Thermoelectric Transport and Microstructure of ZnSb

by

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Thesis submitted in partial fulfillment of the requirements
for the degree of Philosophiae Doctor

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University of Oslo
February 2016

Summary

Research in thermoelectrics has been intensively carried out in recent years, partly motivated by global energy and environmental management. Material improvement is essential for further development and a wider utilization of thermoelectrics. This PhD thesis focuses on the thermoelectric material ZnSb, which has among its advantages of high abundance, low toxicity and low cost compared to other thermoelectric materials. This three-year PhD work was built upon an understanding of semiconductor transport, and the investigation of thermoelectric properties of ZnSb has led to a deeper knowledge of thermoelectrics. The experiments have been designed for improving the thermoelectric transport properties and new knowledge and insight have been acquired.

Manuscript I

Impurity band conduction in the thermoelectric material ZnSb

Physica Scripta, T148 (2012) 014001

Bulk polycrystalline ZnSb samples were prepared and low-temperature electrical transport measurements (6 K to room temperature) were carried out. The data was interpreted in terms of the hole impurity band conduction: intrinsic acceptor defects creating bands that are conducting when there are also compensating donors. Modelling the transport revealed qualitatively good agreement. Quantitative differences were discussed in terms of the structure of the samples, which has been studied by using X-ray diffraction, scanning electron microscope and electron microprobe. The systematics of adding different amounts of Mn and Cr to ZnSb was studied and had the effect of varying the density of states in impurity bands and varying the hole concentrations. In Chapter 2 of this thesis there are some findings on impurity bands put further in context of thermoelectrics operated at elevated temperature.

Manuscript II

A study of transport properties in Cu and P doped ZnSb

Journal of Applied Physics, 117, 045709 (2015)

A study of adding Cu acceptors with and without P in ZnSb has been carried out. We varied the doping concentration and showed that the carrier concentration could be increased to an optimum value of $1.6 \times 10^{19} \text{ cm}^{-3}$ at room temperature. The relationship between the measured Seebeck coefficient *vs.* the carrier concentration (Pisarenko plot) at different temperatures did not follow the model of a single parabolic band except for carrier concentrations above $1 \times 10^{19} \text{ cm}^{-3}$. For lower carrier concentrations an impurity band model could fit the measurements well. For the samples containing both Cu and P,

the Pisarenko plot could either be modeled by single parabolic band models with different density of states effective mass at high and low carrier concentrations respectively or by impurity band models. Also some interesting anomalies were observed for Cu doping, such as a double hump in the Seebeck coefficient with temperature, hysteresis in temperature cycling, and sharp increase in thermal conductivity with Cu addition.

Manuscript III

Nanostructuring of Undoped ZnSb by Cryo-Milling

Journal of Electronic Materials, Vol. 44, No. 8, 2015

The most direct benefit of nanostructuring on thermoelectric devices is by introducing grain boundaries which increases phonon scattering. In this work we demonstrated reduction of the thermal conductivity by means of cryomilling. The samples were fabricated by different combinations of synthesis procedures. The optimum nanostructured ZnSb for reducing the thermal conductivity was achieved by milling at cryogenic temperature followed by rapid hot-pressing. The nanocomposition was investigated and confirmed by different techniques. The thermal conductivity was reduced a factor of two due to the increase of phonon scattering by adjusting the process conditions, and less than one third that was reported for single crystal ZnSb.

Manuscript IV

Enhancement of thermoelectric properties by energy filtering: Theoretical potential and experimental reality in nanostructured ZnSb

Journal of Applied Physics, 119, 125103 (2016)

Nanostructuring also offers other possibilities to affect the properties of the samples. One of them is energy filtering. In this work we tested a principally simple model for energy filtering. We calculated theoretically the transport coefficients of idealized ZnSb crystals. The temperature variation was calculated and compared to the experimental measurements. The best fit to experiments was found for a constant relaxation time and an energy barrier of 0.25 eV.

Manuscript V

Zn vacancy formation, Zn evaporation and decomposition of ZnSb at elevated temperatures:

Influence on the microstructure and the electrical properties

Journal of Alloys and Compounds, 710 (2017) 762-770

Zn has a high vapor pressure that results in a tendency of Zn loss during synthesis or high temperature measurements. It is believed that the tendency of ZnSb to be a p -type semiconductor is due to Zn vacancies that may be created during heat treatment. Experimental results related to solid solubility of vacancies and evaporation of Zn were presented in this work. We used a thermogravimetric method to estimate the enthalpy of vaporization of Zn and discussed the measured net increase in hole concentration for

undoped ZnSb after heat treatment in terms of Zn vacancies acting as acceptors. It was further discussed in Chapter 2 how the measured results can potentially have large impact on our understanding of temperature dependent measurements of transport coefficients in ZnSb and the high temperature operation of devices.

Manuscript VI

A study on S doped ZnSb

To be submitted

A thermoelectric module usually contains both n -type and p -type doped semiconductors. It is ideal to use the same semiconductor material, for the n - and p -type respectively, to minimize the thermal stress between the two legs. This work shows our attempt to synthesize n -type ZnSb by sulfur doping. There has not been any other study on S doping of ZnSb yet. As the element is in the same group as Te, which has been studied and showed temporary n -type conduction, we expected that S can act as a donor. We have used two different synthesis techniques. Direct solidification from the melt in one series yielded vastly non-uniform samples which were improved by ballmilling and hot-pressing in another series. However, no n -type conduction was observed in any of the series of samples with different S concentrations. This can be due to very low solubility of S, combined by the tendency for intrinsic defects in ZnSb, notably, Zn vacancies to be acceptors. Some interesting observations on the systematics in sign of temperature coefficient of mobility and resistivity were discussed.

Acknowledgments

First and foremost I would like to express my sincere and greatest gratitude to my main supervisor, Terje Finstad, who has been supportive since the day I began working on thermoelectrics as a MENA-master student 7 years ago. He offered me so much advice and patiently guided me on a path to grow from one who did not even know the "band gap" to one who today is equipped with knowledge and skills, and expertise in semiconductor physics and thermoelectrics. I am grateful for all his help.

This PhD thesis does not only represent my own work, but includes also contributions from many people. I would like to thank my co-workers in NanoThermo project, particularly Kjetil Valset who generously shared his knowledge and work, and provided interesting samples. Many from SINTEF deserve a call out and big thanks: Patrícia Carvalho who incites critical but valuable discussions; Joachim Graff who helped me with the cryomilling; Espen Flage-Larsen who read through my thesis and offered helpful suggestions and comments; and my co-supervisor Ole Martin Løvvik who has always been available and provided suggestions through my entire PhD period. I would also like to acknowledge Jeff Snyder at the California Institute of Technology for being part of the project as a collaborator, and thank him for his hospitality in my visiting period at the thermoelectric group at Caltech. My appreciate also goes to Jaya Nolt at University of California, Santa Barbara for helping the temperature scanning XRD measurements.

My special thanks to two persons who engaged themselves to ZnSb purely because of their scientific passions and interests: Matthias Schrade and Kristian Berland. Matthias has been a kind, fun and enthusiastic colleague and friend. A lot of experiments have been accomplished with his assistance, and several results can be credited to his strict and critical input. It was an amazing experience to work with Kristian. He sent about ten emails with intensive but fruitful discussions every night during the period we were working on the manuscript. It would not have gone so smooth without his intensity and efficiency.

A big hug to the folks in BATE (The Basic and Applied ThermoElectrics initiative) and Structure Physics group: Øystein, Mauro, Cecilie, Asbjørn, Simen, Andrey, Wei, Lars, Adrian who offered so many joyful out-of-office moments in Friday-beer, hiking trip, sommerpark, *etc.*. It was wonderful to be part of the company. Ole Bjørn Karlsen deserves an individual thank you for his initial help and fantastic ideas in many scientific and non-scientific activities; an appreciation goes to Anette Gunnæs for enrolling me in the MENA-program in the first place so that I could be in this journey thereafter and for continuously

supporting and hosting me in Structure Physics; I am so grateful to Johan Taftø who put a firm faith in me so that I can start a PhD program and continue my interest and research. Moreover, I am also thankful to the neighbor group Solid State Electrochemistry (FASE) who has been supportive to many of the instruments and facilities.

To my dearest friends who made my life easy and make me feel like home in Norway: Marit Grøvdal, Manolis Platakis, Elizabeth and Ireneusz (and little Alexander) Underdal, you are just amazing. I give a heartfelt thank you to Evangelos Tasoulas, who has lightened my life up and has always been a truly trusting friend keeping me cheerful company for many years.

A great gratitude hereby is dedicated to my mother who have raised me up, taught me values and given her fully understanding for pursuing my dream.

I would like to thank the University of Oslo and Centre for Materials Science and Nanotechnology for being the platform for my studies and research, as well as the Norwegian Research Council for funding my project. I am thankful for the Kristine Bonnevie stipend which supported my stay at Caltech; Norwegian PhD Network on Nanotechnology for Microsystems for funding me to attend several conferences; and NorFab for offering the long term financial support enabling me to work at UiO MiNaLab.

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Preface

We live in a world that has a huge demand for energy. In past decades, we have become increasingly aware of the energy shortage as well as the impact of the greenhouse effect. To cope with the predicted energy- and associated climate- crisis, many different technologies for energy generation and storage have been developed, for instance nuclear-, hydro-, natural gas- and biofuel- power generation. These technologies can provide sustainable energy for the daily needs of our society, such as transport, industrial activities and residential requirements. The need for many systems to reject heat as a byproduct of their operation is fundamental to the laws of thermodynamics and reports on the efficiency of the energy management are alarming. Fig. 1 shows an example in the USA that more than half of the total managed energy was wasted since the 1970s [1]. In addition, the trend is predicted to remain in the coming years. Significant measures have to be taken to change these trends and explore the strategies for better energy management.

One promising alternative to avoid a large energy crisis is to combine different energy technologies and utilize the waste heat, thus enhancing the available output and exploitation efficiency. For example rejected heat in one process can be utilized by another. Rankine steam engine and turbo steam engines are among the most efficient energy conversion devices, converting heat into mechanical energy or into electrical energy. Successful use of these engines into automobiles to improve the overall efficiency has been reported [2]. Thermoelectric converters are competing against these machines for the same type of applications, and have some advantages such as flexibility (scalability and compactness), environmental friendliness (recycling waste heat and low carbon), human friendliness (no noise and toxicity), no moving parts (less wear). Thermoelectric devices could play an important role in the global energy management and climate crisis prevention if more efficient thermoelectric materials can be developed. Transporta-

Fig. 1.: Share of useful energy and waste heat in the USA since the 1970s. Data from Lawrence Livermore National Laboratory.

tion industry in general has the potential to become a large market for thermoelectric generators. Nevertheless, there are many other applications of thermoelectric materials. Thermoelectric modules have been simply installed on stoves for remote-area power supply [3]. The development of nanotechnology allows thermoelectric modules to become thinner and smaller for different medical use cases, such as pacemakers or wearable devices [4]. Thin film thermoelectric refrigerators (Peltier coolers) have been manufactured by screen-printing techniques on PCB boards or IC chips for removal of excess heat to improve electronics device performance [5,6]. Large scale usage, such as underwater thermoelectric power plants that generate electricity by the temperature gradient of ocean water at different depths, has been proposed and embedded in modern global energy management [7].

Fig. 2.: Timeline of development of thermoelectrics.

The discovery of thermoelectric phenomena can be traced back 200 years. In 1820s Thomas Johann Seebeck observed the deflection of a compass when heating a nearby junction between two metals. However, he at first misinterpreted the observation as due to the thermomagnetism. This was refuted by many who had followed Hans Christian Ørsted's work on induction, and it was soon acknowledged by the scientific community that Seebeck's observation was due to current generated in response to a temperature gradient and the word *thermoelectrics* was born. Seebeck studied a series of alloys with high thermoelectric activities, including Zn-Sb, the material studied in this thesis [8–10]. In 1834, Jean Charles Athanase Peltier found that heat was absorbed or emitted at the junction of two dissimilar metals when the current passed through [11]. This observation was confirmed by the Russian physicist Heinrich Emil Lenz in 1838, who froze a droplet of water by Peltier cooling. In 1851 Gustav Magnus discovered the independency between the Seebeck voltage and the distribution of temperature along the metals, indicating that the thermopower is a thermo-

dynamic state function, which built the physical basis for a thermocouple. Twenty years later, William Thomson (also known as Lord Kelvin) described the thermodynamic inter-relationship between the Seebeck and Peltier effects: heat was absorbed or emitted when current flows in a material with a temperature gradient, and the heat was proportional to both the electrical current and the temperature gradient.

In the middle of the last century, the study of semiconductors brought about a revolution to thermoelectrics. In 1949, Abram Fedorovich Ioffe proposed a parameter called thermoelectric figure of merit, which tied semiconductor physics to the thermoelectric performance [12]. The dimensionless figure of merit zT reveals the balance between the electrical and thermal properties of the materials, offering a measure of the thermoelectric efficiency and performance. Fig. 3 lists the development of some thermoelectric materials since the 1940s [13]. The progress on semiconductor physics brought zT up to 1, which is considered as a feasible thermoelectric performance measure and often serves as a go/no-go criterion for the development of high performance thermoelectric modules. Into the 21st century, the research on thermoelectrics has integrated quantum physics and nanotechnology. With the superlattices structure, for instance in Bi_2Te_3 , the figure of merit zT can be doubled compared to the bulk materials.

This PhD thesis is dedicated to a narrow gap semiconductor, ZnSb . The elements are non-toxic, cheap, and abundant, which contributed to the choice. This thesis is conducted at the University of Oslo and in collaboration with SINTEF. Some experiments were done at the California Institute of Technology during a three-month visit. The thesis is organized as follows: Chapter 1 covers the physics behind the thermoelectric phenomena. Two approaches are introduced: the Boltzmann transport equations and

the Landauer approach. The strategies to improve thermoelectric materials are also pinpointed. Chapter 2 reviews the material ZnSb . Much of the relevant knowledge from past research is systematized including discussions on the aspects of crystal structure, electronic structure, electrical properties, doping effects, intrinsic defects and impurity band conduction. Since the experimental methods used in this PhD thesis are included in each manuscript, Chapter 3 briefly summarizes the different techniques, rather than providing an in-depth explanation of each method. Chapter 4 summarizes a list of manuscripts in chronological order and some conclusions and notes on future work are presented in

Fig. 3.: Development of mainstream thermoelectric materials since the 1940s. [13]

Chapter 5. Moreover, Appendix A is written as a mini manuscript and document a few experiments on hysteresis in conductivity with thermal cyclings as well as characterization of oxygen in one ZnSb sample.

There are still a lot of mysteries and nuances in the ZnSb system that I was not able to solve. One may not be able to solve them in a short time. However, I believe the ZnSb system still has remaining unexploited potential. I wish my research work contributes to understanding of thermoelectric materials, particularly the ZnSb system. And I wish the reader can find the charm of this particular material ZnSb via this thesis.

February 2016, Oslo

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1. Introduction to thermoelectric transport

The purpose of this chapter is to provide an understanding of thermoelectric phenomena. Starting with an introduction to the thermoelectric transport coefficients, the theories for calculating these coefficients are briefly described via two approaches: Boltzmann transport equation and Landauer formalism, each offering a different avenue, but a consistent physical scheme. The following section discusses the interaction between the transport coefficients, and pinpoints some keys of how to improve the thermoelectric performance.

1.1. Phenomenological introduction to thermoelectrics

Thermoelectric phenomena include charge flow induced by a temperature gradient, or vice versa. The flow of charge and heat are given by the transport coefficients which can be measured. When there is neither a temperature gradient nor a carrier concentration gradient, the electrical current density, J , for a particular material is characterized by the transport coefficient, σ , called the electrical conductivity. It is given by

$$J = \sigma \cdot \mathcal{E}, \quad (1.1)$$

where $\mathcal{E}$ is the electrical field. This is the intensive form of Ohm's law.

The most well-known thermoelectric transport coefficient is the Seebeck coefficient, α , defined by

$$\alpha = \frac{\Delta V}{\Delta T}, \quad (1.2)$$

where ΔV is the voltage that is developed in the presence of a temperature gradient ΔT along a sample. The process is referred to as the Seebeck effect.

