Shifting up the optimum figure of merit of \( p \)-type bismuth telluride-based thermoelectric materials for power generation by suppressing intrinsic conduction

Li-Peng Hu\(^1\), Tie-Jun Zhu\(^{1,2,3}\), Ya-Guang Wang\(^1\), Han-Hui Xie\(^1\), Zhao-Jun Xu\(^1\) and Xin-Bing Zhao\(^{1,3}\)

The abundance of low-temperature waste heat produced by industry and automobile exhaust necessitates the development of power generation with thermoelectric (TE) materials. Commercially available bismuth telluride-based alloys are generally used near room temperature. Materials that are composed of \( p \)-type bismuth telluride, which are suitable for low-temperature power generation (near 380 K), were successfully obtained through Sb-alloying, which suppresses detrimental intrinsic conduction at elevated temperatures by increasing hole concentrations and material band gaps. Furthermore, hot deformation (HD)-induced multi-scale microstructures were successfully realized in the high-performance \( p \)-type TE materials. Enhanced textures and donor-like effects all contributed to improved electrical transport properties. Multiple phonon scattering centers, including local nanostructures induced by dynamic recrystallization and high-density lattice defects, significantly reduced the lattice thermal conductivity. These combined effects resulted in observable improvement of \( ZT \) over the entire temperature range, with all TE parameters measured along the in-plane direction. The maximum \( ZT \) of 1.3 for the hot-deformed \( \text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3 \) alloy was reached at 380 K, whereas the average \( ZT_{av} \) of 1.18 was found in the range of 300–480 K, indicating potential for application in low-temperature TE power generation.

**Keywords:** bismuth telluride; donor-like effect; hot deformation; low-temperature power generation; texture

**INTRODUCTION**

Thermoelectric (TE) devices have attracted extensive interest over the past few decades because of their potential use in direct thermal-to-electrical energy conversion and solid-state refrigeration. The TE conversion efficiency of a material can be gauged by the dimensionless figure of merit \( ZT = \frac{a^2 \sigma T}{k} \), where \( a \), \( \sigma \), \( k \) and \( T \) are the Seebeck coefficient, the electrical conductivity, the thermal conductivity and the operating temperature, respectively.\(^1\) Continuous effort has been invested toward improving the \( ZT \) values of TE materials, resulting in significant advances through phonon engineering\(^2\text{–}^9\) and band engineering.\(^10\text{–}^{14}\) For example, remarkable increases in \( ZT \) have been achieved in bulk nanomaterials via the enhancement of phonon scattering at boundaries to reduce lattice thermal conductivities.\(^2\text{,}^4\text{,}^6\text{,}^7\)

Currently, the best commercial TE materials near room temperature are still rhombohedral bismuth tellurides and related solid solutions fabricated by unidirectional crystal growth.\(^15\text{–}^{17}\) Nanostructuring strategies have been devised to prepare high-performance bismuth telluride-based alloys, including bottom-up and top-down approaches. In the bottom-up approach, nanostructures are first obtained by low-temperature hydrothermal synthesis,\(^1\text{,}^5\) ball milling\(^6\text{,}^{18}\text{,}^{19}\) or melt spinning\(^4\text{,}^{20}\) and are subsequently sintered and consolidated by hot pressing (HP) or spark plasma sintering to yield bulk alloys. Recently, Shen \textit{et al.}\(^7\text{,}^{21}\) have developed a novel top-down approach to improve the TE performance of \( p \)-type bismuth telluride-based alloys utilizing hot deformation (HD)-induced \textit{in situ} nanostructures and high-density lattice defects. More recently, we found that HD can also be used to improve the TE performance of \( n \)-type bismuth telluride-based materials because of multi-scale microstructural effects including \textit{microscale} texture enhancement, lattice defects and donor-like effects at the \textit{atomic scale}, and recrystallization-induced local nanostructures.\(^22\text{,}^{23}\)

The ternary alloy \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \) has been so far the best-known \( p \)-type materials for room-temperature refrigeration. Various advanced powder metallurgical techniques\(^4\text{,}^5\text{,}^7\) have been implemented to induce high \( ZT \) values (approximately 1–1.3) in polycrystalline \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \) alloys through structural modification.

\(^1\)State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China; \(^2\)Cyrus Tang Center for Sensor Materials and Applications, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China and \(^3\)Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China

Correspondence: Professor X-B Zhao or Professor T-J Zhu, State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China.

