Supplementary Information

High ZT in p-Type Thermoelectric (Bi,Sb)₂Te₃ with Built-in Nanopores

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Part I. Supplementary Data and Diagrams

Table. S1. Density of $(Bi_{0.4}Sb_{1.6})_{1-\nu/2}Zn_{\nu}Te_{3-x}I_x$ samples in this work.

x	у	Density (g/cm ³)	Relative density
0	0	6.651	98.1%
0.003	0	6.630	97.8%
0.005	0	6.625	97.7%
0.007	0	6.620	97.5%
0.010	0	6.605	97.4%
0.005	0.004	6.640	97.9%
0.005	0.007	6.632	97.8%
0.005	0.010	6.612	97.5%



Fig. S1 A Low-magnification TEM images for nanopores in y = 0.004 sample with the EDS mapping for Bi, Sb, Te, Zn, and I elements.



Fig. S2 An HRTEM image for the surface of a nanopore of the x = 0.005 sample with the FFT and IFFT image of regions A and B.



Fig. S3 Thermodynamic behavior of BiI_3 measured through thermal gravimetry analysis (TGA). The weight loss begins to occur at around 595 K, indicating the sublimation of BiI_3 into vapor.



Fig. S4 The comparison of high-resolution I 3d spectrum by XPS analysis for the MAed x = 0.005 and y = 0.004 samples before and after the SPS process, indicating that BiI₃ escaped from the matrix after the SPS process.



Fig. S5 EPMA point analysis for x = 0.005, y = 0.004 and y = 0.010 samples with backscattered electron image of the matrix and some Te-rich phases.



Fig. S6 The area composition analysis by the STEM mode of TEM for x = 0.005 and y = 0.004 samples.



Fig. S7 Temperature dependence of the (a) power factor and (b) weighted mobility for $Bi_{0.4}Sb_{1.6}Te_{3-x}I_x$ and $(Bi_{0.4}Sb_{1.6})_{1-y/2}Zn_yTe_{2.995}I_{0.005}$ samples with the corresponding amounts of BiI_3 and Zn (inset shows the values and their variation trend with different *x* and *y* at 303 K).



Fig. S8 The XRD patterns for $Bi_{0.4}Sb_{1.6}Te_{3-x}I_x$ and $(Bi_{0.4}Sb_{1.6})_{1-y/2}Zn_yTe_{2.995}I_{0.005}$ samples with the corresponding amounts of BiI₃ and Zn along the direction of parallel to the direction of SPS pressure. The enlarged image for 2θ range from 27.8 to 28.5 is shown on the right side.



Fig. S9 Pisarenko curve at 308 K for $Bi_{0.4}Sb_{1.6}Te_{3-x}I_x$ and $(Bi_{0.4}Sb_{1.6})_{1-y/2}Zn_yTe_{2.995}I_{0.005}$ samples with the corresponding amounts of BiI_3 and Zn using the effective mass model (Seebeck coefficient dependence of Hall carrier concentration).



Fig. S10 The data for repeatedly prepared samples. Temperature dependence of the (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) the total thermal conductivity, (e) lattice, and bipolar thermal conductivity, and (f) the *ZT* values.



Fig. S11 The data of repeated measurement for the y = 0.004 sample. Temperature dependence of the (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) the total thermal conductivity, (e) lattice, and bipolar thermal conductivity, and (f) the *ZT* values.

As shown in **Fig. S11**, the electrical and thermal transport properties changed a little after the first time of measurement, but after that no apparent change was observed. The *ZT* value kept almost unchanged of > 1.5, which confirmed the cycle stability of the sample.



Fig. S12 The SEM images for the morphology of grains for $Bi_{0.4}Sb_{1.6}Te_{3-x}I_x$ and $(Bi_{0.4}Sb_{1.6})_{1-y/2}Zn_yTe_{2.995}I_{0.005}$ samples with the corresponding amounts of BiI₃ and Zn.



Fig. S13 The electric current dependence of (a) heat flow and (b) output power under different hot-side temperatures for the segmented single-leg for the y = 0.004 sample. The cold-side temperature was 298 K.



Fig. S14 The Mini-PEM measuring data for two single-leg modules under the cold-side temperature of 298 K. The electrical current dependence of the (1) measured TE conversion efficiency, (2) heat flow, and (3) output power under different hot-side temperatures for (a) Device 2 and (b) Device 3.

The Mini-PEM measuring data for two single-leg modules are shown in **Fig. S14**. Both of them exhibited high TE conversion efficiency of >4.7%, which confirmed the reproducibility of the single-leg module.

