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SILVER AND LEAD TELLURIDE BASED THERMOELECTRIC NANOSTRUCTURED MATERIALS

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Abstract

Lead telluride (PbTe) and its multi-phased alloy are well accepted as promising materials for high figure of merit (ZT) thermoelectric devices because of their high Seebeck coefficient, S , low thermal conductivity, k , and high electric conductivity, σ , in the temperature range 400-700 K. For further enhancement of the thermoelectric performance, reducing the dimension of the thermoelectric semiconductor has been reported as a successful strategy to further improve their thermoelectric property (ZT value) because of the quantum size effect and the enhancement of phonons interface scattering.

In this thesis, systematic work started from synthesis of single phased PbTe nanostructures. Both PbTe nanoparticles and nanowires were successfully synthesized using a simple solvothermal process. It was found that the structure, size and morphology can be tuned by synthetic parameters like temperature, synthesis time, surfactants, and solvents. The growth mechanism was proposed based on synthesis parameters investigation. The thermoelectric property measurements including electrical conductivity, Seebeck coefficient and thermal conductivity were carried out on thin film samples to confirm the improvement in Seebeck of p - type PbTe nanostructured materials. Meanwhile, the sign change of Seebeck coefficient (from '+' to '-') in the temperature range of 575~650 K was observed for PbTe nanostructure sample, which was not observed for bulk ingot. This unique phenomenon was mainly attributed to the extrinsic-to-intrinsic-semiconductor transition for PbTe nanocrystals due to the competing factors between quantum size effect increasing band gap and self-purification process decreasing their charge carrier concentration, which shifted the transition point of nanocrystals to lower range as comparing to that of bulk samples.

For comparison of the quantum confinement effect in thermoelectric characterization, an *n*-type thermoelectric material: Ag_2Te which is usually used as dopant in thermoelectric (TE) materials was studied. The Ag_2Te nanoparticles investigated were prepared with the same synthesis method as synthesizing PbTe nanoparticles. From thermoelectric property characterization, it was found that the 15-nm Ag_2Te nanoparticles exhibited a maximum ZT value of ~ 0.8 at $T=550$ K. It is 33% higher than that highest reported for bulk Ag_2Te . The increase of the ZT value was mainly attributed to the reduction of thermal conductivity, which is possibly related to the increase of phonon scattering in Ag_2Te nanostructure.

Due to the self-purification phenomena in nanostructured systems, adjusting carrier concentration for single phased nanomaterials is difficult. To further improve the thermoelectric performance of nanostructured PbTe , the PbTe based binary phased nanomaterials were investigated. The systematic experiments started from TE characterization of the binary phased $\text{PbTe-Ag}_2\text{Te}$ nanocomposites prepared by hot pressing. However, the thermoelectric properties of these nanocomposites did not exhibit improvement probably due to the non-coherent interfaces in the composites. Then two secondary phases: PtTe_2 (metallic phase) and Ag_2Te (semiconductor phase) were chosen to introduce into the nanostructure systems separately for study. The increased electrical conductivity was observed in PbTe-PtTe_2 binary phased nanoparticles due to the carrier concentration enhancement by adding the PtTe_2 phase. With the enhancement, the maximum power factor of PbTe-PtTe_2 binary phased nanoparticles was improved by more than two orders of magnitude as compared to that of pure PbTe particles. The promising results revealed the advantages of the multi-phased nanostructured materials in thermoelectric application. Therefore, a binary phased $\text{Ag}_2\text{Te/PbTe}$ core-shell nanoparticle prepared with a two-step approach was studied. Both electrical conductivity

and Seebeck coefficient were improved in these binary phased core-shelled nanoparticles due to the synergetic effects. A high ZT value was predicted based on preliminary thermoelectric characterization results. This indicated that the binary phased system can be a promising approach on the development of new types of highly efficient thermoelectric materials.

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Chapter 1 Introduction

1.1 Motivation

In recent years, energy crisis has become one of the most concerned issues to the whole world. Generating new power by recycling the waste heat that is totaled up to 70% of the total primary energy produced from transport tools, factories, or other similar sources will be extremely significant. With the ability of inter-convert between heat and electricity, thermoelectric materials offer one feasible approach to recycle energy. Thermoelectricity (abbreviated as *TE*) was discovered in 1821, and it has attracted lots of interest since then [1]. It refers to a class of phenomena, in which a temperature gradient creates an electric potential or an electric potential creates a temperature gradient. After about 100 years of efforts since TE was discovered, it was found that the effect can be applied to refrigeration and power generation in 1950's [2]. After that, thermoelectronics are used widely in refrigeration applications like portable refrigerators, beverage coolers, electronic component coolers, metal alloy sorting devices etc. However, for power generation, thermoelectric materials currently find only niche applications because of their limited efficiency. Therefore, the development of more efficient thermoelectric materials is designated as a priority research field [3].

Thermoelectric efficiency is quantified by the dimensionless parameter ZT , where $Z = S^2 \sigma / \kappa$, and S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the total thermal conductivity. Total thermal conductivity is often approximately described as $\kappa = \kappa_l + \kappa_e$, where κ_l is the heat conducted by phonons (lattice vibration) and κ_e is the heat conducted by mobile electrons [4]. Large values of ZT indicate high thermoelectric efficiency and require high S , high σ , and low κ . Since an increase in S normally implies a decrease in σ because of lower carrier concentration, and since an increase in σ implies an

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increase in the electronic contribution to κ as given by the Wiedemann-Franz law, it is very difficult for further enhancement of Z value in typical bulk thermoelectric materials [5]. The best commercial bulk thermoelectric material is the $\text{Bi}_{2(1-x)}\text{Sb}_{2x}\text{Te}_{3(1-y)}\text{Se}_{3y}$ family with room temperature $ZT \approx 1$ for $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ [6]. Recently, it was found that lowering the material structure's dimensionality offers one strategy to increase ZT value relative to that of bulk material. Independent measurements of the Seebeck coefficient, the electrical conductivity and the thermal conductivity, combined with theoretical analysis, indicate that the improved efficiency originates from phonon effects [7].

Lead telluride (PbTe) and PbTe based alloys are reported as one of the best TE materials in the temperature range between 650K and 800K [8]. The maximum ZT values of traditional PbTe bulk materials are reported as 0.8 for n-type and 0.6 for p-type [9]. In recent years, with the development of TE nanostructured materials, their thermoelectric performance has been significantly enhanced. The most popular system investigated for PbTe based high ZT value materials is $\text{AgPb}_m\text{SbTe}_{2+m}$ (lead antimony silver telluride: LAST) which belongs to inhomogeneous nanostructured materials. It is a solid solution of PbTe and AgSbTe_2 with excess Ag and Sb as nano inclusion to enhance the power factor and lower the thermal conductivity. The maximum ZT value of LAST can reach 1.7 at approximately 700 K [10]. After that, similar systems like $\text{AgPb}_m\text{Sn}_n\text{SbTe}_{2+m+n}$ (lead antimony silver tin telluride: LASTT) [11, 12], $\text{NaPb}_m\text{SbTe}_{2+m}$ (sodium antimony lead telluride: SALT) [13] were investigated and the reported $ZT > 1$. Beside, the binary phased PbTe-PbS prepared using spinodal decomposition which produced coherent nanoscale heterogeneities expressed maximum $ZT \approx 1.5$ at 642 K [14].

It is noted that the currently reported systems with high ZT value are most focusing on nanocomposites with nano-inclusions inhomogeneously dispersed in bulk matrix [9, 30]. And the nanocomposites are prepared with various methods such as solid state reaction,

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chemical synthesis, ball-milling [90], melt spinning [121], etc. In fact, the investigation on homogeneous nano-system still remains as a challenge due to the limitation of fabrication technology, such as the morphology and size controlling difficulties during synthesis. Solvothermal synthesis is one of the effective bottom-up methods to produce large scale nanomaterials with controllable homogeneity [8, 30, 90]. Therefore, the main effort of this work is to fabricate PbTe and PbTe based alloy nanostructures with solvothermal method for thermoelectric study.

1.2 Objective

The main objective of this project is to synthesize PbTe and PbTe based single-phased or binary-phased nanostructures using simple solvothermal processes to achieve high ZT value.

Systematic work will start from synthesis of single-phased PbTe nanostructures. PbTe nanoparticles and nanowires will be the main structures for study. In order to illustrate morphology control and growth mechanism, the synthesis parameters like temperature, synthesis time, surfactants, and solvents will be studied. And then the thermoelectric property measurements (electrical conductivity, Seebeck coefficient and thermal conductivity) will be carried out to demonstrate the advantages of nanostructures in TE materials and also to find out the problems of pure nanostructures.

Another thermoelectric material Ag_2Te nanostructure which is usually used as dopant in TE will also be investigated for comparison. Ag_2Te nanoparticles will be prepared with the same synthesis system as PbTe nanoparticles. The investigation of quantum confinement effect on TE performance is conducted for these single phased nanostructures.

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To further improve the thermoelectric performance to get high ZT value, the binary phased nanostructures fabrication will be investigated. The metallic phased $PtTe_2$ and semiconductor phase Ag_2Te will be introduced into the nanostructure separately for study. The phase homogeneity and structure morphology is controlled by synthesis temperature, surfactants and precursors ratio. The growth mechanism is also investigated. As electrical conductivity of pure $PbTe$ is low and doping in nanocrystals is not easy due to the self-purification phenomena, tuning the charge carrier concentration in the $PbTe$ nanostructure most probably rely on the secondary phase. Therefore, the two secondary phases chosen are highly electrical conductive. The thermoelectric performance is characterized according to different phase composition.

1.3 Organization of the Thesis

The thesis contains six chapters.

In Chapter 1, the motivation and objectives of this work, as well as the outline of the thesis are depicted.

In Chapter 2, the basic theories of thermoelectric materials are briefly introduced. In addition, the new generation high ZT thermoelectric materials are summarized based on literatures. And then, an introduction to $PbTe$ and $PbTe$ based thermoelectric alloys is included with the recent work have been reported for high ZT achievement. Finally, the fabrication and property enhancement of multi-phased thermoelectric nanomaterials are introduced.

Chapter 3 presents synthesis of $PbTe$ single phased nanostructures including nanoparticles, nanocubes and nanowires with different solvothermal processes. The growth mechanisms are proposed based on the synthesis parameters investigation. The

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preliminary thermoelectric properties of these nanostructures are characterized. After that, further investigation of the sign change of seebeck coefficients for pure PbTe nanostructures phenomenon are reported in detail. The physical mechanism is proposed.

Chapter 4 presents the synthesis of single phased Ag_2Te nanoparticles with oil-based solvothermal process. The synthesis parameters which control both particle size and shape are analyzed. The enhanced ZT value is reported based on thermoelectric properties characterization.

In Chapter 5, Ag_2Te based binary phased nanocomposites are obtained by hotpressing the blends of Ag_2Te nanoparticles and PbTe micro-powders. The thermoelectric properties of nanocomposites with different phase ratio are characterized and analyzed. The second part of this chapter presents the fabrication of PbTe- PtTe_2 based binary phased nanostructures using simple one-step solvothermal synthesis. The growth mechanism is proposed by analyzing the effects of synthesis parameter. The enhancement in power factor is observed due to introducing the secondary phase in each single nanoparticle. Finally, further investigation of the binary phased nanocrystals is conducted in the PbTe/ Ag_2Te system. The PbTe/ Ag_2Te core shell structures fabricated with two-step solvothermal method are discussed. The improvement of thermoelectric performance of these nanostructures is reported due to the synergetic effect.

Chapter 6 presents the conclusions as well as the recommendation for future development of the present topic.

Chapter 2 Literature review

In this chapter, a brief introduction to the physical effects of thermoelectric (TE) materials is given. Lead telluride, as one of the most promising TE materials used at intermediate temperature range, is highlighted. The recent technology of lead telluride and lead telluride based nanostructure synthesis for improving their thermopower will also be reviewed.

2.1 Thermoelectric (TE) review

2.1.1 Seebeck and Peltier effects

Thermoelectric materials have been extensively studied and developed. These materials were first discovered by Thomas Seebeck in the early 1800s [1]. He found that if a closed loop was formed by connecting a bismuth bar with a copper wire, the north end of the magnetic needle in the middle of the loop would turn a few degrees towards east when the bottom of the bismuth bar was heated, and the needle turned towards west if the bismuth bar was replaced with an antimony bar (see Figure 2-1 as illustration). The reason he recognized is that the temperature difference between the top and the bottom Bi-Cu junctions, which leads to a voltage difference (ΔV) between the two junctions and produces a current in the loop. And ΔV is directly proportional to the temperature difference across the two junctions, $K_h - K_c$, and ΔV is not affected by the temperature distribution along the materials between the junctions. The factor of proportionality, S , is called the Seebeck coefficient, or thermoelectric power, or just simplified as thermopower, of the bi-metallic couple[15]. In general, the Seebeck coefficient varies with the levels of the temperature where the temperature difference occurs. The Seebeck coefficient is very low for pure metals (only a few $\mu V/K$) but much larger for semiconductors (typically

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several hundred $\mu V/K$) [16] as the absolute value of the seebeck coefficient is affected by band structure. A few years later, a related effect—the Peltier effect, was discovered by Jean-Charles Peltier (a French physicist) in 1834. Peltier showed that when an electrical current passes through the junction of two dissimilar materials, heat is either absorbed or rejected at the junction, depending on the direction of the current.

Figure 2-1 Illustrate of Seebeck effect

$$\Delta V = S \cdot (K_h - K_c) \tag{2.1}$$

The Peltier effect describes the fact that when the carriers flow through a conductor, beside charge, they also carry heat. The heat current Q is proportional to the charge current I and

$$Q = \Pi_{AB} I = (\Pi_B - \Pi_A) I \tag{2.2}$$

Where Π is the Peltier coefficient and Π_{AB} represents the coefficient of entire thermocouple. Π_A and Π_B are the coefficients of each material, respectively. N-type silicon typically has a negative Peltier coefficient, and p-type silicon is typically positive [17]. The Peltier effect is a result of the change in the entropy of the electrical charge carriers as they cross a junction. It is not an electromotive force (emf) despite the fact that Π_{AB} can be expressed in energy units involving volts. Both the Peltier effect and the Seebeck effect are unrelated to the contact potential [4].

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A typical thermoelectric cooler based on the Peltier effect is shown in Figure 2-2(a). P-type and n-type semiconductor elements are interconnected on the cold and the hot sides. In a Peltier cooler, the external D.C. power will be supplied, which drives electrons in the n-type element move opposite to the direction of current and holes in the p-type element move in the direction of current with carrying heat, thereby cooling the top surface of the device.

Energy conversion based on the Seebeck effect for power generation is shown in Figure 2-2(b). Just opposite to the thermoelectric cooler, a thermoelectric generator uses heat flow across a temperature gradient to power an electric load through the external circuit. The temperature difference initiates the voltage difference ($V=S\Delta T$) from the Seebeck effect as the heat flow creating a current through the circuit.

Figure 2-2(c) shows a practical device, which contains many thermoelectric couples consisting of p-type (containing free holes) and n-type (containing free electrons) thermoelectric elements which are wired electrically in series and thermally in parallel. In both devices, the heat rejected must be removed through a heat sink.

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Figure 2-2 Illustration of the thermoelectric devices (a) cooler [18], (b) power generator [19], (c) practical device (d) image of typical thermoelectric device with multiple stages. [20, 21]

2.1.2 Figure-of-Merit

The potential, based on the efficiency, of thermoelectric material is measured by the dimensionless Figure-of-Merit, Z [22]:

$$ZT = \frac{TS^2\sigma}{\kappa} \tag{2.3}$$

Where T is the temperature in Kelvin (usually equal to $(T_2 + T_1) / 2$ for device), σ is the electrical conductivity, κ is the total thermal conductivity, and S is the Seebeck coefficient or thermopower (conventionally in $\mu\text{V/K}$). Values of $ZT=1$ are considered good, and values of at least the 3–4 range are considered to be essential for thermoelectric to compete with mechanical generation and refrigeration in efficiency. In order to maximize ZT , large values for the Seebeck coefficient and electrical conductivity, and low value of the thermal conductivity are necessary.

All the three parameters (S , σ and κ) can be defined as functions of the carrier concentration (n) [9].

σ : The electrical conductivity is relative to n through the carrier mobility μ :

$$\sigma = ne\mu \tag{2.4}$$

S : The Seebeck coefficient of p- type semiconductor can be expressed by n as [23]

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$$\alpha_P = \frac{k_B}{e} \left(\frac{3}{2} + \frac{E_F - E_v}{k_B T} \right) \quad 2.5$$

where,

$$\frac{E_F - E_v}{k_B T} = -\ln \frac{n \cdot h^3}{2(2\pi m^* k_B T)^{\frac{3}{2}}} \quad 2.6$$

For an n- type semiconductor, the Seebeck coefficient is [23]

$$\alpha_N = -\frac{k_B}{e} \left(\frac{3}{2} + \frac{E_c - E_F}{k_B T} \right) \quad 2.7$$

where,

$$\frac{E_c - E_F}{k_B T} = -\ln \frac{n \cdot h^3}{2(2\pi m^* k_B T)^{\frac{3}{2}}} \quad 2.8$$

where, n is the carrier concentration and m^* is the effective mass of the carrier, k_B is the Boltzmann constant, $E_F - E_v$ is the difference between the Fermi level and the valence band, and the $E_c - E_F$ is the difference between the conduction band and the Fermi level. In general, the Seebeck coefficient increases with increasing effective mass m^* of the carrier, and decreasing with increases carrier concentration. The effective mass m^* is determined by the structure of the semiconductor.

