Controlled growth of bismuth antimony telluride $\text{Bi}_x\text{Sb}_2-\text{xTe}_3$ nanoplatelets and their bulk thermoelectric nanocomposites

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Abstract
Solution synthesis as a scalable bottom-up growth method shows considerable advantages for designing novel nanostructured bulk composites with augmented thermoelectric performance. Tuning the composition of synthesized materials in the solution process is important for adjusting the carrier type and concentration. Here, we report a modified solvothermal synthesis method for the controlled growth of $\text{Bi}_x\text{Sb}_2-\text{xTe}_3$ nanoplatelets, which can be sintered into nanostructured bulk pellets by using the spark plasma sintering process. We further demonstrate the tuning of the stoichiometric composition in ternary $\text{Bi}_x\text{Sb}_2-\text{xTe}_3$ nanoplatelets with high crystallinity and homogenous phase purity, which is proved by X-ray diffraction and Raman spectroscopy. The composition dependence of the thermoelectric performance of $p$-type $\text{Bi}_x\text{Sb}_2-\text{xTe}_3$ pellets is also systematically studied. The optimized nanostructured bulk $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ sample is found to have $\text{ZT} \sim 0.51$ at 375 K, which shows great potential for further improving the thermoelectric performance by this solution synthesis method. Considering the progress in $n$-type Bi-Te-Se composites, our results advocate the promise of bismuth/antimony chalcogenide nanocomposites towards practical thermoelectric applications.

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Introduction

Thermoelectric materials are widely used to harvest waste heat to produce useful electricity based on the Seebeck effect, or to produce heating or cooling when a current runs through two complementary junctions—the so-called Peltier effect. To make the practical applications of thermoelectric materials viable, it is crucial to improve the efficiency of thermoelectric materials by enhancing the materials’ dimensionless figure of merit (ZT) [1], where $\text{ZT} = \frac{S^2\sigma/\kappa}{T}$, and $S$, $\sigma$, $\kappa$, $T$, PF is the thermoelectric power (Seebeck coefficient), electrical conductivity, thermal conductivity, absolute temperature, power factor, respectively. Thus, an ideal thermoelectric material should have large power factor and low thermal conductivity. There have been consecutive efforts in achieving high-ZT thermoelectric materials since 1940s, but the highest ZT in thermoelectric materials had been remained around 1 lasting to the end of last century [2]. The challenge in improving the ZT value is that the parameters $S$, $\sigma$, $\kappa$ in a material are mutually constrained, for example, increasing $S$ usually leads to a simultaneous decreasing of $\sigma$, and increasing the $\sigma$ leads to the increase of $\kappa$ at the same time because of the Wiedemann-Franz law [3]. In 1993, Hicks and Dresselhaus predicted that the ZT value could be greatly enhanced in the quantum-well [4] and quantum-wire [5] structures due to enhanced thermoelectric power and the reduced lattice thermal conductivity, which inspires the nanostructuring approach for high-ZT thermoelectric materials. Nanostructuring engineering in bulk alloys has been proven to be an effective strategy to enhance the thermoelectric performance by reducing the lattice thermal conductivity [6-9]. Moreover, band structure engineering strategies have also been proposed to increase the power factor for high thermoelectric performance [10,11].

Along with the emergence of various new approaches and new materials in the past decade, the ZT values of the bulk materials for high-temperature applications have been greatly improved, such as multiple-filled skutterudites CoSb$_3$ [12], lead antimony silver telluride and its alloy [13], PbTe-based alloys and nanocomposites, [14,15] and the highest ZT peak has been recorded to be $\sim2.6$ at 923 K for the SnSe crystal [16]. However, for the low-temperature (about 200-500 K) cooling and power generation applications, Bi$_2$Te$_3$-based bulk materials (n-type Bi$_2$Te$_3$-xSe$_x$ and p-type Bi$_2$Sb$_{2-x}$Te$_3$) still dominate. Compared with commercial Bi$_2$Te$_3$-based alloy ingots, enhanced thermoelectric performances were also observed in nanostructured bulk Bi$_2$Te$_3$-based alloys because of the reduced thermal lattice conductivity, which were carried out by various nanostructure engineering approaches such as ball-milling hot-pressing process [17,18], melt-spinning spark-plasma-sintering process [19], hot forging process [20], and solution-synthesis sintering process [21,22].

