Thermoelectric Properties of P-Type Nanostructured Bismuth Antimony Tellurium Alloyed Materials

Author: Yi Ma

This work is posted on eScholarship@BC, Boston College University Libraries.

Boston College Electronic Thesis or Dissertation, 2009

Copyright is held by the author, with all rights reserved, unless otherwise noted.
Boston College
The Graduate School of Arts and Sciences
Department of Physics

THERMOELECTRIC PROPERTIES OF P-TYPE
NANOSTRUCTURED BISMUTH ANTIMONY TELLURIUM
ALLOYED MATERIALS

a dissertation

by

Yi Ma

submitted in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

August 2009
© copyright by Yi Ma

2009
THERMOELECTRIC PROPERTIES OF P-TYPE NANOSTRUCTURED BISMUTH ANTIMONY TELLURIUM ALLOYED BULK MATERIALS

by

Yi Ma

Advisor: Professor Zhifeng Ren

Abstract

Solid-state cooling and power generation based on thermoelectric effects are attractive for a wide range of applications in power generation, waste heat recovery, air-conditioning, and refrigeration. There have been persistent efforts on improving the figure of merit ($ZT$) since the 1950’s; only incremental gains were achieved in increasing $ZT$, with the $(\text{Bi}_{1-x}\text{Sb}_x)_{2}(\text{Se}_{1-y}\text{Te}_y)_3$ alloy family remaining the best commercial material with $ZT \sim 1$. To improve $ZT$ to a higher value, we have been pursuing an approach based on random nanostructures and the idea that the thermal conductivity reduction that is responsible for $ZT$ enhancement in superlattices structures can be realized in such nanostructures.

The synthesis and characterization of various nanopowders prepared by wet chemical as well as high energy ball milling methods will be discussed in this dissertation. The solid dense samples from nanopowders were prepared by direct current induced hot press (DC hot press) technique. The thermoelectric properties of the hot pressed samples have been studied in detail.
By ball milling ingots of bulk alloy crystals and hot pressing the nanopowders, we had demonstrated a high figure-of-merit in nanostructured bulk bismuth antimony telluride. In this dissertation, we use the same ball milling and hot press technique, but start with elemental chunks of bismuth, antimony, and tellurium to avoid the ingot formation step. We show that a peak $ZT$ of about 1.3 can be achieved. Our material also exhibits a $ZT$ of 0.7 at 250 °C, close to the value reached when ingot was used. This process is more economical and environmentally friendly than starting from bulk alloy crystals. The $ZT$ improvement is caused mostly by the low thermal conductivity, similar to the case using ingot. Transmission electron microscopy observations of the microstructures suggest that the lower thermal conductivity is mainly due to the increased phonon scattering from the high density grain boundaries and defects.

The performance of thermoelectric materials is determined by its dimensionless figure-of-merit ($ZT$) which needs to be optimized within a specific temperature range for a desired device performance. Hence, we show that by varying the Bi/Sb ratio, the peak $ZT$ can be shifted to a higher or lower temperature for power generation applications or a cooling mode operation. A peak $ZT$ of about 1.3 is achieved from a Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composition which is highest among the different compositions. These nanostructured bulk samples have a significantly low lattice thermal conductivity compared to the bulk samples due to the increased phonon scattering in the grain boundaries and defects. This study shows that Bi$_{0.5}$Sb$_{1.5}$Te$_3$ may potentially perform better for cooling devices, while Bi$_{0.3}$Sb$_{1.7}$Te$_3$ should be able to show better power generation efficiency.

Several issues related to accurate measurement of thermoelectric properties were identified and many of them were solved during my studies and these are discussed in this
thesis. With the data we obtained, it is clear that nanopowder-based thermoelectric materials hold significant promise. Therefore, a review of synthesis of nanostructured materials by solution-based methods, including a hydrothermal process for the Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_2$Te$_{2.25}$Se$_{0.75}$ nanoparticles, a solvothermal route for Sb$_2$Te$_3$ nanostructures, and a polyol process for the preparation of Bi nanostructures is presented in this dissertation. These new nanostructures may find applications in enhancing the thermoelectric performance. Although small sized and well dispersed nanopowders of various thermoelectric materials could be prepared by a solution method in large scale, contamination and partial oxidation are always big challenges in a chemical approach. Hence, a high energy ball milling technique to prepare thermoelectric nanopowders in large scale and without major contamination is still found to be more efficient and preferred.
Acknowledgements

I am extremely indebted to my advisor, Prof. Zhifeng Ren, for his enlightening mentoring, detailed instructions, high-standard education and fatherly generosity. It is beyond words to describe how much his characters and guidance affected me in a very positive way, towards not only more substantial accomplishments down the road as a professional but also a higher class of life as a person. His door is always open to all students for discussions and help. Time after time, his easy grasp of problem at its most fundamental level helped me in the struggle for my own understanding. I would like to express my sincere appreciation to him.

I would like to express my most sincere thinks to the committee members of this dissertation who offered tremendous guidance and contributions to my efforts involved in this dissertation and to my general academic activities during the pursuit of my degree. It is truly a privilege to be working with and under the instruction of such a group of prestigious scholars, Prof. Zhifeng Ren, Prof. David Broido, Prof. Michael Graf, Prof. Cyril P. Opeil, SJ and Prof. Gang Chen., who have always been ready to spend time and effort in my education and personal development. I especially thank to Professor Gang Chen for his insightful opinions and extremely valuable advices.

Thanks and gratitude are also given to Dr. D. Z. Wang, Dr. B. Poudel, Dr. Y. C. Lan, Dr. J. Rybczynski, Dr. Y. Tu, Dr. D. Banerjee, Mr. B. Yu, Mr. J. Yang, Mr. X. Yan, Mr. H. Wang, Mr. X. W. Wang, Mr. G. H. Zhu, Mr. G. R. Joshi, Dr. S. Chen and many others who helped walk me through daily research in every aspect along the way. Their kindly help and unselfishness is fully appreciated and will never be forgotten.

Finally, I would like to offer special thanks to my family, my grandparents, uncles and aunts, for their long term support to my career and for the joy of my life. It is certainly beyond thanks could say about how much I owe to my beloved parents for their complete devotion and unconditional support before and ever after.

Yi Ma
August 2009
Chapter 1 Introduction

1.1. Fundamentals of Thermoelectrics

1.1.1. The Thermoelectric Effects

1.1.1.1. The Seebeck and Peltier Effects

1.1.1.2. The Thomson Effect

1.1.1.3. Kelvin Relations

1.1.2. Thermoelectric Figure of Merit and Efficiency of Thermoelectric Devices

1.1.2.1. The Figure of Merit

1.1.2.2. Efficiency of Thermoelectric Devices

1.1.2.3. Necessary Criteria for High Performance Thermoelectric Materials

1.1.3. Thermoelectric Transport Theory

1.1.3.1. The Boltzmann Equation

1.1.3.2. Electrical Conductivity

1.1.3.3. Seebeck Coefficient
Chapter 2 Measurement Techniques of Thermoelectric Properties………38

2.1. Introduction.................................................................38
2.2. Measurement Principles..................................................40
  2.2.1. Electrical Conductivity.................................................40
  2.2.2. Seebeck Coefficient..................................................43
  2.2.3. Thermal Conductivity................................................45
2.3. Integrated Measurement using a Vacuum Cryo-chamber....................46
  2.3.1. Electrical Conductivity Measurement..........................47
  2.3.2. Seebeck Coefficient Measurement..............................48
  2.3.3. Thermal Conductivity Measurement.............................50
2.4. Electrical Conductivity and Seebeck Coefficient Measurement by Commercial Equipment (ZEM-3, Ulvac Inc.)..........................................................55
2.5. NanoFlash Technique for Thermal Diffusivity Measurement................60
2.6. Specific Heat Measurement.............................................64
2.7. Hall Measurements at Room Temperature................................67
2.8. References....................................................................72
Chapter 3 Synthesis of p-type Nanostructured Bismuth Antimony Tellurium Alloys and Their Thermoelectric Properties

3.1. Introduction

3.2. General Properties of Bismuth Telluride and Its Alloys

3.3. Experimental Procedures

3.3.1. Preparation of Nanostructured Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloys by Mechanical Alloying

3.3.2. Consolidation of As-prepared Nanopowders

3.4. Results and Discussion of p-type Nanostructured Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloy Samples

3.4.1. Measurement Results and Theoretical Analysis for Our Best Hot-pressed Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloy Samples

3.4.2. Microstructures Study of p-type Hot-pressed Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloy Samples

3.4.3. Optimization of p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloy Samples

3.4.3.1. Effect of Ball Milling Time

3.4.3.2. Effect of Hot-press Temperature

3.4.3.3. Effect of Holding Time

3.5. Results and Discussion of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ Alloy Samples

3.6. Summary

3.7. References

Chapter 4 The Effect of Bi/Sb Ratio on Thermoelectric Properties in p-type Nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ Alloys

4.1. Introduction
4.2. Experimental and Results of p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ Alloy Samples Made from Planetary Ball Mill Machine………………………………………………………………..111

4.3. Experimental and Results of p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ Alloy Samples Made from High Energy Mixer/Mills Machine……………………………………………………………..121

4.3.1. Thermoelectric Properties of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Composition…………………...123
4.3.2. Thermoelectric Properties of $\text{Bi}_{0.45}\text{Sb}_{1.55}\text{Te}_3$ Composition…………………125
4.3.3. Thermoelectric Properties of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ Composition…………………...126
4.3.4. Thermoelectric Properties of $\text{Bi}_{0.35}\text{Sb}_{1.65}\text{Te}_3$ Composition…………………128
4.3.5. Thermoelectric Properties of $\text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3$ Composition…………………...129
4.3.6. Thermoelectric Properties of $\text{Bi}_{0.25}\text{Sb}_{1.75}\text{Te}_3$ Composition…………………132

4.4. Summary………………………………………………………………………….134

4.5. References………………………………………………………………………...136

Chapter 5 Synthesis and Characterization of Various Nanostructures by Wet Chemical Methods………………………………………………………………………..138

5.1. Introduction………………………………………………………………………….138

5.2. Bi-based Nanostructures Synthesized by Wet Chemical Methods…………….140

5.2.1. Motivation and Background…………………………………………………..140

5.2.2. $\text{Bi}_2\text{Se}_3$ Nanoparticles Synthesized by Hydrothermal Method……………..143

5.2.3. $\text{Bi}_2\text{Te}_3$ Nanoparticles Synthesized by Hydrothermal Method……………..146

5.2.4. $\text{Bi}_2\text{Te}_{2.25}\text{Se}_{0.75}$ Nanoparticles Synthesized by Hydrothermal Method……..149

5.2.5. Single Crystalline Bismuth Nanostructures by Polyol Process…………………151

5.3. Synthesis of Single-Crystalline Antimony Telluride Hexagonal Nanoplates Using a
Summary

166
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC hot press</td>
<td>Direct current induced hot press</td>
</tr>
<tr>
<td>TE</td>
<td>Thermo-electric</td>
</tr>
<tr>
<td>BM</td>
<td>Ball mill or ball milling</td>
</tr>
<tr>
<td>SOA</td>
<td>State-of-the-art</td>
</tr>
<tr>
<td>QDSL</td>
<td>Quantum dot superlattice</td>
</tr>
<tr>
<td>PF</td>
<td>Power factor</td>
</tr>
<tr>
<td>COP</td>
<td>Coefficient of performance</td>
</tr>
<tr>
<td>LAST</td>
<td>Silver lead antimony telluride</td>
</tr>
<tr>
<td>D</td>
<td>Dimensions</td>
</tr>
<tr>
<td>ac</td>
<td>Alternating current</td>
</tr>
<tr>
<td>dc</td>
<td>Direct current</td>
</tr>
<tr>
<td>amb</td>
<td>Ambient</td>
</tr>
<tr>
<td>avg</td>
<td>Average</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
</tr>
<tr>
<td>EMF</td>
<td>Electro-motive force</td>
</tr>
<tr>
<td>TC</td>
<td>Thermocouple</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>EDA or EDX</td>
<td>Energy diffraction x-ray analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-energy TEM</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>DI water</td>
<td>De-ionized water</td>
</tr>
<tr>
<td>NTs</td>
<td>Nanotubes</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>NWs</td>
<td>Nanowires</td>
</tr>
<tr>
<td>PF*T</td>
<td>Power factor times temperature</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Z</td>
<td>Figure-of-merit</td>
</tr>
<tr>
<td>ZT</td>
<td>Dimensionless-figure-of-merit</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>S or $\alpha$</td>
<td>Seebeck coefficient</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>Peltier coefficient</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Thomson coefficient</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Fermi energy</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Scattering time</td>
</tr>
<tr>
<td>$e$</td>
<td>Electronic charge</td>
</tr>
<tr>
<td>$w_D$</td>
<td>Debye frequency</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Shear modulus</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility</td>
</tr>
<tr>
<td>$W$</td>
<td>Thermal resistance</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Debye temperature</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Coefficient of performance</td>
</tr>
<tr>
<td>$n$</td>
<td>Carrier concentration</td>
</tr>
<tr>
<td>$m^*$</td>
<td>Effective mass</td>
</tr>
<tr>
<td>$k_L$</td>
<td>Lattice thermal conductivity</td>
</tr>
<tr>
<td>$R_H$</td>
<td>Hall coefficient</td>
</tr>
<tr>
<td>$q''$</td>
<td>Heat flux</td>
</tr>
<tr>
<td>$T_h$</td>
<td>Hot side temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Cold side temperature</td>
</tr>
<tr>
<td>$A$</td>
<td>Area of cross section</td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>Half time</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Diffusivity</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat capacity</td>
</tr>
</tbody>
</table>
$E_b$  
Energy barrier

$N_d$  
Carrier density

$J$  
Current density
Lists of Figures and Tables

Fig. 1.1.1. Thermoelectric effects in a single material. A temperature difference induces a voltage through the material, and current flow induces heat flow through the material. .................................................................5

Fig. 1.1.2. A simple sketch showing heat transfer across the junctions (Presentation at DTEC by T. Hogan, MSU). .................................................................6

Fig. 1.1.3. Schematic of a thermoelectric power generator (left) and a thermoelectric cooler (right). .................................................................8

Fig. 1.1.4. Thermoelectric properties as a function of carrier concentration. .................11

Fig. 1.1.5. Maximum temperature difference for a single stage thermoelectric refrigerator plotted against $ZT$. The heat sink is set at 300 K. ........................................12

Fig. 1.1.6. Theoretical efficiency of ideal thermoelectric devices working at different temperatures as a function of the materials’ figure of merit. .........................14

Fig. 1.1.7. State-of-the-art thermoelectric materials. ........................................16

Fig. 1.2.1. Quantum well superlattice (left) and quantum wire (right). Each layer thickness in superlattice is 2 nm. Quantum confinement and boundary scattering are expected to result in the high Seebeck coefficient and low thermal conductivity without a decrease in electrical conductivity. ..............................31

Fig. 1.2.2. Experimental and calculated thermal conductivity of SiGe superlattices in both in-plane and cross-plane, normalized to thermal conductivity of SiGe bulk alloy. Solid lines were calculated by lattice dynamics simulation. The experimental results are lower than the calculated results. ........................................32

Fig. 2.2.1. Schematic of four probe electrical conductivity measurement. .......................41

Fig. 2.2.2. Slope method for electrical conductivity measurement. ..............................41

Fig. 2.2.3. Schematic of the Seebeck coefficient measurement. ...................................44

Fig. 2.3.1. Picture of integrated measurement system probe head. ................................46

Fig. 2.3.2. Picture of the home built electrical, Seebeck, and thermal properties measurement system from liquid nitrogen up to 350 °C. .................................47
Fig. 2.3.3. Demonstration of measurement results of two temperature points along a sample by Angstrom method. The red one corresponds to the thermocouple, which is to heat source at \( x=x_1 \), and the blue one is at \( x=x_2 \), which is farther from the heater showing reduction of amplitude. \( M \) and \( N \) are the amplitudes of each signal, and \( dt \) is the phase difference between signals. 53

Fig. 2.4.1. Schematic of electrical conductivity measurement system. 56

Fig. 2.4.2. A picture of sample holder with mounted sample (left) and sample dimensions (right). 57

Fig. 2.4.3. A picture of Seebeck and electrical properties measurement system (ZEM-3, Ulvac Inc.). 57

Fig. 2.4.4. Schematic of Seebeck coefficient measurement system. 59

Fig. 2.4.5. Computation of Seebeck coefficient from \( \Delta V \) vs. \( \Delta T \) plot. 60

Fig. 2.5.1. A simple sketch of Nanoflash setup system. 61

Fig. 2.5.2. Nanoflash LFA 447 (Netzsch Instruments, Inc.) equipment for thermal diffusivity measurement. 62

Fig. 2.5.3. Temperature rise curve plotted against dimensionless time \( \omega \). 63

Fig. 2.6.1. A simple sketch of DSC setup system. 65

Fig. 2.6.2. DSC 200 F3 Maia® (Netzsch Instruments, Inc.) instrument for specific heat measurement. 66

Fig. 2.6.3. DSC data from an actual measurement. 67

Fig. 2.6.4. The calculated \( C_p \) for a typical sample. 67

Fig. 2.7.1. Schematic of the Hall Effect in a long, thin bar of semiconductor with four ohmic contacts. The direction of the magnetic field \( B \) is along the \( z \)-axis and the sample has a finite thickness \( t \). 68

Fig. 2.7.2. Schematic of the measurement set-up. 69

Fig. 2.7.3. Home-built Hall measurement system. 69

Fig. 2.7.4. Graph demonstration for the determination of the magnetic field direction. 70

Fig. 3.2.1. Crystal structure of bismuth telluride: (a) rhombohedric unit cell, (b) hexagonal unit cell, and (c) projection in YZ plane. 77
Fig. 3.2.2. Band structure of bismuth telluride. .............................................................78

Fig. 3.3.1. Pictures of A) planetary ball mill machine (PM100, Glen Mills Inc.), B) and C) a ball milling jar (open and sealed respectively). .............................................81

Fig. 3.3.2. (A) XRD pattern of the nanopowders after ball milling, (B) SEM, (C) bright-field TEM image, and (D) HRTEM image of the mechanically alloyed nanopowders from elements. .................................................................82

Fig. 3.3.3. A simple sketch of dc hot-press system (left) and a real picture of it (right). ...84

Fig. 3.3.4. Pictures of a hot-pressed sample (left) and a cut bar sample (right) for power factor measurement. .................................................................84

Fig. 3.4.1. (A) Electrical conductivity, (B) Seebeck coefficient, (C) power factor, (D) thermal conductivity, and (E) ZT dependence of temperature of hot-pressed nanocrystalline bulk samples with Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$ nominal composition made from elemental chunks in comparison with a commercial ingot and a nanocrystalline bulk sample made from ingot. ..............................................87

Fig. 3.4.2. Thermal conductivities of BiSbTe samples. Pink and navy blue lines represent measured total thermal conductivities for crystalline ingot and our nanograinied samples, respectively. Sky blue and yellow lines represent the corresponding calculations of the lattice part of the thermal conductivity, respectively. ..........90

Fig. 3.4.3. TEM images showing the microstructures of hot-pressed nanocrystalline dense bulk samples made from elemental chunks. (A) low-magnification image showing the submicrometer grains, (B) HRTEM image showing high crystallinity and random orientation, (C) bright-field TEM image and (D) HRTEM image showing Sb precipitates of about 50 nm in the matrix, EDX patterns (inset of Fig. 3.4.2C) show that the precipitates are pure Sb (marked with 1) and the matrix are BiSbTe alloy (marked with 2). HRTEM images (E) and (F) showing the nanodots of various sizes (2-3 nm in E indicated by the arrows and 10-15 nm in F) inside the BiSbTe matrix. .................................................................92

Fig. 3.4.4. XRD patterns for powders with different lengths of ball milling time. ..........94

Fig. 3.4.5. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D), and ZT (E) of various samples
from powders with different lengths of ball milling time. …………………..95

**Fig. 3.4.6.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D), and $ZT$ (E) of various samples hot-pressed at different temperatures. …………………………………………..97

**Fig. 3.4.7.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various samples pressed at 500 °C and held for 0, 1, 2, and 6 mins, respectively. ………………99

**Fig. 3.5.1.** (A) XRD pattern of Sb$_2$Te$_3$ nanopowders after 90 hrs ball milling, (B) SEM, (C) bright-field TEM images, and (D) HRTEM image of the mechanically alloyed nanopowders. ………………………………………………………………….101

**Fig. 3.5.2.** (A) XRD pattern of Bi$_2$Te$_3$ nanopowders after 44 hrs ball milling, (B) SEM, and (C) HRTEM image of the mechanically alloyed nanopowders. ………………102

**Fig. 3.5.3.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), thermal conductivity (C) and $ZT$ (D) of a typical Sb$_2$Te$_3$ composition sample hot-pressed at 500 °C and held for 2 mins. ……………………………………103

**Fig. 3.5.4.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), thermal conductivity (C) and $ZT$ (D) of a typical Bi$_2$Te$_3$ composition sample hot-pressed at 500 °C and held for 0 min. …………………………………….104

**Fig. 4.2.1.** XRD patterns of the nanopowders with different nominal compositions. ………113

**Fig. 4.2.2.** Typical SEM (A), low- (B), and high- (C) magnification TEM images of fully mechanically alloyed nanopowders from a typical composition (Bi$_{0.6}$Sb$_{1.6}$Te$_3$ here). …………………………………………………………………………...114

**Fig. 4.2.3.** Temperature dependence of electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D), and $ZT$ (E) of hot-pressed nanocrystalline bulk samples with different nominal compositions. …………118

**Fig. 4.2.4.** Temperature dependence behavior of specific heat for samples with different nominal compositions. ………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………… …
dense grains, (C) high-magnification TEM images showing Sb precipitates of about 50 nm in the grains, and (F) high-magnification TEM image showing the boundaryless nanodots inside the BiSbTe matrix.

Fig. 4.3.1. Pictures of A) high-energy ball mill machine (SPEX SamplePrep 8000M Mixer/Mills) and B) a ball mill vial (open and sealed respectively).

Fig. 4.3.2. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ composition samples pressed at 530 °C and held for 2 mins.

Fig. 4.3.3. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various Bi$_{0.45}$Sb$_{1.55}$Te$_3$ composition samples.

Fig. 4.3.4. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composition samples.

Fig. 4.3.5. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various Bi$_{0.35}$Sb$_{1.65}$Te$_3$ composition samples hot-pressed at different temperatures.

Fig. 4.3.6. XRD pattern of the as-prepared Bi$_{0.3}$Sb$_{1.7}$Te$_3$ nanopowders after 20 hrs ball milling.

Fig. 4.3.7. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various Bi$_{0.3}$Sb$_{1.7}$Te$_3$ composition samples hot-pressed at different temperatures.

Fig. 4.3.8. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various Bi$_{0.25}$Sb$_{1.75}$Te$_3$ composition samples hot-pressed at different temperatures.

Fig. 5.2.1. A) Nanoparticles into a host material and B) two different types of nanoparticles forming nano-composites.

Fig. 5.2.2. Predicted thermal and electrical properties of SiGe nanocomposite materials.

Fig. 5.2.3. Picture of a high temperature high pressure reaction vessel.

