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# The Anisotropic High Thermoelectric Performance in $(Bi_xSb_{1-x})_2Te_3$

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### Abstract

The anisotropy of thermoelectric properties for  $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$  (0.16  $\leq x \leq$  0.24) are investigated in the temperature range of 300K to 523K. Anisotropy ratios of the specimens are around 0.72-0.93 and 1.0-1.26 for the resistivity and the thermal conductivity, respectively. In addition, a relation of  $k_{\perp} \approx k_{//} / (1 - f)$  is found to hold, suggesting the validity of the rule of mixture for its k and *f*. The maximum ZT=1.37 (at 416K) are achieved for  $(\text{Bi}_{0.16}\text{Sb}_{0.84})_2\text{Te}_3$ . Besides,  $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$  sample shows good mechanical properties. The compression strength for  $(\text{Bi}_{0.16}\text{Sb}_{0.84})_2\text{Te}_3$  is 60MPa and 65MPa in the two measured directions, which is 6 folds and 1.6 times as larger as that of commercial ingot parallel and normal to the solidification direction, respectively.

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### Introduction

Thermoelectric (TE) materials are among the important potential candidates for alternative and complementary sources for energy, wherein heat can be directly converted into electrical energy and vice versa [1]. Efficient TE materials should exhibit a high thermoelectric figure of merit defined as ZT=S\_T/( $\rho\kappa)$ , where T, S,  $\rho,$  and  $\kappa$  are the absolute temperature, Seebeck coefficient, electrical resistivity and thermal conductivity, respectively [2]. Among the traditional thermoelectric materials, Bi<sub>2</sub>Te<sub>3</sub>-based materials, including p-type  $(Bi_xSb_{1-x})_2Te_3$  and n-type  $Bi_2Te_{3-y}Se_y$ , are well known as the most efficient TE materials that operate near room temperatures [3,4].  $Bi_{7}Te_{3}$  has a rhombohedra structure with the space group R3m. Along the c-axis, the atom layers array in the structure of -Te(1)-Bi-Te(2)-Bi-Te(1)-; the -Te(1)-Te(1)- atomic layers are bonded by the weak van der Waals force, so they are liable to cleavage [5]. Originating from this unique structural anisotropy, anisotropies in resistivity and thermal conductivity are observed for Bi<sub>2</sub>Te<sub>3</sub>-based compounds [6-9]. The experiments suggest that the anisotropy ratios range from 4.3 to 6.7 for the resistivity, and 2.1 to 2.5 for the thermal conductivity. Due to the isotropy for Seebeck coefficient, ZT along the cleavage planes is approximately twice to three times as large as that along the c-axis. The anisotropic characteristics of ZT will inevitably result in reduced efficiency in utilization of Bi<sub>2</sub>Te<sub>3</sub>-based alloys. On the other hand, Bi, Te, -based alloys with high structural anisotropy have poor mechanical properties due to cleavage fractures, which causes problems in cutting or/and operating the material. Hence, it is of vital significance to obtain highly isotropic superior thermoelectric performance for anisotropic Bi<sub>2</sub>Te<sub>3</sub>-based alloys with good mechanical properties for large-scale commercial applications.

Several methods have been used to obtain isotropic  $Bi_2Te_3$ -based bulk materials. For example, by sintering nano-sized spherically shaped powder synthesized via chemical reaction method, Kim et al. [6] obtained isotropic p-type  $Bi_{0.5}Sb_{1.5}Te_3$  bulk sample that had no directional difference in TE properties, and the ZT value of 1.1 in both parallel and normal to the consolidated direction was obtained. Through ball milling and hot pressing of  $Bi_2Te_3$ -based n-type single crystals, isotropic ZT had been achieved for  $Bi_2Te_3$ -Se\_{0.3} bulk sample with the peak ZT of 0.85 in both directions parallel and normal to the pressing direction [8]. Unfortunately, although there have been a few reports related to the preparation of isotropic  $Bi_2Te_3$ -based alloys, the obtained ZT values for the isotropic materials are not high to meet the requirements of large scale applications. As a matter of fact, to achieve isotropic superior thermoelectric performance for  $Bi_2Te_3$ -based alloys with good mechanical properties, one needs not only to reduce (or eliminate) the anisotropy in their microstructures, but also to enhance (or maintain) both power factor (PF) and phonon blocking in  $Bi_2Te_3$ -based alloys. In this aspect, nano-inclusions have been shown to be efficient. They are found to be able to simultaneously scatter the phonons and filter the lower-energy carriers so that both the power factor and thermal conductivity contributions could be synergistically improved [10,11]. To our knowledge; however, the attempt to achieve superior thermoelectric performance for  $Bi_2Te_3$ -based alloys in different measured direction is not successful until today [6].

