Thermoelectric Properties of Bismuth Antimony Telluride Alloys

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ABSTRACT

Commonly used ozone-depleting refrigerants in refrigerators will be completely phased out in less than 15 years according to the Montreal Protocol. This imminent challenge can be tackled effectively by replacing the current vapor-compression cooling with environmentally sustainable thermoelectric cooling. \( P \)-type \( (\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3 \) alloys have been intensively studied over the past 50 years for cooling applications because of their high thermoelectric performance near room temperature. However, the electronic origin of the high thermoelectric efficiency of \( (\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3 \) alloys is often understated or ignored completely. In this thesis, the underlying physics of high electronic performance observed in the particular alloy composition, \( (\text{Bi}_2\text{Te}_3)_{0.25}-(\text{Sb}_2\text{Te}_3)_{0.75} \), is investigated. It was demonstrated with two-band transport calculation that the convergence of bands occurred at \( (\text{Bi}_2\text{Te}_3)_{0.25}-(\text{Sb}_2\text{Te}_3)_{0.75} \). A \( zT \) improvement of 17% was also achieved in zone-levelled \( (\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3 \) crystals by controlling their carrier concentration while using the two-band model as a guide. With the optimum electronic efficiency theoretically calculated and achieved experimentally, the thesis moves on to minimize lattice thermal conductivity of \( (\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3 \) for the maximum \( zT \). A new liquid compaction method was devised to produce dense arrays of dislocations in grain boundaries of nanostructured \( (\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3 \). The grain boundary dislocations were found to be highly effective in scattering phonons and a substantial improvement in \( zT \) was possible \((zT = 1.86 \text{ at } 320 \text{ K})\). The understanding of phonon scattering by dislocations was in turn applied to phonon scattering at grain boundaries of polycrystalline materials. By demonstrating that the frequency-dependent dislocation scattering can replace the commonly used frequency-independent boundary scattering by Casimir, this thesis suggests that the grain boundary dislocation scattering may be responsible for the mechanism of phonon scattering at grain boundaries.

H.-S. K. participated in theoretically comparing different band gap calculations with different assumptions, producing an engineers’ chart for facile and accurate determination of band gap, and participated in the writing of the manuscript.


H.-S. K. participated in devising a simple equation as a function of Seebeck coefficient which can calculate Lorenz number without having to solve Boltzmann transport numerically, and participated in the writing of the manuscript.


H.-S. K. participated in analysis of data by achieving experimentally obtained low lattice thermal conductivity with lattice thermal conductivity modelling. H.-S. K. also estimated bipolar contribution to the total thermal conductivity by employing two-band transport calculation. H.-S. K. theoretically calculated the maximum coefficient of performance of modules and compared with experimental data. H.-S. K. participated in the writing of the manuscript.


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Chapter 1

Introduction

1.1 History of refrigeration

Early history of refrigeration is closely related to our efforts to preserve food by keeping it cool. Centuries ago, when natural ice was the only available refrigerant people harvested ice in winter and stored it underground year-round to keep their food cold. With the advent of an icebox (Fig. 1.1) in early 19th century, harvested ice could be stored domestically. When a block of ice was placed in a compartment at the top of the icebox, chilled air around the ice would travel down the box keeping food in lower compartments fresh. Insulating materials such as cork and sawdust were inserted in wooden walls of the icebox to prevent the ice from melting. When the ice eventually melted, it was drained through a spigot. However, with increasing pollution in rivers (source of natural ice) ice harvesting and the use of iceboxes faded away by early 1910.

Fig. 1.1. Schematic diagram of an icebox from an advertisement in 1874. Image from Google
In 1930, electricity-powered refrigerators using synthetic refrigerant based on chlorofluorocarbon (CFC) were commercially available (the very first refrigerator powered by electricity was developed in 1927, but it utilized flammable and toxic methyl formate as its refrigerant). Unlike icebox where harvested ice was used as a refrigerant, mechanically circulating refrigerant (CFC) which changed its state between liquid and gas was used in the refrigerator (vapor-compression cooling).

The refrigerant in gas (low pressure and low temperature, blue line entering the compressor in Fig. 1.2) is compressed to high pressured gas at high temperature. This work is done by a compressor powered by electricity. As the gas (high pressure and high temperature) enters the condenser and passes through vent fins (red line coming out of the compressor), it condenses to a liquid at a reduced temperature. Some of the liquid then quickly expands to a vapor at an expansion valve. This change of state suddenly drops the temperature of the liquid. The cold liquid lowers the temperature of the air inside the refrigerator and changes back to gas (low pressure, low temperature) in an evaporator in the refrigerator.

Fig. 1.2. Schematic diagram of a mechanical refrigerator. Image redrawn from a website run by The Institute of Refrigeration in the UK (www.fantasticfridge.com).
Despite the fact that it was less harmful to use CFC (or other newly developed hydrochlorofluorocarbon (HCFC) based refrigerant) than methyl formate (used in the first electric refrigerator in 1927) as refrigerants, both CFC and HCFC were identified as ozone-depleting gases. Currently, the CFCs are prohibited in the Montreal Protocol and even the HCFCs are scheduled for a complete phase-out by 2030\(^7\). Many efforts have been focused on developing a better refrigerant which is not ozone-depleting, but in order to tackle this ambitious task a completely different approach to refrigeration is necessary.

1.2 Thermoelectric solid-state cooling

Thermoelectric solid-state cooling does not require any refrigerants for it to operate. All it needs are thermoelectric modules in Fig. 1.3 and an external electric current source. When an external electric potential is applied to the module, as the current runs through thermoelectric elements (\(p\)-type in green and \(n\)-type in purple) in series, heat is absorbed from one side of the module and released to the other (with the current flowing as in Fig. 1.3, the top surface of the module cools).
The thermoelectric module can absorb heat from one side (and dissipate the heat at another side) due to a thermoelectric phenomenon called Peltier effect. When current flows through \( n \)-type and \( p \)-type thermoelectric elements connected in series (Fig. 1.4), charge carriers from each thermoelectric element are forced to move. Both electrons (from \( n \)-type element) and holes (from \( p \)-type element) travel downwards (white dotted arrows in Fig. 1.4) while carrying heat along with them. This movement of charge carriers induced by electric potential makes one side of the thermoelectric module cold and the other side hot. A thermoelectric material’s ability to convert the applied electric potential to a temperature difference is expressed in Seebeck coefficient, \( S = \frac{V}{\Delta T} \) (\( V \) and \( \Delta T \) are the applied voltage and induced temperature difference, respectively). Even though a material with a high Seebeck coefficient is not necessarily a good thermoelectric material, the good thermoelectric material has a high Seebeck coefficient (reason to be discussed in Chapter 1.3).

![Fig. 1.4. Schematic diagram of a Peltier effect](image)

Thermoelectric cooling is superior to its mechanical counterpart in many aspects. For instance, it is environmentally sustainable (refrigerant-free), free of vibration/noise (no compressor required), and even capable of zonal cooling. Commercially available thermoelectric wine refrigerator is a good example, which demonstrates thermoelectric cooling’s advantages. A wine refrigerator cannot be made with a vapor-compression cooling, as the vibration it accompanies will agitate sediments in wines and eventually cause
the wines to age prematurely. Only vibration-free thermoelectric refrigerator can serve its purpose as a suitable wine cellar. Unfortunately, efficiency of the thermoelectric module is lower than that of the vapor-compression cooling which hinders thermoelectric refrigerator from replacing household mechanical refrigerator. For thermoelectric refrigerator to be more competitive than current vapor-compression refrigerator, development of highly efficient thermoelectric materials is needed.

1.3 Thermoelectric materials for cooling application

Efficiency of a thermoelectric material is characterized by a dimensionless figure-of-merit, $zT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, electrical conductivity, temperature (absolute temperature), and thermal conductivity. Both charge carriers transporting heat ($\kappa_e$) and phonons propagating through lattice of a material ($\kappa_l$) contribute to the thermal conductivity ($\kappa = \kappa_e + \kappa_l$). In theory, an efficient thermoelectric material can be achieved by increasing both $S$ and $\sigma$ while keeping $\kappa$ minimum. Nonetheless, optimizing $zT$ is nontrivial because the variables in $zT$, which are expressed separately, are in fact coupled to each other. For example, the $S$ is known to be inversely proportional to carrier concentration and directly proportional to entropy. Qualitatively, it can be reasoned that a material with a high carrier concentration has a low entropy as there is not much more room to accommodate additional carriers. In contrast, another material with low carrier concentration will have a high entropy for the exactly opposite reason. Thus, by decreasing carrier concentration of a material, its $S$ will increase but its $\sigma$ will decrease along with $\kappa_e$. A more detailed interrelationship among thermoelectric parameters is depicted in Fig. 1.5. Approximately, an optimized thermoelectric material (with high $zT$) has a carrier concentration in a range between $10^{18} \sim 10^{20}$ (cm$^3$), where a typical heavily-doped semiconductor lies.
Among other thermoelectric materials, Bi$_2$Te$_3$-based alloys have been found to have the highest $zT$ near room temperature (~300 K) as shown in Fig. 1.6. Because of their high $zT$ near 300 K, they have been studied extensively for their application in cooling devices.

Bi$_2$Te$_3$ crystal has a layered hexagonal crystal system (also a rhombohedral structure) as drawn in Fig. 1.7. Tellurium (Te) in Bi$_2$Te$_3$ can be situated in two different positions (distinguished by Te (1) and Te (2)). While layers of bismuth (Bi) and Te are strongly held together by covalent-ionic bonds, the connection
between Te (1) layers (between orange layers in Fig. 1.7) is much weaker (van der Waals bonding)\textsuperscript{11}. Therefore, Bi\textsubscript{2}Te\textsubscript{3} single crystal easily cleaves along \textit{a-b} basal plane.

![Fig. 1.7. Crystal structure of Bi\textsubscript{2}Te\textsubscript{3}. Te atoms in two different positions are distinguished by Te (1) and Te (2).](image)

In addition to the anisotropy in mechanical property, some thermoelectric properties of Bi\textsubscript{2}Te\textsubscript{3} single crystal are observed to be anisotropic as well (i.e. electrical conductivity and Hall coefficient, which is related to carrier concentration)\textsuperscript{11,12}. Drabble\textsuperscript{13} explained the observed anisotropy in transport with a multiple Fermi surfaces in its band structure. For \textit{p}-type Bi\textsubscript{2}Te\textsubscript{3}, it was found that the highest valence band had a valley degeneracy ($N_v$) of 6\textsuperscript{(13)}. The complex band structure with anisotropic Fermi pockets (Fig. 1.8) in \textit{p}-type Bi\textsubscript{2}Te\textsubscript{3} makes its high thermoelectric performance possible\textsuperscript{14}. 

Fig. 1.8. Valence band structure of $p$-type Bi$_2$Te$_3$. Only the Fermi surfaces which correspond to the highest valence band are present (in purple). High symmetry points are noted as z, a, and U in orange.

1.4 Summary of research

This thesis focuses on improving current best thermoelectric material for cooling (Bi$_2$Te$_3$-based alloys) in order to help advance a new era of solid-state cooling refrigerators. Because the substitution of isoelectronic Sb$^{3+}$ for Bi$^{3+}$ in Bi$_2$Te$_3$ has the potential to improve $zT$ by reducing the thermal conductivity, (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$, especially (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ ($x = 0.75$) alloys have been studied extensively in literature (composition $x = 0.75$ has the best $zT$ among $0 \leq x \leq 1$).

The first part of the thesis explores possibilities to further enhance thermoelectric performance of (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ alloys. To begin with, the reason that the (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloys have the highest $zT$ at $x = 0.75$ is examined. Historically, it has been assumed that only the highest valence bands in Bi$_2$Te$_3$ and Sb$_2$Te$_3$ contribute in transport. Consequently, the transport properties of (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloys interpreted with a single valence band model results in a conclusion that the density-of-states effective mass of the band suddenly peaks at $x = 0.75$ (hence the highest Seebeck coefficient and $zT$). However, it is proposed that the maximum Seebeck coefficient is not because of the abrupt increase in the effective mass but because of the convergence of bands (between the first valence band and the second valence band). Based on this two band model, an improved $zT$ is achieved from careful carrier concentration tuning by changing the amount of excess Te in oriented (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_{3+\delta}$ crystals.
Strategies to reduce thermal conductivity of (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ polycrystalline material are also investigated. A liquid-phase compaction method, which involves Spark Plasma Sintering (SPS) of (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ powders with excess Te is found to produce dense arrays of dislocations in grain boundaries of polycrystalline (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ when melted excess Te is expelled during the SPS process. Phonon scattering by the dislocations reduces thermal conductivity significantly with a very high $zT$ of 1.86 at 320 K. Further phonon scattering due to modulation of solute concentration near dislocation strain fields is also presented.

Secondly, important physics behind thermoelectric parameters are analyzed. Developing a theoretical tool that accurately describes properties of a material is important as it broadens our understanding of the physics behind. Furthermore, it will guide us to new strategies for improving performance of the material as well. First of all, an alternative approach to boundary scattering is proposed. A frequency-independent phonon mean free path has been commonly used to describe phonon boundary scattering in polycrystalline materials. However, recently it was discovered that at low temperature, the frequency-independent boundary scattering could no longer describe thermal conductivity of nanostructured materials. Therefore a better analytical model which works in all temperature range is suggested. Tools for an accurate determination of energy band gap and Lorenz number (both important in calculating $zT$ accurately) as a function of measured thermopower (absolute value of $S$) are discussed as well.

Lastly, mechanical strength of Bi$_2$Te$_3$-Sb$_2$Te$_3$ alloys fabricated by hot extrusion, vertical zone melting, and SPS are compared. This study is relevant to the practical application of the material in a thermoelectric module as thermoelectric elements in the module are subjected to stress when they are assembled in the module and when the module is in use.
Chapter 2

Experimental methods

2.1 Summary of experimental methods

Experimentally, this thesis studies (Bi_{0.25}Sb_{0.75})_2Te_3 synthesized by two very different methods: zone-melting and Spark Plasma Sintering (SPS). Because the samples synthesized by SPS were made by our collaborators in Samsung Advanced Institute of Technology (SAIT) and Sungkyunkwan University in the Republic of Korea, tools used to characterize the samples are also different from those used to analyze samples fabricated by zone-melting at Caltech. Therefore, this chapter is first divided by material synthesis technique. Under each different synthesis method, synthesis procedure and sample characterization are detailed.

2.2 Starting charge zone-melting for (Bi_{0.25}Sb_{0.75})_2Te_{3+\delta}

This section contains contents that have been submitted to a journal. Once it is accepted, permission will be asked.

2.2.1 Synthesis procedures

Samples of Te-rich (Bi_{0.25}Sb_{0.75})_2Te_3 were synthesized from solidus compositions (SC) of (Bi_{0.25}Sb_{0.75})_2Te_{3+\delta} with \delta in the range of 0 - 0.0585 and liquidus compositions (LC) of (Bi_{0.25}Sb_{0.75})_2Te_{3+\delta} with \beta/\alpha < 3 and \delta from 0 - 0.0585 as listed in Table 2.1. Elements of Bi, Sb, and Te (99.999 % purity metals basis) from Alfa Aesar were used to synthesize the SC and LC compounds separately. For both SC and LC, stoichiometric amounts of each element were weighed in air. They were then loaded into carbon coated quartz ampoules, and evacuated to a pressure of \sim 10^{-5} Torr. The SC and LC (in sealed ampoules) were melted at 1073 K for 12 hours using a vertical tube furnace, and rapidly quenched in water. The obtained ingots were ground for 20 minutes using a mortar and pestle in an Argon glove box to prevent oxidation of the ground powders.
Table 2.1 Starting solidus and liquidus compositions for Te-excess (Bi_{0.25}Sb_{0.75})_2Te_3

<table>
<thead>
<tr>
<th>Sample</th>
<th>LC/SC</th>
<th>Bi (at. %)</th>
<th>Sb (at. %)</th>
<th>Te (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.73E19</td>
<td>LC</td>
<td>18.00</td>
<td>22.00</td>
<td>60.00</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td>10.00</td>
<td>30.00</td>
<td>60.00</td>
</tr>
<tr>
<td>4.57E19</td>
<td>LC</td>
<td>10.30</td>
<td>28.10</td>
<td>61.60</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td>9.97</td>
<td>29.90</td>
<td>61.30</td>
</tr>
<tr>
<td>3.61E19</td>
<td>LC</td>
<td>10.30</td>
<td>28.10</td>
<td>61.60</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td>9.92</td>
<td>29.78</td>
<td>60.30</td>
</tr>
<tr>
<td>3.57E19</td>
<td>LC</td>
<td>10.45</td>
<td>28.38</td>
<td>61.17</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td>9.862</td>
<td>29.58</td>
<td>60.55</td>
</tr>
<tr>
<td>3.29E19</td>
<td>LC</td>
<td>10.45</td>
<td>28.38</td>
<td>61.17</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td>9.862</td>
<td>29.58</td>
<td>60.55</td>
</tr>
<tr>
<td>2.64E19</td>
<td>LC</td>
<td>10.46</td>
<td>27.92</td>
<td>61.61</td>
</tr>
<tr>
<td></td>
<td>SC</td>
<td>9.71</td>
<td>29.12</td>
<td>61.17</td>
</tr>
</tbody>
</table>

† Sample name = nH of the resulting oriented crystal at 300 K. ‡ LC = liquidus composition, SC = solidus composition

To create the starting ingot for crystal growth, the resulting LC powder was melted (in a quartz tube under ~10^{-5} Torr) at 1073 K for 5 minutes, and quenched in water (Fig. 2.1a to 2.1c). The newly formed LC ingot (inside of the tube) was about 10 ~ 15 mm in length (green ingot in Fig. 2.1c). The top of the sealed quartz tube (with LC ingot still inside) was cut and SC powder (purple spheres) was placed on top of the LC ingot as shown in Fig. 2.1d. The quartz tube was vacuum sealed to ~10^{-5} Torr yet again. While keeping the LC ingot at room temperature, the SC powder (which slid to the bottom of the tube as the tube was held upside-down) was melted at 1073 K for 5 minutes (Fig. 2.1e). The upside-down quartz tube with melt SC was flipped and gently shaken once or twice to ensure that the melt SC flowed down to be in contact with the LC ingot. The instant that all the melt SC is on top of the LC ingot, the whole tube was quenched in water as in Fig. 2.1f. This “flip and quench” step, which took less than 5 seconds, formed an interface free of voids between the LC ingot (~10 mm in length) and SC ingot (~70 mm in length).
Fig. 2.1. Schematic description of preparing a sealed ampoule with two ingots with different compositions in contact for zone-melting.

The ampoule with \(LC\) ingot at the bottom and \(SC\) ingot on top (as in Fig. 2.1f and Fig. 2.2) was zone-levelled with a home-built vertical zone-levelling furnace\(^{15}\) at 890 K with a solidification rate of 2.7 mm/hr. Temperature of the molten zone was measured by a pyrometer (Modline 5, Ircon). A temperature controller (UP550, Yokogawaka) controlled the power input to the induction coil to keep the molten zone temperature at 890 K. The length of the \(LC\) ingot (orange part in Fig. 2.2) was controlled to be approximately the length of the molten zone in the zone-levelling furnace by adjusting the amount of \(LC\) powder in Fig. 2.1a. As the molten zone passed through the \(LC\) ingot, the melt \(LC\) froze to a solid with a composition of \(SC\) \((k < 1)\). Because the composition of frozen solid from the molten zone is the same as that fed into the molten zone (\(SC\) ingot), this zone-levelling resulted in oriented polycrystalline material with a homogeneous composition of \(SC\).
2.2.2 Characterization

2.2.2.1 Composition characterization

An iterative process was employed to determine the compositions of LC and their corresponding SC. Each \((\text{Bi}_x\text{Sb}_y)\text{Te}_{3+\delta}\) powder (prepared as above) with different composition was melted (in a quartz tube under ~10^{-5} \text{ Torr}) at 1073 K for 5 minutes, and quenched in water (as in Fig. 2.1a to 2.1c). Final ingots (40 mm in length) were zone-levelled at 890 K with a growth rate of 2.9 mm/hr. Composition of each crystal's region where the first solidification happened was examined by electron probe microanalysis (EPMA). Only those samples which melt and froze into Bi : Sb = 10 : 30 (at. %) with Te higher than 60 at. % (SC) were used as LC to synthesize \((\text{Bi}_{0.25}\text{Sb}_{0.75})\text{Te}_{3+\delta}\) oriented crystals (Table 2.1).
For example, as a candidate for $LC$, an ingot with a composition of Bi : Sb : Te = 10.45 : 28.38 : 61.17 (in at. %) was zone-melted as in Fig. 2.3b. Unlike in Fig. 2.2, there was only one ingot (with $LC$) present in Fig. 2.3b which would result in changing composition of the zone-melted crystal along the height of the crystal. Therefore in order to accurately measure the freezing composition of the melted $LC$, electron probe microanalysis (EPMA) was done on the region where the molten zone was first started (orange square in Fig. S1b). The orange dotted line in Fig. 2.3a clearly defines the boundary between textured crystal (curved layers) and ingot (below the line). Since the start of the textured crystal corresponds to that of the molten zone, EPMA measurements from ten different spots (yellow circles in Fig. 2.3a) were taken from above the orange dotted line (but still close to the line). Those spots were deliberately chosen to be closer to the surface of the crystal as the cooling air (via air tube in Fig. 2.3b) first froze the melted ingot near the surface. According to the EPMA, the averaged (from ten data points) ratio of Sb to Bi was $\sim 2.95$ and the averaged Te was 60.55 at. %. As the freezing composition satisfied the two conditions of $SC$, $(Bi_{0.25}Sb_{0.75})_2Te_{3+\delta}$, the composition of Bi : Sb : Te = 10.45 : 28.38 : 61.17 (in at. %) and its freezing composition were adopted as
LC and SC, respectively. This combination of LC and SC was used in the samples “3.57E19” and “3.29E19” as listed in Table 2.1. After the sample “3.29E19” was synthesized, the same synthesis procedure was repeated to make “3.57E19” from the very beginning for a brief reproducibility test. All the LC used in Table 2.1, their freezing compositions estimated by EPMA are given in Table 2.2. For SC of the sample “4.57E19”, the lower limit of the estimated Te (at. %) from the freezing composition was used.

Table 2.2. Freezing composition of each LC measured by EPMA.

<table>
<thead>
<tr>
<th>Sample†</th>
<th>LC</th>
<th>freezing composition‡</th>
<th>SC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bi (at. %)</td>
<td>Sb (at. %)</td>
<td>Te (at. %)</td>
</tr>
<tr>
<td>3.57E19</td>
<td>10.45</td>
<td>28.38</td>
<td>61.17</td>
</tr>
<tr>
<td>3.29E19</td>
<td>10.46</td>
<td>27.92</td>
<td>61.61</td>
</tr>
</tbody>
</table>

† Sample name = nH of the resulting zone-levelled crystal at 300 K
‡ freezing composition = composition that melted LC ingots freeze into

2.2.2.2 Thermolectric transport characterization

Parallelepiped shape samples (4.0×1.5×12.0 mm³) were prepared for resistivity and Hall effect measurements under dynamic vacuum. A total of 5 contacts were made on the samples to measure the resistivity (via 4-point method) and Hall effect (with the 5th contact at opposite side of resistance voltage contacts) at the same time without having to change contact geometry (Fig. 2.3). A modified MMR technologies variable temperature Hall measurement system with a 1.0 T field up to 520 K was utilized.

Disk shape samples (6.0 mm diameter and 1.5 mm thick) cut from one end of the zone-levelled ingot piece for the parallelepiped samples were used in the Seebeck coefficient (house built)⁶ and thermal diffusivity (via Netsch LFA 457) measurements.
2.2.3 Two-band transport model

A two-band (TB) model was employed to compute transport properties of the zone-levelled (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_{3+\delta}$ samples at 300 K. For each nonparabolic band, Boltzmann transport equations (as functions of chemical potential) were numerically solved (in Python) to obtain chemical potential dependent thermoelectric parameters (i.e. Seebeck coefficient, mobility, etc.) while assuming acoustic phonon scattering\textsuperscript{17} and alloy scattering\textsuperscript{18} (except Bi$_2$Te$_3$ and Sb$_2$Te$_3$). The resulting transport properties from the two valence bands (VB$_1$ and VB$_2$ in Fig. 3.1d) were calculated by taking conductivity-weighted averages of the thermoelectric parameters of each band\textsuperscript{19}.

The energy gaps between the lowest conduction band (CB) and the highest valence band for 0 ≤ $x$ ≤ 0.75 (VB$_1$) used in the TB model were taken from Sehr et al.\textsuperscript{20} (Fig. 3.1d and $\Delta E_{CB-VB1}$ in Table 2.3). For $x$ > 0.75, the $\Delta E_{CB-VB1}$ was linearly extrapolated to minimize complexity. The density-of-states effective mass ($m^*$) and deformation potential ($E_{def}$) for each valence band at $x = 0$ and $x = 1$ were fitted to experimental data from literatures while adjusting their energy differences between CB and VB$_2$ ($\Delta E_{CB-VB2}$). Because it was assumed that the bands were crossing at $x = 0.75$, we knew $\Delta E_{CB-VB2}$ at $x = 0.75$ ($\Delta E_{CB-VB2} = \Delta E_{CB-VB1}$). The $\Delta E_{CB-VB2}$ at $x = 0.75$ and those determined from $x = 0$ and 1 could approximately be joined in a straight line. Therefore, the $\Delta E_{CB-VB2}$ for other $x$ were obtained from the straight line (Table 2.3). For 0.75 < $x$ ≤ 1, the...
highest valence band is the $VB_2$ and the $\Delta E_{CB-VB_2}$ serves as the energy gap (between the lowest $CB$ and the highest valence band). The fitted energy gap at $x = 1$ used in the model (0.2007 eV of $\Delta E_{CB-VB_2}$ in Table 2.3) is about 16 % smaller than degeneracy-corrected optical energy gap from Sehr et al.\textsuperscript{20} (reasonable given the tendency to overestimate the optical energy gap as degeneracy increases)\textsuperscript{21}.