κ : The total thermal conductivity contribution comes from two sources: (1) electrons and holes transpoting heat κ_e and (2) phonons travelling through lattice κ_l [9]. The lattice contribution is nearly invariant with carrier concentration, and depends on the properties of the material lattice. The electrical contribution is relative to the electrical conductivity through the Wiedemann-Franz law, where L is the Lorenz number:

$$\kappa_e = LT\sigma \quad 2.9$$

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where σ will be affected by carrier concentration.

The variation of thermoelectric figure-of-merit ZT , Seebeck coefficient S , electrical conductivity σ , and total thermal conductivity κ values with changing the materials carrier concentration is shown by figure 2-3. In order to obtain a high ZT value, the ideal carrier concentration is between $10^{19}/\text{cm}^3$ and $10^{20}/\text{cm}^3$, which is mostly found in heavily-doped semiconductors.

Figure 2-3 Dependence of figure-of-merit ZT , Seebeck coefficient, electrical conductivity, and thermal conductivity on carrier concentration [24].

2.2 Thermoelectric materials

2.2.1 Traditional thermoelectric materials

Figure 2.4 [9] shows ZT as a function of temperature for bulk materials that have been developed over the last decade. Based on their thermoelectric ZT performance, different materials can be chosen for different applications. According to their application temperature, TE materials can be classified as low temperature, intermediate temperature and high temperature TE materials [25]. For near-room-temperature applications, such as refrigeration and waste heat recovery up to 200°C , Bi_2Te_3 alloys have been shown to

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possess the greatest ZT value for both p- and n- type thermoelectric system. For mid-temperature power generation (500-900K), materials based on group-IV telluride are typically used, such as PbTe and its similar compounds $\text{AgPb}_m\text{SbTe}_{2+m}$. For high temperature (>900K), thermoelectric generators have typically used silicon-germanium alloys for both n- and p-type legs. The ZT value of these materials is fairly low, particularly for the p-type materials, because of the relatively high lattice thermal conductivity of the diamond structure.

Figure 2-4 Non-dimensional figure-of-merit ZT as function of temperature for state of the art materials [9].

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2.2.2 New generation of thermoelectric materials

2.2.2.1 Low dimensional thermoelectric materials

During the last 40 years, the efficiency of thermoelectric devices has increased only marginally which is much less than alternate cooling and power generation techniques [26]. Recently, there has been a great interest in thermoelectric phenomena as both theoretical [27] and experimental [28] results of low dimensional structured materials such as quantum wells (2D) or quantum wires (1D) showed that the reduced dimensionality offers a strategy for further increasing ZT and enables much more efficient thermoelectric devices.

According to the definition of figure of merit, high ZT value achievement requires high power factor and low thermal conductivity. To gain high power factor, both high electrical conductivity and thermopower (Seebeck) are needed. However, in bulk materials system, these two parameters are co-related and both depend on carrier concentration, which means that increasing one of these parameters always goes with dragging down the other one. Then the greatest challenge to further improve the power factor is to make high electrical conductivity and large thermopower separate and coexist in one compound.

Thermopower can be described with Boltzmann transport theory and expressed in the Mott equation[29]

$$S = \frac{\pi^2}{3} \frac{k^2 T}{e} \left. \frac{d \ln \sigma(E)}{dE} \right|_{E=E_F} \quad 2.10$$

Where $\sigma(E)$ is the electronic conductivity which depends on the band filling or Fermi energy E_F . When we assume the electronic scattering does not relate to energy, the electrical conductivity is just proportional to the density of states (DOS). Then the

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variation of the DOS near the Fermi level is the key to affect thermopower. The structures with DOS rapidly increasing near E_F will result in larger thermopower (See Figure 2-5).

Figure 2-5 Hypothetical schematic plot of density of state (D.O.S.) with a) a large slope ($d\ln\sigma(E)/dE$) and (b) a small slope near E_F [30].

Reducing the dimensionality is an effective method for high ZT achievement because it offers a strategy for enhancing the density of states near E_F , and hence leads to an enhancement of the Seebeck coefficient [31]. In low dimensional material systems, especially when the system size approaches the nano-scale, it will induce significant difference in electronic density of state (See Figure 2-6) [32] and electrical transport properties such as effective mass, or electron distribution due to the quantum confinement effect. These physical properties changing offer an opportunity to vary thermopower, electrical conductivity and thermal conductivity independently.

Figure 2-6 Electronic density of states for (a) a bulk semiconductor (3D), (b) a quantum well (2D), (c) a quantum wire (1D), and (d) a quantum dot (0D) [32].

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In 1993, Hicks, L. D *et al* suggested that significant enhancement in ZT could indeed be attained for a good thermoelectric material when it is prepared as a 2D quantum well with a simple calculation of a quantum confined 2D electron gas [33]. They used Bi_2Te_3 system as the basic thermoelectric material for study, and the results showed substantial enhancement for 2D systems at small quantum well widths (shown in Figure 2-7), an even larger enhancement in ZT was predicted for Bi_2Te_3 when it is prepared as a 1D quantum wire.[27, 34]

Figure 2-7 Calculated dependence of ZT within the quantum well or quantum wire on the well or wire width for Bi_2Te_3 based material at the optimum doping level for transport in the highest-mobility direction. And the dots line indicates the ZT for bulk Bi_2Te_3 calculated using the corresponding 3D model for comparison [33].

Based on the theoretical modeling analysis, we can conclude that a good thermoelectric material in 3D might be accepted to achieve even higher ZT value with reducing dimensionality. However, the confinement lengths required for further improvement of ZT are quite small, which are 10~20 Å for Bi_2Te_3 . Therefore, to increase the size of quantum confinement, selecting thermoelectric materials with smaller effective masses is necessary.

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To further study the quantum confinement effect in low dimensional system, *M. S. Dresselhaus, et al* did modeling with bismuth nanowire as study object and calculated its bandgap energy as the function of its diameter. Analyzing from the electric energy band structure of nanowires in comparison with bulk, the quasi-1D electron movement is limited inside a cylindrical potential well, then the quantization of the transverse momentum makes energy level E_{ij} , which is occupied by electrons (and also holes), quantized, so that E_{ij} can be determined by [31]

$$E_{ij} = \frac{\hbar^2 k_x^2}{2m_x^*} + \frac{\hbar^2 \chi_{ij}^2}{2m_d^* r_0^2} \quad 2.11$$

where k_x stands for the momentum, m_x^* and m_d^* are the effective mass components of the electron (or hole) along the wire axis and in the plane perpendicular to the wire, respectively, $2\pi\hbar = h$ is Planck's constant, χ_{ij} are roots of the Bessel function $J_i(\chi_{ij}) = 0$ and r_0 is the radius of the wire. Figure 2-8 shows the calculated effective band gap E_{geff} of Bi nanowires in the function of the wire diameter with crystal orientations along the three primary crystallographic directions of the rhombohedral crystal structure of Bi. And it consists with the calculation of the critical diameter d_c based on value of effective mass for the semimetal to semiconductor transition of Bi [35]. Due to the quantum confinement effect, the Bi 1D nanosystem with the wire diameters $\leq 10 \text{ \AA}$ is expected to be good thermoelectric material.

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Figure 2-8 Wire diameter dependent band gap energy calculated between the lowest electron subband and the highest hole subband of Bi nanowires oriented along the three primary crystalline directions: a) binary b) trigonal and c) bisectrix [35].

Besides the power factor improvement induced by quantum confinement, the low-dimensional system also offers an opportunity to increase the boundary scattering of phonons at the barrier-well interfaces without a large increase in electron scattering at the interface, which will effectively reduce thermal conductivity. The total thermal conductivity can be expressed as $\kappa_{total} = \kappa_{lat} + \kappa_e$, where κ_{lat} and κ_e depend on phonon transport in the lattice and electron (or holes) transport, respectively. As κ_e is determined by Lorenz factor and carrier concentration which is correlated to electrical conductivity, reducing κ_{lat} is a better approach for ZT improvement.

According to the classical theory, a good approximation for the lattice thermal conductivity can be given as [30]:

$$\kappa_{lat} = \frac{1}{3} C_v l v_s \tag{2.12}$$

where C_v is the specific heat at constant volume, l is the phonon mean free path, and v_s is the average velocity of sound. For TE materials, their application temperatures are

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normally above the Debye temperature, thus, C_v approaches $3R$ (R is ideal gas constant) and κ_{lat} depends primarily on l which is associated with phonon scattering.

For bulk materials, one of the great ideas to decrease κ_{lat} is referred to the “phonon-glass/electron-crystal” (PGEC) concept proposed by *Slack et al* [36]. In a new family of advanced bulk material systems, PGEC refers to cages or tunnels in its crystal structure which the small metal guest atoms without bounding can reside in. These massive atoms can act as obstacles to perturb phonon and thermal energy transport. In recent years, the PGEC approach has attracted great attention, and has given rise to remarkable increase in ZT .

For low- dimensional nano-systems, phonon scattering will significantly increase when the size of the system approaches the mean free path of phonon. Meanwhile, the electrical conductivity will not be affected if the system size goes beyond the de Broglie wavelength of the electron. (Equation 2.13)

$$\lambda_i = \left(\frac{\hbar^2}{2m_i^* k_B T} \right)^{1/2} \quad 2.13$$

where λ_i is the de Broglie wavelength in the i - direction ($i = x,y,z$), $\hbar$ is the Planck’s constant, k_B is Boltzmann’s constant, T is the temperature, and m_i^* is the effective mass of an electron in the i - direction. Some notable value of the de Broglie wavelength are 12 Å for a free electron ($m^* = m_e$), 86 Å for Bi_2Te_3 ($m^* = 0.02 m_e$ in one direction), and 150 Å for Bi ($m^* = 0.0065 m_e$ in one direction) [26], which means the mean free path for electrons in most of the component is in the range of 1~10nm. For most of traditional thermoelectric materials, the phonon mean free path is in the range of 10-50nm. Therefore, we can conclude that 10-50nm is possibly the ideal size for low thermal conductivity achievement without lowering down its electrical property (see Figure 2-9).

Figure 2-9 Schematic graph indicated size influence to the phonon and electron transport

2.2.2.2 Complex thermoelectric materials

Increasing the system complexity is another approach for further enhancement of ZT value. It can be expected that compounds with complex structures and compositions have a good chance of possessing complex electronic structures. Then we can make an assumption of the electronic band structure for simple semiconductor and complex semiconductor system (see Figure 2-10).

Figure 2-10 Hypothetical electronic band structure with (a) a simple semiconductor component with single extremum and (b) a complex structure system with multiple extrema in the valence and conduction bands [30].

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As the maximum of figure of merit can be expressed as [30]

$$Z_{\max} \propto \gamma \frac{T^{\frac{3}{2}} \tau_z \sqrt{\frac{m_x m_y}{m_z}}}{\kappa_{lat}} e^{(r+\frac{1}{2})} \quad 2.14$$

where γ refers to the number of valleys in the conduction band for n-type materials or peaks in the valence band for p-type materials. When the two systems are doped in the same level E_F' , each band extremum, which is occupied by carriers (electrons or holes), contributes a certain thermopower and electrical conductivity and hence the total power factor is improved for the complex system b. Therefore, to achieve a large number of such valleys in the band structure could be an effective approach to increase ZT because the total power factor for the material derives from the summation of contributions from all extrema. However, this improvement allows only one type of carrier present in the system (electrons or holes) as the mixed carrier systems may lower down its Seebeck coefficient because of cancellation of thermal currents, ($S=S_n+S_p$).

From the above discussion, a few important parameters need to be considered when we do material systems selection and design, including the band-gap (E_g), the shape and width of the bands structure near the Fermi level (E_F), even the carrier effective mass and mobility. In figure 2-11 [30], the temperature dependent ZT values of the new generated thermoelectric materials have been investigated. The nanostructure inclusion and the complexity increasing are the main focusing directions which can enhance their thermoelectric performance.

Figure 2-11 ZT performance of new generation thermoelectric materials [30]

2.3 Lead Telluride and Lead Telluride based thermoelectric materials

2.3.1 Introduction of PbTe

Lead telluride and lead telluride-based thermoelectric materials, like $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ (lead-tin-telluride), belong to a class of semiconductors represented by the general formula $\text{A}^{\text{IV}}\text{B}^{\text{VII}}$. Their physicochemical properties have much in common: they have the same type of chemical bond (ionic-covalent) and they are isomorphous (cubic sodium chloride-type lattice, Figure 2-12).

Figure 2-12 Cubic crystal structure of PbTe

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Lead telluride has a congruent melting point in the lead telluride-rich zone of the phase diagram (923 or 924°C). The composition at this point is 50.012% of tellurium. Below the melting point, lead telluride exhibits a homogeneous range of composition extending from the tellurium-rich to the lead-rich region and having its maximum width around 780°C (from 50.012 % of tellurium to 49.994 % of tellurium). The lead-tellurium system forms an eutectic at 85.5 % of tellurium and a melting point of 405°C [37].

2.3.2 Thermoelectric property of PbTe

The electrical and thermoelectric properties are dependent on the carrier concentration and temperature. With doping elements, the carrier concentration of normal p-type materials can be increased from 3.5×10^{17} to $1.5 \times 10^{20} \text{ cm}^{-3}$ calculated from Hall measurement [4]. This behavior is attributed to the presence of a second valance band, separated from the first by about 0.1 eV. An analysis of the experimental temperature dependence of the Hall coefficient gives the following value for the energy gap between the valence bands:

$$E = 0.17 - 4 \times 10^{-4} T \text{ eV} \quad 2.15$$

Consequently, the edges of the two valence bands are at approximately the same level at 425 K. At temperatures higher than 425 K, the main contribution to the transport properties is the heavy hole band and the energy gap between the edges of the conduction and heavy hole bands remains constant. Therefore, for p-type lead telluride, the Hall coefficient reaches a maximum at 425 K and the carrier concentration variation will influence the maximum value but not the peak temperature point.

2.3.3 Recent work for pure PbTe nanomaterials

One dimensional (1D) structures, e.g., nanowires (NWs), attract a lot of interests recently because they are suitable for building device circuits, and then allows the study of thermal and electrical properties of individual nanostructure. The current work for PbTe-based nanowires fabrication mostly use electrochemical deposition into hard templates [38, 39], which gives polycrystalline products and requires a tedious process to remove the hard template for further device integration. Chemical vapor deposition has also been applied in fabricating PbTe nanowires, however the diameter of the nanowires (100-200nm) is beyond the size at which quantum confinement takes place. By solution-based soft-templating approaches, the reported results mostly yield spherical or cubic nanoparticles [40-43], possibly because of the cubic crystal structure favoring isotropic growth. In a successful attempt, PbTe nanorods are synthesized with Te nanotubes as the template. The nanorods are 75-100 nm in diameter with unreacted Te as the second phase [44].

For 0-dimensional nanostructures, the fabrication of PbTe quantum dots has been reported many times using a high-temperature solution phase synthesis (HTSPS) which is a promising method for developing IV-VI lead chalcogenide quantum dots including PbS [45, 46], PbSe [21, 47, 48] and PbTe [41-43, 49]. The synthesis is conducted in oil phase system with oleic acid presence as the capping agent. The obtained quantum dots using this approach can be monodispersed in a non-polar solvent. And the particle size can be controlled in the range of 10~50 nm by varying synthesis parameters.

All the pure PbTe nanostructures including nanowire and nanoparticles discussed above show large enhancement in thermopower. However, the power factors obtained from these nanostructures are lower due to the substantially reduction of electrical conductivity.

2.3.4 Complex PbTe based thermoelectric materials (LAST family)

The first PbTe system reported for high ZT achievement is an inhomogeneous system: $\text{AgPb}_m\text{SbTe}_{2+m}$ (LAST-m: lead antimony silver telluride) [10]. The maximum ZT achieved is ≈ 2 in high temperature range 600-900K. The large enhancement in ZT is mainly contributed to the low thermal conductivity in this complex system. The Ag or Sb rich nano inclusions exhibit coherent or semicoherent interfaces with the matrix (see Figure 2-13) and effectively enhance phonon scattering, hence the total thermal conductivity decreases substantially. The preparation methods for LAST are listed as: solid state reaction which achieved $\text{ZT} > 1.0$ in the intermediate temperature range 600-800 K [50, 51], spark plasma sintering achieved a ZT value of 1.5 at 700 K [29] and solid state reaction with heat treatment which achieved $\text{ZT} \sim 2.2$ at 800K [10].

Figure 2-13 HRTEM images of the nano-inclusion shows (a) coherent, and (b) semicoherent with matrix [30]

After that, some similar system were investigated including $\text{AgPb}_m\text{Sn}_n\text{SbTe}_{2+m+n}$ solid solution (LASTT) which is p-type semiconductor and the maximum ZT obtained is 1.4 at 700K. For n-type semiconductor, the sodium-substituted system $\text{NaPb}_m\text{SbTe}_{2+m}$ (SALT-m: sodium antimony lead telluride) was discovered with high ZT value ~ 1.6 at 675K. Beside the nano-inclusion effect, the SALT system is found to exhibit complex electronic

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band structure because of the Na^+ doping which holds the promise for further improvement of power factor.

2.3.5 Binary phased PbTe nanomaterials

In most thermoelectric materials design, doping is the major part for adjusting the charge carrier concentration. However, there have been few successful reports to date for doping in nano system. As in nano-systems, a hypothesis named ‘self-purification’ phenomena intrinsically exists and limits the introduction of impurities into nanocrystals [52]. Recent theoretical and experimental works show that ‘self-purification’ mechanisms are energetically favorable compared with dopant incorporation, particular for small nanocrystals [53]. Therefore, there is a need for alternative approaches to nanocrystal doping using the nanostructures themselves as dopants in a multiphase nanocrystalline structure.