Fig. 5.2.4. A) Low magnification TEM image, B) high magnification TEM image, C) XRD
pattern, and D) EDX spectra of as prepared Bi$_2$Se$_3$ nanoparticles. ...............145

**Fig. 5.2.5.** A) Low magnification SEM image, B) high magnification SEM image, C) XRD pattern, D) EDX spectra, E) low magnification TEM image, and F) high magnification TEM image of as prepared Bi$_2$Te$_3$ nanoparticles. ...............147

**Fig. 5.2.6.** A) XRD pattern, B) medium resolution TEM image, and C) high resolution TEM image of as prepared Bi$_2$Te$_{2.25}$Se$_{0.75}$ nanoparticles. ........................................150

**Fig. 5.2.7.** a) Low-magnification TEM image of the as-prepared Bi nanocubes, b) HRTEM image and corresponding SAED pattern of a single cube, and c) XRD pattern of the as-prepared Bi nanocubes. ................................................153

**Fig. 5.2.8.** TEM images of A) triangular Bi nanoplates, B) spherical nanoparticles prepared with molar ratio of PVP and Bi of 5, and C) typical Bi nanobelts. D) Low-magnification SEM image of as-prepared Bi nanobelts. .........................154

**Fig. 5.3.1.** A) High-magnification SEM image and B) XRD pattern of the as-prepared Sb$_2$Te$_3$ nanoplates. C) Typical TEM image of an individual hexagonal nanoplate and D) HRTEM image of the marked area shown in C). Both the HRTEM and the SAED pattern show that the nanoplate is a single crystal. .........................157

**Table 3.4.1.** Mobility and carrier concentration at room temperature of our nanocrystalline bulk samples with Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nominal composition made from elemental chunks in comparison with the commercial ingot and the nanocrystalline bulk samples made from ingots. ...........................................88

**Table 4.2.1.** Room temperature carrier concentration and mobility data of our hot pressed nanocrystalline bulk samples with the different nominal compositions. ......116
List of Publications


Chapter 1

Introduction

Providing a sustainable supply of energy to the world’s population will become a major societal problem for the 21st century as fossil fuel supplies decrease and world demand increases. Thermoelectric phenomena, which involve the conversion between thermal and electrical energy and provide a method for heating and cooling materials, are expected to play an increasingly important role in meeting the energy challenge of the future. The thermoelectric effects were discovered early in the 19th century but it was only in the second half of the 20th century when Ioffe [1] found that doped semiconductors alloys have better thermoelectric performance than pure metals or semiconductors. This was when thermoelectric generation became reasonably efficient and thermoelectric refrigeration became even practicable. Despite high cost and relatively low efficiency of thermoelectric devices, these devices promised some revolutionizing features compared to conventional power generators or cooling devices. Because there are no moving parts, these devices are silent, reliable, and have a long lifetime without maintenance. Also, these devices are environmentally friendly, can be made portable or very small for local cooling, and have better temperature accuracy when needed.

During 1960-1990, the thermoelectrics field received little attention from the worldwide scientific research community. Nevertheless, the thermoelectrics industry grew
slowly and steadily by finding niche applications for space missions, laboratory equipment, and medical applications. In these applications, cost and energy efficiency were not as important as energy availability, reliability, predictability, and the quiet operation of equipment. In the early 1990s, the US Department of Defense (DoD) became interested in the potential of thermoelectrics for new types of applications. As a result the DoD encouraged the research community to re-examine research opportunities for advancing thermoelectric materials to the point that they could be used more competitively for cooling and power-conversion applications from a performance standpoint [2]. As a result of this stimulation, thermoelectric research experienced a rebirth. Two different research approaches were taken for developing the next generation of new thermoelectric materials. One uses new families of advanced bulk thermoelectric materials [3-5], which focused on new categories of materials that contained heavy-ion species with large vibrational amplitudes (rattlers) at partially filled structural sites, thereby providing effective phonon-scattering centers. The most prominent of these advanced bulk materials are the so-called phonon-glass/electron-crystal (PGEC) materials [6] (such as the partially filled skutterudites based on alloys of CoSb3 [7]). Another approach is the use of nanostructures that improve or maintain electron performance through quantum size effects [8-9] or interface energy filtering, while concurrently reducing the phonon thermal conductivity through interface scattering [10]. Large increases in ZT have been observed in Bi2Te3/Sb2Te3 superlattices (SL) and PbTe/PbSeTe quantum dot superlattices (QDSL) [11-12].
Recently, the two approaches seem to be coming together again. Firstly, the most successful new bulk thermoelectric materials are host materials containing nanoscale inclusions that are prepared by using chemical approaches [13]. Secondly, low-dimensional materials systems are now being assembled as nanocomposites containing a coupled assembly of nanoclusters showing short-range low dimensionality embedded in a host material [14-15], thereby producing a bulk material with nanostructures and many interfaces that scatter phonons more effectively than electrons. In this chapter, a brief review of thermoelectric phenomena and current challenges are presented. Additionally, our approach [16-17] for the development of new thermoelectric materials to achieve better performances will be discussed.

1.1. Fundamentals of Thermoelectrics

1.1.1. The Thermoelectric Effects

When a material is subjected to a thermal gradient, an electrical field is created in the opposite direction. Conversely, when an electrical current is passed through a material, a temperature gradient is created. These phenomena are called thermoelectric effects. The physical principles used to explain thermoelectric effects, the use of these principles, and how they relate to the development of the new advanced materials which have large thermoelectric effects, will be discussed and reviewed in this chapter.
1.1.1. The Seebeck and Peltier Effects

Seebeck discovered the effect that bears his name in 1821 [18]. In this effect, a voltage appears when two different conductors are joined together and the junction is heated. This phenomenon is familiar to all scientists and engineers, as it has long been used in the measurement of temperature. This is also the principle of power generation. The Peltier effect, discovered in 1834, is not so well known. When an electric current passes through the junction between two conductors, that junction becomes heated or cooled according to the direction of the current. As we shall see, it is possible to choose the conductors so that the Peltier effect can be used to produce worthwhile cooling and so that the efficiency of generation through the Seebeck effect becomes large enough for certain purposes.

The thermoelectric effects can also occur for any single isolated material. Figure 1.1.1 illustrates the thermoelectric effects in a single material. A material that is subjected to a temperature gradient can generate a voltage and the ratio of the voltage to the temperature difference is called the Seebeck coefficient $S$

$$S = -\frac{dV}{dT}. \quad (1.1.1)$$

The Seebeck coefficient is assigned a positive value if the voltage tends to drive a current from end 1 to end 2 through the conductor when 1 is at a higher temperature than 2.

The Peltier coefficient $\Pi_{ab}$ of a pair of materials at a junction is defined as the ratio of heat flow $Q$ to current flow $I$. 
Here Π is the Peltier coefficient, Π_{ab} is the coefficient of the entire thermocouple, and Π_a and Π_b are the coefficients of each material. The Peltier effect is caused by the fact that a heat current in a homogeneous conductor accompanies an electric current even at constant temperature. The heat current accompanies an electric current is explained by the different flow velocities of the electrons carrying the electric current. The flow velocities depend on the energies of the conduction electrons. Thus, if the flow velocity of electrons with energy above the chemical potential (Fermi energy) is higher than that for electrons with lower energy, the electric current is accompanied by a heat current in the opposite direction (since the electronic charge is negative!).

![Diagram](image)

**Fig. 1.1.1.** Thermoelectric effects in a single material. A temperature difference induces a voltage through the material, and current flow induces heat flow through the material.

A physical picture of heat transfer mechanism in using semiconducting thermoelements is shown in Fig. 1.1.2. When holes are charge carriers (p-type), the heat is transported along the direction of the hole current. Similarly, when electrons are charge carries (n-type), the heat is transported along the direction of the electron current. The holes
move in the valance band and the electrons move in the conduction band which have energies different from the metal Fermi energies ($E_F$) at the junctions. Thus the carriers either emit or absorb the energy at the junctions creating cooling or heating effects.

Fig. 1.1.2. A simple sketch showing heat transfer across the junctions (Presentation at DTEC by T. Hogan, MSU).

Since heat is absorbed at one junction, the Peltier effect can be used to transfer heat from one to another junction, which is the principle of thermoelectric cooling. However, in typical conductors, Joule heating dominates, making efficient Peltier cooling a difficult task.

1.1.1.2. The Thomson Effect

The Thomson effect describes the heating or cooling of a current-carrying conductor with a temperature gradient. Any current-carrying conductor with a temperature difference between two points will either absorb or emit heat, depending on the material. If a current
density $J$ is passed through a homogeneous conductor, heat production per unit volume is

$$q = \frac{J^2}{\sigma} - \tau \Delta T,$$

(1.1.3)

where $\sigma$ is the conductivity of the material, $\Delta T$ is the temperature gradient along the wire and $\tau$ is the Thomson coefficient.

The first term $\frac{J^2}{\sigma}$ is simply the Joule heating which is not reversible. The second term is the Thomson heat, which changes sign when $I$ changes directions.

1.1.1.3. Kelvin Relations

The three transport parameters introduced above are not independent. The theory of irreversible thermodynamics proves the validity of the Kelvin relations as follows

$$\Pi = S \cdot T,$$

and

$$\tau = T \frac{dS}{dT},$$

(1.1.4) (1.1.5)

where $T$ is the absolute temperature of the material.

1.1.1.4. Bipolar Thermoelectric Devices

When holes are the majority of electrical carriers, the Seebeck coefficient is positive and the materials are called “p-type”. When electrons are the majority of electrical carriers, the Seebeck coefficient is negative and the materials are called “n-type”. Thermoelectric devices can be made with a pair of p-type and n-type materials.
Thermoelectric devices convert energy between heat and electricity. Electric coolers and power generators are good examples of the thermoelectric devices that use the Peltier and the Seebeck effect respectively. Figure 1.1.3 shows a schematic of the two types of thermoelectric devices. The most typical applications of these devices are for a deep-space spacecraft and mobile refrigerators. When a spacecraft travels far away from the sun, solar radiation is too weak to be used as an energy source. In this case, nuclear heat powered thermoelectric power generators are often used to generate electric power. A radio-isotope reactor creates heat, from which electricity is generated by the thermoelectric devices.

![Schematic of a thermoelectric power generator (left) and a thermoelectric cooler (right).](image)

**Fig. 1.1.3.** Schematic of a thermoelectric power generator (left) and a thermoelectric cooler (right).

**1.1.2. Thermoelectric Figure of Merit and Efficiency of Thermoelectric Devices**

**1.1.2.1. The Figure of Merit**

Thermoelectric cooling and power generation conversion are attractive practical
applications of the thermoelectric effects described in section 1.1.1. The strength of these effects and suitability for application are determined by the dimensionless figure of merit $ZT$, which is defined as

$$ZT = \frac{S^2 \sigma T}{k}. \quad (1.1.6)$$

This dimensionless parameter is a function of the usual transport coefficients. Here, $S$ is the Seebeck coefficient, $\sigma$ is electrical conductivity, $k$ is thermal conductivity, and $T$ is the operation temperature. The expression $S^2 \sigma$ is called the power factor. It is reasonable that $ZT$ is proportional to the square of the Seebeck coefficient because the efficiency is proportional to the amount of power generated and because the power is proportional to the square of the voltage created by the Seebeck effect (equation (1.1.1)). It is also reasonable that $ZT$ is linearly proportional to electrical conductivity because high electrical conductivity reduces energy leakage by Joule heating within the material. On the other hand, a high thermal conductivity will decrease energy conversion efficiency, because a high thermal conductivity enhances heat transfer through the sample, so the temperature difference cannot be sustained. And the equation is multiplied by operation temperature to give it a dimensionless form. As all of these parameters ($S$, $\sigma$, $k$, and eventually $ZT$) vary with temperature, it is important to indicate at which temperature those properties are measured.

Therefore, a good thermoelectric material requires a high Seebeck coefficient, a high electrical conductivity, and a low thermal conductivity. However, in bulk materials all of the
three thermoelectric properties are strongly interrelated to each other so it is hard to change only one property without changing the others. For example, increasing the number of electrical carriers not only increases electrical conductivity but also increases thermal conductivity. Moreover, the Seebeck coefficient is inversely proportional to carrier concentration. Figure 1.1.4 shows each of three properties as a function of carrier concentration. As the figure shows, metals have not only high electrical conductivities, but also high thermal conductivities because of the Widemann-Franz ratio and the low Seebeck coefficients (~10 \( \mu \) V/K). Insulators have high Seebeck coefficients and low thermal conductivities, but the electrical conductivities are too low, making \( ZT \) low. The best materials for thermoelectric applications are found in the region of the semiconductors. Moreover, in semiconductors, electrical conductivities and carrier type can be easily changed without affecting other properties simply by changing the doping type and doping concentration. With dopants, electrical conductivity can reach to a fairly high value of \( \sim 10^5 \) S/m, which is comparable to electrical conductivities of metals. Because the contribution of electrons to thermal conductivity is not significant for semiconductors, a change in doping concentration has little effect on thermal conductivity.
1.1.2.2. Efficiency of Thermoelectric Devices

Presently, the use of thermoelectric devices is limited by their low efficiency. The efficiency of a refrigerator is expressed by the coefficient of performance (COP) $\Phi$, which is the amount of cooling divided by the electrical power input needed to obtain that cooling [19]:

$$\Phi = \frac{q}{w}$$  \hspace{1cm} (1.1.7)

where

$$q = S_w T_c I - \frac{1}{2} I^2 R - k(T_H - T_C)$$  \hspace{1cm} (1.1.8)

$$w = S_w (T_H - T_C) I + I^2 R$$  \hspace{1cm} (1.1.9)

Not surprisingly, there is a current for which the coefficient of performance reaches its highest value. When this current is applied,
\[
\Phi = \frac{T_c[(1 + ZT)^{1/2} - T_H/T_C]}{(T_H - T_C)[(1 + ZT)^{1/2} + 1]}.
\]  

(1.1.10)

For refrigeration purposes, an important quantity is the maximum temperature
difference that can be achieved when the thermal load is zero. It is found that

\[
\Delta T_{\text{max}} = \frac{ZT_C^2}{2}.
\]

(1.1.11)

In Figure 1.1.5, this maximum temperature difference is plotted against \(ZT\) with the sink
temperature, \(T_H\), set at 300 K.

![Fig. 1.1.5. Maximum temperature difference for a single stage thermoelectric refrigerator plotted against \(ZT\). The heat sink is set at 300 K.](image)

Similarly, the efficiency of a thermoelectric power generation device is defined as
the ratio of the electrical power delivered to the load to the heat absorbed at the hot junction.

\[
\eta = \frac{w}{q} = \frac{I^2 R_L}{k(T_H - T_C) + \alpha_{ab} IT_H}
\]

(1.1.12)

The efficiency for a given thermocouple varies with the resistance of the load. In 1957, Ioffe
showed that the highest efficiency is given by [1]

$$\eta = \frac{(T_H - T_C)}{T_H} \frac{(1 + ZT)^{1/2} - 1}{(1 + ZT)^{1/2} + T_C / T_H},$$  \hspace{1cm} (1.1.13)

where $T$ is taken to be equal to $(T_H + T_C)/2$, i.e. the mean temperature over which the device operates. $(T_H - T_C)/T_H$ is defined as the Carnot efficiency of an ideal thermodynamic machine.

As seen in these equations, both the COP of a refrigerator and the efficiency of a power generator depend only on the dimensionless figure of merit $ZT$, where a higher $ZT$ results in a higher efficiency. Also in equation 1.1.13, if $ZT \to \infty$ then $\eta \to$ Carnot efficiency. Thus it is customary to express efficiency in terms of percentage of Carnot efficiency. The best bulk thermoelectric materials each achieve peak efficiency values up to about 17% of the Carnot efficiency, a value that has increased only by a few percent since 1950s. However, there is no known upper theoretical limit to the efficiency of thermoelectric conversion beyond the usual Carnot limit. For example, 30% of Carnot efficiency (comparable to home refrigerators) could be reached by a thermoelectric device with a $ZT$ of 3. Figure 1.1.6 shows the variation of efficiency with $ZT$ for different hot bath temperatures.
Fig. 1.1.6. Theoretical efficiency of ideal thermoelectric devices working at different temperatures as a function of the materials' figure of merit.

1.1.2.3. Necessary Criteria for High Performance Thermoelectric Materials

For the systematic search of good thermoelectric materials, the transport parameters, $S$, $\sigma$, and $k_{tot}$ have to be expressed by more fundamental properties like energy gap, carrier concentration and mobility, and so on. Attempts are also made to relate these parameters to practically useful parameters like crystal structure or the constituting elements [20]. Based on the extensive theoretical analysis and experimental evidence, materials suitable for thermoelectric applications fall mainly into two categories: semiconductors and mixed-valent compounds, although some semimetals may also be viable. For semiconductors, the best materials should have the following properties:

1. Carrier concentration should range in between $10^{18}$ to $10^{20}$ cm$^{-3}$.

2. Electronic bands near the Fermi level with many valleys preferably away from
the Brillouin zone boundaries. This requires high symmetry.

3. Elements with large atomic weight with large spin-orbit coupling [21].

4. Compositions with more than two elements (i.e., ternary, quaternary compounds).

5. Low average electronegativity differences between elements [22-23].

6. Large unit cell sizes.

7. Energy gaps equals to \(10 k_B T\), where \(k_B\) and \(T\) stand for the Boltzmann constant and absolute temperature respectively. For room temperature operation this should be \(0 < E_g < 0.3\) eV.

These basic criteria, if satisfied, should give rise to high carrier mobility (criteria 2 and 5), low thermal conductivity (criteria 3, 4, and 6) and large Seebeck coefficient (criteria 2 and 7). The last criterion (7) suggests that low temperature thermoelectrics \((T < 300 \text{ K})\) have very small band gaps. For operation at higher temperature (e.g., power generation applications) higher band gaps must be used.

Several materials were investigated for their potential use as high performance thermoelectric devices. However, only a few materials explored so far were found to achieve relatively high efficiencies over a specific temperature ranges that are summarized in Figure 1.1.7. Among those materials, Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) and Bi\(_2\)Te\(_3-y\)Se\(_y\) were the most efficient low temperature p- and n-type thermoelectric materials with a \(ZT\) of about 1 at room temperature. To make a major contribution to electronic cooling, a \(ZT\) of \(~1.5\) would be required. Also, to
significantly impact air-conditioning technology, a $ZT$ of $\sim 2.5$ would be needed. This suggests that in order for the thermoelectric materials to be competitive with current energy conversion technology, more research is needed to enhance $ZT$.

![Graph showing thermoelectric materials and their $ZT$ values](image)

**Fig. 1.1.7.** State-of-the-art thermoelectric materials.

### 1.1.3. Thermoelectric Transport Theory

#### 1.1.3.1. The Boltzmann Equation

In the unperturbed equilibrium state with no electric field, magnetic field or temperature gradient, the charge carrier distribution in a material is given by Fermi-Dirac distribution function [24]

$$f_0(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}, \quad (1.1.14)$$

where $E$ is the energy of the charge carrier, $E_F$ denotes the Fermi energy, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature.
Under the presence of an electric field, magnetic field or a temperature gradient, this distribution is no longer valid. The perturbation due to external fields and forces is assumed to be small so that the distribution function can be liberalized and written as

\[ f(\vec{r}, \vec{k}) = f_0(E) + f_1(\vec{r}, \vec{k}). \]  

(1.1.15)

In a non-equilibrium state, scattering of the electrons on lattice defects, phonons, grain boundaries etc. will force the distribution back to its equilibrium state. The rate of change of the distribution function will be proportional to its difference to the equilibrium distribution. The constant of proportionality is the relaxation time \( \tau \) which is a function of crystal momentum \( \tau = \tau(\vec{k}) \). The physical interpretation of the relaxation time is the time associated with the rate of return to the equilibrium distribution when the external fields or thermal gradients are switched off.

The equation to describe this relaxation process is the Boltzmann equation:

\[ \frac{df(\vec{r}, \vec{k}, t)}{dt} = \frac{f(\vec{r}, \vec{k}, t) - f_0(E)}{\tau(E)} = \frac{f_1(\vec{r}, \vec{k}, t)}{\tau}. \]  

(1.1.16)

Solution to equation 1.1.16 (when the fields are switched off at \( t = 0 \)) leads to

\[ f(t) = f_0 + [f(0) - f_0] \exp\left(-\frac{t}{\tau}\right), \]  

where \( f(0) \) is the distribution function at time \( t = 0 \).

1.1.3.2. Electrical Conductivity

To calculate the static electrical conductivity, we will assume that there is no
magnetic field and that there are no thermal gradients present. Using the Boltzmann equation, the electrical conductivity is expressed in terms of the conductivity tensor $\sigma$

$$\sigma = \frac{e^2}{4\pi^2} \int \tau \bar{v}(\vec{k}) \bar{v}(\vec{k}) \frac{\partial f_0}{\partial E} d^3k,$$

(1.1.18)

where $\sigma$ is a symmetric second rank tensor ($\sigma_{ij} = \sigma_{ji}$), $\tau$ is relaxation time, $\bar{v}(\vec{k})$ is velocity of carriers, and $f_0$ is distribution function. The evaluation of the integral in equation 1.1.18 over all $k$-space depends on the $E(\vec{k})$ relations through the $\bar{v}\bar{v}$ terms and the temperature dependence comes through the $\frac{\partial f_0}{\partial E}$ term.

In deriving the electrical conductivity for an intrinsic and non-degenerate semiconductor, we make three approximations:

1. In the case of electron states in intrinsic semiconductors that have no donor or acceptor impurities, we have the condition $(E - E_F) >> k_B T$. Then the Fermi-Dirac distribution function is

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

(1.1.19)

Since $E$ is usually measured with respect to the bottom of the conduction band, $E_F$ is a negative energy and it is therefore convenient to write $f_0(E)$ as

$$f_0(E) \approx \exp\left(-\frac{|E_F|}{k_B T}\right) \exp(-\frac{E}{k_B T}).$$

(1.1.20)

2. For simplicity, we assume a constant relaxation time $\tau$ independent of $\vec{k}$ and $E$.

3. We consider the simplest case: an isotropic, parabolic band $E = \hbar^2 k^2 / 2m^*$. 

18
Under these approximations, the electrical conductivity now can be expressed as

\[ \sigma = \frac{2e^2 \tau}{m} \left( \frac{m^* k_B T}{2 \pi \hbar^2} \right)^{3/2} \exp\left(-\frac{|E_F|}{k_B T} \right). \]  

(1.1.21)

The carrier concentration calculated using the Drude model, \( \sigma = \frac{n e^2 \tau}{m^*} \) becomes

\[ n = 2 \left( \frac{m^* k_B T}{2 \pi \hbar^2} \right)^{3/2} \exp\left(-\frac{|E_F|}{k_B T} \right). \]  

(1.1.22)

1.1.3.3. Seebeck Coefficient

In many metals and semiconductors, there exits a coupling between the electrical current and the thermal current. This coupling can be understood by observing that when carriers carry thermal current, they are also transporting charge and therefore generating an electric field. In our discussion of thermoelectric phenomena we start with a general derivation of the coupled equations for the electrical current density \( \vec{j} \) and the thermal current density \( \vec{j}_T \):

\[ \vec{j}(\vec{r}, t) = \frac{1}{4\pi^3} \int e \vec{v}(\vec{k}) f_0(\vec{k}) d^3k - \frac{1}{4\pi^3} \int e \vec{v}(\vec{k}) f_0(\vec{k}) d^3k \]  

(1.1.23)

\[ \vec{j}_T(\vec{r}, t) = \frac{1}{4\pi^3} \int \vec{v}(\vec{k})(E - E_F) f_0(\vec{k}) d^3k - \frac{1}{4\pi^3} \int \vec{v}(\vec{k})(E - E_F) f_0(\vec{k}) d^3k \]  

(1.1.24)

since under equilibrium conditions,

\[ \int e \vec{v}(\vec{k}) f_0(\vec{k}) d^3k = 0 \]  

(1.1.25)

\[ \int \vec{v}(\vec{k})(E - E_F) f_0(\vec{k}) d^3k = 0. \]  

(1.1.26)

The solution to the Boltzmann equation in the presence of an electric field and a
temperature gradient is

\[ f_i = \mathbf{v}_i \left( \frac{\partial f}{\partial \mathbf{r}} \right) = \mathbf{v}_i \left( \frac{\partial f_0}{\partial \mathbf{r}} \right) \left[ \frac{E - E_F}{T} \right] \nabla T - e \mathbf{E} + \nabla E_F . \]  

(1.1.27)

Substituting \( f_i \) into equation 1.1.23 and using open circuit conditions \( \tilde{j} = 0 \), we obtain the general expression for Seebeck coefficient

\[ S = \frac{1}{eT} \int \int \int \tau(k) \mathbf{v}_i(k) \mathbf{v}_f(k) \left[ E(k) - E_F \right] \frac{\partial f_0}{\partial E} d^3k \]  

(1.1.28)

For metals or highly degenerate semiconductors, the Seebeck coefficient can be represented by Mott’s formula as a logarithmic derivative of the electrical conductivity, \( \sigma \), evaluated at the Fermi energy \( E_F \) [25]

\[ S = -\frac{\pi^2 k_B^2 T}{3} \frac{\partial \ln \sigma}{\partial E} \bigg|_{E=E_F} . \]  

(1.1.29)

For a spherical constant energy surface \( E = \hbar^2 k_y^2 / 2m^* \) and assuming a relaxation time \( \tau \) that is independent of energy, we can readily evaluate the Seebeck coefficient

\[ S = \frac{\pi^2 k_B^2 k_y T}{2e E_F} . \]  

(1.1.30)

From this equation, we can see the Seebeck coefficient exhibits a linear dependence on \( T \) and sensitivity to the sign of carriers. We note that a low carrier concentration implies a large Seebeck coefficient. Thus degenerate (heavily doped with \( n \sim 10^{18} - 10^{19} / \text{cm}^3 \)) semiconductors tend to have a higher Seebeck coefficient than metals.