Based on the band structure information (\(\Delta E_{CB-VB_1}\) and \(\Delta E_{CB-VB_2}\)) obtained from the literature and the fitting to the experimental literature data of $x = 0$ and 1, the $m^*$ and $E_{def}$ of each band for $0 < x < 1$ were determined while controlling the alloy scattering potential $U$ (Table 2.3). The $U$ describes the magnitude of the alloy scattering in an alloy. The relaxation time equation for the alloy scattering from Heng et al.\textsuperscript{18} was used in the TB model. The total relaxation time was calculated by Matthiessen’s rule: \(\tau_{\text{total}}^{-1} = \tau_{\text{ac}}^{-1} + \tau_{\text{alloy}}^{-1}\), where \(\tau_{\text{ac}}\) and \(\tau_{\text{alloy}}\) are the relaxation times for acoustic phonon scattering and alloy scattering, respectively. A constant $U$ of 0.35 eV was used for all $x$ except $x = 0$ and 1 (where the alloy scattering was absent).

Table 2.3. Band parameters used in the two-band transport model.

<table>
<thead>
<tr>
<th>$x$\textsuperscript{†}</th>
<th>$VB_1$ (the first valence band)</th>
<th>$VB_2$ (the second valence band)</th>
<th>$\Delta E_{VB_1-VB_2}$ (meV)</th>
<th>$U$ (eV)</th>
<th>$C_l$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m^*$</td>
<td>$E_{def}$</td>
<td>$\Delta E_{CB-VB_1}$ (eV)</td>
<td>$N_V$</td>
<td>$m^<em>/m_{l</em>}$</td>
<td>$m^*$</td>
</tr>
<tr>
<td>0.00</td>
<td>0.750</td>
<td>14.36</td>
<td>0.1442</td>
<td>6</td>
<td>2.56</td>
</tr>
<tr>
<td>0.02</td>
<td>0.750</td>
<td>15.61</td>
<td>0.1575</td>
<td>6</td>
<td>2.26</td>
</tr>
<tr>
<td>0.03</td>
<td>0.730</td>
<td>13.42</td>
<td>0.1661</td>
<td>6</td>
<td>2.79</td>
</tr>
<tr>
<td>0.05</td>
<td>0.728</td>
<td>15.29</td>
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<td>0.2107</td>
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</tr>
</tbody>
</table>

\textsuperscript{†}Composition $x$ in ($\text{Bi}_{1-x}\text{Sb}_x$)$_2\text{Te}_3$.

\textsuperscript{‡}\(\Delta E_{CB-VB_1}\) = Energy difference between conduction band (CB) and the first valence band ($VB_1$).

\textsuperscript{‡}Similarly, \(\Delta E_{VB_1-VB_2}\) denotes the energy difference between the first and second valence bands.

\textsuperscript{‡}\(m^*/m_{l*}\) = Parameter describing the anisotropy of a single band.

\textsuperscript{†}The ratios of $m^*$ to $m_{l*}$ are effective masses along longitudinal and transverse ellipsoid directions, respectively.

\textsuperscript{¶}For different compositions ($x$) are calculated from ref. 22.

\textsuperscript{¶}$U$ = Alloy scattering potential. \textsuperscript{§}$C_l$ = elastic constant.
Anisotropy of the bands was also taken into account in the TB model. Stordeur et al.\textsuperscript{22} have optically measured effective masses along longitudinal ($m_{\parallel}$\textsuperscript{*}) and transverse ($m_{\perp}$\textsuperscript{*}) ellipsoid directions. However, since Stordeur et al. assumed that only a single band was participating in transport only composition-dependent $m_{\parallel}$\textsuperscript{*} and $m_{\perp}$\textsuperscript{*} for a single valence band was available. Thus, only the highest valence band ($VB_1$ for $0 \leq x \leq 0.75$ and $VB_2$ for $0.75 < x \leq 1$) was treated as anisotropic (Table 2.3). The second highest band was assumed to be isotropic for simplicity ($m_{\parallel}$\textsuperscript{*}/$m_{\perp}$\textsuperscript{*} = 1 for an isotropic band).

The elastic constants ($C_i = d \times v_l^2$ where $d$ and $v_l$ are the density and the longitudinal sound velocity, respectively) of Bi$_2$Te$_3$ ($x = 0$) and Sb$_2$Te$_3$ ($x = 1$) were calculated from the $d$ and $v_l$ of $x = 0$ ($d = 7700$ kg/m\textsuperscript{3} and $v_l = 2143$ m/s from ref. 23,24) and $x = 1$ ($d = 6500$ kg/m\textsuperscript{3} and $v_l = 2333$ m/s from ref. 23,24). The $C_i$ for the rest $x$ were linearly interpolated between those of $x = 0$ and 1 (Table 2.3).

As shown in Figs. S4, S5, and S6, band parameters used in the TB model (Table 2.3) yielded satisfactory fits to the experimental literature data at 300 K. However, equally adequate fits may be obtained for different sets of parameters. Nonetheless, the underlying physics of the measured transport properties in (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ single/oriented crystals is satisfactorily captured in the fits provided by the TB model.

### 2.3 Spark Plasma Sintering (SPS) for (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te

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#### 2.3.1 Synthesis procedures

The Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ingots were prepared with a melt process; high-purity (> 99.999 %) Bi, Sb, and Te granules were weighed according to the composition Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and loaded into a vacuum-sealed quartz tube of 10 mm diameter, and the contents were melted and homogeneously mixed in a rocking furnace for 10 h at 1073 K.
Bi$_{0.5}$Sb$_{1.5}$Te$_3$ bulk ingots were pulverized and mixed with excess Tellurium (25 wt. %), then the homogeneously mixed materials were put into a quartz cylinder with 0.3 mm diameter nozzle in melt spinning system. The materials were induction-molten, and were injected under a pressure of 40 kPa Ar onto a Cu wheel rotating with linear speed of 45 m s$^{-1}$ under the Ar atmosphere of 300 mTorr. Thin ribbons (5–10 μm thick, 1.5–2 mm wide, and 5–10 mm long) were obtained by rapid solidification (cooling rate $\sim$106 K s$^{-1}$) using this melt spinning process.

The melt spun ribbons were pulverized, then compacted using spark plasma sintering (SPS) at 480 $^\circ$C for 3 min under 70 MPa. During the compacting, the liquidified excess Te was expelled from the graphite die.

![Image of excess Te expelled from the graphite die after the SPS process.](image)

### 2.3.2 Characterization

X-ray diffraction (XRD) (D/MAX-2500/PC, Rigaku, Japan) analysis with Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) was performed on powder and bulk samples. The microstructure was investigated using scanning electron microscopy (SEM) (JSM-7600F, JEOL) and transmission electron microscope (TEM) (JEM-2100F, JEOL). Transport measurements were performed in directions both parallel and perpendicular to the pressing direction. Only the measurements perpendicular to the pressing directions are shown in the main text and used for calculation of $zT$. The electrical conductivities ($\sigma$) and Seebeck coefficients ($S$) were measured from 300 to 480 K by a four point probe method using a ZEM-3 (ULVAC-RIKO, Japan). Hall effect
measurements were performed using Physical Property Measurement System (Quantum Design). The thermal conductivity values \( (\kappa = \rho_s \times C_p \times \lambda) \) were calculated from measurements taken separately. Sample density \( (\rho_s) \) was measured by Archimedes method. The thermal diffusivity \( (\lambda) \) was measured by laser-flash method using TC-9000 (ULVAC-RIKO, Japan). The Dulong-Petit heat capacity \( (C_p = 124.6 \text{ J mol}^{-1} \text{ K}^{-1}) \) was used and confirmed by measurements at 300 K by the thermal relaxation method using a Physical Property Measurement System (Quantum Design).
Chapter 3

Convergence of valence bands in (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$

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3.1 Introduction

Since commonly used refrigerants (hydrochlorofluorocarbons) were identified as ozone-depleting, there has been a worldwide agreement to eliminate their production by 2030\(^7\). Progress towards this task can be aided if current vapor-compression cooling is replaced by environmentally sustainable thermoelectric cooling. The development of high-efficiency thermoelectric material, whose performance is evaluated by its figure of merit, \( zT = S^2 \sigma T / \kappa \), where \( S \), \( \sigma \), \( T \), and \( \kappa \) are the Seebeck coefficient, electrical conductivity, temperature, and the thermal conductivity, respectively, is essential to make thermoelectric refrigerators more competitive than their ozone-depleting counterparts.

For decades, \( p \)-type Bi$_2$Te$_3$-Sb$_2$Te$_3$ alloys have been the best candidates for cooling applications because of their high \( zT \) near room temperature\(^{10} \). Among single-crystal (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$, the composition near \( x = 0.75 \) has been found to have the maximum \( zT \) (0.87 – 0.9 at 300 K)\(^{12,25} \). Since then, many efforts have focused on nanostructured polycrystalline (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ to improve the \( zT \) by \( \kappa \) reduction\(^{1,26-28} \).

In order to further enhance \( zT \) in (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$, optimizing both the thermal and electronic properties will be required. Recently, a high \( zT \) (1.86 at 320 K) was reported in (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ from phonon engineering through dislocations\(^1 \). This material is made with excess Te and lower hole concentration than typical materials of the same nominal composition\(^1 \), suggesting charge carrier optimization may also have been involved. The maximum attainable electronic performance of a thermoelectric material is proportional
to the quality factor\textsuperscript{29}, which in turn depends on the number of Fermi pockets ($N_v$)\textsuperscript{13,30}. Because $N_v$ is not coupled to any other property related to $zT$, converging separate carrier pockets provides a straightforward strategy for improving $zT$ (ref. 30). To date, band convergence in (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ has not been sufficiently investigated, probably because many experiments assumed only one band participating in transport\textsuperscript{12,31-33} despite the fact that it has a high crystal symmetry like PbTe.

Using a single band model, the density-of-states effective mass ($m^*$) for the valence band can be calculated from the Seebeck Pisarenko plot ($S$ versus Hall carrier concentration) for each composition. A peak was found in $m^*$ at $x = 0.75$ (ref. 34,35) as shown in Fig. 3.1a. Optical investigations\textsuperscript{22} of single-crystal (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ confirmed the $m^*$ peak at $x = 0.75$ and concluded this was due to an increase in mass along one direction only near $x = 0.75$. Unfortunately, the single band theory could not explain the abrupt change in the effective mass\textsuperscript{33}.

Here we propose, providing additional evidence, that the high $zT$ at $x = 0.75$ is not due to sudden flattening of the valence band to increase $m^*$, but instead is due to the convergence of the two different valence bands that cross as $x$ changes (Fig. 3.1d). We develop a two-band transport model for (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloys that predicts an improvement in $zT$ when the carrier concentration of (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ is carefully tuned. Preparing homogeneous, crystalline material by zone-melting, we observe a $zT$ of $\sim 1.05$ at 300 K. This value is significant when compared to the state-of-the-art single-crystal (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ ($zT \leq 0.9$), as it is achieved without nanostructuring or external doping.
3.1 Band related properties as a function of composition ($x$) for (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ at 300 K. (a) Density-of-states effective mass (red circle) showing an abrupt peak (grey line as guide to the eye) while the mobility prefactor (b) shows no such change at $x = 0.75$. (c) Brillouin zone of Bi$_2$Te$_3$ ($x = 0$) showing hole pockets for the first valence band (in purple) and for the second valence band (in green). (d) Semi-empirical band structure (300 K) with the first valence band (purple line), second valence band (green line), and the lowest conduction band (dark grey line). For simplicity, the energy of the first valence band (purple) of Bi$_2$Te$_3$ ($x = 0$) is set to 0.0 eV. $\Delta E_{VB1-VB2}$ denotes energy difference between the first and second valence bands. The energy gap between the lowest conduction band (dark grey) and the highest valence band (purple for $0 \leq x \leq 0.75$ and green for $0.75 \leq x \leq 1$) is the band gap $E_g(x)$.

3.2 Experimental

In order to understand band structure of (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ with pronounced anisotropy\(^{36}\), the transport properties carefully measured from its textured or single crystal along the same direction are required. Among various methods to grow textured and/or single crystals, simple solidification from the melt (Bridgman method) works well for congruently melting systems, but for alloys this will generally produce materials with a composition gradient as the material solidifies and the composition of the liquid phase changes\(^{37}\). This is due to the composition difference between the solid and liquid phase at the growth
temperature characterized by the segregation coefficient $k$ (concentration of a particular component in solid phase divided by that in the liquid phase).

Zone-levelling (shown schematically in Fig. 3.2) is ideal for producing homogeneous crystals in systems with segregation coefficients not equal to unity ($k \neq 1$). Unlike the Bridgman method where the entire molten ingot solidifies from end to end, in zone-levelling only a portion (or zone) of the ingot is in the molten state at any given time. The compressed air flowing below and above the molten zone ensures sufficient temperature gradients for solidification and a smooth liquid-solid interface (Fig. 3.2a). The two regions of different compositions (solute concentration) in the ingot before the zone-levelling is depicted with a blue dashed line in Fig. 3.2b. The initial composition is the liquidus composition ($LC$) $C_0/k$ at the bottom of the ingot (with a length the size of the molten zone) and solidus composition ($SC$) $C_0$ for the remainder of the ingot. These compositions correspond to liquidus and solidus composition in the ternary phase diagram of Bi-Sb-Te system at the growth temperature of 890 K (since $k < 1$ for (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$, $C_0 < C_0/k$). When the zone-levelling is performed on this ingot, the crystal has a solute concentration of $C_0$ ($SC$) throughout the crystal as liquid $LC$ freezes to $SC$ except at the top of the crystal where the molten zone is stopped (blue solid line in Fig. 3.2b). Therefore, it is particularly important to control the initial liquid-solid interface to coincide with the $LC$-$SC$ junction (between orange and grey regions of the ingot in Fig. 3.2a). For $k \neq 1$, the normal freezing method (i.e. Bridgman method) would result in a gradually changing solute concentration (green solid line in Fig. 3.2b) and not a homogeneous ingot with the desired composition $C_0$. 

Fig. 3.2. Apparatus and method of zone-levelling. (a) Schematic diagram of zone-levelling apparatus. A sealed ampoule with an ingot of liquidus composition \((LC\) in orange\) and another ingot of solidus composition \((SC\) in grey\) in contact is positioned at the center of induction coil. The \(LC\) and \(SC\) correspond to solute concentration of \(C_0/k\) and \(C_0\) in Fig. 2b, respectively. All the \(LC\) ingot is currently in molten state (part of ingot in orange is within the induction coil). For uniform mixing of solute, the sealed ampoule rotates while moving downwards in a constant rate. (b) Concentration profile for the zone-levelling method compared to normal freezing (Bridgman method). Solute concentration of an ingot before zone-levelling is shown in blue dashed line. That of another ingot before normal freezing is in green dotted line. Resulting solute concentrations of crystals after zone-levelling and normal freezing are expressed in blue and green solid lines, respectively.

Although pseudo-binary phase diagram for \(\text{Bi}_2\text{Te}_3–\text{Sb}_2\text{Te}_3\) can be found in literature\(^{12}\), in order to tune hole carrier concentration with excess Te in \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_{3+\delta}\) a ternary phase diagram of Bi-Sb-Te is required. However, because a sufficient Bi-Sb-Te ternary phase diagram is not available (only the liquidus projection has been studied) numerous melted ingots with a single composition have been solidified to characterize their solid (frozen) compositions. Only those ingots \((LC)\) which freeze (after being melted) to \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_{3+\delta}\) \((SC)\) are presented in this paper. Preparing a sealed ampule with both ingots of \(LC\) and \(SC\) is illustrated in Fig. 3.3.
Fig. 3.3. Schematic description of preparing a sealed ampoule with two ingots with different compositions in contact for zone-levelling and picture of cut crystal after zone-levelling. All the sealed ampoules from Fig. 3.3a to 3.3f are under vacuum. Powder is depicted in spheres. Once the powder is melted in furnace (3.3b) and quenched in water an ingot is formed as in 3.3c. Top of the ampoule in 3.3c is cut and SC powder is poured on top of the LC ingot (3.3d). Only SC powder is melted while keeping the LC ingot in room temperature (3.3e). The ampoule in 3.3e is inverted upside down for the melted SC to flow down to LC ingot. As soon as the melted SC is in contact with the LC ingot the entire ampoule is quenched in water to prepare a sealed ampoule with LC and SC in contact (3.3f). Picture of a parallelepiped shape sample set up for electrical resistivity and Hall coefficient measurement (3.3g). Inset shows the sample alone.

Parallelepiped (4×1.5×12 mm³) and disk shape samples (6 mm diameter and 1.5 mm thick) were cut from the zone-levelled crystals for electrical resistivity, Hall effect, Seebeck coefficient, and thermal conductivity measurements along the growth direction. The parallelepiped shape sample mounted on an apparatus for measuring electrical resistivity and Hall coefficient is shown in Fig. 3.3g.

3.3 Two valence band behavior in p-type (Bi₁₋ₓSbₓ)₂Te₃

The band structure of Bi₂Te₃ and Sb₂Te₃ has been extensively studied³⁶,³⁹-⁴² showing the bands and Fermi surfaces are clearly complex with several distinct band extrema off the high symmetry points (all on the plane containing the G, Z, U, A, F, L points). The combination of complex band structure and anisotropic Fermi pockets (Fig. 3.1c) found in Bi₂Te₃ contributes to the high η and σ at the same time¹⁴. Different density functional theory (DFT) methods predict different energies for the different band extrema. Based on locations of valence band edges⁴⁰,⁴² and calculated hole mass tensor parameters associated with the valence band edges⁴², Fermi pockets of Bi₂Te₃ are illustrated as in Fig. 3.1c. The second valence band (VB₂, green ellipsoids in Fig. 3.1c) close to the first valence band (VB₁, purple ellipsoids) in energy is also shown
(calculated $\Delta E_{VB1-VB2}$ is 27 meV from ref. 42 and 3.8 meV from ref. 40 – our fitted $\Delta E_{VB1-VB2}$ is 30 meV as in Fig. 3.1d). Because both hole pockets for $VB_1$ and $VB_2$ lie in a mirror plane of $Bi_2Te_3$ Brillouin zone ($k_y-k_z$ plane in Fig. 3.1c), they both have three-fold rotation and inversion symmetry; by being off the $\Gamma$–$Z$ line their degeneracies are $N_y = 6$.

Here we propose a schematic band structure of $(Bi_{1-x}Sb_x)_{2}Te_3$ alloys with two valence bands contributing to transport, contrary to previous reports in which only a single valence band was considered$^{22,34,35}$. After Drabble showed that a model assuming one valence band with $N_y = 6$ could be made to fit galvanomagnetic measurements on single crystal of $p$-type $Bi_2Te_3$ ($x = 0$)$^{13}$, the band structure of even other compositions was assumed to have a single valence band. Gaidukova et al.$^{35}$ determined the density-of-states effective mass ($m^*$) from measured Seebeck data of the alloys ($0.5 \leq x \leq 1$) using the Single Parabolic Band (SPB) model$^8$. When the $m^*$ was plotted against the composition ($x$), a peak was observed at $x = 0.75$. A similar result was reported by Stordeur et al.$^{22}$ where the $m^*$ and its components along different directions in k-space (as a function of $x$) were calculated from thermoelectric transport data and reflection spectra concluding that the single valence band suddenly becomes heavy in one direction.

To understand the cause of the maximum $m^*$ at $x = 0.75$, we have first conducted semi-empirical SPB modelling$^8$ on experimental Seebeck coefficient ($S$) and the Hall mobility ($\mu_H$) from the literature ($0 \leq x \leq 1$) and the samples prepared here ($x = 0.75$) to extract single band $m^*$ and intrinsic mobility ($\mu_0$, which scales with $\mu_H$) for different $x$ (Fig. 3.1a and 3.1b). Because of the marked anisotropy of the layered structure of $(Bi_{1-x}Sb_x)_{2}Te_3$ (i.e., hexagonal crystal system)$^{36}$, only the S and the $\mu_H$ measured perpendicular to the trigonal axis of single-crystal samples ($c$-axis in the hexagonal system) were used in the modelling (the $zT$ perpendicular to the $c$-axis is higher than that along the $c$-axis$^{11}$).

The fact that the $\mu_0$ does not change dramatically with $x$ like $m^*$ suggests that this is not due to a change in mass of a single band (Fig. 3.1b). This is because the mobility is not only inversely proportional to the inertial effective mass in the direction of transport ($a$-$b$ plane) but also inversely proportional to the density
of states mass $m_b^{*3/2}$ of electron states it can scatter into (deformation potential e.g. acoustic phonon scattering dominates)\textsuperscript{29}.

For a Fermi surface consisting of $N_f$ equivalent conducting carrier pockets (or valleys in the band structure) each with density-of-states mass, $m_b^*$, the overall equivalent density of states mass is given by $m^* = N_f^{2/3}m_b^*$. Thus $\mu_0$ directly reflects the shape of the band around a charge carrier regardless of the total number of conducting bands while $m^*$ is a measure of the total density of states including the number of bands contributing.

According to Fig. 3.1a, where the $m^*$ peaks at $x = 0.75$ (equivalent to previous results\textsuperscript{22,35}), it can be said that $N_f$ or $m_b^*$ (or even both) peaks around $x = 0.75$. The absence of a dip in $\mu_0$ at $x = 0.75$ (Fig. 3.1b) eliminates the possibility of $m_b^*$ increasing at $x = 0.75$ but instead suggests that the increase in $m^*$ is a result of the $N_f$ peaking around $x = 0.75$.

We postulate that convergence of two valence bands is responsible for the high $N_f$ at $x = 0.75$. The existence of the second valence band has been reported for both Bi$_2$Te$_3$ ($x = 0$)\textsuperscript{43-45} and Sb$_2$Te$_3$ ($x = 1$)\textsuperscript{46-50} from Shubnikov–De Haas measurements. Although $\Delta E$ between the first and second valence bands at $x = 0$ (15 meV)\textsuperscript{44} and $x = 1$ (150 meV)\textsuperscript{47} were also deduced, because these values were estimated at a low temperature (4.2 K) they could be significantly different at 300 K. Band movements with temperature of this magnitude are observed in PbTe\textsuperscript{51}. Therefore we only assume that the $VB_1$ (purple line in Fig. 3.1d) and the $VB_2$ (green line in Fig. 3.1d) cross each other at $x = 0.75$ (for simplicity, energies of both bands are assumed to vary linearly with composition $x$). The energy difference between $VB_1$ and $VB_2$ at $x = 0$ and $x = 1$ are fitted ($\Delta E_{VB_1-VB_2}$ in Fig. 3.1d).

Besides $\Delta E_{VB_1-VB_2}$, the composition-dependent energy band gap $E_g(x)$ between the lowest conduction band and the highest valence band was required to construct the band diagram for (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ (Fig. 3.1d). The true optical energy band gap (at 300 K) utilized here is from Sehr and Testardi\textsuperscript{20}. They estimated it by subtracting the Burstein–Moss shift from the observed energy band gap. As the intrinsic hole carrier density
increases rapidly as \( x \) gets close to 1, this correction increases and with it the uncertainty in the optical gap\(^{21}\). Sehr and Testardi’s data only for \( 0 \leq x \leq 0.75 \) were used. Based on the \( E_g(x) \) \((0 \leq x \leq 0.75)\), two fitted \( \Delta E_{VB1-VB2} \) \((x = 0 \text{ and } 1)\), and proposed band convergence at \( x = 0.75 \) \((\Delta E_{VB1-VB2} = 0)\) the energies of the two bands for other compositions were extrapolated as in Fig. 3.1d.

### 3.4 Transport properties calculated by the two-band model

We incorporated the band structure information given in Fig. 3.1d into multi-band and nonparabolic-band\(^{52}\) (due to its narrow energy band gap\(^{22,45}\)) modelling of the thermoelectric properties of \((\text{Bi}_{1-x}\text{Sb}_x)\text{Te}_3\). Approximately linearly varying density-of-states effective mass \( (m^*) \) and deformation potential \( (\Xi \propto \mu_0^{-1/2}) \) throughout the composition \( (x) \) for each valence band were determined by fitting them to \( S \) and \( \mu_H \) (both as functions of \( n_H \) for \( 0 \leq x \leq 1 \)) under the acoustic phonon scattering and alloy scattering assumptions (Fig. 3.4a). A constant valley degeneracy \( (N_v) \) of 6 was used in all \( x \) for both valence bands\(^{40,53,54}\) (see Fig. 3.1c). Anisotropy in the Fermi pockets \( (m_{||}^*/m_\perp^* \neq 1) \), where \( m_{||}^* \) and \( m_\perp^* \) are effective masses along the longitudinal and transverse ellipsoid direction, respectively) of \((\text{Bi}_{1-x}\text{Sb}_x)\text{Te}_3\) (Fig. 3.1c), which was obtained by Stordeur et al.\(^{22}\) was included in the two-band (TB) modelling. Stordeur et al.\(^{22}\) assumed that a single valence band \( (N_v = 6) \) contributed to transport to calculate the anisotropy. Thus the anisotropy was only adopted in the highest valence band in Fig. 3.1d \((VB_1 \text{ for } 0 \leq x < 0.75 \text{ and } VB_2 \text{ for the rest } x)\). Lastly, the \( \mu_H \) reduction due to alloy scattering was also taken into account for alloy compositions (except \( x = 0 \) and 1)\(^{18}\). The TB model results (orange line in Fig. 3.4b and 3.4c), those of the SPB model (green line), and experimental data are given in Fig. 3.4b and 3.4c for \( x = 0.75 \). Even though both TB model and SPB model closely followed the measured \( S \) in all \( n_H \), the TB model was slightly better at describing measured \( \mu_H \) at \( n_H > 10^{20} \text{ cm}^{-3} \).
Fig. 3.4. Two-band related property as a function of composition ($x$) and transport properties as a function of Hall carrier concentration ($n_H$) for (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ at 300 K. (a) Density-of-states effective masses ($m^*$) used in the two-band (TB) model to calculate Seebeck coefficient ($S$) (b) and Hall mobility ($\mu_H$) (c). The TB model (orange line) was fitted to the experimental results (empty circles in orange) and the literature data from Ref. 35, 22, 55, and Ref. 56 (empty shapes in blue). The result of SPB model (green line) was also plotted for comparison.

