Supplementary Materials for

Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics

Sang Il Kim,* Kyu Hyoung Lee,* Hyeon A Mun,* Hyun Sik Kim, Sung Woo Hwang, Jong Wook Roh, Dae Jin Yang, Weon Ho Shin, Xiang Shu Li, Young Hee Lee, G. Jeffrey Snyder, Sung Wng Kim*

*Corresponding author.
E-mail: sang.il.kim@samsung.com (S.I.K.); kimsungwng@skku.edu (S.W.K.)

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Materials and Methods

Ingot preparation

The Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ingots were prepared with a melt process; high-purity (> 99.999%) Bi, Sb, and Te granules were weighed according to the composition Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and loaded into a vacuum-sealed quartz tube of 10 mm diameter, and the contents were melted and homogeneously mixed in a rocking furnace for 10 h at 1073 K.

Melt spinning

Bi$_{0.5}$Sb$_{1.5}$Te$_3$ bulk ingots were pulverized and mixed with excess Tellurium (25 wt%), then the homogeneously mixed materials were put into a quartz cylinder with 0.3 mm diameter nozzle in melt spinning system. The materials were induction-molten, and were injected under a pressure of 40 kPa Ar onto a Cu wheel rotating with linear speed of 45 m s$^{-1}$ under the Ar atmosphere of 300 mTorr. Thin ribbons (5–10 μm thick, 1.5–2 mm wide, and 5–10 mm long) were obtained by rapid solidification (cooling rate ~10$^6$ K s$^{-1}$) using this melt spinning process.

Spark plasma sintering

The melt spun ribbons were pulverized, then compacted using spark plasma sintering (SPS) at 480 °C for 3 min under 70 MPa for S-MS and Te-MS materials. During the compacting, the liquidified excess Te was expelled from the graphite die.

Characterization and Measurement

X-ray diffraction (XRD) (D/MAX-2500/PC, Rigaku, Japan) analysis with Cu K$_\alpha$ radiation ($\lambda$ = 1.5418 Å) was performed on powder and bulk samples. The microstructure was investigated using scanning electron microscopy (SEM) (JSM-7600F, JEOL) and transmission electron microscope (TEM) (JEM-2100F, JEOL). Transport measurements were performed in directions both parallel and perpendicular to the pressing direction. Only the measurements perpendicular to the pressing directions are shown in the main text and used for calculation of $zT$. The electrical conductivities ($\sigma$) and Seebeck coefficients ($S$) were measured from 300 to 480 K by a four point probe method using a ZEM-3 (ULVAC-RIKO, Japan) with confirming measurements using a custom system (section S7). Hall effect measurements were performed using Physical Property Measurement System (Quantum Design) and confirmed with a custom system (section S7). The thermal conductivity values ($\kappa = \rho_s \times C_p \times \lambda$) were calculated from measurements taken separately. Sample density ($\rho_s$) was measured by Archimedes method. The thermal diffusivity ($\lambda$) was measured by laser-flash method using TC-9000 (ULVAC-RIKO, Japan) and confirmed using Netzsch LFA 457 (section S6). The Dulong-Petit heat capacity ($C_p = 124.6$ J mol$^{-1}$ K$^{-1}$) was used and confirmed by measurements at 300 K by the thermal relaxation method using a Physical Property Measurement System (Quantum Design) (section S10).
S1. SEM images of melt spun stoichiometric $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (S-MS) and 25 wt% Te excess $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (Te-MS) samples.

**Figure S1.** A, Phase diagram of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$–Te system showing an eutectic composition at 92.6 at% Te. Blue and red arrows indicate the nominal composition of melt spun stoichiometric $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (S-MS) and 25 wt% Te excess $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (Te-MS) material, respectively (Fig. 3A). B and C, Scanning electron microscope (SEM) images of melt spun ribbons of S-MS and Te-MS material showing platelets of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. D, An enlarged view of (C) showing the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ platelets surrounded by the eutectic phase of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$–Te mixture, in which the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ particles (white spots) have the size of 10–20 nm (Fig. 3B).
S2. Structural characterization of melt spun Te-MS ribbons with Te excess (25 wt% Te excess Bi$_{0.5}$Sb$_{1.5}$Te$_3$) and compacted Te-MS samples.

