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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

SYNTHESIS AND CHARACTERIZATION OF THERMOELCTRIC

NANOMATERIALS

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

PHYSICS

by

Kamal Kadel

2014

To: Dean Kenneth G. Furton College of Arts and Sciences

This dissertation, written by Kamal Kadel, and entitled Syntehsis and Characterization of Thermoelectric Nanomaterials, having been approved in respect to style and intellectual content, is referred to you for judgement.

We have read this dissertation and recommend that it be approved.

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Date of Defense: March 18, 2014

The dissertation of Kamal Kadel is approved.

Dean Kenneth G. Furton College of Arts and Sciences

Dean Lakshmi N. Reddi University Graduate School

Florida International University, 2014

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DEDICATION

I dedicate this dissertation to my beloved parents.

ACKNOWLEDGMENTS

I would like to extend my great appreciation and gartitude to my advisor Professor Wenzhi Li for his invaluable guidance, mentoring and support during my entire research work and dissertation writing.

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ABSTRACT OF THE DISSERTATION

SYNTHESIS AND CHARACTERIZATION OF THERMOELECTRIC

NANOMATERIALS

by

Kamal Kadel

Florida International University, 2014

Miami, Florida

Professor Wenzhi Li, Major Professor

As existing energy sources have been depleting at a fast pace, thermoelectric (TE) materials have received much attention in recent years because of their role in clean energy generation and conversion. Thermoelectric materials hold promise in terrestrial applications such as waste heat recovery. Bismuth selenide (Bi₂Se₃), lead telluride (PbTe), skutterudites CoSb₃, and Bi-Sb alloys are among the widely investigated thermoelectric materials.

Synthesis of above mentioned thermoelectric materials in nanostructured form and their characterization were investigated. Highly crystalline Bi₂Se₃, undoped and indium (In) doped PbTe, unfilled and ytterbium (Yb) filled CoSb₃ nanomaterials were synthesized using hydrothermal/solvothermal technique and Ca-doped Bi-Sb alloy was synthesized using ball milling method. The mechanism of indium doping to the PbTe matrix was investigated using X-ray diffraction, laser-induced breakdown spectroscopy (LIBS) and a first principle calculation. It was found that indium doping, at a level below 2%, is substitution on Pb site. The effects of the amount of sodium borohydride (NaBH₄) as the reducing agent and the annealing treatment on the phase transition of $CoSb_3$ were investigated. It was found that a sufficient amount of $NaBH_4$ along with the specific annealing condition was needed for the formation of pure phase $CoSb_3$.

Thermoelectric properties of Bi₂Se₃ and Ca-doped Bi₈₅Sb₁₅ were also investigated. A lower thermal conductivity and a higher Seebeck coefficient were achieved for a Bi₂Se₃ sample prepared in dimethyl formamide (DMF) at 200°C for 24 h as compared to bulk Bi₂Se₃. The decrease in thermal conductivity can be attributed to the increased phonon scattering at the interfaces of the nanostructures and at the grain boundaries in the bulk nanocomposite. The increase in the Seebeck coefficient of Bi₂Se₃ nanostructures is likely the result of the quantum confinement of the carriers in nanostructures. The effect of calcium doping on Bi₈₅Sb₁₅ nanostructures were investigated. It was found that 2% calcium doped Bi-Sb alloy showed the best TE efficiency due to the enhanced power factor and reduced thermal conductivity.

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CHAPTER 1: INTRODUCTION AND BACKGROUND

As a consequence of the continuous depletion of existing energy sources, the biggest challenge for humankind is to find alternate sources of energy. For several years, effort has been concentrated in search for alternate sources of energy that are environmentally friendly. Thermoelectricity is one of the widely studied and investigated phenomena in the direction of alternate energy due to its unique features and applications. In general, thermoelectricity explains the direct conversion of heat to electrical energy and vice versa. Thermoelectric (TE) technology finds application in solid state cooling and power generation [1] and plays a great role in recovering waste heat. Thermoelectrics could recover useful electric energy from heat generated by automotive exhaust and home and industrial heating that otherwise will be wasted. The quality of thermoelectric material is measured by a quantity called thermoelectric figure-of-merit (ZT). Despite the advantages of the state-of-the-art thermoelectric devices such as quietness and environmental friendliness, their practical application as a power generator or refrigerator is greatly reduced due to their low efficiency. At present, practical bulk thermoelectric materials have a ZT value of about 1 whereas a ZT value of 3 or more is needed for competitive power generation and refrigeration. If the efficiency can be enhanced, thermoelectric devices can provide the best solution for today's need for clean alternate energy. In the past several years, significant progress was made in increasing the efficiency of thermoelectric materials in various ways, for example, exploring the novel thermoelectric materials such as skutterudites with high ZT or developing novel techniques such as nanostructuring to increase the ZT value of existing thermoelectric materials

1.1 Thermoelectric phenomena

1.1.1 Seebeck effect

The Seebeck effect is the conversion of heat to electricity when the junctions of two different materials are subjected to a temperature gradient. It is related to the power generation phenomenon in the thermoelectric effect. It is named after German physicist Thomas Seebeck who in 1821 first noticed a potential difference between two ends of a metal bar when the metal bar is placed in the temperature gradient along its length [2]. The same phenomenon was discovered later for a closed loop of two dissimilar metals in the presence of a temperature difference between the junctions as shown in Fig. 1.1.



Fig. 1.1 Seebeck effect: *A*, *B* are two types of conductors, a temperature difference induces a voltage between the junctions.

In the presence of temperature difference, charge carriers (electrons or holes) in the material tend to diffuse from the hot side to the cold side, hence, creating an internal electric field and building up a thermoelectric voltage. The internal electric field thus

developed opposes the further movement of charge carriers to the cold side when there is an equal amount of charge carriers diffusing back to the hot side. At the equilibrium stage, an increase in the temperature difference is needed to resume the transfer of charge carriers to the cold end to further increase the thermoelectric voltage. The thermoelectric voltage, also called the thermoelectric *emf*, generated between the hot and the cold ends is defined as,

$$\Delta V = -S\Delta T \tag{1.1}$$

where *S* is the Seebeck coefficient of the material and ΔT is the temperature difference between the hot and cold junctions. The Seebeck coefficient, also known as the thermopower of the material, is defined as the ratio of the thermoelectric voltage to the temperature difference,

$$S = -\frac{\Delta V}{\Delta T}$$
 1.2

The voltage generated between the junctions can be written as,

$$\Delta V = \int_{T_2}^{T_1} S_{AB} dT = \int_{T_2}^{T_1} (S_A - S_B) dT$$
 1.3

where S_A and S_B are the (absolute) Seebeck coefficients of materials A and B, and T_1 and T_2 are the temperatures at the junction 1 and 2, respectively.

1.1.2 Peltier effect

Peltier effect is the reverse of the Seebeck effect and is associated with the thermoelectric refrigeration. The effect is named after Jean Peltier who first observed this phenomenon in 1834 [3]. When an electric current passes through junctions of two dissimilar materials such as metals or semiconductors, heat will be absorbed at one junction and cooling will be developed at the other junction. The heating and cooling of the junctions depends on the flow of the current. The Peltier effect reflects the fact that the charge carriers are also the carriers of heat and heating or cooling will be developed across the junctions when they diffuse due to the applied voltage.



Figure 1.2 Peltier effect in two dissimilar materials A and B in the presence of external voltage ΔV .

As shown in Fig. 1.2 when a potential difference is applied across the junction in the direction as shown, heat is generated at one junction, T^+ , and cooling is developed at another junction, T^- . Reversing the current reverses the heating and cooling at the

junctions. In the Peltier effect, the heat produced Q at one junction is proportional to the current flowing through the junction I,

$$Q = \Pi I$$
 1.4

and the constant Π is called the Peltier coefficient of the material. For two materials A and B equation 1.4 can be written as,

$$Q = \Pi_{AB} I; \Pi_{AB} = \Pi_A - \Pi_B$$
 1.5

where Π_{AB} is called Peltier coefficient of the entire thermocouple, and Π_A and Π_A are the respective coefficients of each material.

When two materials are joined together and a current is passed through the junction, there will be an excess or deficiency in energy at the junction because of the different Peltier coefficients of the materials. The excess energy is released to the lattice, generating heating and the deficiency in energy is supplied by the lattice, creating cooling [4].

1.1.3 Thomson's effect

Thompson's effect describes the heating or cooling of a current carrying conductor because of a temperature gradient and was first observed by William Thomson (later known as Lord Kelvin) in 1851. Every current carrying conductor when subjected to a temperature gradient absorbs or emits heat depending on the material. The Thomson coefficient, for a conductor carrying current I, can be defined as,

$$\mu = \frac{\Delta Q / \Delta l}{I \Delta T / \Delta l} \tag{1.6}$$

Where $\Delta Q/\Delta l$ is the rate of heating or cooling per unit length and $\Delta T/\Delta l$ is the temperature gradient.

1.1.4 Kelvin relation

The Seebeck effect, the Peltier effect, and the Thomson effects are related to each other as explained by the equations 1.7 and 1.8,

$$\Pi = ST$$
 1.7

$$\mu = T \frac{\Delta S}{\Delta T}$$
 1.8

where T is the absolute temperature of the material. Eqs.1.7 and 1.8 are known as the Kelvin relations [5] after the founder of these relationships, Lord Kelvin.

1.2 Thermoelectric figure-of-merit

The concept of the thermoelectric figure-of-merit was first introduced by E. Altenkirch in the early 1900's [6-7]. Qualitatively, a good thermoelectric material should have high electrical conductivity to minimize thermal noise from Joule heating which is generated when a current passes through the thermoelectric element, a low thermal conductivity to minimize the heat leakage to maintain a large temperature gradient across the junction, and large Seebeck coefficients to produce a large voltage. Incorporating all these qualities to a good thermoelectric material, the figure-of-merit (Z) of a thermoelectric material can be formulated as:

$$ZT = \frac{S^2 \sigma}{\kappa} T$$
 1.6

where *S* is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity and *T* is the absolute temperature at which *Z* is determined. κ consists of an electronic component κ_e and a lattice component κ_L . *Z* is most commonly referred to as *ZT* to make it a dimensionless figure-of-merit. Nowadays, $S^2\sigma$ is most commonly known as power factor [8]. Since the efficiency of a thermoelectric power generator and the coefficient of performance (COP) of a thermoelectric cooler are directly related to *ZT* of the TE material, which will be explained in detail in section 1.4, a good TE material requires a higher power factor and a low thermal conductivity.

1.3 Optimization of thermoelectric performance

As evident from equation 1.6, an increase in the power factor and a decrease in the thermal conductivity are required for a higher *ZT* value of a TE material. However, for bulk materials σ , κ , and *S* all are coupled together in such a way that each of them cannot be optimized independently in order to fulfill the conditions for increasing *ZT*. Moreover, σ , κ , and *S* are also strongly dependent on the materials crystal structure, electronic structure, and carrier concentration [9-10]. In the past, various materials were studied extensively in search of a good TE material that fits the abovementioned quality. Depending upon the carrier concentration and electronic structure, most materials can be classified into metals, semiconductors, and insulators. Thermoelectric properties of metals, semiconductors, and insulators at 300 K are tabulated in Table 1.1 and plotted in Fig. 1.3.

 Property
 Metals
 Semiconductor
 Insulators

 S, (μVK⁻¹⁾
 ~ 5
 ~ 200
 ~ 1000

 σ, (Ω⁻¹cm⁻¹)
 ~ 10⁶
 ~ 10³
 ~ 10⁻¹²

 $\sim 2 \times 10^{-3}$

 $\sim 3 \times 10^{-6}$

 $\sim 5 \times 10^{-17}$

 $Z, (K^{-1})$

Table 1.1 Comparison of thermoelectric properties of metals, semiconductors and insulators at 300 K [11]

From Table 1.1, it is clear that among the bulk materials, semiconductors exhibit the best thermoelectric properties with a maximum *Z* value of $\sim 2 \times 10^{-3}$ K⁻¹. The best thermoelectric materials with a large power factor are located in the narrow band gap semiconductor region (Fig. 1.3), with an optimized carrier concentration of about 1×10^{-19} cm⁻³. Slack [12] also suggested that a narrow band gap semiconductor with high mobility careers is the best candidate for a good TE material. Later, Mahan also stated the character of a good TE material is a narrow band-gap semiconductor (Eg~0.25 eV at 300 K) in agreement with Slack [13, 14]. Though, semiconductors are the best available bulk TE materials, their efficiency (*Z*= $\sim 2 \times 10^{-3}$) is very low for wide applications. In the past, efforts were made in the direction of increasing the TE efficiency of those materials.



Figure 1.3 Seebeck coefficient (S), electrical conductivity (σ), power factor ($S^2\sigma$), and electronic (κ_e) and lattice (κ_l) thermal conductivity as a function of free-charge-carrier concentration n, the optimal carrier concentration is about 1×10^{19} cm⁻³, which is indicated by an arrow [adapted from ref. 10,11].

In my dissertation work, two different approaches, which have been widely used since early 1990's, were undertaken to increase the TE efficiency of several types of advanced TE materials. One approach is synthesizing TE materials in the nanostructure form [15], and the other approach is searching the novel complex bulk materials having good TE properties. As explained earlier, *S*, σ and κ should be decoupled for increasing *ZT* value. An increase in S normally results in a decrease in σ , and an increase in σ implies an increase in κ_e as given by Weidmann-Franz Law,

$$\frac{k_e}{\sigma T} = L \tag{1.9}$$

where *L* is known as Lorentz number and *T* is absolute temperature. The nanostructuring technique enables us to decouple σ and κ and to optimize the power factor and reduce thermal conductivity, simultaneously. Nanostructuring helps increase the TE efficiency in two ways: a) using quantum-confinement phenomena to enhance *S* and to control *S* and σ independently and b) using the interface and grain boundaries in nanostructures to scatter phonons more effectively than electrons aiming at reducing the lattice thermal conductivity without significantly affecting the electrical conductivity.

The electronic property of nanostructured materials is different from their bulk counterpart due to the distortion of the electronic density of states (DOS) by quantum confinement effects of carriers in nanostructures [16-18].



Figure 1.4 Electronic densities of states for a) a bulk 3D crystalline semiconductor, b) a 2D quantum well, c) a 1D nanowire or nanotube, and d) a 0D quantum dot [adapted from ref. 18].

As the particle size decreases and approaches the nanometer length, it is possible to cause dramatic change in electronic density of states with sharp steps or edges for 1-D and 0-D materials as shown in Fig 1.4. The sharp peaks in electron DOS results in an increase in the Seebeck coefficient without any significant decrease in the electrical conductivity. The quantum confinement effect is more pronounced in 0D materials like quantum dots with a size up to a few nanometers.

Another advantage of the nanostructuring is that it increases the number of grain boundaries and interfaces between the nanostructures. The increased grain-boundary density results in stronger scattering of phonons in those boundaries compared to the scattering of charge carriers. The strong scattering of phonons will reduce the phonon mean free path [19] and, consequently, the thermal conductivity of the TE materials [20].

The other approach for improving the performance of TE materials is the selection of the novel complex bulk materials guided by the so-called phonon-glass-electron-crystal (PGEC) [12] concept. A PGEC material generally possesses a very low phonon thermal conductivity as in glass and very high electronic conductivity as in a single crystal, which are the ideal conditions for an enhanced thermoelectric efficiency. Skutterudites and clathrates are the most commonly investigated PGEC materials that possess very high carrier mobilities and a high power factor among the bulk semiconductor materials, which will be favorable for high-efficiency thermoelectric device applications [21].

1.4 Thermoelectric application

Thermoelectric materials can be used in the fabrication of various power generating and refrigerating devices. These devices consist of thermocouples made by nand p-type thermolements as shown in Fig. 1.5 (a) for TE power generation using the Seebeck effect, and Fig. 1.5 (b) for TE cooling using the Peltier effect. As explained earlier, charge carriers (electron for n-type and holes for p-type thermolements) tend to diffuse from the hot side to the cold side in case of power generation (Fig. 1.5 (a)) and diffuse along with the direction of the applied voltage in the case of cooling (Fig. 1.5(b)).



Figure 1.5 Thermoelectric devices for a) power generation and b) cooling.

The efficiency of thermoelectric power generator is defined as the ratio of electric power delivered to the load W to the total power drawn from heat source Q and can be expressed as equation 1.10,

$$\eta = \frac{W}{Q} = \frac{T_H - T_C}{T_H} \left[\frac{(1 + ZT)^{1/2} - 1}{(1 + ZT)^{1/2} + \frac{T_C}{T_H}} \right]$$
 1.10

where $T_{\rm H}$ and $T_{\rm C}$ are temperatures at hot and cold junctions respectively, ZT is the aforementioned dimensionless figure-of-merit and the term $(T_{\rm H}-T_{\rm C}/T_{\rm H})$ is known as the Carnot's efficiency.

Similarly, the coefficient of performance (COP), which measures the efficiency of a refrigerator or cooling device is defined as the ratio of heat drawn from the source Q to the total power consumption, and can be expressed as equation 1.11,

$$\phi = \frac{Q}{W} = \frac{T_C \left[(1 + ZT)^{1/2} - \frac{T_H}{T_C} \right]}{T_H - T_C \left[(1 + ZT)^{1/2} + 1 \right]}$$
 1.11

Equations 1.10 and 1.11 clearly show that the efficiency of the thermoelectric power generator and the COP of the TE refrigerator directly depend on ZT of the materials used in thermolements. Hence a higher ZT is required for better performance of TE generators and refrigerators. As explained in section 1.3, the search for high ZT is the main motive of this dissertation work.