A related effect is the Peltier effect. If an electrical current passes through a material, the material absorbs heat at one end and emits heat at another end. The direction of the heat flow can be reversed by reversing the current direction. This effect is associated with the

Peltier transport coefficient, Π , defined phenomenologically by

$$\Pi = \frac{J_Q}{J}, \quad (1.3)$$

where J_Q is the heat current density and J is the electrical current density. The Seebeck coefficient and the Peltier coefficient are related to each other because the heat flux and the charge carrier flux are coupled, thus the Onsager relationships apply for the transport coefficients. The two coefficients are related by the Kelvin relation

$$\Pi = \alpha T. \quad (1.4)$$

The third thermoelectric transport coefficient is the Thomson coefficient, β , defined by the Thomson effect: heat is absorbed or emitted when an electrical current flows in a material with a temperature gradient; the heat current can be positive or negative and is linear in the electrical current and the temperature gradient such that

$$J_Q = -\beta \cdot J \cdot \nabla T. \quad (1.5)$$

This turns out to be small and is often ignored. However, for a large ΔT , it becomes important. It is related to the Seebeck coefficient through

$$\beta = T \frac{\partial \alpha}{\partial T}. \quad (1.6)$$

1.2. Theories for thermoelectric transport coefficients

The thermoelectric transport coefficients can be measured and also be estimated from specific idealized situations. The most common theoretical calculation strategies today are using the first principle calculations for the density of electron- and phonon- quantum states. They are combined with the semiclassical Boltzmann transport equations (BTE) for charge carrier transport, and classical molecular dynamics simulations combined with quantum non-equilibrium Green's functions. These fundamental approaches are described in textbooks and several review articles [14–16]. Recently there has also been an initiative to introduce the Landauer formalism to thermoelectric transport. The Landauer formalism was launched in the 1950s [17] and has been proved to be fruitful for modeling nanoscale electronic devices [18–21]. It has been shown that this approach can yield similar or identical expressions for the thermoelectric transport coefficients as the BTE approach does, and its derivation is easy to grasp. Some find it is appealing and having a good pedagogical value. For the interested readers, a thorough introduction and rigid justification can be sought in the textbooks [20–22].

1.2.1. Boltzmann Transport Equations (BTE) for transport coefficients

The Boltzmann transport equation [23]

$$\frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} \Big|_{\text{diffusion}} + \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} \Big|_{\text{fields}} + \frac{\partial f(\vec{r}, \vec{k}, t)}{\partial t} \Big|_{\text{collisions}} = 0, \quad (1.7)$$

expresses that in steady states there is no net change in the distribution function $f(\vec{r}, \vec{k}, t)$, thus giving the probability for occupancy of an electron state wavevector $\vec{k}$ at position $\vec{r}$ at time t . The thermoelectric transport coefficients can be obtained by solving BTE in the relaxation time approximation to find the electron distribution function $f(\vec{r}, \vec{k}, t)$ for non-equilibrium conditions by series expansion of f around f_0 , the Fermi-Dirac equilibrium distribution, which is given by

$$f_0(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}}, \quad (1.8)$$

where E_F is the Fermi level which is the same as the electrochemical potential μ_0 . Each coefficient that was found in this way expressed in the following while the details can be sought into Ref. [23].

Electrical conductivity

Using BTE, the electrical conductivity can be derived as the ratio between the current density and the electrical field, giving

$$\overleftrightarrow{\sigma} = \frac{q^2}{4\pi^3} \int \tau \vec{v} \otimes \vec{v} \left(-\frac{\partial f_0}{\partial E} \right) d^3 k, \quad (1.9)$$

where $\overleftrightarrow{\sigma}$ is a symmetric second rank tensor ($\sigma_{ij} = \sigma_{ji}$). Here q is the elementary charge, $\vec{v}$ is the group velocity associated with state $\vec{k}$, which can be found from the slope of the dispersion relation $E(\vec{k})$ at $\vec{k}$, τ is the relaxation time and the volume element in k -space $\int d^3 k = \int_0^\infty 2\pi \left(\frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$ for a parabolic energy band.

For a semiconductor with a single parabolic energy band with an energy independent relaxation time, and when $E - E_F \gg k_B T$, the electrical conductivity can be written as

$$\sigma = qn \left(\frac{q\tau}{m^*} \right) = qn\mu, \quad (1.10)$$

where $\mu = \frac{q\tau}{m^*}$ is the charge carrier mobility, and m^* is the density of states effective mass. Here, Eq. (1.10) has been brought into the form derived from the simple Drude model of conduction.

Seebeck coefficient

The Seebeck coefficient obtained from Eq. (1.3), Eq. (1.4) and BTE with a temperature gradient is

$$\alpha = \frac{1}{qT} \frac{\int \tau \vec{v} \otimes \vec{v} (E - E_F) \left(-\frac{\partial f_0}{\partial E}\right) d^3k}{\int \tau \vec{v} \otimes \vec{v} \left(-\frac{\partial f_0}{\partial E}\right) d^3k}. \quad (1.11)$$

For the case of the energy dependent relaxation time, the Seebeck coefficient for a non-degenerate n -type semiconductor can be calculated from Eq. (1.11) [14], giving

$$\alpha = -\frac{k_B}{q} \left[\eta - \left(r + \frac{5}{2} \right) \right]. \quad (1.12)$$

η is the reduced Fermi energy, here written out for an n -type semiconductor $\eta = \frac{E_C - E_F}{kT}$; E_C is the energy at conduction band onset, and r is the scattering factor that defines the energy dependent relaxation time via $\tau = \tau_0 E^r$, and r equals to $-1/2$, 0 , $1/2$, and $3/2$ for the scattering from acoustic lattice vibrations, neutral impurity atoms, strongly screened impurity atoms and ionized weakly screened impurity atoms, respectively [24]. From Eq. (1.12) we readily see the important trend that α will decrease with increasing doping concentration, when the Fermi level comes closer to the conduction band edge. The sign of the Seebeck coefficient is sensitive to the carrier type. For the presented n -type case the Seebeck coefficient is negative, while for a p -type semiconductor with hole carriers, Eq. (1.12) will have a positive sign.

For a highly degenerate semiconductor or a metal, Eq. (1.11) can be calculated by assuming a parabolic band, energy-independent scattering and approximations from the Drude-Sommerfeld electron gas model. The resulting expression for the Seebeck coefficient can be written as the form of Mott relation [25, 26]

$$\alpha = \frac{8\pi^2 k_B^2}{3qh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}}. \quad (1.13)$$

Thermal conductivity

The thermal conductivity of thermoelectric materials, κ , has two contributions [23]

$$\kappa = \kappa_e + \kappa_{ph}. \quad (1.14)$$

Here, κ_e is called the electron thermal conductivity and κ_{ph} is called the lattice thermal conductivity. κ_e is due to a charge carrier flux and κ_{ph} is due to a phonon flux through

the lattice. The thermal conductivity from the charge carrier flux is given by

$$\begin{aligned} \overleftrightarrow{\kappa}_e = & \frac{1}{4\pi^3 T} \int \tau \vec{v} \otimes \vec{v} (E - E_F)^2 \left(-\frac{\partial f_0}{\partial E}\right) d^3 k \\ & - \frac{1}{q} \left(\frac{q}{4\pi^3 T}\right)^2 \frac{[\int \tau \vec{v} \otimes \vec{v} (E - E_F) \left(-\frac{\partial f_0}{\partial E}\right) d^3 k]^2}{\frac{q^2}{4\pi^3} \int \tau \vec{v} \otimes \vec{v} \left(-\frac{\partial f_0}{\partial E}\right) d^3 k}. \end{aligned} \quad (1.15)$$

In the absence of an electric field, we can drop the second term. Then the electron thermal conductivity of a non-degenerate semiconductor can be calculated by replacing $E - E_F$ by E since only electrons in the conduction band can conduct heat, giving

$$\overleftrightarrow{\kappa}_e = \frac{1}{4\pi^3 T} \int \tau \vec{v} \otimes \vec{v} E^2 \left(-\frac{\partial f_0}{\partial E}\right) d^3 k \quad (1.16)$$

For a degenerate semiconductor or a metal with a spherical Fermi surface, the electron thermal conductivity can be written as

$$\kappa_e = \frac{1}{3q^2} \pi^2 k_B^2 \sigma T = \sigma \mathcal{L} T, \quad (1.17)$$

where $\mathcal{L}$ is the Lorenz number, which is often taken as a constant. It is usual to write κ_e as the last part of Eq. (1.17). In different materials, the relationship between σ and κ_e is different. Then it is better to call $\mathcal{L}$ the Lorenz coefficient, or Lorenz factor, which in general depends upon the material, the scattering mechanisms, the doping concentration and the temperature [27]. An accurate value for the Lorenz factor $\mathcal{L}$ is needed if κ_e is directly calculated from measured values of σ via the Wiedemann–Franz law

$$\kappa_{ph} = \kappa - \kappa_e = \kappa - \sigma \mathcal{L} T. \quad (1.18)$$

1.2.2. Landauer approach for charge flow

The so-called Landauer approach was successful first for describing the transport in nanostructured devices where the transport through the material could be ballistic (no collisions in the material) or via tunneling. One is then considering a system that consists of contacts on each side. The contacts act as large reservoirs of electrons that are in local equilibrium and the energy distribution of electrons is given by the Fermi-Dirac distribution function with a local electrochemical potential, which is the same as the Fermi level. The "material" between the contacts is simply considered as transport channels. Therefore, the current through the channel at energy E simply related to (i) the difference between the quasi-Fermi functions at both ends, $f_1 - f_2$; (ii) the conductance function, $G(E)$, whose average around the Fermi level gives the conductance of a material. Integrating over all transport channels, the current is given by [21, 22]

$$I = \frac{1}{q} \int G(E) (f_1 - f_2) dE. \quad (1.19)$$

Carrier flux under a small bias

When a small bias is applied while keeping a constant temperature along the channels, the quasi-Fermi level of the negative "-" end E_{F1} will be pulled higher, and the one at the positive "+" end E_{F2} will be pushed lower, as shown in Fig. 1.1. The electrons will move from high occupancy to low occupancy, which gives rise to a net charge flow.

Fig. 1.1.: Illustration of *Ohmic conductance* driven by a small bias. E_{F0} is the equilibrium Fermi level at room temperature in the material, E_F , E_{F1} and E_{F2} , respectively, are the quasi-Fermi level in the material and at each end. The difference of quasi-Fermi level at each end is the driving force for the carrier flux. Only the charge carriers between f_1 and f_2 participate in the transport. Note that in the basic Landauer model, the medium between contacts is just channels for transport at constant energy, while this drawing approximates how the conduction band and valence band will vary for a real situation.

The difference between Fermi functions can be linearized in $f_1 - f_2 \approx (-\frac{\partial f_0}{\partial E})(E_{F1} - E_{F2})$ when $\Delta T = 0$. And the net flow is driven by the small bias ΔV , giving rise to a potential energy difference $q\Delta V = E_{F1} - E_{F2}$. Therefore Eq. (1.19) can be written as [21, 22]

$$I = \frac{1}{q} \int G(E) \left(-\frac{\partial f_0}{\partial E}\right) dE \cdot q\Delta V = G\Delta V, \quad (1.20)$$

which is essentially Ohm's law. Further on in the chapter we may refer to this conductance as *Ohmic conductance*; it is characterized by the current being driven by a voltage difference $G_\Omega = I_\Omega/\Delta V$. G_Ω is the integral of the conductance function, G , as expressed by Eq. (1.20), written as [21, 22]

$$G_\Omega = \int_{-\infty}^{+\infty} G(E) \left(-\frac{\partial f_0}{\partial E}\right) dE = \frac{2q^2}{h} \int T(E) M(E) \left(-\frac{\partial f_0}{\partial E}\right) dE. \quad (1.21)$$

Here $T(E)$ is the transmission of electrons passing through the channels. In ballistic transport, $T(E) = 1$ (meaning perfect transmission, no scattering). In diffusive transport where the elastic scattering occurs, the quasi-Fermi level will vary continuously between the contacts and one needs to consider the velocity of the charge carriers. Then the transmission can be generalized into multichannel conductance formula [18, 28]. $M(E)$

is the number of channels with energy E and it is proportional to the density of states, $D(E)$, times the average group velocity in the current direction. For simplicity we here neglect the details of $T(E)$ and $M(E)$ and only leave some important dominating energy dependencies in the integrand of Eq. (1.21). Thus for ballistic transport, we can write Eq. (1.21) schematically:

$$G_{\Omega} \propto \int D(E) \left(-\frac{\partial f_0}{\partial E} \right) dE. \quad (1.22)$$

Under a small bias, the net charge carrier flux only has contributions between f_1 and f_2 , which means it is close to the Fermi level, as shown in Fig. 1.1.

Carrier flux under temperature gradient

Fig. 1.2 illustrates the Fermi distribution functions $f_1(E)$ and $f_2(E)$ in the hot and cold ends on each side of a semiconductor under open circuit conditions. Unlike for *Ohmic conduction* the shapes of the Fermi functions are different, being more smeared out in the hot end. For a small temperature gradient ΔT , the linearization of $f_1 - f_2$ gives $f_1 - f_2 = \left(-\frac{\partial f_0}{\partial E} \right) \left(\frac{E - E_F}{T} \right) (T_2 - T_1)$. If we only consider the charge current that is driven by the temperature gradient in an open circuit, no net current will flow because a voltage will develop to cancel any current driven by a temperature gradient. If we short circuit the contacts, then the voltage between the contacts is zero and a net electrical current is flowing. Under closed circuit conditions with a temperature gradient, Eq. (1.19) can be written as

$$I = \frac{1}{q} \int [G(E) \left(\frac{E - E_F}{T} \right) \left(-\frac{\partial f_0}{\partial E} \right) dE] \cdot \Delta T = G_S \Delta T, \quad (1.23)$$

where G_S is sometimes called the Soret coefficient. And in this thesis we call it *Seebeck conductance*. In a similar schematic fashion applied in writing Eq. (1.22), we apply the same to Eq. (1.23) and get

$$G_S \propto \int \left(\frac{E - E_F}{qT} \right) D(E) \left(-\frac{\partial f_0}{\partial E} \right) dE. \quad (1.24)$$

Figs. 1.2 (i) – (iii) illustrate the charge flows due to a temperature gradient in the case of a semiconductor with different doping concentrations: intrinsic, lightly doped and heavily doped cases. For the purpose of illustration, the right contact is set to room temperature (low temperature, LT) and the left contact has a few thousands Kelvin (high temperature, HT), while our rigid assumption is still based on a small temperature gradient.

(i) Intrinsic semiconductor

In an intrinsic semiconductor, the concentration of electrons and holes are equal, and the Fermi level is located close to the middle of the band gap (small deviation if the density of states effective mass for electrons is different than that for holes). Therefore, the

Fig. 1.2.: Illustration of *Seebeck conductance* with a driving force ΔT while $\Delta V = 0$. CB and VB are the edge of the conduction band and the valence band, respectively. (i) Intrinsic semiconductor: The *Seebeck conductance* is very small due to canceled carrier flux contributions from holes and electrons. (ii) Lightly doped n -type semiconductor: the quasi-Fermi level E_F is close to CB. The carrier flux flows from high occupancy to low occupancy in both directions depends on the sign of $\frac{\partial f_0}{\partial E_F}$. The most of electrons that participate in transport are in the conduction band, yielding a larger net charge flux; (iii) Heavily doped n -type semiconductor: E_F is located inside of conduction band. The *Seebeck conductance* is inhibited due to both directions of the charge flux are in the conduction band.

electrical current contributions tend to cancel each other, resulting in a very small *Seebeck conductance*, as shown in Fig. 1.2 (i).

(ii) Lightly doped semiconductor

A lightly doped semiconductor is usually non-degenerate. In the case of an n -type semiconductor, the Fermi level is close to the conduction band. The *Seebeck conductance* is larger than that for the intrinsic case because the asymmetry in the contribution from holes and electrons due to the factor $\int (E - E_F) dE$ in Eq. (1.24), as shown in Fig. 1.2 (ii).

(iii) *Heavily doped semiconductor*

A heavily doped semiconductor is often degenerate. In the case of n -type semiconductor, the Fermi level is located in the conduction band, as for a metal. The *Seebeck conduction* becomes small because the factor $\int (E - E_F) dE$ is small, giving rise to contributions of different sign to the current for states above and below the E_F respectively. The situation is sketched Fig. 1.2 (iii).

Total charge flow

With both a potential-, ΔV , and a temperature-, ΔT , difference as driving forces, the total current consists of both *Ohmic conductance* (Eq. (1.20)) and *Seebeck conductance* (Eq. (1.23)), giving:

$$I_{total} = G_{\Omega} \Delta V + G_S \Delta T, \quad (1.25)$$

In most experiments the voltage is directly measured. It is then convenient to write Eq. (1.25) as

$$\Delta V = \frac{I}{G_{\Omega}} - \frac{G_S}{G_{\Omega}} \Delta T. \quad (1.26)$$

In the absence of a temperature gradient ($\Delta T = 0$), Eq. (1.26) is just the Ohm's law. In an open circuit (no current flow, $I = 0$) with a temperature gradient, the Seebeck coefficient α can be derived from Eq. (1.26)

$$\frac{\Delta V}{\Delta T} = -\frac{G_S}{G_{\Omega}} = \alpha. \quad (1.27)$$

Note that Eq. (1.27) leads the same result of the Seebeck coefficient from Boltzmann transport in Eq. (1.11). The sign of the Seebeck coefficient is dependent upon the polarity of the majority carrier flux. A measurement of the sign of the Seebeck coefficient is thus made in the standard "hot-probe-test" to determine if a sample is n -type or p -type.