In the present work, isotropic microstructure and high ZT are obtained for  $(Bi_x Sb_{1-x})_2 Te_3$  with x=0.16, 0.18 and 0.20 in the both measured directions. The largest ZT=1.37 (at 416K) are achieved for  $(Bi_{0.16}Sb_{0.84})_2 Te_3$ , which is attributed to both the lowering of  $\kappa$  from enhanced phonon scattering due to  $Sb_2O_3$  nano-inclusions and the elevated S via intensified energy filtering effect from interphase potentials. In addition, the compression strength for  $(Bi_{0.16}Sb_{0.84})_2 Te_3$  in this work is 60MPa and 65MPa in the two measured direction, which is six folds and 1.60 times as larger as that of commercial ingot parallel and normal to the directional solidification direction, respectively.

### **Experimental Section**

#### Sample preparation

Elemental Bi (99.99%, Alfa Aesar), Sb (99.5%, Sigma Aldrich) and Te (99.999%, Alfa Aesar) powders are weighted according to the formula of  $(Bi_xSb_{1-x})_2Te_3(x=0.16-0.24)$  doped with 3 wt% Te. The powder mixture is loaded into quartz ampoule sealed under vacuum at  $10^{-2}$  Pa, and then heated at 800°C for 10 h. Then the ingots are ground into powder by using a mortar for one hour.

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The powders about 28g are compacted by spark plasma sintering (SPS)at a pressure of 50 MPa in a diameter of 20 mm graphite mould in vacuum for 5 min. The sintering temperature, heating rate and cooling rate are 673 K, 373 K/min and 373K/min, respectively. After SPS, bulk samples with dimensions of cylinder 20 mm od  $\times$  12 mm length are obtained.

### Microstructure characterization

The sample is characterized by X-ray diffraction (XRD) using Philips X'Pert PRO X-ray diffractometer equipped with graphite monochromatic Cu K $\alpha$  radiation ( $\lambda$ = 1.54056 Å). The operation voltage and current are kept at 40 kV and 400 mA, respectively. TEM (transmission electron microscope) observations were performed on a JEOL-F2010 instrument with an acceleration voltage of 200 kV. The morphology is characterized by field emission scanning electron microscopy (FESEM; SU8020).

## Measurements of thermoelectric properties and mechanical properties

A commercial four-probe apparatus (ULVAC-RIKO ZEM-3) is applied to measure the electrical resistivity and Seebeck coefficient of the bar samples. The thermal diffusivity D is obtained by a laser flash method (Netzsch LFA-457) performed on rectangle samples. The specific heat,  $C_p$ , is determined from the DSC measurement (Pyris Diamond DSC, Perkin-Elmer). The thermal conductivity is calculated from  $\kappa = DC_p d$ , where d is the density of the sample determined by Archimedes' method. The hole concentration at 300K is measured using a physical properties measurement system (Quantum Design). The measurements of room-temperature compression strengths of the samples are carried out on Instron 3369.