Calculated density-of-states effective masses ($m^*$) for both bands in the TB model (Fig. 3.4a) decrease linearly with $x$ (Fig. 3.4a). It should be noted that, for example at $x = 0$, $m_{VB2}^*$ is heavier than $m_{VB1}^*$ (Fig. 3.4a) but $VB2$ is lower than $VB1$ in energy (Fig. 3.1d). The $m_{VB1}^*$ and $m_{VB2}^*$ decrease only by ~5% and
~15%, respectively, as \( x \) increases from 0 to 1. The greater change in \( m_{VB2}^* \) allows the lower energy valence band (\( m_{VB2}^* \) for \( 0 \leq x < 0.75 \) and \( m_{VB1}^* \) for the rest \( x \)) to stay heavier than the highest band for all \( x \) (Fig. 3.4a and 3.1d) despite the bands crossing at \( x = 0.75 \). Literature on the band parameters of the first and second valence bands in \((\text{Bi}_1-x \text{Sb}_x)_2\text{Te}_3\) was scarce to support the reliability of the TB model for all compositions \( (x) \). For example, Sologub et al.\textsuperscript{53} could not determine relative energies of the two bands in \( \text{Bi}_2\text{Te}_3 \) despite the band parameters acquired for both bands from galvanomagnetic measurements. However, Köhler et al.\textsuperscript{48} tentatively extrapolated the \( m^* \) of the highest valence band for \( 0 \leq x \leq 0.6 \) (0.3 \( m_e \)) up to \( x = 1 \) with a brief mention of the \( m^* \) in the second valence band being comparable to that estimated for \( \text{Bi}_2\text{Te}_3 \) \( (x = 0) \) by von Middendorff and Landwehr\textsuperscript{44} for all \( x \) (1.25 \( m_e \)). In spite of the fact that the extrapolation of both the \( m^* \) to \( x = 1 \) was based on a tentative assumption, we could at least find that the second band being heavier than the first band at \( x = 0 \) was in agreement with our results. For \( x = 0 \), Kulbachinskii et al.\textsuperscript{57} and Biswas et al.\textsuperscript{43} confirmed that the second valence band was heavier than the first band. While the \( m^* \) of the highest valence band in \( \text{Sb}_2\text{Te}_3 \) \( (x = 1) \) was deduced by von Middendorff et al.\textsuperscript{47}, the lack of information on the \( m^* \) of the second band made direct comparison of the literature and our study difficult. Nonetheless, the \( m^* \) of the second band (\( m_{VB1}^* \) at \( x = 1 \) in Fig. 4a) being heavier than that of first band (\( m_{VB2}^* \)) at \( x = 1 \) was also reported by Kulbachinskii et al.\textsuperscript{58}.

### 3.5 Optimizing the \( zT \) at 300 K via carrier concentration control

The carrier concentration of \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3\) was controlled via the amount of excess Te. Based on the TB model and the lattice thermal conductivity taken from Goldsmid\textsuperscript{59}, the \( zT \) (for \( x = 0.75 \)) was predicted as in Fig. 3.5 (orange solid line) with its maximum of 1.03 at \( n_H = 1.3 \times 10^{19} \text{cm}^{-3} \) (300 K). However, when stoichiometric \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3\) was synthesized with the liquidus composition (\( LC \)) of Bi : Sb : Te = 18 : 22 : 60 in at. %, and solidus composition (\( SC \)) of Bi : Sb : Te = 10 : 30 : 60 (at. %) in reference to the pseudo-binary phase diagram\textsuperscript{12} of \( \text{Bi}_2\text{Te}_3\)--\( \text{Sb}_2\text{Te}_3 \) the resulting \( n_H \) was close to 6.7\( \times 10^{19} \text{cm}^{-3} \) (with \( zT \approx \)
0.6). As an excess Te should suppress Sb$_{Te}$ antisite defects that produce holes$^{12}$ and hence increase $S$, attempts to produce homogenous (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ oriented crystals with excess Te were made. As the complete ternary phase diagram including solidus and liquidus tie-lines is not known, the compositions used resulted from an iterative process.

![Graph of $zT$ versus $n_H$](image)

**Fig. 3.5.** $zT$ as a function of Hall carrier concentration ($n_H$) for (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ at 300 K. The experimental results (empty shapes in orange) and the literature data of Ref. 12 (empty diamond in grey), and prediction from the TB model were plotted.

Experimentally, the 17–20 % improvement in $zT$ (1.05 at $n_H = 2.6 \times 10^{19}$ cm$^{-3}$) was achieved via carrier concentration tuning when compared to $zT = 0.87$ from Scherrer and Scherrer$^{12}$ (empty grey diamond in Fig. 3.5), and the $zT$ of 0.9 (at 300 K) of Yim and Rosi$^{25}$ (not be shown in Fig. 3.5 as its $n_H$ was not provided).

In summary, the best $zT$ performance from $x = 0.75$ in (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloys is explained with two valence bands converging at $x = 0.75$. A two band transport model satisfactorily explains the experimental thermoelectric transport data for (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloys within a framework consistent with low temperature measurements and theory indicating a complex band structure. Based on the two-band model predicting higher $zT$ for lower carrier concentrations, a (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_{3+\delta}$ oriented crystal was fabricated via zone levelling with excess Te. The successful suppression of holes from Sb$_{Te}$ anti-site defects results in a $zT$ of
1.05 at 300 K. This value is about 17 % higher than the commonly known best $zT$ for $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}$ crystals. Further improvements in $zT$ are expected in fine-grained and nanostructured materials due to reduced lattice thermal conductivity.
Chapter 4

Phonon engineering through grain boundary dislocations in polycrystalline (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$

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4.1 Introduction

Bismuth antimony telluride alloys are the most widely used thermoelectric bulk material developed in the 1960’s for Peltier cooling with $p$-type composition close to Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and peak $zT$ of 1.1 near 300 K (ref. 12). The Bi-Sb atomic disorder in Bi$_{0.5}$Sb$_{1.5}$Te$_3$ scatters the heat carrying phonons, reducing $\kappa_l$ that permits such high $zT$ values. Matched with Bi$_2$Te$_3$ based $n$-type alloys, devices are commercially produced that provide a maximum temperature drop ($\Delta T_{\text{max}}$) of 64 – 72 K with 300 K hot side ($T_h$) (ref. 11). Recent measured improvements in $zT$ of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ bulk alloys have been reported using strategies primarily based on nanometer-scale microstructures to add boundary scattering of phonons at the composite interface or grain boundaries$^{27,60-62}$. However, improvements in the performance ($\Delta T_{\text{max}}$) of Peltier cooling devices have not been realized since the development of bismuth antimony telluride$^{11}$.

Heat carrying phonons cover a broad spectrum of frequencies ($\omega$) and the lattice thermal conductivity ($\kappa_l$) can be expressed as a sum of contributions from different frequencies$^{11,63}$: $\kappa_l = \int \kappa_s(\omega) d\omega$. The spectral lattice thermal conductivity $\kappa_s(\omega)$ can be expressed as arising from the spectral heat capacity of phonons $C_p(\omega)$, their velocity $v(\omega)$, and their scattering time $\tau(\omega)$ such that $\kappa_s(\omega) = C_p(\omega) \times v^2(\omega) \times \tau(\omega)$. Phonons in all crystalline materials are scattered by other phonons by Umklapp scattering, which generally has a $\tau_U^{-1} \sim \omega^2$ dependence. Combining this with the Debye approximation for heat carrying phonons ($C_p(\omega) \sim \omega^3$)
gives $\kappa(\omega) = \text{constant}$. This leaves a wide range of phonon frequencies where all frequencies contribute to the thermal conductivity (Fig. 4.1a).

![Fig. 4.1. Full-spectrum phonon scattering in high-performance bulk thermoelectrics. (a) The inclusion of dislocation scattering (DC + DS) is effective across the full frequency spectrum. Boundary (B) and point defect (PD) are effective only at low and high frequencies. The acoustic mode Debye frequency is $f_a$. (b) Lattice thermal conductivity ($\kappa_l$) for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloys produced by melt-solidification (Ingot), solid-phase compaction (BM, S-MS) and liquid-phase compaction (Te-MS). The lowest $\kappa_l$ of Te-MS can be explained by the mid-frequency phonon scattering due to dislocation arrays embedded in grain boundaries (inset). (c) The figure of merit ($zT$) as a function of temperature for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloys. The data points (red) give the average ($\pm$standard deviations) of all 30 Te-MS samples (inset), which shows excellent reproducibility. (d) A Peltier cooling module (right) with 127 couples made from $p$-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ Te-MS pellet (left) and $n$-type 1 wt. % SbI$_3$ doped Bi$_2$Te$_2.7$Se$_0.3$ ingot. (e) The maximum coefficient of performance ($\text{COP}_{\text{max}}$) measured on modules of (d) where the high-performance is confirmed with notably high $\Delta T_{\text{max}}$ of 81 K with 300 K hot side.

The $\kappa_l$ can be further reduced with additional scattering mechanisms. Traditional mechanisms are only effective at the high or low frequency ends\textsuperscript{11}. Point defect scattering of phonons from the Bi-Sb disorder in Bi$_{0.5}$Sb$_{1.5}$Te$_3$ targets high frequency phonons with a scattering time depending on frequency as $\tau_{PD}^{-1} \sim \omega^4$ (ref. 11), similar to Rayleigh scattering. However, boundary scanning of phonons targets low frequency phonon as it is frequency independent\textsuperscript{64} ($\tau_B^{-1} \sim \text{constant}$). Even the scattering of nanometer-sized particles can be well described with these two models as the small size Rayleigh regime rapidly crosses over to the boundary regime as the particle size increases\textsuperscript{65}. A full-spectrum strategy targeting the wide spectrum of phonons including mid-frequency phonon scattering is necessary for further reduction in $\kappa_l$. However, at the same time the high carrier mobility ($\mu$) must be maintained because the maximum $zT$ of a material is
determined by the ratio \( \mu/\kappa \) (quality factor). Thus, any reduction in \( \kappa \) by phonon scattering must not be compensated by a similar reduction in \( \mu \) due to electron scattering for there to be a net benefit.

### 4.2 Liquid-phase compacting process

![Figure 4.2](image)

Fig. 4.2. Comparison of thermoelectric properties of Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) between different fabrication methods. Introduction of dislocation arrays has a large effect on thermal conductivity but a small effect on electronic conductivity. (a) Temperature dependence of electrical conductivity (\( \sigma \)). Charge carrier mobilities of S-MS (190 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) are lower than for Te-MS (280 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) materials (Inset). (b) Temperature dependence of Seebeck coefficient (\( S \)) and power factor (\( \sigma S^2 \)) (Inset). Temperature dependences of total (c) and lattice (d) thermal conductivity (\( \kappa_{\text{total}}, \kappa_{\ell} \)) for all samples. The error bars of Te-MS in all panels are the standard deviations from the measurements of 30 samples.

Liquid-phase sintering produces low energy, semi-coherent grain boundaries that one can expect to have a minimal impact on electron scattering. The techniques to engineer and characterize grain boundaries have
been well established in materials science due to their importance in engineering the mechanical strength\textsuperscript{66},
magnetism\textsuperscript{67}, and other material properties\textsuperscript{68}. Most importantly, the periodic dislocations that can arise from
such low energy grain boundaries add a new mechanism that targets the mid-frequency phonons with both
\( \tau^{-1} \sim \omega \) and \( \tau^{-1} \sim \omega^3 \) dependence that is between those for point defect and boundary scattering\textsuperscript{11,63}. In
order to produce the periodic dislocations at low energy grain boundaries in Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} alloys, we applied
a simple liquid-phase compacting process. The process differed from typical liquid-phase sintering as it
included applied pressure and transient flow of the liquid phase during compaction. The process greatly
reduced \( \kappa_l \) to 0.33 W m\textsuperscript{-1} K\textsuperscript{-1} at 320 K (Fig. 4.1b, Fig. 4.2d) and resulted in an exceptionally high \( zT \) of 1.86 ± 0.15 at 320 K for dozens of independently measured Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} samples (Fig. 4.1c) used to make a
Peltier cooling module with 127 couples (Fig. 4.1d). The module outperforms all known single stage Peltier
cooling modules\textsuperscript{11,69}, demonstrating a \( \Delta T_{\text{max}} \) of 81 K with \( T_h \) of 300 K (Fig. 4.1e). We compare ingot, ball
milled (BM), and stoichiometric melt spun (S-MS) Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} materials (Figs. 4.1 and 4.2). The latter
two types of samples were fabricated by using spark plasma sintering (SPS). Two different melt-spun
materials were synthesized, stoichiometric (S-MS), and with excess Te (Te-MS, Fig. 4.3a, red arrow).

Melt-spun samples have plate-like microstructure of S-MS and Te-MS ribbons with platelets several
micrometers wide and several hundred nanometers thick (Fig. 4.3b). The Te excess composition has an
eutectic microstructure over the entire ribbons that forms between the Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} platelets (Fig. 4.3b). The
eutectic phase consists mostly of elemental Te and a small amount of Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} nano-particles. During
the high temperature (480 °C) and pressure (70 MPa) process of SPS, above the melting point of Te (450
°C), the excess Te in the eutectic phase was liquidified and expelled to the outer surface of the graphite die
(Fig. 4.3c and Fig. 2.5).
4.3 Periodic arrays of dislocations at grain boundaries

The morphology of the grain boundary structure in the Te-MS material is remarkably different than the typical grain boundaries as found in the S-MS material. TEM images (Figs. 4.4b to 4.4j) reveals a Moiré pattern (up to 50 nm wide) at the grain boundaries between the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains in the Te-MS material (Fig. 4.4b), compared to the few nanometer width as observed in the S-MS material (Fig. 4.4a). Moiré patterns can be observed when the grain boundary plane is oblique to the TEM zone axis so the two crystals overlap along the viewing direction. The Moiré patterns indicate the grains are highly crystalline with clean grain boundaries in which the obscured dislocations exist. From the elemental mapping (TEM-EDS) in the Te-MS material, we confirmed no presence of excess Te at the grain boundaries, suggesting that the abnormal contrast is not due to a secondary phase.
Fig. 4.4. Dislocation arrays embedded in grain boundaries. (a) Low magnification TEM image of S-MS material. (b) Low magnification TEM image of a Te-MS material. (c) Enlarged view of boxed region in (b). The grain boundary indicated by red arrow is aligned along the zone axis showing only strain effects while the two grain boundaries at upper part show Moiré patterns. The high magnification TEM image of circled area is shown in fig. S15. (d) Enlarged view of boxed region in (c). The insets are FFT images of adjacent grains crossing a twist-type grain boundary (GB). (e) FFT image of $(0 \, 1 \, 5)$ and $(0 \, 1 \, \bar{4})$ atomic planes of left and right grains in the inset (d). Along the boundary, edge dislocations, indicated as red symbols, are clearly shown. Burgers vectors of each dislocation is $\mathbf{B}_n = <0 \, 1 \, 5>$, parallel to the boundary. The misfit between the two planes are $\sim 0.15 \, \AA$ ($\sim 4.5 \%$), which compensates the misfit spacing of $\sim 6$ nm and is identical to the periodic patterns ($\sim 6$ nm spacing) in (f) and (g). (f) Enlarged view of boxed region in (b). A view of tilted zone axis from (c), showing periodic Moiré patterns along GBs. (g) Enlarged views of boxed region in (f). (h) Enlarged view of boxed region in (b). (i) Enlarged view of boxed region in (h). The insets are FFT images of adjacent grains crossing a tilt-type GB. (j) FFT image of $(0 \, 1 \, 5)$ atomic planes in the inset of (f). Burgers vectors of the each dislocation is $\mathbf{B}_n = <2 \, 1 \, 0>$, perpendicular to the boundary. The misfit spacing of $\sim 2.5$ nm was obtained. Insets of (c) and (j) are the IFFT images of boxed areas, respectively, clearly identifying the dislocations.
The clean grain boundary structure observed in Te-MS material requires the presence of periodic arrays of
dislocations that form at low energy grain boundaries. Figure 4.4c shows a grain boundary (indicated by
red arrow) aligned along the zone axis showing only strain effects. The indexing of fast Fourier-transformed
(FFT) images confirmed the coincidence of (0 1 4) and (0 1 5) atomic planes along the two adjacent grains
at the twist-type grain boundary with lattice spacing of 3.30 and 3.15 Å, respectively. Edge dislocation
arrays are found in inverse FFT (IFFT) images of Fig. 4.4d (Fig. 4.4e, red symbols). The dislocations
compensate for the $d$-spacing mismatch between the crystallographic planes of adjacent grains, which is ~
0.15 Å (4.5 %) between (0 1 5) and (0 1 4) atomic planes, introducing misfit spacing of ~ 6 nm. This
mismatch is identical, as expected$^{70}$, to the periodicity in the translational Moiré patterns of the grain
boundary observed in Figs. 4.4f and 4.4g, which were taken by slightly tilting the zone axis from that of
Figs. 4.4c and 4.4d. Dislocation arrays with the periodic spacing of ~ 2 nm were observed together with
Moiré fringes at the circled area (in blue) of upper grain boundary in Fig. 4.4c. Another array of dislocations
was observed in tilt-type boundary in Fig. 4.4h. The FFT images in the inset of Fig. 4.4i revealed the 5°
misorientation between two adjacent grains and inverse IFFT image of (0 1 5) atomic planes in Fig. 4.4j
and dislocation arrays with the misfit spacing of ~ 2.5 nm. Such dislocation arrays are expected to be present
in low angle grain boundaries or between grains with small $d$-spacing mismatch to lower the interfacial
energy$^{71}$. The dislocation arrays observed here have a close spacing between cores of ~2.5 – 6 nm, which
considering the size of the grains corresponds to an areal dislocation density of ~$2\times10^{11}$ cm$^{-2}$ that is 100
times higher than that observed in grains of Bi$_2$Te$_3$ (ref. 72).

In a typical solid-phase sintering, the grain boundaries have random alignment due to a limited diffusion
length of atoms/dislocations, and so the chance of low angle boundary ($< 11^\circ$) is very low$^{71}$. In contrast, in
liquid-phase sintering, the wetting liquid penetrates into the grain boundaries$^{73}$. Atoms in a liquid have
much higher diffusivities and also dislocations at the grain boundaries have much higher diffusion lengths$^{74}$.
The high solubility of Bi and Sb in the Te liquid and insignificant solubility of Te in the solid phase
contributes to the very rapid mass transport (over 100 times faster than in solids) and rapid rearrangement
of the grains\textsuperscript{73}. In addition, the capillary force of the liquid at the grain boundary exerts a force facilitating grain rearrangement\textsuperscript{73,75}.

However, the liquid-phase becomes absorbed in the matrix of the grain in a typical transient liquid phase sintering, leading to compositional variation of the matrix. This prohibits the application of traditional liquid-phase sintering for thermoelectric Bi-Sb-Te because compositional variation will degrade the TE properties. In contrast, the liquidified excess Te in the eutectic phase is expelled during the high pressure-assisted liquid-phase compacting processing. Any slight amount of Te remaining is nearly insoluble in Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} and does not as dramatically affect the carrier concentration. Furthermore, the applied pressure induces additional stresses which helps create dislocations\textsuperscript{75} and accelerate grain rearrangement\textsuperscript{73}. As a result, the grain interfaces rearrange to allow low energy grain boundaries, which results in dislocation arrays within much of the grain boundary.

From the thermal and electrical transport properties it appears that the semi-coherent grain boundaries of Te-MS material do maintain high charge carrier mobility but provide sufficient atomic strain to scatter heat carrying phonons. The small increase in Seebeck coefficient is due to a slight decrease in carrier concentration for S-MS and Te-MS materials compared to the Ingot material (Fig. 4.2b). The reduced grain size of the S-MS and Te-MS materials leads to lower carrier mobility. This decrease is less dramatic for Te-MS indicating the semi-coherent grain boundaries in Te-MS are less disruptive to charge carriers than those in the S-MS material (Fig. 4.2a). Low energy grain boundaries in Bi-Sb-Te are likely formed when atomic displacements are primarily in the Te-Te van der Waals layer, which have been observed experimentally\textsuperscript{76}. Displacements in this layer are also likely to be least disruptive to the charge carriers and maintain high mobility.

While the dense dislocation arrays embedded in grain boundaries do little to scatter charge carriers, they are remarkably efficient at scattering phonons and greatly reducing thermal conductivity in the Te-MS material (Fig. 4.2d). The $\kappa_i$ values were extracted from $\kappa_{\text{total}}$ by subtracting the electronic thermal
conductivity ($\kappa$), which was estimated using the Wiedemann-Franz relation. We calculated the Lorenz number ($L_0$) using the reduced Fermi energy obtained from measured $S$ values at different temperatures. The calculations indicate that dislocation arrays embedded in grain boundaries cause the reduction of $\kappa$. The $\kappa$ value at 320 K (0.33 W m$^{-1}$ K$^{-1}$) of the Te-MS sample is comparable to the reported value (0.29 W m$^{-1}$ K$^{-1}$) in highly deformed Bi$_{0.2}$Sb$_{1.8}$Te$_3$ with high-density lattice defects[77], indicating that dense dislocation arrays at grain boundaries are effective to reduce the $\kappa$.

### 4.4 Reinforced phonon scattering from dislocation strain field

We have modeled the temperature dependent $\kappa$ of BM, S-MS and Te-MS materials based on Debye-Callaway model[78] using parameters derived from independently measured physical properties (Fig. 4.1b). The total phonon relaxation time ($\tau_{\text{total}}$) was estimated by including scattering from Umklapp processes ($\tau_U$) and point defects ($\tau_{PD}$) using parameters based on bulk alloys[63,79,80]. We used microscopy to determine the parameter of average grain size ($d$) for the grain boundary scattering[70] ($\tau_B$). The calculated $\kappa$ (0.66 W m$^{-1}$ K$^{-1}$ at 300 K) for BM matches the measured data well, verifying the values used for Umklapp processes ($\tau_U$) and point defects ($\tau_{PD}$) of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloys. The 18 % reduction in $\kappa$ observed in S-MS material relative to BM material at 300 K is explained by a grain size reduction from 50 μm to 300 nm. The additional 29 % reduction in $\kappa$ for Te-MS material is explained by introducing phonon relaxation times associated with additional scattering from dislocation cores ($\tau_{DC}$) and strain[81-83] ($\tau_{DS}$), using the experimentally determined dislocation density (~2×10$^{11}$ cm$^{-2}$) and the effective Burgers vector ($B_D$ of ~12.7 Å).

This analysis shows that the periodic spacing of dislocation arrays plays a vital role for reducing $\kappa$. When the spacing between dislocation cores is small as observed in Te-MS material, the scattering from dislocation strain is reinforced[84]. This effect was experimentally observed in Ag-Cd alloys with the large scattering effect as due to the dislocation pile-up[64]. When dislocations are closely spaced the effective Burgers vector ($B_D$) is the sum of the individual Burgers vectors involved[85]. As the scattering rate is...
proportional to \( B_D^2 \), this pile-up of dislocation strain leads to a non-linear increase in scattering. The exact amount of reinforcement is not precisely specified in the theory and leads to the only adjustable parameter in the model. Nevertheless, the Burgers vector that precisely fits the data is well within the range observed experimentally\(^76\) (more details regarding the \( \kappa \) modelling can be found in Chapter 5).

The dislocation scattering mechanism is particularly effective because it targets phonons not scattered sufficiently by the other mechanisms providing a full-spectrum solution to scatter phonons. Compared to Umklapp scattering (Fig. 4.1a), boundary scattering from grain boundaries (\( \tau_B^{-1} \sim \omega^0 \)) is efficient at scattering low frequency phonons but quickly become ineffective at higher frequencies. Conversely, point defects scatter mostly high frequency phonons (\( \tau_{PD}^{-1} \sim \omega^4 \)). However, most of the remaining heat carrying phonons have intermediate frequency around 0.63 THz (Fig. 4.1a) and avoid scattering from boundaries and point defects. The 0.63 THz phonons still carry 74\% of the heat they would have carried without any scattering from boundaries or point defects in the S-MS material. Including the dislocation scattering as found in the Te-MS material, the \( \kappa \) of 0.63 THz phonons drops to less than 45\% of the heat they would have carried with only Umklapp scattering (Fig. 4.1a).

The low thermal conductivity while maintaining high mobility results in a dimensionless figure of merit (\( zT \)) for Te-MS that reaches a maximum value of 2.01 at 320 K within the range of 1.86 ± 0.15 at 320 K for 30 samples (Fig. 4.1c), a much higher value than for S-MS or Ingot materials. Most importantly, for cooling applications, the \( zT \) at 300 K is high (1.72 ± 0.12), suggesting it should provide superior refrigeration than other materials. For example, the \( zT \) is the higher than that of nanograin\( \)n\( \) Bi\( \text{0.5Sb1.5Te3} \) alloy (dotted line in Fig. 4.1c) near room temperature. These results from the ability of dislocation arrays to enable a full-spectrum scattering of phonons due to a compounding effect not found in randomly dispersed dislocations inside grains. The present liquid-phase compaction method assisted with a transient liquid flow is highly scalable for commercial use and generally applicable to other thermoelectric systems such as PbTe, CoSb\( _3 \), Si-Ge alloys, and even engineer thermal properties of other thermal materials such as
thermal barrier coatings. This may accelerate practical applications of thermoelectric systems in refrigeration and beyond to waste heat recovery and power generation.

