PERFORMANCE ENHANCEMENT IN BULK THERMOELECTRIC MATERIALS

by

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To My Parents
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Chapter 1 Introduction

With recent rising demand for energy all over the world, renewable energy resources are considered as necessary alternatives for the traditional fossil fuels since the oil reserves on the earth are shrinking. Another widely accepted issue of using petroleum, coal, or natural gas is global warming, which is caused by the emission of CO₂. Renewable energy resources include solar, wind, biomass, hydropower, geothermal, and etc. These energy resources are constantly replenished and generate almost zero CO₂ during the energy conversion process. As a result, renewable energy resources can help replace the finite-lifetime and polluting fossil fuels. Based on the latest U.S. energy consumption report published by the Lawrence Livermore National Laboratory,[1] which is also known as the energy flow chart, renewable energy resources contribute to approximately 10% of the total usable energy generated. This number is still increasing since a great many scientists and engineers in both academia and industry dedicate themselves to enhancing the efficiency of renewable energy conversion and reducing the cost. The energy flow chart does not take energy conversion efficiency into account; however, it quantitatively illustrates the efficiency of energy consumption. It is important to note that more than 60% of the total usable energy dissipates as waste heat. While improving the efficiency of energy consumption is an effective approach, directly converting waste heat energy into electricity is also appealing. Unfortunately, most of the traditional heat engines are not capable of making use of waste industrial heat energy effectively.
An interesting phenomenon related to heat conversion was discovered by German physicist Thomas Johann Seebeck more than two centuries ago, and is now known as the Seebeck effect. It is a fundamental material property that a temperature gradient across a piece of material leads to an electrical potential difference between the hot end and the cold end. Such a property opens up a possibility to directly convert waste heat energy to electricity, the process referred to as the thermoelectric energy conversion. The direct application of the Seebeck effect was restricted to accurate temperature measurement using thermocouples until the mid of last century, when NASA successfully implemented thermoelectric generators (TEG) on spacecraft for reliable electricity generation.[2] Containing no moving parts makes thermoelectric generators are much more reliable and maintenance free compared to traditional heat engines.
Because of the advantages mentioned above, thermoelectric generators stood out among other heat engines and were selected to serve in deep space missions.

With the success of thermoelectricity in deep space missions, it is natural to extend its potentials to daily life. As mentioned at the beginning of the chapter, more than 60% of the total usable energy generated dissipates in the form of waste heat. If only 15% of waste heat energy was recovered by thermoelectricity, it would be equal to the total energy generated by all other renewable resources. Alphabet Energy, a thermoelectrics startup, has developed thermoelectric generators recovering exhaust-gas heat to optimize its use with large engines.[3] Such generators can also be rescaled for waste heat recovery in vehicles to save gasoline. Thus, thermoelectricity has held scientists’ and engineers’ attention during the past two decades.

Fortunately, the University of Michigan led a project funded by both the U.S. and China Department of Energy. As part of the team, we focus on engineering bulk polycrystalline inorganic materials for thermoelectric energy conversion efficiency enhancement. The engineered materials will eventually be used for thermoelectric generators fabrication. The project created an opportunity for us to make an improvement in the fundamental material-wise problem, which plays a crucial role in the commercialization of thermoelectricity.

1.1 Basic Concepts
As mentioned above, the Seebeck effect is a fundamental material phenomenon that a temperature gradient results in an electrical potential difference. A coefficient quantifying the ratio of the electric field and the temperature gradient is defined as the Seebeck coefficient $S$:

$$ S = \frac{\partial V}{\partial x} \frac{1}{\partial T} \frac{1}{\partial x} = \frac{\partial V}{\partial T} $$

Equation 1.1

The Seebeck coefficient depends on other properties of the material, such as band structure and scattering processes of the carriers, and thus can be used to characterize the fundamental properties of materials in many areas of condensed matter physics, including superconductivity, for example. In the field of thermoelectricity, the Seebeck coefficient is a material-dependent parameter directly measuring the voltage generated by a unit temperature difference. Obviously, high Seebeck coefficient is desired for thermoelectric applications because high electrical voltage is desired. The Seebeck coefficient can be either positive or negative, corresponding to holes or electrons as the majority carriers, respectively.

The efficiency of thermoelectric energy conversion does not only depend on the Seebeck coefficient. Insulators usually have large Seebeck coefficients; however, it is not hard to imagine that insulators cannot be used for thermoelectricity since the carriers hardly move in these materials. This leads to another material-dependent property, the electrical conductivity or resistivity, which quantifies how conductive the materials are. High electrical conductivity (or low resistivity) is desired for thermoelectric applications. Another important material-based property that affects thermoelectric performance is thermal conductivity, which characterizes how much heat conducts through the materials per unit temperature gradient without being converted into electricity. Low thermal conductivity is desired since it prevents heat from “escaping”. It can be understood in another way that a low thermal conductivity results in a large
temperature gradient per unit heat flow, hence a large voltage. In summary, combining the three factors discussed above, we define a material-wise thermoelectric figure of merit as:

\[ ZT = \frac{S^2 \sigma T}{\kappa} \]

\[ \text{Equation 1.2} \]

where \( \sigma \) is the electrical conductivity, \( \kappa \) is the thermal conductivity, and \( T \) is the absolute temperature. The thermoelectric figure of merit \( ZT \) is directly related to the thermoelectric energy conversion efficiency as:[4]

\[ \phi_{\text{max}} = \frac{T_H - T_C}{T_H} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \]

\[ \text{Equation 1.3} \]

where \( \phi_{\text{max}} \) is the maximum thermoelectric conversion efficiency, assuming energy loss in other forms to be zero, \( T_H \) is the hot-end temperature, \( T_C \) is the cold-end temperature, and \( \bar{T} \) is the average temperature of the thermoelectric material. A high thermoelectric figure of merit leads to high thermoelectric energy conversion efficiency and it is only a material-dependent parameter. Thus, increasing \( ZT \) is the main goal of engineering materials for thermoelectric applications.

Besides power generation at high temperatures, thermoelectricity also possesses a great potential for cooling applications at room or lower temperatures. The inverse Seebeck effect, also known as the Peltier effect, describes that passing an electric current through a junction between two different semiconductors will result in absorption of heat, which is different from the normal irreversible Joule heating associated with charge carrier scattering. Since thermoelectric cooling systems require neither Freon refrigerants nor moving parts, they are exceptionally reliable and quiet. Similarly, the thermoelectric cooling coefficient of performance is positively related to the thermoelectric figure of merit. Thus, engineering thermoelectric materials to enhance \( ZT \) is beneficial for both power generation and cooling.
1.2 Challenges and Approaches

The major challenge for enhancing the thermoelectric figure of merit is the three interrelated material-dependent parameters. A high Seebeck coefficient usually results in a low electrical conductivity, and vice versa. A high electrical conductivity also leads to a high thermal conductivity, since charge carriers also carry heat energy during the electrical conduction. Extensive research has been carried out to reduce the thermal part of the total thermal conductivity by scattering phonons; however, few significant progresses on the enhancement of the power factor, defined as $S^2\sigma$, have been made. Since the Seebeck coefficient and electrical conductivity are closely related to the details of the band structure and scattering processes, the work in this thesis focuses on engineering the band structure and scattering processes to enhance the power factor. In the following chapters, I will demonstrate the detailed approach and discoveries of my Ph.D. research. The contents of the following chapters are summarized as follows: in Chapter 2, I will discuss experimental aspects of the work including sample synthesis and measuring techniques; in Chapter 3, I will demonstrate the approach and discoveries of enhancing the thermoelectric figure of merit in $p$-type binary skutterudite CoSb$_3$ via incorporation of Sn dopants; in Chapter 4, thermoelectric properties of $p$-type filled skutterudites are discussed; in Chapter 5, a novel doping method to improve the average thermoelectric performance over a wide temperature range is proposed and its application in GeTe-CuInTe$_2$ composites is presented. in Chapter 6, I will present the numerical calculation results on the relation between the power factor and band dispersion index and a high dispersion index is
suggested for improving power factor; Chapter 7 will present the conclusion and suggestions for future work.
Chapter 2 Synthesis and Measurement Setup

In this chapter, I will demonstrate the experimental setups for thermoelectric materials synthesis and characterization.

2.1 Thermoelectric Materials Synthesis

An OmniLab glovebox provides an inert gas (N₂ or Ar) environment to minimize oxidation during sample preparation, such as raw elements weighing and mixing. The oxygen and moisture levels are maintained below 0.12 ppm and 0.5 ppm, respectively. A quartz sealing station provides a vacuum environment (~10⁻⁴ Torr) for ampoule creation to minimize oxidation during the process of high temperature heat treatment. Programmable high temperature furnaces calibrated beforehand are used for the synthesis and heat treatment of thermoelectric materials. Powders ground from the as-cast ingots are densified using spark plasma sintering (SPS) apparatus, with the sintering pressure and temperature programmable. An SPS and a homemade hot press setup are installed at the General Motors Research Labs and at the Michigan State University for pellet sintering, respectively.
2.2 Crystallographic and Microstructural Characterization

Powder X-ray diffraction (XRD) characterization was carried out using Rigaku and Scintag XRD diffractometers at the Electron Microbeam Analysis Laboratory – Central Campus (EMAL) at the University of Michigan. Phase identification and lattice parameters were determined by analyzing the diffraction peak patterns using the Rietveld method with the Maud.[5] The XRD equipment generally has a detection limit of ~5%. Backscattered Electron (BSE) Microscopy, Energy Dispersive X-ray Spectroscopy (EDS), and Secondary Electron Microscopy (SEM) were carried out with an FEI Helios and a JEOL – 7800FLV FE scanning electron microscope at the Michigan Center for Materials Characterization (MC$^2$) at the University of Michigan for micron-scale phase identification and structural analysis. Actual elemental composition and its distribution were characterized with an SX-100 Electron Microprobe at EMAL. Transmission electron microscopy (TEM) was performed by Dr. Douglas Medlin at the Sandia National Laboratory and Dr. Wenpei Gao at the Oak Ridge National Laboratory for the determination of nano-scale phase identification and structural analysis. Ultraviolet and X-ray photoemission spectroscopy (UPS and XPS) were performed in Professor Stephen Forrest’s Lab at the University of Michigan for Fermi level detection.

2.3 Transport Measurements

2.3.1 High Temperature Electrical Properties Measurement
High temperature measurements of the Seebeck coefficient and electrical conductivity were performed from room temperature to 800 K using a custom setup. 3×3×10 mm³ specimens were cut from sintered pellets and the measurement configuration shown schematically in Figure 2.1 was used. A heater was attached on top of the bar-shaped sample to generate a temperature gradient. Two Type-R (Platinum-Platinum/Rhodium) thermocouples were attached with silver epoxy on the side of the sample to measure the temperature. The platinum wires of the thermocouples were also used to measure the voltage signal across the sample between the tips of the two thermocouples. Two copper wires were connected to the bottom and the top of the sample to generate a current through the sample. The whole setup was placed in a high temperature furnace, which can reach a temperature of 1000 K. The Seebeck coefficient was measured by fitting the voltage vs. temperature curve, the data taken continuously after the heater was turned on. Electrical conductivity was measured by fitting the voltage vs. current curve. The furnace, together with the sample, was installed in an argon environment with a constant argon flow to prevent oxidation at high temperatures.
2.3.2 Low Temperature Thermoelectric Transport Properties Measurement

Low temperature measurements of the Seebeck coefficient and electrical conductivity were very similar to those at high temperature. In addition, low temperature thermal conductivity was measured at the same time in our setup. 3×3×10 mm³ bars were cut from sintered pellets. A
A strain gauge heater was attached on top of the bar-shaped sample using varnish as the glue to build up a temperature gradient across the sample for Seebeck coefficient and thermal conductivity measurements. To provide an electrical current for resistivity measurements, a copper wire was also attached on top of the sample, under the heater, using indium. The sample was placed on a bronze holder used as the heat sink and electrical conductor. Two Type-T thermocouples (Constantan-Copper) were attached on the side of the sample using indium as contact points and the copper wires were used to read the voltage signal. A steady-state method was used to measure the Seebeck coefficient and thermal conductivity. The voltage and the temperatures of the two thermocouples were read when they stabilized at a certain heating power. Taking the temperatures of the hot and cold end of the sample as $T_h$ and $T_c$, the Seebeck voltage as $V_s$, the power generated in the heater as $W_h = I_h V_h$, the cross-sectional area of the sample to be $A$ and the distance between the two thermocouple tips as $l$, then the thermal conductivity and Seebeck coefficient can be expressed as, respectively:

$$Seebeck = \frac{V_s}{T_h - T_c} \quad \text{Equation 2.1}$$

$$Thermal\ Conductivity = \frac{W_h l}{(T_h - T_c) A} \quad \text{Equation 2.2}$$

The sample with the holder was placed in a cryostat, and liquid nitrogen or liquid helium was used to cool the samples to ~70 K or 4 K, respectively. The sample was surrounded by a radiation shield to reduce thermal radiation induced measurement error, and the cryostat was pumped down to $10^6$ Torr to suppress convection induced measurement error. The temperatures of the holder and the radiation shield were kept at a known temperature using a heater controlled by a Cernox thermometer. The measurement setup is schematically shown in Figure 2.2a.
Although thermal conductivity can be measured at room temperature or below, thermal radiation losses introduce a large error especially near room temperature, for low thermal conductivity materials. Thus, it is crucial to correct for radiation loss. Taking the holder and the radiation shield to be at temperature $T_0$, the temperatures of the cold and hot thermocouple tips to be $T_c$ and $T_h$, the emissivity to be $\varepsilon_e$, and Stefan’s constant to be $\sigma_r$, the radiation loss in steady state is:

$$W_{\text{radiation loss}} = \sigma_r \varepsilon_e \left\{ \left( \frac{T_h + T_c}{2} + T_0 \right)^4 - T_0^4 \right\} \quad \text{Equation 2.3}$$

Since we cannot accurately determine the value of $\sigma_r \varepsilon_e$, this amount of heat must be measured experimentally. Each time after the regular measurement (with the samples attached to the holder), we detached the sample from the holder with all of the other wires untouched. The detached sample was then suspended in the chamber using a thin thread (a thermal and electrical isolator). The radiation loss power was then measured by adjusting the heater power to make the average temperature rise of the sample identical with the previous value during the regular measurement:

$$T_h + T_c = T'_h + T'_c \quad \text{Equation 2.4}$$

where $T'_h$ and $T'_c$ are the temperatures of the hot and cold tips of the two thermocouples during the radiation loss measurement. Then the heater power will be equal to the radiation loss power and the value of $\sigma_r \varepsilon_e$ solved by Eqn. 2.3 will be used to estimate the radiation loss at lower temperatures. The radiation loss measurement setup is schematically shown in Figure 2.2b.
2.3.3 High Temperature Thermal Conductivity Measurement

High temperature thermal conductivity cannot be measured using the steady state method due to the much larger radiation loss at elevated temperatures. Instead, high temperature thermal conductivity is measured using an indirect method, according to the relation:

\[ \kappa = D \cdot C_p \cdot \rho \]

\textit{Equation 2.5}

where $D$ is the thermal diffusivity, $C_p$ is the specific heat capacity, and $\rho$ is the density. Thermal diffusivity was measured using the laser flash method [6] on a disc-shaped sample of thickness from 1 mm to 3 mm. The time-dependent temperature profiles of the bottom of the sample were detected after a laser pulse hit on the top of the sample. Thermal diffusivity was then determined by fitting the temperature profile with the solution of the thermal diffusion equation. Specific heat capacity was measured using differential scanning calorimetry (DSC). Density was then measured using the Archimedes method.

\[ \text{Figure 2.2 Low temperature thermoelectric transport measurement setup for (a) normal measurement and (b) radiation loss} \]
2.3.4 Hall Effect Measurement

The high temperature Hall coefficient was measured using a custom setup with a superconducting magnet cooled to 4.2 K to generate a steady magnetic field up to 1T. Low temperature Hall coefficient was measured using a Quantum Design Magnetic Properties Measurement System (MPMS). For both high temperature and low temperature Hall characterization, an AC resistance bridge was implemented to measure the Hall signal.
Chapter 3 Resonant Density of States in p-type CoSb3

3.1 Background

As discussed in Chapter 1, thermoelectric technology has been recognized as a promising technique to make use of waste heat energy. Since many applications of high temperature thermoelectric power generation occur in environments with significant vibrations, such as car electricity recovery, thermoelectric devices should possess good mechanical properties to survive occasional mechanical vibrations. Among many promising thermoelectric materials, skutterudites have attracted a lot of attention during the past several decades not only due to their excellent electrical properties, but also their outstanding mechanical properties. Both measurements and calculations have verified that CoSb$_3$, a binary paradigm of this large class, is a narrow-gap semiconductor possessing high mobility.[7-11] However, the high thermal conductivity (on the order of 10 Wm$^{-1}$K$^{-1}$ at room temperature) is too high for practical thermoelectric applications.[9, 10] The special crystal structure of this class of materials opens the possibility of reducing its intrinsic thermal conductivity by filling the structure with guest elements. The near square planar rings composed of 4 pnicogen atoms fill up 6 out of the 8 cubes formed by the M atoms in the binary skutterudites MX$_3$, where M stands for Co, Rh, or Ir while X represents P, As, or Sb.[12] Guest elements with small ionic radius can then be filled in the two remaining “empty” cubes in the unit cell, which are often referred to as “voids” or “cages”.

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These guest elements are often denoted as “fillers”, and the resulting filled lattice structure is known as a filled skutterudite. The weakly bonded fillers significantly reduce thermal conductivity by resonantly scattering phonons without dramatically affecting the electrical properties; this effect has been studied using a variety of elements.[13-21] A ZT as high as 1.7 was reported in the n-type filled skutterudites Ba$_{0.08}$La$_{0.05}$Yb$_{0.04}$Co$_4$Sb$_{12}$.[18] which is a dramatic enhancement compared to the binary CoSb$_3$ compound (~0.1). Unfortunately, due to an unfavorable valence band structure, p-type skutterudites, even filled with guest elements, have proven to be a challenging area of study to achieve a ZT value above 1.[19-21]

On the one hand, introducing dopants to create mass disorder or “rattling” states to reduce the lattice thermal conductivity is an effective means to improve the thermoelectric performance of CoSb$_3$-based materials. On the other hand, the numerator of ZT, known as the thermoelectric power factor $S^2\sigma$, offers a complementary approach in which electronic transport properties are improved. Here, the Seebeck coefficient $S$ and the electrical conductivity $\sigma$ are both determined by the band structure, the Fermi level position, and the scattering processes. Usually, $S$ and $\sigma$ are closely interdependent, and increasing both factors simultaneously is very difficult. A promising approach to improve the power factor given the trade-off between $S$ and $\sigma$ is to explore dopants that may form resonant density of states that can increase the density of states over a small range of carrier energies.[22-24] In order to realize an increase in Seebeck coefficient over typical dopant concentrations without sacrificing electrical conductivity, the Fermi level must also fall in the range of energies at which the band experiences a distortion due to the impurity. This approach has been successfully demonstrated using the dopant Tl in PbTe[25] and the dopant Sn in Bi$_2$Te$_3$.[26]
In this chapter, I report the exploration on Sn substitution for Sb as a potential means to form a resonant contribution to the density of states of CoSb$_3$. I predicted by band structure calculations that Sn, when substituted for Sb, should distort the density of states in a way that is reminiscent of the behavior of Tl in PbTe and Sn in Bi$_2$Te$_3$. I then conducted experiments where we substitute Sn for Sb, and find that the solubility limit of Sn in CoSb$_3$ is too low to achieve hole concentrations sufficient to make the Fermi level reach the energies at which the valence band is distorted.

### 3.2 Prediction of Resonant Density of States in CoSb$_3$ through incorporation of Sn by Band Structure Calculation

*Ab initio* calculations were carried out at AGH University of Science and Technology by Dr. Janusz Tobola. Electronic structure calculations of skutterudite-type (space group Im-3, No. 204) CoSb$_{3-x}$Sn$_x$ (x=0, 0.01, 0.025, 0.05 and 0.1) were performed using the all-electron self-consistent Korringa-Kohn-Rostoker (KKR) method, combined with the coherent potential approximation (CPA), which allows us to model the chemical disorder on the Sb site.[27, 28] In all computations, experimental values of the lattice constants and atomic positions, determined from XRD, were used. A self-consistent crystal potential of muffin-tin form was constructed with the local density approximation (LDA) framework and employed the Perdew-Wang expression for the exchange-correlation part.[29] For well-converged atomic charges (below $10^{-3}$ e) and potentials (below 1 mRy), the total and partial density of states (DOS) decomposed according to site (atoms) and angular momentum (s orbit, p orbit, d orbit, etc.) were computed.
using the integration tetrahedron method in reciprocal space (~130 k-space points in the irreducible part of the Brillouin zone). The Fermi level ($E_F$) was precisely determined from the generalized Lloyd formula,[30] which appears to be particularly important in systems on the verge of semiconductor-metal crossovers. Core states were calculated fully relativistically, while valence states were treated in a nonrelativistic approach.