Multiphased structures in nano scale provide access to unique combinations of stoichiometry and symmetry which are not available in single-phase bulk solids. The binary superlattice structures composed by ordered co-crystallization of nanoparticles enable close contact of nanocrystals and show distinct physical properties, which will provide an approach to ‘metamaterials’ design and exhibit novel chemical or physical properties [54]. The synergetic effect offers an opportunity to further enhance thermoelectric property of these systems. The electronic measurement of multiphase nanocrystal solids composed of PbTe and Ag_2Te supperlattice structure is shown in figure 2-14a, demonstrating synergistic effects leading to enhanced p-type conductivity (Figure 2-14b) [55].

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Figure 2-14 (a) TEM image of PbTe/Ag₂Te supper-lattice arrangement, (b) dependence of conductivity on composition ratio of PbTe to Ag₂Te [55]

Chapter 3 Single phase PbTe nanostructures synthesis and thermoelectric characterization

As discussed in the literature review chapter, reducing the dimensions of the thermoelectric semiconductor is a key point to gain further enhancements in ZT, because of the quantum size effect and the enhanced interface scattering of phonons. In this chapter, two PbTe nanostructures (nanoparticles and nanowires) synthesized using solvothermal method will be discussed.

3.1 Synthesis and thermoelectric characterization of PbTe nanoparticles and nanocubes by an oil based solvothermal method

3.1.1 Introduction

Mono-dispersed PbTe nano particles synthesized using solvothermal approach has been reported in many papers [41-43, 49]. Their good uniformity and morphology controllability provide possibility for large amounts of fabrication. Thin film device can be easily achieved using these nanoparticles through self-assembly. However, the organic capping impurity layers or bonds are very difficult to be removed completely which may cause errors during property measurements. In this part, an oil phased, solvent based, solvothermal synthesis approach for fabricating PbTe nanostructures including nanocubes and nano- cuboctahedral structures will be discussed. Preliminary thermoelectric characterization on these nanostructures will be reported for analysis.

3. Single phase PbTe nanostructures

3.1.2 Materials and Experimental Method

Materials: Lead (II) oxide (99.9+%, PbO), oleic acid (OA, technical grade 90%), trioctylphosphine (TOP, technical grade 90%) and 1-octadecene (ODE, tech. 90%) were obtained from Sigma-Aldrich. N-hexane (99%) and hydrazine monohydrate (98+ %) were obtained from Alfa Aesar. All chemicals were used without further purification.

Synthesis: The trioctylphosphine-telluride solution (1M, TOP-Te) was prepared in advance by dissolving 1.27 g of tellurium powder into 10 mL of TOP with moderate stirring at 50 °C temperature. In a typical synthesis, 223mg PbO (1mmol), 1ml oleic acid and 5ml ODE were loaded into a 100ml three-neck flask. The solution was stirred at 120 °C for 30 min under Ar protection to form lead oleate. After that, the temperature of the solution was raised to 170 °C and 1ml as-prepared TOP-Te was injected into the flask. The reaction happens upon injection and was stopped within 2 minutes. The black precipitates were washed with ethanol and dispersed in hexane.

Sample characterization: The synthesized samples were characterized using various characterization methods to verify both structure morphologies and their thermoelectric properties.

Materials and structure characterization: The as-prepared samples were drop-casted onto $1 \times 1 \text{ cm}^2$ silicon substrates for XRD (X-ray Diffraction), FESEM (Field Emission Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray) measurements and onto carbon coated 200 mesh Cu grids for TEM (Transmission Electron Microscopy), and HRTEM (High Resolution Transmission Electron Microscopy).

Phase analysis was performed through XRD, which was obtained using Shimadzu 6000 diffractometer. Monochromatic CuK_α radiation with wavelength (λ) of 1.5406Å was used under $V = 50 \text{ kV}$ and $I = 50 \text{ mA}$. The XRD data were collected over the 2θ range of

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20°~60° at the scanning speed of 1 °/min with the step kept at 0.02 °. The determination of the peak position and peak heights, as well as the phase analysis of the collected XRD raw data was done by using the Match and Topas software.

The size and morphology of the nanostructures were characterized using a FESEM (JEOL JSM7600F) operated at $V = 5$ kV. EDX element analysis was carried out using TEM (JOEL 2100F) to determine the sample composition.

The lattice information and diffraction pattern were obtained using TEM (JEOL JSM2100F) operating at 200 kV. The TEM specimens were prepared by drop-coating the NPs dispersed in ethanol onto carbon-coated copper grid. The TEM specimens were then dried in ambient for 8 hours.

Thermoelectric properties characterization: The as-prepared samples in hexane were centrifuged out and re-dispersed into the $N_2H_4 \cdot H_2O$: ethanol = 1:4 mixture to remove the capping surfactants. After 1 hour, the precipitates were again centrifuged out and dispersed into the $N_2H_4 \cdot H_2O$: ethanol = 1:8 mixture. The solution was then used for film preparation onto glass substrate by using an air brush spray system. Then, the samples were annealed at 400 °C under 95%Ar + 5% hydrogen gas environment for half an hour. The thickness of the film was measured using a surface profile scanning system (Alpha-step IQ Surface Profile).

The Seebeck coefficient and electrical conductivity were determined by a standard four probe method using ULVAC ZEM-3 at pre-selected temperature range of 300 - 673K in a He atmosphere. The ΔT was set as 10K, 15K and 20K intervals.

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3.1.3 Materials and structure study

Figure 3-1 Powder XRD pattern for PbTe Nps and ingots for comparison

The x-ray diffraction patterns (see Figure 1h) show that the synthesized precipitates using this solvothermal method are PbTe (JCPDF 038-1435) and there are no detectable impurity phases in the as-prepared samples. The large peak widths as compared to the ingot samples indicate that the size of the obtained products is quite small.

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Figure 3-2 (a) SEM and (b) TEM (d) HRTEM images of PbTe Nps obtained with reaction temperature of 170 °C (c) TEM images of PbTe nanocubes obtained at 190°C.

The TEM images (see Figure 3-2a) reveal that the morphology of the black precipitates obtained from the solvothermal synthesis is uniformly distributed. The particles' shapes are either cuboctahedral or cubic and the particle size can be controlled in the range of 5~20 nm (see Figure 3-2b-d) by varying synthesis temperature and reaction time. The high resolution TEM image (see Figure 3-2d) shows that the growth of the nanocubes is along the $\langle 100 \rangle$ direction, as the distance between lattice fringes is 0.32nm which is the inter-planar distance of PbTe $\{200\}$ facet. The HRTEM image also reveals that all nanoparticles are single crystals which are consistent with the XRD results.

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3.1.4 Synthesis parameter effects

Reaction temperature and time: As shown in Fig 3-2, the uniformly cuboctahedral nanoparticles formed with injection temperature below 180 °C. The morphology changed to PbTe nanocubes if the injection temperature exceeded 190 °C as the reaction temperature affected the particles growth mechanism. For inorganic component growth, facets normally tend to form on low-index planes for surface energy minimization. Therefore, during PbTe particles growth, {200} facet is more favorable. As the molecules motion was enhanced by higher temperature (e.g. 200 °C), the particles grew along $\langle 100 \rangle$ direction to minimize their surface energy [41, 49]. It is in good agreement with Wuff construction theory.

The longer reaction time resulted in larger particles. The cuboctahedral particles size will reach 50-100 nm when the reaction time is extended to an hour. However, for nanocubes growth, the higher reaction temperature induced faster growth rate. Cubes lager than 50nm were observed in samples with reaction taken for 5min at 190 °C (see Figure 3-3).

Figure 3-3 TEM images of PbTe nanocubes with reaction taken for (a) less than 10seconds (b) 5min at 190 °C

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Surfactants: During the synthesis process, oleic acid acts as both stabilizer and indirect reaction precursor react with PbO to form lead oleate in the first stage. If we change the PbO to lead acetate, the amount of oleic acid will affect the particle size. Figure 3-4 shows that with the same reaction temperature and time, the larger the amount of oleic acid used, the larger particles are obtained. It is due to the different reaction kinetics of lead acetate and lead oleate. Lead oleate is more stable in organic solvent hence the reaction is slower compared with lead acetate [49]. Increasing the oleic acid amount will promote more lead oleate in the first stage, and decreases the nucleation rate. Then the larger amount of Pb and Te precursors used will be consumed on particles growth instead of nuclei formation and leads to larger particles formation [49, 56]. Oppositely, if the oleic acid concentration is lower, the more reactive lead acetate precursor leads to a lot of nuclei formation in short time, and then much smaller particles are obtained, as much less Pb and Te precursor feedstock left for nucleus growth. Size control of oleic acid can not be observed in PbTe quantum dots synthesis with PbO as Pb precursor [41, 43, 56]. This phenomenon confirms above discussion.

Figure 3-4 TEM images of PbTe NPs synthesized with lead acetate at 180 °C for 2min with (a) $I_{\text{oleic/Pb}} = 1$ (b) $I_{\text{oleic/Pb}} = 3$ where $I_{\text{oleic/Pb}}$ indicates molar ratio of oleic acid and Pb precursor.

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3.1.5 Thermoelectric properties characterization

The thermoelectric property measurements were conducted on ZEM-3 (see fig 3-5) for thin film samples was PbTe NPs sprayed on glass slide followed by high temperature annealing.

Figure 3-5 Demonstration of prepared thin film sample and ZEM-3 measurement

Measurements of the Seebeck coefficient, S of NPs films with different particle size were conducted in the temperature range 315-470 K (Figure 3-6). When increasing the temperature, the electrical resistivity tends to be lower. This is a typical semiconductor behavior as higher temperature excites more electrons or holes as effective charge carriers. The larger particles provide better electrical conductivity. The resistivity decreases to $\sim 10^{-2}$ from $\sim 10^{-1} \Omega \text{ m}$ as the particle size increases to 20nm from 5nm. This is probably due to the reduction of interface scattering as smaller particles have larger surface area. Smaller particles also led larger amount of organic capping trapped in measuring samples which may block the charge carrier movement and lower its electrical conductivity. The highest electrical conductivity of the PbTe nanostructure is $\sim 71.6 \Omega^{-1} \text{ m}^{-1}$, which is extremely low compared to bulk PbTe reported [8-10]. The main reason for the low electric conductivity is their low charge carrier concentration, $\sim 3 \times 10^{17} \text{ cm}^{-3}$ measured on the thin film samples using an Accent HL5500 Hall system. For thermoelectric materials, the optimized charger carrier concentration is around $10^{19} \sim 10^{21} \text{ cm}^{-3}$ and doping with a light element is normally used to achieve that concentration. Therefore, for the pure PbTe

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without doping, their electrical conductivities are much lower. In addition, the un-optimized network connection between the NPs in the measurement sample also affects the electrical conductivity. However, it can be recovered with the low thermal conductivity contributed by un-optimized connection.

It is noted that there is not much difference in both electrical resistivity and Seebeck measurement results for samples made by cuboctahedral structure or cubic structure NPs in same size. The SEM images (Figure 3-6) show that the particle edges have merged together after annealing process due to the sintering effect, which means the particle's original shape has been lost. Therefore, it will not affect properties.

Figure 3-6 Temperature dependence of (a) electrical resistivity (b) seebeck coefficient, and (c) power factor of PbTe NPs of 5nm, 15nm and 20nm. (d) SEM image of PbTe nanoparticles after annealing

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The positive Seebeck coefficient (see Figure 3-6b) indicates that the NPs are p-type semiconductors. The maximum Seebeck $\sim 475 \mu\text{V/K}$ at $T = 370\text{K}$ was measured on sample made by 5nm NPs, and it is $\sim 80\%$ higher than that of bulk PbTe reported ($265 \mu\text{V/K}$) [57]. The enhancement of Seebeck is possibly due to the quantum confinement of the nanostructures, which is able to effectively improve density of energy states (DOS) which has been discussed in Chapter 2. The seebeck values achieve $>470 \mu\text{V/K}$ for all samples with different particle sizes because all the sizes are smaller than 46nm, which is excitonic Bohr radius of PbTe [58]. However, different particle sizes did not create trend for Seebeck measurement. The high seebeck coefficient may also be due to their low charge carrier concentration [9] which will be discussed in detail in the next chapter.

Finally, the power factor, P , was calculated based on the S and ρ results obtained (see Figure 3-6c). The thin film sample fabricated with 20nm nanocubes exhibits the highest power factor. The maximum power factor of $\sim 15 \mu\text{W/K}^2$ at $T = 450\text{K}$ is much lower than bulk PbTe reported [8, 57, 59, 60], which is mainly due to the low electrical conductivity. Therefore, for nanostructures, the enhancement in their electrical property is the key for better performance.

3.1.6 Concluding remarks

The PbTe NPs with different structures cuboctahedral or cubic were successfully synthesized using an oil based solvothermal approach. The particles size can be controlled in the range of 5-50nm by varying the synthesis parameters (e.g. temperature, reaction time, etc.). The NPs were sprayed into thin film for thermoelectric property characterization. High Seebeck up to $475 \mu\text{V/K}$ was achieved due to quantum confinement. However, extremely low electrical conductivities were measured because of

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their low charger carrier concentration and un-optimized sample network connection. Therefore, electrical conductivity enhancement of these nanostructures is the main challenge for improving the thermoelectric property of current nanostructures.

3.2 *Synthesis and thermoelectric characterization of PbTe nanowires by simple solvothermal method*

3.2.1 Introduction

One dimensional (1D) nanowires have attracted more attention as they are potential to be used in many applications like field-effect transistors [61-63], light-emitting diodes [64], photo-detectors [65], solar cells [66], ultrahigh-density memory and logic devices [67] or thermoelectric devices [68, 69]. In addition, NWs are suitable for building device circuits, which can be studied for thermal and electrical properties of individual nanostructures through contact formation. Several fabrication techniques have been developed for fabricating PbTe nanowires including electrical chemical deposition [59, 70], hydrothermal synthesis, chemical vapor deposition, etc. In this work, a simple chemical synthesis approach for PbTe nanowire fabrication will be reported, and their thermoelectric properties characterization will be conducted and analyzed.

3.2.2 Materials and Experimental Method

Materials: 1, 5-Pentanediol (97%), lead acetate trihydrate (99+%), $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, orthotelluric acid (99.99%, H_6TeO_6), trioctylphosphine oxide (99%, TOPO), sucrose, hydrazine monohydrate, were obtained from Aldrich and used without further purification.

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Synthesis: In a typical synthesis, 23 mg orthotelluric acid (0.1 mmol) and 114 mg lead acetate trihydrate were dissolved into 3 mL pentanediol in two separate vials at $T = 160\text{ }^{\circ}\text{C}$ in ambient, respectively. In a separate three-neck round flask, 160 mg sucrose were added into 20 mL pentanediol and heated to $190\text{ }^{\circ}\text{C}$ for 5 minutes under Ar flow. The orthotelluric acid and lead acetate trihydrate in pentanediol solution were then mixed and quickly injected into three-neck round flask under moderate magnetic stirring. Upon injection, black precipitates were observed immediately. The reaction was stopped after 30 seconds by quenching the round flask in an ice water bath. The black precipitates were cleaned by repeated washing with ethanol and centrifuging. The NWs were then dispersed in ethanol and stored in N_2 gas environment, which were used for characterization.

Both structure and thermoelectric properties characterization of the PbTe NWs obtained were conducted with the same procedure as PbTe NPs in part 3.1.

3.2.3 Phase analysis

Figure 3-7 shows the XRD patterns of PbTe NWs synthesized at various temperatures ($165\text{ }^{\circ}\text{C}$, $180\text{ }^{\circ}\text{C}$ and $240\text{ }^{\circ}\text{C}$). At $165\text{ }^{\circ}\text{C}$, beside PbTe (JCPDF 38-1435), Te (JCPDF 36-1452) as the secondary phase was also detected. By further increasing the reaction temperature to $180\text{ }^{\circ}\text{C}$ or $240\text{ }^{\circ}\text{C}$, only PbTe phase can be detected in the XRD results, which indicates that the precipitation of Te takes place at lower temperature than that of Pb. Based on our experimental results, the critical point to form pure PbTe is $180\text{ }^{\circ}\text{C}$.

Energy-dispersive X-ray (Figure 3-8) analysis of the sample prepared at $180\text{ }^{\circ}\text{C}$ revealed that the Pb:Te molar ratio is close to 50:50, which can be modified by varying the precursor ratio.

Figure 3-7 Powder XRD pattern for PbTe NWs synthesized with different temperatures.

Figure 3-8 EDX analysis of as-prepared PbTe NWs at 180 °C.

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3.2.4 Morphology characterization

Scanning electron microscopy (SEM) image in Figure 3-9a shows the PbTe nanowires obtained from samples prepared at 180 °C and quenched after 90 s. The nanowires are straight (see Figure 3-9b and d) and have uniform lengths spanning 2-3 μm . The width of the nanowires has a narrow distribution in the range of 20-30 nm. By further increasing the reaction temperature (e.g. 210 °C) or decreasing the reaction time (e.g. 30s), shorter and smaller nanowires can be obtained (Figure 3-9 c and d). The size of the nanowires can be controlled in the range of 0.5-3 μm in length and 10-30nm in width. Phase contrast atomic resolution TEM (Figure 3-9e) and the selected area electron diffraction (SAED) (Figure 3-9d) pattern indicate that each nanowire is a single crystal. The long axis of the nanowires is along $\langle 111 \rangle$ direction analyzed from the HRTEM image in Figure 3-9e.

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Figure 3-9 (a) A SEM image of PbTe nanowires prepared at 180 °C. (b) Representative TEM images of a PbTe NW from the same batch as (a), (c) SEM image of PbTe NWs prepared at 210 °C. Representative (d) TEM (e) HRTEM images of a single NW from the same batch as (c), and inset in (d) is the corresponding SAED pattern.