4.5 $\Delta T_{\text{max}}$ calculation of the Peltier cooler with the $p$-type Te-MS

The ultimate verification of the exceptional $zT$ comes from testing the performance of a Peltier cooler (Fig. 4.1d) made using Te-MS materials. A state-of-the-art Peltier device using the Te-MS as the $p$-type material and an $n$-type ingot material was made with cutting edge commercial methods. The device not only greatly outperforms a similar device made with the $p$- and $n$-type ingot materials (Fig. 4.1e), but also outperforms all commercial Peltier devices. We determined the coefficient of performance (COP = cooling power/input power) to assess the cooling performance of both Peltier devices. Maximum values for coefficient of performance (COP$_{\text{max}}$) were taken at different $\Delta T$ in COP versus input current. The values of COP$_{\text{max}}$ for two modules were plotted as filled circles in Fig. 4.1e. By assuming asymmetric thermal contact resistivity of the modules, following equation was derived from Gao Min’s equation for a module with symmetric thermal contacts.

$$\text{COP}_{\text{max}} = \left( \frac{1}{1+\frac{l_c}{T}} \right) \left[ \frac{R_c}{R_{th} - R_c} \left( \frac{1+Z R_c}{2} \right)^{1/2} \frac{R_h}{R_c} \right]^{1/2}, \quad \text{(Eqn. 4.1)}$$

where $l_c$ and $l$ are the length as shown in Fig. 4.5 and $r$ corresponds to thermal conductivity of thermoelements divided by that of the contact layers (substrate + contact + metal bonding in Fig. 1.3). Variables $r$ and $Z$ were adjusted to fit calculated COP$_{\text{max}}$ (lines in Fig. 4.1e) to experimental COP$_{\text{max}}$ (filled circles in Fig. 4.1e) data. The $\Delta T_{\text{max}}$ values are easily extracted from the COP measurements as the temperature difference reached when the cooling power vanishes.
A key characteristic performance metric of a Peltier cooler is $\Delta T_{\text{max}}$, which is directly related to the $zT$ of materials. While the $\Delta T_{\text{max}}$ of Peltier cooler made from the ingot materials falls within the range of current commercial devices, $64 \text{ K} < \Delta T_{\text{max}} < 72 \text{ K}$ for $T_h$ of 300 K, the Peltier cooler made with the Te-MS $p$-type material exhibits an $\Delta T_{\text{max}}$ of 81 K for $T_h$ of 300 K (Fig. 4.1e).


Chapter 5

Phonon scattering by grain boundary dislocations at low temperature

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5.1 Introduction

Significant improvements in thermoelectric materials have been achieved by suppressing heat conduction via phonons. Other than $\kappa_l$, all the materials variables in $zT$ are highly coupled to one another making the optimization of $zT$ a nontrivial task. Therefore, much effort has been devoted to reduce $\kappa_l$ in order to improve $zT$. Phonons scatter off any irregularities in the lattice. For example, alloy atoms, rattling atoms, and other point defects can reduce the phonon mean free path. If the unit cell contains a large number of atoms, phonon heat conduction is also impeded because of a large fraction of heat carrying optical phonons with low group velocities. The frequency dependence of the point-defect scattering ($\tau_{PD}^{-1} \sim \omega^4$, where $\tau$ and $\omega$ are the phonon relaxation rate and the phonon frequency, respectively) and Umklapp scattering ($\tau_{U}^{-1} \sim \omega^2$) makes both scattering mechanisms effective at high phonon frequencies.

Phonons at low frequencies can be targeted by frequency-independent boundary scattering ($\tau_B^{-1} \sim \omega^0$). The majority of efforts to decrease the grain size in nanostructured materials aim to maximize scattering of phonons at an increased density of boundaries (for low $\kappa_l$ superlattices, many efforts were focused on phonon localization). However, when the composition of nanostructures embedded in a matrix differs from that of the matrix the boundary scattering alone cannot describe the intensity of scattering at the interfaces accurately. He et al. observed misfit dislocations at the interfaces of spinodally decomposed...
PbTe and PbS (nanoscale in size). In addition to the boundary scattering, He et al. included scattering from dislocations to predict the phonon scattering at interfaces/boundaries. However, amid many other scattering mechanisms considered, the importance of dislocation scattering in reducing $\kappa_l$ was not fully stressed. 

Recently, Kim et al.\(^1\), developed a pathway to encircle grains of polycrystalline $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with dense dislocation arrays to achieve a substantial $\kappa_l$ reduction ($zT = 1.86$ at 320 K). In contrast to the previous misfit dislocations at interfaces of a two-phase material\(^8\), the dislocation arrays were formed along grain boundaries of single phase $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. Kim et al. demonstrated that the grain boundary dislocation scattering was responsible for the dramatic reduction in $\kappa_l$. Nonetheless, the effect of dislocation scattering mechanism at low temperature was not studied.

In this work, we present the low temperature experimental $\kappa_l$ of the sample whose maximum $zT$ is 1.86 (at 320 K). Here we show that grain boundary dislocation scattering mechanism is required to model the $\kappa_l$ satisfactorily at low temperatures where boundary and dislocation scatterings are dominant. Both models used separately to calculate the $\kappa_l$ at high temperatures ($T > 300$ K) and at low temperatures ($T < 200$ K) are thoroughly discussed and compared.

### 5.2 Lattice thermal conductivity model for $T > 300$ K

The $\kappa_l$ can be calculated from the heat capacity of phonons ($C$), phonon velocity ($v$), total relaxation time ($\tau_{\text{total}}$), and the phonon frequency ($\omega$) as shown in Eqn. 5.1.

$$\kappa_l = \frac{1}{3} \int C(\omega) \cdot v^2(\omega) \cdot \tau_{\text{total}}(\omega) \, d\omega.$$  \hspace{1cm} (Eqn. 5.1)

Assuming that the phonon group velocity is constant (Debye model) and that scattering mechanisms are independent of each other, Callaway’s equation for the $\kappa_l$ can be approximated to

$$\kappa_l = \frac{k_B}{2\pi^2v} \left(\frac{k_B\hbar}{\pi}\right)^3 \int_0^{\theta_B/T} \frac{\tau_{\text{total}}(z) z^4 e^z}{(e^z-1)^2} \, dz,$$  \hspace{1cm} (Eqn. 5.2)
where \( k_B, h, \theta, \) and \( z \) are the Boltzmann constant, reduced Planck’s constant, acoustic Debye temperature, and \( \hbar \omega / k_B T \), respectively\(^97\). When the \( \tau_{total} \) is obtained from individual relaxation times \( (\tau_i) \) for different scattering mechanisms according to \( \tau_{total}(z)^{-1} = \sum_i \tau_i(z)^{-1} \) the calculation of \( \kappa_i \) using Eqn. 5.2 is straightforward. Therefore, a careful characterization of each \( \tau_i \) is essential to model \( \kappa_i \) with high predictive power.

Recently, a drastic \( \kappa_i \) reduction led to dramatic \( zT \) improvement in Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\)\(^{(1)}\). The \( \kappa_i \) of the polycrystalline samples (named as BM, S-MS, and Te-MS) produced using three different methods were computed consecutively to single out a cause for the reduction in thermal conductivity (Fig. 5.1). The BM sample was fabricated by ball-milling (hence the name BM) Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) ingots followed by Spark Plasma Sintering (SPS) the ball-milled powder. The S-MS and Te-MS samples were also sintered via SPS at the end. However, powders used in SPS for the S-MS and Te-MS were melt-spun from Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) ingots (S-MS, which stands for stoichiometric-MS) and from those with 25 wt. % Tellurium excess (Te-MS), respectively.

First, in order to calculate \( \kappa_i \) of the BM sample with 20 \( \mu \)m average grain size, relaxation times associated with Umklapp scattering \( (\tau_U) \), point-defect scattering \( (\tau_{PD}) \)\(^18\), and boundary scattering \( (\tau_B) \) were considered as relevant scattering mechanisms (Table 5.2). Although the \( \tau_B \) given by\(^63\)

\[
\tau_B^{-1} = \frac{v}{\alpha_d} , \quad \text{(Eqn. 5.3)}
\]

where \( d \) and \( \alpha_d \) are the experimentally determined grain size and the grain boundary transmission coefficient, respectively, has no free parameter \( (\alpha_d = 1 \) was used for \( T > 300 \) K), the \( \tau_U \) and the \( \tau_{PD} \) include variables, which need to be adjusted to the measured \( \kappa_i \). The Umklapp scattering is a phonon-phonon scattering in which the total crystal momentum is not conserved. Its relaxation time, \( \tau_U \), is of the form\(^63\)

\[
\tau_U^{-1} = A_N \frac{2}{(6\pi^2)^{1/3}} \frac{k_B V^{1/3}}{M v^3} y^2 \omega^2 T , \quad \text{(Eqn. 5.4)}
\]
where $V$, $γ$, $M$, and $A_N$ are the atomic volume, Grüneisen parameter, average atomic mass, and the free parameter, which takes momentum-conserving Normal scattering into account. Point-defect scattering originates from alloy atoms scattering phonons, which is expressed as:

$$τ_P^{-1} = \frac{V_4}{4πν^4} \Gamma,$$  \hspace{1cm} (Eqn. 5.5)

where $\Gamma$ is the scattering parameter. In Eqn. 5.5, another free parameter ($G$) is hidden inside of the $\Gamma$:

$$\Gamma = x(1 - x) \left[ \left( \frac{ΔM}{M} \right)^2 + \frac{2}{9} (G + 6.4γ) \left( \frac{Δa}{a} \right)^2 \right],$$  \hspace{1cm} (Eqn. 5.6)

where $x$, $ΔM$, $G$, $r$, and $Δa$ are the fractional concentration of either of constituents, difference in mass, parameter representing a ratio of fractional change of bulk modulus to that of local bond length, Poisson ratio, and the difference in lattice constant, respectively. The $A_N$ and $G$ in Eqn. 5.4 and 5.6, respectively were fit to experimental $κ_l$ varying with $x$ in (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloy by Stordeur and Sobotta to model $κ_l$ of BM sample in Fig. 5.1 (purple solid line). The use of reliable experimental literature data by independent scientists, which give values that are consistent with other studies and expected for this material, demonstrates the reasonableness of the model. Including parameters that were fitted, other material-dependent or experimentally determined parameters used to calculate theoretical $κ_l$ of the BM, S-MS, and Te-MS samples at high temperature (as shown in Fig. 5.1) are listed in Table 5.1. All the parameters in Table 5.1 except $A_N$, $B_{D, eff}$, $N_D$, and $α_t$ were also used in low temperature $κ_l$ modeling in Fig. 5.2.
Table 5.1. Parameters used to model $\kappa_l$ of BM, S-MS and Te-MS samples in Fig. 5.1 (at high temperature from ref. 1) and in Fig. 5.2 (at low temperature except $A_N$, $B_{\text{eff}}$, $N_D$, and $\alpha_t$).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Description</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_d$</td>
<td>acoustic Debye temp.</td>
<td>94 K</td>
<td>100</td>
</tr>
<tr>
<td>$v$</td>
<td>avg. phonon velocity</td>
<td>2147 m/s</td>
<td>101</td>
</tr>
<tr>
<td>$v_L$</td>
<td>longitudinal velocity</td>
<td>2884 m/s</td>
<td>101</td>
</tr>
<tr>
<td>$v_T$</td>
<td>transverse velocity</td>
<td>1780 m/s</td>
<td>101</td>
</tr>
<tr>
<td>$M$</td>
<td>atomic mass of BST†</td>
<td>2.22×10$^{-25}$ kg</td>
<td>–</td>
</tr>
<tr>
<td>$V$</td>
<td>atomic vol. of BST†</td>
<td>31.26 Å$^3$</td>
<td>63</td>
</tr>
<tr>
<td>$M_{\text{Bi}_2\text{Te}_3}$</td>
<td>atomic mass of Bi$_2$Te$_3$</td>
<td>2.79×10$^{-25}$ kg</td>
<td>–</td>
</tr>
<tr>
<td>$M_{\text{Sb}_2\text{Te}_3}$</td>
<td>atomic mass of Sb$_2$Te$_3$</td>
<td>2.07×10$^{-25}$ kg</td>
<td>–</td>
</tr>
<tr>
<td>$V_{\text{Bi}_2\text{Te}_3}$ ‡</td>
<td>atomic vol. of Bi$_2$Te$_3$</td>
<td>3.40×10$^{-29}$ m$^3$</td>
<td>–</td>
</tr>
<tr>
<td>$V_{\text{Sb}_2\text{Te}_3}$ ‡</td>
<td>atomic vol. of Sb$_2$Te$_3$</td>
<td>3.13×10$^{-29}$ m$^3$</td>
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</tr>
<tr>
<td>$A_N$</td>
<td>parameter in Eqn. 5.4</td>
<td>2.6</td>
<td>fit</td>
</tr>
<tr>
<td>$G$</td>
<td>parameter in Eqn. 5.6</td>
<td>23.8</td>
<td>fit</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Grüneisen parameter</td>
<td>2.3</td>
<td>102</td>
</tr>
<tr>
<td>$r$</td>
<td>Poisson’s ratio</td>
<td>0.24</td>
<td>103</td>
</tr>
<tr>
<td>$N_D$</td>
<td>dislocation density</td>
<td>2×10$^{11}$ cm$^{-2}$</td>
<td>exp.</td>
</tr>
<tr>
<td>$B_{\text{D,eff}}$</td>
<td>effective Burgers vector</td>
<td>12.7 Å</td>
<td>fit</td>
</tr>
<tr>
<td>$d_{\text{BM}}$</td>
<td>BM grain size</td>
<td>20 μm</td>
<td>exp.</td>
</tr>
<tr>
<td>$d_{\text{MS}}$</td>
<td>S-MS, Te-MS grain size</td>
<td>300 nm</td>
<td>exp.</td>
</tr>
<tr>
<td>$\alpha_t$</td>
<td>transmission coefficient</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>$c_0$</td>
<td>conc. of Bi$_2$Te$_3$</td>
<td>0.25</td>
<td>–</td>
</tr>
<tr>
<td>$K$</td>
<td>bulk modulus of Sb$_2$Te$_3$</td>
<td>44.8 GPa</td>
<td>102</td>
</tr>
<tr>
<td>$T_a$</td>
<td>annealing temp.</td>
<td>753 K</td>
<td>exp.</td>
</tr>
</tbody>
</table>

† BST = Bi$_{0.5}$Sb$_{1.5}$Te$_3$
‡ Lattice constant ($a$) was obtained by taking cube root of the atomic volume

Since, the only difference between the BM sample and the melt-spun Bi$_{0.5}$Sb$_{1.5}$Te$_3$ sample with 300 nm grain size (S-MS) was the size of the grain (20 μm in BM), $\kappa_l$ of the S-MS was calculated by simply changing the $\tau_B$ (to $d = 300$ nm) in the $\tau_{\text{total}}$ of the BM sample (Table 5.2) while keeping $\tau_U$ and $\tau_{PD}$ the same as for BM. A good fit between the theory (blue solid line) and the experimental data (empty blue circle) was achieved for the S-MS sample (Fig. 5.1).

Lastly, in order to compute $\kappa_l$ of melt-spun Bi$_{0.5}$Sb$_{1.5}$Te$_3$ sample with 25 wt. % Te excess (Te-MS), scattering relaxation times from dislocation cores ($\tau_{DC}$) and dislocation strain field ($\tau_{DS}$) were introduced to $\tau_{\text{total}}$ of S-MS (Table 5.2). Because the excess Te flowed out of the Te-MS sample during SPS (keeping its composition the same as the S-MS), and the grain size of the Te-MS was similar to that of S-MS, we could use the same $\tau_U$, $\tau_{PD}$, and $\tau_B$ in $\tau_{\text{total}}$ of the S-MS for that of the Te-MS. However, unlike S-MS, Moiré fringes indicative of dense dislocation arrays were observed in grain boundaries of the Te-MS sample. As arrays
of dislocations at grain boundaries can be equally treated as a sum of isolated dislocations inside a grain. The following equations can be used to describe grain boundary dislocation scattering in Te-MS:

\[ \tau_{DC}^{-1} = N_D \frac{v^{4/3}}{v^2} \omega^3, \quad \text{(Eqn. 5.7)} \]

\[ \tau_{DS}^{-1} = 0.6 \times B_{D,eff}^2 N_D (\gamma + \gamma_1)^2 \omega \left[ \frac{1}{2} + \frac{1}{24} \left(\frac{1-2r}{1-r}\right)^2 \left\{ 1 + \sqrt{2} \left(\frac{v_L}{v_T}\right)^2 \right\}^2 \right]. \quad \text{(Eqn. 5.8)} \]

where \( B_{D,eff}, N_D, \gamma, v_L, \) and \( v_T \) are the magnitude of effective Burgers vector, dislocation density, change in Grüneisen parameter, longitudinal phonon velocity, and the transverse phonon velocity, respectively. While determining \( \tau_{DC} \) is straightforward (\( N_D \) was computed with measured spacing between dislocation cores), an explanation is required on the details of the \( \tau_{DS} \) equation before using it. First of all, the numerical prefactor 0.6 in \( \tau_{DS} \) (Eqn. 5.8) is a product of the most recent constant of proportionality (1.1) Klemens placed in the \( \tau_{DS} \) formula (Klemens has modified the number multiple times and another factor of 0.55 to account for arrays of dislocation oriented in random directions. A factor of 18 was multiplied by Klemens to the first constant of proportionality (0.06) he theoretically calculated to minimize the discrepancy between the theory and experiments.

Further phonon scattering from inhomogeneously distributed solute atoms in alloys near grain boundary dislocations (due to the strain field) was accounted by a change of the Grüneisen parameter, \( \gamma_1 \), in Eqn. 5.8. Even though the solute atoms were treated as point defects to theoretically quantify \( \gamma_1 \), this scattering was different from the point defect scattering (Eqn. 5.5) in that it only described the combined scattering from modulation of the point defect concentration, not the scattering from individual point defects as in Eqn. 5.5. The \( \gamma_1 \) changes the intensity of scattering from the dislocation strain field. Eqns. 5.9 and 5.10 can be utilized to determine \( \gamma_1 \)

\[ \gamma_1 = \frac{V_{Sb_2Te_3} c_p k}{k_B r_a} (\gamma a^2 - \alpha \beta), \quad \text{(Eqn. 5.9)} \]
\[
\alpha = \frac{(V_{\text{Bi}_2\text{Te}_3} - V_{\text{Sb}_2\text{Te}_3})}{V_{\text{Sb}_2\text{Te}_3}} \quad \beta = \frac{1}{2} \frac{(M_{\text{Sb}_2\text{Te}_3} - M_{\text{Bi}_2\text{Te}_3})}{M_{\text{Sb}_2\text{Te}_3}},
\]  
(Eqn. 5.10)

where \(V_{\text{Bi}_2\text{Te}_3}\), \(V_{\text{Sb}_2\text{Te}_3}\), \(M_{\text{Bi}_2\text{Te}_3}\), \(M_{\text{Sb}_2\text{Te}_3}\), \(K\), \(c_0\), and \(T_a\) are the atomic volume of \(\text{Bi}_2\text{Te}_3\), that of \(\text{Sb}_2\text{Te}_3\), the average atomic mass of \(\text{Bi}_2\text{Te}_3\), that of \(\text{Sb}_2\text{Te}_3\), the bulk modulus of \(\text{Sb}_2\text{Te}_3\), the concentration of \(\text{Bi}_2\text{Te}_3\) in \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3\) and the sample annealing temperature. Because Te-MS is an alloy between \(\text{Sb}_2\text{Te}_3\) (75%) and \(\text{Bi}_2\text{Te}_3\) (25%), the \(\gamma_1\) estimated for Te-MS is 1.1 strengthening the scattering from the dislocation strain field (Eqn. 5.8) by a factor of \(~2.2\). Although this strengthening factor would vary depending on the details of alloys considered, the factor of 2.2 was physically attainable (order of magnitude wise) when considering that of copper-aluminum alloy \(^{109}\) (10 atomic % Al), which was experimentally estimated to be \(~2\) \(^{110}\).

Moreover, because the spacing between dislocations situated in grain boundaries of Te-MS (~2.5 nm) is smaller than the wavelength of most phonons (the median phonon wavelength contributing to \(\kappa_l\) of \(\text{Bi}_2\text{Te}_3\) is approximately 3.6 nm according to Wang’s calculation \(^{111}\)) those parallel dislocations can be grouped into one dislocation with larger effective Burgers vector \((B_{D,\text{eff}})\) \(^{106,112}\) fortifying the scattering from dislocation strain (Eqn. 5.8). However, owing to the uncertainty involved in this compounding effect and characterization of Burgers vector in dislocation arrays, the \(B_{D,\text{eff}}\) was fit to the experimental \(\kappa_l\) of Te-MS (green empty circles in Fig. 5.1). The fit \(B_{D,\text{eff}}\) value (12.7 Å) is reasonable when compared to the reported Burgers vectors in \(\text{Bi}_2\text{Te}_3\) \(^{113}\). The theoretical \(\kappa_l\) of Te-MS (green solid line in Fig. 5.1) agrees well with the measured data (green empty circles in Fig. 5.1) showing how effective scattering by dislocations is for reducing \(\kappa_l\). Individual relaxation times chosen to calculate \(\kappa_l\) of BM, S-MS, and Te-MS at high temperatures \((T > 300 \text{ K})\) are shown in Table 5.2.
Table 5.2 Contributions to the total relaxation rate ($\tau_{total}^{-1}$) used to model $\kappa_l$ of BM, S-MS and Te-MS samples from ref. 1 at high temperatures (“HT grey model” in Fig. 5.1 only).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_{total}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>$\tau_U^{-1} + \tau_{PD}^{-1} + \tau_{B(dBM, a_i=1)}^{-1}$</td>
</tr>
<tr>
<td>S-MS</td>
<td>$\tau_U^{-1} + \tau_{PD}^{-1} + \tau_{B(dMS, a_i=1)}^{-1}$</td>
</tr>
<tr>
<td>Te-MS</td>
<td>$\tau_U^{-1} + \tau_{PD}^{-1} + \tau_{B(dMS, a_i=1)}^{-1} + \tau_{DS}^{-1} + \tau_{PC}^{-1}$</td>
</tr>
</tbody>
</table>

5.3 Estimation of bipolar thermal conductivity at $T > 300$ K

Significant bipolar effects were present in the thermal conductivities of all three samples (BM, S-MS, and Te-MS) at high temperatures as observed in Fig 5.1. The bipolar contributions ($\kappa_{bp}$) were estimated by a two (parabolic) band model (an extension of a single parabolic band model (SPB)) assuming acoustic phonon scattering. In the two band model, thermoelectric parameters of each band (valence and conduction bands in this case) computed from Boltzmann transport equations (see ref. 8) can be substituted into the following equations,

\[
\sigma_{total} = \sum_i \sigma_i , \quad \text{(Eqn. 5.11)}
\]

\[
S_{total} = \frac{\sum_i S_i \sigma_i}{\sum_i \sigma_i} , \quad \text{(Eqn. 5.12)}
\]

\[
R_{H_{total}} = \frac{\sum_i R_{Hi} \sigma_i^2}{(\sum_i \sigma_i)^2} , \quad \text{(Eqn. 5.13)}
\]

\[
\kappa_{total} = \kappa_l + \sum_i L_i \sigma_i T \left( \sum_i S_i^2 \sigma_i - S^2 \sigma \right) T , \quad \text{(Eqn. 5.14)}
\]

where $R_{Hi}$ and $L_i$ are the Hall coefficient and the Lorenz number of each band (properties with subscript $i$ represent those of an individual band), respectively, used to calculate the total thermoelectric properties from the two bands. In Eqn. 5.14, $\sum_i L_i \sigma_i T$ and $\left( \sum_i S_i^2 \sigma_i - S^2 \sigma \right) T$ describe electronic and bipolar contributions to the total thermal conductivity, respectively. The $\kappa_{bp}$ of the BM, S-MS, and Te-MS samples were taken from $\left( \sum_i S_i^2 \sigma_i - S^2 \sigma \right) T$. 
In order to obtain theoretical $\kappa_{bp}$, calculated $\sigma_{total}$ and $S_{total}$ of one sample were fitted to experimental electrical conductivity and Seebeck coefficient of the sample by adjusting deformation potentials and density-of-states (DOS) effective masses ($m^*$) of its valence and conduction bands (Table 5.3). Due to high crystal symmetry of Bi$_{0.5}$Sb$_{1.5}$Te$_3$, more than one pocket of Fermi surface contribute to $m^*$ as $m^* = N_F^{1/3}m_b^*$ where $N_F$ and $m_b^*$ are the valley (pocket) degeneracy and the band-mass of a single valley, respectively. While the $N_F$ for the highest valence band of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ is known to be 6 (Fig. 3.1c) that for the lowest conduction band is found to be 2 as listed in Table 5.3$^{(41)}$. Since Bi$_{0.5}$Sb$_{1.5}$Te$_3$ is a $p$-type material, its carrier concentration of holes ($p$) and electrons ($n$) follow the charge neutrality equation,

$$p = N_{AC} + n,$$  \hspace{1cm} (Eqn. 5.15)

where $N_{AC}$ is the number of acceptors. The $R_{Hi}$ (inversely proportional to $p$ for valence band and $n$ for conduction band) was calculated by fitting $N_{AC}$, for experimental $R_{Hi}$ data at high temperatures (> 300 K) were not available.

### Table 5.3 Band parameters used to model $\kappa_{bp}$ of the BM, S-MS and Te-MS samples from ref. 1 using the two band model at high temperatures (“HT grey model” in Fig. 5.1 only).

