## Supporting Information

# Rare three-valence-band convergence leading to ultrahigh

thermoelectric performance in all-scale hierarchical cubic SnTe

Fan Li,<sup>a</sup> Xin Liu,<sup>a</sup> Shu-Rong Li,<sup>c</sup> Xiao-Fan Zhang,<sup>d</sup> Ni Ma,<sup>a</sup> Xin-Jing Li,<sup>a</sup> Xin-Yun Lin,<sup>a</sup> Ling Chen, \*,<sup>a,b</sup> Hai-Jun Wu, \*,<sup>c</sup> and Li-Ming Wu\*,<sup>a,b</sup>

<sup>a</sup> Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, *People's Republic of China* 

<sup>b</sup>Center for Advanced Materials Research, Beijing Normal University, Zhuhai 519087, *People's Republic of China* E-mails: chenl@bnu.edu.cn, wlm@bnu.edu.cn

<sup>c</sup> State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, *People's Republic of China* 

<sup>d</sup> Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, *People's Republic of China* 

#### 1. EXPERIMENTAL SECTION

#### 1.1 Materials fabrication.

High-purity reactants of stoichiometric Sn shot (99.99%, Alfa Aesar), Mn powder (99.995%, Alfa Aesar), Cd powder (99.99%, Aladdin element), Ge powder (99.999%, Aladdin element) and Te shot (99.99%, Aladdin element) were weighed and mixed under a glove box with nitrogen atmosphere, and then loaded into a carbon-coated quartz tube (10 mm in diameter), which was subsequently flame-sealed at 10-3 Pa. And then, the tubes were heated up to 1273 K in 12 h and dwelt at this temperature for 25 h followed by quenching in liquid nitrogen to room temperature and subsequently annealed at 923 K for 50 h. The obtained ingots were grinded into fine powders in an agate mortar and densified at 923 K for 60 min under a pressure of 60 MPa by hot pressing. With the experimental measured mass and dimensions, the density of the pellet was evaluated to be greater than 95% of the theoretical density. Afterwards, the pellets were polished by an abrasive before cut into  $\sim 2.5 \times 2.5 \times 9 \text{ mm}^3$  for the electrical performance measurements, and  $\sim 6 \times 6 \times 1.2 \text{ mm}^3$  for the thermal diffusivity and Hall coefficient measurements, respectively. In order to fabricate the single-leg module and junction of  $SnTe_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  and Ni electrode, the obtained SnTe<sub>0.92</sub>(MnCd<sub>0.6</sub>Ge<sub>0.4</sub>Te<sub>2</sub>)<sub>0.08</sub> powder and the Ni powders were sequentially loaded into a graphite die for one-step hot pressing at 923 K for 60 min under 60 MPa, obtaining a Ni/ SnTe<sub>0.92</sub> (MnCd<sub>0.6</sub>Ge<sub>0.4</sub>Te<sub>2</sub>)<sub>0.08</sub>/Ni cylinder with dimensions of ~10 mm in diameter and  $\sim 8$  mm in thickness. Afterwards, the junctions were polished by an abrasive before cut into  $\sim 3 \times 3 \times 8 \text{ mm}^3$  for the contact resistance and the thermoelectric conversion efficiency measurements.

1.2 Characterization.

The phase purity was evaluated at room temperature by the X-ray diffraction instrument (Bruker D8 ADVANCE, Cu K $\alpha$ 1 radiation  $\lambda$  = 1.5406 Å). The field emission Scanning electron microscopy (Oxford Instruments, JSM-7800F), electron back-scattering diffraction (EBSD) and energy-dispersive X-ray (EDX) analyses were applied to investigate the microstructure and elemental mapping. The optical band gap was measured on the finely ground powders using the infrared Fourier transform

spectroscopy in a frequency of 4000 - 400 cm<sup>-1</sup>. The The ultraviolet photoelectron spectroscopy (UPS) valence band maxima spectra were measured on a Thermo ESCALAB XI + with a He I radiation source (hv = 21.2 eV) in high vacuum. Furthermore, High-resolution transmission electron microscopy (HRTEM, 2100F, investigate microstructure Japan) was also applied to the of the  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  sample, which was prepared by conventional mechanical thinning to a thickness of  $\approx 10 \mu m$ , and then followed by ion milling. Atomic resolution STEM-HAADF imaging and energy dispersive X-ray mapping (EDX) experiments were performed on a JEOL ARM200F transmission electron microscope with a probe aberration corrector and an Oxford X-MaxN 100TLE spectrometer, operated at 200 keV. Pulse-echo method was used to measure the speed of sound and the waveforms were recorded using a Tektronix TBS 1102 oscilloscope.

