compounds are prone to decomposing and forming gas products during synthesis. In order not to lose any material and change the stoichiometry, they have to be synthesised in sealed crucibles (Figure 4.3c). As crucible material Ta was chosen, due to its ductility, chemical resistivity and high melting point of approximately 3020 °C. While this makes it the perfect choice to withstand the temperatures achieved at synthesis, it also complicates the preparation. After all, the crucible can only be welded at very high temperatures. Many starting materials, however, have lower boiling points. Therefore they must be constantly cooled during welding, so that they do not vaporise. For this reason a Cu heatsink, which encloses approximately two thirds of the crucible, was specially designed (Figure 4.3a).



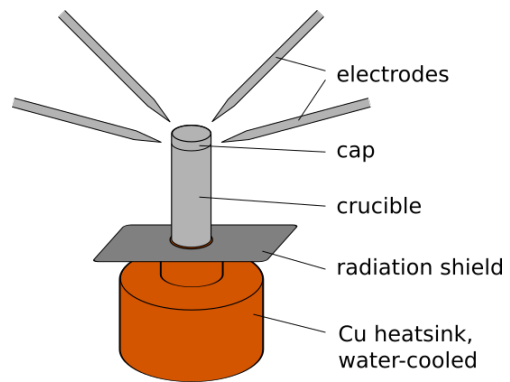
(a)



(b)



(c)



(d)

Figure 4.3.: a) Cu heatsink with inlay and crucible. b) Heatsink with crucible and radiation shield inside the opened tetra-arc furnace. c) Sealed crucible. d) Schematic of sealing a crucible via tetra-arc welding.

It is placed on an already existing water-cooled heatsink (Figure 4.3b) and cools down very well, thus shielding the crucibles content from heat. The inlays allow it to be used for differently sized crucibles and ensure a good contact between the crucible and heatsink. Furthermore, a radiation shield, made of Ta foil, is placed on top of it and gives additional protection from the heat.

To weld the crucibles shut, a tetra-arc is used. First, the crucible is filled with material and then closed with a cap, also made of Ta. It is placed in the heat sink, which is then put inside the tetra-arc furnace. After the furnace is closed and evacuated, it is filled with Ar gas to a pressure of ~ 0.6 bar. The four electrodes are positioned close to the cap (Figure 4.3d). After the positioning, the heating power is turned on and the current through the electrodes can be increased manually. Depending on the crucible, a current of 15-28 A per electrode is deemed appropriate. When the cap starts to melt, a rotation of the heat sink and the crucible is turned on, ensuring that the melting takes place evenly.

4.2. Structural and compositional characterisation of samples

A material's properties can change a lot, depending on the exact stoichiometry and defects in the material. For this reason, it is essential to analyse the samples' structure and composition carefully before measuring their physical properties. This way, one can find out if the produced samples deviate from the desired stoichiometry or if there are inclusions of secondary phases. Often the samples' quality can be improved through annealing, as demonstrated in the following chapters by comparing XRD data before and after annealing. Only samples with sufficient purity are considered for further measurements.

To analyse the phases and the structure, two methods were used, which will be

presented in the following.

4.2.1. X-ray powder diffraction

All information that can be obtained from X-ray diffraction (XRD) is based on Bragg's law:

$$2d \cdot \sin\theta = n\lambda \quad (4.1)$$

with d being the interplanar distance, θ the diffraction angle, n the ordinal number and λ the wavelength.

This means that an X-ray beam is only reflected from, or transmitted through, a sample, if a specific relation between the incident angle and the crystal structure is given. Furthermore, symmetries in the crystal structure can cancel out certain diffracted beams. Therefore, each crystal structure has a characteristic XRD pattern.

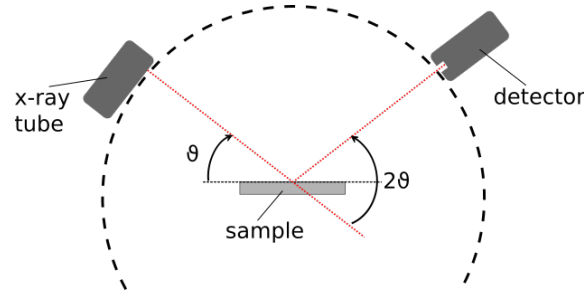


Figure 4.4.: Bragg-Brentano geometry

In case of powder diffraction, a small part of the sample has to be ground into fine powder, which is then fixed on a small glass plate using silicon grease. The prepared sample is placed in a diffractometer with Bragg-Brentano-geometry, as shown in Figure 4.4, and a radiation source that provides an X-ray beam with $\lambda_{\alpha 1} = 1.540598 \text{ \AA}$ and $\lambda_{\alpha 2} = 1.544426 \text{ \AA}$ (Cu-target). A goniometer, on which either

the X-ray source and the detector (θ : θ -scan) or the sample holder and the detector (θ : 2θ -scan) are mounted, ensures that the incident angle of the X-ray beam is always the same as the diffraction angle.

Due to the previous pulverisation, the sample now has the form of tiny crystallites, which are oriented statistically in all directions. A small percentage of crystallites is oriented in such a way, that Bragg's law is fulfilled at a certain angle and reflected X-rays can be detected. Plotting the measured intensity against the incident angle leads to the characteristic diffraction pattern that can be used to identify the crystal structure. Once this is known, a refinement of the cell parameters can be performed using the Rietveld method, which is based on a least-squares approach. For the data's evaluation, two programs were used: A rough refinement of the lattice constants, as well as the phase composition in case of multiphase materials, was conducted with *Powdercell 2.3*. For a more detailed refinement of the cell parameters, *PANalytical XPert HighScore Plus 3.0* was used.

4.2.2. Scanning electron microscopy

For analysis via scanning electron microscopy (SEM) a sample has to be prepared by sanding and polishing it to a mirror finish. Then it is scanned with a focussed electron beam (20 kV). The electrons are reflected (backscattered electrons), but not without transferring part of their energy to the atoms in the sample. The excited atoms emit secondary electrons, which are detected and used to create an image. Due to their low energy ($\sim$ eV) they can be easily distinguished from the backscattered electron ($\sim$ keV). Furthermore, the low energy allows only the electrons from a few nm beneath the surface to reach the detector, making this a surface sensitive imaging method with good spatial resolution ($\sim$ 1 nm). There is also the possibility of using backscattered electrons for imaging, but their higher energy makes the volume, from which they can be detected, larger and the reso-

lution therefore lower (several μm).

When an electron is emitted from an inner shell, the vacancy is filled by an electron from a higher-energy shell, while the energy difference is emitted in form of an X-ray photon. By measuring the energy of these X-ray photons, which is characteristic for each element, it is possible to determine the chemical composition of a given spot. This method is called energy dispersive X-ray spectroscopy (EDX).

4.3. Transport properties

4.3.1. Ulvac

The thermopower and the electrical resistivity at high temperatures (300 K - 870 K) were measured on the *ULVAC ZEM-3*, using a four-point method. For the measurement a sample with a defined geometry (rectangular or cylindrical) is positioned between two electrodes, then two thermocouples are brought into contact with it (Figure 4.5). The whole is surrounded by an infra-red furnace, which is evacuated and filled with He to a pressure of ~ 0.15 bar. Then the furnace heats up according to the temperature program, while the heater in the lower block sets the temperature difference ΔT between the thermocouples. The resulting voltage U can be measured and provides information about the thermopower S

$$S = \frac{U}{\Delta T} \quad (4.2)$$

Usually, measurements are taken three times for each temperature (with $\Delta T = 10, 15, 20$ K) and then averaged out.

By sending normalised current (I) through the electrodes without applying a temperature gradient and measuring the voltage, it is possible to determine the elec-

trical resistivity ρ , using:

$$\rho = \frac{U}{I} \frac{l}{A} \quad (4.3)$$

with l being the distance between the thermocouples and A the sample's cross section.

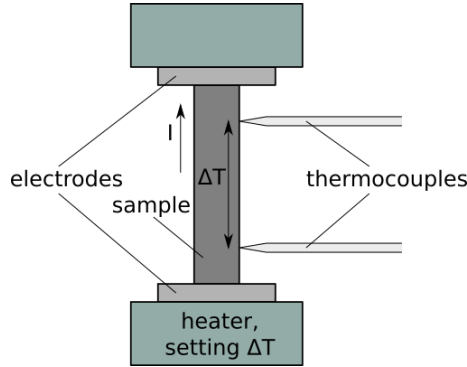


Figure 4.5.: Schematic of the thermopower measurement in the ULVAC.

Although the measurements were conducted in a He environment, all samples showed signs of oxidation afterwards. More than that, Yb_2InGe_2 was covered in what appeared to be metal filings. Upon closer examination, they turned out to be mainly Ge and small droplets of In, which presumably formed due to the depletion of Yb through its preferred oxidation. Since one cannot say for sure, at which exact point in the high-temperature range these changes happened, the results of the high-temperature Ulvac measurements have to be viewed with care and used only as rough guide values.

4.3.2. Laser flash method

For measuring the thermal conductivity at high temperatures (420 K - 820 K), Anter Corporation's *Flashline 3000* was used. This set-up requires a disc shaped sample, which is blackened with graphite spray. It is placed inside a furnace, where it is brought to a certain temperature. Then a laser pulse hits one side,

thus warming the sample. The heat diffuses to the other side of the sample, where it can be detected by an infra-red sensor. Plotting the detected heat against time leads to $\tau_{1/2}$, which is the time to reach half of the peak temperature. This value, together with the sample thickness d , is used by the measurement's computer program to calculate the thermal diffusivity α .

The thermal conductivity can then be determined using following relation:

$$\kappa = \alpha \cdot c_V \cdot \rho \quad (4.4)$$

with c_V being the sample's specific heat per unit volume and ρ its density.

4.3.3. Physical property measurement system (PPMS)

The physical property measurement system was used to measure the electrical resistivity and the Hall effect at low temperatures (2 K - 300 K). For the measurement, six thin wires are spot-welded to the sample (Figure 4.6). It is then glued onto a puck, where the wires are contacted through soldering. The wires I_1 and I_2 provide the sample with normalised current, while U_1 and U_2 measure the voltage and therefore the resistivity. By applying a magnetic field (9 T) perpendicular to the current, it is possible to induce the Hall effect (Section 2.3), which is used to determine the charge carrier concentration. Here, the wires H_1 and H_2 measure the Hall voltage U_H , which is perpendicular to both current and magnetic field.

To prevent measuring errors that arise from the Hall contacts not being fixed on the same equipotential line, the measurements are carried out twice, with opposite magnetic fields $+B$ and $-B$. This leads to the Hall voltage

$$U_H = \frac{U_H(+B) - U_H(-B)}{2} = \frac{(U_{B=0} + U_H) - (U_{B=0} - U_H)}{2} \quad (4.5)$$

which is used to determine the Hall coefficient R_H

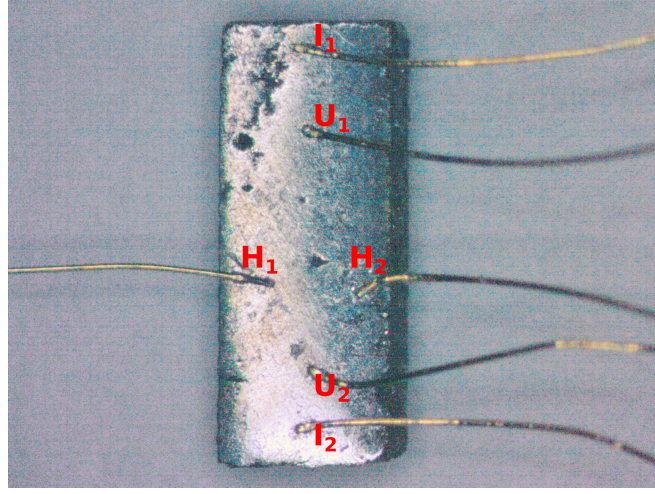


Figure 4.6.: Yb_2InGe_2 sample with attached Au wires for current supply (I_1 and I_2), measuring the voltage (U_1 and U_2) and measuring the Hall-voltage (H_1 and H_2).

$$R_H = \frac{U_H}{I} \frac{d}{B} \frac{b}{b^*} \quad (4.6)$$

with the current I , the magnetic field B and the sample thickness d . A comparison with (2.40) shows an additional correction factor $\frac{b}{b^*}$. This is due to the fact, that the sample width b is not exactly the same as the distance b^* between H_1 and H_2 , which has to be taken into account.

Based on R_H it is easy to calculate the charge carrier density n and the charge carrier mobility μ :

$$n = \frac{1}{qR_H} \quad (4.7)$$

$$\mu = \frac{|R_H|}{\rho} \quad (4.8)$$

with the electron charge $q \approx -1.602 \times 10^{-19}$ C and the electrical resistivity ρ , which was measured using U_1 and U_2 .

5. Materials with the formula $A_2M'M''_2$ ($A = \text{Sr, Yb}$; $M' = \text{In, Sn, Pb}$; $M'' = \text{Si, Ge}$)

5.1. Motivation

The mixed tetrelides Yb_2SnGe_2 (space group $P4/\text{mbm}$, no. 127, $Z = 2$) and Sr_2PbGe_2 (space group Cmmm , no. 65, $Z = 2$) were discovered in 2015 by M. Jehle et al. as part of an alkaline-earth/lanthanoid family with the general formula $A_2M'M''_2$ ($M' = \text{In, Sn, Pb}$; $M'' = \text{Si, Ge}$). They were obtained by melting stoichiometric amounts of their elements inside sealed Ta crucibles and appeared without any by-products. In case of Yb_2SnGe_2 , it was also said to be obtainable in its pure form by simply arc-melting the right amounts of Yb, Sn and Ge. The authors determined the crystal structure of these new phases on microcrystals, which had been separated mechanically from the polycrystalline samples. No physical properties of the phases were measured. [13]

Yb_2SnGe_2 crystallises in the Mo_2FeB_2 -type structure, with the tetragonal space group $P4/\text{mbm}$. Two formula units build the unit cell with the lattice parameters $a = 7.4027 \text{ \AA}$ and $c = 4.3526 \text{ \AA}$. Viewed down the a -axis, one can see that the Yb atoms form a layer between SnGe_2 planes (Figure 5.1). According to Jehle, these planes consist of Ge dumbbells with a double bond, which are connected by square

planar coordinated Sn atoms (Figure 5.2). Therefore, Yb_2SnGe_2 can be written as an electron precise Zintl phase: $2\text{Yb}^{2+} \text{Sn}^0 \text{Ge}_2^{4-}$. In this case, the material is likely to be a semiconductor. [13]

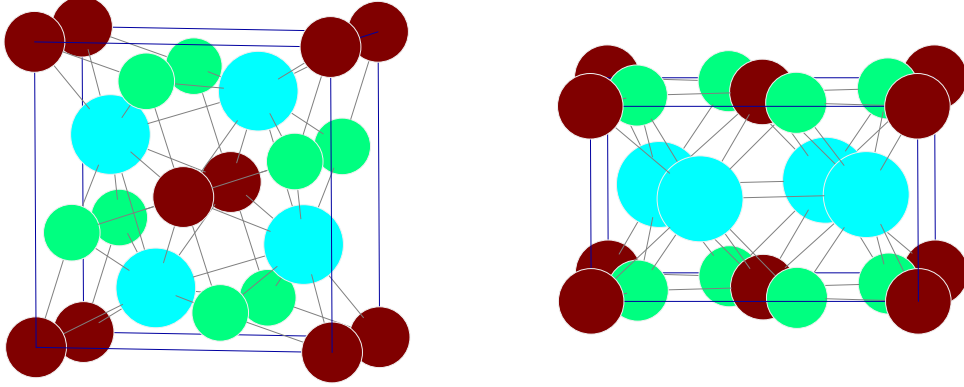


Figure 5.1.: Unit cell of Yb_2SnGe_2 from two different perspectives. The Yb (light blue) is situated between two layers of Sn (red) and Ge (green).

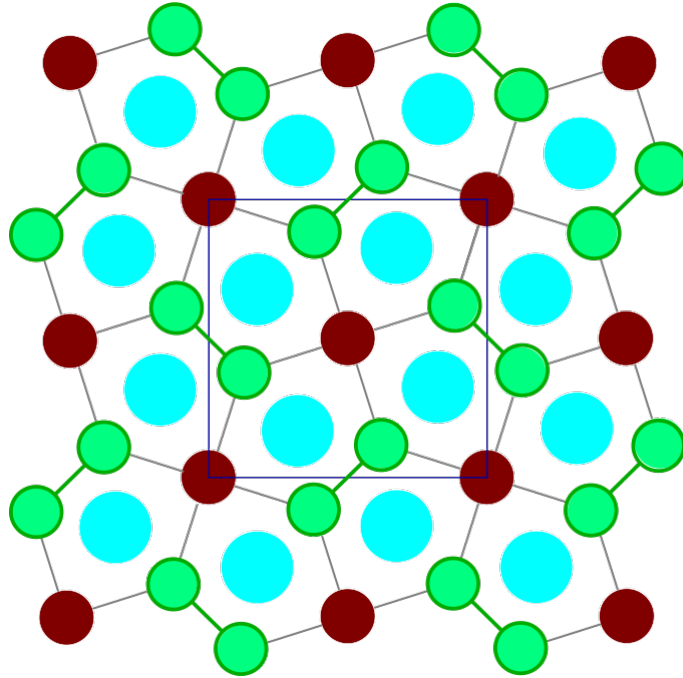


Figure 5.2.: Crystal structure of Yb_2SnGe_2 , viewed down the c -axis, showing the Ge-Ge bonds (green).

Sr_2PbGe_2 crystallises in the orthorhombic Mn_2AlB_2 structure (Figure 5.3). Contrary to Yb_2SnGe_2 , the Ge atoms form infinite zig-zag chains with alternating single and double bonds, while the Pb connects linearly with the Ge. This gives rise to the formula $2\text{Sr}^{2+} \text{Pb}^{2-} [\text{Ge}_2]^{2-}$, making the compound electronically compensated and therefore also a semiconductor. [13]

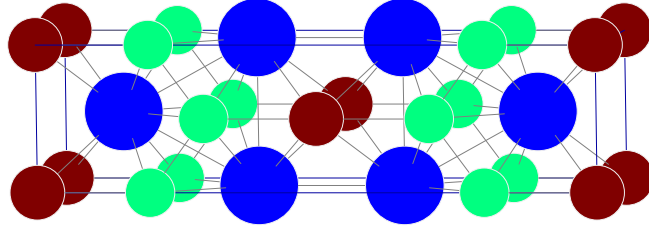


Figure 5.3.: Unit cell of Sr_2PbGe_2 , with Sr (dark blue), Pb (red) and Ge (green).

Density functional theory (DFT) calculations of the electronic density of states (DOS) [13], on the other hand, may show a reduced DOS at the Fermi level, but not a band gap (Figure 5.4), which is a sign of both materials being metallic. However, these calculations have to be viewed with caution, since delocation errors in the exchange-correlation functionals could change the outcome significantly. For example, measurements of SrZn_2Sb_2 show a band gap of 0.26 eV, which is not predicted by traditional DFT calculations [14]. Therefore, Yb_2SnGe_2 and Sr_2PbGe_2 have to be examined properly, in order to know for sure whether the Zintl formalism can be applied or not.

Another reason for the interest in the materials can be also found in Figure 5.4. Here, sharp features near the Fermi level can be seen. The peak for Sr_2PbGe_2 is not exactly at the Fermi level, but this could be improved by doping the material. For instance, by partially replacing some elements in the materials with others that have less electrons, one could shift the Fermi level to lower energies, which would

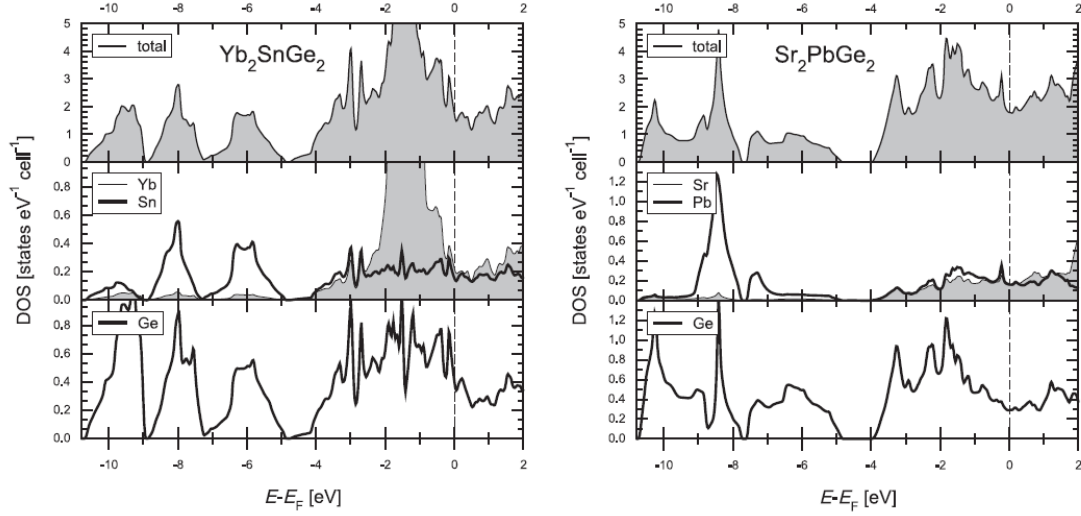


Figure 5.4.: Electronic density of states of Yb_2SnGe_2 and Sr_2PbGe_2 . [13]

put it closer to the mentioned peaks. Since the Mott formula (2.36) states that a steep DOS at the Fermi level causes a high Seebeck coefficient, these modifications could cause interesting thermoelectric properties.

But not only the Seebeck coefficient can be improved through doping. As mentioned in Section 3.1, a material's charge carrier concentration is an important parameter, affecting all relevant thermoelectric properties. Being able to influence it is crucial. Therefore, in order to find the optimal version of a material, one first has to find suitable dopants with more or less electrons that can be integrated into the existing crystal structure.

In case of Yb_2SnGe_2 the goal was to achieve a smaller charge carrier concentration. Since it was assumed that the Yb in the compound already appeared in its divalent form Yb^{2+} , replacing it with another alkaline-earth metal or lanthanide seemed futile. Instead, it was decided to replace Sn with In, which has one electron less. Furthermore, it is known that Yb_2InGe_2 also crystallises in the Mo_2FeB_2 structure, as noted by P. Tobash et al. [15]. The authors confirm the divalent state of Yb for this compound through magnetic measurements (Figure 5.5). However, they

count the electrons differently, considering only one covalent bond for Ge, which leads to following calculation: $2\text{Yb}^{2+} \text{In}^{3+} 2\text{Ge}^{3-}$. The resulting extra electron per formula unit implies metallic behaviour. Even so, the lack of experimental data for the compound's transport properties in Tobash's paper, as well as the fact that their Zintl reasoning differs greatly from the one used in [13], is reason enough to investigate this material.

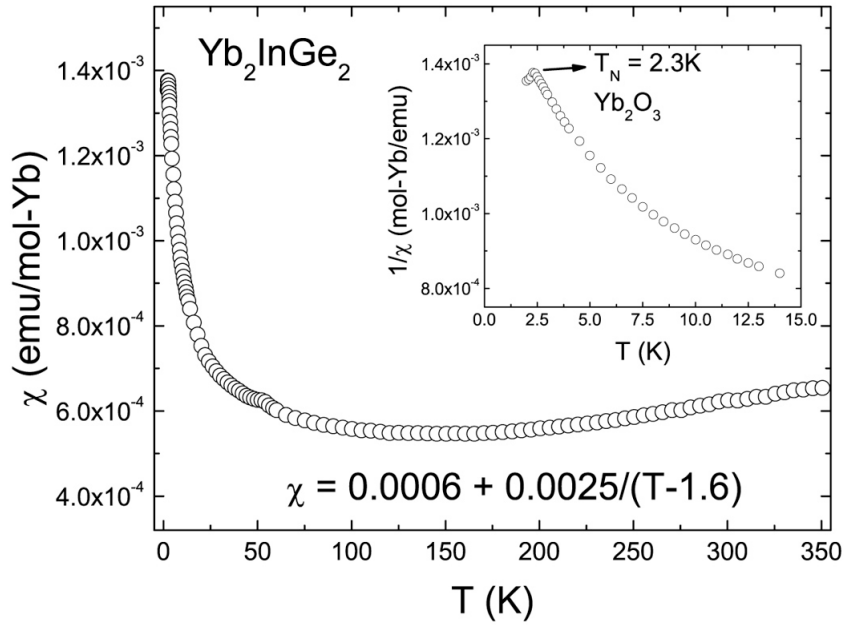


Figure 5.5.: Magnetic susceptibility of Yb_2InGe_2 versus temperature, as measured by P. Tobash et al. [15]. Note that there is an error in the labelling of the inset's y-axis: It should be χ (emu/mol-Yb).

5.2. Synthesis and characterisation via XRD and SEM

5.2.1. Yb_2SnGe_2

Since Yb_2SnGe_2 reportedly can be obtained by simple melting without a Ta crucible, it was decided to synthesise a sample in the cold boat. First, stoichiometric amounts of the elementary metals were weighed. Then, Yb was melted several times in the cold boat, using HF induction, while Sn and Ge were added stepwise to prevent violent reactions. After weighing the final ingot, it was found to be approximately 5 % shy of the expected mass. This big difference was accredited to the volatile Yb, therefore it was decided to add more Yb to compensate for the mass loss. The whole was melted two more times to ensure a homogeneous sample.

