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Minority Carrier Blocking to Enhance the Thermoelectric Performance of Solution-processed $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ Nanocomposites via Liquid-phase Sintering Process

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Abstract

Minority carrier blocking through hetero-interface barriers has been theoretically proposed to enhance the thermoelectric figure of merit ZT of bismuth telluride based nanocomposites at elevated temperatures recently (*Phys. Rev. B* **2016**, 93, 165209). Here, to experimentally realize the minority carrier blocking, liquid-phase sintering process enabled by excess Te is applied to the solution-processed $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ nanocomposites for introducing interfacial energy barriers. The controlling parameters in the liquid-phase sintering process such as the amount of excess Te, sintering temperature and holding time, and the Bi composition (x) are systemically tuned and investigated to fully understand the minority carrier blocking mechanism. These interface-engineering parameters are optimized for introducing maximum lattice imperfections and band-bending interfaces that are responsible for blocking the minority carrier and wide-range

scattering of the phonons towards enhanced thermoelectric performance. High $ZT > 1.4$ at 375 K is realized in the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ sample, which is much higher than that of the state-of-art commercial ingots ($ZT \sim 1$) and other solution-processed nanocomposites. The enhanced ZT at elevated temperatures is mostly due to the suppression of bipolar thermal conductivity by minority carrier blocking as well as the reduction of lattice thermal conductivity. Adapting this solution synthesis process to design favorable hetero-interfaces for minority carrier blocking in the liquid-phase sintering process holds promise to further enhance the ZT values.

Keywords: minority carrier blocking, liquid-phase sintering, bismuth antimony telluride, solution-processed, thermoelectrics

1. Introduction

Solid-state thermoelectric devices are silent, reliable and scalable, making them ideal for distributed electric power generation from waste-heat and on-demand cooling of electronic components.¹⁻⁶ The widespread use of thermoelectric device in daily life is still limited by their low energy efficiency.¹ The efficiency of thermoelectric materials can be evaluated by the dimensionless figure of merit (ZT), $ZT = (S^2/\rho\kappa)T$, where S is Seebeck coefficient, ρ is resistivity, κ is thermal conductivity and T is the absolute temperature. The κ is usually the sum of three contributions, which are lattice thermal conductivity (κ_l), electronic thermal conductivity (κ_e) and bipolar thermal conductivity (κ_{bi}). Recently, various approaches such as the band-structure engineering⁷ (e.g., introducing resonant state,⁸⁻⁹ quantum confinement,⁴ and increasing valley degeneracy¹⁰) to enhance power factor (PF , S^2/ρ) and the nanostructuring^{3,6,11} to decrease the thermal conductivity have been proposed and demonstrated to improve the ZT values effectively. Although nanostructuring engineering was first theoretically proposed to increase the power factor by the quantum confinement effect,^{4,12} most of the following experiments on

nanostructured bulk (nanobulk) materials show that the reduction of lattice thermal conductivity is the dominant effect because of the wide-frequency phonon scattering by different nanostructures and interfaces.^{11, 13-15} Besides the reduction of lattice thermal conductivity, the suppression of bipolar thermal conductivity is also a potential way to enhance the ZT values, especially for applications at elevated temperatures such as for power generation by scavenging the waste heat. Actually, the bipolar carrier transport (thermally excited electron-hole pairs) is detrimental to thermoelectric performance as it decreases the Seebeck coefficient and increases the bipolar contributions to the total thermal conductivity. To block the bipolar carrier transport, some theoretical models of minority carrier blocking by hetero-barrier have been proposed recently.¹⁶

Bismuth telluride based materials (like p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ and n-type $\text{Bi}_2\text{Te}_{3-y}\text{Se}_y$) are the best commercialized thermoelectric materials for electric power generation and refrigeration in the near room-temperature region.^{1, 17} Commercial bismuth telluride based ingots are produced by high-temperature solid-solution-alloying method, and their ZT values can reach up to ~ 1.0 with appropriate composition and doping levels.¹⁷ Recently the enhancement of the ZT values of bismuth telluride based materials, especially the p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$, are mainly realized by various nanostructuring approaches,^{11, 18-20} which is effective to the reduction of lattice thermal conductivity. Usually, to achieve nanobulk materials, nanostructured powders are firstly prepared and then are sintered to bulk samples. Nanostructured powders can be prepared by top-down methods using bulk ingot as starting materials, or bottom-up approaches starting from chemical precursors. Nanostructured p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ materials with $ZT > 1.4$ in the near room temperature region have been achieved by top-down approaches like ball milling followed by hot pressing,¹¹ and melt spinning combined with spark plasma sintering (SPS).²⁰ Comparing with top-down methods, bottom-up approaches like chemical solution synthesis are another type of facile and non-energy-intensive ways to achieve nanostructured

powders.²¹ Although there are many reports on the thermoelectric properties of bottom-up solution-processed bismuth telluride based samples,²²⁻³⁴ most of them usually have much lower power factor ($< 1.8 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$) at room temperature, even though the lattice thermal conductivity is indeed greatly reduced. This limits any further enhancement of their ZT values. Reducing the lattice thermal conductivity without compromising much of the power factor is still a challenge for further improving the ZT values in bottom-up solution-processed samples.

