Solution-processed n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites with enhanced thermoelectric performance *via* liquid-phase sintering

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ABSTRACT The much slower progress in enhancing the thermoelectric performance of n-type Bi_2Te_3 than that of p-type Bi_2Te_3 based materials in the past decade hinders the widespread use in power generation and refrigeration. Here, a facile bottom-up solution-synthesis with spark plasma sintering (SPS) process has been developed to build n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites, which substantially improves the power factor and decreases the lattice thermal conductivity by tuning the interface scattering of phonons and electrons. The stoichiometric composition in ternary $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites is also tuned to optimize the carrier concentration and lattice thermal conductivity. The optimized bulk nanocomposite $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ exhibits a ZT of 1.1 at ~ 371 K, which is comparable to the corresponding commercially available ingots. Our results demonstrate the great potential of the solution-processed n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites for cost-effective thermoelectric applications.

Keywords: thermoelectric, liquid-phase sintering, nanocomposites, solution-processed, bismuth telluride

INTRODUCTION

Thermoelectric (TE) technology has attracted great attention in clean and more sustainable energy sources [1]. TE materials are capable of harvesting waste heat into electricity based on the Seebeck effect, or inducing a cooling effect by passing an electric current through two complementary junctions based on the Peltier effect [1]. For economic viability and minimizing cost, the efficiency of TE materials must be further improved by enhancing their dimensionless figure of merit, termed as ZT , where $ZT = (S^2/\sigma)\kappa T = (\text{PF}/\kappa)T$ with S , σ , κ , T , and PF representing

the Seebeck coefficient (thermoelectric power), electrical conductivity, thermal conductivity, absolute temperature, and power factor respectively [2]. Therefore, an excellent TE material should possess a large PF and low κ . Usually, the κ is contributed by the lattice thermal conductivity κ_l and the electronic thermal conductivity κ_e , where $\kappa_e = L\sigma T$ according to the Wiedemann-Franz law (the proportionality constant L , known as the Lorenz number). Due to the carrier concentration (n) dependence of S and σ and the inter-dependence between κ_e and σ , increasing S usually results in a decrease of σ and increasing σ results in an increase of κ_e simultaneously [2]. And thus, achieving an optimized n and reducing the κ_l are the two strategies mostly used for enhancing the ZT values [2,3].

With the development of new approaches and strategies, such as nanostructuring [4,5] and band engineering [6,7], the ZT of both n-type and p-type TE materials have been greatly improved in the past two decades [5]. Many TE materials have ZT exceeding 1, and some larger than 2. In the big family of TE materials for applications in different temperature regions, Bi_2Te_3 -based alloys (mostly the n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$) remain the best choice for cooling and power generation applications near the room-temperature region ranging in ~ 200 – 500 K [5,8]. Nanostructuring approaches such as the ball-milling [9], melt-spinning process [10] and hot-deforming [11] have improved the maximum ZT of p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ to 1.4 and above. Recently, $ZT \sim 1.86$ at 320 K has also been obtained in the p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ by a modified melt-spinning process through introducing liquid-phase sintering (LPS) process [12]. On the other hand, although nanostructuring approaches like ball-

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milling [13,14] and hot deforming process [15–17] have also been applied to n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, the achieved maximum ZT are only in the range of 1.1–1.2, which is insufficient to match the present p-type counterparts. Thus, it is in great need to develop high-performance n-type Bi_2Te_3 based TE materials for constructing TE devices with matching n-type and p-type legs.