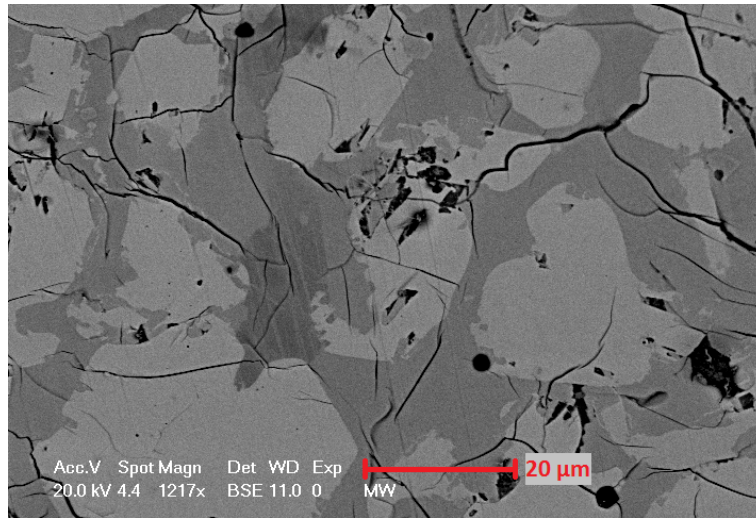


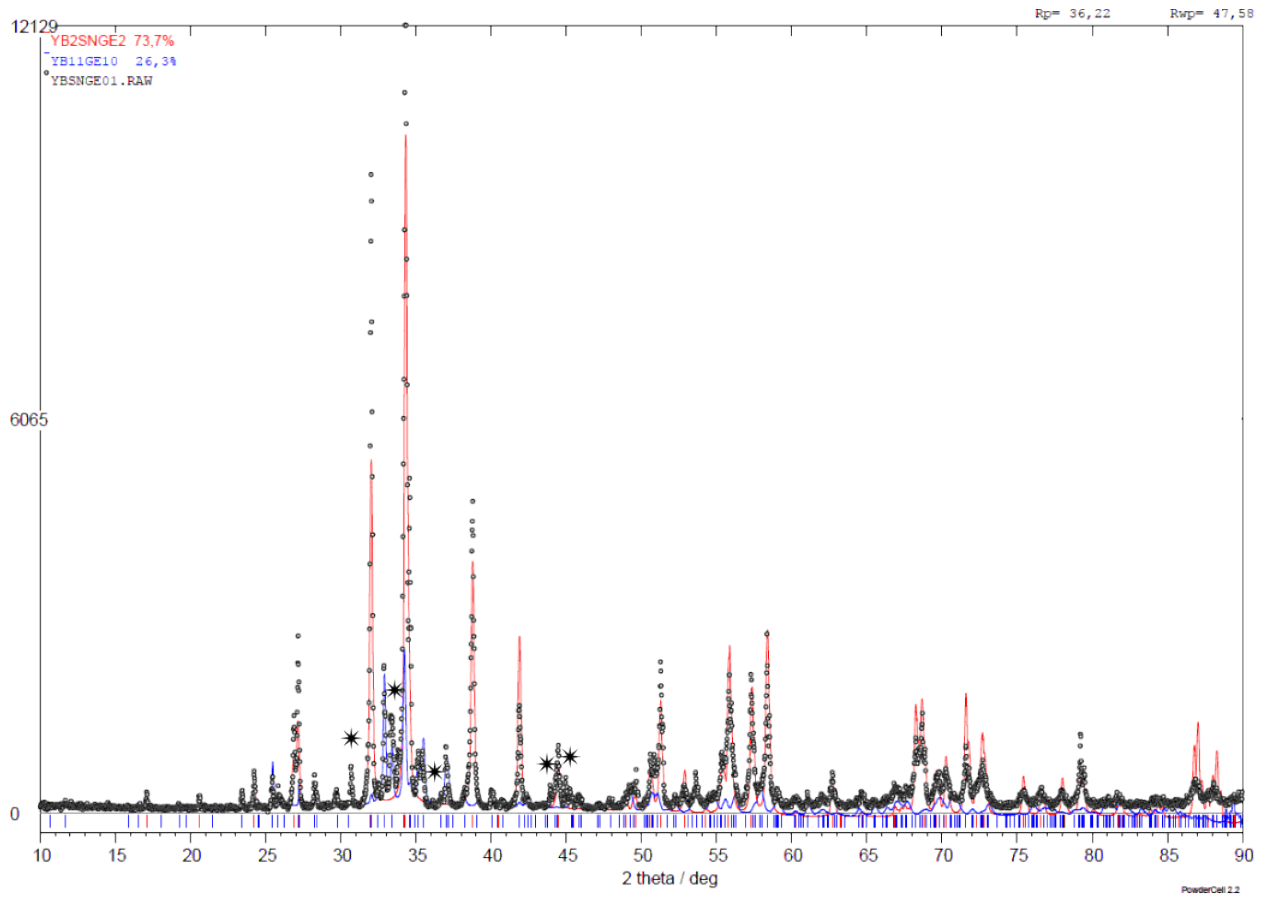
Figure 5.6.: SEM image of the Yb_2SnGe_2 sample before annealing, revealing a main phase with $\text{Yb}=2.1$, $\text{Sn}=0.8$, $\text{Ge}=2.1$ (dark grey) and a second phase with $\text{Yb}=2.8$, $\text{Sn}=0.2$, $\text{Ge}=2.1$ (light grey).

A piece of the sample was analysed via SEM/EDX. Here, a second phase, which consisted primarily of Yb and Ge, was visible (Figure 5.6). According to our EDX measurements, the main phase had a composition of 2.1:0.8:2.1, rather than 2.0:1.0:2.0. The second phase consisted of Yb=2.8, Sn=0.2, Ge=2.1. Therefore, its most probable crystal structure would be Yb_5Ge_4 , followed by Yb_5Ge_3 . However, neither of these crystal structures matches the XRD pattern. Instead, $\text{Yb}_{11}\text{Ge}_{10}$ appears to be a better fit and a conducted Rietveld refinement with Yb_2SnGe_2 and $\text{Yb}_{11}\text{Ge}_{10}$ yields an approximate ratio of 3:1 (Figure 5.7a).

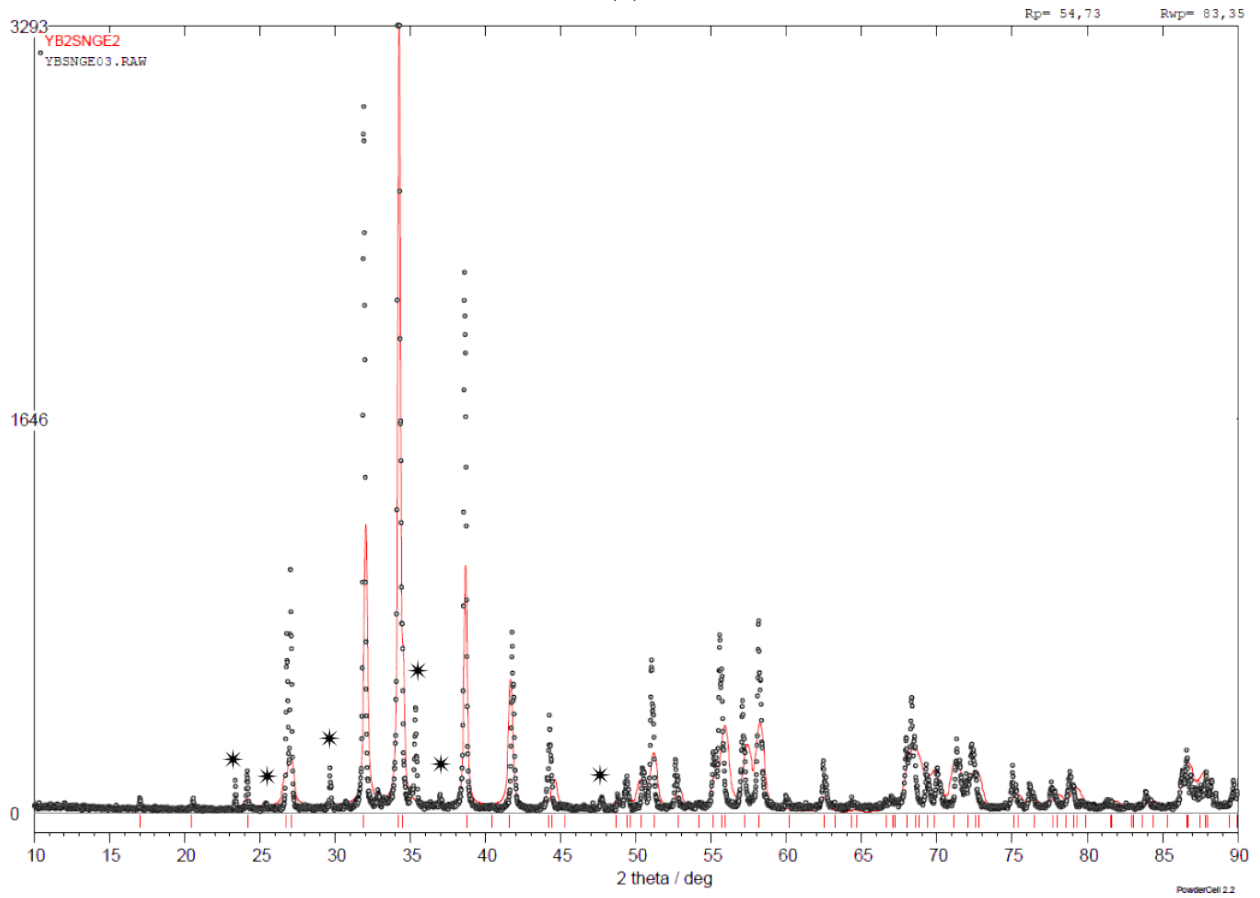
Wrapping the sample in Ta foil and annealing it at 700 °C for one week improved the material's quality, although some traces of another phase remained (Figure 5.7b). The refined lattice constants turned out to be significantly smaller than the literature value, with $a = 7.379 \text{ \AA}$ and $c = 4.326 \text{ \AA}$ instead of $a^* = 7.403 \text{ \AA}$ and $c^* = 4.353 \text{ \AA}$.

We synthesised several other samples in the cold boat, without adding extra Yb after melting the starting materials. Nevertheless, the XRD showed impurities that partly remained after annealing (Figure 5.8).

A thorough refinement of the lattice parameters using *High Score Plus* once again showed smaller lattice constants than expected. Figure 5.9 illustrates the samples' $a : c$ interrelation, including the literature value [13] and the values of our two annealed samples. Since annealing the samples, which evidently improves their quality, leads to bigger cell parameters, the low values apparently are caused by an off-stoichiometric ratio of the elements. Unfortunately, the samples YbSnGe05, YbSnGe06 and YbSnGe07 were melted and YbSnGe11 was annealed right after the XRD measurements, without analysing the samples via SEM/EDX. Therefore, we do not possess systematic EDX measurements to trace the relationship between the lattice parameters and the composition. However, it is interesting that the measured values a and c are in a linear correlation. Following this law,

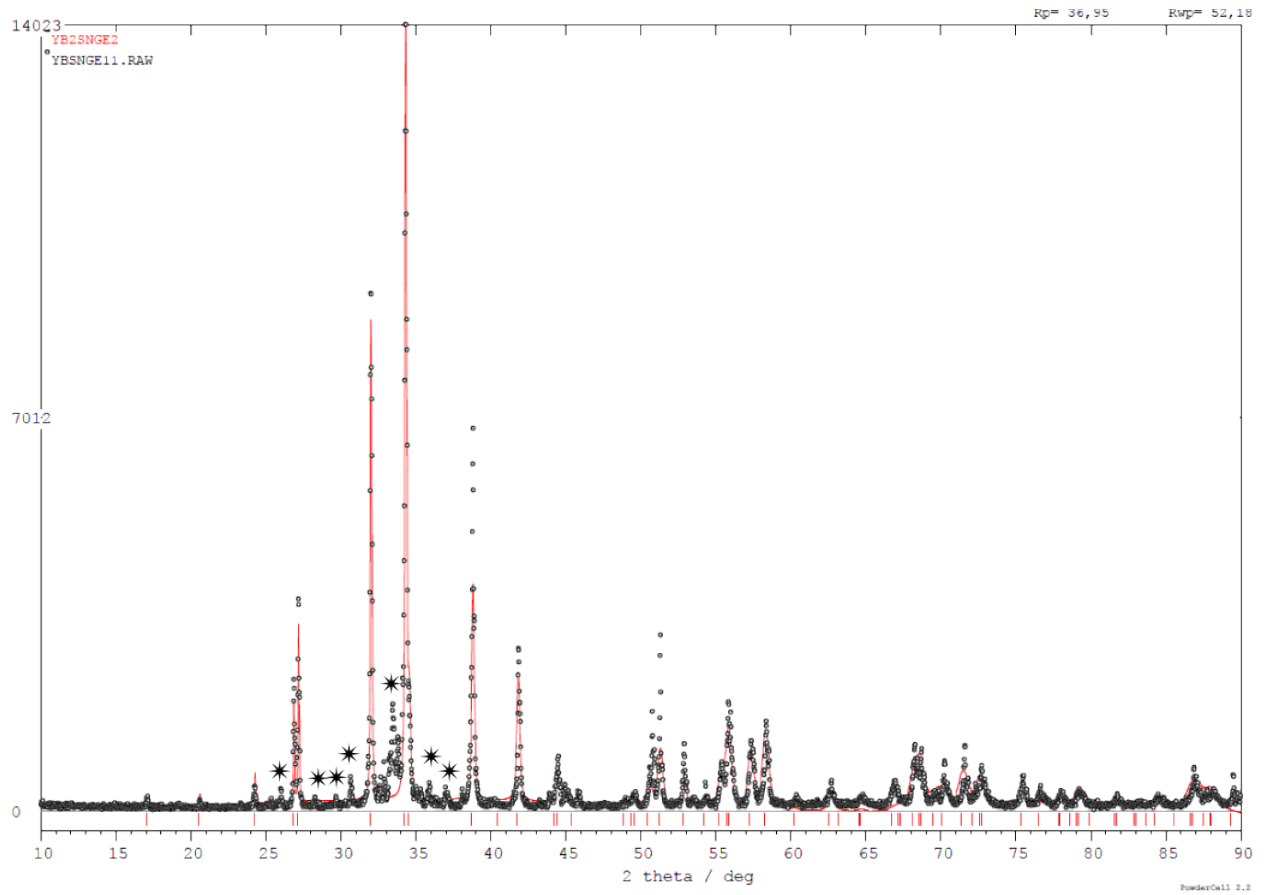


(a)

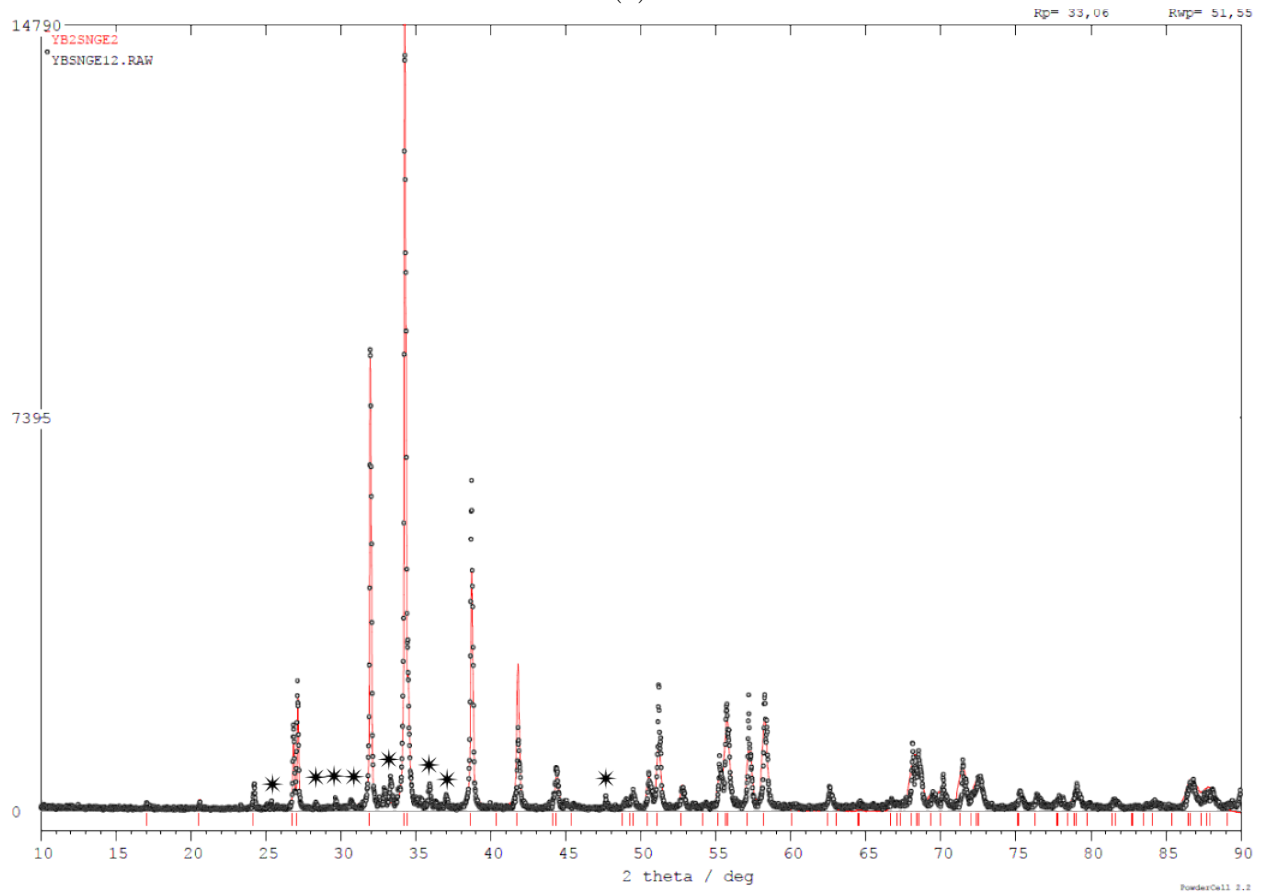


(b)

Figure 5.7.: XRD of a sample with the nominal composition Yb_2SnGe_2 a) before and b) after annealing for one week. The calculated XRD patterns of Yb_2SnGe_2 (red) and $\text{Yb}_{11}\text{Ge}_{10}$ (blue) are included. The unidentified phases are marked with *.



(a)



(b)

Figure 5.8.: XRD of a sample with the nominal composition Yb_2SnGe_2 without extra Yb a) before and b) after annealing for one week. The red line symbolises the calculated XRD pattern of Yb_2SnGe_2 , while the unidentified phases are marked with *.

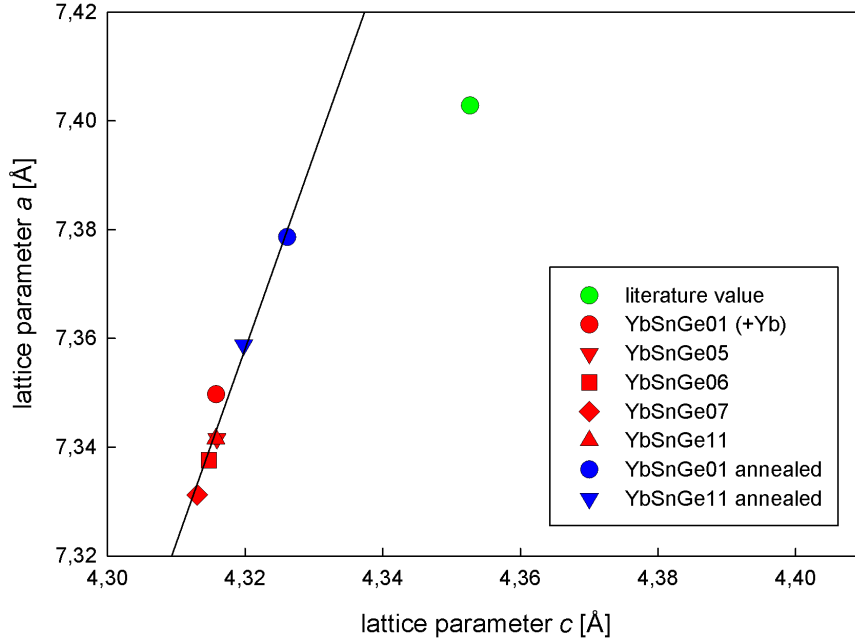
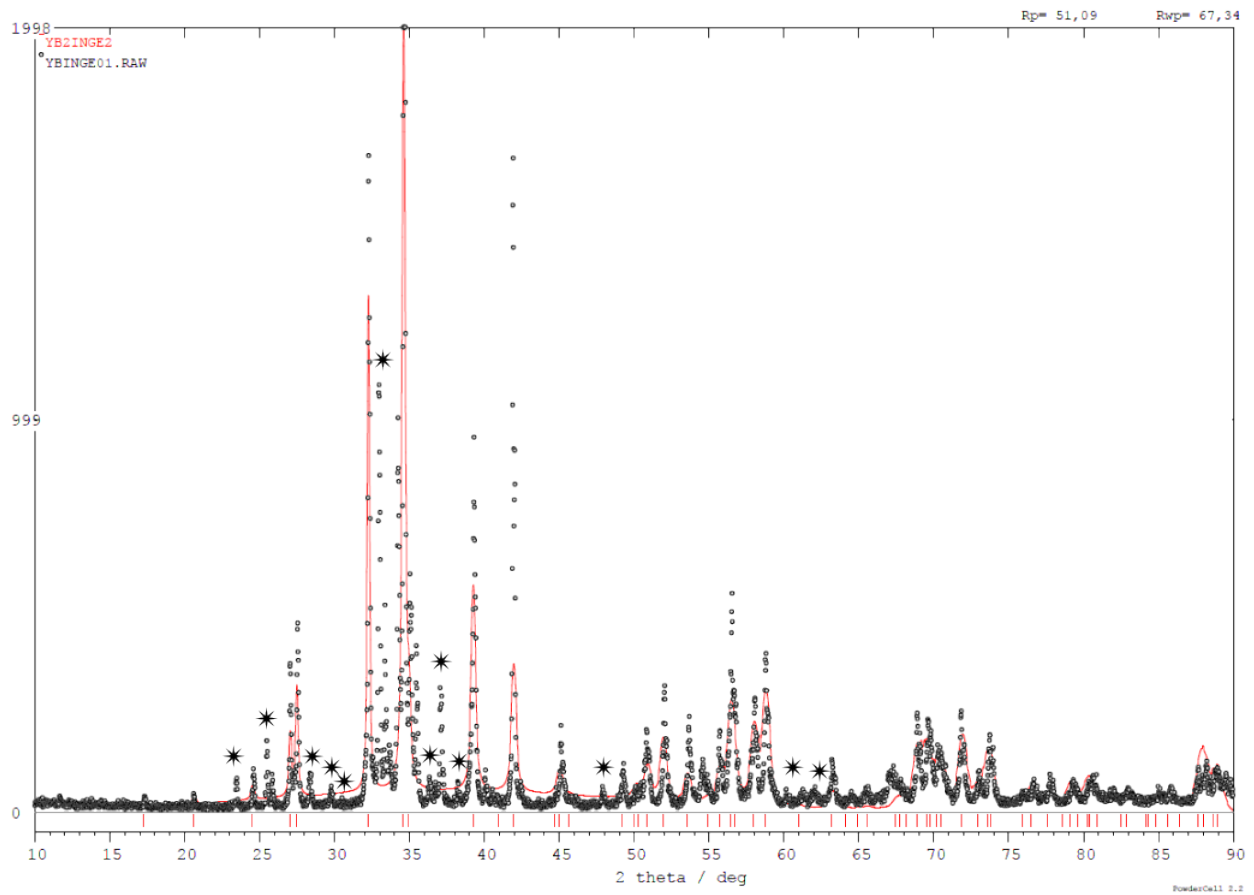
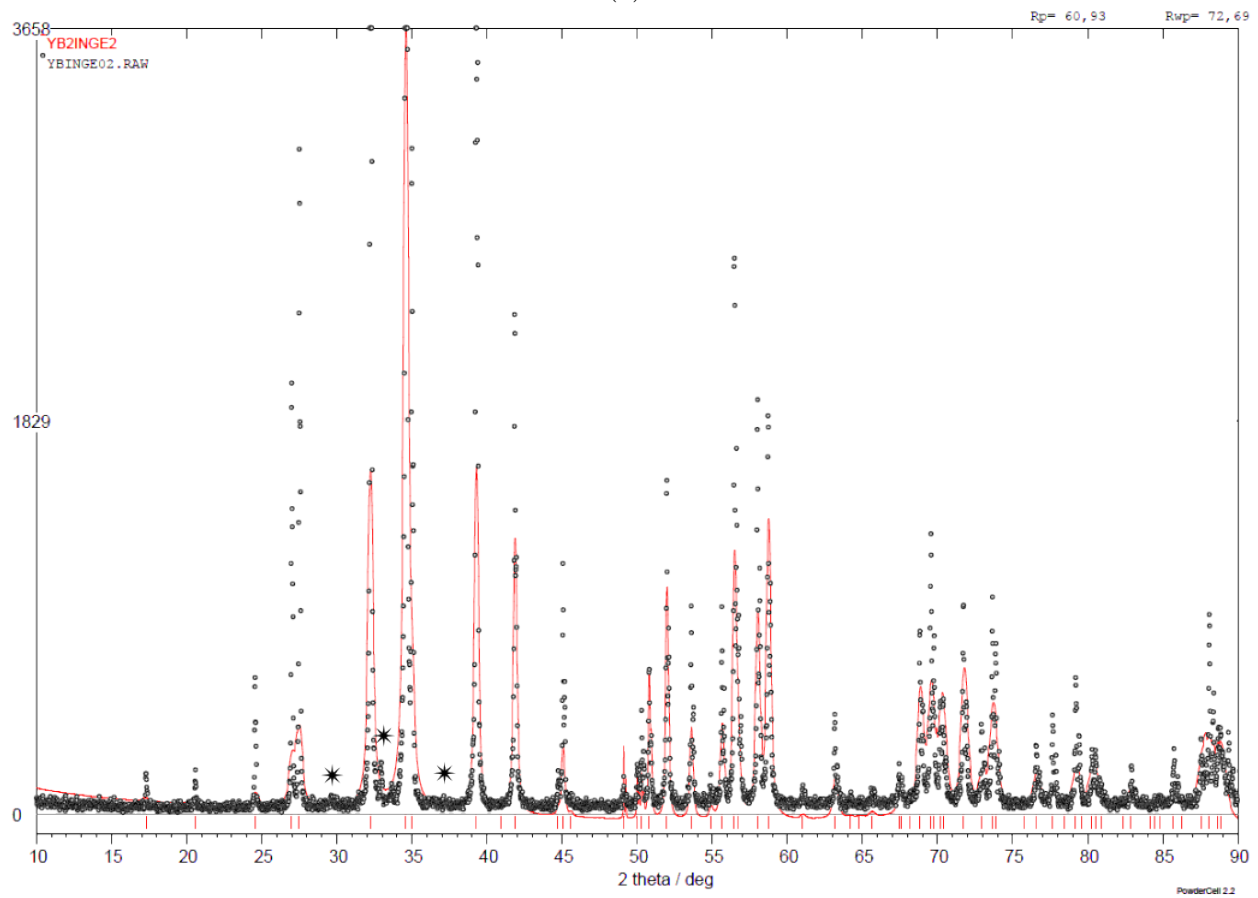


Figure 5.9.: Lattice parameters a and c of Yb_2SnGe_2 . Annealed samples generally have bigger lattice parameters than the others, but even with additional Yb (YbSnGe01) they are nowhere near the literature value [13].

the literature value c^* should be about $0.02 \text{ \AA}$ smaller. A possible explanation for the different lattice constant is that the measured samples contain primarily Yb^{3+} , which is smaller than Yb^{2+} . Recalling Figure 5.1, this difference would be mostly noticeable in the lattice constant c . This possibility will be further discussed in Section 5.3.3.