A

B

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<td>Sb</td>
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<td>Te</td>
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B: dashed circle: detection range (~1 μm), Black (#1, #3): Primary Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains, Red (#2): Eutectic phases

C

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<td>59.69</td>
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C

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<td>Te</td>
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Figure S2. A, X-ray diffraction patterns of melt spun ribbons with Te excess samples. The peak indicated by red arrows is of Te elements and the others are well matched with the diffraction pattern of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloy, indicating melt spun ribbons with Te excess samples still have an excess Te elements. B, SEM-EDS measurements on melt spun ribbons of Te-MS samples. The distinct difference in the amount of Te elements between primary Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains (#1 and #3) and eutectic phases (#2) was clearly observed, indicating excess Te elements exist between primary Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains. It was hard to independently analyze each Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grain and eutectic phase due to the limit of detecting range (~ 1 µm) in energy dispersion spectroscopy of scanning electron microscopy. C, SEM-EDS measurements on compacted Te-MS samples. The results clearly showed no distinct region of excess Te elements and Te-rich Bi$_{0.5}$Sb$_{1.5}$Te$_3$ composition. D, Electron backscatter diffraction (EBSD) image showed a nearly random crystallographic orientation of polycrystalline compacted Te-MS samples with an average grain size of ~ 280 nm.
Table S1. Inductively coupled plasma mass spectrometry (ICP-MS) results for compacted S-MS and Te-MS samples. The results indicate the compacted Te-MS samples are stoichiometric Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloys without excess Te elements.

<table>
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<tr>
<td></td>
<td>Sb</td>
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<tr>
<td>Bi$<em>{0.5}$Sb$</em>{1.5}$Te$_3$ (standard)</td>
<td>28.9</td>
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<tr>
<td>S-MS</td>
<td>29.6</td>
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<td>Te-MS #1</td>
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<td>Te-MS #2</td>
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<td>Bi$<em>{0.5}$Sb$</em>{1.5}$Te$_3$ (Nominal)</td>
<td>30</td>
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<td>25 wt% Te excess</td>
<td>23.8</td>
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<tr>
<td>Bi$<em>{0.5}$Sb$</em>{1.5}$Te$_3$ (Nominal)</td>
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</table>
S3. Expelled excess Te along with Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nano-particles from graphite die.

Figure S3 shows the pictures after transient liquid flow compacting process (using spark plasma sintering) for Te-MS sample, where the solidified eutectic phases (mixture of solidified excess Te and Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nano-particles) are shown on the top of graphite die. Excess Te was expelled as a liquid along with solid Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nano-particles (that is, eutectic phases) during the compaction at 480 °C. Figure S4 shows the X-ray diffraction patterns of expelled excess Te along with Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nano-particles from graphite die. As a result, the compacted Te-MS samples were single phase BST alloys with stoichiometric composition of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloy, as confirmed from XRD and ICP measurements (Fig. S2A and Table S1). Furthermore, the SEM-EDS showed no distinct region of excess Te elements and Te-rich Bi$_{0.5}$Sb$_{1.5}$Te$_3$ composition (Fig. S2C).
**Figure S3.** Pictures after transient liquid flow compacting process (spark plasma sintering) for 25 wt% Te excess Bi$_{0.5}$Sb$_{1.5}$Te$_3$ (Te-MS) material.
Figure S4. Powder X-ray diffraction patterns of expelled excess Te along with Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} nano-particles (eutectic phases).
S4. Samples for thermoelectric transport properties measurements

The inner diameter of graphite die was about 10.4 mm. We fabricated the disk-shaped samples of 10.4 mm in diameter and 12.5–13 mm in thickness as shown in Fig. S5A. The acquired samples were ground into disk of 10 mm in diameter and 12 mm in thickness as shown in Fig. S5B. In order to measure the thermoelectric properties in both directions parallel and perpendicular to the press direction, disks of 10 mm diameter and 1.5 mm thickness and bars of about 3 mm × 1 mm × 9 mm were made from both directions by grinding of the 4 samples shown in Fig. S5C. Disk for the thermal diffusivity measurement along the perpendicular to the press direction was made from square-shaped sample (10 mm × 10 mm × 1.5 mm).
Figure S5. A and B, Pictures of the final product after transient liquid flow compacting process (spark plasma sintering). C, Pictures after cutting the compacted samples.
S5. Anisotropic crystal structure and thermoelectric transport properties.

Figure S6 shows the X-ray diffraction patterns of both the planes parallel (||) and perpendicular (⊥) to the press directions for BM, S-MS, and Te-MS samples. The texture fraction of the \{0 0 l\} planes was calculated from X-ray diffraction patterns scanned from 2θ = 10° to 60° by Lotgering method. The degree of orientation (f) is defined as \( f_{00l} = \frac{p_{00l} - p_0}{1 - p_0} \), where \( p_{00l} = \frac{\sum I_{00l}}{\sum I_{hkl}} \) and \( p_0 = \frac{\sum I_{00l}^{0}}{\sum I_{hkl}^{0}} \) with \( I_{hkl} \) and \( I_{hkl}^{0} \) being the intensities of \((h k l)\) peaks for the textured and randomly oriented sample, respectively.