Bottom-up solution-processed synthesis offers another nanostructuring approach for enhancing the TE performance, which has drawn much attention because of its unique advantages such as cost-effectiveness, mild synthesis temperature and most importantly the facility and scalability in achieving various nanostructures [3,8,18]. Various bottom-up solution-processed methods have been reported to achieve n-type Bi_2Te_3 based nanocomposites [19–30], but the achieved maximum ZT of these nanocomposites varies largely from 0.04 to 1.23. For example, Zhao *et al.* [27] reported the solution synthesis of Bi_2Te_3 nanotubes and achieved a $ZT \sim 1$ in the corresponding bulk nanocomposites; Mehta *et al.* [19] reported the solution synthesis of Bi_2Te_3 based nanoplates and prepared bulk nanocomposites with $ZT \sim 1.1$. However, on the other hand, solution-processed Bi_2Te_3 based bulk nanocomposites with low ZT (<0.3) were also reported in other groups [28–30]. The instability of the TE performance in solution-processed samples can be ascribed to the poor interface connection that hinders the transport of majority carriers although the phonons are greatly scattered on the interfaces [3,8]. Synergetic approaches to compromise between thermal and electrical transport are needed to further enhance the TE performance of solution-processed n-type Bi_2Te_3 based materials. LPS process has been applied to a wide range of engineering materials [31], and has also been introduced to TE materials recently [12,32,33]. The phase diagram, widely used in designing the microstructures of TE materials [34], is also powerful for designing the LPS process [12,32]. Wetting liquid between solid grains in the sintering process provided by the LPS process is favorable for enhancing the interface connecting between grains to attain smooth carrier transport without affecting the scattering of phonons.

We reported the solution synthesis of the Bi_2Te_3 based nanoplatelets and bulk nanocomposites, and proved the validity of LPS process for enhancing TE performance, especially for p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ samples [32,33]. However, the impact and mechanism of LPS process applied to n-type solution-processed $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites are still not fully revealed and understood. Here, we demonstrate n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites with en-

hanced TE performance that were prepared by the bottom-up solution-synthesis and LPS-involved spark plasma sintering (SPS) process. Here, the LPS process is enabled by introducing excess Te in the chemical synthesis process. As an interface-engineering approach, the LPS process effectively reduces the lattice thermal conductivity without compromising much the power factor by optimizing the transport of electrons and phonons. Synergistically, the carrier concentration is also optimized by tuning the Se composition in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites to maximize the power factor. Maximum ZT as high as 1.1 at ~ 371 K is obtained in the optimized $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites, showing great potential for further enhancement of the TE performance in n-type solution-processed Bi_2Te_3 based materials *via* composition tuning and LPS process.

EXPERIMENTAL SECTION

Bottom-up chemical solution-synthesis of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanoplates with excess Te

To synthesize 4 mmol Te-excess- $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ mixtures, 8 mmol bismuth acetate ($\text{Bi}(\text{OOCCH}_3)_3$), $4(3-x)(1+28.5\%)$ mmol potassium tellurite monohydrate ($\text{K}_2\text{TeO}_3 \cdot \text{H}_2\text{O}$) (28.5 at.% excess compared with the stoichiometric ratio), $4x$ mmol potassium selenite (K_2SeO_3), 40 mmol potassium hydroxide (KOH) and 0.4 g polyvinylpyrrolidone (PVP, average $M_w \sim 55,000$) were dissolved in 160 mL ethylene glycol (EG) with the aid of sonication. The milky mixed solution was transferred into a 250-mL round bottom flask equipped with a condenser for refluxing, then heated to the boiling temperature of EG at $\sim 190^\circ\text{C}$ for 3 h. A 100-mL flask was also used to synthesize 1 mmol Te-excess- $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ mixtures. After reaction, the product was washed in acetone and isopropyl alcohol (IPA) for several cycles with the assistance of sonication followed by centrifugation. Next, Te-excess- $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ mixtures were collected, dried overnight in a dry cabinet and milled into powders.

Spark plasma sintering of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk samples with LPS process

Through the SPS process, the dried Te-excess- $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ powders were then sintered into bulk nanocomposites at 460°C for 3 min with an applied pressure of 60 MPa. With the sintering temperature higher than the melting temperature of Te ($\sim 450^\circ\text{C}$) and the eutectic temperature of the Te and $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ($\sim 410^\circ\text{C}$), the LPS process was enabled. The Te-excess eutectic mixtures were expelled out from the graphite dies during the sintering process.

The yielded bulk nanocomposites achieved a density of about 89%–95% of the theoretical densities, which is 6.95, 7.06, 7.35, 7.03 g cm⁻³ for the Bi₂Te_{3-x}Se_x bulk samples with $x=0, 0.3, 0.375$ and 0.5 respectively. The bulk nanocomposites were then shaped into bars with dimensions of 9–10 mm in length and 1–2 mm in thickness, polished with sandpapers and attached with leads in the four-probe geometry by applying silver-filled H20E-HC epoxy.