(a)



(b)

Figure 5.10.: XRD of a sample with the nominal composition Yb_2InGe_2 a) before and b) after annealing for one week. The red line symbolises the calculated XRD pattern of Yb_2InGe_2 , while the unidentified phases are marked with *.

5.2.2. Yb₂InGe₂

The Yb₂InGe₂ sample was also prepared in the cold boat with additional Yb to compensate for the mass loss after the first melting. Here, the quality could be improved greatly through annealing, although traces of a foreign phase remained (Figures 5.10a and 5.10b). With $a = 7.249 \text{ \AA}$ and $c = 4.315 \text{ \AA}$ the lattice parameters appeared to be much larger than the literature values $a^* = 7.199 \text{ \AA}$ and $c^* = 4.303 \text{ \AA}$, which is mainly due to the different measuring temperatures. In case of this sample, the powder XRD measurement was conducted at RT, while Tobash et al. determined the cell parameters from single-crystal XRD at $T = -153 \text{ }^\circ\text{C}$. [15] SEM/EDX analysis of the annealed sample (Figure 5.11) shows a single-phase material with a slightly increased Yb-concentration, i.e. Yb=2.1, In=1.0, Ge=1.9. However, this deviation from the wanted composition might be simply a measurement uncertainty.

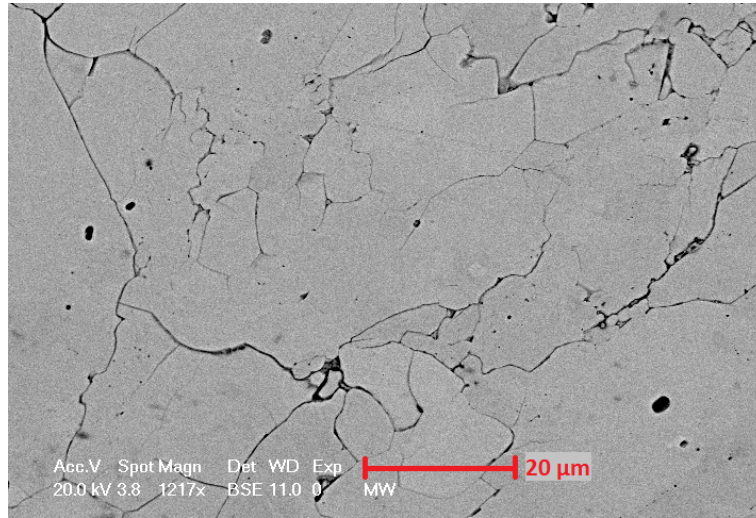
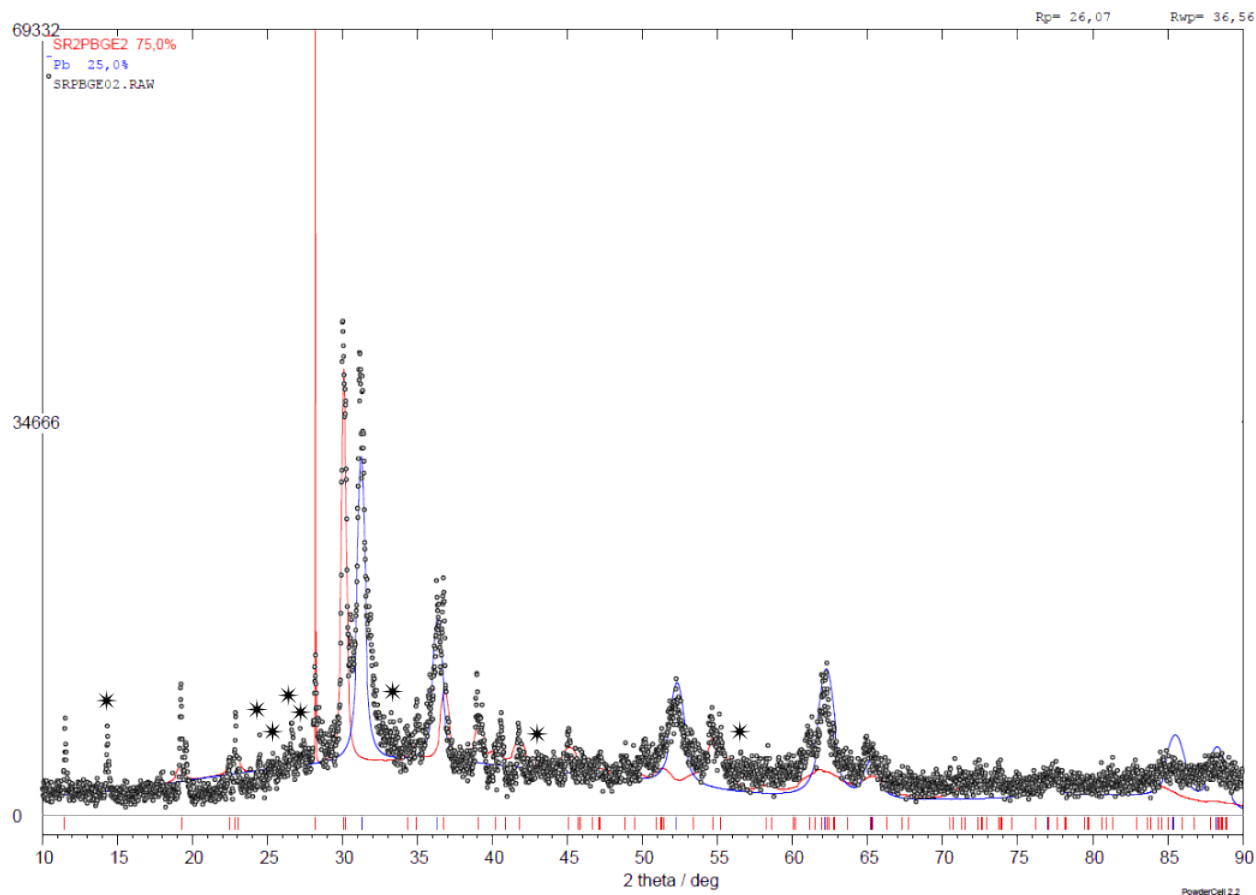
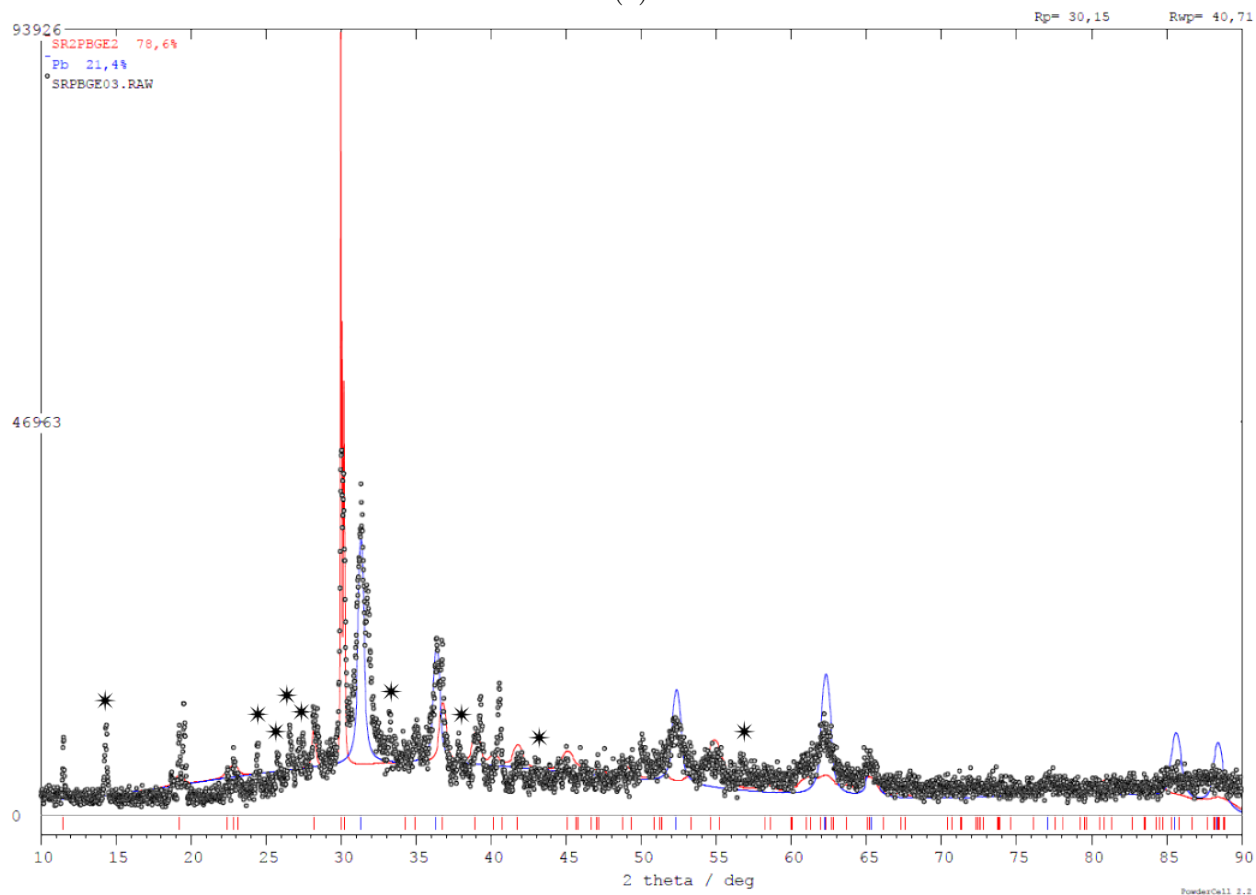


Figure 5.11.: SEM image of an annealed Yb₂InGe₂ sample, with the composition Yb=2.1, In=1.0, Ge=1.9



(a)



(b)

Figure 5.12.: XRD of a sample with the nominal composition Sr_2PbGe_2 : a) synthesised in the cold boat. b) synthesised in a sealed Ta-crucible. The calculated XRD patterns of Sr_2PbGe_2 (red) and Pb (blue) are included. The unidentified phases are marked with *.

5.2.3. Sr_2PbGe_2

Sr_2PbGe_2 samples were prepared in two ways. At first, a small amount of Sr, Pb and Ge was melted several times in the cold boat. Since, in a previous attempt, a violent reaction had appeared during the pre-synthesis of the sample, this synthesis was carried out very carefully, first melting the more electropositive Sr and Pb and then adding the more electronegative Ge. However, the volatility of Sr lead to some mass loss. Therefore, it was decided to synthesise an other sample in a sealed Ta crucible, heating it slowly to 1200 °C. Interestingly, the XRD shows no significant difference between the two samples (Figure 5.12). Apart from the desired phase, Pb was detected. Unfortunately, the phase purity did not improve much after annealing (Figure 5.13). Anticipating that Sr_2PbGe_2 would be air-sensitive and that obtaining a single-phase sample would cost too much time and effort, further work on this material was put on hold.

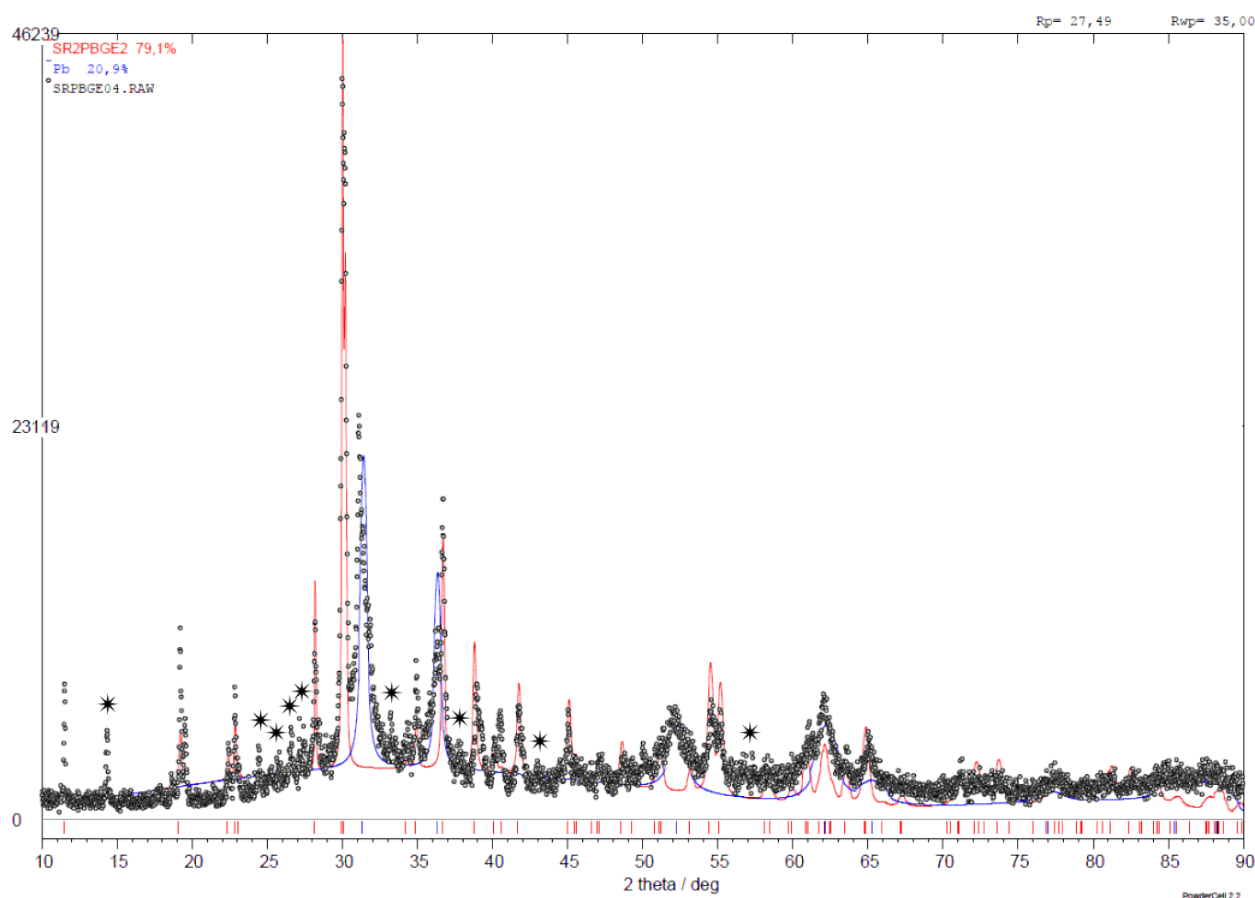


Figure 5.13.: XRD of a sample with the nominal composition Sr_2PbGe_2 after annealing, including the calculated XRD patterns of Sr_2PbGe_2 (red) and Pb (blue). The unidentified phases are marked with *.

5.3. Physical properties of Yb_2SnGe_2 and Yb_2InGe_2

5.3.1. Electrical resistivity

Figures 5.14a and 5.15a show the electrical resistivity of Yb_2SnGe_2 and Yb_2InGe_2 at low temperatures (2 K - 300 K), measured in the PPMS, while Figures 5.14b and 5.15b show the electrical resistivity for the temperature ranges 300 K - 870 K and 300 K - 770 K, measured in the ULVAC. The high-temperature data do not follow a smooth curve, which might be due to some changes in the bulk material during the measurement (Section 4.3.1). Furthermore, the electrical resistivity $\rho(300\text{ K})$ is significantly higher in the ULVAC measurement than it is in the PPMS measurement. This disruption is caused by a different contact resistance. For this reason, the low temperature (LT) and high temperature (HT) measurements are presented separately, with the combined results only being shown in insets. In general, the LT measurements were deemed more reliable, which is why in the insets the data points of the HT curves were adjusted by multiplying them with the coefficient $\frac{\rho_{\text{LT}}(300\text{ K})}{\rho_{\text{HT}}(300\text{ K})}$.

Yb_2SnGe_2

The electrical resistivity of Yb_2SnGe_2 starts with $\rho_0 = 74.68\ \mu\Omega\text{cm}$ and rises almost linearly to $\rho(300\text{ K}) = 582.62\ \mu\Omega\text{cm}$, with an average slope of $\frac{\Delta\rho}{\Delta T} \approx 1.69\ \mu\Omega\text{cm/K}$. Upon closer examination, one can distinguish two sections with different behaviour. While the electrical resistivity above 180 K rises in fact linearly, with $\frac{\Delta\rho}{\Delta T} = 1.63\ \mu\Omega\text{cm/K}$, the slope gets steeper at temperatures below 180 K, which is shown in the inset in Figure 5.14a. A possible explanation for the behaviour at low temperatures is the strong temperature dependence of the charge carrier density. As described in Section 5.3.3, Yb_2SnGe_2 exhibits an unusually high charge carrier concentration that rises with $5.36 \times 10^{25}\text{m}^{-3}/\text{K}$. With such high changes in the

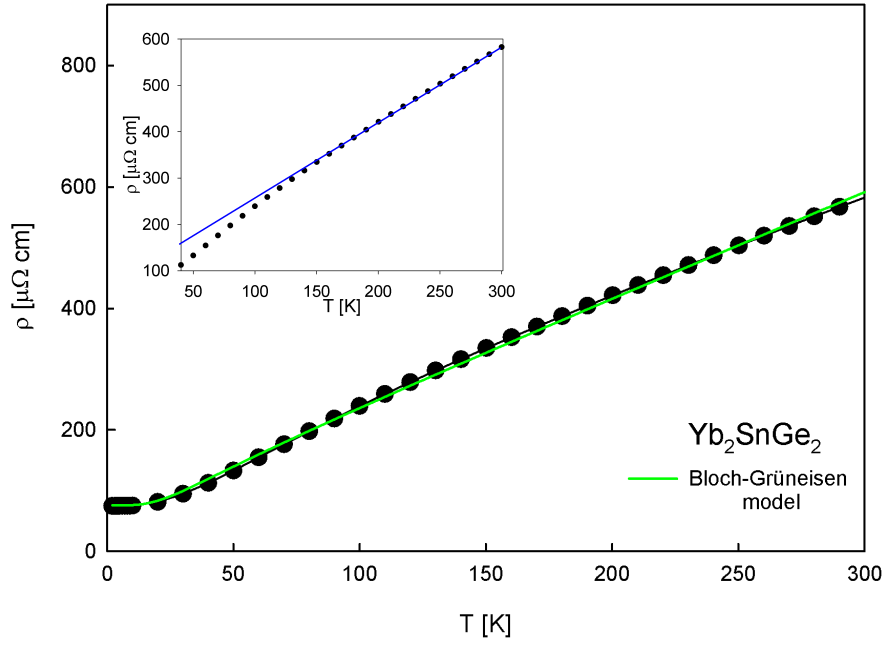
charge carrier concentration, the electron-phonon interaction might not be the only scattering mechanism that has to be considered.

A curve was fitted to the data based on the Bloch-Grüneisen model and the fit is shown as a green line in Figure 5.14a. It deviates somewhat from the measurement data. This is due to the nonlinear behaviour in the temperature region 40 K - 180 K, which is not accounted for by the Bloch-Grüneisen model. The fitting procedure is described in Appendix A and yields a Debye temperature $\Theta_D = 121.07$ K. In the high-temperature range, the model cannot be applied at all, since the electrical resistivity loses its linear behaviour (Figure 5.14b). Nevertheless, it is mainly rising with the temperature, spanning from $\rho(300 \text{ K}) = 807.62 \mu\Omega\text{cm}$ to $\rho(870 \text{ K}) = 1979.12 \mu\Omega\text{cm}$.

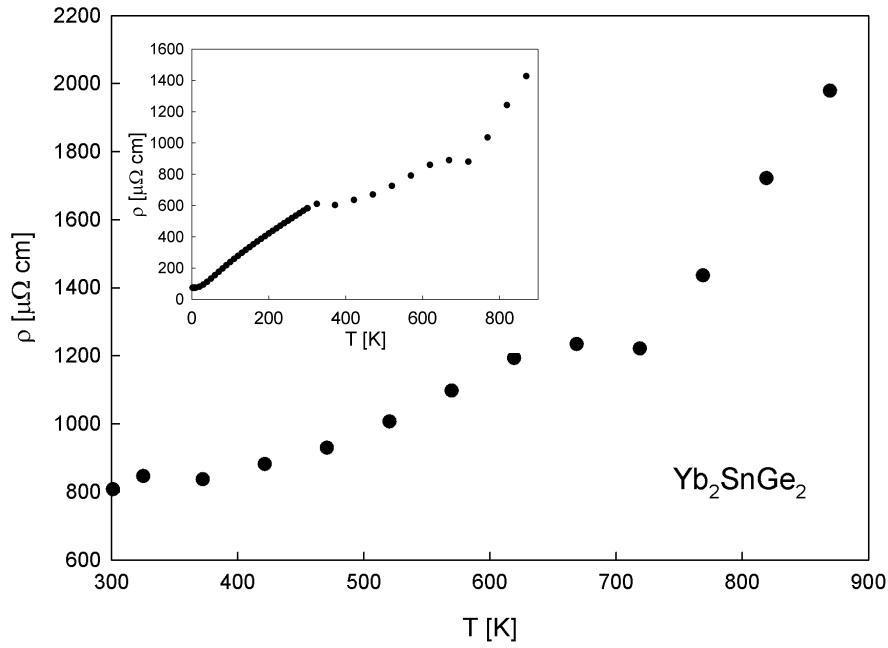
The **residual resistivity ratio** (RRR) compares the resistivity at 300 K with the residual resistivity ρ_0 , which is primarily defined by scattering due to defects and impurities and not electron-phonon scattering, as at high temperatures. Therefore, it can be a measure of the main phase's quality, with higher ratios generally meaning less defects. The RRR of commercial Cu, for instance, is 50-100, whereas annealing can increase the value up to 300 and passivating magnetic impurities can increase it even to several 1000 [16]. Compared to that, the measured RRR of Yb_2SnGe_2 , which is $\frac{\rho(300\text{K})}{\rho_0} = 7.8$, seems to be very low. However, in order to determine whether this is due to a low quality of the sample or due to interactions between the electrons, a comparison with a reference value of a similar sample would be necessary.

Yb_2InGe_2

Yb_2InGe_2 also behaves like a metal at low temperatures (Figure 5.15a). It starts at $\rho_0 = 28.26 \mu\Omega\text{cm}$ and increases to $\rho(300 \text{ K}) = 196.93 \mu\Omega\text{cm}$, with an approximate slope of $\frac{\Delta\rho}{\Delta T} \approx 0.56 \mu\Omega\text{cm}/\text{K}$. Fitting a curve, based on the Bloch-Grüneisen model,



(a)



(b)

Figure 5.14.: a) Low temperature electrical resistivity of Yb_2SnGe_2 and fitting, following the Bloch-Grüneisen model. The inset shows a slight deviation from the linear behaviour. b) Electrical resistivity of Yb_2SnGe_2 at high temperatures. The combined LT and HT measurements, where the HT values were adjusted with a coefficient, are shown in the inset.

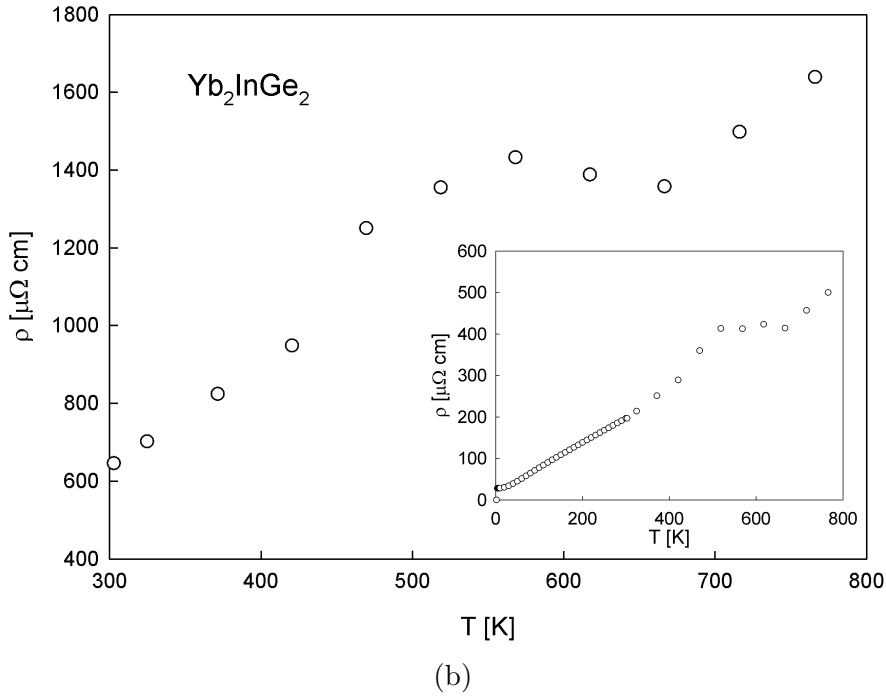
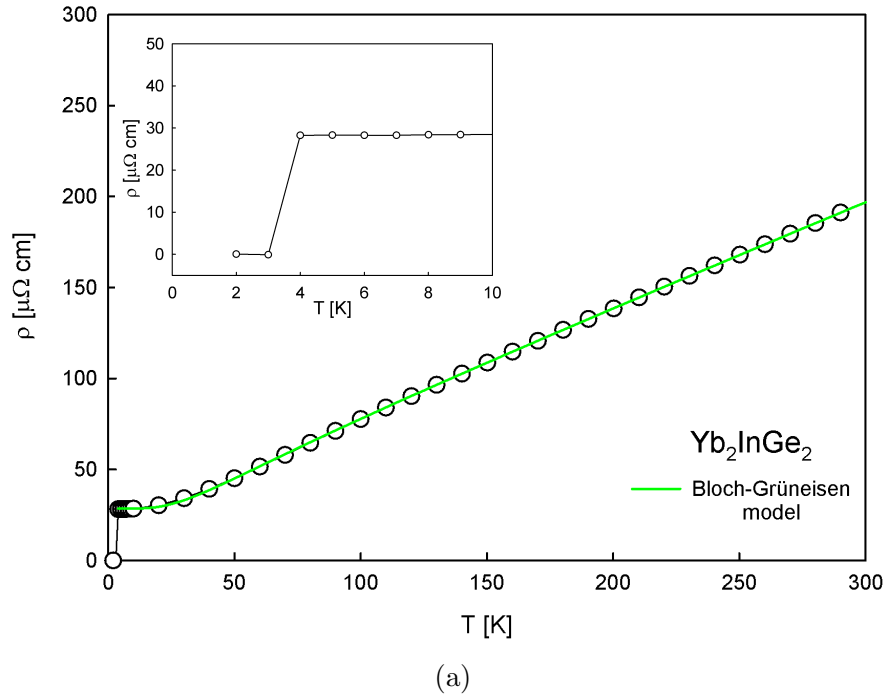


Figure 5.15.: a) Low temperature electrical resistivity of Yb_2InGe_2 and fitting, following the Bloch-Grüneisen model. The superconducting behaviour of the sample below 4 K can be seen in the inset. b) Electrical resistivity of Yb_2SnGe_2 at high temperatures, as well as the combined LT and HT measurements, with adjusted HT values.

yields $\Theta_D = 163.87$ K. Since the green curve in Figure 5.15a shows no deviation from the measured data, the model seems to apply very well to the LT electrical resistivity. This cannot be said for the HT measurement, where the electrical resistivity shows irregularities in the range 450 K - 650 K (Figure 5.15b).