The calculated density of states (DOS) is shown in Fig. 3.1. The figure clearly shows that Sn shifts the Fermi level into the valence band, and thus it should act as a $p$-type acceptor impurity. Fig. 3.1c shows a maximum in the DOS due to Sn impurity at approximately 0.3 eV below the valence band edge, and 0.05 eV below the Fermi energy. Fig. 3.1d suggests that substituting 3% of the Sb atoms with Sn atoms ($x=0.1$) should bring the Fermi level into the region of the valence band that is distorted by the presence of Sn. The $ab$ initio calculations clearly predict that Sn impurities should enhance the Seebeck coefficient without sacrificing too much electrical conductivity by generating the resonant density of states and moving the Fermi level to their vicinity simultaneously.[24] In the following sections, I explore this possibility experimentally.
3.3 Sample Synthesis and Pellet Sintering
Polycrystalline CoSb$_3$,Sn$_x$ samples with various Sn doping concentrations ($x = 0$, 0.01, 0.025, 0.05, 0.1 and 0.15) were prepared for this study. Cobalt (powder, 99.998%), antimony (shot, 99.9999%), and tin (99.995% pure powder for $x>0.01$ and 99.9999% pure shot for $x=0.01$) were weighed and mixed in quartz tubes in the OmniLab glovebox to minimize oxidation. The tubes were then evacuated to a pressure below 10$^{-3}$ Torr and sealed to prevent oxidation during the high temperature heat treatment. The materials were melted at 1373 K for 12 hours followed by annealing at 1023 K for 7 days. The annealed ingots were ground by hand to micron-size powders, of which a portion was examined by powder XRD. The remaining powders were sintered to high density ingots (cylinders of 12 mm diameter and 10 mm height) using SPS at 923 K and 50 MPa for 5-10 min. Ingot density was measured using the Archimedes method, after which the ingots were cut into various sizes for transport measurements. Small ingot pieces were reserved for high-temperature heat capacity measurements, and others were polished for electron microprobe analysis (EMPA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) studies. Certain pieces that contained secondary phases of Sb or Sn (based on the results of XRD before SPS), were ground to powders again for XRD after SPS to study whether SPS suppressed the formation of Sb or Sn secondary phases with low melting point.

### 3.4 Crystallographic and Microstructural Characterization

Powder XRD results before and after the SPS process are shown in Fig. 3.2a and Fig. 3.2b, respectively. Three CoSb$_{3-x}$Sn$_x$ with $x=0.01$, 0.05, and 0.1 were selected in particular to
clearly show the trend. The majority phase was confirmed to be CoSb$_3$. Secondary phases were identified as Sb for lightly and moderately doped samples ($x=0.01$ and 0.05) and Sn and CoSb$_2$ for the heavily doped one ($x=0.1$). Powder elements adhering to the inner walls of the ampoules caused the unavoidable loss of cobalt powder during the preparation process. This resulted in an excess of Sb in lightly and moderately doped samples, while the appearance of Sn and CoSb$_2$ phases in the heavily doped sample ($x=0.1$) were due to the small solubility limit ($x<0.1$ for CoSb$_{3-x}$Sn$_x$) of Sn on the Sb sites. The moderately doped sample ($x=0.05$) was verified to be free of Sn or CoSb$_2$ secondary phases, suggesting a solubility limit larger than 0.05 for the CoSb$_{3-x}$Sn$_x$ compounds. A decrease in the concentration of the secondary phases was observed after the samples were subjected to SPS, suggesting that SPS significantly suppressed the formation of Sb and Sn secondary phases. The Rietveld refinement results performed using the MAUD program are shown in Table 3.1.[5] The lattice parameter was verified to increase with Sn concentration for $x<0.15$, which is consistent with the fact that Sn ions have a larger atomic radius [31] (0.294nm) than Sb atoms (0.245nm). The most heavily doped sample ($x=0.15$) constitutes an exception: it has a smaller lattice parameter than the $x=0.1$ sample, indicating that not all the Sn went into solution.
<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Density (g/cm³)</th>
<th>Actual matrix composition</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSb₃</td>
<td>7.04</td>
<td>CoSb₃.0487</td>
<td>9.0323</td>
</tr>
<tr>
<td>CoSb₂.₉₉Sn₀.₀₁</td>
<td>7.14</td>
<td>CoSb₃.₀₄₁₉Sn₀.₀₀₂₈</td>
<td>9.0394</td>
</tr>
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<td>7.2</td>
<td>CoSb₃.₀₂₈₄Sn₀.₀₀₅₉</td>
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</tr>
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<td>7.65</td>
<td>CoSb₃.₀₁₂₂Sn₀.₀₁₅₈</td>
<td>9.0462</td>
</tr>
<tr>
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<td>CoSb₂.₉₇₁₉Sn₀.₀₇₇₂</td>
<td>9.0462</td>
</tr>
<tr>
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<td>7.62</td>
<td>CoSb₂.₉₇₃₇Sn₀.₀₈₆₇</td>
<td>9.0443</td>
</tr>
</tbody>
</table>

Table 3.1 Density, actual matrix composition, and lattice parameter of CoSb₃₋ₓSnₓ samples.

Figure 3.2 (a) Powder XRD patterns of three samples (CoSb₃₋ₓSnₓ with x=0.01, 0.05, and 0.1) before SPS. (b) Powder XRD patterns of two samples (with x=0.01 and 0.1) after SPS.

The results of the density and actual matrix elemental compositions are also included in Table 3.1 to show the quality of the polycrystalline (with micron-size grains) CoSb₃₋ₓSnₓ samples synthesized in this work. CoSb₃₋ₓSnₓ samples with x=0, 0.01, and 0.025 have densities only 92%
of the theoretical value that was calculated from the lattice parameter determined from the Rietveld analysis of the powder XRD results. Heavily doped samples ($x=0.05, 0.1$ and $0.15$) exhibit larger densities in excess of $98\%$. Taken from at least 5 random positions selected within the matrix region for each sample, the results from Electron Microprobe Analysis (EMPA) reflect the actual composition of the matrix instead of the total composition that counts the sediments between the grains. The pure, lightly and moderately doped samples with $x=0.01, 0.025$, and $0.05$ still exhibit an excess of Sb. This is consistent with the XRD observation of the Sb peak after SPS, indicating that the SPS process cannot eliminate the secondary phases that have already segregated in the matrix. The actual Sn concentration is lower than the nominal values for all of the samples, due to the unavoidable loss of Sn powder during the preparation process (similar to cobalt), evaporation during the melting process, and sedimentation of Sn between the grains. Yet, except for the $x=0.15$, the actual Sn concentration in solid solution increases with the nominal concentration $x$ as expected.

More accurate phase information from backscattered electron microscopy (BSE) for three lightly and moderately doped samples ($x=0.01, 0.05$ and $0.1$) is shown in Fig. 3.3a-c. Since BSE images are more sensitive for detecting secondary phases than SEM images, we used BSE instead of SEM to show the phase composition more accurately. In Fig. 3.3a, many dark spots were present, verifying that the low density of the lightly doped samples ($x=0.01$) was caused by severe porosity, which is also shown by SEM in Fig. 3.3d. Heavily doped samples ($x=0.05$ and $0.1$) are much denser than the lightly doped ones as much fewer dark spots are present in Fig. 3.3b and Fig. 3.3c. Secondary phases with the size of approximately $50 \mu$m (gray spots) in the heavily doped sample ($x=0.1$) were observed, which is consistent with the conclusion drawn from powder XRD that the solubility limit of Sn on Sb sites is below $x=0.1$. Similar gray spots
observed in the CoSb$_{2.9}$Sn$_{0.1}$ sample are barely visible in the CoSb$_{2.95}$Sn$_{0.05}$, suggesting that the solubility limit is still larger than $x=0.05$. I believe that the porosity of the lightly doped sample was due to the fact that the SPS condition used in this work was only optimized for high Sn concentration. This suggested explanation is consistent with a previous study using SPS for ceramics,[32] which also found that an additional low melting impurity (Sn in this case) can improve densification during SPS.

Figure 3.3 (a) BSE image of the $x=0.01$ sample. (b) BSE image of the $x=0.05$ sample. (c) BSE image of the $x=0.1$ sample. (d) SEM image of the $x=0$ sample.
Scanning transmission electron microscopy (STEM) images from three samples \((x=0, 0.05\) and 0.15) are shown in Fig. 3.4 to show finer microstructure down to nanometer scale. Energy dispersive x-ray spectroscopy (EDS) measurements in STEM identified Sb as a secondary phase at grain boundaries in the undoped sample, which further confirmed the results obtained from the powder XRD and EMPA. An example of one such inclusion is shown in Figure 3.4a. A small amount of Sn-rich inclusions was also observed at grain boundaries in the moderately doped sample \((x=0.05)\) and heavily doped sample \((x=0.15)\). These cannot be detected by either powder XRD due to its detection limit or BSE because of its limit in spatial resolution. These observations suggest that the solubility limit is close to \(x=0.05\) and that the precipitation of a small amount of Sn or Sn-rich phase is due to local inhomogeneity. Analysis of diffractograms from high resolution high angle annular dark field STEM images obtained at several different orientations, an example of which is shown in Figure 3.4d, were consistent with SnO\(_2\).[33] The presence of SnO\(_2\) impurities explains why the Sn concentration of the \(x=0.15\) sample is larger than that of the \(x=0.1\) sample in the matrix, even though \(x=0.1\) is already greater than the solubility limit. An imperfect vacuum during annealing or SPS likely caused the formation of the SnO\(_2\) impurities.
Figure 3.4 STEM analyses found the presence of some secondary phases localized to intergranular regions. (a) $x=0$ sample: example of Sb-rich intergranular phase. (b) $x=0.05$ and (c) $x=0.15$ samples show Sn-rich inclusions at grain-boundaries. (d) High resolution HAADF-STEM image of inclusion in (c). Inset shows diffractogram calculated from Fourier transform of STEM image. Spacings and angular relationships from this and other orientations identify the phase as SnO$_2$ (Cassiterite). The image in (d) is oriented along a $[111]$ zone axis.

To summarize the structural characterization of the samples, I observed that the solubility limit for Sn is between $x=0.05$ and 0.1 for CoSb$_3$,Sn$_x$, and probably more toward the lower end
of that range, as the TEM results suggest that the solubility limit is close to 0.05. This value falls within the range from 0.0045 reported by Zobrina et al.[34] to 0.3 reported by Kim et al.[35] and comparable to the value of 0.14 by Tobola et al.[36] Moderately doped samples were confirmed to be homogenous and dense, lightly doped samples were found to be porous and heavily doped samples were found to contain Sn-rich impurities.

3.5 Thermoelectric Properties

Before I move to the discussion of the thermoelectric transport properties, the possibility that the secondary phases observed in the previous chapter will influence the transport coefficients needs to be ruled out. Indeed, the type and size of the inclusions observed in Fig. 3.3 and Fig. 3.4 were not expected to affect the Seebeck coefficient of the samples significantly, which is the most sensitive probe of the presence of a resonant state. The thermoelectric properties of composites have been theoretically studied by Bergman and co-workers,[34,35] who showed that spherical or cube-like inclusions of a metallic phase with a low Seebeck coefficient in a matrix of a more insulating semiconductor material with a high Seebeck coefficient reduces the Seebeck coefficient only slightly at inclusion concentrations below the percolation limit. Experimentally[37] adding metallic silver (S ~ +2 μV/K at 300 K) into polycrystalline Bi (S ~ -72 μV/K at 300 K) reduces the absolute value of the Seebeck coefficient of the composite (S ~ -60 μV/K at 300 K) by only 15% when the Ag concentration is 40% by volume, and much less for the concentrations observed in Fig. 3.3. The electrical conductivity is expected to be linearly dependent on the volume percentage of the inclusions or pores, which can be seen to be small in
Fig. 3.3. So, we do not need to worry about the influence of the secondary phases on the Seebeck coefficient and electrical conductivity.

High temperature Hall measurement results for all samples are shown in Fig. 3.5. For a single band with only one type of carrier (here holes), the Hall coefficient can be expressed as:[38]

\[ R_H = \frac{A}{pe} \]  \hspace{1cm} \text{Equation 3.1}

where \( R_H \) is the Hall coefficient, \( p \) is the hole concentration, \( e \) is the elementary charge (of a hole), and \( A \) is the Hall factor, a parameter accounting for the anisotropy of the Fermi surface and the dominant scattering mechanism. The positive Hall coefficients of all samples and the greatly reduced Hall coefficients of the doped CoSb\(_{3-x}\)Sn\(_x\) samples compared to pure CoSb\(_3\) verify that Sn is an effective \( p \)-type dopant in CoSb\(_3\). The Hall coefficient peaked at a certain temperature, presumably due to the interband excitation of minority electrons at high temperatures, and the peaks occur at progressively higher temperatures with increasing Sn content. An interesting feature of the Hall data for samples with \( x > 0 \) is the rising magnitude of \( R_H \) from room temperature to a peak value between 673K and 773K. Under the assumption of \( A = 1 \) (valid for simple bands with parabolic band dispersion) in Eqn. 3.1, carrier concentration decreases as temperature increases. Because this is not physically reasonable, a more complex band dispersion is warranted. Singh and Pickett[8] have shown previously that the top of the valence band of CoSb\(_3\) exhibits linear dispersion. Replacing parabolic band dispersion with a linearly dispersing valence band, the carrier concentration deduced from the Hall coefficient indeed rises with temperature at high temperatures, as shown in Fig. 3.5b, up to the temperature at which minority electrons are thermally excited and \( R_H \) decreases again.
Figure 3.5 (a) Hall coefficients measured in all of the samples from room temperature to 800 K. The x values in the legend correspond to the Sn fraction in CoSb$_3$-xSn$_x$. (b) The calculated temperature dependence of the Hall coefficient using a linearly dispersing valence band, assuming two constant carrier concentrations and a constant scattering parameter.

The Seebeck coefficient was measured over a wide temperature range from 300 K to 800 K, as shown in Fig. 3.6a-b. The positive Seebeck coefficient measured confirms hole conduction in all samples. At low temperatures before the onset of interband excitation, S increases with T, confirming that the samples are degenerately doped and have metallic behavior. At higher temperatures above the appearance of minority electron thermal excitation, a negative slope for $dS/dT$ sets in at temperatures coinciding with the Hall coefficient peaks. For a degenerate carrier system, the Seebeck coefficient can be described by the Mott relation:[39]

$$S = -\frac{\pi^2 k}{3e} T \left[ \frac{d \ln(\mu g(E))}{dE} \right]_{E=E_F}$$  \hspace{1cm} \text{Equation 3.2}$$

where $\mu$ is the carrier mobility and $g(E)$ is the carrier density of states. If the term in brackets remains temperature-independent, the Seebeck coefficient is then expected to be linearly

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dependent on temperature. This linear dependence was observed in the two most heavily doped samples \((x=0.1\) and 0.15\) at high temperatures. Figure 3.6b shows that the Seebeck coefficients of the \(\text{CoSb}_{3-x}\text{Sn}_x\) samples typically follow the conventional Pisarenko relation at low temperatures. The deviation from the conventional Pisarenko relation at high temperatures originate from the intrinsic excitation of the minor carriers in the lightly doped samples. The Pisarenko relation at low temperatures will also be discussed in detail later in this section.

![Figure 3.6](image)

**Figure 3.6** (a) Seebeck coefficients measured in all of the samples from room temperature to 800 K. The \(x\) values in the legend correspond to the Sn fraction in \(\text{CoSb}_{3-x}\text{Sn}_x\). (b) Seebeck coefficients as a function of nominal Sn concentration \(x\) at 330 K, 560 K, and 800 K.

Electrical conductivity was measured from 300 K to 800 K, as shown in Fig. 3.7. The increase in hole concentration introduced by Sn dopants results in an enhanced electrical conductivity at room temperature. Electrical conductivity was observed to be highest for the \(x=0.025\) sample and decreases with a further increase in Sn concentration beyond \(x=0.025\) due to deterioration of carrier mobility. All Sn-doped samples exhibit a decreasing electrical
conductivity with temperature, reflecting metallic behavior. At high temperatures, all samples tend to converge to a similar value of approximately 375 S/cm.

Figure 3.7 Electrical conductivity measured in all of the samples from room temperature to 800 K. The x values in the legend correspond to the Sn fraction in CoSb$_{3-x}$Sn$_x$.

The thermoelectric power factor ($S^2\sigma$) is shown in Fig. 3.8. Below 573 K, the highest power factor is achieved with pure CoSb$_3$, confirming that such binary compounds possess
excellent electrical properties. At higher temperatures (above 673 K), the best power factor is obtained for $x=0.05$, reaching a value of $9 \, \mu\text{Wcm}^{-1}\text{K}^{-2}$, due to the carrier concentration enhancement with the introduction of Sn dopants.

Figure 3.8 Power factor from room temperature to 800 K. The $x$ values in the legend correspond to the Sn fraction in CoSb$_{3-x}$Sn$_x$.

A Pisarenko plot, which illustrates the relationship between Seebeck coefficient and carrier concentration, is shown in Fig. 3.9 to determine whether or not any improvement in the
Seebeck coefficient due to the presence of band resonant states is realized. If the parabolic band structure is not altered (no resonant levels present near Fermi level), the relationship between Seebeck coefficient and carrier concentration should simply follow the solid line of $S(p)$ plotted in Fig. 3.9, which is calculated using:[9]

$$S = \left(\frac{2\pi k_B^2 T}{3ea}\right)\left(\frac{\pi}{3p}\right)^{\frac{1}{3}}$$  \hspace{1cm} \text{Equation 3.3}

Unfortunately, at room temperature and above, no significant improvement due to the presence of resonant impurity levels can be observed. The experimental data points generally lie on the calculated solid line without any distortion.