The \( f_{00l} \) values for BM, S-MS, and Te-MS samples in the perpendicular direction are 0.089 (BM), 0.095 (S-MS), and 0.108 (Te-MS), while those for the plane parallel to the press direction are 0.076 (BM), 0.068 (S-MS), and 0.061 (Te-MS). All samples showed the anisotropy in crystal structure, but the degree of anisotropic orientation was not much significant in all samples.
Figure S6. X-ray diffraction patterns of both the planes parallel (||) and perpendicular (⊥) to the press directions for BM, S-MS, and Te-MS samples, showing the anisotropic properties in all samples.
We measured all thermoelectric transport properties (electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and thermal conductivity ($\kappa$)) both in parallel and perpendicular to the press directions. In Fig. S7, we showed the temperature dependence of $\sigma$, $S$, power factor (PF), $\kappa$ and $zT$ of the BM, S-MS, and Te-MS samples in both the directions perpendicular ($\sigma_\perp$, $S_\perp$, $\kappa_{\text{tot}\perp}$, $\kappa_{\text{lat}\perp}$, and $zT_\perp$) and parallel ($\sigma_\parallel$, $S_\parallel$, $\kappa_{\text{tot}\parallel}$, $\kappa_{\text{lat}\parallel}$, and $zT_\parallel$) to the press direction. For Te-MS sample, the $\sigma_\perp$ is about 16.5% higher than $\sigma_\parallel$ for the whole temperature range, which clearly shows that there is a little $ab$ plane orientation along the perpendicular to the press direction, while $\sigma_\perp$ values of BM ($\sim$ 6.7%) and S-MS ($\sim$ 11.4%) samples are slightly higher than $\sigma_\parallel$, consistent with the results of X-ray diffraction data (Fig. S7A). On the other hand, $S$ values for BM, S-MS, and Te-MS samples are very similar in both directions (Fig. S7B). The $\kappa_{\text{tot}\parallel}$ value of Te-MS sample is $\sim$ 6.1% lower (0.62 W m$^{-1}$ K$^{-1}$ at 320 K with a lattice contribution of 0.34 W m$^{-1}$ K$^{-1}$) than $\kappa_{\text{tot}\perp}$ (0.66 W m$^{-1}$ K$^{-1}$ at 320 K with a lattice contribution of 0.33 W m$^{-1}$ K$^{-1}$) mainly due to the reduction in electronic contribution by decrease in $\sigma$ (Figs. S7D and S7E). The maximum $zT_\perp$ is about 1.86 at 320 K, which is about a 11% higher than $zT_\parallel$ ($\sim$ 1.67 at 320 K) as shown in Fig. S7F.
Figure S7. Anisotropic thermoelectric properties of BM, S-MS and Te-MS samples. 

A, Temperature dependence of electrical conductivity ($\sigma$). B, Temperature dependence of Seebeck coefficient ($S$). C, Temperature dependence of power factor ($\sigma S^2$). D, Temperature dependence of total thermal conductivity ($\kappa_{\text{tot}}$). E, Temperature dependence of lattice thermal conductivity ($\kappa_{\text{lat}}$). F, Temperature dependence of dimensionless figure of merit ($zT$).
S6. Thermal diffusivity of Te-MS samples

The values of thermal diffusivity for 4 different Te-MS samples were cross-checked by using the instrument LFA-457 of Netzsch. There is no significant difference between the values of thermal diffusivity measured with TC-9000 (ULVAC-RIKO) and LFA as shown in Fig. S8A. Furthermore, Figure S8B showed the comparison of the values in Fig. S8A and the values of 30 Te-MS samples (measured with TC-9000) in Fig. S9D. All values of Fig. S8A are in the range of values of 30 Te-MS samples
Figure S8. Thermal diffusivity of Te-MS samples. A, Comparison of the values measured with TC-9000 (ULVAC-RIKO) and LFA (Netzsch) for 4 Te-MS samples. B, Comparison of the values measured by LFA (Netzsch) for 4 Te-MS samples with the values measured by TC-9000 (ULVAC-RIKO) for 30 Te-MS samples of Fig. S9D.
S7. Reproducibility of high-performance thermoelectric properties of Te-MS samples