As shown in the magnified plot in Figure 5.15a, the electrical resistivity of Yb_2InGe_2 drops to 0 below temperatures of 4 K. This would point to superconducting behaviour in that temperature region. Since superconductors are ideal diamagnets, the material's susceptibility should drop to negative values at this point. However, measurements of the magnetic susceptibility of Yb_2InGe_2 , which were performed in [15], show no sign of diamagnetic behaviour (Figure 5.5). Therefore, it is more probable that the observed superconducting behaviour is caused by a percolation of microscopic In inclusions, which were not spotted by neither SEM nor XRD. This guess is also supported by the fact that the superconducting transition temperature of In is 3.72 K, which fits very well into the observed values.

The main phase's RRR is $\frac{\rho(300\text{K})}{\rho_0} = 6.97$, which is only a little bit smaller than for Yb_2SnGe_2 . Apparently, the main phases of both samples have a comparable quality. Moreover, this shows that the higher resistivity of Yb_2SnGe_2 is not due to sample imperfections, but rather due to enhanced scattering mechanisms.

5.3.2. Seebeck coefficient

The Seebeck coefficient is negative for both Yb_2SnGe_2 and Yb_2InGe_2 , which points to the charge carriers being electrons. Furthermore, the highest values measured were $S \approx -18 \mu\text{V/K}$ and $S \approx -24 \mu\text{V/K}$, which is quite low, compared to commercial TE materials like single-crystalline Bi_2Te_3 with $S(300 \text{ K}) = 240 \mu\text{V/K}$ [17]. Since a low thermopower is usually caused by too high charge carrier concentrations, all of this implies that the materials are metal-like. This is in accordance with the results from the measurements of the electrical resistivity.

Yb₂SnGe₂

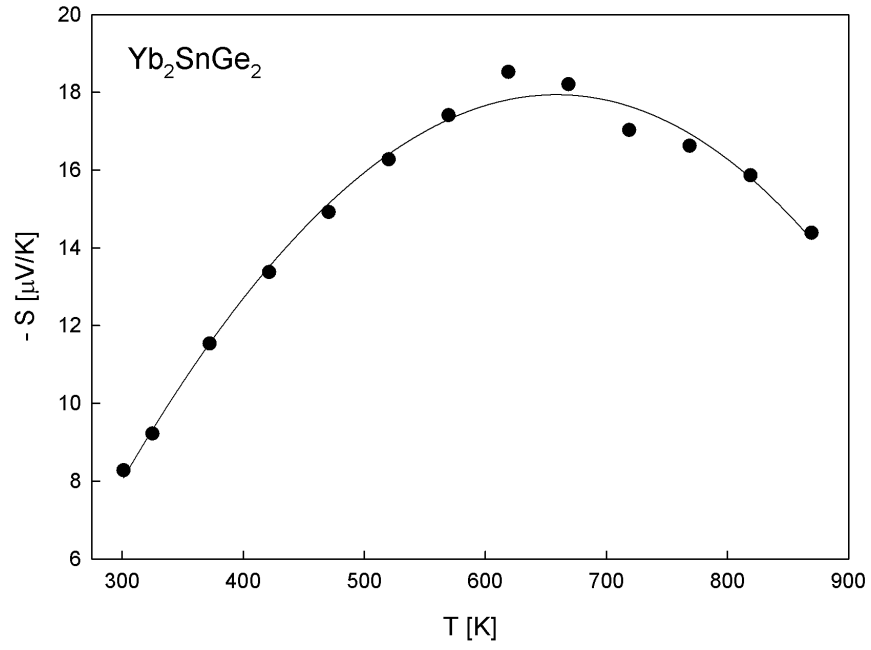
Figure 5.16a shows the thermopower of Yb₂SnGe₂, with a fitted polynomial function to guide the eye. It rises continuously until approximately 650 K, where it reaches a maximum of $S \approx -18 \mu\text{V/K}$. Afterwards, the values start decreasing. In semiconductors, this marks the onset of intrinsic conductivity, where minority charge carriers are generated and the thermopower is lowered. However, since we have a good metal, another explanation should be given: According to (2.36) the Seebeck coefficient is proportional to the slope in the DOS, i.e. a negative Seebeck coefficient corresponds to a decrease in the DOS. Based on the measured data (Figure 5.16a), the slope is steepest at 650 K and then levels off. Considering the calculated DOS (Figure 5.4), it seems plausible that at higher temperatures the slope gets smaller, until a minimum in the DOS is reached.

Based on the Seebeck coefficient and electrical resistivity, the so-called **power factor** was calculated, which gives an estimate for a material's usefulness as a thermoelectric, disregarding the thermal conductivity (Figure 5.16b). Similar to the thermopower, it rises in a parabolic manner and reaches its maximum value at roughly 620 K, although it remains very small in comparison to Bi₂Te₃, where measurements on single crystals yield $S^2/\rho = 57,6 \mu\text{W/cmK}^2$ [17].

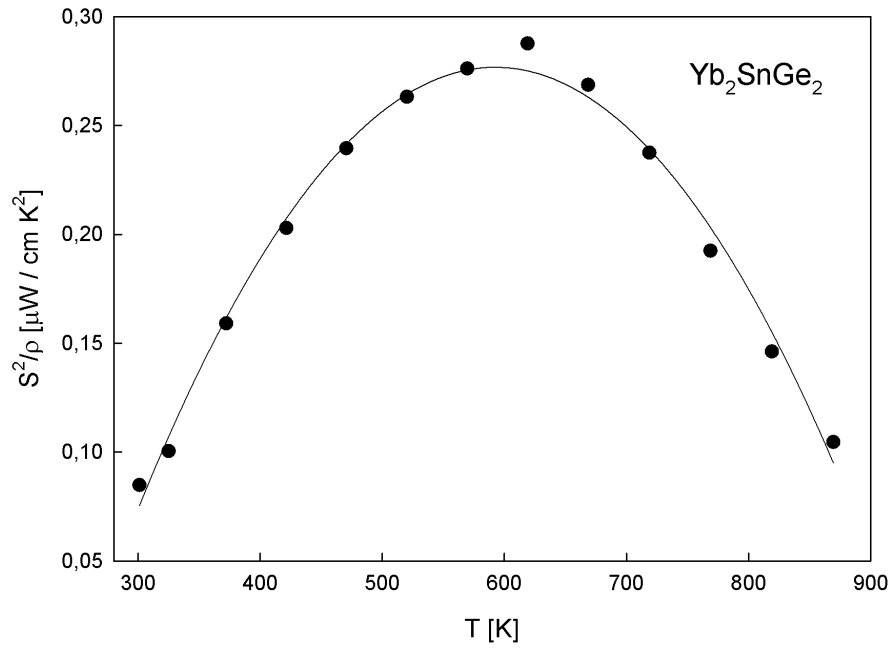
Yb₂InGe₂

Looking at the fitted function in Figure 5.17a, the Seebeck coefficient of Yb₂InGe₂ seems to have a maximum of $S \approx -24 \mu\text{V/K}$ near RT. With increasing temperature the thermopower gets smaller, until it reaches values comparable to Yb₂SnGe₂ at approximately 700 K.

The power factor of Yb₂InGe₂ can be seen in Figure 5.17b. It is shown to be constantly decreasing in the measured range, which suggests that there might be slightly higher values below RT.



(a)



(b)

Figure 5.16.: a) Thermopower of Yb_2SnGe_2 as a function of temperature. b) Power factor of Yb_2SnGe_2 as a function of temperature.

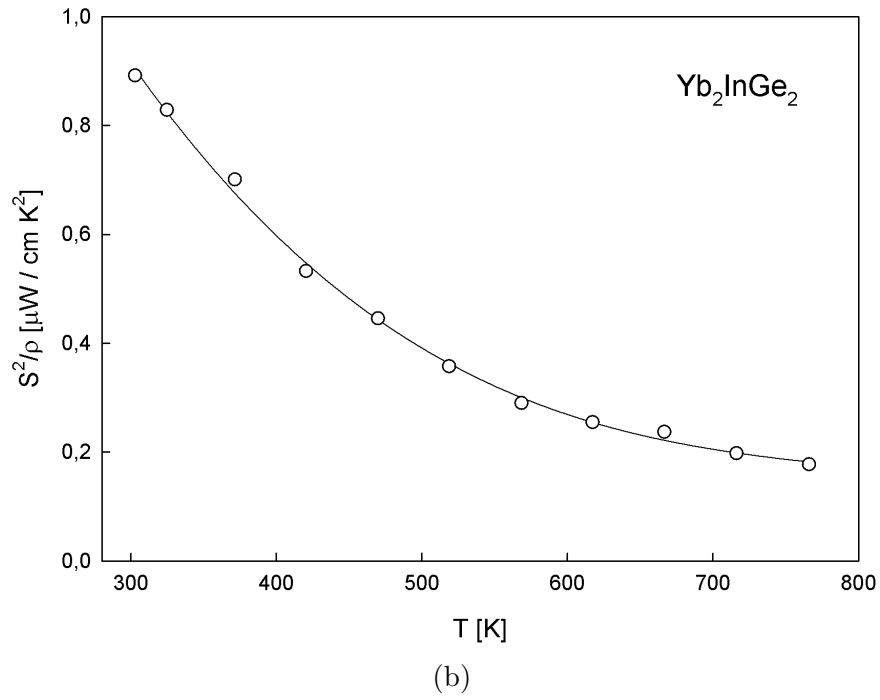
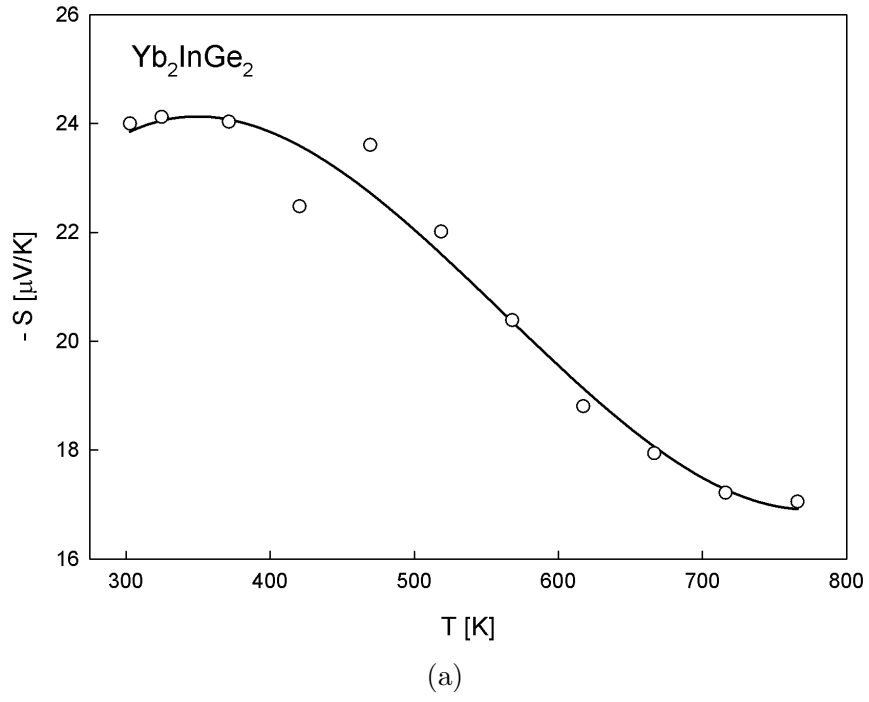


Figure 5.17.: a) Thermopower of Yb_2InGe_2 as a function of temperature. b) Power factor of Yb_2InGe_2 as a function of temperature.

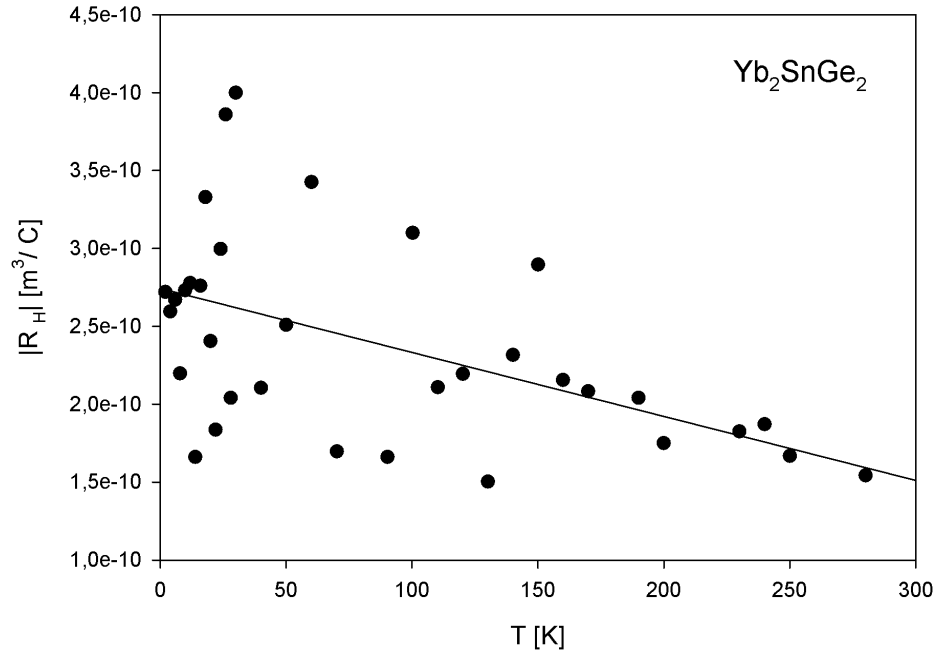
5.3.3. Charge carrier concentration

In order to confirm the speculation in Section 5.3.1, an investigation of the charge carrier concentration was deemed helpful. Therefore, it was decided to measure the charge carrier concentration using the Hall effect. At first, the Hall coefficient was determined from the measured electrical resistance $\frac{U_H}{I}$ using (4.6). Then, using (4.7), the charge carrier concentration was calculated.

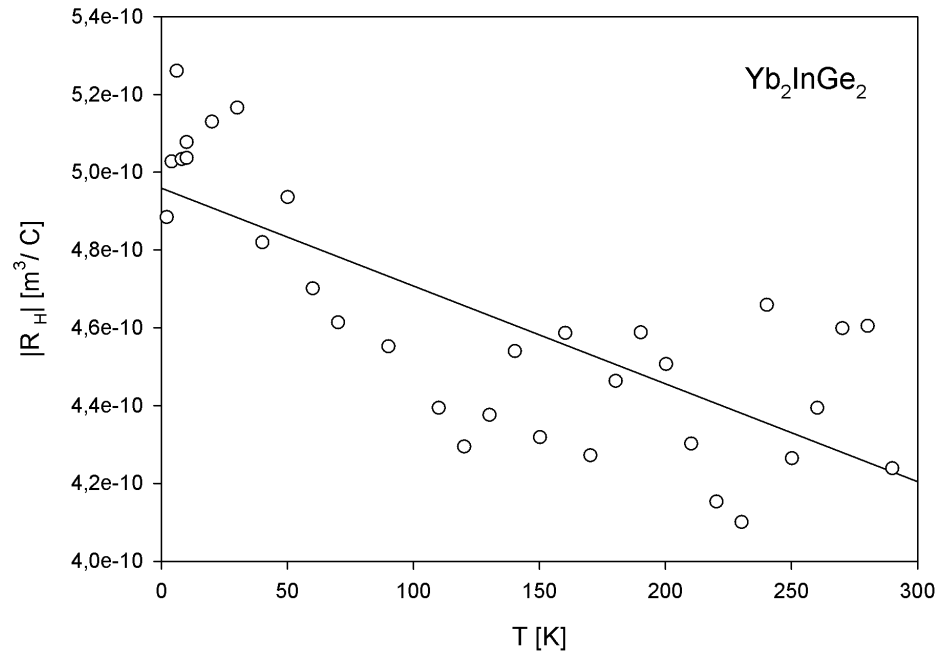
The temperature dependencies of the Hall coefficients of Yb_2SnGe_2 and Yb_2InGe_2 are shown in Figure 5.18. The Hall coefficients are quite small, which is no surprise, considering that the measured materials are metals and therefore have a low electrical resistance. Unfortunately, small quantities are difficult to measure correctly, which results in scattered values. While scattering in an order of magnitude of $10^{-10} \text{ m}^3/\text{C}$ does not seem like a lot at first glance, it causes a big problem for further calculations. Due to the fact, that the charge carrier concentration is calculated with the reciprocal value of R_H , the small values not only cause high charge carrier concentrations, but also strong data scattering, which can be seen in Figure 5.19.

Yb_2SnGe_2

Despite the strong data scattering a trend in the temperature dependence of the charge carrier concentration of Yb_2SnGe_2 can be found in Figure 5.19a. To illustrate the general trend, a linear function was fitted to the data. It has a starting value of $2.36 \times 10^{28} \text{ m}^{-3}$ at 2 K and reaches $3.96 \times 10^{28} \text{ m}^{-3}$ at 300 K, with an approximate slope of $5.36 \times 10^{25} \text{ m}^{-3}/\text{K}$. Using the charge carrier concentration at RT, as well as the unit-cell volume, it is possible to determine the number of free electrons per unit cell, i.e. 9.32 electrons. Since a unit cell of Yb_2SnGe_2 contains 2 formula units, this results in 4.66 electrons per formula unit. Considering the Zintl formalism that was used in Section 5.1, the number should be close to 0. Even if



(a)



(b)

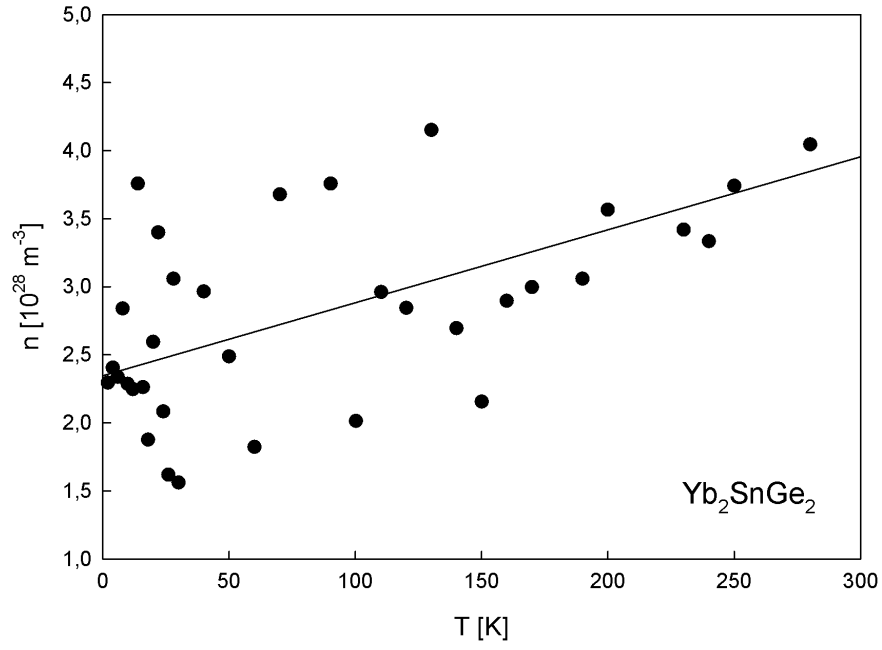
Figure 5.18.: Hall coefficients of a) Yb₂SnGe₂ and b) Yb₂InGe₂ at low temperatures.

taking the approach suggested by Tobash et al. [15], i. e. considering single bonds between the Ge atoms, there would only be 2 resulting electrons ($2\text{Yb}^{2+} \text{Sn}^{4+} 2\text{Ge}^{3-}$). There is the possibility of the Yb being trivalent ($2\text{Yb}^{3+} \text{Sn}^{4+} 2\text{Ge}^{3-}$), which would result in 4 electrons per formula unit, but this does not explain the high electron count completely either.

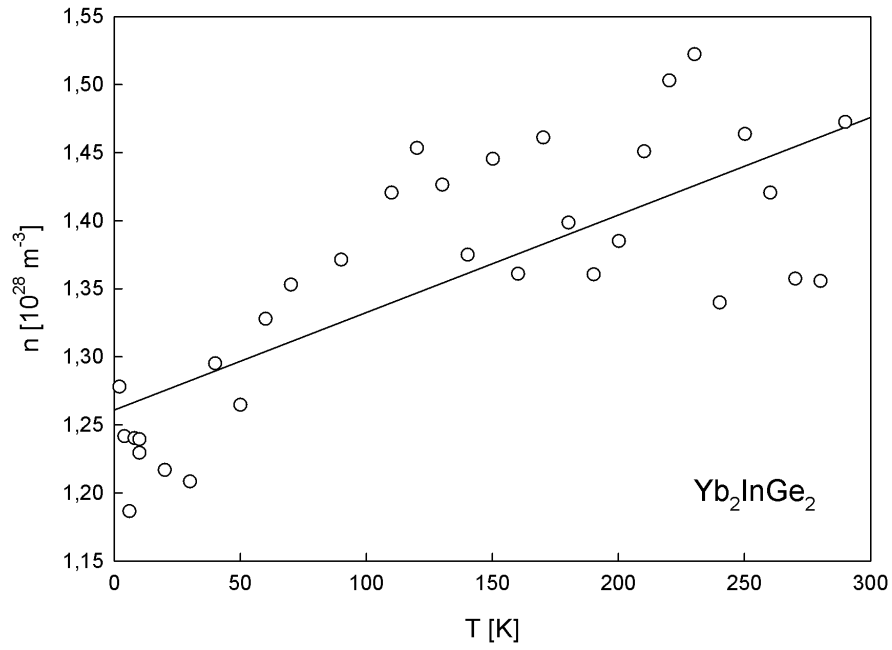
Yb^{3+} has the configuration $4f^{13}$ and is thus a magnetic ion. This means that the electronic state of Yb could be determined by magnetic measurements. Unfortunately, a very pure sample is needed for the measurements and it was neither possible to produce a single-phase sample, nor to identify the additional phases completely. Therefore, a magnetic measurement could not be conducted.

Yb_2InGe_2

The charge carrier concentration of Yb_2InGe_2 is lower and less scattered than for Yb_2SnGe_2 (Figure 5.19b). A linear fit has been done to illustrate the general trend in the temperature dependence of n . It shows values of $1.26 \times 10^{28}\text{m}^{-3}$ at 2 K and $1.48 \times 10^{28}\text{m}^{-3}$ at 300 K, which is smaller than the 2K value of Yb_2SnGe_2 . The approximate slope is $7.16 \times 10^{24}\text{m}^{-3}/\text{K}$. Calculating the number of electrons per formula unit at room temperature leads to 1.67 electrons, which is more than expected from the Zintl calculation. However, if one considers a mixture of divalent and trivalent Yb in a ratio of 2:1, due to the material's deviation of the composition from the stoichiometric one, the formalism yields a fitting value: $\frac{4}{3}\text{Yb}^{2+} \frac{2}{3}\text{Yb}^{3+} \text{In}^{3+} 2\text{Ge}^{3-} \rightarrow 1.67e$. Once again, magnetic measurements would be helpful for a better understanding, especially since the measurements conducted by Tobash et al. suggest divalent Yb [15], but were neglected, due to the unidentified phases that can be seen in Figure 5.10b.



(a)



(b)

Figure 5.19.: Charge carrier concentration of a) Yb_2SnGe_2 and b) Yb_2InGe_2 at low temperatures.

5.3.4. Electron mobility

Knowing the Hall coefficient and the electrical conductivity allows to calculate the electron mobility, using (4.8).

The temperature dependent electron mobility of Yb_2SnGe_2 can be seen in Figure 5.20a. It is very low in comparison with conventional TE materials, starting with $3.4 \text{ cm}^2/\text{Vs}$ at 2 K and decreasing to approximately $0.2 \text{ cm}^2/\text{Vs}$ at RT.

Yb_2InGe_2 exhibits a higher electron mobility, with a maximum of approximately $18 \text{ cm}^2/\text{Vs}$ at 2 K . Unfortunately, a strong decrease follows and leads to a value of only $2.2 \text{ cm}^2/\text{Vs}$ at RT (Figure 5.20b).

