ABSTRACT

CHAN, TSUNG-TA ETHAN. N- and P-type Nano Bi(Sb)Te(Se) Alloy Materials with Enhanced Thermoelectric Figure of Merit and Device Performance. (Under the direction of Carl Koch.)

To make thermoelectric device technology competitive in energy harvesting and power generation, it requires both high performance n- and p-type materials through nano-engineering. In contrast to p-type materials, the development of n-type Bi$_2$Te$_3$-based materials has been rather lackluster and consequently limits the device performance.

This work presents both n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ and p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk nanocomposite materials with significantly enhanced figures of merit ($ZT$) through an optimized high-pressure consolidation process of mechanical alloyed powders that maintains a high concentration of nanoscale structures. With electron microscopy, our materials possess a wide distribution of grain sizes with 5 to 20 nm precipitates dispersed throughout. The nanoscale structuring leads to increased Seebeck coefficients and reduced lattice thermal conductivities while maintaining good electrical conductivities over a wide range of temperature.

The combination of these improvements results in a significantly enhanced $ZT$ between 25 $^\circ$C and 175 $^\circ$C, with peak $ZT$ of $\sim$2.5 at $\sim$100 $^\circ$C for the best n-type and $\sim$3 at 50 to 100 $^\circ$C for the best p-type. Both types of material have peak $ZT$ at similar temperature range around 100 $^\circ$C which is ideal for coupling them into the thermoelectric device.

Incorporation of these nano-materials into early heat-to-electricity conversion devices is shown to result in a efficiency of 7.9% compared to $\sim$5.6% in state-of-the-art commercially available devices using non-nano materials, representing about 41% improvement in device efficiency. Furthermore, the conversion efficiencies are 52% better than commercial devices at commonly available lower temperatures of energy harvesting around 50 $^\circ$C. Thus this work demonstrates an important transition of materials to device technology for real world power generation and cooling applications by waste heat recovery and solar thermal energy.

An optimal hot pressing pressure to obtain the best Seebeck coefficient was found for Bi(Se)Te material, about 2 GPa. This phenomenon could be contributed by the pressure-driven changes in the density of antisite defects and electronic band structure at elevated temperatures. Microstructure analysis as a function of hot pressing pressure are presented and discussed.

From the discoveries of thermoelectric phenomena to their definitions by modern physics, conventional thermoelectric materials have been revived by nano engineering such as quantum confinement and energy filtering effect introduced by low-dimensional structure. Their roles are discussed via mathematically formulated thermoelectric properties to better understand their inter-relationships and the challenge and approach in the $ZT$ enhancement.
N- and P-type Nano Bi(Sb)Te(Se) Alloy Materials with Enhanced Thermoelectric Figure of Merit and Device Performance

by
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APPROVED BY:

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Salah Bedair           Carl Koch
Chair of Advisory Committee
DEDICATION

To my parents, my wife Yiyi, my singleton Ziyi and my twins Ziyao, Zixu.
Tsung-ta Ethan Chan came to North Carolina State University in 2008 to continue his study in Materials Science and Engineering after receiving a M.S. from University of Pennsylvania and a B.S. from National Cheng Kung University in Taiwan in the same major. To deepen his interests in electronic materials, Tsung-ta also completed a minor in Electrical and Computer Engineering during his pursuit of the Ph.D degree in the NC State University.

In addition to the research and course work, Tsung-ta was also a teaching assistant to the X-ray diffractometer and undergraduate lab sessions in the department. In 2012, he was honored to be one of the few graduate students in the department to present his work in the University Graduate Research Symposium of NC State University and became a member of Alpha Sigma Mu International Professional Honor Society.

Tsung-ta enjoys music, traveling, reading, skiing, jogging, weight training, hiking, basketball, baseball, softball, etc. (looking forward to biking and snowboarding in the future) as well as a cup of coffee on Sunday afternoon with his family. He is proud of having their singleton, Ziyi, a couple days before the preliminary exam and the twins, Ziyao and Zixu, a couple months before the final oral defense.
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Dr. James Lebeau provided many insights and experience on microstructure analysis. Dr. Thomas Rawdanowicz also enriched my skills in transmission electron microscope and X-ray diffractometer. Both of them polished my professionalism from little things. Dr. Lewis Reynolds guided my teaching assistantship to lead hundreds of undergraduate lab sections and grade thousands of lab reports.

I would like to acknowledge all the former and present members in Dr. Koch and Dr. Scattergood’s group. It is my pleasure to meet and work with you guys.

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# TABLE OF CONTENTS

List of Tables .................................................................................. ix

List of Figures .................................................................................. x

Chapter 1 Introduction ..................................................................... 1

Chapter 2 Fundamentals of Thermoelectric Materials ..................... 3
  2.1 Thermoelectric Phenomenon ...................................................... 3
  2.1.1 Figure of Merit .................................................................. 5
  2.1.2 Seebeck, Peltier and Thomson Effect .............................. 6
  2.2 Thermoelectric Materials ........................................................ 8
    2.2.1 Development of Thermoelectric Materials .................... 8
    2.2.2 Modern Thermoelectric Material Systems ................. 9

Chapter 3 Electrical Transport in Thermoelectric Materials ............ 11
  3.1 Boltzmann Transport Equation ................................................ 11
  3.2 Formulations of Transport Properties .................................... 13
    3.2.1 Carrier Velocity and Relaxation Time .......................... 13
    3.2.2 Single Band Seebeck Coefficient and Electrical Conductivity ........ 13
    3.2.3 Multiple Bands Seebeck Coefficient and Electrical Conductivity ........ 14
    3.2.4 Carrier Concentration and Mobility ............................. 15
  3.3 Analysis of Individual Electrical Transport Properties ............ 16
    3.3.1 Diffusive Seebeck Coefficient ........................................ 16
    3.3.2 Phonon Drag Seebeck Coefficient ............................... 17
    3.3.3 Electrical Conductivity and Mobility ............................ 18
  3.4 Interrelationships Between Electrical Transport Properties ........ 19

Chapter 4 Thermal Transport in Thermoelectric Materials ............. 22
  4.1 Electronic Thermal Conductivity ............................................ 23
    4.1.1 Formulation of Electronic Thermal Conductivity .......... 23
    4.1.2 Analysis of Electronic Thermal Conductivity ............... 24
  4.2 Lattice Thermal Conductivity ................................................ 26
    4.2.1 Phonon Dispersion Relationship .................................. 26
    4.2.2 Formulation of Lattice Thermal Conductivity ............... 28
    4.2.3 Analysis of Lattice Thermal Conductivity ................... 29
  4.3 Lattice Thermal Conductivity Reduction ................................ 30
    4.3.1 Phonon-Glass/Electron-Crystal (PGEC) Approach ........ 31
    4.3.2 Size Effects on Thermal Transport ............................... 32
Chapter 5 \textit{ZT Enhancement by Low-dimensional Structures} ........................................ 36
5.1 Power Factor Enhancement .................................................. 36
5.1.1 Quantum Confinement .................................................. 37
5.1.2 Energy Filtering .......................................................... 39
5.2 Lattice Thermal Conductivity Reduction .................................. 42
5.2.1 Nano-structure Approach ................................................ 42
5.3 Proof-of-principle Low-dimensional Structures .......................... 42
5.3.1 Nanowires–1D ............................................................. 42
5.3.2 Thin Film Superlattices–2D .............................................. 43
5.3.3 Nanocomposites–3D ...................................................... 44

Chapter 6 \textit{Experimental Background and Methods} ................................. 51
6.1 Mechanical Alloying .......................................................... 51
6.2 Hot Pressing ................................................................. 52
6.3 Material Properties of Bi(Sb)Te(Se) Alloys ............................... 53
6.3.1 Structure ................................................................. 53
6.3.2 Phase Diagram .......................................................... 55
6.3.3 Transport Properties .................................................... 56
6.4 Preparations of Bi(Sb)Te(Se) Nanocomposites ......................... 57
6.4.1 Challenges and Approaches .......................................... 57
6.4.2 Mechanical Alloying .................................................... 60
6.4.3 Consolidation ............................................................ 60
6.5 Characterizations of Bi(Sb)Te(Se) Nanocomposites ................... 61
6.5.1 X-ray Diffraction ........................................................ 62
6.5.2 Differential Scanning Calorimetry ................................... 62
6.5.3 Transmission Electron Microscope ................................... 63
6.5.4 Seebeck Coefficient ..................................................... 64
6.5.5 Electrical Resistivity .................................................... 65
6.5.6 Thermal Conductivity ................................................... 65

Chapter 7 \textit{Nanocrystalline Bi(Sb)Te(Se) Powders} ............................. 67
7.1 N-type BiTe(Se) ............................................................. 67
7.1.1 Composition: XRD and DSC ......................................... 67
7.1.2 Microstructure: TEM .................................................... 68
7.2 P-type Bi(Sb)Te .............................................................. 69
7.2.1 Composition: XRD and DSC ......................................... 69
7.2.2 Microstructure: TEM .................................................... 70

Chapter 8 \textit{N-type BiTe(Se) Nanocomposites by 300K As-milled Powders} .... 76
8.1 Microstructure ............................................................... 77
8.1.1 Composition ............................................................ 77
8.1.2 TEM and EDS Analysis ................................................. 78
8.2 Transport Properties ........................................................ 79
8.2.1 Seebeck Coefficient ................................................. 80
8.2.2 Resistivity .............................................................. 80
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Comparison of different operation modes of a thermoelectric module.</td>
<td>4</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>Lattice parameters ($a$ and $c$) in angstrom (Å) and density for Bi$_2$Te$_3$, Sb$_2$Te$_3$ and Bi$_2$Se$_3$ compounds at 300 K.</td>
<td>55</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>Transport properties of various Bi(Sb)Te(Se) compounds at 300 K: type of conduction (p or n); $n$, carrier concentration in $10^{19}$ cm$^{-3}$; $\rho$, electrical resistivity in $\Omega\cdot$m; $\mu$, carrier mobility in cm$^2$V$^{-1}$sec$^{-1}$; $S$, absolute Seebeck coefficient in $\mu$VK$^{-1}$; $k$, thermal conductivity in Wm$^{-1}$K$^{-1}$; $ZT$, figure of merit, dimensionless. After reference [114].</td>
<td>56</td>
</tr>
<tr>
<td>Table 6.3</td>
<td>Optimized process settings for making n- and p-type bulk nanocomposite materials in this work.</td>
<td>63</td>
</tr>
<tr>
<td>Table 6.4</td>
<td>Ion milling settings for Bi(Sb)Te(Se) TEM specimens.</td>
<td>64</td>
</tr>
<tr>
<td>Table 8.1</td>
<td>Weight percentage analyzed by EDS of various spots at Figure 8.4. Rows highlighted by color yellow are the results from the precipitates. The ideal weight percentage for Bi$<em>2$Te$</em>{2.7}$Se$_{0.3}$ is included in the bottom row.</td>
<td>79</td>
</tr>
<tr>
<td>Table 9.1</td>
<td>Weight percentage analyzed by EDS of various spots at Figure 9.4. Rows highlighted by color yellow are the results from the precipitates. The ideal weight percentage for Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ is included in the bottom row.</td>
<td>91</td>
</tr>
<tr>
<td>Table 9.2</td>
<td>Weight percentage analyzed by EDS of various spots at Figure 9.5. Rows highlighted by color yellow are the results from the precipitates. The ideal weight percentage for Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ is included in the bottom row.</td>
<td>91</td>
</tr>
<tr>
<td>Table 10.1</td>
<td>Comparison of efficiencies at optimal power for various $T_{\text{hot}}$ and $\Delta T$, for the thermoelectric generators (TEGs) made with the p- and n-type nano materials, state-of-the-art COTS materials and published work by KELK Ltd.</td>
<td>111</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Basic illustration of thermoelectric module configuration for (a) power generation and (b) refrigeration mode. The diffusion of charge carriers, $h^+$ and $e^-$, converts the input energy to other format depends on the operation mode.</td>
<td>4</td>
</tr>
<tr>
<td>2.2</td>
<td>Basic configuration of a thermocouple that output temperature readings based on Seebeck effect. The isothermal cold junction connected to the voltage meter is used as reference to the hot junction. It is a K-type thermocouple if metal A is nickel-chromium and metal B is Alumel.</td>
<td>6</td>
</tr>
<tr>
<td>2.3</td>
<td>$ZT$ of selected n- and p-type thermoelectric materials system at different temperature: (a) n-type and (b) p-type systems. After reference [38].</td>
<td>10</td>
</tr>
<tr>
<td>3.1</td>
<td>A plot of $ZT$ versus the reduced Fermi energy ($\xi^<em>$ in the figure) in a 3D material. The $ZT$ peaks when the reduced Fermi energy is at an optimal value ($\xi_{opt}^</em>$ in the figure). After reference [5].</td>
<td>19</td>
</tr>
<tr>
<td>3.2</td>
<td>Thermoelectric properties as a function of carrier concentration. The Seebeck coefficient is denoted as $\alpha$ in the figure. For the highest $ZT$ value, the material should have carrier concentration in between $10^{19}$ to $10^{20}$ cm$^{-3}$ according to the plot. Namely a heavily doped semiconductor usually shows potentials to have high $ZT$ value. After reference [38].</td>
<td>20</td>
</tr>
<tr>
<td>3.3</td>
<td>Experimental data showing $ZT$ as a function of the dopant concentration in PbTe system. As the dopant concentration changes, the $ZT$ increases while the peak value shifts to different temperature as well. After reference [38].</td>
<td>20</td>
</tr>
<tr>
<td>4.1</td>
<td>The relationships between the figure of merit ($ZT$) and the electronic and lattice thermal conductivity. Reducing $k_L$ from 0.8 to 0.2 W/m-K directly increases $ZT$ from point (2) to point (3). The $ZT$ can be further enhanced to point (3) with an optimized carrier concentration which contributes to less electronic thermal conductivity. After reference [38].</td>
<td>23</td>
</tr>
<tr>
<td>4.2</td>
<td>The plot of Lorentz numbers ($L$) as a function of the reduced Fermi level ($\eta$) of different scattering factors ($r$) and dimensionality ($D$). The value of $L$ changes as the material transits from metallic regime ($\eta \gg 0$) to degenerate semiconductor ($\eta \sim 0$) and non-degenerate semiconductor ($\eta \ll 0$) regimes. After reference [41].</td>
<td>25</td>
</tr>
<tr>
<td>4.3</td>
<td>An illustrations of lattice vibration modes of a two-atom basis material. Compared to equilibrium atom positions in (a), the atoms on the unit cell vibrate along the same direction in acoustical mode (b) while they vibrate in the opposite direction in optical mode (c).</td>
<td>27</td>
</tr>
<tr>
<td>4.4</td>
<td>Dispersion relation for a diatomic linear lattice. The frequencies at the limits $k=0$ and $k=\pm \frac{\pi}{a}$ are shown if $M_1 &gt; M_2$. After reference [56].</td>
<td>27</td>
</tr>
</tbody>
</table>
Figure 4.5 Illustrations of possible collision process in the three phonon model, (a) normal process and (b) umklapp process, in a two dimensional square lattice. Incident phonons, $k_1$, $k_2$ collide and create transmitted phonon, $k_3$. The momentum completely transferred to the transmitted phonon in the normal process, but only partial momentum is transferred in the umklapp process. 

Figure 4.6 Illustrations of the empty CoSb$_3$ in (a) and FeSb$_3$ filled with Ce/La in (b) skutterudite structures. After reference [60].

Figure 4.7 Material systems with reduced lattice thermal conductivity ($k_l$ in the figure) achieved by complex crystal structures. After reference [38].

Figure 4.8 Plot of the ratio of the lattice thermal conductivity of a solid solution ($\lambda_L$) to a perfect crystal ($\lambda_0$) and the $x$-axis is ratio of the phonon frequency with point defect ($\omega_D$) to that of perfect crystal ($\omega_0$). The curve is based on theoretical modeling and the points represents experimental thermal conductivity data for various solid solutions. After reference [63].

Figure 4.9 Schematic plot of thermal conductivity ($k$) as a function of the phonon frequency ($\chi$ in the plot). Point defect scattering (single-hatched area) removes most of the high frequency phonon contributions so that the remaining lattice thermal conductivity is mainly due to low frequency phonons, where the double-hatched area indicates the reduction due to the boundary scattering. After reference [62].

Figure 5.1 Density of states ($g(E)$) for a bulk 3D semiconductor, a 2D quantum well and a 1D nanowire. The figures show multiple sub-bands, each of which is shifted up from the ground state energy ($E_0$). After reference [41].

Figure 5.2 The $S^2n$ values of the PbTe/Pb$_{0.958}$Eu$_{0.042}$Te multiple quantum well structure (full circle) with the calculated results (solid line) and the best experimental bulk PbTe material as a function of the well thickness (a) and a function of the carrier concentration (b). After reference [70].

Figure 5.3 Electron distributions in the conduction bands of the (a) bulk Si and (b) 2 nm by 2 nm Si nanowire at 300 K. The electron distributions are defined by the Fermi-Dirac distribution and density of state, as in Eq. 3.20, indicated as the gray area in the figures. When the structure dimension decreases from 3D to 1D, a four-fold increase in the power factor is predicted by the modeling. It is mainly a result of the changes in the average electron energy, $\langle E \rangle$, and the Fermi level, $E_F$. The carrier mobility and carrier concentration are the same for both 3D and 1D structures, $3.86$ and $1.7 \times 10^{20}$ cm$^{-3}$ respectively. The band ground state energy is set to be zero. After reference [41].
Figure 5.4 Band alignment and TEM micrograph of the Pt-Sb₂Te₃ material. The bandgap ($E_g$), electron affinity (E. A.), ionization potential (I. P.) and work function ($\Phi$) values are shown in (a), the band diagram before the formation of Pt-Sb₂Te₃ interfaces. At equilibrium, band-bending potential well are formed at the interface that blocks low energy holes as shown in (b). The TEM micrograph, (c), shows the nanocomposite structure: Pt nanocrystals about size 13 nm dispersed in the matrix Sb₂Te₃. After reference [78].

Figure 5.5 a. A scanning electron microscopy (SEM) image of the Si nanowire. b. The temperature dependency of thermal conductivities of various diameter Si nanowires. After reference [82].

Figure 5.6 Temperature dependency of $ZT$ of the 20 and 10 nm wide Si nanowires. The $ZT$ peaks around 200 K in the 20 nm wide nanowires. After reference [83].

Figure 5.7 a. PbTe superlattice structure and b. $ZT$ versus temperature plot. Such structure showed $ZT$ as high as 3 at 500 K. After reference [8, 84, 85].

Figure 5.8 The $ZT$ of the p-type Bi₂Te₃/Sb₂Te₃ superlattice (dark blue circles), about 2.4 at room temperature, compared to other thermoelectric material systems, which are generally below 1.2. After reference [7].

Figure 5.9 (a) An illustration of a cross-section view of the nanocomposite structure. Different types of "inclusions", aligned, staggered and random, embedded in the matrix used in Monte Carlo simulation are shown in (b). After reference [74].

Figure 5.10 The calculated thermal conductivity versus the volumetric fraction of Si of the SiₓGe₁₋ₓ nanocomposite. The heat flow is along the wire direction while the wires are aligned in the matrix. The solid line represents a bulk alloy with the same chemical composition as the nanocomposites. After reference [89].

Figure 5.11 The calculated thermal conductivity versus the volumetric fraction of various Si particle and nanowire inclusions in the SiₓGe₁₋ₓ nanocomposite. It shows an universal curve that all types of inclusions can reduce the thermal conductivity when the interface density is higher than 0.08 nm⁻¹. After reference [74].

Figure 5.12 TEM micrographs of the Bi₀.₅Sb₁.₅Te₃ nanocomposite. Low magnification image, A, shows the grains in the nanometer scale and high magnification image showing the grain boundaries and crystallinity in B. After reference [90].

Figure 5.13 Transport properties of the Bi₀.₅Sb₁.₅Te₃ nanocomposite. Solid squares represents the nanocomposite and open squares represents the state-of-the-art (SOA) ingot. The thermal conductivity reduction contributes the improvement of the $ZT$ which peaks at 100 °C to be about 1.4. The electrical conductivity of nanocomposites is better than the SOA ingot due to the charge build up at grain boundaries. After reference [90].
Figure 5.14 Transport properties of Si$_{80}$Ge$_{20}$ nanocomposite. The solid line is the SiGe material used in the radioisotope thermoelectric generator (RTG) for comparison. After reference [91].

Figure 5.15 TEM images showing the microstructure of the Si$_{80}$Ge$_{20}$ nanocomposite. The contrast in the dark dots in the low magnification image, a, is due to the dopant (boron). Both dark dots and background contains small grains as shown in b. After reference [91].

Figure 5.16 Thallium-doped PbTe nanocomposite which has $ZT \sim 1.5$ at 500 °C. The figures shows microstructure are taken by (a) TEM and (b) SEM. After reference [92].

Figure 6.1 The illustration of the collision between grinding medium such as stainless steel balls and the material during mechanical alloying. After reference [99].

Figure 6.2 An illustration of the lamellar structure of Bi$_2$Te$_3$ showing the quintuple layers and the locations of the van der Waals gap. The green, red and dark blue dots represent the Te$_{(1)}$ atoms, the Bi atoms and the Te$_{(2)}$ atoms, respectively. After reference [107].

Figure 6.3 The phase diagram of the Bi-Te system. After reference [115].

Figure 6.4 The phase diagram of the Sb-Te system. After reference [115].

Figure 6.5 An exaggerated illustration of the stoichiometry deviation around the Bi$_2$Te$_3$ compound. After reference [114].

Figure 6.6 A schematic illustration of 3D Bi-Te-Se ternary phase diagram. The shaded area represents solid solution containing 5% of Bi$_2$Te$_3$. After reference [114].

Figure 6.7 Liquidus and iso-concentration lines ($L$) of the Bi-Te-Se system. After reference [114].

Figure 6.8 Partial 3-dimensional Bi-Sb-Te ternary phase diagram. After reference [116].

Figure 6.9 Partial Bi-Sb-Te ternary phase diagram on the tellurium-rich side with experimental isothermal curves of the liquids at different temperature and experimental iso-concentration lines ($L_1$, $L_2$) for $S_1$: 20% and $S_2$: 25% of Bi$_2$Te$_3$ in Sb$_2$Te$_3$. After reference [116].

Figure 6.10 Summary of the processing steps in this work including the products after each step.

Figure 6.11 SEM images of the FIB "Lift-out" process for TEM sample preparation. (a) Lift-out needle attached to the membrane. (b) A Pt protection layer is deposited on the edge of the membrane. (c) Final sample where part of it are of electron transparent thickness. The V-shape TEM grid in (b) is at the top.

Figure 6.12 Basic illustration of the Seebeck coefficient measurement setup. The disc-shaped sample is placed on top of the copper blocks. Both temperature and voltage differences are measured at the same time.
Figure 6.13 Basic illustration of the thermal conductivity measurement setup. There are five thermocouples attached to the Q-Meter at specific locations. After reference [121].

Figure 7.1 XRD spectra of the n-type powders milled at room, (a), and cryogenic temperature, (b). The intensity is in arbitrary units (a. u.).

Figure 7.2 The DSC data of the n-type room temperature as-milled powders. An endothermic peak is at around 410 °C.

Figure 7.3 TEM images show the microstructure of the n-type room temperature as-milled powders in low, (a), and high, (b), magnification. The SAD pattern from materials in (a) is inserted in the upper right corner in (a).

Figure 7.4 The grain size distribution plot of the n-type room temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.

Figure 7.5 Bright field, (a), and dark field, (b), TEM images of the n-type cryogenic temperature as-milled powders with the SAD pattern inserted in the upper right corner in (a). The grain boundaries are better recognized in the dark field image in (b).

Figure 7.6 The grain size distribution plot of the n-type cryogenic temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.

Figure 7.7 XRD spectra of the p-type powders milled at room, (a), and cryogenic temperature, (b). The intensity is in arbitrary units (a. u.).

Figure 7.8 The DSC data of the p-type room temperature as-milled powders. An endothermic peak is at around 413 °C.

Figure 7.9 TEM images show the microstructure of the p-type room temperature as-milled powders in low, (a), and high, (b), magnification. The SAD pattern from materials in (a) is inserted in the upper right corner in (a).

Figure 7.10 The grain size distribution plot of the p-type room temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.

Figure 7.11 Bright field, (a), and dark field, (b), TEM images of the p-type cryogenic temperature as-milled powders with the SAD pattern inserted in the upper right corner in (a). The grain boundaries are better recognized in the dark field image in (b).

Figure 7.12 The grain size distribution plot of the p-type cryogenic temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.

Figure 8.1 XRD spectra of (i) n-type bulk sample made from room temperature as-milled powders on the top and (ii) room temperature (RT) as-milled powders on the bottom.

Figure 8.2 Microstructure figures of a n-type bulk sample made by room temperature as-milled powders with various magnification by TEM: (a) - (d) low magnification, (e) SAD pattern, (f) HRTEM of a precipitate.
Figure 8.3 Calculated grain size distribution of the n-type bulk samples made by room temperature as-milled powders. Only grains/precipitates less than 50 nm are considered. ......................................................... 84
Figure 8.4 TEM figures of different n-type bulk samples made by room temperature as-milled powders showing the locations of the EDS probe indicated by the numbers. ......................................................... 84
Figure 8.5 Transport properties of n-type material made by room temperature as-milled powders along with reference data. .......................................................... 85
Figure 8.6 Transport properties of the best n-type sample and the average made by room temperature as-milled powders. .......................................................... 86
Figure 8.7 TEM figures of commercial polycrystalline n-type BiSeTe materials. 87

Figure 9.1 XRD spectra of (i) p-type bulk sample made from room temperature as-milled powders on the top and (ii) room temperature (RT) as-milled powders on the bottom. ......................................................... 89
Figure 9.2 Microstructure figures of a p-type bulk sample made by room temperature as-milled powders with various magnification by TEM: (a) - (d) low magnification, (e) SAD pattern, (f) HRTEM of a precipitate. ......................................................... 94
Figure 9.3 Grain size distribution of p-type bulk samples made by room temperature as-milled powders. Only grains/precipitates less than a hundred nm are considered. ......................................................... 95
Figure 9.4 TEM figures of different region in the second p-type bulk samples made by room temperature as-milled powders showing the locations of the EDS probe indicated by the numbers where (b) is acquired by the dark field imaging to better outline the precipitates. ......................................................... 95
Figure 9.5 TEM figures of different region in the first p-type bulk samples made by room temperature as-milled powders showing the locations of the EDS probe indicated by the numbers. ......................................................... 95
Figure 9.6 Transport properties of p-type material made by room temperature as-milled powders along with reference data. ......................................................... 96
Figure 9.7 Transmission electron microscope figures of the p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ by Poudel, et al. [90] (d), (e): Sb-rich nano-dots; (f): pure Te precipitates. The materials were processed by ball milling and spark plasma sintering. ......................................................... 97
Figure 9.8 Transmission electron microscope figures of the p-type BiSbTe by Fang, et al. [123] (c): Sb-rich precipitates. Nano-inclusions produced by melt spinning were ball milled with single crystal Bi$_{0.6}$Sb$_{1.4}$Te$_3$ followed by hot pressing. ......................................................... 97
Figure 9.9 Transport properties of the best p-type sample and the average made by room temperature as-milled powders. ......................................................... 98
Figure 9.10 TEM figures of commercial polycrystalline p-type BiSbTe materials. ......................................................... 99

Figure 10.1 An illustration of a radioisotope thermoelectric generator. After reference [124]. ......................................................... 101
Figure 10.2 Thermoelectric generator in a BMW 5 series. The thermoelectric module, indicated by the white arrow, is designed to be incorporated with the exhaust system. After reference [126].