Materials with a high Seebeck coefficient are heavily doped degenerate
semiconductors for which the Fermi level is close to the band edge and the complete Fermi function must be used. Since the Seebeck coefficient typically depends on the sign of the charge carriers, good thermoelectric materials must be heavily doped as either p-type or n-type semiconductors to prevent the cancellation of the contribution from electrons and holes. This cancellation occurs in intrinsic semiconductors which have equal concentrations of electrons and holes because of thermal excitations of carriers.

1.1.3.4. Heat Conduction and Thermal Conductivity

The electrons in solids not only conduct electricity but also heat because they transfer energy from a hot junction to a cold junction. Just as the electrical conductivity characterizes the response of a material to an applied voltage, the thermal conductivity characterizes the material with regard to heat flow or an applied $\Delta T$. In fact the electrical conductivity and thermal conductivity are coupled since thermal conduction also transports charge and electrical conduction transports energy.

Thermal transport, like electrical transport, also follows the Boltzmann equation. The thermal conductivity is defined by the equation

$$\mathbf{j} = -\mathbf{k} \left( \frac{\partial T}{\partial r} \right), \quad (1.1.31)$$

where $\mathbf{j}$ is the heat flow through the material (equivalent to the current density in the electrical case) and $\mathbf{k}$ is the thermal conductivity tensor. The total thermal conductivity $\tilde{k}$ of any material is the superposition of the electronic part $\tilde{k}_e$ (heat transported by electrons
moving through the material) and the lattice part \( \tilde{k}_l \) (thermal excitation of lattice vibrations):

\[
\tilde{k} = \tilde{k}_e + \tilde{k}_l. \tag{1.1.32}
\]

**Heat Conduction from Electronic Part**

We now consider the calculation of the electronic contribution to the total thermal conductivity. The application of a temperature gradient to a solid gives rise to a heat flow. We define \( \tilde{j}_T \) as the thermal current which is driven by the heat energy \( E - E_F \), which is the excess energy of an electron above the equilibrium energy \( E_F \)

\[
\tilde{j}_T(\tilde{r},t) = \frac{1}{4\pi^3} \int \tilde{v}(\tilde{k})(E - E_F)f(\tilde{r},\tilde{k})d^3k. \tag{1.1.33}
\]

Under equilibrium conditions there is no thermal current density so that the thermal current is driven by the thermal gradient which causes a departure from the equilibrium distribution:

\[
\tilde{j}_T(\tilde{r},t) = \frac{1}{4\pi^3} \int \tilde{v}(\tilde{k})(E - E_F)f_i(\tilde{r},\tilde{k})d^3k. \tag{1.1.34}
\]

Substituting equation 1.1.27 in the absence of an electric field into the equation for the thermal current, we get

\[
\tilde{j}_T = \frac{1}{4\pi^3T} \int \nabla \tilde{v}(E - E_F) \left( \frac{\partial f_0}{\partial \tilde{r}} \right) d^3k \tag{1.1.35}
\]

and

\[
\tilde{k}_e = \frac{1}{4\pi^3T} \int \nabla \tilde{v}(E - E_F) \left( \frac{\partial f_0}{\partial \tilde{r}} \right) d^3k. \tag{1.1.36}
\]

In the case of a metal, the electronic contribution to the thermal conductivity simply yields Wiedemann-Franz relation [26]
\[ \tilde{k}_e = \bar{\sigma}T \left( \frac{\pi^2 k_B^2}{3e^2} \right), \]  
\hspace{1cm} (1.1.37)

which suggests that the ratio \( k_e / \bar{\sigma}T \) should be a constant, which is defined as the Lorenz constant. The quantity is equal to \( 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2 \).

For the case of non-degenerate semiconductors (assuming a parabolic band, a constant relaxation time and replacing \( (E - E_F) \) with \( E \)), the electronic contribution to the total thermal conductivity can be written as

\[ k_{exx} = \sigma_{xx}T \left( \frac{35 k_B^2}{2e^2} \right). \]  
\hspace{1cm} (1.1.38)

The coefficient \( (35/2) \) for this calculation for semiconductors corresponds to \( (\pi^2 / 3) \) for metals. Except for numerical constants, the formal relations between the electronic contribution to the total thermal conductivity \( k_e \) and the electrical conductivity \( \sigma \) are similar for both metals and semiconductors. A major difference between semiconductors and metals is the magnitude of the electrical conductivity and hence of the electronic contribution to the thermal conductivity. Since \( \sigma \) is much smaller for semiconductors than for metals, \( k_e \) for a semiconductor is relatively unimportant and the thermal conductivity is dominated by the lattice contribution.

**Heat Conduction by the Lattice**

All the material parameters discussed above are related to the electronic structure of the material and are correlated to each other in several ways. Therefore, they cannot be
optimized independently. The lattice thermal conductivity is the only parameter in the figure of merit $ZT$ that is not determined by the electronic structure. Therefore, it has to be discussed separately.

The fact that metals are good conductors of heat can be attributed to the transport of heat by the charge carriers. Of course, heat can also be conducted through electrical insulators. The thermal conductivity of diamond, for example, exceeds that of any metal. It is, in fact, the transfer of vibrational energy from one atom to the next that causes this process.

We may draw on the kinetic theory of gases to express the lattice thermal conductivity $k_l$ in terms of the mean free path $l$ of the phonons:

$$k_l = \frac{C_V v_s l}{3},$$  \hspace{1cm} (1.1.39)

where the specific heat $C_V$ is defined for a unit volume and $v_s$ is the speed of sound.

At high temperatures, i.e. above the Debye temperature, according to Debye’s theory $C_V$ approaches the classical value of $3R$, making $k_l$ primarily determined by the behavior of phonon mean free path since phonon velocity can be considered independent of temperature. At very low temperatures, the behavior of $k_l$ is dominated by the Debye $T^3$ law for $C_V$. Phonon scattering is insignificant in this temperature range because of the low number of excited phonons and their very long wavelength [27].

In a perfect crystal at zero temperature the phonons would move through the crystal uninhibited which would result in an infinite thermal conductivity. However, different scattering mechanisms lead to a finite thermal conductivity. The goal in thermoelectric
research would be to get very strong phonon-scattering without affecting the electrical properties.

1.1.3.5. Electron Scattering Process

The transport properties of a conductor depend not only on the charge carrier concentration but also on the free path length between collisions. Electron scattering brings an electronic system, which has been subjected to external perturbations back to its equilibrium. Collisions also alter the momentum of the carriers as the electrons are brought back to equilibrium. Electron collisions can occur through a variety of mechanisms such as electron-phonon, electron-impurity, electron-defect, and electron-electron scattering process. Scattering probabilities for more than one scattering process are additive and therefore so are the reciprocal scattering time or scattering rate. This is called Mattesien’s Rule:

\[
\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \cdots + \frac{1}{\tau_j} .
\] (1.1.40)

The most important electron scattering mechanism for both metals and semiconductors is electron-phonon scattering (scattering of electrons by the thermal vibration of the lattice) even though the scattering process for metals differs in detail from that for semiconductors. In the case of metals, much of the Brillouin zone is occupied by electrons. In the case of semiconductors, most of the Brillouin zone is unoccupied and represents states into which electron can be scattered. In metals, electrons are scattered from one point on the
Fermi surface to another point and a large change in momentum occurs, corresponding to a large change in the wave vector $\mathbf{k}$. In semiconductors, changes in the wave vector from $\mathbf{k}$ to $\mathbf{k}'$ normally correspond to only a very small change in the wave vector and hence only low phonon $\mathbf{q}$ vectors participate. Therefore, small angle scattering is especially important for semiconductors. The probability that an electron makes a transition from an initial state $i$ to a final state $f$ is proportional to the availability of final states for electrons, the probability of absorbing or emitting a phonon, and the strength of the electron-phonon coupling or interaction.

1.1.3.6. Phonon Scattering

Whereas electrons scattering is important in electronic transport properties, phonon scattering is important in thermal transport, particularly for the case of insulators where heat is carried mainly by phonons. The major scattering mechanisms for phonons are alloy disorder scattering, phonon-phonon scattering, phonon-boundary scattering, and defect-phonon scattering.

Alloy Disorder Scattering

Alloy disorder scattering is one of the most thoroughly understood mechanisms related to defect scattering and is based on mass-difference scattering. Abeles et al. have described this mechanism both experimentally and theoretically [28]. Considering
phonon-phonon and phonon-isotopic point-defect scattering as major scattering mechanisms, the expression for the phonon thermal resistance, \( W (= k^{-1}) \), can then be written in the form:

\[
W = U / (k_p \tan^{-1} U),
\]

where \( U = 8.7 \times 10^{-2} \Gamma^{3/2} M^{3/2} \delta \varphi^{-1} T^{-3/2} \), \( k_p = 5.7 \times 10^{-8} M \delta \varphi^{3} \gamma^{-2} T^{-1} (W / \text{deg} - cm) \), and

\[
\Gamma = \sum_i f_i \left[ (M_i - M) / M \right]^2.
\]

Here \( \Gamma \) is disorder parameter, \( \theta \) is Debye temperature, and \( f_i \) is the fractional concentration of mass \( M_i \) and \( \gamma \) is the Grüneisen anharmonicity parameter. In SiGe alloy materials, the thermal conductivity is reduced by almost an order of a magnitude by this mechanism, thereby enhancing the figure of merit significantly compared to pure Si or Ge.

**Phonon-phonon Scattering**

Phonon-phonon scattering is usually the most important scattering mechanism at high temperatures. Phonons are scattered by other phonons because of anharmonic terms in the restoring potential. This scattering process permits two phonons to combine to form a third phonon or one phonon to break up into two phonons. In these anharmonic processes, energy and wave vector conservations apply: \( \vec{k}_1 + \vec{k}_2 = \vec{k}_3 \) (which is called normal processes) and \( \vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{K} \) (which is called Umklapp processes) where \( \vec{K} \) corresponds to a phonon wave vector of magnitude to that of reciprocal lattice vector. Only collisions with \( \vec{K} \neq 0 \) produce thermal resistance because the flow direction of the phonon is inversed by
such a process.

From second-order perturbation theory, the relaxation time for three-phonon Umklapp scattering at high temperature ($T>300$ K) is given by [29]

$$\frac{1}{\tau_U} = 2\gamma^2 \frac{k_B T \omega^2}{\mu V_0 \omega_D},$$  \hspace{1cm} (1.1.45)

where $\gamma$ is the Grüneisen anharmonicity parameter, $V_0$ is the volume per atom, $\omega_D$ is the Debye frequency, and $\mu$ is the shear modulus which is related to the transverse sound velocity through $\mu = \frac{v_T^2}{\rho}$.

**Phonon-boundary Scattering**

Phonon-boundary scattering is important at low temperatures where the phonon density is low. However, in highly disordered materials, boundary scattering may become significant at high temperatures [30]. Powdering a material and subsequently pressing it into pellets generally lowers the lattice thermal conductivity due to the phonon-boundary scattering processes. Although in most cases the electron mobility is lowered as well, in some materials the effects on the phonons are stronger than the effects on the mobility. Therefore it is possible to improve the figure of merit of certain materials by this technique [2].

Boundary scattering relaxation time is given by

$$\frac{1}{\tau_B} = \frac{\nu}{D} (1 - p).$$  \hspace{1cm} (1.1.46)

Here $D$ is the grain diameter, $\nu$ is the phonon group velocity, and $p$ is a parameter that
characterizes the interface roughness and its effect on the phonon-boundary scattering [28].

The value of $p$ represents the probability that the phonon is undergoing a specular scattering event at the interface. In the case of purely diffuse scattering, $p = 0$, equation 1.1.46 reduces to the well-known Casimir limit [31]:

$$\frac{1}{\tau_b} = \frac{\nu}{D}. \quad (1.1.47)$$

**Defect-phonon Scattering**

Defect-phonon scattering includes a variety of crystal defects, charged and uncharged impurity sites and different isotopes of the host constituents [29]. The phonon relaxation time on point defects can be written as:

$$\frac{1}{\tau_D} = \frac{V_0 \Gamma \omega^4}{4\pi^2}, \quad (1.1.48)$$

where $\Gamma$ is the measure of the strength of the point defect scattering. In general we can assume for simplicity that the point defect scattering is only due to the difference in mass of substitutional foreign atoms and the strain field effect. Thus the strength of the point defect scattering is given by

$$\Gamma = \sum_i f_i \left[ \left( 1 - \frac{M_i}{M} \right)^2 + 2 \left( 6.47 \left( 1 - \frac{R_i}{R} \right) \right) \right]. \quad (1.1.49)$$

Here $M_i$ is the mass and $R_i$ is the Pauling ionic radius of the $i$th impurity atom or defect and $f_i$ is the fractional concentration of the impurity atoms.
1.2. The Objective and Outline of This Work

During the 1950s, when a space science was a matter of great importance, rapid progress was made on the development of alloy-based semiconductors. Among those materials, Bi$_{0.5}$Sb$_{1.5}$Te$_3$ was the most efficient p-type thermoelectric material with a $ZT$ of 1 at room temperature [31]. However, the equivalent $ZT$ for typical mechanical power generators or refrigerators is more than 3. In order for thermoelectric materials to be competitive with current energy conversion technology, more research was needed to enhance $ZT$. Within the last 10 years, significant enhancement in $ZT$ has been made with the help of nanotechnology. In 1993, Hicks and Dresselhaus theoretically presented a possible enhancement in $ZT$ through the use of quantum well superlattices and quantum wires [8-9]. Reduced dimensionality, as occurs in quantum well superlattices (2D) or in quantum wires (1D), enhances the density of states and can have energy filtering effect by quantum confinement. This leads to an increase in the Seebeck coefficient without decrease in electrical conductivity. Meanwhile, thermal conductivity can be reduced by increasing the phonon scattering by nanostructures. The idea was successfully demonstrated in the PbTe/PbSeTe superlattice [12] and other systems later [11]. Figure 1.2.1 shows pictures of these nanostructures.
Fig. 1.2.1. Quantum well superlattice (left) and quantum wire (right). Each layer thickness in superlattice is 2 nm. Quantum well superlattice was made by Professor Wang’s group at UCLA and quantum wire was made by our group. Quantum confinement and boundary scattering are expected to result in the high Seebeck coefficient and low thermal conductivity without a decrease in electrical conductivity.

There are two groups that explain the thermal conductivity reduction in low dimensionality. The first group treats phonon as a coherent wave just as in electron wave [32-36]. Periodicity of nanostructures causes modification of phonon modes and, in turn, reduces the phonon group velocity. Reduced phonon group velocity is proposed as an explanation for the thermal conductivity reduction in cross-plane direction of superlattices [36]. However, experimental results showed more decrease in thermal conductivity than simulation results [37-40] (Fig. 1.2.2). This fact suggests that only modification in phonon modes cannot explain the thermal conductivity reduction in nanostructures. The other group treats phonon as incoherent particles and considers interface scattering as the classical size effect [41-44]. These approaches are based on solving the Boltzmann transport equation. They consider the thermal conductivity reduction comes from phonon scattering at boundaries. Phonons can easily scatter away at every interface because the wavelength of phonons (1~2 nm at room temperature) is comparable to the length scale of surface
roughness (3 Å at room temperature). On the other hand, the electrical conductivity is not significantly affected by boundary scattering because electrons have a longer wavelength (8 nm at room temperature) than phonons. With partially diffuse and partially specular interface scattering, modeling studies match experimental results. Thermal conductivity reduction by the classical size effect is conspicuous when the mean free path of phonon (100–200 nm at room temperature) is comparable to or larger than the characteristic length of structures [41-43]. Hence, not periodic structures but increased amount of boundaries in nanostructures is critical factor for thermal conductivity reduction.

![Graph showing the thermal conductivity of SiGe superlattices](image)

**Fig. 1.2.2.** Experimental and calculated thermal conductivity of SiGe superlattices in both in-plane and cross-plane, normalized to thermal conductivity of SiGe bulk alloy. Solid lines were calculated by lattice dynamics simulation [40]. The experimental results are lower than the calculated results [37-39].

Several experimental studies followed to prove the increase in $ZT$ of nanostructures
The highest $ZT$ value of 2.4 occurs at room temperature and was observed for Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices [11]. However, these superlattices are not practical for use in thermoelectric products because the time and cost of fabrication are not competitive enough for mass production to be possible.

In this dissertation, we proposed the semiconductor nanocomposites for highly efficient materials development where the reduction of thermal conductivity is a blessing for efficiency enhancement. Dr. Bed Poudel demonstrated the high figure-of-merit in nanostructured bulk bismuth antimony telluride by ball milling alloyed bulk crystalline ingots into nanopowders and hot-pressing them [16]. Inspired by his work, now we use the same ball milling and hot press technique, but start with elemental chunks of bismuth, antimony, and tellurium to avoid the ingot formation step. These materials have been investigated as high performance thermoelectric materials for waste heat recovery, power generation, and cooling applications. This work involves an extensive experimental study (including the study of nominal compositions effect) coupled by theoretical analysis of the thermoelectric-related properties in bismuth antimony telluride systems which are summarized in Chapters 3 and 4. The measurement techniques for three transport properties ($S, \sigma, k$) have been introduced in Chapter 2. Synthesis and morphology characterization of a few nanostructured thermoelectric materials by wet chemical methods with the study of their physical properties are presented in Chapter 5. Also, summary of the work and some guidelines for further research into the topic have also been given in Chapters 3 and 4.
1.3. References


Chapter 2
Measurement Techniques of Thermoelectric Properties

2.1. Introduction

The performance of a thermoelectric device can be expressed in terms of the figure of merit $ZT$. Clearly this quantity is of utmost importance. Although there are more direct methods to determine the thermoelectric performance of a material such as $Z$-meter [1], it is often necessary to make independent measurements of the electrical conductivity $\sigma$, the Seebeck coefficient $S$, and the thermal conductivity $k$. Such measurements are required, for example, in optimizing the properties of any particular semiconductor and in selecting new materials. Measurements of $\sigma$ and $S$ are also used in routine testing of production of thermoelectric material.

One of the first steps in improving the accuracy of a particular experimental setup is to identify and quantify any systematic errors in the measurement. One way to do this is to develop standards (materials with known and established thermoelectric properties) to check the apparatus and measurement techniques for accuracy and reproducibility. However, very few good thermoelectric standards exist today. For this reason, it is very important to develop different independent characterization techniques which can be used to compare between each other and build a confidence of any measurement.

Another mistake that is often made results from calculating $ZT$ using values of the
various thermoelectric properties as measured from different samples. Thermoelectric materials have often proven to be notoriously inhomogeneous even among samples taken from the same batch. Therefore, it is best to take all measurements on the same sample. In addition, these measurements should be taken as closely together in time as possible in order to eliminate sample deterioration effects. In general, electrical and thermal transport properties can have a very strong dependence on crystallographic direction. Thus, even “pressed pellet” polycrystalline samples can exhibit anisotropy in their properties and sample orientation must be consistent when measuring and comparing the different thermoelectric properties.

Establishing excellent electrical contacts to these thermoelectric materials is also an essential factor. Unfortunately, some of the materials of interest in thermoelectrics are susceptible to the formation of oxide layers or sample decomposition at the surface. Therefore, careful surface preparation is often one of the most crucial steps in achieving good adhesion and low resistance contacts. Also, most of the potential thermoelectric materials are semiconductors which require metal-semiconductor electrical contacts. Thus, this incorporates all the problems and issues that exist in making electrical contacts between metals and semiconductors.

In this chapter, various measurement techniques used in characterization of the thermometric properties will be summarized. Underlying measurement principles and challenges will also be briefly described. In our measurements, we employed a home built
system capable of measuring electrical conductivity, Seebeck coefficient, and thermal conductivity simultaneously from liquid nitrogen temperature to 350 °C (MIT). We also used a commercially available equipment for electrical conductivity and Seebeck coefficient measurement up to 1000 °C (ZEM-3, Ulvac Inc.), a commercial Nanoflash equipment for thermal diffusivity measurement up to 300 °C (Nanoflash LFA 447, Netzsch Instruments, Inc.), a commercial equipment for specific heat measurement up to 600 °C (DSC 200 F3 Maia®, Netzsch Instruments, Inc.), and a home built Hall measurement system (BC) for carrier concentration and mobility measurement.

2.2. Measurement Principles

2.2.1. Electrical Conductivity

For many materials, the determination of the electrical conductivity is a simple and straightforward measurement. A four-probe method is typically used in which current is injected through one set of current leads and voltage is measured using another set of voltage leads. Figure 2.2.1 below shows a schematic of an electrical conductivity measurement system.

Electrical conductivity is usually measured indirectly by resistivity $\rho$. The resistivity $\rho$ can be found from the relation $\rho = AR/L$, where $R$ is resistance, $L$ is sample’s length, and $A$ is sample’s cross sectional area. The resistance is deduced from the slope of voltage drop to current flow into the sample (Fig. 2.2.2).
Although the electrical conductivity measurement of conducting materials has been studied for a long time, there are special problems that arise for thermoelectric materials. Because the Peltier effect sets up temperature gradients which, in turn, generate electric fields
through the Seebeck effect, thermoelectric voltages (Seebeck voltages) are superimposed on the potential differences that arise from electrical resistance which hinder the accurate measurement for electrical conductivity of the sample. There are two ways of avoiding errors from temperature gradients in samples. One method, which is usually impractical, is to make the probes from a substance that has precisely the same Seebeck coefficient as the sample being measured. The more usual method takes advantage of the fact that a temperature gradient, arising from the Peltier effect, takes some time to develop. Thus, it was found that either an ac current source [2] or a chopped dc current source [3] can be used to measure electrical conductivity without interference from the Seebeck voltage. Experimental observation [1] suggests that an ac current with the frequency of 60 Hz is enough to neglect the Peltier effect.

Another problem with electrical conductivity measurement is the contact resistance. This intrinsic contact resistance is caused by the gap between the work function of the metal and the Fermi level of the semiconductor called Schottky Barrier [4]. This contact resistance becomes worse when there is an oxide layer on the surface, which can be as much as one hundred ohms. Resistance of samples is expected to be less than ten ohms. Reliable electrical conductivity data can be obtained only after the contact resistance problems have been solved. A four probe method, as discussed before, is typically used to eliminate the contributions of contact resistance.

Although the effect of contact resistance can be eliminated by the four probes
method, inconsistent contact resistance leads to an unstable result. Moreover, growth of the oxidation layer in the air can increase the contact resistance up to a few tens of kilo-ohms. Bismuth telluride and lead telluride alloys can be easily oxidized in the air, even at room temperature. The oxide layers in Bismuth telluride alloys can be removed chemically by dipping into bromine liquid, or mechanically by polishing the surface of a sample right before the measurement is done.

2.2.2. Seebeck Coefficient

The Seebeck coefficient is conceptually the easiest among the three quantities to measure because it is defined as the ratio of an open-circuit potential difference to a temperature difference. It is independent of geometric parameters and, to some extent, is not sensitive to the heat loss problem either. When a temperature gradient is applied across the sample, the Seebeck coefficient $S$ can be expressed as the ratio of the voltage $\Delta V$ created to the temperature difference $\Delta T$, $S = -\Delta V / \Delta T$. The temperature difference is determined by using thermocouples, while the voltage difference is usually measured by one of the legs of the thermocouples. This measurement technique involves fixing the sample temperature, $T$, and varying a small temperature gradient across the sample. The induced voltage is recorded as a function of temperature difference and the slope yields the Seebeck coefficient. A simple schematic of a Seebeck measurement system is shown below in Fig. 2.2.3.
Fig. 2.2.3. Schematic of the Seebeck coefficient measurement.

However, this approach has possible sources of error. For instance, heat may be conducted along the thermocouple wires to the sample, changing the temperature at the contact regions. Additionally, there may be a temperature gradient within the junction of the thermocouple wires so that the measured temperature is different from that at the position where the electric potential is taken up. This problem becomes more severe as the thermal conductivity of the sample becomes smaller. To minimize the errors from this cause, the thermocouple wires should be of very small diameter.

In principle, the induced voltage vs. temperature difference curve should pass through zero when there is no temperature gradient. But in practice there is always some non-zero intercept which is called dark emf. To understand the source of this emf, one should note that there is always some heat transport through the thermocouple wires to the port which is coupled with the data accusation system. If this port is not at exact thermal equilibrium
because of the transported heat or by other means (which means two thermocouples will see a thermal gradient), it creates a dark emf. Seebeck coefficient measurement is considered reliable when the dark emf doesn’t exceed 10 % of the Seebeck voltage signal.