E-mail: zhaoxb@zju.edu.cn or zhutj@zju.edu.cn

Received 1 August 2013; revised 19 November 2013; accepted 25 November 2013
However, maximum ZT values are only obtained at room temperature, as rising temperatures dramatically decreased ZT because of intrinsic excitation.\textsuperscript{4,7,24} For low-temperature power generation applications below 500 K, the maximum ZT of p-type bismuth telluride-based alloys must be shifted to higher temperatures, employing a composition other than Bi$_2$Sb$_2$Te$_3$. One feasible solution toward the optimization of ZT at elevated temperatures, making them suitable for low-temperature power generation, is to actively suppress intrinsic conduction at elevated temperatures via two strategies. The first is to broaden the band gap; the second is to increase the hole concentration. The origin of hole concentration in the form of antisite defect mainly depends on bond polarity. The lower the polarity of the bonds between cations and anions, the lower the energy for antisite defects.\textsuperscript{25,27} Raising the Sb content in Bi$_{2-x}$Sb$_x$Te$_3$ mixed crystals can reduce the formation energy of antisite defects, thereby increasing the hole concentration because of the smaller difference in electronegativity for Sb–Te compared with Bi–Te.\textsuperscript{27} The hole concentration may be further tuned through donor-like effects induced during the deformation process by grinding and pressing.\textsuperscript{22,23,28,29} The binary compound Bi$_2$Te$_3$ has a narrow band gap (approximately 0.13 eV).\textsuperscript{30–33} which can be adjusted through the formation of solid solutions by alloying with Sb$_2$Te$_3$ (a larger band gap of approximately 0.28 eV).\textsuperscript{34,35} The band gap increases with the addition of Sb to the rich-Sb$_2$Te$_3$ region, which can be attributed to increasing degeneracy of charge carriers and the larger band gap of Sb$_2$Te$_3$ compared with Bi$_2$Te$_3$.\textsuperscript{35} Thus, Sb substitution can effectively shift the optimum ZT to higher temperatures.\textsuperscript{37} Nonetheless, systematic work on the effects of Sb-substitution on the TE performance of polycrystalline Bi$_{2-x}$Sb$_x$Te$_3$ is rare.

In this work, we fabricated a series of p-type Bi$_{2-x}$Sb$_x$Te$_3$ (x = 1.4–1.8) polycrystalline solid solutions by a top-down, HD method to explore the effect of Sb-alloying on the suppression of intrinsic conduction. The optimum ZT was shifted to higher temperatures (approximately 380 K) by increasing the values of both band gap and hole concentration. The maximum ZT of 1.3 was attained at 380 K with the composition x = 1.7 and TE parameters measured along the same direction. More importantly, the average ZT$_F$ of approximately 1.18 was achieved in the range of 300–480 K, indicating potential for the application of this composition in low-temperature power generation.

EXPERIMENTAL PROCEDURES

Melting

Commercial high-purity elemental chunks of 99.999% Bi, 99.999% Sb, and 99.999% Te were used as raw materials. Appropriate quantities of each were weighed according to the nominal composition of Bi$_{2-x}$Sb$_x$Te$_3$ (x = 1.4, 1.5, 1.6, 1.7 and 1.8) and sealed in a quartz tube at 10$^{-3}$ Pa. The element mixture was melted at 1023 K for 10 h and cooled in the furnace.

Consolidation of powders and HD

Ingots were ball milled (MM 200, Retsch GmbH, Haan, Germany) for 20 min at 15 Hz to yield fine powders. These powders were pressed hot into cylindrical shapes in a φ10 mm graphite die at 673 K for 30 min under 80 MPa. The initial hot-pressed bulk samples with different Sb content (x) were named HP-Sbx. Subsequently, HD was performed by repressing the HP samples in a larger graphite die with an inner diameter of 16 mm at 823 K for 30 min at the same pressure. This HD approach eventually yielded 16 mm disk-shaped samples, labeled ‘HD-Sbx’.