Heat flux

The Peltier coefficient has been introduced by Eq. (1.3). The premise for the Kelvin relation (Eq. (1.4)) shows that the heat flux and the charge carrier flux are coupled. For each energy channel the conductance function is $G(E)$, which is defined by Eq. (1.19). We can replace the charge in Eq. (1.19) by the thermal energy $E - E_F$ to get the heat flux, yielding the heat current I_Q .

$$I_Q = \frac{1}{q} \int \left(\frac{E - E_F}{q} \right) G(E) (f_1 - f_2) dE. \quad (1.28)$$

The electrical current has ΔV and ΔT as driving forces. The same applies for the heat current and similarly to Eq. (1.25), we have the heat current:

$$I_Q = G_P \Delta V + G_Q \Delta T \quad (1.29)$$

$$= \int_{-\infty}^{+\infty} G(E) \frac{E - E_F}{q} \left(-\frac{\partial f_0}{\partial E} \right) dE \cdot \Delta V + \int_{-\infty}^{+\infty} G(E) \frac{(E - E_F)^2}{q^2 T} \left(-\frac{\partial f_0}{\partial E} \right) dE \cdot \Delta T. \quad (1.30)$$

Inserting Eq. (1.26) into Eq. (1.29), the heat current becomes

$$I_Q = \frac{G_P}{G_\Omega} I + \left(G_Q - \frac{G_P G_S}{G_\Omega} \right) \Delta T, \quad (1.31)$$

where G_P is the Peltier heat conduction. Applying the adiabatic approximation, i.e. set the second term in Eq. (1.31) to zero, we get the Peltier coefficient, Π ,

$$\frac{I_Q}{I} = \frac{G_P}{G_\Omega} = \int \frac{E - E_F}{q} = \Pi. \quad (1.32)$$

Eq. (1.27) and Eq. (1.32) form the Kelvin relation, which is the same as Eq. (1.4)

$$\frac{G_P}{G_\Omega} = \frac{G_S}{G_\Omega} T \implies \Pi = \alpha T. \quad (1.33)$$

Fig. 1.3.: Peltier effect. In the case of an n -type semiconductor, E_{C1} and E_{C2} are the onsets of the conduction band at each end. Electrons absorb $E_{C1} - E_{F1} + \delta$ amount of heat from the left contact in order to enter the conduction band and release $E_{C2} - E_{F2} + \delta$ amount of heat at the right contact to be thermally equilibrated.

One can also illustrate the Peltier effect for an average charge carrier as in Fig. 1.3. An average electron will absorb the energy $E_{C1} - E_{F1} + \delta$ in order to enter the conduction band of n -type semiconductor from the left contact. The average energy in the semiconductor is δ above E_{C1} . The value of δ is of the order of $2k_B T$ but depends on the band structure and the scattering processes. When the average electrons has been transported across the material they will give away energy from $E_{C2} + \delta$ to E_{F2} , in the form of heat, in

order to be thermally equilibrated. If one considers open circuit conditions, then no net current is flowing. From the previous treatment this occurs when $f_1 - f_2 = 0$. Stating that it is equally probable for an average electron in the left contact to acquire the energy $E_{C1} + \delta - E_{F1}$, as it is that an electron in the right contact to release that energy. Setting $f_1 = f_2$ means setting $f_1(E_{C1} + \delta) = f_2(E_{C2} + \delta)$. We introduce $q\Delta V = E_{F1} - E_{F2}$, and solve for ΔV , which yields

$$\Delta V = -\alpha_n \Delta T, \quad (1.34)$$

$$\alpha_n = -\frac{E_{C1} + \delta - E_{F1}}{qT_1}. \quad (1.35)$$

This is an expression for the Seebeck coefficient and is equivalent to that obtained in Eq. (1.11) by integrating Fermi integrals for a parabolic band.

Thermal conductivity

The term $G_Q - \frac{G_P G_S}{G_\Omega}$ in Eq. (1.31) is the heat current conductance under short circuit ($V=0$) conditions. Under a steady flow conditions, the flux of electrons into the semiconductor material is considered to be equal to the flux of electrons out, but the heat absorbed by each electron is not the same as the heat released. (This applies to each electron, as well as to the average electrons.) Therefore, the net heat $G_Q - \frac{G_P G_S}{G_\Omega}$ always contributes to the thermal conduction κ_e .

1.3. Thermoelectric efficiency

A conventional configuration for a thermoelectric device, often called thermoelectric module, consists of n -type and p -type bar-shaped elements. They are connected thermally in parallel, and electrically in series. The coefficient of performance (COP) for a thermoelectric generator is [29]

$$\eta_{COP} = \left(\frac{T_H - T_C}{T_H}\right) \left(\frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}\right), \quad (1.36)$$

where T_H and T_C are the temperature at hot and cold reservoirs, respectively. The efficiency of thermoelectric device is fundamentally limited by the Carnot efficiency and depends on the dimensionless figure of merit

Fig. 1.4.: Optimum thermoelectric efficiency as a function of ZT . At a given temperature, the higher the figure of merit ZT , the higher the efficiency [29].

ZT . The optimum efficiency as a function of ZT is plotted in Fig. 1.4. At a given temperature, the higher the ZT , the higher the efficient. Here, ZT is for a pair of n - and p -type thermoelectric materials. For an individual material, the figure of merit reduces to zT . It shows the correlations between material's intrinsic parameters and limites, written as a combination of the thermoelectric transport coefficients:

$$zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T. \quad (1.37)$$

It is governed by the Seebeck coefficient α which qualitatively is the key to generating electrical power from a temperature gradient, the electrical conductivity σ which expresses the material's ability to have a flow of carriers while generating a minimum of Joule heat, and the thermal conductivity κ which expresses the ability to maintain a large temperature gradient along the material. The product $\alpha^2 \sigma$ is termed the thermoelectric power factor.

1.4. Strategies to enhance the thermoelectric properties

The present section will introduce some of the strategies to improve the thermoelectric performance considering the interactions between the thermoelectric coefficients. These considers enhanced performance of a given material, such as the ZnSb presented in manuscripts of this PhD thesis, as well as selection or even design of improved thermoelectrics.

1.4.1. Carrier concentration

We have demonstrated the two types of carriers: electrons in the conduction band and holes in the valence band in Fig. 1.2. This becomes significant at high temperature when the semiconductor enters the intrinsic zone, where both electrons and holes participate in the transport. Thus the Seebeck coefficient is weighted by both types of carriers:

$$\alpha = \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\sigma_n + \sigma_p}, \quad (1.38)$$

where n and p refer to electron and hole, respectively. Mix of electrons and holes will lead to both charge carriers moving to the cold end, canceling the induced Seebeck voltage. The total Seebeck coefficient becomes smaller at high temperature due to the partial Seebeck coefficient for electrons and holes have opposite sign. It is also worth mentioning that one can have considerable so-called bipolar effects similar to that in bipolar transistors under heavy injection due to the coupling of electron and hole fluxes. To ensure a large Seebeck coefficient, one would preferably select a material that has a single type of carrier. Having the Fermi level close to the band edge can minimize the effect of minority carriers at the maximum temperature.

The competition between the Seebeck coefficient and the electrical conductivity can be illustrated from Eq. (1.10) (the electrical conductivity) and Eq. (1.11) (the Seebeck coefficient). The electrical conductivity becomes directly proportional to the carrier concentration n while the Seebeck coefficient α is proportional to the $n^{-2/3}$ [31]. This competition is schematically shown by the Seebeck coefficient and the electrical conductivity as a function of the doping concentration n in Fig. 1.5. Since these coefficients have opposite dependency on n , the maximum of the power factor, $\alpha^2\sigma$, will occur at some particular value for n . The peak typically occurs for a carrier concentrations between 10^{19} and 10^{21} cm^{-3} (depending on the material system), which indicates the Fermi level of the material will be at or near the band edge.

A good thermoelectric material requires a narrow distribution of energy for the carriers [32]. To a large extent it is the effect of the integrand of the transport parameters $(-\frac{\partial f_0}{\partial E})$ and $(E - E_F)(-\frac{\partial f_0}{\partial E})$, that gives the optimum carrier concentration since the Fermi level is influenced by the doping concentration.

In this thesis, *manuscripts 4.1, 4.2, 4.5 and 4.6* deal with the study of self-doping by vacancies and effect of external dopant element, such as Cu and S, from concentration of $\sim 10^{17}$ to $\sim 10^{19} \text{ cm}^{-3}$ on the thermoelectric material ZnSb.

1.4.2. Band gap and the effective mass

For a material with good thermoelectric performance, a relative narrow band gap semiconductor has proven to be preferable. A wide band gap semiconductor usually yields low mobility and high thermal conductivity, albeit a very large Seebeck coefficient. However, a very small gap will also enhance the bipolar effect due to the concurrent electron and hole fluxes, thus minifying the Seebeck coefficient at elevated temperature. The band gap E_g between $6k_B T$ to $10k_B T$ has been stated to be favorable for high zT [33–35]. Fig. 1.6 shows the maximum of zT as a function of band gap in the unit of $k_B T$ [36]. One can

Fig. 1.5.: Correlations between the thermoelectric transport coefficients as a function of carrier concentration. The competition between Seebeck coefficient and the electrical conductivity yields a maximum value for the power factor, $\alpha^2\sigma$, at a particular carrier concentration, n , when E_F is close to the band edge. For an insulator, the Seebeck coefficient is relatively large while the electrical conductivity is infinitely small and vice versa in the metal. The electron thermal conductivity increases with the electrical conductivity while the lattice thermal conductivity is often assumed to be constant [30]. The figure of merit, zT is not drawn but will have a maximum at slightly lower doping concentration than that giving maximum in the power factor.

see that for $E_g < 10k_B T$, zT increases with the band gap; while when $E_g > 10k_B T$, zT strongly depends on the scattering mechanisms.

Eq. (1.10) and Eq. (1.13) (the electrical conductivity and the Seebeck coefficient for a degenerate semiconductor) also reveal the competition between the density of states effective mass dependency. A larger effective mass refers to the flat band (in a $E(\vec{k})$ plot) while the small effective mass refers to a band with a large curvature. Accordingly a large effective mass corresponds to a higher density of states, thus a high Seebeck coefficient. However, heavy carriers will yield a low mobility, which in turn leads to a lower

Fig. 1.6.: Maximum value of zT as a function of band gap E_g for parabolic bands and for non-parabolic bands with two different scattering mechanisms [36].

electrical conductivity. The relationship between the effective mass and the mobility depends on the electronic structure, scattering mechanisms and anisotropy in the material. Experience has shown that, as a rule of thumb, high mobility and low effective mass are typically found in materials made from elements with small electronegativity differences, whereas high effective mass and low mobility are found in materials with narrow bands such as ionic compounds. It is not obvious at which value the effective mass is optimum: good thermoelectric materials can be found within a wide range of effective masses and mobilities, such as from low-mobility, high-effective-mass oxide to high-mobility, low-effective-mass semiconductors SiGe and GaAs. Therefore, a balance between the effective mass and mobility needs to be reached by the band structure engineering. This may require the architectural buildup of the materials, for instance, introducing alloys of the wide gap and narrow gap semiconductors, and organizing them as quantum wells and superlattices. No deliberate band engineering has been done in this thesis.

1.4.3. Reducing thermal conductivity

An effective way to reduce the thermal conductivity applicable to most materials is to reduce the lattice thermal conductivity, i.e. phonon propagation. The lattice thermal conductivity can be separated from the measured total thermal conductivity via the Wiedemann-Franz law (Eq. (1.18)). Notice that in Fig. 1.5 the lattice thermal conductivity is assumed to be constant. This is similar to setting the Lorenz coefficient equal to the Lorenz number. The Lorenz coefficient is a function of carrier concentration, leading to a variation of lattice thermal conductivity with temperature in one material. Thus one needs to take special

caution when using Weidemann- Franz law, particularly for low-carrier-concentration materials. The Lorenz coefficient in such material can be reduced by as much as 20 % from the free-electron value, thus introducing uncertainty and even leading to negative κ_{ph} value during interpretation [27].

Phonons are characterized by their different wavelength. For an imperfect crystal, impurities are the most effective scatterers to the short-wavelength phonons. The impurities give rise to the local variations of both the density and the interatomic forces, particularly at low temperature when the mean free path for phonon-phonon scattering is large. Another route for reducing the lattice thermal conductivity is to introduce atoms or regions with a mass contrast, such as alloys. Moreover, in a single crystal which only contains one isotropic element, the isotopes of different atomic mass can lead to a substantial reduction in phonon mean free path [37]. For the phonon with mid- and long- wavelength, the grain boundary and interface play a role. By introducing grain boundaries, for instance by nanocomposite structure, the lattice thermal conductivity can be reduced due to the increased phonon scattering. *Manuscript 4.3* demonstrates the reduction of thermal conductivity by means of nanostructuring that has been achieved by different synthesis processes.

1.4.4. Energy filtering

Potential barriers can be introduced into materials and may block low energy carriers. It is called to filter out low energy carriers and can have a large positive effect on the Seebeck coefficient. Various nanostructuring techniques can be introduced for the filtering and could simultaneously have a positive effect by scattering phonons. The filter height can in principle be adjusted with many different approaches. In a material made of nanosized grains, the barriers can form because of charge trapping on the grain boundaries, and for a given material the barrier height will be a function of grain size, doping concentration and interface state density. Given the band gap of a nanoparticle depends upon the nanoparticle size, the quantum confinement effects can be exploited for nanoinclusions. Fig. 1.7 shows that the band gap of PbS varies from 0.37 eV to 1.3 eV by going from bulk size down to a nanoparticle of 3 nm. When PbS nanoinclusion are embedded in the bulk of another semiconductor, the mismatch of the band alignment and the band gap will create an energy barrier that will backscatter the low energy carriers. Large energy barriers at the interfaces of materials thus may be created [39].

Fig. 1.7.: Schematic illustration of energy levels and band gap of PbS by particle size [38].

However, if the nanoinclusions are randomly distributed, then it is not sufficient to filter the carriers due to the energy dependent cross-section. The energy filtering may occur only when the nanoinclusions accumulate at the grain boundaries [40]. In such a case the scattering cross-section increases because all the carriers will have to pass through the grain boundaries, as shown in Fig. 1.8.

Fig. 1.8.: Energy filtering by (left) nanoprecipitates randomly distributed within an embedding phase and (right) grain boundaries in polycrystalline materials. Note that only in the latter case all carriers are filtered out in energy [40].

How large the energy barrier can be depends upon the energy relaxation time τ . Often the dependency is modeled by setting $\tau = \tau_0 E^{r-1/2}$, where r is the scattering factor (same as in Eq. (1.12)) that is sought to be modified by nanoinclusions. Nanoinclusions have been suggested to have an energy filtering effect by giving much longer relaxation time compared to the corresponding bulk material if we assume grain boundary scattering is dominant. The larger the value r , the larger the energy filtering effect and the larger the enhancement of the Seebeck coefficient [41]. A study of testing for the possibility of energy filtering in nanostructured ZnSb can be found in *manuscript 4.4*.

2. Review on the thermoelectric ZnSb

This chapter reviews the research literature on the thermoelectric material ZnSb, starting with the equilibrium phases of the Zn-Sb system, followed by the crystal and electronic structure. The electrical properties and doping effect are listed and discussed. The importance of the intrinsic defects on the transport and the impurity band conduction are discussed. Finally, the thermal transport is being reviewed.

The thermoelectric effect in ZnSb has been known for almost two centuries. The first documented encounter can be traced back to the original work of Seebeck on thermoelectric current generation on different materials and alloy pairs in 1819 – 1827 [9]. Quantitative measurements of the Seebeck voltage of ZnSb have been done by Becquerel in 1866 [42]. From the early 20th century, many attempted to solve the crystal structure but were barely successful [43–45]. Until 1948, Almin finally determined the crystal structure of ZnSb together with CdSb [46]. A large interest in ZnSb followed due to the progress on semiconductors since the 1950s. Fig. 2.1 shows thermoelectric devices made by ZnSb at that time. (a) – (c) show a solar thermoelectric generator prototype built by ZnSb (p) and $\text{Bi}_{91}\text{Sb}_9$ (n) with overall efficiency of 0.63 %, which was good in comparison with other materials at the time [47]. In the meantime, a thermoelectric refrigerator made by n -PbTe ($z = 1 \times 10^{-3} \text{ K}^{-1}$) and p -ZnSb ($z = 0.8 \times 10^{-3} \text{ K}^{-1}$) was demonstrated by USSR in the 1950s, as shown in Fig. 2.1 (d) [12]. However, the research reporting on ZnSb faded in the 1970s and there was little improvement in terms of its efficiency. Until in recent years, a renewed attention appeared following the nanostructuring boom in material science, and the thermoelectric properties of ZnSb have been intensively studied and improved. There are also other energy related applications of ZnSb actively being explored such as electrodes for rechargeable Li ion batteries [48], or phase change memory cells [49].