Part II. Supplementary discussion on electrical transport properties

The temperature dependence of Hall carrier concentration $(n_{\rm H})$ and mobility $(\mu_{\rm H})$ are presented in **Fig. 5c and 5d**, which can explain the variation of σ and *S*. The $n_{\rm H}$ slightly increased for x = 0.003, and further increasing the amount of BiI₃ caused $n_{\rm H}$ to decrease. All samples added BiI₃ had the $n_{\rm H}$ higher than the pristine (Bi,Sb)₂Te₃. Therefore, the increase of σ was mainly attributed to the increased $n_{\rm H}$. This variation trend was distinct from the effect of Idoping reported by previous literature and could be explained by the forming process of nanopores. The sublimation of BiI₃ decreased the ratio of Bi: Sb below its nominal value, which increased the antisite defects Sb'_{Te} and therefore increased the carrier concentration. The varied ratio of Bi: Sb also led the XRD peaks to shift to higher angles by the shrink of lattice, as shown in **Fig. S8**. Although much of the BiI₃ escaped during the sintering process, there was a proportion of BiI₃ doped into the matrix that reduced the $n_{\rm H}$ based on equation (1):

$$BiI_{3} \xrightarrow{(Bi,Sb)_{2}Te_{3}} Bi_{Bi,Sb} + 3I_{Te} + 3e'$$
(1)

which led to the reduction of positive carrier charges. This doping effect of the I atoms might be the reason for the decreased $n_{\rm H}$ when $x \ge 0.005$. In addition, the $n_{\rm H}$ for all samples increased with increasing temperature due to the intrinsic excitation, which led to the decrease of *S* with increasing temperature. The unchanged onset temperature of ~373 K for the intrinsic excitation indicates that the addition of BiI₃ did not change the bandgap. The Pisarenko curve at 303 K is plotted in **Fig. S9**, which demonstrates that the density of state (DOS) effective mass (m^*) maintained ~1.38 m_e for a different amount of BiI₃, indicating that the band structure may not change. In contrast, the $\mu_{\rm H}$ barely changed for x ≤ 0.007 , as demonstrated in **Fig. S**d. When the *x* increased to 0.01, the $\mu_{\rm H}$ became slightly lower than the pristine (Bi,Sb)₂Te₃. Intrinsically, the weight mobility ($\mu_{\rm w}$) also generally decreased with increasing *x* as shown in **Fig. S7**b, indicating that some potential scattering centers were formed with added BiI₃.^[1] As mentioned before, it would be the nanopores that slightly scattered the charge carriers.

The reasons for the improvement in electrical transport properties after Zn doping are attributed to increased carrier concentration with a low decrease in carrier mobility, as shown in **Fig. 5**c **and 5**d. The increase of carrier concentration could be described by the equation:

$$2Zn \xrightarrow{(Bi,Sb)_2 Te_3} 2Zn_{Bi,Sb} + 3Te_{Te}^{\times} + 2h^{\bullet}$$
(2)

The (015) XRD peak shifting to a higher angle in **Fig. S8** reveals the successful doping of a portion of Zn into the matrix. In general, the introduced $Zn_{Bi,Sb}$ would decrease the carrier mobility accordingly. However, in this work, the lower decrease in carrier mobility was probably due to the tendentious distribution of Zn atoms around the nanopores, as shown in **Fig. 3d and S1**. These aggregated defect clusters reduced the widely distributed point defect scattering centers into a single scattering center, thereby reducing the decrement in carrier mobility when doping. Because of this, the μ_w slightly increased when doping with Zn (y = 0.004), as shown in **Fig. S7**b.

The reason for the deterioration in electrical transport properties for the y = 0.01 sample can be analyzed by the EPMA, as demonstrated in **Fig. S5**. With the introduction of the Zn element, some Te-rich phases were observed in the sample. It is possible that the overmuch Zn doping would induce Te to precipitate, which would leave $V_{Te}^{\bullet\bullet}$ in the matrix that accompanies the generation of negative charges, thereby decreasing the carrier concentration. The introduced $V_{Te}^{\bullet\bullet}$ would enhance the charge carrier scattering, leading to the decrease of μ_w for $y \ge 0.007$.