Recently, p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with a higher ZT of $\sim 1.86 \pm 0.15$ at 320 K is realized by modified melt spinning followed by SPS method, where excess tellurium enabled the liquid-phase sintering (LPS) process.¹⁹ By introducing the LPS process to bottom-up solution-processed samples, we have achieved p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ bulk samples with nanoscale grains (from ~ 1 nm to ~ 20 nm) and other nanostructured interfaces.³⁵ These nanobulk samples have ZT of $\sim 1.59 \pm 0.16$ at 370 K,³⁵ which is much higher than those solution-processed samples previously reported.^{22, 26, 31, 33-34, 36-38} Unlike dense dislocation arrays at grain boundaries in melt-spun samples, our solution-processed samples show composition segregated phases between the boundaries,³⁵ which can serve as interfaces for phonon scattering and most importantly the hetero-barrier for blocking minority carrier. LPS is a process where solid grains meet wetting liquid phase in the sintering conditions.³⁹ In the LPS process, controlling the starting solid-liquid ratio and the following grain coalescence and arrangements is especially important for the interface engineering. Other processing parameters such as sintering temperature and holding time, and the grain sizes of starting powders can also influence the LPS process.³⁹ In the LPS process of solution-processed samples, the interfaces between grains can be well developed to scatter more phonons and minority carrier but less majority carrier, which is favorable for improving the ZT values. To make full advantage of this strategy, systemic understanding on the tuning of thermoelectric performance by LPS process is essential to further improve the ZT values.

Here, we have studied the optimization of the LPS process for enhancing the ZT values of the solution-processed p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ (especially $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$) nanobulk samples. The excess tellurium (Te) is introduced in the chemical solution-synthesis process to enable the LPS process. To understand the LPS process, the excess amount of Te, sintering temperature, sintering time, grain sizes and composition are systemically studied. The band bending mechanism at the grain interfaces can be introduced to understand the phonon and electron scattering between the interfaces, especially the minority carrier blocking. Optimized LPS conditions are crucial for reducing the lattice thermal conductivity and suppressing bipolar thermal conductivity while maintaining the power factor of solution-processed $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ nanocomposites. With the important enhancement in ZT by LPS process, solution-processed bismuth telluride based nanocomposites show great promise for their widespread use in thermoelectric devices.

2. Experimental Section

2.1. Solution chemical synthesis and spark-plasma sintering

In the chemical synthesis of 4 mmol $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ ($x=0, 0.2, 0.4, 0.5, 0.6$) with 25% excess Te, $4x$ mmol bismuth acetate ($\text{Bi}(\text{OOCCH}_3)_3$), $4(2-x)$ mmol antimony acetate ($\text{Sb}(\text{OOCCH}_3)_3$), 15 mmol potassium telluride monohydrate ($\text{K}_2\text{TeO}_3 \cdot \text{H}_2\text{O}$), 40 mmol potassium hydroxide (KOH), and 0.4 g polyvinylpyrrolidone (PVP, average $M_w \sim 55,000$) were dispersed in 160 ml diethylene glycol (DEG) solvent with the aid of sonication. Then 0.4 g L-cysteine was added to the solution as reducing agent. The mixed solution was transferred to a 250 ml flask with a condenser for refluxing, and heated at the boiling temperature of DEG ($\sim 240^\circ\text{C}$) for 3 hours. To achieve other excess amounts ($y\%$, $y=0, 6, 12.5, 50$) of Te, the amount of potassium telluride monohydrate was set to $12(1+y\%)$ mmol. After synthesis, the as-prepared products were washed and centrifuged in acetone and isopropyl alcohol for several cycles, and finally dried

in a dry cabinet at room temperature. Then the powders were sintered to bulk disk samples using an spark-plasma sintering (SPS) system (Dr. Sinter 1050, Sumitomo Coal Mining, Japan) under the pressure of 60 MPa in vacuum (4-6 Pa), with the application of tunable temperatures (400, 460, 480 °C) and holding time (3, 4, 6 minutes). The densities of the bulk disk samples were measured by the Archimedes method, which were about 86%-91% of the commercial ingot samples.