Characterization

The solution-processed nanostructures and sintered bulk nanocomposites were characterized using the scanning electron microscopy (SEM, JEOL 7100F and Hitachi SU-70 equipped with energy dispersive spectrometer (EDS)) for morphology and elemental analysis, and X-ray diffraction (XRD) spectra were taken using a Bruker D8 advance diffractometer with Cu K α radiation ($\lambda=0.15404$ nm; 40 kV, 40 mA) in the locked couple mode between the X-ray gun and detector. The measurements of the temperature-dependent TE properties (parameters S , σ , κ and ZT) were performed using the physical properties measurement system (PPMS, Quantum Design) with thermal transport option in the “single timed mode” for experience users. Each measurement period was fixed at 2,000–3,000 s in order to ensure steady-state measurement at each temperature. The infrared emissivity ε for correcting the radiation loss is set to 1, and a commercial Bi_{0.5}Sb_{1.5}Te₃ ingot was used as a reference sample to calibrate the thermal conductivity. All TE measurements were conducted along the disc-plane direction, which is perpendicular to the SPS press direction. The Hall measurements were performed using the physical properties measurement system (PPMS) with alternating current (AC) transport option by sweeping the magnetic strength between -2 T and 2 T. The carrier density (n) was calculated from the measured Hall coefficient (R_H) using the formula $n=-1/(eR_H)$, where e is the elementary charge.

RESULTS AND DISCUSSION

Morphology and structure characterization

As displayed in Fig. 1a, the solution-processed Te-excess-Bi₂Te_{3-x}Se_x mixtures were synthesized by a common wet-chemical synthesis method [33,35]. Chemical precursor (K₂TeO₃·H₂O) is added excessively in the reaction solution to introduce excess Te in the final reaction product. The as-obtained products are dripped onto SiO₂/Si substrates for SEM characterization. Fig. 1b–e show the SEM

Figure 1 (a) Photo image of the setup for solution synthesis. SEM images of the as-grown (b) Bi₂Te₃, (c) Bi₂Te_{2.7}Se_{0.3}, (d) Bi₂Te_{2.625}Se_{0.375} and (e) Bi₂Te_{2.5}Se_{0.5} nanoplates with excess tellurium. (f) SEM image of the Bi₂Te_{2.7}Se_{0.3} pellet after LPS process. The inset in (f) shows the photo image of the sintered pellet.

images of the as-grown Te-excess-Bi₂Te_{3-x}Se_x mixtures with different stoichiometric ratio of parameter x . The Bi₂Te_{3-x}Se_x nanoplatelets are hexagonal or truncated-edge hexagonal, which are consistent with their layered and rhombohedral crystal structures [36]. Some nanowires are also displayed, which can be identified as Te nanowires as reported in our previous p-type bismuth telluride based samples [32]. The collected solution-synthesized powders can weigh up to 95% of their theoretical weight, revealing that this solution synthesis obtains Te-excess-Bi₂Te_{3-x}Se_x mixtures with high yield. Through the SPS process, these Bi₂Te_{3-x}Se_x nanopowders were sintered into bulk nanocomposites (Fig. 1f), demonstrating that the solution synthesis method can be scaled up for the preparation of large-quantity bulk TE materials. Liquid-phase items formed in the SPS process can be expelled out from the graphite die, which are attached around the punch (see Supplementary information Fig. S1).

As shown in Fig. 2a, the XRD patterns of the as-grown solution-synthesized powders reveal two different sets. Referring to the standard single phase Te data (PDF#36-1452) and the Bi₂Te_{3-x}Se_x data (PDF#15-0863 for Bi₂Te₃, PDF#50-0954 for Bi₂Te_{2.7}Se_{0.3} and PDF #51-0643 for Bi₂Te_{2.5}Se_{0.5}), the two sets of XRD patterns in Fig. 2a can be ascribed to Te and Bi₂Te_{3-x}Se_x, respectively. The peak of Te-excess-Bi₂Te₃ seems to be only one set of XRD pattern, due to the quite similar XRD patterns of Te (PDF#36-1452) and Bi₂Te₃ (PDF#15-0863). With increasing Se concentration, the (015) peaks of Bi₂Te_{3-x}Se_x gradually shifts from 27.63° to 27.9°, as shown in Fig. 2a. On the other hand, the XRD patterns of the Te (PDF#36-

Figure 2 XRD patterns of the as-synthesized powders (a) and sintered bulk pellets (b) of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ samples with excess Te added in the solution synthesis process. The (015) peak is enlarged in the right sides of both (a) and (b).