Figure 10.3 Seiko Thermic™ wrist watch. After reference [128].

Figure 10.4 Schematic diagram of the SiGeC/Si thin film thermoelectric coolers. After reference [131].

Figure 10.5 A thermoelectric module consists of n- and p-type element.

Figure 10.6 Calculated ideal device conversion efficiency as a function of $Z_d T_M$ based on Eq. 10.11. The cold side temperature $T_c$ is set to be 25 °C.

Figure 10.7 A schematic view of thermoelectric device components. After reference [38].

Figure 10.8 The picture of a single p-n couple thermoelectric device made by nano-bulk materials in this work.

Figure 10.9 The picture of a multiple p-n couples thermoelectric device.

Figure 10.10 A three stage cascade thermoelectric module. After reference [136].

Figure 10.11 Average and the best conversion efficiency of nano-bulk modules. Data points from commercial state-of-the-art BiTe based materials are also included.

Figure 11.1 XRD spectra of (i) n-type bulk sample made from cryogenic temperature as-milled powders on the top and (ii) cryogenic temperature as-milled powders on the bottom.

Figure 11.2 Calculated grain size distribution of the n-type bulk samples made by cryogenic temperature as-milled powders. Precipitates are not included in the calculation.

Figure 11.3 Microstructure of the n-type bulk sample consolidated from cryogenic temperature as-milled powders with various magnification by TEM, (a) to (d), and SAD pattern, (e).

Figure 11.4 Average transport properties of n-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively.

Figure 11.5 Transport properties of the best n-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively.

Figure 11.6 Transport properties of n-type material made by cryogenic temperature as-milled powders (solid triangle) along with data from the work by Yan et al. [52] (open triangle).

Figure 12.1 XRD spectra of (i) p-type bulk sample made from cryogenic temperature as-milled powders on the top and (ii) cryogenic temperature as-milled powders as-milled powders on the bottom.

Figure 12.2 Calculated grain size distribution of the p-type bulk samples made by cryogenic temperature as-milled powders. Precipitates are not included in the calculation.
Figure 12.3  Microstructure of the p-type bulk sample made by cryogenic temperature as-milled powders with various magnification by TEM, (a)-(e), and SAD pattern, (f) ................................................................. 125

Figure 12.4  Transport properties of p-type material made by cryogenic temperature as-milled powders (solid triangle) along with data from the work by Poudel et al. (solid squares) [90] ................................................................. 126

Figure 12.5  Average transport properties of p-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively ................................................................. 127

Figure 12.6  Transport properties of the best p-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively ................................................................. 128

Figure 13.1  X-ray diffraction spectra of bulk Bi$_2$Te$_{2.7}$Se$_{0.27}$ samples hot pressed at pressure from 1.75 to 2.1 GPa as well as that from materials before hot pressing (as-milled powder). The peaks are indexed according to PDF #15-0863 ................................................................. 132

Figure 13.2  Microstructure figures of consolidated Bi$_2$Te$_{2.7}$Se$_{0.27}$ hot pressed at 1.75 GPa, (a), and 2 GPa, (b) by TEM along with absolute Seebeck coefficients and carrier concentration as a function of hot pressing pressure, (c). The solid squares and triangles represent the absolute Seebeck coefficients from n-type Bi$_2$Te$_{2.7}$Se$_{0.27}$ and Bi$_2$Te$_{2.7}$Se$_{0.3}$ respectively. The carrier concentration of Bi$_2$Te$_{2.7}$Se$_{0.27}$ is indicated by the open squares to the right axis ................................................................. 134
Materials that possess the thermoelectric (TE) phenomenon have been highlighted recently due to the search for new energy sources to supplement traditional fossil fuels. The performance of thermoelectric devices depends on the material’s figure-of-merit ($ZT$) given by

$$ZT = \frac{S^2 T}{\rho k}$$

where $S$ is the Seebeck coefficient, $T$ is the absolute temperature, $\rho$ is the electrical resistivity, and $k$ is the total thermal conductivity, respectively. The highest $ZT$ in conventional bulk thermoelectric alloys at room temperature (RT) is around 1 for both n-type and p-type materials in the past three decades.

The objective of this study is to improve the $ZT$ of the $\text{Bi}_2\text{Te}_3$ TE material system in the form of bulk material and ultimately increase the efficiency of its TE device. In contrast to p-type nano-materials, there has been no significant enhancement in $ZT$ reported for n-type nano-bulk $\text{Bi}_2\text{Te}_3$-based materials, preventing the demonstration of device efficiency advantage of the bulk nano-materials over conventional materials, for the important areas of heat-to-electric conversion or thermoelectric cooling, solar-thermal systems and energy efficiency through waste-heat harvesting. Further improvement of thermoelectric device performance requires high $ZT$ for both n- and p-type materials, with similar transport properties, to fabricate matched n-p couples. In this work, we report an approach starting with elemental components and creating nanocrystalline alloy powders by either liquid nitrogen or room temperature high energy ball-milling with subsequent compaction by conventional high pressure hot-pressing.
Fundamental theories of thermoelectric materials are first introduced. Chapter 2 will discuss some basic thermoelectric phenomena that lead to the application of energy conversion. Development of various thermoelectric material systems in the past 30 years are discussed as well as their strength and limits. Chapter 3 focuses on the mathematical explanations of electrical transport in TE materials including Seebeck coefficient and electrical conductivity. Formulations and their inter-relationships are discussed. Details of heat transport by both electrons and the lattice in the TE materials as well as the approaches to reduce the thermal conductivity are presented in Chapter 4.

Chapter 5 is devoted to the thermoelectric figure of merit enhancement specifically by low-dimensional structures, such as nanowires, thin films, nanocomposite, etc. The effects of low-dimensional structure on electrical and thermal properties are discussed.

The experimental details start from Chapter 6, which contains experimental methods including methodology of the process design as well as the challenges and approaches to create nanocomposite Bi(Sb)Te(Se). Background information of mechanical alloying and hot pressing are introduced as well as basic structure and transport properties of BiTe alloys and characterization techniques. Chapter 7 steers toward the experimental development of nanocrystalline powders, including n- and p-type processed at either room or cryogenic temperature.

Chapters 8, 9, 10 focuses on the results and discussions from n- and p-type materials made by room temperature as-milled powders as well as their resulting device performance. Their nanocomposite structure successfully improved the $ZT$ and thus the efficiency of their power generation device.

The results and discussions from n- and p-type materials made by a slightly modified approach: cryogenic temperature as-milled powders are presented in Chapters 11, 12. The significant differences from different starting powders are observed which also reflect to the thermoelectric properties.

Finally, Chapter 13 is directed to the relationship between consolidation pressure and the Seebeck coefficient that could further enhance the material’s thermoelectric performance.
CHAPTER 2

Fundamentals of Thermoelectric Materials

This chapter serves as introductory discussion and general review to the field of thermoelectrics including theories, applications and materials. The first half of this chapter introduces basic thermoelectric behaviors and scientific explanations to them by reviewing the discoveries of this phenomenon in history. By applying the thermoelectric materials, a device can either generate potential difference or absorb heat. Some formulations are used to mathematically describe the heat-electricity conversion as well as the important thermoelectric figure of merit ($ZT$) of both single and coupled materials. The second half of this chapter reviews recent developments in the thermoelectric field. Several notable high $ZT$ achievements as well as modern thermoelectric material systems are discussed. Selected high $ZT$ material systems at different temperature regimes are highlighted.

2.1 Thermoelectric Phenomenon

Thermoelectric phenomenon is the direct conversion between thermal and electrical energy. The conversion is two-way: when a temperature gradient is applied, a thermoelectric material will generate voltage which can drive a current; when a electric current is applied, it will absorb or reject heat. The former operation is usually called "power generation mode", and the later is called "refrigeration mode" or "cooling mode". A basic comparison of these two modes is listed in Table 2.1. A single thermoelectric material can be used in either mode without changing the material, namely, the input can be either heat or power and the material will generate corresponding output. The basic configuration of a thermoelectric module in power generation
Table 2.1: Comparison of different operation modes of a thermoelectric module.

<table>
<thead>
<tr>
<th>Operation mode</th>
<th>Power generation</th>
<th>Refrigeration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input</td>
<td>Heat</td>
<td>Power (electrical potential)</td>
</tr>
<tr>
<td>Output</td>
<td>Power (electrical potential)</td>
<td>Cooling (Heat absorption)</td>
</tr>
</tbody>
</table>

mode and refrigeration mode is shown in Figure 2.1 (a) and (b) respectively. It consists of two types of materials: the n-type leg is doped with excess electrons ($e^-$) and the p-type leg with excess holes ($h^+$). The charge carriers diffuse in response to the applied temperature gradient or electric current at one end of the module and then either create voltage in power generation mode or absorb/reject heat in refrigeration mode at the other end of the module. The thermoelectric elements are connected in parallel thermally and in series electrically. The conversion efficiency and the involving thermoelectric phenomena, Seebeck effect, Peltier effect, and Thompson effect, will be described in Section 2.1.2.

Figure 2.1: Basic illustration of thermoelectric module configuration for (a) power generation and (b) refrigeration mode. The diffusion of charge carriers, $h^+$ and $e^-$, converts the input energy to other format depends on the operation mode.
2.1.1 Figure of Merit

Material’s Figure of Merit

The dimensionless figure of merit ($ZT^1$) represents the thermal-electrical energy conversion efficiency. The figure of merit of a thermoelectric material [1, 2] is given by

$$ZT = \frac{S^2T}{\rho k}$$

(2.1)

where $S$ is the Seebeck coefficient, $T$ is the absolute temperature, $\rho$ is the electrical resistivity, and $k$ is the total thermal conductivity, which is a combined contribution from lattices ($k_L$) and electrons ($k_e$), i.e., $k = k_L + k_e$. These parameters are somewhat related to each other and more details are discussed in Chapter 3 and 4.

Device Figure of Merit

A thermoelectric device requires both n-type and p-type materials coupled together to complete the circuit and the figure of merit of such device is given by

$$ZdT = \frac{S^2T}{(\rho_p k_p)^{\frac{1}{2}} + (\rho_n k_n)^{\frac{1}{2}}}$$

(2.2)

and

$$S = S_p - S_n$$

(2.3)

where the subscript $n$ and $p$ denote the corresponding parameters of n- or p-type material.

In general, the higher the material’s figure of merit ($ZT$), the better the device conversion efficiency\(^2\). As indicated in Eq. 2.1, high $ZT$ materials should have high Seebeck coefficient, low electrical resistivity (or high electrical conductivity) and low thermal conductivity. These properties are interrelated and the materials need to have a good balance between material composition, crystal structure, atomic bondings, etc. to achieve high thermal-electrical energy conversion. However, for the past three decades, $ZT \sim 1$ has been the value of "upper limit" set by the commercially available thermoelectric materials [3]. While this value is not predicted by thermodynamics or theory to be a physical limit, much effort was carried out to increase the $ZT$ over 1 or higher.

\(^1\)Some define the figure of merit as "$Z$" where the temperature part is absent on both side of Eq. 2.1.

\(^2\)The relationship between material’s figure of merit and the resulting device efficiency is described later in Chapter 10.
2.1.2 Seebeck, Peltier and Thomson Effect

Seebeck Effect

In 1821, Thomas Johann Seebeck, a Estonian physicist with a medical degree, discovered that the temperature difference applied to the junction made of two different metals (or electrical conductors) produced electric potential\(^3\). It was found that the voltage produced is proportional to the magnitude of the difference in temperature between the junction and the voltage meter. The proportionality constant is called Seebeck coefficient \((S)\) and sometimes thermopower. This phenomenon was named after him and is the basic principle of the thermocouple, which is used for acquiring temperature readings. For example, a K-type thermocouple made of nickel-chromium (90Ni-10Cr) and Alumel (95Ni-2Mn-2Al-1Si), as shown in Figure 2.2. The junction will produce about 4.09 and 12.2 mV at 100 and 300 °C respectively [4].

![Figure 2.2: Basic configuration of a thermocouple that output temperature readings based on Seebeck effect. The isothermal cold junction connected to the voltage meter is used as reference to the hot junction. It is a K-type thermocouple if metal A is nickel-chromium and metal B is Alumel.](image)

Nowadays it is realized that the creation of potential difference is due to the response of charge carriers (electrons and holes) to the temperature gradient. Mobile charge carriers diffuse from the hot side to the cold side when there is a difference in temperature. The accumulation of charge carriers along with the oppositely charged nuclei they left behind give rise to the electric potential difference across the material. Eventually the buildup of the charge carriers stops and reaches equilibrium with the internal electrical field resulting from the separation of charge carriers. The potential difference thus reaches some maximum and will not change unless the temperature gradient changes and charge carriers start to diffuse. Incidentally \(S\) also represents entropy per charge carrier in the material. The Seebeck coefficient from charge carrier diffusion, \(S_d\), is defined as the ratio of the potential difference \((\Delta V)\) to the temperature.

\(^3\)This electric potential is sometimes called the Seebeck voltage.
gradient ($\Delta T$):

$$S_d = \frac{\Delta V}{\Delta T}$$ (2.4)

In addition to the diffusion of charge carriers, the $\Delta V$ could be from: 1) the work function difference between the contact and the materials that gives $S_\phi$ and 2) the interaction between charge carriers and crystal lattice while electrons move past atoms (phonon drag) that leads to $S_{ph}$. So the overall Seebeck coefficient is

$$S = S_d + S_\phi + S_{ph}$$ (2.5)

Typically the diffusive Seebeck coefficient is the most dominant part at general temperature range. Therefore only $S_d$ is considered and referred to as $S$ in this work unless otherwise specified. Although $S_{ph}$ is considered more effective at low temperature regime (less than 200 K), it has been observed around room temperature\(^4\). $S_\phi$ arise from the work function difference between the contact and thermoelectric materials. The effect of $S_\phi$ is still under investigation and it is mainly important in thermionic thermal to electrical applications.

In general, metals have low Seebeck coefficient (typically 1-10 $\mu$V/K) because they have half-filled energy band. Both electrons and holes participate in the temperature induced diffusion and cancel out each other’s contribution. On the other hand, semiconductors heavily doped with excess electrons (n-type) or holes (p-type) can have large Seebeck coefficient (1 mV/K or more). It is one of the reasons why heavily doped semiconductors are favored for thermoelectric materials. The sign of Seebeck coefficient indicates which charge carrier dominates in electric transport: negative for n-type and positive for p-type.

**Peltier Effect**

Thirteen years after the findings by Seebeck, a French watch maker Jean Charles Athanase Peltier found heat can be removed or generated by passing the electrical current at the material junction and the heat absorbed or created is proportional to the electrical current. The proportionality constant is then called *Peltier coefficient* ($\Pi$), which is defined as the ratio of the rate of heating or cooling ($q$) per unit volume to the electric current ($I$):

$$\Pi = \frac{q}{I}$$ (2.6)

\(^4\)More details are discussed in Section 3.3.2
Thomson Effect

Later in 1855, the interdependency between Seebeck and Peltier effect was explained by William Thomson, also later known as Lord Kelvin. He predicted and observed a third thermoelectric effect, now known as Thomson effect, i.e., that carriers in a homogeneous conductor gained or released energy while traveling through the temperature gradient and this heating or cooling process is reversible. The relationship between the rate of heat absorbed/released ($q$) and the current density ($J$) is:

$$q = \rho J^2 - \tau J \frac{dT}{dx}$$  \hspace{1cm} (2.7)

where $\tau$ is the Thomson coefficient. For a single conductor, it can be written as

$$\tau = T \frac{dS}{dT}$$  \hspace{1cm} (2.8)

He also described that the Peltier coefficient is the Seebeck coefficient times the absolute temperature ($T$) based on thermodynamics such that:

$$\Pi = ST$$  \hspace{1cm} (2.9)

Eq. 2.8 and Eq. 2.9 are called Thomson (Kelvin) relations.

2.2 Thermoelectric Materials

2.2.1 Development of Thermoelectric Materials

Around 1957, a Russian scientist Abram Ioffe suggested to make an all solid-state refrigerator by doped semiconductors which opened the door of thermoelectric materials. However, the efficiency was too low to be competitive and the researches became latent. It wasn’t until 1990 that thermoelectric materials received another attention by U.S. government’s Office of Naval Research (ONR) and Defense Advanced Research Projects Agency (DARPA). They asked interested researchers to propose a way to improve the $ZT$. In 1993 the quantum well structure was predicted to be able to enhance Seebeck coefficient while depressing the thermal conductivity [5, 6]. Later on Venkatasubramanian achieved $ZT \sim 2.4$ at room temperature in 2001 by creating superlattice structured PbTe [7]. Next year Harman published $ZT \sim 3.2$ around 300 °C from PbTe superlattice with quantum dots structure [8]. Around 500 °C, Hsu reported $ZT$ at least 1.4 from AgPbSbTe by appropriate stoichiometry in 2004 [9] and Heremans published $ZT \sim 1.5$ from PbTe with thallium impurity in 2008 [10].

In the search of potential high performance thermoelectric material, Dr. Slack proposed the concept of a “Phonon-Glass Electron-single-Crystal” (PGEC) in 1995: a good thermoelectric
material should possess low thermal conductivity like that in amorphous materials such as glass and high electronic properties like that in a single crystal. This approach started the investigations in semiconductors that have PGEC quality and became a breakthrough innovation in the field of thermoelectric research [11].

2.2.2 Modern Thermoelectric Material Systems

In general, common materials that possess good thermoelectric properties can be classified as the following:

- **Bulk binary semiconductors:** Bi$_2$Te$_3$, PbTe, alloys containing Te, Ag, Ge, Sb (TAGS), SiGe, Zn$_4$Sb$_3$ [12], etc. Intermetallic compounds consist of heavy elements such as Pb, Hg, Bi, Tl, Sb, Te or Se. Their highly covalent bonds and crystal structures allow good balance between electrical and thermal transport properties to achieve high $ZT$.

- **Complex inorganic structures:** CsBi$_4$Te$_6$, CsBi$_4$Te$_6$ [13], ZrTe$_5$ and HfTe$_5$ [14], lead antimony silver tellurium materials (AgPb$_m$SbTe$_{m+2}$ (LAST), Ag(Pb$_{1-x}$Sn$_x$)$_m$SbTe$_{2+m}$ (LASTT), Na$_{1-x}$Pb$_m$Sb$_y$SbTe$_{m+2}$ (SALT) and NaPb$_{18-x}$Sn$_x$SbTe$_{20}$ (SALTT) [9, 15, 16, 17] and half-Hauser alloys: MNiSn $M=$(Zr, Hf, Ti), etc. [18, 19, 20] These ternary and quaternary compounds show very low thermal conductivity and can be good thermoelectric materials with proper composition. Half-Hauser alloys usually possess high Seebeck coefficient but the challenge exists of reducing thermal conductivity.

- **Crystal structure with phonon "rattlers":** clathrate (Ba,Sr)$_8$(Al,Ga)$_{16}$(Si,Ge,Sn)$_{30}$ [21, 22, 23] and skutterudites Co$_4$Sb$_{12}$ system [24, 25, 26, 27, 28, 29]. This structure exhibit low thermal conductivity by introducing "guest" atoms, usually heavy metals, into the voids in the material to act as phonon scattering centers. The smaller and heavier the ions, the greater the reduction in thermal conductivity due to the structure disorder.

- **Complex oxides:** Co based layer oxides: NaCo$_2$O$_4$, Ca$_3$Co$_2$O$_4$ [30, 31, 32] and Al-doped ZnO [33]. Among numerous oxides with metals, few can be considered as prospective candidates for thermoelectric materials mainly due to their strong ionic behavior: their narrow conduction band widths lead to localized electrons and thus limit the electron mobility. Cobalt oxide is promising in its layered structure provides electric transport while the compositional misfit between the layers helps reduce the thermal conductivity. Complex oxide thermoelectric materials are renowned by their thermal stability at elevated temperature ($\sim$730 °C and above) [34, 35]. Thermoelectric modules made by oxide

---

$^5$Being the material system studied in this work, Bi$_2$Te$_3$ will be solely discussed in later chapters.
Figure 2.3: $ZT$ of selected n- and p-type thermoelectric materials system at different temperature: (a) n-type and (b) p-type systems. After reference [38].

materials have been reported [36] but the performance is limited by the high contact resistance at the junctions between metal and oxide.

- Rare earth compounds: YbAl$_3$, CePd$_3$, etc. [37] Although metallic compounds typically have low Seebeck coefficients, these rare earth intermetallics show good power factor by having reasonable Seebeck coefficients and metal-like electrical conductivity. However, the $ZT$ is still less than 1 so far due to high thermal conductivity.

Different thermoelectric material systems have peak $ZT$ values at different temperature regimes as shown in Figure 2.3. The temperature dependence is a critical factor in applying a thermoelectric device. Bi(Sb)Te is the best in room and lower temperature (200 °C) for both n- and p-type. PbTe and CoSb$_3$ dominate in intermediate temperature (300 to 700 °C) among n-type materials and TAGS among p-type materials. At higher temperature regime, 800 °C and above, n-type SiGe and p-type Yb$_{14}$MnSb$_{11}$ shows the best $ZT$. 


In this chapter, transport properties involving electrons such as the diffusive and phonon drag Seebeck coefficients \( S, S_{ph} \), charge carrier mobility \( \mu \) and electrical conductivity \( \sigma \) will be discussed mathematically in order to see the physical origins and their dependences of the temperature and carrier concentration. Based on the Boltzmann transport equation, the expressions for each coefficient are derived to better understand the inter-relationships between them which ultimately leads the way to optimize thermoelectric performance in a given materials. (The discussions in this chapter are to better understand the factors that could change the thermoelectric properties but not meant for strict physical explanations. Due to the complexity of these topics, the materials presented have been selected to fit the best interest of this work.)

### 3.1 Boltzmann Transport Equation

The Boltzmann transport equation describes the evolution of distribution density of particles in a non-equilibrium system. It can be used to find the electrical transport properties by solving the equation when the perturbations such as the electric field \( \varepsilon \) and the temperature gradient are applied to the system. The Boltzmann transport equation\(^1\) can be written as

\[
\left( \frac{df}{dt} \right)_{coll} = \frac{df}{dt} + \frac{d\vec{k}}{dt} \nabla_{\vec{k}} f + \frac{d\vec{r}}{dt} \nabla_{\vec{r}} f
\]

\(^{1}\)More extensive explanations are referred to Ashcroft and Mermin [39].
where $f$ is the non-equilibrium distribution function, $t$ is time, $k$ is the wave vector and $r$ is the position vector of electrons. To find the solution, the *relaxation time approximation* is applied to describe the scattering/collision process of the electrons\(^2\) as a function of relaxation time $\tau$: when the system is disturbed by the external force field, the electrons will reach equilibrium ($f_0$) through random scatterings within time $\tau$. Therefore

$$\frac{df}{dt}_{\text{coll}} = -\frac{f - f_0}{\tau} \quad (3.2)$$

Since electrons are "fermions", particles with half-integer spin, the electron distribution at equilibrium follows the Fermi-Dirac statistic:

$$f_0(E) = \frac{1}{\exp \left( \frac{E - E_F}{k_B T} \right) + 1} \quad (3.3)$$

where $E$ is the electron energy, $E_F$ is the Fermi level\(^3\) and $k_B$ is the Boltzmann constant. Let the perturbations for electrons arise from the electric field ($\varepsilon$) and the temperature gradient along the x direction such that

$$\nabla_k f = \frac{\partial f}{\partial E} \frac{\partial E}{\partial x} \text{ and } \nabla_r f = \frac{\partial f}{\partial T} \frac{\partial T}{\partial x} \quad (3.4)$$

By combining Eq. 3.2 and Eq. 3.4, the first order solution to the Boltzmann transport equation at steady state ($df/dt = 0$), $f - f_0$ in the left hand side of the Eq. 3.1, can be obtained as

$$f(E) - f_0(E) = -\tau v \frac{df_0(E)}{dE} \left[ -\frac{dE_F}{dx} - \left( \frac{E - E_F}{T} \right) \frac{dT}{dx} \right] \quad (3.5)$$

where $v$ is the velocity of the electrons in the x direction. Both $v$ and $\tau$ are functions of the electron energy ($E$). The electric field ($\varepsilon$) is given by $\pm \frac{1}{e} \left( \frac{dE_F}{dx} \right)$ so that the $f(E) - f_0(E)$ can be represented as a function of both the electric field and the absolute temperature:

$$f(E) - f_0(E) = -\tau (E)v(E) \frac{df_0(E)}{dE} \left[ \mp e \varepsilon - \left( \frac{E - E_F}{T} \right) \frac{dT}{dx} \right] \quad (3.6)$$

While applying the $f(E) - f_0(E)$ term into the charge current density ($J$), in Section 3.2.2, one can derive the Seebeck coefficient and the electrical conductivity. If it is plugged into the heat current density ($Q$), in Section 4.1.1, the electronic thermal conductivity can be described.

\(^2\)The sources of electronic scattering include impurities, defects in the crystal, and deviation from periodicity due to the thermal vibration of the ions [39].

\(^3\)Often Fermi level is used as synonymous with Fermi energy in the field of solid state physics. They are the same at 0 K but different at other temperature.
3.2 Formulations of Transport Properties

3.2.1 Carrier Velocity and Relaxation Time

Without the external electric field, the temperature provides the charge carriers thermal energies to have random, bouncing motions between scattering sites including the lattice points, defects, interfaces, impurities and other charge carriers at temperatures above absolute zero. From the classical mechanics, we can obtain the carrier velocity \(v\) as a function of energy \(E\)

\[
v(E) = \sqrt{\frac{2(E - E_0)}{m_\sigma}}
\]

where \(E_0\) is the ground state energy and \(m_\sigma\) is the conductivity effective mass\(^4\).

Typically the relaxation time is described as a power law function:

\[
\tau(E) = \tau_0 \left(\frac{E - E_0}{g(E)}\right)^r
\]

where \(r\) is the scattering factor which is determined by a particular scattering process and \(\tau_0\) is a constant which depends on the material properties and scattering processes. It is noted that the frequency \(\tau^{-1}(E)\) of the elastic collisions is proportional to the density of state function \(g(E)\). The value and sign of \(r\) can be measured from the resistivity, Hall, Seebeck and Nernst coefficients [40]. In some cases, the values of \(r\) have been determined\(^5\) for the parabolic band model: \(r = 2\) for ionized impurity scattering, \(r = 1/2\) for neutral impurity scattering and \(r = 0\) for acoustic and optical phonon scattering [40, 41].