<table>
<thead>
<tr>
<th>Band parameters</th>
<th>BM</th>
<th>S-MS</th>
<th>Te-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence band (VB) $E_{def}^{†}$ (eV)</td>
<td>10.5</td>
<td>9.45</td>
<td>8.75</td>
</tr>
<tr>
<td>VB $m^*$ (in $m_0$)$^{‡}$</td>
<td>1.33</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>VB $N_V$$^{§}$</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Conduction band (CB) $E_{def}^{†}$ (eV)</td>
<td>8.34</td>
<td>10.6</td>
<td>12.4</td>
</tr>
<tr>
<td>CB $m^*$ (in $m_0$)$^{‡}$</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>CB $N_V$$^{§}$</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>No. of acceptors ($10^{19}$ cm$^{-3}$)</td>
<td>2.22</td>
<td>2.00</td>
<td>1.75</td>
</tr>
<tr>
<td>Energy band gap (eV)</td>
<td>0.145</td>
<td>0.145</td>
<td>0.145</td>
</tr>
<tr>
<td>$C_l$ (GPa)$^{‖}$</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>

$^{†}$ $E_{def}$ = deformation potential
$^{‡}$ $m^*$ = density-of-states effective mass ($m_0$ = electron mass)
$^{§}$ $N_V$ = number of valley degeneracy

The approximated $\kappa_{bp}$ for each sample was added to corresponding $\kappa_l$ predicted above to obtain theoretical $\kappa_l + \kappa_{bp}$ in Fig. 5.1 (solid lines). These results are labelled as “HT grey model” for BM and S-MS because
the frequency-independent boundary scattering term (grey model) in Eqn. 5.3 was used to model $\kappa_l$ at high temperature (HT). For Te-MS sample, it is called “HT grey + dislocation” as dislocation scattering terms (Eqns. 5.7 and 5.8) were included in addition to the boundary scattering (Eqn. 5.3) to explain phonon scattering at grain boundaries of the Te-MS sample (Table 5.2).

Fig. 5.1. Lattice and bipolar contributions to thermal conductivities of BM, S-MS, and Te-MS samples of ref. 1. Empty circle – experimental data, solid line – sum of calculated $\kappa_l$ and $\kappa_{bp}$. Corresponding experimental $zT$ curves are given in the inset.

5.4 Lattice thermal conductivity model for $T < 200$ K

At low temperatures, the frequency-independent boundary scattering dominates ($\tau_B^{-1} \sim \omega^0$). Among the other scattering mechanisms considered to calculate the “HT grey model” (“HT grey + dislocation” for Te-MS) in Fig. 5.1, the dislocation scattering from strain field ($\tau_{DS}^{-1} \sim \omega^1$, Eqn. 5.8) is also prominent due to its frequency dependence. As the scattering from the dislocation strain field is stronger than that from the core ($\tau_{DC}^{-1} \sim \omega^3$, Eqn. 5.7)\textsuperscript{105}, especially at low temperature it can be concluded that the scattering from grain boundary dislocations (strain field + core) and the boundary scattering play a vital role in determining the low temperature $\kappa_l$. 
The $\kappa_l$ of the S-MS and Te-MS samples were measured at low temperatures ($T < 200$ K) by a Quantum Design Physical Property Measurement System (PPMS). Because the average grain size for both the samples was 300 nm (the same boundary scattering effect), by comparing their $\kappa_l$ the effect of dense dislocation arrays, only observable in the Te-MS sample, on reducing $\kappa_l$ at low temperature could be examined more closely.

![Fig. 5.2. Lattice contribution to thermal conductivities of the S-MS, and Te-MS samples. Empty circle – experimental data measured with PPMS at $T < 200$K, empty square – experimental data measured by laser-flash method using TC-9000, ULVAC-Riko at $T > 300$K, dashed line – calculated $\kappa_l$ with “LT grey model” (“LT grey + dislocation” for Te-MS), and solid line – calculated $\kappa_l$ with “LT GBDS model”.

Similar to the high temperature $\kappa_l$ calculation ($T > 300$ K), Umklapp, point-defect, and boundary scatterings were taken into account to compute low temperature $\kappa_l$ of S-MS. However, different equation for Umklapp scattering ($\tau_{U,LT}^{-1}$ for low temperatures) and $\alpha_t > 1$ (from Eqn. 5.3) were employed while utilizing the same $\tau_{PD}^{-1}$ as in Eqn. 5.5. The $\tau_{U,LT}^{-1}$ has an exponential term ($e^{-\theta_a/3T}$) as

$$\tau_{U,LT}^{-1} = A_{N,LT} \frac{h\gamma^2\omega^2T}{Mv^2\theta_a} e^{-\theta_a/3T},$$  

(Eqn. 5.16)

where $A_{N,LT}$ is a fitting parameter that accounts for the momentum-conserving Normal scattering contribution. The absence of this exponential term in $\tau_U^{-1}$ (Eqn. 5.4) makes it only applicable at high temperatures. As grain boundaries of a polycrystalline material are not as effective as sample boundaries in
limiting phonon mean free path, it is not surprising that the phonon mean free path can be much greater than the grain size at low temperatures\(^{114,115}\) (hence \(\alpha_t > 1\)). The total scattering relaxation rates for the low temperature \(\kappa_l\) calculation of the S-MS and Te-MS samples are given in Table 5.4 including the parameters required for the computation (in addition to the ones in Table 5.1).

<table>
<thead>
<tr>
<th>Model</th>
<th>Sample</th>
<th>(\tau_{total,LT}^{-1})</th>
<th>(A_{N,LT})</th>
<th>(\alpha_t)</th>
<th>(B_{\text{eff},LT}) (Å)</th>
<th>(N_D) (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT grey</td>
<td>S-MS</td>
<td>(\tau_{U,LT}^{-1} + \tau_{PD}^{-1} + \tau_{B(d_{MS},\alpha_t&gt;1)}^{-1}) (+ \tau_{DC}^{-1} + \tau_{DS}^{-1})</td>
<td>3</td>
<td>8.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Te-MS</td>
<td>(\tau_{U,LT}^{-1} + \tau_{PD}^{-1} + \tau_{B(d_{MS},\alpha_t&gt;1)}^{-1}) (+ \tau_{DC}^{-1} + \tau_{DS}^{-1})</td>
<td>10</td>
<td>8.3</td>
<td>3.3</td>
<td>2\times10^{11}</td>
</tr>
<tr>
<td>LT grey + dislocation</td>
<td>S-MS</td>
<td>(\tau_{U,LT}^{-1} + \tau_{PD}^{-1} + \tau_{DC}^{-1} + \tau_{DS}^{-1})</td>
<td>3</td>
<td>–</td>
<td>3.3</td>
<td>5.2\times10^{10}</td>
</tr>
<tr>
<td></td>
<td>Te-MS</td>
<td>(\tau_{U,LT}^{-1} + \tau_{PD}^{-1} + \tau_{DC}^{-1} + \tau_{DS}^{-1})</td>
<td>10</td>
<td>–</td>
<td>3.3</td>
<td>2.1\times10^{11}</td>
</tr>
</tbody>
</table>

For low temperature \(\kappa_l\) of the S-MS sample calculated using “LT grey model” (blue dashed line in Fig. 5.2), \(\alpha_t = 8.3\) was obtained (Table 5.4). The name “LT grey model” originates from the frequency-independent \(\tau_B^{-1}\) (Eqn. 5.3) used in the model. For \(T < 20\) K, the trend of experimental data of the S-MS (blue empty circle in Fig. 5.2) differed from that of the “LT grey model” (blue dashed line). The slope of the “LT grey model” below 20 K was not affected by changing \(\alpha_t\).

Once a reasonable fit between the experimental data and the “LT grey model” was achieved in the S-MS sample, the same scattering mechanisms and parameters (i.e. \(A_{N,LT}\) and \(\alpha_t\)) were adopted for the Te-MS sample (with the same composition and grain size). To account for the fact that the Te-MS sample had dense dislocations at grain boundaries which were not observed in the S-MS sample, dislocation scattering relaxation rates were also included to determine \(\tau_{total,LT}^{-1}\) of the Te-MS (Te-MS “LT grey + dislocation” in Table 5.4). A larger \(A_{N,LT}\) for Te-MS than for S-MS was required to describe the low \(\kappa_l\) of Te-MS at \(~200\) K (lower than that of S-MS). Nonetheless this discrepancy did not influence the \(\kappa_l\) behavior at \(T < 20\) K where the Umklapp scattering is negligible. Furthermore the large measurement error systematically present in PPMS at higher end of the low temperatures\(^{116}\) \((~100\) K) might provide an explanation for different \(A_{N,LT}\) obtained for S-MS and Te-MS (Table 5.4). Experimental \(\kappa_l\) measured via laser-flash method for \(T > 300\) K...
(empty square in Fig. 5.2) were also provided for reference. The further reduction of $\kappa_l$ in Te-MS compared to S-MS at low temperatures was explained with added phonon scattering from dislocations (“LT grey + dislocation” - green dashed line in Fig. 5.2) with the effective Burgers vector close to Bi$_2$Te$_3$ lattice constant and the dislocation density ($N_D = 2\times10^{11}$ cm$^{-2}$) also used in “HT grey + dislocation” (Table 5.4). Unfortunately, the reason for $B_{D,\text{eff},LT}$ (for LT model) being different from $B_{D,\text{eff}}$ (for HT model) is not known.

5.5 Frequency-independent boundary scattering at low temperature

Below 10 K in Fig. 5.2, particularly for the S-MS sample, the “LT grey model” deviated from the experimental data ($\sim T^2$ trend for measured data and $\sim T^3$ for S-MS “LT grey model” – guided with dashed lines in grey color). According to Wang et al., the discrepancy between the experiment and the “LT grey model” (dashed lines in Fig. 5.2) stemmed from frequency-independent boundary scattering relaxation rate ($\tau_B^{-1}$ in Eqn. 5.3) utilized in the model. Wang et al. showed that the use of frequency-dependent boundary scattering relaxation rate, $\tau_B^{-1}$, much improved the predictive power of $\kappa_l$ modelling at low temperatures. In Fig. 5.2, Te-MS “LT grey + dislocation” (green dashed line) followed closer to $\sim T^2$ instead of $\sim T^3$ as in S-MS “LT grey model”. This was because the scattering from dislocation strain field ($\tau_{DS}^{-1} \sim \omega^1$) considered along with the frequency-independent boundary scattering (Eqn. 5.3) in Te-MS “LT grey + dislocation” contributed to $\tau_{total,LT}^{-1}$ greater than $\tau_B^{-1}$ did due to the significant scattering of dislocation strain field from the dense dislocation arrays.

As an alternative to the frequency-dependent boundary scattering suggested by Wang et al., the frequency-independent boundary scattering term (Eqn. 5.3) was completely substituted by dislocation scattering terms (Eqns. 5.7 and 5.8). This model is named as low temperature grain boundary dislocation strain model (“LT
GBDS model”) as the frequency-independent boundary scattering term is completely removed from \( \tau_{\text{totall},LT}^{-1} \) (Table 5.4). Although the dense dislocation arrays were not observed in the S-MS sample, as grain boundaries were composed of dislocations by definition replacing boundary scattering by scattering from dislocations formed at grain boundaries was not far-stretched.

As presented in Table 5.4, for S-MS “LT GBDS model”, with theoretical dislocation density of \( 5.2 \times 10^{10} \) (cm\(^{-2}\)) (with the same \( B_{D,\text{eff},LT} \) as in Te-MS “LT grey + dislocation”), the boundary scattering could be translated into the scattering by dislocations at grain boundaries (blue solid line in Fig. 5.2). For the Te-MS sample, where the dislocation scattering term was already present even when “LT grey + dislocation” was used, removing the boundary scattering was compensated only by 5 % increase in the dislocation density (“LT GBDS model” in Table 5.4 and green solid line in Fig. 5.2). As expected, according to “LT GBDS model”, about 5 time denser dislocation density was required to predict the \( \kappa_l \) of Te-MS (green solid line in Fig. 5.2) as opposed to that of S-MS (blue solid line in Fig. 5.2).

At low temperature, drastic lattice thermal conductivity reduction in Te-MS was observed. We modelled the low temperature \( \kappa_l \) of Te-MS satisfactorily with grain boundary dislocation scattering. Although the parameters in the phonon scattering mechanisms differ between the high and low temperature models for the \( \kappa_l \) calculation, both models provide strong evidence for the presence of grain boundary dislocation scattering in polycrystalline \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3\).
Chapter 6

Dislocation strain as the mechanism of phonon scattering at grain boundaries

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6.1 Introduction

A reduction of lattice thermal conductivity has been one of the most productive routes towards improving thermoelectric figure of merit. The thermal conductivity, \( \kappa \), can be attributed to heat transported along with the conduction of electrons and holes (\( \kappa_e \)), and from phonons (lattice vibrations) travelling through the lattice (\( \kappa_l \)). The lattice thermal conductivity, \( \kappa_l \), can be suppressed with disorder among many length scales, ranging in size from as small as an atom (point-defect scattering) up to a few millimeters (boundary scattering). The effects of boundary scattering especially are of utmost importance for thermoelectric performance.

Boundary scattering was first observed in a single crystal by de Haas and Biermasz. The phonon scattering at sample boundaries was explained by Casimir who suggested that the phonon mean free path (MFP) could be approximated as the sample size (frequency-independent). The frequency independence of the Casimir model means that the sample boundaries are just as effective at limiting the MFP of short wavelength phonons as they are for long wavelength phonons. The Casimir model could be considered phenomenological, in the sense that it does not specify a real condition (at the atomic level) of the interface.

Berman suggested that scattering of phonons at grain boundaries could limit the MFP the same way phonon scattering on sample boundaries did, and since then the grain size of polycrystalline materials has been adopted as the MFP in the Casimir model (also known as grey model). Although it may be suitable to
use sample dimension as the MFP due to perfect acoustic mismatch at perfectly rough sample surfaces, it is not entirely appropriate for grain size because adjacent grains have similar acoustic impedance.

Recently, Wang et al. demonstrated that the grey model failed to explain the $\kappa_l$ of nanocrystalline silicon$^{117}$. At low temperature, it was observed that the measured $\kappa_l$ followed a $T^2$ trend instead of a $T^3$, which was predicted in the grey model. This result implies a MFP that depends on frequency as $\Lambda_B^{-1} \sim \omega$, where $\Lambda_B$ and $\omega$ are the boundary scattering MFP and phonon frequency, respectively.

Frequency-dependent $\Lambda_B$ was first introduced by Ziman in an attempt to apply the Casimir model to materials with real boundaries$^{104}$. Roughness of sample boundaries was taken into consideration in a frequency-dependent specularity term included in the $\Lambda_B$. However, the Ziman model did not predict $\Lambda_B^{-1} \sim \omega$; it can be considered a phenomenological term. Hua and Minnich$^{122}$ successfully predicted Wang et al.’s results via Monte Carlo simulations which included frequency-dependent phonon transmissivity at grain boundaries$^{117}$ (consistent with $\Lambda_B^{-1} \sim \omega$). The frequency-dependent interfacial (Kapitza) resistance of grain boundaries manifested itself even in molecular-dynamics simulations$^{123,124}$. For example, Young and Maris$^{125}$ found phonon transmission coefficient decreasing with increasing frequency for the Kapitza resistance at an interface between two dissimilar solids. Moreover, the thermal conduction in thin films was commonly depicted with Fuchs-Sondheimer equation with the frequency-dependent specularity term from the Ziman model$^{126-128}$. Unfortunately, above models and simulations for frequency-dependent $\Lambda_B$ are only phenomenological without any mechanisms because they do not specify real conditions of the boundaries.

In this work, we propose that interface scattering could be due to strain at grain boundaries described analytically as dislocation strain as formulated by Klemens$^{105}$. Here we show that the $\kappa_l$ calculated previously with the grey model can be equally satisfactorily modelled with Klemens’ grain boundary dislocation scattering term by using appropriate value for dislocation density. A most promising example is a recent demonstration of exceptional $zT$ ($\sim 1.86$ at 320 K) in Bi$_{0.5}$Sb$_{1.5}$Te$_3$ where grain boundary dislocations are produced by liquid-phase compaction$^1$. The grey model plus dislocation scattering we used
in Kim et al.\textsuperscript{1} is here entirely replaced by the dislocation scattering. The dislocation model demonstrates its superiority by predicting a $T^2$ trend instead of the $T^3$ of the grey model for the nanocrystalline silicon system of Wang et al.\textsuperscript{117}.

Finally we show that the Klemens model suggests dislocation boundary scattering can be enhanced by engineering compositional changes around dislocations in alloys as observed in silicon-germanium alloys\textsuperscript{129-131} (not predicted by Casimir model).

### 6.2 Models for phonon scattering

From the kinetic theory of gases, the lattice thermal conductivity ($\kappa_l$) can be expressed as arising from the heat capacity of phonons ($C$), phonon velocity ($v$), and total relaxation time ($\tau_{\text{total}}$), as a function of $\omega$ such that

$$\kappa_l = \frac{1}{3} \int C(\omega) v^2(\omega) \tau_{\text{total}}(\omega) \, d\omega. \quad \text{(Eqn. 6.1)}$$

Using the Debye model (phonon group velocity is constant), Callaway’s equation for the $\kappa_l$ becomes

$$\kappa_l = \frac{k_B}{2\pi^2 v} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta/T} \tau_{\text{total}}(z) \frac{z^4 e^z}{(e^z - 1)^2} \, dz, \quad \text{(Eqn. 6.2)}$$

where $k_B$, $\hbar$, $\theta$, and $z$ are the Boltzmann constant, reduced Planck’s constant, Debye temperature, and $\hbar \omega/k_B T$, respectively\textsuperscript{97}. The $\kappa_l$ of a material can be calculated using Eqn. 6.2, once its $\tau_{\text{total}}(z)$ is determined from individual relaxation times ($\tau_i$) for different scattering processes according to Matthiessen’s rule

$$\tau_{\text{total}}(z)^{-1} = \sum_i \tau_i(z)^{-1} = \tau_U^{-1} + \tau_{PD}^{-1} + \tau_B^{-1}. \quad \text{(Eqn. 6.3)}$$

Relaxation times associated with Umklapp scattering ($\tau_U$), point-defect scattering ($\tau_{PD}$), and frequency-independent boundary scattering ($\tau_B$), which assumes completely inelastic (specularity zero) scattering at the grain boundaries are most commonly considered. The $\tau_B$ has been found to be a good model for surfaces
(of nanowires for instance) where there is perfect acoustic mismatch at the interface between the material and vacuum. Frequency-independent $\tau_B$ is given by:

$$\tau_B^{-1} = \frac{V}{d^2}, \quad \text{(Eqn. 6.4)}$$

where $d$ is the experimentally determined grain size. Umklapp scattering occurs when phonons in a crystal are scattered by other phonons. Its relaxation time is of the form:

$$\tau_U^{-1} = A_N \frac{2 k_B V^{1/3} \gamma^2 \omega^2 \tau}{M v^3}, \quad \text{(Eqn. 6.5)}$$

where $V$, $\gamma$, and $M$ are the atomic volume, Grüneisen parameter, and the atomic mass. The parameter $A_N$ takes normal phonon-phonon scattering (total crystal momentum conserving process) into account. Point-defect scattering arises from an atomic size disorder in alloys. The disorder is described in terms of the scattering parameter ($\Gamma$) within the $\tau_{PD}$ formula as:

$$\tau_{PD}^{-1} = \frac{V \omega^4}{4 \pi v^3} \Gamma. \quad \text{(Eqn. 6.6)}$$

In Eqn. 6.6, $\Gamma$ is related to the difference in mass ($\Delta M$) and lattice constant ($\Delta a$) between two constituents of an alloy as:

$$\Gamma = x(1-x) \left[ \left( \frac{\Delta M}{M} \right)^2 + \frac{2}{9} \left( \frac{G + 6.4 \gamma}{1+r} \right) \left( \frac{\Delta a}{a} \right)^2 \right], \quad \text{(Eqn. 6.7)}$$

where $x$ and $r$ are the fractional concentration of either of constituents and the Poisson ratio, respectively. The parameter $G$ represents material dependent ($\Delta K/K)(\Delta R/R)$ where $\Delta K$ and $\Delta R$ are the contrast in the bulk modulus and that in the local bond length, respectively. The $G$ was regarded as an adjustable parameter in the calculation.

Phonon scattering of dislocations in a grain boundary can be treated as resulting from scattering by dislocation cores ($\tau_{DC}$) and by the dislocation strain ($\tau_{DS}$) as:

$$\tau_{DC}^{-1} = \frac{V \omega^4}{4 \pi v^3} \Gamma.$$
\[ \tau_{DC}^{-1} = \left( \frac{2}{s_d} \right) \frac{V^{4/3}}{v^2} \omega^3, \quad \text{(Eqn. 6.8)} \]

\[ \tau_{DS}^{-1} = 0.6 \times B_{D,\text{eff}}^2 \left( \frac{2}{s_d} \right) (\gamma + \gamma_1)^2 \omega \left[ \frac{1}{2} + \frac{1}{24} \left( \frac{1-2r}{1-r} \right)^2 \left( 1 + \sqrt{2} \left( \frac{v_L}{v_T} \right)^2 \right) \right]^2, \quad \text{(Eqn. 6.9)} \]

where \( B_{D,\text{eff}}, \gamma, \gamma_1, v_L, \) and \( v_T \) are the magnitude of effective Burgers vector, Grüneisen parameter, change in Grüneisen parameter, longitudinal phonon velocity, and the transverse phonon velocity, respectively. The change in Grüneisen parameter \( (\gamma_1) \) in \( \tau_{DS}^{-1} \) describes the modulation of solute atom concentration by strain fields around dislocations in alloys. Initially, Klemens derived Eqns. 6.8 and 6.9 for collections of single dislocations (with density \( N_D \)) within a grain. As dislocations could be easily introduced into grains by deformation, Klemens’ equations were often used to compute \( \kappa_l \) of strained materials\textsuperscript{132,133}. When arrays of dislocations at boundaries (or interfaces) were found physically equivalent to a sum of individual dislocations within a grain\textsuperscript{104}, \( \kappa_l \) reductions from dislocations, which originated due to lattice mismatch between thin film and substrate\textsuperscript{134}, or between different phases in polycrystalline materials\textsuperscript{81} were explained by Klemens’ equations. Nevertheless, the consideration of the scattering effect of dislocation arrays at grain boundaries of single-phase polycrystalline materials has been scarce. Here we replace the density of dislocations per unit area \( (N_D) \) used by Klemens with \( N_D = 2/(d \times s) \), where \( d \) is the average grain size and \( s \) is the average spacing between dislocation cores in order to apply Klemens equations to phonon scattering of grain boundary dislocations where average grain size can be an observed parameter.

### 6.3 Dislocation scattering can explain \( \kappa_l \) without the need for boundary scattering

Recently, a dramatic \( zT \) improvement in Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} was attributed to substantially low \( \kappa_l \).\textsuperscript{11} In ref. 1 we showed that modelling the boundary scattering with the normally expected \( \tau_B^{-1} \) along with the experimentally determined \( \tau_U^{-1} + \tau_{PD}^{-1} \) was insufficient to explain the low \( \kappa_l \) of Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} with dense dislocation arrays at grain boundaries. The additional scattering mechanisms, \( \tau_{DC}^{-1} \) and \( \tau_{DS}^{-1} \) from
dislocations were required to explain the \( \kappa_l \). In this section we show that within the range of physically reasonable parameters, once dislocation scattering is included, since an array of dislocations situated in the plane makes a grain boundary the traditional boundary scattering \( \tau_B^{-1} \) is not necessary to satisfactorily model the data.

In ref. 1 various forms of Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) samples were considered to self-consistently model the \( \kappa_l \). The parameters \( A_N \) and \( G \) in \( \tau_U^{-1} \) and \( \tau_{PD}^{-1} \) (Eqns. 6.5 and 6.6), respectively were determined by fitting the modelled \( \kappa_l \) to the experimental \( \kappa_l \) of large grained (Bi\(_{1-x}\)Sb\(_x\))\(_2\)Te\(_3\) alloys with varying \( x \). The use of reliable literature values determined experimentally eliminates or minimizes the parameters needed for the \( \kappa_l \) calculation.

The \( \kappa_l \) of the samples fabricated via different processing routes (Ball milling: BM, melt spun with stoichiometric tellurium: S-MS, and melt spun with excess tellurium: Te-MS) were modelled using the \( \tau_B^{-1} \) expected from the average grain size (\( d \)) observed in the microscopy (“grey model” in Table 6.1) where significant bipolar contributions (\( \kappa_{bp} \)) were present at high temperatures. For BM and S-MS samples, the scattering terms \( \tau_U^{-1} + \tau_{PD}^{-1} + \tau_B^{-1} \) were sufficient to explain the \( \kappa_l \). However, the Te-MS required the introduction of dislocation scatterings \( \tau_{DC}^{-1} \) and \( \tau_{DS}^{-1} \) using values of the observed \( N_D \) and the fitted \( B_{D,\text{eff}} \) as listed in Table 6.1, “grey + dislocation”. The fitted \( B_{D,\text{eff}} \) was within reasonable expectation, especially considering the compounding effect leading to reinforcement of grain boundary dislocation scattering expected by Klemens.

Table 6.1. Theoretical total relaxation rate (\( \tau_{total}^{-1} \)) considered for grey model and GBDS model.
Now that we have concluded that $\tau_{DC}^{-1}$ and $\tau_{DS}^{-1}$ are required to model some of the grain boundary scattering in some samples, we can explore the possibility of this mechanism replacing the $\tau_B^{-1}$ term entirely to model all of the boundary scattering in all the samples studied.

Indeed, an equally satisfactory model exists by entirely replacing the $\tau_B^{-1}$ term in $\tau_{total}^{-1}$ of BM, S-MS, and Te-MS with $\tau_{DC}^{-1}$ and $\tau_{DS}^{-1}$ by using reasonable values of $B_{D,\text{eff}}$ and $N_D$ as shown in Table 6.1 ("GBDS model"). The scattering from strain field induced by the dislocations is stronger than that from dislocation cores\textsuperscript{105}. Therefore the scattering by grain boundary dislocations (from both strain field and
cores) is termed as grain boundary dislocation strain (GBDS) scattering for simplicity. The $B_{D,\text{eff}}$ and $\gamma_i$ values were kept unchanged from those acquired for Te-MS in the “grey + dislocation”.

There are different kinds of grain boundaries, consisting of different kinds of defects, that produce the strain that scatters phonons. Nevertheless, it has been suggested that most if not all defects at grain boundaries can be described as some combination of dislocations$^{105,135-140}$. Even if all types of grain boundaries cannot be entirely defined by dislocations, the usefulness of GBDS model requires only that dislocation strain is a dominant mechanism for boundary scattering.