RESULTS AND DISCUSSION

Texture evolution

Figure 1a shows the in-plane X-ray diffraction patterns of the as-pressed Bi$_{2-x}$Sb$_x$Te$_3$ bulk samples before and after HD. All the reflection peaks can be indexed to a rhombohedral phase (JCPDS #49-1713). The (00l) diffraction intensities of the HD sample are much higher than those of the HP samples, revealing the formation of preferred orientation during the HD process. To investigate the texture evolution, the degree of preferred orientation ($F$) of the (00l)-planes was calculated by the Lotgering method.\textsuperscript{39} As shown in Figure 1b, the F values increase from 0.14–0.17 in the HP series to 0.20–0.28 in the HD samples. Obviously, HD causes enhanced texture in the bulk samples because of the occurrence of plastic deformation. In our previous study, a similar process yielded reduced textures, which was ascribed to deformation-induced dynamic recrystallization.\textsuperscript{2} The possible cause of the difference may be the different degree of deformation applied to the samples.

It is well known that both plastic deformation and dynamic recrystallization take place in HD process and have opposite impacts on the degree of texture. The deformation strain ($\varepsilon$), defined by $\varepsilon = (H_0-H)/H_0$, where $H_0$ and $H$ are the initial thicknesses of the HP samples and the final thicknesses of the HD samples, represents the degree of plastic deformation. A value of $\varepsilon = 0.37$ was obtained in the earlier report,\textsuperscript{2} whereas a value of $\varepsilon = 0.61$ was observed in this work. The larger deformation strain induced in the present work led to the formation of texture as a result of the comparatively stronger role played by plastic deformation than dynamic recrystallization. The F values reported here are higher than those observed in materials prepared using the MA-spark plasma sintering (MA: mechanical alloying)\textsuperscript{37} or MA-HP\textsuperscript{40} techniques. However, processes such as zone melting accompanied by spark plasma sintering\textsuperscript{41} or shear extrusion\textsuperscript{42} provide stronger textures, with $F$ values of 0.61 (zone melting) and 0.63 (shear extrusion). Scanning Electron Microscopy (SEM) fractographs of the bulk samples give results consistent with X-ray diffraction measurements (Supplementary Figure 2). It should be mentioned that even small degrees of texture will result in large differences between in-plane and out-of-plane thermal conductivities.

Effects of Sb content and HD on TE properties

In p-type Bi$_{2-x}$Sb$_x$Te$_3$ alloys, the hole concentration is primarily created by antisite defects in the form of Te sites occupied by Bi or Sb atoms.\textsuperscript{25–27} The incorporation of Sb atoms into the Bi$_2$Te$_3$ lattice decreases the difficulty associated with the formation of antisite defects in Bi$_{2-x}$Sb$_x$Te$_3$ mixed crystals is mainly associated with Sb substitution. The optimum ZT solution toward the optimization of ZT is achieved in the range of 300–480 K, indicating potential for the application of this composition in low-temperature power generation.
defects and thereby increases the hole concentration\textsuperscript{27,43} Thus, as illustrated in Figure 2a, the hole concentration ($n_H$) monotonically rises with increasing $x$. The $n_H$ values of Bi$_2$Te$_3$-based alloys are sensitive to both chemical composition and processing-induced lattice defects\textsuperscript{22,23,29}.

Tellurium vacancies can be generated by a process of deformation-induced non-basal slip that provides the lattice with excess negative carriers, referred to as the donor-like effect\textsuperscript{28,44}. The donor-like effect can partially compensate for the hole concentration in Sb-rich $p$-type solid solutions\textsuperscript{28}. This phenomenon explains the slight reduction in $n_H$ observed in the HD samples compared with their HP counterparts (Figure 2a). Single crystals prepared by the Bridgeman method without mechanical deformation show the highest $n_H$.\textsuperscript{27,43} The influence of Sb content on the carrier mobility is illustrated in Figure 2b. The markedly increased $n_H$ achieved with increasing $x$ leads to strong electron–electron scattering and decreased $\mu_H$. However, it is interesting that both $n_H$ and $\mu_H$ increase with increasing $x$. The increase of $\mu_H$ with increasing $x$ (a reduced Bi/Sb ratio) is mainly attributed to weakened alloy scattering, which is consistent with previous studies\textsuperscript{24,45}. In addition, the HD samples show much higher $\mu_H$ values than the HP samples by virtue of their lower $n_H$ and slightly enhanced textures\textsuperscript{22,23,47}. Nevertheless, the measured $\mu_H$ values of the HD samples are still smaller than the $\mu_H$ for the single crystals\textsuperscript{43} and MA-HP\textsuperscript{48} samples of the same composition. Further improvements in $\mu_H$ may be possible through the formation of a highly preferred orientation via repetitive HD or optimization of the process parameters.