#### 1.3 Transport Property Measurement.

The electrical transport properties of the Seebeck coefficient S and the electrical conductivity  $\sigma$  were synchronously measured on the commercial ZEM-3 (Ulvac Riko, Inc.) from 300 to 900 K under the constant helium atmosphere. The total thermal conductivity was calculated by the formula  $\kappa = D \times C_p \times d$ , where the thermal diffusivity (D) was measured on a Netzsch LFA-457 in the temperature range of 300 - 900 K, the specific heat  $(C_p)$  was derived using standard sample (pyroceram9606) in LFA-457, which is in good agreement with Dulong Petit limit (Fig. S12), and the density  $(\rho)$ determined by the measured mass and dimensions (Table S4). The Hall measurement was carried out by using the van der Pauw technique under a reversible magnetic field of 1.5 T on a home-made apparatus. The carrier concentration n and mobility  $\mu$  were calculated by relations of  $\mu = \sigma R_{\rm H}$  and  $n = 1/eR_{\rm H}$ , where e is the electron charge,  $R_{\rm H}$  is the Hall coefficient, and  $\sigma$  is the electrical conductivity. The measurement of low temperature heat capacity (Cp) was performed in a Physical Property Measurement System (PPMS-9: Quantum Design). The room temperature longitudinal and transverse sound velocities were measured by Pulse-echo method and the waveforms were recorded using a Tektronix TBS 1102 oscilloscope.

1.4 Theoretical Calculation.

DFT calculations within the generalized gradient approximation (GGA) were employed to calculate band structures of the compounds<sup>1</sup>, and a plane-wave basis with the projector augmented wave (PAW) potentials were applied.<sup>2</sup> To accurately obtain the electronic band structures of SnTe, spin-orbital interactions (SOC) were included in all calculations. The pseudopotentials were used to simulate the ion electron interaction of all constituent elements: Sn 5s<sup>2</sup>5p<sup>2</sup>, Te 5s<sup>2</sup>5p<sup>4</sup>, Mn 3p<sup>6</sup>3d<sup>5</sup>4s<sup>2</sup>, Cd 4d<sup>10</sup>5s<sup>2</sup>, Ge 3d<sup>10</sup>4s<sup>2</sup>4p<sup>2</sup>. A kinetic energy cutoff of 500 eV was chosen with Monkhorst-Pack k-point meshes spanning less than 0.05/Å<sup>3</sup> in the Brillouin zone.<sup>3</sup> Periodic boundary conditions and a plane wave basis set as implemented in the Vienna ab initio simulation package (VASP) were used.<sup>4</sup> And then we use the optimized structures to calculate the static self-consistency, the density of state and energy band with a dense 0.02/Å<sup>3</sup> k-point spacing mesh. A  $2 \times 2 \times 2$  supercell based on primitive cell of SnTe containing 54 atoms was constructed for simulation. The special quasi-random structure (SQS) of Sn<sub>27</sub>Te<sub>27</sub>, Sn<sub>25</sub>MnCdTe<sub>27</sub>, Sn<sub>24</sub>Mn<sub>2</sub>CdTe<sub>27</sub> Sn<sub>23</sub>Mn<sub>2</sub>CdGeTe<sub>27</sub> and Sn<sub>25</sub>Mn<sub>2</sub>Te<sub>27</sub> were generated using the mcsqs tool as implemented in the alloy theoretic automated toolkit (ATAT).<sup>5</sup> Lattice parameters and atomic positions were optimized, and the configuration that had the lowest energy was chosen for the defect-containing supercell. The lattice dynamical properties were calculated utilizing the Phonopy package.<sup>6</sup> A 2  $\times 2 \times 1$  supercell for Sn<sub>8</sub>Te<sub>8</sub>, Sn<sub>6</sub>MnCdTe<sub>8</sub> was constructed to realize the convergence of Hellmann-Feynman forces. The convergence criteria of 10<sup>-5</sup> eV Å<sup>-1</sup> per atom for the relaxation process of a unit cell and  $10^{-7}$  eV for self-consistent calculations was employed. The temperature-dependent phonon dispersions and density of states for Sn<sub>8</sub>Te<sub>8</sub> and Sn<sub>6</sub>MnCdTe<sub>8</sub> were calculated through the ab initio molecular dynamics (AIMD) simulations within the isothermal-isovolume NVT ensemble (ran for 20 ps with a time step of 1 fs, excluding the first 4 ps steps) at 300 K. Then we used the power spectrum fitting model-spectrum-function shape in Dynaphonopy<sup>7</sup> to process the trajectory of the AIMD by fitting the power spectrum of the atomic velocity projected into the phonon modes coordinates into model-spectral-function shapes with Fourier transform.



