INTRODUCTION
Thermoelectric materials, which enable direct conversion between heat and electrical energy, show great promise for applications in waste heat recovery. Thermoelectric energy conversion generates no emissions, is quiet, and is exceptionally reliable (1–4). The conversion efficiency is defined by the dimensionless thermoelectric figure of merit ZT = a2α2σ2/kL, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and k and kL are the electronic and lattice contributions to the overall thermal conductivity (5–7). Thus, an excellent thermoelectric material should simultaneously have a large Seebeck coefficient, high electrical conductivity, and as low as possible lattice thermal conductivity (8–10). Extensive experimental and theoretical investigations have shown that electronic band structure engineering (11), doping (12–15), nanostructuring (16–20), formation of solid solutions (21, 22), and fabrication of nanocomposites (23–27) are effective strategies to optimize the thermoelectric performance.

Bismuth telluride–based materials are the most investigated systems among thermoelectric materials and have been the top-performing materials near room temperature (28–33). Innumerable research efforts have focused on improving the thermoelectric figure of merit ZT, but values significantly in excess of unity have rarely been observed (19, 23–25). This is why it was remarkable when Kim et al. (16) recently claimed a record ZT ~ 1.85 at 320 K, which has the potential to revolutionize the thermoelectric industry. The report described adding an extra 25 weight % (wt %) excess of Te to Bi0.5Sb1.5Te3 that was melt-spun and subsequently spark plasma–sintered (SPS) at 480°C and a pressure of 70 MPa, during which the excess amount of Te was expelled (squeezed out) and pure Bi0.5Sb1.5Te3 was obtained. However, as the structure is subjected to an applied pressure during SPS and the excess Te is being squeezed out, the atomic planes of Bi0.5Sb1.5Te3 are being rearranged and reoriented, giving rise to a high density of dislocation arrays between grains. These dislocations were proposed to strongly scatter midfrequency phonons markedly reducing the lattice thermal conductivity to an extremely low value of 0.33 Wm−1 K−1 with only a marginal impact on the electrical conductivity. Despite the record-high value of ZT ~ 1.85 reported for the (Bi1−xSbx)2Te3-based structure, the result has so far not been reproduced or confirmed. The subsequent effort by Jo et al. (17) incorporated a comparable amount of Te into Bi0.5Sb1.5Te3 by chemical means, whereby a ball-milled powder of Bi0.5Sb1.5Te3 was added to a solution of Te2+ polyanions dissolved in thiol-amino. The suspension was drop-cast over ceramic plates, dried, and sintered by SPS at 480°C and 70 MPa. Although the authors also observed the molten Te seeping out regardless of the amount of Te2+ polyanions, the final product always contained about 6 wt % excess of Te that formed interfacial layers between the nanograins of Bi0.5Sb1.5Te3 contrary to the findings of Kim et al. (16). However, despite the arrays of dislocations observed, the lattice thermal conductivity perpendicular to the pressure direction was still around 0.50 Wm−1 K−1 at room temperature even when the Lorenz number was used as 2.0 × 10−8 V2/K2, which is much higher than the 0.33 Wm−1 K−1 value reported by Kim et al. (16). Jo et al. (17) reported ZT values of up to 1.3 at about 400 K for their 6 wt % excess of Te incorporated in their Bi0.5Sb1.5Te3 bulk structures. This small improvement in the thermoelectric performance of Te-containing Bi0.5Sb1.5Te3 falls significantly behind the value reported by Kim et al. (16).
The impact of extra Te on the orientation of grains, the microstructure, and eventually the thermoelectric properties remains substantially obscure. In addition, there are doubts whether dense dislocation scattering can be as effective in lowering the lattice thermal conductivity to these low levels as claimed given that the well-known Bi$_{0.5}$Sb$_{1.5}$Te$_3$ structure already has a very short phonon mean-free path. Therefore, it is critical to investigate in detail the influence of the excess Te content on the microstructure and composition of melt-spun Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ribbons and the impact of Te melting and its expulsion during the SPS process on the composition, microstructure, and thermoelectric properties of sintered samples. The results show that the extra Te distributes homogeneously at the boundaries of melt-spun ribbons of Bi$_{0.5}$Sb$_{1.5}$Te$_3$. Subsequent melting and extraction of Te during SPS promotes recrystallization and directional realignment of grains to improve the orientation factor $F$ and the electrical conductivity perpendicular to the pressure direction (18). The obtained samples have a dense array of dislocations in the grain boundaries, as described by Kim et al. (16). However, the lattice thermal conductivity of these samples at 300 K, despite the large amount of dislocations and defects generated during the SPS process, shows a similar value of 0.65 Wm$^{-1}$K$^{-1}$ (17) and is much higher than 0.33 Wm$^{-1}$K$^{-1}$ reported by Kim et al. (16). As a result, the highest ZT of our samples is comparable to that measured by Jo et al. (17) but well below the value reported by Kim et al. (16). The discrepancy arises despite us following as closely as possible the procedures and techniques reported by Kim et al. (16), and our structural characterization indicates that we have obtained the samples as described by Kim et al. (16).