2.2.3. Thermal Conductivity

Thermal conductivity $k$ is defined as the ratio of heat flux $q''$ (which is rate of heat transfer per unit cross-sectional area) to the temperature gradient $\nabla T$ caused by the heat flux, $k = q'' / \nabla T$. The schematic used for the Seebeck coefficient measurement can also be applied for the thermal conductivity measurement (Fig. 2.2.3). However, the thermal conductivity measurements are by far the most difficult to make with relatively high accuracy. There are many excellent texts and techniques available that discuss in detail many of the corrections and potential errors one must consider [5-10]. The thermal conductivity, $k$, of good thermoelectric materials is very low, typically $k \leq 2$ W/m-K. This makes the measurement even more difficult since the heat will flow through other paths of higher thermal conductivity, such as down lead wires and conduction by any gases or air flow around the sample. These result in an error in determination of the power input into the sample and thus the exact thermal conductivity is unattainable. Therefore, calculating the heat loss corrections and proper thermal shielding techniques to minimize these corrections and radiation effects is critical for these thermoelectric materials. The thermal conductivity measurement systems we used as well as their advantages and disadvantages will be
described in the following sections.

2.3. Integrated Measurement using a Vacuum Cryo-chamber

Figure 2.3.1 is the picture of the home-built integrated measurement setup with a mounted sample which is used for measuring electrical conductivity, Seebeck coefficient, and thermal conductivity simultaneously. On the top and bottom of the sample, two thermocouple wires are connected to inject the current into the sample and to read the temperature during Seebeck coefficient measurement. The sample holder is placed inside a cryogenic chamber, as shown in Fig. 2.3.2, which can be connected to a turbo pump to create a good vacuum.

Fig. 2.3.1. Picture of integrated measurement system probe head.
2.3.1. Electrical Conductivity Measurement

During the electrical conductivity measurement, we used spark-welding to connect voltage probes and soldering of thermocouple wires into the sample to achieve a good contact. In the case of voltage probes, platinum wires with the diameter of 1 mille-inch (~25 μm) were used which can be easily spark-welded into the sample surface with low welding energy, without severely damaging the sample surface. Larger sized wires need more welding energy which may locally damage the sample surface. Also, they will cause more heat loss, causing the less accuracy of the measurement at higher temperatures.

Thermocouple wires (chromel and alumel) were used to inject the current for the electrical conductivity measurement. The wires with diameter of 2 milli-inches were chosen, which are strong enough for easy handling and do not cause too much heat loss. These
thermocouples were soldered onto the top and bottom of the sample (2×2×12 mm rectangular bar) using a suitable solder. For low temperature measurements (less than 130 °C), a Bi-Pb alloy solder is preferred for securing good contact. Before soldering into the thermocouple wires, both ends are cleaned with Bromine liquid to remove any oxide layer and electroplated using a Ni-plating pen. Ni-plating has two advantages: making soldering better and preventing any diffusion of silver (silver epoxy was used to mount the sample onto the stage). The sample stage was electrically insulated but thermally connected to the holder by Boron Nitride spray paint, as shown in Fig. 2.3.1.

Several problems had been encountered during the measurement, such as non-linear or non-overlapping (increasing and decreasing current stages) $I-V$ plot. These problems can be solved by carefully examining the system. More attention was paid to the contacts and temperature distribution was made better by putting a Cu-shielding in place to make an isothermal area across the length of the sample. After that, linear and reproducible $I-V$ plots and reliable electrical conductivity measurement were achieved as shown in Fig. 2.2.2.

### 2.3.2. Seebeck Coefficient Measurement

Although the Seebeck coefficient measurement is less sensitive to the heat loss problem, unsteady heat loss is still not desirable for good results. However, if the heat loss from the sample to the thermocouple is large, the temperature measurement will have error which eventually causes error in the Seebeck coefficient. Thermocouples with diameter of
two milli-inches are utilized to minimize conductive heat loss through the thermocouple wires. In our measurement setup, a small heater is mounted on top of the sample to create a temperature gradient. To measure the temperature difference across the sample, we attach thermocouples on top and bottom of the sample by a solder or silver paste as shown in the Fig. 2.3.1. For temperatures below 350 °C, solder would be the best choice since it is easy to handle, saves time, and works well. For higher temperature measurements, it is hard to find a suitable solder which can work at such temperatures. Silver paste can be used, but it needs to be baked at 250 °C in a vacuum before use to insure a good contact at high temperatures.

Measurements are usually done in vacuum of \(\sim 10^{-5}\) Torr in order to minimize temperature fluctuations due to convection. Several data points are collected and plotted in the \(\Delta V-\Delta T\) curve by changing the power that goes through the electric heater (which is controlled by a computer using a LabVIEW program). The Seebeck coefficient was acquired by a slope of the \(\Delta V-\Delta T\) curve, similar to the electrical conductivity measurement case.

Since thermocouples are used to measure the voltage which themselves have some Seebeck voltage, the result should be compensated by the Seebeck coefficient of the wires that are used for voltage measurement. Let’s consider \(T_a\) the ambient, \(T_h\) the hot side and \(T_c\) the cold side temperatures of the sample respectively. Then we can write the following relation for the voltage drop across the two thermocouple contacts:

\[
V = (T_a - T_h)S_n + (T_h - T_c)S_s + (T_c - T_a)S_w = (T_h - T_c)(S_s - S_w),
\]

where \(S_s\) and \(S_w\) are the Seebeck coefficient of sample and wire respectively. Hence, we should add the Seebeck
coefficient of wires to the value we got from the slope. When we use the alumel side of the thermocouple wire for voltage reading, we should add the Seebeck coefficient of alumel, which is \(-18.53 \mu V/K\), to the following expression

\[ S_s = \frac{dV_{\text{Seebeck}}}{dT} + S_{\text{Alumel}} . \]  

(2.3.1)

2.3.3. Thermal Conductivity Measurement

Non-steady-state methods to measure the thermal transport property are well established [11] and considered to be more reliable for lower thermal conductivity materials. Most of these methods measure the thermal diffusivity rather than conductivity, which indirectly determines thermal conductivity with the value of specific heat and density

\[ k = \rho C \alpha , \]  

(2.3.2)

where \( \rho \) is density, \( C \) is specific heat, and \( \alpha \) is thermal diffusivity. The density can be easily determined by Archimedes’ principle. Specific heat can be calculated by several measurement techniques or by using a table for standard materials. The diffusivity is acquired by solving one dimensional diffusion equation:

\[ \frac{1}{\alpha} \frac{\partial T}{\partial t} + m^2 T = \frac{\partial^2 T}{\partial t^2} , \]  

(2.3.3)

where \( T \) is temperature difference to ambient temperature and \( m \) is the coefficient of surface heat loss which takes into account heat loss by radiation, conduction, and convection. Depending on the boundary conditions, a wide range of solutions are possible.
In 1961, Angstrom developed the thermal diffusivity measurement method with sinusoidal heat source for a semi-infinite sample [12]. It has been modified and improved by numerous investigators and has become a well-established method for thermal diffusivity measurement [13-15]. Although Angstrom’s method was established long time ago, it has not been properly replaced by other recent techniques due to its mathematical clearance and convenience of installation. The theory is based on the fact that if a heat source, whose temperature varies sinusoidally with time, is located at one end \((x = 0)\) of a semi-infinite sample, these temperature oscillations will propagate along the sample with a velocity \(V\):

\[
V = \omega / \beta ,
\]

where \(\omega\) is the angular frequency and \(\beta\) the phase shift per unit length. In such a case, a general solution to the equation 2.3.3 is given by:

\[
T(x,t) = A(x) + B(x)e^{i\omega t} .
\]

In this equation only the \(B(x)\) term, which is the amplitude of sinusoidal wave, matters for the derivation of the thermal diffusivity. The sinusoidal wave is realized by applying ac current to the electric heater in Fig. 2.3.1. When the \(T\) of equation (2.3.3) is substitute by the \(T\) in equation (2.3.5), the second order ordinary differential equation for \(B(x)\) becomes:

\[
B_{xx}(x) - \left( \frac{i\omega}{\alpha} + m^2 \right) B(x) = 0 ,
\]

where \(B_{xx}\) is the second derivative of \(B\) with respect to \(x\). The general solution of equation (2.3.6) is
\[ B(x) = C_1 e^{\beta x} + C_2 e^{-\beta x} \]

\[ \beta^2 = m^2 + \frac{i \omega}{\alpha}, \quad (2.3.7) \]

where \( C_1 \) and \( C_2 \) are constants to be determined by the following two boundary conditions.

One of the boundary conditions is determined by the sinusoidal heat source,

\[ T(x=0,t) = a + \beta(x) e^{i \omega t}. \]
\[ B(x=0) = b. \quad (2.3.8) \]

Theoretically, the method we used for deriving the thermal diffusivity assumes semi-infinite sample for which the solution becomes

\[ B(x) = b e^{-\beta x}. \quad (2.3.9) \]

When \( \beta \) is split into real part \( P \) and imaginary part \( Q \), we can get the following relation:

\[ PQ = \frac{\omega}{2 \alpha}. \quad (2.3.10) \]

And we can rewrite the solution of the diffusion equation as:

\[ T(x,t) = A(x) + b e^{-\beta x} \cos(\omega t - Q x). \quad (2.3.11) \]

From this equation, it is clearly seen that amplitude and phase of a sinusoidal temperature wave will be different from each measurement point. Measurements of only two temperature waves at two points \( x=x_1, x_2 \) are enough to determine the coefficients \( P \) and \( Q \) without knowing \( b \). Hence, Angstrom’s method is useful in the sense that thermal diffusivity can be measured regardless of heat loss or the amount of heat that goes through. Figure 2.3.3 shows a measurement result of the Angstrom’s method.
Fig. 2.3.3. Demonstration of measurement results of two temperature points along a sample by Angstrom method. The red one corresponds to the thermocouple, which is closer to heat source at $x=x_1$, and the blue one is at $x=x_2$, which is farther from the heater showing reduction of amplitude. $M$ and $N$ are the amplitudes of each signal, and $dt$ is the phase difference between signals.

From the measurement result, we can acquire amplitude $M$ and $N$, and phase difference $dt$ between two sinusoidal temperature waves. From the two amplitudes, $P$ in equation (2.3.11) can be determined:

$$
\frac{M}{N} = \frac{be^{-P_2}}{be^{-P_1}} = e^{P_1 - P_2},
$$

where $l$ is the length between two measurement points. Also the phase difference $Q$ is determined:

$$
P = \frac{1}{l} \ln \left( \frac{M}{N} \right),
$$
\[
\omega t - Qx_1 = \omega(t + dt) - Qx_2 \\
Q(x_2 - x_1) = \omega \cdot dt \quad . \\
Q = \frac{\omega \cdot dt}{l} 
\]

With \( P \) and \( Q \) in equations (2.3.12) and (2.3.13), we can derive the thermal diffusivity \( \alpha \) from equation (2.3.10):

\[
PQ = \frac{\omega dt \ln \frac{M}{N}}{l^2} = \frac{\omega}{2\alpha} \\
\alpha = \frac{l^2}{2 dt \ln \frac{M}{N}} \quad . 
\]

By this relation, we can get thermal diffusivity without any knowledge of the amount of power that goes into a sample and without any consideration of heat loss from sample surface.

In the above calculation of the thermal diffusivity, a semi-infinite sample was assumed. This is not possible to have in practice. A simple analysis can be done to find an error coming from a finite size of the sample [16]. With a 10 W/m-K magnitude for the thermal conductivity, a sample of 2 mm diameter, and a low heat source frequency such as 10 mHz, calculations show that \( l \) for the sample should be much longer than 1 mm in order for the semi-infinite method to be valid. The lengths of the samples that were used for the measurement were around 12 mm, which can be thought of as long enough.
2.4. Electrical Conductivity and Seebeck Coefficient Measurement by Commercial Equipment (ZEM-3, Ulvac Inc.)

As discussed in the previous sections, the most dependable method to determine electrical conductivity currently available is the high-speed, high-resolution current switching dc measurement technique. ZEM-3 (Ulvac, Inc.) equipment utilizes the recommended [17] setup to produce the most reliable electrical conductivity and Seebeck coefficient measurement. Figure 2.4.1 shows a simple sketch of the method used for the electrical conductivity measurement and Fig. 2.4.2 shows a picture of actual sample mounted on the sample holder. The sample holder is enclosed in an infra-red furnace. A picture of ZEM-3 equipment is shown in Fig. 2.4.3. The holder is surrounded by an isothermal nickel radiation shield to provide a uniform temperature environment across the sample length. All measurements are carried out in a helium atmosphere at approximately 10 kPa absolute pressure.

The sample is held between the jaws with moderate pressure from a clamping spring. The lower jaw is heated by an electrical resistance heater which creates a temperature gradient along the sample. Temperature and voltage are measured by the two probe thermocouples which are held against the sample by light spring pressure. This type of pressure contact is advantageous to apply constant force on the sample. Hence the contact resistance can have stable value. To ensure a one-dimensional heat and current flow, the distance between the probes and end-plates should be 1.5 times larger than the sample’s
characteristic lateral dimension \((L)\). All the samples were rectangular bars with approximate geometry of \(2 \times 2 \times 12\) mm. The probe spacing was \(\sim 6\) mm for all the measurements. The upper and lower probe temperatures are measured by a pair of chromel-alumel (Type-K) thermocouples using two channels of a Keithley 2010 digital multimeter. The chromel leads are also used to measure the voltage differential between probes for the Seebeck and conductivity measurements.

**Fig. 2.4.1.** Schematic of electrical conductivity measurement system.

Electrical conductivity is measured by the four probe current switching method. Electrical current is injected from one side of the thermocouple wires and voltage is measured by the probe wires as shown in Fig. 2.4.1. An \(I-V\) plot before the start of the actual measurement is utilized to check the contact; a linear plot with no intercept guarantees a good ohmic contact. Lower and upper electrodes with spring force hold the sample firmly in the
upright position. This also makes good thermal contact between heat source/sink and sample surface. Temperature controllers, data accusation, and analyses are fully automated using a computer. From the plotted $I-V$ curve, resistance (and consequently the resistivity) is determined at various temperatures of interest.

**Fig. 2.4.2.** A picture of sample holder with mounted sample (left) and sample dimensions (right).

**Fig. 2.4.3.** A picture of Seebeck and electrical properties measurement system (ZEM-3, Ulvac Inc.).

The electrical conductivity of the sample is computed from its measured resistance using the specimen geometry. The current duration is short and the probe voltage is measured.
very quickly to minimize errors caused by the transient temperature differential which is produced by the Peltier effect. In addition, there is also a small, steady-state temperature gradient along the sample during the resistivity measurement. Consequently, the measured voltage has both Seebeck and ohmic contributions. To eliminate the steady-state Seebeck contribution, two measurements are taken with opposite current polarity. These two measurements are combined to compute the sample resistance using the following relation:

\[ R = \frac{V_1 - V_2}{2I}, \]  

(2.4.1)

where \( V_1 \) and \( V_2 \) are the voltages measured at \(+I\) and \(-I\). The sample dimensions are measured using a micrometer with accuracy of \(\pm 0.001\) mm. Unfortunately, due to the ZEM-3 configuration, the probe distance is very difficult to measure and we always assume it to be 6 mm. Probe spacing uncertainty dominates the other contributions and therefore controls the accuracy of the resistivity measurements. It can be assumed that all conductivities reported in our work have uncertainties \(\sim 5\%\).

During the Seebeck coefficient measurement, no current flows through the sample. The only source of emf is due to the Seebeck effect in the sample and probe leads. The ZEM-3 system determines the sample’s Seebeck coefficient from the upper and lower probe temperatures and the measured emf, which are represented by \(\Delta T\) and \(\Delta V\) respectively. The equation used for computing the Seebeck coefficient \(S\) is given as:

\[ S = -\frac{\Delta V}{\Delta T} + S_{TC}, \]  

(2.4.2)

where \(S_{TC}\) is the Seebeck coefficient of thermocouple. A detailed schematic of the Seebeck
measurement configuration is shown below (Fig. 2.4.4). A temperature differential exists between the lower and upper probes. The measurement probes are connected to copper leads at an isothermal junction ($T_0$). The copper leads feed into instruments at ambient temperature ($T_A$).

![Diagram of Seebeck coefficient measurement system]

**Fig. 2.4.4.** Schematic of Seebeck coefficient measurement system.

To increase the accuracy of the Seebeck coefficient measurement, the ZEM-3 system measures voltages at three or more temperature differentials. A linear regression is performed on these data points. From the slope of the $\Delta V$ vs. $\Delta T$ curve, Seebeck coefficient is computed after compensating the thermocouple Seebeck value. A typical Seebeck computation plot is shown in Fig. 2.4.5. The measured Seebeck value at room temperature (-42.5 $\mu$V/K) for a constantan standard sample agrees very closely with the actual value, which shows the reliability of the measurement.
2.5. NanoFlash Technique for Thermal Diffusivity Measurement

As discussed previously, thermal conductivity measurement is considered to be the most difficult measurement among the various thermoelectric properties. This is due to difficulties in satisfying the assumed boundary conditions caused by surface heat losses and thermal contact resistance between the sample surface and its associated heat sources and sinks. As mentioned before, the thermal conductivity $k$ can be indirectly determined by measuring thermal diffusivity $\alpha$ and specific heat $C$. A Nanoflash LFA 447 (Netzsch Instruments, Inc.) apparatus is utilized to measure the thermal diffusivity by the laser flash technique, whose formulation was first deduced by Parker et al. in 1961 [15] and reviewed several times by many researchers [18-20], simply a high-performance Xenon flash lamp.
taking the place of the laser. This technique makes use of a flash tube to eliminate the problem of thermal contact resistance while the heat loss is minimized by making the measurements in short enough time so that the cooling effect can be neglected.

A simple sketch of the setup system is shown in figure 2.5.1 and picture of the equipment is shown in Fig. 2.5.2. Diffusivity is a measure of how quickly a body can change its temperature; it increases with the ability of the body to conduct heat $k$ and it decreases with heat capacity. A short description of calculating diffusivity by laser flash technique is given as follows.

Consider a solid with uniform thickness $d$ with an initial temperature distribution $T(x,0)$. The temperature distribution at a later time $T(x,t)$ is given by

$$T(x,t) = \frac{1}{d} \int_0^d T(x,0)dx + \frac{2}{d} \sum_{n=0}^{\infty} \exp\left(-\frac{n^2 \pi^2 \alpha t}{d^2}\right) \times \cos\frac{n \pi x}{d} \int_0^d T(x,0) \cos\frac{n \pi x}{d} dx.$$  \hspace{1cm} (2.5.1)

If a laser pulse of energy $Q$ is incident on the surface $x = 0$
and absorbed in a small depth $g$, then the temperature distribution is given by

$$T(x,0) = \frac{Q}{\rho C_p g}, \text{ for } 0 < x < g$$  \hspace{1cm} (2.5.2)

and  $$T(x,0) = 0, \text{ for } g < x < d.$$  \hspace{1cm} (2.5.3)

For a small $g$, equation 2.5.1 at the rear surface $x = d$ together with equations 2.5.2 and 2.5.3 can be written as

$$T(d,t) = \frac{Q}{\rho d C_p} [1 + 2 \sum_{n=0}^{\infty} (-1)^n \exp(-n^2 \pi^2 \alpha t / d^2)].$$  \hspace{1cm} (2.5.4)

Equation 2.5.4 further can be simplified as

$$V = 1 + 2 \sum_{n=0}^{\infty} (-1)^n \exp(-n^2 w),$$  \hspace{1cm} (2.5.5)

where,  $$V = T(d,t) / T_M,$$  \hspace{1cm} (2.5.6)

and  $$w = \pi^2 \alpha t / d^2.$$  \hspace{1cm} (2.5.7)

Here, $T_M$ is the maximum temperature at the rear surface.

Fig. 2.5.2. Nanoflash LFA 447 (Netzsch Instruments, Inc.) equipment for thermal diffusivity measurement.
The equation can be plotted against \( w \) and it can be shown that when \( V \) is equal to 0.5 \( (t = t_{1/2}) \), \( w \) is equal to 0.138. With these values, diffusivity \( \alpha \) can be written as

\[
\alpha = 0.138d^2 / \pi^2 t_{1/2}.
\]  

(2.5.8)

**Fig. 2.5.3.** Temperature rise curve plotted against dimensionless time \( \omega \).

In an actual experiment, a sample of 12.7 mm in diameter and 1-2 mm in thickness is aligned between heat beam and a liquid-nitrogen-cooled InSb (Indium Antimonide) infrared detector and the temperature increase on the rear of the sample is measured. A high-performance Xenon flash lamp is applied to produce the heat pulse on the front of the sample causing a heat pulse to travel through the sample’s thickness. The non-contact measurement of the temperature increase guarantees an easy sample change and a short response time for the signal acquisition system. The equipment is fully automated to control all the functions and record, analyze, and report the thermal diffusivity. All the samples here are graphite coated using a dry graphite lubricant.

There are a few issues related to more accurate determination of thermal diffusivity in this technique. A finite width of the heat pulse can affect the measurement of thin or high
diffusivity samples because the heating of the front surface can’t be considered instantaneous relative to the time it takes to diffuse through the sample. Also, there are non-measurement errors related to heat losses and non-uniform heating. These problems hinder the accurate determination of half time using the temperature rise curve. The software in use contains a set of theoretical analyses that take these issues into account and we can choose the one that fits our experimental conditions and sample constituents. After the correct account of the problems, a fairly accurate value of diffusivity can be obtained with the error range of ~ 2 %, most of which is attributed to the error in thickness measurement.

2.6. Specific Heat Measurement

As seen in equation 2.3.2, to accurately determine the thermal conductivity the exact measurement of the specific heat is another key challenge. A commercial DSC 200 F3 Maia® (Netzsch Instruments, Inc.) instrument is utilized to measure the specific heat by Differential Scanning Calorimetry (DSC) technique, which is one of the most frequently used techniques in the field of thermal characterization of solids and liquids. The principle of DSC technique is that the difference in energy input into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. Both the sample and reference material are maintained at nearly the same temperature throughout the measurement. Generally, the temperature program is designed for the temperature of sample holder to increase linearly as a function of
time. The reference material should have a well-defined heat capacity over the temperature range of interest. In our system, sapphire disc is used as reference material. A simple sketch of the setup system is shown in figure 2.6.1 and picture of the instrument is shown in Fig. 2.6.2.

![Fig. 2.6.1. A simple sketch of DSC setup system.](image)

In an actual measurement, a sample with the diameter of about 5.5 mm and the thickness of 0.5-1.0 mm is placed inside a crucible which is then placed inside the measurement cell (furnace) of the DSC system along with a reference pan which is normally empty. The optimum sample thickness depends on the thickness of the reference sapphire disc. By applying a controlled temperature program (isothermal, heating or cooling at constant rates), caloric changes can be characterized. In principle, three measurements need
to be done before calculating the specific heat of the sample: for baseline, reference sapphire
disc, and the sample. The specific heat of a material can be calculated and given by

\[ C_p = \frac{\text{signal difference (sample - baseline)}}{\text{sample mass} \cdot \text{heating rate} \cdot \text{sensitivity}}, \]  

(2.6.1)

where the sensitivity is obtained from the sapphire measurement and given by

\[ \text{sensitivity} = \frac{\text{signal difference (sapphire - baseline)}}{\text{mass (sapphire)} \cdot \text{heating rate} \cdot \text{theoret. } C_p (\text{sapphire})}. \]  

(2.6.2)

The actual measured DSC data for a typical sample is shown in Fig. 2.6.3. By applying the ratio method, \( C_p \) value of the sample can be calculated using the built-in software and shown in Fig. 2.6.4.

**Fig. 2.6.2.** DSC 200 F3 Maia® (Netzsch Instruments, Inc.) instrument for specific heat measurement.
2.7. Hall Measurements at Room Temperature

If a current carrying conductor is put into a magnetic field, the charge carriers experience additional force due to the magnetic field and are deflected due to the Lorentz force, which creates a potential difference across two sides of the conductor. This is called the Hall Effect. A simple sketch showing this effect is shown in Fig. 2.7.1. In heavily doped...
semiconductors (as in the case of good thermoelectric materials), only one type of carriers carry most of the current. They are called majority carriers and their resistivity behavior with temperature is similar to metal. Hall measurement is used to determine fundamental transport properties including carrier mobility, carrier concentration, and electrical conductivity of a material.