### 2. XRD RESULTS AND TE PERFORMANCE.

Figure S1. PXRD patterns of the  $(SnTe)_{1-x}(MnCdTe_2)_x$  samples.



Figure S2. Temperature dependence of (a)  $\sigma$ , (b) *S*, (c)  $\kappa_{T}$ , (d) *ZT* (e) *PF* and (f)  $\kappa_{L}$  for the (SnTe)<sub>1-x</sub>(MnCdTe<sub>2</sub>)<sub>x</sub> samples.



Figure S3. PXRD patterns of the (SnTe)<sub>0.92</sub>(MnCd<sub>1-y</sub>Ge<sub>y</sub>Te<sub>2</sub>)<sub>0.08</sub> samples.



Figure S4. Temperature dependence of (a)  $\sigma$ , (b) *S*, (c) *PF* (d)  $\kappa_{T}$ , (e)  $\kappa_{L}$  and (f) *ZT* for the (SnTe)<sub>0.92</sub>(MnCd<sub>1-v</sub>Ge<sub>v</sub>Te<sub>2</sub>)<sub>0.08</sub> samples.



Figure S5. In situ XRD patterns versus temperature for the  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  samples from 303 to 923 K.

## 3. MICROSTRUCTURE.



Figure S6. Elemental mappings of Sn (a), Mn (b), Cd (c), Ge (d), Te (e) and electronic image (f) by EDS for the  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  sample as shown in Fig 2c.



Figure S7. BSE images of the polished surfaces of the  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  sample (a), elemental mappings (b - f), electronic image (g) and EDS spectra taken from both the precipitate and matrix (h-j).



Figure S8. BSE images of the polished surfaces of  $(SnTe)_{0.92}(MnCdTe_2)_{0.08}$  sample (a), elemental mappings (b - e), electronic image (f) and EDS spectra taken from both the precipitate and matrix (g-i).



Figure S9. SEM images with EDS elemental mappings for  $(SnTe)_{0.92}(MnCdTe_2)_{0.08}$  (a) and  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  (b), respectively. With Ge alloying,  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  exhibits much smaller precipitates than those of  $(SnTe)_{0.92}(MnCdTe_2)_{0.08}$ .



Figure S10. Statistics precipitate size distributions for  $(SnTe)_{0.92}(MnCdTe_2)_{0.08}$  (a) and  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  (b) obtained by the software nano measurement.



Figure S11. BSE imagines taken from different areas of  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$ , indicating wide distributions of nanoprecipitates with multiple scales.



Figure S12. EBSD grain boundary map and grain size distribution statistics for the high performance  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  sample (a, b) and the

(SnTe)<sub>0.92</sub>(MnCdTe<sub>2</sub>)<sub>0.08</sub> sample (c, d). 4. HEAT CAPACITIES, HALL DATA AND *PF*.



Figure S13. Measured temperature dependent heat capacities of the  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  samples, with a comparison to literature results.<sup>8,9</sup>



Figure S14. (a) Alloying *x* dependence of  $n_{\rm H}$  and  $\mu_{\rm H}$  for the (SnTe)<sub>1-x</sub>(MnCd<sub>1-y</sub>Ge<sub>y</sub>Te<sub>2</sub>)<sub>x</sub> samples. (b) DFT calculated Sn vacancy formation energies of Sn<sub>27</sub>Te<sub>27</sub>, Sn<sub>25</sub>MnCdTe<sub>27</sub>, Sn<sub>24</sub>Mn<sub>2</sub>CdTe<sub>27</sub> and Sn<sub>23</sub>Mn<sub>2</sub>CdGeTe<sub>27</sub>, respectively.