RESULTS AND DISCUSSION

Phase and structure characterization

Powder x-ray diffraction (XRD) patterns of melt-spun ribbons of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ with $x$ wt % excess of Te ($x = 5, 10, 15, 20, 25$) are presented in fig. S1A. The expanded view of XRD in the range of 20° to 35° in fig. S1B shows that the main Bragg peak of elemental Te is detected at 27° to 28° when $x \geq 5$. The intensity of this peak increases notably with increasing content of Te. This indicates that Te is present in its elemental form and segregates during the rapid solidification of the melt-spun ribbons. The crystal lattice of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ does not accommodate any overstoichiometric amount of Te because it is essentially a line compound. To further analyze the form and distribution of elemental Te in the ribbons, their microstructure containing various different excess amounts of Te was characterized in detail. The contact surface (the ribbon’s surface in direct contact with the rotating copper drum as the molten charge rapidly solidifies) and the free surface of ribbons containing 0 and 20 wt % of Te are shown in fig. S2A. The cross section of a ribbon with the thickness of 5 μm is shown in fig. S2B. The grain size increases gradually from the contact surface to the free surface because of the cooling rate gradient, where the contact surface experiences a much faster rate of cooling than the free surface. Consequently, the grain growth on the contact surface is significantly inhibited.

Field-emission scanning electron microscopy (FESEM) images of the contact surface of ribbons with 0 and 25 wt % excess of Te are shown in fig. S2 (C and D, respectively). In both cases, the grains are fine with the size of about 100 to 300 nm, but it is difficult to tell the difference between the two samples because of the limit of detection. FESEM images of the free surface of ribbons with 0, 5, 15, and 25 wt % excess of Te are shown in Fig. 1 (A to D, respectively). The free surface has a typical dendritic structure with the size of dendrites of about 100 to 200 nm and width and 2 μm in length. Grain boundaries in ribbons having no Te excess are smooth and clear and with no sign of the presence of any secondary phases. In contrast, grain boundaries of ribbons that have some excess of Te are blurred, and the color tone near the boundaries turns deeper than that of the matrix, as marked by red arrows. The difference in contrast increases with the increasing Te content. The composition analysis shows that grain boundaries of ribbons containing extra Te are Te-rich zones. Results of energy-dispersive spectroscopy performed on the free surface of a ribbon with 25 wt % excess of Te are shown in fig. S3. Here, spots 1 and 2 represent grains of the matrix having the main component of Bi$_{0.5}$Sb$_{1.5}$Te$_3$, JCPDS (Bi$_{x}$Te$_{y}$: 00-001-0727).
spots 3 and 4 represent a typical Bi0.5Sb1.5Te3-Te eutectic structure, and spots 5 and 6 depict pure elemental Te. This confirms that any Te excess has segregated at the boundaries of the Bi0.5Sb1.5Te3 matrix during melt spinning, in accordance with observations described in the literature (16).

Displacement motions of a puncher die during the SPS process of samples having different content of Te are shown graphically in Fig. 1E. Two large displacements are observed: The first one occurs at 260°C and corresponds to a vanishing of big pores between the grains and densification of the grains. The other one at 410°C reflects melting of the excess Te (Tm = 449°C for Te) and its ejection from the interior of the sample. This temperature corresponds to the eutectic point of BiSbTe and Te mixture, which is slightly lower than the melting temperature of Te. In addition, the real temperature of the BiSbTe sample is usually higher than the temperature detected by the thermocouple inserted in the die. The above puncher die motion is to be contrasted with only one notable puncher die displacement observed for a pure sample of Bi0.5Sb1.5Te3 at 260°C that corresponds to the densification of grains in the structure. Moreover, in samples containing excess of Te, the absolute size of the displacement and its slope notably increase with the increasing Te excess.