Part III. Single Parabolic Band (SPB) modeling

As a kind of degenerate semiconductor, the samples can be analyzed by the Single Parabolic Band (SPB) Model with relaxation time approximation.^[1-3] The Seebeck coefficient can be expressed as:

$$S = \frac{k_B}{e} \left[\frac{\left(\frac{5}{2} + \lambda\right) F_3}{\left(\frac{3}{2} + \lambda\right) F_{\frac{1}{2} + \lambda}}(\eta)} - \eta \right]$$
(3)

The charge carrier concentration can be expressed as:

$$n_{H} = 4\pi \frac{\left(2k_{B}Tm^{*}\right)^{\frac{3}{2}}}{h^{3}} F_{\frac{1}{2}}(\eta)$$
(4)

1

where *e* is the elementary charge, λ is the scattering parameter taken as $\overline{2}$ for acoustic phonon scattering ($\mu_H \propto T^{-\frac{3}{2}}$ around room temperature), m^* is the density-of-state (DOS) effective

mass, η is the reduced Fermi level. $\eta = \frac{E_F}{k_B T}$, where E_F is the Fermi level. The $F_j(\eta)$ is Fermi integral, which can be expressed as:

$$F_j(\eta) = \int_0^\infty \frac{x^j}{1 + e^{(x-\eta)}} dx$$
(5)

The charge carrier mobility is directly correlated with the nondegenerate limits of drift mobility (μ_0) , which can be expressed as:

$$\mu_{H} = \mu_{0} \frac{F_{-\frac{1}{2}}(\eta)}{2F_{0}(\eta)} \tag{6}$$

The weighted mobility is always defined as:

$$\mu_W = \mu_0 \left(\frac{m^*}{m_e}\right)^{\frac{3}{2}} \tag{7}$$

The electrical transport coefficient can be given as:

$$\sigma_{E_0} = \frac{8\pi e (2m_e k_B T)^{\frac{3}{2}}}{3h^3} \mu_W$$
(8)

Then the electrical conductivity can be expressed as:

$$\sigma = \sigma_{E_0} F_0(\eta) \tag{9}$$

Therefore, by solving the equations above, a simple analytic form for the weighted mobility within 3% for thermopower values $|S| > 20 \ \mu V \cdot K^{-1}$ can be obtained, which can be expressed as:^[1]

$$\mu_{W} = \frac{3h^{3}\sigma}{8\pi e (2m_{e}k_{B}T)^{\frac{3}{2}}} \left[\frac{exp \left[\frac{|S|}{k_{B}/e} - 2 \right]}{1 + exp \left[-5 \left(\frac{|S|}{k_{B}/e} - 1 \right) \right]} + \frac{\frac{3}{\pi^{2}k_{B}/e}}{1 + exp \left[5 \left(\frac{|S|}{k_{B}/e} - 1 \right) \right]} \right]$$
(10)

Part IV. Calculation of thermal transport properties

1. Effective medium theory (EMT)

The effective medium theory (EMT) was applied to correct the effect of the lost medium on phonon transport. The nanopores can be regarded as another medium of air. The relationship for the thermal conductivity between the porous and dense materials can be expressed as:^[4,5]

$$\kappa_p = \kappa_d f_\kappa(\varepsilon) \tag{11}$$

where ε is the porosity volume fraction, κ_p and κ_d are the thermal conductivity for the porous and dense sample, respectively. As confirmed in other literature, supposing the pores to be spherical does not overestimate the effects of pores on decreasing the thermal conductivity.^[4,6] Therefore, the pores were simply supposed as spherical, of which the EMT function *f* can be expressed as:^[4,7]

$$f_{\kappa}(\varepsilon) = 1 - \frac{3\varepsilon}{2} \tag{12}$$

2. Debye-Callaway's model

To better understand the main factor of the reduced lattice thermal conductivity, Debye-Callaway's model was adopted, which integrates the relaxation time from Umklapp processes, Normal processes, grain boundary scattering, point defect scattering, second phase scattering, and dislocation scattering. The expression of the model is shown as follows:^[4,8-13]

$$\kappa_{L}(\omega) = \frac{k_{B}}{2\pi^{2}\nu} \int_{0}^{\overline{T}} \tau_{C}(\omega) \left(\frac{\hbar\omega}{k_{B}T}\right)^{2} \frac{\omega^{2} e^{\frac{\hbar\omega}{k_{B}T}} d\omega}{\left(e^{\frac{\hbar\omega}{k_{B}T}} - 1\right)^{2}}$$
(13)

The frequency dependence of the lattice thermal conductivity can be calculated using the following model:^[8,14]

$$\kappa_{s}(\omega) = \frac{k_{B}}{2\pi^{2}v} \tau_{C}(\omega) \left(\frac{\hbar\omega}{k_{B}T}\right)^{2} \frac{\omega^{2} e^{\frac{\hbar\omega}{k_{B}T}}}{\left(e^{\frac{\hbar\omega}{k_{B}T}} - 1\right)^{2}}$$
(14)