1452) and $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ (PDF#51-0643) can be separated more clearly. Since the SPS process takes place at 460°C , higher than the melting temperature of Te ($\sim 450^\circ\text{C}$) and the eutectic temperature of Te and $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ($\sim 410^\circ\text{C}$), the excess Te combined with other eutectic mixtures become liquid and can be expelled out from the graphite dies under press conditions. As shown in Fig. 2b, Te-related peaks are not identified in the XRD spectra of SPS-derived $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ pellets. The peak shift in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ pellets ascribes to the replacement of Te with Se composition. According to Bragg's law and the geometry of the hexagonal crystal structure, the lattice constants a and c are determined as the stoichiometric parameter x increases from 0 to 0.5. From Bi_2Te_3 to $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$, and the in-plane lattice constants (a, b) decreases by about 1.3%. The decrease of out-plane lattice constant c of only about 0.8% may be due to the smaller atomic radius of Se atoms as compared to Te atoms.

Therefore, the introduction of Se as a dopant into the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ material generally affects the distance of in-plane atoms. Compared with the powder mixtures shown in Fig. 2a, the pellets shown in Fig. 2b display stronger diffraction intensities in the (006) and (0015) peaks, demonstrating that the reorientation of the nanoplatelets towards the ab planes during the SPS process. This reorientation trend was also observed in other n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ TE materials [14,21,36].

The EDS mapping of the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ bulk nanocomposites after LPS-involved SPS process was conducted to identify that the excess Te can be expelled out from the solid matrix, as shown in Fig. 3. Although some scratches are observed on the surface of the samples (Fig. 3d), the elemental distribution of Bi, Te and Se is unchanged in the test region (Fig. 3a–c), and there is no element-segregation, especially no aggregated Te. The corresponding EDS elemental also quantitatively reveals

Figure 3 The EDS elemental mapping of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ pellet after liquid-phase sintering process. The elemental mapping graph of (a) Bi, (b) Te and (c) Se are taken from the region of (d).

that the final stoichiometric atomic ratio agrees well the theoretical atomic ratio of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ (see Fig. S2).

Electrical transport properties

Fig. 4a–c show the temperature dependent electrical transport of the sintered bulk $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites with various compositions of Se ($x = 0, 0.3, 0.375$ and 0.5). All the electrical transport properties (S , σ and PF)

were measured by PPMS in the same disc-plane direction with the four-probe geometry configuration. In Fig. 4a, the negative S of all $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites in the test temperature range of 10 to 375 K indicates their n-type conducting behavior. The absolute S of all the n-type nanocomposites increases with increasing temperature from 10 to 375 K. By employing a simple parabolic band structure and energy-independent scattering approximation, the S can be modeled after the Mott relation given as [2]:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* \left(\frac{\pi}{3n} \right)^{2/3} T, \quad (1)$$

where k_B , e , h , m^* , n is the Boltzmann constant, electronic charge, Planck's constant, effective mass of carriers, carrier density, respectively. Hence, the gradient of the temperature dependence of the S is generally determined by the m^* and n . The dash line plotted in Fig. 4d (known as Pisarenko plot) represents the plot of Equation (1) at 300 K with $m^*=0.76 m_e$, where m_e is the electron mass. The S of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites at 300 K is 125, 178, 186, 197 $\mu\text{V K}^{-1}$ for Se content at $x=0, 0.3, 0.375, 0.5$, respectively, while the corresponding n is 4.17, 2.53, 2.50, $2.22 \times 10^{19} \text{ cm}^{-3}$, respectively. The measured n dependence on S in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites agrees well with the plotted dash line, indicating that the change of S

Figure 4 Temperature dependence of Seebeck coefficient (a), electrical resistivity (b), power factor (c) of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites with different Se content defined by parameter x , with excess tellurium added in the chemical synthesis process, and (a, b and c) share the same annotation. (d) Carrier density dependence of Seebeck coefficient at 300 K (known as Pisarenko plot) of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites.