Solution synthesis is a typical bottom-up assembly approach, which is a facile and scalable method to achieve various nanostructures such as nanowires [23], nanobelts [24], nanoplatelets [25-27], nanonetworks [28], and even heterostructures [29]. Using these nanostructures as building blocks one can harness great possibilities to achieve various novel nanostructured bulk materials for enhancing the thermoelectric performance. However, the solution derived nanostructured bulk materials usually show a low ZT value comparing with the ones made by ball-milling hot-pressing approaches because of the low power factor [30-32], although the lattice thermal conductivity is greatly reduced. For example, a nanostructured bulk Bi$_2$Te$_3$ material made from solution synthesized nanoparticles only shows a ZT of 0.04 at room temperature because of the poor electrical conductivity even though the thermal conductivity is as low as 0.51 W m$^{-1}$ K$^{-1}$ [30]. Thus, to make full advantage of the solution approaches, further systematic controlling on the morphology, structure and composition of nanostructures is greatly needed to optimize the three thermoelectric parameters $S$, $\sigma$, $\kappa$ for high-ZT bulk nanocomposites. Composition tuning in thermoelectric materials is especially important to adjust the band structure and doping level of the materials for improving the power factor [10]. Up to date, various solution approaches have been widely proposed to synthesize binary Bi$_2$Te$_3$ [25,32,33] and Sb$_2$Te$_3$ [26,31,34] nanoplatelets, but the research on the solution synthesis of ternary Bi$_2$Te$_3$-xSe$_x$ and Bi$_2$Sb$_{2-x}$Te$_3$ with tunable composition is still limited. Previously we reported the solution synthesis of n-type Bi$_2$Te$_3$-xSe$_x$ nanoplatelets and characterizations of the thermoelectric performance of their bulk pellets [22]. In a complete Bi$_2$Te$_3$-based thermoelectric device, both n-type Bi$_2$Te$_3$-xSe$_x$ and p-type Bi$_2$Sb$_{2-x}$Te$_3$ materials are required. Although some solution approaches have also been reported recently for the synthesis of stoichiometric ternary p-type Bi$_2$Sb$_{2-x}$Te$_3$ [35,36], it is still a challenge to improve the power factor of these bulk nanocomposites.

Here, we report a modified solvothermal synthesis method for the controlled growth of Bi$_2$Sb$_{2-x}$Te$_3$ nanoplatelets, in which the L-cysteine is used as reducing agent to obtain homogeneous stoichiometric composition. Using this solution synthesis method, the tuning of the stoichiometric composition in ternary Bi$_2$Sb$_{2-x}$Te$_3$ is successfully realized. Phase segregation problem is overcome by this modified approach. By spark plasma sintering (SPS) of the Bi$_2$Sb$_{2-x}$Te$_3$ nanoplatelets, the corresponding nanostructured bulk pellets are prepared for thermoelectric characterizations. The optimized nanostructured bulk Bi$_2$Sb$_{2-x}$Te$_3$ sample is found to have ZT $\sim0.51$ at 375 K, which shows great potential for further improving the thermoelectric performance by the solution synthesis method.

Experimental details

Sample preparation

In a typical synthesis of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanoplatelets, 3.26 g potassium telluride monohydrate ($K_2TeO_3\cdot H_2O$), 0.77 g bismuth acetate (Bi(OOCCH$_3$)$_3$), 1.79 g antimony acetate (Sb(OOCCH$_3$)$_3$), 2.24 g KOH and 0.4 g Polyvinylpyrrolidone (PVP) as stabilizing agent were dissolved in the 160 mL diethylene glycol (DEG) solvent with the aid of sonication. To tune the composition $x$ in the Bi$_2$Sb$_{2-x}$Te$_3$, the amount of Bi and Sb precursors also changes following the stoichiometric ratio. The mixed solution were transferred to a 250-mL round
bottom flask equipped with a condenser for refluxing. Then 0.8 g L-cysteine was added to the solution and the color changed from white to black immediately. After that, the flask was put on an electrothermal mantel with stirring part. The reaction temperature of the mix solution was set at the boiling temperature of DEG (~240 °C). The electrothermal mantel power was turned off after heating the blended solution at ~240 °C for 3 h, and solution was allowed to cool down to room temperature. The black solution was washed in acetone and isopropyl alcohol with the assistance of sonication and followed by centrifuging. The washing process repeated for several cycles. After that, the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples were dried in oven at 60 °C for 1 h. Dried Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples were milled to powders and re-dried at 60 °C for 0.5 h.