2.2. Sample characterizations

X-ray diffraction (XRD, Bruker D8) with Cu K_α radiation and scanning electron microscopy (SEM, JEOL 7100F) were carried out to investigate the structures and morphology of the as-synthesized and sintered samples. The sintered bulk samples were cut to bar shapes and their thermoelectric properties (S , ρ , κ and ZT) were characterized by the physical properties measurement system (PPMS, Quantum Design) equipped with thermal transport option, using single-timed mode (the fixed period set at each testing temperature was long enough to meet the requirement of steady-state measurement). The detail of thermal transport measurement can be found in the Supporting Information or elsewhere.³⁵ The Hall coefficient (R_H) was measured by the PPMS equipped with AC transport option sweeping the magnetic field up to $\pm 2T$, and the carrier density n was calculated from the Hall coefficient R_H .

3. Results and discussion

3.1. Morphology and structure characterization

The solution-synthesized $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples are usually hexagonal or the truncated-edge hexagonal disc morphologies, while the excess Te usually appears as wire shape, as reported in our previous results.³⁵ As a representative, the morphology of as-synthesized $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with 50% excess Te is displayed in **Figure 1a**, which reveals the typical $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$

nanoplates and Te nanowires. As demonstrated by XRD patterns in Figure 1b-c, the corresponding Te phase is noticeably shown in the as-synthesized powder with excess Te added in the solution synthesis. The $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ phase is nearly the same no matter whether the excess Te is added or not. During the SPS process, the excess Te in the powders is liquefied with other eutectic mixtures and can be expelled out under the high pressure conditions, as proved in our previous experiment³⁵ and Kim et al.'s work¹⁹. As shown in Figure 1b-c, the sintered pellets all reveal the single $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ phase for both the samples with and without excess Te in the powders. However, comparing with the powder samples, the pellets have preferred (006), (0015), and (0018) peaks, indicating that the alignment and reorientation of those nanoplates occurred under such sintering conditions. As revealed in Figure S1-S2, the positions of the XRD peaks in sintered $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ pellets are nearly independent of the adding amount of excess Te, sintering temperature and holding time. By tuning the compositions in $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$, the positions of XRD peaks can be gradually shifted (Figure S3), which is the same as previous reports^{31, 33}.

3.2. Excess Te dependence

Figure 2 shows the temperature-dependent thermoelectric properties of solution-processed nanobulk $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ samples with different amount of excess Te added in the chemical synthesis process, revealing that the parameters S , ρ , PF , κ , κ_l and ZT do vary with the amount of excess Te. As shown in Figure 2a, the S increases with the temperature without reaching the maximum in the region 10-375 K for most samples except the sample without added excess Te, which has a maximum value of $\sim 246 \mu\text{VK}^{-1}$ at 350 K. The S value at 300 K can vary from 192 to $224 \mu\text{VK}^{-1}$, whose variation is mainly ascribed to the variation of carrier density ($n \sim 1.13\text{-}1.55 \times 10^{19} \text{ cm}^{-3}$, confirmed by Hall measurement) depending on the amount of excess Te added in the synthesis process, as demonstrated by the carrier density dependent S

(Pisarenko plot at 300 K) in **Figure 3a**. The relationship between S and n can be described by:⁴⁰

$$S = \frac{2k_B^2 T}{3e\hbar^2} \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} m^* (1 + r) \quad (1)$$

where k_B is the Boltzmann constant, e is the elementary charge, $\hbar$ is the reduced Planck constant, m^* is the effective mass of the carrier, r is the scattering parameter ($r = 0$ for acoustic phonon scattering, which is used for the fitting of our experiments). The solid curve in Figure 3a represents the plot of Equation 1 with $m^* = 0.58 m_e$, where the m_e is the electron mass. The solid curve fits our data well except for the sample-12.5% which has a larger deviation from the fitting line.

The ρ of all samples increases with the temperature, revealing the heavily doped degenerate semiconducting behavior, as shown in Figure 2b. In the entire temperature region, the ρ in the sample without excess Te is noticeably higher than those in the samples with excess Te added in the synthesis process. At 300 K, the ρ varies from 1.42 to $1.82 \times 10^{-5} \Omega \cdot \text{m}$ for different amount of excess Te (from 6% to 50%), while the ρ in the sample without excess Te can be as high as $2.63 \times 10^{-5} \Omega \cdot \text{m}$. As the ρ is dependent on the carrier density n and mobility μ with the relationship $1/\rho = ne\mu$, the excess Te dependence of μ at 300 K can be calculated as shown in Figure 3b. The μ at 300 K of the sample without adding excess Te is $\sim 210 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is lower than that of the sample with adding excess Te, varying from 242 to $289 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. As displayed in Figure 2c, the PF (S^2/ρ) increases at low temperature and decreases at high temperature, exhibiting a peak around 275 K. Compared to the sample without adding excess Te ($PF \sim 1.9 \times 10^{-3} \text{ Wm}^{-1} \text{K}^{-2}$ at 300 K), the PF values of the samples with adding excess Te have been significantly improved ($PF \sim 2.1\text{-}3.0 \times 10^{-3} \text{ Wm}^{-1} \text{K}^{-2}$ at 300 K).