With currently available efficiencies, TE devices have already started finding applications such as on heat sinks for microchips, car seat heating, small picnic coolers or cordless temperature-controlled food containers. The auto industry has been utilizing waste heat from the engines of automobiles to generate the electricity, which can later be used to heat the car seat. Thermoelectric cooling can be applied in small area cooling or spot cooling like the cooling of a computer processor. Some advantages of the thermoelectric devices are, as in the case of radio-active thermoelectric generators (RTGs), they can function without fueling and have a power density independent of the environment unlike solar panels. Radio-active thermoelectric generators used in space by NASA utilize heat from the radioactive decay of ²³⁸Pu to generate the electricity for space probes. National Aeronautics and Space Administration (NASA) has used RTGs in its spaceflights like Apollo, Cassini, Viking, and Voyager and so on.

1.5 Research progress in the field of thermoelectrics

Earlier, the thermoelectric effect had very few applications. The early application of the TE effect was in metallic thermocouples, which have been used to measure temperature for many years [11]. The extensive study in the field of thermoelectric research begun in the early 1950's when the semiconductor bismuth telluride (Bi₂Te₃) was first used for refrigeration. During the next 40 years, alloys constructed on the Bi₂Te₃ system, such as Bi_{2(1-x)}Sb_{2x}Te_{3(1-y)}Se_{3y} were extensively investigated as the primary solid state TE material for application in solid state power generation and refrigeration. Alloying is a very efficient technique to reduce the phonon thermal conductivity in bulk materials without a significant reduction in the electrical conductivity [22]. However, the challenge is to reduce the thermal conductivity beyond the alloy limit. Among the traditional bulk TE materials, the best TE efficiency is displayed by the family of Bi_{2(1-x)}Sb_{2x}Te_{3(1-y)}Se_{3y} with a room temperature *ZT* value of 1 for Bi_{0.5}Sb_{1.5}Te₃ [23]. Extensive investigations have been carried out on these bulk materials to optimize their thermoelectric property and it has been found that only small improvements are possible for further increasing ZT of these materials in bulk form. Since then the progress in improving ZT of the traditional bulk TE materials had not been very effective for almost 40 years and the value of ZT had fairly remained around 1. Research activities in the field of thermoelectricity had been dwindling during that time. There was a renewed research interest in the field of thermoelectric research in the 1990's after the findings of efficient novel bulk materials and the development of techniques like nanostructuring for increasing ZT of such materials. Progress in TE research is indicated by the improvement of the TE efficiency as shown in Fig. 1.6 (a). The ZT values of the materials first increased slowly until the 1970's, then remained almost constant at 1 until the 1990's, after which it increased sharply. It indicates a very significant increment in the efficiency of the TE material in recent years.



Figure 1.6 a) Improvement of ZT of some thermoelectric materials with year, b) the number of papers on thermoelectric published as the function of year [adapted from ref. 10].

Research interest on thermoelectric materials can be explained by analyzing the growth of the publication with the timeline displayed in Fig. 1.6 (b). It is evident from the figure that the growth of publications almost remained flat during 1970-1990, increased linearly during 1955-1970 as indicated by region I and increased exponentially after the 1990's. The increase in publication indicates the surge of research interests on thermoelectric materials after the development of various techniques, such as nanostructuring, in TE materials processing which has provided the opportunity to increase ZT of the TE materials.

As mentioned in section 1.3, in the 1990's there emerged two leading ways for increasing the *ZT* of TE material: one is the investigation of the complex structure guided by the so-called phonon-glass-electron-crystal (PGEC) concept [12], and the other is the study of low-dimension materials to optimize *S*, σ , and κ , independently [15].

Phonon-glass-electron-crystal concepts is mostly applicable to complex materials with open structures or voids that act as the scattering site for phonons when introduced with "rattlers", such as smaller but heavier atoms with large atomic displacements. Though a perfect PGEC material is still very far from realization, a large number of complex materials such as skutterudites [24, 25], clathrates [26, 27], and other zintl compounds [28] have been investigated as the prospective PGEC materials to obtain *ZT* values in the range of 1-1.5. Soon after Hicks and Dresselhaus [15] theorized that lowering the dimension of the material could lead to a significant increase in *Z*T as a result of quantum confinement of charge carriers, a large variety of nanostructures have been synthesized and their TE properties have been investigated. It has been found from

initial experiments that the nanostructuring concept is indeed effective for improving ZTfor materials such as Bi₂Te₃-Sb₂Te₃ super lattices [29] and PbTe-PbSe quantum dots [16]. It was found that the large reduction of thermal conductivity can be achieved in lowdimensional materials because of the scattering of phonons in boundaries and interfaces of nanostructures and is greatly responsible for increasing ZT along with the increase in the power factor, as a result of the quantum confinement effect. Later, the approach of the reduction of thermal conductivity was applied to the structures like nanotubes and nanowires [18, 30], 2-dimensional superlattices such as GaAs/AlAs/ErAs [31, 32] and Si/Si-Ge [33, 34] superlattices. Despite the promising perspective of enhancement of ZT of these nanomaterials, the wide applications of these TE materials are hindered because of very limited high temperature applications and difficulties in scale-up production for TE device fabrication. Hence, a relatively new method has been developed to produce nanomaterials in bulk scale also known as nanostructured bulk materials. With nanostructured bulk approach, nanostructured TE materials are synthesized in a powder form using the precursor materials and then consolidated to a dense solid to form nanocomposites. Mahan [35] also suggested that nanostructuring in bulk scale is the ideal solution for increasing ZT for practical TE devices. The nanostructured bulk materials have grain size of up to a few hundred nanometers with a very high density of grain boundaries that scatter phonons over a large mean free path range. The phonon scattering will cause the reduction of thermal conductivity without compromising carrier mobilities and hence electronic properties. A typical HRTEM image of the first ball milled and then hot pressed $(Bi,Sb)_2Te_3$ nanostructured bulk material or nanocomposite [36] is shown in Fig. 1.7, which reveals the presence of nanograins of a few hundred nanometer sizes with

very clear and distinct grain boundaries. With the nanocomposite approach, one can produce nanocomposite materials such as Bi_2Te_3 , PbTe, CoSb₃, and Si-Ge alloys that have very good bulk electronic properties along with rather high thermal conductivity. Recently, the maximum *ZT* of about 1.3-1.4 at 100°C has been reported for Bi_2Te_3 nanocomposite prepared with ball milling and then hot pressing techniques [37, 38].



Figure 1.7 HRTEM image of several nanograins in a p-type $(Bi,Sb)_2Te_3$ nanocomposite produced by the ball-milling and hot-pressing method [adapted from ref. 36].

In the past, various techniques have been employed to synthesize the thermoelectric materials in nanostructured form and to consolidate the nanostructures to bulk nanocomposites. However, care should be taken in selecting the synthetic technique

that can produce a large quantity of material that can be used to fabricate practical TE devices. Hence, the following two guidelines would help select the best synthetic and fabrication techniques for practical TE devices: 1) the synthetic technique needs to be scalable at low cost for the mass production of TE materials with controllable morphology, uniform particle size and distribution, and high crystallinity, and 2) for the application in practical TE devices, the material's density must be 95% or greater of the theoretical density and the condensed nanocomposite must be thermally stable in the entire range of the operating temperature [39]. Guided by the above mentioned qualities, various synthesis techniques have been developed in the course of TE research. Among these techniques, hydrothermal/solvothermal methods [40, 41], wet chemical reactions [42, 43], and ball milling [37, 38] are the most widely employed techniques for nanomaterial synthesis. To make the as-synthesized nanostructured material applicable for TE device fabrication and transport characterization, it must be consolidated to a bulk dense nanocomposite. In order to get a dense nanocomposite, the as-prepared thermoelectric nanoparticles are densified using various approaches such as cold pressing-hot sintering [44], hot pressing [45,46], and spark plasma sintering [47,48]. Hot pressing and spark plasma sintering can produce pellets of density of 95-100 % of the theoretical density, while cold pressing-hot sintering can only yield about 90% of the theoretical densities. In my dissertation research, hydrothermal/solvothermal and ball milling methods were employed as the material synthesis techniques and hot pressing was used as the consolidation technique. A detail description of these methods will be included in chapter 2, which deals with the research methodology.

Along with the synthesis technique, another important task for improving ZT is the selection of good thermoelectric materials. Since Bi₂Te₃ alloys were first investigated in the 1990's as the near room temperature material for refrigeration and power generation, it was immediately found that ZT can be improved by making a solid solution of Bi_2Te_3 with isomorphic compounds such as Sb_2Te_3 and Bi_2Se_3 [11,49]. For room temperature application, $(Sb_0 Bi_0 2)_2 Te_3$ and $Bi_2(Te_0 Se_0 2)_3$ have been mostly investigated as p-type and n-type materials, respectively. The peak ZT values for these materials (Bi₂Te₃ for n-type and Sb₂Te₃ for p-type) are in the range of 0.8-1.1 as shown in Fig. 1.8 [50]. For intermediate-temperature-range (500K-900K) power generation applications, group IV chalcogenides (e.g., PbTe) are most commonly used [11, 51] with peak ZT values of about 0.8 (Fig.2.3). For high temperature application (>900 K), Si-Ge alloys are widely used as both n-type and p-type materials for temperatures above 1100 K and skutterudites such as $CoSb_3$ (n-type) and $CeFe_4Sb_{12}$ (p-type) are the most common materials for temperatures about 900 K-1100 K with fairly small ZT values (Fig. 2.3). The Bi-Sb alloys have been commonly used in the low temperature (>180K) cooling application [52]. In the dissertation work, Bi_2Se_3 was chosen as the material for room temperature application, PbTe as the material for medium temperature application, and skutterudite CoSb₃ as the complex novel material for medium to high temperature application, and Bi-Sb alloy as the material for low temperature cooling. A more detailed introduction of the materials is presented in the next section.



Figure 1.8 ZT of some state-of-the-art thermoelectric materials. a) n-type and b) p-type TAGS refers to the Te-Ag-Ge-Sb alloy [adapted from ref. 35].
1.6 Materials of interest in this dissertation research

1.6.1 Bismuth selenide (Bi₂Se₃)

As Slack suggested, narrow band gap semiconductors are promising TE materials [12]. Group V-VI alloys such as Bi₂Se₃ and Bi₂Te₃ are narrow band gap semiconductors with an energy gap of about 0.3 eV. For example, Bi₂Se₃ has a gap of 0.28 eV [11, 53]. Bismuth selenide may be n-type or p-type depending upon the synthesis conditions. A unit cell of Bi₂Se₃ crystal has a rhombohedral structure with space group of *R3m*. Bismuth selenide has potential applications in optical recording system [54], photoelectrochemical devices [55], and thermoelectric devices [56]. Group V-VI semiconductors are considered to be good thermoelectric materials because of their low thermal conductivity which can be attributed to their high anharmonic lattice vibrations and low Debye temperature [57]. These materials have a low melting point (~900K) [11], which limit their use in the high temperature range but are considered as the best TE material in the room temperature range.

In recent years, various synthesis techniques have been developed to obtain different nanostructures of Bi₂Se₃.Wang *et al.* [58] reported low temperature solvothermal synthesis of Bi₂Se₃ nanosphere in ethylenediamine (EN), and Jiang *et al.* [59] synthesized Bi₂Se₃ nanosheets by microwave heating in the presence of ionic liquid. Recently, Bayaz *et al.* reported a room temperature Seebeck Coefficient of 120 μ V/K for Bi₂Se₃ thin film grown by metal organic chemical vapor deposition technique [56]. In a similar work, Lin *et al.* [60] reported a room temperature Seebeck coefficient of 84 μ V/K and power factor of $7x10^{-5}$ Wm⁻¹K⁻² for Bi₂Se₃ nanoplates obtained from decomposition of a single source precursor.

1.6.2 Lead telluride (PbTe)

Lead Telluride (PbTe) is another narrow band gap (0.33 eV) semiconductor, which has higher melting point (1200 K) compared to bismuth chalcogenides. Hence PbTe can be employed as a good TE material in the medium and high temperature range (500-900 K) [11]. A PbTe unit cell belongs to face centered cubic space group Fm3m. Lead telluride can be made n-type or p-type by controlling the content of lead and tellurium when they are alloyed. While doping with various elements such as indium, thallium, and iodine excess lead in stoichiometric ratios leads to n-type, and excess tellurium results in p-type PbTe. In recent years PbTe has gained increased research interest because of its potential application in thermoelectric devices [61], IR photoelectronics [16], and IR laser devices [62].

Recently, the synthesis and thermoelectric properties of PbTe nanostructures have been extensively studied. Beyer *et al.* [63] reported an enhanced TE efficiency of PbTe superlattice grown using molecular beam epitaxy (MBE). Wang *et al.* [64] synthesized PbTe nanoboxes by an alkaline solution hydrothermal route. To enhance the thermoelectric property of PbTe through the reduction of thermal conductivity, PbTe can be doped with silver (Ag) and antimony (Sb) to get the so-called lead-antimony-silvertelluride (LAST) material. Hsu *et al.* [61] investigated the thermoelectric property of the AgPb_mSbTe_{m+2} system and obtained a high thermoelectric figure of merit of ~2.2 at 800K

for m=18. Figure 1.9 shows the variation of ZT of AgPb₁₈SbTe₂₀ with temperature, which reveals the ZT_{max} is ~2.2 at 800K.



Figure 1.9 Thermoelectric figure of merit of $AgPb_{18}SbTe_{20}$ as a function of temperature [adapted from ref. 61]

In another approach, Heremans *et al.* [65] reported enhancement of the Seebeck coefficient of PbTe through the distortion of the electronic density of state. By the use of thallium to create an impurity level in PbTe, a thermoelectric figure of merit of above 1.5 was obtained for p-type PbTe at 773 K. The approach of manipulating density of states via doping PbTe with group III elements like thalium is becoming more popular. In my dissertation work, In-doped PbTe was investigated hoping to achieve an enhancement in *S*, and hence, in the power factor.

1.6.3 Skutterudite (CoSb₃)

Binary skutterudite has the form MX₃ (M: Co, Rh, Ir and X: P, Sb, As). The skutterudite unit cell belongs to body centered cubic, space group *Im3*. The skutterudite unit cell consists of 8 MX₃ units having 32 atoms. A prototype CoSb₃ unit cell is shown in Fig. 1.10. Two of the eight units of the CoSb₃ unit cell have voids that can be filled with some filler atoms. The skutterudite unit cell with two voids can be represented as $\Lambda_2M_8X_{24}$, where Λ represents the void. For the purpose of convention, people often consider only a half of the unit cell designated as ΛM_4X_{12} . The structure has a total valence electron count (VEC) of 72, which is required in determining semiconductor skutterudites. For the unfilled skutterudites, such as CoSb₃ each Sb atom has four nearest neighbors: two Sb atoms and two Co atoms. Both the Sb-Sb bond and the Co-Sb bond are short in length, however, the Co-Co bond length is quite large indicating no bond exists between the metals. In a very simple bonding scheme, each transition metal, M, contributes nine electrons and X atom contributes three electrons to make a total valence electron count to 72 in a half unit cell ΛM_4X_{12} .

State-of-the-art TE materials like Bi_2Te_3 have limited isostructural compounds and have very limited possibilities to optimize their bulk transport properties to enhance their operational efficiency over a wide temperature range. But at least 11 binary compounds and many solid solutions of skutterudites are known to exist to date [4], which triggers the wide research interests in the skutterudite materials in pursuit of enhanced efficiency in a wide range of operational temperatures.



Figure 1.10 A $CoSb_3$ unit cell. Small dark spheres represent Co atoms, which form the simple cubic lattice as shown. White spheres are Sb atoms, which form nearly square rings and the two large grey spheres, represent two voids in a $CoSb_3$ unit cell [adapted from ref. 4].

As discussed earlier, filled skutterudites are gaining much research interest as a promising TE material with the introduction of the PGEC concept [12, 66, 67]. Previous works [68, 69] suggest that the thermal conductivity of skutterudites can be decreased significantly with the introduction of rare earth metals or lanthanides (Yb, La, Ce, Eu and Pr) and alkaline earth metals into the voids of skutterudite unit cell. Since these filler atoms have high atomic mass and small ionic diameters, they 'rattle' around in the voids to generate disorders, scatter phonon vibrations, and reduce thermal conductivity.



Figure 1.11 Lattice thermal conductivity as a function of temperature for $Yb_xCo_4Sb_{12}$ (with x=0, 0.06, and 0.19) [adapted from ref. 68].

Recently, Nolas *et al.* [68] investigated the effect of ytterbium filling on the thermal conductivity of $CoSb_3$ and found that the thermal conductivity of $CoSb_3$ decreases with the content of ytterbium filling as displayed in Fig. 1.11. This shows that the lattice thermal conductivity of the skutterudites can be greatly reduced due to the anharmonic vibration of the "rattlers" inside the open structures of the skutterudites.

In the past, various synthesis techniques, such as chemical alloying [70], melt spinning [71], ball milling [72], mechanical alloying [73], spark plasma sintering [74], and hydrothermal/solvothermal method [75] have been employed to synthesize filled and

unfilled CoSb₃ in nanostructured form. In the present dissertation work, the solvothermal technique was employed to synthesize unfilled and ytterbium filled CoSb₃.