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3.2.5 Effects of synthesis parameters (reaction temperature, reaction time, and surfactant template)

The size and morphology of the PbTe nanowires synthesized are sensitive to the reaction temperature, reaction time and surfactant templates.

Reaction temperature and time

As discussed in 3.2.4, the nanowires (Figure 3-9 a and b) with 2-3 μm in length and 20-25nm in width were synthesized at injection temperature of 180 °C. When precursors were injected into pentanediol at 210 °C and quenched after 30 seconds, the obtained nanowires were 10-16 nm in width and 400-600 nm in length (Figure 3-9 c-e). Higher injection temperature initiated higher seeding rate which may lead larger numbers of NWs produced with same precursor stock, hence smaller and shorter NWs were obtained. We note that the measured width is smaller than those reported to date [70], which hold promise for the good performance of thermoelectric devices. With increased temperature, the crystal size decreases, which can also be estimated from the width of the diffraction peaks in XRD patterns using Sherrer's equation [71] (see Figure 3-7).

In addition to the effect of reaction time on the size of the nanowires, the sample morphology was also affected. PbTe nanoparticles with large size distribution e.g. 10-50 nm were observed with the presence of PbTe nanowires when the reaction time was extended to 30 mins or 60 mins (Figure 3-10). This indicates that the 1D templating effect was lost after long time reaction, which is possibly due to the decomposition of sucrose under high temperature. We note that the solvent became dark brown color after reaction which reveals the existence of carbon from sucrose decomposition.

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Figure 3-10 SEM images of PbTe samples prepared at 180 °C with reaction a time of (a) 30 minutes and (b) 60 minutes

Surfactant template

PbTe nanowires can only be obtained when sucrose was used as the surfactants in the synthesis. Without sucrose, precipitation of PbTe under the same conditions led the formation of cubes with size of 100nm or larger (see Figure 3-11a). And if sucrose was replaced with trioctylphosphine oxide (TOPO), flower shaped nano-cluster forming from folded thin film (see Figure 3-11b) was observed from precipitates. The above phenomenon reveals that sucrose is the key to direct the 1D growth in this particular reaction. On the other side, without sucrose, the reaction temperature was raised to 230 °C for precipitate forming, which is much higher compared to the 190°C when sucrose is present in synthesis. This indicates that sucrose also acts as reducing agent as well as soft template to direct 1D growth.

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Figure 3-11 SEM images of (a) PbTe cubes precipitate in the synthesis without sucrose, (b) PbTe clusters formed in the synthesis by replacing sucrose by TOPO, inset (b) TEM image of PbTe cluster from the same batch as (b).

3.2.6 Structure forming mechanism

Based on the experimental observation, the growth mechanism (Scheme 3-1) was proposed. Due to the π - π electron interaction, the sucrose molecule form stacking templates. And the hydroxyl groups in the sucrose preferentially interact with only Pb atoms. When Pb was replaced with Pt, highly agglomerated and random-shaped PtTe crystals were precipitated (Figure 3-12a), which indicates the lack of effective interaction between sucrose and both elements of Te and Pt. Therefore, the precipitation sequence of Te and Pb is very important to control the growth morphology. During the process of gradually heating to grow PbTe, Te precipitates faster than Pb, because of the higher reduction potential of Te^{6+} as compared to that of Pb^{2+} . It was found that non-uniform shaped mixtures (Figure 3-12b) are formed due to the absence of passivation by sucrose during the initial Te nucleation stage. By injecting the precursors into the solvent at high temperature, precipitation of Pb is accelerated, which allows the effective interaction with

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sucrose to passivate the nanostructure and the translation of the template to direct the 1D structure growth.

Scheme 3-1 Proposed Growth Mechanism of the PbTe NWs

Figure 3-12 (a) TEM image of PtTe₂ agglomerated crystals synthesized at 180 °C, and (b) SEM images of the PbTe clusters formed by heating the precursors from room temperature gradually to 180 °C with a heating rate of 5 K/min.

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Figure 3-13 SEM images of the sprayed hydrazine treated PbTe NWs on glass substrates after annealing at 300 °C under gas forming environment for 30 minutes with (a) low magnification and (b) high magnification

3.2.7 Thermoelectric properties characterization

For the thermopower and electric resistivity measurement, the PbTe NWs were sprayed on the glass substrates to make uniform films. The films were annealed at 300 °C under Ar (95%) and H₂ (5%) forming gas protection to remove organic capping layer. The films are highly porous and the NWs are randomly aligned without noticeable coalescence, which can be observed from SEM images (Figure 3-13).

Measurement of the Seebeck coefficient, S , on the NW film was conducted in the temperature range of 315-475 K (Figure 3-14a). High seebeck coefficients of $> 470 \mu\text{V/K}$ at $T = 425\text{K}$ were measured, which is at same level compared with PbTe NPs and higher than that of bulk PbTe. Positive Seebeck values suggest a p-type semiconductor. Besides the quantum confinement effect of the NWs with diameter smaller than 20nm, the enhancement of the Seebeck effect is also possibly due to some other factors, e.g. phonon drag [7] which is caused by the increased scattering between phonons and charge carriers [60]. As the phonon mean free path in PbTe is estimated between 280~440nm [72] which

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is smaller than the length of PbTe NWs (1~3 μ m) obtained. Phonon drag results in both increased seebeck and electrical resistivity. The interface electron temperature gradient in the PbTe NWs network may also cause high Seebeck coefficient measured.

The resistivities of the annealed films are plotted versus temperatures (Figure 3-14b). It is noted that the variation of the film thickness contributes to the error (less than 10%) of the resistivity values. The resistivity of the NWs films is about 1 order lower than PbTe NPs. This is possibly due to reduction of electron scattering in 1D transporting and indicates the promise of PbTe nanowires for further thermoelectric property enhancement. We note that the resistivity of the NWs thin film is still 3-4 times higher than that of bulk PbTe due to un-optimized interconnection in the NW network (see Figure 3-13). However, the development of single wire device can be considered as one of the solutions. Further investigation is currently undergoing.

The power factor of NWs thin film is 5~6 times higher than that of PbTe NPs film which attributes to the enhancement of electrical conductivity. The maximum value of power factor is ~90 μ W/K² at T $\approx$ 430K.

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Figure 3-14 (a) Seebeck coefficients measured on the film sample of PbTe NW film in the temperature range of 315-525 K. (b) The corresponding resistivity of film sample at $T \sim 315\text{-}475$ K.

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3.2.8 Concluding remarks

In short conclusion, a simple solvothermal approach to synthesize PbTe NWs with tunable size has been demonstrated. Sucrose passivation is the key to induce the 1D growth of PbTe. The size and morphology of the NWs are affected by the reaction temperature, reaction time and type of surfactants used. Enhanced Seebeck coefficient has been observed, which is possibly due to the quantum confinement of small dimension nanowire or phonon drag effect. The resistivity of the nanowire has been decreased compared to PbTe NPs discussed in 3.1 due to the advantages of 1D transport of the electrons or holes. However, its electrical conductivity is still lower than that of bulk PbTe. Further improvement of electrical property is still under the working direction.

3.3 *Extrinsic-to-intrinsic transition and sign changes of Seebeck coefficients for PbTe nanocrystals*

3.3.1 Introduction

Enhanced Seebeck coefficients have been demonstrated in chapter 3 and also in several other nanocrystal systems, e.g. PbSe quantum dots [73], and PbTe nanowires [72, 74] and nanoparticles [75]. However, apart from increasing the Seebeck coefficient, quantum size effect on TE materials also gives rise to significantly varying the charge carrier concentration, n , [73, 75] mainly due to the increased band gap. Direct tuning of the charge carrier concentration in nanocrystal system is not easy [52, 55, 76], while the change of n can directly affect many aspects of TE semiconductors.

Herein, we will highlight an important potential issue regarding applications of nanocrystal in TE modules: the extrinsic-to-intrinsic transition temperature, at which the sign of the Seebeck coefficient may change from '+' to '-', falls into the operating

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temperature range. Thus, a designed p-type TE semiconductor component may perform as an n-type component at certain operating temperature range. This phenomenon has not been systematically reported for TE nanocrystals before, while it can definitely affect the proper performance of TE modules. In this work, our study is mainly focused on the PbTe system by comparing three types of samples, bulk ingots, nanowires (NWs) and nanoparticles (NPs). But the discussion is extendable to other TE semiconductors, which needs to be considered in designing and applications of TE devices using nanocrystals [77, 78].

3.3.2 Experimental section

3.3.2.1 Synthesis

Preparation of PbTe NWs and NPs: The PbTe nanoparticles and nanowires were synthesized with the same solvothermal approaches as reported in Chapter 3.

Preparation of PbTe ingots: Lead powders (2.07g) and tellurium shots (1.66 g) were mixed, and heated up to 950 °C for 12 h in a vacuum sealed quartz ampoule. The ampoule was quenched by immersing into water and the sample was polished to a standard shape for characterization.

3.3.2.2 Characterization

The phase and morphology characterization were conducted on PbTe NPs, NWs and ingot samples followed by the steps reported in section 3.1 and 3.2.

For characterization of thermoelectric properties, both as-prepared PbTe NWs and NPs were sprayed onto glass substrates as thin films after washing with hydrazine using air brush spray system. The thin films were then annealed at 350 °C for 40 min under Ar atmosphere. The Seebeck coefficients were measured on samples (films or ingots) using ULVAC ZEM-3 at pre-selected temperature range of 300–675 K. The effective charge

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carrier concentrations were investigated using an Accent HL5500 Hall system. Near-IR absorption spectroscopy was performed with a Hitachi U-3010 spectrophotometer.

3.3.3 Results and discussion

The SEM and TEM images (Figure 3-15a-b) reveal that the as-prepared PbTe NPs are nearly spherical in shape and have a narrow size distribution, e.g. 10~12 nm. The inter-particle spacing is around ~4 nm as indicated by the TEM image (Figure 3-15b), which is in good agreement with the length scale of oleic acid [79]. The as-prepared PbTe NWs by the polyol process have a moderate size distribution with width of 15-25 nm and length of 500-1200 nm (Figure 3-15c and d). The SEM image (Figure 3-15e) displays that the PbTe ingot is composed of large crystal grains with size of 100-500nm. EDX analysis shows that the molar ratios of Pb:Te ($X_{\text{Pb:Te}}$) are 50 : 50, 50 : 50, and 44 : 56 for NPs, NWs and ingots, respectively. It should be noted that $X_{\text{Pb:Te}}$ cannot be readily adjusted for NPs and NWs by varying the molar ratio of Pb:Te precursors during the synthesis similar to previously reported [74]. XRD patterns (Figure 3-16) show that there are no detectable impurity phases in the as-prepared PbTe samples. The crystal sizes estimated from the width of the XRD peaks using Scherrer Equation [80] are 10 nm for PbTe NPs and 15 nm for PbTe NWs, which are consistent with the TEM observations.

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Figure 3-15. SEM, and TEM images of as-prepared (a-b) PbTe NPs and (c-d) PbTe NWs. (e) A SEM image of the microstructure of the bulk PbTe ingot.

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Figure 3-16 Powder X-Ray Diffraction patterns of PbTe NPs, NWs and ingots

The thermoelectric characterization were carried out on PbTe ingots and films composed of PbTe NWs and NPs, which were sprayed onto glass substrates and annealed at 350 °C under Ar atmosphere. The electrical resistivities of the samples were investigated at different temperatures (Figure 3-17a) using the four probes in a commercially available ULVAC ZEM-3 system. PbTe ingots show the lowest electrical resistivity, e.g. 1.5×10^{-4} - $4.4 \times 10^{-4} \Omega\cdot\text{m}$, in the temperature range of 300-700 K, which is around 1~2 orders lower than that of PbTe NPs and NWs. The electrical resistivities of all three types of samples decrease at higher temperature, which is the typical trend for metals or heavily doped semiconductors.[81] The effective charge carrier concentration, n , investigated using an Accent HL5500 Hall system shows that all three samples are p-types, while n of NPs and NWs is about one order lower than that of the ingots (Table 3-1), which is consistent with their higher electrical resistivity (Figure 3-17a). Here, it is noted that we have intended to try to vary the charge carrier concentration in NPs and NWs by changing the ratio of Pb precursor to Te precursor during the synthesis, because

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it is reported that adjusting Pb:Te ratio can effectively tune the charge carrier concentration n of PbTe.[82] However, the resulting PbTe nanocrystals show no obvious change in the charge carrier concentration.

Figure 3-17 (a) Resistivity and (b) Seebeck coefficients as a function of temperature for PbTe NWs, NPs and bulk ingots.

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Sample	n (10^{17} cm^{-3})	Hall coefficient ($\text{cm}^3 \cdot \text{C}^{-1}$)	Room- temperature ρ ($\text{ohm} \cdot \text{cm}$)
PbTe NPs	3	20.81	2.43
PbTe NWs	5	12.48	0.69
PbTe Bulk Ingots	50	1.25	0.03

Table 3-1 Charge carrier concentration and resistivity of PbTe samples

The Hall measurement suggests that all three types of samples are p-type, possibly due to their slight Te rich composition [4] or the presence of extra oxygen in the samples, which is difficult to eliminate during synthesis [4]. The results correspond to positive Seebeck coefficients [83], as characterized in the ULVAC ZEM-3 system. Increasing the measurement temperature, the coefficients clearly undergoes a sign change from ‘+’ to ‘-’ for PbTe NPs (~575 K) and NWs (~650 K). No such changes are observed for the PbTe ingot within the measurement temperature range of 300~700 K. A similar transition phenomenon was reported for pure CoSb₃ [84], attributed to the variation of composition, e.g. Co:Sb ratio, at different measurement temperatures. Here, in PbTe samples, the high temperature did not cause obviously change of both morphologies (Figure 3-18a) and the composition ratio of Pb:Te. The composition ratio is still around 1:1 after high temperature measurement (see Figure 3-18c). The XRD pattern (Figure 3-18b) indicates that there is no secondary phase after measurement. In addition, the sign change of Seebeck coefficient can also be repeated for the same samples during temperature variation cycles. Therefore, we concluded that such a transition for PbTe nanocrystals is not closely related to the change of the sample after a high temperature measurement.

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Figure 3-18 (a) SEM image (b) XRD patterns of PbTe NWs after heat treatment under 400 °C, and (c) Energy-dispersive X-ray spectroscopy of PbTe NWs of as-prepared with composition ratio $X_{\text{Pb:Te}} = 49:51$ and after ZEM-3 measurement with $X_{\text{Pb:Te}} = 49.65:50.34$

Theoretically, the S can be expressed [85] as

$$S = \frac{S_h \sigma_h - S_e \sigma_e}{\sigma} = S_h - \frac{n_e \mu_e}{n_h \mu_h + n_e \mu_e} \left(\frac{E_g + 4k_B T}{eT} \right),$$

where S_p and S_n are Seebeck contribution of holes and electrons, respectively, and are directly related to the effective mass of the charge carrier, band gap and temperature; $\sigma = \sigma_h + \sigma_e$ is the electrical conductivity, σ_h and σ_e are hole conductivity and electron conductivity, respectively; n_h and n_e are electron concentration and hole concentration, respectively; μ_h and μ_e are hole's mobility and electron mobility, respectively; E_g is the band gap and k_B is Boltzmann constant. Thus, we attributed the observed sign change of the Seebeck coefficient to a crossover from extrinsic to intrinsic semiconductor for PbTe

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nanocrystals as the temperature is raised and more electrons are excited thermally from the highest full band to the lowest empty band, significantly altering S_n and S_p . The transition temperature from extrinsic to intrinsic semiconductor depends on both the external carrier concentration and activation energy of the intrinsic carriers. For PbTe bulk samples with proper charge carrier concentration [10, 86, 87], the transition points are normally well above the decomposition temperature. For nano-structured PbTe, such as NWs and NPs, the bandgap E_g increases due to the quantum effect, which is expected to increase the transition temperature and is opposite to our observation in Figure 3-17b. The quantum confinement effect in varied sized PbTe nanoparticles has been reported by other groups [42]. In our case, the broad peak in the near-IR absorption spectrum (see Figure 3-18) for nanoparticles indicates that the PbTe NPs used for the measurements have a moderate size distribution. Based on the peak position at around 2060 nm, the estimated band gap for PbTe NPs is ~ 0.6 eV as compared to the theoretical value of 0.23 eV for bulk PbTe [42, 49]. For PbTe NWs, we could not observe well-resolved absorption peaks, possibly due to their non-uniform size and intrinsic physical properties broadening the excitonic transition [88]. Besides the effect of increasing band gap happened in nanocrystals leading to the trend to increase the transition temperature, self-purification phenomenon [52, 55, 76] in nanocrystals makes external carrier doping very difficult hence the charge carrier concentration will be lower [73, 75] (see Table 3-1) and tend to decrease the transition temperature, which is more dominant as judged from the Seebeck results in Figure 3-17b and shift the transition temperature to a lower range, e.g. 550-650 K.

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Figure 3-18 Near-IR absorption spectrum of PbTe nanowires and nanoparticles sized in 8-13nm

On the other hand, for p-type materials, the Seebeck coefficient can be expressed as

$$S_p = \frac{k_B}{h} \left(\frac{3}{2} + \frac{E_F - E_V}{k_B T} \right)$$

where k_B is Boltzmann's constant, h is Planck's constant, T is temperature, E_F and E_V are energy level of Fermi level and valence band, respectively. This formula describes Seebeck as a function of temperature and its value depends on the energy difference of valence level and Fermi level. For nanocrystals, the band gap increased compared with bulk materials, which has been confirmed by IR absorption results. In addition, the lower doping concentration shifted the Fermi level towards the intrinsic Fermi level which is the center of the band gap, and then the difference between E_F and E_V was enlarged, hence the Seebeck of PbTe nanocrystals was 80% higher than that of bulk PbTe samples. The mechanism is described clearly using band structure in Scheme 3-2. With the Fermi level

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shifting closer to the intrinsic Fermi level, the excitation energy required for transition from extrinsic to intrinsic is lower. Therefore, the transition temperature decreases.