Powder XRD patterns of melt-spun ribbons, sintered bulk, and ejected material during the SPS process are shown in Fig. 1F. Before SPS, both Bi0.5Sb1.5Te3 and elemental Te were detected in ribbons containing excess amounts of Te. After SPS, only Bi0.5Sb1.5Te3 is detected in the sintered ingot because all excess Te was “squeezed out” during the SPS process, as described by Kim et al. (16). XRD of this squeezed-out material indicates that it is mostly Te with a small amount of Bi0.5Sb1.5Te3, as confirmed also by images of back-scattered electrons. The actual graphite dies containing samples with 5, 15, and 25 wt % of excess Te after SPS are shown in Fig. 1 (G to I). The amount of ejected material increases with the increasing content of excess Te. More characterization of the resulting bulk Bi0.5Sb1.5Te3 and Te samples obtained after the squeeze-out process is given in the Supplementary Materials.

XRD patterns collected on planes of samples perpendicular to the pressing direction during SPS are presented in Fig. 2A. The intensity of peaks corresponding to planes of (006), (009), and (0015) increases with the increasing Te content, and this indicates an enhanced orientation. The relationship between the orientation factor F and the content of extra Te is shown in Fig. 2B. Excess Te in the structure seems to enhance texturing (orientation) in these samples. The values of F for samples with 0 and 25 wt % excess of Te are 0 (no orientation) and 0.17 (high orientation), respectively.

To assess the influence of excess Te on the orientation and microstructure of sintered samples, two typical samples were selected for detailed microstructural characterization. FESEM images of a freshly fractured surface of a sample having no Te excess are presented in Fig. 2 (C and D). Figure 2 (E and F) shows similar images for a sample having 25 wt % excess of Te. The orientation of the surfaces with respect to the pressing direction during SPS is shown in the upper right corners of the above figures. Lamellar structures with a typical size of about 10 to 50 μm are apparent. The grains of samples having no excess Te are randomly arranged in all directions, as depicted in Fig. 2 (C and D). The morphology is, however, quite different in samples that have some excess of Te. For instance, the sample with the excess amount of 25 wt % of Te, shown in Fig. 2E, has a distinctly layered structure with blocks of about 30 μm in thickness that extend along the direction perpendicular to the pressure applied during SPS. The microstructure of this sample observed in the direction parallel to the pressure is shown in Fig. 2F. Thus, on the basis of the different microstructures that develop in the perpendicular and parallel directions, it appears that liquid Te during the sintering process promotes plane slipping and recrystallization, making a-b planes extend perpendicular and stack parallel to the pressing direction. The resulting much enhanced orientation is quantified by an increase in the orientation factor F that rises from 0 (no excess Te) to 0.17 (25 wt % Te excess). This is a key finding because it affects the directions of thermal transport measurements, which will be discussed below.

High-resolution transmission electron microscopy (HRTEM) was carried out to look more closely at the microstructure of the sample made from melt-spun ribbons containing 25 wt % excess of Te. A low-magnification TEM image, including an inset displaying selected-area electron diffraction (SAED) corresponding to the Bi0.5Sb1.5Te3 matrix, is shown in Fig. 3A. Numerous pleated structures (overlaps of two grains in the boundaries) with the width of 40 nm are embedded at grain boundaries (marked with red lines). Images of fast Fourier transforms (FFTs) of the centered regions in Fig. 3B reveal that the grain boundaries tend to be polycrystalline. Figure 3C shows a Moiré pattern of two adjacent crystalline grains. A high density of dislocations is found in this region, as shown in the inverse FFT (IFFT) in Fig. 3D. Rearrangement of grains that takes place during the application
of high pressure expedites the creation of dislocations at the grain boundaries. In general, we observe that the microstructure of our sample is very similar to that reported by Kim et al. (16).