1.6.4 Bi-Sb alloy

Bismuth is a semimetal that crystallizes in the spatial group R3*m* and exhibits a layered structure. Being a semimetal, it possesses a small energy overlap between the conduction and valence bands, high carrier mobilities, and small effective masses. By alloying bismuth with small amounts of antimony, the energy overlap decreases and a gap begins to form. Since Sb is also a semimetal that exhibits a similar rhombohedral crystal structure of point group R3*m*, the Bi_{100-x}Sb_x alloys form a solid solution over the entire composition range [76]. Drastic changes in the band structure are observed in Bi_{100-x}Sb_x solid solution that depends on the Sb content. The band structure determined at T = 0 K shows that Bi_{1-x}Sb_x alloys are narrow band gap semiconductors for *x*=7-18 with an energy gap less than 25 meV [77-79]. Bi_{100-x}Sb_x alloys behave as a semimetal for 7>*x*>18.

Though properly oriented semiconducting single crystals of $Bi_{100-x}Sb_x$ have been found to be the best n-type thermoelectric materials for low-temperature (80 K) thermoelectric cooling [80, 81], the tendency of $Bi_{100-x}Sb_x$ single crystals to cleave along the basal planes and the difficulty to scale up the production of single crystals drastically limit their use in thermoelectric devices. Hence, synthesis of a nanostructured bulk Bi-Sb alloy has gained much attention because the nanostructured material allows for further optimization of TE properties as previously found in other TE materials [47, 82]. In the past, nanostructured Bi-Sb alloys have been synthesized using various techniques. Datta [83] *et al.* synthesized Bi rich $Bi_{1-x}Sb_x$ alloy nanocrystals using low temperature polyol process. Lopez *et al.* [84] employed a mechanical alloying technique to synthesize homogeneous poly-crystalline $Bi_{1-x}Sb_x$ (*x*=0.12, 0.15, and 0.22) and Lukas [85] *et al.* synthesized Ho-doped $Bi_{1-x}Sb_x$ (*x*=0.12, 0.15, and 0.22) alloy nanoparticles using ball milling techniques. During the current dissertation work, arc melting and ball milling techniques were employed to synthesize Ca-doped $Bi_{1-x}Sb_x$ (*x*=0.15) alloy.

1.7 Research projects and research goals

The main objective of the proposed research is to synthesize the above mentioned thermoelectric materials in their nanostructure form and to study how their nanostructure affects their thermal conductivity, Seebeck coefficient, electrical conductivity and figure-of-merit. Bismuth selenide was chosen because of its low room temperature thermal conductivity, lead telluride because of its high power factor and higher temperature applications compared to bismuth selenide, skutterudites as near PGEC material for medium to high temperature applications, and Bi_{1-x}Sb_x alloy for its application to low temperature cooling. In my dissertation work, two approaches were used to lower the thermal conductivity of the concerned materials. 1) Synthesizing all materials of interest in nanostructures. The nanostructuring process is expected to cause significant reduction in the thermal conductivity due to the scattering of phonons in those boundaries without scattering charge carriers. 2) Introduction of filler atoms as 'rattlers' into skutterudites.

the skutterudites can significantly decrease their thermal conductivity and hence increase their efficiency. Ytterbium was chosen as the principal filler atom in my dissertation research because it is comparatively heavier in the lanthanide series and it can produce a large disorder to cause considerable reduction in thermal conductivity [55]. As explained earlier, the power factor is also expected to increase in nanostructures as the quantum confinement phenomenon becomes more evident in the nanoscale regime.

A hydrothermal/solvothermal method was employed as the principal synthesis technique along with the ball milling method for the nanomaterial synthesis. Hydrothermal techniques have the advantages of high yield, low synthesizing temperature, and the ability to control the size and shape of the material with the assistance of suitable surfactants or capping agents compared to other synthesis methods. Similarly, ball milling has the advantage of producing nanomaterials with high yield, high purity, and high crystallinity. Using the two synthesis techniques, highly crystalline pure phase nanostructures were successfully prepared.

In my dissertation work, synthesis and characterization of various thermoelectric materials were investigated. Firstly, the synthesis and characterization of bismuth selenide nanostructures were studied. Highly crystalline semiconductor hexagonal flake-like bismuth selenide nanopaticles were synthesized using a hydrothermal synthesis technique and their surface morphology and structural analysis were carried out. It was found that the as- prepared samples are highly crystalline rhombohedral phase of Bi₂Se₃. A more detail description is provided in chapter 3. Secondly, the synthesis and characterization of indium doped thermoelectric lead telluride was carried out. In this

project, indium was successfully doped into the nanostructured lead telluride synthesized via a solvothermal method. A first-principle calculation was also conducted to investigate the mechanism of indium doping into the PbTe matrix. Chapter 4 provides detailed information about the research on lead telluride. Thirdly, unfilled and ytterbium (Yb)filled skutterudites cobalt antimony (CoSb₃) as a PGEC material were studied owing to its superior thermoelectric property coupled with the abundant presence of less volatile constituent elements. The unfilled and Yb-filled CoSb₃ nanoparticles were successfully synthesized via a solvothermal route. Effects of various amounts of sodium borohydride (NaBH₄) as the reducing agent and annealing conditions on the formation of CoSb₃ were investigated. Chapter 5 of the current dissertation explains the project on skutterudites. Finally, synthesis and characterization of Ca-doped Bi-Sb alloy was studied. Nanostructured Ca-doped $Bi_{85}Sb_{15}$ alloy was synthesized using first arc melting and then ball milling process and its structural characterization was carried out. A detail explanation of synthesis and characterization of Ca-doped Bi-Sb alloy is presented in chapter 6.

The study of thermoelectric properties of Bi_2Se_3 and Ca-doped Bi-Sb alloy are also presented in this dissertation. It was found that the thermal conductivity of Bi_2Se_3 sample prepared in dimethyl formamide (DMF) at 200°C for 24 h was lowered significantly compared to bulk Bi_2Se_3 The effects of calcium (Ca) doping in $Bi_{85}Sb_{15}$ on the structure and thermoelectric properties were investigated. It was found that a 2% Cadoped Bi-Sb alloy showed the best TE efficiency at room temperature. A detail explanation on TE property measurement is presented in chapter 7.

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CHAPTER 2: EXPERIMENTAL METHODS

The current chapter describes the techniques that were used to synthesize, characterize, and measure the transport properties of the materials in the dissertation work.

2.1 Material synthesis techniques

The hydrothermal/solvothermal method was employed for the synthesis of bismuth selenide, lead telluride, and cobalt antimony skutterudite and ball milling technique was used for the synthesis of Bi-Sb alloy.

2.1.1 Hydrothermal/solvothermal method

As explained in chapter 1, solvothermal or hydrothermal technique has been proposed as one of the efficient methods for the large- scale synthesis of nanostructured materials. It has been employed to synthesize various kinds of semiconducting materials including thermoelectric materials with different morphologies and sizes from large ingots to nanostructures [1, 2]. In a typical synthesis process, starting materials in the specific end-product stoichiometry were mixed with reductant and/or pH controlling agent in the presence of either a solvent (for the solvothermal route) or an aqueous solution (for the hydrothermal route). Figure 2.1 shows a schematic of the hydrothermal/solvothermal technique employed for nanomaterial synthesis. In this dissertation work, different kinds of organic solvents including ethanol, dimethyl formamide (DMF), ethylene glycol (EG), and inorganic solutions including a water/glycerol mixture were used as the solvent for solvothermal synthesis and water was used as the solvent for hydrothermal synthesis. Sodium borohydride (NaBH₄) and sodium hydroxide (NaOH) were used as reductant and pH controlling agent, respectively.



Figure 2.1 Schematic of the synthesis of nanomaterials by hydrothermal/solvothermal method.

The mixture was then loaded into a Teflon-liner; the Teflon-liner was filled up to 80% of its volume with the respective solvents. Later, the Teflon-liner was placed in an ultrasonicator for 30 minutes to obtain a uniform reaction mixture. After the sonication, the Teflon-liner was placed in an autoclave and sealed. The autoclave was then heated in a furnace to the required temperature, which was usually above the critical point (i.e. no distinction between the liquid and gas phases) of the solvent, and for a desired duration. The autoclave was then allowed to cool to room temperature naturally. The precipitate that resulted from the reaction was vacuum filtered, rinsed with ethanol and distilled water several times repeatedly, and dried at 120°C in for 4 h to get the sample in powder form. The samples, which were selected for transport property measurement, were dried

again in the presence of hydrogen and argon at 100°C for 4 h to eliminate any oxygen in the sample.

The hydrothermal method provides a very good control over the morphology and the structure of the end products with the use of capping or templating materials during the reduction of the precursor materials in the solvent matrix. Most commonly used capping agents or surfactants are materials such as ethylenediaminetetraacetic acid (EDTA) trimethylammonium bromide (CTAB), Triton X-100 and sodium dodecyl sulfate (SDS). With the aid of these materials, various morphologies such as nanocubes [3], nanoparticles [1, 3], nanowires [1], and nanosheets [4] have been achieved. Fine PbTe nanoparticles of size ranging from 50- 120 nm were synthesized in water /glycerol solution at 140°C for 24 h in the presence of Triton as shown in Fig. 2.2.



Figure 2.2 PbTe nanocubes synthesized in water/glycerol mixture with Triton as surfactant at 140 °C for 24 h.

The hydrothermal/solvothermal method provides an excellent control over the particle size distribution and its morphology. However, it has some disadvantages too. One problem is the lack of control over the end-product stoichiometry, especially for complex materials like CoSb₃ based alloys, which results in phase impurity in the final product [6]. The other limitation is the difficulty to sinter these nanomaterials to get high density pellets [6, 7]. Solvothermally synthesized CoSb₃ nanoparticles showed the presence of impurity phases CoSb₂ and Sb in the end product. However, annealing at suitable conditions could eliminate the impurities. Details about the annealing work will be discussed in chapter 6.

2.1.2 Ball milling method

Recently, the ball milling process has been developed as one of the widely used techniques for the synthesis of nanostructured thermoelectric materials [8, 9]. During the ball milling process, mechanical alloying and nanostructuring occurs simultaneously through a sequence of collision events inside a high energy ball mill [10]. In a typical ball milling process, elemental chunks or powders of precursor materials in the specific resulting alloy stoichiometry were placed inside a ball mill jar containing stainless steel balls. The whole process was operated inside an argon filled glove box to reduce the possibility of oxidation of rather reactive precursor materials. The ball mill jar was then placed in a high energy ball mill machine. Figure 2.3 shows photographs of (a) stainless steel ball jar and balls, and (b) high energy ball milling machine from Prof. Zhifeng Ren's lab (University of Houston) used to synthesize Bi-Sb alloys.



Figure 2.3 Photographs of a) stainless steel ball mill jar and balls and b) high energy ball mill machine (Spex 8000), courtesy Prof. Zhifeng Ren's lab (University of Houston).

The ball milling process has several advantages such as highly scalable yield up to kilograms of material in a few hours. The ball milled nanomaterials are easy to sinter to form high density pellets with a large number of grain boundaries, which is favorable for increasing the Seebeck coefficient and decreasing the thermal conductivity to optimize the power factor. There are also some disadvantages in the ball milling process. For example, the size distribution of the particles is difficult to control and the materials can lose their crystallinity after long-time ball milling. In the current dissertation work, Bi-Sb nanomaterials were produced by the ball milling method. First, an arc melting technique was used to make a Bi-Sb ingot from the precursor materials, and then the ingot was subjected to ball milling process. The ball milling process resulted Bi-Sb alloy nanostructure with average particle size ranging from 30-50 nm as presented in chapter 6.

2.2 Examination techniques for structural characterization

2.2.1 X-ray diffraction (XRD)

An x-ray diffraction (XRD) technique was used to identify the phase of the nanocrystals and to get the information on the crystal structure. The XRD measurement was carried out using a Siemens D5000 diffractometer equipped with a Cu anode operated at 40 kV and 40 mA. The XRD patterns were collected with a step size of 0.01° and a scan rate of 1 sec/step. The intensity of X-rays diffracted by the sample was constantly recorded as the detector and the sample were rotated by respective angles. A peak in intensity occurs at an angle θ when the sample contains lattice planes with d-spacings that diffract X-rays at that value of θ . Finally, the result was presented as peaks at 2 θ on the x-axis and intensity of X-ray on the y-axis. The XRD pattern, thus obtained was compared to the standard XRD profiles of different materials that are available from International Center for Diffraction Data as the Powder Diffraction File (PDF), commonly known as a JCPDS file. Unit cell parameters could be calculated after indexing each reflection peak to corresponding *hkl* (Miller indices) values.

2.2.2 Scanning electron microscopy (SEM)

A field emission scanning electron microscope (SEM) was used to analyze the surface morphology of nanocrystals. In SEM, a high-energy beam of electrons interacts with the atoms inside the sample generating signals that consist of the information about the morphology of the sample. Surface morphology analysis of the sample was performed by JEOL JSM-6330F SEM, which was operated at a15kV accelerating voltage

and gives magnifications up to 500k. To prepare a sample for SEM measurement, the powder sample was ultrasonicated in alcohol for 30 minutes. A very small drop of sample solution was dropped onto silicon substrate and the alcohol was allowed to evaporate. Most of the time, the sample was coated with gold film to make it conductive to get a better SEM image.

2.2.3 Transmission electron microscopy (TEM)

The structural analysis of the nanostructures was carried out by a transmission emission microscope (TEM). Transmission emission microscope works on the principle that an electron can behave as a wave (de Broglie hypothesis). Smaller de Broglie wavelengths of electrons, which are on the order of spacing of atoms, enable TEM to image atoms at significantly higher resolution. The electrons generated thermionically and accelerated with an accelerating voltage transmit through the sample and the transmitted beam is used to form the image. The images are of various types such as low magnification TEM, high resolution TEM (HRTEM), selected area diffraction (SAED) pattern, and electron dispersive X-ray spectroscopy (EDS). The HRTEM images provide the information about the phase of the crystal, and SAED patterns give the information about the crystallinity of sample. The dots on the SAED pattern indicate single crystallinity while the rings indicate polycrystallinity of the samples. The EDS pattern reveals the chemical composition of the material. TEM images, SAED patterns, and EDS spectra of the samples were obtained from a FEI Tecnai F30 apparatus operated at an accelerating voltage of 300 kV with a point-to-point resolution of 2Å.

2.2.4 Laser-induced breakdown spectroscopy (LIBS)

In the dissertation work, LIBS was used to detect the very small content of elements such as indium doping in the PbTe matrix and ytterbium filling in the CoSb₃ structure. Equipped with a highly energetic laser as an excitation source, LIBS works on the principle of atomic emission spectra. When the laser beam strikes the sample, it initiates highly energetic luminous plasma from the ablated sample mass, which consists of free electrons, excited atoms, and ions. A typical plasma spectrum is a signature of the chemical species in the sample and provides information about the chemical species composition and relative abundance [11].

The LIBS analyses of the samples were conducted on a RT100HP system (Applied Spectra, Fremont, CA) equipped with a 1064nm ns-Nd:YAG laser. The detector has a CCD linear array (Avantes, Broomfield, CO) with possible gate delay adjustment from 50 ns to 1 ms with a 25 ns step resolution and a fixed integration time of 1.1ms. Data interpretation and data analysis were conducted with the TruLIBS TM emission database and Aurora data analysis software (Axiom 2.1, Applied Spectra, CA).

2.3 Sample consolidation technique

Powder samples need to be consolidated into compact discs in order to carry out the transport property measurement of the sample. Nano powders were consolidated using a DC power controlled hot press.



Figure 2.4 a) A schematic of a hot press system where T is a thermocouple and b) lab made hot press system, courtesy Prof. Zhifeng Ren's lab (University of Houston) [adapted from ref. 12].

Figure 2.4 shows (a) a schematic of the hot press, and (b) a photograph of a homemade hot press system. The powder sample was loaded into a 12 mm inner diameter graphite die and sealed with two graphite rods on top and bottom as shown in Fig. 2.4 (a). Then the die with the powder was mounted on the hot-press system as shown in Fig. 2.4 (b) and the powder was pressed (~80 MPa) along with the application of a high DC voltage across the sample through the graphite plunger (graphite rods on top and bottom). The temperature of the sample was controlled by a current (200-2000 A) passed through the sample and the sample was heated according to Joule's heating to a temperature below the melting point of the material. When the temperature reached the set peak value, it was held under the desired pressure for few minutes, depending on the samples, to ensure the uniform density of the pellets. The density of the resulting pellet mainly depended on the hot press pressure and the temperature. Then these bulk pellets were cut

into 2 mm \times 2 mm \times 12 mm bars for four-probe electrical conductivity and Seebeck coefficient measurements and were also cut into 12 mm diameter and 1 or 2mm thick disks for the thermal conductivity measurements.

2.4 Transport property measurement techniques

Electrical conductivity (σ), Seebeck coefficient (S), and thermal conductivity (κ) are the fundamental transport properties that characterize the efficiency of a thermoelectric material. Electrical conductivity and Seebeck coefficients were measured by commercial equipment, Ulvac ZEM 3 and thermal conductivity was measured using a laser flash system (Netzsch LFA 457).

2.4.1 Electrical conductivity and Seebeck coefficient measurement

Figure 2.5 shows the measurement system that was used to measure the electrical properties of the samples. Figure 2.5 (a) displays the photograph of the commercial ZEM-3 system and Fig. 2.5 (b) shows a sample mounted in the ZEM-3 apparatus for electrical resistivity and Seebeck coefficient measurement. In the ZEM-3 system, electrical resistivity was measured using a four probe technique and electrical conductivity was calculated from the electrical resistivity. The four probe technique for measuring the resistivity simply accounts for the contact resistance between metal electrodes and the semiconducting samples. Figure 2.6 (a) displays a schematic diagram of the four probe used by the ZEM-3 system. As shown in Fig. 2.6 (a), in the four probe technique current I was passed through one set of probes (blue blocks) and the voltage



Figure 2.5 a) A commercial ZEM-3 system, and b) magnified sample holder region (indicated by red circle in (a)) with a sample mounted for measurement, courtesy Prof. Zhifeng Ren's lab (University of Houston).