### **Results and Discussion**

Figure 1 shows the X-ray diffraction (XRD) patterns of bulk samples sliced normal ( $\perp$ ) to the pressing direction for (Bi<sub>x</sub>Sb<sub>1</sub>, <sub>x</sub>)<sub>2</sub>Te<sub>3</sub>(0.16≤x≤0.24), respectively. The main diffraction peaks can be indexed to the standard Bi<sub>0.4</sub>Sb<sub>1.6</sub>Te<sub>3</sub> (JCPDS No.72-1836) phase belonging to the rhombohedra structure, and the additional peak located at about 28° is observed, which is attributed the excessive Te (JCPDS No. 01-1313) added. In order to quantitatively describe the anisotropy of the sample, orientation factor (f) was calculated by

the Lotgering method,  ${}^{12}f=(P-P_0)/(1-P_0)$ , where P is the fractional intensity of the (00l) diffraction peak, P=I(00l)/ $\Sigma$ I(hkl), and P<sub>0</sub> is the diffraction intensity of (0 0 l) peak for isotropic (i.e. no preferred orientation) Bi<sub>0.4</sub>Sb<sub>1.6</sub>Te<sub>3</sub> (JCPDS No.72-1836). Based on the XRD diffractograms, the orientation factor for (Bi<sub>x</sub>Sb<sub>1.x</sub>)<sub>2</sub>Te<sub>3</sub> sliced normal to the pressing direction (*f*) is 0.05, 0.03, 0.11, 0.06 and 0.11 for x=0.24, 0.22, 0.20, 0.18 and 0.16, respectively, as seen Table 1. The density for samples (as shown in Table 1)basically decreases with decreasing bismuth content. For example, *d* decreases from 6.68 gcm<sup>-3</sup> for x=0.24 to 6.51 gcm<sup>-3</sup> for x=0.16. The relative densities *d*<sub>R</sub> for samples have almost the same porosity.

| Sample   | f    | d (g/cm <sup>3</sup> ) | dR    | $\sigma_{\perp}$ (MPa) | σ <sub>//</sub> (MPa) |  |  |
|--|------|------------------------|-------|------------------------|-----------------------|--|--|
| x=0.24   | 0.05 | 6.68                   | 96.8% | /                      | /                     |  |  |
| x=0.22   | 0.03 | 6.65                   | 96.9% | /                      | /                     |  |  |
| x=0.20   | 0.11 | 6.63                   | 97.2% | /                      | /                     |  |  |
| x=0.18   | 0.06 | 6.53                   | 96.5% | /                      | /                     |  |  |
| x=0.16   | 0.11 | 6.51                   | 96.6% | 65                     | 60                    |  |  |
| x=0.16 ingot   | 1    | 1                      | /     | 40                     | 10                    |  |  |
| Table 1: List of orientation factor $f_{1}$ density $d_{2}$ relative density |      |                        |       |                        |                       |  |  |

 $d_{\rm p}$ , compression strength  $\sigma_{\rm l}$  and  $\sigma_{\rm ll}$ .

The low-magnification FESEM image for  $(Bi_{0.16}Sb_{84})_2Te_3$  fractured normal to the pressing direction (Figure 2a) reveals that a large number of small particles are randomly embedded among the particles with micron dimension. A high-magnification FESEM image (Figure 2b) demonstrates that the small particles are around the size of 30-80 nm. The low-magnification FESEM image for  $(Bi_{0.16}Sb_{84})_2Te_3$  fractured parallel to the pressing direction (Figure 2c) reveals many small dots embedded among the layered structure. The high-magnification FESEM image (Figure 2d) confirms that the small particles are around the size of 30-80 nm and the thickness of the lamellar structure is in the range of 100-200nm.

Figure 3 shows the TEM results for  $(Bi_{0.16}Sb_{84})_2Te_3$  sliced normal (Figure 3(a-c)) and parallel (Figure 3(d-h)) to the pressing direction. The low magnification TEM image for  $(Bi_{0.16}Sb_{84})_2Te_3$  sliced normal to the pressing direction (Figure 3(a)) demonstrates that many nanoparticles with size of 50-80nm existed in the matrix with submicron size



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Figure 2: FESEM images of the fracture surfaces of bulk samples for  $(Bi_{0.16}Sb_{0.84})_2Te_{35}$  fractured normal and parallel to the pressing direction