Figure S15. Comparison of PF values of this work and literature results<sup>10–18</sup> for SnTe.

## 5. TRANSPORT PROPERTY CALCULATIONS.

Based on the Boltzmann transport theory, <sup>19</sup> the modeling of transport properties can be estimated by Eqs. S8–S14:

The Hall factor:

$$r_{H} = \frac{3F_{1/2}(\eta)F_{-1/2}(\eta)}{4F_{0}(\eta)^{2}}$$
(S3)

The Hall carrier concentration:

$$n_{H} = \frac{n}{r_{H}} = \frac{\left(2m_{d}^{*}k_{B}T\right)^{3/2} 2F_{0}(\eta)^{2}}{3\pi^{2}\hbar^{3} F_{-1/2}(\eta)}$$
(S4)

The Seebeck coefficient:

$$S = \frac{k_B}{e} \left[ \frac{(r+5/2)F_1(\eta)}{(r+3/2)F_0(\eta)} - \eta \right]$$
(S5)

The Hall carrier mobility, assuming an isotropic band  $(m_b^* = m_l^*)$ :

$$\mu_{H} = \mu r_{H} = \frac{2^{1/2} \pi \hbar^{4} e \rho v_{l}^{2} N_{V}^{5/3} F_{-1/2}(\eta)}{m_{d}^{*5/2} (k_{B}T)^{3/2} E_{def}^{2} 4 F_{0}(\eta)}$$
(S6)

The Fermi integral:

$$F_j(\eta) = \int_0^\infty \frac{\xi^j}{1 + exp^{[i0]}(\xi - \eta)} d\xi$$
(S7)

The reduced Fermi level:

$$\eta = (E_V - E_F) / (k_B T)$$
(S8)

The Lorenz Factor:

$$L = \left(\frac{k_B}{e}\right)^2 \left\{ \frac{(r+7/2)F_{(r+5/2)}(\eta)}{(r+3/2)F_{(r+1/2)}(\eta)} - \left[\frac{(r+5/2)F_{(r+3/2)}(\eta)}{(r+3/2)F_{(r+1/2)}(\eta)}\right]^{-2} \right\}$$
(S9)

where *n* is the chemical carrier concentration,  $r_H$  is the Hall factor,  $m_d^*$  is the density of state effective mass,  $k_B$  is the Boltzmann constant,  $\hbar$  is the reduced Planck constant,  $\mu$  is the drift mobility, and  $N_v$  is the band degeneracy  $[m_d^* = N_V^{2/3} m_b^*]$ .  $E_{def}$  is the deformation potential coefficient,  $v_1$  is the longitudinal sound velocity,  $\rho$  is the density, e is the electron charge,  $F_j(\eta)$  is the Fermi integral, and r is the scattering parameter, r= -1/2 for the acoustic phonon-dominated scattering.



Figure S16. (a) Temperature dependence of  $\kappa_e$  for the  $(SnTe)_{1-x}(MnCd_{1-y}Ge_yTe_2)_x$ samples. (b) Composition-dependent  $\kappa_L$  for  $(SnTe)_{1-x}(MnCd_{1-y}Ge_yTe_2)_x$  at 300 and 626 K.

As can be observed in Fig S16b, irrespective of the temperature, the  $\kappa_L$  exhibited an initial decrease followed by a gradual increase with increasing Ge content, reaching its minimum values at y = 0.4. This phenomenon bears resemblance to the findings reported in Sb-doped PbTe.<sup>20</sup> This is because the decrease in  $\kappa_L$  does not follow a monotonic trend with an increasing concentration of nanoparticles; instead, there exists an optimum concentration beyond which the lattice thermal conductivity actually

increases. In our experiment, the optimum concentration of MnCdTe<sub>2</sub> may be reached around y = 0.4. With the Ge concentration increases, the solid solubility of MnCdTe<sub>2</sub> precipitates continues to rise, and the concentration of precipitates gradually deviates from the optimal value. And thus, the  $\kappa_L$  for y = 0.5 is higher than that of y = 0.4.