**Thermoelectric properties**

Now that we have established that oriented samples with a high density of dislocations at the grain boundaries have been obtained, we can examine in detail their electrical and thermal transport properties. Figure 4 (A and B) presents the temperature dependence of the total thermal conductivity measured perpendicular (\(k_\perp\)) and parallel (\(k_\parallel\)) to the pressing direction for samples sintered from melt-spun ribbons with various excess content of Te. The perpendicular thermal conductivity \(k_\perp\) increases slightly with increasing excess of Te in the whole temperature range. The minimum value of \(k_\perp\) is about 0.94 and 1.03 Wm\(^{-1}\)K\(^{-1}\) for samples with 0 and 25 wt % excess of Te, respectively, and both values were reached at 350 K. In samples prepared from melt-spun ribbons having excess content of Te, the perpendicular thermal conductivity is enhanced on two counts. The increased perpendicular electrical conductivity contributes a larger charge carrier thermal conductivity term according to the Wiedemann-Franz formula.

\[ \frac{k_\perp}{\sigma_\perp} = L T \]

where \(\sigma_\perp\) is the electrical conductivity, \(L\) is the Lorenz number, and \(T\) is the absolute temperature (see Materials and Methods for details). Our data obtained lattice thermal conductivity in the perpendicular direction is shown in Fig. 4C. The inset shows data of Kim et al. (16). The lattice thermal conductivity varies little with the increasing excess amount of Te, and the minimum value reaches \(\sim 0.65\) Wm\(^{-1}\)K\(^{-1}\) for the sample with 25 wt % excess of Te. This lattice thermal conductivity value is almost twice as large as the value reported by Kim et al. (16) for the sample prepared with a comparable excess of Te.

Figure 5 depicts the temperature-dependent electrical conductivity, Seebeck coefficient, and power factor of all samples with different excess Te measured perpendicular to (designated with ‘\(k_\perp\)’) and parallel to (designated with ‘\(k_\parallel\)’) the pressing direction to document the effect of texturing. Figure 5A shows clearly that the perpendicular electrical

\[ k_{\perp,\parallel} = \frac{1}{\sigma_{\perp,\parallel}} \]
conductivity rises with increasing Te content, whereas the parallel electrical conductivity decreases with the increasing Te content. At room temperature, the electrical conductivity for a sample with 25 wt % excess of Te measured in the direction perpendicular to the pressure is 857 S/cm, some 30% enhancement over the sample with no extra Te. The electrical conductivity of all samples decreases monotonically with increasing temperature and, on the basis of Hall effect measurements, all show the similar carrier concentration of $\sim 2.25 \times 10^{19} \text{cm}^{-3}$. Therefore, the increase in the electrical conductivity of samples prepared with excess amounts of Te must originate from higher carrier mobility. The increase in mobility occurs because of the enhanced electrical conductivity and the only mildly decreased Seebeck coefficient, the power factor $PF$ in the perpendicular direction increases with the increasing excess Te and reaches 4.2 mWm$^{-1}$K$^{-2}$ at room temperature for the sample with 25 wt % excess of Te, some 20% higher than for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ itself. In contrast, the more significant decrease in electrical conductivity along the parallel direction with increasing excess Te, despite the increase of Seebeck coefficient, leads to reduction of the power factor $PF$ from 3.7 mWm$^{-1}$K$^{-2}$ for pure Bi$_{0.5}$Sb$_{1.5}$Te$_3$ to 3.1 mWm$^{-1}$K$^{-2}$ for the sample with 25 wt % excess of Te.

The values of $ZT$ are shown in Fig. 5D. Fabricating Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples from melt-spin ribbons with excess of Te seems to slightly benefit the thermoelectric performance as documented by a $ZT$ value of 1.24 achieved at 350 K with a sample containing 20 wt % excess of Te (in the perpendicular direction). This is about a 15% improvement over the sample processed by the exact same route but with no excess of Te. Nevertheless, this value falls far short of $ZT = 1.86$ reported in the literature (16). However, if one would naively assume that, following the SPS processing, the samples are isotropic structures and combine thermal conductivity measurements parallel to the pressing direction with electrical conductivity and the Seebeck coefficient measurements obtained perpendicular to the pressing direction, then $ZT$ values of 1.7 at 350 K with our samples can be obtained, as shown by open triangles and open hexagons in Fig. 5D.