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in three forms: along grain boundaries, inside grains and filling the pores. The typical HRTEM image (Figure 3(b)) of an individual nanoparticle reveals that the products are well crystallized and the lattice fringes can be observed clearly. The regular parallel fringe spacing is about 6.44 Å and 3.93 Å, which can be assigned to the interplanar spacing of the (11 1) and (2 2 0) lattice plane of cubic Sb<sub>2</sub>O<sub>2</sub>. The Fourier transfer diffraction pattern of white square part for nanoparticle is given in the inset of Figure 3(b), confirming that the nanoparticle is Sb<sub>2</sub>O<sub>2</sub>. The energy dispersive X-ray spectroscopic (EDX) patterns (Figure 3(c)) obtained on the nanoparticle confirm that they are compound of element Sb and O with the atomic ratio of Sb: O=2: 2.95. As indicated in the low magnification TEM image of Figure 3(d) for  $(Bi_{0.16}Sb_{84})_2$  Te<sub>3</sub> sliced parallel to the pressing direction, the dark triangle submicron particles are observed to exist along the grain boundaries, and the bright nanoparticles with size of around 50nm in the pore are found in the matrix. The EDX analysis for the dark triangle particle as shown in Figure 3(e) indicates that it is Tellurium. The selected-area electron diffraction (SAED) image taken from the dark triangle particle in theinset of Figure 3(e) confirms that it is a well-crystallized Te crystal. An amplified HRTEM image focusing on theedge of Te particle is presented in Figure 3(f), which indicates that the lattice spacing of about 5.96Å corresponds to (001) planes ofhexagonal Te. The HRTEM image of bright nanoparticle as shown in Figure 3(g) reveals that the interplanar spacing of about 6.44 Å can be assigned to the (11 1) lattice plane of cubic  $Sb_2O_3$ . The amplified HRTEM image for matrix is presented in Figure 3(h). The lattice spacing of about 1.02nm corresponds to  $(0 \ 0 \ 3)$ planes of rhombohedral (Bi<sub>0.16</sub>Sb<sub>84</sub>)<sub>2</sub>Te<sub>3</sub>. SAED image taken from

the matrix in the inset of Figure 3(h)shows that spacing distance of 1.02nm is a five-layer lamellae with orientation arrangement along the [0 0 1] direction. EDX results obtained on the matrix indicate that the atomic ratio for Bi: Sb:Te in  $(Bi_{0.16}Sb_{84})_2Te_3$  is 0.34:1.59:3.

Temperature dependence of electrical resistivity measured normal ( $\rho_{\perp}$ ) and parallel ( $\rho_{\mu}$ ) to the pressing direction is plotted in Figure 4(a) and Figure 4(b), respectively. The dependence of  $\rho$  on temperature for the samples as shown in Figure 4(a) and Figure 4(b) is similar: the electrical resistivity increases with the increase of temperature, whic hindicates that the materials exhibit metallic-like or degenerate semiconductor behavior. In addition,  $\rho$  for  $(Bi_{s}Sb_{1,s})_{2}Te_{3}$  $(0.16 \le x \le 0.24)$  decreases with decreasing Bi content. For example,  $\rho_{1}$  and  $\rho_{1}$  at room temperature decreases from  $1.87 \times 10^{-5} \Omega$  m and  $2.24 \times 10^{-5} \Omega$  m to  $0.86 \times 10^{-5} \Omega$  m and  $1.08 \times 10^{-5} \Omega$  m with decreasing x from 0.24 to 0.16, respectively. Moreover, for the same sample,  $\rho_{1/2}$  is larger than  $\rho_{1/2}$  at the same temperature. The ratio  $\rho_{1/2}/\rho_{1/2}(=\mu_{1/2}/2)$  $\mu_1$ ) for  $(Bi_x Sb_{1-x})_2 Te_3$  (0.16 $\leq x \leq 0.24$ ) is presented in Figure 3(c), which is in the range of 0.72-0.93 and basically independent on the temperature. The positive values of Seebeck coefficient for (Bi\_Sb, ), Te, (0.16 $\leq$ x $\leq$ 0.24) measured normal (S<sub>1</sub>) and parallel (S<sub>1</sub>) to the pressing direction determined over the temperature range of 300 K to 523 K, as shown in Figure 5(a) and Figure 5(b), respectively, means that the major charge carriers in the samples are holes. The Seebeck coefficient for the samples is observed to increase with increasing temperature, and after reaching a maximum value, it shows a decrease with further increase in temperature. This behavior has been reported previously and is probably due to the excitation of minority carrier at