Figure 2.6 a) Schematic diagram of four probe technique in ZEM-3 system, and b) a typical I-V curve for resistance measurement.

difference (ΔV) was measured using another set of probes (small red spheres). These four probes were connected to four thermocouples. The voltage and current control, data

acquisition, and interpretation were fully automated and computer controlled. The electrical resistivity was found from the relation

$$\rho = \frac{A}{l} \left(\frac{\Delta V}{\Delta I} \right) \tag{2.1}$$

where $(\Delta V/\Delta I)$ is the slope of the I-V curve as shown in Fig. 2.6(b), A is the crosssectional area of the sample and l is the distance between the voltage probes. The electrical conductivity was then calculated as the reciprocal of the resistivity. During the resistivity measurement, the temperatures at both probes were kept constant to minimize the Seebeck voltage.

The same ZEM-3 system (Fig. 2.5) was used for Seebeck coefficient measurement. The Seebeck coefficient is simply defined as the ratio of an open-circuit potential difference (ΔV) to a temperature gradient (ΔT),

$$S = \frac{\Delta V}{\Delta T}$$
 2.2

For Seebeck coefficient measurement, the voltage and temperatures were measured simultaneously by the same thermocouple probe (small red spheres) as shown in Fig. 2.6 (a). Then, the voltage difference (ΔV) was measured for a set of temperature differences (ΔT) between the two probes and the Seebeck coefficient was calculated from the slope of ΔV - ΔT plot.

2.4.2 Thermal conductivity measurement

A laser flash technique was used to measure the thermal conductivity of the samples in the dissertation work. In the laser flash technique, thermal conductivity was calculated using the relation,

$$\kappa = C \alpha \rho$$
 2.3

where *C* is specific heat capacity, α is the thermal diffusivity, and ρ is the density of the sample. A laser flash system (Nestzsch LFA 457) was used to measure α and *C*, and Archimedes' principle was used to measure ρ of the material. A Nestzsch LFA 457 system (shown in Fig. 2.7 (a)) can measure α and *C* from room temperature to 950°C.



Figure 2.7 a) A laser flash system (Nestzsch LFA 457), courtesy Prof. Zhifeng Ren's lab (University of Houston) and b) schematic diagram of the laser flash technique.

The laser flash system used a disk of diameter 12.7 mm and thickness ranging from 1-2 mm. All samples, together with the reference sample needed for specific heat calculation were graphite coated to match the absorptivity and emissivity that is specifically important for specific heat calculation. The samples were then placed with one side facing the laser beam and the other side facing an Indium Antimonide (InSb) IR detector inside an argon-environment furnace as shown in Fig. 2.7 (b). A heater was used to adjust the furnace temperature as needed for temperature dependent diffusivity and specific heat measurement. A laser beam struck the front sample surface causing a heat pulse to travel through the sample's thickness. The actual IR signal was detected by the IR detector on the other side of the system and transferred the required data for the measurement of α and C to the computer. The equipment was fully automated and controlled to record, analyze, and interpret the data of thermal diffusivity and specific heat capacity. Then thermal conductivity was calculated using equation 2.3.

2.5 References

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CHAPTER 3: SYNTHESIS AND CHARACTERIZATION OF BISMUTH SELENIDE (Bi₂Se₃) NANOMATERIALS

This chapter presents a detailed investigation on the synthesis and structural characterization of Bi₂Se₃ nanomaterials.

3.1 Introduction

According to Slack [1], semiconductors having a narrow band gap and highmobility carriers are best suited as thermoelectric materials. Bismuth selenide (Bi_2Se_3) is a V-VI semiconductor with a narrow band gap of about 0.3 eV [2, 3], which has potential applications in optical recording systems [4], photoelectrochemical devices [5], thermoelectric devices [2, 3]. In recent years, bismuth chalcogenides gained much research interest due to their good thermoelectric properties and high *ZT* values at room temperature [6, 7].

Theoretical predictions and experimental results show that a nanostructured low dimensional TE material can exhibit high thermoelectric efficiency [8-10]. A wide variety of synthesis techniques have been developed to synthesize various nanostructures of Bi₂Se₃. Wang *et al.* [11] reported a low-temperature solvothermal method to obtain Bi₂Se₃ nanostructures in ethylenediamine (EN), Giani *et al.* [12] used chemical vapor deposition method to synthesize Bi₂Se₃ thin films, and Jiang *et al.* [13] synthesized Bi₂Se₃ nanosheets by microwave heating in the presence of an ionic liquid. Among the various synthesis techniques employed for the formation of Bi₂Se₃ nanostructures, the solvothermal/hydrothermal process is attracting much interest because of the advantages

of high yield, low synthesizing temperature, and high crystallinity. Xie *et al.* [14] and Yu *et al.* [15] synthesized Bi_2Se_3 nanostructures using ethylenediamine (EN) as a solvent and Batabyal *et al.* [16] synthesized Bi_2Se_3 nanorods using dimethyl formamide (DMF) as a solvent. In this dissertation work, flake-like Bi_2Se_3 nanostructures were synthesized via the solvothermal route in DMF at various synthesis temperatures for different durations. The effect of the synthesis temperatures on the structure and morphology of Bi_2Se_3 nanostructures has been investigated.

3.2 Experimental

The general explanation of experimental technique for material synthesis and characterization has already been presented in chapter 2. The specific details of the synthesis and characterization of Bi₂Se₃ nanoparticles is presented in the current section.

3.2.1 Material synthesis

In a typical synthesis process, analytically pure bismuth nitrate pentahydrate (Bi(NO₃)_{3.}5H₂O, Fisher Scientific) and selenium (Se, Acros) powder were used as precursor materials in a 2:3 molar ratio and mixed in a Teflon liner. Then 4 mmol of sodium hydroxide (NaOH, Acros) as a pH controlling and reducing agent, and 2 mmol of ethylenediaminetetraacetic acid (EDTA, Acros) as a shape directing additive were used. DMF was used as the solvent to facilitate the reaction process. The synthesis process was carried out at 140°C and 200°C for 24 h. Samples prepared in DMF at 140°C and 200°C for 24 h are termed as BiSe-1 and BiSe-2 respectively.

3.2.2 Structural characterization

I used X-ray diffraction (XRD) measurements to perform crystal structure analyses of the as-prepared samples. Surface morphology analysis was performed by a field emission scanning electron microscope (SEM, JEOL JSM-6330F, 15 kV). Transmission electron microscopy (TEM) images, selected-area electron diffraction (SAED) patterns, and energy dispersive X-ray spectroscopy (EDS) spectra were obtained from an FEI Tecnai F30 apparatus operated at an accelerating voltage of 300 kV with a point-to-point resolution of 2Å.

3.3 Results and discussion

Figure 3.1 shows the XRD patterns of the samples prepared in DMF for 24 h at 140°C (BiSe-1) and 200°C (BiSe-2), respectively. The peaks in the XRD pattern can be indexed as rhombohedral Bi₂Se₃ (JCPDS: 033-0214) with a space group $R\bar{3}m(166)$. The strong (015) diffraction peak represents the prominent growth orientation of Bi₂Se₃ nanoparticles along the [015] direction. The sharp peaks in the XRD profiles indicate the high crystallinity of the as-prepared Bi₂Se₃ samples. No peaks for other elements were detected indicating the high purity of the Bi₂Se₃ samples.

The surface morphology and structure of the as-prepared samples were analyzed by SEM and TEM. Figure 3.2 shows the SEM and TEM examination results of the sample BiSe-1. The SEM image (Fig. 3.2(a)) shows thin and appreciably fine flake-like nanostructures of Bi_2Se_3 with an average size of 300 nm.



Figure 3.1 XRD patterns of the as-prepared Bi_2Se_3 samples synthesized in DMF for 24 h, BiSe-1 at 140°C, and BiSe-2 at 200°C.

The process of formation of Bi_2Se_3 nanoflakes can be attributed to the layered nature of Bi_2Se_3 structure [17, 18]. The isolated nanoflake is very thin and translucent to electron beams when examined by TEM. A previous work by Wang *et al.* [19] also reported on the solvothermal synthesis of flake-like crystal of Bi_2Se_3 in diethyl glycol at $160^{\circ}C$ for 22 h. The size of the flake was in the range of 200-400 nm which is comparable to the size of the nanoflakes reported in the present work. It should be pointed out that



Figure 3.2 SEM and TEM images of the as-prepared Bi₂Se₃ samples synthesized in DMF at 140°C for 24 h (BiSe-1). a) SEM image, b) TEM image, c) HRTEM image, d) SAED pattern, and e) EDS pattern.

although both the solvent and the temperature are different between the dissertation work and the reported work (ref. 19), the Bi_2Se_3 nanoparticles from the two methods have similar morphology and size, indicating that the solvents (diethyl glycol and DMF) and a temperature in the range of 140-200 °C have the same or a similar effect on the formation of the Bi_2Se_3 nanoflakes. A large repertoire of solvents and a broad range of temperature will provide us some flexibility in the selection of the synthesis conditions of these materials.

Figure 3.2(c) shows a high resolution TEM image of a Bi₂Se₃ nano-flake. The lattice fringes are clearly distinguishable and the calculated lattice spacing of 0.172 nm is in agreement with the d-spacing of the (205) planes of rhombohedral Bi₂Se₃. Figure 3.2(d) shows the clearly distinguishable SAED ring patterns, which can be indexed to different lattice planes of rhombohedral Bi₂Se₃. The chemical composition of the asprepared Bi₂Se₃ sample was analyzed by an EDS spectrum (Fig. 3.2(e)) which shows that the as-prepared sample consists of Bi and Se only, hence confirming the chemical purity of the sample. The peak corresponding to Cu in the EDS spectrum arises from the TEM grid used for preparing the TEM specimen. From the TEM analysis, it can be concluded that the well-defined and clear lattice fringes in the HRTEM image as well as the distinct rings in the SAED pattern reveal the high crystalline quality of the as-synthesized Bi₂Se₃ nano-flakes.

The SEM and TEM images of the BiSe-2 sample are shown in Fig. 3.3. A typical SEM image of BiSe-2 (Fig. 3.3(a)) reveals the presence of the flake-like nanostructures similar in shape but slightly bigger in size as compared to the nanoflakes of BiSe-1


Figure 3.3 SEM and TEM images of the as-prepared Bi₂Se₃ samples synthesized in DMF at 200°C for 24 h (BiSe-2). a) SEM image, b) TEM image, c) HRTEM image, d) SAED pattern, and e) EDS pattern

sample (see Fig. 3.2(a)). The increase in size of the nanoflakes can be attributed to the increase of the synthesis temperature. Wang *et al.* [11] reported the increase in particle size of hydrothermally synthesized Bi_2Se_3 nanospheres from about 30 nm to 100 nm when the temperature was increased from 130°C to 200°C. Figure 4.3(b) is a TEM image of the as-prepared sample, which shows the thin and translucent nanoflakes with a size ranging from 180-400 nm.

Figure 3.3(c) is a HRTEM image of the BiSe-2 sample, and it shows clearly the equally spaced lattice fringes. The calculated fringe separation is 0.311 nm which corresponds to the d-spacing of (015) plane of rhombohedral Bi₂Se₃. Figure 3.3(d) shows the SAED spot pattern which is indexed to corresponding lattice planes of rhombohedral Bi₂Se₃. The EDS spectrum of the sample, shown in Fig. 3.3(e), shows that the as-prepared sample consists of Bi and Se only, hence confirming the chemical purity of the sample. Clearly distinguishable lattice fringes in HRTEM image indicate the high crystallinity of the sample and the spotty SAED pattern reveals the single-crystalline nature of the BiSe-2 sample.

3.4 Conclusions

Bismuth selenide (Bi_2Se_3) nanoflakes were synthesized via a solvothermal route at different synthesis conditions using DMF as a solvent. The surface morphology and crystal structure of the nanoflakes were analyzed and the results show that the asprepared samples are rhombohedral phase of Bi_2Se_3 . The effect of temperature on the size of the as-synthesized nanoparticles was also studied and found that the size of the Bi_2Se_3 nanoflakes increases with the synthesis temperature.

3.5 References

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CHAPTER 4: SYNTHESIS AND CHARACTERIZATION OF UNDOPED AND INDIUM DOPED LEAD TELLURIDE (PbTe) NANOMATERIALS

The current chapter presents the investigation on the synthesis and characterization of undoped and indium doped PbTe and the doping mechanism of indium to PbTe matrix.

4.1 Introduction

Lead Telluride and its solid solutions have been extensively investigated as thermoelectric materials since mid twentieth century [1]. As Slack suggested [2], semiconductors having narrow band gap and high mobility carriers are best suited for thermoelectric materials. PbTe is a narrow band gap semiconducting material with a direct band gap of 0.33 eV at 300 K [3] and has great applications in IR photoelectrics [4], IR laser devices [5] and thermoelectric devices. PbTe is considered as one of the best thermoelectric materials for the medium and high temperature range (450-800K) [3].

It is shown theoretically and experimentally that the TE property of PbTe can be improved by doping it with some donor or acceptor atoms [6, 7]. Recently, there has been renewed research interest in PbTe after Heremans *et al.* [8] reported the enhancement of the Seebeck coefficient of PbTe through the distortion of electronic density of states by doping it with thallium. The electric property of PbTe can vary significantly when it is doped with group IIIA elements, such as In and Ga, which generate a deep lying impurity level in IV-VI compounds [9]. A previous work by Dashevsky *et al.* [10] reported a higher *ZT* value of about 0.92 at 700K for a functionally graded indium doped single crystal of PbTe.

Lead Telluride nanostructures have been synthesized using various techniques. Beyer *et al.* [11] reported an enhanced thermoelectric efficiency of molecular beam epitaxially (MBE) grown superlattices based on PbTe. Palchik *et al.* [12] synthesized PbTe from solutions under microwave radiations. Earlier works also reported the synthesis of 3-D structures of PbTe such as dendrite like structure via electrochemical deposition [13] and sponge like structures from sonochemistry [14]. Among the various synthesis techniques employed for the formation of PbTe nanostructures, the solvothermal/hydrothermal process has attracted much interest due to advantage of high yield, low synthesis temperature, high purity and high crystallinity. Zhu *et al.* reported the synthesis of PbTe three dimensional hierarchical superstructures via an alkaline hydrothermal method [16]. The solvothermal/hydrothermal technique produces various PbTe nanostructures such as nanotubes [17, 18], nanospheres [19], and nanoboxes [20].

This chapter reports the synthesis of undoped and In-doped PbTe nanostructures using the solvothermal and hydrothermal routes in alkaline solution medium with or without a surfactant at different temperatures and reaction time durations. The synthesis of the undoped and In-doped PbTe nanostructures is carried out in water/glycerol mixture as a solvent. The surface morphology and crystal structure of the as-synthesized undoped and In-doped PbTe nanostructures have been discussed in detail. The In-doped and undoped PbTe nanostructures are intended to be utilized in future thermoelectric applications. A pseudo-potential first principle calculation has been conducted to study the mechanism of indium doping into PbTe matrix. In-doped PbTe is expected to exhibit the enhanced thermoelectric property as a result of the enhanced electronic properties upon indium doping.

4.2 Experimental

The general explanation of experimental techniques for material synthesis and characterization for the materials of study for the dissertation work has already been presented in chapter 2. Only a specific detail for the synthesis and characterization of undoped and In-doped PbTe nanoparticles is presented in the current section.

4.2.1 Material synthesis

Analytically pure lead nitrate (PbNO₃), indium chloride (InCl₃) and tellurium (Te) powder were used as precursor materials for the synthesis of PbTe and In-doped PbTe. These materials were put in the Teflon-liner in the appropriate molar ratios according to the formula $In_xPb_{1-x}Te$, x=0, 0.005, 0.01, 0.015, and 0.02. Then, 6.25 mmol of sodium hydroxide (NaOH) as a pH controlling agent, 2.6 mmol of sodium borohydrate (NaBH₄) as a reducing agent, and 1 mmol of ethylenediaminetetraacetic acid (EDTA) as a shape directing additive, were added. Water was used as a solvent in the hydrothermal process; either ethanol or a mixture of glycerol and water in 1:3 volume ratio were used as solvents for the solvothermal route. The hydrothermal/solvothermal reaction process was then carried out at 140°C and 200°C for 24 h. The above synthesis process was repeated with the addition of 1 mmol each of cetyltrimethylammonium bromide (CTAB), sodium

dodecyl sulfate (SDS), and Triton X-100 as cationic, anionic, and non-ionic surfactants/capping agents, respectively at 140°C for 24 h in water/glycerol solution (3:1 volume ratio). The PbTe nanostructures synthesized without surfactants at 140°C and 200°C for 24 h in ethanol are termed as PbTe-1 and PbTe-3 and in the water-glycerol mixture are named as PbTe-2 and PbTe-4, respectively. $In_xPb_{1-x}Te$ (x= 0.005, 0.01, 0.015, and 0.02) synthesized at 140°C for 24 h in water/glycerol solution are named as In005PbTe, In015PbTe, and In02PbTe, respectively.