In the total thermal conductivity $\kappa = \kappa_l + \kappa_e + \kappa_{bi}$, the κ_e is calculated by the Wiedemann-Franz law $\kappa_e = LT/\rho$, where the Lorenz number L is estimated using an approximation equation $L = 1.5 + \exp(-|S|/116)$ for degenerated semiconductors (where L is in the unit 10^{-8}

$\text{W}\cdot\Omega\cdot\text{K}^{-2}$ and S in μVK^{-1}).⁴¹ As the κ_{bi} from thermally generated electron-hole pair is only significant at high-temperature region, the κ_l is usually estimated by subtracting the κ_e from κ as $\kappa - \kappa_e$, though the κ_{bi} is still included in the calculated κ_l . Theoretically, the κ_l can be expressed as a sum of contributions from different-frequency phonons and written as:^{19, 42}

$$\kappa_l = \int \kappa_s(\omega) d\omega = \int \frac{1}{3} C_p(\omega) v(\omega) l(\omega) d\omega \quad (2)$$

where $\kappa_s(\omega)$, $C_p(\omega)$, $v(\omega)$, $l(\omega)$ are the spectral lattice thermal conductivity, specific heat capacity, phonon-group velocity, and phonon mean free path respectively. As shown in Figure 2d, the κ firstly increases at low temperature (<50 K) and then starts to decrease with temperature up to ~300 K. At higher temperature (> 300 K), the κ of most of the samples starts to stop decreasing with temperature, except that the κ of the sample-25% continues to decrease with temperature. As displayed in Figure 2e, the increase of κ_l in the low-temperature region (<50 K) is mainly ascribed to the Debye T^3 law of the heat capacity, while the decrease of κ_l is due to the dominated phonon-phonon scattering (*Umklapp process*) when the temperatures are sufficiently high.³⁵ At higher temperatures (>300 K), the κ_{bi} starts to contribute to the increase of κ , leading to the increase of calculated κ_l .

Compared with commercial $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ingots with $\kappa_l \sim 0.8\text{-}0.9 \text{ Wm}^{-1}\text{K}^{-1}$ at 300 K,^{11, 19} our solution-processed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanobulk samples have much lower κ_l ranging from 0.36 to $0.56 \text{ Wm}^{-1}\text{K}^{-1}$ at 300 K, especially the sample-25%, as shown in Figure 3b. What's more, the suppression of κ_{bi} is quite significant in the sample-25% comparing with other samples, as shown in Figure 2e, 3c-d. As the theoretical κ_l exhibits a $1/T$ temperature dependence due to the *Umklapp process* at high temperature region, the bipolar contribution is evaluated by subtracting the linearly $1/T$ fitting data from the experimental $\kappa - \kappa_e$, as displayed in Figure 3c. The approach that we adopted to determine the bipolar thermal conductivity has also been widely used in previous literatures⁴³⁻⁴⁵. For the sample-0%, the κ_{bi} becomes noticeable from

300 K and starts to increase with the temperature (Figure 3c-d, Figure S4). However, the sample-25% still agrees well with the $1/T$ fit even up to 375 K, indicating the great suppression of κ_{bi} at high temperature region. Adding excess Te is quite effective for reducing the κ_l and κ_{bi} , and the optimized amount of excess Te is crucial to realize the outstanding reduction of κ_l and κ_{bi} (Figure 3b, 3d, Figure S4). The minimum κ_l can reach to $\sim 0.23 \text{ Wm}^{-1}\text{K}^{-1}$ at 375 K for the sample-25%, which is lower than the reported values of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with dense dislocations ($\sim 0.33 \text{ Wm}^{-1}\text{K}^{-1}$ at 320 K)¹⁹ and other solution-processed samples ($\sim 0.29 \text{ Wm}^{-1}\text{K}^{-1}$ at 300 K).³⁴