 $\begin{array}{l} \mbox{Figure 4: Temperature dependent (a, b) electric resistivity}(\rho_{\perp}, \rho_{//}), (c) \\ \mbox{ratio of } \rho_{\perp}/\rho_{//} \mbox{for } (Bi_x Sb_{1,x})_2 Te_3 \ (0.16{\le}x{\le}0.24) \end{array}$ 

high temperature [6]. The ratio of S<sub>1</sub> to S<sub>1</sub> is presented in Figure 5(c). It can be seen that the ratio of S<sub>1</sub> to S<sub>1</sub> ( $Bi_xSb_{1-x})_2Te_3$  (0.16≤x≤0.24) in the measured temperature range is in the range of 0.9-1.1, which indicates that the Seebeck coefficient for ( $Bi_xSb_{1-x})_2Te_3$  (0.16≤x≤0.24) are isotropic within the experimental error.

The Hall coefficient, RH, at room temperature (RT) is positive for  $(Bi_xSb_{1,x})_2Te_3$  (0.16 $\leq$ x $\leq$ 0.24), indicating *p*-type or hole conduction in this system, which agrees with the results of Seebeck coefficient. Assuming parabolic bands and a single band conduction process at 300 K, the carrier concentration, *p*, is estimated from the formula: *p*=1/eRH, where e is the carrier charge. The carrier concentrations *p* are 1.54×1019, 2.10×1019, 2.76×1019, 3.33×1019 and 3.73×1019 cm<sup>-3</sup> for samples with x=0.24, 0.22, 0.20, 0.18 and 0.16, respectively (Table 2). Hence, it is the increase incarrier concentration that causes the decrease in electrical resistivity with decreasing bismuth content. The RThole mobility calculated from the equation  $\mu$ =1/( $\rho$ pe), and is listed in Table 2. One can see that for the same sample,  $\mu_{\perp}$  is larger than  $\mu_{//}$ , and thus the larger  $\rho_{//}$  than that of  $\rho_{\perp}$ . Conflicting with the Mott formula[13]

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Figure 5: Temperature dependent (a, b) Seebeck coefficient  $(S_{\perp}, S_{//})$ , (c) ratio of  $S_{\perp}/S_{//}$ , (d) variation of Seebeck coefficient with carrier concentration for x=0.16. Thesolid line is Pisarenko relation for ingot  $(Bi_xSb_{1,x})_2Te_3$ .

$$S = \frac{\pi^2}{3} \frac{k_B}{q} k_B T \left\{ \frac{d \ln(\sigma(E))}{dE} \right\}_{E=E_F}$$
(1)

| Sample | $\mu_{\perp}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) | $\mu_{//}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) | p(×10 <sup>19</sup> cm <sup>-3</sup> ) | $r_{\perp}$ | r <sub>//</sub> |
|--------|--|---|--|-------------|-----------------|
| x=0.24 | 217  | 181   | 1.51                                   |             |                 |
| x=0.22 | 212  | 184   | 2.10                                   |             |                 |
| x=0.20 | 213  | 160   | 2.76                                   |             |                 |
| x=0.18 | 196  | 141   | 3.33                                   |             |                 |
| x=0.16 | 195  | 155   | 3.73                                   | 1.43        | 1.49            |

Table 2: List of room temperature Hall mobility  $\mu, {\rm carrier}$  concentration p, and scattering factor r for (Bi\*Sb1-x)²Te³ (0.16≤x≤0.24)