The electrical transport properties of the Bi$_{2-x}$Sb$_x$Te$_3$ bulk samples have been measured and plotted in Figure 3, wherein a transition from semiconducting ($x \approx 1.4$) to metal-like ($x < 1.5$) conduction behavior is observed. The remarkable enhancement in $\sigma$ with increasing $x$ can be attributed to increases in both $n_H$ and $\mu_H$ because of the incremental concentration of antisite defects\textsuperscript{27,43} and reduced alloy scattering,\textsuperscript{24} respectively. Post-HD changes in $\sigma$ were different for materials with $x < 1.6$ and $x > 1.6$ because of the different magnitudes of the $n_H$ reduction and the $\mu_H$ increase. In particular, $\sigma$ is improved, to some extent, because of texture enhancement in materials with Sb content $x > 1.6$. The electrical conductivities of the Bi$_{2-x}$Sb$_x$Te$_3$ ($x = 1.5–1.8$) bulk samples roughly follow a $T^{-1.5}$ dependence near room temperature, indicative of acoustic phonon
Figure 3 (a) Temperature dependence of electrical conductivity, (b) temperature dependence of Seebeck coefficient and (c) Sb content dependence of temperature for the $n_{\text{max}}$ and $n_{\text{H}}$ of the Bi$_{2-x}$Sb$_x$Te$_3$ bulk samples before and after hot deformation.

Table 1 Hole concentration $n_{\text{H}}$, Hall mobility $\mu_{\text{H}}$, Seebeck coefficient $\alpha$, reduced Fermi levels $\xi_F$, carrier effective mass $m^*$ and sample density $\rho_0$ of the Bi$_2$Sb$_x$Te$_3$ bulk samples at 300 K before and after hot deformation.

| Samples  | $n_{\text{H}}$ ($10^{19}$ cm$^{-3}$) | $\mu_{\text{H}}$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $\alpha$ ($\mu$V K$^{-1}$) | $\xi_F$ | $m^*$ | $\rho_0$ (g cm$^{-3}$) |
|----------|-----------------------------------|-----------------------------------------|------------------|--------|------|-------------------|
| HP-Sb1.4 | 2.4                               | 65                                      | 156              |        |      | 6.82              |
| HD-Sb1.4 | 0.9                               | 94                                      | 191              |        |      | 6.73              |
| HP-Sb1.5 | 2.6                               | 122                                     | 218              | -0.2   | 1.4  | 6.77              |
| HD-Sb1.5 | 2                                 | 140                                     | 255              | -0.8   | 1.6  | 6.77              |
| HP-Sb1.6 | 3.4                               | 157                                     | 199              | 0.1    | 1.4  | 6.71              |
| HD-Sb1.6 | 3.1                               | 173                                     | 215              | -0.2   | 1.5  | 6.65              |
| HP-Sb1.7 | 4.6                               | 164                                     | 176              | 0.5    | 1.4  | 6.67              |
| HD-Sb1.7 | 4.3                               | 185                                     | 187              | 0.3    | 1.5  | 6.44              |
| HP-Sb1.8 | 5.8                               | 184                                     | 144              | 1.2    | 1.2  | 6.72              |
| HD-Sb1.8 | 5.9                               | 217                                     | 139              | 1.3    | 1.2  | 6.57              |

The parabolic nature of the valence band and complex scattering processes, the trends in the values of $\xi_F$ and $m^*$ can provide information about the band structure upon the introduction of Sb. The increase in $n_{\text{H}}$ with increasing $x$ is accompanied by a gradual increase in $\xi_F$ indicating the progressive movement of the Fermi level deeper into the valence band. However, the Fermi level slightly shifts toward the valence band edge after HD, as evidenced by the decreased $\xi_F$ of the HD samples in comparison to their HP counterparts. $m^*$ remains nearly unchanged with increasing $x$. The slight decrease in $m^*$ at $x = 1.8$ can be attributed to variations in the valence band constituents, consistent with Stordeur’s results.\textsuperscript{38} Deformation does not cause changes in $m^*$.