Figure 2f reveals the temperature dependence of ZT values for samples with different amount of excess Te. The sample-0% and sample-50% have the similar ZT performance, showing ZT peaks of 0.94 and 0.97 at 350 K respectively, which are close to the value of commercial ingots ~ 1 . The ZT values of sample-6% and sample-12.5% are improved compared with sample-0%, reaching to 1.14 and 1.22 at 370 K respectively. Although the sample-25% does not have the highest carrier mobility, the great reduction of κ_l and suppression of κ_{bi} make the sample-25% exhibit the best TE performance, especially at high temperatures ($>300 \text{ K}$). The ZT of sample-25% can reach up to 1.48 at 375 K, which is much higher compared with other reported solution-processed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ samples.^{22, 26, 31, 33-34}

3.3. Band bending at the boundary

As shown in **Figure 4a**, we propose the band bending structure at the boundaries to understand the excess Te dependence of thermoelectric performance. The local electrostatic force built in the interfaces because of the enrichment or the devoid of charge densities will lead to the band bending at the interfaces, which has also been proposed to enhance the thermoelectric performance⁴⁶. Without excess Te to enable LPS process, the devoid of hole-carrier at the solid-solid connection boundary can lead to the downward band-bending at the interfaces, which will

scatter the majority hole-carrier more significantly than the minority electron-carrier, especially those low-energy holes. This kind of energy filtering effect for scattering low-energy majority carriers has been widely proposed to enhance the Seebeck coefficients.⁴⁷⁻⁵⁰ However, the energy filtering effect can also lead to the decrease of carrier density and mobility,⁵¹⁻⁵² which agrees well with our observation (Figure 3a-b). Thus, this kind of downward band bending is not conducive to improve the hole-carrier mobility and suppress the bipolar transport, which agrees well with the lowest μ at 300 K and high κ_{bi} for sample-0% (Figure 3b and 3d). In contrast, with the excess Te to enable the LPS process at high SPS-sintering temperature (460 °C, larger than ~420 °C, the eutectic temperature of the mixture of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and Te, as presented in the phase diagram in Figure 4b), liquid Te with other eutectic phases exists between solid grains, which facilitates the grain coarsening and rearrangement. After the liquid Te and other eutectic phases are expelled out during high pressure sintering, the trace of liquid phase between solid grains can be found as Sb-rich region, as observed in our previous samples by transmission electron microscopy.³⁵ For p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples, the hole-carrier density will increase as the amount of Sb increases, which can be proved in our previous results³¹ and as discussed below. The composition of matrix agrees well with the nominal composition of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, though the segregated Sb-rich region exists in the nanoscale boundaries³⁵. The hole-carrier-rich phase (Sb-rich region) between the grain boundaries can lead to the upward band-bending at the boundaries, based on the alignment of the final Fermi level in the matrix. As shown in Figure 4a, the built-in energy barrier (ΔE) by the upward band-bending will not scatter the transport of hole-carrier much, but it will greatly suppress the transport of thermally excited minority carrier electrons (especially the low-energy electrons). Compared with sample-0%, the higher carrier mobility of the samples with excess Te added (from 6% to 50%) is benefited from this upward band-bending besides the good grain rearrangement enabled by LPS process. However, ultimately to reduce the κ_l and suppress κ_{bi} , the interface contacting

areas or interface densities between the grains and the Sb-rich region at the boundaries has to be optimized to the maximum for intensively scattering phonons and minority electrons. An optimized ratio of liquid phase versus solid grains in the LPS process is the key to achieve the largest band-bending interfaces. As shown in the phase diagram of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3\text{-Te}$ (Figure 4b) by applying the lever rule, the amount of liquid phase will increase with the amount of excess Te added in the synthesis process. Thus, an optimized amount of excess Te for maximizing the interfaces densities between the solid $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ phase and Te-rich liquid phase is expired for minimizing the κ_l and suppressing κ_{bi} , as observed in the sample-25% under our experimental conditions.

Introducing designed energy barrier to prevent the transport of minority carrier without affecting the transport of majority carrier has also been theoretically proposed recently to drastically enhance the ZT value.¹⁶ The κ_{bi} is usually estimated with the T and bipolar transport bandgap E_g^* , using the following exponential relation:^{16, 53}

$$\kappa_{bi} \propto \exp\left(-\frac{E_g^*}{2k_B T}\right) \quad (3)$$

which indicates that the κ_{bi} exponentially increases with the temperature. Near the intrinsic regime ($n \approx p$), the bandgap of bipolar transport is equal to the bandgap of semiconductors E_g .¹⁶ At high doping levels, the κ_{bi} will also be dependent on the carrier concentration (related to energy difference between the Femi level E_F and the valence band edge E_v for hole carrier, $E_F - E_v$) besides the bandgap.⁴⁴ The potential barrier (E_b) at boundaries will also be served as blocking barrier for minority carriers. As shown in Figure 4, the built-in barrier ΔE for the transport of the minority electron carrier through the boundaries is dependent on three parameters, E_g , $E_F - E_v$ and E_b . Besides the sufficiently high barrier ΔE , much longer barrier width (w) between the boundaries is also important to ensure the minority carriers to be blocked

without tunneling.¹⁶ Thus, besides the amount of excess Te, the sintering temperature and holding time and the composition are also tuned to systemically understand the band bending at the interfaces by the LPS process, as to be discussed below.