Scheme 3-2 Schematic configuration of band structures of bulk and nano materials

Here, it should be noted that this transition temperature range for nanostructured PbTe is in the operation temperature range for many thermoelectric module design using PbTe [9, 10, 30, 89] . Thus, we want to emphasize that the concept of enhancing the performance with low dimensionality [32, 91, 92] in thermoelectric materials needs more consideration. In the intrinsic stage, the Seebeck coefficient can be expressed as [85]

$$S = \frac{k_B}{e} \frac{(C-1)}{(C+1)} \left(\frac{E_g}{2k_B T} + 2 \right),$$
 where k_B and e are Boltzmann's constant and electron charge,

E_g is the band gap, and C is the ratio of the mobility of holes and electrons, $\mu_p : \mu_e$. Thus, the negative sign of Seebeck coefficient for PbTe nanocrystals in the intrinsic stage is mainly due to that of C being less than one or $\mu_p < \mu_e$, although the charge carrier concentrations of holes and electrons are comparable to each other at this temperature.

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To further examine the extrinsic to intrinsic transition of PbTe nanocrystals, field effect measurements were carried out on PbTe NW networks at the pre-selected temperature range of 300-675 K. The field effect devices were fabricated by drop casting the PbTe NWs onto SiO₂ (300 nm)/Si substrates with patterned Au electrodes. The PbTe NWs connecting the source and drain electrodes act as the conducting channel. The channel length (L) and width (W) are 150 and 75 μm , respectively, as illustrated in Scheme 3-3. The devices were annealed at 300 °C under Ar gas protection for 40 min to remove any possible remaining capping ligands and to enhance the electrode contacts. Figure 3-19a shows the typical source-drain current (I_{ds}) vs. voltage (V_{ds}) curves at different gate voltages (V_{g}) at room temperature. The linear shapes indicate typical ohmic contacts between the Au electrodes and PbTe NWs. The $I_{\text{ds}}-V_{\text{g}}$ responses of PbTe NWs at different temperatures were further investigated under a fixed drain voltage (Figure 3-19b-d). At room temperature, I_{ds} increases at decreased V_{g} that reveals a hole dominant behavior (see Figure 3-19b), which is attributed to the much higher hole concentration as compared to that of electrons. Increasing the measurement temperature to 625 K, the $I_{\text{ds}}-V_{\text{g}}$ curve reveals that both n-type and p-type charge carriers contribute effectively to the field effect transport, which indicates the transition stage of PbTe NWs [93]. Further increasing the measurement temperature to 675 K, we observed that I_{ds} shows a downward trend with increased V_{g} , revealing an electron dominating behavior possibly due to their much higher mobilities as compared to holes, which indicates the transition to intrinsic stage. The mobility estimated [94] from the $I_{\text{ds}}-V_{\text{g}}$ for PbTe NWs are 0.567 $\text{cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$ and 0.133 $\text{cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$ for electrons and holes, respectively. The higher electron mobility obtained from the field effect measurement is consistent with the negative Seebeck coefficients obtained in the intrinsic stage (Figure 3-17).

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Scheme 3-3 Schematic configuration of the PbTe NW-based field-effect transistor device.

Figure 3-19 (a) Source to drain current-voltage curves at various gate voltages at room temperature. (b-d) Drain current vs. gate voltage curves at (b) room temperature, (c) 625 K and (d) 675 K, respectively. The drain voltage is fixed at 5 V.

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3.4 Concluding remarks

In summary, nano-structured PbTe, e.g. NWs and NPs, shows the extrinsic to intrinsic transition in the temperature range of 575-650 K, possibly due to their low extrinsic charge carrier concentration, while this phenomenon is not observed for bulk PbTe ingots up to 700 K. Such transition can lead to the sign change of Seebeck coefficient and may affect the proper performance of TE modules in their operation temperature range. As the adjustment of charge carrier concentration is not easy in nanocrystals due to self-purification process, such phenomenon should be considered carefully during the design of TE devices using nano-structured semiconductors [32, 74] .

4. Ag_2Te nanoparticles with high figure-of-merit**Chapter 4 High figure of merit n -type Ag_2Te nanoparticles****synthesized using solvothermal process***Introduction*

Based on the property investigation of p-type PbTe nanostructures reported in Chapter 3, it was found that solution based synthesis process for PbTe had not been demonstrated successfully to prepare nanocrystals with much improved ZT values as compared to the bulk ones, while PbTe based nanocomposites prepared by solid state reaction have shown promising ZT values. The reason could be due to: (1) the usage of strong binding surfactants leading to the formation of insulating layer on the nanocrystal surface, (2) un-optimized integration process of the TE nanocrystals into modulus, (3) low charge carrier concentration in nanocrystals, which can not be adjusted by extrinsic doping due to the self-purification phenomenon.

In this Chapter, another nanostructured material, Ag_2Te , which is an n -type semiconductor, has been investigated. As pure Ag_2Te has higher electrical conductivity as compared to pure PbTe, the nanostructured Ag_2Te is expected to exhibit better thermoelectric performance. A simple solvothermal approach was demonstrated to prepare Ag_2Te nanoparticles with controllable uniform sizes, e.g. 5-10 nm. The size and shape of the Ag_2Te nanoparticles can be controlled by changing the reaction time and temperature. Although Ag_2Te is not directly used as TE materials [95, 96], it was demonstrated that such quantum dots prepared by the solvothermal process can exhibit more enhanced ZT values than the highest reported for bulk Ag_2Te . For example, the samples showed improved power factors ($\sim 4.77 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 570K) and low thermal conductivity ($0.31 \text{ W m}^{-1} \text{ K}^{-1}$). The obtained maximum ZT values are ~ 0.8 as compared to that of bulk Ag_2Te (e.g. ~ 0.4) prepared by solid state reaction [97].

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4.2 Synthesis and characterization procedure

Synthesis of Ag_2Te nanoparticles: In a typical synthesis, 170mg (1mmol) silver nitride (AgNO_3) was dissolved in 10 mL H_2O and then loaded into a 100ml flask containing 0.24 ml dodecanethiol (1mmol) and 10 ml toluene. The mixture was stirring for 1-2 h at room temperature for ligand attachment. After that, the stirring was stopped for a while and the clear aqueous phase was removed. 10 ml oleylamine was added into the organic phase which contained Ag precursor following by raising the temperature to 443K and maintained for 10 min for toluene evaporation. Next, 0.5 ml TOP-Te solution (1 M), prepared by dissolving tellurium shot (1.27 mg) into trioctylphosphine (10 mL), was rapidly injected into the flask. The black precipitates were observed upon injection, and the reaction was stopped within 2~10 min by quenching the flask in cold water. The black color precipitates obtained were washed by re-dispersed in hexane and centrifuge out with ethanol for several times.

The As-prepared samples were characterized using XRD, FESEM, TEM and EDS for morphology characterization.

For thermoelectric measurement, the as-prepared Ag_2Te nanoparticles were centrifuged out and re-dispersed into the mixture of hydrazine and ethanol with volume ratio ~1:5 and maintained for overnight to remove the capping surfactants. The precipitates were then washed with ethanol and dried in vacuum oven at 353 K. The collected powders were sent for hot pressing at 673 K for 30mins under vacuum with a uniaxial pressure of approximately 50MPa to form pellets. Both electrical resistivity and seebeck coefficient measurements were carried on the pellet samples using ULVAC ZEM-3 at pre-selected temperature range of 300–575 K. The thermal conductivities were measured under argon atmosphere using laser flash (NETZSCH LFA 447).

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4.3 Morphology and synthesis parameter study

Figure 4-1 (a) Assembly of densely packed Ag_2Te nanoparticles synthesized with at 463 K for 10 min. TEM images of Ag_2Te nanoparticles prepared at (b) 443 K for 2min, (c) 443 K for 10min and (d) 463 K for 10min. (e) HRTEM images of one Ag_2Te nanoparticle in the same batch as (c). (f) SAED pattern on the sample in (c).

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The Scanning electron microscopy (SEM) image shown in Figure 4-1a indicates that the self-assembled superlattice of Ag_2Te nanoparticles with uniform size ~ 15 nm was achieved by drop-casting. Transmission electron microscopy (TEM) image shown in Figure 4-1b reveals that mono-dispersed nanoparticles with an average size of ~ 15 nm were obtained by injecting the TOP-Te into oleylamine containing AgNO_3 at 463 K and stopping the reaction after 10 minutes by quenching in ice water. The high resolution (HR) TEM image (see Figure 4-1c) indicated that the nanoparticles are single crystalline. The energy-dispersive X-ray (EDX) analysis of the as-prepared nanoparticles indicated that the ratio of Ag:Te is 33: 67. The selected area electron diffraction (SAED) pattern (see Figure 4-1d) exhibited rings corresponding to the monoclinic Ag_2Te [space group: $P2_1/n$ (13)] (JCPDS 34-0142). The size of the nanoparticles can be tuned by changing the reaction temperature and time. For example, particles with an average size ~ 9 nm were obtained by injecting TOP-Te at 443 K and stop the reaction after 10 minutes (See Figure 4-1e) or ~ 5 nm particles were obtained by injecting TOP-Te at 443 K and stop the reaction after 2 minutes (See Figure 4-1f). The XRD patterns (see Figure 4-2) of nanoparticles prepared at different temperatures revealed that only Ag_2Te monoclinic phase was obtained, which was consistent with the HRTEM and SAED results. There was no detectable impurity phase. Here, it is worth to note that the phase transition temperature of Ag_2Te is 418 K [97]. The phase transition of Ag_2Te at 418 K is a reversible process. It is α - phase with cubic *fcc* structure (JCPDS 34-0142) at above 418 K and it is β -phase with monoclinic structure below 418 K. It is then interesting that the as-obtained Ag_2Te nanoparticles are β -phase although the synthesis temperature is >418 K, which indicates that the Ag_2Te nanoparticles can quickly convert from α - phase to β - phase during the cooling process.

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Figure 4-2 X-ray diffractogram of Ag₂Te nanoparticles prepared at different temperatures: 443 K and 463 K. A XRD pattern of pellet sample after annealing is also displayed.

The morphology of these Ag₂Te nanoparticles is also sensitive to the synthesis parameters. Decreasing the injecting temperature to 383 K, the obtained product was non-uniform-shaped sample composed of nanoparticles and nanoplates (see Figure 4-3a). The size of these mix-shaped nanostructures were much larger as compared to that prepared at T = 443~463 K. The larger sized Ag₂Te nanocrystals obtained in oleylamine indicates possible slower nucleation process [98]. The HRTEM images of the nanoplate taken from the primary surface and the side surface (e.g. by tilting the sample) are shown in Figure 4-3(b) and (c), respectively. The HRTEM image and SAED pattern in Figure 4-3(b) reveal that the nanoplate is single crystalline β -Ag₂Te with preferred exposure of (001) facets for the primary surfaces. The HRTEM image taken from the side surface of the plate (see Figure 4-3c) also indicates that the zone axis in the plate structure growth is along [001] direction. Therefore, the plate structures are mainly due to the confined growth of β -Ag₂Te within the (001) planes, which is possibly due to the preferred attachment of oleylamine onto the (001) facets. By comparing the two types of morphologies of the

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Ag_2Te nanocrystals obtained at $T > 418\text{ K}$ and $T < 418\text{ K}$, we conclude that the shape of the Ag_2Te nanocrystals is directly related to the crystal structure, e.g. cubic *fcc* α - phase corresponds to spherical particles and monoclinic β -phase (hexagonal-symmetry) leads to the possible growth of nanoplates. The oleyamine is also critical to induce the formation of plate-shaped Ag_2Te . If we replaced the oleyamine with toluene, injected TOP-Te at 383 K and stopped the reaction after 10 min, only spherical Ag_2Te particles with the size of 5~10 nm (see Figure 4-3d) were obtained. Such observation supports the assumption on the effect of oleyamine in controlled growth of nanoplates. The XRD patterns (see Figure 4-3e) confirm that all samples prepared at 383 K are $\beta\text{-Ag}_2\text{Te}$, which is consistent with the HRTEM and SAED measurements.

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Figure 4-3 (a) TEM and (b) HRTEM images of Ag_2Te nanoplates synthesized at 383 K with oleylamine (c) HRTEM image of the side surface of same nanoplate in (b) (d) Ag_2Te nanoparticles synthesized at 383 K with toluene (e) X-ray diffractogram of Ag_2Te nanoparticles prepared in different solvents: toluene and oleylamine at 383K

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The role of the dodecanethiol is also important during the synthesis of the Ag₂Te nanoparticles, which serves also as the surfactants to confine the particle growth. Without addition of the dodecanethiol, injecting the TOP-Te at 443 K and stopping the reaction after 10 minutes lead to the formation of large spherical particles with size > 500 nm (see Figure 4-4a and b). It is interesting to see that ordered hexagonal crystal facets well aligned on the surface of the particles, which corresponds to the β -Ag₂Te crystal structures as revealed by the XRD result (see Figure 4-2).

Figure 4-4 SEM images of Ag₂Te particles synthesized without dodecanethiol at 210 °C for 30s

4.4 *Thermoelectric property characterization*

To characterize their thermoelectric properties, the as-prepared Ag₂Te nanoparticles were dried and cold-pressed into pellets. The density of the pellet samples is ~6.5 g/cm³, which is ~ 80% of the theoretical density of bulk Ag₂Te. Figure 4-5a shows the electrical resistivity, ρ , of the pellets prepared from nanoparticles with two different sizes, e.g. 5 or 15 nm, as shown in Figure 4-1b and d, respectively. The highest electrical resistivity of pellets of 5-nm particles in the measurement temperature range is 11.35 mΩ.cm at 620 K,

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which is about 2-3 times higher than that of pellets of 15-nm particles. There is a big increase of ρ for both samples in the temperature range 370 to 420 K. This is expected to be closely related to the phase transition in such temperature range, which is confirmed by DSC measurements (see Figure 4-5b). The electrical conductivity of pellets of 15-nm particles is slightly lower than that of bulk Ag₂Te ingots prepared by solid state reaction.

Figure 4-5 Temperature dependent (a) Resistivities, and (b) DSC result

4. Ag_2Te nanoparticles with high figure-of-merit

The measured Seebeck coefficients, S , of both nanoparticle pellets in the temperature range 300-650 K (see Figure 4-6a) revealed n-type semiconductor behavior, e.g. with '-' sign. The maximum values of S were 147 $\mu\text{V/K}$ for pellets of 15-nm particles and 200 $\mu\text{V/K}$ for pellets of 5-nm particles at $T = 570\text{K}$. The maximum Seebeck coefficient of 5-nm particle pellets is $\sim 30\%$ higher than that highest reported for bulk Ag_2Te [99]. The higher Seebeck coefficients obtained for 5-nm Ag_2Te nanoparticles are possibly to be related to energy filtering process [100] as there are many interfaces in such pellets to scatter the low energy charge carriers. Other possibilities, e.g. quantum size effect [32, 74, 101], were also noted. Based on the measurements on Seebeck coefficients and electrical resistivities, the corresponding power factors ($S^2/\rho T$) were plotted and shown in Figure 4-6 (b). As compared to the bulk samples, the power factors of nanoparticles are lower due to their lower electrical conductivities. And it has been reported that the power factor may be possibly improved in more dense pellet samples [99]. For the Ag_2Te ingot, the power factor of α -phase is lower than that of β -phase. Therefore, the maximum power factor appears at $T = 350\text{K}$ (e.g. lower than the phase transition temperature $T = 418\text{K}$), which is consistent with the value reported. However, for Ag_2Te nanoparticles, the maximum power factor shifts to a high temperature range and the maximum value is $\sim 4.77 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at $T = 570\text{K}$ for 15-nm Ag_2Te nanoparticles.

4. Ag₂Te nanoparticles with high figure-of-merit

Figure 4-6 Temperature dependent (a) Seebeck coefficients and (b) power factor of pellet samples of Ag₂Te nanoparticles of ~5nm, ~15nm and bulk ingot.

The thermal conductivities, κ , of the pellets were measured by laser flash and displayed in Figure 4-7 (a). For the pellet of 15-nm nanoparticles, the lowest thermal conductivity is ~0.3 W/mK at 450K. It is well known that the total thermal conductivity κ_{total} can be expressed as $\kappa_{total} = \kappa_{lat} + \kappa_{el}$, where κ_{lat} is the lattice contribution and κ_{el} refers to the electrical contribution which can be calculated with Wiedemann–Franz–Lorenz relation [4]: $\kappa_{el} = L\sigma T$, where L is the Lorenz number, σ is the electrical conductivity, and

4. Ag₂Te nanoparticles with high figure-of-merit

T is the temperature. By subtracting κ_{el} , we calculated κ_{lat} and plotted in Figure 4-7 (a). The κ_{lat} for the 15-nm Ag₂Te nanoparticles is 0.6 Wm⁻¹ K⁻¹ at 300 K and 0.31 Wm⁻¹ K⁻¹ at T = 550 K. These values are significantly lower than that of Ag₂Te ingot, which is 1.18 Wm⁻¹ K⁻¹ at 300 K and 0.74 Wm⁻¹ K⁻¹ at 550 K. Here, the measured κ_{total} of Ag₂Te ingot is comparable to that previous reported [97]. The reduction of the total thermal conductivity of Ag₂Te nanoparticles is mainly due to the decrease of κ_{lat} , which is expected to be close related to the increased interface scattering of phonons in Ag₂Te nanoparticle pellets.