**CONCLUSION**

To conclude, introducing excess amounts of Te to a stoichiometric charge of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ during the melt-spinning process has considerable impact on the microstructure, composition, and transport properties of SPS structures. Our results show that the excess Te distributes homogeneously at the boundaries of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains following rapid solidification of the melt-spin ribbons. Melting and squeezing out the excess Te during the SPS process promotes recrystallization and reorientation of grains because they are forced to fill empty spaces left by the expelled Te liquid. This gives rise to dense dislocation arrays embedded in grain boundaries, as reported by Kim et al. (16), as well as to a partial directional alignment of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains in all samples prepared with excess amounts of Te. It seems as if liquid Te plays a role of an efficient lubrication agent (for example, lubricant and flux) facilitating the directional alignment that increases with the increasing content of excess Te. Whereas the SPS-processed samples prepared from melt-spin ribbons without excess of Te turned out to be essentially isotropic structures with a minimal degree of transport anisotropy, the structures sintered from ribbons containing excess of Te acquired distinct structural anisotropy reflected in the anisotropy of their transport parameters. The directional alignment makes it imperative to take into careful account the direction in which the
transport properties are measured with respect to the pressing direction applied during the SPS process. Power factors obtained for the direction perpendicular to the pressing direction for our samples that contained some excess of Te are very high and comparable to the power factor reported by Kim et al. (16). With the Seebeck coefficients showing a rather small directional effect, the enhanced perpendicular electrical conductivity as the excess of Te increases results in progressively increasing power factors. The induced grain alignment following SPS has also a significant impact on heat transport. Unfortunately, here, the effect is less favorable from the perspective of thermoelectricity. The perpendicular lattice thermal conductivity, although rather small at 0.65 Wm$^{-1}$K$^{-1}$ for a sample with 25 wt % excess of Te, remains significantly higher than claimed by Kim et al. (16). The anisotropy in the heat transport of structures fabricated from melt-span ribbons that contained large excess of Te is substantial. Measured in the parallel orientation, the thermal conductivity is much lower (0.74 Wm$^{-1}$K$^{-1}$ for the sample with 25 wt % excess of Te) because it is more difficult for phonons to propagate across the van der Waals gaps of the crystal structure because the grains of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ are partly c axis–oriented. The maximum value of ZT that we have measured reached 1.24 at 350 K for samples with 20 and 25 wt % excess of Te, representing about 15% increase over the figure of merit of identically prepared Bi$_{0.5}$Sb$_{1.5}$Te$_3$ having no excess of Te.

**MATERIALS AND METHODS**

**Sample preparation and measurement**

High-purity Bi, Sb, and Te granules were weighed according to the stoichiometric composition Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and loaded into a vacuum-sealed quartz tube with the diameter of 15 mm. The charge was melted and homogeneously mixed in a rocking furnace for 10 hours at 1073 K and then furnace-cooled down to room temperature. The obtained ingots were ground into a fine powder, sieved through a 200 size mesh, mixed with the excess amount of Te powder (0.5, 10, 15, 20, and 25 wt %), and finally cold-pressed into pellets under a pressure of 10 MPa.

Each obtained pellet was put into a quartz tube with a 0.3-mm-diameter nozzle at the bottom, and the tube was mounted on a melt-spinning apparatus. The chamber was filled with Ar (0.04 MPa) to protect the ingot from oxidation while the ingot was melted by radio frequency heating. The melt was ejected under a pressure pulse of 40 kPa of Ar onto a copper roller rotating with a linear speed of 45 m s$^{-1}$. Thin ribbons (5 to 10 μm in thickness, 2 mm in width, and 5 to 10 mm in length) were obtained through this rapid solidification process.

The melt-span ribbons were hand-ground into fine powders and compacted using SPS at 480°C for 3 min under 70 MPa. During the SPS process, the liquefied excess Te was expelled from the structure into a graphite die. The fully condensed bulks with the relative density over 99% were obtained in sizes of Φ12.7 mm × 13 mm. The entire synthesis process, including melting spinning and SPS processing, is identical to that used by Kim et al. (16).

Phase composition of bulk samples was identified by powder XRD analysis (PANalytical-Empyrean; Cu Kα). Composition and morphology of the bulk samples was investigated by electron probe microanalysis (EPMA) with wavelength-dispersive spectroscopy (JXA-8230, JEOL), FESEM (Hitachi SU-8020), and HRTEM (JEM-2100F, JEOL) equipped with an energy-dispersive spectroscope to determine the actual composition.