3.4. Sintering temperature and holding time

Figure 5 shows the temperature dependence of thermoelectric properties (S , ρ , PF , κ , κ_l and ZT) of solution-processed nanobulk $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ samples with different sintering temperatures and holding time (the amount of excess Te is set to 25%). As shown in Figure 5a, the S values are nearly the same in the temperature region 10-375K for the samples prepared with the same sintering temperature (460 °C) but different holding durations (3 min, 4 min and 6 min), which is in good agreement with their nearly the same hole-carrier concentration as revealed in Figure 5g ($n \sim 1.38\text{-}1.42 \times 10^{19} \text{ cm}^{-3}$, $S \sim 196\text{-}200 \mu\text{VK}^{-1}$ at 300 K). As shown in Figure 5b, the resistivity decreases as the holding time increases from 3 min to 4, 6 min (sintering temperature set at 460 °C), which can be understood by the increase of the carrier mobility (Figure 6c, corresponding μ is 242, 276, 299 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at 300 K). By increasing the temperature (from 400 °C, 460 °C to 480 °C, with holding time set at 3 min), the S and n have a bit variation as revealed in Figure 5a and 5g ($n \sim 1.18\text{-}1.42 \times 10^{19} \text{ cm}^{-3}$, $S \sim 196\text{-}209 \mu\text{VK}^{-1}$ at 300 K), while the resistivity ρ decreases as shown in Figure 5b (corresponding ρ at 300 K is $2.04, 1.82, 1.71 \times 10^{-5} \Omega\text{m}$, respectively), which can be ascribed to the increase of the μ (Figure 5i, corresponding μ is 231, 242, 310 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at 300 K, respectively). The PF values show noticeable dependence on the SPS temperature and holding time, which reveals that higher sintering temperature and longer holding time are favorable for achieving high PF (Figure 5c).

Besides the μ , the κ , κ_l and κ_{bi} also show significant dependence on the sintering temperature and holding time, as shown in Figure 5d-e, Figure 5g-h and Figure S5. Same as the μ , the κ , κ_l and κ_{bi} increase as the holding time increases from 3 min to 6 min (temperature set at 460 °C).

Generally speaking, with longer sintering time, grain coarsening, rearrangement and composition relaxation will last much longer, which will reduce the densities of lattice and composition imperfections and the barrier width (w) as well. The reduction of lattice and interfaces defects will decrease the scattering of phonons, which increases the κ_l . As shown in Figure 4a, the tunneling transport of minority carriers will increase as the barrier width shortens, which increases the κ_{bi} . On the other hand, although the μ increases with the temperature from 400 °C to 480 °C (holding time set at 3 min), the κ , κ_l and κ_{bi} have an extraordinary minimum at 460 °C. Basing on the phase diagram $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ -Te systems (Figure 4b), increasing the temperature can also increase the ratio of liquid phase to solid grains in the LPS process same as the increase of excess Te amount as discussed in Figure 2-3. To achieve the optimized ratio of liquid phase versus solid grains, an optimized temperature is preferred for reducing the κ_l and κ_{bi} as much as possible. To achieve a higher ZT value, a higher μ/κ_l (quality factor) is desirable. Although the samples with the highest sintering temperature (sample-480 °C 3min) and longest holding time (sample-460 °C 6 min) have much higher PF (Figure 5c) and μ (Figure 5i), their κ , κ_l and κ_{bi} are also much higher, which limits their ZT value to be still around 1.0 like the commercial $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ingot from 300 K to 375 K (Figure 5f). The much higher κ_{bi} for sample-480 °C 3min leads to the decrease of ZT at high temperature region (>325 K) with a ZT peak ~ 0.94 at 325 K. The sample-460 °C 3 min have the lowest κ , κ_l and κ_{bi} and moderate μ , which makes the quality factor μ/κ_l quite high for enhanced ZT values.