Figure S9. Temperature dependence of thermoelectric properties for 30 Te-MS samples with dislocation arrays embedded in grain boundaries. A, Electrical conductivity ($\sigma$). B, Seebeck coefficient ($S$). C, Power factor ($\sigma S^2$). D, Total thermal conductivity ($\kappa_{\text{tot}}$). E, Lattice thermal conductivity ($\kappa_{\text{lat}}$). F, Dimensionless figure of merit ($zT$).
Table S2. Cross-check of carrier concentration ($n$) and mobility ($\mu$) of compacted Te-MS samples. The results of the table were obtained at Caltech are similar to those of the compacted Te-MS samples.

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<th>$n$ ($10^{19}$ cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ S$^{-1}$)</th>
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<tr>
<td>#1</td>
<td>1.96 ± 0.03</td>
<td>275 ± 5</td>
</tr>
<tr>
<td>#2</td>
<td>1.75 ± 0.05</td>
<td>309 ± 2</td>
</tr>
<tr>
<td>#3</td>
<td>1.60 ± 0.01</td>
<td>321 ± 4</td>
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Figure S10. Anisotropic mobility of Te-MS sample.
Figure S11. Cross-check of thermoelectric transport properties for Te-MS samples.

A, Temperature dependence of electrical conductivity ($\sigma$). B, Temperature dependence of Seebeck coefficient ($S$). Inset is the power factor ($\sigma S^2$). C, Temperature dependence of total thermal conductivity ($\kappa_{\text{tot}}$). Arrows indicate the direction of measurements. The measurements at Caltech are described elsewhere (35, 36).
S8. Compatibility factor of Te-MS sample

Figure S12. Comparison of compatibility factors of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ between different fabrication methods. The compatibility factor ($s_c$) was calculated with the equation of $s_c = -\sqrt{1 + z} - \frac{1}{S T}$ (37). The compatibility factor for Te-MS sample showed a similar value as those of other samples in the whole measured temperature ranges.
S9. TEM images of dislocation arrays embedded in grain boundaries for Te-MS samples.

Figure S13 shows the TEM images observed at slightly tilted zone axis from Fig. 4B of the manuscript. Figure S14 shows the TEM images observed by tilting the TEM zone axis of boxed region B and E in Fig. S13A. Figure S15A shows the classical Moiré fringe. From the fast Fourier-transformed (FFT) image of Fig. S15A as shown in Fig. S15B, it is clearly shown that the (1 1 0) atomic planes of the right grain and the (1 1 6) atomic planes of the left grain match, forming the misfit dislocations as indicated with the red symbols. The misfit between the two planes is ~ 0.05 Å, which is the 2.8% of d-spacing. The misfit of 2.8% is energetically favorable to form misfit dislocations. And, the misfit compensates the misfit spacing of ~ 2.5 nm, as shown in Fig. S15B. This spacing is identical to the periodic spacing of the Moiré fringes of Fig. S15A. Figure S16C shows the high resolution TEM image of dislocation arrays (encircled in white) embedded in grain boundary of Fig. 4H. Figures S17 and S18 show other TEM images of dislocation arrays embedded in grain boundaries for compacted Te-MS samples.
Figure S13. Dislocation arrays embedded in grain boundaries. A, TEM images observed at slightly tilted zone axis from Fig. 4B. B–E, Enlarged views of boxed regions in A. F–G, Comprised TEM images of the pink-colored grain boundary area of F.
Figure S14. Grain boundary images by tilting the TEM zone axis. Images of central grain boundary change by tilting the TEM zone axis, showing the appearance and disappearance of Moiré fringes.
Figure S15. Dislocation arrays embedded in grain boundaries. A, High resolution TEM image of a grain boundary. B, Inverse FFT (IFFT) image with (1 1 6̅) and (1 1 0) planes for the left and right grains, respectively, of boxed region in A. C, Strain mapping of B, showing the dislocation cores with the high intensity. Inset is the enlarged view of boxed region in B. D–F, FFT images of left, center and right grains, respectively.
Figure S16. Dislocation arrays embedded in grain boundaries. A, High resolution TEM image of a grain boundary of Fig. 4H in main text. B, Enlarged view of boxed region in A. C, Enlarged view of boxed region in B, showing some dislocations encircled in white.
Figure S17. Dislocation arrays embedded in grain boundaries. A, Low-magnification TEM image of a grain boundary. B, High resolution TEM image of a grain boundary. Inset, IFFT image of boxed region. C and D, FFT images of top and bottom grains in B. The FFT images revealed the $3^\circ$ misorientation between two adjacent grains. The arrays of alternating edge dislocation pairs are quite similar to the periodic dislocations observed in low angle ($7^\circ$) grain boundary of Bi$_2$Se$_3$ thin film (38).
Figure S18. Low-magnification TEM images of dislocation arrays embedded in grain boundaries. Images show a Moiré pattern (~90 nm wide) at central grain boundary and the other grain boundaries without Moiré pattern have an width up to ~60 nm that is quite wide compared to the few nanometer width as observed in the S-MS material (Fig. 4A).
S10. Energy dispersion spectroscopy measurement around grain boundaries in compacted Te-MS sample.