There are materials, which show low mobilities and are nevertheless considered to be promising thermoelectric materials (e.g. La_3Te_4 with $\mu(300 \text{ K}) = 11.5 \text{ cm}^2/\text{Vs}$), because their Seebeck coefficient causes a high power factor $S^2/\rho \propto (m^*)^{3/2}\mu$ [18]. However, as a rule, efficient TE materials have a high charge carrier mobility, like Bi_2Te_3 ($\mu(300 \text{ K}) = 212 \text{ cm}^2/\text{Vs}$) [17]. Keeping these values in mind, it comes as no surprise that the power factors of Yb_2SnGe_2 and Yb_2InGe_2 are so small.

5.3.5. Thermal conductivity

The laser flash method was used to measure the thermal diffusivity at high temperatures (420 K - 820 K), which is shown in Figures 5.21a and 5.21b. Then relation (4.4) was used to calculate the thermal conductivity. For this, the specific heat was needed, as well as the material's temperature-dependent density $\rho(T)$. Since the latter was not known for neither Yb_2SnGe_2 nor Yb_2InGe_2 , it was evaluated from an extrapolation by comparing the unit cell volume and resulting density of Yb_2InGe_2 measured at 120 K [15] with our value from the XRD measurement at 300 K. With the linear dependence $\rho(T) = \rho_0 + \alpha\Delta T$, the thermal expansion coefficient α was found to be $-8.28 \times 10^{-4} \text{ g/cm}^3\text{K}$. This value was also used for

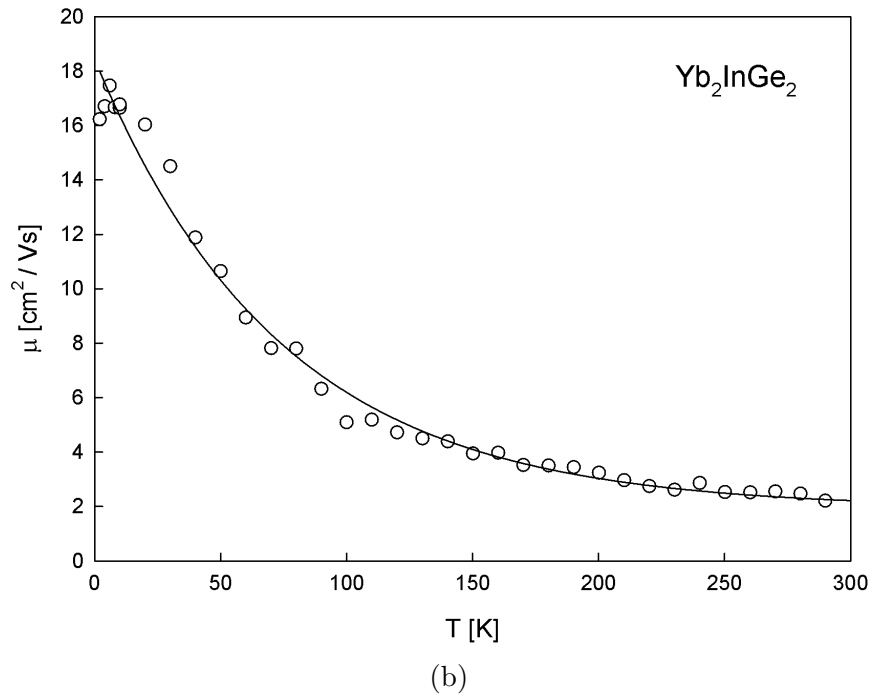
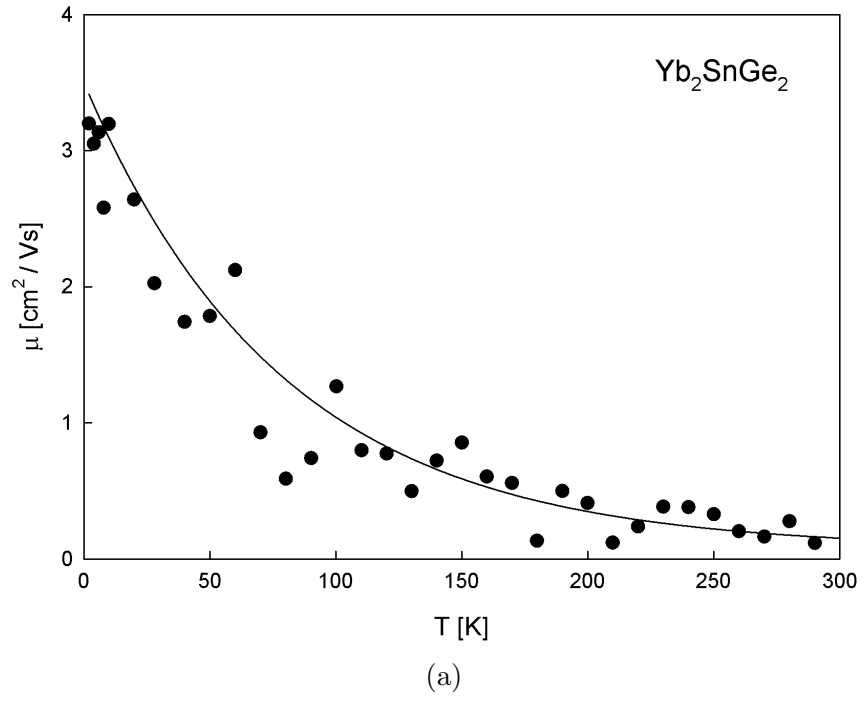


Figure 5.20.: Electron mobility of a) Yb_2SnGe_2 and b) Yb_2InGe_2 at low temperatures.

calculating the density of Yb_2SnGe_2 , since it was assumed that both materials behave similarly. Using the **Dulong-Petit law** (2.33), the molar specific heat was estimated to be $c_V = 24.9 \text{ J/mol K}$ for both materials.

Yb_2SnGe_2

The thermal conductivity of Yb_2SnGe_2 is depicted in Figure 5.22a as a function of temperature. The black curve represents the measured data. The values between 7.3 W/mK at 470 K and 4.1 W/mK at 670 K are high for a TE material. This comes as no surprise, considering the low electrical resistivity. However, as mentioned in Section 2.2.2, the thermal conductivity is not only determined by the electronic contribution κ_{el} , but also by the phononic contribution κ_{ph} . Therefore, to truly realise a material's potential for designing a high figure of merit, it is necessary to split the total thermal conductivity into these contributions. Since both Yb_2SnGe_2 and Yb_2InGe_2 are good metals, κ_{el} can be calculated via the **Wiedemann-Franz law** (2.28), using the electrical resistivity ρ and the Lorenz number $2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$. κ_{el} is depicted in Figure 5.22a as a red curve. These values were subtracted from the total thermal conductivity, thus revealing κ_{ph} (green curve), which is still rather high. For comparison, Bi_2Te_3 has a thermal conductivity of $\kappa_{\text{ph}} \approx 1.5 \text{ W/mK}$ and bulk Si-Ge alloys have $\kappa_{\text{ph}} \approx 4 \text{ W/mK}$ [4].

Yb_2InGe_2

Figure 5.22b shows the thermal conductivity of Yb_2InGe_2 . It depends weakly on temperature, showing a slight increase from 7.5 W/mK to 8.2 W/mK over the measuring range. This behaviour is rather unusual, since in most metals κ decreases with increasing temperature.

Subtracting κ_{el} (red) from the measurement values, leaves $\kappa_{\text{ph}} \approx 6 \text{ W/mK}$.

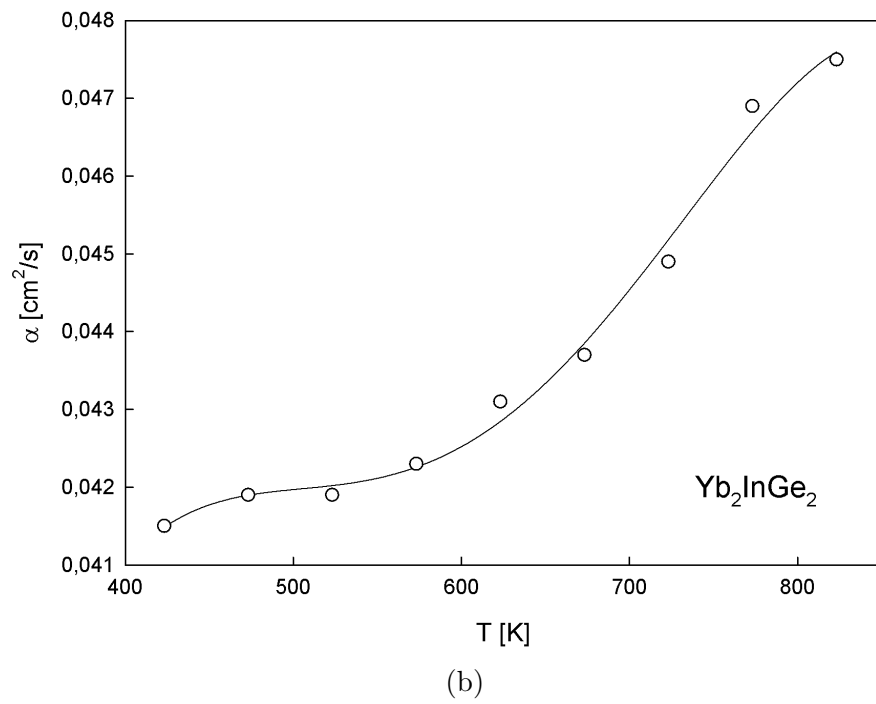
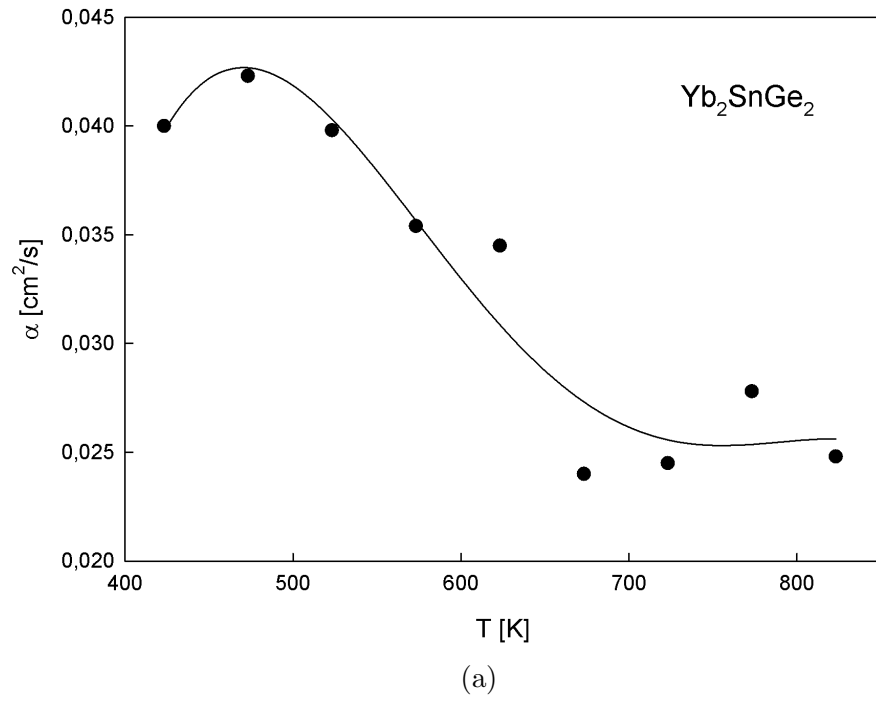
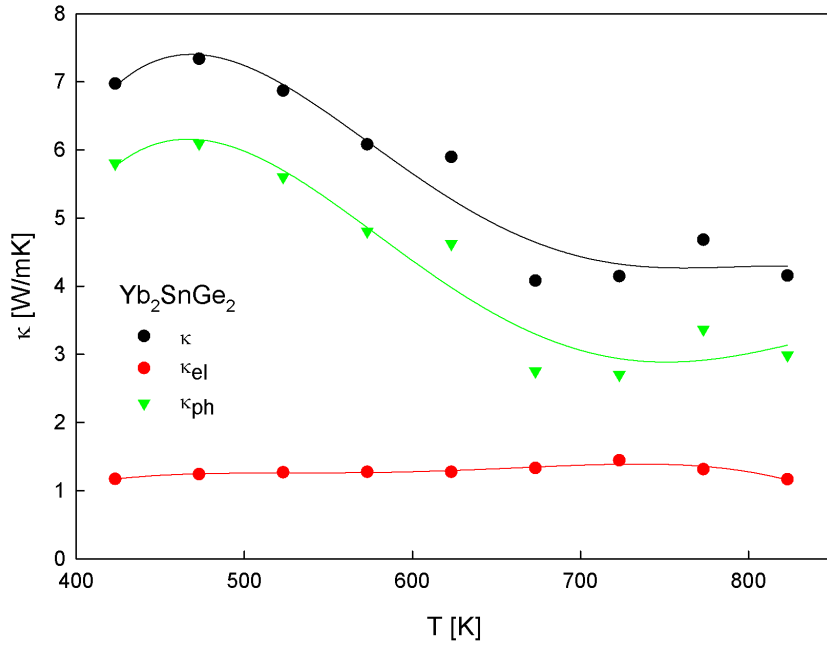
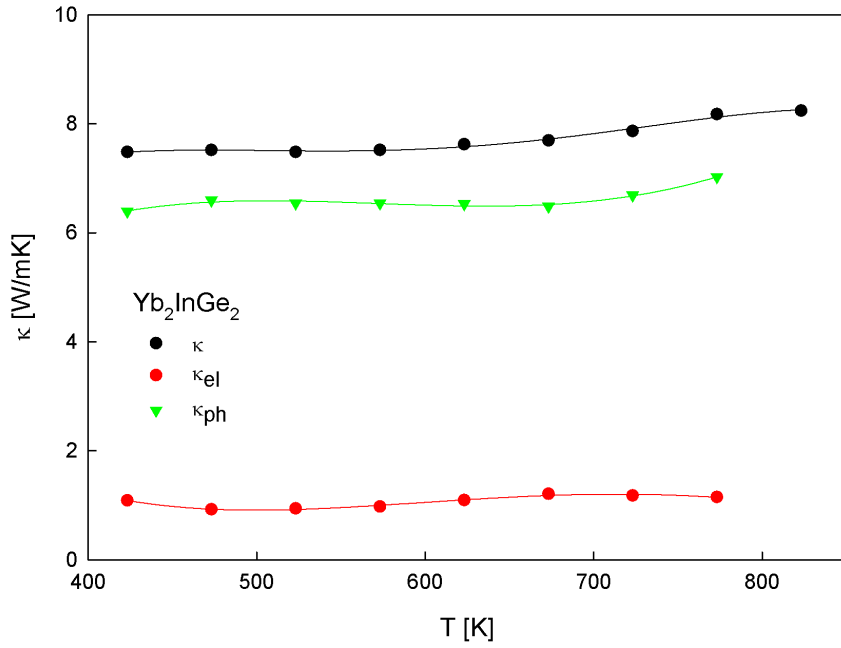


Figure 5.21.: Thermal diffusivity of a) Yb_2SnGe_2 and b) Yb_2InGe_2 at high temperatures.



(a)



(b)

Figure 5.22.: Thermal conductivity of a) Yb₂SnGe₂ and b) Yb₂InGe₂, showing the total thermal conductivity (black), the electronic contribution (red) and the phononic contribution (green).

5.3.6. Figure of merit

Figure 5.23 shows the temperature dependence of ZT for Yb_2SnGe_2 and Yb_2InGe_2 . Yb_2SnGe_2 reaches its highest figure of merit around 700 K. However, this value is approximately 0.0045, which is too small to be of any practical interest.

The maximum of Yb_2InGe_2 is more difficult to pinpoint, since ZT appears to be only decreasing in Figure 5.23. Based on the almost constant thermal conductivity (Figure 5.22b) and the fact, that the power factor increases with decreasing temperature (Figure 5.17b), one could expect it to be near RT or even below. Assuming that $\kappa(300 \text{ K}) \approx 7.5 \text{ W/mK}$ and with $PF(300 \text{ K}) = 0.9 \times 10^{-4} \text{ W/mK}^2$, one gets the value $ZT(300 \text{ K}) \approx 0.0036$. Being even smaller than the maximum of Yb_2SnGe_2 , this low ZT shows that the material is not suited for TE applications. Unfortunately, due to the high charge carrier concentration and the high lattice thermal conductivity in both materials, the chances of improving the figures of merit significantly by charge carrier optimisation via composition variation are very small. Therefore, Yb_2SnGe_2 and Yb_2InGe_2 do not appear to be good candidates for thermoelectric materials.

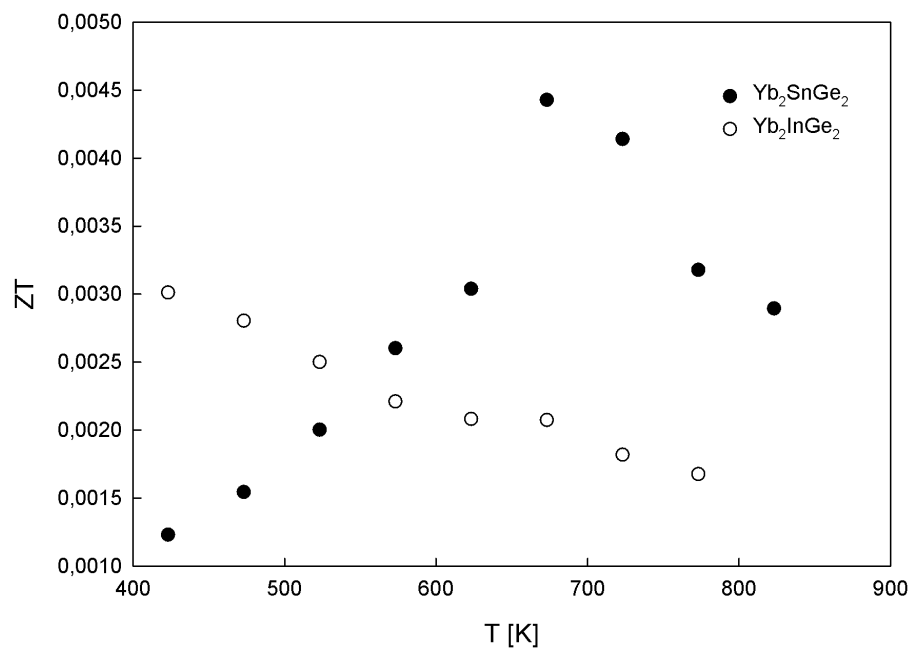


Figure 5.23.: Figure of merit of Yb_2SnGe_2 and Yb_2InGe_2 .

6. Materials with anti-Th₃P₄ structure

6.1. Motivation

Rare-earth chalcogenides with the Th₃P₄ structure type (space group I-43d, no. 220, $Z = 4$, Figure 6.1a) have been studied for decades due to their good thermoelectric properties [18]. Promising features include a low thermal conductivity and the existence of the homogeneity range of the phase R₃X₄-R₂X₃ (R = rare-earth, X = S, Se or Te), with R₃X₄ being metallic and R₂X₃ being an insulator, which allows for a good control over the charge carriers [18]. (The phase R₂X₃ can also be viewed as a variant form of R₃X₄, namely as R_{2.67}V_{0.33}X₄, where V stands for vacancies.) In fact, one of the most efficient materials for high-temperature use known today is the n-type lanthanum telluride La_{3-x}Te₄ with $x = 0.25$, showing a $ZT \approx 1.2$ at 1273 K [19].

The search for materials with a comparable figure of merit, but with lower toxicity than tellurium-based compounds has led some researchers to investigate rare-earth antimonides R₄Sb₃ that crystallise in the anti-Th₃P₄ structure (Figure 6.1b) [20]. As antimony-based compounds, they were expected to exhibit properties ideally situated between metallic and insulating behaviour [21]. Although they do not have a homogeneity range like that of R₃X₄, their complex structure and the possibility to partially substitute both the anionic and the cationic site make them

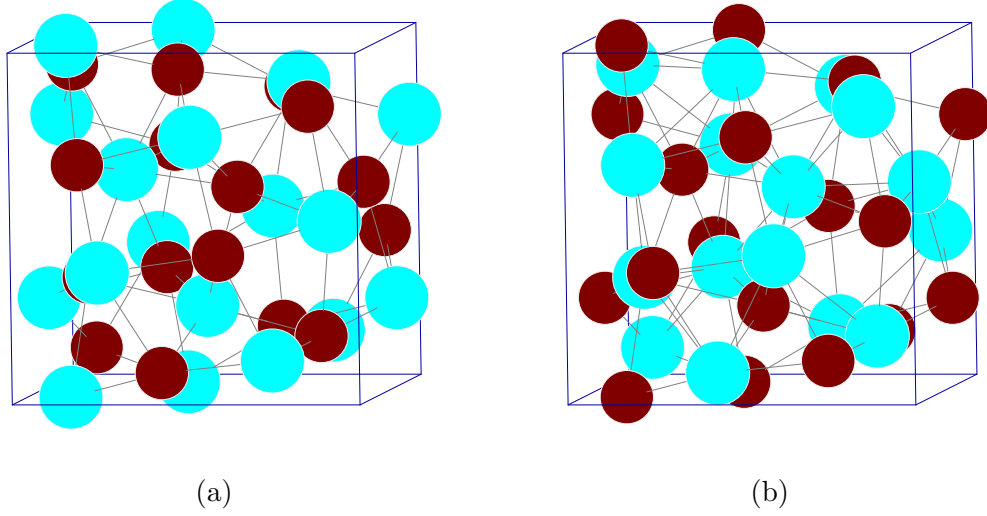


Figure 6.1.: a) Th_3P_4 structure, where the Th-atoms (light blue) occupy the 12a Wyckoff position and the P-atoms (red) can be found at the 16c site. b) Anti- Th_3P_4 structure, with Th-atoms at the 16c site and P-atoms at the 12a site.

materials of interest [22].

In recent years, A. Chamoire et al. have primarily conducted studies on Yb_4Sb_3 [20, 21, 22]. They stated that it was a "semi-metal or heavily doped semiconductor" with p-type conduction. Considering the Zintl formalism, one can write the formula as follows: $\text{Yb}_4^{2+}\text{Sb}_3^{3-}$, which leaves one extra hole per formula unit, resulting in a material that is too metallic for TE applications. This calculation suggests, that the transport properties can be improved by introducing more electrons, which, in fact, was successfully done by partially substituting Yb with a trivalent rare earth like Sm or La to the limit of the substitution range ($x = 0.5$ - 0.6) and nearly doubled the thermopower to $120 \mu\text{V K}^{-1}$ at 1000°C [21].

Another way to achieve more electronically compensated materials with anti- Th_3P_4 structure is the synthesis of rare-earth chalcopnictides $\text{R}_4\text{Y}_2\text{X}$ (R = rare-earth, Y = pnictogen, X = chalcogen). For example, by replacing one third of Sb in the previously described Yb_4Sb_3 with S, it should be possible to achieve a

completely valence precise material: $4\text{Yb}^{2+} 2\text{Sb}^{3-} \text{S}^{2-}$. This could increase the thermopower significantly.

Some rare-earth chalcopnictides were reported by F. Hullinger in 1978. Researching the Eu-chalcopnictides $\text{Eu}_4\text{Y}_2\text{X}$ (Y = pnigogen, X = chalcogen), which crystallise in the anti- Th_3P_4 structure, he also discovered the isostructural compounds $\text{Ca}_4\text{Bi}_2\text{Te}$, $\text{Sm}_4\text{Bi}_2\text{Te}$ and $\text{Yb}_4\text{Bi}_2\text{Te}$. These compounds were obtained by reacting the elements in quartz ampoules below 1000 °C and melting the heavier compounds in Ta or Mo crucibles at temperatures near 1500 °C. All compounds were stated to be semiconductors, a claim, which was supported by the high Seebeck coefficients. $\text{Eu}_4\text{As}_2\text{Te}$, for instance, displayed a Seebeck coefficient of $S(\text{RT}) = 140 \mu\text{V}/\text{K}$ and $\text{Sm}_4\text{Bi}_2\text{Te}$ an even higher Seebeck coefficient of $S(\text{RT}) = 230 \mu\text{V}/\text{K}$. Measurements of the magnetic moment concluded that Sm appeared in its divalent form Sm^{2+} . Therefore, Zintl counting rules confirm by Hullinger's description of this compound being a semi-conductor: $\text{Sm}_4^{2+}\text{Bi}_2^{3-}\text{Te}^{2-}$. [23]

$\text{Sm}_4\text{Bi}_2\text{Te}$ is in fact an interesting candidate for thermoelectric materials. First of all, it has a high thermopower and its structure supposes a rather low thermal conductivity. Secondly, Sm has the tendency of appearing in a mixed valence state $\text{Sm}^{(2+\delta)+}$, thus making Sm-based compounds more flexible for controlling the charge carrier density and more interesting as materials for basic research than, for instance, compounds with Eu, which solely appears as Eu^{2+} . Therefore, it was decided to recreate and study $\text{Sm}_4\text{Bi}_2\text{Te}$.