with different Se composition in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ is ascribed to the n rather than m^* . The decrease of n by replacing Te with Se is ascribed to the suppression of Te vacancies, which is usually regarded as donor like defects that donate electrons to the matrix [13]. Compared with other reported n-type Bi_2Te_3 based materials (Fig. 4d) [16,23,24,26], our Pisarenko plot is among the middle level. The carrier mobility (μ) of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites can be calculated by the relationship $\sigma = ne\mu$, which is 141.4, 177.8, 141.3, 125.6 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 300 K for Se content at $x=0, 0.3, 0.375, 0.5$, respectively. The room-temperature μ of our solution-processed n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ is comparable with that of other non-solution-processed samples [13,17] and higher than that of many other solution-processed n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites [20,26,28–30].

Fig. 4b shows that the resistivity (ρ , $\rho=1/\sigma$) of the sintered $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites increases with T , indicating their metallic conduction behavior. The ρ of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites increases with increasing Se content x at each T , which is mostly ascribed to the decrease of n in $x=0$ to 0.5 and 0.3 to 0.5. The temperature dependent the power factor (PF, $S^2\sigma$) for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites in Fig. 4c is derived from Fig. 4a, b. As S and σ ($1/\rho$) exhibit opposite temperature dependent behavior, the PF first increases at low temperatures and then decreases at high temperatures, with the maximum power factor at mid-temperature. The optimal PF is realized in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, in accordance with previous studies [23,36]. The maximum PF of our $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk samples in the measured temperature region is $2.47 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at $\sim 275 \text{ K}$ for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. At the highest measured temperature of around 370 K, the maximum PF of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is $2.29 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$. It is comparable with other nanostructured bulk samples produced by ball-milling [13,14] and higher than most of the solution-processed $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ samples [22–26,29,30,37,38]. In order to further enhance PF, continuous efforts for optimizing the S and σ are required.

Lattice thermal conductivity

Fig. 5a and the inset depict the temperature dependent thermal conductivity κ of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites measured using the PPMS. In the PPMS, the κ together with S and σ is measured in one sample in the same test direction to avoid measuring errors from choosing different samples. As the temperature increases to 325 K and above, the thermal conductivity of all $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites falls below $1 \text{ W m}^{-1} \text{ K}^{-1}$. Fig. 5b shows the temperature dependent lattice thermal conductivity κ_l of

$\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites. These κ_l are determined by subtracting electronic thermal conductivity κ_e ($\kappa_e = L\sigma T$) from the total κ . The Lorenz number L varies from 2.44 (degenerate limit) to $1.5 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ (non-degenerate semiconductor) depending on different material system. In this study the L was computed using an approximation equation [39]: $L = 1.5 + \exp(-|S|/116)$, where S is in the unit $\mu\text{V K}^{-1}$ and L in $10^{-8} \text{ W } \Omega \text{ K}^{-2}$. In the low temperature region, the grain boundaries dominate the phonon mean free path, and the only temperature-dependent specific heat capacity increases at lower temperature, following the Debye's T^3 law, which leads to the increase of κ_l at low temperature [40]. Then the κ_l reaches a peak when defect scattering mechanism dominates the phonon scattering process. The introduction of Se into Bi_2Te_3 greatly reduces the κ_l from a maximum of $\sim 6 \text{ W m}^{-1} \text{ K}^{-1}$ at $\sim 25 \text{ K}$ for the binary Bi_2Te_3 to $\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$ at $\sim 25 \text{ K}$ for the ternary $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites. The reduction of κ_l at low-temperature ($\sim 25 \text{ K}$) by Se alloying can be explained by the reduction of the mean-free path of phonons limited by the point defects due to the added Se. At high temperature, the dominated Umklapp process leads to the decrease of lattice thermal conductivity with $1/T$ temperature dependence [40]. At higher temperature $>300 \text{ K}$, the increase of κ_l can be ascribed to bipolar thermal conductivity by thermally excited electron-hole pairs, which is not included in the κ_e . The lattice thermal conductivity of $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ near the room temperature region is larger than that of other $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites (inset of Fig. 5b), which can be ascribed to their larger crystal size compared with other samples, as shown in Fig. 1. The lowest κ_l attained in these $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites between 350 to 375 K lies in the range of ~ 0.35 to $0.55 \text{ W m}^{-1} \text{ K}^{-1}$. The κ_l of our $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites is much smaller than that of commercial n-type ingots produced by the solid-state alloying method (~ 0.8 – $0.9 \text{ W m}^{-1} \text{ K}^{-1}$) [40], and is comparable with that of nanostructured composites produced by ball milling [13], hot deforming [15] and bottom-up solution process [22–26].