## 6. REPRODUCIBILITY AND STABILITY OF TE PROPERTIES.

Figure S17. Temperature dependence of (a)  $\sigma$ , (b) *S*, (c) *PF* (d) *D*, (e)  $\kappa_{T}$  and (f) *ZT* for three different batches of (SnTe)<sub>0.92</sub>(MnCd<sub>0.6</sub>Ge<sub>0.4</sub>Te<sub>2</sub>)<sub>0.08</sub> samples.



Figure S18. Five full heating and cooling cycles between 300 and 900 K for  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$ .

## 7. ELECTRONIC STRUCTURES.



Figure S19. The partial and angular momentum-projected densities of states for  $Sn_{27}Te_{27}$  (a) and  $Sn_{23}Mn_2CdGeTe_{27}$  (b). Total DOS of  $Sn_{27}Te_{27}$ ,  $Sn_{25}Mn_2Te_{27}$ ,  $Sn_{25}Mn_2CdTe_{27}$ ,  $Sn_{24}Mn_2CdTe_{27}$  and  $Sn_{23}Mn_2CdGeTe_{27}$  (c).



Figure S20. Optical absorption spectra of  $(SnTe)_{1-x}(MnCd_{1-y}Ge_yTe_2)_x$ . Although no obvious band gaps can be derived from the FTIR measurement, the blue shift of the absorption edges with MnCdTe<sub>2</sub>/Ge alloying suggest the bandgap increase.



Figure S21. DFT calculated band structure and PDOS for (a)  $Sn_{25}MnCdTe_{27}$ , (b)  $Sn_{24}Mn_2CdTe_{27}$  and (c)  $Sn_{25}Mn_2Te_{27}$ , respectively. The three-valence band-convergence related bands at L,  $\Sigma$  and  $\Lambda$  are labelled as 1, 2 and 3, respectively.



Figure S22. The atomic orbital projected band structure of  $Sn_{23}Mn_2CdGeTe_{27}$ . The weight is proportional to the size of the symbol.



Figure S23. UPS VBM spectra of the typical  $(SnTe)_{1-x}(MnCd_{1-y}Ge_yTe_2)_x$  samples (a). Extrapolating the tangent of excitation edge in the low energy region to the baseline determines the VBM energy (b), and the VBM energy is taken from the UPS measurement (c).



Figure S24. The temperature dependent  $R_{\rm H}$  for the typical  $({\rm SnTe})_{1-x}({\rm MnCd}_{1-y}{\rm Ge}_y{\rm Te}_2)_x$  samples.



8. ANALYSIS OF CARRIER TRANSPORT PROPERTIES.

Figure S25. Temperature dependent  $R_{\rm H}$  and  $\mu_{\rm H}$  for  $({\rm SnTe})_{1-x}({\rm MnCdTe}_2)_x$  (a, b), and  $({\rm SnTe})_{0.92}({\rm MnCd}_{1-y}{\rm GeyTe}_2)_{0.08}$  (c, d). Generally, the temperature at which  $R_{\rm H}$  peaks is used to identify the band convergence. With the dual incorporation of MnCdTe<sub>2</sub> and Ge (c),  $R_{\rm H}$  presents weak temperature dependence below 600 K, indicating that the valence bands are effectively aligned to mimic the behavior of a single band transporting at these temperatures.



Figure S26. Temperature dependent  $\mu_W$  for the (SnTe)<sub>0.92</sub>(MnCd<sub>1-y</sub>GeyTe<sub>2</sub>)<sub>0.08</sub> samples.



Figure S27.  $n_{\rm H}$  dependence of S (a) and  $\mu_{\rm H}$  (b) at 300 K with a comparison to literature.<sup>14,16,21–25</sup> The solid gray lines: theoretically calculated according to the two band model, considering the contributions from both the light and heavy hole valence bands with a  $\Delta E$  of 0.35 eV in SnTe.

# 9. DFT PHONON DISPERSIONS AND LOW TEMPERATURE $C_{\rm p}$ .



Figure S28. Calculated phonon dispersions without (blue) and with the imaginary modes renormalized to the calculated (red) in (a)  $Sn_8Te_8$  and (b)  $Sn_6MnCdTe_8$  at 300 K.