Besides the excess amount of Te and sintering temperature as two thermodynamic parameters in the phase diagrams, the sizes of nanoplates in the starting powers as a kinetic parameter can also greatly influence the thermoelectric performance as well (Figure S6). Nanobulk samples using much smaller nanoplates show un-suppressed bipolar thermal conductivity in the high temperature region, as shown in Figure S6, which is similar to those samples having more excess Te (50%) or higher sintering temperature (480 °C) discussed above, indicating the effect

of nanoplates size on the solid-liquid ratio as well. In the LPS process, smaller grains usually have higher diffusion rate which makes them much easier to be liquefied or dissolved in the liquid,³⁹ increasing the liquid fraction. Thus, optimal thermodynamic and kinetic parameters are especially important to suppress the bipolar thermal conductivity for enhancing ZT values.

3.5. Composition tuning in $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$

As revealed in Figure 4a, the potential barrier (ΔE) for minority carrier blocking can be reduced when the Fermi level is lifted up, relating to the reduction of carrier density. The carrier density can be adjusted by tuning the composition in $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples. Although the composition tuning of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ has been widely investigated in solid-solution-alloying derived ingots,¹⁷ the composition dependence of thermoelectric properties (S , ρ , PF , κ , κ_l and ZT) of solution-processed nanobulk $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples is important for the understanding of the LPS process for minority carrier blocking (the amount of excess Te is set to 25% and sintering condition is 460 °C 3 min), as shown in **Figure 6**. The S increases as the composition Bi (x) increase from 0 to 0.6 in all the temperature region from 10 K-375K (Figure 6a), which is mostly attributed to the decrease of carrier density (Figure 6g). The maximum S value of $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ can reach to 254 μVK^{-1} at 350 K. As shown in Figure 6b, the ρ also increases as the composition Bi (x) increases, which is ascribed to the decrease of carrier density (Figure 6g) and μ (Figure 6i, though the μ of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ is exceptionally a bit lower than that of $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$). The PF of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ shows similar temperature dependence except that the PF peak of $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ shifts to lower temperature (Figure 6c). As the composition Bi (x) increases, the reduction of the κ and κ_l is quite clear, especially in the low temperature region (Figure 6d-e). The peak of κ is reduced from 6.30 $\text{Wm}^{-1}\text{K}^{-1}$ in Sb_2Te_3 at 30 K to 1.45 $\text{Wm}^{-1}\text{K}^{-1}$ in $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ at 50 K (Figure 6d), while the corresponding peak of κ_l is reduced from 4.72 $\text{Wm}^{-1}\text{K}^{-1}$ in Sb_2Te_3 at 20 K to 1.19 $\text{Wm}^{-1}\text{K}^{-1}$ in $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ at 20 K (Figure 6e). All the κ_l of the $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples

with $\text{Bi}(x) \leq 0.5$ still decrease with temperature in high temperature region (>300 K), indicating the great suppression of κ_{bi} as revealed in Figure 6h and Figure S7. As the $\text{Bi}(x)$ increases to 0.6, the great reduction of hole-carrier density lifts the Fermi level and decreases the block barrier for minority electron transport. Therefore, the κ_{bi} starts to contribute to the increase of κ_l from 350 K in $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$, which leads to the decrease of ZT in $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$, having a peak ~ 1.16 at 350 K (Figure 6f). In lower temperature region $T < 300$ K, the $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ have the best thermoelectric performance (Figure 6f), making it more attractive for low-temperature thermoelectric cooling. For other $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples with $\text{Bi}(x) \leq 0.5$, the ZT increases with temperature and the magnitude of ZT at each temperature increases with $\text{Bi}(x)$, as shown in Figure 6f. It can be seen in Figure 6i that the μ and κ_l show similar composition dependence behavior (first decrease with $\text{Bi}(x)$ and then increase with $\text{Bi}(x)$, having a lowest value at $\text{Bi}(x)=0.5$), which can be ascribed to scattering of hole-carriers and phonons by the variation of elements in the lattice.

4. Conclusion

In conclusion, the experimental parameters such as the amount of excess Te, sintering temperature, holding time, nanoplate sizes and composition $\text{Bi}(x)$ are systemically tuned to reveal the underlying mechanism of liquid-phase-sintering (LPS) process for enhancing the thermoelectric performance of solution-processed p-type bismuth antimony telluride based nanocomposites. The carrier mobility is enhanced by introducing LPS process, which can be ascribed to the reduction of carrier scattering between grains by the grain coalescing and rearrangement. The composition segregated region as the trace left after LPS provides an energy barrier between different grains, which blocks the transport of minority carrier but without affecting much of the transport of majority hole-carrier. Besides the suppression of bipolar thermal conductivity, the trace left after LPS also provides a large number of lattice