4.2.2 Structural characterization

Crystal structure analysis was performed by X-ray diffraction (XRD) measurements (Siemens D5000 diffractometer). Surface morphology analysis was performed by a field emission scanning electron microscope (SEM, JEOL JSM-6330F, 15 kV). Transmission electron microscopy (TEM), selected-area electron diffraction (SAED) patterns, and energy dispersive X-ray spectroscopy (EDS) spectrum were obtained from a FEI Tecnai F30 apparatus. Laser induced breakdown spectroscopy (LIBS) analyses were conducted on a RT100HP system (Applied Spectra, Fremont, CA), equipped with a 1064nm ns-Nd:YAG laser.

4.2.3 First principle calculation

A first principle calculation was conducted to investigate the effect of indium doping into PbTe. First, lattice constant of PbTe was calculated based on NaCl structure and then a simple cubic (SC) $2 \times 2 \times 2$ supercell with 32 PbTe units was constucted for further calculation of substitution energy and interstitial insertion

energy. The carrier concentration of 1.5% In-doped PbTe was also calculated.

4.3 Results and discussion

Figure 4.1 shows the XRD patterns of the as-prepared samples. Figure 4.1(a) shows the XRD pattern of undoped PbTe samples PbTe-1, PbTe-2, PbTe-3, and PbTe-4. All the diffraction peaks in the XRD patterns can be indexed as a face centered cubic PbTe (JCPDS: 78-1905) [18] which confirms the crystalline phase of the as-synthesized PbTe. The strong (200) diffraction peak represents the prominent growth orientation of PbTe nanostructures along the [200] direction. The sharp peaks in the XRD profiles indicate the high crystallinity of the PbTe sample. However, the XRD profile for PbTe-1 sample shows two weak peaks on either side of the (220) peak, which can be attributed to the presence of some elemental Te [21]. The residual Te is supposed to have come from the starting material indicating that the synthesis in ethanol at relatively low temperature (140°C) is an incomplete reaction. The results indicate that if ethanol is used as the solvent, a high reaction temperature is needed to promote a complete reaction and achieve high purity PbTe (see the XRD pattern labeled PbTe-3 in Fig 4.1a). Furthermore, if a water-glycerol mixture is utilized as the solvent, pure phase of PbTe can be formed at either low temperature of 140 °C (see the XRD pattern labeled PbTe-2 in Fig. 4.1a) or high temperature of 200 °C (see the XRD pattern labeled PbTe-4 in Fig. 4.1a). It is clear that solvent of a water-glycerol mixture facilitates the reaction. Because only water-glycerol mixture yields a pure phase of PbTe at all synthesis conditions including lower temperature (140° C) synthesis, all doped samples were prepared in water-glycerol solution at 140° C for 24 h as undoped sample PbTe-2.



Figure 4.1 a) XRD patterns of the as-prepared undoped PbTe samples synthesized without surfactants for 24 h. PbTe-1 at 140 °C in ethanol solution, PbTe-2 at 140 °C in water/ glycerol solution, PbTe-3 at 200 °C in ethanol, and PbTe-4 at 200 °C in water/ glycerol solution. b) XRD pattern of In-doped PbTe samples synthesized at 140 °C for 24 h, In005PbTe, In01PbTe, In015PbTe, and In02PbTe, synthesized in water/glycerol solution.

Figure 4.1(b) represents the XRD patterns of In-doped PbTe (In005PbTe, In01PbTe, In015PbTe, and In02PbTe) synthesized at 140°C for 24 h in water-glycerol solution. All the diffraction peaks belong to face centered cubic structure same as those of PbTe and the very sharp peaks indicate the high crystallinity of the as-synthesized In-doped PbTe samples. The XRD patterns do not show any peaks corresponding elemental indium, indicating that indium is likely doped in PbTe. Lattice constants of undoped (PbTe-2) and indium doped samples were calculated from the respective XRD profiles using Bragg's law and were tabulated in table 4.1. As indium atoms are smaller in diameter than Pb atoms, lattice constants of the In-doped PbTe sample are almost identical (average value~6.434 Å) which is in agreement with the reported value of undoped cubic PbTe, 6.454 Å (JCPDS: 78-1905).

Figure 4.2 shows the variation of lattice constant of PbTe samples prepared at 140° C for 24 h in water-glycerol solution with the different molar fractions of indium doping. The graph indicates that PbTe samples do not exhibit any consistent variation in lattice constant with the doping level of indium. Samoylov *et al.* [22] reported a very small decrease (on the order of 10^{-3} Å) in lattice constant of In-doped PbTe films within the molar fraction interval of 0 < x < 0.064 of indium. The decrease is one order of magnitude smaller than the uncertainty in lattice constant of these samples (see table 4.1). Another work by Belokon *et al.* [23] also reported almost constant lattice parameter with the doping level of indium up to 2 at% of indium. The bigger uncertainty in the lattice

Table 4.1 Lattice constant calculation for as-synthesized un-doped PbTe; PbTe-2 and In-doped PbTe; In005PbTe, In01PbTe, In015PbTe, and In02PbTe

Doping type	Sample Name	Lattice Constant, Å
Undoped	РЬТе-2	6.423±0.017
Doped	In005PbTe	6.452±0.019
	In01PbTe	6.437±0.014
	In015PbTe	6.418±0.013
	In02PbTe	6.441±0.015



Figure 4.2 Graph of lattice constant versus doping level of indium in In-doped PbTe samples synthesized at 140 °C for 24 h in water/glycerol solution

constant calculation in these samples can be attributed to the observational errors attributable to the simple method used in this calculation. Any minute change in lattice constant with the indium content is beyond the capability of the simple method of lattice constant calculation. A more accurate and sophisticated method of lattice parameter calculation will be necessary to reveal any minute variation of lattice constant at such a small doping level of indium.

To further investigate the doping mechanism, the favorability of indium atom to substitute Pb was studied by conducting a pseudo-potential first principle calculation using a single cubic $2 \times 2 \times 2$ supercell with 32 units of PbTe. In the beginning, a 64 atom Pb₃₂Te₃₂ cell was used to calculate the lattice constant of PbTe crystal. The calculated value of lattice constant is found to be 6.33 Å which is in close agreement with the reported value of cubic PbTe, 6.454 Å (JCPDS: 78-1905). The calculation of lattice constant is followed by calculation of the formation energy for substitution with one indium in the $2 \times 2 \times 2$ supercell (1.5 at % of In) which is slightly higher in indium level compared to the highest doped experimental sample In_{0.02}Pb_{0.98}Te (1.0at %). The formation energy of the substitution is defined as $E_{sub} = E(Pb_{32}Te_{32}) + E(In) - E(InPb_{31}Te_{32})$ -E(Pb). The calculated value of the formation energy of the substitution is 3.21 eV which is larger than the calculated cohesive energy of indium crystal (E_{in}) , 2.52 eV. Since $E_{sub} > E_{in}$, it can be concluded that indium is highly favorable to substitute Pb into the PbTe for 1.5 at % doping level. The conclusion is consistent with the result from the XRD analysis of In-doped PbTe samples which shows no presence of indium in the XRD pattern. The formation energy of substitution for InPb₁₅Te₁₆ (3.12 at % of In) and

InPb₇Te₈ (6.24 at% of In) were also calculated in order to investigate the solubility of the indium into PbTe. It is found that formation energy for substitutions reduced to -0.6 eV and -1.17 eV respectively for 3.12 at% and 6.24 at% of indium doping. The reduced value of substitution energy indicates that substitution of Pb with indium becomes less favorable with the increased In doping concentration. The very large negative substitution energy, -1.17 eV for 6.24 at % of In doping suggests that it is almost impossible for In to substitute Pb at such high doping level which corresponds well with the solubility limit of indium in PbTe. The doping of indium into interstitial sites of PbTe lattice was also tested. At most likely (0.25, 0.25, 0.25) interstitial site the insertion energy comes to be 0.068 eV. From these energy calculations, as well as from the X-ray measurement, it can be concluded that In doping, at the level of 1.5 at %, is substitution on Pb site. Zhang et al. [24] also investigated the effect of aluminum (Al) doping on PbSe by conducting a first principle calculation and found that Al atoms prefer to replace Pb rather than take interstitial sites. The reported band structure and density of states (DOS) calculation showed that upon low level doping of Al, the enhanced density of states of PbSe near the Fermi energy is responsible for the enhanced carrier density, which leads to higher conductivity. Since In doping to our PbTe sample is also substitution on Pb site, we expect a similar effect on electronic properties of our PbTe samples upon doping. Indium concentration in 1.5% In-doped PbTe sample is calculated and found that the concentration of indium is about 2.14×10^{20} cm⁻³. Total carrier concentration n, for 1.5 % In-doped PbTe sample is also calculated using the equation 4.1,

$$n = n_{int} \left[1 + \left(\frac{N_d}{n_{int} e^{\frac{E_g}{2K_B T}}} \right)^{\frac{1}{2}} \right] e^{\frac{E_{c-}E_d}{E_g}}$$

$$4.1$$

where, n_{int} is carrier concentration of undoped PbTe, N_d is the concentration of Indium in 1.5% In-doped PbTe, E_c and E_d are the conduction and the donor energy levels, and E_g is the band gap energy for undoped PbTe. With $n_{int}=1\times10^{18}$ cm⁻³ [25] $N_d=2.14\times10^{20}$ cm⁻³, $E_g=0.33$ eV and indium impurity sitting in the middle of the band gap, the total carrier concentration for 1.5% In-doped PbTe comes to be about 1.76×10^{18} cm⁻³, which is consistent with the reported experimental value of room temperature carrier concentration of about 3.9×10^{18} cm⁻³ for 1.5% In-doped PbTe sample [26]. Hence, the conclusion of indium substitution on Pb-site for 1.5% of In-doped PbTe sample from first principle calculation is consistent with the carrier concentration measurement.

To further investigate the incorporation of indium to the PbTe matrix, the LIBS analyses were performed on the undoped (PbTe-2) and two indium doped (In01PbTe and In02PbTe) samples, respectively. The LIBS emission spectra were obtained in the wavelength range of 200-1040 nm. The presence of indium on samples In01PbTe and In02PbTe was confirmed by the detection of 9 different emission lines at: 256.0nm, 271,0nm, 275.4nm, 293.3 nm, 303.9 nm, 325.6 nm, 410.2 nm, 451.1nm and 465.6nm, respectively. Figure 4.3 shows typical spectra and some emission peaks detected for In and Pb on sample In02PbTe. Tellurium (Te) peaks were not detected because of the very high ionizing potential of Te for the operational range of the LIBS instrument used. LIBS spectra shows the presence some prominent impurity peaks like magnesium (Mg) which

may have come from some trace metal impurities ($\sim 0.2\%$) present in precursor materials used before the synthesis. Figure 4.3 (a) is the LIBS emission spectra of In02PbTe for selected range from 300 nm to 466 nm which shows the presence of atomic indium peaks at different wavelengths from 256.0 nm to 466 nm.



Figure 4.3 a) LIBS spectra of In02PbTe for selected range from 300 nm to 466 nm. b) LIBS indium emission lines at 410 nm for samples PbTe-2 (blue), In01PbTe (green), and In02PbTe red), respectively. c) LIBS indium emission lines at 325 nm for samples PbTe-2 (blue), In01PbTe (green), and In02PbTe (red), respectively.

Figure 4.3 (b) and (c) show the LIBS indium emission lines at 410 nm and 325 nm for undoped PbTe (blue), In01PbTe (green) and In02PbTe (red), respectively. Undoped PbTe does not show any indium peak at both the wavelengths indicating the absence of indium. However, In01PbTe and In02PbTe samples show the presence of indium lines at 410 nm and 325 nm with almost linear increase in intensity with increasing indium content. The presence of multiple indium emission lines and linear increase in intensity from the samples In01PbTe and In02PbTe confirms the incorporation of indium to the PbTe matrix of doped samples in proportion with the doping level of indium. From the result of LIBS analyses, first principle energy calculations, and from the X-ray measurement, it can be concluded that at the level of 1.5 at % doping, indium is doped in the PbTe matrix with the substitution on Pb site.

Figure 4.4 shows the SEM images of the PbTe samples prepared at 140°C and 200°C with different solvents, respectively. Figure 4.4(a) is the SEM image of the sample prepared with ethanol as the solvent at 140°C for 24 h which shows particles with appreciably uniform shape and average particle size of about 200 nm. However, with ethanol at 200°C for 24 h (Fig. 4.4(b)), particles grow larger to an average size of about 300 nm. For comparison, the synthesis of PbTe sample was attempted with water as the solvent. Figures 4.4(c) and (d) present the SEM images of the PbTe samples synthesized with water as the solvent at 140°C and 200°C for 24 h, respectively. From the images it is clear that the PbTe samples formed with water as the solvent have chunks with various shapes and sizes. The PbTe sample prepared at 200°C for 24 h with water as solvent (Fig. 4.4(d)) shows nano to micron size spherical particles along with irregularly shaped



Figure 4.4 SEM images of undoped PbTe nanoparticles prepared without surfactants for 24 h in ethanol a) at 140 °C, and b) at 200 °C, in water c) at 140 °C, and d) at 200 °C, and in water/glycerol solution e) at 140 °C, and f) at 200 °C.

particles. The result indicates that water alone is not sufficient for the formation of uniform small size PbTe nanoparticles. Figure 4.4(e) is the SEM image of the PbTe sample formed with water/glycerol (3:1 volume ratio) at 140 °C for 24 h. It shows clearly the fine particles with similar shape and a size in the range of 70-200 nm. The SEM image of the sample prepared with water/glycerol at 200°C for 24 h (Fig. 4.4(f)) shows larger particles in the range of 200-500 nm in various shapes. The SEM results indicate that the particle size increases with the increase in the synthesis temperature when waterglycerol is used as solvent. From the SEM images, it can also be concluded that the combination of water and glycerol gives rise to nanoparticles with similar shape and small size compared to the use of alcohol or water alone as solvents. The use of ethanol or a water/glycerol mixture as solvent yields PbTe nanoparticles with uniform shape and size as compared with the PbTe particles prepared with only water. A report by Zhu et al. [14] also suggests that solvothermal route of synthesis is more favorable than the hydrothermal one caused by the strong polarity of the organic material in the solvothermal route which accelerates the dissolution of Te in the reaction process.

To further understand the effect of addition of the surfactant on the surface morphology of the PbTe samples, the synthesis process was repeated with a water/glycerol (3:1) solution at 140°C for 24 h using CTAB, SDS, and Triton, respectively, as surfactants. Figure 4.5 (a) shows the SEM image of the PbTe prepared with CTAB, which indicates the formation of mostly cube-shaped nanoparticles with size in the range of 65-145 nm. Sample synthesized with SDS (Fig. 4.5(b)) shows fewer nanocubes and more irregular nanoparticles compared to the nanoparticles synthesized



Figure 4.5 SEM images of undoped PbTe synthesized with (a) CTAB, (b) SDS, and (c) Triton, respectively, as surfactants in water/glycerol (3:1 volume ratio) solution at 140°C for 24 h.

with CTAB; the size of nanoparticles ranges from 70-230 nm. The synthesis of the PbTe sample with Triton (Fig. 4.5(c)) yields fine particles with the size in the range of 40-120 nm. From the SEM images, it can be concluded that the PbTe nanoparticles synthesized at 140°C for 24 h with a water/glycerol solution with the addition of different surfactants (Fig. 4.5) are more uniform in shape and size compared to the nanoparticles synthesized without surfactants (Fig. 4.4(e)). The modification of shape can be attributed to the presence of surfactant as shape directing agent to control the size and shape of the particles. The PbTe nanoparticles synthesized with CTAB and Triton are smaller in size, while nanoparticles synthesized in SDS are bigger in size which are comparable to the nanoparticles synthesized without surfactants. Zhu et al. [15] reported the synthesis of three dimensional hierarchical structure of PbTe by a hydrothermal method with or without surfactants using different molar concentration of NaOH and concluded that the morphology of the PbTe crystals depends on the synthesis temperature, time, and most importantly on the concentration of NaOH. The cited work also reported the synthesis of PbTe nanoparticles without any hierarchical structure, similar to these PbTe nanostructures, with or without 1M NaOH at 160°C and without the use of any surfactants.

The structure of the as-prepared PbTe sample synthesized at 140°C for 24 h with a water/glycerol solution (sample PbTe-2) was analyzed by TEM, HRTEM, SAED, and EDS. Figure 4.6(a) is the low-magnification TEM image of the PbTe nanoparticles with various sizes of 75-220 nm. The high-magnification TEM image of the PbTe sample (Fig. 4.6(b)) indicates that the nanoparticles have cube-like shape. Poudel *et al.* [27] also



Figure 4.6 TEM images of undoped PbTe synthesized without surfactants at 140° C for 24 h with water/glycerol (3:1 volume ratio) solvent. (a) Low-magnification TEM image, (b) high-magnification TEM image, (c) HRTEM image of the magnified region indicated by an open box in Fig. (b), (d) SAED pattern, and (e) EDS pattern

reported the cube-like PbTe nano- and micro-particles synthesized hydrothermally at 100°C and 160°C, respectively, for 10 h without surfactant. But, with surfactants, various morphologies of PbTe crystals including hierarchical structures were obtained. Recently, PbTe microcubes were prepared using a composite-hydroxide-mediated approach [28]. Instead of using organic or inorganic solvents, the reported work used a mixture of NaOH and potassium hydroxide (KOH) to yield PbTe micro cubes with the size of several micrometers. Figure 4.6(c) shows the HRTEM image of the magnified region on the nanocube indicated by the open box in Fig. 4.6(b). The HRTEM image indicates equally spaced lattice fringes separated by a distance of 0.314 nm that corresponds to the dspacing of the (200) plane of the cubic PbTe [13]. Figure 4.6(d) shows the clearly distinguishable SAED ring patterns, which can be indexed to different lattice planes of cubic PbTe. The chemical composition of the PbTe sample was analyzed by an EDS spectrum (Fig. 4.6(e)), which shows that the as-prepared sample consists of only Pb and Te, hence confirming the chemical purity of the sample. The peak corresponding to Cu in the EDS spectrum arises from the TEM grid used for preparing the TEM specimen. From the TEM analysis, it can be concluded that the clear lattice fringes in the HRTEM image and the distinct rings in the SAED pattern reveal the high crystalline quality of the assynthesized PbTe nanostructures.