Dried nano powders were loaded in 10.5 mm (inner diameter) graphite dies and sintered to bulk disk samples (10.5 mm in diameter and 1-2 mm in thickness) using the spark plasma sintering (SPS) system. After pumping the working chamber to a vacuum ~5 × 10⁻⁷ mbar, the sintering power was turned on to increase the temperature to 350 °C at a rising rate of 50 °C/min and maintained for 10 min at an applied pressure of 40 MPa. Then the temperature was set to 50 °C at a decreasing rate of 50 °C/min, and the applied pressure also decreased to 10 MPa. The densities of the SPS yielded pellets are about 89-95% of the theoretical densities. After SPS, the bulk samples were cut to bars with length 9-10 mm, width 2-3 mm and thickness 1-2 mm. The bars were polished with sandpapers, and four-probe leads were attached to the bars by applying the silver-ﬁlled H2O-E-HC epoxy.

**Characterization methods**

Morphology characterizations of the samples were taken by using scanning electron microscopy (SEM, JEOl 7100F), atomic force microscopy (AFM, scanning probe microscopy model DI dimension V, tapping mode). X-ray diffraction (XRD) patterns were performed using a Bruker D8 advance diffractometer with Cu Kα radiation (λ = 0.15404 nm; 40 kV, 40 mA) in the locked couple mode between the X-ray gun and detector. Raman spectroscopy data were collected on a micro-Raman spectrometer (Horiba-JY T64000, 532 nm, 0.07 mW). The temperature dependence of the thermoelectric performances (parameters $S$, $\sigma$, and $k$) was measured in a physical properties measurement system (PPMS, Quantum Design) with thermal transport option, using the timed single mode (each fixed period is set at 2000–3000 s that is long enough to make sure the steady-state measurement at each temperature). Hall measurements were conducted in the same PPMS apparatus using AC transport option. All the thermoelectric measurements were taken along the disc-plane direction that was perpendicular to the SPS-pressing direction.

**Results and discussions**

**Morphology and structure**

The synthesized Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets were dropped on SiO$_2$/Si substrates for morphology characterization. Figure 1 (a)-(g) show the SEM images of the as-grown Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets with different stoichiometric parameters $x$, and all the samples display the hexagonal or the truncated-edge hexagonal morphologies, which are consistent with their layered and rhombohedral crystal structures of the space group $R3m$(D$_{3d}$) [37,38]. Comparing Figure 1(a) with (b)-(g), the lateral sizes of the binary Sb$_2$Te$_3$ nanoplatelets are about ten times larger than that of other ternary Bi$_{x}$Sb$_{2-x}$Te$_3$ and binary Bi$_2$Te$_3$ nanoplatelets. As shown in the statistical analysis of the lateral size distributions (Supporting information Figure S1), the mean sizes of Sb$_2$Te$_3$ (Figure 1(a)) and Bi$_{0.5}$Sb$_{1.5}$Te$_3$ (Figure 1(d)) nanoplatelets are 2.8 μm and 240 nm, respectively. And the corresponding thickness of Sb$_2$Te$_3$ nanoplatelets is about few tens of nanometers while that of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanoplatelets is around 10 nm (Supporting information Figure S2). Excluding Sb$_2$Te$_3$ nanoplatelets, the size and thickness of other ternary Bi$_{x}$Sb$_{2-x}$Te$_3$ and binary Bi$_2$Te$_3$ nanoplatelets are in the same level, as shown in Figure 1(b)-(g). Thus, adding Bi atoms into the lattice of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ greatly reduces the sizes of these nanoplatelets. Because the formation speed of Bi$_2$Te$_3$ is much faster than Sb$_2$Te$_3$ (Supporting information Figure S3), adding Bi precursors can increase the initial formation rate of ternary Bi$_{x}$Sb$_{2-x}$Te$_3$ cluster, which may lead to much more nucleuses for epitaxial growth. Thus more nucleuses will lead to smaller size of nanoparticles. After washing and drying, the weight of the collected Bi$_{x}$Sb$_{2-x}$Te$_3$ powders can reach above 95% of the theoretical weight, which suggests a high yield production of Bi$_{x}$Sb$_{2-x}$Te$_3$ nanopowder with this modified solvothermal synthesis method. Figure 1 (h) exhibits a photograph of a Bi$_{0.5}$Sb$_{1.5}$Te$_3$ pellet sample after SPS process, which indicates that this chemical approach has great advantage for scale-up preparations of bulk thermoelectric materials.