If there are more than one scattering processes, which is typically the case in bulk materials, the relaxation time from each scattering event should be taken into account by the Matthiessen’s rule as

\[
\frac{1}{\tau_{\text{total}}(E)} = \frac{1}{\tau_{\text{phonon}}(E)} + \frac{1}{\tau_{\text{defect}}(E)} + \frac{1}{\tau_{\text{impurity}}(E)} + \ldots
\]

3.2.2 Single Band Seebeck Coefficient and Electrical Conductivity

The charge current density \(J\) can be determined as

\[
J \equiv \pm nev = \pm e \int_{-\infty}^{+\infty} g(E) v(E) [f(E) - f_0(E)] dE
\]

where \(n\) is the carrier concentration, \(g(E)\) is the material’s density of states (DOS).

\(^4\)The harmonic average of the effective mass of all degenerate conduction bands: \(m_\sigma = \left(\sum_{i=1}^{N} \frac{1}{m_{\sigma,i}}\right)^{-1}\).

\(^5\)Depends on the expression of scattering factor, the values of \(r\) could be different.
From Eq. 3.5, Eq. 3.10 with single parabolic band structure approximation, the Seebeck coefficient and the electrical conductivity can be derived [42]:

- **Seebeck coefficient** \( (S) \), single band

\[
S \equiv \frac{1}{e} \frac{dE_F}{dx} \left| \frac{dE}{dx} \right|_{J=0} \equiv \frac{\varepsilon}{dT} \left| \frac{dT}{dx} \right|_{J=0} = \mp \frac{1}{eT} \left( \frac{K_1}{K_0} - E_F \right) \tag{3.11}
\]

- **Electrical conductivity** \( (\sigma) \), single band

\[
\sigma \equiv \frac{J}{\varepsilon \left| \frac{dT}{dx} \right|_{J=0}} = e^2 K_0 \tag{3.12}
\]

where

\[
K_i = \int_{-E_0}^{+\infty} g(E) \tau(E) v^2(E) E^i \left( \frac{df_0(E)}{dE} \right) dE \tag{3.13}
\]

The integral in Eq. 3.13 can be solved by the introductions of the Fermi-Dirac integral \( (F_j(\eta)) \) and the reduced Fermi level \( (\eta) \). Along with the expression of the density of state \( (g(E)) \), \( K_i \) for a bulk, 3-Dimensional (3D) material can be written as

\[
K_i = \frac{1}{2\pi^2} \left( \frac{2m_d}{\hbar^2} \right)^{3/2} \frac{\tau_0}{m_\sigma} (k_B T)^{r+\frac{3}{2}+i} \left( \frac{2(r+i)}{3} + 1 \right) F_{r+\frac{3}{2}+i}(\eta) \tag{3.14}
\]

where

\[
F_j(\eta) = \int_{0}^{+\infty} \frac{x^j}{\exp(x - \eta) + 1} dx \tag{3.15}
\]
is the \( j \)th order Fermi-Dirac integral which can be evaluated numerically \( (x = E \) in this case) and the reduced Fermi level \( (\eta) \) is defined as

\[
\eta = \frac{E_F - E_0}{k_B T} \tag{3.16}
\]

### 3.2.3 Multiple Bands Seebeck Coefficient and Electrical Conductivity

Common thermoelectric materials usually have multiple band minima\(^6\) that have the same energy level and contribute to thermoelectric properties. The contributions could be from conduction band, valence band or both. This degeneracy arises from the symmetry of the material structure. The number of these degenerate bands is called "degeneracy factor \((N)\)". Taking band degeneracy into account yields the following based on Eq. 3.11 and Eq. 3.12 [42]:

\(^6\)Sometimes referred to as "carrier pockets" where the electrons have energy close to \( E_F \) and can be activated.
• Seebeck coefficient \((S)\), multiple bands

\[
S = \frac{\sum_{i=1}^{N} S_i \sigma_i}{\sum_{i=1}^{N} \sigma_i} \tag{3.17}
\]

• Electrical conductivity \((\sigma)\), multiple bands

\[
\sigma = \sum_{i=1}^{N} \sigma_i \tag{3.18}
\]

where the \(i^{th}\) term denotes a transport property from a band minimum and basically the total transport property is the sum of that from each degenerate band.

These formulations of transport properties allow showing how the parameters such as the effective mass, Fermi level and relaxation time change the Seebeck coefficient, electrical conductivity and thermal conductivity and thus the overall figure of merit of the material. They are not meant for mathematical calculations due to the extent of complexity in real bulk thermoelectric materials.

### 3.2.4 Carrier Concentration and Mobility

The carrier concentration \((n)\) and the carrier mobility \((\mu)\) are related with each other through the electrical conductivity \((\sigma)\) (or the electrical resistivity \((\rho)\)) as the following:

\[
\sigma = n e \mu = \frac{1}{\rho} \tag{3.19}
\]

where carrier concentration \((n)\) is described as

\[
n \equiv \int_{E_0}^{+\infty} g(E)f_0(E)dE \tag{3.20}
\]

For a bulk 3D material, the carrier concentration is then to be

\[
n = \frac{1}{2\pi^2} \left( \frac{2k_B T m_d}{\hbar^2} \right)^{3/2} F_1(\eta) \tag{3.21}
\]

after the expressions of the 3D density of state and the Fermi-Dirac integral are replaced. \(m_d\) is the density of state effective mass. Relate Eq. 3.12 and Eq. 3.21, the mobility \((\mu)\) is then deduced as

\[
\mu = \frac{e}{m_\sigma} \left( \tau_0 (k_B T)^r \frac{F_{r+\frac{1}{2}}(\eta)}{F_{\frac{1}{2}}(\eta)} \right) \tag{3.22}
\]
3.3 Analysis of Individual Electrical Transport Properties

3.3.1 Diffusive Seebeck Coefficient

From Eq. 3.11, the diffusive Seebeck coefficient from a single band, with the assumptions of \( g(E) \) and \( \tau(E) \) are power law functions, the 3D Seebeck coefficient can be written as [42, 41]

\[
S = \pm \frac{1}{eT} \left( \frac{\langle \tau E \rangle}{\langle \tau \rangle} - E_F \right) \approx \pm \frac{1}{eT} \left( \langle E \rangle - E_F \right) = \pm \frac{k_B}{e} \left( \frac{(r + \frac{5}{2}) F_{r + \frac{3}{2}}(\eta)}{(r + \frac{3}{2}) F_{r + \frac{1}{2}}(\eta)} - \eta \right) \quad (3.23)
\]

In the case of constant relaxation time, \( \frac{\langle \tau E \rangle}{\langle \tau \rangle} \) becomes \( \langle E \rangle \) and it is clear that the Seebeck coefficient is proportional to \( \langle E \rangle - E_F \), i.e., the difference between the average electron energy and the Fermi level. In other words, the higher the average electron energy, the bigger the separation from the Fermi level and thus the higher the Seebeck coefficient. In addition, \( S \) will change with changes in the \( E_F \) and temperature from Eq. 3.23. Their relationships are discussed as the following:

- **\( S \) v.s. \( E_F \):** The decreases in \( E_F \), i.e., the decreases in \( \eta \), will lead to the increases in \( S \) according to Eq. 3.23. Although the decreases in \( E_F \) indicate the decreases in carrier concentration and thus the decreases in the average carrier energy, \( \langle E \rangle \), the amount of the decrease in \( E_F \) is relative larger than that in \( \langle E \rangle \) so that \( S \) will always increase as \( E_F \) decreases.

- **\( S \) v.s. \( T \):** As temperature increases, both the carrier concentration and average carrier energy increase and result in the higher Seebeck coefficient. Typical thermoelectric materials are extrinsic semiconductors whose carrier concentration is pretty much fixed by the dopant concentration. Therefore the average carrier energy does not increase as the temperature increases. However, the reduced Fermi level \( \langle \eta \rangle \) decreases as the temperature increases so that the overall Seebeck coefficient still increases. With sufficient high temperature, extrinsic semiconductors start to behave like intrinsic semiconductors and the Seebeck coefficient decreases as the temperature keeps increasing. This is because both the electrons in the conduction band and the holes in the valance band participate in the charge carrier diffusion and cancel out each other’s contribution to the overall Seebeck coefficient.

- **\( S \) v.s. \( r \):** According to Eq. 3.23, the Seebeck coefficient will increase as the scattering factor \( r \) increases. In other words, the Seebeck coefficient is larger if ionized impurity scattering \( (r = 2) \) dominates in the material compared to the other scattering events caused by neutral impurities \( (r = 1/2) \) or phonons \( (r = 0) \).
S v.s. \( m^* \): The Seebeck coefficient is independent of the effective mass \((m^*)\) according to Eq. 3.23.

It is possible to evaluate the Seebeck coefficient using appropriate approximations. All of the following expressions are based on the assumptions of parabolic band structure and single band contribution. For the multi-band Seebeck coefficient, individual band coefficient has to be calculated and combined together using Eq. 3.17 and Eq. 3.23.

**Non-degenerate Semiconductor Approximation**

Non-degenerate approximation is applicable when \( \eta \ll 0 \) and acceptable when \( \eta < -2 \). The physical meaning is that the Fermi level lies within the band gap well away from the band edge. The Seebeck coefficient of a non-degenerate 3D semiconductor from Eq. 3.11 [2, 41, 42] is

\[
S \approx \pm \frac{k_B}{e} \left( r + \frac{5}{2} - \eta \right)
\]

**Degenerate Semiconductor Approximation**

When \( \eta \gg 0 \), i.e., the Fermi level is above the conduction band edge or below the valence band edge, the material is considered under the degenerate condition and behaves like a metallic conductor. The Seebeck coefficient is approximated with the series expansion of the Fermi-Dirac integral [42] and Mott’s formula [43, 44] to be

\[
S \approx \pm \frac{\pi^2 k_B}{3e\eta} \left( \frac{\partial \ln(g(E))}{\partial \ln(E)} + \frac{\partial \ln(\tau(E))}{\partial \ln(E)} + \frac{\partial \ln(v^2(E))}{\partial \ln(E)} \right) \approx \pm \frac{\pi^2 k_B}{3e\eta} \left( r + \frac{3}{2} \right)
\]

It is more intuitive to show the interrelationship between the Seebeck coefficient and the carrier concentration \((n)\) by assuming energy independent scattering and parabolic band structure [38, 45]. Eq. 3.25 can then be rewritten as

\[
S = \left( \frac{2\pi^2 k_B^2}{3e\hbar^2} \right) m_d T \left( \frac{\pi}{3n} \right)^{2/3}
\]

**3.3.2 Phonon Drag Seebeck Coefficient**

As the charge carriers flow past atoms in the lattice, they change or disturb the polarity of nearby lattice points. The momentum was then transferred to phonons (and other imperfections). This effect results in lower carrier mobility and consequently lower electrical conductivity. This interaction causes the slow down of the flow of the charge carriers and is called ”phonon drag” effect. It was first observed in measuring the Seebeck coefficient of germanium below 100 K that showed much larger value [46, 47], and below 200 K with the presence of the impurity atoms
[48, 49]. Nonetheless, it was also found in semi-conducting diamond above room temperature [50]. The modeling of a Si nanowire contributed phonon drag Seebeck coefficient ($S_{ph}$) to enhance the overall $S$ in the temperature range of 150 to 300 K [51].

If there is $x$ fraction of collisions of the charge carriers that involve phonons and the relaxation time for the phonon system to return to un-disturbed state is $\tau'$, the contribution from phonon drag to the Seebeck coefficient can be expressed as

$$S_{ph} = \mp \frac{xv^2\tau'}{\mu T}$$

(3.27)

where $v$ is the charge carrier velocity and $\mu$ is the carrier mobility. Typically $S_{ph}$ is strongly dependent on temperature as it is proportional to $T^{-9/2}$ [42].

3.3.3 Electrical Conductivity and Mobility

Electrical Conductivity

The electrical conductivity, given in Eq. 3.19, is a function of temperature because the carrier concentration (Eq. 3.21) and the mobility (Eq. 3.22) are both dependent on the temperature. However, the carrier concentration could be a constant or a variable at different conditions and is also a function of the Fermi level ($E_F$). The details are discussed as the following:

- Intrinsic semiconductor: $E_F$ lies in the middle of the band gap in intrinsic semiconductors and can be considered as a constant. Therefore as the temperature increases, the carrier concentration increases with the dependency of $T^{3/2}$ resulting in an increase in the electrical conductivity.

- Extrinsic semiconductor: The carrier concentration is a constant value which is set by the dopant concentration in extrinsic semiconductors. As temperature increases, the carrier concentration will not change and $E_F$ has to decrease in order to satisfy Eq. 3.21 (which will lead to an increase in $S$ as discussed in Section 3.3.1). Then the electrical conductivity depends on the carrier mobility. In general, the higher the carrier mobility, the higher the electrical conductivity.

Carrier Mobility

The carrier mobility ($\mu$) is more challenging to predict because it involves the scattering factor ($r$) according to Eq. 3.22. Since a material typically consists of several types of scattering mechanism, i.e., a combination of different $r$ values, the experimentally measured mobility values can be used as an rough estimation of which scattering mechanism dominates in the material. In general, its temperature dependency is determined by the value of $r$. 

18
3.4 Interrelationships Between Electrical Transport Properties

The group of the electrical properties in the \( ZT \) defined in Eq. 2.1 is called “power factor (PF)”, i.e., the \( S^2 \sigma \) or \( S^2/\rho \) part. Apparently the higher the power factor, the higher the potential \( ZT \) of the material. Often the power factor is the first criteria for a sample to be considered as a “good” thermoelectric material before it is moved on to thermal property measurements.

From the previous discussions, the value of the Seebeck coefficient at a certain temperature is decided by the reduced Fermi energy (\( \eta \)) and it is found that the peak Seebeck coefficient is achieved when \( \eta \) is equal to its optimal value \( \eta_{opt} \), based on the calculations by Hicks and Dresselhaus [5] as shown in Figure 3.1. Once \( \eta_{opt} \) is found, the maximum Seebeck coefficient can be found. For extrinsic semiconductors, \( \eta \) can be varied by impurity doping concentration so that \( \eta = \eta_{opt} \) while the carrier concentration is also determined by the impurity doping concentration. As a result, the carrier concentration controls both the Seebeck coefficient and electrical conductivity simultaneously.

![Figure 3.1: A plot of ZT versus the reduced Fermi energy (\( \xi^* \) in the figure) in a 3D material. The ZT peaks when the reduced Fermi energy is at an optimal value (\( \xi_{opt}^* \) in the figure). After reference [5].](image)

In general, as the carrier concentration increases, the Seebeck coefficient decreases and the electrical conductivity increases as shown in Figure 3.2. Therefore the power factor increases to
a maximum then starts to decrease. The overall $ZT$ behaves similarly with the power factor that peaks at certain carrier concentration value. The peak values of both power factor and $ZT$ are predicted to be located at carrier concentration ranging from $10^{19}$ to $10^{20}$ cm$^{-3}$ indicating good thermoelectric properties could come from a heavily doped semiconductor. Also the thermal conductivity$^7$ ($k$) increases as the carrier concentration increases, which then decreases the $ZT$.

Figure 3.2: Thermoelectric properties as a function of carrier concentration. The Seebeck coefficient is denoted as $\alpha$ in the figure. For the highest $ZT$ value, the material should have carrier concentration in between $10^{19}$ to $10^{20}$ cm$^{-3}$ according to the plot. Namely a heavily doped semiconductor usually shows potentials to have high $ZT$ value. After reference [38].

Figure 3.3: Experimental data showing $ZT$ as a function of the dopant concentration in PbTe system. As the dopant concentration changes, the $ZT$ increases while the peak value shifts to different temperature as well. After reference [38].

$^7$The thermal transport properties will be discussed in detail in Chapter 4.
Optimization of the carrier concentration not only enhances the performance but also allows the tuning of the materials for specific applications at different temperatures. Figure 3.3 shows an example of the carrier concentration dependency. The PbTe alloys were doped with various concentrations of PbI$_2$ and their $ZT$ was plotted versus temperature. The peak $ZT$ increases from 0.6 to 0.85 as the dopant concentration increases from 0.01% to 0.1% while the peak value shifts from $\sim$50 to $\sim$460 °C [38]. This behavior allows tuning of the PbTe system to be a power generation or refrigeration thermoelectric material in a wide temperature range by adjusting the dopant concentration.
Thermal Transport in Thermoelectric Materials

The ability of a material to conduct heat is described as "thermal conductivity (k)". Good heat conduction materials such as diamond, Cu, and Ag are able to transfer heat across the material at a faster rate compared to poor heat conduction materials such as air, wood and glass. In terms of thermal conductivity, the higher the value, the more efficient the heat transfer. For example, the $k$ value for Cu is about 400 W/m-K while for air is about 0.025 W/m-K.

There are two mechanisms that participate in the heat conduction in a solid. Heat can be carried by electrons and lattice vibration waves. The total thermal conductivity is the sum of these two contributions as

$$k = k_e + k_L$$  \hspace{1cm} (4.1)

where $k_e$ is the electronic thermal conductivity and $k_L$ is the lattice thermal conductivity. The lattice thermal conductivity is generally much greater than the electronic thermal conductivity.

The benefit of thermal conductivity reduction for the thermoelectric figure of merit is shown in Figure 4.1. In a model Bi$_2$Te$_3$ system, the reduction of lattice thermal conductivity from 0.8 to 0.2 W/m-K leads to an increase of $ZT$, from point (1) to point (2) in the figure. In addition, with an optimized carrier concentration, both electronic and lattice thermal conductivity are reduced and result in a higher $ZT$ at point (3) in Figure 4.1.

This chapter will present the formulations and analysis of electronic and lattice thermal conductivity individually. The magnitude of $k_e$ can be obtained by Wiedemann-Franz law for a given electrical conductivity and therefore it can be adjusted by changing the carrier concentrations. However, the Lorentz number of heavily doped semiconductors may be different from that of conventional metals which gives some uncertainties in determining the value of $k_e$. 

22
Figure 4.1: The relationships between the figure of merit (ZT) and the electronic and lattice thermal conductivity. Reducing $k_L$ from 0.8 to 0.2 W/m-K directly increases ZT from point (2) to point (3). The ZT can be further enhanced to point (3) with an optimized carrier concentration which contributes to less electronic thermal conductivity. After reference [38].

and $k_L$.

Most modern thermoelectric material studies are focus on the reductions in the lattice thermal conductivity by either decreasing the heat transport velocity or limiting the phonon mean free path. The former is the concept of creating Phonon-Glass/ Electron-Crystal (PGEC) material and the latter is the main interest of most low dimensional thermoelectric materials. They are discussed in Section 4.3 following the formulations of lattice thermal conductivity and a brief introduction of heat transport quanta: phonons. Some theoretical and modeling works are presented along with the experimental data.

4.1 Electronic Thermal Conductivity

4.1.1 Formulation of Electronic Thermal Conductivity

The expression of electronic thermal conductivity is similar to that of the Seebeck coefficient and electrical conductivity. Based on the Boltzmann transport equation (Eq. 3.1) and its first order, steady state solution (Eq. 3.5), heat current density $(Q)$ is determined as

$$Q \equiv n(E - E_F)v = \int_{-\infty}^{+\infty} g(E)(E - E_F)v(E)[f(E) - f_0(E)]dE$$

(4.2)

and $E - E_F$ represents the total thermal energy transported by a charge carrier.
Then the single band electronic thermal conductivity \( k_e \) is defined \([42]\) and derived to be

\[
k_e \equiv - \frac{Q}{dT} \bigg|_{J=0} = \frac{1}{T} \left[ K_2 - \frac{K_1}{K_0} \right]
\](4.3)

where \( J \) is the charge current density and \( K_i \) can be solved by Fermi-Dirac integral for 3D materials, as discussed in Section 3.2.2, to be

\[
K_i = \frac{1}{2\pi^2} \left( \frac{2m_d}{\hbar^2} \right)^{3/2} \frac{\tau_0}{m_\sigma} (k_B T)^{r+\frac{3}{2}+i} \left( \frac{2(r + i)}{3} + 1 \right) F_{r+\frac{3}{2}+i}(\eta)
\](4.4)

where \( r \) is the scattering factor and \( \eta \) is the reduced Fermi level \( (\eta) \) defined as

\[
\eta = \frac{E_F - E_0}{k_B T}
\](4.5)

For materials with multiple band minima, the multi-band \( k_e \) is the sum of the contribution from individual band \( (k_{e,i}) \):

\[
k_e = \sum_{i=1}^{N} k_{e,i}
\](4.6)

### 4.1.2 Analysis of Electronic Thermal Conductivity

The electronic thermal conductivity \( (k_e) \) represents the heat transfer by electrons. In general, the more the carriers involve in the conduction and/or the faster the electrons move, i.e., the higher the carrier concentration \( (n) \) and/or the higher the carrier mobility \( (\mu) \), the higher the \( k_e \). Electronic thermal conductivity can be optimized through varying carrier concentration, which also changes the power factor. Its influence to the overall \( ZT \) is relatively small so that the priority is usually given to obtaining a better power factor.

**Wiedemann-Franz Law**

The electronic thermal conductivity \( (k_e) \) is proportional to the product of electrical conductivity \( (\sigma) \) and absolute temperature \( (T) \). This relationship is described by the Wiedemann-Franz law:

\[
k_e = \sigma LT = n e \mu LT
\](4.7)

where the proportional factor \( L \) is the Lorentz number. Combining Eq. 4.7 with Eq. 3.12 and Eq. 4.3, the Lorentz number is then given by
\[ L = \left( \frac{k_B}{e} \right)^2 \left[ \frac{(r + \frac{7}{2})F_{r+\frac{7}{2}}(\eta)}{(r + \frac{7}{2})F_{r+\frac{7}{2}}(\eta)} - \left( \frac{(r + \frac{7}{2})F_{r+\frac{7}{2}}(\eta)}{(r + \frac{7}{2})F_{r+\frac{7}{2}}(\eta)} \right)^2 \right] \]  

(4.8)

The modeling results of the dependency of the Lorentz number versus the reduced Fermi level based on Eq. 4.8 is shown in Figure 4.2. Different values of scattering factors \((r)\) and dimensionality \((D)\) are also included. When \(\eta \gg 0\), the metallic regime, \(L\) is close to the experimental value from Wiedemann-Franz law: \(L = \pi^2/3(k_B/e)^2 = 2.44 \times 10^{-8} \text{ W}\Omega^{-2}\). As \(\eta\) gets closer to zero, i.e., less metallic and more semi-conductive, \(L\) starts to decreases. As \(\eta \ll 0\), \(L\) reaches to a constant value ranging from 1.6 to 2.2 \(\times 10^{-8} \text{ W}\Omega^{-2}\) depending on the scattering factor.

Figure 4.2: The plot of Lorentz numbers \((L)\) as a function of the reduced Fermi level \((\eta)\) of different scattering factors \((r)\) and dimensionality \((D)\). The value of \(L\) changes as the material transits from metallic regime \((\eta \gg 0)\) to degenerate semiconductor \((\eta \sim 0)\) and non-degenerate semiconductor \((\eta \ll 0)\) regimes. After reference [41].

It is important to have accurate \(k_e\) values because \(k_L\) is usually obtained by the difference between \(k\) and \(k_e\) using the experimentally measured electrical conductivity. However, some uncertainties arise due to the determinations of scattering factor and dimensionality which reflects in the past studies: several different \(L\) values have been used to calculate the electronic thermal conductivity such as 1.6 \(\times 10^{-8} \text{ W}\Omega^{-2}\) for nanocrystalline samples [52] and 2.0 \(\times 10^{-8} \text{ W}\Omega^{-2}\) for heavily doped semiconductor [53, 54].

The other source of uncertainty is from multiband conduction nature of the material that introduces a bipolar term into the thermal conductivity which is not included in the Wiedemann-Franz law [2]. This results in perceived increase in \(k_L\) at high temperature. The onset of
the bipolar thermal conduction occurs at the temperature where the Seebeck and electrical resistivity peak, which are similarly due to bipolar effects [38].

### 4.2 Lattice Thermal Conductivity

#### 4.2.1 Phonon Dispersion Relationship

The harmonic vibration of lattices as a response to the thermal energy can be modeled by Hooke’s Law, where the force is proportional to the displacement. The solutions to the lattice motion equation (harmonic oscillator) are the vibration modes\(^1\), represented as *phonons*, with different frequencies. In each allowed mode of vibration with frequency \(\omega\) there are \(n\) quanta of phonons with energy \(E_n = \left(n + \frac{1}{2}\right) \hbar \omega\). The frequency \(\omega\) is related to the wave vector \(k\) as the phonon dispersion relationship which is analogous to the electron dispersion relationship: energy \((E)\)-wave vector \((k)\).

For a crystal with single lattice point basis, there is one allowed solution of the wave function, namely acoustical mode, which results from the inter-unit cell response to the temperature. The lattice point on the unit cell vibrates toward the same direction. The phonon dispersion relationship \((\omega-k)\) can be found as\(^2\)

\[
\omega^2 = \frac{2C}{M} (1 - \cos k a)
\]

where \(M\) is the atom mass and \(a\) is the repeat distance of the lattice. \(C\) is the force constant between the nearest-neighbor planes.

For a crystal with more than one type of atoms in a primitive cell, optical mode of phonon arises representing the intra-cell interactions, the atoms vibrate in opposing motion, in addition to the acoustic phonons. An illustration of lattice vibration of a two-atom basis material is shown in Figure 4.3 for a cubic crystal where atoms of mass \(M_1\) and atoms of mass \(M_2\) lie on alternative planes. The motion equations can be solved again and the dispersion relationships at the boundary of the first Brillouin zone are:

at \(k=0\)

\[
\begin{align*}
\omega^2 &\approx 2C \left( \frac{1}{M_1} + \frac{1}{M_2} \right) &\text{(optical branch)} \\
\omega^2 &\approx \frac{1}{2} \left( C \frac{1}{M_1 + M_2} \right) k^2 a^2 &\text{(acoustical branch)}
\end{align*}
\]

\(^1\)Phonon "mode" is the same concept as electron "band". There are certain allowed modes/bands in a solid depending on the material structure.

\(^2\)The detail \(\omega-k\) derivations of acoustical and optical mode of phonons are referred to reference [55].
and at $k = \pm \frac{\pi}{a}$

$$\omega^2 = \frac{2C}{M_2} \quad \text{(optical branch)} \quad (4.12)$$

$$\omega^2 = \frac{2C}{M_1} \quad \text{(acoustical branch)} \quad (4.13)$$

respectively. A plot of optical branch and acoustical branches of the dispersion relation is shown in Figure 4.4 if $M_1 > M_2$.

Figure 4.3: An illustrations of lattice vibration modes of a two-atom basis material. Compared to equilibrium atom positions in (a), the atoms on the unit cell vibrate along the same direction in acoustical mode (b) while they vibrate in the opposite direction in optical mode (c).