Smaller grain size, $d$, which leads to increased scattering in $\tau_B^{-1}$ (“grey model”) translates into a larger dislocation density ($N_D$) in “GBDS model” (Table 6.1). Besides, the stronger GBDS (given the same $d$) which could not be described in terms of phenomenological $\tau_B^{-1}$ was taken into account in a greater $N_D$. Therefore, $N_D$ for different samples were fit to the experimental $\kappa_l$ ($\kappa_{bp}$ is the same for both models, more details on estimation of the $\kappa_{bp}$ can be found in Chapter 5.3) whose numbers are given in Table 6.1 (“GBDS model”).

Previously, the $N_D$ estimated from experimentally determined dislocation spacing in Te-MS and used in “grey + dislocation” was $2.0\times10^{11}$ (cm$^{-2}$)$^1$, but with only a 10% increase in $N_D$, $2.2\times10^{11}$ (cm$^{-2}$) (which is still physically reasonable), we can equally adequately describe the exceptionally low $\kappa_l$ of Te-MS using “GBDS model” (orange solid line in Fig. 6.1). As anticipated, much weaker scatterings from GBDS in BM and S-MS are manifested in their fitted $N_D$ (Table 6.1), which are one or two orders magnitude smaller than that of Te-MS while in the range expected for polycrystalline materials$^{141}$. Similar results can be applied to PbTe given removing boundary scattering by GBDS scattering can sufficiently explain the data like we show in Bi-Sb-Te.

Effect of scatterings from dislocation cores and strain field can be best understood when the spectral thermal conductivity ($\kappa_s$) is plotted.
\[ \kappa_s = \frac{3k_B \omega^2}{2\pi^2 v} \tau(\omega) \]  
\text{(Eqn. 6.10)}

As described in the \( \kappa_s \) for S-MS (Fig. 6.2), while Umklapp scattering is effective in all frequency range, point defect scattering and boundary scattering (frequency-independent) only scatter high and low frequency phonons, respectively. Similar to the boundary scattering (green line – grey model), dislocation cores and strain field scatterings reduce thermal conductivity at low frequencies (orange line – GBDS model). Although the \( \kappa_s \) curves for the grey model (green curve Fig 6.2) and the GBDS model (orange curve Fig 6.2) do not coincide exactly in Fig. 6.2, their \( \kappa_l \) agree well (green curves Fig 6.1) with each other because the \( \kappa_l \) is the area under the \( \kappa_s \) curve.

Fig. 6.2. Spectral thermal conductivity of S-MS. U (Umklapp), PD (Point-Defect), and B (frequency-independent Boundary scattering) are accounted for the calculation. For grey model, U, PD, and B are considered as relevant scattering mechanisms (green solid line). Meanwhile, in GBDS model B has entirely been replaced by DC and DS (orange solid line).
6.4 Dislocation scattering model superior to boundary scattering model at low temperatures

In a recent study by Wang et al. on nanocrystalline Si\textsuperscript{117}, it was shown that the traditional frequency-independent boundary scatterings fails to correctly predict the observed \(\kappa\), even qualitatively. The grey model predicts a \(T^3\) temperature dependence (green dotted line in Fig. 6.3) while the experimental measurements show a temperature dependence closer to \(T^2\) at low temperatures.

Wang et al. were able to predict a \(T^2\) temperature dependence using Born von Karman (BvK) model (group velocity is not constant), along with frequency-dependent boundary scattering relaxation rate (\(\tau_{B,\omega}^{-1}\)) approximated as

\[
\tau_{B,\omega}^{-1} = c \frac{v\omega}{d},
\]  
(Eqn. 6.11)

where \(c\) is the dispersion relation dependent constant. The model in ref. 117, however, is phenomenological in that no mechanism was given for the frequency dependence (although it is consistent with atomistic calculations predicting the same frequency dependence).

Here we propose that GBDS may be the mechanism that leads to the frequency dependence. Because the GBDS model includes both a dislocation strain field term with \(\omega\) dependence and a dislocation core term with \(\omega^3\) dependence (for scattering relaxation rates) it cannot exactly reproduce the model in ref. 117, instead we show the GBDS model gives a satisfactory fit (Fig. 6.3). All the parameters and constants from Debye model in ref. 117 were re-utilized except for the boundary scattering, which was replaced by \(\tau_{DC}^{-1}\) and \(\tau_{DS}^{-1}\). The \(\gamma_l\) for Si was taken to be zero as Si is not an alloy, and for simplicity, lattice constant of Si (5.4 Å) was substituted for \(B_{D,\text{eff}}\). Similar to the (Bi\(_{0.25}\)Sb\(_{0.75}\))\textsubscript{2}Te\(_3\) case, the dislocation spacing (\(s\)) was adjusted to match the experimental results. The fitted \(s\) (0.76 ~ 0.94 nm) for nanocrystalline Si was still above the minimum theoretical dislocation spacing (lattice constant ~ 0.5 nm). The fit is nearly as good
as the frequency-dependent BvK model in ref. 117, suggesting dislocation scattering may be the underlying mechanism in $\kappa_l$ reduction due to grain boundary scattering.

6.5 Alloys

Experimental $\kappa_l$ data of Si-Ge alloys by Savvides and Goldsmid$^{129,130}$ were also examined to show that the GBDS model can replace the grey model completely, which also revealed a new strategy for further suppressing $\kappa_l$. This mechanism utilizes the change in Grüneisen parameter that accompanies the compositional changes around dislocations in alloys.

The change in Grüneisen parameter ($\gamma_1$) of $\tau_{DS}^{-1}$ can strengthen or weaken the scattering due to GBDS depending on mass and volume mismatch between constituents of the alloy. The $\gamma_1$ can be estimated as

$$\gamma_1 = \frac{\nu_{ca} K}{k_BT_a} (\gamma \alpha^2 - \alpha \beta),$$

(Eqn. 6.12)

with $\alpha$ and $\beta$ being
\[ \alpha = \frac{(V' - V)}{V}, \quad \beta = \frac{1}{2} \frac{(M - M')}{M}, \]  

(Eqn. 6.13)

where \( V', V, M', M, K, c_0, \) and \( T_a \) are the atomic volume of impurity, that of host, average atomic mass of impurity, that of host, bulk modulus of host, concentration of impurity in the alloy, and the sample annealing temperature, respectively. For Te-MS, which is a \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3\) alloy, the theoretical \( \gamma_1 \) is positive reinforcing the GBDS scattering.1

Savvides and Goldsmid129,130 compared the relative change in \( \kappa_l \) from nanostructuring for different Si-Ge alloy compositions. In particular, they plotted the \( \kappa_l \) ratio of polycrystalline Si-Ge with different grain sizes (containing boundaries and point defects, \( \kappa_{PD,B} \)) relative to that of single crystal alloy (containing only point defects, \( \kappa_{PD} \)). Simply comparing two 30% alloys (Fig. 6.4) cannot provide any information on relative strength of the boundary scatterings in the alloys since the Fig. 6.4 plots the ratio of \( \kappa_{PD,B} / \kappa_{PD} \). In fact, according to Savvides and Goldsmid’s calculated \( \kappa_{PD,B} / \kappa_{PD} \) using the grey model (dashed lines in Fig. 6.4), less intense point-defect scattering in Si0.7Ge0.3 was held responsible for the lower \( \kappa_{PD,B} / \kappa_{PD} \) of Si0.7Ge0.3.

Replacing the \( \tau_B^{-1} \) in the Savvides and Goldsmid’ model with the GBDS model, a reasonable fit to the experimental data was achieved (solid lines in Fig. 6.4) considering the uncertainty involved in determining the size of the grains (represented with error bars in Fig. 6.4).

For Si0.7Ge0.3 and Si0.3Ge0.7, \( s = B_{D, eff} = 7 \) Å (in Eqns. 6.8 and 6.9) was adopted to produce the solid lines in Fig. 6.4. Even if the effective Burgers vector is larger than that normally expected for Si and Ge (5.4 Å and 5.5 Å, respectively), given the uncertainty of the models, we can still deduce that the GBDS model can provide an alternative to the Casimir model for boundary scattering.

If GBDS is indeed the correct mechanism for boundary scattering, the Klemens theory implies that the scattering due to impurity modulation around grain boundary dislocation strain field in Si-Ge alloys plays a vital role in further reducing the \( \kappa_l \). The change in Grüneisen parameter (\( \gamma_1 \) in Eqn. 6.12) of the Si-Ge alloys increase the overall Grüneisen parameter (\( \gamma + \gamma_1 \)) in Eqn. 6.12 by 3.4 times for Si0.7Ge0.3 and about
2.1 times for Si$_{0.3}$Ge$_{0.7}$ reinforcing GBDS scattering accordingly. Now that the increased GBDS scattering becomes the dominant scattering mechanism, the discrepancy in $\kappa_{PD,B}/\kappa_{PD}$ for the two 30% alloys can be explained with the degree of impurity modulation ($\gamma_1$). The theoretical $\gamma_1$ for various thermoelectric materials are listed in Table 6.2.

![Figure 6.4](image)

Fig. 6.4. Ratio of thermal conductivities whose departure from unity measures the boundary scattering effect. The ratio between $\kappa_{PD,B}$ ($\kappa_1$ where point-defect and boundary scatterings are present) and $\kappa_{PD}$ ($\kappa_1$ where only point-defect scattering is present) for different grain sizes ($d$) is shown at 300 K. Plots in orange are for Si$_{0.3}$Ge$_{0.7}$ alloy and blue for Si$_{0.7}$Ge$_{0.3}$ alloy. Filled circle – experimental data, dashed line – Savvides and Goldsmid’ model using grey model (grey model), and solid line – Savvides and Goldsmid’ model using our GBDS scattering model in lieu of the grey model (GBDS model).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$K$ (GPa)</th>
<th>$T_a$ (K)</th>
<th>$\gamma_1$</th>
<th>$(\gamma + \gamma_1)/\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bi$<em>{0.25}$Sb$</em>{0.75}$)$_2$Te$_3$</td>
<td>0.09 a)</td>
<td>-0.18</td>
<td>2.3 b)</td>
<td>45 d)</td>
<td>753 c)</td>
<td>1.1</td>
<td>1.49</td>
</tr>
<tr>
<td>PbTe$<em>{0.75}$Se$</em>{0.25}$</td>
<td>-0.15 a)</td>
<td>0.07</td>
<td>1.45 a)</td>
<td>39 d)</td>
<td>700 e)</td>
<td>1.4</td>
<td>1.99</td>
</tr>
<tr>
<td>Pb$<em>{0.97}$Mg$</em>{0.03}$Te</td>
<td>-0.02 a)</td>
<td>0.27</td>
<td>1.45 a)</td>
<td>39 d)</td>
<td>700 e)</td>
<td>0.03</td>
<td>1.02</td>
</tr>
<tr>
<td>Si$<em>{0.7}$Ge$</em>{0.3}$</td>
<td>0.13 f)</td>
<td>-0.79</td>
<td>0.56 a)</td>
<td>98 d)</td>
<td>1200 h)</td>
<td>1.3</td>
<td>3.32</td>
</tr>
<tr>
<td>Si$<em>{0.3}$Ge$</em>{0.7}$</td>
<td>-0.12 f)</td>
<td>0.31</td>
<td>0.76 a)</td>
<td>75 d)</td>
<td>1200 h)</td>
<td>0.8</td>
<td>2.07</td>
</tr>
<tr>
<td>Mg$<em>2$Si$</em>{0.7}$Sn$_{0.3}$</td>
<td>0.19 a)</td>
<td>-0.09</td>
<td>1.32 a)</td>
<td>49 d)</td>
<td>1000 h)</td>
<td>1.6</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Table 6.2. Theoretical change in Grüneisen parameter ($\gamma_1$) for thermoelectric materials.

Taken from: a)ref. 63; b)ref. 142; c)ref. 1; d)ref. 143; e)ref. 144; f)ref. 145; g)ref. 146; h)ref. 147
In summary, straightforwardly applicable frequency-dependent phonon scattering due to dislocation strain in grain boundaries (GBDS model as illustrated in Fig. 6.5) can replace the most commonly used frequency-independent boundary scattering (grey model) to accurately predict the $\kappa_l$. Although the grey model is in wide use, it has been difficult to align with observed phenomena. The theoretical $\kappa_l$ of Bi-Sb-Te, Si, and Si-Ge previously modelled with grey model were recalculated using GBDS model with equally satisfactory results. At low temperatures, boundary scattering is better described with scattering due to GBDS. We revisited Wang et al.’s thermal conductivity calculation (Debye model) using frequency-independent boundary scattering ($\sim T^3$) which deviated from experimental thermal conductivity ($\sim T^2$) at low temperatures. Accuracy of the Debye model is much improved when frequency-independent boundary scattering is changed to GBDS scattering. It is concluded that the scattering from GBDS is the more likely mechanism for the grain boundary scattering than the grey model derived for boundary scattering at the sample boundaries. Strengthening of the GBDS scattering via impurity modulation around dislocations in alloys opens possibilities for grain boundary engineering as a means toward more efficient thermoelectric materials.

Fig. 6.5. Schematic diagram of phonon scattering by a single dislocation (a) and a grain boundary (b)
Chapter 7

Band gap estimation from temperature dependent Seebeck measurement


7.1 Introduction

In a typical plot of $zT$ versus temperature for a good thermoelectric material (Figure 7.1 inset), the $zT$ will rise until reaching a peak value after which it decreases. Since the peak $zT$ values are often the measure by which materials are compared, it is worthwhile to understand the origins of the peak and what factors can influence it. Typical degenerate thermoelectric semiconductors display thermopower (magnitude of the Seebeck coefficient, $|S|$) which rises linearly with temperature to a maximum (Figure 7.1) followed by a decrease. Because the Seebeck coefficient is squared in the formula for $zT$, a maximum in the thermopower also results in a maximum in the temperature dependent $zT$.

It is well known that the origin of the thermopower peak is most often related to the onset of bipolar conduction which involves thermal excitation of both electrons and holes across the band gap. The contribution to the overall Seebeck coefficient by both the positive and negative charge carriers can be described by the conductivity weighted average:

$$S = \frac{\sigma_p S_p - \sigma_n |S_n|}{\sigma_p + \sigma_n}.$$  \hfill (Eqn. 7.1)

Because the minority carriers are (by definition) fewer in number, they will also have higher thermopower contributions (Seebeck coefficient is inversely proportional to carrier concentration). However, at low temperatures the population of minority carriers is small, meaning that they will not contribute much to the
overall $S$. At higher temperatures, though a broadening Fermi distribution leads to an exponential increase in minority carrier conductivity resulting in a reduction (and therefore peak) in the thermopower\textsuperscript{148}.

The strength of bipolar conduction is determined by the value of the semiconductor band gap. Goldsmid and Sharp developed an analytical expression relating the band gap and the maximum thermopower, $|S|_{\text{max}}$ (defined as the magnitude of the Seebeck coefficient), and the temperature at which it occurs ($T_{\text{max}}$) in the bipolar regime by: $E_g = 2e|S|_{\text{max}}T_{\text{max}}$\textsuperscript{148}. This simple method of estimating the band gap is ubiquitous in the thermoelectrics community because temperature dependent Seebeck coefficient is so commonly measured. Figure 7.1 shows a calculated temperature dependent Seebeck coefficient and corresponding $zT$ (inset) for a valence and conduction band model with a band gap of 0.13 eV at various carrier concentrations. We can see that the Goldsmid-Sharp band gap formula (dashed line) accurately predicts the maximum thermopower over a wide range of carrier concentrations and temperatures.

While the Goldsmid-Sharp gap serves as a quick estimate of the band gap in a given material, it is important to understand where deviations might occur when using this analysis. In Goldsmid-Sharp’s full equation, the weighted mobility ratio: $A = \frac{\mu_{\text{maj}} N_{\text{maj}}}{\mu_{\text{min}} N_{\text{min}}} \left( \frac{m_{b,\text{maj}}}{m_{b,\text{min}}} \right)^{3/2} = \frac{\mu_{\text{maj}}}{\mu_{\text{min}}} \left( \frac{m_{b,\text{maj}}}{m_{b,\text{min}}} \right)^{3} = \frac{\mu_{b,\text{maj}}}{\mu_{b,\text{min}}} \left( \frac{m_{b,\text{maj}}}{m_{b,\text{min}}} \right)^{3/2}$ (where $\mu$ is the mobility, $N_v$ is the valley degeneracy, $m^*$ and $m_b^*$ are the density-of-states and single valley effective mass, and $B$ is the quality factor for majority and minority charge carriers) governs the relative contributions of the electron and hole bands to the electronic properties in the case of bipolar conduction. We can also consider $A$ as the ratio of the quality factors, $B = \frac{\mu_0 m^{*3/2}}{\kappa_1}$ (where $\mu_0$ is the non-degenerate mobility, and $\kappa_1$ is the lattice thermal conductivity), between the majority and minority bands, which relate directly to the maximum attainable $zT$ (for any doping level) for a given band\textsuperscript{149-153}. One of the primary conclusions of the Goldsmid-Sharp paper was that the $2e|S|_{\text{max}}T_{\text{max}}$ band gap was within ~20\% of the actual value and was roughly independent of the weighted mobility ratio, but this assumed that the dimensionless band gap ($\epsilon_g = \frac{E_g}{k_B T}$) — the parameter that governs the strength of bipolar conduction — was equal to 10. For some common
thermoelectric materials (Bi$_2$Te$_3$\textsuperscript{154,155}, PbSe\textsuperscript{156,157}, PbTe\textsuperscript{144,158}) the value of the band gap is actually $5 - 6 \ k_B T$ at $T_{\text{max}}$. Recent work by Schmitt, Gibbs \textit{et al.} shows that for ZrNiSn half-Heuslers, the Goldsmid-Sharp band gap can deviate by $50 - 100 \%$ of the optical band gap value mainly due to the large majority-to-minority weighted mobility ratio ($A = 5$) and an $\epsilon_g$ much lower than 10 as used in the derivations by Goldsmid-Sharp\textsuperscript{159}. Further, because $E_g$ is often within $\sim 6 \ k_B T_{\text{max}}$ ($\epsilon_g \sim 6$), Maxwell-Boltzmann statistics — applied in Goldsmid-Sharp’s derivation — should be replaced with Fermi-Dirac statistics which can more accurately represent semiconductor processes in narrow-gap ($\epsilon_g < 10$), heavily doped materials. We thoroughly probe the limitations of the $2e|S|_{\text{max}}T_{\text{max}}$ relation, particularly by exploring the effect of varying majority-to-minority weighted mobility ratio ($A$) and the dimensionless band gap ($\epsilon_g$). We generate a chart that can be used to quickly estimate the relationship between the true and the Goldsmid-Sharp band gaps depending on $A$ and $|S|_{\text{max}}$.

Fig. 7.1. Calculated temperature dependent Seebeck coefficient and $zT$ (inset) for various defect concentrations ($N_{\text{ac}} = p - n = 1 \times 10^{15} \ \text{cm}^{-3}$ in blue to $1 \times 10^{20} \ \text{cm}^{-3}$ in red) for two parabolic bands with a band gap of 0.13 eV, $m^* = 1.0 \ m_e$, and $\mu_0(300 \ \text{K}) = 820 \ \text{cm}^2/\text{Vs}$ (valence and conduction bands). Dashed line indicates the Goldsmid-Sharp band gap: $S = E_g/2eT$. The lattice thermal conductivity was estimated as $\kappa_l(T) = 1.7 \ (300/T) \ \text{W/m-K}$, following Umklapp scattering is used for the $zT$ estimate.
7.2 Different methods of estimating the $|S|_{\text{max}}$

The expression for the Seebeck coefficient in a multi band (valence/conduction) can be expressed by rearranging Eqn. 7.1(19):

$$S = \frac{1}{1 + \frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}} S_{\text{maj}} + \frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}} S_{\text{min}}} \quad \text{(Eqn. 7.2)}$$

where $S$, $S_{\text{maj}}$, and $S_{\text{min}}$ are the overall, majority carrier, and minority carrier Seebeck coefficients, respectively. $\sigma_{\text{maj}}$ and $\sigma_{\text{min}}$ are the majority and minority carrier conductivities, respectively. In the interest of maintaining general relationships applicable for either $p$ or $n$-type materials, we chose to use the majority and minority carrier labels; in the case of a primarily $p$-type material, the majority carrier will be holes.

While Goldsmid and Sharp proceed assuming Maxwell-Boltzmann, non-degenerate statistics: $\frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}} = A \exp(\eta_{\text{maj}} - \eta_{\text{min}})$, where $A = \frac{\mu_{\text{maj}}N_{\text{maj}}}{\mu_{\text{min}}N_{\text{min}}} \left(\frac{m_{\text{maj}}}{m_{\text{min}}}\right)^{3/2}$, we will consider the Fermi integral solution to the Boltzmann transport equation (assuming scattering by acoustic phonons and parabolic bands). In this context, the Seebeck coefficient of a specific carrier type ($S_i$) and electrical conductivity ratio between the majority and minority carriers can be written as a function of the dimensionless chemical potential ($\eta = \xi/k_BT$) — where $\xi$ is the electronic chemical potential:

$$S_i = \frac{k_B}{e} \left(\frac{2F_0(\eta_i)}{F_0(\eta_i)} - \eta_i\right) \quad \text{(Eqn. 7.3)}$$

$$\frac{\sigma_{\text{maj}}}{\sigma_{\text{min}}} = A \frac{F_0(\eta_{\text{maj}})}{F_0(\eta_{\text{min}})} \quad \text{(Eqn. 7.4)}$$

where $A$ has the same definition as in the Goldsmid-Sharp formulation and represents the weighted mobility ratio and $F_j$ represents the Fermi integral:
\[ F_j(\eta) = \int_0^\infty \frac{e^{\frac{1}{\epsilon - \eta}}}{1 + \exp(\epsilon - \eta)} \, d\epsilon . \]  
(Eqn. 7.5)

<table>
<thead>
<tr>
<th>Method Name</th>
<th>Criterion for Maximum</th>
<th>Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goldsmid-Sharp</td>
<td>(dS/d\eta = 0)</td>
<td>Maxwell-Boltzmann</td>
</tr>
<tr>
<td>Fermi</td>
<td>(dS/d\eta = 0)</td>
<td>Fermi</td>
</tr>
<tr>
<td>Exact</td>
<td>(dT = 0)</td>
<td>Fermi</td>
</tr>
</tbody>
</table>

Table 7.1. Description of the three different methods of estimating the maximum thermopower in this work.

In order to find the maximum thermopower, several methods can be used as differentiated in Table 7.1. The derivation of the Goldsmid-Sharp band gap does not explicitly find the maximum in thermopower with temperature; rather, Goldsmid-Sharp find a maxima with respect to reduced chemical potential, \(dS/d\eta = 0\), which is equivalent to \(dS/dT = 0\) when \(d\eta/dT\) is much larger than \(d(\epsilon_g)/dL\) as pointed out by Goldsmid and Sharp. In this work, the “Fermi” method (Table 7.1) also assumes \(dS/d\eta = 0\), as in the “Goldsmid-Sharp” method, but it uses Fermi-Dirac rather than Maxwell-Boltzmann statistics. We can test the \(dS/d\eta = 0\) approximation by performing a full, temperature dependent calculation of the Seebeck coefficient — the “Exact” method. This is accomplished by applying a charge counting balance, \(N_{AC} - N_{DO} = p - n\), at various temperatures, where \(N_{AC}\) and \(N_{DO}\) are the number of electron acceptors and donors respectively, and \(p\) and \(n\) are the number of holes and electrons, respectively (for simplicity we have assumed that \(A_m^* = \frac{m_{maj}^*}{m_{min}^*} = 1\)). The full, temperature dependent, numerically calculated results (“Exact” method) will be presented along with the simpler \(dS/d\eta = 0\) solutions using both Maxwell-Boltzmann (“Goldsmid-Sharp”) and Fermi-Dirac (“Fermi”) statistics. The expression for \(\frac{dS}{d\eta}\) used in the “Fermi” method derived using the single parabolic band Fermi integrals with acoustic phonon scattering can be written as:
\[
\frac{dS}{d\eta} = F_0(\eta)^2 - 2F_{-1}(\eta)F_1(\eta) + A \left[ 2F_1\left(-\eta - \frac{E_g}{k_BT}\right)F_{-1}(\eta) + F_0\left(-\eta - \frac{E_g}{k_BT}\right)\left\{ E_g \frac{F_{-1}(\eta)}{F_1(\eta)} + 2F_0(\eta) \right\} + F_{-1}\left(-\eta - \frac{E_g}{k_BT}\right)\left(E_g \frac{F_0(\eta) + 2F_1(\eta)}{F_1(\eta)} \right) \right] + A^2 \left[ F_0\left(-\eta - \frac{E_g}{k_BT}\right)^2 - 2F_{-1}\left(-\eta - \frac{E_g}{k_BT}\right)F_1\left(-\eta - \frac{E_g}{k_BT}\right) \right].
\]

(Eqn. 7.6)

### 7.3 Deviations from Goldsmid-Sharp band gap due to degeneracy

First, in order to probe the applicability Goldsmid-Sharp’s assumption of Maxwell-Boltzmann (non-degenerate) statistics, Figure 7.2 considers a weighted mobility ratio of \( A = 1 \). Figure 7.2a shows the chemical potential dependent Seebeck coefficient (with \( \eta = 0 \) being the valence band edge, \( \epsilon_g = 5 \) being the conduction band edge). As expected, the “Goldsmid-Sharp” result overlaps well with the “Fermi” result for chemical potentials in the gap (0 < \( \eta < 5 \)), but deviations begin for chemical potentials of about 1.5 \( k_B T \) from either band edge which become larger as the chemical potential becomes degenerate (chemical potential within the band, \( \eta < 0 \) or \( \eta > \epsilon_g = 5 \)).