6.2. $\text{Sm}_4\text{Bi}_2\text{Te}$

We made several attempts to produce a pure $\text{Sm}_4\text{Bi}_2\text{Te}$ sample. A pre-melting of the elements in an Al_2O_3 crubile at 1000 °C, which was placed in a sealed silica tube, yielded mostly SmBi and SmTe . Figure 6.2a shows the XRD of the melted

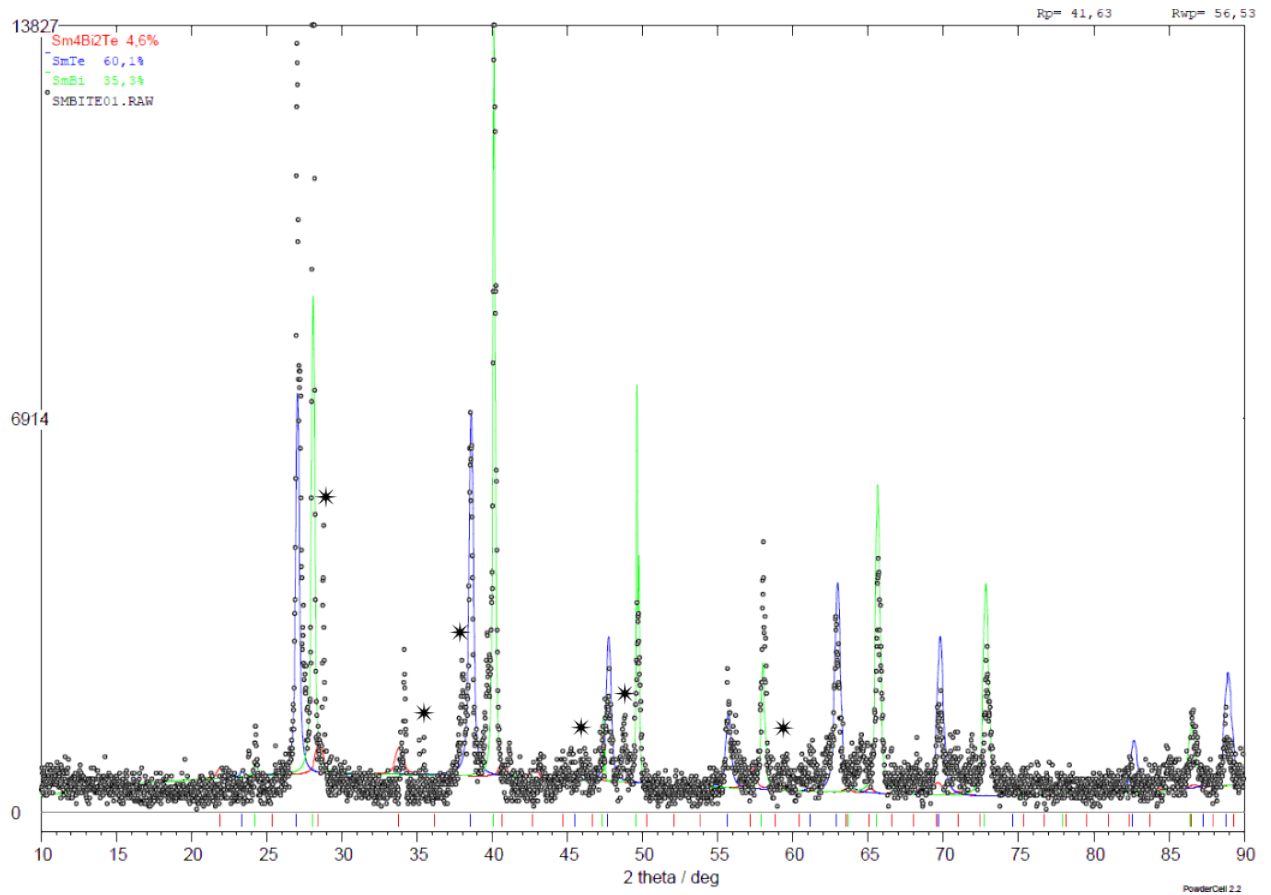
material, consisting of approximately 60 % SmTe and 35 % SmBi, with almost no $\text{Sm}_4\text{Bi}_2\text{Te}$. The intermediate product was filled in a Ta crucible, which was then sealed and heated to 1500 °C. This resulted in the desired phase $\text{Sm}_4\text{Bi}_2\text{Te}$, although with a rather large amount of SmTe (Figure 6.2b).

In a second attempt, a stoichiometric amount of the elements was melted together directly in a sealed Ta crucible at 1600°C. The resulting phase composition (Figure 6.3a) was comparable to the first attempt as to the amount of the foreign SmTe phase. Annealing it at 900 °C for five days did not improve the quality (Figure 6.3b). These results indicate a limited Te incorporation into the phase $\text{Sm}_4\text{Bi}_{3-x}\text{Te}_x$ (with $x < 1$).

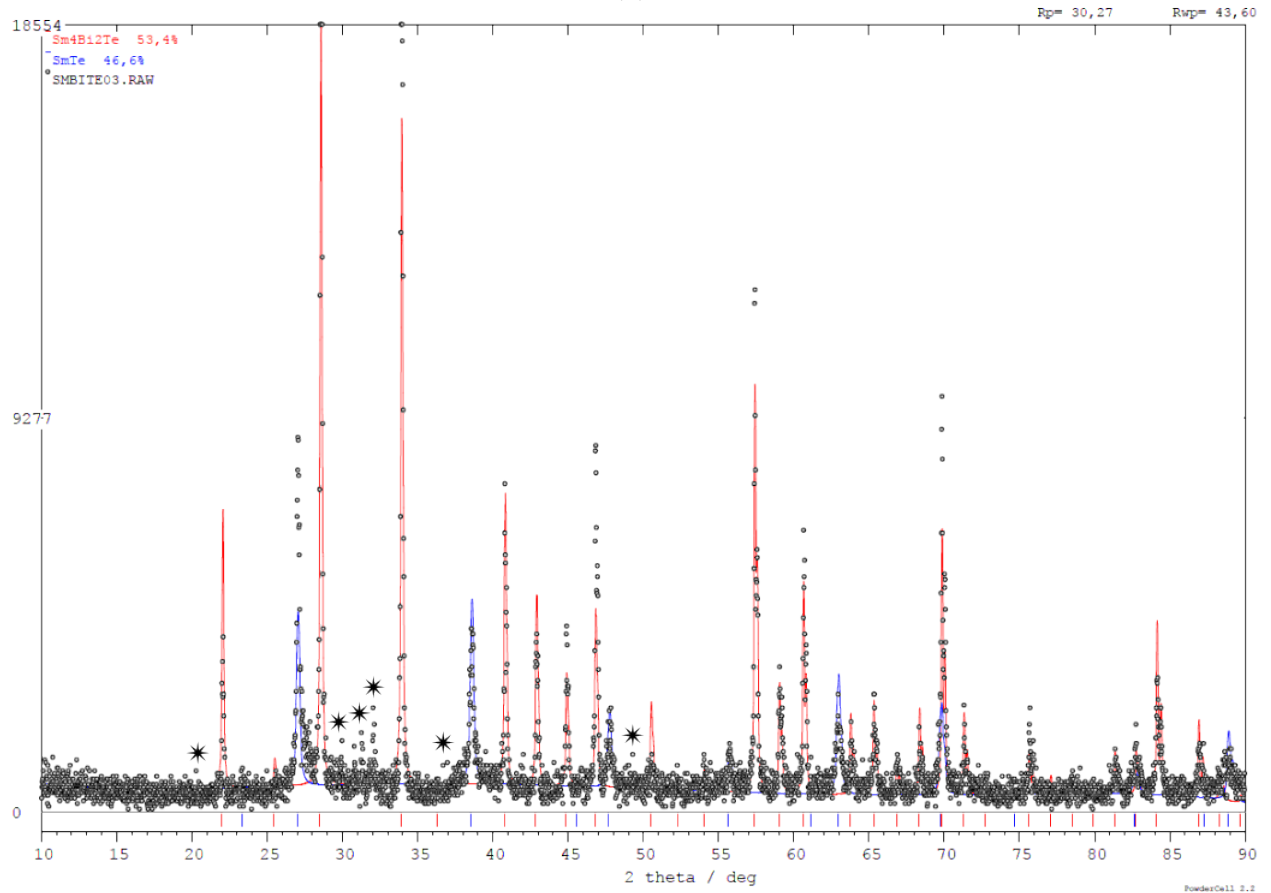
Difficulties in obtaining a single phase material were also reported by Hullinger. According to the author, most samples contained traces of a second phase. [23]

An attempt was made to synthesise this phase with a reduced amount of Te, i.e. $x = 0.5$. In the Zintl formalism, this would look like: $4\text{Sm}^{2+} 2.5\text{Bi}^{3-} 0.5\text{Te}^{2-}$, which would leave 0.5 holes, resulting in a p-doped semiconductor.

However, this synthesis at 1500 °C inside a sealed Ta crucible yielded mainly SmBi, with only traces of the anti- Th_3P_4 compound and SmTe (Figure 6.4).

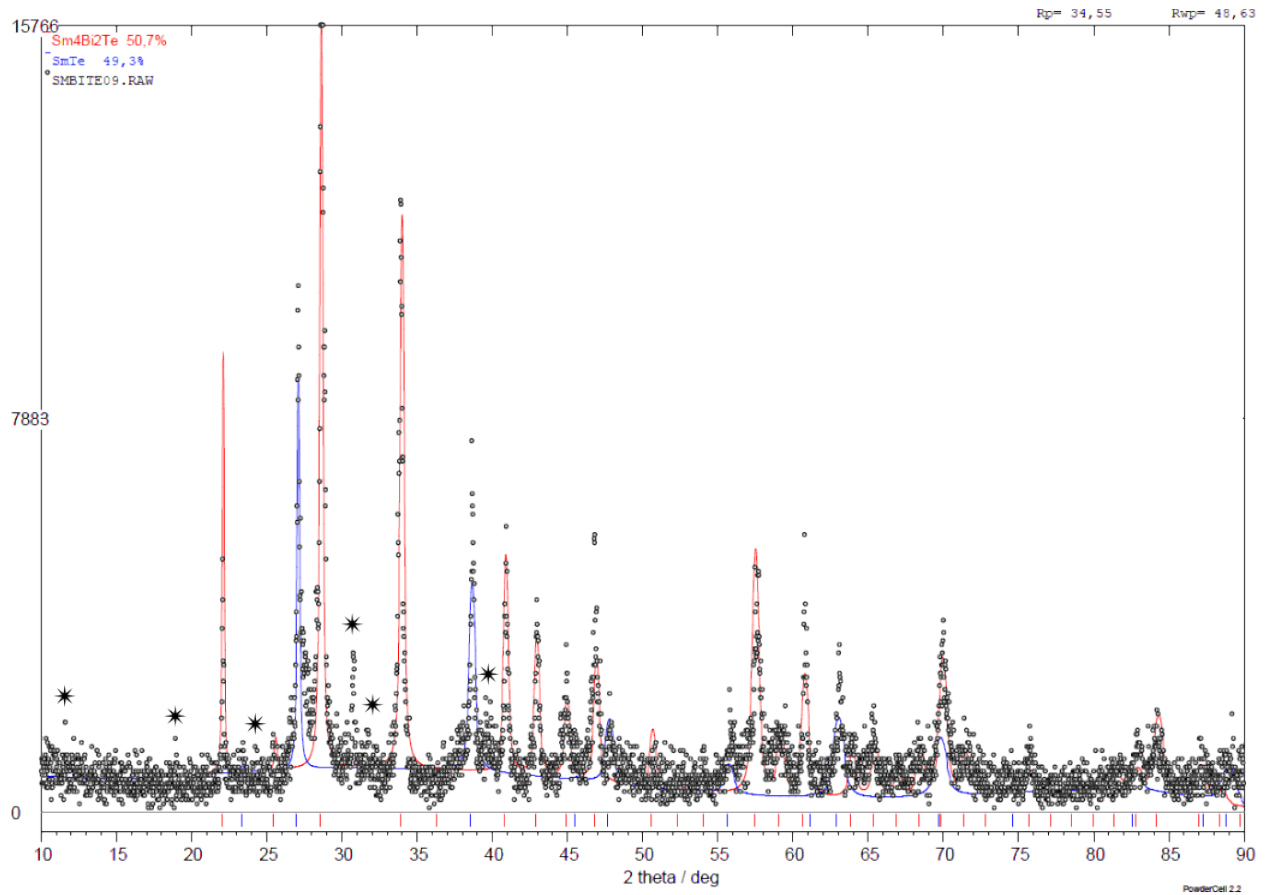


(a)

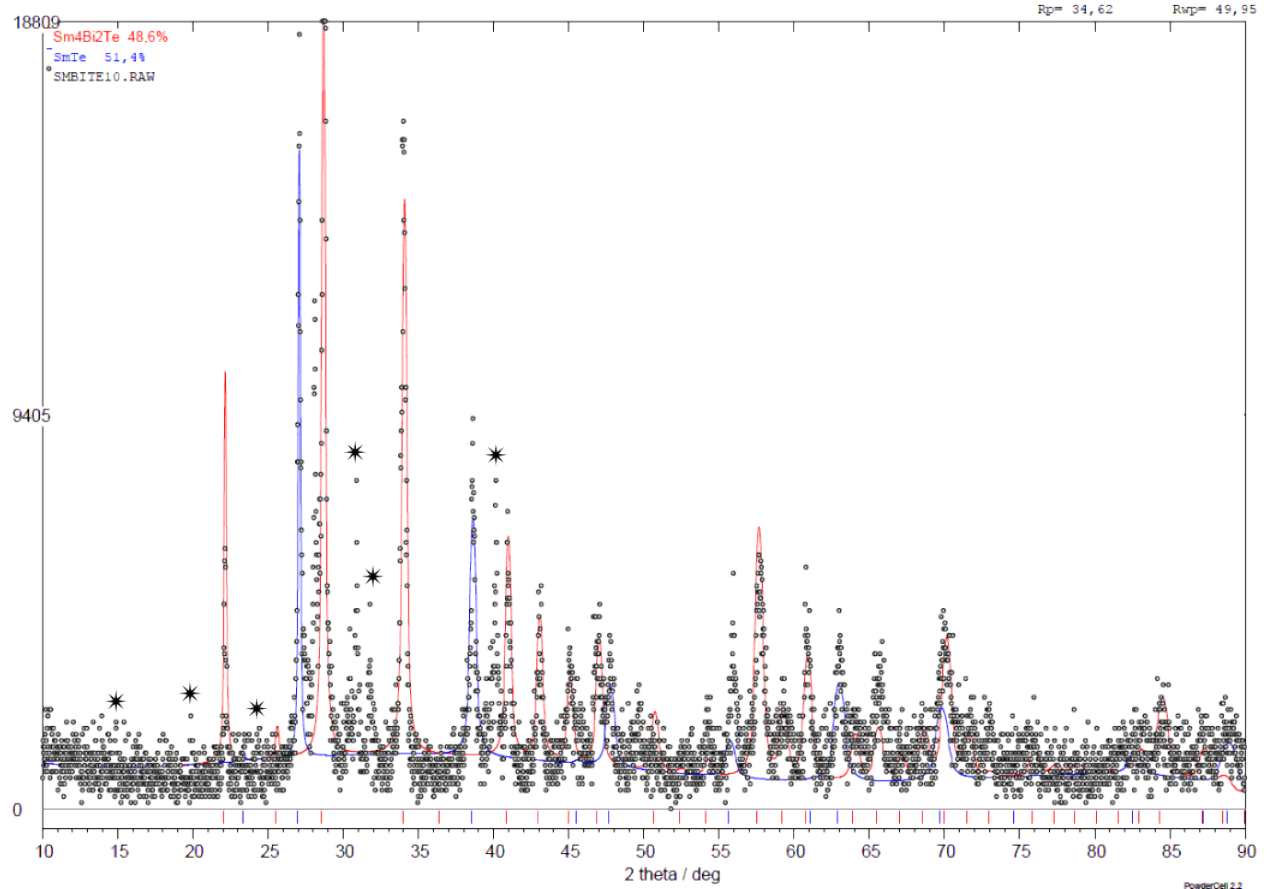


(b)

Figure 6.2.: XRD of a sample with the nominal composition $\text{Sm}_4\text{Bi}_2\text{Te}$, including the calculated XRD patterns of $\text{Sm}_4\text{Bi}_2\text{Te}$ (red), SmTe (blue) and SmBi (green): a) after pre-synthesis in an Al_2O_3 crucible and sealed quartz tube at 1000 °C. b) after synthesis in a Ta crucible at 1500 °C. The unidentified phases are marked with *.



(a)



(b)

Figure 6.3.: XRD of a sample with the nominal composition $\text{Sm}_4\text{Bi}_2\text{Te}$, including the calculated XRD patterns of $\text{Sm}_4\text{Bi}_2\text{Te}$ (red) and SmTe (blue): a) before and b) after annealing at 900 °C. The unidentified phases are marked with *.

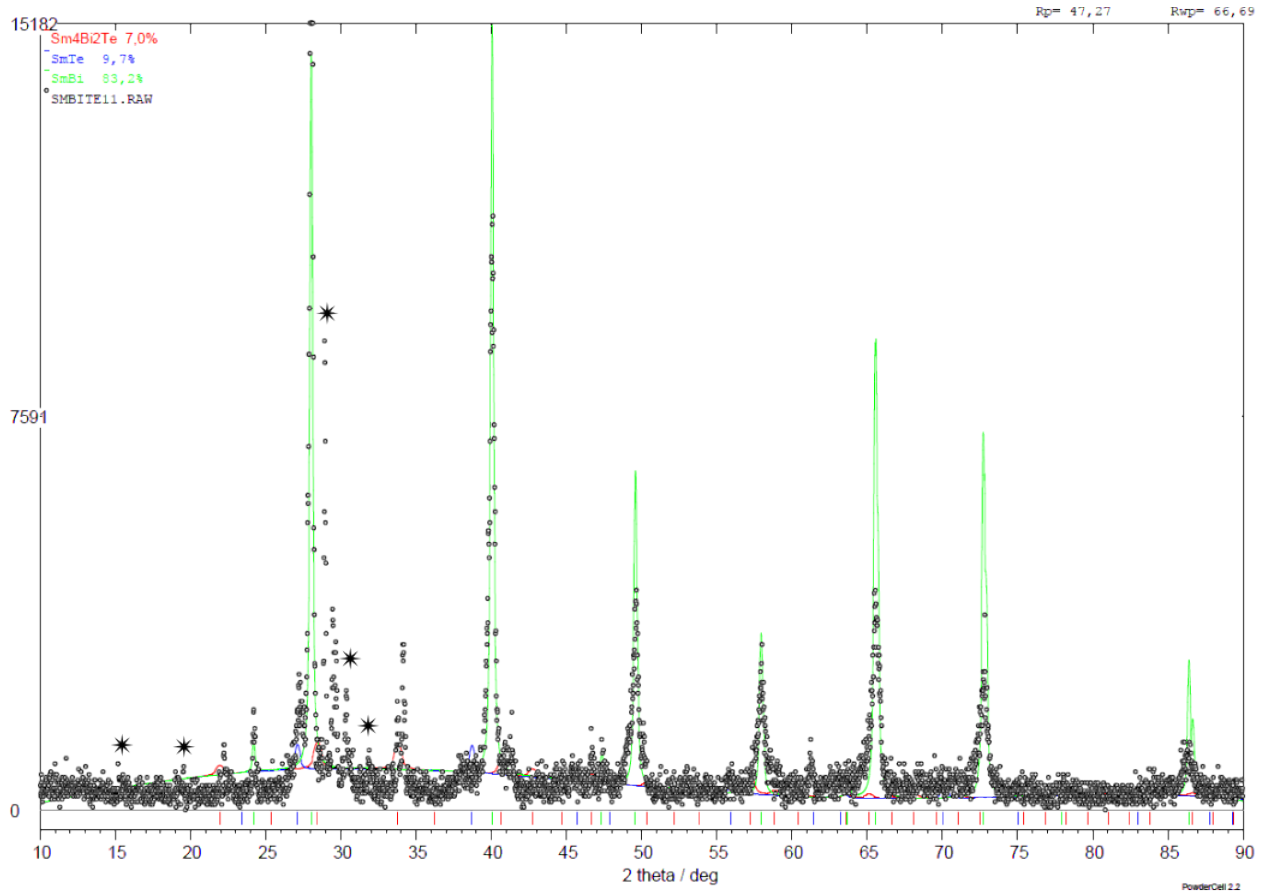


Figure 6.4.: XRD of a sample with the nominal composition $\text{Sm}_4\text{Bi}_{2.5}\text{Te}_{0.5}$, including the calculated XRD patterns of $\text{Sm}_4\text{Bi}_2\text{Te}$ (red), SmTe (blue) and SmBi (green). The unidentified phases are marked with *.

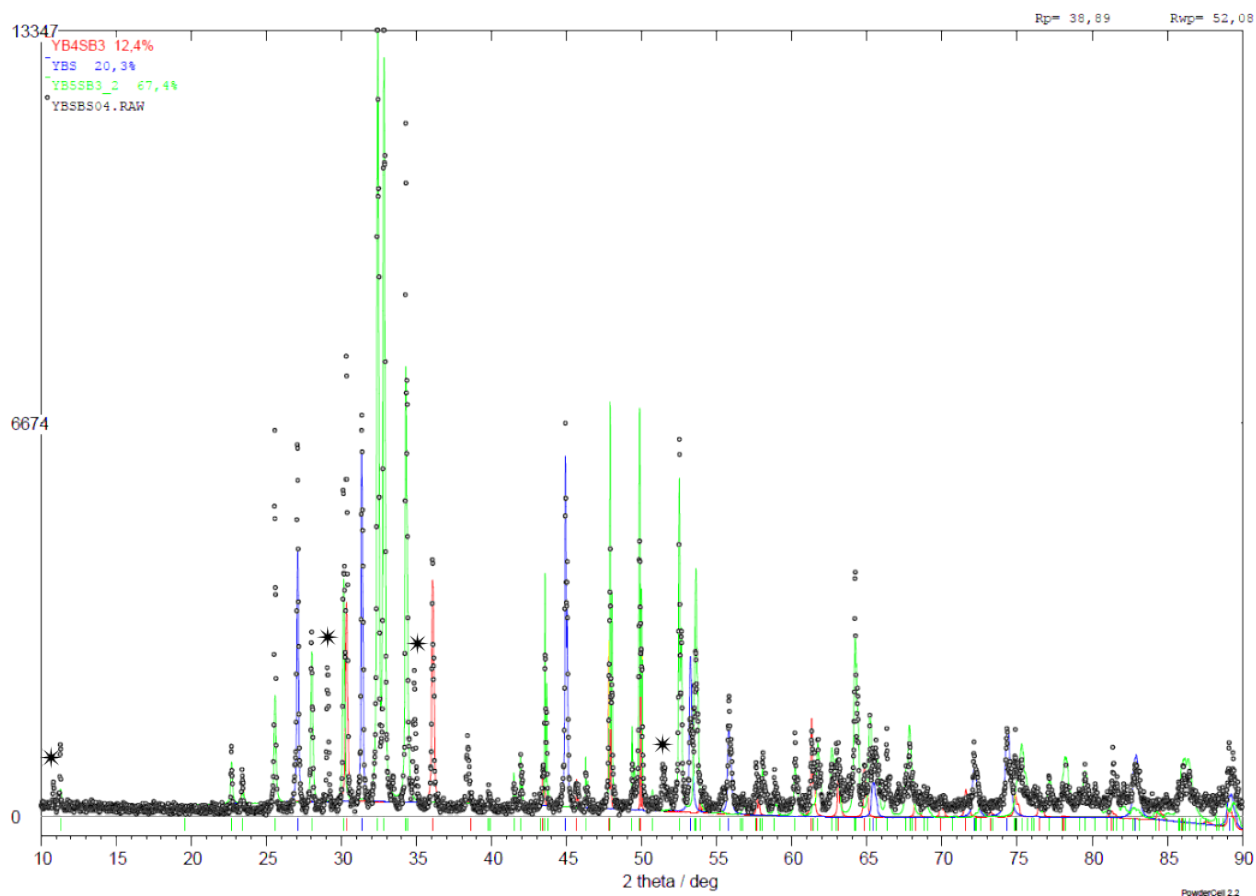
Obviously, the phase diagram of the compound appeared to be complex and a thorough SEM/EDX analysis would have been necessary. For further investigation, all samples needed to be cut and polished to a mirror finish. However, the phase under investigation appeared to be chemically very unstable: a violent reaction with H_2O occurred during cutting, forming the toxic H_2Te . Therefore, it was decided to stop the research on $\text{Sm}_4\text{Bi}_2\text{Te}$ and to concentrate on materials that are less toxic than Te-based compounds. Herein, $\text{Yb}_4\text{Sb}_2\text{S}$ was found to be an interesting, non-toxic alternative.

6.3. Yb₄Sb₂S

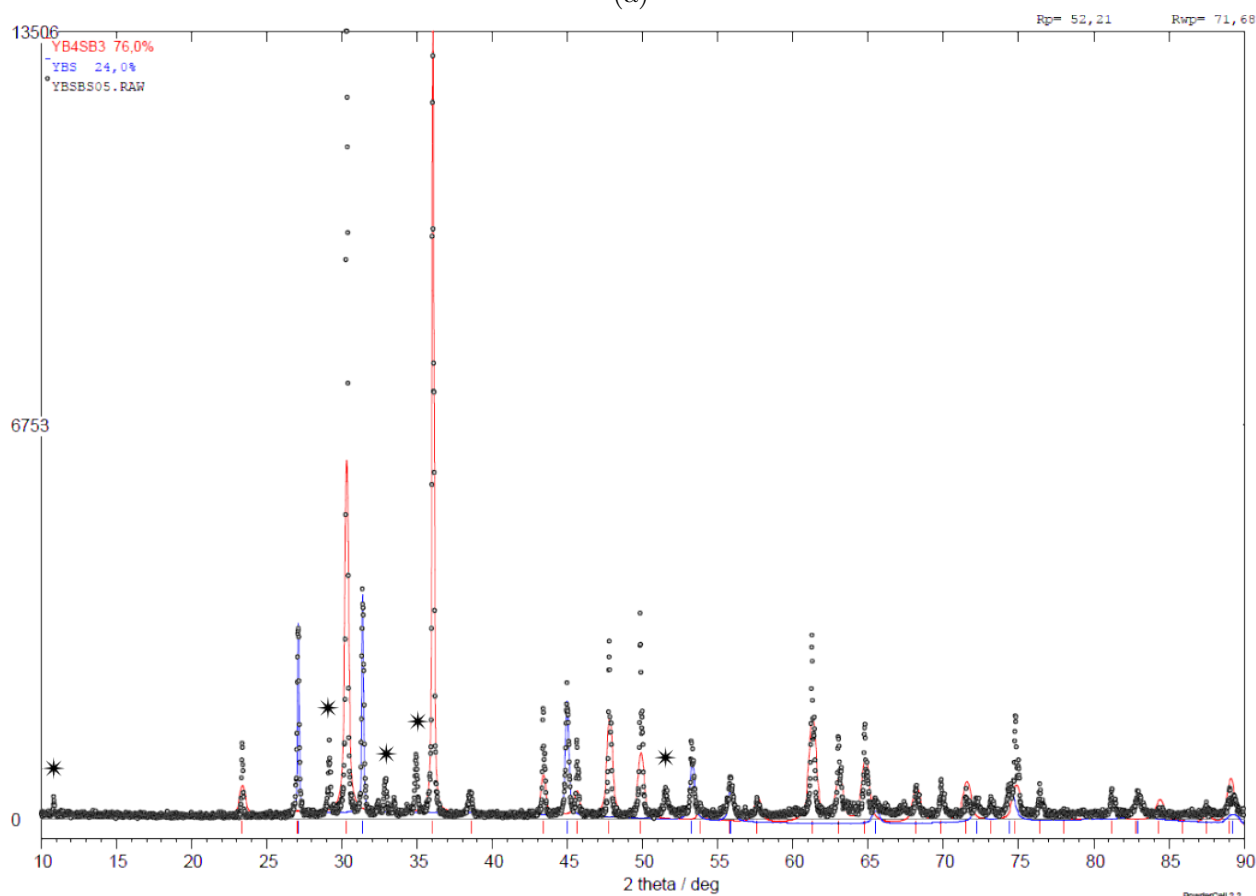
For obtaining Yb₄Sb₂S, first YbS was produced by reacting Yb and S inside a sealed quartz tube. This had to be done very carefully, because S has a very low boiling point of 445 °C. Therefore, Yb was placed at one end of the quartz tube and S at the other. The natural temperature gradient of a resistance tube furnace, which is hottest in the center, was used to keep the S at lower temperatures with a controlled vapour pressure and the Yb at higher temperatures, at which it could react with the S vapour through diffusion. The temperature was raised carefully, until all the material had reacted, always keeping an eye on the temperature at the colder end.