Table 2.1 lists the reported figure of merit zT . The performance of ZnSb strongly depends on the doping concentration and operation temperature. In addition, the preparation-induced defects (phase impurity, oxidation, and grain size) and intrinsic defects (vacancies, interstitials, clusters) influence strongly the material's performance. These need to be controlled in order to bring further progress, and in general the handling of the material is a long learning curve and a detailed understanding of the material, per se, is needed.

Fig. 2.1.: (a) – (c) Solar thermoelectric generator [47]: (a) Open circuit EMF (Seebeck coefficient) as a function of temperature on ZnSb-alloys comparing with other thermal couples. Materials: (1) ZnSb (Sn, Ag, Bi)-Bi₉₁Sb₉, (2) ZnSb (Sn, Ag, Bi)-constantan, (3) Bi₉₁Sb₉Sn₅-Bi₉₁Sb₉, (4) Chromel P-constantan; (b) Thermoelectric efficiencies on aforesaid materials; (c) Solar radiation thermopile contained 25 junctions built by *p*-ZnSb in plot (a) and (b) and *n*-Bi₉₁Sb₉. Above: front surface exposed to the sun; below: rear view shows the thermoelectric junctions. (d) Thermoelectric refrigerator with 16 pair of *n*-PbTe ($z = 1 \times 10^{-3} \text{ K}^{-1}$) and *p*-ZnSb ($z = 0.8 \times 10^{-3} \text{ K}^{-1}$, labeled as "4"), made at Physical-Technical Institute in 1950s [12].

Table 2.1.: List of reported zT of ZnSb

Report year	zT	At temperature	Sample	Reference
(1961)	0.6	460 K	single crystal	[50]
(1964)	0.42	300 K	single crystal	[51]
(1964)	0.3	300 K	polycrystalline	[51]
(1966)	0.2	273 K	single crystal	[52]
(2010)	0.07	300 K	polycrystalline	[53]
(2010)	0.8	573 K	polycrystalline	[54]
(2012)	0.9	659 K	polycrystalline with Cu	[55]
(2013)	1.15	670 K	polycrystalline with Ag doping	[56]
(2014)	0.9	635 K	polycrystalline with Ag	[57]
(2014)	0.8	600 K	polycrystalline with Cu	[57]
(2014)	1	630 K	polycrystalline with Sn+Cd	[58]
(2015)	0.8	700 K	polycrystalline with Zn vacancies	[59]

2.1. Thermal equilibrium phases in Zn-Sb system

The Zn-Sb binary phase diagram is shown in Fig. 2.2 [60]. The phases ZnSb, Zn₃Sb₂ and Zn₄Sb₃ have been well-recognized for a long period [60, 64–66]. Zn₄Sb₃ has been much studied due to its phonon-glass electron-crystal structure that leads to a remarkably low thermal conductivity, typically 0.65 W/m·K at room temperature [67]. High $zT = 1.4$ has also been reported. However, the static-to-dynamic phase transition (β to γ) reduces its reliability and applicability [68]. On the other hand, ZnSb is relatively thermally stable until 506 °C [69], but its peritectic decomposition at 544.5 °C makes it difficult to produce either perfect single crystal or homogeneous polycrystalline samples from a molten solution.

Fig. 2.2.: ZnSb Phase diagram and binary compounds in Zn-Sb system. (a) Equilibrium diagram of Zn-Sb system [60]; (b) and (c) are the crystal structures of Zn_4Sb_3 and Zn_6Sb_5 at room temperature: both contain Sb_2^{-4} and Sb_2^{-3} dimers [61]; (d) Crystal structure of $\beta\text{-Zn}_6\text{Sb}_5$ at room temperature. Zn atoms are inside the antimony tetrahedra, which are connected by Sb_2^{-4} dimers [62]; (f) Projection of $\text{Zn}_{13}\text{Sb}_{10}$ structure on [001] [63].

The recent studies have discovered phases that were unknown previously: $\text{Zn}_{6-\delta}\text{Sb}_5$, which is a product when Zn_4Sb_3 undergoes a transition below 767 K (before β to γ) [62]; Zn_8Sb_7 , which has high Seebeck coefficient and is entropically stable at high temperature [61]; and $\text{Zn}_{13}\text{Sb}_{10}$, which was obtained by using Zn_4Sb_3 nanoparticle precursors [63]. The aforesaid compounds are predicted to be good thermoelectric materials as ZnSb and Zn_4Sb_3 . However, the stabilities of these newly discovered phases need further investigation through the whole temperature range before choosing strategies for further improvement.

2.2. Synthesis of the material

Single crystal ZnSb was grown in order to understand the inherent material properties. There has been several reports on the zone melting method [51, 52, 70–74] that the single crystal was pulled from a Sb rich liquid phase, Bridgeman’s method [75, 76], and Czochralski method [70, 77, 78]. The hole concentrations on the sample obtained by these methods were reported to be about $1 - 2 \times 10^{16} \text{ cm}^{-3}$ [51, 52, 74].

Polycrystalline ZnSb ingots can be synthesized by melting the elements followed by solidification in air or quenching in cold water. The purity of starting material has a significant impact on the resulting electrical properties. The starting materials with purities of 99.99 % and 99.9999 % leading to be a carrier concentration of $\sim 10^{19} \text{ cm}^{-3}$ and $\sim 10^{16} \text{ cm}^{-3}$, respectively, on undoped polycrystalline ZnSb have been reported [51]. Since ZnSb does not melt congruently, solidification will result in a mix of the phases, Zn_4Sb_3 , ZnSb and Sb. This mix can be homogenized by sufficient heat treatments to reach the thermody-

namic equilibrium state with a single uniform ZnSb phase [51, 52]. Another problem with the solidification is that the sample contains cracks that significantly influence the electron transport [50]. The solidified ingots are often milled into fine powder and pressed to pellets. The milling offers access to nanosized grains, thus a possibility to enhance the thermoelectric properties. Earlier studies show that different milling techniques led to a trend of grain size as 80.0 nm, 44.6 nm and 32.4 nm for manually grinding, dry-milling and wet-milling respectively [53].

There are different kinds of compaction techniques, the so-called pressing, that are used in powder metallurgy and have been used for fabrication of ZnSb samples. The most common ones are cold-pressing (at room temperature with ultra-pressure 2 – 10 GPa [79, 80]), hot-pressing ($> 450^\circ\text{C}$ with pressure of 20 – 300 MPa [53, 56, 57, 81]), and Spark Plasma Sintering (SPS) (the electrical current is passed through the sample with 5 minutes reaction time at $350 - 450^\circ\text{C}$ [80, 82]). One important difference among hot-presses is secondary phases; both removal and proportioning are possible, and obviously depends upon the temperature and duration, but also on details of the instrument design and the environment of the ZnSb powder. Xiong *et al.* have reported that the volume fraction of Sb phase was estimated to be $\sim 2\text{ wt}\%$ by Rietveld refinement in a hot-pressed sample [56]. A recent study on SPS-samples also showed the Sb phase was distributed along the samples, accompanied with Zn_4Sb_3 on the surface [82].

2.3. Crystal structure of ZnSb

2.3.1. Crystallographic structure

The crystallographic structure of ZnSb has been determined by Almin [46]. According to this determination, ZnSb has orthorhombic crystal structure, oP16, and belongs to the space group $Pbca$ No.61. The structure of ZnSb has been studied and confirmed by different techniques, albeit gave slightly different interatomic distances [62, 69, 83, 84]. Fig. 2.3 shows a ZnSb crystal structure that was generated by the structural data from Mozharivskyj [62]. The lattice parameters are $a = 6.203(9)\text{ \AA}$, $b = 7.740(8)\text{ \AA}$ and $c = 8.097(7)\text{ \AA}$ and the position of the atoms in the unit cell are listed in Table 2.2: one atom for each species is given and the coordinators of the rest of atoms can be obtained by the symmetric operation. The interatomic distances for each bond are annotated in Fig. 2.3 (a).

Table 2.2.: Positions of Zn and Sb atoms in the unit cell [62]

Atom	x	y	z
Zn	0.4580(3)	0.1104(3)	0.8673(4)
Sb	0.1416(2)	0.0822(2)	0.1090(2)

The structure can be viewed as a deformed zinc blende structure. In a standard zinc blende structure each atom is surrounded by four atoms of the other kind (four-fold coordination), and the complete structure is exclusively made up of corner-sharing tetrahedra. In ZnSb there are also distorted Sb-Sb edge-sharing ZnSb_4 tetrahedra, as seen in Fig. 2.3 (a). The tetrahedral distortion also causes a peculiar five-fold coordination of each atom: one of the same kind and four of the other kind. In the context of bonding and its relation to conduction, all the atoms in the structure are tied together in a network – a point we will return to below.

Fig. 2.3.: Crystal structure, bonding and coordination environment of ZnSb. (a) Structure in $1 \times 2 \times 3$ unit cell generated by Mozharivskyj's data [62]. Both the deformed tetrahedral and the Zn_2Sb_2 -ring, as well as the interatomic distance between the nearest neighbors are annotated; (b) Scanning transmission electron microscopic (STEM) imaging reveals atomic scale structure that is recognized corresponding to (a) and (c); (c) $3 \times 1 \times 3$ cell shows the Zn_2Sb_2 -rings network. Each of the ring has 6 nearest neighbors, connected by bonds ix_{1-6} ; (d) The angles between Sb-Zn-Sb are similar to that of the standard tetrahedra, 109.5° . Bonds $i - vi$ are the covalent bonds for building up the tetrahedron, while vii and $viii$ are the bonds to form the Zn_2Sb_2 -ring; bond ix_{1-6} in (c) are the dimers that connect the Zn_2Sb_2 -rings. (e) Hybrides of four atomic orbitals (AO) and six molecular orbitals (MO) in Zn_2Sb_2 -ring [69].

Another way to systematize the structure is to group the atoms together in planar rhomboid rings of Zn_2Sb_2 that have short Zn-Zn bonds connected to two different longer Zn-Sb bonds, as seen in Fig. 2.3 (a). These motifs are also tied together in a network that completes the crystal structure. The structure can be recognized in atomic scale by scanning transmission electron microscopy (STEM), as shown in Fig. 2.3 (b).

2.3.2. Bonding

The bonds in ZnSb have been categorized in 3 groups, shown in Fig. 2.3 (c) and (d): bonds $i - vi$ are the covalent bonds for building up the tetrahedron; bonds vii and $viii$ form the Zn_2Sb_2 -ring; and bonds ix_{1-6} are the dimers that connect the Zn_2Sb_2 -rings. The angles between each Sb-Zn-Sb bond are also annotated in Fig. 2.3 (d). Notice that the angles are close to that in a regular tetrahedron, 109.5° . Therefore even though the structure

has five-fold coordination, one can still expect that ZnSb satisfies the tetrahedron rules to some extent. One of them is the electron count per bond. ZnSb has 7 valence electrons per formula unit, whereas a regular tetrahedral binary semiconductor has 8 valence electrons. Such electron-poor valence often indicates a metallic bond. Yet, ZnSb behaves as a semiconductor. The clue about the semiconducting property is probably due to the sp^3 -hybrid orbitals in the tetrahedron that often represents the semiconducting bond [85]. The counting rules cannot be applied on a per bond basis without considering the complete network. Therefore, all the atoms in the structure are bonded together in a network. ZnSb, thereby, has been classified as an electron-poor framework semiconductor (EPFS) [69, 86]. A quite similar interpretation for the structure has been applied to the family compounds CdSb [76, 85, 87, 88] and ZnAs [81].

2.3.3. Charge transfer in bondings, covalency, ionicity

The valence electrons in ZnSb are not distributed evenly. Fig. 2.4 (a) shows the theoretical *ab initio* calculations of the so-called deformation charge in two different cross-sections through the structure of ZnSb; while (b) shows that in an individual Zn_2Sb_2 -ring [89]. The deformation charge density is the electron concentration in the framework minus the electron concentration of the free atoms. Red indicates excess of electron and blue indicates electron deficiency compared to the free atoms. It is seen that there is a small transfer of electrons between the Zn and Sb along Zn-Sb bond, as typical for covalent bonds. The figure thus shows the dominating bonding to be of covalent nature, as expected.

Fig. 2.4.: Deformation charge density calculated by GGA-PBE. Red indicates accumulation of electrons, whereas blue shows loss of electrons in the relaxed structure of the compound compared with the number of electrons in the free atoms. (a) Deformation charge density for two crossing Zn_2Sb_2 -rings; (b) deformation charge density in a single Zn_2Sb_2 -ring. [89]

Regarding the direction, the electronegativity is usually used as an indicator for an element's tendency to attract an electron: the higher the electronegativity, the more attraction. Zn has a Pauling electronegativity of 1.65 eV, and that of Sb is 1.96 eV. Thus, one would expect a charge transfer from Zn atom to Sb atom. Niedziolka *et al.* shows the result of *ab initio* calculations by GGA-PBE (Generalized Gradient approximation with the Perdew-Burke-Ernzerhof exchange functionals) that Zn atom transfers a small average fraction of 0.26 electrons to Sb [89]. Essentially the same transfer was found in the calculations of Benson *et al.* [90]. On the other hand, Niedziolka *et al.* also reported a charge transfer

of 0.36 electrons by using another presumably more accurate calculation approach (Heyd-Scuseria-Ernzerhof (HSE)) in the same study [89]. X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) measurements indicated a shift of a Zn Auger peak and softening of EELS fine structure could be caused by a small net charge transfer of 0.1 electron from Zn to Sb [91]. The apparent difference between reported experiments and calculations can be related to experimental uncertainties and different volume that was chosen for the calculation.

2.4. Electronic structure

2.4.1. Band calculations

The band structure of ZnSb has been calculated by *ab initio* methods by many groups in recent years [69, 86, 89–91, 93–96]. The calculations are based upon density functional theory (DFT) but with varying detailed approximations and tradeoffs between computational cost and accuracy. By comparing different calculated band diagrams one can see some features that are common for most of the calculations and expect to filter out methodological errors in the different reports.

Fig. 2.5 shows our calculation of a ZnSb band diagram in *manuscript 4.4*. The zero energy location corresponds to the largest energy of filled states. Thus the states below 0 correspond to the valence

Fig. 2.5.: Band diagram of ZnSb showing energy states along high symmetry directions in k -space calculated by Berland using GGA - PBE. (See *manuscript 4.4*). The Brillouin zone for orthorhombic lattice with the high symmetry symbols are shown to the right for indication [92].

band while those above correspond to the conduction band. The value of the band gap is severely underestimated by the computational approximations. By using more accurate methods but at the expense of increased computation time, such as HSE-hybrid functional, the band gap was calculated to be around 0.5 eV [89]. This value is close to the one in single crystal ZnSb. On the other hand, the shape of the bands may be less affected by the computational approximations. The band diagram in Fig. 2.5 shares some of the features found in most of the calculations listed. The band gap is indirect with the maximum of the valence band along the symmetry line X- Γ and the minimum of the conduction band along Γ -Z. One can see that the conduction band contains more satellites within 0.5 eV of

the minimum than the pockets of the maximum in the valence band. Thus one can expect ZnSb would have acted better as an n -type material than a p -type material if stable n -type doping could have been achieved (See Section 2.6).

Beyond the general trends there are some differences in the reported band diagrams, for example the Γ point for the valence band in Fig. 2.6 (a) and (b), which are encircled in red. The computational methods were reported to be identical except for the number of k -points used for Brillouin zone integrations [95, 96].

Fig. 2.6.: Two published band diagrams of ZnSb band diagram used apparently the same software package and approximation (Monkhorst-Pack) except for difference the number k -grid points performed for Brillouin zone integrations. (a) k -point sampling of $15 \times 15 \times 15$ for both relaxation and band structure are performed by Jund *et al.* [95]; (b) a $3 \times 3 \times 3$ k -points grid for the relaxation while a $5 \times 5 \times 5$ grid for the density of states are calculated by Niedziolka *et al.* [96].

Finally it is worth mentioning the band diagram that was calculated by Yamada in 1978 by using pseudopotentials. [97] The maximum of the valence band was found to be on the line from Γ -X at $k = (0.93\pi/a, 0.0)$, which is close to the DFT values, further a band gap of 0.6 eV. However a minimum of conduction band is located at $k = (0.47\pi/a, 0.0)$ along Γ -X, which is not in agreement with most DFT calculations, and it is hard to determine experimentally due to the difficulty in preparing n -type ZnSb.

2.4.2. Experimental band gap

The band gap has been measured by different methods. The value of 0.5 – 0.53 eV on single crystal ZnSb, which were measured by optical absorption, have been reported [71, 77]. These values are essentially identical when considering the uncertainties, and 0.5 eV has been considered to be a reference value for single crystal ZnSb.

Many have also determined the thermodynamic band gap from the temperature dependence of carrier concentration in the intrinsic regime. The carrier concentration is determined from the Hall coefficient, R_H . A linear fit of $\ln(R_H T^{\frac{3}{2}})$ *vs.* $1/T$ will yield the

activation energy, which is half of the thermodynamic energy gap. (This assumes an effective density of states proportional to $T^{\frac{3}{2}}$.) Values of 0.47 – 0.65 eV have been reported in literature for single crystal ZnSb based upon Hall effect measurements [72, 74].