Figure 7.2b quantifies the effectiveness of the \( 2e|S|_{\text{max}}T_{\text{max}} \) estimate for band gap at different \( \epsilon_g \) for the three cases of interest: the \( dS/d\eta = 0 \) model using both the “Fermi” and “Goldsmid-Sharp” methods, as well as the \( dS/dT = 0 \) (or “Exact”) case. For large \( \epsilon_g \), the “Fermi” and “Goldsmid-Sharp” solutions (\( dS/d\eta = 0 \)) converge to \( 2e|S|_{\text{max}}T_{\text{max}}/E_g \) very near 1.0 (although the exact value is \( \sim 10 \% \) less at \( \epsilon_g = 10 \)). However, as the band gap becomes small, (\( \epsilon_g < 5 \)), \( 2e|S|_{\text{max}}T_{\text{max}}/E_g \) increases for all three methods. The divergence for small gaps is a consequence of increasingly degenerate chemical potentials which yield the maximum thermopower. Experimentally, this would be observed for heavily doped samples that do not reach a maximum thermopower until very high temperatures.
7.3.1 Theoretical $|S|_{max}$ for materials with $A = 1$

Fig. 7.3a shows the magnitude of the maximum Seebeck coefficient predicted using the three different methods (as shown in Table 7.1). The result is useful for estimating the maximum attainable thermopower at a given temperature (which would be set to $T_{max}$) for a material which has an electron-to-hole weighted mobility ratio ($A$) near 1 and a known band gap. As demonstrated in Fig. 7.1, one would not be able to obtain higher thermopower regardless of extrinsic doping concentration. For example, $E_g/k_B T$ for Bi$_2$Te$_3$ ($A \sim 1^{(160)}, E_g \sim 0.13$ eV$^{(160,161)}$) is ~5.2 for operation at room temperature ($T_{max} = 300$ K), yielding a maximum Seebeck coefficient near 230 $\mu$V/K — a reasonable estimate$^{162-165}$. 

---

**Fig. 7.2.** Result of the “Exact”, “Fermi”, and “Goldsmid-Sharp” methods calculated assuming $\epsilon_g = 5$ and $A = 1$ for (a) Seebeck coefficient as a function of $\eta$, (b) the ratio of the $2e|S|_{max}T_{max}$ estimate to $E_g$ as a function of the dimensionless band gap $\epsilon_g$. 

---
By evaluating \( dS/d\eta = 0 \) from Fig. 7.2a for different dimensionless band gaps, the value of chemical potential \( (\eta_{\text{max}}) \) that yields these maxima can be obtained — the results are plotted in Fig. 7.3b. \( \eta_{\text{max}} \) converges with the classical solution from the “Goldsmid-Sharp” method when the band gap is larger than \(~6 k_B T\). Below this value, the \( \eta_{\text{max}} \) values start to deviate.

7.4 Deviations from Goldsmid-Sharp band gap due to weighted mobility ratio

We have shown that the degree of degeneracy can result in some deviations to the Goldsmid-Sharp band gap, but the weighted mobility ratio \( (A) \) can also play a substantial role. While Bi2Te3 has similar majority and minority carrier weighted mobility\(^{160,161}\), other systems such as ZrNiSn\(^{159}\), Si, Ge, and others\(^{166}\), are believed to have values that exceed two (5 in the case of ZrNiSn). In order to illustrate the effect of an increasing weighted mobility ratio, the \( \eta \)-dependent Seebeck is plotted for ZrNiSn \( (\varepsilon_g \sim 5 \) at room temperature)\(^{159}\) in Figure 7.4a. We see that the magnitude of the maximum Seebeck coefficient obtained for \( p \)-type ZrNiSn \( (A = 1/5) \) is significantly lower than that for \( n \)-type ZrNiSn \( (A = 5) \). The effect of having an \( A \) different from one is that the magnitude of the maximum Seebeck coefficient \( (|S|_{\text{max}}) \) as well as the
temperature where it occurs ($T_{\text{max}}$) is increased for the carrier type with higher weighted mobility while those of the lower weighted mobility carrier are decreased. So in a system like ZrNiSn, the $n$-type material maintains a high thermopower to much higher temperatures than might be expected from its narrow band gap (~0.13 eV) and therefore can reach an impressive $zT$ from 0.5 – 1.0\textsuperscript{(167,168)}. On the other hand, the $p$-type ZrNiSn prematurely experiences reduced thermopower due to compensating high-mobility electrons.

In Figure 7.4b, it is obvious that $2e|S|_{\text{max}} T_{\text{max}}/E_g$ is larger than 1.0 for all values of $\epsilon_g$ when $A = 5$ while it is less than 1.0 for all $\epsilon_g$ for $A = 1/5$ (except at quite low $\epsilon_g$). Figure 7.4c shows how $2e|S|_{\text{max}} T_{\text{max}}/E_g$ increases with increasing $A$ values; larger deviations are observed as $E_g/k_B T$ becomes smaller. In comparison with Goldsmid-Sharp’s conclusion that only ~20% deviation is observed for $A = 10$, we find that 50 - 100% errors in the estimated gap can be obtained for $\epsilon_g$ values reasonable for many relevant thermoelectric materials ($\epsilon_g \approx 4 - 5$).
Fig. 7.4. Result of the “Exact”, “Fermi”, and “Goldsmid-Sharp” methods assuming $\epsilon_g = 5$ and $A = 5$ (weighted mobility ratio) for (a) Seebeck coefficient as a function of $\eta$, (b) the ratio of the $2e|S|_{\text{max}}T_{\text{max}}$ estimate to the actual model $E_g$ as a function of $\epsilon_g$, and (c) the same ratio with respect to the weighted mobility ratio $A$ at different $E_g$ values (3, 5, and 10 $k_B T$ as indicated on the figure).

7.4.1 Theoretical $|S|_{\text{max}}$ for materials with $A = 5$

In the case of non-unity $A$ value, $|S|_{\text{max}}$ is always larger for the $A=5$ (majority carrier five times the weighted mobility as minority) case than for the $A=1/5$ (minority carrier five times the weighted mobility as majority) for all values of $E_g/k_B T$ as shown in Fig. 7.5a. Although some differences between the “Goldsmid-Sharp”
and the other two methods occur for small values of $E_g/k_B T$ in the $A = 1/5$ calculation (probably breaking down of the classical approximations in favor of Fermi statistics), all three methods show qualitatively the same trends. In terms of the chemical potential which yields the maximum Seebeck coefficient, Fig. 7.5b shows that if the majority carrier has a lower weighted mobility ($A = 1/5$), $\eta_{max}$ tends to occur nearer to the band edge ($\eta_{max} = 0$ at a larger value of $E_g/k_B T_{max}$). This results in larger deviations from the Goldsmid-Sharp band gap.

![Graphs showing thermopower and chemical potential trends](image)

**Fig. 7.5.** Maximum attainable thermopower (a) and the reduced chemical potential which yields it (b) as a function of reduced band gap (at the rollover temperature). The dashed line in Figure (b) represents half way between the valence and conduction bands, the dotted grey lines represent the position of the valence and conduction bands. All calculations are done for a majority-to-minority carrier weighted mobility ratio of $A = 5$ and $1/5$.

### 7.5 Engineering guide for estimation of the real band gap

While the Goldsmid-Sharp band gap has proven to be a simple and useful estimate for the real band gap, it is not without its limitations. In this work, we have shown several cases for which this simple approximation breaks down. Fig. 7.6 shows the deviation between the Goldsmid-Sharp band gap and the true band gap for a wide variety of these parameters. Ultimately, we observe that the magnitude of the deviation is largest for materials with large differences between the weighted mobility of electrons and holes ($A \neq 1$). From an experimental perspective, $A \neq 1$ will result in a larger value of $2e|S|_{max} T_{max}$ for the higher weighted mobility species, and a lower value for the one with lower weighted mobility. In the case of ZrNiSn, the more mobile
electrons ($A = 5$) result in an observation of about a five-fold difference in the $p$-type ($\sim 0.05$ eV) and the $n$-type ($\sim 0.25$ eV) Goldsmid-Sharp band gaps.$^{159}$

Figure 7.6 can be useful in determining either an unknown $A$ value for a material if the true band gap is known, or it can show the expected deviations of the Goldsmid-Sharp band gap relative to the true band gap for a given $A$ value. For instance, in the case of $n$-type ZrNiSn with $2e|S|_{\text{max}}T_{\text{max}}/E_g = 2.1$ (using $E_{g,\text{optical}} = 0.13$ eV$^{(159)}$) and observed maximum Seebeck coefficient ($\sim 200$ $\mu$V/K), we determine $A \sim 5$. Alternatively, if the majority-to-minority carrier weighted mobility ratio ($A$) is known, one can (based on the magnitude of the maximum Seebeck coefficient) obtain an estimate a value for $2e|S|_{\text{max}}T_{\text{max}}/E_g$ from Figure 7.6, which can be used to estimate the true band gap (as described in the numbered list below).

1. Measure temperature dependent thermopower and obtain a maximum.

2. Calculate the Goldsmid-Sharp band gap: $E_g = 2e|S|_{\text{max}}T_{\text{max}}$.

3. If $|S|_{\text{max}} < 150$ $\mu$V/K, be aware that the true $E_g$ may significantly differ from $2e|S|_{\text{max}}T_{\text{max}}$ (see below).

4. For $|S|_{\text{max}} > 150$ $\mu$V/K, estimate the majority-to-minority carrier weighted mobility ratio, $A$.

5. Find the $2e|S|_{\text{max}}T_{\text{max}}/E_g$ ratio ($r$) from Figure 7.6 that is consistent with that $A$ and $S_{\text{max}}$ value to then calculate the corrected $E_g = 2e|S|_{\text{max}}T_{\text{max}}/r$.

The $S_{\text{max}} < 150$ $\mu$V/K describes the degenerate crossover that leads to the upward trend in Figure 7.6 mentioned previously for low values of $S_{\text{max}}$. For degenerate, heavily doped samples ($\eta_{\text{max}}$ in the majority band) $E_g/k_B T_{\text{max}}$ becomes a poor metric for describing the bipolar effects; rather, we believe the thermal band gap ($\frac{E_g,\text{thermal}}{k_B T} = \epsilon_g + \eta$) is the relevant parameter. This effect is even more pronounced as $A$ is decreased because the lower mobility majority carrier requires a chemical potential deep within the band (large $\eta$) to mitigate the effects of a highly mobile minority carrier.
In summary, the Goldsmid-Sharp band gap \((E_g = 2e|S|_{\text{max}}T_{\text{max}}/E_g)\) is an extremely useful tool for obtaining an estimate for a material’s band gap through temperature dependent Seebeck measurements. While most researchers understand that this is not an exact estimate, it is important to understand when and why the simple relation can break down and to what extent. In this work, we show that large deviations can occur for several reasons: a breakdown of Maxwell-Boltzmann statistics (used to derive the Goldsmid-Sharp band gap) for materials with narrow gaps, or materials with very large (or small) majority-to-minority carrier weighted mobility ratio \((A)\). Because bipolar conduction is detrimental to thermoelectric performance, results from this work using the Goldsmid-Sharp gap could be used to validate strategies for suppressing bipolar effects beyond altering band gap and doping\(^{155,169-171}\) but also by other methods (including nanostructures\(^{27,172-174}\)) given that both \(n\)-type and \(p\)-type samples are obtainable.
Chapter 8

Characterization of Lorenz number with Seebeck coefficient measurement

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8.1 Introduction

A semiconductor with large Seebeck coefficient, high electrical conductivity, and low thermal conductivity is a good candidate for a thermoelectric material. Because the charge carriers (electrons in n-type or holes in p-type semiconductors) transport both heat and charge, the electronic contribution to the thermal conductivity ($\kappa_e$) is commonly estimated from the measured electrical conductivity ($\sigma$) using the Wiedemann-Franz law: $\kappa_e = L\sigma T$, where $L$ and $T$ are the Lorenz number and the temperature, respectively. Once $\kappa_e$ is known, lattice thermal conductivity ($\kappa_l$) is computed by subtracting the $\kappa_e$ from the total thermal conductivity, $\kappa_{total} = \kappa_e + \kappa_l$. For this method, the bipolar thermal conductivity ($\kappa_{bp}$) will also be included, which can be written $\kappa_{bp} + \kappa_l = \kappa_{total} - L\sigma T$.

Since a high $zT$ requires low $\kappa_{total}$ but high $\sigma$ simultaneously, one of the more popular routes towards improving $zT$ has been to reduce $\kappa_l^{10}$. However, depending on the value of $L$, which maps from $\sigma$ to $\kappa_e$, the resulting $\kappa_l$ can often be misleading. For instance, in the case of lanthanum telluride, incautious determination of $L$ can even cause $\kappa_l$ to be negative, which is not physical$^{175}$. Therefore, careful evaluation of $L$ is critical in characterizing enhancements in $zT$ due to $\kappa_l$ reduction.

For most metals, where charge carriers behave like free-electrons, $L$ converges to $\frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8}$ W$\Omega K^{-2}$ (degenerate limit). Although some heavily doped semiconductor thermoelectric materials have an $L$ very close to the degenerate limit, properly optimized materials often have charge carrier concentrations...
between the lightly doped (non-degenerate) and heavily doped (degenerate) regions\(^{176}\) (\(\xi_{optimum}\) is near the band edge where \(\xi\) is the electronic chemical potential) which can result in errors of up to \(\sim 40\%\)\(^{177}\).

Direct measurement of \(L\)\(^{178}\), requires high mobility — typically beyond that attainable at the temperatures of interest (> 300 K). Thus \(L\) is typically estimated either as a constant \((2.44 \times 10^{-8} \text{ W} \Omega \text{K}^{-2})\) or by applying a transport model — such as the single parabolic band (SPB) model obtained by solving the Boltzmann transport equations — to experimental data.

For example, Larsen \textit{et al.} proposed an approximate analytical solution of \(L\) based on the SPB model as a function of carrier concentration \((n)\) and \((m^*T)^{3/2}\) (where \(m^*\) is the density-of-states effective mass) along with various sets of parameters for distinct carrier scattering mechanisms\(^{179}\). However, when the Hall carrier concentration, \(n_H\), of a material is not available, the use of the approximate solution by Larsen is not possible. It can be shown that for the SPB model with acoustic phonon scattering (SPB-APS), both \(L\) and \(S\) are parametric functions of only the reduced chemical potential \((\eta = \xi/k_B T\), where \(k_B\) is Boltzmann constant); thus no explicit knowledge of temperature \((T)\), carrier concentration \((n)\), or effective mass \((m^*)\) is required to relate them\(^{180}\). We have utilized this correlation between \(L\) and measured \(S\) to estimate \(\kappa_l\) for a few known thermoelectric materials including: PbTe\(^{144,181,182}\), Zintl materials\(^{183-185}\), Co-doped FeV\(_{0.6}\)Nb\(_{0.4}\)Sb Half Heusler\(^{186}\), La\(_{3-x}\)Te\(_4\)\(^{175}\), resulting in much more satisfactory values for \(\kappa_l\) than the degenerate limit result \((L = 2.44 \times 10^{-8} \text{ W} \Omega \text{K}^{-2})\) would have.

While the SPB model works well to estimate \(L\), a transcendental set of equations is needed to solve for \(L\) in terms of \(S\) — requiring a numerical solution. Considering that the typical measurement uncertainty for \(\kappa_{total}\) is 10% and that SPB-APS is only an approximation, a much simpler equation would supply sufficient accuracy. Here we propose the equation

\[
L = 1.5 + \exp\left[\frac{|S|}{116}\right], \quad \text{(Eqn. 8.1)}
\]

where \(L\) is in \(10^{-8} \text{ W} \Omega \text{K}^{-2}\) and \(S\) in \(\mu\text{V/K}\) as a satisfactory approximation for \(L\).
8.2 Lorenz number as a function of thermopower – from Single Parabolic Band model

We examine the $L$ function in terms of $S$ for the SPB-APS case and provide a simple expression relating the two (Eqn. 8.1). Eqn. 8.1 allows for a facile estimation of $L$ from an experimental $S$ only without requiring a numerical solution. We characterize the effectiveness of this estimate for $L$ using some experimental data from some relevant thermoelectric materials (PbSe\(^{(187)}\), PbS\(^{(188)}\), PbTe\(^{(30,189)}\), Zintl material (Sr\(_3\)GaSb\(_3\))\(^{183}\), Half Heusler (ZrNiSn)\(^{190}\), and Si\(_{0.8}\)Ge\(_{0.2}\)\(^{191}\)).

For a single parabolic band, $L$ and $S$ are both functions of reduced chemical potential ($\eta$) and carrier scattering factor ($\lambda$) only:

$$L = \left(\frac{k_B}{e}\right)^2 \frac{(1+\lambda)(3+\lambda)F_{\lambda}(\eta)F_{\lambda+2}(\eta)-(2+\lambda)^2F_{\lambda+1}(\eta)^2}{(1+\lambda)^2F_{\lambda}(\eta)^2}$$

(Eqn. 8.2)

$$S = \frac{k_B}{e} \left(\frac{(2+\lambda)F_{\lambda+1}(\eta)}{(1+\lambda)F_{\lambda}(\eta)} - \eta\right),$$

(Eqn. 8.3)

where $F_{\lambda}(\eta)$ represents the Fermi integral:

$$F_{\lambda}(\eta) = \int_0^\infty \frac{e^{\lambda e}}{1+\exp(e-\eta)}.$$

(Eqn. 8.4)

By assuming that the carrier relaxation time is limited by acoustic phonon scattering (one of the most relevant scattering mechanisms for thermoelectric materials above room temperature\(^{30,192}\)), Eqns. 8.2 and 8.3 can be solved numerically for $L$ and the corresponding $S$ as shown in Fig. 8.2 along with the proposed approximation (Eqn. 8.1).
According to the Fig. 8.1, the degenerate limit of $L \times 10^{-8}$ $\text{W} \Omega^{-2}$ K is valid with errors less than 10% for materials whose thermopower is smaller than 50 $\mu$V/K (highly degenerate). In contrast, if the thermopower is large, the discrepancy with the degenerate limit can be up to 40%.

To decide an appropriate value of $L$ with a known $S$ easily, rather than graphically extracting it from Fig. 8.1, Eqn. 8.1 can be used to quickly estimate $L$, given a measured thermopower. Eqn. 8.1 is accurate within 5% for single parabolic band where acoustic phonon scattering is dominant scattering mechanism when $|S| > \sim 10$ $\mu$V/K. For $|S| < 10$ $\mu$V/K, while the SPB model converges to the degenerate limit, Eqn. 8.1 increases exponentially, thus reducing the accuracy of the Eqn. 8.1. Although estimation of $L$ with an accuracy within 0.5% for SPB-APS is possible, this requires an approximate equation more complex than Eqn. 8.1 (see Chapter 8.5 for the more complex equation).
Fig. 8.2. Thermopower dependent Lorenz number obtained from materials whose band structure and scattering assumptions are different from those assumed in SPB-APS along with Eqn. 8.1 calculation. For comparison, the degenerate limit of $2.44 \times 10^{-8}$ $\text{W} \Omega K^{-2}$ is also presented in a red dashed line.

### 8.3 Lorenz number for non-parabolic band model

Exceptions are known where $L$ has been found to be outside the uncertainty described above for SPB-APS which are presented in Fig. 8.2 and Table 8.1. Temperature dependent $S$ and $L$ were directly extracted from corresponding literature for Sr$_3$Ga$_{0.97}$Zn$_{0.07}$Sb$_3$ (183), ZrNiSn$_{0.99}$Sb$_{0.01}$ (190), and PbTe$_{0.85}$Se$_{0.15}$ (30). Pairs of $S$ and $L$ at each temperature were then plotted in Fig. 8.2. In cases of PbTe$_{0.998}$I$_{0.002}$ (189), Pb$_{1.002}$Se$_{0.998}$Br$_{0.002}$ (labeled as 3E19 in the literature) (187), and PbS$_{0.9978}$Cl$_{0.0022}$ (4E19 in the literature) (188), temperature dependent $L$ was calculated from temperature dependent resistivity ($\rho = 1/\sigma$), $\kappa_{\text{total}}$, and $\kappa_l$ from $\kappa_l = \kappa_{\text{total}} - L \sigma T$ (temperature dependent $S$ was given in the literature). For Si$_{0.9}$Ge$_{0.2}$ (191), theoretical carrier concentration ($n_c$) dependent Hall mobility ($\mu_{H}$) and $\kappa_c$ were used to calculate theoretical $n_c$ dependent $\sigma$ and $L$ using the relations: $\sigma = n_c e \mu_H$ and $\kappa_c = L \sigma T$. The acquired $n_c$ dependent $\sigma$ along with theoretical $n_c$ dependent $zT$ and $\kappa_{\text{total}}$ given in the literature were utilized to obtain $n_c$ dependent $S$ at 1300 K ($zT = \sigma S^2 T / \kappa_{\text{total}}$). From the theoretical $n_c$ dependent $S$ and $L$, pairs of $S$ and $L$ at each $n_c$ were extracted for Si$_{0.9}$Ge$_{0.2}$ at 1300 K. Since Vining provided experimental temperature dependent $S$ (labeled as T373) in the range 700 K $\sim$ 1300 K, the
$S$ value at 1300K was taken for T373 and corresponding $L$ was found from the theoretical pairs of $S$ and $L$, where the theoretical $S$ corresponds to that of T373.

These exceptions typically involve either non-parabolic band structures (PbTe, PbSe, PbS) or alternative scattering mechanisms (other than acoustic phonons). Narrow-gap semiconductors (lead chalcogenides for example) are often better described by the non-parabolic Kane model which yields a different $\eta$ dependence of $L$ and $\kappa$ which depends on the non-parabolicity parameter: $\alpha = \frac{k_B T}{E_g}$ (ref. 17,193). For well-studied lead chalcogenides (PbTe, PbSe, PbS), a reasonable range of $\alpha$ is from 0.08 (300 K) to 0.16 (850 K). Figure 8.2 shows that $L$ is at most ~26 % lower than that of the SPB-APS and Eqn. 8.1 result over the entire range of temperatures. In other words, $\kappa_l$ estimates will maintain the order: $\kappa_{l,deg} < \kappa_{l,SPB-APS} < \kappa_{l,SKB-APS}$ (where SKB stands for the single Kane band model) with the largest errors being for the degenerate limit when applied in the non-degenerate case.

For narrow-gap semiconductors, because the energy gap ($E_g$) between the valence and conduction band extrema is small, the two nearest bands interact to each other making the energy dependence of crystal momentum non-quadratic, and effective mass a function of energy. A thermoelectric transport model incorporating the non-parabolicity of a band is called a single Kane band (SKB) model194. For a single Kane band (assuming acoustic phonon scattering), $L$ and $S$ are both functions of reduced chemical potential ($\eta$) and non-parabolicity parameter ($\alpha = \frac{k_B T}{E_g}$):

$$L = \left( \frac{k_B}{e} \right)^2 \left[ \frac{2 F_{1/2}^{1/2}}{\partial F_{1/2}^{1/2}} - \left( \frac{1 F_{1/2}^{1/2}}{\partial F_{1/2}^{1/2}} \right)^2 \right] \quad \text{(Eqn. 8.5)}$$

$$S = \frac{k_B}{e} \left( \frac{1 F_{1/2}^{1/2}}{\partial F_{1/2}^{1/2}} - \eta \right), \quad \text{(Eqn. 8.6)}$$

where $\frac{\eta F_{K}^{m}(\eta)}{p}$ represents the following integral with the Fermi-Dirac distribution, $f$: 
\[ nP_k^m(\eta) = \int_0^\infty \left( -\frac{\partial f}{\partial \epsilon} \right) \epsilon^n (\epsilon + \alpha \epsilon^2)^m [(1 + 2\alpha \epsilon)^2 + 2]^{k/2} d\epsilon . \] 

(Eqn. 8.7)

The thermopower dependent \( L \) calculated for different \( \alpha \) using SKB model for acoustic phonon scattering is shown in Fig. 8.3. At a given temperature, the narrower the \( E_g \) gets (the larger the \( \alpha \)), the more \( L \) deviates from the SPB result (“SPB model (APS)” in Fig. 8.3). Although it is not presented in the figure, the SKB result without non-parabolicity (\( \alpha = 0, E_g \sim \infty \)) exactly coincides with the SPB model result as there is no interaction between valence and conduction band due to their infinite separation. Narrow-gap thermoelectric materials (\( \text{PbTe}_{0.9988}\text{I}_{0.0012}(189), \text{Pb}_{1.002}\text{Se}_{0.998}\text{Br}_{0.002}(187), \text{and PbS}_{0.9978}\text{Cl}_{0.0022}(188), \) and \( \text{PbTe}_{0.85}\text{Se}_{0.15}(30) \)) require temperature dependent \( E_g \) (between conduction and valence bands) for accurate determination of \( S \) and \( L \) using SKB model (Eqns. 8.5 and 8.6 in functions of \( \eta \) and \( \alpha \) for acoustic phonon scattering). For instance, \( E_g/eV = 0.17 + 4 \times 10^{-4} T/K \) is employed for SKB model of \( \text{Pb}_{1.002}\text{Se}_{0.998}\text{Br}_{0.002}(187) \).

![Fig. 8.3](image) Calculation of thermopower dependent Lorenz number for a single Kane band with assumption of acoustic phonon scattering for different band non-parabolicity parameter (\( \alpha \)). For comparison, the SPB-APS result (orange) and the degenerate limit of \( 2.44 \times 10^{-8} \text{W}\Omega\text{K}^{-2} \) (red) are also presented.

Alternative scattering mechanisms can also yield deviations from the SPB-APS. For example, when ionized impurity scattering dominates (\( \lambda = 2 \)), the \( L \) actually increases with increasing \( S \), however, this example is not particularly prevalent in materials which have high dielectric constants (including the lead...
chalcogenides) or at high temperatures. At low temperatures (< 100 K), as $S$ approaches zero, it is expected that $L$ converges to the degenerate limit regardless of carrier scattering mechanism and parabolicity of bands involved in transport. However, a pronounced inelastic electron-electron scattering due to high mobility of carriers decreases $L$ from the degenerate limit, even for strongly degenerate materials. In case of $n$-type PbTe, $L$ at 100 K is approximately 40% lower than its value at 300 K.