Figure 4.4: Dispersion relation for a diatomic linear lattice. The frequencies at the limits $k=0$ and $k=\pm \frac{\pi}{a}$ are shown if $M_1 > M_2$. After reference [56].
4.2.2 Formulation of Lattice Thermal Conductivity

The formal derivation of lattice thermal conductivity is somewhat similar to the electronic thermal conductivity. It starts with Boltzmann transport equation while \( k \) and \( r \) in Eq. 3.1 are now wave and position vector of the phonon, the particle that is involved in heat transport in a solid. Again the relaxation time approximation is applied to describe the collision process of phonons

\[
\left( \frac{df}{dt} \right)_{\text{coll}} = -\frac{f - f_0}{\tau}
\]  

(4.14)

where \( f \) and \( f_0 \) are the perturbed and equilibrium distribution function of phonons respectively. Different from electrons, the distribution function follows Planck distribution\(^3\). Assuming at steady state \( (df/dt = 0) \) and momentum dispersion of the phonons are negligible \( (\nabla_k f \approx 0) \), the solution to the Boltzmann transport equation can be obtained as

\[
f - f_0 = -\tau v \nabla f
\]  

(4.15)

where phonon velocity \( v \) equals to \( dr/dt \). Inserting this solution into heat flux \( (Q(r,t) = \sum_k vfE(k)) \), it becomes

\[
Q(r,t) = \int v(f_0 - \tau v \nabla f)E(k)g(E)dE
\]  

(4.16)

Replacing \( \nabla f \) with \( \nabla T f \nabla T \), the equation becomes

\[
Q(r,t) = \nabla T \int \tau v^2 \nabla T fE(k)g(E)dE
\]  

(4.17)

The lattice thermal conductivity \( (k_L) \) is defined as the ratio of the heat flux \( (Q) \) to the temperature gradient \( (\nabla T) \), therefore

\[
k_L = \int \tau v^2 \nabla T fE(k)g(E)dE
\]  

(4.18)

By introducing the lattice heat capacity \( (C_L) \) defined as

\[
C_L = dU/dT = \frac{d[\int fE(k)g(E)dE]}{dT}
\]  

(4.19)

\(^3\)Planck distribution: \( \langle n \rangle = \frac{1}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} \), where \( \langle n \rangle \) is the average excitation quantum number of an oscillator.
\[ l = v \tau \]  

(4.20)

, then the lattice thermal conductivity can be simply expressed as

\[ k_L = C_L v l \]  

(4.21)

### 4.2.3 Analysis of Lattice Thermal Conductivity

Modern thermoelectric material designs primarily aim at lowering phonon velocity \( v \) and decreasing the phonon mean free path \( l \) to minimize the lattice thermal conductivity and thus the total thermal conductivity to improve the overall \( ZT \). The theories behind their approach are discussed as the following.

**Phonon Velocity**

Phonons travel in a medium as a wave packet with "group velocity". It can be found through the dispersion relationship of phonons as

\[ v = \frac{d\omega}{dk} \]  

(4.22)

, which is the gradient of the frequency with respect to wave vector. As indicated in Figure 4.4, the acoustic phonons have larger spread of energy, i.e., greater group velocity, while the optical phonons have relatively small \( \frac{d\omega}{dk} \), i.e., slower group velocity. Since the goal is to contain heat inside the material, ideally it can be achieved by creating large amount of optical phonons, the slowly propagating phonons.

The origin of optical phonons is the differences of atoms in the material as discussed in Section 4.2.1. It can be shown that with \( p \) atoms in the unit cell and \( N \) unit cells, there can be a total of \( 3N \) acoustical modes and \( 3N(p - 1) \) optical modes, each mode consists of a longitudinal and two transverse branches of polarization. Consequently structures with larger number of unit cells and atoms per unit cells in the structure, namely larger \( p \) and \( N \), there will be more optical phonons and total thermal conductivity will be reduced.

Based on this concept, several materials are considered as potential good thermoelectric material such as PbTe, MgAl\(_2\)O\(_4\) and \( \beta \)-boron based materials because their lattice thermal conductivity could be lowered by introducing many optical phonons.
**Phonon Mean Free Path**

The phonon mean free path \((l)\) is mainly determined by two scattering mechanisms, geometrical scattering and phonon-phonon interaction. There are situations where these effects are dominant.

- **Geometrical scattering**
  Crystal boundaries, the distribution of isotropic masses in natural chemical elements, chemical impurities, lattice imperfections, amorphous structures, etc. are important in limiting the phonon mean free path \([55]\). The theories of phonon scatterings by grain boundaries were investigated: a simplified model to calculate the phonon boundary scatterings at high temperature was reported by Parrott \([57]\) while Bhandari and Rowe studied the thermal conductivity in fine-grained alloys of silicon and germanium \([58, 59]\).

- **Phonon-phonon interaction**
  With a simple three phonon model, there are two possible collision processes. If the phonon momentum \((J)\)\(^4\) is conserved, it is called "normal process" or "N-process" in which incident phonon momentums are all transferred to the transmitted phonon, i.e., \(k_1 + k_2 = k_3\) in Figure 4.5 (a). This implies infinite value of \(k_L\) because there is no loss during the conduction of heat energy.

  On the other hand, if the phonon momentum is NOT conserved, it is called "umklapp process" or "U-process". This anharmonic process results in excess momentum represented as the reciprocal lattice vector \((G)\): \(k_1 + k_2 = k_3 + G\), where \(G = \frac{2\pi}{a}\) and \(a\) is the lattice parameter as shown in Figure 4.5 (b). The presence of \(G\) indicates there is a net change in phonon momentum\(^5\) in each collision event which creates thermal resistance during the U-process and thus a finite \(k_L\).

  At high temperature, where all phonon modes are excited \((k_BT > \hbar\omega)\), a substantial proportion of phonon collisions will be U-process along with a large amount of momentum change in the collision which results in a decrease in \(k_L\). In general, this effect has to be considered for thermoelectric materials operated between room temperature and beyond.

**4.3 Lattice Thermal Conductivity Reduction**

Modern thermoelectric research mainly focuses on the reduction in \(k_L\). Based on the previous discussions, there are two ways to reduce the lattice thermal conductivity from the materials structure design perspective: 1) creating complex structures to reduce the phonon velocity such

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\(^4\)Phonon momentum: \(J = \sum_k n_k \hbar k\)

\(^5\)Unlike momentum, energy is conserved in both N- and U-process.
Figure 4.5: Illustrations of possible collision process in the three phonon model, (a) normal process and (b) umklapp process, in a two dimensional square lattice. Incident phonons, \(k_1\), \(k_2\) collide and create transmitted phonon, \(k_3\). The momentum completely transferred to the transmitted phonon in the normal process, but only partial momentum is transferred in the umklapp process.

as skutteruditeliike materials and 2) utilizing low dimensional structure features—for example, thin films, nanowires, quantum dots—to limit the phonon mean free path.

4.3.1 Phonon-Glass/Electron-Crystal (PGEC) Approach

The phonon-glass/electron-crystal (PGEC) approach is mostly highlighted by the skutterudite structure materials. It is a cubic structure with the space group composed of eight corner-shared octahedra. The linked octahedra have vacant sites at the center of the cluster that can accommodate large atoms. By introducing "guest" atoms into these voids, strong phonon scattering sites are created by the "guest" atoms thus reducing the lattice thermal conductivity of the compounds. The vacant sites can be completely or partially filled, as shown in Figure 4.6, such that the guest atoms "rattle" and scatter the acoustic phonons. This thermal conductivity reduction from the disorder within the unit cell can also be achieved by interstitial sites and partial occupancies in addition to the rattling atoms. More details about lattice disorder scattering of phonons are discussed later in Section 4.3.2.

The results of various material systems by PGEC approach are experimentally obtained as shown in Figure 4.7. Several complex material systems exhibit extremely low values such as \(\text{Yb}_{14}\text{MnSb}_{11}\), \(\text{CeFe}_3\text{CoSb}_{12}\), \(\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}\) compared to \(\text{Bi}_2\text{Te}_3\) system. Other than skutterudite structure, this approach also works on materials with highly covalent bonding, which enables high carrier mobility and therefore good electron-crystal properties, such as Si, Ge or Sn [3].
4.3.2 Size Effects on Thermal Transport

At low temperature, the size effect from geometrical scattering dominates such that the lattice thermal conductivity becomes

\[ k_L \approx C_L v D \]  \hspace{1cm} (4.23)\]

where \( D \) is the order of the diameter of the specimen. This effect is appreciable when \( l \) is comparable to the \( D \). Therefore low dimensional structures such as thin films, nanowires and quantum dots can take advantage of the size effect to limit the phonon mean free path which is usually on the order of nanometers. Conceivably, if \( l \) is of the order of the minimum phonon wave length (\( \approx 2a \)), the minimum \( k_L \) would be achieved. In a polycrystalline material, the maximum mean free path is expected to be set by the grain size. By the same token, an amorphous material could have phonon mean free path comparable to interatomic spacing.
Although the size effect is conventionally considered as a low temperature phenomenon (at $T < 200$ K), it has been found to play an important role in lowering $k_L$ in modern high $ZT$ nanostructured thermoelectric materials [42, 61, 62].

**Point Defect Scattering**

The local changes in density and elastic constants associated with different atoms result in the scattering of phonons in solid solutions. This effect is applicable for low frequency phonons because their wavelength is larger than the point defects. The modeling of this effect has been studied and compared to experimental values as shown in Figure 4.8 [57, 63]. The y-axis is the ratio of the lattice thermal conductivity of a solid solution ($\lambda_L$ in the plot) to a perfect crystal ($\lambda_0$ in the plot) and the x-axis is ratio of the phonon frequency with point defect ($\omega_D$) to that of perfect crystal ($\omega_0$). The plot shows that the lattice thermal conductivity can be reduced with local mass-fluctuation by the fact that no data points lie above the theoretical curve. Some data points are in good agreement with the theoretical predictions but some data points fall below. It could be due to the addition of strain scattering to the point defect scattering.

![Figure 4.8: Plot of the ratio of the lattice thermal conductivity of a solid solution ($\lambda_L$) to a perfect crystal ($\lambda_0$) and the x-axis is ratio of the phonon frequency with point defect ($\omega_D$) to that of perfect crystal ($\omega_0$). The curve is based on theoretical modeling and the points represents experimental thermal conductivity data for various solid solutions. After reference [63].](image)

Rare earth chalcogenides with the Th$_3$P$_4$ structure also show low thermal conductivity due to the point defect scattering [64], for example, the La$_{3-x}$Te$_4$ in Figure 4.7. It is believed that a large number of random vacancies are responsible for low lattice thermal conductivity because the phonon scattering depends on the mass ratio of the alloy constituents.
The random alloying mixture of filling atoms and vacancies in partially filled skutterudites and clathrates, as discussed in Section 4.3.1, enable the point defect scattering of phonons as well. On the other hand, filling the voids with ions creates additional source of lattice disorder because it will be requiring compensating cations for charge balance. This partially filling method may also allow the tuning of free-carrier concentration by offsetting the charge balanced composition [38].

**Boundary Scattering**

This "boundary scattering" of phonons originates from the fact that the mean free path of the phonons \( l \) strongly depends on their vibrational frequency \( \omega \) [62]. Since \( l = v\tau \) and both \( v \) and \( \tau \) are both dependent on the \( \omega \). The low frequency phonons, although they are relatively small in number, have a large mean free path and thus make substantial contributions to the lattice thermal conductivity.

The contributions of low frequency phonons to the lattice thermal conductivity can be demonstrated in Figure 4.9. The single-hatched area represents the reduction in thermal conductivity due to point defect scattering and the double-hatched area indicates the reduction due to the boundary scattering of the phonons. The upper curve is applicable when only phonon-phonon scattering occurs, i.e., the area under the upper curve represents the lattice thermal conductivity of large pure crystals. Since the contributions from most of the high frequency phonons are reduced by the point defect scattering, the remaining lattice thermal conductivity is mainly dependent on low frequency phonons, which are sensitive to the boundary scattering because of their long mean free path.

Boundary scattering becomes important in low dimensional structures because the relaxation time in a polycrystalline material depends on the average size of the sample or the layer thickness \( d \) [65], which is given by

\[
\tau = \frac{v}{d} \left[ \frac{1 - p(\omega)}{1 + p(\omega)} \right]^{-1} \quad (4.24)
\]

where \( p(\omega) \) represents the boundary surface roughness. The value \( p = 1 \) indicates a smooth surface and infinite relaxation time and there is no boundary scattering effect. The value \( p = 0 \), there are very rough surfaces in the material and the boundary scattering dominates. Several researches have successfully shown reduced lattice thermal conductivity by boundary scattering at and around room temperature such as superlattice, nanowires and nanocomposites, which will be discussed later in Section 5.3. The detailed modeling and theories are referred to the references [61, 66, 67, 68].

Boundary scattering of phonons may also affect the Seebeck coefficient, especially the phonon drag part \( S_{ph} \) which is sensitive to the phonon scattering mechanisms. The \( S_{ph} \) is
Figure 4.9: Schematic plot of thermal conductivity ($k$) as a function of the phonon frequency ($\chi$ in the plot). Point defect scattering (single-hatched area) removes most of the high frequency phonon contributions so that the remaining lattice thermal conductivity is mainly due to low frequency phonons, where the double-hatched area indicates the reduction due to the boundary scattering. After reference [62].

mainly associated with low frequency phonons and therefore could be sensitive to the boundary scattering effects. Experimental studies of the boundary scattering effect on both the Seebeck coefficient and thermal conductivity have been carried out in Ge crystals [69].
Due to the interrelationship between thermoelectric properties ($S$, $\sigma$, and $k$), the $ZT$ of traditional 3D bulk thermoelectric materials have been limited to be about 1 for the past three decades. This chapter introduces the low-dimensional structure approach, such as quantum confinement and energy filtering, to break the barrier of the $ZT$ in 1D nanowire, 2D thin film lattice and 3D bulk nanocomposites structures.

This approach is expected to be able to both improve the power factor and limit the thermal conductivity according to the computer simulation. The former is mainly from the quantum confinement effect that increases the number of charge carriers and changes the average energy, $\langle E \rangle$, and the Fermi level, $E_F$. The later is benefit from increased interface density by embedding nano-scale features in the microstructure.

The computer modeling, resulting experimental performance and contributing factors in structures of different dimensionality are presented. Focused on 3D nanocomposite, the modeling of the phonon transport are discussed and various thermoelectric material systems in this structure configuration are introduced.

### 5.1 Power Factor Enhancement

As discussed in Section 3.4, the Seebeck coefficient ($S$) and the electrical conductivity ($\sigma$) are linked by the carrier concentration ($n$). In general, an increase in $S$ comes with a decrease in $\sigma$. To quasi-independently vary these properties, Hicks and Dresselhaus proposed the use of low-dimensional structure such as quantum wells and nanowires [5, 6]. As the dimensionality
of the structure decreases, the length scale and new physical phenomena such as quantum confinement and energy filtering become available for the control of material properties. These phenomena are discussed in the following.

5.1.1 Quantum Confinement

The quantum confinement effect can be observed when the structure size is comparable to nanometer scale or less as the number of atoms in any direction becomes small. It is an approach to enhance the Seebeck coefficient without affecting the electrical conductivity through changes in the magnitude of the density of state while the dimensionality of the material decreases.

The density of state per unit volume ($g(E)$) including a spin factor of two for 3D, 2D and 1D structures can be derived as the following respectively [55]:

$$g_{3D}(E) = \frac{1}{2\pi^2} \left(\frac{2m_d}{\hbar^2}\right)^{3/2} E^{1/2}, \quad m_d = (m_xm_ym_z)^{1/3} \quad (5.1)$$

$$g_{2D,n}(E) = \frac{m_d}{a\pi\hbar^2}, \quad E \geq E_n, \quad m_d = (m_xm_y)^{1/2} \quad (5.2)$$

$$g_{1D,nm}(E) = \frac{1}{a^2\pi} \left(\frac{2m_d}{\hbar^2}\right)^{1/2} (E - E_{nm})^{-1/2}, \quad E \geq E_{n,m}, \quad m_d = m_x \quad (5.3)$$

where $m_d$ is the density of state effective mass, $n, m = 1, 2, 3..., \text{ representing an integer for the sub-band index}$, $\hbar$ is the reduced Planck constant and $a$ is the size or length scale of the structure, i.e., width/thickness of the quantum well or nanowire.

As indicated in these equations, the resulting energy dependency of the density of state changes dramatically from $1/2$ (3D bulk) to $0$ (2D quantum well) and $-1/2$ (1D quantum wire), as shown in Figure 5.1. Also the length factor, $a$, shows up in 2D and 1D material structures and has inverse proportionality of the density of the states, i.e., smaller $a$ can result in higher density of state.

Seebeck Coefficient Enhancement

Due to the shape of the 1D density of state, the electron distribution in 1D nanowire is skewed toward the lower energy state (the band edge). Given the same carrier concentration, this results in lower average electron energy, $\langle E \rangle$, compared to that in the 3D bulk materials. The Fermi energy, $E_F$, is also reduced and the amount of reduction is much greater than that in the average electron energy. Consequently the Seebeck coefficient is still increased since it is proportional to the difference between the average electron energy and the Fermi energy, i.e., $S \propto (\langle E \rangle - E_F)$, as discussed in Section 3.3.1.

The power factor is enhanced by the increases in the Seebeck coefficient while the electrical
conductivity is fixed by the carrier concentration assuming the carrier mobility remains the same in the bulk, quantum well and nanowire structures. This assumption was made because the carrier mobility is rather challenging to predict. For example, in the 2D or 1D structures, the Fermi energy could be increased or decreased due to the changes in the density of the states and this may lead to a change in the scattering mechanism compared to the 3D materials. Therefore, often \( S^2n \) in the power factor \( (S^2\sigma, \text{or} \ S^2ne\mu) \), is emphasized when \( \mu \) is assumed to be a constant and now the power factor is determined by the Seebeck coefficient and carrier concentration in this discussion.

**Modeling of the Quantum Confinement Effect**

The validity of these concepts were first tested in modeling a 2D PbTe\(_{1-x}\)Eu\(_x\)Te multiple quantum well system [70]. The structure was grown by molecular beam epitaxy with PbTe well widths varying between 17 and 55 Å separated by Pb\(_{0.958}\)Eu\(_{0.042}\)Te barriers of about 450 Å. The \( S^2n \) values were found to match the predictions of the theory [5]: it is higher than the bulk PbTe and increases as the well thickness decreases as shown in Figure 5.2 (a). The study also demonstrated the \( S^2n \) as a function of carrier concentration: the optimal carrier concentration changes as the well width changes as shown in Figure 5.2 (b).

The modelings of bulk and nanowire Si reinforce the advantages of the quantum confinement effect [41]. Using optimal carrier concentration and the corresponding Fermi energy, \( n = 1.7 \times 10^{20} \text{ cm}^{-3} \) and \( E_F = 0.1 \text{ eV} \) respectively in the bulk Si, the calculated Seebeck coefficient is -0.1 mVK\(^{-1}\), the \( S^2n \) is \( 17 \times 10^{23} \mu\text{V}^2\text{K}^{-2}\text{cm}^{-3} \) and the average electron energy is 0.13 eV as shown in Figure 5.3 (a). Assuming the carrier mobility and carrier concentration remain the same, when the structure changes from 3D bulk to 2 nm by 2 nm nanowire, the average electron energy decreased to 0.05 eV because the majority of the electrons has lower energy defined by the 1D density of states. Meanwhile, the \( E_F \) decreased as well from 0.1 to 0.01 eV. The combination of the changes in \( \langle E \rangle \) and \( E_F \) doubles the Seebeck coefficient and therefore a four-fold increase
Figure 5.2: The $S^2n$ values of the PbTe/Pb$_{0.958}$Eu$_{0.042}$Te multiple quantum well structure (full circle) with the calculated results (solid line) and the best experimental bulk PbTe material as a function of the well thickness (a) and a function of the carrier concentration (b). After reference [70].

in $S^2n$ from $17 \times 10^{23}$ to $68 \times 10^{23}$ $\mu V^2K^{-2}cm^{-3}$ as shown in Figure 5.3 (b).

**Carrier Pocket Engineering**

The other use of the quantum confinement effect is the so-called “carrier pocket engineering” proposed by Koga et al. to enhance the power factor [71]. This method looks for shifting energy levels in the carrier pockets/conduction valleys as well as increasing the number of active conduction valleys. It requires precise matching of materials with defect-free, compatible crystal structure and similar configurations of the electronic band structures. Therefore Si/Ge and GaAs/AlAs superlattice showed promising enhancements in the power factor and overall figure of merit through carrier pocket engineering [72, 73].

**5.1.2 Energy Filtering**

The concept of energy filtering is to selectively scatter charge carriers according to their energy level [74, 75]. This could be done by introducing interfaces as barriers to restrict the flows of low energy carriers in a material. On the other hand, those carriers with energy significantly higher than the Fermi energy can pass through the interfaces and become dominant in the transport properties. Therefore the Seebeck coefficient increases because the average electron energy increases. This “filtering” happened because the carrier mean free path strongly depends on the energy due to the presence of the potential barriers [76].

The interfaces, however, could reduce the electrical conductivity as well. Therefore the
Figure 5.3: Electron distributions in the conduction bands of the (a) bulk Si and (b) 2 nm by 2 nm Si nanowire at 300 K. The electron distributions are defined by the Fermi-Dirac distribution and density of state, as in Eq. 3.20, indicated as the gray area in the figures. When the structure dimension decreases from 3D to 1D, a four-fold increase in the power factor is predicted by the modeling. It is mainly a result of the changes in the average electron energy, $\langle E \rangle$, and the Fermi level, $E_F$. The carrier mobility and carrier concentration are the same for both 3D and 1D structures, 3.86 and $1.7 \times 10^{20}$ cm$^{-3}$ respectively. The band ground state energy is set to be zero. After reference [41].

Energy filtering approach relies on appropriate interfaces such that the reduction in the electrical conductivity is more than compensated for by the increase in the Seebeck coefficient through the process to result in a net increase in the power factor. The positively effective interfaces could be from proper dopant, the degree of deviation from stoichiometry and optimized crystalline size relative to the mean free path length, etc. [76]

**Seebeck Coefficient Enhancement**

Grain-boundary potential barrier scatterings were observed to be the dominant scattering mechanism in both pure PbTe and Ag-doped PbTe nanocomposites\(^1\) [77]. The material has a dispersion of nanostructure within a bulk matrix, with grain size ranging from 100 nm to over 1 µm. The charge carriers trapped in the grain boundaries form energy barriers that allow only carriers with energy higher than the barrier height to go through. Therefore the carriers participating in the transport are those with higher energy so that $\langle E \rangle$ increases. Consequently both the Seebeck coefficient and power factor increase: the former is about 325 and 200 µVK$^{-1}$ and the later becomes 8 and 14 µWcm$^{-1}$K$^{-2}$ for the pure and Ag-doped PbTe at 300 K respectively. The power factor is still low due to the poor electrical conductivity even with the

\(^1\)Being the main structure configuration in this work, more details of its role in bulk thermoelectric material are discussed in Section 5.3.3.
enhanced Seebeck coefficient.

Oxidation was found by X-ray diffraction during the sample preparation and enhanced the energy filtering process according to the author. The chemisorption of oxygen forms acceptor states by removing electrons from the grain surface so that more charge carriers are trapped at the grain boundaries and the energy barriers are established [77].

Similar Seebeck coefficient enhancement via carrier energy filtering has also been reported in Pt-Sb$_2$Te$_3$ nanocomposites [78]. The Pt nanocrystals, average size 13.7 nm, are embedded in a p-type Sb$_2$Te$_3$ matrix by chemical solution process. The band-bending potential well is formed at the interfaces between the Pt nanocrystals and the matrix such that low energy holes are preferentially scattered as shown in Figure 5.4 (a), (b). The TEM micrograph of such a nanocomposite structure is shown in Figure 5.4 (c). The resulting Seebeck coefficient increases from 79 $\mu$VK$^{-1}$ from pure single crystal Sb$_2$Te$_3$ with similar carrier concentration value to 151 $\mu$VK$^{-1}$ from Pt-Sb$_2$Te$_3$ nanocomposite. The power factor value, however, is only 1 $\mu$Wcm$^{-1}$K$^{-2}$ again due to the poor electrical conductivity in the nanocomposite structure.

![Figure 5.4: Band alignment and TEM micrograph of the Pt-Sb$_2$Te$_3$ material. The bandgap ($E_g$), electron affinity (E. A.), ionization potential (I. P.) and work function (\(\Phi\)) values are shown in (a), the band diagram before the formation of Pt-Sb$_2$Te$_3$ interfaces. At equilibrium, band-bending potential well are formed at the interface that blocks low energy holes as shown in (b). The TEM micrograph, (c), shows the nanocomposite structure: Pt nanocrystals about size 13 nm dispersed in the matrix Sb$_2$Te$_3$. After reference [78].](image)

In addition to the potential barriers, impurities and defects in the material can create resonant levels near the allowed band edge. With additional doping of electrically active materials, these impurity bands can be filled and increase the average carrier energy. This phenomenon offers the possibility of increasing the Seebeck coefficient from 56 up to 140 $\mu$VK$^{-1}$ in Na-doped samples and was observed in In-doped PbTe, PbSe and SnTe samples [76].
5.2 Lattice Thermal Conductivity Reduction

In addition to electrical transport properties, thermal transport properties plays an important role in the $ZT$ enhancement. As presented in Section 4.3, the heat energy can be conducted by electrons or phonons with thermal conductivity $k_e$ and $k_L$. Within these two mechanisms, lattice thermal conductivity is more of interest because the contribution from $k_e$ is relatively small and it is fixed by the Wiedmann-Franze law, $k_e = \sigma LT$ where $L$ is the Lorenz number, when the electrical conductivity is determined.

5.2.1 Nano-structure Approach

As discussed in Section 4.2.3, by introducing interfaces, crystal boundaries, lattice imperfections and/or chemical impurities, the lattice thermal conductivity will decrease due to the decreases in the phonon mean free path provided their sizes are comparable to the phonon wavelength, in the order of nanometer scale in general. This effect aims at the long wavelength (or low frequency) acoustic phonons because they have long mean free path and contributed significantly to thermal conductivity at high temperature as well as increases the rate of the U-process phonon-phonon scatterings [42, 79, 80, 81]. Structures, such as nanocomposite, superlattice, nanowire, have shown promising thermoelectric performance benefiting from the reduction in the lattice thermal conductivity, which will be discussed in detail in the following sections.

5.3 Proof-of-principle Low-dimensional Structures

5.3.1 Nanowires–1D

Although bulk Si is a poor thermoelectric material, Si nanowires seem to be a promising high performance thermoelectric materials benefit from its low dimensional structure. The reduction in thermal conductivity is dramatic in 50 nm in diameter Si nanowires: about 100-fold reduction while the Seebeck coefficient and the electrical resistivity remain the same as the bulk Si. The resulting $ZT$ is much improved from 0.01 (bulk Si) to 0.6 (Si nanowire) at room temperature [82]. The thermal conductivity has been reduced from $\sim$150 W/m-K in bulk Si to $\sim$1.6 W/m-K ($k_L$ is about 1.2 W/m-K) in Si nanowire, which is already close to the amorphous limit. The phonon mean free path was limited from about 300 nm to 50 nm by the structure.