For polycrystalline ZnSb the band gap is often reported to be around 0.31 – 0.35 eV [50, 98], which is smaller than that of single crystal material. It is justified to discuss whether the band gap really is different, or if it is due to the idealizations of the measurement methods do not hold for polycrystalline material. One of the methods that has been used for estimating the band gap is to measure the temperature dependence of the Seebeck coefficient. By determining the temperature, T_{max} , for the maximum of the absolute value of the Seebeck coefficient, α_{max} , the band gap can be estimated from the Goldsmid formula, $E_g = 2q\alpha_{max}T_{max}$ [99]. This method works well for many semiconductors, for instance Zr-NiSn half-Heusler [100]. However, there have been reports on some systems that the Goldsmid formula does not apply [101, 102]. ZnSb may be one of them. Guo and Luo have reported that Goldsmid formula returned a value of $E_g = 0.3$ eV for their polycrystalline ZnSb samples [59]. However, Böttger *et al.* justified that for the samples that has a band gap of 0.3 eV obtained by Goldsmid formula, the temperature dependent resistivity was fitted better with a value of 0.44 eV [103]. It is fair to state that it depends upon the context whether it is best to reconsider the band gap value for polycrystalline or reconsider the idealizations used in the measurement methods.

We should also keep in mind that heavily doping may influence the density of states near the band edges, forming tails that are extending into the band gap. The defect states in the band gap also influences the values. This is a well-documented phenomenon (for Si) [104] even if the precision in a detailed quantitative understanding may be lacking. In **manuscript 4.2** we reported that the maximum of the Seebeck coefficient of ZnSb could be varied considerably by the presence of the defect states in the band gap.

We have discussed in Section 1.4.2 that the "best thermoelectric material" has a band gap around $6k_B T$ to $10k_B T$. Considering ZnSb operating at 600 K, this means a band gap of 0.5 eV would fit that rule of thumb, and is a reason why ZnSb is considered a good thermoelectric material that draws a lot of attentions.

2.4.3. Effective mass and density of states

The idealized single parabolic band (SPB) model is convenient for analyzing experimental results. The model has been successful for finding the optimum doping concentration of many thermoelectric materials [105–107]. When applied to Seebeck measurements on ZnSb with different doping concentrations, it has been observed that Pisarenko plot (Seebeck coefficient *vs.* carrier concentration) does not follow the SPB model with a single density of states effective mass m^* , which was defined as 0.42 – 0.49 [52, 103], but rather a different

mass fit for different ranges of doping concentrations. A previous study by Böttger *et al.* has suggested that the deviations from the idealized SPB behavior could be induced by impurity band states [103]. In *manuscript 4.2*, we showed that deviations from simple SPB behavior at varying doping concentration could be modeled by introducing an impurity band. One may comment that a best fit with varying m^* is not necessary to imply that the energy band curvature varies. It suffices that the temperature dependent position of Fermi level varies differently than that in an idealized SPB case.

2.5. Electrical properties

2.5.1. Summary of electrical transport coefficients

Table 2.3 lists the band gap, carrier concentration and other electrical and thermal properties reported for ZnSb in the literature.

2.5.2. Anisotropic conductivity

Given the crystal structure, single crystal ZnSb exhibits anisotropic conduction [78]. Fig. 2.7 shows the anisotropic hole mobility along different crystal orientations on an undoped p -type single crystal ZnSb. The ratio of the hole mobility along a -, b - and c - is $\mu_{11} : \mu_{22} : \mu_{33} \approx (2.6 - 2.9) : 1.0 : (4.1 - 4.5)$, indicating the highest mobility is along the c -axis [52, 77]. The electrical conductivities are consistent along the same orientations $\sigma_{11} : \sigma_{22} : \sigma_{33} \approx 1.7 : 1 : 2.5$, as well as yielding the highest $zT = 0.2$ along c -axis at 0°C [52]. The hole mobility varies with temperature as T^r , where r is $-1 - -1.5$ for extrinsic region and approaches 2.5 in the intrinsic region. Notice that r along a -axis is higher than that of b - and c -axis, indicating a slightly higher lattice scattering along a -axis. Interestingly, both the thermal conductivity and the piezoresistance showed anisotropy in the corresponding orientations, $\kappa_{11} > \kappa_{22} \approx \kappa_{33}$ and $\pi_{11} < 0$, and $\pi_{22} > 0$, $\pi_{33} > 0$ [76].

Fig. 2.7.: Hall mobilities as a function of temperature for undoped p -type ZnSb along different crystal axes. Data from Shaver and Blair are plotted with the linear fitting; r values from Komiya *et al.* are annotated in the parentheses [52, 77].

Table 2.3.: Summary of electrical properties of ZnSb

Ref.	Report year	Structure	Dopant	σ S	ρ $\Omega\cdot\text{cm}$	μ $\text{cm}^2/(\text{V}\cdot\text{s})$	p cm^{-3}	α $\mu\text{V}/\text{K}$	E_g eV	κ $\text{W}/(\text{m}\cdot\text{K})$
[108]	(1947)	—	—	—	0.0072	—	—	250	—	1.4
[47]	(1954)	—	2 at% Sn+0.1 at% Ag	—	0.0019	—	—	210	—	—
[75]	(1960)	Single crystal	—	2.8	3.57	350	5.1×10^{16}	440	0.52 – 0.57	—
[72]	(1961)	Single crystal	—	3	0.33	480	3×10^{16}	550	0.49	560
[70]	(1963)	Single crystal	—	1.6	0.63	248	4.1×10^{16}	—	—	—
[70]	(1963)	Single crystal	—	5.6	0.18	1150	3.1×10^{16}	—	—	—
[77]	(1963)	Single crystal	—	6.4	0.16	10	4×10^{18}	110	0.53	1.1
[51]	(1964)	Single crystal	—	19.7	0.05	384	3.2×10^{17}	490	—	—
[51]	(1964)	Polycrystalline	—	20	0.05	95.2	1.3×10^{18}	375	—	1.3
[51]	(1964)	Polycrystalline	0.1 at% Ga	2.04	0.49	210	6×10^{16}	675	—	—
[51]	(1964)	Polycrystalline	0.1 at% Cu	110	—	680	1.1×10^{18}	—	—	—
[109]	(1964)	Single crystal	—	—	—	—	3×10^{17}	—	0.48	—
[52]	(1966)	Single crystal	—	825	0.001	800	2×10^{16}	182	—	3.7
[52]	(1966)	Single crystal	Cu	42	0.02	660	4×10^{17}	—	—	—
[52]	(1966)	Single crystal	Cu	898	0.001	510	1×10^{19}	—	—	—
[74]	(1967)	Single crystal	Au	26.9	0.04	233	4.2×10^{17}	404	0.47 – 0.65	—
[74]	(1967)	Single crystal	In	37.5	0.03	326	7.7×10^{17}	288	0.47 – 0.65	—
[74]	(1967)	Single crystal	Te	51	0.02	379	8.3×10^{17}	400	0.47 – 0.65	—
[53]	(2010)	Polycrystalline	2 wt% Ag	—	0.01	—	—	185	—	2.3
[54]	(2010)	Polycrystalline	—	28.2 – 32.1	—	—	—	400 – 500	—	1.41
[56]	(2013)	Polycrystalline	0.002 at% Ag	—	0.0016	111	2.6×10^{19}	181	—	1.5
[57]	(2014)	Polycrystalline	Sn	180	—	—	4.9×10^{18}	250	—	1.8
[110]	(2014)	Polycrystalline	0.6 at% Cu	640	—	—	2.5×10^{19}	134	—	—
[58]	(2014)	Polycrystalline	0.15 at% Cu	935	—	—	2.4×10^{19}	142	—	—
[59]	(2015)	Polycrystalline	3 at% V _{Zn}	800	0.0012	66	7.9×10^{17}	275	0.29	1.75

Comments: Data are reported at room temperature data unless special comment. Data in [51–53, 72, 75, 95] are read off from the original plot. Some electrical parameters in [52, 77] are calculated from the other transport coefficients, according to $\rho = R_H/\mu$

The anisotropies of electrical conductivity can be influenced by the anisotropy in the effective mass of holes (the valence band curvature) and/or the relaxation time (the scattering events). Mlnaríková *et al.* determined the effective mass from experimental data and found the ratio of m^* in different orientations corresponds to the ratio of the hole mobility ($m_{11}^* : m_{22}^* : m_{33}^* \approx \mu_{11} : \mu_{22} : \mu_{22}$), while no difference in relaxation times in different orientations ($\tau_{11} : \tau_{22} : \tau_{22} = 1 : 1 : 1$), thus concluding that the electrical conductivity is strongly dependent on the anisotropic effective mass [78].

Stevenson has measured the anisotropic effective mass by cyclotron resonance, and determined m^* to be 0.175 in the a - c plane, and 0.146 in b - c plane. The results indicated that the constant energy surface in k -space in ZnSb is a spheroid [73]. The anisotropic energy surface has also been observed by optical absorption. Fig. 2.8 shows the reflectivity when the polarization is along different crystal orientations [109]. The energy towards lower when $\vec{E} \parallel \vec{c}$, corresponding to the highest electrical conductivity along c -axis.

Fig. 2.8.: The absorption edge at low levels in ZnSb at room temperature. The notation of the curves corresponds to the polarized radiation with $\vec{E}$ parallel to $\vec{a}$, $\vec{b}$, $\vec{c}$ [109].

Böttger *et al.* determined each mass tensor component from the band diagram calculation [103]. Different components were given by $m_{11}^* = 0.1811$; $m_{22}^* = 0.4913$; $m_{33}^* = 0.0837$. And the average effective mass is, therefore, $m^* = (m_{11}^* m_{22}^* m_{33}^*)^{1/3} \times 2 \cdot 2^{2/3} = 0.49$, which is similar to Shaver's results, $m^* = 0.42 \pm 0.15$ [52].

According to the Seebeck coefficient in Eq. (1.11) [52]

$$\alpha = \frac{1}{Tq} \frac{\langle (E - E_F) \tau_{ii} \rangle}{\langle \tau_{ii} \rangle} \delta_{ij}, \quad (2.1)$$

where the Kronecker delta δ_{ij} is 1 when $i = j$ and δ_{ij} is 0 when $i \neq j$, the Seebeck coefficient should be isotropic if the relaxation time τ is isotropic, and the experiments of Mlnaríková *et al.* indeed did not show an anisotropic relaxation time [78]. Shaver and Blair's found that α did not depend upon the crystal orientation by measuring the same sample in different directions, for several samples with different carrier concentrations. However, the power factor ($\alpha^2 \sigma$) depended significantly on the direction due to the anisotropic electrical conductivity [52].

2.5.3. Scattering mechanisms

There is much literature devoted to the scattering mechanisms in semiconductors [111], while there are fewer reports dealing with that topic specifically for ZnSb. It is expected that ZnSb has similar behavior to those semiconductors which have been much studied and follows similar trends. ZnSb appears to have favorably small polarity due to small electronegativity difference between Zn and Sb. This would in turn lead to a negligible polar optical phonon scattering than other III-V and II-VI compounds where polar optical phonon scattering may be dominant. Roughly, transport in ZnSb is dominated by the impurity scattering at low temperature, while at higher temperature when lattice vibrations are stronger, the longitudinal acoustic phonon scattering dominates (deformation potential scattering). The hole mobility varies with temperature as $\mu \propto T^r$, thus the plot of $\ln \mu$ vs. T will give the scattering factor r that implies the scattering mechanism. A value of -1 to -1.5 typically indicates the longitudinal acoustic phonon scattering dominates. In Fig. 2.9 (a) the slopes of Hall mobility approaches -1.5 (-1.4 in the plot) as the doping concentration decreases, which indicates that the acoustic phonon scattering dominates within the temperature range. The deviation from -1.5 for each individual curve is attributed to additional ionized impurity scattering [14]. It is also seen that the higher hole concentration corresponds to an increase of ionized impurity scattering, which limits the hole mobility.

Fig. 2.9.: (a) Hall mobilities along c -axis as a function of temperature for p -type ZnSb at various hole concentration (1) $3 \times 10^{16} \text{ cm}^{-3}$; (2) $4 \times 10^{17} \text{ cm}^{-3}$; (c) $5.5 \times 10^{17} \text{ cm}^{-3}$; (4) $1 \times 10^{19} \text{ cm}^{-3}$ [52]; (b) Resistivity vs. temperature of ballmilled and hot-pressed samples with varying silver content. Inset: unprocessed sample (Ingot) [53].

Not only the intentional dopants, but also defects that are ionized or neutralized, screened or unscreened, contribute to scattering. Likely scattering centers are Zn vacancies, interstitials, internal strain, grain boundaries and dislocations. Fig. 2.9 (b) shows the resistivity for

an unprocessed ZnSb ingot that was obtained directly from solidification and hot-presses ZnSb pellets with different dopants. The temperature coefficient, $\frac{d\rho}{dT}$, for the unprocessed ingot is positive, which is commonly observed for metals and semiconductors in a certain temperature range where phonon scattering dominates. For the processed samples, either with or without Ag, the temperature coefficient is negative. The reason for the negative temperature coefficient could be the dominant Coulomb scattering due to charged defects or impurities. We observed the change of the mobility by sulfur doping and discuss it in *manuscript 4.6*.

2.6. Doping effects

The most direct purpose of doping is to vary the carrier concentration. A broad range of dopant elements has been reported for ZnSb. The selection of dopant is often rationalized based on the same valence electron counting scheme that is applied to the elemental group IV, III-V or II-VI tetrahedrally bonded semiconductors. These considerations are applied for the acceptors, while donors are challenging. One will have acceptors by replacing group I elements for Zn or group IV elements for Sb. It is expected the donors can be the substitution of group III elements on Zn sites and group VI elements on Sb sites. In all cases there may be an issue with doping efficiency, i.e. not all the added dopant atoms will be electrically active. It is common and qualitatively well understood for other semiconductors that this inefficiency involves segregation (solid solubility limit), clustering of dopant atoms, and/or agglomeration of complexes of dopant atoms and point defects. A theoretical calculation predicts that the optimum hole concentration for thermoelectric efficiency of ZnSb is around $2 \times 10^{19} \text{ cm}^{-3}$ [103], which is achievable in *p*-type ZnSb. For donors in ZnSb there may also be additional issues to what has been mentioned above.

2.6.1. Acceptors

I_{Zn} – acceptors as elements of Group I

Cu_{Zn} , Au_{Zn} , Ag_{Zn} all yield *p*-type conduction [74, 112]. Most of the reported carrier concentrations are below the optimum value, and probably depend upon the details of sample preparation. However, the highest doping concentrations that have been reported are $4 \times 10^{19} \text{ cm}^{-3}$ doped by 0.02 *at%* Ag [56] and $2 \times 10^{19} \text{ cm}^{-3}$ doped by 0.1 *at%* Cu [52, 58, 110]. There are several interesting behaviors that involve additional states in the band gap when doped with Cu. The details can be seen in *manuscript 4.2*.

IV_{Sb} – acceptors as the elements of group IV

Hole concentrations around $4.9 - 19.1 \times 10^{18} \text{ cm}^{-3}$ were obtained by 0.6 – 3 *at%* Sn_{Sb} , and

the lowest Sn concentration yielded the highest hole mobility [57, 103]. A hole concentration of $2.7 \times 10^{18} \text{ cm}^{-3}$ has been achieved by 1 at% Ge_{Sb} [57]. The change of the hole concentration was considered as a consequence of introducing the temperature dependent acceptor levels.

I_{ZnIVSb} – co-doping

Hole concentrations of $2 - 2.5 \times 10^{19} \text{ cm}^{-3}$ have been reported by co-doping of group I (0.15 at% Cu or Ag)/IV (0.6 at% Pb, Sn, or Ge)/Cd [57, 58]. The measured transport coefficients at different regions indicate two types of impurity acceptor: one embedded into Zn sites, and another into Sb sites. Here, Cd is not expected to act as a acceptor but for increasing the phonon scattering and thereby reducing the thermal conductivity. The same function of P has been used to introduce the alloy scattering in the Cu doped ZnSb [55, 113].

2.6.2. Donors

n -type ZnSb is desired because *i*) thermoelectric modules are preferably built of parallel legs of n -type and p -type materials and it is preferable to use the same material (ZnSb) for minimizing the thermal stress; *ii*) although, theoretically n -type ZnSb is believed to be a much better thermoelectric material than p -type [94–96], no real successful stable n -type doping has been achieved. However temporary n -type behaviors have been reported by doping of group III and group VI elements.