We now show that our experimental findings are consistent with the theory, and no enhancement of the Seebeck coefficient was observed because the Fermi energy simply never reaches the valence band distortion predicted in Fig. 3.1, because the solubility limit of Sn precludes the introduction of more carriers.
In order to calculate the Fermi energy $E_F$ (with respect to the valence band edge) from the Hall carrier concentration, we assume a linear band dispersion and primarily acoustic phonon scattering at room temperature. We write the Hall coefficient by solving the Boltzmann transport equation within the relaxation time approximation as:

$$ R = \frac{3}{1 + \exp(-\eta^*)} \left( \frac{\eta^*}{kT} \right)^3 F_{1/2}(\eta^*) \frac{n}{(\pi \alpha)^2} $$

Equation 3.4
where $\eta^* = \frac{E_F}{kT}$ is the reduced Fermi level, $F_j(x)$ is the j-th order Fermi integral and $a$ is the proportionality constant of the linear band dispersion $E = a |\vec{k}|$ with a value of 3.1eVÅ from the literature.[9] From the Hall coefficient, we can calculate $E_F$ for various samples at room temperature and then calculate the carrier concentration through the equation I derived:

$$p = \frac{\pi}{(\pi a)^3} (kT)^3 F_2(\eta^*)$$

*Equation 3.5*

The results are shown in Fig. 3.10. Here, the energy of holes increases as they move deeper into the valence band, and so does Fermi level. It is obvious that as the Sn concentration increases, the Fermi level is pushed deeper into the valence band, and reaches $E_F = 0.3$ eV for the most heavily doped samples. This should have been sufficient to observe the effect of Sn as a resonant level according to Fig. 3.1. It is possible that the overestimation of the Fermi level assuming only one linear band over the whole energy range in all the model calculations is such that the resonant levels are much deeper, and in the end, it is impossible to add enough Sn in solid solution into the Sb sites of CoSb$_3$ to enhance the Seebeck coefficient at high temperature. Indeed, the fact that the Fermi level does not change when the Sn concentration increases from 0.1 to 0.15 suggests that the solubility limit of Sn in CoSb$_3$ is less than $x=0.1$, consistent with the microscopy data in Figs 3.3 and 3.4 and indicative of the inability to further push down the Fermi level.
Thermal conductivity data above room temperature, presented in Fig. 3.11a, exhibit a decrease as Sn dopant concentration increases. The lowest room-temperature thermal conductivity of approximately 2 W/m-K was achieved in the most heavily doped sample (x=0.15), presumably due to strong impurity scattering of acoustic phonons. The temperature dependence of the thermal conductivity is indicative of Umklapp scattering. A slight upturn in the high-temperature thermal conductivity (T>770 K) is likely due to an electronic contribution from the onset of the minority electrons, which also contributes to downturns in the Seebeck coefficient and Hall coefficient. Using the Wiedemann-Franz law (with a fully degenerate value of the Lorenz number of $2.44 \times 10^{-8} \text{W} \Omega \text{K}^{-2}$) to approximately separate the electronic and lattice
contributions to thermal conductivity, the lattice contribution is plotted in Fig. 3.11b. The fact that this value does not decrease monotonically with temperature is an indication that the assumption of a constant Lorenz number was only very approximate, and it does not account for a bipolar contribution one might expect in the presence of minority electrons. The lattice thermal conductivity is reduced quite effectively by Sn dopants; at room temperature, the samples with highest Sn doping have a lattice thermal conductivity that is lower than that of pure CoSb$_3$ by a factor of more than five. Because Sn and Sb are neighboring elements in the periodic table and their atomic masses (118.69 for Sn and 121.75 for Sb) are similar, it is unlikely that this arises from alloy scattering alone. Rather, Sn may also be filling voids in the crystal structure and scatter acoustic phonons by rattling. The filler (Sn in voids) together with the dopant (Sn substituting for Sb) may also cause a change in the temperature dependence of the lattice thermal conductivity from negative to temperature-independence, as has also been observed elsewhere (Yb filler together with Sn dopant).[40] However, the fraction of Sn dopants that acts as fillers is believed to be small, since it does not influence electronic transport as dramatically as thermal transport.
Figure 3.11 (a) Total thermal conductivity from room temperature to 825 K. The x values in the legend correspond to the Sn fraction in CoSb$_3$$_{-x}$Sn$_x$. (b) Lattice thermal conductivity from room temperature to 825 K derived by subtracting the electronic thermal conductivity (approximated using the Wiedemann-Franz law) from the total measured thermal conductivity. x values in the legend correspond to the Sn fraction in CoSb$_3$$_{-x}$Sn$_x$.

Calculated ZT values are shown in Fig. 3.12. The highest ZT (~0.2) was achieved for the x=0.05 sample at 723 K. Improvements in ZT arise primarily from reductions in thermal conductivity rather than improvements in power factor.
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3.6 Summary

By using spark plasma synthesis, I successfully made Sn-doped CoSb$_3$,$_x$Sn$_x$ materials with various $x$ values. The solubility limit was determined to be $x \approx 0.05$. Based on transport measurements and calculations, I did not observe any significant evidence of band resonant states in Sn-doped CoSb$_3$ within the dopant concentration range explored. I explained this by the fact that the Sn solubility limit is too low to achieve the hole concentration levels needed to put
the Fermi level near the Sn resonant state as calculated \textit{ab-initio}. As a consequence, the figure of merit was enhanced only slightly; this enhancement is primarily due to a reduction in thermal conductivity potentially caused by a small portion of Sn filling voids in the crystal structure. My study indicates that the doping limit of Sn in CoSb$_3$ is below 2\% and that the synthesis of samples with very low Sn concentrations is difficult because of porosity and inhomogeneous dopant distribution. Other approaches to enhance the thermoelectric properties in \textit{p}-type skutterudites are desired.
Chapter 4 Thermoelectric Properties of $p$-type Filled Skutterudites

$\text{Yb}_z\text{Fe}_y\text{Co}_{4-y}\text{Sb}_{12-y}\text{Sn}_x$

4.1 Background

In Chapter 3, I have shown by both calculation and experiment that low solubility of Sn dopants on Sb sites in CoSb$_3$ is not capable of introducing enough charge carriers to push the Fermi level deep into the valence band to the vicinity of the generated resonant levels. A straightforward approach to solve such problem is to further push the Fermi level by introducing a second $p$-type dopant. The solubility limit of a second $p$-type dopant on Sb sites is likely to be low, and thus incorporating Fe on Co sites is selected. Indeed, numerous previous work indicates that Fe is able to substitute all Co, though adding interstitial fillers is required for stabilizing the crystal structure.[41, 42] In this chapter, Yb was selected as the filler and Fermi level is tuned by varying both Yb and Fe concentrations. Sn concentration is fixed at ~1%. In addition to experiments, numerical thermoelectric transport coefficient fitting is attempted. Thermoelectric measurements suggest that substituting Co by Fe is able to increase the carrier concentration; however, the Fermi level is still pinned above the energy vicinity of the generated resonant states by Sn. Such Fermi level pinning is caused by the moving Fe heavy band as the Fe concentration increases. Though transport coefficient fitting fails probably due to the unknown temperature dependence of the scattering processes, I am still able to conclude that the convergence of the
Fe-d band and the Sb-p band is beneficial for thermoelectric performance. An approach to further improve the thermoelectric performance of \( p \)-type filled skutterudites is also proposed.

### 4.2 Materials Synthesis and Pellets Sintering

Ytterbium (99%, Alfa Aesar), iron (99.98%, Alfa Aesar), cobalt (99.98%, Alfa Aesar), antimony (99.9999%, Alfa Aesar), and tin (99.9999% Alfa Aesar) elements were weighed based on the chemical formula of 6 various compositions: \( \text{Yb}_{0.3} \text{FeCo}_3 \text{Sb}_{12} \), \( \text{Yb}_{0.3} \text{FeCo}_3 \text{Sb}_{11.9} \text{Sn}_{0.1} \), \( \text{Yb}_{0.6} \text{Fe}_2 \text{Co}_2 \text{Sb}_{12} \), \( \text{Yb}_{0.6} \text{Fe}_2 \text{Co}_2 \text{Sb}_{11.9} \text{Sn}_{0.1} \), \( \text{Yb}_{0.8} \text{Fe}_3 \text{CoSb}_{12} \), and \( \text{Yb}_{0.8} \text{Fe}_3 \text{CoSb}_{11.9} \text{Sn}_{0.1} \) in the glovebox. The reason I selected these 6 particular compositions will be discussed in the following sections. The weighed elements are then mixed and sealed in the evacuated quartz tubes. The mixed raw elements are heated up to 1373 K at a rate of 0.5 K/min, held at 1373 K for 6 hours, and then quenched in cold salt water. The quenched ingots were then sealed again in quartz tubes and annealed at 923 K for 4 days. Following annealing, the as-cast ingots were hand-ground to powders, after which SPS was performed under 50 MPa pressure and 873 K temperature for \( \sim \)15 min.

### 4.3 Crystallographic and Microstructural Characterization

Powder XRD patterns of 6 \( \text{Yb}_2 \text{Fe}_{4-y} \text{Co}_y \text{Sb}_{12-x} \text{Sn}_x \) samples are shown in Fig. 4.1. The major phase is identified as skutterudite with minor secondary phases identified as FeSb\(_2\), Yb\(_2\)O\(_3\),
and Sb. The existence of the secondary phases in \( p \)-type filled skutterudites seems unavoidable and these microscale secondary phases do not influence the thermoelectric properties much.[40-43] The measured density, actual elemental composition of the matrix, lattice parameters determined by the Rietveld analysis of the powder XRD patterns, and the calculated carrier concentration for the nominal composition of \( \text{Yb}_{2}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12-x}\text{Sn}_x \) are listed in Table 4.1. The valence state of Yb is taken to be 2.62 in filled skutterudites.[44] All samples are well densified and have densities greater than 94% of the theoretical value. The actual elemental composition only deviates slightly from the nominal value, probably due to the unavoidable oxidation of the elements or segregation of the secondary phases. The lattice parameter increases with Yb and Fe concentration, caused by the larger Fe ionic radius with respect to Co and the interstitial Yb incorporation. The effect of Sn dopants on the lattice parameter is observed to be negligible. The calculated carrier concentration from the nominal composition shows that the carrier concentration increases as the Fe concentration increases.
Figure 4.1 Powder XRD results of all the skutterudite samples from 5° to 85°. Secondary phases in the skutterudites samples can be identified by comparing the powder XRD results of the samples to the powder XRD patterns of the references.
Table 4.1 Nominal composition, density measured by Archimedes method, actual matrix composition measured by electron microprobe analyzer (EMPA), lattice parameters calculated from the Rietveld analysis of the powder XRD data, and estimated carrier concentration calculated from the nominal composition.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Density (g/cm³)</th>
<th>Actual matrix composition</th>
<th>Lattice parameter (Å)</th>
<th>Estimated carrier concentration based on nominal composition(cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb₀.₃FeCo₃Sb₁₂</td>
<td>7.55</td>
<td>Yb₀.₂₃Fe₁₀Co₂.₉₉Sb₁₂</td>
<td>9.068</td>
<td>5.740×10⁲⁰</td>
</tr>
<tr>
<td>Yb₀.₃FeCo₃Sb₁₁.₉Sn₀.₁</td>
<td>7.59</td>
<td>Yb₀.₂₃Fe₀.₉₄Co₃.₀₅Sb₁₁.₉Sn₀.₀₇</td>
<td>9.073</td>
<td>8.₄₀₈×10²⁰</td>
</tr>
<tr>
<td>Yb₀.₄Fe₂Co₂Sb₁₂</td>
<td>7.36</td>
<td>Yb₀.₅₉Fe₂.₀₆Co₂.₀₄Sb₁₂</td>
<td>9.₁₀₂</td>
<td>1.₁₃₅×10²¹</td>
</tr>
<tr>
<td>Yb₀.₄Fe₂Co₂Sb₁₁.₉Sn₀.₁</td>
<td>7.₈₄</td>
<td>Yb₀.₅₅Fe₁.₈₀Co₂.₁₈Sb₁₁.₉Sn₀.₀₆</td>
<td>9.₁₀₁</td>
<td>1.₄₀₁×10²¹</td>
</tr>
<tr>
<td>Yb₀.₅Fe₃CoSb₁₂</td>
<td>7.₅₀</td>
<td>Yb₀.₈₄Fe₃.₀₂Co₁.₀₃Sb₁₂</td>
<td>9.₁₄₀</td>
<td>2.₃₆₈×10²¹</td>
</tr>
<tr>
<td>Yb₀.₅Fe₃CoSb₁₁.₉Sn₀.₁</td>
<td>7.₆₉</td>
<td>Yb₀.₈₄Fe₂.₈₀Co₁.₁₈Sb₁₁.₉Sn₀.₃</td>
<td>9.₁₂₄</td>
<td>2.₆₄₄×10²¹</td>
</tr>
</tbody>
</table>

4.4 Transport Fitting Theory

*Ab initio* band structure calculation results reported by Yang et al. suggest that three valence bands contribute to the hole conduction in *p*-type filled skutterudites Yb₄Fe₄⁻ₓCoₓSb₁₂.[45] The three valence bands include a light non-parabolic Sb-p band and a heavy parabolic Fe-d band with both of their energy maximums located at Γ point, and another light parabolic band with its energy extreme located between H and N points. Electrical transport coefficients of each band will be derived in this section. The total transport coefficients will then be calculated from the contribution of each band.
For the light Sb-p band, the band dispersion relation is described by the Kane model:[46]

\[ \frac{\hbar^2 k^2}{2m_{v_1}^*} = E(1 + \alpha E) \]  

\textit{Equation 4.1}

where \( \hbar \) is the reduced Planck constant, \( k \) is the wave vector, \( m_{v_1}^* \) is its effective mass, \( E \) is the energy, and \( \alpha \) is the nonparabolicity parameter. The electrical transport coefficients can be written as:[46-48]

\[ \sigma_{v_1} = \frac{e^2}{3\pi^2} \frac{2(2m_{v_1}^*)^2}{\hbar^3} \int_0^\infty \left( -\frac{\partial f_0}{\partial E} \right) \tau_{\text{total}v_1}(E + \alpha E^2)^{3/2}(1 + 2\alpha E)^{-1} dE \]  

\textit{Equation 4.2}

\[ S_{v_1} = \frac{1}{eT} \left[ \int_0^\infty \left( -\frac{\partial f_0}{\partial E} \right) \tau_{\text{total}v_1}(E + \alpha E^2)^{3/2}(1 + 2\alpha E)^{-1} dE \right] + E_F \]  

\textit{Equation 4.3}

\[ R_{Hv1} = \frac{\int_0^\infty \left( -\frac{\partial f_0}{\partial z} \right) \tau_{\text{total}v_1}(z + \beta z^2)^{3/2}(1 + 2\beta z)^{-1} d\beta}{\int_0^\infty \left( -\frac{\partial f_0}{\partial z} \right) \tau_{\text{total}v_1}(z + \beta z^2)^{3/2}(1 + 2\beta z)^{-1} d\beta} e_{v_1} \]  

\textit{Equation 4.4}

where \( f_0 \) is the Fermi distribution function, \( \tau_{\text{total}v_1} \) is the total relaxation time of Sb-p band, \( \beta = \alpha k_B T, z = \frac{E}{k_B T} \), and \( p_{v_1} \) is the carrier concentration of Sb-p band. Various scattering processes contribute to the total relaxation time obeying Matthiessen’s rule as:[46]

\[ \frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{ac}} + \frac{1}{\tau_{npo}} + \frac{1}{\tau_{po}} + \frac{1}{\tau_{imp}} + \frac{1}{\tau_{iv}} \]  

\textit{Equation 4.5}

in which \( \tau_{ac}, \tau_{npo}, \tau_{po}, \tau_{imp}, \) and \( \tau_{iv} \) are the relaxation times of acoustic phonon scattering, nonpolar optical phonon scattering, polar optical phonon scattering, ionized impurities scattering, and the intervalley transition scattering. The intervalley transition scattering can be broken down into two parts as:

\[ \frac{1}{\tau_{iv}} = \frac{1}{\tau_{iv12}} + \frac{1}{\tau_{iv13}} \]  

\textit{Equation 4.6}
where \( \tau_{iv12} \) and \( \tau_{iv13} \) account for intervalley transitions between the Sb-p band and the Fe-d band and between the Sb-p band and the light H-N band, respectively. The detailed expressions for the relaxation time of various scattering processes are:[46-49]

\[
\frac{1}{\tau_{ac}} = \frac{(2m_{v1})^{3/2}E^2_{acv1}k_BT}{2\pi\hbar^4\rho v_l^2}(E + \alpha E^2)^{1/2}(1 + 2\alpha E)F_{ac} \quad \text{Equation 4.7}
\]

\[
\frac{1}{\tau_{po}} = \frac{e^2}{4\pi} \frac{(2m_{v1})^{1/2}k_BT}{\hbar^2} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \right) \frac{1 + 2\alpha E}{(E + \alpha E^2)^{1/2}} F_{po} \quad \text{Equation 4.8}
\]

\[
\frac{1}{\tau_{imp}} = \frac{\pi N_{imp}}{(2m_{v1})^{1/2}} \left( \frac{e^2}{4\pi\varepsilon_s} \right)^2 \frac{1 + 2\alpha E}{(E + \alpha E^2)^{3/2}} F_{imp} \quad \text{Equation 4.9}
\]

\[
\frac{1}{\tau_{npo}} = \frac{1}{2} \frac{E_{npo}}{E_{acv1}} \frac{\theta_D}{T} \left( e^{\theta_D/T} - 1 \right)^{-1} \times \left[ \left( 1 + \frac{k_B\theta_D}{E} \right)^{1/2} + e^{\theta_D/T} \left( 1 - \frac{k_B\theta_D}{E} \right)^{1/2} \right] \frac{1}{\tau_{ac}} \quad \text{Equation 4.10}
\]

\[
\frac{1}{\tau_{iv12}} = \frac{M_{v2}}{2} \left( \frac{m_{v2}}{m_{v1}} \right)^{3/2} \frac{E_{iv}}{E_{acv1}} \frac{\theta_{iv}}{T} \frac{1}{\exp(\theta_{iv}/T) - 1} \times \left[ \left( 1 + \frac{k_B\theta_{iv}}{E} \right)^{1/2} + \exp(\theta_{iv}/T) \left( 1 - \frac{k_B\theta_{iv}}{E} \right)^{1/2} \right] \frac{1}{\tau_{ac}}
\]

\text{Equation 4.11}

where \( E_{acv1} \) is the acoustic-phonon deformation potential of Sb-p band, \( \rho \) is the density, \( v_l \) is the sound velocity of longitudinal acoustic phonons, \( \varepsilon_\infty \) is the high frequency dielectric constant, \( \varepsilon_s \) is the static dielectric constant, \( N_{imp} \) is the concentration of ionized impurities, \( E_{npo} \) is the nonpolar optical phonon deformation potential, \( \theta_D \) is the Debye temperature, \( k_B\theta_{iv} = \hbar\omega_{iv} \) with \( \omega_{iv} \) being the phonon angular frequency, \( E_{iv} \) is the intervalley transition deformation potential, \( F_{ac}, F_{po}, \) and \( F_{imp} \) are the functions of \( E \) defined by Zawadzki.[49] The electrical transport coefficients shown above can easily be extended to parabolic bands (Fe-d band and light H-N band in this work) by setting the nonparabolicity parameter to be zero. \( \theta_{iv} \) can be assumed to be approximately equal to the Debye temperature.[46]
The charge carrier concentration of the non-parabolic Sb-p band is expressed as:[46]

\[ p_{v1} = 2 \left( \frac{m_{v1} k_B T}{2 \pi \hbar^2} \right)^{3/2} \frac{4}{3 \sqrt{\pi}} L_{0}^{3/2} (\eta, \beta) \]  

Equation 4.12

where \( n L_{k}^{m} (\eta, \beta) \) is the generalized Fermi-Dirac integral defined as:[46]

\[ n L_{k}^{m} (\eta, \beta) = \int_{0}^{\infty} (- \partial f_{0}/ \partial z) z^{n}(z + \beta z^{2})^{m}(1 + 2 \beta z)^{k} dz \]  

Equation 4.13

For the Fe-d and light H-N parabolic bands, the charge carrier concentration is:[38]

\[ p_{v2,v3} = 2 \left( \frac{2 \pi m_{v2,v3} k_B T}{\hbar^2} \right)^{3/2} F_{1/2} \left( \frac{E_f - E_{g2,g3}}{k_B T} \right) \]  

Equation 4.14

where \( F_{j}(\eta) = \int_{0}^{\infty} \frac{\eta^{j}}{1+\exp(\eta-\eta^{*})} d\eta \) is the Fermi integral of \( j \)-th order. \( E_{g2} \) and \( E_{g3} \) are the energies at the top of the Fe-d band and the light H-N band with respect to the energy at the top of the Sb-p band.