Figure S19 shows the STEM-EDS elemental-mapping image of Te for the similar image as Fig. S13C, indicating no presence of remaining Te at grain boundaries and no distinct Te increase in the compositions of adjacent Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains.
Figure S19. STEM-EDS elemental-mapping image of Te for compacted Te-MS sample.
S11. Heat capacity ($C_p$) of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples

We measured the heat capacity of BM, S-MS and Te-MS materials for the calculation of thermal conductivity and used the reference data for Ingot material ($124.6 \text{ J mol}^{-1} \text{ K}^{-1}$) (38). Figure S20 shows the temperature dependence of BM, S-MS and Te-MS materials, showing a similar value (BM: $124.6 \text{ J mol}^{-1} \text{ K}^{-1}$, S-MS: $124.8 \text{ J mol}^{-1} \text{ K}^{-1}$, Te-MS: $124.6 \text{ J mol}^{-1} \text{ K}^{-1}$) at 300 K. The densities ($\rho$) of Ingot (6.88 g cm$^{-3}$), BM (6.78 g cm$^{-3}$), S-MS (6.77 g cm$^{-3}$) and Te-MS (6.76±0.03 g cm$^{-3}$) materials measured by Archimedes method were used for thermal conductivity calculation.
Figure S20. The temperature dependence of heat capacity ($C_p$) for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ samples (BM, S-MS and Te-MS) measured in the range from 100 K to 300 K by thermal relaxation method using Physical Property Measurement System (Quantum Design). The heat capacity value of 124.6 J mol$^{-1}$ K$^{-1}$ was used for Ingot material (39).
S12. Calculation of Lorenz number

The value of $\kappa_{\text{lat}}$ was calculated by subtraction of $\kappa_{\text{ele}}$ from $\kappa_{\text{tot}}$, which was estimated using the Wiedemann-Franz law ($\kappa_{\text{ele}} = L_0 T \sigma$), where $L_0$, $T$, and $\sigma$ denote the Lorenz number, absolute temperature and electrical conductivity. The Lorenz number, $L_0$ was obtained using following equation:

$$L_0 = \left(\frac{k_B}{e}\right)^2 \left(\frac{(r + 7/2)F_{r+5/2}(\eta)}{(r + 3/2)F_{r+1/2}(\eta)} - \left[\frac{(r + 5/2)F_{r+3/2}(\eta)}{(r + 3/2)F_{r+1/2}(\eta)}\right]^2\right),$$

where $k_B$ is the Boltzmann constant, $e$ is the electron charge, $r$ is the scattering parameter, $F_n(\eta)$ is the $n$-th order Fermi integral, $F_n(\eta) = \int_0^\infty \frac{x^n}{1 + e^{x-\eta}} dx$, and $\eta$ is the reduced Fermi energy, respectively. For the $L_0$ calculation, $\eta$ was calculated from the following relationship using the measured Seebeck coefficient ($S$):

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

and $r$ was derived from the temperature dependence of the carrier mobility. The values of $L_0$ at 300 K were found 1.603$x10^{-8}$, 1.574$x10^{-8}$, 1.614$x10^{-8}$ V$^2$ K$^{-2}$ for BM, S-MS, Te-MS materials, respectively.
S13. Calculation of $\Delta T_{\text{max}}$ of modules

Two thermoelectric modules of the same size (127 couples) were fabricated, where the only difference between them lied in the materials used for p-type legs. For one module, the ingot was utilized for the p-type legs, while the Te-MS was used in another one.