Surface morphology and structural analysis of the as-prepared In-doped PbTe samples were performed with SEM and TEM examinations, respectively. Figure 4.7 shows the SEM and TEM images of In01PbTe sample synthesized at 140°C for 24 h in water/glycerol solution. SEM image (Fig. 4.7(a)) shows the presence of nanoparticles in

various shapes with size in the range of 120-250 nm. The nanoparticles are bigger in size as compared to the nanoparticles present in undoped PbTe sample synthesized at the same conditions (see Fig. 4.4(e)). The high magnification TEM image (Fig. 4.7(b)) of the as-prepared sample reveals the nanoparticles with size of around 150-265 nm. Figure



Figure 4.7 SEM and TEM images of the as-prepared In_{.01}Pb_{.99}Te samples synthesized in water/glycerol solution at 140°C for 24 h (sample name: In01PbTe). (a) SEM images, (b) TEM image, (c) HRTEM image, and (d) SAED pattern.

4.7(c) shows the magnified region of a nanoparticle as indicated by the letter 1 in the Fig. 7(b). It shows equally spaced and clear lattice fringes separated by 0.319 nm, which is in agreement with *d*-spacing of (200) plane of cubic PbTe. SAED pattern (Fig. 4.7(d)) shows the distinguishable diffraction spots which indicate the single-crystalline nature of the In01PbTe cubic structure.

SEM and TEM images of In02PbTe sample are shown in Fig. 4.8. A typical SEM image (Fig. 4.8(a)) reveals that the nanoparticles have similar shapes and small size in the range of 70-125 nm. The high magnification TEM image (Fig. 4.8(b)) of the as-prepared sample shows the nanoparticles with size of around 160-280 nm. The difference in particle size measured from SEM and TEM images comes from the fact that SEM and TEM images are taken from different areas of the sample with various particle sizes indicating that the particle sizes are not uniform within the entire sample. Figure 4.8(c)presents the high resolution TEM image of an In02PbTe nanoparticle, taken from the region marked by "1" in the Fig. 4.8 (b). The HRTEM image shows equally spaced lattice fringes with separation of 0.378 nm that corresponds to the *d*-spacing of (111) plane of cubic In-doped PbTe. The similar values of the d-spacing for In01PbTe, In02PbTe and PbTe indicate the doping of small amount of indium will not cause significant change of the unit cell of crystals unit cell. Figure 4.8(d) shows the isolated SAED spots, which indicate the single-crystalline nature of the In02PbTe cubic structure. From the TEM analysis, it can be concluded that the well-defined and clear lattice fringes in the HRTEM image as well as the distinct SAED pattern confirm the high crystalline quality of the as-synthesized In01PbTe and In02PbTe nanoparticles.



Figure 4.8 SEM and TEM images of as-prepared $In_{.02}Pb_{.98}Te$ samples synthesized in water/glycerol solution at 140°C for 24 h (In02PbTe). (a) SEM images, (b) TEM image, (c) HRTEM image, and (d) SAED pattern

4.4 Conclusions

Undoped and In-doped PbTe nanoparticles were synthesized via the solvothermal and hydrothermal routes with or without surfactant at different preparation conditions. It is found that solvent plays a very important role in the size and shape of the PbTe and Indoped PbTe nanoparticles. The use of water/glycerol mixture as the solvent yields nanoparticles with relatively uniform shapes and narrow size distribution while use of water as the solvent results in nanoparticle with irregular shapes and wide range size distribution. Absence of any impurity phase of indium in XRD pattern indicated that indium was likely doped into the lattice sites of Pb in PbTe. The presence of multiple indium lines in the LIBS emission spectra for indium doped PbTe samples; In01PbTe and In02PbTe, confirms the incorporation of indium to the PbTe matrix. The results from the theoretical calculation also indicate that indium is likely to replace the lead during the doping process for the smaller concentration of indium (< 3 at %) which complements the result from LIBS and XRD analyses. Lattice constants for In-doped PbTe samples derived from the XRD pattern did not show marked change in the lattice constant with the doping level of indium, which can be attributed to the observational limitation of the method of calculation.

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CHAPTER 5: SYNTHESIS AND CHARACTERIZATION OF UNFILLED AND YTTERBIUM FILLED COBALT ANTIMONY

Chapter 5 presents the detailed study of the synthesis and characterization of unfilled and ytterbium (Yb) filled cobalt antimony (CoSb₃) nanoparticles synthesized via a solvothermal route. The effect of the amount of sodium borohydride reductant and the annealing condition on the phase transformation of CoSb₃ has also been investigated.

5.1 Introduction

During the past few years, there has been a renewed research interest in the families of novel and advanced thermoelectric materials which have the potential for increasing their thermoelectric (TE) efficiency. Skutterudites are among the best of these novel materials [1-3]. Investigation of skutterudites as a promising thermoelectric material is guided by the so called 'phonon-glass-electron-crystal (PGEC)' concept proposed by Slack [4]. A PGEC material generally possesses a very low phonon thermal conductivity as in glass and very high electronic conductivity as in a single crystal which are the ideal conditions for an enhanced thermoelectric efficiency. Binary skutterudite has the form MX₃ (M: Co, Rh, Ir and X: P, Sb, As) with cubic (space group *Im3*) unit cell which possesses an open crystalline lattice with two icosahedral voids. Among the various skutterudite systems, cobalt antimony (CoSb₃) has been widely studied owing to its superior thermoelectric property coupled with the abundant presence of less volatile constituent elements [5]. Binary skutterudite possesses very high carrier mobility among the bulk semiconductor materials which will be favorable for high efficiency thermoelectric device application [6]. However, for practical applications, the high

thermal conductivity (~ $10-25 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature) of the binary skutterudite [7] needs to be reduced to further increase its efficiency. It is now widely known that various techniques, such as nanostructuring [8] and lanthanides (Yb, La, Ce, Eu and Pr) filling [9, 10], can drastically alter the thermal and electrical properties of the skutterudite to enhance its thermoelectric efficiency. Slack [4] first pointed out that some smaller atoms may be introduced into the icosahedral voids of skutterudites to scatter the phonons and to suppress the thermal conductivity via their "rattling" inside these voids. Later, Morelli et al. [11] experimentally confirmed the same idea in their work on cerium filled iron antimony. Since ytterbium (Yb) is comparatively heavier in lanthanide series, it has been widely used as a filler atom. The heavier and the smaller the filler atom, the greater is the reduction in thermal conductivity [12].

In the past, various techniques such as chemical alloying [13], melt spinning [14], ball milling [15], mechanical alloying [16], sol-gel [17], spark plasma sintering [18] and hydrothermal/solvothermal method [8,19] have been employed to synthesize filled and unfilled CoSb₃ in nanostructured form. In the present work, a solvothermal synthesis technique is employed because it is a very cost effective method to yield fine and regular nanoparticles with high yield, low synthesis temperature, high purity, and good size and shape control. A systematic study of the effect of both the annealing temperature and the amount of sodium borohydride reductant on the phase formation during the synthesis of CoSb₃ is still lacking. In the current work, the effects of annealing temperature and various amounts of reductant on the phase transformation of the synthesized nanomaterials have been discussed.

5.2 Experimental

The general approach for material synthesis and characterization in the dissertation work has already been presented in chapter 2. The specific detail for the synthesis and characterization of unfilled and Yb-filled CoSb₃ nanoparticles will be presented below.

5.2.1 Material synthesis

Analytically pure CoCl₂.6H₂O, SbCl₃ and YbCl₃ were used as starting materials for the synthesis of CoSb₃ and Yb-filled CoSb₃. These precursor materials were put into a Teflon-lined autoclave in the appropriate molar ratio according to the formula CoSb₃ and Yb_xCo₄Sb₁₂ (x=0.1 and 0.2). In a typical synthesis process of CoSb₃, 1mmol CoCl₂.6H₂O, 3 mmol of SbCl₃ were used as precursors and 11 mmol (0.4 g) of NaBH₄ was used as the reductant and about 14 mL(0.24 mol) of ethanol was used as solvent. Then the solution was subjected for solvothermal reaction at 240 °C for 72 h. The assynthesized CoSb₃ nanostructure using the abovementioned typical synthesis process was named as CoSb₃-T. To study the effect of annealing on the phase transformation, the sample CoSb₃-T was annealed at various temperatures for different duration. To investigate the effect of NaBH₄ on the formation of CoSb₃, a various amount of NaBH₄ from 0.4 g to 1.2 g and the same amount of CoCl₂.6H₂O and SbCl₃ in 1:3 molar ratios were used. The samples prepared with 0.4 g, 0.6 g, 0.8 g, 1.0 g, and 1.2 g of NaBH₄ and annealed at 500 °C in argon for 5 hours were designated as CoSb₃-0.4, CoSb₃-0.6, CoSb₃-0.8, CoSb₃-1.0, and CoSb₃-1.2 respectively. Since the experimental results indicated that the highest phase purity was exhibited in the CoSb₃ sample synthesized with 0.8 g of NaBH₄, all Yb-filled CoSb₃ (Yb_{0.1}Co₄Sb₁₂ and Yb_{0.2}Co₄Sb₂) samples were synthesized with 0.8 g of NaBH₄.

5.2.2 Characterization

X-ray diffraction measurements were taken using Siemens D5000 diffractometer for the crystal structure analysis of the samples. Surface morphology analysis of the CoSb₃ and Yb-filled CoSb₃ materials was performed by a field emission scanning electron microscope (SEM, JEOL JSM-6330F, 15 kV). TEM, HRTEM, and SAED measurement were carried out by A FEI Tecnai F30 apparatus. LIBS spectrum was collected using a J200 system (Applied Spectra, Fremont, CA), equipped with a 266nm ns-Nd:YAG laser.

5.3 Results and discussion

5.3.1 Effect of synthesis conditions on the formation of CoSb₃ and Yb_xCo₄Sb₁₂ (x=0.1 and 0.2)

The crystal structure of the as-synthesized CoSb₃-T nanostructures was studied with powder X-ray diffraction. An XRD profile of the CoSb₃-T sample is presented in Fig. 5.1, which shows the presence of very prominent peaks corresponding to elemental antimony (Sb) and cobalt antimonide (CoSb₂) along with the peaks of CoSb₃. The impurity peaks of Sb and CoSb₂ are marked with "+" and "*" respectively and all unmarked peaks correspond to pure CoSb₃ in the XRD profiles in Fig. 5.1. A similar work by Mi *et al.* [8] also reported the presence of the CoSb₂ impurity phase in the sample prepared solvothermally in ethanol using NaBH₄ as reductant at reaction temperature of

 250° C for 72h and the transformation of the CoSb₂ to CoSb₃ after the sample was hot pressed. An annealing process is also expected to have similar effect on the phase transformation of the as-prepared CoSb₃-T sample. To investigate the effect of annealing on its phase transformation, the CoSb₃-T sample was then annealed for various durations from 2 h to 5 h in the temperature range from 300°C to 700°C. The annealing at different time from 2h to 5h all resulted in similar reduction in the peak intensity of the impurity phases, but a 5 h annealing showed comparatively greater reduction in the peak intensity of the impurity phases. Therefore, an annealing time of 5 h is chosen for further studying the effect of annealing temperatures on the phase transformation. The sample CoSb3-T was annealed at 400°C to 700°C for 5 h. The XRD profiles of the samples annealed at 400°C, 500°C, 600°C, and 700°C are named as An400C, An500C, An600C, and An700C, respectively, as shown in Fig. 5.1. The XRD profiles of the samples An300 (XRD not shown here) and An400 show no significant change in the intensity of the peaks of Sb and CoSb₂ compared to that of the unannealed sample CoSb3-T. Since annealing at 300°C and 400°C resulted in the products with the very similar XRD profiles, only the XRD profile of the sample annealed at 400°C is presented in Fig. 5.1. It is found that the Sb peaks disappeared and the relative intensity of the $CoSb_2$ peaks was reduced after the sample was annealed at the temperature of 500°C. Although the samples annealed at 600°C and 700°C did not show the Sb peaks, the relative intensity of the CoSb₂ peaks did not change much compared with those in the sample annealed at 400 °C and the asprepared sample. The above results indicate that an annealing temperature of 500 °C and an annealing time of 5 h are the optimal conditions for reducing the impurity phases in the skutterudite.



Figure 5.1 XRD profiles of the CoSb₃ nanoparticles before and after annealing at various temperatures for 5 hours. CoSb₃-T denotes the as-synthesized sample, An400C the sample annealed at 400°C, An500C the sample annealed at 500°C, An600C the sample annealed at 600°C, and An700C the sample annealed at 700°C.

Use of various amounts of NaBH₄ may be another route to obtain the pure phase CoSb₃. Ji *et al.* [20] reported the effect of various amounts of NaBH₄ on the phase of CoSb₃ synthesized with ethanol at 220°C for 24 h. It was found that the as-synthesized sample mainly contained elemental Sb and CoSb₂ if small amount of NaBH₄ (from 0 g to 0.4 g) was used during the sample synthesis while the as-synthesized sample mainly contained CoSb₃ phase if high amount of NaBH₄ (0.8 g-1.6 g) was employed during the synthesis. Since a high amount of NaBH₄ in the synthesis process in the current work resulted in the high purity of CoSb₃ phase, various amounts of NaBH₄ (0.4 g-1.2 g) were used to synthesize CoSb₃ at 240 °C for 72 h to investigate the effect of NaBH₄ in the phase purity of the skutterudite sample.

Figure 5.2 shows the XRD profiles of samples CoSb₃-0.4, CoSb₃-0.6, CoSb₃-0.8, CoSb₃-1.0, and CoSb₃-1.2 synthesized with NaBH₄ of 0.4, 0.6, 0.8, 1.0 and 1.2 g, respectively, followed by annealing in argon at 500 °C for 5 hours. The majority of the diffraction peaks can be indexed as the binary skutterudite CoSb₃ with space group *Im3* according to JCPDS 65-3144. The XRD pattern of CoSb₃-0.4 shows presence of some weak peaks of impurity CoSb₂ along with strong peaks of CoSb₃. With the increasing amount of NaBH₄, as in the case of the samples CoSb₃-0.6, CoSb₃-0.8, CoSb₃-1.0, and CoSb₃-1.2 the peaks corresponding to impurity CoSb₂ disappeared, indicating that a large amount of NaBH₄ is necessary to complete the reaction process to form the pure CoSb₃ phase. However, samples CoSb₃-1.0 and CoSb₃-1.2 showed the presence of some


Figure 5.2 XRD profiles of the CoSb₃ nanoparticles synthesized with different amount of NaBH₄ and annealed in argon at 500°C for 5h. CoSb₃-0.4 with 0.4 g , CoSb₃-0.6 with 0.6 g, CoSb₃-0.8 with 0.8 g, CoSb₃-1.0 with 1.0 g, and CoSb₃-1.2 with 1.2 g of NaBH₄ respectively.

Among all the samples, CoSb₃-0.6, and CoSb₃-0.8 demonstrated the best CoSb₃ phase purity, with CoSb₃-0.8 showing more distinct peaks over the whole range of diffraction

angles. From the XRD analysis, it can be concluded that the addition of 0.8 g of NaBH₄ as reducing agent results in the formation of CoSb₃ with the best phase purity.

To understand the effect of $NaBH_4$ in the formation of $CoSb_3$, a detail study of the complete reaction process during the synthesis is required. A typical reaction process can be stated in the following steps.

$$6SbCl_3 + 18NaBH_4 \longrightarrow 6Sb + 18BH_3 + 18NaCl + 9H_2$$
(1)

$$CoCl_2 + 2NaBH_4 \longrightarrow Co + 2BH_3 + 2NaCl + H_2$$
(2)

$$Co + 2Sb \longrightarrow CoSb_2$$
 (3)

$$Co + 3Sb \longrightarrow CoSb_3$$
 (4)

In the beginning of the reaction, Co^{2^+} and Sb^{3^+} ions were formed and reduced to Co and Sb by the strong reducing action of NaBH₄ as shown in steps (1) and (2). However, Sb^{3^+} ions can be reduced more easily and quickly compared to Co^{2^+} since standard reduction potential of Sb^{3^+} ion is much higher compared to that of Co^{2^+} ion ($Sb^{3^+}/Sb = 0.204$, and $Co^{2^+}/Co = -0.28$) [20]. The more positive the reduction potential, the greater is the ion's tendency to be reduced. The presence of very stable elemental Sb (once it is reduced) and the excess of Co^{2^+} in the solution may be the reason for the impurity phase of elemental Sb and $CoSb_2$ in the final product as indicated by the above reaction step (3). In step (3), Sb may possess negative valence state ($Sb^{(-)}$) and react with Co^{2^+} to form $CoSb_2$. An increased amount of NaBH₄ can promote the reduction of excess Co^{2^+} to Co to form single phase CoSb₃ as shown in reaction (4). Hence, in this work, it is evident that a sufficient amount of NaBH₄ is required to obtain the pure phase $CoSb_3$ in the final sample.