### 10. CALCULATED ELASTIC PROPERTIES.

The average sound velocity  $v_a$ , Young's modulus *E*, shear modulus  $\mu$ , Poisson ratio *v*, Grüneisen parameter  $\gamma$ , and Debye temperature  $\theta_D$  are calculated according to the following equations:<sup>26</sup>

$$v_{a} = \left[\frac{1}{3}\left(\frac{1}{v_{l}^{3}} + \frac{2}{v_{t}^{3}}\right)\right]^{-1/3}, (S10)$$

Young's modulus

$$E = \frac{\rho v_t^{\ 2} (3v_l^{\ 2} - 4v_t^{\ 2})}{v_l^{\ 2} - v_t^{\ 2}}, (S11)$$

Poisson ratio

$$u_{\rho} = \frac{\frac{1 - 2(\frac{v_{t}}{v_{l}})^{2}}{2 - 2(\frac{v_{t}}{v_{l}})^{2}}}{\frac{1 - 2(\frac{v_{t}}{v_{l}})^{2}}{2 - 2(\frac{v_{t}}{v_{l}})^{2}}}, (S12)$$

Grüneisen parameter

$$\gamma = \frac{3}{2} \left( \frac{1 + v_{\rho}}{2 - 3v_{\rho}} \right), \text{ (S14)}$$

Debye temperature

$$\Theta_D = \frac{h}{k_B} \left[ \frac{3N}{4\pi V} \right]^{1/3} v_a, \quad (S15)$$

Where  $v_1$  and  $v_t$  are longitudinal and transverse sound velocities obtained from ultrasonic measurements, and  $\rho$  represents the sample density. *h* represents Planck's constant,  $k_B$  represents the Boltzmann constant, *N* represents the number of atoms in a unit cell, *V* represents the unit-cell volume, and  $v_a$  represents the average sound. velocity.



Figure S29. Measured sound velocities for the  $(SnTe)_{1-x}(MnCd_{1-y}Ge_yTe_2)_x$  samples at room temperature.

Table S1. Measured sound speeds and elastic properties for the  $(SnTe)_{1-x}(MnCd_{1-x}Ge_yTe_2)_x$  samples at room temperature.

Samples	TA	LA	Vave	γ	Ε	μ	В	$\Theta_{ m D}$
$\mathbf{x} = 0$	2000	3496	2222	1.53	63.3	25.2	43.4	189.7
x = 0.03	1957	3513	2179	1.62	61.5	24.1	45.5	185.9
x = 0.05	1885	3485	2104	1.73	57.9	22.4	46.6	179.1
x = 0.07	1858	3420	2073	1.72	56.1	21.7	44.7	176.3
x = 0.08	1856	3421	2071	1.72	56.1	21.7	44.8	176.3
x = 0.1	1831	3487	2048	1.83	55.4	21.1	48.4	174.3
x = 0.12	1795	3384	2007	1.80	52.9	20.3	45.0	170.4
x = 0.08, y = 0.25	1854	3455	2070	1.76	56.2	21.6	46.3	176.4
x = 0.08, y = 0.35	1869	3385	2083	1.66	56.4	22.0	42.8	177.7
x = 0.08, y = 0.375	1861	3430	2076	1.72	56.4	21.8	45.0	177.2
x = 0.08, y = 0.4	1837	3437	2052	1.77	55.3	21.2	46.1	171.9
x = 0.08, y = 0.43	1861	3431	2076	1.72	56.4	21.8	45.1	177.3
x = 0.08, y = 0.45	1888	3481	2107.6	1.72	58.1	22.4	46.3	180.3
x = 0.08, y = 0.5	1850	3425	2065.4	1.74	55.8	21.5	45.2	176.4



Figure S30. Measured  $C_P/T$  as a function of T<sup>2</sup> for  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  with a comparison to the fitting results of a single Debye model (a) and the Debye + 1 Einstein mode (b).

Table S2. Fitting parameters of the heat capacity ( $C_P$ ) for  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$ .