Maximum values for coefficient of performance ($\text{COP}_{\text{max}}$) were taken at different $\Delta T$ in COP versus input current. The values of $\text{COP}_{\text{max}}$ for two modules were plotted as filled circles in Fig. 1E. By assuming asymmetric thermal contact resistivity of the modules, following equation was derived from Min’s equation (40, 41) for a module with symmetric thermal contacts.

$$\text{COP}_{\text{max}} = \left( \frac{1}{1+\frac{r l}{l_c}} \right) \left[ \frac{r c}{r h - r c} \frac{(1+Z\frac{T_h+T_c}{2})^{1/2}}{(1+Z\frac{T_h+T_c}{2})^{1/2} + 1} \right]$$

where $l_c$ and $l$ are the length as shown in Fig. S21 and $r$ corresponds to thermal conductivity of thermoelements divided by that of the contact layers (ceramic plate + conducting strip). Variables $r$ and $Z$ were adjusted to fit calculated $\text{COP}_{\text{max}}$ (lines in Fig. 1E) to experimental $\text{COP}_{\text{max}}$ (filled circles in Fig. 1E) data. The $\Delta T_{\text{max}}$ of a module was obtained from a $\Delta T$ value when $\text{COP}_{\text{max}}$ becomes zero.
Figure S21. Schematic illustration of thermoelectric module.
S14. Model of lattice thermal conductivity

Lattice thermal conductivities (κ_{lat}) of BM, S-MS and Te-MS were explained using the Debye-Callaway model (26, 29). We followed the Bessas’ model (42) who found the acoustic phonons are the dominant contribution to lattice thermal conductivity. In the Debye-Callaway model, the total phonon relaxation time (τ_{tot}) is a reciprocal sum of the relaxation times of the pertinent scattering mechanisms. Once τ_{tot} is obtained, it is used to calculate the lattice thermal conductivity from eqn. 1.

\[
\kappa_{lat} = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar}\right) \int_0^{\theta_a/T} (x) \frac{\tau_{tot}(x)}{x^4 e^{x}} \frac{\theta_a z}{(e^{x-1})^2} \, dx
\]  

(1)

The three dominant scattering mechanisms relevant to all (Bi_{0.25}Sb_{0.75})_{2}Te_{3} polycrystalline samples are Umklapp phonon-phonon scattering, point-defect scattering and boundary scattering. The relaxation time associated with Umklapp phonon-phonon scattering (τ_{U}) (9, 27, 28) is calculated from eqn. 2 (see Table S4).

\[
\tau_{U}^{-1} = A_{N} \frac{2}{(6\pi^2)^{1/3}} \frac{k_B V^{1/3} y^2 \omega^2 T}{M v^3}
\]  

(2)

The impact of normal phonon-phonon scattering (τ_{N}) in the calculation of κ_{lat} can be expressed in terms of τ_{U} (29) which leads to an additional factor (A_{N} = 2.6 see Table S3). This factor is determined by fitting experimental literature data from Stordeur (43) on well characterized crystalline material.

The relaxation time associated with point-defect scattering (τ_{PD}) (12, 30, 31) is given by eqn. 3 (see Table S4).

\[
\tau_{PD}^{-1} = \frac{\nu w^4}{4\pi v^3} \Gamma
\]  

(3)

The mass and lattice constant contrasts between Bi and Sb in (Bi_{0.25}Sb_{0.75})_{2}Te_{3} are the sources of point-defect scattering, and they are described in Γ (12, 30). The value of Γ = 0.145 (in Table S4) for (Bi_{0.25}Sb_{0.75})_{2}Te_{3} is determined by fitting experimental literature data from Stordeur (43).

The relaxation time associated with boundary scattering (τ_{B}) (9, 31, 44) is given by eqn. 4 (see Table S4).

\[
\tau_{B}^{-1} = \frac{\nu}{d}
\]  

(4)

We use the observed average grain size of 50 μm for BM and 300 nm for S-MS and Te-MS samples to calculate τ_{B} (τ_{U} and τ_{PD} were kept unchanged since all these samples have the same composition - see Table 3).

Finally, to model the κ_{lat} of Te-MS, introduction of additional relaxation times associated with dislocations was necessary. The scattering mechanism from dislocations can be divided into scattering from dislocation strain and that from dislocation cores; hence they have separate phonon relaxation times τ_{DC} (10, 29, 46, 47) and τ_{DS} (10, 29, 45, 46), respectively (see eqn. 5–6). Because an array of dislocations at grain boundaries can be physically treated as a collection of single dislocations inside a grain (47), we include τ_{DC} and τ_{DS} to calculate the τ_{tot} of Te-MS.
\[
\tau_{DC}^{-1} = N_D \frac{\rho^{4/3}}{\nu^2} \omega^3
\]

\[
\tau_{DS}^{-1} = 0.6 \times B_D^2 N_D (\gamma + \gamma_1)^2 \omega \left[ \frac{1}{2} + \frac{1}{24} \left( \frac{1-2r}{1-r} \right)^2 \left( 1 + \sqrt{2} \left( \frac{\nu_T}{\nu_L} \right)^2 \right) \right]
\]