In these equations, $k_{\rm B}$ is the Boltzmann constant, θ_D is the Debye temperature, \hbar is the reduced Planck constant, v is the average phonon-group velocity, ω is the phonon angular frequency and T is the absolute temperature, respectively. τ_C is the total relaxation time, which follows Matthiessen's rule as:^[9,11]

$$\tau_{C}^{-1} = \tau_{U}^{-1} + \tau_{N}^{-1} + \tau_{GB}^{-1} + \tau_{PD}^{-1} + \tau_{D}^{-1} + \tau_{NS}^{-1} \cdots$$
(15)

The contribution of Umklapp (τ_{U}^{-1}) and Normal (τ_{N}^{-1}) processes to the relaxation time can be expressed as:^[12,15]

$$\tau_{U}^{-1} + \tau_{N}^{-1} = A \frac{2 k_{B} \overline{v}^{3} \gamma^{2} \omega^{2} T}{(6\pi^{2})^{\frac{1}{3}} M v^{3}}$$
(16)

where A is a comprehensive coefficient, since τ_U^{-1} is in proportion to τ_N^{-1} . V is the atomic volume of Bi_{0.4}Sb_{1.6}Te₃, γ is the Grüneisen parameter, M is the average atomic mass of Bi_{0.4}Sb_{1.6}Te₃.

The contribution of grain boundary scattering to the relaxation time can be expressed as:^[9]

$$\tau_{GB}^{-1} = \frac{v}{d} \tag{17}$$

where d is the average grain size.

The point defect scattering in $Bi_{0.4}Sb_{1.6}Te_3$ mainly comes from the disordered arrangement of Bi and Sb atoms in the equivalent position, which can be expressed as:

$$\tau_{PD}^{-1} = \frac{\bar{V}\omega^4}{4\pi\nu^3}\Gamma\tag{18}$$

where the Γ is the point defect scattering parameter.

The contribution of dislocation scattering to the relaxation time τ_D^{-1} contains two parts, which can be respectively described as:^[9]

Dislocation core:

$$\tau_{DC}^{-1} = N_D \frac{V^{\frac{4}{3}}}{v^2} \omega^3 \tag{19}$$

Dislocation strain:

$$\tau_{DS}^{-1} = 0.6B_D^2 N_D \gamma^2 \omega \left[\frac{1}{2} + \frac{1}{24} \left(\frac{1-2r}{1-r} \right)^2 \left\{ 1 + \sqrt{2} \left(\frac{\nu_L}{\nu_T} \right)^2 \right\}^2 \right]$$
(20)

where ${}^{B}{}_{D}$ is the effective Burger's vector, ${}^{N}{}_{D}$ is the dislocation density, r is the Poisson's ratio, ${}^{v}{}_{L}$ is the longitudinal phonon velocity and ${}^{v}{}_{T}$ is the transverse phonon velocity, respectively.

When regarding the nanopores and Zn-rich defect clusters as a solid spherical second phase (Zn_2Te_3) , the contribution of their scattering to the relaxation time can be expressed as:^[11,16]

$$\tau_{S}^{-1} = v \left(\sigma_{s}^{-1} + \sigma_{l}^{-1} \right)^{-1} V_{S}$$
(21)

In this equation, σ_s and σ_l are the scattering cross-section in short- and long- wavelength regimes, respectively. Their expressions are as follows:

$$\sigma_s = 2\pi R^2 \tag{22}$$

$$\sigma_l = \frac{4}{9}\pi R^2 \left(\frac{\Delta D}{D}\right)^2 \left(\frac{\omega R}{v}\right)^4 \tag{23}$$

where R is the equivalent mean radius of the second phase; D and ΔD are the mass density of host and density difference between host and second phase, respectively; V_S is the number density of the second phase.

All parameters involved above are given in Table S2.

Parameters	Notes	Values	Methods
θ_D	Acoustic mode Debye temperature	124	Calculated ^[17]
v	Average speed of sound	1911 m·s ⁻¹	Calculated ^[17]
Α	Comprehensive coefficient between	2.6	Ref. ^[12]
	Umklapp and Normal processes		
\overline{V}	Average atomic volume of Bi _{0.4} Sb _{1.6} Te ₃	3.23×10 ⁻²⁹ m ³	Ref. ^[18]
\overline{M}	Average atomic mass of Bi _{0.4} Sb _{1.6} Te ₃	2.20×10 ⁻²⁵ kg	Calculated
$M_{Bi_2Te_3}$	Average atomic mass of Bi ₂ Te ₃	2.66×10 ⁻²⁵ kg	Calculated
$M_{Sb_2Te_3}$	Average atomic mass of Sb ₂ Te ₃	2.08×10 ⁻²⁵ kg	Calculated
γ	Grüneisen parameter	1.5	Calculated