When there is more than one dominant scattering mechanism affecting the transport of a non-parabolic band, Eqns. 8.5 and 8.6 need to be replaced by the following equations:

$$L = \left( \frac{k_B}{e} \right)^2 \left[ \frac{\int_0^\infty \left( \frac{\partial f}{\partial \epsilon} \right) \tau_{\text{total}}(\epsilon) \epsilon^{7/2}(1+\alpha \epsilon)^{3/2}(1+2\alpha \epsilon)^{-1} d\epsilon}{\int_0^\infty \left( \frac{\partial f}{\partial \epsilon} \right) \tau_{\text{total}}(\epsilon) \epsilon^{3/2}(1+\alpha \epsilon)^{3/2}(1+2\alpha \epsilon)^{-1} d\epsilon} \right]^2 \left( \int_0^\infty \left( \frac{\partial f}{\partial \epsilon} \right) \tau_{\text{total}}(\epsilon) \epsilon^{5/2}(1+\alpha \epsilon)^{3/2}(1+2\alpha \epsilon)^{-1} d\epsilon \right)$$

(Eqn. 8.8)

$$S = \frac{k_B}{e} \left( \int_0^\infty \left( \frac{\partial f}{\partial \epsilon} \right) \tau_{\text{total}}(\epsilon) \epsilon^{5/2}(1+\alpha \epsilon)^{3/2}(1+2\alpha \epsilon)^{-1} d\epsilon \right) \eta,$$

(Eqn. 8.9)

where $\tau_{\text{total}}(\epsilon)^{-1} = \sum \tau_i(\epsilon)^{-1}$ ($\tau_i(\epsilon)$ is a relaxation time of a scattering mechanism $i$). Detailed equations for acoustic phonon, polar, and alloy scattering can be found in literatures for PbS$_{0.9978}$Cl$_{0.0022}$ and ZrNiSn$_{0.99}$Sb$_{0.01}$.

Table 8.1. Estimated maximum error to Eqn. 8.1 for $L$ with different band structure and scattering assumptions.

<table>
<thead>
<tr>
<th>Band</th>
<th>Scattering</th>
<th>Examples</th>
<th>Max. error (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>AP</td>
<td>SrGa$<em>{0.93}$Zn$</em>{0.07}$Sb$_3$</td>
<td>4.4</td>
<td>183</td>
</tr>
<tr>
<td>2$P$</td>
<td>AP+II</td>
<td>Si$<em>{10.8}$Ge$</em>{0.2}$</td>
<td>7.5</td>
<td>191</td>
</tr>
<tr>
<td>$K$</td>
<td>AP</td>
<td>PbTe$<em>{0.9985}$I$</em>{0.0012}$</td>
<td>19.7</td>
<td>189</td>
</tr>
<tr>
<td>$K$</td>
<td>AP+PO</td>
<td>Pb$<em>{1.005}$S$</em>{0.998}$B$_{0.002}$</td>
<td>19.5</td>
<td>187</td>
</tr>
<tr>
<td>$K$</td>
<td>AP+PO+AL</td>
<td>PbS$<em>{0.9978}$Cl$</em>{0.0022}$</td>
<td>19.4</td>
<td>188</td>
</tr>
<tr>
<td>2$K$+P</td>
<td>AP</td>
<td>ZrNiSn$<em>{0.99}$Sb$</em>{0.01}$</td>
<td>25.6</td>
<td>190</td>
</tr>
<tr>
<td>2$K$+P</td>
<td>AP</td>
<td>PbTe$<em>{0.935}$Se$</em>{0.065}$</td>
<td>14.9</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$Band is the type and number of bands involved in evaluating $L$. For instance, “2K+P” means two non-parabolic Kane bands (K) and a parabolic band (P).

$^b$Scattering is the type of scattering mechanism assumed in estimating $L$. AP, II, PO, and AL are acoustic phonon, ionized impurities, polar, and alloy scattering, respectively. For example, “AP+PO” means that both acoustic phonon and polar scatterings are assumed in calculating $L$. 


8.4 Lorenz number for multiple-band model

Multiple band behavior (present in $p$-type PbTe$_{0.85}$Se$_{0.15}$, and $n$-type Si$_{0.8}$Ge$_{0.2}$ Fig. 8.2) can also lead to deviations in the thermopower-dependence of the Lorenz number. In the case of PbTe, hole population of both the light and heavy bands yields a more complicated relationship between $L$ and $S$; it is not simply a parametric function of $\eta$ and depends on the specific effective mass and mobility contributions from each band.

When more than a single band is involved in a transport, total $S$ and $L$ are expressed as follows:

\[
L = \frac{\sum L_i \sigma_i}{\sum \sigma_i} \quad \text{(Eqn. 8.10)}
\]
\[
S = \frac{\sum S_i \sigma_i}{\sum \sigma_i}, \quad \text{(Eqn. 8.11)}
\]

where $S_i$, $\sigma_i$, and $L_i$ are Seebeck coefficient, electrical conductivity, and Lorenz number for a band denoted as $i$, respectively. Total $S$ and $L$ were calculated using Eqns. 8.10 and 8.11 for Si$_{0.8}$Ge$_{0.2}$(191) (valence band and conduction band, both parabolic bands) and PbTe$_{0.85}$Se$_{0.15}$(30) (one conduction band and two valence bands where the lower valence band in parabolic while other bands are all Kane type bands).

One last, prevalent source of error occurs because the Wiedemann-Franz law does not take the bipolar thermal conductivity into consideration. $\kappa_i$ calculated from the difference between $\kappa_{total}$ and $\kappa_e$ does include varying portion of bipolar conduction with respect to temperature and band structure of materials (which can become important for lightly doped materials with narrow gaps at high temperatures190).

An equation for $L$ entirely in terms of the experimentally determined $S$ is proposed and found to be accurate (within 20 %) for most common band structures/scattering mechanisms found for thermoelectric materials. Use of this equation would make estimates of lattice thermal conductivity much more accurate without requiring additional measurement.
8.5 Approximate $L$ function with an accuracy within 0.5 %

\[ L = 1.49 - 0.49 \exp\left[\frac{-|S|}{21}\right] + 1.40 \exp\left[\frac{-|S|}{85}\right] \]  

(Eqn. 8.12)

Eqn. 8.12 estimates results of SPB model under APS with a maximum error less than 0.5 % for $|S| > 10 \mu V/K$.

![Graph](image-url)  

Fig. 8.4. $L$ calculated from Eqn. 8.1 and Eqn. 8.12 in comparison to results of SPB model under APS
Chapter 9

Improved Mechanical Properties of Thermoelectric (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ by Nanostructuring

This section contains contents that have been accepted to *APL Materials*. Once it is published online, permission will be asked.

9.1 Introduction

Thermoelectric (TE) devices based on Bi$_2$Te$_3$ are important for cooling and emerging power generation applications\textsuperscript{197}. TE devices are relatively robust and reliable because they are made of solid-state components without any moving parts. However, significant thermal stresses placed on TE materials during material processing, device fabrication, and use can ultimately lead to a mechanical failure if stresses exceed the strength of the materials\textsuperscript{198,199}. Although the mechanical strength of a TE material is often overlooked in comparison with its TE figure of merit, $zT = \alpha^2 \sigma T / \kappa$ ($\alpha$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, electric conductivity, absolute temperature, and the thermal conductivity, respectively), it is also an important parameter to consider especially when the material is to be included within a TE module.

TE materials are commonly prepared by zone-melting\textsuperscript{200}, Czochralski\textsuperscript{201} or Bridgman methods\textsuperscript{202}. In Bi$_2$Te$_3$-based alloys, these growth methods produce single or oriented polycrystals due to anisotropy in the solidification rate – faster within the $a$-$b$ cleavage plane and slower parallel to the $c$-direction. Producing preferentially oriented crystals is advantageous as these materials show a maximum in $zT$ parallel to the growth direction and normal to the $c$-direction\textsuperscript{12}. The $zT$ of (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ single crystal was reported to be $\sim$0.87 at 300 K\textsuperscript{12}. Among the listed crystal growth methods, the vertical zone-melting is the most widespread method for the industrial production of textured (Bi, Sb)$_2$Te$_3$ crystals with large-sized grains.
However, in lab-scale experiments, higher $zT$ has been observed in polycrystalline (Bi, Sb)$_2$Te$_3$ with micron sized grains. Although the grinding of material to decrease grain size disrupts the preferable orientation of grains thereby lowering $\sigma$, the $zT$ of $p$-type (Bi, Sb)$_2$Te$_3$ at 300 K increases to the value $\sim$1.0 because of increased grain boundary scattering of phonons, which results in a much lower $\kappa$. Further enhancement in $zT$ was achieved by reducing the average grain size of the polycrystalline (Bi, Sb)$_2$Te$_3$ down to nanoscale ($zT \approx 1.1$-$1.3$)\textsuperscript{27,203-205}. Many methods of synthesizing bulk nanocrystalline (Bi, Sb)$_2$Te$_3$ involve ball-milling powders to nanosize and subsequently compacting the powders by hot pressing or spark plasma sintering (SPS)\textsuperscript{27,203-205}. Some of the preferred grain orientation lost during ball-milling can also be recovered through high-temperature extrusion of (Bi, Sb)$_2$Te$_3$ samples\textsuperscript{206-209}.

Although there are many reports on thermoelectric properties of (Bi, Sb)$_2$Te$_3$ samples prepared via different processing routes, the temperature-dependent mechanical properties of the samples are not sufficiently investigated\textsuperscript{210-212}. In particular, there are few studies comparing the mechanical properties of nanostructured (Bi, Sb)$_2$Te$_3$ with those of state-of-the-art zone-melted (Bi, Sb)$_2$Te$_3$\textsuperscript{213-215}. In this work, temperature-dependent fracture strengths of (Bi, Sb)$_2$Te$_3$ processed by vertical zone-melting, hot extrusion, and SPS are presented. In addition, a mechanism is proposed for the low brittle-ductile transition temperature observed in the nanostructured sample prepared by SPS. These strength data along with an understanding of their underlying mechanisms are essential for developing TE materials optimized for high and reliable performance within TE modules.

### 9.2 Experimental

Ingots were produced with a stoichiometric composition of (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ by melting the elemental components in sealed quartz ampoules at a temperature of 720 °C for 2 hours followed by quenching. The ingots were confirmed to be single phase by X-ray diffraction (XRD). These ingots were further processed by three different methods, vertical zone-melting, hot extrusion, and hot compaction, using SPS. Vertical zone-melting was performed using a Kristall-810 with resistive heating. Temperature of the molten zone
was between 700-780 (±1) °C and the temperature gradient at the crystallization front was ~100 °C/cm. The molten zone passed through the ingot twice: downwards with a speed of ~0.5 mm/min followed by upwards at a reduced speed of ~0.1-0.15 mm/min.

Hot extrusion was performed using an IP2500 250-ton hydraulic press equipped with a temperature control system maintained between 400-450 °C. Samples were extruded at a pressure of 250-300 MPa at a punch speed of 0.5 mm/min producing an extrusion factor of 18.

For the SPS processed materials, ingots were first ball-milled to a particle size of ~8-10 nm using a Retsch PM 400 high-speed planetary mill. The techniques for obtaining nano-sized powders and estimating size of the powders are described in more details in refs. 203-205. The nanopowder was compacted into disks 20 mm diameter and 5 mm thickness under a pressure of 250 MPa in protective atmosphere at room temperature. Next, the disks were sintered using a Fuji SPS-511S SPS at a temperature of 450-500 °C for 10 min under pressure of 50 MPa. The speed of heating and cooling was 16 °C/min.

To determine the mechanical properties, rectangular samples of size 5 × 5 × 6 mm³ were cut using electrical discharge machining (EDM) from the materials fabricated by each of the three methods. The length scale of material affected by EDM is in the order of 10 µm, significantly lower than the dimensions of the samples for mechanical testing. This was estimated from changes of width in XRD peaks before and after EDM. Any change in strength due to EDM is negligible regardless of the processing route. An Instron model 5982 controlled using “Bluehill Materials Testing Software” was used for mechanical tests under uniaxial compression. The uncertainty of loading on the sample is not expected to exceed 0.4 %, and the uncertainty of travel is ± 0.001 mm. Tests were performed with speed of 0.05 mm/min. A demountable hinged electric furnace was used for heating samples during measurement; temperature was measured using a Type-K thermocouple. The cut samples were placed under uniaxial compression in such a way that the compression direction was along the growth direction and the extrusion direction for the zone-melted and extruded
samples, respectively. For SPS processed samples, loading was normal to the compaction direction during SPS.

9.3 Fracture strength of materials prepared via different methods

Fig. 9.1. Stress – strain curves for the samples processed by zone-melting (a), hot extrusion (b), and SPS (c) at temperatures: (■) – 25 °C; (▲) – 100 °C; (●) – 150 °C; (♦) – 170 °C; (○) – 200 °C; (◇) – 250 °C; (◊) – 300 °C; (●) – 350 °C
The stress-strain curves recorded during sample deformation are presented in Fig. 9.1. For all of the (Bi0.2Sb0.8)2Te3 samples at low strains, the deformation is elastic and follows Hooke's law. At 25 °C, the slope of the plots, a measure of the elastic stiffness of the material, is highest in the SPS processed nanograin material, followed by the extruded and then zone melted materials. The nanograin material is roughly fifty percent more stiff than the zone melted. Compounds of the form (Bi,Sb)2(Te,Se)3 are highly anisotropic in their mechanical properties. This is due to the strong covalent bonding present within the a-b planes and weak van der Waals bonding between neighboring Te/Se planes. For example, in Bi2Te2Se, the elastic stiffness constant is over 7 times smaller parallel to the c-axis as compared to the a or b axes22. The stiffness variation between materials produced via different methods can be understood in terms of grain size and preferred orientation. In the nanograin materials, the random orientation of grains results in an averaging effect of the elastic properties within the material. In contrast, the extruded and zone melted materials exhibit more preferential orientation in their grains making them weaker in specific directions and easier to deform.

Brittle fracture is observed in all samples without appreciable plastic deformation at temperatures below 200 °C. In the stress-strain curves for the zone-melted sample, pronounced jumps in the deformation curves are observed due to the formation of cracks or deformation twinning (purple curves in Fig. 9.1a for 25 °C). Overall, the stress at failure is highest in the nano-grained SPS material and lowest in the zone-melted material. This difference is attributable to grain size and orientation differences. Nano-grained materials are known to fracture through grain boundaries (inter-granular fracture) while coarse-grained materials (> 10 μm) fracture along specific crystallographic planes within grains (transgranular fracture)216. In the larger grained zone melted material, failure occurs via transgranular cleavage between the weakly bonded neighboring Te planes. The cleavage planes throughout the sample are far more aligned in zone melted materials than randomly oriented SPS materials. At smaller grain sizes, cleavage planes no longer align over appreciable distances and failure proceeds by inter-granular means. The small grain size limits the length of any initiating cracks which can be present and the material is markedly more resistant to
fracture. Unlike others, the zone-melted sample went through partial plastic deformation before the fracture even at $T < 200^\circ$C. Because grains in the zone-melted sample have not experienced heavy deformation like those in extruded or SPS sample during the synthesis, there may be more room for the movement of dislocations in the sample under stress\textsuperscript{217}.

As the temperature is raised, a marked brittle-ductile transition is observed and plastic deformation begins to occur. For samples produced by zone-melting or extrusion, the brittle-ductile transition occurs within a broad temperature range from 200 to 300 °C. When average grain size of the samples prepared by zone-melting and extrusion was reduced to tens of μm (from the order of mm) the materials became much stronger at low temperatures. Nonetheless, even with smaller grain size, they also weakened above 200 °C. In the nanostructured material (SPS sample), the transition occurs at lower temperatures between 170-200 °C.

At high temperatures, there was no ultimate destruction of the sample during the course of testing; instead plastic deformation was accompanied by deformation hardening. This behavior was observed for the extruded sample at 300-350 °C and for nanostructured at 200-300 °C. Therefore, the maximum stress values for these samples cannot be considered as true strengths-to-failure although they effectively characterize the mechanical strength of the materials.

![Fig. 9.2. Temperature-dependent strength of the samples fabricated by zone-melting (▲), extrusion (♦), and SPS (■). The maximum pressure during the course of high-temperature testing of the extruded and SPS samples without destruction were obtained from Fig. 2.1.](image-url)
The temperature dependence of the maximum stress values is shown in Fig. 9.2. A rapid decrease in mechanical strength above 200 °C is found for all of the (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ samples. Above 100 °C the samples prepared by zone-melting, have strength of only 20-30 MPa which varies only slightly with temperature.

The plastic deformation behavior of the samples prepared by zone-melting and extrusion at elevated temperature can be described by dislocation slip and dislocation pile-up within grains$^{218-223}$. During deformation, the dislocation density is increased by bowing of dislocations between pinning points such as in Frank-Read sources or screw dislocations which have experienced a segment of double cross-slip. Materials which possess high initial dislocation density are able to generate more during deformation.

Dislocation motion is impeded at grain boundaries due to the misalignment of slip planes between neighboring grains. As grain size decreases, the interactions between dislocations and grain boundaries can have a significant strengthening effect. Dependence of the grain size ($L$) reduction to strengthening is described by the Hall–Petch relationship:

\[ \sigma_T = \sigma_0 + KL^{1/2}, \]  
(Eqn. 9.1)

where $\sigma_T$ is yield strength, $\sigma_0$ is the yield strength of a single-crystal, and $K$ is the material dependent Hall–Petch factor$^{224}$. Our experimental work qualitatively follows the Hall–Petch equation. The grain size of extruded samples is smaller than that in the zone-melted samples approximately by a factor of 18 (from the extrusion factor). If we assume $\sigma_0$ to be negligible, the ratio of the $\sigma_T$ of the extruded sample to that of the zone-melted sample can be roughly estimated to be $\sim 18^{1/2} \approx 4.2$. Accordingly, the strength of extruded samples at room temperature ($\approx 130$ MPa), is 4-5 times higher than that of the zone-melted sample (Fig. 9.2 green and blue lines).

The Hall-Petch relationship is related to stress-induced dislocation motion near grain boundaries. A pile-up of dislocations against a grain boundary exerts a reinforced stress proportional to the number of dislocations within the pile-up$^{85}$. Yielding occurs when the stress concentration of the pile-up exceeds the threshold
required to activate dislocation generation and slip to neighboring grains. Due to the repulsive interactions between dislocations with Burger’s vector of the same sign, the dislocation spacing within a pile-up is determined by the applied stress. Smaller grain size can effectively limit the number of dislocations which can be present in a pile-up, thereby limiting the stress compounding effect. A material with smaller grain size is thus expected to require a higher applied stress to yield via this mechanism.

However, for materials with grain size below 100 nm, the Hall-Petch equation overestimates the yield strength\textsuperscript{225-227}. For a given applied stress, at a small enough grain size only a single dislocation can be present near a boundary and the compounding effect of a pile-up will no longer exist\textsuperscript{228}. Consequently, the Hall-Petch relation breaks down\textsuperscript{229}. Dislocations are either absent in nanograins or present in only small quantities. As a result there are no heterogeneous sources for dislocation generation and reproduction, and homogeneous formation of dislocations requires stresses on the order of $\tau \approx 900$ MPa (from $\tau \approx G/30$ where the shear modulus, $G$, for Bi$_2$Te$_3$ is $\approx 27$ GPa), well beyond the fracture strength of the nanostructured sample in Fig. 9.2 (orange line)\textsuperscript{230,231}.

Alternatively, grain-boundary sliding has been proposed as the dominant deformation mechanism for the nanostructured SPS sample. This process is characterized by grain-restricted slippage, migration, and dynamic recrystallization\textsuperscript{224,232-234}. Simulation has shown that in nano-grained material, deformation occurs by grain-boundary sliding instead of dislocation slip within grains typically observed in large grains\textsuperscript{39}. This behavior has been confirmed experimentally in the grain-size dependent flow stress of Cu\textsuperscript{80}. Thermally-activated grain boundary shear was found to be the deformation mechanism in nano-scale grains. If a second phase other than (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ were present on the grain boundaries, this could negatively influence on the strength of the material. However, when the SPS nanostructured sample was analyzed by high-resolution transmission electron microscopy (HRTEM) equipped with energy dispersive spectroscopy (EDS) detector from EDAX, the composition of grain boundaries was found to be homogeneous and the same as within the grains. Furthermore, the grain boundaries were atomically-sharp without any chemical heterogeneity or intermediate phases. Even if the Te-phase separation (Fig. 9.6) did happen at high
annealing temperature, the temperature at which the strength of the nanostructured sample started to drop was even lower than the annealing temperature. Thus, in this case, the deformation of the nanostructured sample may be related to the reduction grain boundary area due to recrystallization at high temperatures.

The nanostructured sample demonstrates much higher fracture strength compared to the other samples (Fig. 9.2), but as temperature increases its strength reduces to that of coarse-grained samples\textsuperscript{226}. This drop in strength of the nanostructured sample can be attributed to increased grain-boundary diffusion coefficient at high temperature which in turn raises the plasticity under stress.

![HRTEM image of the sample produced by SPS at a temperature of 500 °C](image)

There is a correlation between the mechanical and thermoelectric properties of (Bi,Sb)\textsubscript{2}Te\textsubscript{3} materials and the sintering temperature. The nanostructured samples sintered at 450-500 °C possess not only the maximum thermoelectric figure of merit\textsuperscript{203}, but also the highest mechanical strength. At these sintering temperatures, there is a fragmentation of the initial grains due to formation of nanograins with the same structure and pores (Fig. 9.3). These may be created by the precipitation of excess elemental Te due to its low melting point (450 °C)\textsuperscript{235}. Although an ingot of stoichiometric composition of (Bi\textsubscript{0.2}Sb\textsubscript{0.8})\textsubscript{2}Te\textsubscript{3} was used
in the nanostructured sample, not all of the Te was included in the matrix. According to the phase diagram\textsuperscript{235} a small amount of Te (less than 0.5 at. %) can exist in elemental form because of anti-site defects (Sb in Te site)\textsuperscript{236}. Another possibility can be the melting of nano-sized (Bi\textsubscript{0.2}Sb\textsubscript{0.8})\textsubscript{2}Te\textsubscript{3}. The SPS sintering temperature (500 °C) of the ball-milled ingot (in 8-10 nm) was only about 15 % lower than the melting temperature of bulk Bi\textsubscript{2}Te\textsubscript{3} (585 °C)\textsuperscript{237}. Given the fact that the melting point of nano-sized Bi-Sn alloy (10 nm) can be reduced by 15 % of its bulk melting temperature\textsuperscript{238}, the precipitation of the nano-sized (Bi\textsubscript{0.2}Sb\textsubscript{0.8})\textsubscript{2}Te\textsubscript{3} during the SPS is physically possible. However, the mechanism involved in the formation of nano-sized pores observed in Fig. 9.3 is still under investigation.

Thermoelectric properties (\(\sigma\) and \(\alpha\)) of the nanostructured sample during thermocycling were measured up to temperatures of 250 °C (Fig. 9.4) and 300 °C (Fig. 9.5). The temperature-dependent \(\sigma\) and \(\alpha\) stayed almost the same during five cycles of heating (up to 250 °C) and cooling (Fig. 9.4). However, upon increasing the maximum temperature to 300 °C, changes in the \(\sigma\) and \(\alpha\) were observed even from the first cycle of heating and cooling (\(\sigma\) decreased and \(\alpha\) increased as shown in Fig. 9.5). It could be concluded that the nanostructured sample was only thermostable at temperatures below 250 °C (its strength was significantly reduced starting at 150-200 °C as in Fig. 9.2).

![Fig. 9.4. Temperature dependences of electrical conductivity (\(\sigma\)) and Seebeck coefficient (\(\alpha\)) of the nanostructured (SPS) sample at cycling (●, ○ - the first cycle; ◊, □ - the fifth cycle).](image-url)
Fig. 9.5. Temperature dependences of electrical conductivity ($\sigma$) and Seebeck coefficient ($\alpha$) of the nanostructured (SPS) sample at cycling (♦, ● - heating; ◊, ○ - cooling).

Fig. 9.6. X-ray diffraction of nanostructured samples before annealing (a) and after annealing at temperature 300 °C for 2 hours (b) (■ - (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$, ▼ - Te).
In the Bi-Sb-Te system, the composition \((\text{Bi,Sb})_2\text{Te}_3\) is homogenous at room temperature, but a tellurium rich phase may phase separate at elevated temperatures depending on the nominal Te content\(^{235}\). As shown in the X-ray diffraction results of Fig. 9.6, annealing the samples in air at 300 °C for 2 hours led to the separation of the elemental tellurium phase. This separation along with grain growth due to recrystallization could contribute to the thermal instability of both the thermoelectric and mechanical properties. During thermocycling to 300 °C (Fig. 9.5), the excess tellurium phase separates into the grain boundaries (Fig. 9.6). However, the thermal activation energy provided by annealing combined with the diffusing Te may have decreased the concentration of anti-site defects\(^{239}\) within the bulk (hence the reduced electrical conductivity of the cooling sample in Fig. 9.6). Even a small amount of Te present in grain boundaries of the nanostructured sample can further weaken the material since it can facilitate rotation of grains at high temperatures. The concurrent loss of thermoelectric and mechanical performance above 250 °C defines a temperature range of practical use of nanostructured \((\text{Bi,Sb})_2\text{Te}_3\) materials within thermoelectric generators.

The temperature-dependent fracture strength under uniaxial compression of \((\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3\) samples produced by either vertical zone-melting, hot extrusion, or SPS were investigated. It was observed that the strength of the nanostructured sample (via SPS) was higher than that of the zone-melted or extruded sample at a room temperature. However, at \(T > 300 \, ^\circ\text{C}\), the strength of the nanostructured sample decreased and became comparable to that of the zone-melted sample. Grain boundary slippage in the nanostructured sample was proposed as a mechanism for this sudden drop in strength at temperatures higher than 170-200°C. Based on the observed Te-phase separation in the nanostructured sample annealed at 300 °C, a maximum operating temperature for a thermoelectric generator made with the nanostructured sample was suggested (< 250 °C).


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