The electrical conductivity $\sigma$ and the Seebeck coefficient $\alpha$ were measured simultaneously by a standard four-probe method in the range of 300 to 473 K using an Ulvac-Riko ZEM-3 system. The total thermal conductivity was calculated from $\kappa = DC_\rho\rho$, where $D$ is the thermal diffusivity obtained by the laser flash method (LFA-457, Netzsch), $C_\rho$ is the specific heat measured by a differential scanning calorimeter (DSC Q20, TA Instruments), and $\rho$ is the density determined by the method of Archimedes. The room-temperature carrier concentration and the Hall mobility were measured using a Physical Property Measurement System (PPMS, Quantum Design). All tests were performed perpendicular to the pressing direction. The orientation factor $F$ was calculated according to the following equations (18, 28)

$$F = \frac{(P - P_0)}{(1 - P_0)}$$

$$P_0 = \frac{I_0(001)}{\sum I_0(hkl)}$$

$$P = \frac{I(001)}{\sum I(hkl)}$$

Here, $P$ and $P_0$ are the ratios of the integral intensities of the (001) planes to the intensities of the (hkl) planes for preferentially and for randomly orientated samples, respectively. A sample has no preferred orientation when the orientation factor $F$ equals to 0, and it is fully oriented when the orientation factor $F$ equals to 1.

**Sample characterization after the squeeze-out SPS process**

Because the ejected material is not just pure Te, we carried out EPMA and collected back-scattered electron images to check the exact composition of the resulting bulk Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples synthesized from melt-spin ribbons containing 0, 15, and 25 wt % excess of Te. The results are shown in fig. S4 (A to C). All samples were homogeneous without any secondary phase, except for a small amount of residue from the polishing reagent. This attests to a complete ejection of excess Te during SPS. Results of the wave-dispersive spectrometer analysis are presented in table S1 and demonstrate that the ejection of the excess Te content has no influence on the composition of the final product because the ratio of Bi/Sb/Te is close to 1:3:6 in all samples. Figure S4D shows a back-scattered electron image of the ejected material during the SPS process.

**Lattice thermal conductivity calculation**

The lattice thermal conductivity perpendicular to the pressing direction was calculated by the Wiedemann-Franz formula $\kappa_L = \kappa_e - \sigma T$, where $\sigma$ is the electrical conductivity, $L$ is the Lorenz number, and $T$ is the absolute temperature (see the Supplementary Materials for details). Assuming, again, a single parabolic band model, the Lorenz number $L$ is calculated from (34, 35)

$$L = \left(\frac{k_B}{e}\right)^2 \frac{\left(r + 7/2\right)F_{r+5/2}^{3/2}(\eta_L)}{\left(r + 3/2\right)F_{r+3/2}^{3/2}(\eta_L)} - \delta^2(\eta_L)$$

$$\alpha = \frac{k_B}{e} \left[\eta_L - \frac{(r + 5/2)F_{r+3/2}(\eta_L)}{(r + 3/2)F_{r+1/2}(\eta_L)}\right]$$

$$F_i(\eta_L) = \int_0^{\eta_L} \frac{x^4dx}{1 + \exp(x - \eta_L)}$$
where $e$ is the elemental charge and $\alpha$ is the Seebeck coefficient. The calculated Lorenz numbers at temperatures of measurement vary within the range from $1.5 \times 10^{-8}$ to $1.6 \times 10^{-8}$ W ohms K$^{-2}$ for all samples with different excess content of Te.

### Density-of-states effective mass calculation

The effective mass was calculated assuming a single parabolic band model and the dominance of acoustic phonon scattering. The effective mass is calculated from (1, 20)

$$
\alpha = \frac{\hbar}{e} \left[ \eta_F - \frac{(r + 5/2)F_{r+3/2}(\eta_F)}{(r + 3/2)F_{r+1/2}(\eta_F)} \right]
$$

(7)

$$
F_1(\eta_F) = \int_0^\infty \frac{x^3 dx}{1 + \exp(x - \eta_F)}
$$

(8)

$$
\eta_F = E_F / (k_B T)
$$

(9)

$$
n = 4\pi(2\hbar T m^*)^{3/2} F_{1/2}(\eta_F)
$$

(10)

where $F_1(\eta_F)$ is the Fermi-Dirac integral, $\eta_F$ is the reduced Fermi level, $k_B$ is the Boltzmann constant, $h$ is the Planck constant, and $r$ is the scattering ($r = -3/2$ for acoustic scattering).