Figure of merit and comparison with other methods

In Fig. 5c, the temperature dependent ZT in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites are calculated based on the measured S , ρ ($1/\sigma$) and κ . The ZT for all nanocomposites increases from 10 to 375 K. The ZT is also dependent on the Se composition, where the maximum ZT of our solution-processed nanocomposites is 1.1 at $x=0.3$ at $\sim 371 \text{ K}$. This ZT of 1.1 performs much better than our previous samples produced without the LPS process (0.54

Figure 5 Temperature dependence of thermal conductivity (a), lattice thermal conductivity (b) and figure of merit (ZT) of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites (c) with different Se compositions defined by parameter x , with excess tellurium added in the chemical synthesis process, and (a, b and c) share the same annotation. The insets of (a) and (b) are the enlarged figures of (a) and (b), respectively. (d) Comparisons of maximum ZT of different n-type Bi_2Te_3 related materials.

at 300 K) [36] and other reported solution-processed n-type Bi_2Te_3 based samples [22,26], and is also comparable to the other reported state-of-the-art nanostructured n-type Bi_2Te_3 based materials [13,14,16,41], as shown in Fig. 5d. Compared with the n-type samples without LPS process (Fig. S3), the n-type sample with LPS process shows optimized S and ρ as well as low κ , making its ZT comparable to the state-of-the-art commercial n-type ingot. The anisotropic TE properties are much more distinct in n-type Bi_2Te_3 based samples than in p-type samples [14]. The anisotropy of the thermal conductivity measured in our n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposite can reach up to ~25% (Fig. S4), which can be attributed to the reorientation of different grains to the ab plane under pressing during the SPS process. We have also tried to add extra dopants like Cu and Sn in the solution to further enhance the ZT of our n-type solution-processed nanocomposites. However no obvious improvements were observed at present.

Compared with commercial Bi_2Te_3 based ingots (both

n-type and p-type) with $ZT \sim 1$ around room-temperature, the ZT of lab-stage p-type Bi_2Te_3 based materials has been reported to be about 1.4 and above [9–12], even higher ZT of ~1.86 near 320 K in p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ recently [12]. However, the best performing n-type Bi_2Te_3 based nanocomposites exhibited ZT ranging only from 1.1 to 1.23 [13,14,16,19,23,41], where ZT enhancement is limited compared to commercial n-type Bi_2Te_3 based ingots, as shown in Fig. 5d. Moreover, considering the usual measurement errors of ZT of 10% to even 20% [42], the enhancement of ZT in lab-stage n-type Bi_2Te_3 based nanocomposites is unapparent. Thus, the enhancement of ZT in n-type Bi_2Te_3 based materials is challenge to match the best performing p-type Bi_2Te_3 based materials, so as to obtain high TE devices. Considering the great advantages of bottom-up solution-processed methods in controlling the composition, size, shape, phase, micro- and nanostructures [3,8], it remains to be seen if the ZT of n-type Bi_2Te_3 based nanocomposites can be further enhanced by solution-processed methods through modified engineer-

Figure 6 (a) Schematic of pseudo binary phase diagram of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and Te based on the binary phase diagram of Bi-Te and Bi-Se. As pointed in red circle, in our sintering condition at higher temperature (460°C) and in the excess Te region ($\text{Te}\% > 60\%$), the solid state of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and liquid state with rich Te composition coexist at the thermodynamic equilibrium state. (b) Schematic of the effect of point defects and interfaces on the transport of phonons and electrons.

ing approaches.