Because Yb\(_2\)Fe\(_{4-y}\)Co\(_y\)Sb\(_{12-x}\)Sn\(_x\) samples are degenerate \( p \)-type semiconductors, the contribution of conduction bands is negligible. Thus, the charge neutrality condition is:

\[ p_{v1} + p_{v2} + p_{v3} = N_A \]  

Equation 4.15

where \( N_A \) is the concentration of the \( p \)-type dopants. The total electric transport coefficients can be written as:[38]

\[ \sigma = \sigma_{v1} + \sigma_{v2} + \sigma_{v3} = e(n_{v1} \mu_{v1} + n_{v2} \mu_{v2} + n_{v3} \mu_{v3}) \]  

Equation 4.16

\[ R_H = \frac{R_{Hv1} \sigma_{v1}^2 + R_{Hv2} \sigma_{v2}^2 + R_{Hv3} \sigma_{v3}^2}{\sigma^2} \]  

Equation 4.17

\[ S = \frac{(\sigma_{v1} S_{v1} + \sigma_{v2} S_{v2} + \sigma_{v3} S_{v3})}{\sigma} \]  

Equation 4.18
4.5 Thermoelectric Transport Properties

Actual carrier concentration at room temperature can be derived from Hall coefficient measurement as:

\[ p = \frac{A}{eR_H} \]  

Equation 4.19

where \( A \) is a numerical proportionality factor, which depends on the band structure and the scattering processes. In this chapter, we set \( A \) to be 1 for a rough estimation.[38] The estimated actual room temperature carrier concentrations and high temperature Hall coefficients of 6 Yb\(_{2}\)Fe\(_{4-y}\)Co\(_y\)Sb\(_{12-x}\)Sn\(_x\) samples are shown in Fig. 4.2. The results confirm that varying Yb and Fe concentration effectively tunes the charge carrier concentration, except for slight deviations from the expected trend shown in the estimated carrier concentration probably caused by the formation of the defects or secondary phases.
Temperature-dependent electrical conductivity and Seebeck coefficient measured from 300 K to 800 K are shown in Fig. 4.3a-b. The electrical conductivity decreases as temperature increases for all 6 samples, suggesting that they are degenerate semiconductors. Positive Seebeck and Hall coefficients confirm that Yb$_2$Fe$_{4-y}$Co$_y$Sb$_{12-x}$Sn$_x$ samples are all $p$-type semiconductors. The influence of Yb, Fe, and Sn dopants on electrical conductivity is quite significant. Electrical conductivity is related to carrier concentration and mobility as:
\[ \sigma = e \rho \mu \]  

Equation 4.20

Since the Fe dopant concentration effectively tunes the carrier concentration, the electrical conductivity dramatically increases with the Fe concentration. On the contrary, Sn dopants have larger impact on the mobility than the carrier concentration, as shown in Figure 4.4a. Thus, Sn-doped samples exhibit lower electrical conductivity compared to their Sn-free counterparts. Incorporating Sn dopants does not significantly affect the Seebeck coefficient, which suggests that the approach to enhance the thermoelectric power factor by generating Sn resonant levels is not successful in Yb\textsubscript{2}Fe\textsubscript{4-y}Co\textsubscript{y}Sb\textsubscript{12-x}Sn\textsubscript{x} filled skutterudites. On the other hand, varying Yb and Fe doping concentration influences the Seebeck coefficient in a complex manner. In addition to modifying the magnitude of thermopower, a significant change of the temperature dependence of the Seebeck coefficient is observed, which implies a significant dependence of the band structure on the Yb and Fe concentrations. The change of the temperature dependence of the Seebeck coefficient likely originates from the energy shift of the heavy Fe-d band as the Fe concentration increases. This change of the band structure details can also be seen from the Pisarenko relation between the Seebeck coefficient and carrier concentration, as shown in Figure 4.4b. The Seebeck coefficients of the 6 Yb\textsubscript{2}Fe\textsubscript{4-y}Co\textsubscript{y}Sb\textsubscript{12-x}Sn\textsubscript{x} samples do not follow the Pisarenko trend in which the Seebeck coefficient decreases as the carrier concentration increases. The increasing Seebeck coefficient with increasing carrier concentration suggests that incorporating Fe dopants significantly enhance the band effective mass.

In order to corroborate this assumption, fitting of electrical transport coefficients was attempted. A least square method was applied to solve for the simultaneous best fit to the Hall coefficient, Seebeck coefficient, and electrical conductivity data. However, no satisfactory fits were found, likely due to the unknown temperature-dependent band structure and scattering
processes. Recently, an *ab initio* band structure calculation corroborated the assumption that the increasing Fe concentration indeed moves the heavy Fe-d band closer to the light Sb-p band.[50] On the one hand, the energy upshift of the heavy Fe-d band pins the Fermi level above the vicinity of the Sn resonant levels, nullifying the influence of the resonant density of states. On the other hand, the convergence of the heavy Fe-d band and the light Sb-p band is beneficial for thermoelectric power factor. The power factor is enhanced approximately 60% from Yb$_{0.3}$FeCo$_3$Sb$_{12}$ to Yb$_{0.8}$Fe$_3$CoSb$_{12}$, as shown in Figure 4.5.

![Figure 4.3](image)

*Figure 4.3 High temperature (a) electrical conductivity and (b) Seebeck coefficient from 300 K to 800 K.*

Though the contribution of the heavy holes from the Fe-d band leads to a moderately high thermopower at high carrier concentration, these heavy holes are much less mobile than the light holes due to their large effective mass. This is detrimental to the mobility, as shown in Fig. 4.4a. The mobility drops significantly as the Fe concentration increases. The reduced mobility
partly negates the enhancement from the increased carrier concentration. Another drawback from incorporating large concentration of Fe dopants is the high carrier concentration. This large carrier concentration leads to a reduction on the thermopower at high temperatures, as shown in Fig. 4.3b. Such influence is not observed at low temperatures due to the narrow Fermi window. This suggests that an optimized Fermi level exists for maximum power factor. To achieve this, carrier concentration needs to be further modified. Incorporating other dopants is not promising, because extra impurities introduce too much scattering, similar with what Sn dopants do in Yb$_{y}$Fe$_{4-y}$Co$_{y}$Sb$_{12-x}$Sn$_{x}$. Novel doping methods will be demonstrated in the next chapter, which has the potential to maintain the mobility.

![Figure 4.4](image)

Figure 4.4 (a) Room temperature mobility vs. carrier concentration for all 6 Yb$_{y}$Fe$_{4-y}$Co$_{y}$Sb$_{12-x}$Sn$_{x}$ samples. (b) Room temperature Seebeck coefficient vs. carrier concentration.
In spite of the strong scattering on the carriers, Sn dopants significantly scatter acoustic phonons. The total and lattice thermal conductivities of the Sn-doped samples were greatly reduced compared to those of the Sn-free samples, as shown in Fig. 4.6. However, Yb and Fe dopants increase the total thermal conductivity. The independence of the lattice thermal conductivity on the Yb and Fe concentration indicates that Yb and Fe dopants mainly contribute
to the electronic part of the total thermal conductivity. A slightly enhanced thermoelectric figure of merit was achieved using Sn dopants, as shown in Fig. 4.7.

Figure 4.6 (a) Thermal conductivity from 300 K to 800 K. (b) Lattice thermal conductivity from 300 K to 800 K.
Figure 4.7 High temperature thermoelectric figure of merit.

4.6 Summary

A secondary $p$-type dopant Fe was successfully incorporated on the Co sites and the carrier concentration was thus increased. However, thermoelectric transport measurements indicate that the influence of Sn resonant levels is still not visible. This is attributed to the upshift
of the heavy Fe-d band as the Fe concentration increases. Sn dopants did prove beneficial for thermoelectric figure-of-merit by reducing thermal conductivity.

In addition, we found that increasing the Fe concentration moves the Fe-d band closer to the Sb-p band, which is confirmed by a recent *ab initio* calculation. Such convergence of the heavy Fe band and the light Sb band is beneficial to the thermoelectric performance, confirmed by an enhancement of power factor from 15 $\mu$Wcm$^{-1}$K$^{-2}$ for Yb$_{0.3}$FeCo$_3$Sb$_{12}$ to 25 $\mu$Wcm$^{-1}$K$^{-2}$ for Yb$_{0.8}$Fe$_3$CoSb$_{12}$. The contribution of the heavy holes in the heavy Fe band keeps the thermopower at a moderate value in spite of a large carrier concentration. Thus the Seebeck coefficient of Yb$_{0.8}$Fe$_3$CoSb$_{12}$ is higher than that of Yb$_{0.3}$FeCo$_3$Sb$_{12}$ at room temperature. However, the situation reverses at higher temperatures. This is attributed to the widening of the Fermi window as the temperature increases. As lower temperature, the contribution from the deep heavy Fe band is negligible and the Seebeck coefficient is determined primarily by the contribution of light holes. As the temperature increases, the widening Fermi level gradually touches the heavy Fe band and thus the Seebeck coefficient of Yb$_{0.3}$FeCo$_3$Sb$_{12}$ exceeds the value of Yb$_{0.8}$Fe$_3$CoSb$_{12}$ at higher temperatures become of a smaller carrier concentration. Such tradeoff between the carrier concentration and the heavy holes suggests an existence of an optimized carrier concentration for maximum power factor. A conventional doping method based on the ionization of impurity atoms has drawbacks due to the severe ionized impurity scattering introduced. A novel doping mechanism is desired, such as that described in the next chapter.
Chapter 5 Engineering Temperature-Dependent Carrier Concentration for Average Power Factor Enhancement via Novel Doping Method

5.1 Introduction

Conventional doping is to incorporate guest elements into the matrix. Such method is effective to adjust the carrier concentration. However, most of the dopants have low excitation energies, and thus they can be fully ionized at low temperatures.\cite{51} As a result, the carrier concentration of conventionally doped materials is temperature independent over a wide temperature range. The simulation results presented later, together with the experimental results reported in literature suggest that the carrier concentration needed to optimize the power factor varies with temperature.\cite{52} Thus, a temperature-dependent carrier concentration is desired for high temperature thermoelectric power generation. In this work, we proposed a novel method of incorporating secondary phase materials with a different temperature dependence of Fermi level than the matrix. The charge transfer across the interface of the matrix and the secondary phase aggregates causes a dramatic change of the carrier concentration in the matrix. Numerical simulation also indicates that the charge transfer is sensitive to the Fermi level offset between the matrix and the aggregates. Since the Fermi level offset is temperature-dependent caused by the
distinct temperature dependence of the Fermi level in matrix and secondary-phase aggregates, the carrier concentration in matrix is temperature-dependent. By applying this method to the GeTe-CuInTe$_2$ composites with CuInTe$_2$ as the secondary-phase dopants, the average power factor within a wide temperature range is achieved. Compared to the mobility of GeTe-In$_2$Te$_3$ solid solutions, the mobility of secondary-phase-doped GeTe is significantly higher. The synthesis process of the composites is suggested to be important for the doping method. Indeed, by changing from mechanically mixing the micron-size particles of the two materials to direct quenching the mixture of the melts, the thermoelectric power factor is doubled. For the GeTe-CuInTe$_2$ composites with GeTe as the secondary-phase dopants, the thermoelectric power factor is also enhanced, though through a different mechanism. The power factor of CuInTe$_2$ is significantly enhanced at approximately 600 K. Such enhancement is attributed to the energy filtering effect.

5.2 Material Synthesis and Pellet Sintering

Raw elements of germanium, copper, indium, and tellurium were purchased from Alfa Aesar with the following purities: Ge (pieces, 99.9999+%), Cu (shot, 99.999%), In (ingots, 99.9999+%), and Te (lumps, 99.999+%). The starting materials were weighed in the glovebox according to the stoichiometric ratio (Ge$_2$Te$_2$)$_x$(CuInTe$_2$)$_{1-x}$ with $x=100, 95, 90, 87.5, 85, 70, 30, 15, 10, and 0. In this chapter, the samples are denoted as GT-$x$, where $x$ represents the concentration of GeTe in the sample. The weighed materials were then put in carefully cleaned quartz ampoules and sealed under the pressure of less than $10^{-4}$ Torr and placed in a furnace
heated according to the following schedule: slow heating up to 1273 K at the rate of 1.5 K/min; rest at 1273 K for 12 hours; slow cooling down to 873 K at 2 K/min; annealing at 873 K for 4 days; and finally slow cooling down to room temperature at 2 K/min. The as-cast ingots were hand-milled to powders under argon atmosphere and hot-pressed at the temperature of ~773 K under the pressure of ~60 MPa for 30 min.

5.3 Crystallographic and Microstructural Characterization

The density of all samples as measured by the Archimedes method is given in Table 5.1. All GeTe rich samples (samples with the GeTe concentration larger than or equal to 70%) have densities above 6.07 g/cm$^3$, while the CuInTe$_2$-rich samples (samples with the content of GeTe less than or equal to 30%) have densities below 5.88 g/cm$^3$. If we take the theoretical density of GeTe from the literature to be 6.14 g/cm$^3$,[53] and 6.07 g/cm$^3$[54] for CuInTe$_2$, then the theoretical density of the composites can be calculated as below, assuming the phases are separated:

$$\rho = \frac{\rho_{\text{CuInTe}_2}(1+\frac{m_{\text{CuInTe}_2}x(1-x\%)}{m_{\text{Ge}_2\text{Te}_2}x\%})}{\rho_{\text{CuInTe}_2}+\frac{m_{\text{CuInTe}_2}x(1-x\%)}{m_{\text{Ge}_2\text{Te}_2}x\%}}$$

Equation 5.1

where $\rho_{\text{CuInTe}_2}$ is the theoretical density of CuInTe$_2$, $\rho_{\text{GeTe}}$ is the theoretical density of GeTe, $m_{\text{CuInTe}_2}$ is the molecular mass of CuInTe$_2$, $m_{\text{Ge}_2\text{Te}_2}$ is the molecular mass of Ge$_2$Te$_2$, and $x$ is the concentration of GeTe in the composites. The results of the theoretical densities of the composites together with the corresponding relative densities of the samples are also listed in
Table 5.1. All the GeTe-rich samples have relative densities above 98.9%, while CuInTe$_2$-rich samples only have relative densities between 93% and 97%. This difference suggests that the optimized hot-pressing conditions for GeTe-rich and CuInTe$_2$-rich composites are different and the one we use in this study is optimized only for GeTe-rich composites. The powder XRD patterns of 5 selected samples (GT-100, GT-90, GT-70, GT-30, and GT-10) are presented in Figure 5.1. The major phases of all the samples are identified as those of GeTe and CuInTe$_2$ for the GeTe-rich and the CuInTe$_2$-rich samples, respectively, according to the known peak positions of the minerals (GeTe: ref. 06-0469 and CuInTe$_2$: ref. 06-0605). There are also traces of the secondary phase of Ge in the pure GeTe sample (Ge: ref. 03-0478). Several major Cu $\beta$ diffraction peaks are also identified and labeled in Figure 5.1, due to the strong Cu $\beta$ radiation of the X-ray source. As the concentration of CuInTe$_2$ increases, the intensity of the CuInTe$_2$ peaks increases, while that of the GeTe peaks decreases. The peak of Ge impurity disappears for all the CuInTe$_2$-added samples, indicating that the amount of trace Ge falls below the detection limit of powder XRD. The coexistence of GeTe and CuInTe$_2$ peaks confirms that GeTe and CuInTe$_2$ can only form composites, due to the different space group of the two compounds (CuInTe$_2$ has a tetragonal structure with the space group $I\overline{4}2d$, while GeTe crystallizes with a rhombohedral structure in the space group $R4m$).[53, 54] The secondary phase of Ge is present because Ge forms as a consequence of native defects in GeTe.
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>GT-100</th>
<th>GT-98</th>
<th>GT-95</th>
<th>GT-92.5</th>
<th>GT-90</th>
<th>GT-87.5</th>
<th>GT-85</th>
<th>GT-80</th>
<th>GT-70</th>
<th>GT-30</th>
<th>GT-15</th>
<th>GT-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Density (%)</td>
<td>99.3</td>
<td>99.7</td>
<td>98.9</td>
<td>99.9</td>
<td>99.3</td>
<td>&gt;100</td>
<td>99.9</td>
<td>&gt;100</td>
<td>99.4</td>
<td>96.5</td>
<td>93.4</td>
<td>93.2</td>
</tr>
</tbody>
</table>

Table 5.1 Measured densities, theoretical densities, and relative densities of \((\text{Ge}_2\text{Te}_2)_{x\%}(\text{CuInTe}_2)_{1-x\%}\).

Figure 5.1 Powder XRD patterns of 5 typically selected samples, GT-100, GT-90, GT-70, GT-30, and GT-10.
The BSE images of the GT-98 and GT-95 samples are presented to illustrate the segregation of CuInTe$_2$ secondary phases, as shown in Figure 5.2a-b. The segregation of CuInTe$_2$ in GT-98 sample suggests that the solubility limit of Cu or In in the GeTe matrix is below 2%. The contrast of light and dark regions in the BSE image clearly confirms the existence of two phases with the light-colored “bubbles” depicting the CuInTe$_2$ phase with its larger average atomic weight of 433.566, while the dark background corresponds to the GeTe matrix having a smaller average atomic weight of 400.460. Two macroscale BSE images of GT-70 and GT-90 are presented for comparison, shown in Figure 5.2c-d. The size of the segregated CuInTe$_2$ varies from several micrometers for GT-90 to 50 micrometers for GT-70, and various shapes of the segregated phase can be identified as bubbles, dots, polygons, or stripes in the GT-70 sample. As the concentration of CuInTe$_2$ decreases from 30% to 10%, the extent of the segregated CuInTe$_2$ also decreases, and the shape tends to be only spherical.
EDS element mapping further verifies the phase separation of GeTe and CuInTe$_2$, as shown in Figure 5.3a, where the target element accumulates in the lighter area. A small amount of pure Ge is detected in the Ge mapping image as a very light spot and this spot corresponds to the dark spot in the Te mapping image, though the concentration of Ge is so small that powder XRD is not able to detect it. No In or Cu rich secondary phases were detected in the region tested. Since BSE or EDS has detection resolution of approximately 1 μm, nano-scale secondary-phase
aggregates cannot be observed using such technique. High resolution TEM image of a small region of the GT-70 sample is shown in Fig. 5.3b to confirm the nanoscale phase aggregation. The large matrix bears a rhombohedral GeTe structure, well fitted with the overlaid GeTe atomic model. In the matrix, the highlighted area shows an atomic lattice corresponding to the chalcopyrite CuInTe$_2$ structure, confirming the existence of the nano-size CuInTe$_2$ secondary phase. The shape of these nano-size segregations is not spherical. The work function of GeTe and CuInTe$_2$ are determined by UPS. An offset of approximately 0.3 eV is determined. The work function shift shown in the GT-95 sample suggests the interface density is high since the Fermi level is a spatial constant and the local vacuum level bends with the band bending, as illustrated in the middle inset of Fig. 5.3c. This is also confirmed in the XPS peak shifts shown in Fig. 5.3d. The top insets of Fig. 5.3c are the spectroscopy data focusing on the lower (left) and higher (right) kinetic energy range. The right inset verifies that the Fermi levels of the tested 3 samples are all aligned with the measurement system during the measurement, calibrated by measuring Fermi step of a freshly deposited Au film.
It will be demonstrated in the next section by calculation that high density of nanoscale CuInTe$_2$ segregations is crucial for the matrix carrier concentration adjustment. However, it is not easy to have a statistical distribution of these nanoscale particles from a single TEM image. Instead, an EDS mapping on a region of ~300 nm size confirms that the signal of Cu and In is
almost everywhere, confirming that the nanoscale CuInTe$_2$ is distributed homogenously in the matrix, as shown in Fig. 5.4.

Figure 5.4 EDS mapping of Cu, Ge, In, and Te on a small region in the GT-70 sample.
5.4 Poisson Model

For simplicity, the inclusions of CuInTe\(_2\) are assumed to be spheres and the GeTe phase surrounds the CuInTe\(_2\) inclusions. The radius of CuInTe\(_2\) inclusions is related to that of the GeTe phase by the mole concentration of CuInTe\(_2\) as:

\[ x = \left( \frac{R_{\text{CIT}}}{R_{\text{GT}}} \right)^3 \]  

\textit{Equation 5.2}

where \(x\) is the doping ratio. The common energy reference is set as the valence band maximum of pure GeTe. Note that we are studying the effect of holes, thus the energy increases deeper into the valence band. The spatial distribution of the electrostatic potential \(V(r)\) is caused by the charge redistribution after the two phases come into contact, and the potential distribution can be determined \textit{via} the Poisson equation.