Figure 4-7 Temperature dependent (a) thermal conductivity and (b) figure of merit of Ag₂Te nanoparticles of ~5nm, ~15nm and bulk ingot

4. *Ag₂Te nanoparticles with high figure-of-merit*

The figures of merit, ZT , of Ag₂Te nanoparticles were calculated based on the measured values of ρ , S , and κ_{total} (See Figure 4-7b). The ZT value increases at higher temperature in the range of 300-550 K and its maximum value reaches ~ 0.8 at $T=550\text{K}$, which is 100 % higher than that of bulk Ag₂Te prepared by us and is 33% higher than than the highest reported value of bulk Ag₂Te [99].

4.5 *Concluding remarks*

In summary, a simple solvothermal approach to synthesize mono-dispersed Ag₂Te nanoparticles has been demonstrated with tunable size and shape. The particle morphology and size are sensitive to reaction temperature, time and types of surfactants. These nanoparticles are highly uniform and form supperlattice arrangements. When tested as thermoelectric materials, the 15-nm Ag₂Te nanoparticles showed a maximum ZT value of ~ 0.8 at $T=550\text{K}$, which is 33% higher than the highest reported value of bulk Ag₂Te. The increase of the ZT value is mainly due to the reduction of thermal conductivity, which is expected to be close related to the increased interface scattering of phonons in Ag₂Te nanoparticle pellets.

Chapter 5 PbTe based Binary phased nanostructures fabrication using chemical synthesis and their thermoelectric characterization

For a given TE material with controlled size and phase, an appropriate charge carrier concentration is required in order to achieve its optimum ZT values, to ensure a high power factor denoted as $S^2\sigma$. For example in PbSe quantum dot assembly, although enhanced Seebeck coefficients of $>1\text{mV}$ have been achieved [36], the low charge carrier concentration ($\sim 10^{17}\text{ cm}^{-3}$), especially in smaller quantum dots, leads to low σ values of $1\text{--}10\text{ V}^{-1}\text{ m}^{-1}$, and subsequently the desired high power factor cannot be attained. In addition, in our previous work in chapter 3, high Seebeck coefficients of above $500\text{ }\mu\text{V/K}$ have been established in both PbTe nanowire and nanoparticles films. But the electrical conductivities of $10^1\text{--}10^2\text{ V}^{-1}\text{ m}^{-1}$ are too low to achieve high power factor in the films.

Ideally, to achieve high ZT values, an optimized charge carrier concentration of above 10^{19} cm^{-3} is required [4]. Normally in bulk semiconductor materials system, the charge carrier concentration can be adjusted easily by doping some foreign elements. However, due to the self-purification phenomenon which usually occur in nanosystem, controlling the charge carrier concentration by doping are not easy in semiconductor nanocrystals [52, 53]. Therefore, an alternative approach which is multiphased nanocrystalline system offers a promising strategy to achieve tunable electrical properties of semiconductor nanocrystals. Recently, it has been demonstrated that the binary nanocrystal thin film which made of assemblies of p-type PbTe and p-type Ag_2Te shows higher electrical conductivity than that of either pure PbTe or pure Ag_2Te nanoparticles [55]. Although the absolute electrical conductivity values of the binary system is still relatively low, ($\sim 1\text{ V}^{-1}\text{ m}^{-1}$), it offers an attractive approach to control the charge carrier concentration in

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nanocrystal system. However, the self-assembly process to achieve the uniform distribution of the binary nanocrystals is not easy and may require lots of controlled deposition conditions, which is not suitable for the large scale production. Instead, the direct synthesis of uniformly mixed multi-phased nanoparticles will be a more attractive option, which can be easily casted into films or pellets by spraying or hot pressing processes for TE device integration. In addition, to improve the efficiency of thermoelectric devices, instead of achieving enhanced electrical conductivity as demonstrated in the PbTe/Ag₂Te nanocrystal assembly [55], it is more desirable to realize improvements in the power factor ($S^2\sigma$), which has yet to be demonstrated.

5.1 PbTe-Ag₂Te nanocomposite

For chapter 2, it has been reported that AgPb_mSbTe_{2+m} (LAST) alloy prepared by solid state reaction as a bulk sample has been reported to show very high ZT value ~2, which are attributed to the Ag-Sb-rich nano-phases embedded in a PbTe matrix [10]. It reveals that Ag can be an effective doping element to improve thermoelectric property of bulk PbTe. Therefore, as an initial attempt, we fabricated the PbTe-Ag₂Te nanocomposite by mixing Ag₂Te nanoparticles synthesized with the method described in chapter 4 with PbTe micro powders.

5.1.1 Materials and Experimental Method

5.1.1.1 Materials

N-type bulk PbTe (99.99%) was obtained from MOS Group and used without further purification. The Ag₂Te nanoparticles were synthesized using the solvothermal approach which has been discussed in chapter 4. Then the obtained particles were

5. PbTe based binary phased nanostructures

dispersed in hydrazine overnight for ligand removal and dried in vacuum oven after centrifugation.

5.1.1.2 Experimental procedure

The n-type PbTe raw material was grinded manually to micro size powder and filtered using the 40 μm pores sieve. The dried Ag_2Te quantum dots were then mixed with PbTe micro powders by horizontal ball milling for 12 hours. After that, the final composites were formed by hot pressing at 400°C for 30mins under vacuum with a uniaxial pressure of approximately 50MPa. The pellet samples with 13mm in diameter and 1~2mm in thickness were sent for thermal conductivity measurement directly using laser flash after preliminary polishing. The pellets were cut into rectangular block with mechanical cutter for electrical resistivity and Seebeck measurement using ZEM-3.

5.1.2 Thermoelectric characterization of the nanocomposites

The curves in Figure 5-1 show temperature dependence of the total thermal conductivity κ of the pellet samples through hot-pressing with different composition ratio. The total thermal conductivities of samples with 10% Ag_2Te nanoparticles and 50% Ag_2Te nanoparticles are significantly lower compared with that of bulk PbTe [102] as phonon scattering is possibly enhanced by introducing nano inclusion into the bulk system. The sample thermal conductivity decreases with increasing the nano inclusion amount. In addition, the sample densities are slightly decreased with same hot pressing parameter after adding nanoparticles into the system whose effect also need to be considered in thermal conductivity analysis.

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Figure 5-1 Temperature dependence of thermal conductivity of pellet samples of pure PbTe, Ag₂Te and PbTe-Ag₂Te nanocomposite different Ag₂Te amount

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Figure 5-2 Temperature dependence of (a) electrical resistivity (b) seebeck coefficient, and (c) power factor of samples of pure PbTe, Ag₂Te and PbTe-Ag₂Te nanocomposite different Ag₂Te amount

5. PbTe based binary phased nanostructures

The electrical resistivity (see Figure 5-2a) is observed to decrease with the amount of Ag₂Te nanoparticles at low temperature range (300-375K). Ag₂Te is a semi-metallic material which has lower band gap as compared to PbTe. However, after 400K, there is a suddenly increase of resistivity for samples containing Ag₂Te nanoparticles which refers to the phase transition of Ag₂Te at 418K. And with Ag₂Te changing to β -phase, the electrical resistivity increases by 1 order of magnitude. Therefore, there is no obvious improvement in electrical conductivity in the binary phased nanocomposite, especially in high temperature range.

The temperature dependences of Seebeck coefficient for all the samples are shown in Figure 5-2b. The results indicate that the total thermopower of the composite decreases by adding Ag₂Te as the second phase which has lower Seebeck coefficient as compared with PbTe.

The calculated power factors of these Ag₂Te samples shown in Figure 5-2c indicate that the maximum point of composite with 10% Ag₂Te has shift to higher temperature (700K) as compared with the peak point of bulk PbTe (580K) which may lead to higher *ZT* value. However, as there is no significant enhancement in either electrical conductivities or thermopower for the composites, the value of power factors calculated based on these two parameters do not exhibit improvement after introducing the second phase. It means that there is no synergetic effect of the dual phases in our nanocomposite samples and it is possibly due to the incoherent interface formation of the two phases in simple hot press processing. Another reason which may affect the sample properties is the homogeneity of the composite. The optical images of the composite surface after polishing are shown in Figure 5-3. The white area is PbTe and grey area is Ag₂Te as PbTe is lighter. The Ag₂Te quantum dots that were used are of very small dimension, which have very high surface energy and are easily agglomerated. The horizontal ball milling

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was not able to uniformly distribute the Ag_2Te phase into the PbTe matrix, which possibly minimized the effects of the nanophase.

Figure 5-3 Optical images for the PbTe- Ag_2Te nanocomposites of (a) 10% Ag_2Te , and (b) 50% Ag_2Te

Figure 5-4 Temperature dependence of thermoelectric figure of merit of samples of pure PbTe, Ag_2Te and PbTe- Ag_2Te nanocomposite different Ag_2Te amount.

The figures of merit (ZT) calculated from the above datas for pure PbTe, Ag_2Te and PbTe- Ag_2Te nanocomposite samples are shown in Figure 5-4. Due to the thermal conductivity measurement equipment limitation, only low temperature ZT values were obtained. In the low temperature range, the PbTe- Ag_2Te nanocomposites exhibit low ZT

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no matter how we changed the composition ratios. And the all the ZT values shown in Figure 5-4 are under 0.5 which is low comparing with most of reported values.

5.1.3 Concluding remarks

Based on the previous results which have been discussed in chapter 4, the binary phased PbTe-Ag₂Te nanocomposite were prepared by hot pressing the mixture of PbTe micro powder and Ag₂Te quantum dots. However, the thermoelectric properties of these nanocomposites did not exhibit improvement as the interfaces of the two phases are non-coherent which can not generate synergetic effect of binary phased system. And the inhomogeneous distribution of the Ag₂Te quantum dots also minimized their quantum effect. The maximum ZT calculated from the measurement of the composite were lower than 0.1 at low temperature range.

5.2 *Synthesis of PbTe/PtTe₂ binary phased nanoparticles for power factor enhancement*

5.2.1 Introduction

From the study reported in 5.1, we found that the coherent interface of different phases plays an important role in synergetic effect generation. Then the binary phased nanostructure directly synthesized from solvothermal process can be an effective approach as there will be some chemical bonding between the two phases during the nanostructure growth. In addition, the system uniformity can be maximized when the two phase co-exist in one single nanostructure.

In this first binary-phased nanostructure material study, we demonstrate the synthesis of PbTe-PtTe₂ binary phased nanoparticles, and each single particle is composed of both

5. PbTe based binary phased nanostructures

PbTe and PtTe₂ phases. PtTe₂ was selected to combine with PbTe, due to its highly conductive property and proper Fermi level position [103]. PtTe₂ provide electrons for PbTe to make an n-type highly doped semiconductor. It was found that such binary-phased nanocrystals material possesses an enhancement of Seebeck coefficient compared to bulk PbTe. In addition, the ratio of PbTe: PtTe₂ is adjustable. Then it allows the optimization of the charge carrier concentration in the range of $10^5 \sim 10^6 \text{ V}^{-1}\text{m}^{-1}$ for the electrical property improvement. The molar ratio of these two phases can be tuned by varying the precursor ratio. As the Fermi level of PtTe₂ has been reported overlap with the valence band of PbTe [45, 47], the injection of charge carriers will be effective from the PtTe₂ phase to PbTe phase in the nanocrystal system. With varying the composition ratio, particle size can be controlled in the range of 40–100 nm. Each nanoparticle consists of PbTe and PtTe₂ small grains with size about 4–12 nm. The crystal grain size is much smaller than the Bohr exciton radius (~46 nm) of PbTe [10], and it will incur the quantum confinement effectively. Additional advantage of this dual phase nanomaterial is substantial increase in phonon scattering inherent to nanocrystalline materials with high interface density [104, 105].

5.2.2 Materials and Experimental Method

5.2.2.1 Materials

1, 5-Pentanediol (97%), lead acetate trihydrate (99+%, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$), platinum (II) acetylacetonate (97%, $\text{Pt}(\text{acac})_2$), orthotelluric acid (99.99%, H_6TeO_6), sodium tellurite (99%, Na_2TeO_3), trioctylphosphine oxide (99%, TOPO), 1,4 phenylenediamine (97%), L-ascorbic acid (99%, $\text{C}_6\text{H}_8\text{O}_6$), sucrose, hydrazine monohydrate, were obtained from Aldrich and used without further purification.

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5.2.2.2 Synthesis of PbTe-PtTe₂ dual phase NPs

PbTe-PtTe₂ nanoparticles were synthesized by co-precipitation of the two constituent phases in 1, 5-pentanediol in presence of surfactants (TOPO and 1, 4 phenylene diamine) and reducing agent (sucrose and L-ascorbic acid). The phase ratio between PbTe and PtTe₂ is controlled by tuning the molar ratio of the precursors, e.g. Pb(CH₃COO)₂·3H₂O : Pt(acac)₂. For a typical synthesis of nanoparticles with PbTe : PtTe₂ = 1 : 1, 25mg lead acetate trihydrate, 35mg platinum acetylacetonate, 15 mg orthotelluric acid, 50mg sucrose (100mg L-ascorbic acid and 100mg phenylene diamine) and 50 mg TOPO were dissolved into 20ml pentanediol in a three-neck round flask at temperature below 80 °C with continuous stirring under Ar flow. After 5 minutes, the temperature was increased to 180 °C to reflux pentandiol for 10 minutes. The mixture was then cooled down to room temperature in ambient for purifying the precipitates by repeated washing with ethanol and centrifuging. After that, the NPs were dispersed in ethanol and stored in desiccators.

The materials and properties were characterized with the same method as that reported in chapter 3.

5.2.3 Phase analysis

Figure 5-5 shows the powder XRD patterns of pure single phase NPs and dual phase NPs synthesized using different ratios of precursors. And the patterns reveal that NPs with molar ratio of PtTe₂ (JCPDF 99-100-9905): PbTe (JCPDF 99-100-9485) = 0.5, 1 and 2 can be successfully obtained by adjusting the precursors ratio. The average grain size (D) calculated from the pattern is around 12-14 nm for PbTe and 5-10nm for PtTe₂ using Scherrer's Equation:

$$D = 0.89 \lambda / (\beta \cos \theta)$$

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where $\lambda = 1.5406 \text{ \AA}$ (Cu $K\alpha$) and β is full width at half maximum (FWHM) at the diffraction angle of θ .

Energy-dispersive X-ray (Figure 5-6) analysis of the sample prepared with different molar ratio of precursors reveals the NPs synthesized with $X_{\text{PtTe}_2} = 0.5, 1$ and 2 . According to the element analysis results, tellurium element was short in the sample which may enhance the n-type charge carrier concentration and improve the sample electrical conductivity.

Figure 5-5 Powder XRD patterns of PbTe-PtTe₂ NPs with different molar ratio synthesized at 180 °C

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Figure 5-6 EDX analysis of NPs of (a) $X_{PtTe_2}=0.5$ (b) $X_{PtTe_2}=1$ (c) $X_{PtTe_2}=2$

5.2.4 Morphology characterization

SEM image in Figure 5-7(a) and (b) reveals the nanoparticles synthesized at 180 °C with $X_{PtTe_2}=1$. The particles are uniform in size which are around 50-60nm in diameter. The HRTEM image (Figure 5-7c) indicates the PbTe and PtTe₂ dual phase existence in one single nanoparticle. Therefore, this is not a single crystalline nanoparticle, and each particle is composed of small grains of both PbTe and PtTe₂. The grain size revealed in the HRTEM image is around 5-10nm for PtTe₂ and 10-15nm for PbTe which are consistent with XRD results.

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Figure 5-7 (a) A SEM image of PbTe-PtTe₂ NPs with $X_{\text{PtTe}_2} = 1$. Representative (b) TEM and (c) HRTEM images of PbTe-PtTe₂ NPs in the same batch as (a), (d) TEM image of PbTe-PtTe₂ NPs with $X_{\text{PtTe}_2} = 0.5$. Inset in (c) is the corresponding SAED pattern.

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Figure 5-8 EDX line scan analysis of PbTe-PtTe₂ NPs with X_{PtTe₂} = 1

The line scan EDX analysis (Figure 5-8) reveals that both Pb and Pt elements are distributed in the whole particle, but more Pt atoms exist at the center of the particle (Figure 5-8 particle b), and more Pb atoms distributed at the particle edges (Figure 5-8 particle c). Based on this observation, the nanoparticles structure is similar as a core-shell structure, which the PtTe₂ is encircled by PbTe.

5.2.5 Effects of synthesis parameters

Both of the morphology and grain size of the PbTe-PtTe₂ NPs depend on the reaction temperature, reaction time, effect of Pt and reducing agent and surfactants chosen.

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5.2.5.1 Reaction temperature and time

As discussed in 5.2.3, the dual phase nanoparticles around 50-60 nm in diameters were obtained from the sample prepared by gradually increasing the temperature to 180 °C with a heating rate of 5 °C /min and keeping for 10 min. If the temperature was increased to 190 °C (Figure 5-9a) with the same heating rate and precursors' ratio, the NPs surface became rough, and at 210 °C (Figure 5-9b), the precipitates become non-uniform mixtures. This indicates that at higher temperature, higher reaction speed of PbTe results in more PbTe crystals precipitation onto one particle and makes the particles' surface rough. In addition, sucrose directs 1-D growth at high temperatures which has been discussed in chapter 3, hence the precipitates obtained from high temperature reaction (e.g. 210 °C) shows some elongated crystals. At the even higher temperature, the excess PbTe crystals just randomly arranged in the precipitates and made the morphology lost. However, the temperature has no effect on the crystal grain size.