Liquid-phase sintering for interface engineering of solution-processed nanocomposites

Interface engineering is crucial for the improvement of ZT in solution-processed nanocomposites [3,8]. In these nanocomposites, the interfaces between liquid composition and solid grains in the sintering process play an important role, and the LPS process provides an effective interface-engineering strategy, which has also been shown in various alloys and composites over a wide range of sintering temperatures [31]. As shown in Fig. 6a, the solid-state $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and liquid-state Te-rich composition coexist in the region with excess Te and high sintering temperature ($> \sim 410^\circ\text{C}$, the eutectic temperature of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and Te) at the thermodynamic equilibrium state. As atoms in liquid phases have high mass diffusivity, liquid phase in the sintering process can serve as a “cement” to penetrate into grain boundaries and facilitate the connection, coarsening and rearrangement between grains. This, in turn, produces low-energy and semi-coherent grain boundaries for better electron transport through grain boundary interfaces. This interface effect is the primary reason for the high carrier mobility and PF in our solution-processed nanocomposites (Fig. 4). As schematically depicted in Fig. 6b, although the boundary interfaces introduced by LPS process have a minimal effect on electron scattering, they still preserve the scattering effect on heat-carrying phonons, especially on low- and mid-frequency phonons, resulting in the low lattice thermal conductivity in our samples (Fig. 5b). For the samples without LPS process (Fig. S3), it is a key problem

to achieve better interface connecting for better electrical properties but lower thermal conductivity as well as optimized carrier density for high TE performance. The pressure applied in the LPS process is crucial to expel out the Te-rich liquid from the solid matrix without significant effect on the composition and carrier concentration (Figs 2b, 3 and 4d). Furthermore, the applied pressure also introduces additional stresses for lattice dislocation [12], which aids in the reduction of the lattice thermal conductivity. To further improve the TE performance of solution-processed n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites and other TE materials, tuning the composition and microstructures combined with the LPS process is a potential strategy.

CONCLUSIONS

In summary, we demonstrated that the TE performance of solution-processed n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ can be enhanced by LPS process and composition tuning. The bottom-up solution synthesis is an efficient and facile method to grow n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanoplatelets with excellent composition control and crystalline quality. The excess Te in the solution-processed samples triggers the liquid-phase sintering process during the SPS of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ bulk nanocomposites. The LPS process plays a key role in interface engineering of solution-processed $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites for improving the PF and reducing the lattice thermal conductivity. The composition-optimized $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample shows a maximum ZT of 1.1 at ~ 371 K. Our results show that bottom-up solution-synthesis can be a potential strategy for developing high-yield and cost-effective TE materials and devices. Further

study on controlling compositions and nano- or micro-structures is desired for enhancing the TE performance of solution-processed n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ nanocomposites and other TE materials.

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Author contributions Zhang C and Xiong Q designed the experiments. Zhang C conducted the material synthesis and characterization. Ng H performed part of the solution-synthesis of the samples. Zhang C contributed to the SEM characterization. Zhang C wrote the paper with support from Xiong Q. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflicts of interest.

Supplementary information Experimental results including the image of expelled items, EDX, comparison of the thermoelectric properties and the anisotropy of the thermal conductivity test are available in the online version of the paper.

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液相烧结增强溶液法制备的n型碲化铋基纳米复合材料的热电性能

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摘要 近十多年来 Bi_2Te_3 基材料热电性能研究中, n型材料的热电性能提升要比p型慢很多, 这极大限制了 Bi_2Te_3 基材料在发电和制冷应用领域中的广泛推广. 本文介绍了一种简单的“自下而上”的溶液合成方法, 并结合放电等离子体烧结工艺来构建n型 $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ 纳米复合块体材料. 在化学溶液合成中引入过量的碲源, 实现在烧结制备样品的过程中引入液相烧结. 这一过程优化了声子和电子在界面的散射行为, 从而增强了材料的功率因子并降低了晶格热导率. 通过调整 $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ 纳米复合材料中的化学成分进一步实现了载流子浓度和晶格热导率的优化. 优化的 $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ 材料在~371K下的ZT值达到了1.1, 与商业化碲化铋材料的ZT值相当. 本研究表明溶液法制备的n型碲化铋基纳米复合材料在大规模低成本的热电应用领域具有重要前景.