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/6/eaar5606/DC1

### REFERENCES AND NOTES

1. J. He, T. M. Tritt, Advances in thermoelectric materials research: Looking back and moving forward. Science 357, eaak9997 (2017).
2. G. S. Nolas, J. Sharp, H. J. Goldsmid, Thermoelectrics- Basic Principles and New Materials Development (Springer, 2001).
3. A. Shakouri, Recent developments in semiconductor thermoelectric physics and materials. Annu. Rev. Mater. Res. 41, 399–431 (2011).
4. D. M. Nguyen, H. Xu, Y. Zhang, B. Zhang, Active thermal cloak. Appl. Phys. Lett. 107, 121901 (2015).
5. Q. H. Zhang, X. Y. Huang, S. Q. Bai, X. Shi, C. Uher, L. D. Chen, Thermoelectric devices for power generation: Recent progress and future challenges. Adv. Eng. Mater. 18, 194–213 (2016).
6. T. M. Tritt, Thermoelectrics run hot and cold. Science 272, 1276–1277 (1996).
7. J. G. Snyder, T. S. UrSELL, Thermoelectric efficiency and compatibility. Phys. Rev. Lett. 91, 148301 (2003).
8. E. S. Toberer, L. L. Baranowski, C. Dames, Advances in thermal conductivity. Annu. Rev. Mater. Res. 42, 179–209 (2012).
9. X. Su, P. Wei, H. Li, W. Liu, Y. Yan, P. Li, C. Su, C. Xie, W. Zhao, P. Zhai, Q. Zhang, X. Tang, C. Uher, Multi-scale microstructure thermoelectric materials: Transport behavior, non-equilibrium preparation, and applications. Adv. Mater. 29, 160203 (2017).
10. R. P. Chasmar, R. Stratton, The thermoelectric figure of merit and its relation to thermoelectric generators. J. Electron. Control 7, 52–72 (1959).
11. Y. Pei, X. Shi, A. LaLonde, H. Wang, L. Chen, G. J. Snyder, Convergence of electronic bands for high performance bulk thermoelectrics. Nature 473, 66–69 (2011).
34. W. Liu, X. Tan, K. Yin, H. Liu, X. Tang, J. Shi, Q. Zhang, C. Uher, Convergence of conduction bands as a means of enhancing thermoelectric performance of n-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions. Phys. Rev. Lett. 108, 166601 (2012).
35. L.-D. Zhao, S.-H. Lo, J. He, H. Li, K. Biswas, J. Androulakis, C.-I. Wu, T. P. Hogan, D.-Y. Chung, V. P. Dravid, M. G. Kanatzidis, High performance thermoelectrics from earth-abundant materials: Enhanced figure of merit in PbS by second phase nanostructures. J. Am. Chem. Soc. 133, 20476–20487 (2011).

Acknowledgments: We thank R. Jiang and T. Luo for help with the HRTEM analysis.

Funding: We acknowledge support from the Natural Science Foundation of China (grant nos. 51521001 and 51632006), the Fundamental Research Funds for the Central Universities (Wuhan University of Technology, 162459002, 2015-061) and the 111 Project of China (grant no. B07040). This work was supported in part by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, under grant DE-SC0014520, DOE Office of Science (sample preparation, XRD, and TEM measurements). Author contributions: X.T., M.G.K., and C.U. designed the experiments. R.D. and X.S. carried out the experiments, measured the thermoelectric properties, and characterized the samples. Z.Z. and W.L. contributed to sample preparations. Y.Y. contributed to sample characterization. All authors analyzed and discussed the data. R.D., X.S., X.T., M.G.K., and C.U. wrote the manuscript with inputs from all authors.

Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.
Thermal conductivity in Bi$_{0.5}$Sb$_{1.5}$Te$_{3+x}$ and the role of dense dislocation arrays at grain boundaries

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Sci Adv 4 (6), eaar5606.
DOI: 10.1126/sciadv.aar5606