Figure 5-9 SEM images of sample prepared by increased temperature to (a) 190 °C (b) 210 °C with a heating rate of 5 °C /min

5. *PbTe based binary phased nanostructures*

If the reaction time was extended to 30 min (Figure 5-10a) or 2 hour (Figure 5-10a), more and more dissociative PbTe small crystals stack on to the separated particles and merged them together. After 2 hours reaction, the nanoparticles morphology is replaced with big clusters.

Figure 5-10 SEM images of sample prepared by extending reaction time to (a) 30 min (b) 2 hour

5.2.5.2 **Pt catalyst effect**

The XRD pattern in Figure 5-5 reveals that the grain size of pure PbTe (~ 11nm) synthesized under the same condition is smaller than that of dual phase NPs (14nm). It may be due to the catalyst effect of *Pt* which accelerated crystal growth of PbTe during reaction. Further investigation needs to be done to verify the details.

5.2.5.3 **Precursor effect**

Figure 5-11 shows the comparison of XRD patterns of the samples prepared using different reducing agent and precursors. During synthesis reaction, both orthotelluric acid (H_6TeO_6) and sodium tellurite (Na_2TeO_3) can provide Te for PbTe and PtTe_2 crystal growth. The only difference is the valence of Te which is +6 for orthotelluric acid and +4 for sodium tellurite. The lower valence number of sodium tellurite led the faster reduction

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of Te, and then increases the PbTe reaction speed. Therefore, the PbTe-PtTe₂ NPs synthesized with sodium tellurite has smaller grain size of 14 nm (Figure 5-11a) for PbTe compared with that obtained from orthotelluric acid which is 20nm (Figure 5-11b) for PbTe.

5.2.5.4 Surfactant and reducing agent effect

As discussed in chapter 3, sucrose is an effective reducing agent which facilitates the reduction of the precursor during PbTe nanowires synthesis. The calculated grain sizes of samples prepared with only sucrose as the reducing agent and TOPO as the stabilizer are 30nm for PbTe and 9 nm for PtTe₂ (Figure 5-11c). However, the crystal size can be reduced to 20nm for PbTe and 6nm for PtTe₂ if sucrose is replaced with L-ascorbic acid and phenylene diamine as the reducing agent. Therefore, the grain size of the NPs is tunable by varying the reducing agent.

Figure 5-11 XRD pattern of sample prepared using (a) ascorbic acid and phenylene diamine as reducing agent and Na₂TeO₃ as Te precursor, (b) ascorbic acid and phenylene diamine as reducing agent and H₆TeO₆ as Te precursor, (c) sucrose as reducing agent and H₆TeO₆ as Te precursor.

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5.2.5.4 Phase effects

The results also reveal that changing X_{PtTe_2} affects the size of the particles (Figure 5-12). For example, decreasing X_{PtTe_2} from 2 to 0.5 leads to an increase of the average particles size from ~30nm to ~52nm (Figure 5-12a and b). Synthesis of pure PbTe under the same synthesis condition results in the formation of polycrystalline particles of average size ~106nm with a large size distribution (Figure 5-12c-d). The grain size, however, is only 5–12nm as indicated in the dark field TEM observation (Figure 5-12c). It reveals a polynuclear growth process happened during formation of each particle. It is noted that homogenous single crystalline PbTe nanoparticles with size around 8–14nm can be synthesized using a protocol reported in chapter 3 using Te^{2-} in trioctylphosphine (TOP) solution as precursor for Te element. Herein, Te^{6+} was used as the precursor instead of TOP-Te, which possibly slowed down the nucleation rate of the PbTe formation and result in the large size distribution of the PbTe particles.

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Figure 5-12 TEM micrographs of PbTe-PtTe₂ particles with (a) $X_{PtTe_2} = 2$, (b) $X_{PtTe_2} = 0.5$, (c) TEM micrographs of pure PbTe particles, and (d) Size distribution of PbTe-PtTe₂ particles with different phase ratio shows the systematic increase of the particle size with decreased X_{PtTe_2} .

5.2.6 Structure formation mechanism

Base on the observation discussed in 5.2.3 and 5.2.4, the PbTe-PtTe₂ dual phase nanoparticles formation mechanism is proposed. The PtTe₂ small grains precipitates as the seeds first, and then PbTe precipitates onto the PtTe₂ small grains to form the dual phase nanoparticles. A phenomenological description that describes the key aspects of the

5. PbTe based binary phased nanostructures

NPs formation is shown below (Scheme 5-1). Pure PtTe₂ precipitates are platelets due to the tendency of trigonal PtTe₂ to grow anisotropically along the (001) direction[106], but the platelets are highly agglomerated (Figure 5-13a and b) in a random fashion due to the absence of passivation, because there is no effective interaction between Pt and the surfactant TOPO [56]. Pure PbTe nanoparticles (Figure 5-13c) with size of 150-160nm in diameter can be obtained under the same condition due to the stabilization of TOPO [107]. When PtTe₂ is present, the seeding effect results in formation of smaller nanoparticles and more uniform morphology. During the gradually heating process, PtTe₂ precipitates faster than PbTe due to the higher reduction potentials [108] of Pt²⁺ and Te⁴⁺ compared to that of Pb²⁺. Therefore, the heating procedure is very important for the formation of uniform morphology. In the case of the precursors are injected to the solvent at high temperature, both PbTe and PtTe₂ precipitates at the same time and will randomly join together (Figure 5-14e).

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Figure 5-13 (a) SEM images of pure PtTe₂ highly agglomerate precipitates, (b) TEM images of pure PtTe₂ in the same batch as (a), (c) SEM images of pure PbTe nanoparticles obtained from the sample prepared with same condition as PbTe-PtTe₂ NPs, and (d) TEM image of pure PbTe nanoparticles in the same batch as (c).

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Figure 5-14 PbTe-PtTe₂ uniform shape precipitates prepared by injection at high temperature.

Scheme 5-1 Proposed Mechanism of the PbTe-PtTe₂ dual phase NPs formation

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5.2.7 Thermoelectric properties characterization

Same as PbTe NWs, for the thermopower and electric resistivity measurement, the as-prepared PbTe-PtTe₂ particles were washed with hydrazine and dispersed in ethanol. Then the washed particles were sprayed onto glass substrates using air brush to make uniform thin films. Finally, the thin film samples were sent for annealing under Ar: H₂ forming gas environment at 300 °C. The hydrazine washing process removed the organic ligands attachment on the surfaces of the particles effectively, which increased the electrical conductivity drastically. The hydrazine washing process did not affect on the size or shape of the particles. And the as-prepared films are highly porous and no obvious coalescence after annealing (see Figure 5-15). Several reports [36, 47, 55] have described that the inter-particle spacing could be decreased after the hydrazine washing, which enhanced the charge transfer among the particles. During our investigation, the difference of inter-particle distance can not be detected from TEM observation as the particles are partially linked together due to hydrogen bonding. The XRD patterns (Figure 5-16) shows that after heat treatment, the crystal grains did not show obvious growth, but the ratio of PbTe and PtTe₂ slightly changed as some of PbTe evaporated under high temperature during annealing.

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Figure 5-15 SEM images of the sprayed hydrazine treated PbTe-PtTe₂ NPs on glass substrates after annealing at 300 °C under gas forming environment for 30 minutes.

Figure 5-16 Powder XRD patterns of PbTe-PtTe₂ NPs with different molar ratio after annealing at 300 °C for 30 minutes

The electrical resistivity were measured with ZEM with selected temperature range (300K~600K), and the temperature dependent plots for samples with different composition ratio are shown in Figure 5-17. For pure PtTe₂, the resistivity increases with increased measurement temperature, which normally observed in metals or heavily doped semiconductors [109]. And the resistivity for the pure PtTe₂ metal is around $1 \times 10^{-6} \Omega/\text{m}$.

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Therefore, the resistivity decreased with increased amount of PtTe₂. This is consistent with the hall measurement results (Table 5-1) refer to Eqn below:

$$\sigma = n e \mu$$

The charge carrier concentration increases with increasing the doping amount of PtTe₂ from X_{PtTe₂} =0 to X_{PtTe₂} =1, and leads the electrical conductivity increasing.

For sample with X_{PtTe₂} =0.5, the resistivity decreases with increased measuring temperature, which indicates a semiconductor behavior. Figure 5-18 shows the fitting of resistivity versus temperature curve to equation $\rho = \rho_0 \exp[E_a/2k_B T]$, where ρ_0 is a constant, $k_B = 8.617\,343\,15\text{E-}5\text{ eV K}^{-1}$ is Boltzmann's constant, and E_a is the activation energy. The result gives the intrinsic resistivity of sample with X_{PtTe₂} =0.5 is $5.9 \times 10^{-5}\,\Omega\cdot\text{m}$, and the activation energy E_a is 0.105eV, which is smaller than the band gap of PbTe with similar carrier concentration level (0.20eV). It indicates the altering of activation energy by adding PtTe₂ due to the bending of the energy level when two phases are present in one nanoparticle. Further investigation is currently on-going to verify this.

Figure 5-17 Temperature dependences of resistivity of pure PtTe₂ and dual phase samples with X_{PtTe₂} = 0.5, 1 and 2.

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X_{PbTe2}	charge carrier concentration n (cm^{-3})
0	$2.00\text{E}+17$
0.5	$4.02\text{E}+18$
1	$9.70\text{E}+20$

Table 5-1 Hall measurement results of samples with $X_{\text{PbTe2}} = 0.5, 1$ and 2 at room temperature

Figure 5-18 Resistivity fitting result of sample with $X_{\text{PbTe2}} = 0.5$

The measured highest electrical conductivity for pure PbTe particle films synthesized using pentandiol is $\sim 15 \, \Omega^{-1} \, \text{m}^{-1}$, which is about two orders higher than that of reported value for 6-nm PbTe superlattice films [55] and comparable with the PbTe nanowires discussed in chapter 3. However, this is still too low to achieve high ZT values. An σ value of above $10^5 \, \Omega^{-1} \, \text{m}^{-1}$ is desired for thermoelectric applications. The effective charge carrier concentration, n , investigated by the Hall effect measurement shows that the pure PbTe particle film is p- type with an effective hole concentration of $\sim 5 \times 10^{17} \, \text{cm}^{-3}$ at 300 K (Table 5-1). Based on the charge carrier concentration data, we can estimate the

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hole mobility, μ , in the pure PbTe particle film to be $1.2 \text{ cm}^2\Omega \cdot \text{V}^{-1}$ using $\sigma = n e \mu$, which is about two orders lower than that of bulk PbTe [60]. In addition, the electrical conductivity of PbTe was not improved if we vary the precursor ratio of Pb : Te. Then the preparation of multi-phased nanocrystals provides an effective strategy to tune the electrical properties of the particle thin films. With increased secondary phase amount (X_{PtTe_2} values), the particle films show significant enhancement in the electrical conductivity (Figure 5-17) and improved charge carrier concentrations (Table 5-1). High electrical conductivity of above $10^4\Omega^{-1} \text{ m}^{-1}$ could be achieved for samples with $X_{\text{PtTe}_2} = 1$. And the films with $X_{\text{PtTe}_2} = 0.5$ show a maximum electrical conductivity of $1 \times 10^5\Omega^{-1} \text{ m}^{-1}$, which is three orders higher than that of pure PbTe particles films. The significant enhancement in the electrical property of PbTe-PtTe₂ binary-phased nanoparticles as compared to that of pure PbTe nanostructures is attributed to the optimization of the charge carrier concentration in the samples. Herein, it is also noticed that the particle films for the measurements are highly porous (Figure 5-15), which may explain the relatively low electrical conductivity compared to conventional thermoelectric materials. Thus, even higher electrical conductivity can be expected for denser samples, e.g. hot pressed or SPS pellets.

The Seebeck coefficient as a function of temperature with different composition ratio is shown as Figure 5-19. For pure PtTe₂, the Seebeck value is less than $2 \times 10^{-6} \text{ V/K}$ which indicates that it is non-thermoelectric phase. For the samples with different PtTe₂ amount, the negative value reveals that they are n-type materials. Comparing with pure PbTe nanostructure which was discussed in chapter 3 and 4, the p-type material has been changed to n-type by doping PtTe₂ as PtTe₂ is a kind of metal alloy which shows metallic property and donates electrons. For n-type materials, the Seebeck coefficient can be expressed as following equations:

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$$\alpha_n = -\frac{k_B}{e} \left(\frac{3}{2} + \frac{E_c - E_F}{k_B T} \right)$$

Which explains the Seebeck coefficient is a function of temperature. For semiconductors, the Fermi level shifts toward the mid line of the band gap with increased temperature. This leads to an increase in the energy difference between the Fermi level and the conduction band, and hence an increase in the absolute Seebeck coefficient value. Above certain temperature, the Fermi level will be stable and the energy difference between the Fermi level and the conduction band become constant, which indicates the peak point of Seebeck value [110]. However, the peak points are not shown in Figure 5-19, which means the Seebeck value have not reach the highest point even the temperature reaches 700 K. While for pure PbTe nanostructure, the peak appears at $T = 425$ K which has been discussed in chapter 3. It indicates that the Seebeck peak point has been shifted to higher temperature by doping another phase PtTe_2 which has a metallic behavior.

From Figure 5-19, the Seebeck coefficient is observed to decrease with increasing the amount of PtTe_2 . This is mainly due to the enhancement of charge carrier concentration by increasing doping level. Refer to equation [111],

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

The Seebeck coefficient decreasing phenomenon is consistent with the conductivity increasing result with increasing doping level. As X_{PtTe_2} increases from 0.5 to 2, the maximum S decreases from $\sim 140 \mu\text{V/K}$ to $\sim 25 \mu\text{V/K}$. For heavily doped semiconductor or metal, the electron contribution to S can be simplified as $\beta T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}}$ [4], where β is a constant related to the effective mass of charge carriers and n is the charge carrier

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concentration. The observed dependence of S on X_{PtTe_2} may come from the variation of charge carrier concentration. Other possibilities like, e.g. carrier-energy filtering caused by the alternation of scattering mechanism [60] may also exist. Herein, it should be noticed that the Seebeck coefficients for samples with $X_{\text{PtTe}_2} = 0.5$ and 1 are 50–100% higher than that of bulk n-type PbTe material with similar charge carrier concentrations [48], which suggests that the beneficial quantum confinement effect could be retained in the multi-phased samples.

Figure 5-19 Temperature dependences of Seebeck coefficient of pure PtTe₂ and dual phase samples with $X_{\text{PtTe}_2} = 0.5, 1$, and 2

Based on the Seebeck coefficient and electrical resistivity, the power factor ($\alpha^2\sigma$) of these samples are calculated and shown in Figure 5-20. Sample with $X_{\text{PtTe}_2} = 0.5$ maximum value of $2.14 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at about 700 K, which is two orders of magnitude higher than that of pure PbTe nanostructure ($2.2 \times 10^{-6} \text{ Wm}^{-1}\text{K}^{-2}$) [55]. The value is still lower than PbTe bulk material reported [4], but further increase the density of the sample may results in higher power factors. On the other hand, the current low power factor can be offset by the reduction of thermal conductivity from highly porous nanostructure and

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result in higher ZT value. The shifting of the peak point to higher temperature range also gives enhancement of ZT . Such enhancement of ZT can be a promising route to achieve highly efficient thermoelectric energy conversion devices.

Figure 5-20 Temperature dependences of power factor of pure PtTe₂ and dual phase samples with $X_{\text{PtTe}_2} = 0.5, 1, \text{ and } 2$

5.2.8 Concluding remarks

In summary, a simple synthesis protocol to produce PbTe-PtTe₂ multi-phase nanoparticles with controlled phase ratio has been demonstrated. The particles are around 50-60 nm in size and composed by small PbTe and PtTe₂ grains which are 5-10 nm and 10-15 nm respectively. The composition ratio of the particles can be adjusted by precursors adding amount. The size and morphology of the NPs depend on reaction temperature, reaction time and surfactant used. Tunable charge carrier concentration can be achieved via changing the molar ratio of PbTe: PtTe₂. Significant increase in the electrical conductivity has been realized due to the optimization of the charge carrier

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concentration, with the samples still showing greatly enhancement in seebeck coefficient as compared to that of bulk n-type PbTe, which possibly benefits from the quantum size effect. The maximum power factor could be improved by more than two orders of in magnitude for samples with $X_{\text{PbTe}_2} = 0.5$ as compared to that of pure PbTe nanostructures. The significantly property improvement indicates that multi-phase nanosystem is a promising approach on the development of new thermoelectric materials with high efficiency.

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5.3 *Synthesis of Ag₂Te/PbTe core-shell nanoparticles for thermoelectric property enhancement*

5.3.1 Induction

From the results discussed in Section 5.2, we found that the charge carrier concentration of the binary phased nanoparticles can be effectively tuned by varying the composition ratio of PbTe to the secondary phase PtTe₂, and then the thermoelectric power factor was enhanced. These preliminary results give impact on development of new types of highly efficient thermoelectric materials.

In the following study on binary phased nanostructure, Ag₂Te was chosen as the second phase as Ag is an effective doping element in PbTe for carrier concentration adjustment [9]. In addition, the electrical property can be effectively improved in PbTe/Ag₂Te superlattice, which could be attributed to synergetic effect of the two phases [55]. The PbTe quantum dots can be synthesized with a facile solvothermal approach, which has been reported in chapter 3. Therefore, in this section, a silver telluride layer was attempted to grow on the surface PbTe particle to form a core shell nanoparticle by using a second step synthesis. The thermoelectric property measurements were conducted on these core shell nanoparticles with different compositions.