For \(r \leq R_{\text{CIT}}\) in the CuInTe\(_2\) region, the Poisson equation can be written as:

\[ \frac{1}{r} \frac{d}{dr} \left( r \frac{dV}{dr} \right) = - \frac{e}{\varepsilon_{\text{CIT}} \varepsilon_0} p_{\text{CIT-net}}(r) \]  

\textit{Equation 5.3}

For \(R_{\text{CIT}} \leq r \leq R_{\text{GT}}\) in the GeTe region, the Poisson equation can be written as:

\[ \frac{1}{r} \frac{d}{dr} \left( r \frac{dV}{dr} \right) = - \frac{e}{\varepsilon_{\text{GT}} \varepsilon_0} p_{\text{GT-net}}(r) \]  

\textit{Equation 5.4}

where \(\varepsilon_{\text{CIT}}\) is the dielectric constant of CuInTe\(_2\), \(\varepsilon_{\text{GT}}\) is the dielectric constant of GeTe, \(\varepsilon_0\) is the vacuum permittivity, \(p_{\text{CIT-net}}(r)\) is the net charge concentration in the CuInTe\(_2\) region, and \(p_{\text{GT-net}}(r)\) is the net charge concentration in the GeTe region.
At a given temperature, the defect concentration in GeTe and CuInTe$_2$ determines their carrier concentrations. If a certain amount of free carriers move away from a region, it will be left with net charges, which can be written as:

\[ p_{\text{net}} = p[\mu(r)] - p_0 \quad \text{Equation 5.5} \]

where \( p[\mu(r)] \) is the new carrier concentration determined by the chemical potential \( \mu(r) \) after the charge redistribution, and \( p_0 \) is carrier concentration under neutral condition before contact, which is decided by the temperature and defect concentration. If we further assume each material possesses a parabolic band structure (more complex band structure can easily be implemented, here we use parabolic band structure for simplicity), then we have:

\[ p_{\text{net}} = \frac{4\pi(2m^*k_B T)^{\frac{3}{2}}}{h^3} \int_0^\infty \frac{1}{1 + \exp\left(\frac{\eta - E_{F-AC} - E_{VBM-AC}}{k_B T}\right)} \eta^2 d\eta - p_0 \quad \text{Equation 5.6} \]

with \( E_{F-AC} \) representing the Fermi energy after two phases come into contact, and \( E_{VBM-AC} \) representing the energy of the maximum of the valence band after two phases come into contact.

Plugging Eqn. 5.6 into 5.3 and 5.4, we have:

For \( r \leq R_{\text{CIT}} \),

\[ \frac{1}{r} \frac{d}{dr} r V(r) = -\frac{e}{\varepsilon_{\text{CIT}} \varepsilon_0} \left\{ \frac{4\pi(2m_{\text{CIT}} k_B T)^{\frac{3}{2}}}{h^3} \int_0^\infty \frac{1}{1 + \exp\left(\eta - \frac{E_{F-AC} - E_{VBM-AC}}{k_B T}\right)} \eta^2 d\eta - p_{\text{CIT}0} \right\} \quad \text{Equation 5.7} \]

where \( E_{\text{off}} \) is the energy offset between the maximum of the valence bands of the two phases.

And for \( R_{\text{CIT}} \leq r \leq R_{\text{GT}} \)
\[
\frac{1}{r} \frac{d^2}{dr^2} rV(r) = -\frac{e^2}{\varepsilon_{GT}\varepsilon_0} \left\{ \frac{4\pi(2m_{GT}k_BT)^2}{h^3} \int_0^\infty \frac{\eta^2 d\eta}{1 + \exp\left\{ \eta - \frac{E_{F-ac} - eV(r)}{k_BT} \right\}} - p_{GT-0} \right\} 
\]

Equation 5.8

In order to solve for \( V(r) \) within the domain that we are interested in, additional boundary conditions are needed. At the center of the CuInTe\(_2\) inclusion, we set the electric field to be zero, that is:

\[-\left. \frac{dV(r)}{dr} \right|_{r=0} = 0 \quad \text{Equation 5.9} \]

On the other hand, since the total charge within the domain of \( r \leq R_{GT} \) is conserved, based on Gauss’s law, the electric field at \( r = R_{GT} \) is also zero:

\[-\left. \frac{dV(r)}{dr} \right|_{r=R_{GT}} = 0 \quad \text{Equation 5.10} \]

On the interface between the CuInTe\(_2\) and GeTe phases, the discontinuity of the electrostatic potential depends on the interface dipole, which is material dependent. Also, the electrical field discontinuity is decided by the interface free charge density. Here, for simplicity, we set them both to be zero. Thus, the third and fourth boundary conditions on the interface are:

\[ V(r = R^+_{CIT}) - V(r = R^-_{CIT}) = 0 \quad \text{Equation 5.11} \]

\[-\varepsilon_{CIT} \left. \frac{dV(r)}{dr} \right|_{r=R^-_{CIT}} = -\varepsilon_{GT} \left. \frac{dV(r)}{dr} \right|_{r=R^+_{CIT}} \quad \text{Equation 5.12} \]

We used the fourth-order Runge-Kutta algorithm with the shooting method to numerically solve the Poisson equation with the above boundary conditions. The electrostatic potential, electric
field, and charge distribution profile at the interfaces are shown as Fig. 5.5a. To estimate the bulk matrix carrier concentration change due to such a charge transfer effect, we divide the total amount of charge transferred across the interface by the total volume of the sample in the manner of “averaging” the charge transfer effect.

The band bending and charge distribution profiles, together with the average carrier concentration change in the matrix, depend on many parameters, including the Fermi level offset, band structure details, the dielectric constant of each phase, the electrostatic potential drop across the interface, the original carrier concentration in each phase before contact, the secondary phase inclusion size, and secondary phase volume fraction. Other parameters are not included in the model, such as surface states, charge accumulation, and the non-spherical geometry of the inclusion shape. Many of these parameters are fixed when two specific materials are selected, thus a more detailed and rigorous model regarding the whole parameter space must be developed as material selection criteria. Here, we focus on the parameters that change significantly in the GeTe-CuInTe₂ system, such as Fermi level offset, secondary inclusion size, secondary phase volume fraction, and the inclusion shape. The average bulk matrix carrier concentration change depending on these parameters is shown as Fig. 5.5b-d.
Figure 5.5 (a): Room temperature carrier concentration change, electric field, and electrostatic potential distribution near the interface between GeTe and CuInTe$_2$ phases. (b): Average room temperature carrier concentration depletion over the bulk region as a function of secondary phase concentration with various secondary phase geometries of different surface area to volume ratio. (The size of the secondary phase is set to be 3 nm) (c): Average carrier concentration depletion over the bulk region as a function of valence band offset. (The size of the secondary phase is set to be 3 nm and the doping ratio is set to be 5 mol%) (d): Average room temperature carrier concentration depletion over the bulk region as a function of the size of the CuInTe$_2$ inclusions. (The doping ratio is set to be 5 mol% and the surface to volume ratio is set to be 10 times larger than that of spheres)

5.5 Transport Properties Calculation
For a single parabolic band, the Hall coefficient, the Seebeck coefficient, and the electrical conductivity can be expressed as below by solving the Boltzmann transport equation with the relaxation time assumption:

\[
R_H = \frac{1}{e} \left( \frac{\hbar^2}{2m^*k_BT} \right)^\frac{3}{2} \frac{3\pi^2 \frac{F_{-\frac{3}{2}}(\eta^*)}{(F_0(\eta^*))^\frac{3}{2}}}{2} \tag{Equation 5.13}
\]

\[
\sigma = e^2 w \frac{2}{3\pi^2\hbar^2} \left( \frac{\hbar^2}{2m^*} \right)^\frac{1}{2} k_B T F_0(\eta^*) \tag{Equation 5.14}
\]

\[
S = \frac{k_B}{e} \left\{ 2 \frac{F_1(\eta^*)}{F_0(\eta^*)} - \eta^* \right\} \tag{Equation 5.15}
\]

where \(e\) is the elementary charge, \(\hbar\) is the reduced Planck’s constant, \(m^*\) is the effective mass, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(w\) is the proportionality constant, \(\eta^* = \frac{E_F}{k_BT}\) is the reduced Fermi level, and \(F_j(\eta^*) = \int_0^\infty \frac{\eta^j}{1 + \exp(\eta - \eta^*)} d\eta\) is the Fermi integral of the \(j\)-th order. The relaxation time has the energy dependence as:

\[
\tau = wE^r \tag{Equation 5.16}
\]

where \(w\) is the proportionality constant, which we set to a value of \(1.2 \times 10^{-23}\) in this work. With acoustic phonon scattering assumed as the dominant scattering process, the scattering parameter \(r\) has the value of \(-\frac{1}{2}\).

The carrier concentration of a parabolic band can be expressed as:

\[
p = \frac{4\pi(2m^*k_BT)^\frac{3}{2}}{\hbar^3} F_{\frac{1}{2}}(\eta^*) \tag{Equation 5.17}
\]
The dependence of power factor on the temperature and carrier concentration is shown in Figure 5.6. Relaxation time assumption is applied here and the dominant scattering mechanism is assumed to be acoustic phonon scattering. An unambiguous conclusion can be drawn that the carrier density for the peak power factor changes with the varying temperatures. The changing effective mass of the parabolic band will only alter the specific carrier concentration value for the peak power factor corresponding to the cases of certain materials. Such special dependence originates from the fact that the Fermi-Dirac distribution, which decides the total carrier density and power factor, highly depends on the temperature.
Figure 5.6 (a)-(c): Normalized power factor as a function of carrier concentration and temperature for single parabolic bands of various effective masses. (d): Temperature-dependent power factor with carrier concentration following the trajectories shown in (c).

5.6 Thermoelectric Transport Properties

The temperature-dependent heat capacity clearly indicates that a phase transition has taken place at around 650 K for all the samples, Figure 5.7. It is also noticeable that both the
phase transition temperature and the heat capacity value generally decrease as the mole fraction of CuInTe$_2$ increases. The decreasing phase transition temperature suggests that a small amount of Cu and In might go into the GeTe lattice to alter the phase transition temperature, which has also been observed in a previous study on the In-doped GeTe$^5$;[55] however, the phase transition temperature shift in our samples is only around 15 K, much smaller than the value observed in the In-doped GeTe of 125 K, indicating that the amount of Cu and In that went into the GeTe lattice in our sample is much smaller than that of In-doped GeTe in the previous study.[55] The decreasing heat capacity value is consistent with our previous microstructure analysis that GeTe and CuInTe$_2$ form composites with two separated phases and each phase contributes to the heat capacity individually. Three consecutive heat capacity measurements were also done on the GT-87.5 sample to confirm the repeatability of the measurement, inset of Figure 5.7. An abnormal upturn of the heat capacity after the phase transition peak can be observed in the GeTe-rich samples. This feature is confirmed by the three consecutive measurements on the GT-87.5 sample and another measurement at Michigan State University. We qualitatively attribute such an upturn feature to Te vaporization at high temperatures, since we observed the Te deposition layer both inside and outside the crucible after each measurement.
High temperature electrical transport properties of GeTe-CuInTe$_2$ composites are shown in Figure 5.8. Pure GeTe exhibits the typical metallic conduction feature that the Seebeck coefficient and electrical conductivity have a positive and negative monotonic dependence on the temperature, respectively, confirming that the natural defects on the Ge site make pure GeTe a heavily doped semiconductor. Though the phase transition of pure GeTe is observed in the specific heat capacity curve, it does not influence the electrical transport properties. However, a
distinct mark from 575 K to 625 K on the temperature dependence of the electrical transport parameters of four GeTe-rich composites was observed, which corresponds to the temperature range that is slightly lower than the phase transition peak in the heat capacity data. In the inverse Hall coefficient data that will be discussed later, the temperature range of 575 K to 625 K features convergent inverse Hall coefficient data for all the GeTe-rich samples. I attributed this distinct mark on both the temperature dependence of the electrical transport parameters and the inverse Hall coefficient between 575 K and 625 K to the convergence of the Fermi energy.

According to Fig. 5.5, the incorporation of CuInTe₂ secondary phases decreases the electrical conductivity and increases the Seebeck coefficient within the whole temperature range. As the molar fraction of CuInTe₂ increases above 70%, the significantly increased Seebeck coefficient and decreased electrical conductivity suggest that the carrier concentration is significantly decreased. The anomalous discontinuity of the temperature dependence of the Seebeck coefficient and electrical conductivity can also be observed for the CuInTe₂-rich samples around 600 K. However, the fact that it occurs over the expanded temperature range from 500 K to 700 K indicates that it is not related to the phase transition. Another anomaly is that both the Seebeck coefficient and electrical conductivity increase from 500 K to 600 K for the GT-15 and GT-30 samples. The simultaneous increasing Seebeck coefficient and electrical conductivity result in a sharp increase in the power factor within the temperature range from 500 K to 650 K, nearly tripling the power factor. Though the simultaneously increasing electrical parameters are not observed for the GT-10 sample, a similar feature of rapidly increasing power factor is still present due to the fact that the increasing electrical conductivity has much larger temperature dependence than that of the decreasing Seebeck coefficient. Despite having almost identical power factors with the pure GeTe sample at high temperatures, the GT-95 and GT-90
samples exhibit significantly enhanced power factors at lower temperatures resulting in a much improved average power factor over the whole temperature range. The GT-85 and GT-70 samples have much lower power factors than that of pure GeTe at elevated temperatures, suggesting that incorporating more than 15% mole fraction of CuInTe₂ is detrimental for the power factor.
Figure 5.8 High temperature (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor of 8 GeTe-CuInTe₂ samples.
In the XRD phase identification and BSE, SEM, and TEM microstructural analyses, we have confirmed that GeTe and CuInTe$_2$ segregate as separated phases. Below we will show in detail that this two-phase separation feature is crucial for understanding the electrical transport properties in the GeTe-CuInTe$_2$ composites. Electronic band structure schematics of the heterojunction at the interface of GeTe and CuInTe$_2$ phases in the GeTe-rich composites before and after contact at various temperatures are shown in Figure 5.9.

Figure 5.9 Schematics of the band alignment on the interface between GeTe and CuInTe$_2$ phases in GeTe-rich composites (a) 300 K before contact, (b) 300 K after contact, (c) 600 K before contact, (d) 600 K after contact, (e) 800 K before contact, and (f) 800 K after contact.

The determination of the temperature-dependent Fermi energy relative to the valence band maximum of the CuInTe$_2$ phase was based on Boltzmann transport theory and the experimental high temperature Seebeck coefficient, assuming a single parabolic valence band
located at the Γ point, as suggested by previous band structure calculations.[56, 57] The Seebeck coefficient for a single parabolic band is expressed as:

\[ S = \frac{k}{e} \left[ \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right] \quad \text{Equation 5.18} \]

where \( k \) is the Boltzmann constant, \( e \) is the elementary charge, \( \eta = E_f/kT \) is the reduced Fermi level, and \( F_r(\eta) \) is the Fermi integral defined as:

\[ F_r(\eta) = \int_0^\infty \frac{e^r}{1+\exp(e-\eta)} \, de \quad \text{Equation 5.19} \]

The determination of the temperature dependent Fermi energy in the pure GeTe phase relative to its light band edge is more complicated. It is believed that GeTe has 4-fold degenerate light valence bands at \( L \) point and deeper 12-fold degenerate heavy valence bands at \( \Sigma \) point with an energy difference of 0.27 eV – 0.38 eV at 300 K.[55, 58-60] Here, we take the value of 0.36 eV obtained by Sun et al.[55] The energy difference between the light \( L \) band and the heavy \( \Sigma \) band also decreases as the temperature increases.[47, 60, 61] Here, we take the temperature dependence of the energy difference to be \(-1.2 \times 10^{-3} \text{ eV/K}\) to meet the requirement that these two bands converge at around 600 K, which was suggested by the Hall coefficient measurement in this work shown in Figure 5.10a and previous work.[47, 60] The two band model for GeTe Fermi energy determination is then expressed as:[55]

\[ p_l = 4\pi \left( \frac{2m^*_l kT}{\hbar^2} \right)^{3/2} F_{1/2}(\eta_l) \quad \text{Equation 5.20} \]

\[ p_h = 4\pi \left( \frac{2m^*_h kT}{\hbar^2} \right)^{3/2} F_{1/2}(\eta_h) \quad \text{Equation 5.21} \]

\[ \Delta E = (\eta_l - \eta_h) \cdot kT \quad \text{Equation 5.22} \]
\[
S = \frac{p_h}{p_h + p_l \cdot b} S_h + \frac{p_l \cdot b}{p_h + p_l \cdot b} S_l
\]

Equation 5.23

\[
S_{l,h} = \frac{k}{e} \left[ \frac{2F_2(\eta_{l,h})}{F_0(\eta_{l,h})} - \eta_{l,h} \right]
\]

Equation 5.24

where \( p \) is the hole concentration, \( m^* \) is the effective mass, \( h \) is the Planck constant, \( T \) is the temperature, \( \Delta E \) is the energy difference between the light \( L \) band and the heavy \( \Sigma \) band, \( b \) is the mobility ratio of light holes to heavy holes. The subscripts \( h \) and \( l \) in all the equations correspond to the heavy and light holes, respectively. In this work, we take the parameters from the literature to be \( m_l^* = 0.5m_0 \), \( m_h^* = 2.5m_0 \), \( \Delta E = 0.36 - 1.2 \times 10^{-3}(T - 300) \) eV, \( b = 4 \).[55] With the room temperature Fermi level offset determined to be 0.3 eV from UPS measurement, the temperature dependent Fermi energy of GeTe and CuInTe\(_2\) relative to the CuInTe\(_2\) \( \Gamma \) valence band maximum before contact is shown in Figure 5.10b. It is also worth noting that the positive energy direction is pointing toward the valence band since we are studying holes instead of electrons. Thus, the positive Fermi energy value in Figure 5.10b means that the Fermi level is below the CuInTe\(_2\) \( \Gamma \) band maximum.
Figure 5.10 (a) High temperature inverse Hall coefficient of 5 GeTe-rich composites, (b) High temperature Fermi energy of pure CuInTe$_2$ and pure GeTe referred to the valence band maximum of CuInTe$_2$ calculated from the measured transport coefficients, and (c) High temperature power factor of the GT-100 and GT-95 samples for comparison. The carrier concentration dependent power factor at various temperatures for a single parabolic band with an effective mass of 0.5 m$_e$ is shown as the inset of (c). The black and red lines in the inset of (c) schematically correspond to the temperature dependence of the carrier concentration of GT-100 and GT-95 samples, respectively.
With the Fermi energy and band offset energy determined, now we are able to discuss in detail how the band alignment and the charge transfer at the interface between the GeTe and CuInTe$_2$ phases influence the transport properties. First, let’s discuss the GeTe-rich composites. Figure 5.10b shows that the Fermi energy of GeTe sits at a higher energy than that of CuInTe$_2$ at 300 K before contact, which is schematically illustrated in Figure 5.9a. After the two phases make contact, the carriers in the GeTe phase with larger Fermi energy start to diffuse into the CuInTe$_2$ to build up an electrostatic potential to compensate the Fermi energy difference before contact, and eventually keep the Fermi energy constant over the whole composite material. Consequently, the bands bend near the interface in both the phases, resulting in an accumulation region and a depletion region in the CuInTe$_2$ phase and GeTe phase, respectively, as shown in Figure 5.9b. Such a depletion effect reduces the carrier concentration in the GeTe phase near room temperature significantly, as confirmed by the Hall coefficient measurement shown in Figure 5.10a. The carrier concentration drops from $8\times10^{20}$ cm$^{-3}$ to below $5\times10^{20}$ cm$^{-3}$ at 300 K.

As the temperature increases, the Fermi energy difference between the GeTe phase and CuInTe$_2$ phase starts to decrease and at around 600 K, the Fermi energy converges before contact, as shown in Figure 5.9c. Since there is no Fermi energy difference between the two phases, the carriers will not diffuse across the interface after contact, resulting in negligible band bending near the interface, as shown in Figure 5.9d. Thus, CuInTe$_2$ will not deplete the carriers in the GeTe phase at this temperature and the inverse Hall coefficient of the pure GeTe and other GeTe-rich composites converges slightly above 600 K, as shown in Figure 5.10a. It is worth noting that the temperature of the converged inverse Hall coefficient is slightly higher than 600 K due to the fact that the carriers are contributed only by the GeTe phase, which is smaller than
the volume that we use to calculate the carrier concentration. Thus, the carrier concentration of GeTe-rich composites is smaller than that of pure GeTe at 600 K.