Fig. 2.7.1. Schematic of the Hall Effect in a long, thin bar of semiconductor with four ohmic contacts. The direction of the magnetic field $B$ is along the $z$-axis and the sample has a finite thickness $t$.

In principle, the system we use can produce a Hall measurement over a temperature range from 77 K to 300 K or above. Our measurement, however, was limited to only room temperature. A magnetic field of 1.5 T is used to provide the magnetic field. A sample with thickness of ~ 0.3 mm and cross sectional area of ~ 2×7 mm is prepared by cutting and mechanical polishing. The sample is mounted into a sapphire holder with five gold wires using silver epoxy. Two of the wires are used to pass the current while the other two measure
the voltage drop $V_z$ placed ~ 5 mm apart. The other two gold wires measure the hall voltage, $V_y$, produced by the magnetic field as demonstrated in Fig. 2.7.2. A picture of home-built Hall measurement system is shown in Fig. 2.7.3. Whole measurement is computer controlled using a LabVIEW program.

![Fig. 2.7.2. Schematic of the measurement set-up.](image)

Once the sample is mounted onto the holder, it is put into the magnetic field. The magnetic field can be rotated with respect to the sample to make itself perpendicular to the

![Fig. 2.7.3. Home-built Hall measurement system.](image)

Once the sample is mounted onto the holder, it is put into the magnetic field. The magnetic field can be rotated with respect to the sample to make itself perpendicular to the
direction of current. To make sure of this, a plot of hall voltage $V_y$ versus rotation angle $\theta$ is obtained as shown in Fig. 2.7.4. Minima or maxima of the plot correspond to the direction perpendicular to the magnetic field. After the magnetic field is made perpendicular to the current flow, a set of data of voltages $V_y$ with varying magnitude of the magnetic field $B_z$ for a constant current is taken. Current $I_x$ and voltage drop $V_x$ are recorded by a multimeter. Finally, using the slope of the $V_y$-$B_z$ plot, $I_x$ and $V_x$, carrier concentration $n$, mobility $\mu$ and electrical conductivity $\sigma$ are calculated using the following equations.

![Fig. 2.7.4. Graph demonstration for the determination of the magnetic field direction.](image)

For a sample having thickness $t$ and width $w$, the Hall voltage is given by:

$$ V_H = \frac{I_x B_z}{qnt} , $$

(2.7.1)

where $n$ is the carrier concentration and $q$ is the electron charge. Hence, we have

$$ n = \frac{I_x}{qI_x(V_y / B_z)} $$

(2.7.2)

$$ \mu = \frac{l}{V_x w B_z} $$

(2.7.3)
\[ \sigma = nq\mu = 1/ \frac{w l V}{l I_x}. \] (2.7.4)

Here, \( l \) is the distance between two voltage wires. The electrical conductivities measured, using this system, are compared with those measured by other techniques and the results agree within \(~10\%\) error. We believe that the major source of the error is coming from the dimension measurement.
2.8. References


Chapter 3
Synthesis of p-type Nanostructured Bismuth Antimony Tellurium Alloys and Their Thermoelectric Properties

3.1. Introduction

The best elemental or simple compound semiconductors for thermoelectric refrigeration applications at near room temperatures is bismuth telluride (Bi$_2$Te$_3$) based alloys [1]. These materials also have potential applications in low grade heat recovery and segmented or cascaded power generation devices, working in the lower temperature side of the module. As described in Chapter 1, the efficiency of a thermoelectric device is determined by a dimensionless figure-of-merit $ZT = (S^2\sigma/k)T$ [1-3], where $Z$ is the figure-of-merit, $T$ the absolute temperature, $S$ the Seebeck coefficient, $\sigma$ the electrical conductivity, and $k$ the total thermal conductivity with contributions from the lattice ($k_l$) and the electrons ($k_e$). Significant efforts have been made to improve and discover higher $ZT$ materials since the 1950’s, but the $ZT$ of dominant commercial materials based on Bi$_2$Te$_3$ and its alloys, such as Bi$_{x}$Sb$_{2-x}$Te$_3$ (p-type) and Bi$_2$Se$_x$Te$_{3-x}$ (n-type), has remained at 1.

With the application of low dimension concept [4-5], superlattice Bi$_2$Te$_3$/Sb$_2$Te$_3$ [6] and quantum dot superlattice PbSe$_{0.98}$Te$_{0.02}$/PbTe [7] have been shown to have a significantly improved thermoelectric figure of merit due to the phonon confinement and enhanced phonon scattering which result in a much lower lattice thermal conductivity. However, it is
difficult to scale up these superlattices for large volume energy conversion applications due to limitations in both heat transfer and cost. On the other hand, high $ZT$s were reported in bulk materials as well such as silver antimony lead telluride (LAST) [8] and its alloys [9], skutterudites [10], and Zintl [11]. These materials benefit mostly from reduced lattice thermal conductivity. These materials with improved $ZT$ are suitable only for high temperature operations. Near room temperature (0-250 °C), Bi$_2$Te$_3$-based materials are still of prime interest.

In order to improve both the thermoelectric and mechanical properties, we have been pursuing a random nanostructuring strategy based on the understanding that the thermal conductivity reduction that is responsible for $ZT$ enhancement in superlattices can be realized in nanostructures as well. Following this strategy, we have achieved a peak $ZT$ of 1.4 in p-type Bi$_x$Sb$_{2-x}$Te$_3$ by ball milling and hot-pressing the alloyed crystalline ingot as the starting material [12]. This approach is simple, economic, and can be readily extended to other materials. Inspired by this accomplishment, we are interested in ball milling elemental chunks of Bi, Sb, and Te into alloy nanopowders first and then hot-pressing them into dense bulk to demonstrate a similar high $ZT$. This process eliminates the ingot formation step and is more cost effective and environmentally friendly. A peak $ZT$ of about 1.3 in the temperature range of 75 and 100 °C, about 1.1 at room temperature, and 0.7 at 250 °C have been achieved. These are about 10 % lower than those obtained by using ingot as the starting material, probably due to a minor microstructural difference and the lack of some minor elements (Zn,
Cd, etc.). In comparison, conventional Bi$_2$Te$_3$-based materials have a peak $ZT$ of about 1 at room temperature and about 0.25 at 250 °C. The high $ZT$ in the temperature ranges of 25-250 °C makes the nanocrystalline bulk materials attractive for cooling and low grade waste heat recovery applications. This material can also be used for thermoelectric power generation by integrating it into segmented thermoelectric devices which operate at high temperatures. Such a simple approach should be readily applied to other thermoelectric materials that cannot be made into crystalline ingot as easily.

In this chapter, after a brief introduction of the general properties of the materials, we will discuss in detail the sample preparation technique including high energy ball milling and hot-pressing of them into a dense bulk sample, the measurement results and analyses, comparing with commercial ingot and nanograined sample made from ingot.

### 3.2. General Properties of Bismuth Telluride and Its Alloys

Although many authors [13-15] have described the compound bismuth telluride (Bi$_2$Te$_3$) as a rhombohedric structure with space group $D_3^5$ ($R3m$), it is easier to represent this structure by a hexagonal cell. The hexagonal cell is formed by the stacking of layers (perpendicularly to the $c$-axis) of like atoms following the sequence (as showed in Fig. 3.2.1):

-Te$^{(1)}$-Bi-Te$^{(2)}$-Bi-Te$^{(1)}$.

The superscripts refer to the two types of bonding. This sequence is called a quintet and the hexagonal cell is formed by three quintets.
Bi$_2$Te$_3$ crystals are remarkable because they can be readily cleaved in planes perpendicular to the trigonal or $c$-axis. It has been shown that the tellurium and bismuth layers are held together by strong ionic-covalent bonds, but no bonding electrons remain to connect the adjacent Te$^{(1)}$ layers. The weak Van der Waals binding between the layers accounts for the ease of cleavage [16]. Besides this striking mechanical anisotropy, most of the transport properties also possess a strong anisotropy. The parameters of hexagonal cell are $a=4.3835$ Å, $c=30.360$ Å at 77 K.

Bismuth telluride has multivalley type of band structure (Fig. 3.2.2) with a six-valley model for both n-and p-type [17]. This compound has an indirect bang gap and the gap value is found to be 0.13 eV at 300 K.

![Fig. 3.2.1. Crystal structure of bismuth telluride: (a) rhombohedric unit cell, (b) hexagonal unit cell, and (c) projection in YZ plane [17].](image)

The (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ solid solutions constituted from the isomorphous compounds
Sb$_2$Te$_3$ and Bi$_2$Te$_3$ crystallize in the same rhombohedral structure ($R\bar{3}m$). The bismuth atoms are substituted for the antimony atoms. The parameters of the hexagonal cell have been obtained by Smith et al. [18]. For example, if $x=0.75$, then $a=4.295$ Å and $c=30.35$ Å. Based on a six-valley model with and without one parabolic valence band, the band gap is estimated at 0.19 and 0.18 eV for $x=0.75$ and 0.7 respectively [19-20].

![Fig. 3.2.2. Band structure of bismuth telluride [17].](image)

In the same way, the solid solutions Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ are formed by the substitution of Te atoms with selenium (Se). Initially Se atoms, being more electronegative, take the place of the Te$^{(2)}$ atoms and increase the ionic bonds. It has been shown that the band gap increases on adding Bi$_2$Se$_3$ to Bi$_2$Te$_3$, reaching a maximum value of 0.31 eV for $x=0.3$ [21]. If more Te atoms are replaced, then the Se atoms occupy the Te$^{(1)}$ sites. The presence of Bi-Se$^{(1)}$ bonds would decrease the ionicity of the Bi-Se$^{(2)}$ bonds and lead to a decrease in the band gap.

One of the most interesting features of Bi$_2$Te$_3$ is the manner in which thermal diffusion of copper, silver, and gold takes place at relatively low temperatures. These
elements act as donor impurities so that the ease with which they can move into or out of the lattice of Bi$_2$Te$_3$ is clearly of extreme importance. For example, it has been observed that during the manufacture of thermoelectric modules it is possible for copper that is dissolved in molten solder to pass through nickel-plated contacts into the thermoelements. This whole process takes only a few minutes. Equally astonishing is the fact that the copper can be removed at ordinary temperatures by immersing the thermoelements in a suitable aqueous sink. The very high diffusion coefficient of copper in the $a$ direction [22] is undoubtedly due to the fact that positively ionized copper atoms can readily occupy interstitial sites between the Te$^{(1)}$ layers. Because of the weak binding and relatively large spacing between these layers, the copper ions can also easily move from one site to another.

3.3. Experimental Procedures

3.3.1. Preparation of Nanostructured Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloys by Mechanical Alloying

There are several ways of preparing nanopowders of bismuth telluride based alloys: chemical synthesis, chemical vapor deposition, mechanical alloying, etc. However, only the mechanical alloying procedure will be described here. Mechanical alloying (MA) was first developed to produce oxide dispersion-strengthened (ODS) alloys [23]. Synthesis of amorphous alloys is an area that has received considerable attention in recent years. Mechanical alloying is a high-energy ball milling technique used to produce alloyed powder
through solid-state reactions. MA occurs basically through a repeated process of fracture and cold welding of powder particles trapped between grinding balls. Although the processing is done at ambient temperature, the localized heat generated by the collisions of the balls with the materials being alloyed can raise the temperature of the alloy 100 to 350 K depending on the thermal properties of the materials. This temperature increase is not large enough to cause melting or recrystallization in most cases, but it does provide a driving force for the interdiffusion of components along atomically clean fracture surfaces [24]. One of the advantages of MA is that it is a room temperature process which removes the problem of volatilization of dopants. Also, the MA process may allow for the incorporation of nanometer-sized inclusions to act as phonon scatterers [25]. Our goal is to prepare clean nanopowders with small particle size for which high-energy ball milling is a good option.

In a typical experiment, appropriate amounts of elemental Bi (99.999%, metal basis polycrystalline lump), Sb (99.999%, metal basis ingot) and Te (99.999+, metal basis lump) were weighed according to the nominal composition of Bi_{0.6}Sb_{1.6}Te_{3}. Next they are loaded into a zirconia jar containing a few zirconia grinding balls and sealed, and then subjected to mechanical alloying in a planetary ball mill machine (PM100, Glen Mills Inc.) for ~70 hours at a speed of 600 rpm. To minimize the oxygen contamination, all weighing and loading of the nanopowders were done in a glove box under a highly purified argon. Pictures of a ball mill machine and a ball milling jar are shown in figure 3.3.1.
To achieve a high $ZT$, the size and quality of nanopowders are important. For good electrical conductivity and carrier mobility, it is especially important to prevent any oxidation. The X-ray diffraction (XRD) pattern of the nanopowders after ball milling for ~ 70 hrs (Fig. 3.3.2A), scanning electron microscope (SEM) image (Fig. 3.3.2B), and bright-field and high-resolution transmission electron microscope (TEM) images (Figs. 3.3.2C and 3.3.2D) are shown in figure 3.3.2. The XRD pattern verifies that the powders are single phase, indicating that the mechanically assisted reaction during ball milling can make elemental chunks Bi, Sb and Te into a single phase alloy. The broadened diffraction peaks indicate that the particles are small, which is also confirmed by the SEM image (Fig. 3.3.2B) and
low-magnification TEM image (Fig. 3.3.2C) which shows that the nanoparticles are about 5 to 20 nm with an average size of about 10 nm. The HRTEM image (Fig. 3.3.2D) confirms the good crystallinity of the nanoparticles and clean surfaces that are desired for good thermoelectric properties.

![Fig. 3.3.2.](image)

Fig. 3.3.2. (A) XRD pattern of the nanopowders after ball milling, (B) SEM, (C) bright-field TEM image, and (D) HRTEM image of the mechanically alloyed nanopowders from elements.

### 3.3.2. Consolidation of As-prepared Nanopowders

As-prepared nanopowders need to be densified into a bulk solid sample with density close to 100 % of the theoretical value to test the thermoelectric properties. We expect to preserve the nanometer-sized grains in the bulk sample after densification, although there is
always some grain growth during the process. High density of the sample is particularly important to have good electrical conductivity and carrier mobility and, consequently, a high ZT. Here, we employed a direct current induced hot-press technique in air to make a solid bulk sample, which is considered to be superior to maintain small grains in the sample after compaction because of its fast heating capability. Also, it is a time saving technique as each sample can be densified within a few minutes while other conventional heating techniques like furnace heating take a few hours for each sample.

As shown in figure 3.3.3, a large dc current is passed through the as-prepared nanopowders which are loaded into a graphite die in the glove box to prevent any oxidation and are sandwiched by two graphite plungers. The heat generated by the joule heating and the plasma created inside the powders by the applied electric field help to quickly heat up the powders to a high temperature. The applied pressure helps to achieve a high density for the sample. For a typical sample, a constant uniaxial pressure of 80 MPa is applied using a Carver Press. The powders are heated up to a temperature of ~ 500 °C within about 4 mins and held for 2 mins. After the hot-press, the bulk sample is quickly cooled down to room temperature using cooling water at top and bottom of the die while maintaining the pressure. The fast cooling helps to maintain uniform composition by preventing severe precipitation. The pressure during cooling is important to attain the high density for the sample. After the press, a disc of $\frac{1}{2}$" in diameter and a few millimeters in thickness is obtained (Fig. 3.3.4). The disc is then cut into a bar of about 2 mm by 2 mm by 12 mm for power factor measurement.
However, for thermal diffusivity measurement by laser flash technique, a disc can be used without dicing.

**Fig. 3.3.3.** A simple sketch of dc hot-press system (left) and a real picture of it (right).

**Fig. 3.3.4.** Pictures of a hot-pressed sample (left) and a cut bar sample (right) for power factor measurement.

3.4. Results and Discussion of p-type Nanostructured Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloy Samples
3.4.1. Measurement Results and Theoretical Analysis for Our Best Hot-pressed Bi\textsubscript{0.4}Sb\textsubscript{1.6}Te\textsubscript{3} Alloy Samples

The transport properties of three types of samples: nanograined sample with Bi\textsubscript{0.4}Sb\textsubscript{1.6}Te\textsubscript{3} nominal composition made from elements, nanograined sample made from crystalline ingot, and the crystalline ingot are summarized in figure 3.4.1 [26]. The temperature dependence of the electrical conductivity (Fig. 3.4.1A), Seebeck coefficient (Fig. 3.4.1B), power factor (Fig. 3.4.1C), thermal conductivity (Fig. 3.4.1D), and ZT (Fig. 3.4.1E) are analyzed in these figures. The behaviors of the two nanograined samples are similar. The electrical conductivity of the nanograined sample from elements is always higher than that of the crystalline ingot sample (Fig. 3.4.1A) because of the higher carrier concentration measured by Hall method (Table 3.4.1) and is almost identical to the nanograined sample made from ingot [12]. The Seebeck coefficient (Fig. 3.4.1B) of nanograined element sample is slightly lower than from nanograined ingot sample, both of which have a lower Seebeck coefficient than that of the crystalline ingot sample below 150 °C, but higher above 150 °C [12]. The smaller Seebeck coefficient near room temperature is due to higher carrier concentration while the larger Seebeck coefficient at higher temperatures is due to suppression of minority carrier (electron) excitation in more heavily doped samples. Figure 3.4.1C shows the corresponding power factor of the three samples. The nanograined samples have a power factor comparable to that of the crystalline ingot below 100 °C, but higher above 100 °C than that of the ingot. The nanograined sample made from elements has a
slightly lower power factor than that made from ingot. Thermal conductivity of the nanograin sample is significantly lower than that of the ingot as expected due to increased phonon interface scattering, but systematically higher than that of the sample made from ingot [12], probably due to the lack of some minor elements that were used in the ingot (Fig. 3.4.1D). The smaller thermal conductivity of the nanograin samples at higher temperatures is due to weakened bi-polar effect resulted from the interface thermionic emission [12]. It is clearly seen that the peak $ZT$ value shifts to a higher temperature and remains significantly higher than that of the ingot at all temperatures, but about 10% lower than that of the nanocrystalline dense bulk made from ingot (Fig. 3.4.1E)[12]. The peak $ZT$ of our hot pressed samples is about 1.3 at 100 °C, which is significantly higher than that of the best Bi$_2$Te$_3$-based alloy ingots. The superior $ZT$ at high temperatures is very important for power generation applications since there are no other materials with a similar high $ZT$ at this temperature.

Here, the electrical conductivity was measured by a four-point current switching technique and the Seebeck coefficient was measured by a static dc method based on the slope of a voltage vs. temperature-difference curve. The measurements were done by using commercial equipment (ZEM-3, Ulvac Inc.) on bars of about 2 mm by 2 mm by 12 mm cut along the disk plane. The same properties were measured on a home-made system on the same sample and the two sets of measurements are within 5% of each other. The thermal diffusivity was first measured by a laser-flash method on disks along the disk axial direction
using a commercial system (Nanoflash LFA 447, Netzsch Instruments Inc.) and the specific
heat was measured by DSC technique using a commercial instrument (DSC 200 F3 Maia®,
Netzsch Instruments Inc.). After that, bars were diced from the disks and their thermal
diffusivities were measured along the bar (disk-plane) direction using an Angstrom’s method
in the same home-built system. The thermal diffusivities of the bars and of the disks are in
agreement within 5 %, confirming the isotropy of the samples.

![Fig. 3.4.1.](image)

(A) Electrical conductivity, (B) Seebeck coefficient, (C) power factor,
(D) thermal conductivity, and (E) ZT dependence of temperature of hot-pressed
nanocrystalline bulk samples with Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nominal composition made from
elemental chunks in comparison with a commercial ingot and a nanocrystalline bulk
sample made from ingot.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Mobility (cm$^2$/V·sec)</th>
<th>Carrier concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial ingot</td>
<td>320 (along a-b plane)</td>
<td>1.8 x 10$^{19}$</td>
</tr>
<tr>
<td></td>
<td>255 (along c direction)</td>
<td></td>
</tr>
<tr>
<td>Nanocrystalline bulk made from ingots</td>
<td>264 (uniform all directions)</td>
<td>2.5 x 10$^{19}$</td>
</tr>
<tr>
<td>Nanocrystalline bulk made from elements</td>
<td>273 (uniform all directions)</td>
<td>2.9 x 10$^{19}$</td>
</tr>
</tbody>
</table>

**Table 3.4.1.** Mobility and carrier concentration at room temperature of our nanocrystalline bulk samples with Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nominal composition made from elemental chunks in comparison with the commercial ingot and the nanocrystalline bulk samples made from ingots.

Usually the commercial Bi$_2$Te$_3$-based ingots made by zone melting have layered structures and the thermoelectric properties are anisotropic. The highest $ZT$ is along the cleavage plane of the crystal, but unfortunately this direction has the worst mechanical properties resulting in a difficult and low yield module fabrication process. However, the hot-pressed samples from nanopowders are expected to be isotropic because of the random orientation of the grains [12]. Therefore, not only the thermoelectric properties but also the mechanical properties of these nanostructured samples are much better than those of the zone melting made crystalline ingots. To confirm the isotropic property in the hot-pressed nanocrystalline sample, a thicker disc was prepared and cut both along and perpendicular to the press direction. Each of the three properties is measured and found in agreement within 5 %, but the $ZT$s are the same since a higher power factor ($S^2\sigma$) (5 %) is always canceled by a similarly higher thermal conductivity ($k$) (5 %).
In comparing the transport properties of the nanograined samples (both made from ingot and from elements) with those of crystalline ingot, one particularly noteworthy aspect is the slow increase in the thermal conductivity as a function of temperature (Fig. 3.4.1D). This indicates a much smaller bipolar contribution \([1]\) to the thermal conductivity by thermally generated electrons and holes than that in crystalline ingot. We explain this reduced bipolar effect by assuming the existence of an interfacial potential that scatters more electrons than holes \([27]\). Past studies for Bi\(_2\)Te\(_3\)-based materials suggested that structural defects such as antisites, i.e. Bi atoms going to Te sites, serve as an important doping mechanism \([27-28]\). We anticipate that such antisites are more likely to occur at interfaces. Uncompensated recombination centers at interfaces associated with defect states and antisites are responsible for charge buildup at grain-boundaries and thus increase the hole density in the grains. This is in accordance with the observed increase in the electrical conductivity and the reduction in the Seebeck coefficient of the nanograined samples compared with those of crystalline ingot sample (Fig. 3.4.1A and 3.4.1B).

For a typical Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) nanograined sample from elements (YM0078) and a crystalline ingot sample, both the lattice contributions to the thermal conductivity and total thermal conductivities have been carried out as shown in Fig. 3.4.2. The lattice contributions are estimated by using Wiedemann-Franz relation \((k_l \approx k_{\text{total}} - k_e \approx k_{\text{total}} - L \sigma T, \ L \) is the Lorenz constant\). The results show that lattice contributions to the total thermal conductivity are reduced by a factor of two.
3.4.2. Microstructures Study of p-type Hot-pressed Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloy Samples

To understand the mechanism of $ZT$ enhancement in hot-pressed samples, a TEM investigation of the nanostructure was carried out. To prepare the TEM specimen, hot-pressed pellets were cut into blocks of about 2 mm by 3 mm by 1 mm and ground down to 2 mm by 3 mm by 0.002 mm using a mechanical Tripod Polisher. The sample was glued to a copper grid and milled using Precision Ion Polishing System (Gatan Inc.) for 30 minutes with an incident energy of 3.2 kV and a beam current of 15 $\mu$A at the incident angle of 3.5 degrees.

Figure 3.4.3 shows the main structural features of the hot-pressed sample [26]. One of the common features is the presence of submicrometer grains and dense packing as shown in the low magnification TEM image (Fig. 3.4.3A). An HRTEM image (Fig. 3.4.3B) shows...
that grains have excellent crystallinity and large angles between them, which explains isotropy of properties. Although the grains are grown to larger sizes in comparison with the starting nanopowders (Fig. 3.3.2), each grain shows nanosized features within it. Figures 3.4.3C and 3.4.3D clearly show Sb nanoparticles of sizes up to 50 nm precipitated inside the grains which may occur during the hot press heating and cooling processes. The energy dispersive x-ray spectroscopic (EDX) patterns (inset of Fig. 3.4.3C) obtained on the precipitates confirm that they are pure Sb. However, we did not see these Sb precipitates. On the other hand, Te does precipitate in the samples from ingots [12]. Also, we have observed boundaryless nanodots of various sizes that are embedded and dispersed inside the BiSbTe matrix as shown in Figs. 3.4.3E and 3.4.3F. These two images were taken at different locations of the sample and clearly show that the sizes are very different: about 2-3 nm (indicated by the arrows) in Fig. 3.4.3E and 10-15 nm in Fig. 3.4.3F. These nanodots are formed due to the composition fluctuation inside the grains and are mostly Sb-rich with a typical composition close to Bi:Sb:Te = 9:41:50 with Sb substitution for Te. Both the large size distribution and the high dispersion of the nanodots are believed to be favorable to the scattering of a wide spectrum of phonons (mid-to-long wavelength) [29]. We believe that the size of the individual grains, Sb-rich nanodots, and Sb precipitates all help enhance the scattering of the phonons in different energy ranges and therefore contribute to the reduction of the thermal conductivity. The reason why the \( ZT \) is systematically about 10 % lower than the dense nanocrystalline bulk samples made of nanopowders from ball milling the ingot is
probably due to lack of some minor elements (Zn, Cd, etc.) that were used in the ingot and also the minor structural difference that Sb instead of Te precipitates in the samples from elements.