Material	Lattice constant
CoSb ₃	9.0316 ± 0.0063
$Yb_{0.1}Co_4Sb_{12}$	9.0308 ± 0.0081
$Yb_{0.2}Co_4Sb_{12}$	9.0331 ± 0.0054

Table 5.1 Lattice constants of the as-synthesized and Yb-filled CoSb₃ samples

As revealed by XRD analysis, since 0.8 g of NaBH₄ is sufficient for the formation of single phase CoSb₃, the Yb-filled samples (Yb_{0.1}Co₄Sb₁₂ and Yb_{0.2}Co₄Sb₁₂) were synthesized with 0.8 g of NaBH₄ while other synthesis conditions were kept the same. Figure 5.3 shows the XRD profiles of CoSb₃, Yb_{0.1}Co₄Sb₁₂, and Yb_{0.2}Co₄Sb₁₂ nanoparticles synthesized at 240°C for 72 h with 0.8 g of NaBH₄ and annealed at 500°C for 5 h. All the diffraction peaks can be indexed as cubic skutterudites phase (JCPDS 65-3144). The lattice constants of the unfilled and Yb-filled samples were calculated from the respective XRD profiles using Bragg's law and were tabulated in table 5.1. Lattice constant for filled CoSb₃ is expected to increase with the increase in filling fraction of ytterbium. However, lattice constants for unfilled and Yb-filled samples are almost identical with the average value of 9.031 Å, which is in agreement with the reported value of cubic CoSb₃ skutterudites, 9.038 Å [21]. Table 5.1 indicates that the assynthesized CoSb₃ samples do not exhibit any consistent variation in lattice constant with the filling fraction of ytterbium. However, the change in lattice constant is within the



Figure 5.3 XRD profiles of the CoSb₃, $Yb_{0.1}Co_4Sb_{12}$, and $Yb_{0.2}Co_4Sb_{12}$ nanoparticles synthesized with 0.8 g of NaBH₄ and annealed in argon at 500°C for 5h.

error of the calculation, indicating the big uncertainty in the calculation. The bigger uncertainty in the lattice constant calculation of these samples is due to the observational errors attributable to the simple method of the calculation. A more accurate and sophisticated method of lattice parameter calculation will be necessary to reveal any minute variation of lattice constant at such a small filling fraction of ytterbium.

To investigate the presence of ytterbium in the filled CoSb₃ samples, the LIBS analyses were performed on the unfiled ($CoSb_3$) and two ytterbium filled ($Yb_{0.1}Co_4Sb_{12}$) and Yb_{0.2}Co₄Sb₁₂) samples. The presence of ytterbium on samples Yb_{0.1}Co₄Sb₁₂ and Yb_{0.2}Co₄Sb₁₂ was confirmed by the detection of 12 different emission lines throughout the spectrum. Figure 6.4 shows typical spectra and some emission peaks detected for Yb, Co, and Sb on $Yb_{0.2}Co_4Sb_{12}$ sample. Figure 5.4 (a) is the LIBS emission spectra of Yb_{0.2}Co₄Sb₁₂ for selected range from 315 nm to 405 nm, which shows the presence of atomic ytterbium peaks at different wavelengths along with Co and Sb peaks. The LIBS spectra shows the presence of some impurity peaks (not labeled in the figure) which may have come from some trace metal impurities (~0.2%) presented in precursor materials used for the synthesis and elements like nitrogen and oxygen presented in the environment during the process of laser ablation. Figure 5.4 (b) shows the LIBS ytterbium emission lines at 398.8 nm for unfilled CoSb₃ (black), Yb_{0.1}Co₄Sb₁₂ (red) and $Yb_{0,2}Co_4Sb_{12}$ (green). Unfilled CoSb₃ does not show any ytterbium peak indicating the absence of ytterbium. However, Yb_{0.1}Co₄Sb₁₂ and Yb_{0.2}Co₄Sb₁₂ samples show the presence of ytterbium lines at 398.8 nm; the intensity of the emission lines increases with the increase in ytterbium content. The multiple ytterbium emission lines in the Yb-filled CoSb₃ samples confirmed the presence of ytterbium most likely in the voids of CoSb₃. The increased Yb emission intensity in the LIBS spectra from CoSb₃ to Yb_{0.1}Co₄Sb₁₂ to Yb_{0.2}Co₄Sb₁₂ indicated that the concentration of Yb in CoSb₃ is proportional to the amounts of Yb used in the sample preparation.



Figure 5.4 a) LIBS spectra of $Yb_{0.2}Co_4Sb_{12}$ for selected range from 315 nm to 405 nm. b) LIBS of ytterbium emission lines at 398.8 nm for samples $CoSb_3$ (black), $Yb_{0.1}Co_4Sb_{12}$ (red), and $Yb_{0.2}Co_4Sb_{12}$ (green).

5.3.2 Surface morphology and structure analysis

Surface morphology and structural analysis of skutterudites samples were performed with SEM and TEM examination, respectively. Figure 5.5 shows the SEM and the TEM images of CoSb₃ sample synthesized at 240 °C for 72 h in ethanol with 0.8 g of

NaBH₄ and annealed at 500 °C for 5 h. The SEM image (Fig. 5.5(a)) shows the presence of nanoparticles with irregular shapes and various sizes; the larger particles have an average size of about 100 nm and the smaller particles have an average size of about 40 nm. Figure 5.5(b) is the high magnification TEM image of the sample which reveals the



Figure 5.5 SEM and TEM images of the $CoSb_3$ sample synthesized with 0.8 g of $NaBH_4$ and annealed in argon at 500°C for 5h a) SEM image, b) TEM image, c) HRTEM image, and d) SAED pattern.

nanoparticles with average size of about 160 nm. The inset in Fig. 5.5(b) shows the presence of smaller nanoparticles of size of about 35 nm that are connected to each other to form the peanut-like structure. Xie *et al.* [22] also reported the solvothermal synthesis

of CoSb₃ nanoparticles with smaller particles of size about 20 nm together with 50-100 nm larger sheets. Figure 5.5(c) shows a high resolution TEM image of the region in a nanoparticle indicated by the letter "1" in Fig. 5.5(b). It shows the equally spaced and clear lattice fringes separated by 0.371 nm that corresponds to the *d*-spacing of (211) plane of the cubic CoSb₃. A SAED pattern (Fig. (5.5(d)) shows the clearly distinguishable spot pattern indicating the single-crystalline nature of the cubic CoSb₃.



Figure 5.6 SEM and TEM images of the $Yb_{0.1}Co_4Sb_{12}$ sample synthesized with 0.8 g of NaBH₄ and annealed in argon at 500°C for 5h a) SEM image, b) TEM image, c) HRTEM image, and d) SAED pattern

The SEM and the TEM images of the $Yb_{0.1}Co_4Sb_{12}$ sample are shown in Fig. 5.6. Figure 5.6(a) is the SEM image of the sample which shows nanoparticles with the size in the range of about 100-240 nm corresponding an average particle size of 150 nm. The high magnification TEM image (Fig. 5.6(b)) of the sample shows that the nanoparticles have size in the range of 120-300 nm and some of them are fused together to form a cluster. The average particle size is measured as 170 nm. The magnified view of the dark square region (encircled with an orange circle) in Fig. 5.6 (b) is presented as the high resolution TEM image in Fig. 5.6(c), which reveals the equally spaced lattice fringes separated by 0.451 nm that corresponds to the *d*-spacing of the (200) planes of cubic CoSb₃ skutterudite. Figure 5.6(d) shows the clearly distinguishable SAED spot pattern, which indicates the single-crystalline-like nature of the sample.

Figure 5.7 reveals the SEM and TEM images of the $Yb_{0.2}Co_4Sb_{12}$ sample. The SEM image (Fig. (5.7(a)) shows the nanoparticles with a size of about 30-75 nm. Figure 5.7(b) is the high magnification TEM image, which shows the nanoparticles with various sizes ranging from 25-65 nm. The particle are connected together to form various shapes. Figure 5.7(c) is the high resolution TEM image of a single nanoparticle showing the clear lattice fringes with separation distance of 0.368 nm that corresponds to interplanar spacing of (211) plane of cubic CoSb₃ skutterudite. Figure 6.7(d) shows the SAED image with clear ring patterns indicating the high crystallinity of the sample.



Figure 5.7 SEM and TEM images of the $Yb_{0.2}Co_4Sb_{12}$ sample synthesized with 0.8 g of NaBH₄ and annealed in argon at 500°C for 5h a) SEM image, b) TEM image, c) HRTEM image, and d) SAED pattern.

5.4 Conclusion

Ytterbium filled and unfilled CoSb₃ nanoparticles were synthesized at 240°C for 72h using solvothermal route in ethanol with various amount of NaBH₄ as reducing agent. It is found that the amount of NaBH₄ has significant effect on the phase of resulting product. The sample synthesized with 0.8 g of NaBH₄ exhibited comparatively better skutterudite phase. The effects of annealing time and temperature on the phase of the as-prepared CoSb₃ sample were also investigated. It is found that the sample annealed at 500°C for 5h has a pure skutterudite phase. Structural analysis of Yb-filled and unfilled CoSb₃ synthesized with 0.8 g of NaBH₄ and annealed at 500°C for 5h has confirmed the formation of a highly crystalline pure cubic phase. The multiple ytterbium lines in the LIBS emission spectra confirm the presence of ytterbium in the Yb-filled CoSb₃ samples, Yb_{0.1}Co₄Sb₁₂ and Yb_{0.2}Co₄Sb₁₂. However, lattice constant calculation based on the XRD data for unfilled and Yb-filled CoSb₃ samples did not show the expected increment in the lattice constant with the increase of the filling fraction of ytterbium and the result is attributed to the observational limit. The Yb-filled and unfilled CoSb₃ nanoparticles could be used as potential thermoelectric material to develop the high-efficiency solid state thermoelectric devices.

5.5 References

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CHAPTER 6: SYNTHESIS AND CHARACTERIZATION OF Ca-DOPED Bi-Sb ALLOY

Chapter 6 reports the synthesis and structural characterization of Ca-doped Bi-Sb alloy. Structural characterization was carried out using X-ray diffraction analysis.

6.1 Introduction

Bismuth-Antimony (Bi-Sb) alloys are the best thermoelectric materials for low temperature cooling applications [1]. Both Bi and Sb are semimetals that exhibit a similar rhombohedral crystal structure of point group R3*m* and have similar lattice parameters. Thus $Bi_{100-x}Sb_x$ alloys form a solid solution over the entire composition range [2]. It is observed that band structure of $Bi_{100-x}Sb_x$ solid solutions change drastically with the Sb content in the solution. The band structure calculation indicates that at *T*=0K, $Bi_{100-x}Sb_x$ alloys are narrow band gap n-type semiconductors with an energy gap less than 25 meV for 7<*x*<22 and semimetal for 7≥*x*≥22 [3-5].

Properly oriented semiconducting single crystals of $Bi_{100-x}Sb_x$ have been found to be the best n-type thermoelectric materials for low-temperature (80 K) thermoelectric cooling when current flows along the trigonal axis [1, 6]. However, difficulties to produce the homogeneous single crystal of $Bi_{100-x}Sb_x$ and its low mechanical strength drastically limit its use in commercial thermoelectric devices [7]. Poly-crystalline Bi-Sb alloy might be more useful for practical application. However, poly-crystalline Bi-Sb alloy exhibits low *ZT* value. As an alternate, synthesis of nanostructured polycrystalline bulk Bi-Sb alloy has gained much attention because of the possibility of improving the TE properties through enhanced phonon scattering and quantum enhancement in nanostructured bulk TE materials [8].

Several methods such as quenching [7], arc plasma [9], mechanical alloying [10], and powder metallurgy [11] have been employed to synthesize nanostructured bulk n-type polycrystalline Bi-Sb samples. The current chapter reports synthesis and structural characterization of mechanically alloyed calcium doped $Bi_{100-x}Sb_x$ for *x*=15, which is found to be the optimized composition of Sb for the best TE efficiency. Thermoelectric properties measurement of as-synthesized calcium doped $Bi_{85}Sb_{15}$ nanostructured alloys will be reported in chapter 7.

6.2 Experimental

To prepare $Bi_{100-x}Sb_x$ alloy samples, Bi, Sb and doping element Ca were first weighed inside the glove box in the appropriate molar ratio according to the formula $Bi_{85}Sb_{15}Ca_x$, x=0.5, 2, and 5. All the precursor materials were arc melted to form an ingot and the ingot was ball milled in a jar for 5 h. The ball milled nanostructured powder was hot pressed at 200 °C under 80 MPa pressure with 2 minute holding time to get bulk alloy samples. The density of the resulting pellet was about 98% of theoretical density. The details of ball milling and hot press procedures are explained in chapter 2. The ball milled powder and hot pressed bulk samples were characterized by the XRD measurement to confirm the phase of the sample.



Figure 6.1 XRD profile of $Bi_{85}Sb_{15}Ca_x$, nanostructured bulk alloys for x=0.5 (black), 2 (red), and 5 (green).

Figure 6.1 is the XRD profile of the as-synthesized and the hot pressed calcium doped Bi-Sb alloys; Bi₈₅Sb₁₅Ca_{0.5}, Bi₈₅Sb₁₅Ca₂, and Bi₈₅Sb₁₅Ca₅, respectively. The entire diffraction peak can be indexed as rhombohedral phase of Bi-Sb alloy (space group

R3m). No visible peaks of elemental calcium were observed in the diffraction pattern indicating that calcium is likely doped to the Bi-Sb matrix. The particle size was calculated from the diffraction peaks using Scherrer's equation and found to be about \sim 30 nm. The small particle size shows that nanostructure were still preserved preventing the grain growth even after the hot pressing of the sample which is required for the optimization of the TE property of these alloys.

6.4 Conclusions

 $Bi_{85}Sb_{15}Ca_x$ (x=0, 0.5, 2, and 5) were synthesized via arc melting and then ball milling process. The phase of the as-synthesized and hot pressed Ca-doped $Bi_{85}Sb_{15}$ alloys were investigated with the X-ray diffraction and found to be pure rhombohedral Bi-Sb phase.

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CHAPTER 7: THERMOELECTRIC (TE) CHARACTERIZATION OF Bi₂Se₃ AND Ca-DOPED Bi₈₅Sb₁₅

Chapter 7 presents a detail study of the thermoelectric characterization of Bi_2Se_3 nanoparticles and Ca-doped $Bi_{85}Sb_{15}$ alloy.

7.1 Introduction

As mentioned in chapter 1, the efficiency of TE material can be defined by dimensionless thermoelectric figure of merit (ZT),

$$ZT = \frac{S^2 \sigma}{\kappa}$$
 7.1

where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity and T is absolute temperature at which the figure of merit is measured. It is clear that increase in power factor (S² σ) and decrease in thermal conductivity are needed for the enhancement of ZT value. The increase in power factor (S² σ) and decrease in thermal conductivity can be achieved through nanostructured thermoelectric materials [1-3]. Details of the synthesis of Bi₂Se₃ nanoparticles and Ca-doped Bi₈₅Sb₁₅ nanoparticles were presented in chapter 3 and 6, respectively.

Though Bi_2Se_3 is a good thermoelectric material for room temperature application, there have been a few reports on its thermoelectric properties. Recently, Lin *et al.* [4] reported the Seebeck coefficient measurement of Bi_2Se_3 nanostructured materials obtained from decomposition of the single-source precursor, tris-chelated diselenophosphato complex of bismuth ($Bi[Se_2P(OiPr)_2]_3$). It was found that the Seebeck coefficient of the nanostructured Bi_2Se_3 is superior to that of bulk Bi_2Se_3 . Patil *et al.* [5] reported a low thermal conductivity and high Seebeck coefficient of Bi_2Se_3 thin films grown by precipitation techniques as compared to the bulk counterpart. However, the electrical resistivity of the thin film is too high which compromises the improvement of the ZT value. In this chapter, thermoelectric properties of the solvothermally synthesized Bi_2Se_3 nanoparticles will be reported.

Bi-Sb alloy is one of the most widely investigated low temperature thermoelectric materials. Several works have been reported to increase the ZT of polycrystalline Bi-Sb samples. Devauex *et al.* [6] reported the reduction in thermal conductivity of polycrystalline Bi-Sb alloy with the decrease in grain size due to the increased phonon scattering. However, there is no increase in ZT caused by the increased resistivity. Previous results show that doping is another effective way to improve the thermoelectric property of Bi-Sb based alloy [7, 8] by controlling the carrier concentration, for example, lead, tin and tellurium doped Bi-Sb bulk and thin film alloys have been reported [9, 10]. However, careful selections of dopant are needed to optimize the TE property of Bi₁₀₀. $_x$ Sb_x alloy. The current chapter reports the thermoelectric property of mechanically alloyed calcium doped Bi_{100-x}Sb_x for *x*=15, which is found to be the optimized composition of Sb for the best TE efficiency.

7.2 Experimental

The detailed reports on material synthesis techniques for Bi₂Se₃ and Ca-doped Bi₈₅Sb₁₅ alloys were presented in chapter 3 and chapter 6, respectively. Only

methodology for the characterization of thermal and electrical transport properties is presented in this chapter.