defects and boundary interfaces for the wide-range scattering of phonons, which greatly reduces the lattice thermal conductivity. However, to make full use of the LPS process for improving the ZT as much as possible, optimized amount of excess Te and sintering temperature and holding time are required to maximize the interfaces densities between solid grains and liquid-phase trace-left region, which will reduce the lattice and bipolar thermal conductivity as low as possible. Moreover, the bipolar thermal conductivity can also be greatly suppressed by increasing the carrier densities, which increases the potential barrier for blocking the transport of minority carriers. In the optimized LPS condition (25% excess Te, 460 °C 3 min), the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanobulk sample has an extremely low lattice thermal conductivity $\sim 0.23 \text{ Wm}^{-1}\text{K}^{-1}$ and enhanced ZT value ~ 1.48 at 375 K, making our solution-chemistry derived $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ samples very attractive for low-temperature power generation. By tuning the composition, the $\text{Bi}_{0.6}\text{Sb}_{1.5}\text{Te}_3$ sample is found to have better performance in low-temperature region ($< 300 \text{ K}$) because of lower carrier density, which is attractive for thermoelectric cooling. Further understanding and designing the band-bending interfaces between grains holds great promise for developing high thermoelectric solution-processed nanobulk samples for both the thermoelectric power generation and cooling.

Supporting Information

Supporting Information is available online

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Figures and Captions

Figure 1. (a) SEM image of the as-synthesized $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanoplates with 50% excess Te. (b) XRD patterns of the as-synthesized powders and sintered bulk pellets for the samples with 50% excess Te and without excess Te added in the solution synthesis process. (c) Zoom-in views of the (015) peak shown in (b).

Figure 2. Temperature dependences of (a) Seebeck coefficient, (b) electrical resistivity, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity and (f) Figure of merit ZT of all the nanostructured $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ samples with different excess Te amount added during the chemical synthesis process. All the figures share the same annotation as indicated in (f).

Figure 3. (a) Pisarenko plots of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanobulk samples with different excess Te amount added in the chemical synthesis process at 300 K. (b) Excess Te amount dependence of carrier mobility and lattice thermal conductivity at 300 K. (c) The plots of $\kappa - \kappa_e$ versus $1000/T$ of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with adding 25% excess Te and without adding excess Te, and the bipolar thermal conductivity is estimated as the difference between $\kappa - \kappa_e$ and the corresponding theoretically linear fitting. (d) Temperature dependence of κ_{bi} of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanobulk samples with different excess Te amount added in the chemical synthesis process. The average error of κ_{bi} is estimated to be $\sim \pm 0.06 \text{ Wm}^{-1}\text{K}^{-1}$ based on the errors of κ_l . A significant suppressing bipolar thermal conductivity at high temperature is identified at 25% excess Te in the processing.

Figure 4. (a) Schematic of band bending in nanostructured p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ at the boundaries between different grains. Devoid (enriched) hot-carriers at the boundary leads to downward (upward) band-bending at the interfaces of those samples without (with) excess Te added in the synthesis process. (b) Schematic of phase diagram of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ -Te based on the binary phase diagrams of Bi-Te and Sb-Te. At higher temperature ($420^{\circ}\text{C} < T < 610^{\circ}\text{C}$) and in the excess Te region ($60\% < \text{atomic Te}\% < 92\%$), the solid state of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and liquid state with rich Te composition coexists at the thermodynamically equilibrium state. The ratio of liquid state to solid state increases as the temperature or the amount of Te increases.

Figure 5. Temperature dependences of (a) Seebeck coefficient, (b) electrical resistivity, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity and (f) Figure of merit ZT of all the nanostructured $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ samples with different sintering temperatures and holding time. Figures (a)-(e) share the same annotation as shown in (f). (g) Pisarenko plots at 300 K, (h) temperature dependence of the bipolar thermal conductivity, and (i) carrier mobility and lattice thermal conductivity at 300 K for the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanobulk samples with different sintering temperatures and holding time.

Figure 6. Temperature dependences of (a) Seebeck coefficient, (b) electrical resistivity, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity and (f) Figure of merit ZT of the nanobulk $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples with varying Bi composition $x=0, 0.2, 0.4, 0.5, 0.6$. The inset of (e) is the zoom-in view of (e) in the high temperature region. Figures (a)-(e) share the same annotation as (f). The dot line shown in (f) is the commercial $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ingot presented in ref [35]. (g) Pisarenko plots at 300 K, (h) temperature dependence of the bipolar thermal conductivity, and (i) carrier mobility and lattice thermal conductivity at 300 K for the $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ nanobulk samples in different compositions.

Graphical abstract

Liquid-phase sintering (LPS) process is systemically studied and optimized to realize the minority carrier blocking and wide-range phonon scattering for enhancing the thermoelectric performance of bismuth antimony telluride nanocomposites.