To confirm the tuning of stoichiometric parameters $x$ in Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets, XRD characterizations were taken on these powder samples, as shown in Figure 2 (a) and (b). The XRD patterns of the as-grown binary Sb$_2$Te$_3$ and Bi$_2$Te$_3$ samples are well matched with the standard rhombohedral single phase Sb$_2$Te$_3$ (PDF-Card 15-0874, lattice parameters $a=b=c=4.262$ Å, $c=30.45$ Å) and Bi$_2$Te$_3$ (PDF-Card 15-0874, lattice parameters $a=b=c=4.385$ Å, $c=30.48$ Å) respectively, as shown in Supporting information Figure S4. By increasing the Bi composition in Bi$_{x}$Sb$_{2-x}$Te$_3$, corresponding XRD peaks for different planes of Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets gradually shift from peaks of the Sb$_2$Te$_3$ sample to that of Bi$_2$Te$_3$ (Figure 2(a)). Figure 2 (b) shows the enlarged view of the most intense XRD peak for (015) plane, which shows that the 2θ value of these peaks gradually shift from 28.2° to 27.6° as the stoichiometric parameters $x$ increases from 0 to 2. The in-plane lattice parameters (a, b) of Bi$_{x}$Sb$_{2-x}$Te$_3$ also shows an appropriate linear dependence on the Bi composition (Supporting information Figure S5). From Sb$_2$Te$_3$ to Bi$_2$Te$_3$, the increase of in-plane parameters a, b is about 2.9% while that of out-plane parameter c is only 0.1%. Thus, the adding of Bi components into the layered Bi$_{x}$Sb$_{2-x}$Te$_3$ materials mostly influences the distance of the in-plane atoms. After SPS process, the XRD pattern of the prepared pellet is compared with that of synthesized powder, as shown in Figure 2(c). In contrast to the random orientation of the synthesized powder, the XRD patterns of the SPS pellet sample in the plane perpendicular to the
The SPS pellet shows much stronger diffraction intensities of the (006) and (0015), which clearly demonstrate that the reorientation of ab planes of nanoplatelets into the disc plane during the SPS process. The reorientation phenomenon is also presented in ball-milling hot-pressing derived bulk samples [18], which shows positive influence on the thermoelectric performance.

To further prove the substitution of Sb atoms by Bi atoms in Bi x Sb2-x Te3 systems, Raman spectroscopy of Bi x Sb2-x Te3 nanoplatelets was taken to investigate the composition dependence of the phonon frequencies, as shown in Figure 3(a). As demonstrated by the XRD above, layered Sb2Te3, Bi2Te3, and Bi x Sb2-x Te3 nanoplatelets have the rhombohedral crystal structure, which are composed of ab-plane hexagonal close-packed atomic layers, periodically stacking along the c-axis. In the c-axis direction, the atomic arrangements can be considered as the repeating stacking of quintuple-layers stacked by van der Waal’s force [37]. Taking Sb2Te3 as a typical example, each quintuple-layer consists of five atomic layers arranged as Te(1)–Sb–Te(2)–Sb–Te(1), in which Te atoms show two different chemical environments (marked as Te(1) and Te(2)), as illustrated in Figure 3(b). Three kinds of peaks are clearly shown in the Raman spectra of different Bi x Sb2-x Te3 nanoplatelets, which are A1g (60-70 cm⁻¹), E₂ (100-115 cm⁻¹) and A1g (130-170 cm⁻¹), as shown in Figure 3(a). Figure 3(b) shows the schematic draw of the linear-chain vibration modes for the three Raman active phonons modes for the three Raman active phonons modes (A₁g, E₂ and A₁g), which are two out-of-plane modes (A₁g and A₁g) and one in-plane mode (E₂). As shown in Figure 3(c), with the substitution of Sb atoms by Bi atoms in Bi x Sb2-x Te3
Figure 3  Raman characterizations of Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets. (a) Raman spectra of Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets with different Bi composition. The nanoplatelets are deposited on SiO$_2$/Si substrate. (b) Schematic draws of the three Raman active modes ($A_{1g}^{1}$, $E_{2}^{g}$, $A_{1g}^{2}$) of Sb$_2$Te$_3$. (c) Phonon frequencies plotted versus the composition parameter $x$ of Bi$_{x}$Sb$_{2-x}$Te$_3$.