The room temperature value of $\alpha$ is reduced from 255 $\mu$VK$^{-1}$ (HD-Sb1.5) to 139 $\mu$VK$^{-1}$ (HD-Sb1.8) with increasing $x$, because of the increase in $n_{\text{H}}$. The noticeable improvement in $\alpha$ achieved after HD is a result of the reduction in $n_{\text{H}}$. Therefore, HD processing enables the improvement of $\alpha$ through $n_{\text{H}}$ reduction, whereas slightly increasing $\sigma$ by enhancing the textures of the Bi$_2$Sb$_x$Te$_3$ samples. The band gaps of the hot-deformed Bi$_{2-x}$Sb$_x$Te$_3$ ($x = 1.4–1.7$) bulk samples were roughly estimated using the relationship between the peak $\alpha$ and the corresponding temperature, that is, $E_g = 2\alpha_{\text{max}}T_{\text{max}}$. Slight band gap enhancement was observed from $x = 1.4$ ($E_g = 0.11$ eV) to $x = 1.7$ ($E_g = 0.18$ eV). The behaviors of $T_{\text{max}}$ and $n_{\text{H}}$ as functions of $x$ are also shown in Figure 3c. It is clear that the temperature at which $\alpha_{\text{max}}$ is observed gradually rises as the Sb content increases from 1.4 to 1.8 because of the suppression of the detrimental effects of minority carriers on $\alpha$.

A plot of the calculated power factors $PF = \sigma \alpha T$ is shown in Figure 4. The value of $PF$ increases considerably with increasing $x$, because of a substantial improvement in $\sigma$. All the HD samples exhibit higher $PF$ values than their HP counterparts, except when $x = 1.4$. A maximum value of $4.5 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$ was achieved at room temperature for the HD-Sb1.7 sample, approximately 20% higher than without HD.

In-plane thermal conductivity was measured using the method introduced by Xie et al.\textsuperscript{38} The variation of in-plane $\kappa$ with temperature is plotted in Figure 5a. The rise of $\kappa$ at room temperature with increasing $x$ is mainly ascribed to an increase in the electronic contribution $\kappa_e$, which is estimated by the Wiedeman–Franz relationship ($\kappa_e = L_0 T$) using the Lorentz constant, $L_0$, of $2.0 \times 10^{-8}$ V$^2$K$^{-1}$. The value of $\kappa_e$ calculated at 298 K for the HD-Sb1.4
The sample is 0.08 Wm$^{-1}$K$^{-1}$. This value increases to 1.22 Wm$^{-1}$K$^{-1}$ for the HD-Sb1.8 sample. The value of $\kappa_{ph}$, approximately equal to $\kappa - \kappa_{el}$ before the intrinsic excitation, is plotted as a function of temperature in Figure 5b. The HD samples have enhanced (00l) texture; therefore, higher in-plane $\kappa$ values are generally expected. However, the HD samples have lower values of $\kappa$ when compared with their HP counterparts, likely as a result of enhanced phonon scattering by local nanostructures and high-density lattice defects created by HD processing, as demonstrated earlier.\textsuperscript{7,21–23} In particular, the extremely low $\kappa_{ph}$ obtained for the HD-Sb1.8 sample (0.28 Wm$^{-1}$K$^{-1}$) at 355 K is only approximately 45% of that for its HP counterpart.

**Suppression of ambipolar thermal conductivity**

Within the intrinsic conduction region, there is an additional component to the thermal conductivity arising from the diffusion of electron-hole pairs, called the ambipolar component $\kappa_{amb}$. Sizeable values of $\kappa_{amb}$ have serious adverse effects on the $\kappa$, which are particularly notable in the samples with low Sb content. We evaluated $\kappa_{amb}$ for the materials presented in this work to compare the ambipolar contribution to $\kappa$ for alloys of different Sb content. In cases where $\kappa_{amb}$ has no role, the relationship between the $\kappa_{ph}$ and the reciprocal of temperature ($1/T$) is theoretically linear ($\kappa_{ph} \propto 1/T$). Assuming a negligible effect of $\kappa_{amb}$ on $\kappa$ before intrinsic excitation, the difference between the calculated $\kappa_{ph}$ and experimental $\kappa - \kappa_{el}$ is approximately equal to $\kappa_{amb}$ (Figure 6a). The value of $\kappa_{amb}$ increases with temperature, but the magnitude of the increase reduces with increasing $x$. This may be ascribed to the suppression of intrinsic
conduction by increases in both the hole concentration and band gap (Figure 6b). For example, the $\kappa_{\text{amb}}$ value calculated at 400 K for the HD-Sb1.5 sample is 0.36 Wm$^{-1}$K$^{-1}$, but it is only 0.07 Wm$^{-1}$K$^{-1}$ for the HD-Sb1.8 sample. This approximate 80% reduction indicates that the detrimental effects of intrinsic conduction are substantially suppressed by increased Sb content.