Table. S2. Parameters for the calculation of lattice thermal conductivity.

d	Grain size	1 µm	Experimental
Γ	Point defect scattering parameter	0.175	Fitted
N _D	Dislocation density	$6 \times 10^{10} \text{ cm}^{-2}$	Experimental
B _D	Magnitude of Burger's vector	12.7 Å	Ref. ^[13]
r	Poisson's ratio	0.25	Calculated
v_L	Longitudinal sound velocity	2988 m·s ⁻¹	Experimental
v_T	Transverse sound velocity	1721 m·s ⁻¹	Experimental
R	Equivalent mean radius of the nanopores	30 nm, 40 nm	Experimental
	and Zn-rich defect clusters as second		
	phases		
D	Mass density of host	6.7932 g·cm ⁻³	Ref. ^[18]
D _S	Equivalent mass density of Zn-rich	5.28 g·cm ⁻³	Calculated
	defect cluster as second phase (solid		
	Zn_2Te_3)		
V _S	Number density of nanopores and Zn-	$4.6 \times 10^{14} \text{ cm}^{-3}$	Experimental
	rich defect cluster		

References

[1] G. J. Snyder, A. H. Snyder, M. Wood, R. Gurunathan, B. H. Snyder, C. Niu, *Adv. Mater.***2020**, 32, 2001537.

- [2] H. J. Goldsmid, P. L. Balise, Applications of Thermoelectricity, 1961.
- [3] T. P. Hogan, T. Shih, D. M. Rowe, *Thermoelectrics Handbook: Macro to Nano*, 2005.

[4] Y. Pan, U. Aydemir, J. A. Grovogui, I. T. Witting, R. Hanus, Y. Xu, J. Wu, C.-F. Wu, F.-

H. Sun, H.-L. Zhuang, J.-F. Dong, J.-F. Li, V. P. Dravid, G. J. Snyder, *Adv. Mater.* 2018, 30, 1802016.

- [5] D. Stroud, *Phys. Rev. B* **1975**, 12, 3368.
- [6] C. Nan, R. Birringer, D. R. Clarke, H. Gleiter, J. Appl. Phys. 1997, 81, 6692.
- [7] H. J. Juretschke, R. Landauer, J. A. Swanson, J. Appl. Phys. 1956, 27, 838.
- [8] J. Callaway, H. C. Von Baeyer, *Phys. Rev.* **1960**, 120, 1149.

[9] S. Il Kim, K. H. Lee, H. A. Mun, H. S. Kim, S. W. Hwang, J. W. Roh, D. J. Yang, W. H. Shin, X. S. Li, Y. H. Lee, G. J. Snyder, S. W. Kim, *Science* **2015**, 348, 109.

[10]F.-H. Sun, J. Dong, H. Tang, P.-P. Shang, H.-L. Zhuang, H. Hu, C.-F. Wu, Y. Pan, J.-F. Li, *Nano Energy* **2019**, 57, 835.

[11]D. Wu, L. D. Zhao, F. Zheng, L. Jin, M. G. Kanatzidis, J. He, Adv. Mater. 2016, 28, 2737.

[12] Y. Yu, D.-S. He, S. Zhang, O. Cojocaru-Mirédin, T. Schwarz, A. Stoffers, X.-Y. Wang, S. Zheng, B. Zhu, C. Scheu, D. Wu, J.-Q. He, M. Wuttig, Z.-Y. Huang, F.-Q. Zu, *Nano Energy* 2017, 37, 203.

[13]B. Zhu, Y. Yu, Z.-G. Chen, X.-Y. Wang, F.-Q. Zu, Z.-Y. Huang, L. Yang, N. Gao, *Nano Energy* **2017**, 42, 8.

[14] Y. Pan, J.-F. Li, NPG Asia Mater. 2016, 8, e275.

[15]E. S. Toberer, A. Zevalkink, G. J. Snyder, J. Mater. Chem. 2011, 21, 15843.

[16] W. Kim, A. Majumdar, J. Appl. Phys. 2006, 99, 084306.

[17]K. Kurosaki, A. Kosuga, H. Muta, M. Uno, S. Yamanaka, *Appl. Phys. Lett.* 2005, 87, 061919.

[18] M. M. Stasova, N. K. Abrikosov, Izv. Akad. Nauk SSSR Neorg. Mater. 1970, 6, 1090.