systems, there is a continuous variation of the three Raman modes, which gradually shift from peaks of Sb$_2$Te$_3$ ($A_{1g}^{1}$~70 cm$^{-1}$, $E_{2}^{g}$~113 cm$^{-1}$ and $A_{1g}^{2}$~165 cm$^{-1}$) to that of Bi$_2$Te$_3$ ($A_{1g}^{1}$~62 cm$^{-1}$, $E_{2}^{g}$~103 cm$^{-1}$ and $A_{1g}^{2}$~139 cm$^{-1}$). The decreasing of the Raman peaks as the increasing of Bi composition mainly originates from the increase of molar mass [37]. The Raman peaks of as-grown Bi$_2$Te$_3$ and Sb$_2$Te$_3$ nanoplatelets agree well with other reported samples [38,40]. The continuous composition dependence of the Raman modes in Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets is also consistent with Bi$_{x}$Sb$_{2-x}$Te$_3$ crystals synthesized by the Bridgman technique [37], which indicates that uniform composition tuning of ternary Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets is realized by our modified solvothermal synthesis method.

As proved by the XRD and Raman characterizations above, the composition of our as-grown Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets can be homogenously tuned. L-cysteine plays a crucial role to obtain homogenous composition in this modified solvothermal synthesis. Control experiments without adding L-cysteine resulted in two separated phases Bi$_2$Te$_3$ and Sb$_2$Te$_3$ rather than a single phase Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets (Supporting information Figure S56). In addition, without L-cysteine the growth speed of Sb$_2$Te$_3$ is much slower than that of Bi$_2$Te$_3$ (Supporting information Figure S53), which can be the reason for the separated phases. By replacing L-cysteine with another normally used reducing agent L-ascorbic acid, single phase Bi$_{x}$Sb$_{2-x}$Te$_3$ nanoplatelets can also be achieved, however the lateral size is much smaller and the morphology is less uniform than that of as-growth samples with adding L-cysteine (Supporting information Figure S57). Thus, L-cysteine serves as both reducing and stabilizing agent. As observed in the synthesis process, the color of the solution changed from white to black immediately when L-cysteine was added, which indicates its strong reducing nature. Compared with other commonly used reducing agent such as sodium borohydride (NaBH$_4$) [26] and hydrazine hydrate (N$_2$H$_4$·H$_2$O) [34] in the solution synthesis of Sb$_2$Te$_3$ nanoplatelets, L-cysteine is much safer for scale-up chemical synthesis process.

Thermoelectric performances

The as-grown Bi$_{x}$Sb$_{2-x}$Te$_3$ nanopowders were made into disk-like bulk pellets by SPS approach, and these pellets were cut into rectangular bars for thermoelectric characterization. Figure 4 shows the temperature-dependent thermoelectric properties of the Bi$_{x}$Sb$_{2-x}$Te$_3$ pellets with various compositions, and Figure 5 summarizes the composition dependence of thermoelectric properties at 300 K. All the properties were measured in the same disc-plane direction with the four-probe device configuration. As shown in Figure 4(a), the electrical conductivity of the Bi$_{x}$Sb$_{2-x}$Te$_3$ pellets decreases as the temperature increases from 20 K to 375 K, which indicates that all the samples have metallic behaviors. The electrical conductivity also shows dependence on the composition of Bi$_{x}$Sb$_{2-x}$Te$_3$. The Sb$_2$Te$_3$ pellet has an electrical conductivity of about 1.5 × 10^5 S/m at 300 K, which is higher than those p-type ternary Bi$_{x}$Sb$_{2-x}$Te$_3$ pellets (range from 0.4 × 10^5 S/m to 1.2 × 10^5 S/m at 300 K). The reason for the decrease of electrical conductivity in the ternary Bi$_{x}$Sb$_{2-x}$Te$_3$ pellets could be the enhancing of the electron scattering when more Bi atoms substitute Sb atoms in the lattice. Nevertheless, the electrical conductivities of our p-type Bi$_{x}$Sb$_{2-x}$Te$_3$ samples are higher than that of other solution derived samples [35,36] and comparable with that of p-type alloy ingot that is on the level of 1 × 10^5 S/m at 300 K [17].