The materials parameter $\beta$ and dimensionless figure of merit $ZT$

The materials parameter ($\beta$, Figure 7) is proportional to $(\mu/k_{\text{ph}})(m^*/m_0)^{3/2}$ and determines the TE efficiency. Enhancing TE performance requires an increased ratio of carrier mobility to lattice thermal conductivity, along with a high effective mass. Obviously, the value of $(\mu/k_{\text{ph}})(m^*/m_0)^{3/2}$ at 300 K rises with increasing Sb content in our bulk polycrystalline samples. HD remarkably improves $\beta$, showing its promise as a preparation technique for high performance TE materials.

The dimensionless figure of merit, with both electrical and thermal properties measured along the in-plane direction as a function

---

Figure 7 $(\mu/k_{\text{ph}})(m^*/m_0)^{3/2}$ as a function of the Sb content, $x$, at 300 K.

Figure 8 (a) Temperature dependences of $ZT$ values, (b) $ZT$ values at 300 and 380 K as a function of Sb content $x$, as well as data from Ivanova,$^{53}$ Yim,$^{24}$ Fan.$^{48}$ (c) Average $ZT_{\text{av}}$ values of the hot-deformed Bi$_{2-x}$Sb$_x$Te$_3$ bulk samples, (d) $ZT$ values of the Bi$_{0.3}$Sb$_{1.7}$Te$_3$ samples prepared several times to demonstrate processing repeatability, and (e) the maximum $ZT$ value compared with some other typical work using the traditional composition Bi$_{0.5}$Sb$_{1.5}$Te$_3$$^{5,6,8,24}$ (The yellow-shadowed part indicates the overvalued $ZT$ determined by in-plane $\sigma$ and out-of-plane $k$).
of temperature, is calculated and displayed in Figure 8a. Considerable enhancement in ZT was obtained via raising $x$, especially at elevated temperatures. Deformation process further optimizes the ZT. The Sb-rich HD-Sb1.7 sample shows the highest ZT (approximately 1.3) at 380 K, almost 45% better than its HP approach (maximum concentration with increasing Sb content, the temperature of the samples for power generation at higher temperatures will be richer in and HD, so the optimum composition of the polycrystalline bulk samples for power generation at higher temperatures will be richer in Sb (Figure 8b).

Owing to the gradual increases in the band gap and hole concentration with increasing Sb content, the temperature of the HD-Sb1.7 sample was re-prepared twice using the same procedure. Highly repeatable, excellent ($ZT = 1.1$)8 or the Bridgman technique ($ZT = 1.0$),24 is comparable to a value achieved with a bottom-up ball milling approach ($ZT = 1.4$),6 as shown in Figure 8e. Li et al.53 also reported a high ZT (approximately 1.33) at 373 K for ball-milled Bi$_{0.3}$Sb$_{1.7}$Te$_3$ alloys with SiC nanoparticles but not for Bi$_{0.3}$Sb$_{1.7}$Te$_3$. It is also worth noting that the use of both the in-plane $\sigma$ and out-of-plane $\kappa$ to determine the ZT would lead to an overvalued figure of 1.9 (the shadow part in Figure 8e), despite its weak texture. However, property anisotropies were neither mentioned nor discussed in detail for the high ZT values reported in previous studies.4,6,8

In summary, we successfully shifted the maximum ZT values of p-type bismuth telluride-based alloys to relatively high temperatures (approximately 380 K) by Sb-alloying. The detrimental effects of minority carriers on the Seebeck coefficient and thermal conductivity were suppressed as a result of increases in both the hole concentration and band gap. High-performance bismuth telluride-based alloys were fabricated utilizing the HD method. The formation of preferred orientation during the HD process is beneficial to the improvement of electrical conductivity. A donor-like effect partially compensated for the hole concentration, increasing the Seebeck coefficient. Aside from this, the lattice thermal conductivity was considerably reduced by the presence of recrystallization-induced in situ nanostructures and high-density lattice defects. As a consequence of these factors, the hot-deformed Bi$_{0.3}$Sb$_{1.7}$Te$_3$ alloy, rather than the typical Bi$_{0.3}$Sb$_{1.7}$Te$_3$ composition, showed a maximum ZT of 1.3 at 380 K and the largest average $ZT_{av}$ of 1.18 in the range of 300–480 K. These data indicate significant promise for these materials in low-temperature power generation. As these results proved extremely reproducible, this is a simple top down route and improved thermoelectric properties. Energy Environ. Sci. 3, 1519–1523 (2010).