\(N_D, B_D, \gamma, \gamma_1, r, \nu_L, \nu_T\) are dislocation density, effective Burger’s vector, Grüneisen parameter, change in Grüneisen parameter, Poisson’s ratio, longitudinal phonon velocity and transverse phonon velocity, respectively (see Table S4). The scatter of dislocation cores only requires \(N_D, \bar{V}\) and \(\nu\) with no fitting parameters (see eqn. 5). It is important to note that different values of constant \((A)\) in front of \(B_D^2\) in \(\tau_{DS}^{-1}\) have been used by Klemens. In 1955, Klemens began with \(A=0.06\) as the constant of proportionality (10). Three years later, he hinted that the constant 0.06 should be multiplied by 16 (45) and used \(0.96B_D^2\tau_{DS}^{-1}\) equation to model thermal resistivity in experiments with copper alloys (48, 49). His latest book presents the equation of \(1.1B_D^2\tau_{DS}^{-1}\) (10). Another factor of 0.55 is needed to account for arrays of dislocations oriented in random direction (46), resulting in the 0.6 used here.

Klemens also pointed out that for an alloy with dislocations, the concentration of the solute atoms could be modulated by the strain fields around the dislocations (10, 45). This can reinforce or oppose the scattering of dislocation strain depending on details of mismatch of masses and volumes of atoms in the alloy. The modified scattering due to dislocation strain can be calculated by changing the initial Grüneisen parameter \((\gamma)\) by adding a change in Grüneisen parameter due to impurity atmosphere \((\gamma_1)\) (50) as given in eqn. 7 (see Table S4).

\[
\gamma_1 = \frac{V_{\text{Sb}_2\text{Te}_3} c_0 K}{k_B T_a} \left( \gamma \alpha^2 - \alpha \beta \right)
\]

\[
\alpha = \frac{(V_{\text{Bi}_2\text{Te}_3} - V_{\text{Sb}_2\text{Te}_3})}{V_{\text{Sb}_2\text{Te}_3}}, \quad \beta = \frac{1}{2} \left( \frac{M_{\text{Sb}_2\text{Te}_3} - M_{\text{Bi}_2\text{Te}_3}}{M_{\text{Sb}_2\text{Te}_3}} \right)
\]

\(V_{\text{Bi}_2\text{Te}_3}, V_{\text{Sb}_2\text{Te}_3}, M_{\text{Bi}_2\text{Te}_3}, M_{\text{Sb}_2\text{Te}_3}, K, c_0, T_a\) are atomic volume of \(\text{Bi}_2\text{Te}_3\), that of \(\text{Sb}_2\text{Te}_3\), average atomic mass of \(\text{Bi}_2\text{Te}_3\), that of \(\text{Sb}_2\text{Te}_3\), bulk modulus of \(\text{Sb}_2\text{Te}_3\), concentration of \(\text{Bi}_2\text{Te}_3\) in \((\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3\) and sample annealing temperature. Since \(\tau_{DS}^{-1}\) is proportional to \(\gamma^2\) (see eqn. 6), the reinforcement of scattering of dislocation strain is substantial, increasing \(\tau_{DS}^{-1}\) by a factor of 2.2.

In addition to the alloy strengthening of \(\tau_{DS}^{-1}\), the close proximity of the dislocations compounds the effect. As described by Klemens, when the spacing between dislocations is small, the scattering from the parallel dislocations is reinforced (10, 45). If the spacing between dislocations is smaller than phonon wavelength, we should group those dislocations into one dislocation with a new effective Burgers vector (10, 45, 51). Since, from a calculation by Wang (52), the median wavelength of phonons contributing to lattice thermal conductivity of bismuth telluride is \(\sim 3.6\) nm (wavelength at 50% cumulative thermal conductivity), we can expect a compounding effect for more than half the phonons as the spacing between dislocations is \(\sim 2.5\) nm. Because of the uncertainty of this compounding effect and the actual Burgers vector in all the dislocation arrays, we fit the experimental data with an effective Burgers vector \(B_D\). The effective Burgers vector \(B_D\) that fits the experimental data for Te-MS has a magnitude of \(\sim 12.7\) Å, which is...
reasonable considering the Burgers vectors (24) observed in Bi$_2$Te$_3$ and the compounding effect.