Another study of Si nanowire shows similar thermal conductivity reduction by limiting the phonon mean free path [83]. It has also shown 100-fold reduction in the 10 and 20 nm wide nanowires which results in $ZT \sim$1 at 200 K as shown in Figure 5.6. Part of the $ZT$ enhancement is considered from the power factor which is increased by the phonon drag Seebeck coefficient contributions.
5.3.2 Thin Film Superlattices–2D

In the development of low dimensional thermoelectric materials, thin film superlattice first demonstrated effective lattice thermal conductivity reductions and their high $ZT$ values set the milestones in the development of thermoelectric materials [7, 8, 10, 84, 85, 86]. In the PbTe superlattices with alternative layers of PbSe$_{0.98}$Te$_{0.02}$ quantum dots, the total thermal conductivity is 6.9 mW/cm-K ($k_L=3.6$ and $k_e=3.3$ mW/cm-K) which enables the $ZT$ to reach as high as 1.6 at 300 K and 3 at 550 K [8, 84, 85]. The superlattice structure and the $ZT$ versus temperature plot are shown in Figure 5.7.

Bi$_2$Te$_3$ based superlattice have also shown high $ZT$ (about 2.4) around room temperature [7]. The $ZT$ versus temperature plot is shown in Figure 5.8. This performance was mainly contributed by a great reduction in the lattice thermal conductivity. The 10Å Bi$_2$Te$_3$ and 50Å Sb$_2$Te$_3$ structure offers $k_L=2.2$ mW/cm-K in c-axis direction due to a localization-like behavior of low frequency phonons since the estimated phonon mean free path (9.6 Å) is comparable to the structure dimensions (10 Å) [87]. Such a localization effect was also observed in Si/Ge superlattice that leads to a significant reduction in thermal conductivity [61].

With $ZT > 2$, thin film thermoelectrics have revived the concept of using thermoelectric phenomenon to recycle, save and generate energy. The potential applications opens up to the fields of aerospace, consumer electronics and medical devices, etc.
Figure 5.6: Temperature dependency of $ZT$ of the 20 and 10 nm wide Si nanowires. The $ZT$ peaks around 200 K in the 20 nm wide nanowires. After reference [83].

5.3.3 Nanocomposites–3D

Similar concept, limiting the phonon mean free path by interfaces, was again adapted to bulk 3D structure to enhance the $ZT$ based on the conclusions from past studies: periodic structures are not necessary for thermal conductivity reduction [88]. Compared to 2D or 1D structures, the 3D bulk materials have potentials of being produced by a more scalable, cost effective approach and having practical applications. Nevertheless, the 3D structure indicates much more complex structure-property relationship that is challenging to resolve individually and leads to fluctuations in the properties within the same material system.

Recently nanocomposite becomes a popular 3D bulk structure for thermoelectric application. The performance of the nanocomposite structure is expected to be promising because 1) high interface density helps scatter phonons and thus reduce the lattice thermal conductivity and 2) the nanoscale inclusions embedded in the matrix help increase the Seebeck coefficient by, for example, energy filtering and/or quantum confinement effect. Figure 5.9 (a) is the cross section view of the basic composite structure. The ”inclusions” needs to be in nanometer scale in order to be effective in $ZT$ enhancement. Evidently the interfaces in nanocomposite materials may decrease the electrical conductivity but the goal is to compensate that with higher $S$ and lower $k$ and thus higher power factor and $ZT$.

Modeling of Phonon Transport

The model calculations show encouraging results and provide guidelines to the structure design requirements. The calculations of Si-Ge composites, Si nanowire inclusions embedded in Ge
matrix, show that the thermal conductivity can be reduced compared to the bulk $\text{Si}_x\text{Ge}_{1-x}$ alloy of the same composition as the nanocomposites when the Si nanowires are smaller than 500 nm. Meanwhile, the reduction increases when the nanowire size decreases [89]. This was based on the solution of the Boltzmann transport equation for a unit cell containing "aligned" Si nanowires, which is shown in Figure 5.9 (b), and the thermal transport is along the wire direction. The calculations also demonstrate that the thermal conductivity changes with the volumetric fraction of the constituents: $0.2 < x < 0.8$ is the most effective volume fraction of the Si nanowires that a significant reduction in thermal conductivity can be achieved.

The results of Si-Ge nanocomposite are plotted in Figure 5.10. The figure also shows that the thermal conductivity increases with increasing Si volumetric fraction for bulk alloy and $\text{Si}_x\text{Ge}_{1-x}$ with 500 nm Si nanowires. This is because the Si has higher thermal conductivity and sound velocity than Ge. On the other hand, when the Si nanowires are of 50 nm or less, the phonon mean free path is limited by the nanostructural width and the thermal conductivity decreases as the Si concentration increases.

The effects of the inclusion size, size distributions, and degree of randomness were predicted by Monte Carlo simulations in a SiGe host material [74]. The inclusions used in the simulation include aligned, staggered, or random 3D Si particles, as shown in Figure 5.9 (b), and 2D Si nanowires. A universal curve was found and the thermal conductivity showed strong dependency on the interface density (area per unit volume) for all configurations of inclusions. The results are shown in Figure 5.11: when the interface density is higher than 0.08 nm$^{-1}$, regardless of the size and alignment of either particle or nanowire inclusions, the thermal conductivity can be reduced to be smaller than that of the bulk alloy material.
The above two model calculations established that 1) the nano-sized inclusions can impede phonon transport, 2) ordered structures and coherent interfaces are not necessary to achieve low thermal conductivity and 3) interface density is critical in determining the thermal conductivity in nanocomposite material.

**Nanocomposite Materials**

- Bi$_2$Te$_3$ nanocomposites$^2$

  Bi$_2$Te$_3$ has been known for good thermoelectric performance for decades at or around room temperature. It can be doped with electron donors or hole acceptors to make the electrical properties n- or p-type. P-type Bi$_{x}$Sb$_{2-x}$Te$_3$ has shown significant improvement

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$^2$As the main research system in this work, more details in material's properties and structure will be discussed later in Chapter 6.
Figure 5.10: The calculated thermal conductivity versus the volumetric fraction of Si of the Si$_x$Ge$_{1-x}$ nanocomposite. The heat flow is along the wire direction while the wires are aligned in the matrix. The solid line represents a bulk alloy with the same chemical composition as the nanocomposites. After reference [89].

by nanocomposite structure. Compared to conventional commercial Bi$_2$Te$_3$, typically in the form of single crystal ingots, which has ZT about 1, the nanocomposite Bi$_x$Sb$_{2-x}$Te$_3$ can reach peak ZT to 1.4 at 100 °C and 1.2 at room temperature [90]. The microstructure figures obtained by TEM are shown in Figure 5.12. The grains are in the nanometer scale and close packed with clean grain boundaries. Meanwhile Sb-rich nanodots about 2 to 10 nm in size are observed as well as pure Te precipitates of 5 to 30 nm in size. Usually the Sb-rich nanodots have composition close to Bi: Sb: Te = 8: 44: 48 with Sb substituted for Te.

The improvement in ZT is mainly due to the large reduction in thermal conductivity. The individual transport property is shown in Figure 5.13. It is noted that the electrical conductivity in the nanocomposite is higher than that in the state-of-the-art ingot included in Figure 5.13 A. The authors attribute this phenomenon to the structural defects, such as antisites, i.e., Bi atoms go to Te sites. These antisites/defects are responsible for charge buildup at grain boundaries and thus increase the hole density and the electrical conductivity.

Compared to p-type material, the advancement of n-type Bi$_x$Sb$_{2-x}$Te$_3$ is rather lackluster. Being the main challenge in the BiTe based alloy, this work will demonstrate a significant improvement in the the bulk 3D n-type materials later in Chapter 8.

- SiGe nanocomposites
  The promising results from the model calculations make SiGe nanocomposites attractive
in the high temperature range. An experimental p-type boron-doped Si_{80}Ge_{20} alloy shows peak $ZT$ about 0.95 at 800 °C [91]. Its transport properties are shown in Figure 5.14 individually. The continuous increase in the Seebeck coefficient give rise to increasing $ZT$ from 100 to 800 °C. The TEM figures showing microstructure is in Figure 5.15. The grains are in the range of 20 to 200 nm. They are highly crystalline and close packed with clean boundaries. There is no difference in crystal structure between the the dark dots and the background. The contrast may be due to the segregation of the dopant (boron). Both dark dots and the background contain small size grains.

Compared to the p-type SiGe used in the radioisotope thermoelectric generator (RTG) for space power missions, the thermal conductivity is reduced over the whole temperature range up to 1000 °C, mainly from the reductions in the lattice part. The nanostructure
Figure 5.13: Transport properties of the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanocomposite. Solid squares represent the nanocomposite and open squares represents the state-of-the-art (SOA) ingot. The thermal conductivity reduction contributes the improvement of the $ZT$ which peaks at 100 °C to be about 1.4. The electrical conductivity of nanocomposites is better than the SOA ingot due to the charge build up at grain boundaries. After reference [90].

enhances the phonon scattering at the numerous interfaces in the material and impedes the flow of the heat.

- **PbTe nanocomposites**
  Thallium-doped PbTe has shown enhanced $ZT$ of 1.5 at 500 °C through an enhancement of the Seebeck coefficient and small reductions in the thermal conductivity [92]. The micrographs by TEM and SEM are shown in Figure 5.16. The starting powder was around or less than 200 nm but the grains grow substantially after consolidation to be more than several microns.

- **Other nanocomposites**
  There are several other nanocomposite material systems which have been reported to potentially have high $ZT$ values. Such as Bi$_{85}$Sb$_{13}$Pr$_2$ and Bi$_{85}$Sb$_{14}$Ag [92], skutterudite YbxCo$_4$Sb$_{12}$ [93], Ga$_m$Sb$_n$Te$_{1.5+m+n}$ [94], Zn$_4$Sb$_3$ [95], Ag$_n$Pb$_m$Sb$_m$Te$_{m+2n}$ [96]. Even though the thermal conductivity is reduced due to the nanocomposite structure of these material systems, the overall $ZT$ is not necessarily enhanced due to the changes in the electrical conductivity and the Seebeck coefficient.
Figure 5.14: Transport properties of Si$_{80}$Ge$_{20}$ nanocomposite. The solid line is the SiGe material used in the radioisotope thermoelectric generator (RTG) for comparison. After reference [91].

Figure 5.15: TEM images showing the microstructure of the Si$_{80}$Ge$_{20}$ nanocomposite. The contrast in the dark dots in the low magnification image, a, is due to the dopant (boron). Both dark dots and background contains small grains as shown in b. After reference [91].

Figure 5.16: Thallium-doped PbTe nanocomposite which has $ZT \sim 1.5$ at 500 °C. The figures shows microstructure are taken by (a) TEM and (b) SEM. After reference [92].
Experimental Background and Methods

Nanocomposites are commonly developed by the bottom-up methods: first create the nanocrystalline powders and then consolidate the powders into a dense bulk solid. Nowadays, the nanostructured powders are typically produced by high energy mechanical alloying process and then hot-pressed into a bulk sample. Brief introduction and discussion about these techniques are presented in this chapter.

The main materials of interest in this work, Bi(Sb)Te(Se) alloys, are introduced in this chapter including their structures, the antisite defects and phase diagrams followed by the experimental methods of preparing Bi(Sb)Te(Se) nanocomposites. Compared to binary Bi$_2$Te$_3$ and Sb$_2$Te$_3$ systems, the ternary Bi-Sb-Te and Bi-Se-Te systems are still much less understood thermodynamically.

Optimized settings in each processing step are obtained and summarized after numerous unsuccessful runs and samples. Important characterization details, such as X-ray diffraction, transmission electron microscope and its specimen preparation, transport properties are also presented in this chapter.

6.1 Mechanical Alloying

Mechanical alloying is a powder processing technique that describes the milling of a mixture of materials. Although it was initially the result of producing nickel-base superalloy [97], mechanical alloying was found to be able to, for example, create fine dispersion of second phase particles, extend the solid solution limits, refine the grains sizes, synthesis novel and
quasi crystalline phases and develop amorphous phases [98, 99, 100]. These metastable phases were created by the severe plastic deformation during this nonequilibrium process. High energy impacts between the grinding medium and the materials increases the defect density in the material to a point where the system converts to a metastable phase because its free energy is lower than that of the ambient equilibrium phase.

The repeated collisions between the materials and the grinding media deform the powder particles and enable them to weld together. After a certain amount of time, the deforming and welding of the materials reach steady state and the size of the internal structure (particle size, grain size, or lamellar spacing, etc.) becomes a constant. The illustration of the collision between grinding medium and the material is shown in Figure 6.1.

The experimental process of mechanical alloying starts with different materials, alloys or elemental powders of appropriate weight ratio, determined by the target composition. They are then loaded into the milling vial along with the grinding medium and milled for the desired length of time. The properties of the resulting products depend on several parameters including the starting material, the types of the mills and process variables such as milling time, type, size and size distribution of the grinding medium, ball-to-powder weight ratio, milling atmosphere and temperature of milling.

Figure 6.1: The illustration of the collision between grinding medium such as stainless steel balls and the material during mechanical alloying. After reference [99].

### 6.2 Hot Pressing

Hot pressing is a powder consolidation process with simultaneous applications of heat and pressure. With the compressive applied stress and high enough temperature, the pores between the particle are eliminated by Ostwald ripening while grain growth occurs. The major advantage
of hot pressing is the fact that the rate of densification of the material is high which results in a fine and uniform microstructure.

Temperature control is critical in hot pressing because diffusion plays an important role in the process. Elevated temperature enhances the diffusion mechanism which leads to the densification. Pressure is obviously another important factor. High enough pressure increases the rate of the densification which helps shorten the processing time and minimize the grain growth. A narrow distribution of the size of the green particles usually result in higher density in the final product given the same pressing condition. Other factors affecting the hot pressing process includes the correlation between the green density and the final density, pressing atmosphere, impurities, particle size, etc. as discussed in the reference [101].

6.3 Material Properties of Bi(Sb)Te(Se) Alloys

Bismuth telluride (Bi₂Te₃) is one of the best elemental compound semiconductors for around room temperature thermoelectric applications. Often antimony telluride (Sb₂Te₃) or bismuth selenide (Bi₂Se₃) is added to Bi₂Te₃ to improve the ZT by reducing the lattice thermal conductivity (k_L) although neither of them are good thermoelectric materials [102]. Essentially the additions make the materials change the electrical properties: p-type Bi(Sb)Te and n-type BiTe(Se).

6.3.1 Structure

The crystal structure of Bi₂Te₃ has a rhombohedral unit cell consisting of five atoms per cell, two Bi and three chalcogen, with space group R̅3m [103, 104, 105]. Both Sb₂Te₃ and Bi₂Se₃ have similar crystal structure to Bi₂Te₃ and share the same space group. Viewing the Bi₂Te₃ structure as an hexagonal cell, one can observe alternate layers of identical atoms perpendicular to the c-axis following the sequence:

\[-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}-\]

which is called a quintuple¹ and three quintets form a hexagonal cell. Such structure is shown in Figure 6.2.

The bondings between Te layers are considered to be of the weak van der Waals type while it is ionic-covalent type between the Te^{(1)}-Bi and Bi-Te^{(2)} layers [106]. Due to the lamellar nature in the material, Bi₂Te₃ suffers anisotropic mechanical properties: the cracks grow rapidly in between the Te layers. Thus a bulk Bi₂Te₃ material seems brittle and needs more attention in the handling and processing.

¹A quintuple is a group containing five members.
Figure 6.2: An illustration of the lamellar structure of Bi$_2$Te$_3$ showing the quintuple layers and the locations of the van der Waals gap. The green, red and dark blue dots represent the Te$^{(1)}$ atoms, the Bi atoms and the Te$^{(2)}$ atoms, respectively. After reference [107].

The lattice parameters, $a$- and $c$-axis, and density of Bi$_2$Te$_3$, Sb$_2$Te$_3$ and Bi$_2$Se$_3$ are listed in Table 6.1. With the same crystal symmetry, similar lattice dimension and chemical properties, all three compounds are inter-miscible. In solid solutions of Bi$_2$Te$_3$-Sb$_2$Te$_3$, the Sb atoms substitute in Bi sites as

$$-\text{Te}^{(1)}-\text{Sb}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}-$$

In Bi$_2$Te$_3$-Bi$_2$Se$_3$ solid solution, the Se atoms may occupy Te$^{(1)}$ or Te$^{(2)}$ sites to be

$$-\text{Te}^{(1)}-\text{Bi}-\text{Se}-\text{Bi}-\text{Te}^{(1)}-$$

$$-\text{Se}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}-$$

**Antisite Defects**

These substitution actions in the solid solutions could form the so called "antisite defect", i.e., excess Bi or Sb atoms go to the Te sites and vice versa. The presence of the antisite defects could change the electrical properties of the bulk materials [113]: Te$_{\text{Bi}}$, i.e., Te atoms at Bi site, are single donors and Bi$_{\text{Te}}$ are single acceptors. Meanwhile, vacancies in the structure have similar effects: V$_{\text{Te}}$ are double donors and V$_{\text{Bi}}$ are triple acceptors.
Table 6.1: Lattice parameters \((a\) and \(c\)) in angstrom \((\text{"Å})\) and density for Bi\(_2\)Te\(_3\), Sb\(_2\)Te\(_3\) and Bi\(_2\)Se\(_3\) compounds at 300 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(d) (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(_2)Te(_3)</td>
<td>4.275 [110]</td>
<td>30.49 [110]</td>
<td>6.57 [111]</td>
</tr>
<tr>
<td>Bi(_2)Se(_3)</td>
<td>4.934 [112]</td>
<td>28.54 [112]</td>
<td>7.308 [111]</td>
</tr>
</tbody>
</table>

### 6.3.2 Phase Diagram

#### Binary Phase Diagram

The binary phase diagrams\(^2\) of Bi-Te and Sb-Te system are shown in Figure 6.3 and Figure 6.4. At ideal stoichiometry, i.e., Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\), the system presents a single melting compound. It is noted that the compounds exhibit deviations from stoichiometry that is too small to be distinguished in a conventional phase diagram. The initial components could be dissolved and show homogeneous solid solutions but part of the dissolved components can rearrange to become substitutional solid solutions, interstitial solid solutions or solid solutions with vacancies [114]. A schematic plot of this deviation is shown in Figure 6.5. The shaded area is the deviation from the ideal compound and depends on the excess component in the final solid solution, the stoichiometry and carrier concentration are also changed.

#### Ternary Phase Diagram

The ternary phase diagrams of the Bi-Te-Se system are shown in Figure 6.6 and Figure 6.7 where \(S\) represents the point containing different concentrations of Bi\(_2\)Se\(_3\), e.g., \(S_5 = 5\%\), and \(L\) is the corresponding experimental iso-concentration line. The intersection between an isothermal curve and an iso-concentration line gives the composition of the liquidus in equilibrium. In Figure 6.6, it is 5\% Bi\(_2\)Se\(_3\) in the enhanced fields of existence of the solid solution.

The 3-dimensional ternary phase diagrams of the Bi-Sb-Te system above 400 °C in the Te-rich field is shown in Figure 6.8. Figure 6.9 represents the ternary phase diagram on the tellurium-rich side from the pseudo binary cross-section [116].

In Figure 6.8, surface a-b-c represents the homogeneity region of Sb\(_2\)Te\(_3\) and surface a’-b’-c’ shows that of Bi\(_2\)Te\(_3\). Volume a-b-c-a’-b’-b’ represents the boundaries of the solid solution of Bi-Te-Sb. The shaded region corresponds to the Te-rich solidus boundary.

In Figure 6.9, there are two experimental iso-concentration lines, \(L_1\) and \(L_2\), representing

---

\(^2\)The use of the phase diagrams are further discussed in Section 6.4.1.
20 and 25% of Bi₂Te₃ in Sb₂Te₃, S₁ and S₂, respectively. The deviations are not taken into account at the diagram scale.

### 6.3.3 Transport Properties

The electrical and thermal transport properties of various Bi(Sb)Te(Se) compounds are listed in Table 6.2. They are experimental results for materials in single crystal form. Because the properties are highly dependent on the crystal structure and composition, those compounds in nanocomposite structure have different properties and are discussed later in Chapters 7-12.

Table 6.2: Transport properties of various Bi(Sb)Te(Se) compounds at 300 K: type of conduction (p or n); n, carrier concentration in 10¹⁹ cm⁻³; ρ, electrical resistivity in Ω·m; μ, carrier mobility in cm²v⁻¹sec⁻¹; S, absolute Seebeck coefficient in µVK⁻¹; k, thermal conductivity in Wm⁻¹K⁻¹; ZT, figure of merit, dimensionless. After reference [114].

<table>
<thead>
<tr>
<th>Compound</th>
<th>type</th>
<th>n</th>
<th>ρ</th>
<th>μ</th>
<th>S</th>
<th>k</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂Te₃∥</td>
<td>n</td>
<td>2.3</td>
<td>1.0</td>
<td>212</td>
<td>240</td>
<td>2.0</td>
<td>0.87</td>
</tr>
<tr>
<td>Sb₂Te₃⊥</td>
<td>p</td>
<td>2</td>
<td>0.32</td>
<td>244</td>
<td>92</td>
<td>1.6</td>
<td>0.48</td>
</tr>
<tr>
<td>Sb₂Te₃∥</td>
<td>p</td>
<td>10</td>
<td>0.19</td>
<td>313</td>
<td>83</td>
<td>5.6</td>
<td>0.18</td>
</tr>
<tr>
<td>Bi₀.₄Sb₁.₆Te₃</td>
<td>p</td>
<td>4.8</td>
<td>1.0</td>
<td>176</td>
<td>194</td>
<td>1.3</td>
<td>0.90</td>
</tr>
<tr>
<td>Bi₀.₅Sb₁.₅Te₃</td>
<td>p</td>
<td>3.5</td>
<td>1.3</td>
<td>177</td>
<td>225</td>
<td>1.4</td>
<td>0.87</td>
</tr>
<tr>
<td>Bi₀.₅Te₂.₉₂Se₀.₇₅</td>
<td>n</td>
<td>4.3</td>
<td>1.1</td>
<td>150</td>
<td>230</td>
<td>1.7</td>
<td>0.87</td>
</tr>
</tbody>
</table>
6.4 Preparations of Bi(Sb)Te(Se) Nanocomposites

6.4.1 Challenges and Approaches

Bi$_2$Te$_3$ based alloys were chosen in this work for their renowned thermoelectric performance around room temperature. The n-type materials are obtained by doping Se and the target composition is Bi$_2$Te$_{2.7}$Se$_{0.3}$. The dopant in the p-type materials is Sb and the final composition is Bi$_{0.4}$Sb$_{1.6}$Te$_3$.

General Challenges

The process, mechanical alloying, consolidation, and device fabrication, is straightforward per se, but there are several requirements need to be met for the Bi(Sb)Te(Se) system. It is
Figure 6.6: A schematic illustration of 3D Bi-Te-Se ternary phase diagram. The shaded area represents solid solution containing 5% of Bi$_2$Te$_3$. After reference [114].

important to avoid oxidation during the whole process because it was known that oxygen degrades the thermoelectric properties for Bi$_2$Te$_3$ based materials [117]. Therefore the elemental powders and the as-milled powders are always stored in the glove box with minimum exposure to the oxygen.

Mechanical alloying is a rather mature technique but the products should match the target composition and have nanometer grains. One of the major advantages of this technique is to create materials with isotropic properties. Due to the crystal structure and bondings of Bi(Sb)Te(Se), as discussed in Section 6.3.1, typical single crystal Bi$_2$Te$_3$ has anisotropic transport properties that differ in different orientations.

On the other hand, there are many challenges in the hot pressing process. First of all, in order to maintain nanometer grains, the process has to be quick. Secondly, the temperature is critical because if it is too high will cause fast grain growth but too low will not produce fully dense consolidations. Thirdly, the appropriate pressure has to be found along with different temperature and materials to reduce the processing time and obtain full density consolidations. Finally, the consolidated materials needs to be physically strong enough for further material characterizations and device fabrications. Bulk Bi$_3$Te$_3$ alloys tends to be too brittle to handle
Figure 6.7: Liquidus and iso-concentration lines ($L$) of the Bi-Te-Se system. After reference [114].

due to the weak van der Waal bondings between Te layers.

**The Ideal Process Settings**

The binary phase diagrams, Figure 6.3 and Figure 6.4, are used to find the ideal hot pressing temperature. From the composition of exact Bi$_2$Te$_3$ and Sb$_2$Te$_3$ to the right hand side of the diagrams (Te rich side), both alloys show eutectic systems with eutectic temperature 413 °C and 422 °C for Bi$_2$Te$_3$ and Sb$_2$Te$_3$ respectively. These temperatures are used as a reference point.

The hot pressing temperatures are set to be around the neighborhood of the eutectic temperatures. Because a proportion of the material would be expected to be in the liquid state around those temperatures. With an appropriate processing time, this leads to rapid and uniform densification of the materials and the best result in grain size and transport properties, which will be discussed in detail in Chapters 7-12. Although the presence of the liquid phase cannot be observed in situ, the marks in the shape of water drops were found on the punches that indicates the melting of the materials during hot pressing.

Different temperature points has been used. At lower temperature, ~350 °C, the resulting products will not be dense enough and usually are crumbles instead of a complete disk although low temperature is presumably ideal to minimize grain growth. At higher temperature, ~450 °C, the grains grow too fast that even with a reduced processing time, the majority of the grains is in the micron meter scale, which would not help in containing the phonons. These
situations apply to both Bi(Sb)Te and BiTe(Se) systems.

6.4.2 Mechanical Alloying

Elemental powders, Bi, Te, Sb and Se (purity 99.99% or higher) supplied by Alfa Aesar, were weighted out in the appropriate atomic ratio and loaded into the stainless steel vials with martensitic stainless steel balls in a glove box with a high purity argon atmosphere (oxygen concentration less than 1 ppm). The ball-to-powder ratio is 10:1. The milling was carried out by the SPEX CertiPrep 8000M Mixer/Mills equipped with a 1725 RPM motor which provides a clamp speed 1060 cycles/minute [118]. The milling times were either 20 hours at room temperature (300 K) or 4 hours at cryogenic temperature (77 K) cooled by continuous flow of liquid nitrogen. Either milling environment results in loose powders instead of chucks and they do not cold-welded to the vials.

6.4.3 Consolidation

The as-milled powders were sieved and particles less than 45 µm were collected for further processing. The consolidation of powders is carried out in a home made chamber attached to a DAKE 70 ton hydraulic press. An appropriate amount of material was transferred in the 10 or 7 mm diameter tungsten carbide die. The punches are also made of tungsten carbide which have
Figure 6.9: Partial Bi-Sb-Te ternary phase diagram on the tellurium-rich side with experimental isothermal curves of the liquids at different temperature and experimental isoconcentration lines ($L_1$, $L_2$) for $S_1$: 20% and $S_2$: 25% of Bi$_2$Te$_3$ in Sb$_2$Te$_3$. After reference [116].

slip fit to the die. The die and the materials were then sealed in the chamber which was pumped to a vacuum and back filled with pure argon several times. Finally a positive pressure of argon was kept during the whole consolidation process. After the temperature reached desired value, 407 - 417 °C for n-type and 400 - 410 °C for p-type, the pressure was applied to 2 GPa for n-type and 1.8 GPa for p-type. The pressure was kept for about 10 minutes and then the heat was turned off and the pressure was released. The total time of the material spent above 200 °C is less than 30 minutes. The resulting bulk disk samples, 10 or 7 mm in diameter and about 800 µm in thickness were polished for further characterizations.