[ACKNOWLEDGEMENTS]

The work was supported by the National Basic Research Program of China (2013CB632503), the Nature Science Foundation of China (51061120455 and 51271165), the PhD program of the Foundation of the Ministry of Education of China (Nos. 20120101100082 and 2010101110024) and the Program for New Century Excellent Talents in University (NCET-12-0495).
29 Oh, T. S., Hyun, D. B. & Kolomoets, N. V. Thermoelectric properties of the hot-pressed (Bi,Sb)2(Te,Se)3 alloys. *Scripta Mater.* **42**, 849-854 (2000).

30 Austin, I. G. The optical properties of bismuth telluride. *Proc. Phys. Soc. Lond.* **72**, 545-552 (1958).

31 Black, J., Conwell, E. M., Seigle, L. & Spencer, C. W. Electrical and optical properties of some M:VBiNVI-B semiconductors. *J. Phys. Chem. Solids* **2**, 240-251 (1957).

32 Kohler, H. Non-parabolicity of highest valence band of Bi2Te3 from Shubnikov-Dehaas effect. *Phys. Status Solidi. B* **74**, 591-600 (1976).

33 Kohler, H. Non-parabolic E(K) relation of lowest conduction-band in Bi2Te3. *Phys. Status Solidi. B* **73**, 95-104 (1976).

34 Langhammer, H. T., Stordeur, M., Sobotta, H. & Riede, V. IR transmission investigations of Sb2Te3 single-crystals. *Phys. Status Solidi. B* **123**, K47-K51 (1984).

35 Sehr, R. & Testardi, L. R. Optical properties of p-type Bi1-xSbxTe3 alloys between 2-15 microns. *J. Phys. Chem. Solids* **23**, 1219-1224 (1962).

36 Smith, M. J., Knight, R. J. & Spencer, C. W. Properties of Bi2Te3-Sb2Te3 alloys. *J. Appl. Phys.* **33**, 2186-2190 (1962).

37 Chen, C., Liu, D. W., Zhang, B. P. & Li, J. F. Enhanced thermoelectric properties obtained by compositional optimization in p-type Bi2Sb3.4Te fabricated by mechanical alloying and spark plasma sintering. *J. Electron. Mater.* **40**, 942-947 (2011).

38 Xie, W. J., He, J., Zhu, S., Holgate, T., Wang, S. Y., Tang, X. F., Zhang, Q. J. & Trit, T. M. Investigation of the sintering pressure and thermal conductivity anisotropy of melt-spun spark-plasma-sintered (Bi,Sb)2Te3 thermoelectric materials. *Mater. Res.** **26**, 1791-1799 (2011).

39 Logerger, F. K. Topological reactions with ferromagnetic oxides having hexagonal crystal structures. *J. Inorg. Nucl. Chem.* **9**, 113-123 (1959).

40 Fan, X. A., Yang, J. Y., Zhu, W., Bao, S. Q., Duan, J. X., Xiao, C. J., Zhang, Q. Q. & Xie, Z. J. Effect of nominal Sb2Te3 content on thermoelectric properties of p-type (Bi2Te3)x(Sb2Te3)1-x alloys by MA–HP. *Phys. D** **39**, 5069-5073 (2006).

41 Zhao, L. D., Zhang, B. P., Li, J. F., Zhang, H. L. & Liu, W. S. Enhanced thermoelectric and mechanical properties in textured n-type Bi2Te3 prepared by spark plasma sintering. *Solid State Sci.* **10**, 651-658 (2008).

42 Fan, X. A., Yang, J. Y., Zhu, W., Bao, S. Q., Duan, X. K., Xiao, C. J., Zhang, Q. Q. & Xie, Z. J. Enhanced thermoelectric properties of n-type Bi2Te3-xSb2xTe3 (0=x=0.3). *Nano Lett.* **10**, 3373-3378 (2010).

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/3.0/