Fitting Parameters	Debye+2E		
γ/10 <sup>-6</sup> Jmol <sup>-1</sup> K <sup>-2</sup>	1.5		
β/10 <sup>-3</sup> Jmol <sup>-1</sup> K <sup>-4</sup>	3.265		
A1/ Jmol <sup>-1</sup> K <sup>-1</sup>	16.38		
$\Theta_{E1}/K$	12.25		
A2/ Jmol <sup>-1</sup> K <sup>-1</sup>	20.57		
$\Theta_{E2}/K$	33.31		
$R^2$	0.9995		
$\chi^2$	4.2873×10 <sup>-6</sup>		

## 11. TEM CHARACTERIZATIONS of (SnTe)<sub>0.92</sub>(MnCd<sub>0.6</sub>Ge<sub>0.4</sub>Te<sub>2</sub>)<sub>0.08</sub>.



Figure S31. Typical low-magnification TEM image for the  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  sample (a), indicating the co-existence of triangular and circular shaped precipitates. (b)-(f) EDS mappings. Medium-magnification TEM image (g) and the enlarged view of the circular precipitates (h).



Figure S32. Low magnification TEM images (a) and EDS mappings (b-f) of the  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  sample exhibiting the presence of multiscale nanoprecipitates.



Figure S33. (a) Low magnification STEM images of a typical  $MnCdTe_2$  precipitate. Atomic-scale structures of the  $MnCdTe_2$  (b) and SnTe (c) obtained from the HAADF mode images. (d) GPA of the area of (a) showing the lattice strains within the whole precipitate grain. Dispersed lattice strains are observed in the SnTe matrix due to the atomic size fluctuations (Mn, Cd and Ge substitution) and the high content of point defects.



Figure S34. Typical medium-magnification TEM images (a–c) of the triangular shaped precipitates in different regions of the bulk  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$  sample. (d) HRTEM image of the boundary region of a precipitate with the IFFT pattern inset.

# 11. LATTICE THERMAL CONDUCTIVITY STUDIED BY DEBYE-CALLAWAY MODEL.

The relevant phonon relaxation times including in the modeling calculations are given

below:

Grain boundary phonon scattering

$$\tau_B^{-1} = \frac{\nu}{d}$$
(S16)

Phonon Umklapp scattering

$$\tau_{U}^{-1} = \frac{\hbar \gamma^{2} \omega^{2} T}{M \nu^{2} \theta_{D}} \exp\left(-\frac{\theta_{D}}{3T}\right) = A \omega^{2} T \exp\left(-\frac{\Theta_{D}}{3T}\right) (S17)$$

Normal process

$$\tau_N^{-1} = \beta \tau_U^{-1} (S18)$$

Point defect scattering

$$\tau_{PD}^{-1} = \frac{\bar{V}\omega^4}{4\pi\nu^3}\Gamma = B\omega^4 (S19)$$

Nano precipitates phonon scattering

$$\tau_{NP}^{-1} = \nu \left[ (2\pi R)^{-1} + \left( \pi R^2 \frac{4}{9} \left( \frac{\Delta D}{D} \right)^2 \left( \frac{\omega R}{\nu} \right)^4 \right)^{-1} \right]^{-1} N_p (S20)$$

Stacking faults scattering

$$\tau_{\rm SF}^{-1} = 0.7 \frac{a^2 \gamma^2 N_s}{v_s} \omega^2 = C \omega^2$$

Acoustic-optical phonon scattering

$$\tau_{AO}^{-1} = \frac{E\omega^2}{\left(\omega^2 - \omega_0^2\right)^2} \left(-\tanh^2\frac{\hbar\omega_0}{2k_BT}\right) (S21)$$

In the above equations, L is the grain size which is obtained by EBSD measurements, v is the average sound velocity,  $\beta$  is the ratio between the normal process and Umklapp process, R is the average radius for the precipitates, D is the matrix density,  $\Delta D$  is the density difference between the precipitate and matrix,  $N_p$  is the number density of precipitates, respectively.  $\omega_0$  is the optical mode frequency obtained from the phonon dispersion of Sn<sub>6</sub>MnCdTe<sub>8</sub>. The remaining constants A, B, and C are the fitting parameters obtained from the lattice thermal conductivity data.

Table S3. Fitting parameters for the lattice thermal conductivity of  $(SnTe)_{0.92}(MnCd_{0.6}Ge_{0.4}Te_2)_{0.08}$ .