The pictorial summary of each processing step and their results are shown in Figure 6.10 and the processing parameters are summarized in Table 6.3.

6.5 Characterizations of Bi(Sb)Te(Se) Nanocomposites

The characterization techniques used in this work are introduced in this section including the manufacturer and model of the machines.
6.5.1 X-ray Diffraction

The X-ray diffraction (XRD) spectra are obtained by a Rigaku Geigerflex D/Max IIA X-ray diffractometer with MDI DataScan4 software at room temperature. The target material is Cu with a $K_\alpha$ radiation which has wavelength equals to 1.54 Å. The tube voltage is 30 kV and the current is 15 mA.

The main information from XRD is to determine the composition and determine the presence of the second phase. Although it is possible to calculate the grain size from XRD based on the Scherrer's formula\(^3\), the author uses the results from the transmission electron microscope (TEM) instead for higher accuracy.

6.5.2 Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) machine is a Netzsch STA 409 PC Luxx. All of the samples were run at 10 K/min ramp rates under ultra high purity (99.9999%) nitrogen in an alumina crucible. The reference crucible was also alumina and left empty. Correction runs were done with both crucibles empty under identical conditions. Sample masses were around 25 mg.

\(^3\)It is found that when the grain sizes are over 30 nm, the XRD results by Scherrer’s formula will be inconsistent with that from TEM.
Table 6.3: Optimized process settings for making n- and p-type bulk nanocomposite materials in this work.

<table>
<thead>
<tr>
<th>Processing Parameters</th>
<th>Composition</th>
<th>Bi$<em>2$Te$</em>{2.7}$Se$_{0.3}$</th>
<th>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milling</td>
<td>mixer</td>
<td>SPEX 8000M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ball-to-powder ratio</td>
<td>10:1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>atmosphere</td>
<td>Ar (O$_2$ less than 1 ppm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>temperature</td>
<td>300 or 77 K</td>
<td></td>
</tr>
<tr>
<td>Hot pressing</td>
<td>die and punch</td>
<td>10 or 7 mm tungsten carbide</td>
<td>400 - 410 °C</td>
</tr>
<tr>
<td></td>
<td>temperature</td>
<td>407 - 417 °C</td>
<td>400 - 410 °C</td>
</tr>
<tr>
<td></td>
<td>pressure</td>
<td>2 GPa</td>
<td>1.8 GPa</td>
</tr>
<tr>
<td></td>
<td>processing time</td>
<td>less than 45 minutes</td>
<td></td>
</tr>
<tr>
<td>Final sample</td>
<td></td>
<td>10 or 7 mm in diameter disk, about 800 µm in thickness</td>
<td></td>
</tr>
</tbody>
</table>

6.5.3 Transmission Electron Microscope

Sample Preparation

The thinning of the transmission electron microscope (TEM) samples are done by either the focused ion beam (FIB) "Lift-out" method or wedge polishing followed by ion milling.

The FIB lift-out was performed by the Quanta 3D dual beam FIB/SEM (scanning electron microscope) with Omniprobe lift out probe. The process includes cutting trenches in the area of interest, attach lift-out needle, remove the membrane from matrix material and attach it to the TEM grid followed by final thinning with ion beam. A Pt layer was deposited on the sides of the membrane for sample protection. The SEM images of the FIB process are shown in Figure 6.11.

The wedge polishing method is to thin the sample by mechanical lapping and then tilt the sample to put a wedge at the edge of the sample with diamond lapping films. After ion milling, the thin part of the wedge are electron transparent. The lapping was carried out by a Multiprep polishing system with diamond lapping films, particle size from 6 to 1 µm. After being glued to TEM grids, wedge specimens were then thinned to electron transparency with a Fischione Model 1010 Ar+ ion mill and sample stage cooled below -70 °C. The general ion milling conditions are listed in Table 6.4. The settings still depend on the real specimen but low beam energy (low kV) is usually required to prevent damage from the ion beam.
Figure 6.11: SEM images of the FIB "Lift-out" process for TEM sample preparation. (a) Lift-out needle attached to the membrane. (b) A Pt protection layer is deposited on the edge of the membrane. (c) Final sample where part of it are of electron transparent thickness. The V-shape TEM grid in (b) is at the top.

Table 6.4: Ion milling settings for Bi(Sb)Te(Se) TEM specimens.

<table>
<thead>
<tr>
<th>Step</th>
<th>minutes</th>
<th>kV</th>
<th>mA</th>
<th>angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>3</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>2</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>1</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

The Microscopes

Three different TEMs have been used in this work. JEOL 2000FX, a LaB$_6$ emitter TEM, and Hitachi HF2000, a cold field emission TEM, both operated at 200 kV. The medium and low magnification, bright and dark field images as well as selected area (electron) diffraction (SAD) patterns are acquired from both of them. The energy-dispersive X-ray spectroscopy (EDS) results are from a Oxford Link INCA system attached to the Hitachi HF2000 TEM.

A JEOL 2010F TEM with a Schottky field-emission gun operated at 200 kV was used for high resolution TEM (HRTEM) imaging.

6.5.4 Seebeck Coefficient

The Seebeck coefficients were measured using a home build test station. A basic illustration of the setup is shown in Figure 6.12. In a closed, inert gas environment, the sample was placed on top of two different copper blocks and one of them is used as a heating source to create a temperature difference ($\Delta T$) across the sample. Both temperature and voltage differences between two edges of the sample are measured at the same time. A second round of measurement was carried out at the same temperature range after switching the thermocouples.
from one side to the other in order to eliminate the errors from the thermocouples. This technique has been cross checked with machines in different labs using the same standard reference as discussed in round-robin measurements [119].

If the hot side temperature is $T_h$ and voltage and the cold side temperature is $T_c$ with a voltage difference $\Delta V$, the Seebeck coefficient is obtained by

$$S = \frac{\Delta V}{T_h - T_c} = \frac{\Delta V}{\Delta T}$$  \hspace{1cm} (6.1)

Figure 6.12: Basic illustration of the Seebeck coefficient measurement setup. The disc-shaped sample is placed on top of the copper blocks. Both temperature and voltage differences are measured at the same time.

#### 6.5.5 Electrical Resistivity

The electrical resistivity was carried out by the well-known van der Pauw method [120] in a Hall-effect set up that measured both electrical resistivity and carrier mobility/concentration with known sample thickness and drive current. The van der Pauw method, using four very small contacts (compared to the size of sample) symmetrically on the four corners of a 5 mm x 5 mm square sample, ensures good measurement accuracy of the bulk electrical resistivity.

In-plane electrical resistivity measurements were made with a Keithley 220 current source, Keithley 6514 electrometer, and Keithley 7001 Switch System with 7065 Hall Effect Card, measurements were performed using 100 mA of current and a magnetic field of 5000 Gauss.

#### 6.5.6 Thermal Conductivity

The thermal conductivity of nano-bulk samples was measured in the same direction as the electrical resistivity and the Seebeck coefficient, with measured heat flow using calibrated power test system (Q-meter). The set up is illustrated in Figure 6.13. The thermal conductivities
were calculated from the Fourier law, given by the relation below:

\[ Q = k_T \left( \frac{a}{l} \right) \Delta T \]  

(6.2)

where \( k_T \) is the average total, lattice plus electronic) thermal conductivity between temperatures \( T_{\text{hot}} \) and \( T_{\text{cold}} \), \( \Delta T \) is the difference between \( T_{\text{hot}} \) and \( T_{\text{cold}} \), \( a \) is the cross-sectional area and \( l \) is the height of the thermoelectric pellet. The Q-meter measurements have been calibrated with electric measurement of heat input, to within 5%.

Figure 6.13: Basic illustration of the thermal conductivity measurement setup. There are five thermocouples attached to the Q-Meter at specific locations. After reference [121].
Nanocrystalline Bi(Sb)Te(Se) Powders

This chapter presents the results and discussions including the X-ray diffraction (XRD) spectra, differential scanning calorimetry (DSC) data and transmission electron microscope (TEM) images, of Bi(Sb)Te(Se) powders, prepared at either room or cryogenic temperature\(^1\). The XRD spectra show that either milling temperature successfully produces n- or p-type materials of targeted compositions without any side reaction. The endothermic peaks in the DSC data indicate phase transitions at about 410 and 413 °C for n- and p-type materials respectively.

The TEM images and selected area electron diffraction (SAD) patterns further confirms the nanocrystalline structures in the materials while powders milled at cryogenic temperature have smaller grains compared to powders milled at room temperature: averaging 12 nm and 20 nm in room temperature milled n- and p-type compare to around 9 nm in cryogenic milled powders in both types from calculations based on about 300 grains.

7.1 N-type BiTe(Se)

7.1.1 Composition: XRD and DSC

Room Temperature As-milled Powders

The XRD spectrum of room temperature (RT) as-milled powders is shown in Figure 7.1 (a). The peaks well matched the binary Bi\(_2\)Te\(_3\) (PDF #15-0863) indicating a successful mechanical alloying process from elemental powders. There are no extra peaks suggesting no side reactions

\(^1\)The details of the experiment procedures have been discussed in Section 6.4.2.
during the process. The peaks are broad due to the nanocrystalline nature.

The DSC results in Figure 7.2 show an endothermic peak at around 410 °C. Compared to the Bi-Te phase diagram in Figure 6.3, it confirms that the materials have composition on the right hand side (Te rich side) of Bi$_2$Te$_3$ in the phase diagram which shows that the melting temperature for Bi$_2$Te$_3$ is 586 °C and the eutectic temperature is 413 °C.

**Cryogenic Temperature As-milled Powders**

The XRD spectrum of cryogenic (Cryo) temperature as-milled powders is shown in Figure 7.1 (b). The peaks again matched the target composition and no side reactions. Compared to the room temperature as-milled powders, the peaks are broader because the milling at cryogenic temperature produced smaller grains in the structure.

![XRD spectra of n-type powders milled at room (a) and cryogenic temperature (b).](image)

Figure 7.1: XRD spectra of the n-type powders milled at room, (a), and cryogenic temperature, (b). The intensity is in arbitrary units (a. u.).

### 7.1.2 Microstructure: TEM

**Room Temperature As-milled Powders**

The TEM images and SAD pattern confirm the nanocrystalline structure in the powders, as shown in Figure 7.3. There are several grains close to 40 nm in the low magnification image, Figure 7.3 (a), while there are small grains less than 10 nm as shown in the high magnification image, Figure 7.3 (b). The SAD pattern, inserted in Figure 7.3 (a), shows nearly complete rings indicating the nano scale structure in the materials.
A more precise calculation shows that the grain size ranges from 6 to 30 nm while the majority of the grains are in the 9 to 17 nm range with an average 12 nm. The grain size distribution is shown in Figure 7.4. The calculation was done by counting about 300 grains from several TEM images using ImageJ.

Cryogenic Temperature As-milled Powders

The powders milled at cryogenic temperature show smaller grains relative to the powders milled at room temperature. In the TEM images, Figure 7.5, the grains are better recognized in the dark field image, Figure 7.5 (b). Most of them are smaller than 20 nm. The nanocrystalline structure is also confirmed by the SAD pattern inserted in Figure 7.5 (a). The spots almost form complete rings indicating small grains in the structure.

The majority of the grains has size around $9 \pm 3$ nm. Compared to the room temperature milled powders, grains larger than 25 nm are rarely seen in the TEM images and the grain size distribution shifts to the left, the smaller size side, as shown in the Figure 7.6. The calculation again is based on about 300 grains from multiple TEM images.

7.2 P-type Bi(Sb)Te

7.2.1 Composition: XRD and DSC

Room Temperature As-milled Powders

The XRD spectrum well matched the binary Sb$_2$Te$_3$ (PDF #15-874) as shown in Figure 7.7 (a). The peaks are broad due to the nanocrystalline structure, which is then confirmed by TEM
images. There are no extra peaks suggesting no side reaction during the mechanical alloying process.

There is an endothermic peak at around 413 °C from the DSC data in Figure 7.8. Compared to the Sb-Te phase diagram, Figure 6.4, it is close to the eutectic temperature (422 °C) at the right hand side (Te rich side) of Sb$_2$Te$_3$ while the melting temperature for Sb$_2$Te$_3$ is 617 °C.

**Cryogenic Temperature As-milled Powders**

Similar to the room temperature as-milled powders, the peaks in the XRD spectrum, Figure 7.7 (b), are all identifiable and no extra peak present. The width of the peaks is slightly broader than that from the room temperature as-milled powders because the grains are smaller.

**7.2.2 Microstructure: TEM**

**Room Temperature As-milled Powders**

Nanocrystalline structure is confirmed by the TEM images and the ring-like SAD pattern in Figure 7.9. There are small grains around 10 nm and large grains around 40, 50 nm as shown in the low magnification TEM image in Figure 7.9 (a). Meanwhile, the high magnification TEM image, Figure 7.9 (b), indicates the majority of the grains is around 20 ± 4 nm. The grain size distribution resulting from about 300 grains is shown in Figure 7.10.

![Figure 7.3: TEM images show the microstructure of the n-type room temperature as-milled powders in low, (a), and high, (b), magnification. The SAD pattern from materials in (a) is inserted in the upper right corner in (a).](image-url)
Figure 7.4: The grain size distribution plot of the n-type room temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.

Cryogenic Temperature As-milled Powders

The powders milled at cryogenic temperature have smaller grains compared to the powders milled at room temperature as observed in the n-type powders. From the TEM images, Figure 7.11, the grains are generally less than 20 nm and result in almost complete rings in the SAD pattern inserted. (The grains are better recognized in the dark field image, Figure 7.11 (b)). Some of them are smaller than 10 nm. The grain size distribution calculation in Figure 7.12 shows that the majority of the grains are in the 6 to 12 nm range.
Figure 7.5: Bright field, (a), and dark field, (b), TEM images of the n-type cryogenic temperature as-milled powders with the SAD pattern inserted in the upper right corner in (a). The grain boundaries are better recognized in the dark field image in (b).

Figure 7.6: The grain size distribution plot of the n-type cryogenic temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.
Figure 7.7: XRD spectra of the p-type powders milled at room, (a), and cryogenic temperature, (b). The intensity is in arbitrary units (a. u.).

Figure 7.8: The DSC data of the p-type room temperature as-milled powders. An endothermic peak is at around 413 °C.
Figure 7.9: TEM images show the microstructure of the p-type room temperature as-milled powders in low, (a), and high, (b), magnification. The SAD pattern from materials in (a) is inserted in the upper right corner in (a).

Figure 7.10: The grain size distribution plot of the p-type room temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.
Figure 7.11: Bright field, (a), and dark field, (b), TEM images of the p-type cryogenic temperature as-milled powders with the SAD pattern inserted in the upper right corner in (a). The grain boundaries are better recognized in the dark field image in (b).

Figure 7.12: The grain size distribution plot of the p-type cryogenic temperature as-milled powders. The results are based on about 300 grains from multiple TEM images.
N-type BiTe(Se) Nanocomposites by 300K As-milled Powders

The n-type disk samples consolidated from room temperature as-milled powders were polished and characterized. The first half of this chapter presents their composition and microstructure and the transport properties are given in the second half.

There are no side reactions or second phases after the consolidation as determined from the X-ray diffraction spectrum and the composition still matched the target $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. The transmission electron microscopy figures confirm their nanocomposite structure with a large grain size distribution: 5 to 50 nm precipitates embedded in 200 to 800 nm grains. High resolution transmission electron microscope shows that the precipitates have a structure that differs from the matrix. The precipitates are then probed by energy-dispersive X-ray spectroscopy and there is no indication of significant compositional differences from the matrix material. However, these results could be incorrect due to the resolution of the probe because it is difficult to exclude the background composition.

The peak thermoelectric figure of merit is greater than two: about 2.65 at 100 °C while it is about 1.54 at room temperature. This is mainly contributed by the enhancement in the power factor, especially the Seebeck coefficient. The nano-scale precipitates may provide additional interfaces to filter out the low energy electrons while the large grains help maintain the electrical conductivity. Individual thermoelectric properties as a function of temperature are presented. Data points from the literature to highlight the difference in structure and material process are also included for reference.

The results confirm that the thermoelectric properties of n-type BiTe(Se) can be optimized by tuning the microstructure with appropriate processing and thus it is possible to break
through the $ZT=2$ barrier. The structure property relationship is further proven by the microstructure of commercial n-type materials which have $ZT$ about one. In addition to the absence of the nano scale features, the interface density is very low compared to our materials.

### 8.1 Microstructure

#### 8.1.1 Composition

The X-ray diffraction (XRD) spectrum of bulk samples is shown in Figure 8.1 along with that from the as-milled powder for reference. Compared to the materials before hot pressing (as-milled powders), there are no extra peaks and all the peaks are identifiable. Therefore there is i) no side reaction or oxidation and ii) no phase transition during the consolidation process.

Most of the peaks in the bulk disk are sharper and can be differentiated from other peaks or background because of the grain growth during the hot pressing, which is observed by TEM, contributing a higher signal to noise ratio in the XRD patterns.

Figure 8.1: XRD spectra of (i) n-type bulk sample made from room temperature as-milled powders on the top and (ii) room temperature (RT) as-milled powders on the bottom.
8.1.2 TEM and EDS Analysis

Nanocomposite Structure

The microstructure observed by transmission electron microscope (TEM) is shown in Figure 8.2 including several different regions and magnifications in the material. The low magnification TEM figures, Figure 8.2 (a), (b), show a typical nanocomposite structure: large grains with small precipitates embedded in the large grains with high interface density. The grains have clean boundaries without voids in between them. Most of the large grains have precipitates less than 10 nm in diameter as shown in Figure 8.2 (c), (d). The selected area electron diffraction (SAD) in Figure 8.2 (e) indicates the polycrystalline nature and some nanoscale features in the material. High resolution transmission electron microscope (HRTEM) imaging, Figure 8.2 (f), confirms that the precipitates are incoherent and have a structure that differs from the matrix.

The grain size distribution was calculated and the results are shown in Figure 8.3. The calculation includes grains/precipitates less than 50 nm but not grains outside of this range. Their sizes are mainly in the range of 5 to 25 nm that are in the scale to be influential to the transport properties. Most of the large grains are in the range of 200 to 400 nm with a few in the range of 700 to 800 nm. There are no grains larger than one micron by observation.

Nano scale voids were also frequently observed at grain boundaries and precipitate-matrix interfaces. Those voids found at the grain boundaries likely originated from gaps between compacted powder particles that were not closed during the consolidation process. Voids located at precipitate-matrix interfaces indicate that some compositional fluctuation is present, likely the result of the mechanical alloying process. Off-stoichiometric compositions would induce the production of vacancies, and combined with the elevated temperatures of hot-pressing, produce agglomeration via diffusion. The structure and chemistry of the observed precipitates and the formation of voids remain for a detailed future investigation. The observed total volume fraction of the voids is so miniscule that essentially both types of materials are consistent with the 99% or higher measured relative density. Similarly, the voids are not expected to have detrimental effects on mechanical stability of the materials, as evidenced by our device results discussed in Chapter 10.

Investigation of Precipitates

Preliminary compositional analysis by energy-dispersive X-ray spectroscopy (EDS) indicates that there are no significant compositional variations in the n-type materials. The results, listed in Table 8.1, correspond to the averages from multiple random measurements of the precipitates and spots inside the matrix grains, as shown in Figure 8.4 where (a) and (b) are different samples. The results from the precipitates are highlighted by color yellow in Table 8.1. In general, the compositions of the matrix materials do not differ much from that.
of the precipitates: they all have similar weight percentage of Se, Te and Bi. The presence of Cu is due to the TEM grid to which the specimen was attached. This result could be limited by the resolution of the EDS probe that it could not precisely resolve objects less than 10 nm. Carbon tends to be deposited on the target area during the signal collection. This is even worse for small objects because the electron beam is more converged and the EDS needs longer time to have enough signal.

The origins of the precipitates need further investigation. The binary phase diagram (Figure 6.3) does not clearly indicate a two phase region for the composition of Bi$_2$Te$_3$. Local deviations from stoichiometric Bi$_2$Te$_3$ could be a possible reason. A Te rich deviation is more likely because the DSC shows an endothermic melting peak at 410 °C (Figure 7.2) that suggests excess Te could precipitate during the consolidation process. And the fact that the peak is not very sharp indicates only part of the materials participate in the phase transition at that temperature. Essentially a ternary phase diagram and a detailed morphology study of these precipitates are necessary to understand the phase transition of this alloy.

Table 8.1: Weight percentage analyzed by EDS of various spots at Figure 8.4. Rows highlighted by color yellow are the results from the precipitates. The ideal weight percentage for Bi$_2$Te$_{2.7}$Se$_{0.3}$ is included in the bottom row.

<table>
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<tr>
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<th>Se</th>
<th>Te</th>
<th>Bi</th>
<th>Spot at (b)</th>
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8.2 Transport Properties

Thermoelectric properties including the Seebeck coefficient, electrical resistivity, and thermal conductivity of the n-type nanocomposites are grouped together and shown in Figure 8.5 and Figure 8.6 as well as the calculated figure of merit. In Figure 8.5, data from the literature
are included along with the best n-type sample. Yamashita and Sugihara produced n-type Bi$_2$(Te$_{0.94}$Se$_{0.06}$)$_3$ ingot codoped with 0.068 wt% I and 0.017 wt% Te by the Bridgman method [122]. Yan et al. used similar bottom-up method: ball milling and powder consolidation to produce n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ but the powders were consolidated by Spark Plasma Sintering (SPS) [52]. In comparison to the present study, Yamashita’s work represents the differences of single crystal structure vs. nanocomposite and Yan’s work represents the differences in the processing.

Each property-structure relationship is discussed in the following sections. Unfortunately there are no TEM figures in both references to show their microstructure. The solid circles are the properties from the best n-type sample while the solid squares represents the average of five samples in Figure 8.6 to show the reproducibility of this work.

8.2.1 Seebeck Coefficient

The absolute Seebeck coefficient\(^1\) of the best sample starts from 245 \(\mu\)V/K at 25 °C and increases to the peak 330 \(\mu\)V/K at 100 °C then decreases to 230 \(\mu\)V/K at 200 °C. While the Seebeck coefficient of the average samples starts from 180 \(\mu\)V/K at 25 °C and increases to the peak 230 \(\mu\)V/K at 125 °C. Both the best and the average n-type show significant improvement compared to the reference data with similar composition.

This phenomenon is attributed to several possible reasons. First, the nanoscale precipitates may provide interfaces to selectively scatter charge carriers, i.e., energy filtering discussed in Section 5.1.2. Low energy carriers are being blocked/trapped at the interfaces thus the average energy of the carriers increases which leads to an increase in the Seebeck coefficient. Second, the grain size distribution is very large in our material. Compared to an all nano structure, Yan’s work for example, the large grains in our material provide more space for the charge carriers to move and enhances their mobility. Therefore more carriers are able to participate in the accumulation and create higher potential differences (higher Seebeck voltage). Finally, there might be local fluctuations in chemical composition inside the large grains, at the interfaces of the precipitates and the matrix grains and grain boundaries that enhanced the energy filtering process.

8.2.2 Resistivity

The advantage of having large grains in the nanocomposite structure can also be seen in the electrical resistivity. Compared to an all nano structure, our material shows better electrical conduction that helps improve the power factor. It is expected to be not as good as that in the single crystal structure, e.g., Yamashita’s work, because the interface density is higher in

\(^1\)The Seebeck coefficient of the n-type material is negative.
our material. The temperature dependence of the electrical resistivity behaves like a metal: it increases as the temperature increases. It is typical for heavily doped semiconductors which have high carrier concentrations.

### 8.2.3 Power Factor

The power factor is almost two- to three-fold improvement over similar materials. It is from the enhancement of both the Seebeck coefficient and electrical resistivity while the former contributed more. At room temperature the power factor is around $63 \mu W/cm-K^2$ while they are $60 \mu W/cm-K^{-1}$ and $35 \mu W/cm-K^2$ from Yamashita and Yan’s work. The peak value is at $100 \degree C$ to be $93 \mu W/cm-K^2$ compared to $48$ and $31 \mu W/cm-K^2$ from Yamashita and Yan’s work.

### 8.2.4 Thermal Conductivity

The thermal conductivity is optimized by the nano-bulk structure with large grains (300 nm and larger), small grains (100 nm and smaller) and perhaps precipitates shown in the TEM figures in Figure 8.2. The volume ratio of the nano-precipitates, although they are small enough to scatter the phonons, may be small to be effective while the bulk thermal conductivity is measured. Therefore the thermal conductivity is similar to that of single crystal and higher than Yan’s work, which has more grains less than 100 nm.

### 8.2.5 Figure of Merit

The peak thermoelectric figure of merit ($ZT$) of this work is about 2.65 at 100 °C while it is about 1.54 at room temperature. The $ZT$ is much improved to be over 2 at the temperature range 50 to 150 °C compared to the references. This improvement is mainly from the power factor, i.e., the ideal combination of high Seebeck coefficient and reasonable electrical resistivity tuned by this nano-bulk configuration, nanocomposite with a large grain size distribution, and thus demonstrated experimentally the thermoelectric property enhancement via ideal structure design and optimized material process.

### 8.3 Microstructure of Commercial N-type

To better contrast the roles of nano-bulk structure in this work, TEM specimens of commercial polycrystalline BiSeTe materials are obtained by the same mechanical polishing technique and observed under the microscope. Several differences were noticed. First, there are no nano scale precipitates/grains in the material. Second, their grains are huge in the scale of microns with very low interface density as shown in Figure 8.7 and thus narrow grain size distribution. Finally,
there are dislocations throughout the materials, Figure 8.7 (b). The $ZT$ of the commercial material is about one. This value is back calculated based on their device performance therefore their individual properties are not shown.
Figure 8.2: Microstructure figures of a n-type bulk sample made by room temperature as-milled powders with various magnification by TEM: (a) - (d) low magnification, (e) SAD pattern, (f) HRTEM of a precipitate.
Figure 8.3: Calculated grain size distribution of the n-type bulk samples made by room temperature as-milled powders. Only grains/precipitates less than 50 nm are considered.

Figure 8.4: TEM figures of different n-type bulk samples made by room temperature as-milled powders showing the locations of the EDS probe indicated by the numbers.
Figure 8.5: Transport properties of n-type material made by room temperature as-milled powders along with reference data.
Figure 8.6: Transport properties of the best n-type sample and the average made by room temperature as-milled powders.
Figure 8.7: TEM figures of commercial polycrystalline n-type BiSeTe materials.
The microstructure and transport properties of the p-type bulk materials consolidated from room temperature as-milled powder are presented in this chapter. The X-ray diffraction spectrum confirms there are neither second phases nor oxidation after the hot pressing and the composition well matched the target.