7.2.1 Transport characterization of Bi₂Se₃

Sample prepared in DMF at 200 °C for 24h (BiSe-2) was chosen for thermoelectric (TE) property measurement. First, a large amount (~ 3 g) of the asprepared BiSe-2 powder sample was annealed in the presence of hydrogen and argon at 100 °C for 4 h. Then, the powder sample BiSe-2 was pressed at 500°C in a graphite die with a 12.7 mm central cylindrical opening diameter using a DC hot-press method to obtain cylindrical bulk discs. Since the pressure applied to the sample is very high (~ 80 MPa), these bulk disc samples are highly dense. The measured density of the sample by using Archimedes's principle is 6.59gcm⁻³, which is about 97% of the material's theoretical density (6.798 gcm⁻³). These bulk samples were then cut into 2 mm \times 2 mm \times 12 mm bars for four-probe electrical conductivity and Seebeck coefficient measurements and also cut with appropriate thickness for the thermal conductivity measurement. The electrical conductivity and the Seebeck coefficient were measured by using commercial equipment (Ulvac, ZEM-3) from room temperature to 523K and the thermal conductivity was measured by using a laser flash system (Netzsch LFA 457) from room temperature to 523K.

7.2.2 Transport characterization of Ca-doped Bi₈₅Sb₁₅

The ball milled nanostructured powder of $Bi_{85}Sb_{15}Ca_x$ (x=0.5, 2, and 5) was hot pressed at 200 °C under 80 MPa pressure with 2 minute holding time in a graphite die with a 12.7 mm inner diameter to get bulk alloy samples. The density of the resulting pellet was about 98% of the theoretical density. The pellet samples received after hot press were cut into 2 mm \times 2 mm \times 12 mm bars for four-probe electrical conductivity and the Seebeck coefficient measurements. The cylindrical pellets were also cut with appropriate thickness for thermal conductivity measurement. The electrical conductivity and Seebeck coefficient were measured using commercial equipment (Ulvac, ZEM-3) in the range from room temperature to 450 K and the thermal conductivity was measured by using a laser flash system (Netzsch LFA 457) from room temperature to 450 K.

7.3 Results and discussion

7.3.1 Thermoelectric property of Bi₂Se₃ nanostructure

The temperature dependence of the transport properties of the BiSe-2 sample is shown in Fig. 7.1. Figure 7.1 (a) shows the plot of the Seebeck coefficient (*S*) versus temperature measured in the range of 300-523K. The negative value of the Seebeck coefficient indicates that the as-prepared Bi₂Se₃ nanostructures are n-type in nature. The graph shows that the Seebeck coefficient increases with temperature, attains a maximum value around 400K and decreases. Zou *et al* [11] has also reported a similar result for the Seebeck coefficient for n-type Bi₂Te₃ thin films, which show the maximum Seebeck coefficient value at about 530K. Further study is required to understand the relationship between the Seebeck coefficient and temperature. The result shows that the magnitude of S for BiSe-2 sample at room temperature (300K) is 1.15×10^{-4} V/K, which is about two times as much as that for the bulk Bi₂Se₃, 0.59×10^{-4} V/K, at room temperature [12]. The increase in the Seebeck coefficient arises from the quantum confinement of electrons

induced by nanostructures and is necessary for the enhancement of the thermoelectric efficiency. From the definition of ZT, the greater the magnitude of S, the larger is the ZT of the material.



Figure 7.1 Temperature dependence of thermoelectric properties of sample prepared in DMF at 200° C for 24 h (BiSe-2) a) Seebeck coefficient (S) versus temperature (T), b) power factor ($S^{2}\sigma$) vs. temperature (T), c) thermal conductivity (k) versus temperature (T), and d) figure of merit (ZT) versus temperature (T).

Recent work by Lin et al. [4] reports a room temperature Seebeck coefficient of 0.84×10^{-4} V/K of Bi₂Se₃ nanoplates obtained from decomposition of single source precursor. Figure 7.1(b) represents the temperature dependence of the power factor of BiSe-2 sample, which shows that the power factor $(S^2\sigma)$ increases with the temperature. The increase in the power factor with temperature can be attributed to the increase in the electrical conductivity with temperature as a result of the semiconducting nature of the Bi₂Se₃ nanostructures. The maximum value of the power factor is 15.2×10^{-5} Wm⁻¹K⁻² at 523K. The room temperature value of the power factor is 2.8×10^{-5} Wm⁻¹K⁻², which is comparable to the room temperature value of about 7×10^{-5} Wm⁻¹K⁻² of Bi₂Se₃ nanoplates [4]. The variation of thermal conductivity (κ) with temperature is shown in Fig. 7.1(c). The lowest value of the thermal conductivity, 0.751 Wm⁻¹K⁻¹, is recorded at room temperature, which is lower than that for the bulk Bi₂Se₃, 4 Wm⁻¹K⁻¹. The significant reduction of thermal conductivity of Bi₂Se₃ nanostructures results in the enhancement of ZT value. The reduction in the thermal conductivity of Bi₂Se₃ nanostructures is expected from the interface or boundary scattering of phonons in nanostructures. Figure 7.1(d) shows the plot of ZT of BiSe-2 versus temperature in the range of 300-523K, indicating nearly linear increase of ZT with the temperature in the given range. The maximum ZT value is 0.096 at 523K and the room temperature ZT value is 0.011. The thermoelectric measurement of the BiSe-2 sample reveals the promising thermoelectric property of the as-prepared Bi₂Se₃ nanostructures at room temperature but optimization of the synthesis condition is needed to further enhance its thermoelectric efficiency.

7.3.2 Thermoelectric property of Ca-doped Bi₈₅Sb₁₅ alloy

Thermoelectric properties of Bi-Sb alloy with different doping levels of calcium were measured from room temperature to 450 K. Figure 7.2 presents the temperature dependent thermoelectric properties of $Bi_{85}Sb_{15}Ca_x$ (*x*=0, 0.5, 2, and 5).



Figure 7.2 Temperature dependent thermoelectric properties of $Bi_{85}Sb_{15}Ca_x$, nanostructured bulk alloys, x=0(black), 0.5 (red), 2 (green), and 5(blue). a) Seebeck Coefficient (S), b) power factor $(S^2\sigma T)$, c) thermal conductivity (k), and d) figure of merit ZT.

Figure 7.2 (a) shows the plot of the Seebeck coefficient versus temperature. The negative value of the Seebeck coefficient indicates that undoped and calcium doped Bi-Sb alloy have n-type conductivity. For all samples, *S* increases with the decrease in temperature which is expected for the low temperature thermoelectric materials like Bi-Sb alloy. It is also evident from Fig. 7.2 (a) that the Seebeck coefficient is increasing with the doping level for most of the temperature range. The doping of Bi-Sb alloy with the more electropositive elements like calcium is expected to make Bi-Sb alloy less n-type and decrease the concentration and mobility of the charge carriers. The decrease in carrier concentration and the mobility leads to the increase in both the Seebeck coefficient and the electrical resistivity with the doping level of Ca that might affect the overall power factor. Hence, selecting the optimum doping level is very important for increasing the power factor.

Figure 7.2 (b) shows the temperature dependence of the power factor for the entire doping level of calcium. The highest power factor is obtained for the sample $Bi_{85}Sb_{15}Ca_2$ although the sample $Bi_{85}Sb_{15}Ca_5$ possessed the maximum Seebeck coefficient. This can be attributed to the much higher resistivity of $Bi_{85}Sb_{15}Ca_5$ sample compared to $Bi_{85}Sb_{15}Ca_2$ sample. The improved power factor for 2% doping level of calcium arises from the optimal combination of the electrical conductivity and the Seebeck coefficient resulted from optimized Ca-doping. As expected for low temperature TE materials, the power factor for all $Bi_{85}Sb_{15}Ca_x$ (x=0, 0.5, 2, and 5) samples decreases with the increasing temperature.

The variation of thermal conductivity (κ) with temperature is shown in Fig. 7.2(c) for all doping concentrations. The room temperature thermal conductivity for all samples is drastically lowered, about by 3 times, from that of a single crystal Bi-Sb alloy [13, 14]. The low value of the thermal conductivity can be attributed to the increasing phonon scattering at the interfaces of nanostructures and in the boundaries of Bi₈₅Sb₁₅Ca_x solid solution. The thermal conductivity of Ca-doped samples progressively decreases as compared to the undoped sample. Further decrease in the thermal conductivity for higher concentration doping is caused by the point scattering mechanism from additional Ca ions presented in the doped samples, which has also been seen in other reported doped samples [15]. As expected, 5% Ca-doping shows the maximum reduction in thermal conductivity.

Figure 7.2 (d) displays the temperature dependent thermoelectric figure-of-merit (*ZT*) for all doping concentration of calcium. There is a progressive increase in the thermoelectric figure-of-merit for 0.5% and 2% doping, which is due to the optimized power factor as revealed by power factor measurement in Fig. 7(b). In contrast, *ZT* decreases for 5% Ca doped sample. Even though the thermal conductivity of the sample with 5% Ca doping is the lowest among all the samples, its *ZT* is still the lowest which can be attributed to the additional point defect scattering from the additional Ca ions, which are responsible for lowering the mobility of the charge carriers and increasing the resistivity [16]. Hence, by optimizing the power factor and the thermal conductivity, 2% doping of calcium showed the enhanced thermoelectric efficiency with a room temperature *ZT* of ~0.39. The peak room temperature *ZT* value is still low in comparison

to previously reported *ZT* value (~0.5) for a single crystal Bi-Sb alloy [17]. However, the ball milling technique is cost effective and efficient process for scale-up production of $Bi_{100-x}Sb_x$ alloy with a decent *ZT* value and will open a new way in synthesizing $Bi_{100-x}Sb_x$ alloy for application in commercial TE devices. The present work only reports the TE property measurement for room temperature and higher temperature. The low temperature TE measurement is the future work of the project.

7.4 Conclusion

From the thermoelectric property measurement, a maximum *ZT* value of 0.096 was obtained at 523K and a *ZT* value of 0.011 was obtained at room temperature. The asprepared Bi₂Se₃ nanoflakes exhibit a higher Seebeck coefficient and a low thermal conductivity compared to the bulk counterpart at room temperature, which can be attributed to their nanoscale size. The improvement of the thermoelectric property indicates the promising aspect of the as-prepared Bi₂Se₃ nanoflakes as a good thermoelectric material at room temperature. Transport property measurement of all Cadoped samples showed that TE property was optimized for 2% doping of calcium with highest room temperature ZT ~0.39. The low temperature TE property measurement will be performed in future.

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CHAPTER 8: SUMMARY AND FUTURE RESEARCH

8.1 Summary of the dissertation research

This dissertation presents the study results of the synthesis and structural characterization of the nanostructured thermoelectric materials including Bi₂Se₃, PbTe, CoSb₃ skutterudites, and Bi-Sb alloy. It also presents the results of the thermoelectric properties of the nanostructured Bi₂Se₃ and Ca-doped Bi₈₅Sb₁₅ alloy. Two basic approaches have been employed in the present work: (i) synthesizing materials in the nanostructured form and (ii) investigating near PGEC materials such as skutterudites aimed increasing the ΤE efficiency. Various techniques including at hydrothermal/solvothermal method, ball milling and arc melting were used to synthesize the nanostructured materials. It was found that all the synthesis techniques yielded mostly fine and regular nanoparticles. A DC hot press technique was used to consolidate the nanoparticles to bulk nanocomposites for further measurement of transport properties. A variety of characterization tools were used to confirm the crystallinity and the phase purity of the nanostructured nanocomposite samples.

A highly crystalline semiconductor Bi₂Se₃ nanostructure was synthesized using hydrothermal synthesis technique at different synthesis conditions using DMF as a solvent. The surface morphology and crystal structure of the nanoflakes were analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The results show that the as- prepared samples are highly crystalline rhombohedral phase of Bi₂Se₃. The effect of temperature on the size of the Bi₂Se₃ nanoparticles was also investigated and found that the size of the nanoparticles increases with the synthesis temperature.

Undoped and indium doped PbTe nanomaterials were synthesized via solvothermal method. The doping of indium to the PbTe matrix was investigated by an X-ray diffraction (XRD) and a laser-induced breakdown spectroscopy (LIBS). XRD patterns of all indium doped samples did not show any peaks corresponding elemental indium, indicating that indium is likely doped to PbTe. The LIBS analysis confirmed the existence of indium in the In-doped PbTe samples. A first principle calculation was also conducted to study the doping mechanism of indium to the PbTe matrix. The formation energy of substitution of the samples with different In doping levels (1.5 at %, 3.12 at %) and 6.24 at %) was calculated and compared with calculated cohesive energy of single indium crystal. The calculation results suggest that it is almost impossible for In to substitute Pb at the doping levels of 3.12 at %, and 6.24 at %. However, at the doping level of 1.5 at %, it is highly favorable for In to substitute Pb. From the result of the Xray measurement, the LIBS analysis, and the first principle energy calculations, it can be concluded that at the level of 1.5 at % doping, indium is doped to the PbTe matrix with the substitution on Pb site.

Unfilled and Yb-filled CoSb₃ nanoparticles were successfully synthesized via a solvothermal route. The effect of the amounts of sodium borohydride (NaBH₄) as the reducing agent and the annealing conditions on the formation of highly pure phase CoSb₃ was investigated. The XRD patterns of undoped CoSb₃ samples prepared with different amounts of NaBH₄ and annealed at various temperatures for different duration were

analyzed. It was found that 0.8 g (22 mmol) of NaBH₄ along with annealing temperature of 500 °C and an annealing time of 5 h were needed to obtain the pure phase CoSb₃. The filling of ytterbium in CoSb₃ was investigated using the XRD and LIBS analyses. The absence of Yb peaks in the XRD pattern and the presence of multiple Yb emission lines in LIBS spectra of Yb-filled CoSb₃ samples confirmed the presence of ytterbium most likely in the voids of CoSb₃. The measurement of the thermoelectric property of the unfilled and Yb-filled CoSb₃ skutterudites is still underway.

Synthesis and characterization of Ca-doped Bi-Sb alloy were studied. Nanostructured Ca-doped Bi₈₅Sb₁₅ alloy was synthesized using first arc melting and then ball milling process and its structural characterization was carried out with X-ray diffraction analysis. It was found that the as-synthesized and hot pressed Ca-doped Bi₈₅Sb₁₅ alloys exhibit pure rhombohedral Bi-Sb phase.

Thermoelectric properties of Bi_2Se_3 and Ca-doped Bi-Sb alloy were studied. It was found that the thermal conductivity of Bi_2Se_3 sample prepared in dimethyl formamide (DMF) at 200°C for 24 h was lowered significantly compared to bulk Bi_2Se_3 . The decrease of the thermal conductivity can be attributed to the increased phonon scattering at the grain boundaries in the consolidated nanocomposite. The lowest value of the thermal conductivity, 0.751 Wm⁻¹K⁻¹, was recorded at room temperature which is lower than that of the bulk Bi_2Se_3 (4 Wm⁻¹K⁻¹). The room temperature Seebeck coefficient of Bi_2Se_3 sample was about 1.15×10^{-4} V/K which is about two times as much as that of the bulk Bi_2Se_3 (0.59×10⁻⁴ V/K) at room temperature. The increase in the Seebeck coefficient of Bi_2Se_3 nanostructures is likely due to the quantum confinement of the carriers in the nanostructures. The effect of doping of calcium (Ca) on the thermoelectric properties of the arc melted and then ball milled $Bi_{85}Sb_{15}$ nanostructures were investigated. Though the 5% Ca-doped sample showed the maximum Seebeck coefficient, the highest power factor was obtained for the 2% Ca-doped sample. A low power factor for the 5% Ca-doped sample is a result of the higher resistivity caused by the scattering of charge carriers by the additional Ca ions. The thermal conductivity of the Ca-doped Bi-Sb samples progressively decreases with increasing Ca content. It was found that 2% Ca-doped Bi-Sb alloy showed enhanced TE efficiency at room temperature by optimizing the power factor and reducing the thermal conductivity. A *ZT* of ~0.39 was obtained at room temperature for 2% Ca-doped sample. In order to make it commercially applicable, the low temperature TE property measurement is needed, which will be the future work for this project.

The hydrothermal/solvothermal method and the ball milling processes are the cost effective and efficient processes for scale-up production of above mentioned TE materials. The synthesis methods developed in this research may be applied for other types of TE nanomaterial synthesis and research.

8.2 Future research

Though significant progress has been made in the respective research areas reported in this dissertation, there is still a plenty of scope for the improvement. An increase in the Seebeck coefficient along with the decrease in the thermal conductivity has been reported for the nanostructured Bi_2Se_3 sample. However, the *ZT* value of the sample is still low with maximum *ZT* of 0.096 at 523 K and room temperature *ZT* of

0.011. The low value of ZT is likely caused by the high resistivity of the sample resulted from impurities in the final products. The low density of the consolidated nanocomposite used for transport property measurement also leads to low ZT value. Difficulty to sinter the powders to highly dense composites is one of the drawbacks of the solvothermally synthesized nanomaterials. The optimization of the synthesis process and the consolidation conditions are needed to obtain the high density nanocomposites. The doping of PbTe with other group III elements such as thallium, gallium, and aluminum can also be investigated to identify the best dopant to achieve the optimal TE efficiency. Similarly, other filler atoms like cerium, calcium may be used to fill the voids of CoSb₃ to compare with the ytterbium filling. Such a comparative study will enable us to choose the right filler atoms for increasing TE efficiency. Though an enhanced TE efficiency of 2% Ca-doped $Bi_{85}Sb_{15}$ was reported with room temperature ZT of ~0.39, it is still lower compared to previously reported ZT value (~ 0.5) for a single crystal Bi-Sb alloy. Hence, search for other doping elements such as thallium, aluminum, and indium along with the optimization of the sintering process will be the future direction in increasing ZT of Bi-Sb alloy. Since Bi-Sb alloy is a good material for the low temperature cooling, the low temperature TE property measurement on Bi-Sb alloy is also an interesting work.

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