As shown in Figure 4(b), the thermoelectric power $S$ for all the Bi$_{x}$Sb$_{2-x}$Te$_3$ pellets with Bi composition from $x=0$ to $x=0.8$ has positive values in the test temperature range 20-
375 K, showing a typical p-type behavior. However, when the Bi composition $x$ in Bi$_x$Sb$_{2-x}$Te$_3$ pellets is larger than 1, the Bi$_x$Sb$_{2-x}$Te$_3$ pellets can have negative thermoelectric power, revealing the n-type behavior, as summarized in Figure 5(a). As the n-type thermoelectric performance of Bi$_x$Sb$_{2-x}$Te$_3$ pellets is much lower than our previous n-type Bi$_2$Te$_3$-Se$_x$ pellets, this work focuses on the tuning and thermoelectric characterization of p-type Bi$_x$Sb$_{2-x}$Te$_3$ pellets. As shown in Figure 4(b), the thermoelectric power value of all the p-type pellets increases with the increasing temperature from 20 K to 375 K, showing nearly linear temperature dependence. Using a simple parabolic band structure and energy-independent scattering approximation, the thermoelectric power $S$ is usually given by [3]:

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

where $k_B$, $e$, $m^*$, $n$ is the Boltzmann constant, electronic charge, Planck’s constant, effective mass of electrons, carrier density, respectively. Thus, the slope of the temperature dependence of thermoelectric power is mostly determined by the effective mass of electrons $m^*$ and carrier density $n$. Hall measurements reveal that charge-carrier concentration varies in the range $1 - 9 \times 10^{19}$ cm$^{-3}$, carrier mobility in the range $40 - 340$ cm$^2$ V$^{-1}$ s$^{-1}$ by varying the composition (Supporting information Table S1), which are comparable to other nanostructured bulk Bi$_x$Sb$_{2-x}$Te$_3$ [21]. As shown in Figure 4(b) and Figure 5(a), the thermoelectric power of the Bi$_x$Sb$_{2-x}$Te$_3$ pellets is adjusted by tuning the Bi composition, which suggests that the control of the composition in Bi$_x$Sb$_{2-x}$Te$_3$ pellets is an effective way to tune the effective mass of electrons $m^*$ and carrier density $n$. Figure 5(a) shows the composition dependence of thermoelectric power at 300 K, and the value of
thermoelectric power increases from 91 $\mu$V/K for binary Sb$_2$Te$_3$ pellet to 168 $\mu$V/K for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ pellet. The maximum $S$ is reached to $\sim$193 $\mu$V/K for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ pellet at 375 K. Figure 4(c) shows the temperature dependence of power factor ($PF$) for Bi$_x$Sb$_{2-x}$Te$_3$ pellets, which is derived from Figure 4(a) and (b). As the $S$ and $\sigma$ show opposite temperature dependence, the power factors of these pellets can increase at low temperatures range and decrease at high temperature range, reaching a maximum value at medium temperature. The composition dependence of power factor is displayed in Figure 5(b). The maximum power factor at 300 K we have achieved at present is about 18 $\mu$W cm$^{-1}$ K$^{-2}$ for the Bi$_0.2$Sb$_{1.8}$Te$_3$ pellet, which is much higher than other solution-derived samples with maximum power factor 1–9 $\mu$W cm$^{-1}$ K$^{-2}$ [35,36], but it is still about 2.5 times smaller than the maximum power factor of the state-of-art $p$-type Bi$_x$Sb$_{2-x}$Te$_3$ alloy ingot [17]. Further efforts are still demanded in order to optimize the Seebeck coefficient and the electrical conductivity for higher thermoelectric performance.