The finished product was ground and pressed into a pellet, and afterwards annealed again. After confirming the purity of the YbS via XRD, it was sealed with stoichiometric amounts of Yb and Sb inside a Ta crucible., which was then slowly heated up to 1600 °C and cooled down rapidly. According to X-ray analysis, the synthesis resulted in the phases Yb₅Sb₃, YbS and Yb₄Sb₃ (Figure 6.5a). The Rietveld-refined lattice parameter of Yb₄Sb₃ turned out to be $a = 9.309 \text{ \AA}$, which is significantly smaller than the literature value $a^* = 9.322 \text{ \AA}$. This could be a sign of S-substitution, since S²⁻ has an ionic radius of $r_S = 1.84 \text{ \AA}$, while the ionic radius of Sb³⁻ is $r_{Sb} = 2.45 \text{ \AA}$. Annealing the sample for 12 hours at 1000 °C and then for four days at 850 °C caused the Yb₅Sb₃ to vanish (Figure 6.5b). Furthermore, the lattice parameter of Yb₄Sb₃ increased from $a = 9.309 \text{ \AA}$ to $a = 9.321 \text{ \AA}$, indicating that the S had disappeared from the main phase. Apparently, Yb₄Sb₃ is energetically more favourable than the substituted phase.

SEM/EDX analysis before annealing (Figure 6.6a) shows the YbS-phase embedded in a Yb₄Sb_{2.6}S_{0.4} matrix, while the matrix after annealing (Figure 6.6b) seems to be almost pure Yb₄Sb₃. However, upon closer examination, one can detect another phase enclosed in the Yb₄Sb₃ matrix, the inclusions being too small to



(a)



(b)

Figure 6.5.: XRD of a sample with the nominal composition $\text{Yb}_4\text{Sb}_2\text{S}$, including the calculated XRD patterns of Yb_4Sb_3 (red), YbS (blue) and Yb_5Sb_3 (green): a) before and b) after annealing at 850 °C for four days. The unidentified phases are marked with *.

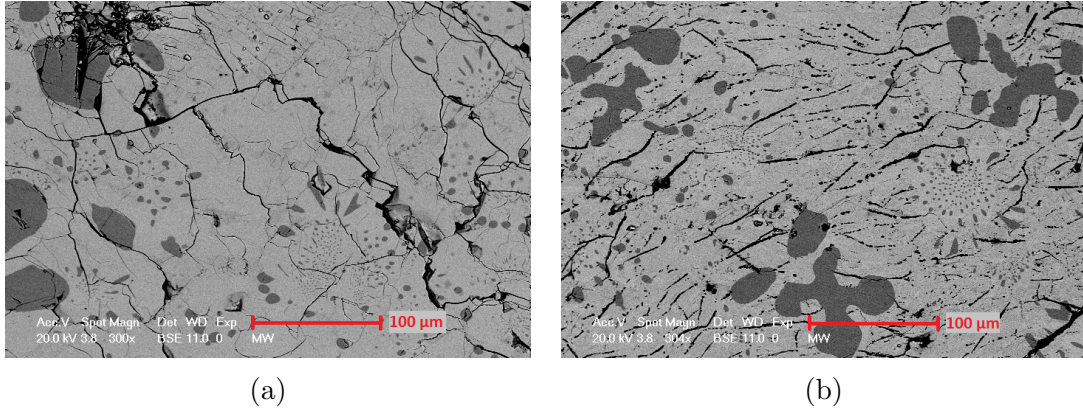


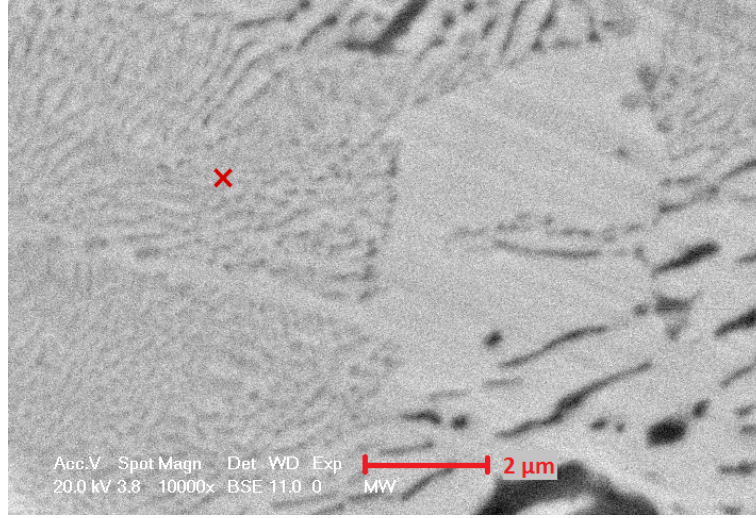
Figure 6.6.: SEM image of a sample with the nominal composition $\text{Yb}_4\text{Sb}_2\text{S}$, showing a YbS-rich phase (dark grey) embedded in a) $\text{Yb}_4\text{Sb}_{2.6}\text{S}_{0.4}$ (light grey) before annealing and b) Yb_4Sb_3 (light grey) after annealing for four days at 850 °C.

analyse them (Figure 6.7a). One can only measure the integrated composition of a $2 \times 2 \mu\text{m}^2$ area: 4.1 Yb, 2.5 Sb, 0.5 S (Figure 6.7b). The small inclusions probably consist of YbS as well.

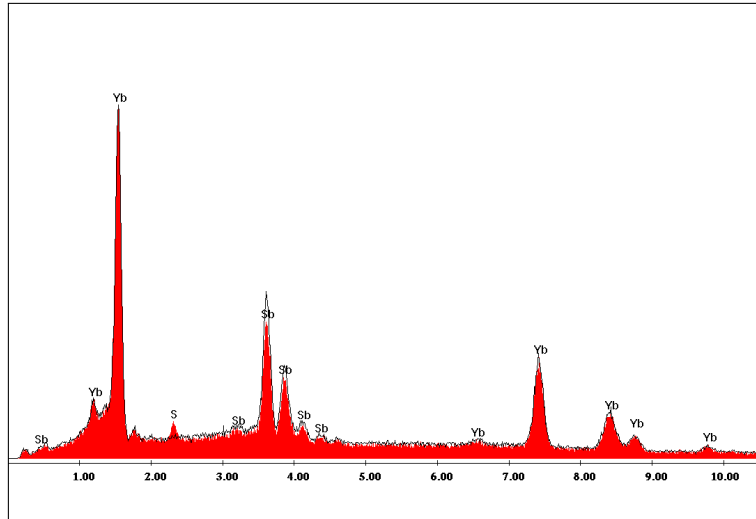
According to the SEM/EDX analysis of the sample before annealing, it does not seem possible to replace Sb by more than 0.4 S. It should be also noted that there were no traces of Yb_5Sb_3 found.

Since the substitution of Yb_4Sb_3 seemed limited to 0.4 S, it was decided to additionally improve the material's TE properties by substituting Yb with Sm, as had been done by Chamoire et al. [21]. Keeping in mind the highly reactive nature of S towards RE metals and Ta, it was decided to carefully synthesise SmS in the same way as the YbS pellet. The less reactive SmS could then be used to synthesise $\text{Yb}_{3.6}\text{Sm}_{0.4}\text{Sb}_{2.6}\text{S}_{0.4}$ without any reactions with the Ta crucible.

The SmS pellet and the stoichiometric amounts of Yb and Sb were melted inside a sealed Ta crucible at 1600°C and afterwards annealed at 700 °C for a week. Upon opening the crucible, the sample was found to have been split into two parts, presumably by a gas bubble. Both parts were measured via XRD (Figure 6.8) and

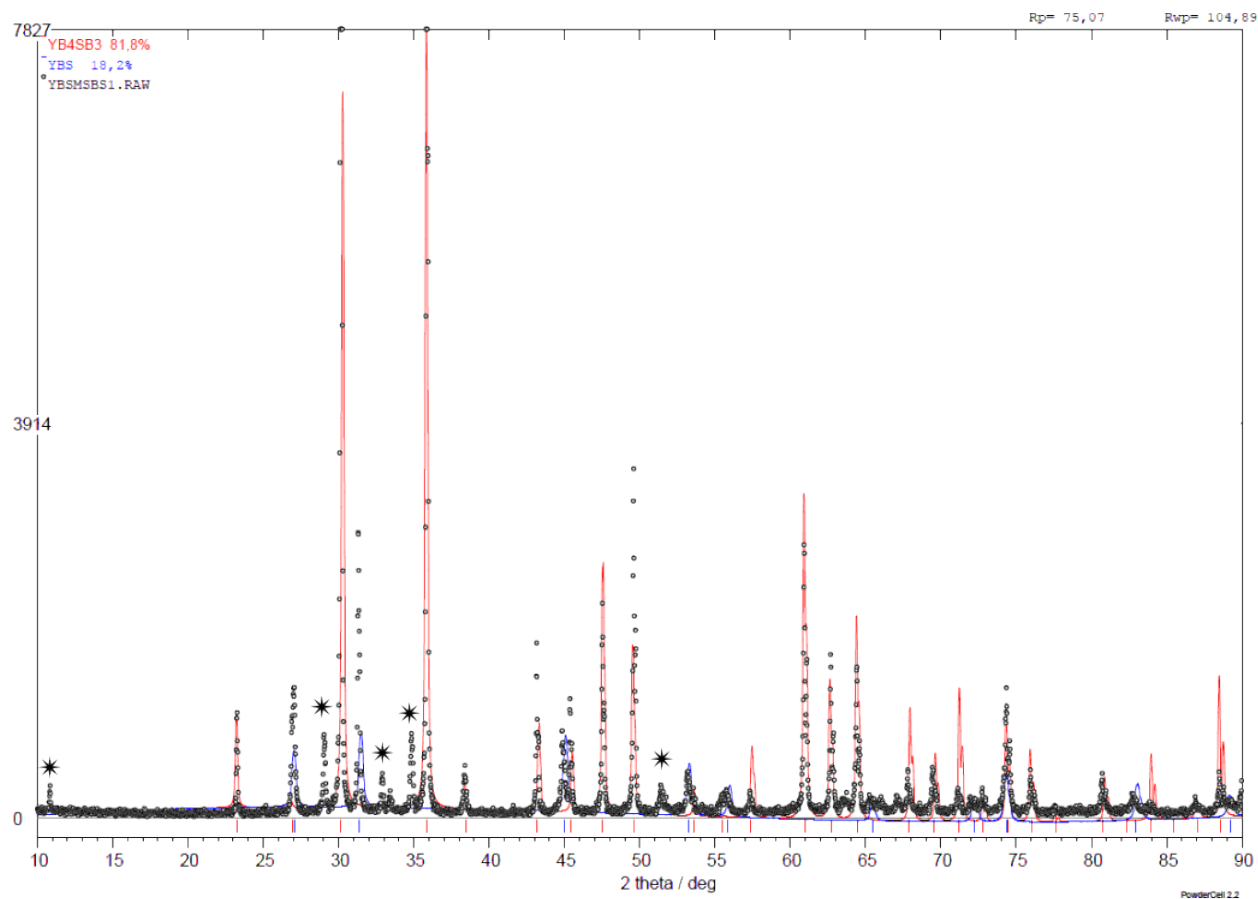


(a)

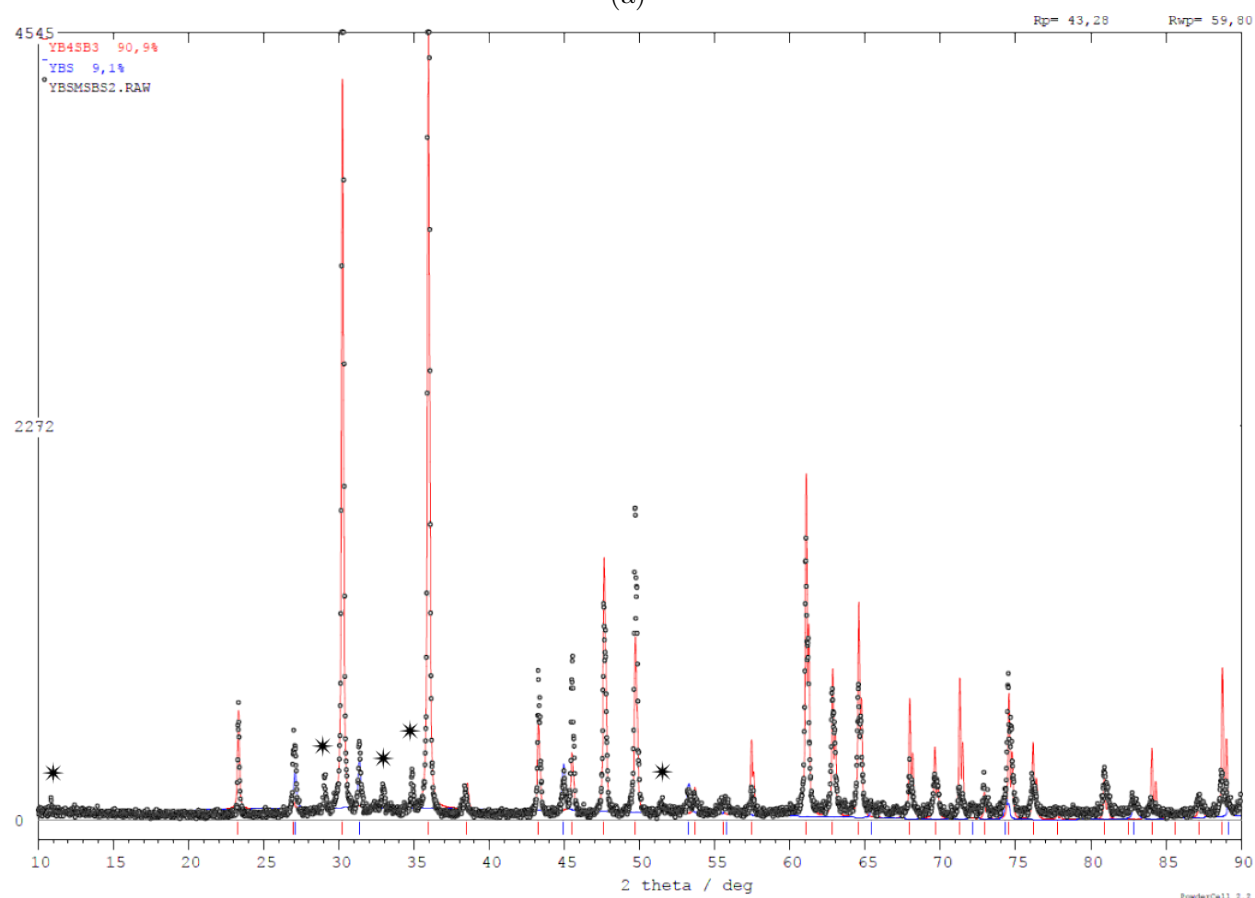


(b)

Figure 6.7.: a) High resolution SEM image of a sample with the nominal composition $\text{Yb}_4\text{Sb}_2\text{S}$ after annealing, showing very small inclusions of a second phase into the overall matrix. The x marks the spot where the EDX was taken. b) EDX analysis of a $2 \times 2 \mu\text{m}^2$ area marked in the SEM image.



(a)



(b)

Figure 6.8.: XRD of the split sample with the nominal composition $\text{Yb}_{3.6}\text{Sm}_{0.4}\text{Sb}_{2.6}\text{S}_{0.4}$, including the calculated XRD patterns of Yb_4Sb_3 (red) and YbS (blue): a) lower part b) upper part. The unidentified phases are marked with *.

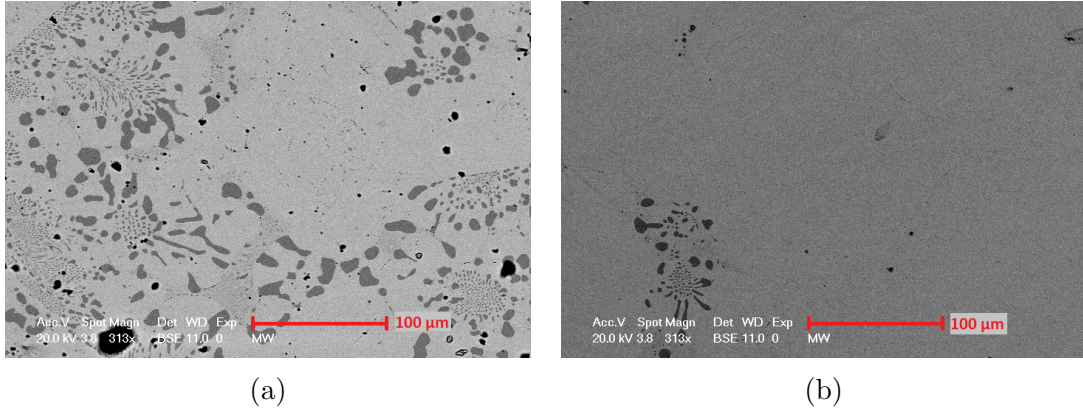


Figure 6.9.: SEM images of the split sample with the nominal composition $\text{Yb}_{3.6}\text{Sm}_{0.4}\text{Sb}_{2.6}\text{S}_{0.4}$: a) lower part b) upper part.

SEM/EDX (Figure 6.9). A Rietveld refinement of the XRD measurements with the phases Yb_4Sb_3 and YbS suggests that the lower part contains more YbS (18.2 %) than the upper part (9.1 %). This claim is supported by SEM/EDX analysis, where the YbS appears in the form of dark grey inclusions in another phase. In the lower part, it is encased by the $\text{Yb}_{3.6}\text{Sm}_{0.5}\text{Sb}_{2.8}\text{S}_{0.1}$ phase, while in the upper part it is mostly the $\text{Yb}_{3.8}\text{Sm}_{0.3}\text{Sb}_{2.8}\text{S}_{0.1}$ phase. Like in the annealed $\text{Yb}_4\text{Sb}_2\text{S}$ sample, the surrounding phases do not seem to be pure, but rather contain very small inclusions of another phase that were too small to be identified.

7. SmGa₆Te₁₀

A brief exploratory experiment was carried out to realize the melting behaviour and to evaluate the efforts of a synthesis of a new compound SmGa₆Te₁₀.

7.1. Motivation

As mentioned in Section 3.2, strongly correlated electrons can give rise to a large Seebeck coefficient, due to a hybridisation between d or f electrons with delocalised conduction electrons. Thus, a strongly correlated material, which shows also low thermal conductivity, would be an excellent candidate for thermoelectric materials. In 2006, A. Bentien et al. presented the rare-earth compound YbGa₆Te₁₀ (space group R32, no. 155, $Z = 6$), which they had obtained by heating the starting materials inside a carbon glass crucible and an Ar filled quartz tube at 700 °C, then grinding and pressing the material and heating it again several times.

It has a low charge-carrier density and a Seebeck coefficient of approximately 110 $\mu\text{V/K}$ at RT. Moreover, it exhibits an extremely low thermal conductivity of $\kappa \approx 0.5 \text{ W/mK}$. This is thought to be the result of the combination of a large unit cell, a low degree of space filling and heavy atoms. Unfortunately, the material also shows a very high electrical resistivity, which could not be completely explained by the authors and diminishes the figure of merit. [24]

Nevertheless, the material class appears to be very promising. It was decided to synthesise a Sm analogue, namely SmGa₆Te₁₀. Since Sm has a different valence

than Yb, it forms compounds with different electrical properties. Therefore, we were hoping to find a material with a similarly low thermal conductivity, but a smaller electrical resistivity.

7.2. Synthesis

In order to synthesise $\text{SmGa}_6\text{Te}_{10}$, 6 parts of Ga and 9 parts of Te were put into an Al_2O_3 crucible and placed inside a sealed silica tube, where they were melted together, thus forming $3\cdot\text{Ga}_2\text{Te}_3$. Then, in the second step, 1 part Sm and 1 part Te were added. The material was melted in a sealed Ta crucible at 1500 °C and analysed via XRD. According to the Rietveld refinement, the sample contained mainly GaTe and Ga_2Te_3 , as well as some unidentified phases (Figure 7.1). Curiously, no phases containing Sm could be detected, The presence of GaTe and Ga_2Te_3 , on the other hand, indicates a lower concentration of Te than planned. A possible explanation for the missing Te would be that it reacted with Sm and formed some air-sensitive phases, which could not be measured via XRD. There is no doubt that the material does not melt congruently. This and the toxicity of Te were the reasons, why there was no second attempt to create this material.

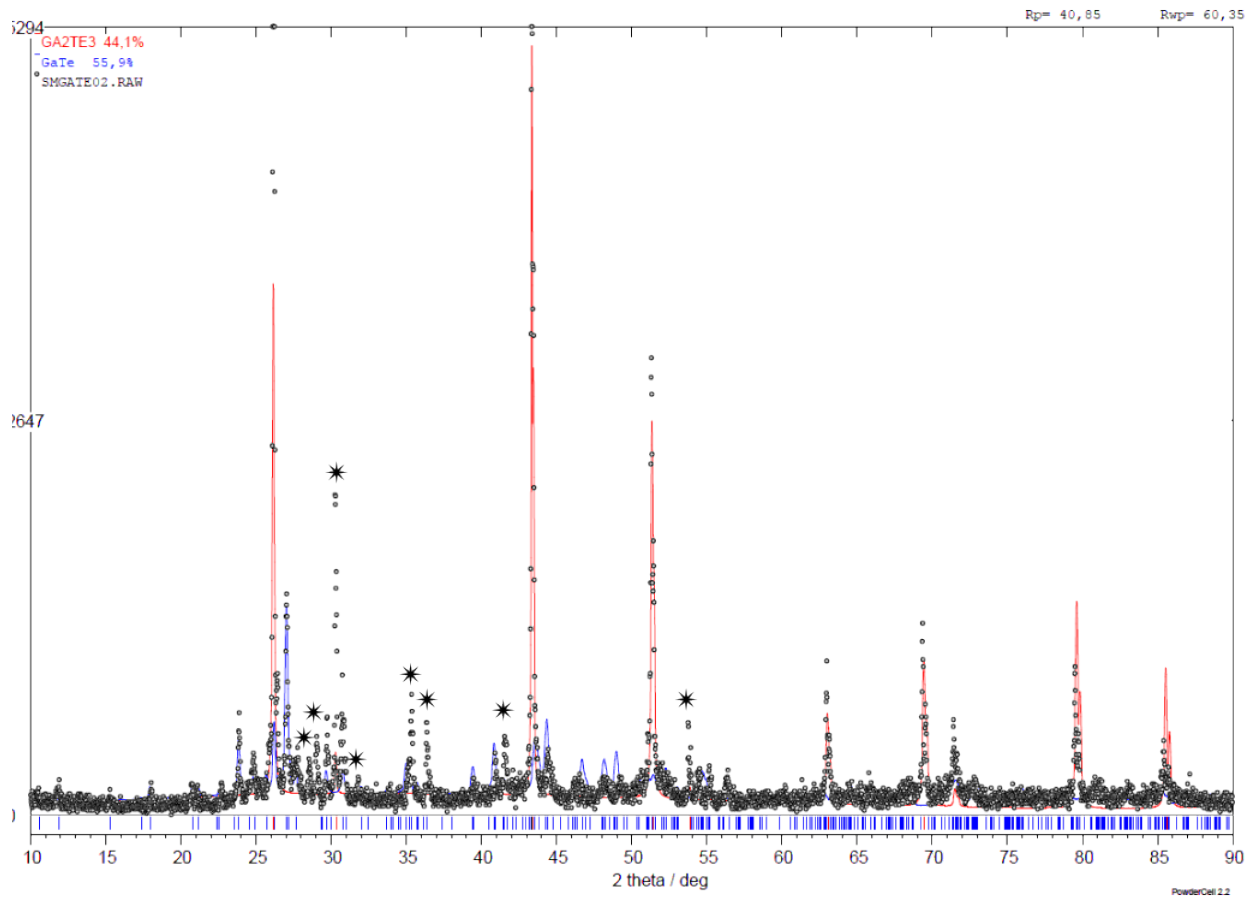


Figure 7.1.: XRD of a sample with the nominal composition $\text{SmGa}_6\text{Te}_{10}$, including the calculated XRD pattern of Ga_2Te_3 (red) and GaTe (blue). The unidentified phases are marked with *.

8. Start-up of the high-frequency induction furnace for closed crucible synthesis and crystal growth technology

The Institute of Solid State Physics (IFP) at the Vienna University of Technology possesses a number of different technologies for material synthesis, including methods for melt synthesis and single crystal growth. Polycrystalline intermetallics can be synthesised in the **Hukin crucible** (up to 40 g) or in the **cold boat** (up to 5×5 g) via induction heating. Both set-ups consist of watercooled Cu crucibles and are powered by a *Hüttinger* HF generator with 30 kW. [25] Another set-up for melt synthesis is the **Tetra arc furnace** of *Techno Search Corp.*, where it is also possible to grow single crystals using the **Czochralski process**. Here, a seed crystal is dipped into the molten material. When it is slowly pulled upwards, a single crystal forms, which has the same orientation as the seed crystal

A rod of polycrystalline material, which, for instance, was produced in a special indentation of the cold boat, can be turned into a single crystal using the **floating zone technique**. It is a crucible-free method, where a **4-mirror furnace** melts a zone of the sample, which is then slowly moved from one end to the other. The surface tension of the melt keeps it in place, until it crystallises in an ordered

manner upon cooling.