Fig. 3.4.3. TEM images showing the microstructures of hot-pressed nanocrystalline dense bulk samples made from elemental chunks. (A) low-magnification image showing the submicrometer grains, (B) HRTEM image showing high crystallinity and random orientation, (C) bright-field TEM image and (D) HRTEM image showing Sb precipitates of about 50 nm in the matrix, EDX patterns (inset of Fig. 3.4.2C) show that the precipitates are pure Sb (marked with 1) and the matrix are BiSbTe alloy (marked with 2). HRTEM images (E) and (F)
showing the nanodots of various sizes (2-3 nm in E indicated by the arrows and 10-15 nm in F) inside the BiSbTe matrix.

We speculate that the larger-sized grains containing nanodots (Fig. 3.4.3A) resulted from the non-uniform ball milling. These large grains may have grown even larger during the longer hot-press compaction via Oswald Ripening mechanism. Therefore, we certainly would like to see more uniform nanograins after ball milling and, better yet, to prevent these nanograins from growing during hot-press. With uniform nanograins, we would expect a further thermal conductivity reduction and a power factor enhancement due to the increase in the electronic density of states that is induced by the quantum confinement effect.

3.4.3. Optimization of p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Alloy Samples

For optimization of the thermoelectric properties of hot-pressed samples, there are several factors that need to be considered. There may be effects of the length of ball milling time, ball milling temperature (regular, air cooling or LN cooling), milling conditions (wet or dry), hot-press pressure, temperature, heating/cooling rate, holding time, and so on. A few of these conditions are briefly discussed in this section.

3.4.3.1. Effect of Ball Milling Time

To find the effect of ball milling time on thermoelectric properties, powders ball milled for different lengths of time were prepared and hot-pressing was done on the same conditions, as described in the previous section. During ball milling, it is believed that many
defects (usually Te vacancies) and antisites are generated. These defects will not only change
the temperature dependence behaviors of electrical conductivity and Seebeck coefficient, but
also help to reduce the thermal conductivity as described in the previous section. X-ray
diffraction (XRD) is used to characterize the powders ball milled for 30, 40, 50, 60, and 70
hrs as shown in Fig. 3.4.4. Temperature dependence behaviors of various thermoelectric
properties for hot-pressed samples from powders with different lengths of ball milling time
are summarized in Fig. 3.4.5. A crystalline ingot sample is also included to compare with our
hot-pressed samples.

![Fig. 3.4.4. XRD patterns for powders with different lengths of ball milling
time.](image-url)

---

---
The XRD patterns verify that the powder becomes single phase with gradually prolonging the milling time, indicating that the mechanically assisted reaction among the Bi, Sb, and Te proceeded and the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ concentration increased with milling time. Full alloying and a single phase, which is very well matched with that of standard Bi$_{0.4}$Sb$_{1.6}$Te$_3$ alloys (see the indexes), is obtained after ball milling for 70 hrs. The electrical conductivities of the hot pressed samples are always higher than the ingot as shown in Fig. 3.4.5A. Meanwhile, the Seebeck coefficient is lower than the ingot which makes the power factor comparable to the ingot at lower temperatures while it is higher at higher temperature. Thermal conductivities of all the hot pressed samples are significantly lower than the ingot.
and the difference increases with temperature as shown in Fig. 3.4.5D. It is also important to note that the electrical conductivity is higher for shorter time ball milled samples and remains similar for samples after 50 hrs ball milling. However, the Seebeck coefficient behaves the opposite way (Fig. 3.4.5A and B). Additionally, the thermal conductivity decreases with the ball milling time until it saturates after 60 hrs. We believe that this reduction is due to the alloying of the nanopowders since the particle sizes are similar after 50 hrs ball milling. This observation proves that the alloyed nanopowders have better thermoelectric properties than composite nanopowders.

3.4.3.2. Effect of Hot-press Temperature

Figure 3.4.6 below shows the summary of the effects of hot-press temperature on thermoelectric properties. Figure 3.4.6A shows the electrical conductivity of various samples hot-pressed at 485, 500, and 515 °C. A general trend that can be observed is that a higher hot-press temperature gives a higher electrical conductivity and both samples pressed at 500 and 515 °C have similar electrical conductivity trends. Fig. 3.4.6B shows the temperature dependence of the Seebeck coefficient of various samples, indicating that a higher press temperature results in a lower Seebeck coefficient. This happens because an increase in carrier concentration (and eventually electrical conductivity assuming same carrier mobility) leads to a decrease in Seebeck coefficient as discussed in chapter 1. Combining these two transport properties together, the 500 °C hot-pressed sample has the highest power factor.
while the 485 °C pressed sample has the lowest power factor as shown in Fig. 3.4.6C. Thermal conductivity is usually lower with a lower hot-press temperature but not in this case here (Fig. 3.4.6D), which could be due to the experimental error coming from a very small press temperature difference for these three samples. A careful observation reveals that $ZT$s of samples hot-pressed in the temperature range of 500 to 515 °C follow a similar trend with a peak value of about 1.3 at temperature ~ 100 °C (Fig. 3.4.6E).

Fig. 3.4.6. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D), and $ZT$ (E) of various samples hot-pressed at different temperatures.
3.4.3.3. Effect of Holding Time

As described in the previous section, a hot-press temperature in the range of 500-515 °C would be the best temperature to use for an optimum $ZT$ value. In this temperature range, different holding times were tested to see the effect of holding time on the $ZT$ value of p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nanograin alloy. Figure 3.4.7 below shows a summary of the effect of the holding time on various thermoelectric properties. Figure 3.4.7A shows the electrical conductivity of various samples that were hot-pressed at 500 °C and held for different times. A general trend can be observed from the plots: a longer holding time usually gives a higher electrical conductivity. Fig. 3.4.7B shows the temperature dependence of the Seebeck coefficients of various samples. As expected, a longer holding time which gives a higher electrical conductivity results in a lower Seebeck coefficient. The power factor is slightly higher for the longer holding time sample as shown in Fig. 3.4.7C. However, a longer holding time also results in a higher thermal conductivity (Fig. 3.4.7D) which makes $ZTS$s almost similar for samples that were held for 1, 2, and 6 mins with a peak value of about 1.3. The 0 min held sample shows much worse performance after 75 °C (Fig. 3.4.7E). This is primarily due to the thermal conductivity for 0 min held sample, which becomes the highest at high temperatures compared to the 1, 2, and 6 minutes held samples (Fig. 3.4.7D).
Fig. 3.4.7. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various samples pressed at 500 °C and held for 0, 1, 2, and 6 mins, respectively.

3.5. Results and Discussion of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ Alloy Samples

The thermoelectric properties of bismuth telluride based alloys are very sensitive to the bismuth and antimony contents. Electrical conductivity is usually increased with the antimony content, but the thermal conductivity increases as well. With a proper bismuth,
antimony and tellurium ratio, the optimum $ZT$ could be obtained for various thermoelectric applications, (i.e. the cooling devices and power generators). In this section, the microstructures and thermoelectric properties of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ composition samples are briefly discussed as a baseline study. The powders preparation and hot-press techniques are the same as that of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ case.

Figures 3.5.1 and 3.5.2 below show the XRD patterns and the main structural features of the as-prepared Sb$_2$Te$_3$ and Bi$_2$Te$_3$ powders (after 90 and 44 hrs ball milling, respectively). Similarly, both XRD patterns (Fig. 3.5.1A and Fig. 3.5.2A) confirm that the powders are single phase, indicating that the mechanically assisted reaction during ball milling can make elemental chunks into single phase alloy. The SEM images (Fig. 3.5.1B and Fig. 3.5.2B) show that the nanoparticles are about tens of nanometers in size and low-magnification TEM image of Sb$_2$Te$_3$ nanoparticles (Fig. 3.5.1C) shows that most of particles aggregate together without clear boundary. This is very different from the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ case. The HRTEM images for both Sb$_2$Te$_3$ and Bi$_2$Te$_3$ powders (Fig. 3.5.1D and Fig. 3.5.2C) confirm the good crystallinity and the clean surfaces of the nanoparticles that are desired for good thermoelectric properties.

Figure 3.5.3 below shows the summary of the various thermoelectric properties of a typical sample prepared from Sb$_2$Te$_3$ powders that was hot-pressed at 500 °C and held for 2 mins. The electrical conductivity is much higher than that of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composition sample and drops from $4 \times 10^5$ to $1.3 \times 10^5$ S/m with the temperature increasing from 25 to
250 °C (Fig. 3.5.3A), indicating a very high hole concentration for binary Sb$_2$Te$_3$ powders. The trend in Seebeck coefficient is as expected: a lower electrical conductivity gives a higher Seebeck coefficient as shown in Fig. 3.5.3B. However, the very high electrical conductivity also results in a very high thermal conductivity (Fig. 3.5.3C), mainly due to the large part of electrical contribution to the thermal conductivity. Hence, the $ZT$ increases with the temperature from 0.28 up to 0.7 at 250 °C (Fig. 3.5.3D). To obtain the best thermoelectric performance by reducing the high electrical conductivity, the ternary composition by Bi doping is essential.

![Fig. 3.5.1.](image)

Fig. 3.5.1. (A) XRD pattern of Sb$_2$Te$_3$ nanopowders after 90 hrs ball milling, (B) SEM, (C) bright-field TEM images, and (D) HRTEM image of the mechanically alloyed nanopowders.
Fig. 3.5.2. (A) XRD pattern of Bi$_2$Te$_3$ nanopowders after 44 hrs ball milling, (B) SEM, and (C) HRTEM image of the mechanically alloyed nanopowders.

Figure 3.5.4 below shows the summary of the various thermoelectric properties of a typical sample prepared from Bi$_2$Te$_3$ powders that was hot-pressed at 500 °C and held for 0 min. Fig. 3.5.4D shows that the peak $ZT$ value of about 0.73 occurs at 50 °C and the $ZT$ curve drops dramatically with the temperature, mainly due to the increased thermal conductivity (Fig. 3.5.4C) and decreased power factor (Fig. 3.5.4A and Fig. 3.5.4B) at higher temperature. One interesting finding is the fact that our Bi$_2$Te$_3$ samples prepared by hot-pressing the ball milled powders show n-type conductivity (Fig. 3.5.4B) (note that single crystals of Bi$_2$Te$_3$ show p-type conductivity for this composition). This can be explained by the creation of many Te vacancies during the milling process. An analysis of data, in agreement with the
literature, suggests that in the p-type materials main doping mechanism is the Bi\textsubscript{Te} and Sb\textsubscript{Te} antisites formation. Between these two types of antisites, Sb\textsubscript{Te} antisites should be the dominant one since Sb is closer to Te in electronegativity and Sb\textsubscript{Te} formation energy is correspondingly smaller at 0.35 eV (Bi\textsubscript{Te} antisites formation energy is 0.40 eV). However, in n-type materials creation of Te vacancies (each vacancy contributes two electrons) which are created during ball milling [30] should be a major source of carriers. Hence, our Sb\textsubscript{2}Te\textsubscript{3} samples show p-type conductivity, indicating Te vacancy doping is not as strong as Bi\textsubscript{2}Te\textsubscript{3} samples.

**Fig. 3.5.3**. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), thermal conductivity (C) and ZT (D) of a typical Sb\textsubscript{2}Te\textsubscript{3} composition sample hot-pressed at 500 °C and held for 2 mins.
Fig. 3.5.4. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), thermal conductivity (C) and $ZT$ (D) of a typical Bi$_2$Te$_3$ composition sample hot-pressed at 500 °C and held for 0 min.

3.6. Summary

By ball milling alloyed bulk crystalline ingots into nanopowders and hot-pressing them, we had demonstrated high figure-of-merit in nanostructured bulk bismuth antimony telluride [12]. Here, we use the same ball milling and hot-press technique, but now we start with elemental chunks of bismuth, antimony, and tellurium to avoid the ingot formation step. Therefore, this process is more economical and environmentally friendly than starting from alloyed bulk crystalline ingots. We show that a peak $ZT$ of about 1.3 in the temperature range
of 75 and 100 °C has been achieved (Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composition). Moreover, our material also exhibits a $ZT$ of 0.7 at 250 °C, similar to the value obtained when ingot was used. Also a $ZT$ of 1.1 is obtained at room temperature, which makes this material very useful not only for cooling but also for efficient power generation. This is not possible with the ingot material because $ZT$ drops to a very low value at 250 °C.

Experimental data coupled with microstructure studies show that the $ZT$ improvement is caused mostly by the lower thermal conductivity, similar as the case using the ingot. Transmission electron microscopy observations of the microstructures suggest that the lower thermal conductivity is mainly due to the increased phonon scattering from the increased grain boundaries of the nanograins, precipitates, nanodots, and defects. This study demonstrates that high $ZT$ values can be achieved in nanostructured bulk materials with ball milling elemental chunks. This suggests that this approach can be applied to other materials that are hard to be made into ingot, in addition to its advantage of lower manufacturing cost.
3.7. References

Muto, D. Vashaee, X. Y. Chen, J. M. Liu, M. S. Dresselhaus, G. Chen, and Z. F. Ren,


Chapter 4

The Effect of Bi/Sb Ratio on Thermoelectric Properties in p-type Nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ Alloys

4.1. Introduction

There is complete solid solubility among bismuth telluride, bismuth selenide and antimony telluride. Depending on the mixture ratio, carrier concentration can be controlled. This virtue of the solid solution is extremely useful in carrier optimization without any need of the external dopants in most cases. It is well known that undoped Bi$_2$Te$_3$ single crystal is strongly p-type [1]. As Sb$_2$Te$_3$ is added, the number of acceptors increases still further such that in the Bi$_{2-x}$Sb$_x$Te$_3$ system it is usually necessary to add donor impurities to reach the optimum positive Seebeck coefficient. When $x$ is greater than about one, it is difficult to introduce enough donor impurity for the alloy to become n-type. On the other hand, the addition of Bi$_2$Se$_3$ to Bi$_2$Te$_3$ leads to a material that is less strongly p-type. If $y$ is large enough in the Bi$_{2-y}$Se$_{3-y}$Te$_y$ system, the alloy tends to be n-type rather than p-type. Note that factors besides composition affect the carrier concentration in the undoped material as well. For example, materials prepared by powder metallurgy are less strongly p-type than those produced by crystal growth from a melt as was discussed in Chapter 3.

However, there are several issues that need to be considered for optimization of thermoelectric performance [2]. First of these considerations is that there are changes in
effective mass and mobility. Electronic measurements indicate that $\mu(m^*/m)^{3/2}$ for holes increases as Sb$_2$Te$_3$ is added to Bi$_2$Te$_3$, probably because of an increase in mobility rather than effective mass [3-4]. For example, at the composition Bi$_{0.5}$Sb$_{1.5}$Te$_3$, the increase amounts to nearly 20 %. On the other hand, the value of $\mu(m^*/m)^{3/2}$ for electrons decreases monotonically with an increase of $y$ in the Bi$_2$Te$_{3-y}$Se$_y$ system. Usually after making a solid solution by alloying the lattice thermal conductivity is reduced too. For example, the lattice thermal conductivity falls with the addition of Sb$_2$Te$_3$ and reaches a minimum when molar concentration of Sb$_2$Te$_3$ amounts to about 70 %. Secondly, the energy gap strongly depends on the alloy composition. Austin et al. first performed optical measurements that showed an increase in the energy gap from adding Bi$_2$Se$_3$ to Bi$_2$Te$_3$ up to the composition Bi$_2$Te$_{2.1}$Se$_{0.9}$ [5]. It seems that adding Bi$_2$Se$_3$ is beneficial in inhibiting the onset of intrinsic conduction, a factor that is of some importance at the upper end of the temperature range at which Bi$_2$Te$_3$ alloys are used.

There are many reports on efforts to optimize the composition and doping during various fabrication processes [6-9]. However, their optimal compositions are uncertain and usually dependent on the preparation processes. Detailed theoretical and experimental studies suggest that Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and Bi$_2$Te$_{2.7}$Se$_{0.3}$ are usually the preferred p- and n-type ternary alloy compositions [10] and a slight improvement in $ZT$ was described by Yim and Rosi [11]. The p-type alloy was Bi$_{0.5}$Sb$_{1.5}$Te$_{2.91}$Se$_{0.09}$ doped with excess tellurium, and the preferred n-type alloy was Bi$_{1.8}$Sb$_{0.2}$Te$_{2.85}$Se$_{0.15}$ doped with SbI$_3$. However, it has been seldom reported
how the doping effect could change the thermoelectric properties and hence shift the $ZT$ peaks which plays an important role to apply to different thermoelectric devices. Since the device performance depends on not only the peak $ZT$ of the material but also the average $ZT$ over the operating temperature range [12], it is important to optimize the $ZT$ curve over the specific temperature range. For example, a device should perform better during a refrigeration application when the $ZT$ peaks are around or lower than the room temperature. On the other hand, one can expect a better device performance for a power generator when the $ZT$ peaks are around 150 °C, assuming that the hot side is placed at ~ 250 °C (maximum operating temperature for Bi$_2$Te$_3$-based alloys).

Following our earlier work described in Chapter 3, in this chapter we report our successful efforts on studying the thermoelectric properties and nominal composition dependence of $ZT$ peak shifts in p-type Bi$_x$Sb$_{2-x}$Te$_3$ nanograined samples prepared by two types of high energy ball milling techniques and hot-pressing of the alloyed nanopowders. This study will have a significant impact in choosing a right composition material to get high performance in cooling devices or power generators.

4.2. Experimental and Results of p-type Bi$_x$Sb$_{2-x}$Te$_3$ Alloy Samples Made from Planetary Ball Mill Machine

To make nanopowders, appropriate amounts of elemental Bi (99.999%, metal basis polycrystalline lump), Sb (99.999%, metal basis ingot), and Te (99.999+, metal basis lump)
from Alfa Aesar were weighed according to the nominal composition of Bi$_{x}$Sb$_{2-x}$Te$_{3}$. Then they were loaded into a zirconia jar containing a few zirconia grinding balls and sealed. Next, they were subjected to mechanical alloying in a planetary ball mill machine (PM100, Glen Mills Inc.) with optimum ball milling time for each composition. Here, for $x = 0.2, 0.3, 0.4, 0.5$, and $0.6$, the optimum ball milling times are 62, 119, 80, 119, and 82 hrs respectively. To minimize the oxygen contamination, all weighing and loading of the nanopowders were done in a glove box under highly purified argon. As-prepared nanopowders with different nominal compositions were characterized by X-ray diffraction (XRD, Bruker-AXS, G8 GAADS) using Cu Kα radiation (Fig. 4.2.1), field emission scanning electron microscopy (SEM, JEOL-6340F), transmission electron microscopy (TEM, JEOL-2010F), and high-resolution TEM (HRTEM) as shown in figure 4.2.2.

Fig. 4.2.1 shows the XRD patterns of the nanopowders with different nominal compositions ($x = 0.3, 0.4, 0.5$, and $0.6$) after optimum time ball milling. A small peak shift is observed when changing the Bi/Sb ratio, which is caused by a change in lattice parameters. All the peaks can be indexed in reference to the Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$ alloy standard patterns which show a single phase of the nanopowders and no crystalline impurities. The broadened diffraction peaks indicate that the particles are small, which is also confirmed by the SEM image (Fig. 4.2.2A) and low-magnification TEM image taken on a typical composition powder (Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$ composition here) (Fig. 4.2.2B). The TEM image (Fig. 4.2.2B) shows that the nanoparticles have sizes of about 5 to about 30 nm with an average size about 10 nm.
The high resolution TEM image (Fig. 4.2.2C) confirms excellent crystallinity of the nanoparticles and the clean boundaries prove that ball milling can produce small, clean nanoparticles.

Fig. 4.2.1. XRD patterns of the nanopowders with different nominal compositions.

As-prepared nanopowders were loaded into a graphite die with ½” inner diameter and pressed into a bulk sample using a direct current heating hot-press technique as mentioned in Chapter 3. For a typical sample, a pressure of 80 MPa was used. The other press conditions were differed slightly depending on the nominal composition. For $x = 0.2$, 0.3, 0.4, 0.5, and 0.6, the optimum press temperatures and holding times were 450, 450, 500, 500, and 565 °C and 2, 2, 2, 2, and 6 mins, respectively. After the press, disks of ½” diameter and 2 mm thick, and bars of about 2 mm by 2 mm by 12 mm were cut and polished from the pressed disks for characterization of thermoelectric properties.
Fig. 4.2.2. Typical SEM (A), low- (B), and high- (C) magnification TEM images of fully mechanically alloyed nanopowders from a typical composition (Bi$_{0.4}$Sb$_{1.6}$Te$_3$ here).

Similarly, the electrical conductivity of the sample was measured by a four-point current-switching dc technique and the Seebeck coefficient was measured by a static dc method based on the slope of a voltage vs. temperature-difference curve using commercial equipment (ZEM-3, Ulvac Inc.) on the same bar-type sample. The thermal diffusivity was measured by a laser-flash method using a commercial system (LFA 447 Nanoflash, Netzsch Instruments Inc.). The specific heat was determined using a commercial instrument (DSC 200 F3 Maia®, Netzsch Instruments Inc.). Hence, the thermal conductivity was calculated by
a product of thermal diffusivity, specific heat and the sample density. The figure of merit $ZT$ was determined according to the equation: $ZT = (S^2/\sigma)(T/k)$. The transport properties measurements of the samples are summarized in Fig. 4.2.3. Electrical conductivity (Fig. 4.2.3A) has a very clear trend: it increases with the decreasing Bi concentration because the carrier concentration measured by the Hall method increases with the decreasing Bi concentration as well (Table 4.2.1). The Seebeck coefficient is the highest in the Bi$_{0.6}$Sb$_{1.4}$Te$_3$ composition which has the lowest carrier concentration. Another noticeable feature in Fig. 4.2.3B is that the temperature dependence trends are different for various compositions. This could be a result of the different bipolar contributions [13]. The Bi$_x$Sb$_{2-x}$Te$_3$ alloy sample with $x = 0.4$ has the highest power factor up to 100 °C while the sample with $x = 0.6$ has the lowest power factor at the entire temperature range (Fig. 4.2.3C). Fig. 4.2.3D shows the temperature dependence of thermal conductivities of various compositions. There is a clear trend that the thermal conductivity decreases with the increasing amount of Bi content at the lower temperature range, mainly due to the dominating electronic contribution to the thermal conductivity. At the higher temperature range, the trend is completely opposite. This indicates an enhanced bipolar contribution with the increasing amount of Bi content. Here, all the thermal conductivities are indirectly determined with the measured values of density, specific heat and diffusivity by the equation below:

$$k = \rho C\alpha,$$  \hspace{1cm} (4.2.1)
where \( \rho \) is density, \( C \) is specific heat, and \( \alpha \) is thermal diffusivity. The density can be easily determined by Archimedes’ principle. Fig. 4.2.4 below shows the temperature dependence behavior of specific heat for samples with different nominal compositions. In general, the specific heat increases with the decreasing amount of Bi content which is consistent with the thermal conductivity behavior (Fig. 4.2.3D). For compositions with \( x = 0.3 \) and \( 0.4 \), the specific heat is very close over the entire temperature range.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Mobility (cm(^2)/V-sec)</th>
<th>Carrier Concentration (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0.2 )</td>
<td>297</td>
<td>( 4.94 \times 10^{19} )</td>
</tr>
<tr>
<td>( x = 0.3 )</td>
<td>235</td>
<td>( 3.64 \times 10^{19} )</td>
</tr>
<tr>
<td>( x = 0.4 )</td>
<td>273</td>
<td>( 2.90 \times 10^{19} )</td>
</tr>
<tr>
<td>( x = 0.5 )</td>
<td>317</td>
<td>( 1.69 \times 10^{19} )</td>
</tr>
<tr>
<td>( x = 0.6 )</td>
<td>329</td>
<td>( 8.97 \times 10^{18} )</td>
</tr>
</tbody>
</table>

Table 4.2.1. Room temperature carrier concentration and mobility data of our hot pressed nanocrystalline bulk samples with the different nominal compositions.