The material has a large grain size distribution from 0.2 to 1.3 $\mu$m. Precipitates/grains of 15 to 50 nm can be found in most of the large grains and they distribute evenly in the large grains. The structure of the precipitates is observed to be different than that of the matrix by high resolution imaging while their composition appears to be Sb rich with less Bi and Te. Local stoichiometry variations could be the origin of these precipitates while their size makes it difficult to be characterized.

The $ZT$ of the best sample is above two from room temperature to 125 °C while the $ZT$ of the average is near or over two at this temperature range. The peak $ZT$ of the best sample is about 3 in the temperature range 50 to 100 °C. Similar to the n-type material, this significant improvement is believed mainly from the increase of the Seebeck coefficient resulting from the structural features: the presence of nano scale precipitates and the large grain size distribution. It allows the quasi-independent tuning of the Seebeck coefficient without suffering from increases in the electrical resistivity. Although the phonon transport is not greatly impeded by the grain boundaries, the enhancement in the power factor is large enough to lift $ZT$ over 3 and over 2 up to 125 °C.

The results suggest that the thermoelectric properties of p-type BiTe(Sb) can be optimized by tuning the microstructure with appropriate processing and $ZT$ over 2 or higher is feasible.
By comparing the microstructure to the commercial p-type materials, $ZT$ enhancement by the nano precipitates and large grain size distribution is supported further.

9.1 Microstructure

9.1.1 Composition

The X-ray diffraction (XRD) spectrum shows no second phase formed after the consolidation process in Figure 9.1. All the peaks can be indexed and almost at the exact same $2\theta$ angle with the as-milled powder therefore their composition is considered the same and matched the target Bi$_{0.6}$Sb$_{1.4}$Te$_3$. The peaks are sharper due to the grain growth during the hot pressing process.

![XRD spectra of (i) p-type bulk sample made from room temperature as-milled powders on the top and (ii) room temperature (RT) as-milled powders on the bottom.](image)

Figure 9.1: XRD spectra of (i) p-type bulk sample made from room temperature as-milled powders on the top and (ii) room temperature (RT) as-milled powders on the bottom.

9.1.2 TEM and EDS Analysis

Nanocomposite Structure

The bulk p-type materials show polycrystalline structure with closely packed grains and abrupt grain boundaries as shown in the transmission electron microscope (TEM) figures, Figure 9.2. The material has a large grain size distribution: the majority of grains are observed to be in
the range of 0.8 ∼ 1.3 μm, along with some smaller 200 nm grains. An important feature in the structure is the presence of the nano scale precipitates/grains distributed inside most of the large grains and at the grain boundaries, Figure 9.2 (c) and (d). The selected area electron diffraction (SAD) in Figure 9.2 (e) reveals the nanocrystalline structure as well with spots forming ring-shape patterns. The structure of the precipitates is different from the matrix materials as shown in the high resolution TEM (HRTEM) figure, Figure 9.2 (f). The white area is a void. Twin boundaries and dislocation lines are also observed within the grains. The sites of grains smaller than 100 nm are measured and their distribution is shown in Figure 9.3. They are mainly within the 15 to 50 nm range with a few larger than 60 nm. Very few voids are observed which is consistent with the 99% dense or higher density measurements.

**Investigation of Precipitates**

Preliminary compositional analysis by energy dispersive X-ray spectroscopy (EDS) was carried out to probe the precipitates. The results from various spots at two different p-type samples both show that the precipitates are mainly Sb rich with less Bi and Te while pure Sb precipitates exist indicated by the EDS. The EDS probe locations at the first sample are shown in Figure 9.4 with the corresponding results listed in Table 9.1 while those at the second sample are in Figure 9.5 and Table 9.2. The results from the precipitates are highlighted by color yellow in both tables. Cu was detected because the TEM specimens were mounted to copper grids.

Similar to the n-type materials in this work, the origins of the precipitates need more investigation. The binary phase diagram (Figure 6.4) does not indicate a two phase region at Sb₂Te₃ composition and deviations from the stoichiometry is suspected. While the endothermic melting peak at 413 °C in the DSC plot (Figure 7.8) is not very large, there should only be part of the materials that have exact Sb₂Te₃ stoichiometry. These deviations could occur during the mechanical alloying process and were then exaggerated by the hot pressing.

**9.2 Transport Properties**

The transport properties, Seebeck coefficient, electrical resistivity, thermal conductivity, etc. of the p-type materials are grouped together and shown in Figure 9.6 and Figure 9.9. In Figure 9.6, the data points from the p-type material with the best performance are shown along with those from the references. Poudel’s work represents slightly different composition (Bi₀.₅Sb₁.₅Te₃), different consolidation technique (spark plasma sintering, SPS) but similar structure (nanocomposite) [90]. Fan’s work represents similar composition (Bi₀.₆Sb₁.₄Te₃), similar structure (nanocomposite) but different processing (melt-spinning inclusions mixed with ingots by ball milling and consolidation by 50 MPa hot pressing at 450 °C) [123].
Table 9.1: Weight percentage analyzed by EDS of various spots at Figure 9.4. Rows highlighted by color yellow are the results from the precipitates. The ideal weight percentage for Bi$_{0.4}$Sb$_{1.6}$Te$_3$ is included in the bottom row.

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<th>Sb</th>
<th>Te</th>
<th>Bi</th>
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<td>23.61</td>
<td>46.03</td>
<td>10.91</td>
<td>3</td>
<td>19.34</td>
<td>24.49</td>
<td>45.31</td>
<td>10.87</td>
</tr>
<tr>
<td>4</td>
<td>18.71</td>
<td>40.23</td>
<td>32.91</td>
<td>8.15</td>
<td>4</td>
<td>18.79</td>
<td>38.6</td>
<td>34.09</td>
<td>8.53</td>
</tr>
<tr>
<td>5</td>
<td>19.18</td>
<td>23.45</td>
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<td>11.54</td>
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<td>19.22</td>
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<td>46.86</td>
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<td>45.5</td>
<td>11.08</td>
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<td>0</td>
<td>25</td>
<td>56.49</td>
<td>18.5</td>
</tr>
<tr>
<td>7</td>
<td>19.45</td>
<td>23.67</td>
<td>45.7</td>
<td>11.18</td>
<td>Ideal</td>
<td>0</td>
<td>25</td>
<td>56.49</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Table 9.2: Weight percentage analyzed by EDS of various spots at Figure 9.5. Rows highlighted by color yellow are the results from the precipitates. The ideal weight percentage for Bi$_{0.4}$Sb$_{1.6}$Te$_3$ is included in the bottom row.

<table>
<thead>
<tr>
<th>Spot at (a)</th>
<th>Cu</th>
<th>Sb</th>
<th>Te</th>
<th>Bi</th>
<th>Spot at (b)</th>
<th>Cu</th>
<th>Sb</th>
<th>Te</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.08</td>
<td>25.71</td>
<td>47.16</td>
<td>15.05</td>
<td>1</td>
<td>8.93</td>
<td>27.24</td>
<td>50.35</td>
<td>13.49</td>
</tr>
<tr>
<td>2</td>
<td>11.12</td>
<td>88.88</td>
<td>1</td>
<td>5.77</td>
<td>2</td>
<td>9.05</td>
<td>71.4</td>
<td>13.67</td>
<td>5.88</td>
</tr>
<tr>
<td>3</td>
<td>11.29</td>
<td>27.18</td>
<td>47.65</td>
<td>13.88</td>
<td>3</td>
<td>8.96</td>
<td>51.82</td>
<td>29.94</td>
<td>9.28</td>
</tr>
<tr>
<td>4</td>
<td>11.19</td>
<td>67.05</td>
<td>15.98</td>
<td>5.77</td>
<td>4</td>
<td>8.87</td>
<td>27.43</td>
<td>49.22</td>
<td>14.48</td>
</tr>
<tr>
<td>5</td>
<td>10.7</td>
<td>26.89</td>
<td>48.83</td>
<td>13.58</td>
<td>Ideal</td>
<td>0</td>
<td>25</td>
<td>56.49</td>
<td>18.5</td>
</tr>
<tr>
<td>Ideal</td>
<td>0</td>
<td>25</td>
<td>56.49</td>
<td>18.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Both works show very good $ZT$ improvement over conventional p-type BiSbTe alloy and have received a lot of attention in this field recently. The TEM figures of their microstructure are shown in Figure 9.7 and Figure 9.8 respectively to differentiate the structure-property relationship by different processing. Compared to the microstructure in this work, a very large grain size distribution, from 15 nm to 1.3 µm, and high density of evenly distributed nano scale precipitates are the main differences. Poudel’s material has smaller grains in general from 20 to 400 nm with 2 to 10 nm Sb-rich nano-dots in Figure 9.7 (d), (e) and pure Te precipitates from 5 to 30 nm in diameter in Figure 9.7 (f). Fan’s material shows large grains in microns, Figure 9.8 (a) with 15 nm Sb-rich precipitates in Figure 9.8 (c). Improved $ZT$ in both work are attributed to the thermal conductivity reduction by nano structure. It is noticed that neither reference explains the origin of the Sb-rich precipitates.

Figure 9.9 shows transport properties of both the best p-type sample (solid circles) and the
average of multiple samples (solid squares). \( ZT \) are greater than two in the temperature range of 50 to 100 °C although the standard deviation is large.

### 9.2.1 Seebeck Coefficient

The Seebeck coefficient of the best sample starts from 298 \( \mu V/K \) at 25 °C and increases to the peak 425 \( \mu V/K \) at 100 °C then decreases to 260 \( \mu V/K \) at 200 °C. While the Seebeck coefficient of the average samples starts from 250 \( \mu V/K \) at 25 °C and increases to the peak 295 \( \mu V/K \) at 100 °C. Compared to the reference data, this is a dramatic improvement which is almost two times and 1.5 times of the reference data at 100 °C and room temperature respectively.

A very large grain size distribution and high density of the nano scale precipitates is believed to be the main contribution to this phenomenon, which are also the main differences in the microstruture between our samples and the references. The nano precipitates act as scattering sites to filter out low energy charge carriers and thus Seebeck coefficient increases because the average energy of the charge carrier increases. Meanwhile, based on the preliminary EDS analysis, the chemical composition of the precipitates are different from that of the matrix material. This fluctuation of the stoichiometry could also enhance the energy filtering process. The effect of the precipitates are expected to be observable despite their size because they can be found in almost every large grain with high density based on the TEM figures.

### 9.2.2 Resistivity

The electrical resistivity of our sample is in the range of \( 1.2 \times 10^{-5} \) to \( 2.7 \times 10^{-5} \) \( \Omega \)-m which is very similar to Fan’s work. Poudel’s work shows lower electrical resistivity with a speculation of defects at the grain boundaries acting as uncompensated recombination centers and thus increasing the hole density in the grain. The temperature dependence of the electrical resistivity is similar to a metal because the carrier concentrations are high.

### 9.2.3 Power Factor

The power factor is obviously improved by the enhancements in the Seebeck coefficient compared to either similar structure or similar chemical composition. It is 75 \( \mu W/cm-K^2 \) at room temperature and the peak is 95 \( \mu W/cm-K^2 \) at 100 °C. The trend of the power factor follows that of the Seebeck coefficient: a curve with a peak value, while it is flat and downward for both references.
9.2.4 Thermal Conductivity

The thermal conductivity increases from 0.9 to 1.6 as the temperature increases from 25 to 200 °C which is higher than either Fan’s or Poudel’s work after 75 °C. It is expected as the density of the grain boundaries, the main phonon scattering sites, is higher in their materials. Although the precipitates in our samples are in the scale to effectively impede phonon transport, their contributions are over-shadowed by the large grains in the matrix.

9.2.5 Figure of Merit

The $ZT$ is above 2 from room temperature to 120 °C with two peaks of 3.06 and 3.07 at 50 and 100 °C respectively and then decreases. The material not only reached $ZT=3$ but is also over 2 in a wide range of temperature. This enhancement is resulting from both the nano scale precipitates and the nano-bulk structure with a large grain size distribution as they increase the Seebeck coefficient and the power factor considerably without scarafice the thermal conductivity. The average $ZT$ of multiple p-type samples is still over two in the temperature range of 50 to 100 °C as shown in Figure 9.9.

9.3 Microstructure of Commercial P-type

The structure-property relationship is further emphasized by comparing our microstructures to the commercial polycrystalline BiSbTe materials, which have $ZT$ about one. They do not have nano-scale features such as grains or precipitates, the grain size is large, in the scale of microns, and the grain size distribution is narrow as shown in Figure 9.10. Dislocations are observed in the materials in Figure 9.10 (b). Their individual transport properties are not available because the $ZT$ is back calculated based on their device performance.
Figure 9.2: Microstructure figures of a p-type bulk sample made by room temperature as-milled powders with various magnification by TEM: (a) - (d) low magnification, (e) SAD pattern, (f) HRTEM of a precipitate.
Figure 9.3: Grain size distribution of p-type bulk samples made by room temperature as-milled powders. Only grains/precipitates less than a hundred nm are considered.

Figure 9.4: TEM figures of different region in the second p-type bulk samples made by room temperature as-milled powders showing the locations of the EDS probe indicated by the numbers where (b) is acquired by the dark field imaging to better outline the precipitates.

Figure 9.5: TEM figures of different region in the first p-type bulk samples made by room temperature as-milled powders showing the locations of the EDS probe indicated by the numbers.
Figure 9.6: Transport properties of p-type material made by room temperature as-milled powders along with reference data.
Figure 9.7: Transmission electron microscope figures of the p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ by Poudel, et al. [90] (d), (e): Sb-rich nano-dots; (f): pure Te precipitates. The materials were processed by ball milling and spark plasma sintering.

Figure 9.8: Transmission electron microscope figures of the p-type BiSbTe by Fang, et al. [123] (c): Sb-rich precipitates. Nanoinclusions produced by melt spinning were ball milled with single crystal Bi$_{0.6}$Sb$_{1.4}$Te$_3$ followed by hot pressing.
Figure 9.9: Transport properties of the best p-type sample and the average made by room temperature as-milled powders.
Figure 9.10: TEM figures of commercial polycrystalline p-type BiSbTe materials.
Experimental thermoelectric (TE) devices have been fabricated from the n- and p-type nano-bulk materials in this work. With an appropriate material matching, the best device shows peak heat-to-electricity conversion efficiency of 7.9% around 300 °C. The average performance from multiple devices also shows peak efficiency about 7% and over 6% in the temperature range of 220 to 330 °C. Compared to the peak efficiency of 5.6% from a commercial state-of-the-art BiTe device, the ZT enhancement from nanostructured materials are successfully transferred to the resulting devices.

The basic design of thermoelectric devices as well as advantages over traditional power generation or cooling devices are introduced. Applications have been developed in various fields, such as radioisotope thermoelectric generators for space missions, waste heat recovery in automotive applications, localized hot spot cooling in computers.

The efficiency of the thermoelectric device is highly dependent on the materials figure of merit. Mathematical definitions of their relationships and the efficiency of the power generation mode are discussed in detail.

10.1 Thermoelectric Applications

Thermoelectric devices can operate in either cooling or power generation mode. There are several advantages of such "solid state" devices over conventional power generating or cooling devices, such as

- No moving parts and silent.
• Small and lightweight.
• Highly reliable.
• Nearly maintenance free and very long life time.
• Wide operating temperature range.
• Operation is independent on orientation or gravity.

In addition to the most common and basic thermoelectric devices, thermalcouples used for temperature readings, further introduction of other applications are discussed below.

10.1.1 Power Generation

Space Mission Applications

Radioisotope thermoelectric generators (RTGs) have been developed for space mission for their long life time and high reliability since '90s. Using radioisotopes such as PuO$_2$ as the heat source, they can output linear voltage-current curve and operate when solar energy is not available. PbTe and SiGe thermoelectric elements are the common materials for RTGs. A typical RTG layout is shown in Figure 10.1. Similar generators have been used on Apollo 12, Pioneer 10, Pioneer 11, etc.[124]

![Figure 10.1: An illustration of a radioisotope thermoelectric generator. After reference [124].](image)

Automotive

More than 60% of energy contained in the fuel is converted into waste heat, mainly to the exhaust and coolant system. Therefore waste heat recovery is attractive as a source of the
thermoelectric generator. Experimental Bi$_2$Te$_3$ modules for automotive applications have been developed to further improve the fuel efficiency and show promising potential [125, 126]. Such a system is usually integrated with the exhaust line as shown in Figure 10.2.

![Figure 10.2: Thermoelectric generator in a BMW 5 series. The thermoelectric module, indicated by the white arrow, is designed to be incorporated with the exhaust system. After reference [126].](image)

**Other**

Thermoelectric effects have been applied to power the wrist watch as well such as Seiko Thermic™, shown in Figure 10.3. It uses the temperature difference between the body heat and the air flow to create current. In the field of microelectromechanical (MEMS) systems, low power thermoelectric generator is designed to be integrated into a complementary metal-oxide-semiconductor (CMOS) system [127].

![Figure 10.3: Seiko Thermic™ wrist watch. After reference [128].](image)
10.1.2 Cooling

In the cooling (refrigeration) mode, embedded thermoelectric cooling (eTEC) presents a solid state approach to reduce the heat in localized hot spots. For example, TEC integrated heat sinks and heat pipes are designed to cool computer processing units (CPU) [129, 130]. Thin film superlattice is a common structure for these micro-coolers. Material systems for this application include Bi$_2$Te$_3$, SiGeC/Si, InGaAsP, etc.[131, 132] Figure 10.4 shows SiGeC/Si micro-coolers that can cool as much as 2.8 and 6.9 K at 25 °C and 100 °C, which is corresponding to power densities on the order of 1000 W/cm$^2$. The design approaches of thermoelectric coolers and their applications have been experimentally studied to optimize their performance curves [133, 134].

![Schematic diagram of the SiGeC/Si thin film thermoelectric coolers. After reference [131].](image)

10.2 Device Efficiency

The conversion efficiency of a TE device is not solely determined by the materials’ ZT because the temperature dependence of Seebeck coefficient, electric resistivity, and thermal conductivity which makes the figure of merit a function of temperature. Even for a state-of -the-art Bi$_2$Te$_3$ with $ZT=1.1$, the resulting device only shows overall effective device figure of merit ($Z_dT$) about 0.7 in either power generation or refrigeration mode [38]. This could be due to several factors such as (1) mismatch between p and n materials in a p-n couple, (2) compatibility factor [38, 135], both within p and n and between p and n over the whole temperature range, (3) thermal losses and (4) device electrical contact losses -which significantly affect the translation of the material $ZT$ into device efficiency.
10.2.1 Power Generation Mode

For a p-n couple with different transport properties\(^1\), the basic module setup can be seen in Figure 10.5 and its properties are as the followings.

![Diagram of a thermoelectric module](image)

Figure 10.5: A thermoelectric module consists of n- and p-type element.

The internal electrical resistance \((R)\) is

\[
R = \frac{\rho_p L_p}{A_p} + \frac{\rho_n L_n}{A_n} \quad (10.1)
\]

The thermal conductance \((K)\) is determined by the length \((L)\) and the cross section area \((A)\) of the thermoelectric element as

\[
K = \frac{k_p A_p}{L_p} + \frac{k_n A_n}{L_n} \quad (10.2)
\]

The device figure of merit \((Z_dT)\), representing the figure of merit of the p-n couple, has been discussed in Section 2.1.1 and the definition is repeated here:

\[
Z_dT = \frac{S^2T}{\left((\rho_p k_p)^{\frac{1}{2}} + (\rho_n k_n)^{\frac{1}{2}}\right)^2} \quad (10.3)
\]

\(^1\)More details of mathematical expressions in this section is referred to Chapter 2 and 10 in reference [42] and Chapter 3 in reference [136].
where the subscript \( n \) and \( p \) denote the corresponding parameters of n- or p-type material and

\[
S = S_p - S_n \tag{10.4}
\]

The power generated \((W)\) can be calculated with current generated by the module \((I)\) and the load resistance \((R_L)\) as

\[
W = I^2 R_L \tag{10.5}
\]

\[
I = \frac{S(T_h - T_c)}{R_L + R} \tag{10.6}
\]

The open circuit voltage \((V_{oc})\) can then be obtained as

\[
V_{oc} = I(R_L + R) \tag{10.7}
\]

The conversion efficiency \((\eta)\) of the module is defined as

\[
\eta = \frac{W}{Q_h} \tag{10.8}
\]

i.e., the ratio between the power generated and the heat flow at the hot side. This can be rewritten by replacing \(Q_h\) with the following

\[
Q_h = ST_h I - \frac{I^2 R}{2} + K(T_h - T_c) \tag{10.9}
\]

to be

\[
\eta = \frac{I^2 R_L}{ST_h I - \frac{I^2 R}{2} + K(T_h - T_c)} \tag{10.10}
\]

Insert the above equation with \(K\) (Eq. 10.2), \(Z_d T\) (Eq. 10.3) and \(I\) (Eq. 10.6), the efficiency then becomes a function of \(Z_d T\) after some math \[137\]:

\[
\eta = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{Z_d T_M + 1} - 1}{\sqrt{Z_d T_M + 1}} \frac{T_c}{T_h} \tag{10.11}
\]

where \(T_h\) is the hot side absolute temperature, \(T_c\) is the cold side absolute temperature and \(T_M\) is the average temperature between \(T_h\) and \(T_c\). The theoretical predictions of conversion efficiency versus temperature difference \((\Delta T)\) are shown in Figure 10.6 where \(Z_d T_M\) from 0.5 to 4 are calculated.
**Maximum Efficiency**

The maximum conversion efficiency happens when the highest thermal efficiency is achieved which is dependent on a ratio $M$ defined as

$$M = \frac{R_L}{R} = \sqrt{Z_d T_M + 1}$$  \hspace{1cm} (10.12)

When $Z_d T_M$ is very large, $M$ could be very large and the efficiency would approach the Carnot cycle limit, i.e.,

$$\eta \to \frac{T_h - T_c}{T_h} \text{ as } Z_d T_M \to \infty$$ \hspace{1cm} (10.13)

![Figure 10.6: Calculated ideal device conversion efficiency as a function of $Z_d T_M$ based on Eq. 10.11. The cold side temperature $T_c$ is set to be 25 \degree C.](image)

10.2.2 **Refrigeration Mode**

The device conversion efficiency in the refrigeration mode is given by the measured maximum temperature drop achieved ($\Delta T_{max}$)

$$\Delta T_{max} = \frac{Z_d T_c^2}{2}$$  \hspace{1cm} (10.14)
10.3 Experimental Nano-bulk Thermoelectric Devices

10.3.1 Device Setups

Thermoelectric elements are connected electrically in series and thermally in parallel in a device. Usually there are ceramic plates on the top and bottom which serve as electrical insulation as well as heat sinks. Copper plates/wires are the electrical connections between the elements. Such setup is shown in Figure 10.7.

![Diagram of thermoelectric device components](image)

Figure 10.7: A schematic view of thermoelectric device components. After reference [38].

Depending on the desired output power and dimensions, the number of the p-n couple can be varied from single (Figure 10.8) to, for example, 71 (Figure 10.9). There are multistage modules as well to obtain greater temperature difference, such as a three stage cascade modules shown in Figure 10.10. The top two stages can operate as heat sinks and provide lower temperature for the third stage. Obviously, this design will take more space.
10.3.2 Performance by Nano-Bulk Materials

Heat-to-electric power generation devices were fabricated using n- and p-type nanostructured Bi$_2$Te$_3$ alloy materials of several combinations, for better p/n matching [138] and also compared with non-nano commercial state-of-the-art Bi$_2$Te$_3$ alloy bulk materials.

The devices were power tested to determine the power output and efficiency that can be achieved with these new materials. Power testing was carried out using a Keithley 2440 source meter for power measurement which sweeps a voltage and measures a current, identifying the maximum power point where the source meter impedance matches the p-n power generation couple. Between voltage sweeps, the source meter voltage is set to provide a continuous electrical load at the last measured maximum power voltage. Temperatures of the cold side and hot side of the device are measured at the same time the maximum power point is measured. Efficiency at peak power is determined from measuring the heat flow ($Q_h$) through the device using a
calibrated $Q$-meter and the measured electric power output ($W$).

Heat-to-electric conversion efficiency results for a nanostructured Bi$_2$Te$_3$ couple and the reference non-nano commercial Bi$_2$Te$_3$ bulk module, which is p/n matched, are shown in Figure 10.11. The maximum efficiency of 5.6% was achieved for a state-of-the-art commercial Bi$_2$Te$_3$ bulk module at $T_{\text{hot}}=250 \, ^\circ\text{C}$. With nanostructured Bi$_2$Te$_3$ couples, device efficiency between 6.4% and 7.9% was achieved for the best p/n matching (device picture in Figure 10.8.). The efficiency of 7.9% represents a 40% improvement over best commercial Bi$_2$Te$_3$ module. The average efficiency from multiple modules still reaches a peak 7.2% at $T_{\text{hot}}=320 \, ^\circ\text{C}$ and over 6% in the range of at $T_{\text{hot}}=200$ to $330 \, ^\circ\text{C}$.

We also observed that the efficiency of the nano-material couples are peaking in efficiency at higher temperatures, around 300 $^\circ\text{C}$, which is consistent with higher Seebeck coefficients in both n- and p-type materials discussed in Chapter 8 and 9. The higher temperature performance is conducive to applications in exhaust automotive waste-heat recovery. This is an important step towards wider application of nanostructured Bi$_2$Te$_3$ materials for efficient power conversion and energy harvesting devices.

10.3.3 Compared to Non-nano Devices

The advantages of our nano p- and n-type materials in a device format are more evident at lower temperatures from the improved $ZT$, over both commercial off-the-shelf (COTS) and KELK Ltd., as shown in Table 10.1. The peak efficiency of 7.9% at maximum power translates to an efficiency of about 8.03% at optimal power. This is to be compared with efficiencies of 7.2% and 7.6%, at peak power and optimal power respectively, reported by KELK Ltd. in their modules based on materials optimized for higher temperatures but utilizing non-nano materials [139].

Here, we observe at optimal power draw from the modules as opposed to peak power, over 52% improvement was obtained in efficiency with the nano materials discussed in this work over
COTS devices at low-temperature heat harvesting scenarios. For $T_{hot} \sim 50\, ^\circ C$, from measured efficiencies, we obtain an average $Z_d T$ of $\sim 0.58$ for the COTS device, 0.73 for the KELK device and 0.99 for the device based on the nano-bulk materials reported in this study.

When the temperature differentials are smaller, the compatibility factor issues are less severe and also thermal losses are reduced, thereby helping to delineate better materials for their intrinsic $ZT$. Thus, we have made a significant step in translating improved nano-material $ZT$ into a device performance. This low-temperature ($T_{hot} \sim 50\, ^\circ C$) advantage is of relevance for applications such as data centers and chip-level energy harvesting. We also notice that the p-n couples made from the nano p- and n-type materials outperform the KELK devices over the whole temperature range. This is an important step towards wider application of nanostructured Bi$_2$Te$_3$ materials for efficient power conversion and energy harvesting devices.
Table 10.1: Comparison of efficiencies at optimal power for various $T_{\text{hot}}$ and $\Delta T$, for the thermoelectric generators (TEGs) made with the p- and n-type nano materials, state-of-the-art COTS materials and published work by KELK Ltd.