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which tells us that *S* decreases with increasing *p*,  $S_{//}$  or  $S_{\perp}$  for (Bi<sub>x</sub>Sb<sub>1</sub>,  $_{x})_{2}$ Te<sub>3</sub> (0.16≤x≤0.24) does not monotonically decrease with increasing *p*. For example, although RT carrier concentration for x=0.22 is 2.10 ×1019cm<sup>-3</sup>, which is smaller than that (2.76 ×1019cm<sup>-3</sup>) of x=0.20, S<sub>//</sub> for x=0.22 is smaller than that of x=0.20 in the measured temperature range, which means that other mechanisms also work. Due to the existence of Sb<sub>2</sub>O<sub>3</sub> nanoparticles phase as observed in TEM results, hetero-junction potential barriers (or wells) should be formed at the phase interfaces, which could cause energy-dependent scattering of carriers. The density of state effective mass  $m_{d}^{*}$  is calculated based on the measured RT *p*=2.60×1019/cm<sub>3</sub> and *S*=182.1µV/K for ingot (Bi<sub>0.16</sub>Sb<sub>0.84</sub>)<sub>2</sub>Te<sub>3</sub> without nano-inclusions (S<sub>0</sub>) using the equations expressed as follows [14]:

$$m_{d}^{*} = \frac{h^{2}}{2k_{B}T} \left[ \frac{p}{4\pi F_{1/2}(\eta)} \right]^{2/3}$$
(2)

$$S = \pm \frac{k_B}{q} \left[ \frac{(r+5/2) F_{r+3/2}(\eta)}{(r+3/2) F_{r+1/2}(\eta)} - \eta \right]$$
(3)

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1 + e^{x - \eta}} dx \tag{4}$$

 $\eta$  is the reduced Fermi energy,  $Fn(\eta)$  is the nth order Fermi integral, h is Plank constant, kB is the Boltzmann constant, and r is scattering parameter of relaxation time. In our calculations, we assume acoustic phonon scattering dominates (i.e., r=-1/2), and the effective mass md\* is obtained to be 1.01m0 (where m0 is the free electron mass) for S0, which is close to the reported value of  $m_0$  [15]. Assuming  $m_1^*$  for the nano-composite samples is the same as that of S<sub>0</sub> and does not change in different samples,  $r_{\!_\perp}\!=$  1.43 or  $r_{\!_/\!}\!=$  1.49 at 300K can be obtained according to the above eqn (2-4) using the measured S and carrier concentration (p), which indicates that r values of  $(Bi_{0.16}Sb_{0.84})_2Te_3$ embedded with  $Sb_2O_3$  are larger than that of  $S_0$ . This increase in  $r_{1/2}$ results in an increase of about 42µV/K above an expected value in S results in an increase of about  $42\mu V/K$  above an expected value in  $S_{11}$  at 300K for the at 300K for the samples with x=0.16, as shown in Figure 5(d)(where the solid line is Pisarenko relation [16] for ingot  $(Bi_{0.16}Sb_{0.84})_2Te_3)$  and shows the dependence of S on p calculated by using Eqs. (2)-(4) and  $m^*=1.01m_0$  for ingot  $(Bi_{0.16}Sb_{0.84})_2Te_3)$ .

The effects of temperature on the thermal conductivity ( $\kappa_{\perp}$  and  $\kappa_{//}$ ) for(Bi sb<sub>1.x</sub>)<sub>2</sub>Te<sub>3</sub> (0.16≤x≤0.24)are presentedin Figure 6(a) and Figure 6(b), respectively. As seen in Figure 6(a) and Figure 6(b), the temperature dependence behavior of the thermal conductivity for the samples is similar: it decreases with increasing temperature and then increases with further increasing temperature. Such behavior is typical of crystalline materials. The ratio of  $\kappa_{\perp}$  to  $\kappa_{//}$  is plotted in Figure 6(c). It can be seen that for x =0.24, the value of  $\kappa_{\perp}/\kappa_{//}$  for (Bi sb<sub>1.x</sub>)<sub>2</sub>Te<sub>3</sub> (0.16≤x≤0.22) is in the range of 1.10-1.26. Interestingly, we find that there exists a relation of  $\kappa_{\perp}/\kappa_{//} = /(1-f)$  or  $\kappa_{\perp} = \kappa_{/}/(1-f)$  in (Bi sb<sub>1.x</sub>)<sub>2</sub>Te<sub>3</sub> system, as shown in Figure 6(d). The result implies that the relationship between thermal conductivity and orientation factor *f* could conform to the rule of mixture as follows

$$k_{ii} = kf_i + (1 - f)k_{\perp}$$
(5)