III_{Zn} – donors as elements of group III

Group III elements have been used as donors to yield n -type conduction in CdSb [114]. It was later reported that ZnSb could also be made n -type by In doping, probably substituting Zn as In_{Zn} . Al_{Zn} and Ga_{Zn} also exhibited temporary n -type behavior [115, 116]. However, the n -type conduction does not always occur. Justi *et al.* did not achieve n -type ZnSb with Ga despite several attempts with single and polycrystalline ZnSb [51]. Niedziolka *et al.* predicted theoretically by DFT calculations that boron would electronically be a good candidate for n -type ZnSb, but did not succeed to synthesize the material and ascribed to the high formation energy of a boron atom on a Zn site [96].

VI_{Sb} – donors as elements of group VI

Some success with Te doping has been reported. Ueda *et al.* reported that a very narrow window around 2 at% Te yielded n -type, possibly by forming substitutions of Te atoms on Sb sites, Te_{Sb} ; while at lower concentration ($< 1 \text{ at\%}$) and higher concentrations ($> 3 \text{ at\%}$) the samples are always p -type. Excess doping with Te results in precipitation of the ZnTe phase and a change in conduction from n - to p -type [117].

p – n transition

A temporary *n*-type behavior with a transition to *p*-type was reported. The factors that have been suggested for explaining these behaviors are related to such factors as oxygen migration on internal surfaces or grain boundaries [116]. Fig. 2.10 shows the *n* to *p* transition on *n*-type $\text{Zn}_x\text{Cd}_{1-x}\text{Sb}$ every time an oxygen gas was flushed into the sample container, and relaxed back to *n*-type after certain time [116]. Another factor entering into explanations are Zn vacancies acting as acceptors and their migration [95, 96, 118]. A similar transition from *n*-type to *p*-type also occurs on the family compound CdSb, which has been attributed to Cd-vacancies [119].

Fig. 2.10.: Seebeck coefficient of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Sb} + 0.1 \text{ at\%}$ with time. Oxygen has been pulsed into the sample container at times a, b and c, yielding *p*-type behavior transition [116].

2.7. Zn vacancies and intrinsic defects

The theoretical intrinsic carrier concentration of perfect ZnSb at room temperature is approximately $2 \times 10^{14} \text{ cm}^{-3}$ given by $p_i = 2 \left(\frac{2\pi m^* k_B T}{h^2} \right)^{3/2} e^\eta$, where $\eta = -E_g/2k_B T$ is the reduced Fermi energy, and taking $E_g = 0.53 \text{ eV}$ and $m^* = 0.42$ [52]. However, the experimental measurements show the carrier concentration of the best single crystals at room temperature is around $1 - 2 \times 10^{16} \text{ cm}^{-3}$ [52, 70, 72, 75] and up to $\sim 10^{18} \text{ cm}^{-3}$ for polycrystalline samples without intended dopants [51, 77]. This deviation is considered due to the intrinsic defects, giving a net hole concentration. The most favored intrinsic defects in ZnSb are Zn vacancies that are believed to yield *p*-type conduction [95, 118]. In the following, we will give several quotes from Bjerg *et al.*'s work on DFT modeling defects in ZnSb, because it is qualitatively simple, while capturing some important characteristics.

Bjerg *et al.* have calculated the formation energies of simple point defects and clusters in different charge states in ZnSb [118]. The calculations gave much lower formation energies for Zn vacancies than other intrinsic defects, meaning that the Zn vacancies will outnumber the other intrinsic defects by orders of magnitude (The Zn vacancy has lowest formation energy among the intrinsic defects was also calculated by Jund *et al.* [95]). The authors considered the dilute limit of defect concentrations. In that limit the electronic band structure is considered to be that of the defect free bulk structure. Discrete defect states are then considered to accept electrons from (or donate electrons to) the bands if they are negatively (or positively) charged. The charge state of the defect will depend on

the Fermi level for electrons. This can in principle be calculated from the condition of electrical charge conservation (charge neutrality). Fig. 2.11 shows a conceptual schematic model of the Zn vacancy in different charge states. It is based upon a combination of interpretation of Bjerg *et al.*'s work [118] and a popularization of Fairs Vacancy model for silicon [120].

The vacancy can in principle have any charge states, but only -2, -1 and 0 seem readily accessible by doping and temperature variation. Fig. 2.12 shows the atomic configuration of the ZnSb with vacancy and the relaxed lattice constant as calculated by Bjerg *et al.* [118]. The formation energy for V_{Zn}^- in this configuration was calculated to be 0.32 eV. The net hole concentration in ZnSb without any doping was then calculated from the requirement of charge neutrality and assuming equilibrium number of vacancies in different charge states (-1 and -2 dominated). The net hole concentration in this configuration was calculated to be $8.8 \times 10^{17} \text{ cm}^{-3}$ at room temperature, which is in the range of the experimental Hall concentrations measured by Böttger *et al.* ($4 - 10 \times 10^{17} \text{ cm}^{-3}$) [53]. One should also compare the calculated net hole concentration to the carrier concentration of undoped single crystal ZnSb that is significantly lower than $8.8 \times 10^{17} \text{ cm}^{-3}$. This apparent discrepancy indicates that the exact values of the formation energies should be used with caution. However, the concepts and the idea of V_{Zn} as a very important defect seem valid. The authors pointed out that at higher vacancy concentration, their approximation of a dilute defect concentration would not hold.

There have been many reports on changes in carrier concentration after heat treatments, both for single crystal and polycrystalline ZnSb. Many observed a slow recovery to the initial carrier concentrations [52, 57, 71, 74, 75, 77, 121]. Andronik *et al.* specifically attributed this change to Frenkel defects [121]: by a Zn atom leaving the lattice and becoming

Fig. 2.11.: Schematic drawing of occupancy of localized states associated with the Zn vacancy in ZnSb. The vacancy will have different charge states -1, -2, -3 dependent upon the position of the Fermi level E_F with respect to the levels E_V^{-1} , E_V^{-2} and E_V^{-3} . E_V is the valence band onset and E_C is the conduction band (CB) onset.

Fig. 2.12.: Atomic arrangement of Zn (gray) and Sb (blue) atoms. (a) Perfect ZnSb lattice; (b) A Zn vacancy with charge state -2. The distance between nearest neighbor atoms are annotated [118].

vacancy-interstitial pair, $V_{\text{Zn}}\text{-Zn}_{\text{I}}$. By assuming that all of the measured changes in carrier concentration were due to Frenkel defect formation, the activation energy of the process could be determined. The Frenkel defect concentration n_{Φ} was assumed to be given by $n_{\Phi} = \sqrt{NN'}e^{-\frac{E_{\Phi}}{2kT}}$, where $n_{\Phi} = n_i - n_0$ is the concentration of Frenkel defect, n_0 and n_i are the concentration before and after heating, N is the concentration of atoms, N' is the concentration of interstitials (there are more than one interstitial position in lattice), E_{Φ} is the formation energy of the Frenkel pair. The formation energy was determined from the experiments to be 0.5 eV. This experimental value seems in the range of formation energies calculated by Bjerg *et al.* [118]. On the other hand, the formation energy for a Zn vacancy calculated by Jund *et al.* gave a different value of 0.8 eV [95]. This calculation used a $\text{Zn}_{64}\text{Sb}_{64}$ supercell with 128 lattice sites and compared it to the energy of a $\text{Zn}_{63}\text{Sb}_{64}$ supercell at 0 K, which corresponds to a vacancy concentration of 1.5 at%.

In *manuscript 4.5*, we have studied the evaporation of Zn by thermogravimetry and Zn vacancy created during vaporization. The net hole concentration was measured to be about $6 \times 10^{18} \text{ cm}^{-3}$, corresponding to a vacancy concentration of about 0.03 at%. Schematically two processes in series were considered as:

Reaction [1] occurs when the V_{Zn} was created but within the dilute limit, while reaction [2] applies to a situation where the Zn vacancy concentration is beyond the solubility limit and ZnSb decomposes into Sb phase and Zn vapor.

2.8. Impurity band conduction

2.8.1. The observation of impurity band conduction

In an idealized semiconductor, which is well approximated by pure Si crystals [122], the carrier concentration shows the so-called "freeze out" feature at low (cryogenic) temperatures: the dopant atoms are not ionized and the carrier concentration goes towards zero, characterized by an infinite Hall coefficient in Hall measurements. However, the Hall coefficient in undoped ZnSb has shown a turning point at low temperatures, typically below 50K, as seen in Fig. 2.13, and then a decrease with further cooling which is explained by an impurity band conduction (see *manuscript 4.1*). Here, the term impurity band is most likely tied to the defects, but the observed phenomena are similar to what can be observed for high doping concentration semiconductors. Impurity band conduction has been reported in many materials [123–125]. It was also observed for ZnSb by Justi *et al.* in 1960s [51]. Recently several others have reported on an impurity band in ZnSb [80, 103].

Let us here analyze sketchily the conditions for observing the characteristics shown in Fig. 2.13. The specifics of this observation are given in *manuscript 4.1*. The changes in the hole concentration in the valence band as the sample was cooled is in principle similar to that of a textbook low doping concentration semiconductor, where the carriers are frozen out of the band. The valence band in the sample of Fig. 2.13 will be nearly empty (for holes) at the lowest temperature. The holes are transferred to the acceptor based impurity band. The holes are however mobile in the impurity band and contribute to conduction and Hall effect. Thus the Hall coefficient decreases with cooling to the lowest temperatures. In order to get conduction in the impurity band some donor compensating centers are needed. (Without donor level, the impurity band would be full of holes (empty) and there is no conduction.) The Fermi level is located above the valence band, while below the impurity band for the lowest temperatures. (This can be found by satisfying the requirement of charge neutrality). The occupancy (of nholes) in the valence band will increase sharply as the Fermi function widens and also will increase in position with temperature. The position of Fermi level as a function of temperature is shown in Fig. 2.14. Thus the hole concentration of the impurity band is depleted.

Fig. 2.13.: The Hall coefficient of an undoped hot-pressed ZnSb sample. The Hall coefficient in ideal cases is inversely proportional to the carrier concentration. If there was a regular freeze out of the carriers, the Hall coefficient goes to infinity at low temperatures. However in the presented case of undoped ZnSb, there is turning point in Hall coefficient, which was interpreted as a signature of an impurity band.

Fig. 2.14.: Temperature dependent Fermi level in undoped ZnSb. (See *manuscript 4.1*)

We turn to the situation where the doping concentration is much higher than that in Fig. 2.13. Would one be able to observe that an impurity band had formed from Hall and resistivity measurement then? Fig. 2.15 compares the Hall carrier concentration and the Hall mobility (inset) at low temperature for high (0.3 at% Cu) and lower concentration (no Cu), respectively (data in *manuscripts 4.1, 4.2*). One can see that the characteristic feature of impurity band conduction vanished in the highly doped sample at the low temperature. The situation is qualitatively as follows: A highly doped sample is equivalent

to a degenerate semiconductor, where the hole concentration is high and the Fermi level is located in the valence band. The native impurity band would be full of holes and so does the top of the valence band. Given the low temperature situation, the conduction will occur within the valence band. Therefore one cannot have a similar change with temperature as in the case of undoped ZnSb. Even if the Fermi level will move into the band gap at higher temperature, the Fermi-Dirac distribution widens and one will never have an emptying of holes in the valence band. The details of the electronic structure of highly Cu doped ZnSb is, however, unknown.

Fig. 2.15.: The Hall carrier concentration at low temperature on highly doped ZnSb (0.3 at% Cu) and low carrier concentration (undoped) ZnSb. Inset: Hall mobility [102,126].

2.8.2. The nature of impurity band and conduction

An impurity band in general

The impurity band comes from interactions which set in for defect concentrations above a certain value. The defects can be dopant atoms, impurities or intrinsic crystal defects. For now, we will use the generic term impurity band, whatever their origin is. Consider one type of impurity (for instance a donor) at low concentrations. It may introduce a localized impurity state with an energy level (for instance a donor level) in the band gap as shown in Fig. 2.16 (a). Such system may show "freeze-out" at low temperature if $k_B T \ll E_{d0}$, where E_{d0} is the ionization energy of the donor. The material will then act as an isolator. For increasingly larger doping concentrations the effective ionization energy, E_d , is reduced for two possible reasons: *i*) overlap of the Coulomb potential from each donor atom as illustrated in Fig. 2.17; *ii*) high electron concentrations will decrease E_d due to screening.

Electrons at a donor level can then be transferred to a neighbor donor by thermal activation and tunneling, but without entering into states in the conduction band. One would then have the hopping region for transport in the material as illustrated in Fig. 2.16 (a). When the donor concentration increases further, the wavefunctions of the donor states overlap and can form a band, where one has impurity band conduction, as illustrated in Fig. 2.16 (b). The mobility in the impurity band is typically small because the band is relatively narrow, and as a consequence one would have a small dispersion curvature in $E(\vec{k})$ and large effective mass. In a semiconductor at low temperature, conduction can occur dominantly in

Fig. 2.16.: Schematics of impurity state/band and conduction band (CB) for n -type semiconductor at low impurity concentration, medium concentration and high concentration at random impurity distribution. Band diagrams illustrate the hopping conduction and impurity band conduction [127]. Inset: A dimensional schematic calculated density of states for high impurity concentration. E_0 is assumed to be the onset of the conduction band; $D_C(E)$ is the number of conduction band and $D_{im}(E)$ is the density of states of impurities in periodically arrangement [128].

the impurity band if there are some compensating levels, such that the impurity band is not fully occupied. At a particular higher concentration there may be a smear of the impurity band and the conduction band, as illustrated in Fig. 2.16 (c). Beyond this concentration the Mott transition, which is a sharp transition from insulator to metal behavior, can take place.

Usually the Mott criterion for the transition occurs when $N_I \geq 0.014a_B^{-3}$, where N_I is the atomic concentration of impurity and a_B is the Bohr radius of the impurity. There are several different treatments yielding essentially the same numbers [127]. The most considered situations are those of high concentrations of shallow donors or acceptors. Here, the Mott criterion gives the insulator-metal transition. However one can create impurity bands with certain energy anywhere in the band gap. Some of the concentrations for the Mott transition then approximately correspond to the concentration to have an impurity band. Rawat *et al.* have suggested a Yb mid-gap impurity band in PbTe affecting the thermoelectric properties [129]. With the doping concentrations for optimum thermoelectric performance that typically is $\sim 10^{19} \text{ cm}^{-3}$, it is reasonable to

Fig. 2.17.: The screened Coulomb potentials at conduction band edge with defects potentials. For high donor concentrations the Coulomb potentials overlap and the ionization energy E_{d0} is reduced to E_d . For high impurity concentration, the screened Coulomb potential does not depend on $1/r$ but is dominated by e^{-r/r_s} , where r_s is the screening radius [127].

expect that the formation of impurity bands is rather common in thermoelectric materials. Also, impurity band formation is just one of several high doping effects one should expect, such as the Mott transition, band tailing, and band gap renormalization [127]. Thus, one should discuss thermoelectric material in the framework of the theory related to heavily doped semiconductors.

Impurity band in ZnSb - its nature, origin and specific points of interest

When it comes to ZnSb specifically, it has been estimated that the impurity band may exist for the impurity concentrations that are well within the observed doping concentrations. In *manuscript 4.1* we have determined the critical impurity concentration in ZnSb to be about $6 \times 10^{17} \text{ cm}^{-3}$ which is around the acceptor concentrations used in the model to fit the low temperature measurements. For the doping concentration of $10^{18} - 10^{19} \text{ cm}^{-3}$ in ZnSb, one can expect impurity bands to form. For undoped or very lightly doped material, we suggested that point defects, especially Zn vacancies can be expected to be involved in impurity bands. From the discussion of vacancy formation in Section 2.7, it appears likely that a high concentration of vacancies can be created by annealing, even to some extent they could combine with any other possible impurities or defects in impurity band. The impurities will likely be dependent on the specific dopants and the preparation technique. For example is oxygen expected to be an impurity in ballmilled material and to the extent being dependent on the atmosphere during processing. It may be different than directly solidified and homogenized materials. However the solid solubility of oxygen is unknown, so presently one cannot make a conclusion about the importance of oxygen in this context. Fedorov *et al.* observed evidence for impurity levels in the band gap associated with different combinations of group I (Ag or Cu) and group IV (Sn or Ge) acceptor elements, which all were similar to each other, but different to those of single acceptor element [58]. Temperature dependent transport coefficients were also measured that were interpreted as a temperature dependent energy state being present with a level in the valence band. The states were considered as hybridized states formed by mixing characters of the valence band and the impurity. In a general case, a temperature dependent level can have a similar effect as growth of position and decrease of population of two levels with temperature due to defect chemistry as suggested in *manuscript 4.2*.

2.8.3. Impact of impurity band on thermoelectric properties

An impurity band will have an effect on the transport properties and the thermoelectric device properties. It may not be immediately transparent how. The conduction in the impurity band is perhaps a minor effect in this context. The most important effect may be on the Seebeck coefficient.