<table>
<thead>
<tr>
<th>Device</th>
<th>$T_{\text{hot}}$ (°C)</th>
<th>$\Delta T$ (°K)</th>
<th>Heat to Electric Conversion Efficiency at Optimal Power</th>
<th>Improvement over best COTS TEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best COTS TEG</td>
<td>49.4</td>
<td>26.3</td>
<td>0.95%</td>
<td>N/A</td>
</tr>
<tr>
<td>KELK</td>
<td>50.0</td>
<td>20.0</td>
<td>0.85%</td>
<td>-10.5%</td>
</tr>
<tr>
<td>This work</td>
<td>49.5</td>
<td>27.2</td>
<td>1.44%</td>
<td>51.5%</td>
</tr>
<tr>
<td>Best COTS TEG</td>
<td>99.0</td>
<td>75.2</td>
<td>3.04%</td>
<td>N/A</td>
</tr>
<tr>
<td>KELK</td>
<td>100.0</td>
<td>70.0</td>
<td>3.20%</td>
<td>5.3%</td>
</tr>
<tr>
<td>This work</td>
<td>100.6</td>
<td>77.2</td>
<td>3.55%</td>
<td>16.7%</td>
</tr>
<tr>
<td>Best COTS TEG</td>
<td>149.0</td>
<td>125.5</td>
<td>4.58%</td>
<td>N/A</td>
</tr>
<tr>
<td>KELK</td>
<td>150.0</td>
<td>120.0</td>
<td>5.00%</td>
<td>9.1%</td>
</tr>
<tr>
<td>This work</td>
<td>140.2</td>
<td>116.3</td>
<td>5.27%</td>
<td>15.1%</td>
</tr>
<tr>
<td>Best COTS TEG</td>
<td>322.6</td>
<td>292.5</td>
<td>5.49%</td>
<td>N/A</td>
</tr>
<tr>
<td>KELK</td>
<td>275.0</td>
<td>245.0</td>
<td>7.60%</td>
<td>38.4%</td>
</tr>
<tr>
<td>This work</td>
<td>317.0</td>
<td>287.4</td>
<td>8.03%</td>
<td>46.3%</td>
</tr>
</tbody>
</table>
In this chapter, the BiTe(Se) materials are consolidated from cryogenic temperature (77 K) as-milled powders by hot pressing at 410 °C with 2 GPa in order to obtain high interface density and reduce thermal conductivity.

The resulting nanocomposite material has peak figure of merit ($ZT$) about 1.54 at 25 °C and 0.8 at 225 °C. The thermal conductivity is reduced below 1.2 W/m-K by high density of nano scale grains. The Seebeck coefficient is also improved by the presence of nano precipitates from 25 to 150 °C. Thus the power factor and $ZT$ are still comparable and higher than Yan’s work [52] even with high electrical resistivity resulting from high density grain boundaries. The n-type made by room temperature as-milled powders in this work still has better performance with larger grain size distribution.

No second phase or side reaction are indicated by the X-ray diffraction after the hot pressing process. The transmission electron microscope (TEM) confirms nanocomposite structure with large grain size distribution and nano scale precipitates inside the grains. The majority of the grains have diameter between 30 to 80 nm and there are no near micron size grains, which are shown in n-type made by room temperature as-milled powders.

### 11.1 Microstructure

#### 11.1.1 Composition

The X-ray diffraction spectrum of consolidated sample shows no extra peak compared to as-milled powder as shown in Figure 11.1. All the peaks can be indexed. The peaks of the bulk
sample are shaper after consolidation due to the grain growth driven by elevated temperature.

Figure 11.1: XRD spectra of (i) n-type bulk sample made from cryogenic temperature as-milled powders on the top and (ii) cryogenic temperature as-milled powders as-milled powders on the bottom.

11.1.2 TEM Analysis

Nanocomposite Structure

Its nanocomposite structure has grains from 20 to 170 nm in diameter while the majority of the grains are in the size of 30 to 80 nm based on the calculation shown in Figure 11.2. The material is composed of closely packed large and small grains with clear boundaries, Figure 11.3 (a), (b). There are also nano scale precipitates inside the grains with very high density, Figure 11.3 (c), (d). Some of the bright spots at the grain boundaries are voids due to incomplete densification. The material still measured 99% dense by the Archimedes method because the voids are miniscule. The nano scale features are confirmed by the selected area electron diffraction (SAD) pattern. The spots almost form complete rings as shown in Figure 11.3 (e).

Compared to the n-type material made by room temperature as-milled powders in Chapter 8, the grains are obviously smaller with higher density of grain boundaries. This is contributed to the smaller grain size in the starting cryo-milled powder. There are no large grains near 700 or 800 nm and the frequency of grains less than 100 nm are much higher. Precipitates and twin
structures can be observed in both materials.

The nature of the precipitates needs further investigations. They could be resulting from local composition deviations from incomplete mechanical alloying process or may simply be impurities. Although XRD did not support these possibilities, they cannot be ruled out yet because they are too small to be characterized independently. The results from Chapter 8 are not applicable either because they are inconclusive.

Figure 11.2: Calculated grain size distribution of the n-type bulk samples made by cryogenic temperature as-milled powders. Precipitates are not included in the calculation.

11.2 Transport Properties

Thermoelectric properties, Seebeck coefficient, electrical resistivity and thermal conductivity, as well as power factor and $ZT$ of samples made by cryogenic temperature as-milled powders (77K-bulk) are shown in Figure 11.4 and Figure 11.5. The former also includes the properties from multiple n-type samples made by room temperature as-milled powders (RT-bulk) while the later shows the differences between 77K-bulk and the best RT-bulk sample.

The properties of 77K-bulk materials are again compared to the work by Yan et al. as shown in Figure 11.6. Their n-type Bi$_2$Te$_2$Se$_{0.3}$ were consolidated from room temperature mechanically milled powders by spark plasma sintering (SPS) representing the subtle difference in the micro structure [52].
11.2.1 Seebeck Coefficient

The absolute Seebeck coefficient starts from 240 $\mu$V/K at 25 °C and increases gradually to the peak value 249 $\mu$V/K at 100 °C then decreases to about 180 $\mu$V/K in the temperature range 175 to 225 °C. This is again a significant improvement compared to Yan’s work [52] due to the presence of the nano scale precipitates inside the material.

Meanwhile, it is slightly better than the average RT-bulk samples but the peak value is not comparable to the best RT-bulk sample. This could be attributed to higher interface density and narrower grain size distribution in the 77K-bulk. Less amount of charge carriers can participate in thermally induced carrier separation and accumulation that leads to smaller Seebeck coefficient.

11.2.2 Electrical Resistivity

Due to the fact that the material consists mostly nano grains, the electrical resistivity is higher than either the RT-bulk in this work or Yan’s work [52]. It increases steadily from $1.7 \times 10^{-5}$ to $2.1 \times 10^{-5}$ $\Omega$-m as the temperature increases from 25 to 225 °C. The temperature dependence is again similar to metal because the carrier concentration is high.

11.2.3 Power Factor

The power factor is low at about 33 $\mu$W/cm-K$^2$ below 150 °C and lower at 175 to 225 °C, which is still comparable to Yan’s work [52] although much lower than RT-bulk in this work. This is expected because the electrical resistivity is higher in 77K-bulk due to higher interface density.

11.2.4 Thermal Conductivity

The phonon transport is apparently limited by the nanostructure. The thermal conductivity is as low as 0.65 W/m-K at room temperature compared to 0.9 W/m-K in Yan’s work [52] and 1.5 W/m-K in RT-bulk sample. It increases to 1.2 W/m-K as the temperature increases to the measurement limit 225 °C.

11.2.5 Figure of Merit

The peak $ZT$ is 1.54 at 25 °C and over 1.2 up to 150 °C. The high electrical resistivity is compensated by the low thermal conductivity while enhanced Seebeck coefficient plays a role as well. This set of data also shows the challenge in obtaining the best $ZT$: while the electrical and thermal properties are both tuned by the micro structure, the material could still possess good $ZT$ while one of them is not a hundred percent optimized.
Figure 11.3: Microstructure of the n-type bulk sample consolidated from cryogenic temperature as-milled powders with various magnification by TEM, (a) to (d), and SAD pattern, (e).
Figure 11.4: Average transport properties of n-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively.
Figure 11.5: Transport properties of the best n-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively.
Figure 11.6: Transport properties of n-type material made by cryogenic temperature as-milled powders (solid triangle) along with data from the work by Yan et al. [52] (open triangle).
The Bi(Sb)Te materials consolidated by hot pressing at 410 °C with 1.8 GPa from cryogenic temperature (77 K) as-milled powders are polished and then characterized to study their microstructure and transport properties.

The X-ray diffraction did not indicate any second phase or side reaction after the hot pressing process. Compared to the materials consolidated from room temperature as-milled powders, since the grains in the starting powders are already smaller, the grains in the bulk samples are expected to be smaller as well, which is then confirmed by the transmission electron microscope (TEM). The materials show nanocomposite structure with large grain size distribution and nano scale precipitates inside the grains. The materials have grains from 25 to 250 nm where the majority of the grains have diameter between 50 and 180 nm. There are no near micron size grains observed, which are shown in materials made by room temperature as-milled powders.

The peak figure of merit ($ZT$) is about 1.3 at 25 °C and decreases to 0.8 at 225 °C. The thermoelectric properties are tuned by the structure: the Seebeck coefficient is improved by the presence of nano precipitates; the thermal conductivity is reduced by high density of grain boundaries. However, the power factor is low compared to materials made by room temperature as-milled powders or Poudel’s work [90] due to high electrical resistivity. It is believed that if there were more large grains to expand the grain size distribution more, like the materials made by room temperature as-milled powders in Chapter 9, the $ZT$ could be higher.
12.1 Microstructure

12.1.1 Composition

The X-ray diffraction (XRD) spectra of as-milled powders and the consolidated materials are shown in Figure 12.1. The peak positions are the same and matched the target p-type composition $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$. There are no second phases or side reactions indicated by the XRD.

![XRD spectra](image)

**Figure 12.1:** XRD spectra of (i) p-type bulk sample made from cryogenic temperature as-milled powders on the top and (ii) cryogenic temperature as-milled powders on the bottom.

12.1.2 TEM Analysis

Nanocomposite Structure

The materials have a typical nanocomposite structure with grains from 25 to 250 nm. The distribution of grain size is calculated and shown in Figure 12.2 where the majority of the grains have diameter between 50 and 180 nm. The microstructure by TEM is obtained with
different magnifications and regions as shown in Figure 12.3 (a)-(e). The grains are closely packed with clean grain boundaries and almost no voids are observed. Grains of different sizes distribute randomly throughout the materials. Twin structure can be found in some large grains. The selected area electron diffraction pattern (SAD) in Figure 12.3 (f) reveals the nanocrystalline structure as well with spots forming ring-shape patterns.

High density precipitates can be observed inside most of the large grains in different regions. Based on the analysis done for the p-type materials consolidated by room temperature as-milled powder discussed in Chapter 9, they are suspected to be Sb-rich as well.

The overall grain size is noticeably smaller than that in the materials consolidated by room temperature as-milled powder. There are no near micron size grains and more grains have size less than 100 nm which shifts the distribution to the smaller side. This is expected because the grains in the starting powders made by cryogenic mechanical alloying is already smaller. On the other hand, precipitates and twin structure can be found in both materials while they both have relative density 99% or higher.

![P-type bulk from 77K milled powder](image)

**Figure 12.2:** Calculated grain size distribution of the p-type bulk samples made by cryogenic temperature as-milled powders. Precipitates are not included in the calculation.
12.2 Transport Properties

The Seebeck coefficient, electrical resistivity and thermal conductivity are grouped together with power factor and thermoelectric figure of merit (ZT) as shown in Figure 12.4. The data points from materials with similar microstructure and composition but different material processing by Poudel et al.[90] are also included. Their bulk samples are consolidated by spark plasma sintering (SPS) with much smaller pressure in the scale of MPa.

In Figure 12.5, both bulk samples made from cryogenic and room temperature as-milled powders in this work, 77K-bulk and RT-bulk, are presented. Data points from the best RT-bulk is also included in Figure 12.6. The differences in their transport properties are discussed in the following sections.

12.2.1 Seebeck Coefficient

The peak Seebeck coefficient is 280 $\mu$V/K at 100 $^\circ$C while it is 242 $\mu$V/K at 25 $^\circ$C and 205 $\mu$V/K at 225 $^\circ$C. This improvement compared to the work by Poudel et al. [90] is again attributed to the large grain size distribution and nano scale precipitates distributed in the matrix materials. The former is beneficial for the charge carrier mobility and the later enhance the energy filtering effect.

The Seebeck coefficient of 77K-bulk is smaller than that of the best RT-bulk but close to the average. It may due to a narrower grain size distribution in 77K-bulk which consists more grains less than 100 nm. This structural difference is indicated not only by the TEM image but also the SAD pattern which has more complete ring pattern in 77K-bulk than in the best RT-bulk. More nano sized grains result in higher interface density thus limit the amount of the charge carrier accumulation which produces less Seebeck voltage.

12.2.2 Resistivity

The electrical resistivity increases from $1.5 \times 10^{-5}$ to $2.8 \times 10^{-5}$ $\Omega$-m as the temperature increases form 25 to 200 $^\circ$C. It is higher than either the data from the work by Poudel et al. [90] or RT-bulk materials because the interface density is higher due to the presence of large amounts of grains less than 100 nm throughout the material.

Although both 77K-bulk and Poudel’s work have many nano scale grains, the defect-induced increase of charge carrier density in Poudel’s work is not shown in 77K-bulk and thus it has higher resistivity.
12.2.3 Power Factor

The peak power factor is about 40 $\mu$W/cm-K$^2$ at 25 °C and decreases as the temperature increases. These values are not as high as either RT-bulk or the work by Poudel et al. [90] because the resistivity is too large even with improved Seebeck coefficient.

12.2.4 Thermal Conductivity

The thermal conductivity is comparable to Poudel’s work while the majority of the grains are nano sized in both materials and the grain boundaries impede the phonon transport. The RT-bulk has higher thermal conductivity because of smaller grain boundary density.

12.2.5 Figure of Merit

The peak $ZT$ is about 1.3 at 25 °C and decreases to 0.8 at 225 °C following the trend of the power factor. It is not as impressive as the RT-bulk due to higher resistivity that results in lower power factor compared to other nanocomposite materials. However, the Seebeck coefficient is improved and the $ZT$ is still higher than one and stable between 1.3 and 1.05 from 25 to 125 °C.
Figure 12.3: Microstructure of the p-type bulk sample made by cryogenic temperature as-milled powders with various magnification by TEM, (a)-(e), and SAD pattern, (f).
Figure 12.4: Transport properties of p-type material made by cryogenic temperature as-milled powders (solid triangle) along with data from the work by Poudel et al. (solid squares) [90].
Figure 12.5: Average transport properties of p-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively.
Figure 12.6: Transport properties of the best p-type materials made by cryogenic and room temperature temperature as-milled powders, solid triangle and open squares respectively.
While most studies focus on the reduction of lattice thermal conductivity to improve $ZT$, this work demonstrates enhanced Seebeck coefficients tuned by hot pressing pressure for n-type nanocomposite Bi(Se)Te alloys consolidated from mechanical alloyed nanocrystalline powders. The peak Seebeck coefficients at room temperature are found to be 210 µV/K from $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.27}$ hot-pressed at 2 GPa and 155 µV/K from $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ hot pressed at 1.75 GPa. Microstructure analysis by X-ray diffraction and transmission electron microscopy as a function of hot pressing pressure are presented.

This phenomenon could be contributed by the pressure-driven changes in the density of antisite defects and electronic band structure at elevated temperatures. The amount of positively charged antisite defects increases as the pressure increases to a point where their contributions are canceled out by other negatively charged antisite defects. Meanwhile, modifications of the energy gap resulting from the lattice distortions at high pressure could be partially maintained as well. This study shows that an optimal hot pressing pressure is required in the consolidation process of Bi(Se)Te based alloy for each given composition in the pursuit of high thermoelectric performance.

### 13.1 Pressure Effects on Seebeck Coefficient

A common way to produce nanocomposite Bi(Sb)Te(Se) alloys is a bottom-up method: create the nanocrystalline powders first followed by a consolidation process. In order to achieve full density, temperature and pressure are important element with which can change the
microstructure and thermoelectric properties dramatically during the consolidation. Here we report an empirical relationship between the hot pressing pressure and the Seebeck coefficient. While it is known that high pressure can change the electrical properties of Bi\textsubscript{2}Te\textsubscript{3} alloys [140, 141, 142], this study directly connects the process parameter with the Seebeck coefficient and provides a practical way to enhance their power factors. Along with limiting thermal conductivity by the nanocomposite structure, further $ZT$ improvement based on this alloy can be expected.

### 13.2 Material Processing and Characterization

The bulk samples are obtained by consolidating Bi(Se)Te powders, which are produced by mechanical alloying. Appropriate amounts of elemental powders, Bi, Se and Te, supplied by Alfa Aesar of purity 99.99% or higher were loaded into the stainless steel vials with stainless steel balls inside a glove box with oxygen less than 1 ppm. The ball to powder ratio was 10:1. The vials were then sealed and milled by SPEX SamplePrep 8000M for 20 hours at room temperature. The resulting powders were then hot pressed at 410 °C with various uniaxial pressures from 1.6 to 2.3 GPa in an inert gas environment. The resulting bulk materials, 10 mm disks with thickness about 800 μm, are then polished for further characterizations. Every sample has identical process parameters except the hot pressing pressure.

The X-ray diffraction (XRD) spectra were obtained for both powder and bulk samples by a Rigaku GeigerFlex DMax/A diffractometer with a Cu radiation to analyze the composition and examine the existence of any side reaction such as oxidation. The density of bulk samples was measured by the Archimedes method. A JEOL 2000 transmission electron microscope (TEM) operated at 200 kV was used to acquire microstructure figures. The TEM specimens were prepared by mechanical polishing followed by low energy ion milling. The carrier concentration of the BiTe(Se) bulk materials were measured by a Hall-effect set up. The Seebeck coefficient of the material was measured using a Seebeck coefficient test station as discussed in the round-robin measurements [119].

### 13.3 Results and Discussion

#### 13.3.1 Pressure Dependency of Seebeck Coefficient

The Seebeck coefficients as a function of the hot pressing pressure of n-type Bi(Se)Te are shown in Figure 13.2 (c). The Seebeck coefficients of Bi\textsubscript{2}Te\textsubscript{2.7}Se\textsubscript{0.27} materials increased from 170 V/K at 1.75 GPa to the peak value of 210 V/K at 2 GPa then decreased to 160 V/K at 2.2 GPa. This phenomenon is also found for materials with a different composition, Bi\textsubscript{2}Te\textsubscript{2.7}Se\textsubscript{0.3}, which
shows a curve with a peak value of Seebeck coefficient 155 V/K at 1.75 GPa indicating this relationship exists for materials with different compositions and the optimal pressure for the highest Seebeck coefficient varies.

There are several possible parameters that could shift the Seebeck coefficient. For heavily doped semiconductors in our case, the Seebeck coefficient is mainly determined by the charge carrier concentration \( n \) according to the Eq. 3.26 which is shown below again

\[
S = \left( \frac{2\pi^2 k_B^2}{3e\hbar^2} \right) m^* T \left( \frac{\pi}{3n} \right)^{2/3}
\]

where \( k_B \) is the Boltzmann constant, \( e \) is the electron charge, \( \hbar \) is the Planck's constant, \( m^* \) is the effective mass and \( n \) is the carrier concentration. This equation suggests that the Seebeck coefficient is roughly inverse proportional to the carrier concentration which is consistent with our measurements as shown in Figure 13.2 (c). The carrier concentration changes with the pressure where the minimum value corresponds to the maximum Seebeck coefficient at 2.0 GPa.

13.3.2 Tuning of Carrier Concentration

The variations in the carrier concentration are attributed to the differences in the density of antisite defects given the same chemical composition. It was found that applied pressure can induce the formation of antisite defects [143].

Antisite Defects

In a perfect Bi\(_2\)Te\(_3\) crystal, the atoms crystalize with alternate layers of Bi and Te as the following,

\[
\text{--Te}_1 - \text{Bi} - \text{Te}_2 - \text{Bi} - \text{Te}_1 --
\]  

(13.2)

When Se atoms were added, they substitute with Te\(_1\) or Te\(_2\). However, some Te\(_1\) or Te\(_2\) sites can be occupied by the Bi atoms that create antisite defects (Bi\(_{Te_1}\), Bi\(_{Te_2}\)) in the event of less Se in the material. Intrinsically, there is a third possible antisite defect: the Te atoms go to the Bi sites (Te\(_{Bi}\)). Bi\(_{Te_1}\) could be the most favorable under pressure as this configuration requires the smallest energy to form among the three possible antisite defects and the formation energy decreases as the pressure increases [143]. Therefore higher concentration of antisite defects is expected at higher pressure. The Bi\(_{Te_1}\) antisite defects are acceptors with a positive charge. When their concentration increases, more negatively charged electrons, the majority charge carriers in the n-type material, are neutralized and therefore the carrier concentration decreases. When the pressure is larger than 2 GPa, it is suspected that the differences in the
formation energy between Bi_{Te_1}, Bi_{Te_2} and Te_{Bi} become smaller and therefore the differences in their concentrations decrease. Their contributions to the overall carrier concentration diminish as the positively charged Bi_{Te_1} and Bi_{Te_2} are canceled out by negatively charged Te_{Bi}.

Another possible reason for this relationship is the modifications in the energy gap at high pressure associated with structure change [144, 145, 146]. It was found that the band gap in the p-type Bi_2Te_3 and In_{0.04}Bi_{1.96}Te_3 alloy decreases as the applied pressure increases from 1 to 6 GPa with a phase transition near 2.5 to 4.5 GPa that adjusts the band extremes. Although the XRD spectra from our samples did not indicate any obvious second phase, as shown in Figure 13.1, the distortion of structure may still play an important role in the variations of the Seebeck coefficients which requires other techniques to characterize.

![X-ray diffraction spectra](image)

**Figure 13.1**: X-ray diffraction spectra of bulk Bi_{2Te_{2.7}Se_{0.27}} samples hot pressed at pressure from 1.75 to 2.1 GPa as well as that from materials before hot pressing (as-milled powder). The peaks are indexed according to PDF #15-0863.

### 13.3.3 Properties by Low Pressure

Compared to the above mentioned studies, the Seebeck coefficient is controlled by relatively lower pressure in the range from 1 to 2.2 GPa. This shift could be due to the simultaneous applications of heat and pressure during the consolidation process. The temperature aids the atom diffusion and alters the lattice parameter therefore this relationship can be observed at
lower pressure. The pressure effect on the Seebeck coefficient in this work was found at room
temperature after the pressure was released. This could be attributed to the process settings.
The hot pressing pressure was kept until the temperature was lower than 220 °C. Meanwhile a
post consolidation heat treatment at 250 °C did not show significant differences in the Seebeck
coefficient and carrier concentration, suggesting the structure is thermally stable below 250
°C. Therefore the material state at high pressure is at least partially maintained at room
temperature and zero applied pressure.

**13.3.4 Microstructure**

To better understand the microstructure, the TEM figures of Bi$_2$Te$_{2.7}$Se$_{0.27}$ consolidated at
1.75 and 2 GPa are obtained, as shown in Figure 13.2 (a) and (b) respectively. There are
no significant differences in their microstructure as expected because either the density of the
antisite defects or the modification of the band gap is out of the resolution of this analysis. Both
materials show typical nanocomposite structures: grain size from 0.1 to a few micron meters
with small precipitates, indicated by the white arrows, about 10 nm and less dispersed inside
the grains. The grains are both closely packed and have clean grain boundaries. There are no
voids observed which is consistent with the fully dense results by Archimedes measurements.
The precipitates can be observed in almost 80% of the grains, especially in the large micron
sized grains.
Figure 13.2: Microstructure figures of consolidated Bi$_2$Te$_{2.7}$Se$_{0.27}$ hot pressed at 1.75 GPa, (a), and 2 GPa, (b) by TEM along with absolute Seebeck coefficients and carrier concentration as a function of hot pressing pressure, (c). The solid squares and triangles represent the absolute Seebeck coefficients from n-type Bi$_2$Te$_{2.7}$Se$_{0.27}$ and Bi$_2$Te$_{2.7}$Se$_{0.3}$ respectively. The carrier concentration of Bi$_2$Te$_{2.7}$Se$_{0.27}$ is indicated by the open squares to the right axis.
In conclusion, we have demonstrated high performance nano-composite materials of both n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ and p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ alloy thermoelectric materials with significantly enhanced figure of merit ($ZT$) between 25 and 175 °C. Using an optimized high-pressure compaction process, we have shown a drastic enhancement in $ZT$ for bulk n- and p-type materials, with $ZT$ as high as 2.5 obtained around 100 °C for n-type and as high as 3 around 50-to-100 °C for p-type, thus allowing us to break through the $ZT > 2$ barrier in bulk thermoelectric materials.

By incorporating a high concentration of nanoscale structures, a significant improvement of the Seebeck coefficient was achieved while reducing lattice thermal conductivity as well. This has allowed us to establish an early heat-to-electric power device with conversion efficiency nearly 40 to 52% better than the state-of-the-art commercially available devices. The material and device results reported in this study therefore represent an important transition of nano-bulk thermoelectric materials to device technology for a wide range of power generation and efficient waste heat recovery applications. For example, a device conversion efficiency of 7.9% is expected to lead to a relative improvement of 5% in fuel efficiency, an important threshold, in automotive waste heat recovery.

The performance of the Bi$_2$Te$_3$ system is very sensitive to their microstructure given the same chemical composition, which is mostly determined by the processing history, especially those involving elevated temperature. Therefore, a more precise and complete ternary phase diagram, or real time electron microscope observations, would be helpful to understand the evolution of microstructure as a function of temperature. On the other hand, it might be interesting to test the materials’ transport properties at low temperatures, such as -50 °C to
room temperature.

The details of the nanoscale precipitates, such as composition, structure, density, in both n and p-type materials require more research by high resolution transmission electron microscope. Their presence obviously tuned the properties significantly. Similarly, the subtle changes in the density of the antisite defects, electron energy gap and microstructure caused by the high pressure need more specific study to resolve the science.

On the road to mass production, the above mentioned are the major concerns to obtain more consistent material microstructure and thus performance, while the fabrication techniques, mainly the mechanical alloying and hot pressing are very mature already. The material process in this work has been optimized for the room temperature as-milled powders, but needs to be fine-tuned for the 77 K as-milled powders in order to improve the power factor in the resulting compactions. Nevertheless, similar processing procedure could be applied to other material systems, such as PbTe, SiGe, CoSb$_3$, to potentially improve their thermoelectric figures of merit.
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