5.3.2 Fabrication of Ag₂Te /PbTe core-shell nanoparticles

The PbTe quantum dots were obtained from synthesis approach discussed in Chapter 3 and dispersed in oleylamine for the following usage. The Ag salt solution was prepared by dissolving 170 mg (1 mmol) silver nitride (AgNO₃) in 10 ml oleylamine. Into the solution, PbTe quantum dots were added and kept stirring for 12 hours under room temperature. And then the black precipitates obtained were washed by re-dispersing in hexane and centrifuge out with ethanol for several times.

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The as-prepared samples were characterized via XRD, Transmission Electron Microscopy (TEM) and Field Emission Scanning Electron Microscopy (FESEM) with the same condition as reported in Chapter 3.

For thermoelectric performance characterization, ZEM-3 measurements were conducted on the thin film samples which were prepared by spraying the as-synthesized particles on glass substrate and followed by annealing at 300 °C for 1 hour under Ar environment for protection. And then the synthesis was scaled up for mass production. The thermal conductivity measurement was conducted on the pellet samples prepared by hot pressing dry powders obtained from mass production using laser flash (NETZSCH LFA 447).

5.3.3 Phase and morphology characterizations of Ag₂Te/PbTe core-shell

nanoparticles

Figure 5-21 shows the TEM images of the PbTe nanoparticles after the second step treatment. It was found that the morphology of the nanoparticles was maintained (see Figure 5-21b) after the second step reaction, but the particle dispersion was not as good as oleic acid capped PbTe particles (see Figure 5-21a). Each particle was found to be coated by an amorphous layer (Figure 5-21c) as marked in Figure 5-21 (d). With these layers, the oleic acid capping was not effective in resulting in good dispersion. Therefore, the particles tend to agglomerate. The HRTEM image shown in Figure 5-21d reveals that the PbTe core is single crystalline.

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Figure 5-21 TEM images of (a) 10 nm PbTe nanoparticles, (b) core-shell nanoparticles after second step reaction and HRTEM images of (c) the agglomerated core-shell nanopates, (d) individual Ag₂Te/PbTe core-shell nanoparticle

To characterize the composition of the amorphous layer, the line scan EDX analysis (see Figure 5-22) was conducted using TEM for single core-shell nanoparticle. From the scan results, we found that Pb and Te were key elements for the core with the atomic ratio of 1:1 which is consistent with the element ratio of PbTe. And the main element of the outer shell was Ag which indicates the amorphous layer is possibly formed by Ag ions in the second step reaction.

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Figure 5-22 EDX line scan analysis of one Ag₂Te/PbTe core-shell nanoparticle

The phases of the Ag₂Te/PbTe core-shell nanoparticle were characterized using X-Ray Diffraction pattern (see Figure 5-23). From the XRD pattern of the as-prepared nanoparticles, only peaks from PbTe phase could be found as the shell is amorphous before annealing. However, after annealing the particles at 300°C, the peaks of Ag₂Te can be observed, which means high temperature is necessary for the formation of secondary phase. In addition, beside the phase of Ag₂Te, Ag_xTe_y (for example Ag₃₅Te₂₀) also existed in the annealed samples as impurities.

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Figure 5-23 Powder XRD patterns of Ag₂Te/PbTe core-shell nanoparticle before and after annealing.

5.3.4 Structure formation mechanism of the Ag₂Te/PbTe core-shell nanoparticles

From the morphology and phase analysis discussed in Section 5.3.3, the growth mechanism of the Ag₂Te/PbTe core-shell nanoparticles was proposed as shown in Scheme 5-2. After mixing the PbTe nanoparticle suspended solution and the Ag solution together, the Ag ions will move to the surface of PbTe nanoparticles and attach to the Te atoms at the surface of the particles due to the electrostatic force between Ag ions, which are electropositive and Te atoms which are electronegative in PbTe phase. With more Ag ions attaching to the particle randomly, an amorphous shell formed and enclosed the whole PbTe nanoparticle and hence the effect of oleic capping for particles monodispersing with self-assembly was lost in the core-shell nanoparticle samples.

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Scheme 5-2 Proposed growth mechanism of the $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticle

5.3.5 Synthesis parameters analysis

There is no surfactant present in the second step reaction, the core-shell particles obtained agglomerated. Then dodecanethiol is tried as surfactant in the second step synthesis to stabilize Ag by forming Ag-S-H. However, the polarity of the *-thiol* (*-S-H*) group is much lower than that of the solvent oleylamine at room temperature, then higher temperature (e.g. 100 °C) required to dissolve Ag-S-H. By using dodecanethiol as surfactant and keeping the reaction at 100 °C for 10min, the core-shell particles were obtained as shown in Figure 5-24. The self-assembly of the particles was enhanced if Ag was capped by *-thiol* group (see Figure 5-24a). However, the excess Ag-S-H precipitated out together with the particles after the solution was cooled down to room temperature. And then the impurities of Ag-S-H (see Figure 5-24b) were introduced into the system and complicated the system composition.

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Figure 5-24 TEM images of Ag₂Te/PbTe core-shell nanoparticle synthesized with dodecanethiol at 100 °C (a) monodispersion of core-shell Nps, (b) core-shell Nps with impurities, (c) HRTEM images of the core-shell Nps, (d) and (e) TEM and HRTEM images of (b) and (c) after TEM burning for 5min, and (f) HRTEM image of one core-shell Np after buring for 5min.

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On the other hand, we found that the amorphous layers coated these particles were not stable during TEM observation. The amorphous layers were burned out after the sample illuminated by electron beam from TEM for 3min (see Figure 5-24 d and e). However, a thin and crystalline layer was observed from the HRTEM. The lattice lattice fringes is 0.21 nm which is consistent with the interplanar distance of Ag_2Te {220} facet. It indicates that the amorphous layers in the as-prepared samples may contain the organic component as the *-thiol* group which has decomposed under the electron beam illumination. And then, the Ag ion re-crystallized with Te to form Ag_2Te . The re-crystallization process observed under TEM is consistent with the XRD results of the core-shell structures after annealing.

5.3.6 Thermoelectric property characterization of $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticles

The electrical conductivity and Seebeck coefficient measurements were conducted with ZEM-3 on thin film samples prepared by spraying the $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticles onto the glass substrates. The electrical resistivity were measured with selected temperature range (300K~650K), and the temperature dependent plots for samples with different composition ratio are shown in Figure 5-25a. The electrical conductivity of the core-shell nanoparticles exhibits a significant increase with the introduction of the secondary phase. With changing the doping amount, the electrical conductivity can be enhanced to $2700 \Omega^{-1}\text{m}^{-1}$ for $X_{\text{Ag:Pb}} = 0.9$ and $25000 \Omega^{-1}\text{m}^{-1}$ for $X_{\text{Ag:Pb}} = 4$ which have been improved by 2~3 order. For the sample with $X_{\text{Ag:Pb}} = 4$, the third phase of pure Ag may also exist in the sample due to the Te shortage if too much Ag introduced into the system. Therefore, the electrical conductivity enhancement is not only attributed to the secondary phase Ag_2Te , but also contributed by the third phase.

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Meanwhile, the metallic phase of Ag also tuned the Seebeck coefficient of the core-shell nanoparticles to negative, which means the semiconductor system could be adjusted to n-type with electrons injection (see Figure 5-25b).

Figure 5-25 Temperature dependence of (a) electrical resistivity, and (b) seebeck coefficient of Ag₂Te/PbTe core-shell nanoparticles with different composition ratios

For sample with $X_{Ag:Pb} = 0.9$, its Seebeck coefficient is positive and observed to increase with temperature increasing which indicates the *p*-type semiconductor behavior. And the p-n transition point was successfully shifted out of to the application temperature

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range (500~700K) by doping the secondary phase Ag_2Te into the system to adjust the charger carrier concentration. In addition, the maximum Seebeck coefficient of the $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticles reaches $\sim 700\text{ }\mu\text{V/K}$ which is 55% higher than that of pure nanoparticles of PbTe and 160% higher than that of bulk PbTe. The large enhancement in Seebeck is possibly attributed to the synergetic effect PbTe and Ag_2Te with composition ratio ~ 1 [55]. Further investigation is under-going to verify this effect.

Figure 5-25 Temperature dependence of power factor of $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticles with different composition ratios

Based on the Seebeck coefficient and electrical resistivity results, the power factor ($S^2\sigma$) of these $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticle samples are calculated and shown in Figure 5-26. The sample with $X_{\text{Ag:Pb}} = 0.9$ achieves the maximum power factor ~ 0.0012 at 680K, and the trend shows the further increasing of the power factor is possible with higher temperature applied.

Based on the results obtained from the thin film samples, mass productions of the $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticles with two different composition ratios were performed and the resulted particles were hot-pressed into pellets for thermal conductivity

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measurement (see Figure 5-26). The thermal conductivity for sample with $X_{\text{Ag:Pb}} = 0.9$ is less than 1 which is attributed to the enhanced phonon scattering in lattice induced by nanostructures. However, the thermal conductivity for the sample with $X_{\text{Ag:Pb}} = 4$ is larger than 3 which is even higher than that of bulk PbTe. Therefore, both enhanced electrical and thermal conductivity due to the excess Ag in the system will cancel each other in thermoelectric performance and therefore high ZT is difficult to achieve.

Figure 5-26 Temperature dependence of thermal conductivity of $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticles with two different composition ratios

Due to the equipment limitation in thermal electric conductivity measurement, the potential good ZT value at high temperature can not be obtained. However, with the maximum power factor at 680K and thermal conductivity measured at highest temperature, the ZT value can be predicted >1.3 for samples with $X_{\text{Ag:Pb}} = 0.9$.

5.3.7 Concluding Remarks

For conclusion of this section, the binary phased $\text{Ag}_2\text{Te}/\text{PbTe}$ core-shell nanoparticles were synthesized with a simple two-step approach. The secondary Ag_2Te phase formed

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after annealing at 300 °C. Dodecanethiol was an effective surfactant to stabilize the core-shell nanoparticle but also introduced impurities into the system. Both electrical conductivity and seebeck coefficient were improved in these binary phased core-shelled nanoparticles due to the synergetic effects. The maximum power factor achieved is 0.0012 at 680K for samples with $X_{\text{Ag:Pb}} = 0.9$. Highest ZT value was predicted >1.3 based on the preliminary characterization results of thermal conductivity and power factor.

Chapter 6 Conclusions and Future work

6.1 Conclusions

This thesis investigates the synthesis of PbTe based single-phased or binary-phased nanostructures with simple solvothermal processes. Characterization of thermoelectric performance of these nanomaterials was also studied. The ultimate goal of this work is to improve the figure of merit (ZT value) of the material system, which is significant for TE application.

The present work starts from synthesis of pure PbTe nanostructures. Firstly, the PbTe nanoparticles with different structures cuboctahedral or cubic were successfully synthesized using an oil based solvothermal approach. The particles size can be controlled in the range of 5-50nm by varying the synthesis parameters (e.g. temperature, reaction time, etc.). And then, the PbTe nanowires with tunable size were obtained via a simple solvothermal approach. Sucrose was used as the key to direct the 1D growth of PbTe. Both size and morphology of the nanowires were affected by the reaction temperature, reaction time and type of surfactants used. Enhanced Seebeck coefficients ($>470 \mu\text{V/K}$) were observed from the thin film samples fabricated by these PbTe nanostructures. The enhancement is possibly due to the quantum confinement of the low dimensional structure. However, extremely low electrical conductivities were measured for these thin film samples because of their low charger carrier concentration and un-optimized sample network connections. Therefore, the thermoelectric performance improvement remains challenging. Meanwhile, a sign change of seebeck coefficient from positive to negative in the temperature range of 575-650 K was observed for PbTe nanostructured samples during ZEM measurement. However, the phenomenon can not be

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observed for bulk PbTe ingots up to 700 K. It is possibly due to the low extrinsic charge carrier concentration for the pure PbTe nanostructures, and then leads the extrinsic to intrinsic transition temperature shift to lower temperature range. Such phenomenon should be considered carefully during the design of TE devices using nano-structured semiconductors [32, 74].

Beside PbTe (*p*-type semiconductor), another nanostructured semiconductor Ag₂Te (n-type) was synthesized using a simple oil-based solvothermal approach for comparison. The obtained nanoparticles are highly uniformed and the size of obtained particles could be tuned by varying reaction temperature, time and types of surfactants. The as-prepared Ag₂Te nanoparticles were washed by hydrazine to remove the capping layer and hot-pressed to pellet for thermoelectric characterization. And the 15-nm Ag₂Te nanoparticles showed a maximum *ZT* value of ~0.8 at *T*=550K, which is 33% higher than the highest reported value of bulk Ag₂Te. The increased *ZT* value is mainly attributed to the reduction of thermal conductivity, which is expected to be close related to the increased interface scattering of phonons in Ag₂Te nanoparticle pellets. While the electrical conductivity of the Ag₂Te nanoparticles remained high as the intrinsic charge carrier concentration of Ag₂Te is high compared to that of PbTe.

In an attempt to improve the thermoelectric properties of PbTe based nanomaterials, the charge carrier concentration enhancement is needed. As doping is very difficult to achieve in a nano-system, the alternative approach, which is multi-phased material system, was applied. A binary phased PbTe-Ag₂Te nanocomposite was fabricated as preliminary attempt by hot-pressing the mixture of PbTe micro powder and Ag₂Te quantum dots. However, the thermoelectric properties of these nanocomposites did not exhibit improvement as the interfaces of the two phases are non-coherent which can not generate

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synergetic effect of binary phased system. And the inhomogeneous distribution of the Ag_2Te quantum dots minimized the quantum effect.

To improve the interaction between different phases at interface, a PbTe/PtTe_2 binary-phased nanoparticle was synthesized by controlling the precipitating rates of two phases (PbTe and PtTe_2). The particles are around 50-60 nm in size and composed by small PbTe and PtTe_2 grains which are 5-10 nm and 10-15 nm respectively. The composition ratio of the particles could be adjusted by precursor ratio. And the size of the nanoparticles was controlled by reaction temperature, reaction time and surfactant used. The improved electrical conductivity was observed for these PbTe/PtTe_2 binary-phased nanoparticles due to the carrier concentration enhancement by adding the secondary phase PtTe_2 . The Seebeck coefficient was adjusted to negative which meant the material system tunes to n -type due to the electron injection with adding the secondary phase PtTe_2 . The high Seebeck coefficient of pure PbTe nanostructures remained due to the quantum confinement, and then led the improvement of the power factor.

On the other hand, the thermoelectric phase Ag_2Te was also chosen as the dopant for the PbTe based binary-phased system study. The binary phased $\text{Ag}_2\text{Te/PbTe}$ core-shell nanoparticles were synthesized with a two-step approach. The secondary Ag_2Te phase formed after annealing at 300 °C. Dodecanethiol was an effective surfactant to stabilize the core-shell nanoparticle but also introduced impurities into the system. Both electrical conductivity and Seebeck coefficient were improved in these $\text{Ag}_2\text{Te/PbTe}$ binary-phased core-shelled nanoparticles due to the synergetic effects. The maximum power factor achieved is 0.0012 at 680K for samples with $X_{\text{Ag:Pb}} = 0.9$. The maximum ZT value could be predicted >1.3 based on the preliminary characterization results of thermal conductivity and power factor. The two-step synthesis is simple and flexible for different

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nanomaterial systems. And the multi-phased nanomaterials exhibit the promise for high efficient thermoelectric device.

6.2 Future works

The results of the present work have inspired the following interesting future works:

6.2.1 1D binary-phased nanostructure

In present works, the binary phased nanostructures are all 0-dimensional nanoparticles. And the particles can not be used in thermoelectric devices directly. However, the one dimensional (1D) nanowires are promising for directly use in many applications like field-effect transistors [29, 112, 113], light-emitting diodes [114], photo-detectors [115], solar cells [116], ultrahigh-density memory and logic devices [117] or thermoelectric devices [14, 118]. In addition, the phonon drag effect in nanowires will lead further increase of the seebeck coefficient. The two-step synthesis will be a good choice for 1D binary-phased core-shell nanowires growth. Any elements (e.g. Ag) can be chosen to attach to the surface of the nanowires (e.g. PbTe) during the second synthesis step. In addition, the secondary phase will be stabilized after annealing. The enhanced thermoelectric properties have been reported for Si/Ge core-shell nanowires [119, 120]. Thus, this direction is worth for future investigation.

6.2.2 Multi-phased nanomaterial system

Complexity is the key for high efficient bulk thermoelectric materials as increasing complexity in material systems manages to decouple the electrical conductivity and thermal conductivity [9]. Thus, to achieve good thermoelectric performance (phonon glass and electron crystal), multi elements doping is normally applied in bulk system. In

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nano system, multi-phased nanostructure could be the alternative approach. With multi phases adding into the materials system, the band structure will be more complex [30], and hence the Seebeck coefficient could be improved. On the other hand, the multi-phased system will introduce more interfaces and further reduce the lattice thermal conductivity because of phonon scattering enhancement. In addition, the interactions between phases may also be effective on the properties which will be very interesting direction for future study.

6.2.3 Nanocomposites with coherent interface

According to the results reported in Chapter 5, the simply hot-pressed nanocomposites did not exhibit improvement in thermoelectric properties as the interface of the two phases is non-coherent due to the surface capping layers formed during synthesis. The capping ligand is difficult to be totally removed with simple washing process. Therefore, there is a need for one step synthesis of nanoparticles embedded in micrograins. For example, the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ nanoprecipitates embedded in $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ micrograins synthesized using melt-spinning [121]. The coherent interface will effectively increase phonon scattering without affect electrons (or holes) movement. The similar composite also can be achieved with solid state reaction [122]. However, the composition ratio and precipitates type of the nanocomposites fabricated with these two technics are limited by the elements solubility. And this limitation does not exist in solution based chemical synthesis. Thus, instant nanocomposite synthesis via solution based process should be a promising direction.

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