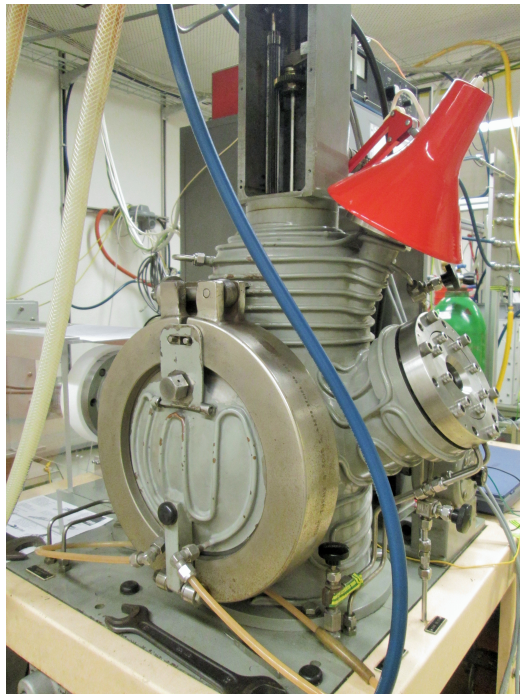
These methods are quite efficient for synthesising some intermetallics, but when handling volatile materials, problems arise. Due to the big volume of the mentioned furnaces, a lot of material can get lost when compounds are synthesised, which tend to decompose and form gas products. This leads to an off-stoichiometry of the produced sample.

A possible solution for this problem is to enclose the compounds in a small, controlled volume. For this reason, crucibles were made of refractory materials like Ta or Mo. They have a cylindrical shape, with $\varnothing$ 0.8 cm or $\varnothing$ 0.65 cm, and can be closed with a cap made of the same material. After a crucible is filled with a sample's starting materials and closed with the cap, it is sealed in the tetra arc (Section 4.1.3). To melt the material inside the crucible, an indirect HF induction furnace is used, which is described in Section 8.1.

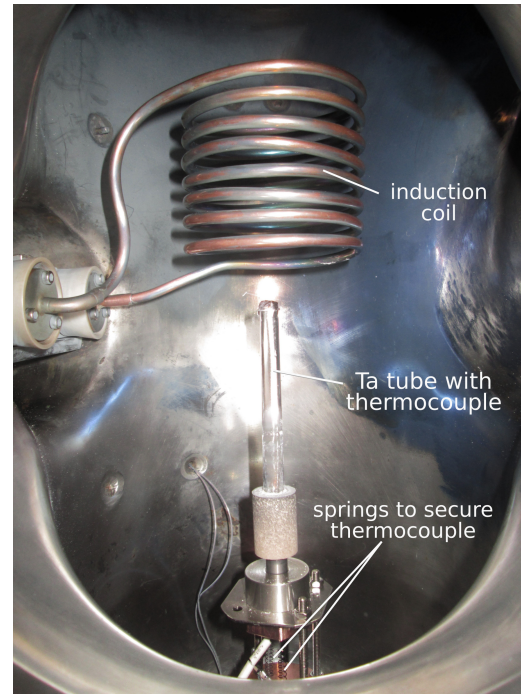
A part of this master's thesis was the first using and optimisation of this newly designed high temperature crucible technology. For this reason, the start-up operations were watched carefully and are documented in Section 8.2.

8.1. Set-up

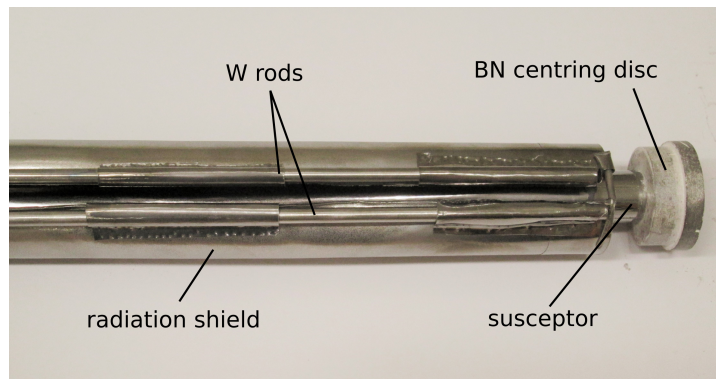
The HF induction furnace consists of a dome-shaped ADL chamber with a large hatch and two small view windows (Figure 8.1a). It is water-cooled and can be evacuated using a booster pump and a turbomolecular pump. The inside is equipped with an induction coil and two water-cooled steel rods that are used to centre the HF Ta susceptor with a crucible inside (Figure 8.1b). They are motor-driven and can be moved up or down, to choose the optimal position inside the induction coil. On the lower steel rod a crucible holder in the form of a Ta tube is mounted. Inside, there is a W-Re thermocouple. Springs at the base of the



(a)

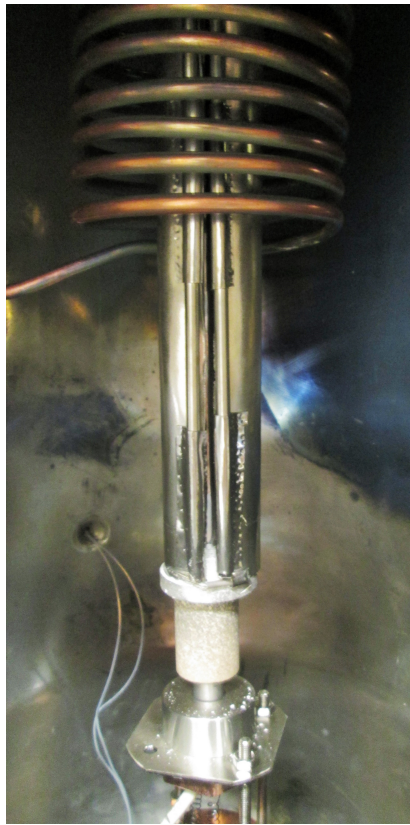


(b)

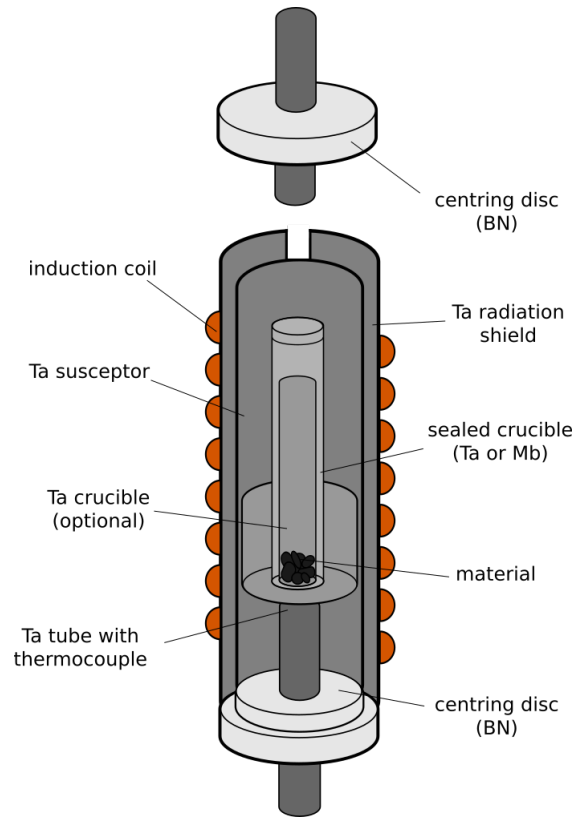


(c)

Figure 8.1.: a) ADL chamber b) Inside of the ADL chamber, showing the induction coil and the lower Ta tube with a thermoelement. Springs at the bottom of the Ta tube secure the thermoelement in place. c) Susceptor, surrounded by a radiation shield, kept in place by centring discs made of BN. W rods in the radiation shield prevent it from deforming.



(a)



(b)

Figure 8.2.: a) ADL chamber with inserted crucible, susceptor and radiation shield. In the picture, the lower Ta tube has yet to be raised a few cm, in order for the crucible to be in optimal position. c) Schematic of the total assembly.

crucible holder prevent the wires from touching.

The actual heat to melt materials is provided by the so-called susceptor, a long cylindrical tube made of Ta foil, which heats up due to the HF electromagnetic field. It is surrounded by a radiation shield, a cylindrical tube with a slit, made of Ta foil with a thickness of 0.1 mm, which stops part of the radiated heat that is directed outwards (Figure 8.1c). Two centring discs made of BN keep the susceptor and the radiation shield in place and ensure that the separate parts are electrically isolated from each other.

To synthesise a material, the sealed Ta crucible is inserted into the susceptor and radiation shield. Next, this assembly is carefully stuck onto the crucible holder inside the ADL chamber (Figure 8.2a). The lower part is raised, until the upper steel rod can be threaded into the susceptor. Now that the crucible and susceptor are secured, one can adjust their position relative to the induction coil by moving both steel rods.. Once the crucible is positioned correctly, a control voltage from a potentiometer is applied to the generator to heat the induction coil. The resulting temperature is measured with the thermocouple, in order to know how much control voltage is necessary to melt a given material.

One can control the voltage either manually or with a computer program. The latter makes it possible to run temperature ramps for different heat treatments of the samples. Since the movement of the steel rods is also controlled electronically, it is also possible to define a speed and move the crucible in the natural temperature gradient of the inductor, thus growing single crystals via the **Bridgeman technique**.

In the schematic of the set-up (Figure 8.2b) an optional small Ta crucible can be seen. It was made by spot welding Ta foil with a thickness of 0.076 mm into the right shape. This way, it was possible to fabricate an absolutely leak-proof crucible. This insertion crucible simplifies the removal of the synthesised material

from the crucible, since it is peeled apart much easier. The crucible is less damaged and can be reused more often. Furthermore, by fabricating a loose cap for the insertion crucible, one can shield the materials inside from the radiated heat during arc welding the outer crucible (Section 4.1.3). Although this method turns out to be effective, the manual production of a leak-proof crucible is quite time consuming and the small diameter of the insertion crucible does not allow for a lot of material. Therefore, it was only used once for proof of principle.

8.2. Initial operation

The first time the induction furnace was used for material synthesis, it was slowly and manually brought to a temperature of 1500 °C. Then, a temperature program was set to cool it to 1400 °C over two hours. After approximately one hour, a metallic mount started to fog up the inside of the chamber. Contrary to the first thought, the crucible, which was examined after the synthesis, turned out to be intact.

The phenomenon also appeared during the second use. To determine the source of this metal mount, some of it was rubbed onto a piece of paper and examined via EDX (Figure 8.3).

According to the EDX analysis, the metal mount consisted primarily of Zn. With that in mind, a few small steal screws, which had probably been passivated with a Zn layer, were found at the bottom of the crucible holder. After replacing them, the induction furnace could be operated without fogging up.

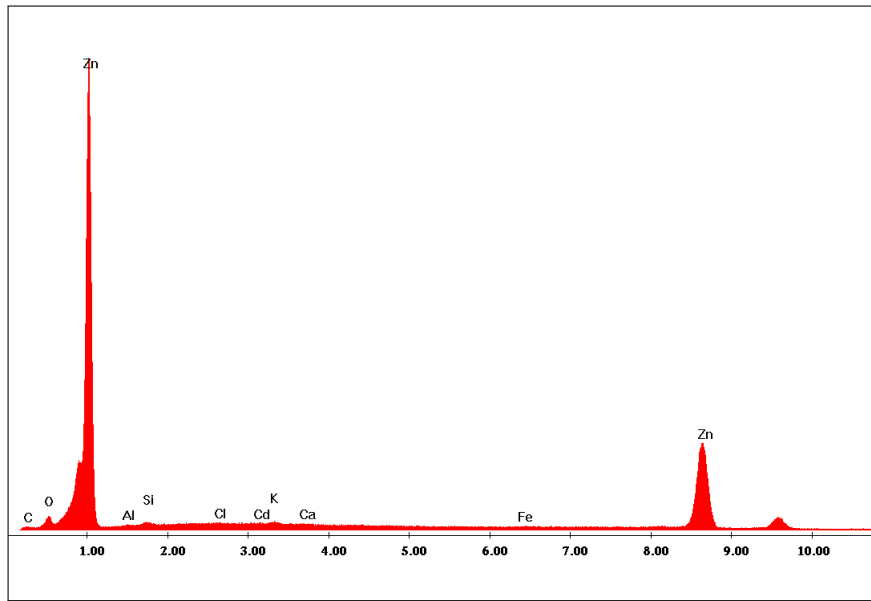


Figure 8.3.: EDX analysis of metal mount inside the chamber.

8.3. Calibration

The purpose of the following calibration curves is to allow for an operating of the induction furnace without depending on the extra temperature measurement, which may drop out at very high temperatures. By reading the temperature at a given applied voltage, a graph was constructed that can serve as a guideline for determining the needed voltage input.

Figure 8.4 shows the calibration curves taken at two different positions of the thermocouple relative to the inductor ($z = 2.5$ cm and $z = 1.5$ cm). The position does not seem to make a big difference, except for the last five data points. Here, the lower position seems to lead to a stronger rise in temperature. Further measurements, however, ascertained that this behaviour was caused by a problem with the thermocouple and was not related to the position.

At a later point in time, a susceptor and radiation shield with a smaller diame-

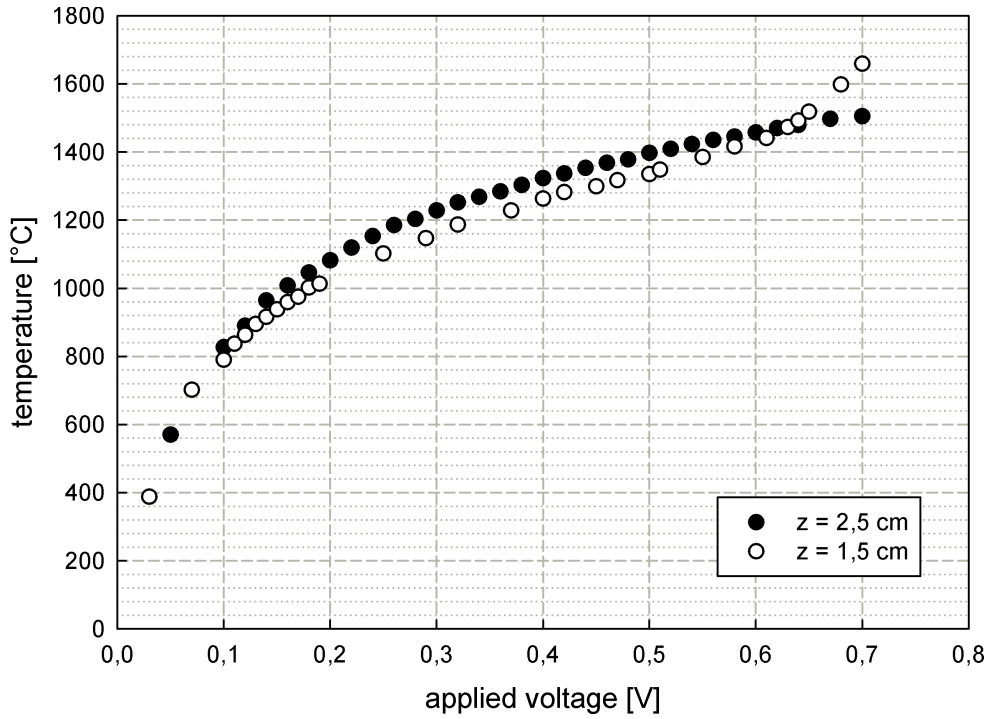


Figure 8.4.: Calibration curves at two different positions of the thermocouple.

ter were used. Although there were no detailed measurements, one can say from experience, that this caused the temperature at high voltages to be higher by approximately 100 °C.

8.4. Deformation of the radiation shield

As mentioned, the radiation shield is a cylindrical tube made of Ta foil, just as the susceptor. The difference is, apart from the diameter, the lengthwise gap in the radiation shield. It is indispensable, since it prevents eddy currents from forming. However, the HF AC still affects the shield, namely by polarising its edges. This causes electrical attraction between them, which becomes a problem

at high temperatures, when Ta gets very soft. Then, the electrical attraction leads to a collapsing of the gap.

To prevent this from happening, the edges were reinforced with two W rods (Figure 8.1c). This material also has a high melting point (3422 °C), but contrary to Ta it is very hard.

9. Summary

The topic of this master's thesis was the search for novel TE materials. For this purpose, materials were chosen, to which the Zintl-Klemm concept could be applied. Polycrystalline samples were produced via melt synthesis and, in a first step, analysed via XRD. In some cases, additional SEM/EDX measurements were conducted. If the material proved to be of a sufficient quality, measurements of the TE properties were conducted. This included measurements of the electrical resistivity at low temperatures (2 K - 300 K) and high temperatures (300 K - 870 K), measurements of the Seebeck coefficient at high temperatures (300 K - 870 K), Hall measurements at low temperatures (2 K - 300 K) and measurements of the thermal conductivity at high temperatures (420 K - 820 K).

Of the synthesised materials Yb_2SnGe_2 , Yb_2InGe_2 , Sr_2PbGe_2 , $\text{Sm}_4\text{Bi}_2\text{Te}$, $\text{Yb}_4\text{Sb}_2\text{S}$ and $\text{SmGa}_6\text{Te}_{10}$, only two could be produced with a minimal amount of secondary phases, so that they could be used for further measurements. These compounds were Yb_2SnGe_2 and Yb_2InGe_2 , both members of a family with the general formula $\text{A}_2\text{M}'\text{M}''_2$ ($\text{M}' = \text{In, Sn, Pb}$; $\text{M}'' = \text{Si, Ge}$), which were synthesised in the cold boat. Both materials turned out to be highly metallic, displaying a typical electrical resistivity and a negative and low Seebeck coefficient, with the highest values being $S = -18 \mu\text{V/K}$ and $S = -24 \mu\text{V/K}$, respectively. Furthermore, they show very high charge carrier concentrations, with $n = 3.96 \times 10^{28} \text{ m}^{-3}$ and $n = 1.48 \times 10^{28} \text{ m}^{-3}$ at RT. In fact, this is a lot higher than expected based on the Zintl formalism.

While these high charge carrier concentrations could be partially explained by the existence of trivalent Yb in the phases, the large content of unidentified foreign phases prevented the confirmation of this conjecture via magnetic measurements. In addition to the low Seebeck coefficients, the samples' thermal conductivities proved to be rather high, with a minimal value of 4.1 W/mK for Yb₂SnGe₂ and 7.2 W/mK for Yb₂InGe₂. Even after subtracting the electronic contribution κ_{el} , the remaining phononic contribution κ_{ph} was still too high to draw any special interest in the material.

A low thermopower and a high thermal conductivity result in a very low figure of merit. Therefore, the highest determined ZT of Yb₂SnGe₂ is 0.0045, while the highest ZT of Yb₂InGe₂ is thought to be near 0.0036. Neither of these values comes close to the ZT of commercial TE materials, thus showing that there is no point in pursuing this class of materials for thermoelectrics any further.

Another member of the A₂M'M''₂ family is Sr₂PbGe₂. This compound was synthesised both in the cold boat and in a sealed Ta crucible, with similar results. Unfortunately, XRD measurements showed the secondary phase Pb and attempts to remove this phase by annealing the material proved to be unsuccessful.

A similar problem occurred during the preparation of Sm₄Bi₂Te, a rare-earth chalcopnictide, which crystallises in the anti-Th₃P₄ structure. Here, the synthesis in a sealed Ta crucible resulted in a mixture of Sm₄Bi₂Te and SmTe, almost in the ratio 1:1. The sample's quality could not be improved through annealing, suggesting that the formation of SmTe is energetically more favourable than the complete incorporation of the chalcogen into Sm₄Bi₂Te. There was an attempt to create a single-phase sample by using off-stoichiometric amounts of the starting materials, i.e. 4 Sm, 2.5 Bi and 0.5 Te, but the resulting material consisted mainly of SmBi. The synthesis of the less toxic Yb₄Sb₂S, which also crystallises in the anti-Th₃P₄

structure, seemed to result in a mixture of the three phases $\text{Yb}_4\text{Sb}_2\text{S}$, YbS and Yb_5Sb_3 , according to the XRD measurement. However, a conducted SEM/EDX analysis revealed only two phases, namely a $\text{Yb}_4\text{Sb}_{2.6}\text{S}_{0.4}$ matrix with YbS inclusions. The third phase, Yb_5Sb_3 , could not be found. After annealing, the XRD showed the phases Yb_4Sb_3 and YbS , which was in accordance with the SEM/EDX measurement. Here, the YbS also seemed to be embedded in a Yb_4Sb_3 matrix. Furthermore, there were microscopically small inclusions found, which were too small to be measured, but probably consisted of YbS as well. These results indicate complex thermal behaviour that requires deeper investigation.

Further attempts of charge carrier compensation consisted of a dual substitution by both S and Sm. A synthesis of the complex phase $\text{Yb}_{3.6}\text{Sm}_{0.4}\text{Sb}_{2.6}\text{S}_{0.4}$ resulted, according to EDX analysis, in the phases $\text{Yb}_{3.6}\text{Sm}_{0.5}\text{Sb}_{2.8}\text{S}_{0.1}$ and $\text{Yb}_{3.8}\text{Sm}_{0.3}\text{Sb}_{2.8}\text{S}_{0.1}$, depending on the material's position inside the crucible. Again, inclusions of YbS could be found. This suggests that Sb cannot be substituted with S by simply melting the compounds, because S tends to form inclusions instead.

Based on $\text{YbGa}_6\text{Te}_{10}$, a material, which shows exceptionally low thermal conductivity, an attempt was made to create the isostructural compound $\text{SmGa}_6\text{Te}_{10}$. The synthesis was carried out in a sealed Ta crucible at 1500 °C and resulted mainly in the phases GaTe and Ga_2Te_3 . No traces of Sm were found, leading to the explanation that Sm and Te had formed air-sensitive phases, which therefore could not be measured. Apparently, the material does not melt congruently, which makes melt synthesis rather difficult. Therefore, if one were to create this compound again, another method might have to be considered.

Most of these compounds were synthesised in a sealed Ta crucible. For this, a newly developed HF induction furnace was used. The start-up of this furnace was closely monitored and some initial problems, like the fogging up of the furnace chamber

or the collapsing of the susceptor, were resolved. Furthermore, calibration curves were taken, allowing for a good estimation of the relation between applied voltage and resulting temperature. Overall, this new method of synthesising volatile compounds proved to be successful.

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A. Fitting procedure of the electrical resistivity at low temperatures

The electrical resistivity ρ of Yb_2SnGe_2 and Yb_2InGe_2 was fitted in the temperature range 2 K - 300 K (Figure 5.14a) and 4 K - 300 K (Figure 5.15a). For this, the program *TableCurve 2D v5.1* was used, where one can write user defined functions (UDFs). The UDF used for fitting was adopted from [26] and is a combination of the Matthiessen rule (2.23) and the Bloch-Grüneisen law (2.24):

$$\rho(T) = \rho_0 + 4\mathcal{R} \left(\frac{T}{\Theta_D} \right)^5 \int_0^{\Theta_D/T} \frac{4x^5}{(e^x - 1)(1 - e^{-x})} dx \quad (\text{A.1})$$

with the residual resistivity ρ_0 , the electron-phonon interaction constant $\mathcal{R}$, the Debye temperature Θ_D and $x = \frac{\hbar\omega_q}{k_B T}$, with the phonon frequency ω_q .

The UDF itself is defined by the three fitting parameters #A1, #A2 and #A3:

$$\begin{aligned} \#F1 &= \#A0 + 4*\#A1*QIN(1,0.01,\#F2,12)/\#F2^5 \\ \#F2 &= \#A2/X \\ Y &= \#F1 \end{aligned}$$

with

$\$$... dummy variable of integration
 $\#F1$... integrand of the Bloch-Grüneisen law
 $\#F2$... $\frac{\Theta_D}{T}$
 X ... temperature T [K]
 Y ... electrical resistivity ρ [$\mu\Omega\text{cm}$]
 $\#A0$... residual resistivity ρ_0 [$\mu\Omega\text{cm}$]
 $\#A1$... electron-phonon interaction constant $\mathcal{R}$ [$\mu\Omega\text{cm}$]
 $\#A2$... Debye temperature Θ_D [K]

The resulting fitting parameters for Yb_2SnGe_2 and Yb_2InGe_2 can be found in Table A.1. By calculating $\frac{\mathcal{R}}{\Theta_D}$ one gets the slope of the linear equation $\rho(T) = \rho_0 + kT$. For Yb_2SnGe_2 this yields $k = 1.73 \mu\Omega\text{cm/K}$ and for Yb_2InGe_2 $k = 0.57 \mu\Omega\text{cm/K}$. Tables A.2 and A.3 compare the fitted values ρ_0 and k with the measured values determined in Section 5.3.1. As one can see, the values for Yb_2InGe_2 are quite similar, while there are distinct differences for Yb_2SnGe_2 . This shows, that Yb_2InGe_2 can be better described by the Bloch-Grüneisen model than Yb_2SnGe_2 .

	ρ_0 [$\mu\Omega\text{cm}$]	$\mathcal{R}$ [$\mu\Omega\text{cm}$]	Θ_D [K]
Yb_2SnGe_2	75.8187	210.0283	121.0747
Yb_2InGe_2	28.5046	93.5351	163.8729

Table A.1.: Fit parameters for Yb_2SnGe_2 and Yb_2InGe_2 .

Yb ₂ SnGe ₂	ρ_0 [$\mu\Omega\text{cm}$]	k [$\mu\Omega\text{cm/K}$]
measured values	74.68	1.69
fitted values	75.82	1.73

Table A.2.: Measured and fitted residual resistivity ρ_0 and slope of $\rho(T)$ for Yb₂SnGe₂.

Yb ₂ InGe ₂	ρ_0 [$\mu\Omega\text{cm}$]	k [$\mu\Omega\text{cm/K}$]
measured values	28.26	0.56
fitted values	28.50	0.57

Table A.3.: Measured and fitted residual resistivity ρ_0 and slope of $\rho(T)$ for Yb₂InGe₂.

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Monika Budnowski