Where  $\kappa_{i//}$  is the intrinsic thermal conductivity along c-axis for a single crystal. Formula (5) illustrates that: (a) as f=1 (which means that the sample is complete anisotropy in its microstructure, just as a single crystal with c-axis along pressing direction),  $\kappa_{p} = \kappa_{i//2}$ 



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Figure 6: The plot of (a,b) thermal conductivity  $(\kappa_{\perp}, \kappa_{//})$ , (c) ratio of  $\kappa_{\perp}/\kappa_{//}$  with temperature, (d) plot of  $\kappa_{\perp}$  and  $\kappa_{//}/(1-f)$  with x in (Bi<sub>0.16</sub>Sb<sub>0.84</sub>)<sub>2</sub>Te<sub>3</sub>).

indicating formula (5) holds; (b) a *f*=0 (that means the sample is complete isotropy in its microstructure and the thermal conductivity measured in any direction is identical),  $\kappa_{//} = \kappa_{\perp}$ , indicating formula (5) holds as well; (c) as f<<1,the first term in the right,  $f\kappa_{i//}$ , can be neglected as compared tothe second term (1-f) $\kappa_{\perp}$ , and formula (5) canbe reduced to  $\kappa_{\perp} = \kappa_{i//} (1-f)$ , which has already been verified by our experimental results (Figure 6(d)); (d) in a more general case, if 0<f<1,

the term  $f_{\kappa_{i/l}}$  cannot be ignored, then formula (6) can be written as:

$$k_{\perp} = \frac{k_{//} - f k_{i//}}{1 - f} \tag{6}$$

Subtracting the carrier thermal conductivity ( $\kappa$ C), expressed as  $\kappa_{\rm C} = L_0 T / \rho$  (here  $L_0$  is the Lorenz number ( $2.0 \times 10^{-8} V^2 K^{-2}$ ) and  $\rho$  is the electrical resistivity [15,17], from  $\kappa$ , the lattice thermal conductivityin the direction normal( $\kappa_{\rm L\perp}$ ) and parallel ( $\kappa_{\rm L\perp}$ ) to the pressing direction, are obtained as shownin Figure 7(a) and Figure 7(b), respectively.



power factor  $(PF_{\perp}, PF_{//})$  with temperature.

The reduction of  $\kappa_{L\perp}$  and  $\kappa_{L//}$  for  $(Bi_x Sb_{1-x})_2 Te_3$  (0.16 $\le$ x $\le$ 0.24) with increasing antimony content is attributed to the scattering phonons of point defects due to mass fluctuation. Due to the layered structures, besides many grain boundaries, the intrinsic lattice thermal conductivity is lower in the direction parallel to the pressing direction than that in the direction normal to the pressing direction, resulting from stronger phonon scattering in the direction parallelto the pressing direction. It should be noted that the thermal conductivity for  $(Bi_x Sb_{1-x})_2 Te_3$  (0.16 $\le$ x $\le$ 0.24) in this work is lower than that reported previously, [18] which is due to the existence of Sb<sub>2</sub>O<sub>3</sub> nano-inclusions in  $(Bi_x Sb_{1-x})_2 Te_3$  (0.16 $\le$ x $\le$ 0.24) matrix.