As the temperature continues going up, the Fermi energy of CuInTe$_2$ sits higher than that of GeTe before contact, as shown in Figure 5.9e. The carriers now diffuse from the CuInTe$_2$ phase into GeTe after contact and an accumulation region and depletion region are formed in the GeTe phase and CuInTe$_2$ phase, respectively, shown in Figure 5.9f. This results in a higher carrier concentration for GeTe-rich composites than that of the pure GeTe, illustrated in Figure 5.10a. The temperature dependent Fermi energy difference between the GeTe and CuInTe$_2$ phases enhances the temperature dependence of the carrier concentration of the GeTe-rich composites compared to that of the pure GeTe by the temperature dependent de-doping effect. The red straight line in the inset of Figure 5.10c represents how the carrier concentration of the GT-95 sample changes as the temperature changes, while the black straight line represents that of the pure GeTe sample. The inset of Figure 5.10c also depicts how the power factor depends on the carrier concentration at various temperatures for a single parabolic band. I conclude that the carrier concentration for the optimized power factor increases as the temperature increases, which is consistent with a previous study.[52] Since the de-doping effect in our sample only happens at lower temperatures while not influencing the carrier concentration at elevated temperatures, the power factor is enhanced at lower temperatures and kept optimized at higher temperatures, resulting in an enhanced average power factor over the whole temperature range. This novel mechanism of temperature-dependent de-doping effect is suitable for enhancing the average power factor of other heavily doped semiconductors that can only be optimized at high temperature via traditional doping method.
While CuInTe$_2$ secondary phases act as de-dopants in the GeTe-rich composites, GeTe secondary phases function quite differently in the CuInTe$_2$-rich composites, which is the next topic of discussion. The band alignment on the interface between the GeTe and CuInTe$_2$ phases at 300 K before and after contact is shown in Figure 5.11. As discussed above, the accumulation region is in the CuInTe$_2$ phase while the depletion region is in the GeTe. However, the Hall coefficient measurement on the CuInTe$_2$-rich samples does not show a dramatic enhancement of the carrier concentration in GT-10 or GT-15 samples compared to the pure CuInTe$_2$ at 300 K, shown in Figure 5.12a. The approximate $4 \times 10^{18}$ cm$^{-3}$ carrier concentration enhancement at room temperature in the GT-10 and GT-15 samples compared to the pure CuInTe$_2$ is much smaller than the $3 \times 10^{20}$ cm$^{-3}$ carrier concentration drop in the GT-95 compared to the pure GeTe. We attribute this large difference to the fact that the GeTe secondary phase segregates at larger size. As mentioned in the Poisson Model section, the nanoscale secondary phase segregation is crucial to the carrier concentration adjustment. The GeTe secondary phases with larger scale do not significantly influence the carrier concentration in CuInTe$_2$. Indeed, no Ge signal can be
observed in CuInTe$_2$ in Fig. 5.3a. Hall measurement shows that the carrier concentration of the GT-15 and GT-10 samples increases faster with temperature than the pure CuInTe$_2$ does. This feature is caused by the temperature dependence of the Fermi energy in the CuInTe$_2$ phase. From Figure 5.10b, the Fermi energy of CuInTe$_2$ is around 60 meV at room temperature, increases to a little above 0.1 eV at around 500 K, and then starts to decrease again above 500 K to a value below 0.1 eV. 60 meV corresponds to an excitation energy of ~700 K, which is well above 300 K. Thus, only a very small amount of carriers in the GeTe phase can be thermally excited over the energy barrier, which is equal to the value of the Fermi energy of CuInTe$_2$. As temperature goes up, more and more carriers in the GeTe tend to be thermally excited, however, the increasing energy barrier keeps the carrier concentration at a fairly low value. This behavior is seen in the carrier concentration plateau from 300 K to 500 K in Figure 5.12a. As the temperature goes up above 500 K, more and more carriers tend to conduct across the barrier and the barrier height starts to decrease, thus a sudden increase in the carrier concentration of the GT-10 and GT-15 samples was observed. I can conclude now that the carrier concentration increase in the GT-10 and GT-15 compared to the pure CuInTe$_2$ comes from the thermal excitation of the carriers from the GeTe phase to the CuInTe$_2$ phase, instead of the depletion or accumulation at the interface, which is the main cause for the de-doping effect in the GeTe-rich composites.
Figure 5.12 (a) High temperature carrier concentration of 3 CuInTe$_2$-rich composites, (b) High temperature Seebeck coefficient and electrical conductivity of the GT-15 sample, and (c) high temperature power factor of the GT-15 sample.
With the charge transfer image in the CuInTe$_2$-rich samples clear in mind, now it is not difficult to explain the simultaneously increasing Seebeck coefficient and electrical conductivity observed in the GT-15 sample. On the one hand, as the temperature increases above 500 K, a large amount of carriers start to be thermally excited over the barrier and contribute to the conduction, thus the electrical conductivity starts to increase dramatically. On the other hand, these excited carriers will continuously move between the CuInTe$_2$ phase and the GeTe phase, thereby experiencing extra scattering. These carriers also tend to occupy the lowest energy in the CuInTe$_2$ bands, since they are excited from even lower energy levels. So a significant amount of low energy carriers have a reduced mobility due to the extra scattering, resulting in an enhanced energy dependence of mobility, which is the well-known effect of energy filtering effect. The enhancement of the Seebeck coefficient is clearly stated in the Mott formula:

$$S = -\frac{\pi^2 k}{3} kT \left\{ \frac{1}{g(E)} \frac{dg(E)}{dE} + \frac{1}{\mu(E)} \frac{d\mu(E)}{dE} \right\}_{E=E_F}$$

Equation 5.25

where $g(E)$ is the density of states, and $\mu(E)$ is the energy-dependent mobility of the carriers. The simultaneously increasing Seebeck coefficient and electrical conductivity of the GT-15 sample, shown in Figure 5.12b, results in a rapid increase of the power factor, shown in Figure 5.12c. The temperature range of this enhancement starts from 500 K, which corresponds to the onset of the thermal excitation discussed earlier. It is also worth noting that this energy filtering effect does not influence the transport properties of the GeTe-rich composites very much by the following argument. At lower temperatures, the carrier concentration increase due to the thermal excitation from the GeTe phase to the CuInTe$_2$ phase in the GT-15 is around $5 \times 10^{18}$ cm$^{-3}$. Taking the fact that GeTe is 95% of the whole material in GT-95 rather than 15% in GT-15, the carrier concentration increase due to such thermal excitation over the barrier at low temperature in GT-
95 will be less than $3.0 \times 10^{19}$ cm$^{-3}$, which is less than 6% of the total carrier concentration of $5 \times 10^{20}$ cm$^{-3}$. Thus, most of the carriers will be blocked by the CuInTe$_2$ secondary phases, and the change of the energy dependence of the mobility contributed by the energy filtering effect is negligible.

In order to uncover the scattering processes in the GeTe-CuInTe$_2$ composites, I performed low temperature transport measurements, the results of which are shown in Figure 5.13. The temperature dependence of the electrical conductivity for the samples GT-x with $x > 30$ is negative, while GT-15 and GT-10 possess positive temperature-dependent electrical conductivity, Figure 5.13a. This suggests that GeTe dominates the electrical transport properties for the samples with GeTe concentration larger than 30%, which is larger than the percolation threshold, where GeTe forms a continuous path through the material. The electrical conductivity generally decreases as the concentration of CuInTe$_2$ increases. The carrier concentration data also confirms that 30% exceeds the percolation threshold of GeTe in the GeTe-CuInTe$_2$ composites as a large jump of carrier concentration from GT-15 to GT-30 sample can be observed, Figure 5.13b. Low temperature Hall mobility was calculated using the relation:

$$\sigma = e\rho\mu \quad \text{Equation 5.26}$$

The negative temperature dependence of the mobility of 5 GeTe-rich composites suggests mixed scattering processes by acoustic phonons, defects and grain boundaries, while a positive temperature-dependent mobility of the GT-10 and GT-15 samples indicates that only scattering by defects and grain boundaries dominates, as shown in Figure 5.13c. GT-30 shows highly temperature-independent mobility, which represents a transition from GeTe-rich composites to CuInTe$_2$-rich composites near the percolation of GeTe, indicating a suppression of the acoustic
phonon scattering. The mobility generally decreases as the CuInTe₂ concentration increases till 70%, when the mobility reaches the minimum. Then the mobility starts to increase as the CuInTe₂ concentration continues increasing until 70%. It is of great interest to compare the room temperature mobility of this work to that of a previous work on In-doped GeTe.[55] As shown in the inset of Figure 5.1, it is obvious that the mobility of GeTe-CuInTe₂ composites is significantly larger than that of GeTe-In₂Te₃ solid solutions. It suggests that forming nano-size secondary phases scatters the carriers less significantly than disturbing the lattice by doping does. As discussed earlier, the carrier de-doping effect from the formation of composites, together with enhanced mobility, is a novel mechanism to optimize the thermoelectric performance of semiconductors.

Low temperature thermal conductivity also shows quite different phonon scattering processes between GeTe-rich and CuInTe₂-rich samples, Figure 5.1d. The exponentially decreasing thermal conductivity for the CuInTe₂-rich samples is due to phonon-phonon scattering processes, while the almost temperature-independent thermal conductivity for the GeTe-rich samples suggests that the phonons are mostly scattered by the grain boundaries and dislocations.
Figure 5.13 Low temperature (a) electrical conductivity, (b) carrier concentration, (c) Hall mobility, and (d) thermal conductivity of GeTe-CuInTe$_2$ composites. The inset of (c) is the comparison of room temperature mobility between GeTe-CuInTe$_2$ composites in this work and GeTe-In$_2$Te$_3$ solid solutions.

High temperature thermal conductivity from room temperature to 800 K of all GeTe-CuInTe$_2$ composites generally exhibit negative monotonic temperature dependence, showing the dominance of Umklapp scattering processes, except an anomalous bump from 650 K to 700 K for the GeTe-rich composites, which is related to the phase transition of GeTe, Figure 5.14a. Since GeTe has a much higher thermal conductivity than that of CuInTe$_2$, the total thermal conductivity generally decreases as the mole fraction of CuInTe$_2$ increases. However, the GT-95
sample shows a remarkable deviation from such a trend with its thermal conductivity lower than that of the GT-90 and GT-85 samples and almost identical with that of the GT-70 sample. Such behavior can be attributed to the large amount of small CuInTe$_2$ phases (~500 nm) that can significantly scatter phonons, which was observed in the BSE and SEM images. The large amount of small secondary phase only happens in the GT-95 sample, suggesting that the size of the micron-size CuInTe$_2$ phase is strongly correlated to the mole fraction of CuInTe$_2$ and 5% of CuInTe$_2$ reaches the optimization for the phonon scattering in our study. Because of the enhanced power factor and the suppressed thermal conductivity of the GT-95 sample, the thermoelectric figure of merit $ZT$ is greatly enhanced within the whole temperature range studied in this paper from room temperature to 800 K. The 800 K $ZT$ is improved from 0.8 to 1.12 by almost 50%, Figure 5.14b. Remember that this $ZT$ value is only a lower bound, since we overestimated the thermal conductivity value due to the high temperature Te evaporation effect mentioned before.
Figure 5.14 High temperature (a) thermal conductivity and (b) thermoelectric figure of merit ZT of GeTe-CuInTe$_2$ composites.
5.7 Summary

The composites of GeTe and CuInTe$_2$ were successfully synthesized over a wide range of GeTe concentration from 0% to 100% using a solid state reaction method followed by hot pressing process. The phase separation of GeTe and CuInTe$_2$ major phases was confirmed by the powder XRD characterization, together with the BSE, SEM, and EDS microstructural study. TEM and nanoscale EDS results confirmed the formation and distribution of the nanoscale segregations. UPS and XPS results determined the Fermi level offset between GeTe and CuInTe$_2$ at room temperature and confirmed the existence of the high density of the nano CuInTe$_2$ segregations. Distinct scattering processes of carriers and phonons between the GeTe-rich and CuInTe$_2$-rich samples were characterized by low temperature thermoelectric transport properties measurement. By detailed theoretical and experimental analysis, we successfully enhanced the average power factor over a wide temperature range in the GeTe-CuInTe$_2$ composites. We proved that such enhancement originated from the temperature-dependent Fermi level offset between the matrix and secondary phase. Such temperature-dependent mechanism results in a temperature-dependent carrier concentration, which is beneficial for thermoelectric power factor enhancement. Small amount of CuInTe$_2$ secondary phases formed nano-size inclusions that strongly scatter phonons and resulted in a much lowered thermal conductivity in the GT-95 sample, confirmed by the BSE and SEM structural analysis and high temperature thermal conductivity measurement. The combined enhanced average power factor and the reduced thermal conductivity made a great improvement on the thermoelectric figure of merit of the GT-95 sample over the whole temperature range from 300 K to 800 K to a peak value of 1.12 at 800 K. The GeTe secondary phases in the CuInTe$_2$-rich samples acted as carrier donors by injecting
carriers at higher temperature into the CuInTe$_2$ phase. Such carrier transfer effect not only increased the electrical conductivity by increasing the carrier concentration, but also increased the Seebeck coefficient by enhancing the energy dependence of the mobility. As a result, the power factor tripled at approximately 600 K. We proposed that this novel secondary-phase doping method demonstrated in the GeTe-CuInTe$_2$ composites in this study can potentially be applied to other composite systems.
Chapter 6 Thermoelectric Power Factor Enhancement from High Order Band Dispersion

6.1 Introduction

The dispersion relation of low energy charge carriers near the band edge is usually parabolic, and thus the thermoelectric transport properties of most of the lightly or moderately doped materials can be well described with a parabolic band model. However, exceptions can exist under certain circumstances. Nonparabolicity has been demonstrated in various narrow bandgap semiconductors and the band dispersion follows the Kane relation.[51] Moreover, some low dimensional materials with high symmetry can have a band dispersion relation other than parabolic. A well-known example in 2D is graphene. In this chapter, we will study how changing the band dispersion influences the electrical transport properties in a thermoelectric material. We derived the transport coefficients by solving Boltzmann transport equation (BTE) with the relaxation time assumption. We also only consider the acoustic phonon scattering, which is the dominant scattering process at room temperature and above for most thermoelectric materials. The numerical calculation results indicate that higher order band dispersion relations indeed dramatically enhance the thermoelectric power factor compared to the parabolic band. Though engineering a material with high order band dispersion relation is very challenging, I propose that the results from this study may open up a new direction to enhance the electrical transport
properties of thermoelectric materials. In addition, real materials may have complex band structures that have parabolic and higher-order contributions,[62] and this work may be considered (from a power series context) quantify non-parabolic contributions to the thermoelectric properties.

6.2 Theory

For simplicity, an isotropic and spherical Fermi surface is assumed in the derivation, which can be extended to more complex cases by changing the one-dimensional integrals to three-dimensional. Applying the relaxation time assumption, the scattering term in the BTE is written as:

$$ - \frac{f(E) - f_0(E)}{\tau} $$  \hspace{1cm} \text{Equation 6.1}

where \( f(E) \) is the perturbed distribution function of the charge carriers, \( f_0(E) \) is the Fermi distribution function, and \( \tau \) is the relaxation time. The band dispersion relation is isotropic for a spherical Fermi surface, and thus we have:

$$ E(\mathbf{k}) = a |\mathbf{k}|^n $$  \hspace{1cm} \text{Equation 6.2}

where \( a \) is the band dispersion proportionality constant that depends on the effective mass of the charge carriers, and \( n \) is the order index of the band dispersion. Then the density of states is:

$$ \varphi(E) = \frac{8\pi}{(2\pi)^3} \frac{1}{an} E^{3-n} $$  \hspace{1cm} \text{Equation 6.3}
with the band effective mass is defined as:

\[ \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2} \]

Equation 6.4

For a parabolic band, band effective mass is independent of the energy of charge carriers; however, higher order dispersive bands have energy-dependent band effective mass. Such a difference makes it necessary to modify the simplified BTE:

\[ \frac{q}{m^*} \left( \vec{E} + \vec{v} \times \vec{B} \right) \cdot \nabla_{\vec{v}} f(E) + \vec{v} \cdot \nabla_{E} f(E) = - \frac{f(E) - f_0(E)}{\tau} \]

Equation 6.5

to a more generalized form:

\[ \nabla_{\vec{p}} E(\vec{k}) \cdot \nabla_{E} f(E) + q \left( \vec{E} + \nabla_{\vec{p}} E(\vec{k}) \times \vec{B} \right) \cdot \nabla_{\vec{p}} f(E) = - \frac{f(E) - f_0(E)}{\tau} \]

Equation 6.6

where \( \vec{p} \) is the momentum of the charge carriers, \( E(\vec{k}) \) is the band dispersion relation, \( q \) is the charge of the carriers, \( \vec{E} \) is the electrical field, and \( \vec{B} \) is the magnetic field. The derivation of the transport coefficients of high order dispersive bands is quite similar with that for parabolic band,[38] though the assumption of a constant effective mass needs to be abandoned throughout the whole derivation, which I present below.

The solution of the BTE, \( f(E) \), which is also the perturbed distribution function, is supposed to have the form of:

\[ f(E) = f_0(E) - \vec{v}(E) \cdot \vec{c}(E) \frac{df_0}{dE} \]

Equation 6.7
where $\tilde{c}(E)$ is a function of carrier energy. Plugging Eqn. 6.7 into Eqn. 6.6, the BTE can be rewritten as:

$$\vec{v} \cdot \nabla r(0 - \vec{v} \cdot \tilde{c} \frac{df_0}{dE}) + q(E + \vec{v} \times \vec{B}) \cdot \nabla \tilde{\rho}(0 - \vec{v} \cdot \tilde{c} \frac{df_0}{dE}) = \frac{\vec{v} \cdot \tilde{c} \frac{df_0}{dE}}{\tau \frac{dE}{dE}}$$  \hspace{1cm} \text{Equation 6.8}

where $\vec{v} = \nabla \rho(E) \hat{K}$ is the velocity of the charge carriers. So far, solving for $f(E)$ is equivalent to solving for $\tilde{c}(E)$. Each term of the BTE can be further simplified in order to solve for $\tilde{c}(E)$.

With the assumption of weak perturbation, the case for thermoelectric applications, the deviation of the perturbed distribution function and its derivative from the unperturbed functions is small:

$$\vec{v} \cdot \tilde{c} \frac{df_0}{dE} \ll f_0$$  \hspace{1cm} \text{Equation 6.9}

$$\nabla \tilde{r} \left(\vec{v} \cdot \tilde{c} \frac{df_0}{dE}\right) \ll \nabla \tilde{r} f_0$$  \hspace{1cm} \text{Equation 6.10}

$$\nabla \tilde{\rho} \left(\vec{v} \cdot \tilde{c} \frac{df_0}{dE}\right) \ll \nabla \tilde{\rho} f_0$$  \hspace{1cm} \text{Equation 6.11}

Thus the first and the second term of the left side of the BTE (Eqn. 6.8) are approximated as:

$$\vec{v} \cdot \nabla \tilde{r}(0 - \vec{v} \cdot \tilde{c} \frac{df_0}{dE}) \approx \vec{v} \cdot \nabla \tilde{r} f_0 = \vec{v} \cdot \nabla \tilde{r} \left(\frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right)+1}\right) = \vec{v} \cdot \nabla \tilde{r} \left(\frac{E-E_F}{k_B T}\right) \frac{df_0}{dE} = \vec{v} \cdot$$

\[
\left\{-k_B T \nabla \tilde{r} \left(\frac{E}{k_B T}\right) + \frac{E}{k_B T} \nabla \tilde{r} (k_B T)\right\} \frac{df_0}{dE}\]

\hspace{1cm} \text{Equation 6.12}

$$q E \cdot \nabla \tilde{\rho}(0 - \vec{v} \cdot \tilde{c} \frac{df_0}{dE}) \approx q E \cdot \nabla \tilde{\rho} f_0 = q \vec{v} \cdot E \frac{df_0}{dE}$$  \hspace{1cm} \text{Equation 6.13}

Since $f_0 = \frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right)+1}$ only depends on the energy of the carriers, thus:
\[ q \vec{v} \times \vec{B} \cdot \nabla_p f_0(E) = q \vec{v} \times \vec{B} \cdot \nabla_{\vec{p}} E \frac{d f_0}{d E} = q \vec{v} \times \vec{B} \cdot \vec{v} \frac{d f_0}{d E} = 0 \]  

Equation 6.14

Then the third term on the left side of the BTE is approximated as:

\[ q \vec{v} \times \vec{B} \cdot \nabla_{\vec{p}} \left( f_0 - \vec{v} \cdot \vec{c} \frac{d f_0}{d E} \right) = -q \vec{v} \times \vec{B} \cdot \nabla_{\vec{p}} \left( \vec{v} \cdot \vec{c} \frac{d f_0}{d E} \right) \]  