Bipolar effects in the total thermal conductivities visible at high temperature of BM, S-MS and Te-MS were estimated by a two band model, which is an extension of a simple parabolic band model (53) (the bipolar effect is less than 10% at 300 K for Te-MS). The band structure of the sample was approximated with a conduction band and a valence band. Each band’s mass and mobility was determined for different samples by fitting calculated electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) to experimental results of different samples (see Fig. 2A and 2B).
Table S3. Types of scatterings used to calculate the $\tau_{\text{tot}}$ where $\tau_U$, $\tau_{PD}$, $\tau_B$, $AB_D^2\tau_{DS}$ and $\tau_{DC}$ are the phonon relaxation times associated with scatterings from Umklapp processes, point defects, boundaries, dislocation strain and dislocation cores, respectively.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\tau_{\text{tot}}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>$\tau_{\text{tot}}^{-1} = \tau_U^{-1} + \tau_{PD}^{-1} + \tau_B^{-1} (20 \mu\text{m})$</td>
</tr>
<tr>
<td>S-MS</td>
<td>$\tau_{\text{tot}}^{-1} = \tau_U^{-1} + \tau_{PD}^{-1} + \tau_B^{-1} (300 \text{ nm})$</td>
</tr>
<tr>
<td>Te-MS</td>
<td>$\tau_{\text{tot}}^{-1} = \tau_U^{-1} + \tau_{PD}^{-1} + \tau_B^{-1} (300 \text{ nm})^{-1} + AB_D^2\tau_{DS}^{-1} + \tau_{DC}^{-1}$</td>
</tr>
<tr>
<td>Parameters</td>
<td>Description</td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\theta_a$</td>
<td>Acoustic mode Debye temperature</td>
</tr>
<tr>
<td>$v$</td>
<td>Average phonon velocity along $a$-plane</td>
</tr>
<tr>
<td>$v_L$</td>
<td>Longitudinal phonon velocity along $a$-plane</td>
</tr>
<tr>
<td>$v_T$</td>
<td>Transverse phonon velocity along $a$-plane</td>
</tr>
<tr>
<td>$\bar{M}$</td>
<td>Average atomic mass of $(\text{Bi}<em>{0.25}\text{Sb}</em>{0.75})_2\text{Te}_3$</td>
</tr>
<tr>
<td>$M_{\text{Bi}_2\text{Te}_3}$</td>
<td>Average atomic mass of $\text{Bi}_2\text{Te}_3$</td>
</tr>
<tr>
<td>$M_{\text{Sb}_2\text{Te}_3}$</td>
<td>Average atomic mass of $\text{Sb}_2\text{Te}_3$</td>
</tr>
<tr>
<td>$V_{\text{Bi}_2\text{Te}_3}$</td>
<td>Atomic volume of $\text{Bi}_2\text{Te}_3$</td>
</tr>
<tr>
<td>$V_{\text{Sb}_2\text{Te}_3}$</td>
<td>Atomic volume of $\text{Sb}_2\text{Te}_3$</td>
</tr>
<tr>
<td>$V$</td>
<td>Average atomic volume of $(\text{Bi}<em>{0.25}\text{Sb}</em>{0.75})_2\text{Te}_3$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Grüneisen parameter</td>
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<tr>
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<td>Poisson’s ratio</td>
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<td>Dislocation density</td>
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<tr>
<td>$B_D$</td>
<td>Magnitude of Burgers vector</td>
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<tr>
<td>$d$</td>
<td>Grain size of BM</td>
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<tr>
<td>$d$</td>
<td>Grain size of S-MS and Te-MS</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Concentration of $\text{Bi}<em>2\text{Te}<em>3$ in $(\text{Bi}</em>{0.25}\text{Sb}</em>{0.75})_2\text{Te}_3$</td>
</tr>
<tr>
<td>$K$</td>
<td>Bulk modulus</td>
</tr>
<tr>
<td>$T_a$</td>
<td>Sample annealing temperature</td>
</tr>
</tbody>
</table>
Additional Author notes

Author Contributions
S.W.K. and K.H.L. organized the research. S.I.K. and H.A.M fabricated the samples and measured the thermoelectric properties. H.A.M and H.S.K analyzed the data. S.W.K and G.J.S wrote the manuscript. All the authors contributed to the experiments, the analysis of the data and editing of the manuscript.
References


17. Materials and methods are available as supplementary materials on *Science* Online.


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