Fig. 4.2.3E summarizes the temperature dependence of \( ZT \) values in comparison with the commercially available ingot whose nominal composition is close to Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\). Our sample, with the same composition \( x = 0.5 \), shows improved \( ZT \) values over the entire temperature range. The highest \( ZT \) peak is about 1.3 and is obtained from the sample with \( x = 0.4 \). The room temperature value is highest (1.13) in the sample with \( x = 0.5 \). However, if we look at the temperature dependence plots over the whole temperature range (25-250 °C), average \( ZT \)s are similar for both samples with \( x = 0.4 \) and \( x = 0.3 \) but much higher than that of the commercial ingot. The \( ZT \) value of the ingot starts to drop after 75 °C and drops much faster at higher temperatures. Our samples, however, retain high values even at 250 °C. This
is especially important for power generation applications where our materials can be used as a leg in the cold side of segmented or cascaded devices. Thus, for a power generation application with a hot side temperature around 250 °C, either of these two compositions should produce a better performance over other compositions and the ingot. On the other hand, samples with $x = 0.5$ or $x = 0.6$ should have better performances in a refrigeration application given the $ZT$ trends around room temperature as shown in Fig. 4.2.3E. Another particular aspect is that the $ZT$ peaks of different compositions continuously shift toward low temperature with the increase of Bi content. This is very important to seek optimum composition for certain application.

All of this data was confirmed by two independent measurements: one commercial and one home built. They agree within the error range. Also, the thermal diffusivity, measured by laser-flash method in a disc sample, agrees very well with the measurement done in the bar sample by Angstrom’s method [14]. The hot-pressed samples from nanopowders are expected to be isotropic because of the random orientation of the grains. To confirm the isotropic properties in the hot-pressed samples, a thicker disc was prepared and cut both along and perpendicular to the press direction. Each of the three properties is measured and found to be within ~ 5 %. 
Fig. 4.2.3. Temperature dependence of electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D), and $ZT$ (E) of hot-pressed nanocrystalline bulk samples with different nominal compositions.
Fig. 4.2.4. Temperature dependence behavior of specific heat for samples with different nominal compositions.

To understand the mechanism of $ZT$ enhancement in hot-pressed samples, SEM and TEM investigations were carried out. The samples for the TEM observation were prepared by ion milling while the SEM images were taken on a freshly broken surface without any further treatment. All the compositions have similar micro-structural features and typical results from $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ composition are shown in Fig. 4.2.5. Very similar to the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ nanograined sample discussed in Chapter 3, one of the common features of the samples with various nominal compositions is the presence of nanosized grains as shown in a SEM (Fig. 4.2.5A) and a low-magnification TEM image (Fig. 4.2.5B). These grains are randomly oriented and densely packed which is consistent with the density measurement (about 100 % of the theoretical density value). Although the grains are grown much larger after the hot-press in comparison to the starting nanopowders, each grain shows nanosized features. Fig. 4.2.5C shows Sb nanoparticles of sizes up to 50 nm precipitated in the grains.
which might occur during hot-press heating and cooling processes [15]. Also, we observed boundaryless nanodots of varying sizes and shapes that are embedded and dispersed inside the BiSbTe matrix as shown in Fig. 4.2.5D. These nanodots are formed due to the composition fluctuation inside the grains and are mostly Sb-rich [15]. Both the large size distribution and the high dispersion of the nanodots are favorable to the scattering of a wide spectrum of phonons (mid-to-long wavelength) [16]. We believe that the size of the individual grains, nanodots (due to composition fluctuation), and Sb precipitates all help to increase the scattering of the phonons in different energy ranges and, therefore, contribute significantly to the reduction of the thermal conductivity in comparison with the commercially available ingot.
Fig. 4.2.5. SEM and TEM images showing the microstructures of a hot-pressed nanocrystalline bulk sample. (A) low-magnification SEM image showing the nanograins, (B) low-magnification TEM image showing randomly oriented and dense grains, (C) high-magnification TEM images showing Sb precipitates of about 50 nm in the grains, and (F) high-magnification TEM image showing the boundaryless nanodots inside the BiSbTe matrix.

4.3. Experimental and Results of p-type Bi$_x$Sb$_{2-x}$Te$_3$ Alloy Samples Made from High Energy Mixer/Mills Machine

As discussed previously, the mechanical alloying of bismuth antimony tellurium alloy powders using the plane planetary ball mill machine (PM100, Glen Mills Inc.) is very time consuming (the typical ball milling time is about 100 hrs). Usually, it takes about one week to prepare one batch of fully alloyed powders. To limit the ball milling time and make the powders more efficiently, a high energy SPEX SamplePrep 8000M Mixer/Mills with fixed 1080 rpm (SPEX SamplePrep®, LLC) was adopted too. This grinds materials by placing them in a container along with one or more grinding elements and imparting motion
to the container.

In a practical experiment, appropriate amounts of elemental Bi, Sb and Te were weighed according to the nominal composition of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ and loaded into a stainless steel vial containing two stainless steel grinding balls and sealed. Then they were subjected to mechanical alloying in the high energy SPEX SamplePrep 8000M Mixer/Mills for several hours. The typical ball milling time needed for full alloying is about 30 hrs, which is much shorter than the time needed for the planetary ball mill machine. To minimize the oxygen contamination, all weighing and loading of the nanopowders were done in a glove box under highly purified argon. Pictures of the ball mill machine and the ball mill vial are showed in figure 4.3.1.

Fig. 4.3.1. Pictures of A) high-energy ball mill machine (SPEX SamplePrep 8000M Mixer/Mills) and B) a ball mill vial (open and sealed respectively).

The thermoelectric properties of Bi$_2$Te$_3$-based alloys are very sensitive to the bismuth to antimony ratio as discussed in the previous sections. Electrical conductivity is usually increased with antimony content. However, in the meantime, the thermal conductivity increases. With a proper combination of the bismuth, antimony and tellurium ratio, not only
can the optimum $ZT$ be obtained, but also the $ZT$ peak position can be shifted to a required temperature range. To obtain the best performance of a device, it is important to match this $ZT$ peak close to the application temperature range. For example, when a material is used for a refrigeration application, it is preferable to shift the $ZT$ peak slightly below room temperature. For a power generation application, $ZT$ peak should fall in the middle of the hot side and cold side temperatures for the best device performance. Following this idea, a few compositions with different Bi/Sb ratios made from SPEX ball mill machine have been prepared and studied in the next sections.

4.3.1. Thermoelectric Properties of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Composition

Following this composition, we prepared $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ composition nanopowders using the SPEX ball mill machine and hot-pressing the powders into solid samples. From there, the thermoelectric properties were investigated. A summary of the thermoelectric properties for two typical samples with different ball milling times (30 and 40 hrs) but same press conditions (530 °C and held for 2 mins) is presented in Fig. 4.3.2. Electrical conductivity is lower and the Seebeck coefficient is therefore higher than those of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ samples which are due to the bigger amount of Bi content (Fig. 4.3.2A and B). The power factor is lower because the increase in the Seebeck coefficient cannot compensate the loss in electrical conductivity (Fig. 4.3.2C). Since the thermal conductivity is also reduced due to the less electronic contribution (Fig. 4.3.2D), a comparable $ZT$ at a low
temperature range is still achieved (Fig. 4.3.2E). Meanwhile, it is clear to see that ZT drops very fast after 100 °C, suggesting that this composition could be a good choice for applications in cooling devices. These two samples show very close transport properties, indicating that 10 hrs difference in ball milling time doesn’t change the thermoelectric performance for this composition.

Fig. 4.3.2. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and ZT (E) of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ composition samples pressed at 530 °C and held for 2 mins.
4.3.2. Thermoelectric Properties of Bi$_{0.45}$Sb$_{1.55}$Te$_3$ Composition

Figure 4.3.3 below shows the summary of various thermoelectric properties of samples prepared from Bi$_{0.45}$Sb$_{1.55}$Te$_3$ powders with different ball milling time and hot-pressed at different temperatures. Figure 4.3.3A shows the temperature dependence of electrical conductivity of various samples. A higher hot-press temperature gives a higher electrical conductivity as was mentioned in Chapter 3. Also, the longer ball milling time gives higher electrical conductivity as shown in the plots. The Seebeck coefficient trend is as expected: a lower electrical conductivity sample has a higher Seebeck coefficient (Fig. 4.3.3B). The power factor data reveals that the power factor is quite sensitive to the hot-press temperature. A sample pressed at a higher temperature has a higher power factor (Fig. 4.3.3C). Combined with thermal conductivity data (Fig. 4.3.3D), sample prepared from 30 hrs ball milled powders and hot-pressed at 530 °C has the best average $ZT$ over the temperature range from 20-125 °C with a peak value of 1.18 at 75 °C as shown in Fig 4.3.3E. This indicates the potential applications for this composition in cooling devices.
4.3.3. Thermoelectric Properties of Bi$_{0.45}$Sb$_{1.55}$Te$_3$ Composition

As described in previous section, the highest peak $ZT$ among various nominal compositions is obtained from the sample with Bi$_{0.45}$Sb$_{1.55}$Te$_3$ composition. Here we prepared Bi$_{0.45}$Sb$_{1.55}$Te$_3$ composition nanopowders by using a SPEX ball mill machine and hot-pressing the powders into solid samples. A summary of thermoelectric properties measurements for various samples is presented in Fig. 4.3.4. The sample prepared from 40 hrs ball milling powders has slightly higher electrical conductivity over all temperature range than those with short ball milling time (Fig. 4.3.4A), which also has a lower Seebeck coefficient below 150
°C but a higher Seebeck coefficient above 150 °C (Fig. 4.3.4B). Fig. 4.3.4D shows that the sample prepared from 40 hrs ball milling powders has a slightly higher thermal conductivity below 125 °C due to the higher electrical conductivity, but a lower thermal conductivity above 125 °C due to the longer ball milling time. Therefore, the sample prepared from 40 hrs ball milling powders has a highest $ZT$ over the entire temperature range with a peak value of about 1.23 at 100 °C, about 1.08 at room temperature, and about 0.7 at 250 °C as shown in Fig. 4.3.4E. This is consistent with the results for samples prepared from the planetary ball mill machine.
4.3.4. Thermoelectric Properties of Bi$_{0.35}$Sb$_{1.65}$Te$_3$ Composition

Figure 4.3.5 below shows the summary of various thermoelectric properties of samples prepared from Bi$_{0.35}$Sb$_{1.65}$Te$_3$ powders and hot-pressed at different temperatures. Figure 4.3.5A and B show the temperature dependence of electrical conductivity and Seebeck coefficient of various samples. Once again, a higher hot-press temperature gives a higher electrical conductivity and a lower Seebeck coefficient. The sample press at 550 °C has the highest power factor due to the very high electrical conductivity and the other samples retain similar power factor (Fig. 4.3.5C). However, the same sample also has a much higher thermal conductivity than other samples pressed at lower temperatures due to the electronic contribution to the thermal conductivity (Fig. 4.3.5D). Figure 4.3.5E shows that both samples pressed at 400 and 450 °C have highest $ZT$ and a similar trend with a peak value of about 1.17 at ~ 125 °C.
Fig. 4.3.5. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various Bi$_{0.35}$Sb$_{1.65}$Te$_3$ composition samples hot-pressed at different temperatures.

4.3.5. Thermoelectric Properties of Bi$_{0.3}$Sb$_{1.7}$Te$_3$ Composition

In an effort to find a better composition to optimize $ZT$ at a higher temperature range,
Bi$_{0.3}$Sb$_{1.7}$Te$_3$ composition powders were prepared. The powders preparation and hot-pressing technique are the same as those of the previous cases. Fig. 4.3.6 shows the XRD pattern of the as-prepared nanopowders with ball milling time of 20 hrs. The peaks can be indexed in reference to the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ alloy standard patterns because of the very small composition variance. This shows a fully alloyed single phase of the nanopowders with no crystalline impurities.

![XRD pattern of the as-prepared Bi$_{0.3}$Sb$_{1.7}$Te$_3$ nanopowders after 20 hrs ball milling.](image)

Figure 4.3.7 shows the summary of various thermoelectric properties of samples prepared from Bi$_{0.3}$Sb$_{1.7}$Te$_3$ powders with ball milling time of 30 hrs and hot-pressed at different temperatures. Not surprisingly, a higher hot-press temperature gives a higher electrical conductivity and a lower Seebeck coefficient again (Fig. 4.3.7A and B). The sample pressed at higher temperature also has a much higher thermal conductivity than other samples pressed at lower temperatures due to the higher electrical conductivity (Fig. 4.3.7D). It can be
seen that at temperatures below 100 °C the samples pressed at lower temperatures have slightly higher $ZT$ than that of the sample pressed at 550 °C due to the much lower electrical conductivity as shown in Fig 4.3.7E. However, the sample hot-pressed at 550 °C has the best $ZT$ performance at temperatures over 125 °C with a peak value of 1.07 at 150 °C and retains the $ZT$ value of 0.77 at 250 °C. This suggests that this composition could be a good choice for applications in power generation devices.
4.3.6. Thermoelectric Properties of Bi$_{0.25}$Sb$_{1.75}$Te$_3$ Composition

Figure 4.3.8 below shows the summary of various thermoelectric properties of samples prepared from Bi$_{0.25}$Sb$_{1.75}$Te$_3$ composition powders and hot-pressed at different temperatures. Figure 4.3.8A and B show the temperature dependence of electrical conductivity and Seebeck coefficient of various samples. Samples pressed at 450 and 500 °C have very similar electrical conductivity and it is much higher than that of the sample pressed at 400 °C. Therefore, these two samples have very similar Seebeck coefficient, while the sample pressed at 400 °C has a much lower Seebeck coefficient. This results in a very similar power factor behavior for all three samples with different hot-press temperatures (Fig. 4.3.8C). However, a sample pressed at a higher temperature has a higher thermal conductivity (Fig. 4.3.8D) due to the larger electronic contribution to the total thermal conductivity. It is clear to see that a sample hot-pressed at 450 °C has the best ZT
performance with a peak value of 1.01 at 150 °C and retains the high $ZT$ value of 0.83 at 250 °C as shown in Fig 4.3.8E, also indicating the potential applications for this composition in power generation devices.

**Fig. 4.3.8.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D) and $ZT$ (E) of various Bi$_{0.25}$Sb$_{1.75}$Te$_3$ composition samples hot-pressed at different temperatures.
4.4. Summary

The performance of thermoelectric materials is determined by its dimensionless figure-of-merit ($ZT$) which needs to be optimized within a specific temperature range for a desired device performance. Here, we show that by varying the Bi/Sb ratio, the peak $ZT$ can be shifted to a higher or lower temperature for power generation applications or cooling mode operations. P-type Bi$_x$Sb$_{2-x}$Te$_3$ nanograin samples were prepared from nanopowders by ball milling the elemental chunks of bismuth, antimony, and tellurium using high energy ball milling techniques and hot-pressing the alloyed nanopowders using a direct current heating hot-press method. The carrier concentration could be tuned by varying the Bi/Sb ratio, thereby effectively shifting the $ZT$ peak to the desired temperature range. A peak $ZT$ of about 1.3 at about 100 °C is achieved from a Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composition which is highest among all the compositions. These nanograin bulk samples have a significantly lower thermal conductivity than that of the bulk samples due to the increased phonon scattering in the grain boundaries.

This study also shows that Bi$_{0.5}$Sb$_{1.5}$Te$_3$ or Bi$_{0.45}$Sb$_{1.55}$Te$_3$ with the peak $ZT$ of ~ 1.2 at about 50-75 °C may potentially perform better for cooling devices, while Bi$_{0.3}$Sb$_{1.7}$Te$_3$ or Bi$_{0.25}$Sb$_{1.75}$Te$_3$ with the peak $ZT$ of ~ 1.1 at about 125-150 °C and retaining the high $ZT$ value of ~ 0.85 at 250 °C, should be able to show better power generation efficiency. This work will have a significant impact in choosing a right composition material to get a high device performance depending on their usage as cooling devices or power generators.
Moreover, a few more ideas which couldn’t be covered during this work may result in an optimized $ZT$. To reduce the thermal conductivity, we could try to form more precipitations inside the samples by adding extra tellurium or create more antisites by adding more antimony. Another approach is to take advantage of interfacial scattering between grains of different types of materials. This can be realized by mixing $\text{Bi}_2\text{Te}_3$ or $\text{Sb}_2\text{Te}_3$ nanoparticles to form composites with different nominal compositions instead of the fully alloyed $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ nanopowders. This approach would be very fruitful in the compositions that are desired for cooling mode operations. Therefore, these compositions need to possess relatively low electrical conductivity since mixing causes the carriers to be trapped on the grain interface (which is usually the case in a composite [17]) thereby reducing the number of carriers.
4.5. References


Muto, D. Vashaee, X. Y. Chen, J. M. Liu, M. S. Dresselhaus, G. Chen, and Z. F. Ren, 


14. P. Poudeu, J. D’Angelo, A. Downey, J. L. Short, T. Hogan, and M. G. Kanatzidis, 


15. Y. Ma, Q. Hao, B. Poudel, Y. C. Lan, B. Yu, D. Z. Wang, G. Chen, and Z. F. Ren, 


Chapter 5
Synthesis and Characterization of Various Nanostructures by Wet Chemical Methods

5.1. Introduction

The physical properties of solids can be tuned up by their microstructures. An example is the arrangement of the atoms (the atomic structure) and the size of a solid in one, two or three dimensions. The properties and behavior of a material may be very different from the bulk counterpart especially when the crystal size reaches the nanoscale. For example, the density of states [1] is changed dramatically when the dimension of the material is reduced from three to one. Similarly, electron and phonon behaviors are modified, thereby affecting many of the physical properties of the material. Two of the many common examples where the mechanical and optical behaviors can be changed with the lower dimension for a material are: the increase of elasticity of carbon nanotubes [2], the change of color of the gold particles below 10 nm from golden yellow to red. Thus, studying and manipulating the material’s properties using nanoscale concepts have received tremendous interests in recent years.

Thermoelectric materials have attracted much attention recently because of their potential applications in superconductors and electronic apparatuses. Most work on thermoelectric materials focuses on improving the figure of merit (ZT). Although several new
thermoelectric materials possessing significantly better properties than conventional materials (such as filled Skutterudites \([3]\), CsBi\(_4\)Te\(_6\) \([4]\), half-Heusler alloys \([5]\), intermetallic clathrates \([6-7]\)) have been developed, the efficiency of thermoelectric generators prepared from such materials is still too low to be suitable for wide-spread application. Recently, thermoelectric nanostructures, quantum wells, quantum wires and quantum dots, have been proven to have much higher thermoelectric coefficients than bulk materials according to both theoretical and experimental investigations \([8-11]\). Our primary goal regarding the synthesis of nanostructured materials is to use them in enhancing the thermoelectric properties by a random nanostructuring strategy as discussed in previous chapters. Using nanoparticles, the thermoelectric properties of a material could be improved due to boundary scattering in the nano-sized grains which leads to a significant reduction of thermal conductivity without affecting the other properties \([12-13]\).

The group V\(_2\)-VI\(_3\) compounds (Bi, Sb)\(_2\)(Se, Te)\(_3\) have been extensively investigated during the past 40 years because of their good thermoelectric cooling at room temperature and their high \(ZT\) values \([14-15]\). In order to obtain advanced thermoelectric materials, several groups have prepared (Bi, Sb)\(_2\)(Se, Te)\(_3\) films with a quantum well structure by sputtering or other physical methods \([3, 16]\). During the past decade, low-cost and time-saving wet chemical methods have been used to synthesize some nanostructures, such as films, nanorods, nanowires, and nanobelts of oxides, metals, alloys, and other compounds \([17-20]\). Up to now, there has been little work on the synthesis of thermoelectric material
nanostructures by wet chemical methods. Sander et al. [9] first reported an electro-deposition method for the synthesis of Bi$_2$Te$_3$ nanowires by using porous anodic alumina templates. Recently, Qian's group has successfully synthesized Sb$_2$Se$_3$ nanowires and Bi$_2$Se$_3$ nanoflakes through a solvothermal reaction [21]. In this chapter, we will discuss the synthesis of various V$_2$-VI$_3$ compound nanostructured materials by the wet chemical methods, the characterization of as-prepared nanostructures, and some of their physical properties.

5.2. Bi-based Nanostructures Synthesized by Wet Chemical Methods

5.2.1. Motivation and Background

We propose to develop nanostructured bulk thermoelectric materials with a significantly enhanced ZT. We have mentioned earlier, in chapter 1, that recent data in literature [11, 15-16, and 22] shows nanostructuring can lead to an enhanced ZT, and will give a more detailed explanation on our proposed approach [23-24]. We would like to first point out that the choice of materials in bulk form comes from the system heat transfer consideration and operational temperatures as discussed before. Thin films are not considered the best for large scale applications due to their heat transfer limitation and their difficulty to produce, although even they can achieve a higher ZT. We focus on V$_2$-VI$_3$ compounds (which are mostly Bi-based materials) because they possess the highest thermoelectric figure of merit known at room temperature. Therefore, their peak ZT temperature matches well with the optimal operational temperature of applications in solid-state cooling devices, which was
the primary goal of this study. In addition, the nanostructured bulk material approach we propose is cost effective and competitive with what is currently used in industry.

The use of nanostructured bulk materials has attractive features. As mentioned before, large increases in $ZT$ have been observed in Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices (SL) and PbTe/PbSeTe quantum dot superlattices (QDSL) [15-16]. Superlattices, however, are expensive and cannot be easily integrated into real thermoelectric devices because it is difficult to match the external heat supply to the heat flux flowing internally through the superlattice-based devices. The recently developed nanostructured bulk material approach [13] is a cost-effective alternative to superlattices, as visualized in figure 5.2.1. This is a heterostructure configuration formed by compacting two kinds of nanoparticles. The use of nanostructures for $ZT$ enhancement was triggered by the recent studies on phonon heat conduction mechanisms in nanostructures [25-27]. The theoretical studies and recent experimental data [13] from the field of thermoelectricity suggests that the most promising approach is to explore the benefit of the thermal conductivity reduction through enhanced phonon scattering at interfaces in nanostructures, while maintaining or enhancing the overall electron performance. This should work for materials with significant differences in lattice properties, but negligible differences in electronic properties. To reduce the thermal conductivity below the level of alloys, a high density of interfaces as illustrated in Fig. 5.2.1 is more effective than the traditionally used random alloys. Also, phonon sequential scattering at interfaces is more important than the coherency of all the interfaces in the whole
structure. Nanocomposites prepared either by addition of nanoparticles into a host material (Fig. 5.2.1A) or by mixing two types of nanoparticles (for example Bi$_2$Te$_3$ and Sb$_2$Te$_3$ (Fig. 5.2.1B) hot-pressed into a bulk solid sample still having nano-sized grains) can satisfy the requirements listed above.

**Fig. 5.2.1.** A) Nanoparticles into a host material and B) two different types of nanoparticles forming nano-composites.

Figure 5.2.2A shows the modeling results for the thermal conductivity of SiGe nanocomposites obtained from Monte-Carlo simulations and by solving the Boltzmann equation [27]. These results show that the thermal conductivity $k$ decreases with the increasing interface density and $k$ can be reduced below that of the corresponding homogeneous SiGe alloy. The thermal conductivity reduction is caused by interface phonon reflection. In Fig. 5.2.2B, the electron power factor ($S^2\sigma$) due to interface scattering controlled by the carrier barrier height is shown. Although in general, interface scattering reduces the electrical conductivity, the Seebeck coefficient is increased because the interfaces preferentially scatter low-energy electrons. This is called the energy filtering effect. With proper control of the electrostatic barrier heights at the interfaces, the electron power factor
can be increased. The experimental results on nanostructured p-type Bi$_2$Te$_3$-based materials described in the previous chapters confirmed these predictions. This shows that the measured thermal conductivity of Bi$_2$Te$_3$-based nanostructured materials is significantly lower than that of a bulk alloy, while the electronic power factor ($S^2\sigma$) can be improved over that of bulk materials at temperatures higher than 50 °C. Such a simultaneous increase in electron performance and reduction in thermal conductivity has been difficult to realize even in superlattices. This observation in p-type bismuth antimony telluride nanocomposite materials has led to a significant increase in $ZT$ over that of a bulk alloy.