Reducing the thermal conductivity by nanostructuring has been widely reported for enhancing the thermoelectric performance. Figure 4(d) shows the temperature dependence of the thermal conductivity for Bi$_x$Sb$_{2-x}$Te$_3$ pellets, which were measured using the four-probe steady-state method on the PPMS. All the Bi$_x$Sb$_{2-x}$Te$_3$ pellets show similar temperature dependence of thermal conductivity from 20 K to 375 K, which increases in low temperature range and decreases in high temperature range, and each sample has a maximum thermal conductivity at about 50-100 K. The measured thermal conductivity has contributions from the phonons and charge carrier. The contribution from phonons (lattice vibrations) is the lattice thermal conductivity $\kappa_l$ and the contribution from charge carriers (electrons or holes) is electronic thermal conductivity $\kappa_e$. According to the Wiedemann-Franz law, the electronic thermal conductivity is related to the electrical conductivity, $\kappa_e = L\sigma T$, where $L$ is the Lorenz number. The Lorenz number $L = 2.45 \times 10^{-8}$ W $\Omega$ K$^{-1}$ is usually taken for metals and degenerate semiconductors [8].

As shown in Figure 4(e), the lattice thermal conductivity shows increasing trend in the low temperature range, which is caused by the excitation of phonons. When enough phonons are excited at high temperature, the phonon-phonon scattering dominates due to the Umklapp process, which leads to the decrease of lattice thermal conductivity at high temperature following $1/T$ temperature dependence. As shown in Figure 4(e), each Bi$_x$Sb$_{2-x}$Te$_3$ pellets has the lowest lattice thermal conductivity at 375 K, which is in the range 0.2–1 W m$^{-1}$ K$^{-1}$. Figure 5(c) displays the composition dependence of the lattice thermal conductivity for Bi$_x$Sb$_{2-x}$Te$_3$ pellets at 300 K, which is in the range 0.4–1 W m$^{-1}$ K$^{-1}$. The lattice thermal conductivity we achieved at present is comparable with the previous reported nanostructured bulk Bi$_2$Te$_3$-based materials [17,21]. Figure 4(f) shows the temperature dependence of Figure of merit (ZT) for Bi$_x$Sb$_{2-x}$Te$_3$ pellets, which is calculated basing on the formula $ZT = (S^2\sigma/k)T$. Increasing the temperature from 20 K to 375 K, the ZT value for all the pellets shows increasing trend with no peaks in this temperature range.
range. Figure 5(d) shows the composition dependence of the ZT value for Bi\_{1-x}Sb\_{2-x}Te\_3 pellets at 300 K, which suggests the tuning of ZT value by composition control. The maximum ZT value we achieved at present is about 0.51 for Bi\_{0.5}Sb\_{1.5}Te\_3 pellets at 375 K. Our Bi\_{1-x}Sb\_{2-x}Te\_3 pellets show relatively low lattice thermal conductivity, so the bottleneck is that the power factor is still low. We ascribed the low power factor of our samples to the influence of some residual chemicals or molecules absorbed on the surface of Bi\_{1-x}Sb\_{2-x}Te\_3 nanoplatelets, and further improvement of the power factor may be realized by using appropriate surface treatment [28].

Conclusions

In summary, we have developed a modified solvothermal synthesis to grow Bi\_{1-x}Sb\_{2-x}Te\_3 nanoplatelets with excellent control of composition tenability and crystalline quality. Nanostructured bulk Bi\_{1-x}Sb\_{2-x}Te\_3 pellets are made from spark plasma sintering of the corresponding nanopowders, which demonstrate the tuning of thermoelectric properties by varying the composition. The p-type Bi\_{1-x}Sb\_{2-x}Te\_3 pellets show low lattice thermal conductivity, though the power factor is still a little lower than state-of-art Bi\_{1-x}Sb\_{2-x}Te\_3 alloy ingot. The ZT value of optimized Bi\_{0.5}Sb\_{1.5}Te\_3 pellet reaches to 0.51 at 375 K. The realization of composition control in p-type Bi\_{1-x}Sb\_{2-x}Te\_3 by this bottom-up solution method opens up great possibilities for future designing of novel nanostructures to lift up the thermoelectric performance. In addition, complete thermoelectric devices for practical applications can be realized by combing our p-type Bi\_{1-x}Sb\_{2-x}Te\_3 with previous reported n-type Bi\_2Te\_3\_xSe\_x.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.05.022.

References

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