Equation 6.15

where:

\[
\nabla_{\vec{p}} \left( \vec{v} \cdot \vec{c} \frac{d f_0}{d E} \right) = \nabla_{\vec{p}} \left( \nabla_{\vec{p}} E \cdot \vec{c} \frac{d f_0}{d E} \right) = \left( \frac{\partial}{\partial p_x} \hat{i} + \frac{\partial}{\partial p_y} \hat{j} + \frac{\partial}{\partial p_z} \hat{k} \right) \left[ \left( \frac{\partial E}{\partial p_x} \hat{c}_x + \frac{\partial E}{\partial p_y} \hat{c}_y + \frac{\partial E}{\partial p_z} \hat{c}_z \right) \frac{d f_0}{d E} \right] = \\
\left\{ \left( \frac{\partial^2 E}{\partial p_x^2} \hat{c}_x + \frac{\partial E}{\partial p_y} \frac{\partial \hat{c}_x}{\partial p_x} + \frac{\partial^2 E}{\partial p_y \partial p_x} \hat{c}_y + \frac{\partial E}{\partial p_z} \frac{\partial \hat{c}_x}{\partial p_x} + \frac{\partial^2 E}{\partial p_z \partial p_x} \hat{c}_z + \frac{\partial E}{\partial p_x} \frac{\partial \hat{c}_x}{\partial p_x} \right) \frac{d f_0}{d E} \right\} \hat{i} + \\
\left\{ \left( \frac{\partial^2 E}{\partial p_y^2} \hat{c}_y + \frac{\partial E}{\partial p_x} \frac{\partial \hat{c}_y}{\partial p_y} + \frac{\partial^2 E}{\partial p_y \partial p_y} \hat{c}_y + \frac{\partial E}{\partial p_z} \frac{\partial \hat{c}_y}{\partial p_y} + \frac{\partial^2 E}{\partial p_z \partial p_y} \hat{c}_z + \frac{\partial E}{\partial p_y} \frac{\partial \hat{c}_y}{\partial p_y} \right) \frac{d f_0}{d E} \right\} \hat{j} + \\
\left\{ \left( \frac{\partial^2 E}{\partial p_z^2} \hat{c}_z + \frac{\partial E}{\partial p_x} \frac{\partial \hat{c}_z}{\partial p_z} + \frac{\partial^2 E}{\partial p_z \partial p_z} \hat{c}_z + \frac{\partial E}{\partial p_y} \frac{\partial \hat{c}_z}{\partial p_z} + \frac{\partial^2 E}{\partial p_z \partial p_y} \hat{c}_z + \frac{\partial E}{\partial p_z} \frac{\partial \hat{c}_z}{\partial p_z} \right) \frac{d f_0}{d E} \right\} \hat{k} = \text{Matrix} \left( \frac{1}{m'} \right) \cdot \vec{c} \frac{d f_0}{d E} + \left( \vec{v} \cdot \frac{\partial}{\partial p_x} \vec{c} \frac{d f_0}{d E} \right) \hat{i} + \\
\left( \vec{v} \cdot \frac{\partial}{\partial p_y} \vec{c} \frac{d f_0}{d E} \right) \hat{j} + \left( \vec{v} \cdot \frac{\partial}{\partial p_z} \vec{c} \frac{d f_0}{d E} \right) \hat{k} = \text{Matrix} \left( \frac{1}{m'} \right) \cdot \vec{c} \frac{d f_0}{d E} + \left( \vec{v} \cdot \frac{\partial}{\partial p_x} \vec{c} \frac{d f_0}{d E} \right) \vec{v} + \\
\left( \vec{v} \cdot \vec{c} \frac{d^2 f_0}{d E^2} \right) \vec{v} \]  

Equation 6.16

where \( \text{Matrix} \left( \frac{1}{m'} \right) \) is the effective mass matrix for the high order dispersive band. A vector is defined as:
\[ \vec{A} = \text{Matrix} \left( \frac{1}{m'} \right) \cdot \vec{c}(E) = \begin{pmatrix} \frac{\partial^2 E}{\partial p_x^2} & \frac{\partial^2 E}{\partial p_x \partial p_y} & \frac{\partial^2 E}{\partial p_x \partial p_z} \\ \frac{\partial^2 E}{\partial p_y \partial p_x} & \frac{\partial^2 E}{\partial p_y^2} & \frac{\partial^2 E}{\partial p_y \partial p_z} \\ \frac{\partial^2 E}{\partial p_z \partial p_x} & \frac{\partial^2 E}{\partial p_z \partial p_y} & \frac{\partial^2 E}{\partial p_z^2} \end{pmatrix} \cdot \begin{pmatrix} c_x \\ c_y \\ c_z \end{pmatrix} \]  

Equation 6.17

Then, the third term (Eqn. 6.15) can be further simplified as:

\[ \text{The third left side term} = -q \vec{v} \times \vec{B} \cdot \vec{A} \frac{df_0}{dE} = -q \vec{v} \cdot (\vec{B} \times \vec{A}) \frac{df_0}{dE} \]  

Equation 6.18

Substituting Eqn. 6.12, 6.13, and 6.18 into the BTE, then we have:

\[ \vec{v} \cdot \left\{ - \left[ k_B T \nabla_r \left( \frac{E_F}{k_B T} \right) + \frac{E}{k_B T} \nabla_r (k_B T) \right] \right\} \frac{df_0}{dE} + q \vec{v} \cdot \vec{E} \frac{df_0}{dE} - q \vec{v} \cdot (\vec{B} \times \vec{A}) \frac{df_0}{dE} = \frac{\vec{v} \cdot \vec{c} \frac{df_0}{dE}}{\tau} \]  

Equation 6.19

The solution \( \vec{c}(E) \) is derived by rearranging the terms in Eqn. 6.19 as:

\[ \vec{c} = -q \tau (\vec{B} \times \vec{A}) + q \tau \vec{E} - \tau k_B T \nabla_r \left( \frac{E_F}{k_B T} \right) - \tau \frac{E}{k_B T} \nabla_r (k_B T) \]  

Equation 6.20

Without losing generality, the electric field and temperature gradient are set in the x-y plane and the magnetic field is set along the z direction:

\[ \vec{E} = E_x \hat{i} + E_y \hat{j}; \quad \vec{B} = B_z \hat{k} \]  

Equation 6.21

Then the vector \( \vec{c}(E) \) only contains x and y components:
\[
\begin{aligned}
\begin{cases}
    c_x = \beta + q\tau B_z \frac{1}{\hbar^2} \left( \frac{\partial^2 E}{\partial k_y \partial k_x} c_x + \frac{\partial^2 E}{\partial k_y^2} c_y \right) \\
    c_y = \gamma - q\tau B_z \frac{1}{\hbar^2} \left( \frac{\partial^2 E}{\partial k_x^2} c_x + \frac{\partial^2 E}{\partial k_x \partial k_y} c_y \right)
\end{cases}
\end{aligned}
\]

where,

\[
\beta = \tau \left\{ qE_x - k_B T \frac{\partial}{\partial x} \left( \frac{E_P}{k_B T} \right) - \frac{E}{k_B T} \frac{\partial}{\partial x} (k_B T) \right\}
\]

\[
\gamma = \tau \left\{ qE_y - k_B T \frac{\partial}{\partial y} \left( \frac{E_P}{k_B T} \right) - \frac{E}{k_B T} \frac{\partial}{\partial y} (k_B T) \right\}
\]

With the weak field assumption, the \(x\) and \(y\) components of the solution \(\vec{c}(E)\) can be further simplified as:

\[
\begin{aligned}
\begin{cases}
    c_x = \left\{ 1 + q\tau B_z \frac{1}{\hbar^2} \right\} \beta + q\tau B_z \frac{\partial^2 E}{\partial k_y^2} \frac{1}{\hbar^2} \gamma \\
    c_y = -q\tau B_z \frac{\partial^2 E}{\partial k_x^2} \frac{1}{\hbar^2} \beta + \left\{ 1 - q\tau B_z \frac{\partial^2 E}{\partial k_x \partial k_y} \frac{1}{\hbar^2} \right\} \gamma
\end{cases}
\end{aligned}
\]

With the perturbed distribution function solved, thermoelectric transport coefficients can now be calculated. The current density along the \(x\)-direction is the integral over the whole \(k\)-space:

\[
j_x = \sum_{k_x,k_y,k_z} q \frac{V(k_x,k_y,k_z)n(k_x,k_y,k_z)}{dSdt} = \iint d\mathbf{k}_x d\mathbf{k}_y d\mathbf{k}_z q \frac{v_x(k_x,k_y,k_z)}{dSdt} f(k_x,k_y,k_z) \varphi(k_x,k_y,k_z) = \iint d\mathbf{k}_x d\mathbf{k}_y d\mathbf{k}_z q v_x(k_x,k_y,k_z)f(k_x,k_y,k_z) \varphi(k_x,k_y,k_z)
\]

where \(V(k_x,k_y,k_z)\) is the volume in the real space in which the electrons or holes with the momentum \((k_x,k_y,k_z)\) will travel through the cross section \(dS\) in the time interval \(dt\); \(n(k_x,k_y,k_z)\) is the electrons or holes concentration with the momentum \((k_x,k_y,k_z)\); \(v_x(k_x,k_y,k_z)\) is the velocity of the electrons or holes with the momentum \((k_x,k_y,k_z)\) in the \(x\)-
direction; \( f(k_x, k_y, k_z) \) is the distribution function of the electrons or holes with the momentum \((k_x, k_y, k_z)\); and \( \varphi(k_x, k_y, k_z) \) is the density of states of electrons or holes with the momentum \((k_x, k_y, k_z)\). For an isotropic and spherical Fermi surface as assumed, the integral can be simplified as:

\[
\hat{j}_x = \sum_{\text{each shell}} \iiint_{\text{Energy Shell}} dk_x dk_y dk_z \varphi(k_x, k_y, k_z) f(k_x, k_y, k_z)
\]

*Equation 6.27*

Since \( f(k_x, k_y, k_z) \) is only a function of the energy of the carriers and:

\[
\varphi(k_x, k_y, k_z) = \frac{2}{(2\pi)^3}
\]

*Equation 6.28*

Thus we have:

\[
\hat{j}_x = \sum_{\text{each shell}} \iiint_{\text{Energy Shell}} dk_x dk_y dk_z \varphi(k_x, k_y, k_z) f(E) \frac{2}{(2\pi)^3}
\]

*Equation 6.29*

Substitute \( f(E) \) solved from BTE into *Eqn. 6.28*, we have:

\[
\hat{j}_x = \sum_{\text{each shell}} \iiint_{\text{Energy Shell}} dk_x dk_y dk_z \varphi(k_x, k_y, k_z) \left[ f_0(E) - \hat{v}(E) \cdot \hat{c}(E) \frac{df_0}{dE} \right] \frac{2}{(2\pi)^3} = \]

\[
\sum_{\text{each shell}} \iiint_{\text{Energy Shell}} dk_x dk_y dk_z \varphi(k_x, k_y, k_z) \left[ f_0(E) - v_x c_x \frac{df_0}{dE} - v_y c_y \frac{df_0}{dE} \right] \frac{2}{(2\pi)^3}
\]

*Equation 6.30*

Similarly, the current density in the \( y \)-direction is:
\[ j_y = \sum_{\text{each shell}} \iiint_{\text{constant energy shell}} dk_x dk_y dk_z q v_y \left\{ f_0(E) - v_x c_x \frac{df_0}{dE} - v_y c_y \frac{df_0}{dE} \right\} \frac{2}{(2\pi)^3} \]

Equation 6.31

Several terms in the integrals are zero due to the high symmetry of the constant-energy surface:

\[ \iiint_{\text{constant energy shell}} dk_x dk_y dk_z q v_x f_0(E) \frac{2}{(2\pi)^3} = \iiint_{\text{constant energy shell}} dk_x dk_y dk_z q v_y f_0(E) \frac{2}{(2\pi)^3} = 0 \]

Equation 6.32

For high order dispersive bands:

\[ E = a|k|^n = a\left(\sqrt{k_x^2 + k_y^2 + k_z^2}\right)^n \]

Equation 6.33

The derivatives of the carrier energy with respect to the momentum are:

\[ \frac{\partial^2 E}{\partial k_x^2} = an(k_x^2 + k_y^2 + k_z^2)^{n-1} + an(n-2)k_x^2(k_x^2 + k_y^2 + k_z^2)^{n-2} \]

Equation 6.34

\[ \frac{\partial^2 E}{\partial k_y^2} = an(k_x^2 + k_y^2 + k_z^2)^{n-1} + an(n-2)k_y^2(k_x^2 + k_y^2 + k_z^2)^{n-2} \]

Equation 6.35

\[ \frac{\partial^2 E}{\partial k_x \partial k_y} = an(n-2)k_x k_y (k_x^2 + k_y^2 + k_z^2)^{n-2} \]

Equation 6.36

\[ v_x = \frac{1}{\hbar} \frac{\partial E}{\partial k_x} = \frac{1}{\hbar} an k_x (k_x^2 + k_y^2 + k_z^2)^{n-1} \]

Equation 6.37

and
\[ v_y = \frac{1}{\hbar} \frac{\partial E}{\partial k_y} = \frac{1}{\hbar} \text{ank}_y (k_x^2 + k_y^2 + k_z^2)^{\frac{n}{2} - 1} \quad \text{Equation 6.38} \]

Substitute Eqn. 6.33 to 6.37 into the current density integrals, we have:

\[
\begin{align*}
    j_x &= \sum_{\text{each shell}} \iiint d k_x d k_y d k_z q \left( \frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right) \left\{ -\frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right\} \\
        &\quad + q \tau B_z \text{an}(n - 2)k_xk_y \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 2} \frac{1}{\hbar^2} \beta \\
        &\quad + q \tau B_z \left[ \text{an} \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 1} + \text{an}(n - 2)k_y^2 \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 2} \right] \frac{1}{\hbar^2} \beta \\
        &\quad - \frac{1}{\hbar} \text{ank}_y \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 1} \left\{ q \tau B_z \left[ \text{an} \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 1} + \text{an}(n - 2)k_y^2 \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 2} \right] \frac{1}{\hbar^2} \beta \\
        &\quad + \left\{ 1 - q \tau B_z \text{an}(n - 2)k_xk_y \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 2} \frac{1}{\hbar^2} \right\} \gamma \right] \frac{d f_0}{d E} \left( \frac{2}{2\pi} \right)^3 \\
        &\quad = \sum_{\text{each shell}} \iiint d k_x d k_y d k_z q \left( \frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right) \left\{ -\frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right\} \beta \\
        &\quad + q \tau B_z \left[ \text{an} \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 1} \right] \frac{1}{\hbar^2} \beta \left( \frac{2}{\hbar^2} \right)^3 \\
        &\quad - \sum_{\text{each shell}} \iiint d k_x d k_y d k_z q \left( \frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right) \left\{ -\frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right\} \beta \\
        &\quad + q \tau B_z \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 1} \frac{1}{\hbar^2} \beta \left( \frac{2}{\hbar^2} \right)^3 \\
        &\quad = \sum_{\text{each shell}} \iiint d k_x d k_y d k_z q \left( \frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right) \left\{ -\frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right\} \beta \\
        &\quad + q \tau B_z \left( \left| \vec{k} \right|^2 \right)^{\frac{n}{2} - 1} \frac{1}{\hbar^2} \beta \left( \frac{2}{\hbar^2} \right)^3 \\
\end{align*}
\]

\[ \text{Equation 6.39} \]

Similarly, the current density in the y direction is:
\[ j_y = \sum_{\text{each shell}} \iiint dk_x dk_y dk_z q v_y \left\{ -v_x c_x \frac{df_0}{dE} - v_y c_y \frac{df_0}{dE} \right\} \frac{2}{(2\pi)^3} \]

\[ = \sum_{\text{each shell}} \iiint dk_x dk_y dk_z q \frac{1}{\hbar} \text{ank}_y \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \left\{ -\frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right\} \left\{ 1 + q \tau B_z \left( an \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} + an(n - 2)k_x^2 \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 2} \right) \frac{1}{\hbar^2} \right\} \frac{df_0}{dE} \]

\[ + \frac{1}{\hbar} \text{ank}_y \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \left\{ -q \tau B_z \left( an \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} + an(n - 2)k_x^2 \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 2} \right) \frac{1}{\hbar^2} \beta \right\} \]

\[ + \frac{1}{\hbar} \text{ank}_y \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \left\{ -q \tau B_z \left( an \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} + an(n - 2)k_x^2 \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 2} \right) \frac{1}{\hbar^2} \beta \right\} \frac{df_0}{dE} \frac{2}{(2\pi)^3} \]

\[ = \sum_{\text{each shell}} \iiint dk_x dk_y dk_z q \frac{1}{\hbar} \text{ank}_y \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \left\{ -\frac{1}{\hbar} \text{ank}_x \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \right\} \left\{ -q \tau B_z an \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \frac{1}{\hbar^2} \beta \right\} \frac{df_0}{dE} \frac{2}{(2\pi)^3} \]

\[ + \frac{1}{\hbar} \text{ank}_y \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} \left\{ -q \tau B_z \left( an \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 1} + an(n - 2)k_x^2 \left( |\vec{k}|^2 \right)^{\frac{n}{2} - 2} \right) \frac{1}{\hbar^2} \beta \right\} \frac{df_0}{dE} \frac{2}{(2\pi)^3} \]

\[ \begin{array}{c}
\text{Equation 6.40}
\end{array} \]

After changing the Cartesian coordinates to the spherical coordinates, the integrals can be simplified as:
\[ j_x = -\int_{0}^{\infty} dk \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} d\theta \frac{2 f_0}{(2\pi)^3} \frac{dE}{dE} q \frac{1}{\hbar^2} a^2 n^2 k^2 \sin^2 \theta \cos^2 \varphi \left[ \beta + \delta \alpha \kappa n^{-2} \gamma \right] \]

\[ = -\int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a n}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n+1} \beta - \int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a^2 n^2 \delta}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n-1} \gamma \]

\[ = -\int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a^{-1} n}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n} \beta - \int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a^{-1} n}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n+1} \gamma \]

Equation 6.41

\[ j_y = \int_{0}^{\infty} dk \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} d\theta \frac{2 f_0}{(2\pi)^3} \frac{dE}{dE} q \frac{1}{\hbar^2} a^2 n^2 k^2 \sin^2 \theta \sin^2 \varphi \left[ \delta \alpha \kappa n^{-2} \beta - \gamma \right] \]

\[ = \int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a n^2 \delta}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n+1} \beta - \int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a^{-1} n^2 \delta}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n-1} \gamma \]

\[ = \int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a^{-1} n^2 \delta}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n} \beta - \int_{0}^{\infty} dE \frac{1}{\hbar^2} \frac{q a^{-1} n^2 \delta}{3 \pi^2} \frac{dE}{dE} \left( \frac{E}{a} \right)^{n+1} \gamma \]

Equation 6.42

where \( \delta = \frac{q R B_z}{\hbar^2} \), and \( k = |\vec{k}| \). Substitute \( \beta \) and \( \gamma \) into the integrals, we have:
\[ j_x = -\int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n+1}{2}} \frac{\partial}{\partial x} \left\{ qE_x - k_B T \frac{\partial}{\partial x} \left( \frac{E_F}{k_B T} \right) - \frac{E}{k_B T} \frac{\partial}{\partial x} \left( k_B T \right) \right\} \]

\[ - \int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n-1}{2}} \frac{\partial}{\partial x} \left\{ qE_y - k_B T \frac{\partial}{\partial y} \left( \frac{E_F}{k_B T} \right) - \frac{E}{k_B T} \frac{\partial}{\partial y} \left( k_B T \right) \right\} \]

\[ = -\int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n+1}{2}} \frac{\partial}{\partial x} \left( \frac{qV + E_F}{k_B T} \right) + qV \frac{\partial}{\partial x} \left( \frac{1}{k_B T} \right) \]

\[ + E \frac{\partial}{\partial x} \left( \frac{1}{k_B T} \right) \]

\[ - \int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n-1}{2}} \frac{\partial}{\partial y} \left( \frac{qV + E_F}{k_B T} \right) + qV \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ + E \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ j_y = \int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n+1}{2}} \frac{\partial}{\partial y} \left( \frac{qV + E_F}{k_B T} \right) + qV \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) + E \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ - \int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n-1}{2}} \frac{\partial}{\partial y} \left( \frac{qV + E_F}{k_B T} \right) + qV \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ + E \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ \text{Equation 6.43} \]

\[ j_y = \int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n+1}{2}} \frac{\partial}{\partial y} \left( \frac{qV + E_F}{k_B T} \right) + qV \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) + E \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ - \int_0^\infty dE \frac{1}{\hbar^2} \frac{q a^{-n} n}{3 \pi^2} \frac{df_0}{dE} E^{\frac{n-1}{2}} \frac{\partial}{\partial y} \left( \frac{qV + E_F}{k_B T} \right) + qV \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ + E \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right) \]

\[ \text{Equation 6.44} \]

where \( \vec{E} = -\nabla V \). Define integrals:
\[
\begin{aligned}
I_1 &= \int_0^\infty dE \frac{1}{\hbar^2} \frac{a^{-n} df_0}{3\pi^2} E^{n+1} \\
I_2 &= \int_0^\infty dE \frac{1}{\hbar^2} \frac{a^{-n} df_0}{3\pi^2} E^{2n+1} \\
I_3 &= \int_0^\infty dE \frac{1}{\hbar^2} \frac{a^{-n} n^2 \delta df_0}{3\pi^2} E^{2n-1} \\
I_4 &= \int_0^\infty dE \frac{1}{\hbar^2} \frac{a^{-n} n^2 \delta df_0}{3\pi^2} E^{3n-1}
\end{aligned}
\]

Equation 6.45

Then, Eqn. 6.43 and 6.44 can be rearranged:

\[
\begin{aligned}
\frac{\partial}{\partial x} \left( \frac{qV + E_F}{k_B T} \right) &= \frac{l_1}{k_B T(l_1^2 + l_2^2)} j_x - \frac{l_3}{k_B T(l_1^2 + l_3^2)} j_y + \left( qV + \frac{l_1 l_2 + l_3 l_4}{l_1^2 + l_3^2} \right) \frac{\partial}{\partial x} \left( \frac{1}{k_B T} \right) \\
&+ \left( \frac{l_1 l_4 - l_2 l_3}{l_1^2 + l_3^2} \right) \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right)
\end{aligned}
\]

Equation 6.46

\[
\begin{aligned}
\frac{\partial}{\partial y} \left( \frac{qV + E_F}{k_B T} \right) &= \frac{l_3}{k_B T(l_1^2 + l_3^2)} j_x + \frac{l_1}{k_B T(l_1^2 + l_3^2)} j_y - \left( \frac{l_1 l_4 - l_2 l_3}{l_1^2 + l_3^2} \right) \frac{\partial}{\partial x} \left( \frac{1}{k_B T} \right) \\
&+ \left( qV + \frac{l_1 l_2 + l_3 l_4}{l_1^2 + l_3^2} \right) \frac{\partial}{\partial y} \left( \frac{1}{k_B T} \right)
\end{aligned}
\]

Equation 6.47

Define the quantities:

\[
\begin{aligned}
A_{11} &= \frac{l_1}{k_B T(l_1^2 + l_2^2)} \\
A_{12} &= \frac{l_3}{k_B T(l_1^2 + l_3^2)} \\
A_{13} &= \left( qV + \frac{l_1 l_2 + l_3 l_4}{l_1^2 + l_3^2} \right) \\
A_{14} &= \left( \frac{l_1 l_4 - l_2 l_3}{l_1^2 + l_3^2} \right)
\end{aligned}
\]

Equation 6.48

Then Eqn. 6.46 and 6.47 turn into a more compact form as:
The electrical transport coefficients can now be calculated based on their own definitions.