![Graph A](image1) ![Graph B](image2)

**Fig. 5.2.2.** Predicted thermal and electrical properties of SiGe nanocomposite materials [27].

### 5.2.2. Bi$_2$Se$_3$ Nanoparticles Synthesized by Hydrothermal Method

As described in the previous section, to realize the concept of nanostructured bulk
materials, nanopowder of a material is needed before hot-pressing them into bulk solid samples. Hydrothermal synthesis [28] is considered to be one of the most cost effective ways to prepare nanoparticles at a large scale. This method can produce small, uniformly sized, and well dispersed nanoparticles. Also, simply by tuning the reaction conditions, various shaped nano/micro crystals can be produced.

For a typical synthesis of Bi$_2$Se$_3$ nanoparticles, 0.5 g of surfactant (EDTA, ethylenediaminetetraacetic acid) was mixed with 80 mL of deionized water. Then 0.9 g of NaOH pellets was added to the solution which makes ~ 0.3 M NaOH aqueous solution. After that, 7.5 mMol of Se powder (325 mesh) and 5 mMol of bismuth nitrate were added to the solution while stirring continuously. 5 mL of hydrazine hydrate (used as a reducing agent) was finally then added to the mixture. Next, the mixture was transferred into a pressure vessel with capacity of 125 mL (Fig. 5.2.3) and kept inside a furnace where the temperature was maintained at 150 °C. After 24 hours of reaction, the product was washed and filtered with deionized water and ethanol many times to strip out the byproducts. Finally, the product was dried at 300 °C under a vacuum for overnight. X-ray diffractometry (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX) were used to characterize the product as shown in Fig. 5.2.4. It is worthy mentioning here that the large scale of bismuth selenide nanoparticles can be prepared even at room temperature, which has not been realized before.
**Fig. 5.2.3.** Picture of a high temperature high pressure reaction vessel.

Figures 5.2.4A and B show low and high magnification TEM images of as-prepared bismuth selenide nanoparticles. The rod-like nanoparticles with an average size of 30 nm were prepared by this method. The broadened XRD pattern (Fig. 5.2.4C) also indicates the small size of the nanoparticles, which is consistent with TEM observation. EDX analysis (Fig. 5.2.4D) shows that the composition of these nanoparticles is Bi:Se = 40:60, which verifies the bismuth selenide nominal composition.
Fig. 5.2.4. A) Low magnification TEM image, B) high magnification TEM image, C) XRD pattern, and D) EDX spectra of as prepared Bi$_2$Se$_3$ nanoparticles.

After the synthesis of nanoparticles, washing, drying and storing of the powder to make bulk samples are very important. In these steps, we need to make sure the particles are clean and not oxidized before further processing. For washing, we used deionized water and alcohol to dissolve all the by-products and filter them out. After washing, we dried the nanopowder in a specially designed quartz tube, which can be pumped to make a vacuum inside. Usually, the powder is dried at 300 °C in the vacuum for about 24 hours to make sure all the water vapor and alcohol are evaporated. After drying them in the vacuum, the nanoparticles inside the quartz are exposed to the argon environment inside a glove box in order to avoid any oxidation. The nanopowder is then stored inside the glove box for future use.

5.2.3. Bi$_2$Te$_3$ Nanoparticles Synthesized by Hydrothermal Method

The preparation of Bi$_2$Te$_3$ nanoparticles follows a similar method to that of Bi$_2$Se$_3$. The only differences are the use of a tellurium source and the capping agent to control
particle size. In a bismuth telluride system, PEG (polyethylene glycol) surfactant is preferable to EDTA (which is what is used in bismuth selenide). For a typical synthesis of Bi₂Te₃ nanoparticles, 50 mg of PEG was mixed with 50 mL of deionized water. Then 2.5 g of NaOH pellets was added to the solution which makes ~ 1.25 M NaOH aqueous solution. After that, 7.5 mMol of Te powder (325 mesh) and 5 mMol of bismuth nitrate were added to the solution while stirring continuously. 8 mL of hydrazine hydrate was then added to the mixture. The mixture was then transferred into a pressure vessel and kept inside a furnace where the temperature was maintained at 150 °C for 24 hours. After the reaction, the product was washed with deionized water and absolute ethanol many times to remove all the impurities.
Fig. 5.2.5. A) Low magnification SEM image, B) high magnification SEM image, C) XRD pattern, D) EDX spectra, E) low magnification TEM image, and F) high magnification TEM image of as prepared Bi$_2$Te$_3$ nanoparticles.

Scanning electron microscopy (SEM), X-ray diffractometry (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX) were used to characterize the as-prepared Bi$_2$Te$_3$ nanoparticles as shown in Fig. 5.2.5. SEM images (Fig. 5.2.5A and B) show that the particles look larger in size but in fact they are clusters formed by an agglomeration of nanoparticles. Fig. 5.2.5C is the x-ray pattern of as-prepared Bi$_2$Te$_3$ nanoparticles. This shows that all the peaks could be indexed to a pure Bi$_2$Te$_3$ rhombohedric structure. The standard pattern of Bi$_2$Te$_3$ is shown on the bottom for comparison. It is clear to see that there are no peaks due to any other phases, exhibiting the single phase of the products. EDX study on individual nanoparticles (Fig. 5.2.5D) confirms that the composition ratio of bismuth to telluride is close to 2:3. There were no other impurity peaks detected (Cu peaks comes from the TEM grid). Figure 5.2.5E is the low magnification TEM image of as-prepared Bi$_2$Te$_3$ nanoparticles and it clearly indicates that the diameters of the particles are
in the range of 20-40 nm. The high resolution TEM picture (Fig. 5.2.5F) of the nanoparticles shows that the crystallinity is excellent and these particles are free of amorphous or oxide layers on the surface. This is particularly important for thermoelectric applications because such a layer can significantly reduce the electrical conductivity leading to a lower figure of merit.

The role of surfactant was found to be very important in the preparation of Bi$_2$Te$_3$ nanoparticles. When surfactant was not used, average particle size increased and crystallinity got worse compared to the case when surfactant was used. If the treatment temperature is increased, the average particle size increases. A similar effect is observed when treatment time is increased.

### 5.2.4. Bi$_2$Te$_{2.25}$Se$_{0.75}$ Nanoparticles Synthesized by Hydrothermal Method

As mentioned in Chapter 4, the mixture of bismuth telluride and bismuth selenide is extremely useful in carrier concentration optimization and thus leads to the optimization of ZT and very good thermoelectric performance of materials. Hence, we have successfully synthesized Bi$_2$Te$_{2.25}$Se$_{0.75}$ nanoparticles following the similar hydrothermal protocol. To prepare Bi$_2$Te$_{2.25}$Se$_{0.75}$ nanoparticles, we first dissolved 50 mg of surfactant (PEG) in 50 mL of water firstly. Then, 3 g of NaOH pellets, 1.875 mMol of Selenium powder, 5.625 mMol Tellurium powder, and 5 mMol of bismuth nitrate were added respectively under strong stirring. Next, 15 mL of hydrazine hydrate was added and sealed in a Teflon-lined reactor
vessel. After about 24 hours of reaction at a temperature of 150 °C, the resulting product is centrifuged and washed many times with deionized water and ethanol. After that, black precipitates of Bi$_{2}$Te$_{2.25}$Se$_{0.75}$ powder were collected. The powder was dried under a vacuum at a temperature of 300 °C overnight and stored inside an argon environment glove box for future use. The characterization tools are the same as those used in Bi$_{2}$Se$_{3}$ nanoparticles.

Figure 5.2.6A is the XRD pattern of as-prepared Bi$_{2}$Te$_{2.25}$Se$_{0.75}$ nanoparticles. This verifies that the particles are a perfect alloy of Bi$_{2}$Te$_{3}$ and Bi$_{2}$Se$_{3}$. No peaks due to any other phases were detected, which proves the single phase of the products. Figures 5.2.6B and C are medium and high resolution TEM pictures of as-prepared Bi$_{2}$Te$_{2.25}$Se$_{0.75}$ nanoparticles after being washed with water and ethanol. The low resolution picture shows that most of the particles possess irregular shapes and has an average diameter of about 20 nm. The high resolution picture shows that the nanoparticles are highly crystallized and have no oxide layers on the surface.
5.2.5. Single Crystalline Bismuth Nanostructures by Polyol Process

Bismuth (Bi), as a semimetal with a rhombohedral structure and a very small band gap, has attracted extensive interest recently as a potentially good room temperature thermoelectric material due to its low effective mass, highly anisotropic Fermi surface, and potential to induce a semimetal-semiconductor transition with decreasing crystallite size [10, 29]. Theoretical studies predicted that nanostructured Bi should have a significantly enhanced thermoelectric figure of merit [30-32]. This has stimulated great efforts to synthesize Bi nanostructured materials [33-35].

Recently, there are a few reports on the synthesis of Bi nanoparticles by a variety of methods, such as inverse micelles [36], radiolytic reduction in aqueous solution [37], high temperature organic solution reduction [38], and solution-based reduction [39-40]. However, there is no report on the control of the shape of Bi nanoparticles up to now. Here, we have
successfully prepared Bi nanoparticles with controlled shape and size by a polyol process [41]. The primary reaction involved the reduction of NaBiO$_3$ (99.6 %, Aldrich) with ethylene glycol (EG, 99.8 %, Aldrich) in the presence of the capping polymer poly (vinyl pyrrolidone) (PVP 1300000, Aldrich) or a trace amount of Fe$^{3+}$ (FeCl$_3$, 99 %, Aldrich) at 200 °C in a Parr reactor (125 mL, model 4750, Parr Company, Moline, IL). The experiments suggested that the morphologies of the product are strongly dependent on the molar ratio of PVP to Bi, and the trace amount of Fe$^{3+}$.

When the molar ratio of PVP to Bi was kept at 1.6, single crystalline Bi nanocubes with an edge length of ~ 60-80 nm were obtained as shown in the low magnification TEM image (Fig. 5.2.7a). The high magnification image (Fig. 5.2.7b) demonstrates the high crystallinity with smooth surfaces. SAED study (inset in Fig. 5.2.7b), obtained by aligning the electron beam perpendicular to one of the faces of the cube, shows a square diffraction pattern which can be indexed based on a rhombohedral cell with a lattice parameter of $a$=4.546 and $c$=11.860 Å. This indicates the single-crystal nature of Bi nanocubes. Figure 5.2.7c shows the typical 2-theta XRD pattern of the as-prepared Bi nanocubes. All diffraction peaks were indexed to the rhombohedral Bi structure ($R\bar{3}m$).
When the molar ratio of PVP to Bi was reduced to 0.8, single crystalline Bi triangular nanoplates were obtained together with cubic and irregular shaped nanoparticles. The percentage of triangular nanoplates in the sample is about 30%. Figure 5.2.8A shows the typical TEM image of the triangular nanoplates. This indicates that the lengths of the three edges of each triangular nanoplate are equal in the range of 200-500 nm. However, if the molar ratio of PVP to Bi is increased to 5, the product is composed of uniform spherical nanoparticles with an average diameter of 75 nm as shown in Fig. 5.2.8B. These
Experimental results indicate that the molar ratio of PVP to Bi plays a key role for the shape control of Bi nanocrystals. We believe that PVP plays multiple roles in our synthetic system. It acts not only as the shape control agent but also as the stabilizing agent. For the present case, PVP molecules could adsorb onto the surfaces of Bi crystals through O-Bi bonding as reported in previous work [34]. PVP molecules adsorbed on some surfaces of the Bi crystals could significantly decrease their growth rates and lead to highly anisotropic growth. A decrease in PVP concentration leads to an ineffectively selective adsorption of the PVP molecule and its respective counter ions on the Bi crystal faces, resulting in the formation of various morphologies, such as triangular nanoplates, cubic, and irregular shape. As for high PVP concentration, excess PVP molecules could act as stabilizing agents to protect particles from aggregating to form big particles and decrease the interaction between ethylene glycol and Bi nanocrystals. So the isotropic growth of Bi crystals was subsequently realized and resulted in the formation of Bi nanospheres with uniform size.
Fig. 5.2.8. TEM images of A) triangular Bi nanoplates, B) spherical nanoparticles prepared with molar ratio of PVP and Bi of 5, and C) typical Bi nanobelts. D) Low-magnification SEM image of as-prepared Bi nanobelts.

It was also found that an introduction of a trace amount of Fe$^{3+}$ species to the reaction system greatly changed the shape of the final Bi nanocrystals. Fig. 5.2.8C and D show the typical low-magnification TEM and SEM images of the Bi nanobelts prepared in the presence of Fe$^{3+}$ species with the molar ratio of PVP to Bi equal 1.6. The SEM image (Fig. 5.2.8D) indicates that large quantities of nanobelts are formed with a length up to 80 $\mu$m. The TEM image (Fig. 5.2.8C) demonstrates that the nanobelts are transparent under the irradiation of electron beam. This reveals that the thickness of the nanobelts is very thin even though the width can be up to 0.6 $\mu$m. As reported before, the organic molecules could play the roles of a surface modifier and assembling agents during the formation of nanostructures by oriented attachment mechanism [42-43]. We speculate that the formation process of Bi nanobelts could be as the following: (i) when a small amount of Fe$^{3+}$ was added into the system, the reduction of Bi$^{3+}$ was significantly slowed down and the nucleation rate of the Bi nanoparticles decreased substantially; (ii) the nanoparticles aligned to the same direction and
then connected to each other to form wire-like structures induced by the assembling agent PVP; (iii) with the prolongation of reaction time and the improvement of crystallinity, these nanoparticles further fused and then grew into single-crystal Bi nanobelts. The role of Fe$^{3+}$ is to oxidize Bi (0) to Bi (III) and thus greatly reduce the nucleation density of Bi.

5.3. Synthesis of Single-Crystalline Antimony Telluride Hexagonal Nanoplates Using a Solvothermal Approach

As discussed in previous chapters, antimony telluride ($\text{Sb}_2\text{Te}_3$) belongs to layered semiconductors with tetradymanite structure. Its doped derivatives are considered to be the best candidates for near room-temperature thermoelectric applications. For instance, specially constructed $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices were reported to exhibit a $ZT$ of $\sim 2.4$ at room temperature [15]. However, so far, there are only a few reports on the synthesis of polycrystalline $\text{Sb}_2\text{Te}_3$ nanowires using electrochemical deposition into the channels of the porous anodic alumina membrane [44]. It is therefore essential to develop an alternative approach to prepare a large quantity of nanosized single-crystalline $\text{Sb}_2\text{Te}_3$ materials to meet the demand of high-performance thermoelectric applications.

We have successfully prepared the hexagonal-shaped $\text{Sb}_2\text{Te}_3$ two-dimensional (2D) nanoplates by a solvothermal approach. First, 1.1 mMol of hexadecyltrimethylammonium bromide (CTAB) (used as the shape controller) was dissolved into 10 mL of deionized water with the help of continuous magnetic stirring, then 80 mL of ethanol was added. Next, the
solution was stirred for 10 min. Then, 10 mMol of SbCl3 was added and dissolved completely, followed by the addition 15 mMol of Te powder (325 mesh) and 20 mMol of NaBH4 as a reducing agent and 15 min of stirring. The mixtures were transferred into a Parr reactor, sealed, and kept at 200 °C for 24 hrs in a furnace and cooled to room temperature. The black precipitates were collected and washed with deionized water and then dried in a vacuum oven at 80 °C for 12 hrs. The yield of a single experiment is about 3 g.

The morphology study by high-magnification SEM, as shown in Fig. 5.3.1A, clearly reveals that the shape of the as-prepared particles is almost hexagonal with an edge length of ~ 200-2000 nm and a thickness of several tens of nanometers. The chemical composition of these nanoplates was further determined by energy dispersive X-ray spectroscopy (EDX). Only peaks of the elements Sb and Te are present in the EDX spectrum with an approximate ratio of 2:3, implying the stoichiometry of Sb2Te3. There are no peaks from other impurities, such as Br and N, indicating that CTAB is not left on the surface of nanoplates. Figure 5.3.1B shows the typical 2-theta XRD spectrum of the as-prepared Sb2Te3 nanoplates. The diffraction peaks can be indexed to the rhombohedral Sb2Te3 structure (R3m). The peak marked with an asterisk is from excess Te.
Fig. 5.3.1. A) High-magnification SEM image and B) XRD pattern of the as-prepared Sb$_2$Te$_3$ nanoplates. C) Typical TEM image of an individual hexagonal nanoplate and D) HRTEM image of the marked area shown in C). Both the HRTEM and the SAED pattern show that the nanoplate is a single crystal.

Figure 5.3.1C shows the TEM image of a single hexagonal Sb$_2$Te$_3$ nanoplate with the HRTEM image (shown in Fig. 5.3.1D) of the selected area marked by the square in Fig. 5.3.1C. The SAED (inset in Fig. 5.3.1C) pattern was obtained by aligning the electron beam perpendicular to the face of this plate. The hexagonally symmetric diffraction pattern indicates the nature of single crystallinity and can be indexed based on a rhombohedral cell with lattice parameter of $a = 4.264$ and $c = 30.458$ Å. The clear lattice fringes shown in Fig. 5.3.1D indicate that the nanoplate is highly crystallized. The spacing of 0.212 nm corresponds to the (110) planes of Sb$_2$Te$_3$. TEM observations also indicated that there were a few Te particles on the surface of some Sb$_2$Te$_3$ plates, as shown in Fig. 5.3.1C; this was why we observed one Te peak in the XRD (Figure 5.3.1B).

Further studies indicate that the concentration of CTAB plays an important role in
the formation of hexagonally shaped Sb$_2$Te$_3$ nanocrystals. The Sb$_2$Te$_3$ nanocrystals prepared without adding CTAB are mainly composed of particles with irregular shapes. Upon adding 0.275 mMol CTAB, the plate-like Sb$_2$Te$_3$ nanocrystals with irregular shape are formed. With CTAB concentration increased to 0.55 mMol, truncated triangular Sb$_2$Te$_3$ nanoplates are formed. However, most nanoplates have irregular shape. When CTAB concentration increases to 1.1 mMol, the product is composed of mainly hexagonally shaped nanoplates.

From analysis of our above experiments, it is obvious that the addition of CTAB leads to formation of Sb$_2$Te$_3$ nanoplates. Therefore, it is reasonable to conclude that the cationic surfactant, CTAB, plays a critical role in the formation of single-crystal Sb$_2$Te$_3$ nanoplates. Our results seem to confirm the conclusion by Pileni et al. that the formation of faceted nanocrystals is related to selective adsorption of ions and their respective counterions on the crystal faces during the growth [45]. In our case, we propose a possible mechanism to illustrate the formation of the hexagonally shaped Sb$_2$Te$_3$ nanoplates: at the initial stage, the dominant process is the formation of tiny Sb$_2$Te$_3$ crystal nuclei. As time passes, these tiny nuclei, which are fixed by CTAB molecules, coalesce with adjacent ones, thus decreasing their surface energy and enhancing plate-like nanocrystal production. During the crystal growth, we believe that the binding between CTAB and Sb$_2$Te$_3$ inhibits crystal growth randomly and favors plate-like single-crystal growth with their preferred facets. With CTAB concentration increasing from 0.275 to 1.1 mMol, the effect of selective adsorption of CTAB molecules and their respective counterions on Sb$_2$Te$_3$ crystal faces induces higher nanocrystal
surface coverage and favors a large-scale production of hexagonally shaped nanoplates. However, when the concentration of CTAB is higher than 1.1 mMol, more irregular nanoparticles appear with a large size ranging from several tens to hundreds of nanometers. This is accompanied by a few irregular plates, indicating that more CTAB molecules will reduce the products’ size and make them irregularly shaped.

5.4. Summary

This chapter provides a review of our current progress for the synthesis of nanostructured thermoelectric materials by wet chemical methods, including a hydrothermal process for the Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Bi$_2$Te$_{2.25}$Se$_{0.75}$ nanoparticles, a solvothermal route for Sb$_2$Te$_3$ nanostructures, and a polyol process for the preparation of Bi nanostructures.

Bi nanoscale materials with different shapes have been successfully synthesized by a polymer-assisted polyol process. The molar ratio of the capping agent PVP to Bi played an important role for the formation of Bi nanocubes, triangular nanoplates, and spheres. The experiments also indicated that introduction of a trace amount of Fe$^{3+}$ species greatly reduced the nucleation density of Bi and the growth rate, leading to the formation of single-crystal Bi nanobelts. In addition, micrometer-sized hexagonal single-crystalline Sb$_2$Te$_3$ nanoplates can be synthesized on a large scale by a solvothermal route. The experimental results showed that the concentration of the surfactant CTAB played a key role in the formation of nanoplates. The as-prepared Sb$_2$Te$_3$ nanoplates are highly crystallized single crystals. These new
nanostructures may find applications in enhancing the thermoelectric performance.

Although small sized and well dispersed nanopowders of various thermoelectric materials could be prepared by a solution method in large scale, contamination and partial oxidation are always big challenges in a chemical approach. Therefore, a high energy ball milling technique (described in previous chapters) to prepare thermoelectric nanopowders in large scale and without major contamination is still found to be more efficient and preferable.
5.5. References


25. G. Chen, in *Semiconductors and Semimetals*, Academic press, San Diego, CA 71,


Summary

In summary, we have developed the concept of nanostructured bulk materials with high thermoelectric performance. The nanostructured bismuth antimony telluride bulk materials were obtained by direct-current induced hot-pressing of the nanoparticles prepared by high-energy ball milling of elemental chunks of bismuth, antimony, and tellurium (mechanical alloying). We show that this p-type material exhibits a $ZT$ of 1.1 at room temperature and 0.7 at 250 °C with a peak $ZT$ of about 1.3 at 100 °C. In comparison, conventional Bi$_2$Te$_3$-based materials have a $ZT$ about 0.9 at room temperature that drops to about 0.25 at 250 °C with a peak value of about 1 at 75 °C. Compositions, hot-press conditions, and nanopowder preparation optimization were investigated in detail to achieve a higher $ZT$. The high $ZT$ in the reported temperature range makes the materials attractive for low-grade waste heat recovery applications or for their integration into segmented thermoelectric devices operations at a high temperature, as well as for cooling applications.

Experimental data coupled with microstructure studies shows that the $ZT$ improvement mainly comes from a lower thermal conductivity due to the increased phonon scattering by defects and grain boundaries. An analysis of data, in agreement with the literature, suggests that the main doping mechanism is the Sb$_{Te}$ antisites formation in our p-type materials.

In addition, by varying the Bi/Sb ratio, the peak $ZT$ can be shifted to a higher or
lower temperature for power generation applications or cooling mode operations. A peak $ZT$ of about 1.3 at about 100 °C is achieved from a $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composition which is highest among all the compositions. This study also shows that $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ or $\text{Bi}_{0.45}\text{Sb}_{1.55}\text{Te}_3$ with the peak $ZT$ of $\sim 1.2$ at about 50-75 °C may potentially perform better for cooling devices, while $\text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3$ or $\text{Bi}_{0.25}\text{Sb}_{1.75}\text{Te}_3$ with the peak $ZT$ of $\sim 1.1$ at about 125-150 °C and retaining the high $ZT$ value of $\sim 0.85$ at 250 °C, should be able to show better power generation efficiency. This work will have a significant impact in choosing a right composition material to get a high device performance depending on their usage as cooling devices or power generators.

Several issues related to accurate measurement of thermoelectric properties were identified and many of them were solved during the measurements, which are discussed in this thesis. With the data we obtained, it is clear that nanopowders-based thermoelectric materials hold significant promise. Therefore, a brief review of synthesis of nanostructured materials by solution-based methods, including a hydrothermal process for the $\text{Bi}_2\text{Te}_3$, $\text{Bi}_2\text{Se}_3$, and $\text{Bi}_2\text{Te}_{2.25}\text{Se}_{0.75}$ nanoparticles, a solvothermal route for $\text{Sb}_2\text{Te}_3$ nanostructures, and a polyol process for the preparation of Bi nanostructures is presented in this dissertation. These new nanostructures may find applications in enhancing the thermoelectric performance. Although small sized and well dispersed nanopowders of various thermoelectric materials could be prepared by a solution method in large scale, contamination and partial oxidation are always big challenges in a chemical approach. Hence, a high energy ball milling technique to
prepare thermoelectric nanopowders in large scale and without major contamination is still found to be more efficient and preferred.