Effect on conduction

The effect of impurity bands on the conductivity is expected to be largest when holes in the valence band (for p -type) do not contribute to the conduction [103]. This is expected to have a strong effect for samples where the doping is below degenerate but sufficiently close to the Mott criterion, and in addition at low temperatures. In a material it is expected that the mobility of carriers in an impurity band is much lower than that in the valence band, thus the impurity band should only have a modest effect on the conductivity.

Effect upon Seebeck - effective density of states mass

The density of states effective mass may be affected by an impurity band. The density of states may change by several high doping effects including the formation of impurity bands. Qualitatively a smear of the impurity band and valence band is expected. Thus, even though the conduction of impurity band is often only observable at low temperature, the Seebeck coefficient can be affected above room temperature. The details to calculate the transport coefficients can be found in *manuscript 4.1*. The Seebeck coefficient is sensitive to the position of the Fermi level and how the density of states varies with energy. Both these factors can be affected by an impurity band. There have been reports on change of density of states effective mass with varying doping concentration [103]. From a Pisarenko plot, one can find the density of states effective mass by fitting the measured data. In *manuscript 4.2* we obtained the best fitting by assuming an impurity band. Further it was shown that camel shaped curves of Seebeck coefficient with temperature, which is unusual in ZnSb, could be modeled by a temperature dependent impurity band. It has been suggested that if one could engineer the energy structure of impurity band, one could have a tool to enhance the thermoelectric performance [130].

Another impact of the impurity band may be on the n to p transition. This was suggested by Schneider by the observation of a sharp increase of electrical conductivity on a temporary n -type and following n to p transition [116] and by Niedziolka based on the calculation of Zn vacancies always leading a p -type behavior [89]. Once the impurity band associated to the vacancies is formed, the Fermi level will be pushed towards the valence band, displaying p -type behavior. On a similar topic, though with different statements, Fedorov *et al.* rationalized the difficulty to dope ZnSb as n -type with the formation of an impurity band close to the conduction band [58].

2.9. Hysteresis in conductivity

Real hysteresis in thermoelectric properties of a sample is discussed in this section and this is not the hysteresis due to temperature gradients in measurement setups. Several

authors have reported that after a heat treatment of ZnSb they have observed an increase in the electrical conductivity and carrier concentration while a decrease in the Seebeck coefficient compared to before the heat treatment. Then they note a slow recovery towards the initial value at room temperature [52, 57, 71, 74, 75, 77, 121]. The changes followed such a loop, thus a hysteresis. The temperature for the hysteresis has varied among different reports. For single crystal ZnSb samples with high purity, Andronik *et al.* [121] and Tuner *et al.* [71] reported 100 °C, Kostur and Psarev reported 150 °C [74], Komiya *et al.* reported 200 °C [77], and Kot and Kretsu reported 250 °C [75]. It can be that the hysteresis effect observed has a single explanation and the one that is presented below seems both simple and plausible: It has been related to the $V_{\text{Zn}}\text{-Zn}_\text{I}$ Frenkel pair formation at elevated temperatures, which was mentioned in Section 2.7. It was rationalized that these hysteresis effects would not be significant at high doping concentration [52]. That seems reasonable, if comparing the same temperatures and assuming the same concentration of vacancies are created for low and high doping concentration, the relative changes associated to Frenkel pairs in the measured values is much smaller in the high doping concentration case under otherwise equal conditions and assumptions.

There are also other observations and phenomena related to that of temperature cycling hysteresis. An apparently necessary but not sufficient condition for hysteresis is a change in the state of the sample by temperature. The nature of this change can be purely redistribution of electrons among energy states, or be structural changes, such as point defect formation and interactions, grain growth, phase segregation, evaporation, oxidation, or mechanical deformation. To get hysteresis, the initial state should be reestablished somehow. Several of the processes leading to the changes are irreversible and would not lead to hysteresis.

Many of the electron state filling processes are expected to have so fast kinetics that the equilibrium filling state is reached at the measurement temperatures. Then it would not lead to hysteresis. Some charge trapping, however, might still occur and this would though depend upon the cooling rate. Point defect chemistry is expected to have a more sluggish response and it may be too fast to establish equilibrium at each measurement point, while a much lower temperature scan rate or a pause in the downward temperature sweep may reestablish equilibrium. Fig. 2.18 shows an example of a hysteresis curve for resistivity as a function of temperature where the sweep was paused during cool down which caused the resistivity regain the value it had on warm-up. Of the mechanisms leading to a change men-

Fig. 2.18.: Resistivity of ZnSb doped by 0.1 at% Cu vs. temperature showed hysteresis. The values depends upon if the temperature is going up or down. The original value can also be obtained by annealing for a longer time at lower temperature (400 K) than branching point (520 K) [131].

Fig. 2.19.: Summary of hysteresis experiments on the Seebeck measurements (a) and the van der Pauw measurements (b) in thermal cycles: cycle 1 – the initial states; cycle 2 – immediately measured after cycle 1; cycle 3 – after stored in air for one week; cycle 4 – after stored in a reducing atmosphere for one week; cycle 5 and cycle 6 are repeating cycle 3 and 4. For each thermal cycle, the decreased the room temperature Seebeck coefficient and the electrical resistivity after heating recovered to initial value when the sample was stored in the air for a week, however, being maintained if the sample was stored in a reducing atmosphere.

tioned, one would further assume that grain growth, which was observed in *manuscript 4.3*, would lead to a change which cannot be restored. The same applies to large scale evaporation as reported in *manuscript 4.5*. By cycling to high enough temperature, there will always be a permanent change in the ZnSb sample properties.

Yet, some reports on ZnSb samples with higher doping concentrations did not show hysteresis [56]. During this thesis work there were also some samples, both undoped and doped, that showed no significant hysteresis effects for reasonable cycling temperatures, such as high sintering temperature or long term annealed samples.

In order to check for the possibility of interactions with the ambient being part of the hysteresis observed in temperature cycling, we did a series of experiments which are further described in the *Appendix A*. The overarching hypothesis was that gas atoms from the ambient can diffuse into the sample and interact with dopants, point defects or the lattice, and that can influence the doping. The sample was measured in reducing atmosphere that

contains hydrogen. Hydrogen may diffuse into ZnSb and get trapped by a compensating site or creating acceptor site. Alternative hypothesis is that if the oxide species can be made volatile by heating in a reducing atmosphere while being able to reform at room temperature in lab air, they indeed influence charge carrier concentration. Then one might observe a hysteresis. Also, doing measurements in a reducing atmosphere changes the state of ZnSb. Oxygen species could affect the electrical conductivity in a number of direct and indirect ways, and we do not have experimental means to tell which.

2.10. Thermal conductivity

In literature ZnSb is not usually considered as a low thermal conductivity semiconductor, particularly compared to its family compound Zn_4Sb_3 , when reviewing material parameters in the context of looking for favorable thermoelectric properties. It is then considered that ZnSb has potential because of its other key thermoelectric properties. On the other hand, Fisher *et al.* considered the thermal conductivity as inherently low and are seeking systematic reasons [81,132]. They then suggested the origin of low thermal conductivity could be a consequence of the multi-center bonded structure of the Zn_2Sb_2 -ring. As their bonding are rationalized as similar to that in the Zintl phase, which has low thermal conductivity, by less electron count. The electron poor multi-centered bond gives rise to a manifold of localized low energy optical modes, which results in the interaction between these modes and acoustic phonons, leading to a low thermal conductivity [81,94].

Thermal conductivity at low temperature may be not important for thermoelectric applications. However, it benefits to the understanding of scattering mechanisms. At low temperature where impurity scattering dominates, the thermal conductivity follows a $1/T$ law. The maximum thermal conductivity occurs at the temperature that equals $1/20 \Theta_D$, where Θ_D is the Debye temperature. The Debye temperature of ZnSb has been determined in a range of 175 K to 225 K. [82, 132, 134] Thus the maximum thermal conductivity in ZnSb is around 10 ± 1.5 K. When the temperature is below the maximum point, the thermal

conductivity changes as T^3 in the single crystals. In polycrystalline samples, the thermal conductivity is limited by grain boundaries and follows T^2 , as shown in Fig. 2.20 [133]. As the temperature increases to above the maximum point, the phonon mean free path is

Fig. 2.20.: Thermal conductivity for cold pressed (CP) and Spark Plasma Sintered (SPS) at different temperature [80]. The inset is thermal conductivity of single crystal and polycrystalline ZnSb, respectively [133].

comparable with the grain size, and the thermal conductivity is dominated by Umklapp scattering, following $T^{1/2}$. The position of the maximum point depends on the relation between grain size and phonon mean free path. Eklöf *et al.* reported the thermal conductivity on samples with different grain size. For the sample with small grains synthesized by Spark Plasma Sintering (SPS) at relatively high temperature of 450°C, the maximum is at 22.1 K, while for cold pressed samples that contain even smaller grains, the maximum occurs at 37.7K due to the fracture structure [80]. This observation is consistent with the report for a single crystal at 15 K [133].

The Wiedemann-Franz law distinguishes the thermal contribution from electrons and phonon by knowing the Lorenz number $\mathcal{L}$. For a metal, $\mathcal{L}$ is weakly temperature dependent, and usually takes Sommerfeld value of $2.44 \times 10^{-8} \text{ (V/K)}^2$. [135] For a semiconductor, it can change to $1.49 \times 10^{-8} \text{ (V/K)}^2$ [136]. Experimentally, the Lorenz number can be estimated by fitting the Seebeck coefficient to the reduced Fermi level. It may give $1.55 \times 10^{-8} \text{ (V/K)}^2$ for undoped ZnSb and $1.65 \times 10^{-8} \text{ (V/K)}^2$ for doped samples [56].

The increase of lattice thermal conductivity at high temperature has been observed by many studies that attribute to the bipolar diffusion due to electron-hole pairs [56, 57, 59, 103]. Theoretically, the bipolar term can be extracted by [137]

$$\kappa_b = \frac{\sigma_p \sigma_n}{\sigma_p + \sigma_n} (\alpha_p - \alpha_n)^2 T \quad (2.2)$$

However, it is difficult to separate the electrons and holes contribution in the Seebeck coefficient and the electrical conductivity. Moreover the bipolar diffusion is a minor effect at the range of operation temperature of ZnSb. Therefore, the bipolar term is often merged in the electron thermal conductivity.

The phonon-glass limit of thermal conductivity has been calculated by Böttger using Cahill's formula for an amorphous solid

$$\kappa_{min} = \frac{1}{2} \left(\frac{\pi}{6} \right) k_B V^{-\frac{2}{3}} (2v_t + v_l), \quad (2.3)$$

where v_t and v_l are the transverse and longitudinal sound velocities. It gives the phonon-glass limit for thermal conductivity to be approximately 0.6 W/(m · K) in ZnSb, which agrees with other reports [59, 95]. Lattice thermal conductivity can be reduced by nanostructuring, by which enormous grain boundaries were introduced to scatter the mid- and long- wavelength phonon. Ballmilling as a technique to reach nanoscale has been widely reported with a reduction on thermal conductivity by 40 % in ZnSb [53]. In *manuscript 4.3*, we report that milling at cryogenic temperature followed by rapid hot press reduced the thermal conductivity to the value that is close to the phonon-glass limit in undoped ZnSb.

3. Experimental methods

The experimental methods vary in different individual work and are described in detail in each manuscript. Many of the techniques are well-known and described in textbooks and review articles. This chapter will systematize the methods used in this thesis, focusing on synthesis and some custom-built setups.

3.1. ZnSb synthesis and sample preparation

The samples that have been used in this thesis were all polycrystalline ZnSb with or without intentional doping. Different processing steps and processing equipments have been used because of a natural evolution in the construction, building of processing equipment and testing of the different synthesis methods. Most of the samples were fabricated at the University of Oslo (UiO). Some processing steps for some of the samples took place at SINTEF and the California institute of Technology (Caltech).

The processing steps are categorized into three groups, namely

- Stoichiometric melts; (SM)
- Powder metallurgic method; (PM)
- Pseudo-Pulverized and Intermixed Elements Sintering method; (Pseudo-PIES)

Fig. 3.1 shows the flow chart for three categories. The purities of the starting materials were: Zn 99.99 % and Sb 99.99 %. The materials were weighted according to the designed stoichiometric atomic ratio and sealed in an evacuated quartz ampule. A typical batch weight was approximately 10 g. The stoichiometric melt (SM) samples were obtained by direct melting of the elements followed by solidification. Since solid ZnSb is fragile and brittle, the melts were cooled in air in order to prolong the solidification and yield larger pieces. In order to improve the homogeneity, the ingot was then annealed at 450 – 550 °C for 120 hours when it was still sealed in the quartz ampule. The resultant ingot was then prepared by scribing (or sawing), lapping and polishing for the needs of measurements. This method yields more cracks and pores than the other methods, as described in *manuscript 4.6* for one sample series. The electrical conductivity is about 1 – 2 order of magnitude lower than the PM samples due to the cracks and pores.

Fig. 3.1.: Flow chart of synthesis procedures.

For many samples we follow a procedure that includes the basic ingredients of standard powder metallurgy (PM). The elements are pulverized, compacted, and sintered. The method(s) have been widely used for making thermoelectric materials. In our PM procedure the ampule is quenched in cold water. The ingots were crushed in an argon atmosphere and loaded into a stainless steel jar with milling balls (containing Fe and 13 at% Cr) for ballmilling. Ballmilling was done at room temperature or at cryogenic temperature. The milling machine at room temperature uses centrifugal force. We used a rotation speed of 400 rpm for 30 minutes, where the centrifuge reversed every 5-minute-cycle with 1 minute pause inbetween to dispose the residual heat. The milling machine at cryogenic temperature (cryomilling) used radial oscillations at horizontal position while the jar was cooled by the flow of liquid nitrogen. The ingot was embrittled and crushed into fine grains by the vibration. Each cryomilling cycle was programed as a 25 Hz oscillation for 20 minutes, followed by 5 Hz low frequency for 5 minutes in order to reduce the residual heat. 3 – 15 cycles, depending on the needs, were performed on different samples. We found out that the duration of the milling time did not have a direct impact on the resultant powder on cryomilling. The resultant powder was then sealed in either an Al foil or a graphite foil in a glove box under an argon flow in order to reduce the oxidization. Hot-pressing was then employed after milling. The sintering temperature was 350 – 525 °C for different samples. Two sets of hot-press setups have been used in this PhD work: slow hot-press (SHP, at UiO) and rapid-hot press (RHP, at Caltech). RHP has been described in details in reference [138]. Here we briefly document the custom-built SHP setup: The SHP is constructed in horizontal position. There is a 10 cm uniform heat zone where the center of the die is located (sample's position). The heating rate was 16 K/min. A pressure up to 30 MPa is loaded from both sides. The sintering chamber was evacuated to 0.2 mbar during the sintering and 3×10^{-3} mbar after sintering due to the shrink of the volume. The dwelling time for SHP was 30 – 60 minutes and the cooling to room temperature took about 24 hours, while the dwelling time for RHP is 10 minutes and it took about 90 – 120 minutes to cool down to the room temperature.

For some individual cases, the pseudo-PIES method was used. The PIES method (Pulverized and intermixed elements sintering method) has been introduced into preparation of thermoelectric $(\text{Bi/Sb})_2(\text{Te/Se})_3$ materials, where all the elements are initially mixed and milled to fine powder before hot-pressing (no melting process) [139, 140]. The electrical conductivity of ZnSb that was synthesized by this method has been reported about 5 times higher than the SM sample [141]. Distinguished from a typical PIES method, we used pseudo-PIES which partially mixed the dopant element with SM ingot in ballmilling, and then processed hot-pressing.

The densities of pellets have been measured by the Archimedes method, adapted to ISO 5017 standard. We have found that the region close to the edge of the hot-pressed pellet is more porous. The pellets were often cut to desired shape by a diamond saw or a micro-saw.

An alternative method is using the diamond pen to initiate cracks in the sample and break it in a way that is often used for Si-wafer. By this way, it would create less mechanical damage than sawing. The sample surface is usually polished optically flat by P4000 sandpaper and finalized by Struers MD 1/4 μm cloth (Abrasive: Diamant).

3.2. Microstructure characterization

The **microstructure** of the samples has been examined by scanning electron microscopy (SEM): Hitachi TM3000 (only equipped with backscattered detector) and FEI Quanta 200 FEG-ESEM. The high temperature stage can be optionally installed for the *in situ* study with only the secondary electron detector and under water vapor. Transmission electron microscopies (FEI-Titan G2 60-300 and JOEL 2000) were used for nanoscale structure. The information, such as grain size, precipitates and grain boundary migration can be revealed by TEM images. Scanning TEM (STEM) mode reveals the local atomic structure. By applying the Fourier transform on a STEM image, one can obtain the diffraction pattern on the selected area. Then the phase composition of the selected area can be analyzed by the crystallographic method. The TEM specimens were prepared by ion milling for 4 – 5 hours, local temperature was 32 °C – 50 °C. The average **phase composition** was determined by Energy Dispersion Spectroscopy (EDS) (applied both in SEM and STEM) and X-ray Diffraction (XRD). *In situ* XRD (Bruker D8 Advance XRD) was performed on both powder and pellets while being heated. The powder was mixed in acetone and cured on a platinum stage. The measurements were run under argon atmosphere from $2\theta = 5^\circ - 125^\circ$, with a step size of 0.010 at a rate of 0.20 sec/steps. The heating was from 50 °C – 350 °C with a step of 50 °.