The electrical conductivity is defined as:

\[
\sigma = \frac{j_x}{E_x}
\]

Equation 6.50

with conditions:

\[
\frac{dT}{dx} = \frac{dT}{dy} = j_y = 0
\]

Equation 6.51

Substituting Eqn. 6.48, 6.50, and 6.51 into 6.49, then we have:

\[
\sigma = -\frac{q^2}{k_B T A_{11}} = -\frac{q^2(I_1^2 + I_3^2)}{I_i}
\]

Equation 6.52

The Seebeck coefficient is defined as:

\[
S = E_x / \frac{dT}{dx}
\]

Equation 6.53

with conditions:

\[
j_x = j_y = \frac{dT}{dy} = 0
\]

Equation 6.54

Plugging Eqn. 6.48, 6.53, and 6.54 into 6.49, then we have:

\[
S = \frac{k_B}{q} (A_{13} \frac{k_B T}{k_B T} \frac{qV}{k_B T} - qV + E_F) = \frac{k_B}{q} \left( \frac{q V + I_1 I_3 I_4}{k_B T} \frac{k_B T}{k_B T} \frac{I_1^2 + I_3^2}{k_B T} \right) = \frac{k_B}{q} \left( \frac{I_1 I_2 + I_3 I_4}{k_B T} \frac{E_F}{k_B T} \right)
\]

Equation 6.55
The Hall coefficient is defined as:

$$R_H = \frac{E_y}{j_B B_z} \quad \text{Equation 6.56}$$

with conditions:

$$j_y = \frac{d\tau}{dy} = \frac{d\tau}{dx} = 0 \quad \text{Equation 6.57}$$

Substitute Eqn. 6.55 and 6.56 into 6.48, then we have:

$$R_H = -\frac{k_B T}{q^2 B_z} A_{12} = -\frac{k_B T}{q^2 B_z} \frac{l_3}{k_B T(l_1^2 + l_3^2)} = -\frac{1}{q^2 B_z l_1^2} \quad \text{Equation 6.58}$$

With the energy-dependent relaxation time having the form of:

$$\tau = wE^r \quad \text{Equation 6.59}$$

where $w$ is the proportionality constant and $r$ is the scattering parameter depending on the scattering processes, the transport coefficients can be written as:

$$\sigma = q^2 \frac{n}{3h^2 \pi^2} a \frac{1}{\pi n W} \left( \frac{n+1}{n} + r \right) \left( k_B T \right)^{\frac{n+1}{n} + r} \frac{F_{n+1}^{n+1+r} \left( \eta^* \right)}{F_{n+1}^{n} \left( \eta^* \right) - \eta^*} \quad \text{Equation 6.60}$$

$$S = \frac{k_B}{q} \left\{ \frac{2(n+1)(n+1+r)}{n(n+1+r)} \frac{F_{n+1}^{n+1+r} \left( \eta^* \right)}{F_{n+1}^{n} \left( \eta^* \right) - \eta^*} \right\} \quad \text{Equation 6.61}$$

$$R_H = \frac{1}{q} \left( \frac{a}{k_B T} \right)^3 3\pi^2 \frac{2(n+1)(n+1+p)}{(n+1)^2} \frac{F_{n+1}^{n+1+2p} \left( \eta^* \right)}{F_{n+1+p}^{n+1+p} \left( \eta^* \right)} \quad \text{Equation 6.62}$$
where \( \eta^* = \frac{E_F}{k_BT} \) is the reduced Fermi level, and \( F_j(\eta^*) = \int_0^\infty \frac{\eta^j}{1+\exp(\eta-\eta^*)} d\eta \) is the Fermi integral of jth order.

### 6.3 Results and Discussion

Firstly, we explore the influence of doping on the electrical transport properties for high order dispersive bands. Since we only focus on the transport properties near room temperature, at which acoustic phonon scattering processes dominate, the dopants are considered to be fully ionized and the carrier concentration is equal to the doping concentration:

\[
p = \frac{8\pi}{(2\pi)^3} \frac{1}{a_n} \left(\frac{1}{a}\right)^{\frac{3-n}{n}} (kT)^{\frac{2}{n}} F_{\frac{3-n}{n}}(\eta^*) = N_A
\]

\[\text{Equation 6.63}\]

where \( p \) is the hole concentration and \( N_A \) is the concentration of the impurities. The proportionality constant \( a \) in Eqn. 6.2 is set to a function of band dispersion order as:

\[
a = e \times \hat{a}^n = (1.6 \times 10^{-19} C) \times (10^{-10} m)^n
\]

\[\text{Equation 6.64}\]

For acoustic scattering in parabolic bands, the scattering parameter \( r \) is equal to -0.5. This value originates from the results of the Fermi Golden Rule that the probability of scattering carriers from their initial states to final states is proportional to the density of the final states:

\[
\frac{1}{\tau} \propto \text{DOS} = \varphi(E)
\]

\[\text{Equation 6.65}\]

Thus, both the scattering parameter \( r \) and the proportionality parameter \( w \) are functions of the band dispersion order \( n \) as:
\[ w = \frac{n}{2} (e \times \text{Å}^2)^\frac{3}{2} (e \times \text{Å}^n)^3 w_0 \quad \text{Equation 6.66} \]

\[ p = 1 - \frac{3}{n} \quad \text{Equation 6.67} \]

The Fermi level, electrical conductivity, Seebeck coefficient, and power factor are then numerically calculated as a function of doping concentration. The results are shown in Fig. 6.1.

In this chapter, I use m\(^{-3}\) instead of cm\(^{-3}\) as the unit of carrier concentration.

Figure 6.1 Carrier concentration dependent (a) Fermi level, (b) Seebeck coefficient, (c) electrical conductivity, and (d) power factor for various band dispersions with acoustic phonon scattering parameter at 300 K.
Without losing generality, we select holes as the charge carriers and thus all conduction is $p$-type. The Fermi level is pushed into the valence band as the doping concentration increases for all the band dispersion orders studied here. Below the doping concentration of $10^{28} \text{ m}^{-3}$, the Fermi level of lower order dispersive bands is pushed deeper into the valence band. This trend is reversed as the doping concentration increases above $10^{28} \text{ m}^{-3}$. This feature is caused by the change of the density of states as the band dispersion index increases, which will be discussed later. The electrical conductivity increases significantly with the increasing doping concentration. As the doping concentration increases above $10^{22} \text{ m}^{-3}$, lower order dispersive bands exhibit higher electrical conductivity. Expectedly, the Seebeck coefficient follows the opposite trend, decreasing as the carrier concentration increases. Higher band dispersion order leads to a larger thermopower. As a result, the peak power factor is enhanced by almost an order of magnitude as the band dispersion order $n$ increases from 2 to 10, as shown in Fig. 6.1d. Interestingly, the optimized doping concentration for the peak power factor also moves to a higher value as the band dispersion order increases.

It is worth noting that the discussion with the acoustic phonon scattering assumption is only valid for $n \geq 2$. If we apply the model to linearly dispersive band, an infinite thermopower and zero electrical conductivity will be obtained. It is not hard to see that the parameter $A_{11}$ is zero and $A_{13}$ is infinity for linear bands. This indicates that the current along $x$ or $y$ direction does not contribute to an electrochemical potential drop along that direction, while a finite temperature gradient yields an infinite electrochemical potential drop. The unreasonable results are probably caused by the assumption that only acoustic phonon scattering exists. On the other
hand, such results also indicate that the carriers scattered by acoustic phonons in a linear band do not contribute to the conduction.

From the discussion above, a conclusion can be drawn that high order dispersive bands are beneficial for the thermoelectric power factor. As the band dispersion order $n$ increases from 2 to 10, as long as the acoustic phonon scattering process dominates, the power factor can be enhanced by an order of magnitude compared to the parabolic bands. In order to understand how high order dispersive band leads to a higher thermoelectric power factor, more details of the change on the band structure caused by the high band dispersion order are needed. Since the improvement mostly comes from the enhancement of the Seebeck coefficient, it may be helpful to explore what causes the Seebeck coefficient to increase. For degenerate semiconductors, the Seebeck coefficient can be expressed as the Mott relation as:

$$ S = \frac{\pi^2}{3} k_B T \left[ \frac{d \ln(\mu(E) \varphi(E))}{dE} \right]_{E_F} $$

*Equation 6.68*

where $\mu(E)$ is the energy-dependent carrier mobility. The enhancement of the Seebeck coefficient suggests that the derivative of the product of the mobility and the density of states with respect to the energy must increase. From *Eqn. 6.3*, the energy-dependent density of states and its derivative with respect to energy are shown in Fig. 6.2.
The energy-dependent density of states is quite different for high order dispersive bands than the parabolic one. The density of states approaches to infinity as the energy approaches to the band edge for band dispersion order larger than 3 and energies near the valence band edge. Such a feature leads to a significantly enhanced magnitude of the derivative of the density of states with respect to the energy near band edge, as shown in Fig. 6.2b. This also explains the trend of the calculated Fermi level shown in Fig. 6.1a. The energy-dependent mobility can be calculated from electrical conductivity:

$$\sigma = \int e\varphi(E)\mu(E)f(E)[1 - f(E)]dE$$  \hspace{1cm} \text{Equation 6.69}$$

The energy-dependent mobility is then written as:

$$\mu(E) = qa^{\frac{2}{3}}\frac{\pi^2}{\hbar^2} \left(\frac{n+1}{n} + p\right)E^{1 - \frac{2}{n+p}}(1 + \exp(\eta^* - \eta))$$  \hspace{1cm} \text{Equation 6.70}$$

The results are plotted in Fig. 6.3 for two different doping concentrations. The corresponding Fermi levels are also labeled in the figures.
It is obvious that the energy dependence of the mobility depends heavily on doping concentration. At the doping concentration of $5 \times 10^{27}$ m$^{-3}$, the energy dependence of the mobility has an abrupt change near the Fermi level. This feature is absent in Fig. 6.3b, since the Fermi level falls out of the energy range presented. The product of the energy-dependent density of states and mobility is shown in Fig. 6.4 for the doping concentration of $5 \times 10^{27}$ m$^{-3}$. As the band dispersion order increases, the Fermi level is pushed closer to the band edge, where the derivative of the product of density of states and mobility with respect to the energy increases. This is why the Seebeck coefficient is significantly enhanced for higher order dispersive bands.
Figure 6.4 The mobility multiplied by the density of states as a function of carrier energy.

Room temperature mobility for various band dispersion orders and various doping concentrations is shown in Figure 6.5a. The mobility of parabolic bands is larger than that of high order dispersive bands up to a doping concentration of $10^{28}$ m$^{-3}$. The results above $10^{28}$ m$^{-3}$ are not discussed here, since most materials do not possess that high carrier concentration. It is also interesting that varying the effective mass of a parabolic band only alters the optimized doping concentration for the maximum power factor. The maximum value is not influenced, as
shown in Fig. 6.5b. It suggests that band engineering of a single parabolic band is not capable of enhancing the power factor.

![Figure 6.5](image)

**Figure 6.5** (a) Room temperature mobility of various band dispersions at different carrier concentrations. (b) Carrier concentration dependent power factor for a single parabolic band with various effective mass.

### 6.4 Summary

Electrical transport coefficients were derived for higher order dispersive bands assuming that the acoustic phonon scattering dominates in this chapter. Numerical calculations are shown for the comparison between the higher order dispersive bands and the parabolic band. I find that the thermoelectric power factor can be enhanced by an order of magnitude by increasing the band dispersion order from 2 to 10. Detailed density of states and mobility analysis suggests that the enhancement mostly originates from the enhanced energy dependence of the product of density of states and mobility. Numerical calculations also show that changing the effective mass
of a parabolic band only changes the optimized carrier concentration for the maximum power factor, but not the maximum power factor value. This suggests that engineering a single parabolic band will not benefit the thermoelectric power factor.
Chapter 7 Conclusion

In this work, we have shown that Sn dopants can be successfully incorporated in the binary skutterudite CoSb\textsubscript{3} via bulk polycrystalline materials synthesis. \textit{Ab initio} calculation predicts that Sn resonant electronic levels lie approximately 0.3 eV below the valence band maximum of CoSb\textsubscript{3}. However, experimental studies did not find a significant enhancement of the power factor. Detailed phase identification and microstructural characterization on the CoSb\textsubscript{3-x}Sn\textsubscript{x} samples using XRD, SEM, and TEM suggests that the solubility limit of Sn in CoSb\textsubscript{3} is too low to move the Fermi level deep enough into the valence band to reach the Sn resonant levels. On the other hand, we have shown that Sn dopants significantly reduce the thermal conductivity of CoSb\textsubscript{3}, leading to an enhanced thermoelectric figure of merit.

An additional approach to further push the Fermi level into the valence band to the vicinity of the Sn resonant levels was pursued. Fe was incorporated on the Co sites as a secondary \textit{p}-type dopant. In order to stabilize the crystal structure and further reduce the thermal conductivity, Yb was also filled in the interstitial sites. Microstructural analysis corroborated that Sn, Fe, and Yb were successfully incorporated in the matrix of Yb\textsubscript{2}Fe\textsubscript{4-\textit{y}}Co\textsubscript{\textit{y}}Sb\textsubscript{12-x}Sn\textsubscript{x}. However, thermoelectric transport measurement results still did not exhibit the influence of the Sn resonant levels. The Sn-doped samples exhibited lower power factor compared to the Sn-free samples. We attributed this to Fermi level pinning by the heavy Fe-\textit{d}-band, which moves to the valence band maximum as the Fe concentration increases.
While Fe doping did not move the Fermi energy sufficiently far to access the Sn resonant levels, we found the convergence of the heavy Fe-d band and the light Sb-p band to be beneficial for the thermoelectric performance of filled skutterudites. Yb$_{0.8}$Fe$_3$CoSb$_{12}$ exhibits the best power factor of ~25 µW/cmK$^2$. In spite of its greatly increased carrier concentration, Yb$_{0.8}$Fe$_3$CoSb$_{12}$ still exhibits an enhanced thermopower compared to Yb$_{0.3}$FeCo$_3$Sb$_{12}$ and Yb$_{0.6}$Fe$_2$Co$_2$Sb$_{12}$ at room temperature due to the contribution of the heavy carriers in the Fe-d band. However, the Seebeck coefficient of Yb$_{0.3}$FeCo$_3$Sb$_{12}$ exceeds that of Yb$_{0.8}$Fe$_3$CoSb$_{12}$ at high temperatures, because the Fermi window at high temperatures becomes so wide that the heavy carriers in the Fe-d band start to contribute to the conduction even in Yb$_{0.3}$FeCo$_3$Sb$_{12}$ and thus the Seebeck coefficient is mainly dependent on the carrier concentration. The benefits from the large effective mass and the drawback of the low mobility suggest that an optimized Fermi level exists for thermoelectric performance. Conventional doping on the Sb sites is able to tune the carrier concentration and adjust the Fermi level; however, ionized impurity scattering makes such a method less promising. Thus, a novel doping mechanism is desired.

In addition to ionic impurity scattering, the low ionization energy of most of dopants results in a temperature-independent carrier concentration above the deionization temperature (this temperature is usually very low). Numerical calculation results indicate that a temperature-independent carrier concentration is not beneficial for thermoelectric applications over a wide temperature range. The peak carrier concentration of the power factor varies with temperature. Instead of using elements, secondary phase materials are intentionally incorporated in the matrix. With the Fermi level offset between the matrix and the secondary phase varying with temperature, the charge transfer across the interface is also temperature-dependent. This leads to a temperature-dependent carrier concentration in the matrix. We demonstrate the novel doping
method in GeTe-CuInTe$_2$ composites. The average power factor over a wide temperature range is significantly enhanced. Moreover, the mobility of GeTe-CuInTe$_2$ composites is significantly larger than GeTe-In$_2$Te$_3$ solid solutions, suggesting that doping with secondary phase materials is able to tune the carrier concentration without sacrificing the mobility. This novel method can be used in other materials, such as filled skutterudites as proposed in Chapter 4.

Finally, engineering band dispersion is proposed as a potential method of enhancing thermoelectric power factor. As the band dispersion index $n$ increases from 2 to 10, the power factor can be enhanced by almost one order of magnitude. Such enhancement originates from the enhancement of the thermopower. Detailed band structure analysis suggests that the enhancement on the thermopower comes from the increased energy dependence of the product of density of states and mobility.

Future work proposed based on the discoveries made in this work has three aspects. Firstly, other elements with their resonant electronic levels in CoSb$_3$ closer to the top of the valence band compared to Sn should be considered. Secondly, the novel doping method devised in Chapter 5 has the potential to be applied to other materials. For those materials which have optimized power factor only at high temperatures, such as heavily doped semiconductors, materials carefully selected based on their temperature dependence of the Fermi level can be incorporated as secondary phases to optimize the matrix carrier concentration over a wide temperature range, and hence enhance the average thermoelectric performance. For materials that need to be further optimized for thermoelectric performance, such as filled skutterudites discussed in Chapter 4, materials with appropriate Fermi level offset with respect to the matrix can be incorporated to further adjust the matrix carrier concentration without deteriorating mobility to further enhance power factor. Finally, engineering band dispersion in materials can
be beneficial for thermoelectric applications. Theoretically, transport coefficients of higher order dispersive bands need to be derived for other scattering processes. Moreover, mechanisms with potentials to achieve higher order dispersive bands, such as introducing strong spin-orbit interaction or altering the symmetry of the lattice structure, need to be confirmed theoretically. Once confirmed by theory, materials with specific properties will be explored experimentally.
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