The calculated power factor (PF<sub>⊥</sub> and PF<sub>//</sub>) for (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub> (0.16≤x≤0.24) is shown in figure 7(c) and figure (d), respectively. Due to the lower  $\rho_{\perp}$ , PF<sub>⊥</sub> is larger than that of PF<sub>//</sub> at the same temperature. For example, RT PF<sub>⊥</sub> is 4.5×10-3 Wm-1K-2 for x=0.16, which is larger than that (3.7×10<sup>-3</sup>m<sup>-1</sup>K<sup>-2</sup>) of PF<sub>//</sub>. Based on the data obtained above, the temperature dependence of ZT<sub>⊥</sub> and ZT<sub>//</sub> for (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub> (0.16≤x≤0.24) are shown in Figure 8(a) and Figure 8(b), respectively. As seen in Figure 8(a&b), the temperature behavior of ZT for the samples is similar: it increases with increasing temperature, and after reaching a maximum, ZT value decreases with further increasing temperature. Although PF<sub>//</sub> for x=0.20, 0.18 and 0.16 is lower than that



Figure 8: Temperature dependent (a, b) figure of merit  $(ZT_{\perp}, ZT_{//})$ , (c) ratio of  $ZT_{\perp}/ZT_{//}$  for  $(B_{i_x}Sb_{\perp_x})_2$ Te<sub>3</sub> (0.16≤x≤0.24).

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is lower than that of PF<sub>1</sub> in the whole temperature range investigated, ZT for x=0.20, 0.18 and 0.16 have no significant differences in the two measured directions as seen in Fig. 8(c), due to its lower thermal conductivity. The maximum ZT is 1.37(368K), 1.26(390K) and 1.37(415K) for x=0.20, 0.18 and  $\overline{0.16}$ , respectively. ZT<sub>1/1</sub> reaches the maximum value of 1.30(390K), 1.30(390K) and 1.37(415K) for x=0.20, 0.18 and 0.16, respectively. Specially, for  $(Bi_{0.16}Sb_{0.84})_2Te_3$  its peak ZT in the two directions both reaches 1.37. In addition, the compression strength  $\sigma$  for  $(Bi_{0.16}Sb_{0.84})_2Te_3$  is 60MPa and 65MPa in the direction parallel ( $\sigma_{II}$ ) and normal ( $\sigma_{II}$ ) to the pressing direction, respectively as seen in Table 1, which is 6 folds and 1.6 times as larger as that of commercial ingot parallel and normal to the directional solidification direction (See details in supplementary materials). The isotropic superior thermoelectric performance obtained for  $(Bi_{0.16}Sb_{0.84})_2Te_3$ with good mechanical properties supplies the possibility to meet the requirements of large scale applications.

### Conclusions

 $(Bi_x Sb_{1,x})_2 Te_3 (0.16 \le x \le 0.24)$  bulk samples are prepared by the melting method, mortar type grinding and spark plasma sintering technique. Due to the isotropic microstructure, highly isotropic resistivity  $(\rho_{\perp}/\rho_{\perp}) = 0.72 - 0.93$ ) and thermal conductivity ( $\kappa_{n}/\kappa_{n} = 1.0 - 1.26$ ) of  $(Bi'_{x}Sb_{1-x})_{2}Te_{3}$  are obtained. Moreover, an empirical equation  $k_{1} \approx$  $k_{\mu}/(1-f)$  holds between the thermal conductivity and orientation factor, suggesting validity of the rule of mixture. As a result, the high figure of merit in both measured directions is obtained. Specifically, the maximum ZT of 1.37 (at 417K) are achieved in both measured directions by simultaneously lowering  $\kappa$  from enhanced phonon scattering due to Sb<sub>2</sub>O<sub>3</sub> nano-inclusions and elevated S via intensified energy filtering effect attributed from the interphase potentials. In addition,  $(Bi_x Sb_{1-x})_2 Te_3$  sample also shows good mechanical properties. The superior thermoelectric performance obtained for (Bi<sub>x</sub>Sb<sub>1,x</sub>)<sub>2</sub>Te<sub>3</sub> with good mechanical properties supplies the possibility to meet the requirements of large scale applications.

### **Competing Interests**

The authors have no competing interests with the work presented in this manuscript.

### **Author Contributions**

All the authors substantially contributed to the study conception, the acquisition of results, and the interpretations as well as drafting the manuscript.

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