The **grain size distribution** can be estimated by applying the Full-Width-Half-Maximum (FWHM) method on the X-ray diffractogram. FWHM offers average grain size through the whole sample, that compensates information of particle size in a local area by mapping on TEM imaging. Another method that has been used for estimating the particle size of ballmilled powders is Dynamic Light Scattering (DLS, Malvern Zetasizer) by suspending the powder particles in methanol and using factory pre-installed routines for data analysis.

The **oxidation** of ZnSb is also an issue. Inert Gas Fusion Analysis (IGFA) has been used to analyze the oxygen content in the bulk of the material. This method has been used for analyzing the oxygen percentage by extracting oxygen from the sample melt as carbon monoxide, and has proved to be a rather accurate method for elements with low concentration [142, 143]. The chemistry of the oxide was also studied by X-ray Photoelectron Spectroscopy (XPS). In XPS, the sample was sputtered by Ar ion beam. The X-ray radiation was directed to the sample, while the ejected photoelectrons, $h\nu$, were measured for calculating the binding energy E_b by $E_k = h\nu - E_b - \Phi$ [144]. The chemical shift between metal and oxide for the element Sb can be used to characterize the oxide according to the

NIST database. For Zn, it might be easier to identify the different phases by Zn LMM Auger line at lower energy, where there is often a clear shift between the metallic and the oxide peak. Time of Flight Secondary ion mass Spectrometry (TOF-SIMS) is another technique for identifying the elemental species on the surface and at certain depth. A pulsed beam of primary ions was sent to the sample surface, producing secondary ions in a sputtering process. The secondary beam corresponding to the molecular or atomic mass suggested the oxide composition [145].

3.3. Reducing atmosphere

The atmosphere used for high temperature measurement is specified in each manuscript. A reducing atmosphere has been used for some experiments with the intention of minimizing oxidation. In the temperature dependent measurements that were performed at UiO, either continuous dry nitrogen flow or a mix of argon and hydrogen flow at a rate of 0.03 l/min was used. However, even when using a nominally inert gas like argon or nitrogen, oxidation can occur due to the presence of spurious oxygen. The used gases had a nominal purity of 5N (purity 99.999 %), i.e. 10 ppm impurities, such as O₂. To reduce the concentration of oxygen, we therefore diluted the gas with hydrogen, which reacts with oxygen to form water according to $\frac{1}{2}\text{O}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O}$. Hydrogen has been used for reducing the oxidation during the growth of single crystal ZnSb [146]. Certainly the kinetics of oxidation by water has been studied in silicon [147,148]. Given for the larger molecule of water, the diffusion rate is significantly reduced. In several experiments, we connected the measurement chamber to a mix of 99 vol.% Ar₂ and 1 vol.% H₂ flow (H-Ar mix). The oxygen partial pressure under above condition can be calculated by the equilibrium condition [149], and changes with temperature. Typically, it ranges from $10^{-25} - 10^{-20}$ atm, thus much lower than the spurious concentration of oxygen in nominally inert gas.

3.4. Thermogravimetric analysis

Thermogravimetric analysis of the rate of Zn evaporation was performed using a CI Electronics MK2 microbalance. The sample and the counterweight were attached to the arms of the balance with thin platinum wires. The sample was hanging in an alumina tube in a vertical tubular furnace and the counterweight was hanging in a glass tube kept at room temperature. The measurement chamber was continuously flushed with H-Ar mix to prevent oxidation. The weight change was monitored versus time at different temperatures to obtain the evaporation rate. Due to the rapid mass loss at higher temperatures, shorter time may be needed to extract a reliable mass loss rate under these conditions. All weights were corrected for buoyancy arising from the asymmetrical temperature of sample and counterweight [150].

3.5. Electrical properties measurements

The electrical conductivity has been obtained by measuring the resistivity by a standard van der Pauw configuration. The Hall voltage is often measured in the same run subsequent to the resistivity measurements with the presence of magnetic field. These measurements then yield the carrier type, p or n , carrier mobility and carrier concentration in addition to the resistivity. Fig. 3.2 shows the configuration for the van der Pauw method, Hall measurements and one hot-pressed pellet with the holder and contacts at the periphery of the sample.

Fig. 3.2.: (a) Configuration of contacts which are used for supplying current and measuring voltages at its periphery for van der Pauw method. (b) Configuration of contacts for Hall measurement at the presence of magnetic field. The contacts for voltage measurements and for supplying current are permuted. (c) One hot-pressed pellet with the holder.

The procedure for resistivity measurements and the philosophy behind it has been described in references [151–153]. The van der Pauw and Hall measurements in this PhD thesis has been performed at different conditions: room temperature, low temperature (6 K) in vacuum when cooled by helium flow, high temperature (up to 450 °C) under H-Ar mix atmosphere or in vacuum. The uncertainty of van der Pauw methods and Hall measurement was estimated to be 5 %.

3.6. Seebeck coefficient measurements

The Seebeck coefficient has been measured cross-plane. Fig. 3.3 shows two main configurations that have been used in this thesis. Fig. 3.3 (a) shows the 2-point method, which has the advantage of minimizing thermal and electrical resistance due to non-direct contact. Fig. 3.3 (b) shows the uniaxial 4-point method which provides lower thermal contact resistance, however, has the risk of cold finger effect [154]. The setups have been described in detail in references [155–157].

Temperatures at hot and cold contacts have been annotated in Fig. 3.3 as T_H and T_C . The Seebeck voltage is measured via the thermocouples that is (i) through the copper blocks in the 2-point method; (ii) directly in contact with the sample in the uniaxial 4-point. The deviation between two methods was estimated to be 7 %. The measured voltage across the

Fig. 3.3.: Two Seebeck configurations used in this thesis. 2-point method (left) and uniaxial 4-point method (right).

sample includes the Seebeck voltage of the sample and two thermocouples [156]:

$$V_{measured} = \int_{T_C}^{T_0} \alpha_w(T) dT + \int_{T_H}^{T_C} \alpha_{sample}(T) dT + \int_{T_0}^{T_H} \alpha_w(T) dT \quad (3.1)$$

where α_w is the Seebeck coefficient for the thermocouple wire. Thus the Seebeck coefficient of the sample at the mean temperature of T_{ave} can be obtained by

$$\alpha_{sample}(T_{ave}) = \frac{V}{T_H - T_C} + \alpha_w(T_{ave}) \quad (3.2)$$

where $T_{ave} = \frac{T_H + T_C}{2}$.

3.7. Laser Flash measurements

Laser flash is a rapid and reliable method to determine the thermal diffusivity and then calculate the thermal conductivity. A commercial laser flash setup NETZSCH[®] LFA 457 MicroFLASHTM has been used in this work. The prepared hot-pressed pellet was coated by graphite for heat conduction. The sample is placed in very small mount of nitrogen flow in order to avoid oxidation, meanwhile satisfy the boundary conditions. When the temperature in the chamber has stabilized at the defined value, a laser pulse hits the front surface of the sample. The heat diffuses through the sample and emitted from the back side that are detected by an IR detector. The timing and intensity of this signal is analyzed to extract the thermal diffusivity, $\mathcal{D}(T)$. The thermal conductivity is then calculated by

$$\kappa(T) = \mathcal{D}(T) \rho_D(T) C_P(T) \quad (3.3)$$

where ρ_D is the density of sample, and the $C_P(T)$ is the specific heat. For ZnSb, $C_P(T)$ fluctuates around 0.3 J/g·K through the temperature range. Therefore, $C_P(T)$ is taken as a constant of 0.3 J/g·K for the calculation of thermal conductivity. The uncertainty of laser flash method was estimated to be less than 3 %.

4. Research results

List of manuscripts

I. Impurity band conduction in the thermoelectric material ZnSb

X. Song, P. H. M. Böttger, O. B. Karlsen, T. G. Finstad, J. Taftø

Physica Scripta T148 (2012) 014001, DOI:10.1088/0031-8949/2012/T148/014001

II. A study of transport properties in Cu and P doped ZnSb

K. Valset, X. Song, T. G. Finstad

Journal of Applied Physics 117, 045709 (2015), DOI:10.1063/1.490640

III. Nanostructuring of Undoped ZnSb by Cryo-Milling

X. Song, K. Valset, J. S. Graff, A. Thøgersen, A. E. Gunnæs, S. Luxsacumar, O. M. Løvvik, J. G. Snyder, T. G. Finstad

Journal of Electronic Materials Vol. 44, No. 8, 2015, DOI: 10.1007/s11664-015-3708-6

IV. Enhancement of thermoelectric properties by energy filtering: Theoretical potential and experimental reality in nanostructured ZnSb

K. Berland, X. Song, P. A. Carvalho, C. Persson, T. G. Finstad, O. M. Løvvik

Journal of Applied Physics, 119, 125103 (2016), DOI: 10.1063/1.4944716

V. Zn vacancy formation, Zn evaporation and decomposition of ZnSb at elevated temperatures: Influence on the microstructure and the electrical properties

X. Song, M. Schrade, N. Masó, T. G. Finstad

Journal of Alloys and Compounds 710 (2017) 762-770, DOI:10.1016/j.jallcom.2017.03.339

VI. A study on S doped ZnSb

X. Song, T. G. Finstad

Submitted to *Material Research Express* in March, 2015

5. Concluding remarks on present and future work

Overarching consideration

The individual papers have their own conclusions of specific results. In retrospect, ZnSb has shown the promising properties as a thermoelectric material for further development. The findings and improvements on its properties in this PhD thesis have contributed to the next steps of designing thermoelectric modules. Yet, there are still many mysteries of ZnSb that remain unsolved. Future work can be planned based on the results in this PhD work. Some of the observed effects can be followed up directly while module realization also will meet other opportunities and challenges.

Defect studies

Systematic studies aimed at a better knowledge of defects in ZnSb are desired. There is a need for theoretical models and improved calculations of native defects, their electronic properties, creation energies and diffusion activation energies. Further, complexes between defects, doping atoms and common contaminants, such as oxygen, hydrogen or carbon need to be systematically computed.

In this thesis several of the observed effects are attributed to defects. Much more experiments are desired to entangle the systematics. Appendix A needs a direct follow up. Using both temperature and hydrogen as an excitation or sensitizing probe while measuring the electrical conductivity, Hall voltage, and Seebeck voltage to reveal kinetic information in a dynamic fashion could be exploited.

Other methods and techniques should be considered, while several would require test samples suitable for the techniques and are thus facing an additional challenge: charge carrier traps can be emptied and filled by applying voltages in p - n junctions, Schottky barriers or metal-insulator-semiconductor (MIS) structures. The latter could be realized by deposition of an insulator (Al_2O_3 , Si_3N_4 , etc.) and metal (Au, Pt, etc.) film. So far, good Schottky barriers have not been reported and an unsuccessful first attempt has been done by others at UiO during this thesis. The traditional technique called electron paramagnetic resonance (EPR) can determine ionization energies and the symmetry of defects. It would require single crystal ZnSb and would be a pioneering challenge.

Nanostructuring

In this thesis it is shown that the thermal conductivity can be reduced by creating small ZnSb crystal grains by nanostructuring. The largest reduction was created by cryomilling and rapid hot-pressing. However this process gave low thermal stability compared to the other process combinations tested, and part of that was attributed to the correlated grain growth. Grain growth is a familiar issue with nanostructured materials. To what extent it would constitute a practical problem, and depends upon the targeted operation temperature. Approaches to minimize grain growth usually consist of adding atoms that segregate in grain boundaries, thereby preventing grain growth. This is an area that needs further study.

There may be other routes to various kinds of nanostructured ZnSb. Some of them may go through various ways of depositing films of ZnSb, such as MOCVD, sputtering and electroplating. Not only for nanostructuring, but other techniques could be feasible for making composites and layered structures with different materials with suitable band offsets for energy filtering. The possibility of making high quality epitaxial films may also be attractive for fundamental material property studies. One might also do band engineering in the material by introducing misfit stress. Thin film deposition may also offer a possibility to grow template nanostructures and exploiting the possibilities of quantum confinement in ZnSb.

***n*-type**

The need for both *n*- and *p*-type materials in thermoelectric modules has been stated in the thesis, as has the challenge of synthesizing *n*-type ZnSb. A practical compromising route towards modules is using another semiconductor than ZnSb for the *n*-type leg. The thesis research project had originally targeted the thermoelectric material $\text{Mg}_2(\text{Sn})\text{Si}$ for this purpose. $\text{Mg}_2(\text{Sn})\text{Si}$ matches ZnSb well in expected operation temperature and has the same environmentally friendly profile. It has also been suggested as the pairing *n*-leg in a module with *p*-ZnSb by the Ioffe group [58]. Unfortunately, the initial tests met synthesis challenges that could not be met within the project. There might also be other suitable material candidates. Any practical problems with thermal expansion mismatch of materials in a module would have to be solved. Fortunately there has been a large development in packaging technology for electronic devices in the last couple of decades. New options for substrates and bonding techniques may be offered and meet the requirements on thermal expansion of the semiconductors. Realization of modern thermoelectric module made of ZnSb may be seen in a new light.

The direct synthesis of *n*-type ZnSb by doping would need a breakthrough. A possibility may arise indirectly from various other investigations on ZnSb; perhaps through a defect engineering or a combination of different approaches, for example modulation doping by embedded higher band gap materials with the appropriate band offsets for supply of electrons combined with compensation of Zn vacancy acceptors.

Module considerations

For new module realizations, the n -type issue should be considered together with thermal expansion and new heat conducting ceramics and new bonding technologies. Long term stability and surface protection coatings to reduce Zn evaporations should be pursued. That approach has improved the thermal stability of III-V materials where the group V elements have higher vapor pressure. The coating might be considered with defect stabilization in mind; (hydrides may supply H from the coating for stabilizing some doping elements). Metallization of ZnSb should be considered more basic. There are still no reported measurements on thermal stability of metallization schemes for ZnSb, no measurements on barrier heights and contact resistance.

Appendix

A. Conductivity hysteresis in Cu-doped ZnSb by thermal cycling in controlled ambients

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C. List of symbols

C_p		Specific heat
D		Diffusivity (gas molecules diffuse in solid)
$D(E)$		Electron density of states
$\mathcal{D}$		Thermal diffusivity
E		Energy
E_g		Band gap
E_F		Quasi-Fermi level
E_C		Energy at conduction band edge
E_V		Energy at valence band edge
E_{F0}		Fermi level in equilibrium state
E_a		Activation energy
E_i		Intrinsic energy level (mid-gap)
E_Φ		Activation energy of Frenkel defect
	n_Φ	Concentration of Frenkel defect
$\mathcal{E}$		Electrical field
$f, (f_0)$		Fermi-Dirac (in equilibrium) distribution
G		Conductance
	$G(E)$	Conductance function
	G_Ω	Ohmic conductance
	G_S	Seebeck conductance
$h, \hbar$		Planck constant, reduced Planck constant
I		Electrical current
I_Q		Heat current
J		Electrical current density
J_Q		Heat current density
k_B		Boltzmann constant
$\vec{k}$		Wave vector in reciprocal space
$\mathcal{L}$		Lorenz factor
m^*		Effective mass
$M(E)$		(Landauer) Charge transport channel
N_{Zn}		Atomic concentration of Zn
n, p		Electron carrier concentration, hole carrier concentration
	n_i, p_i	Intrinsic electron carrier concentration, intrinsic hole carrier concentration
q		Elementary charge
r		Scattering factor
$\vec{r}$		Position in real space

$\vec{v}$	Group velocity
v_t, v_l	Transverse and Longitudinal sound velocities
V_{Zn}	Zn vacancy
V_{Zn}^-	Zn vacancy with charge state -1
$N_{v,\text{Zn}}^-$	Concentration of Zn vacancy with charge state 1
z, zT	Thermoelectric figure-of-merit
α	Seebeck coefficient
α_n, α_p	Seebeck coefficient in n or p type material
β	Thomson coefficient
η	Reduced Fermi energy
η_{COP}	Coefficient of performance for thermoelectric generator
κ	Thermal conductivity
κ_e	Electron thermal conductivity
κ_{ph}	Lattice thermal conductivity
κ_b	Bipolar term in thermal conductivity
μ	Charge mobility
μ_H	Hall mobility
σ	Electrical conductivity
σ_n, σ_p	Electrical conductivity in n or p type material
$\alpha^2 \sigma$	Power factor
Π	Peltier coefficient
π_{ij}	Piezoresistance tensor
ρ	Electrical resistivity
ρ_D	Archimedes density
ρ_{ijk}	Magnetoresistance tensor
τ	Relaxation time
$\frac{\partial f_0}{\partial E}$	Derivative of Fermi Dirac distribution

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