Parameter	Value
Sound velocity $v$ (ms <sup>-1</sup> )	2222
Grain size d (μm)	5.8
A $(10^{-43}  \text{s}^{-3})$	3.38
Debye temperature $\theta_D(\mathbf{K})$	195
B $(10^{-16}  \mathrm{sK}^{-1})$	9.8
Matrix density $D$ (gcm <sup>-3</sup> )	6.4
Density difference $\Delta D$ (gcm <sup>-3</sup> )	0.35
Number density of precipitates $N_p$ (m <sup>-3</sup> )	4×10 <sup>18</sup>
$C(10^{-14}s)$	3.062
$E(10^{10}s^{-1})$	5.6
$\omega_0$ (THz)	0.72

12. AVERAGE ZT.



Figure S35. Composition dependent average ZT for the typical  $(SnTe)_{0.92}(MnCd_{1-}_yGeyTe_2)_{0.08}$  samples.



Figure S36. Maximum output power density  $P_{\text{max}}$  as a function of the temperature different  $\Delta T$ , and other typical TE modules were also included for contrast.<sup>11,25,27,28,29</sup> Table S4. Densities of all samples investigated in this study.

Samples	Density (gcm <sup>-3</sup> )	Samples	Density (gcm <sup>-3</sup> )
x = 0	6.45	x = 0.08, y = 0.25	6.19
x = 0.03	6.34	x = 0.08, y = 0.35	6.09
x = 0.05	6.35	x = 0.08, y = 0.375	6.26
x = 0.07	6.25	x = 0.08, y = 0.4	6.12
x = 0.08	6.25	x = 0.08, y = 0.45	6.31
x = 0.1	6.23	x = 0.08, y = 0.5	6.28

#### Reference

- 1 Perdew, J. P., Burke, K. & Ernzerhof, M, Phys. Rev. Lett. 1996, 77, 3865-3868.
- 2 G. Kresse and D. Joubert, *Physical Review B*, 1999, 59, 1758–1775.
- 3 H. J. Monkhorst, J. D. Pack, Phys. Rev. B. 1976, 13, 5188.
- 4 G. Kresse, J. Furthmüller, Phys. Rev. B. 1996, 54, 11169.
- 5 A. Zunger, S.H. Wei, L. G. Ferreira, J. E. Bernard, Phys. Rev. Lett. 1990, 65, 353.
- 6 A. Togo, F. Oba, I. Tanaka, Phys. Rev. B 2008, 78, 134106.
- 7 A. Carreras, A. Togo and I. Tanaka, Comput. Phys. Commun., 2017, 221, 221–234.
- 8 G. Tan, L. D. Zhao, F. Shi, J. W. Doak, S. H. Lo, H. Sun, C. Wolverton, V. P. Dravid,
- C. Uher and M. G. Kanatzidis, J. Am. Chem. Soc., 2014, 136, 7006–7017.
- 9 Q. Zhang, B. Liao, Y. Lan, K. Lukas, W. Liu, K. Esfarjani, C. Opeil, D. Broido, G. Chen and Z. Ren, *Proc. Natl. Acad. Sci.*, 2013, *110*, 13261–13266.
- 10 G. Tan, F. Shi, J. W. Doak, H. Sun, L.-D. Zhao, P. Wang, C. Uher, C. Wolverton,
- V. P. Dravid and M. G. Kanatzidis, Energy Environ. Sci., 2015, 8, 267–277.
- 11 D. An, J. Wang, J. Zhang, X. Zhai, Z. Kang, W. Fan, J. Yan, Y. Liu, L. Lu, C.-L.

Jia, M. Wuttig, O. Cojocaru-Mir'edin, S. Chen, W. Wang, G. J. Snyder and Y. Yu, *Energy Environ. Sci.*, 2021, 14, 5469–5479.

- 12 Q. Zhang, Z. Guo, R. Wang, X. Tan, K. Song, P. Sun, H. Hu, C. Cui, G. Q. Liu and J. Jiang, *Adv. Funct. Mater.*, 2022, *32*, 2205458.
- 13 L. Hu, Y. Zhang, H. Wu, J. Li, Y. Li, M. McKenna, J. He, F. Liu, S. J. Pennycook and X. Zeng, *Adv. Energy Mater.*, 2018, *8*, 18021.

14 H. Wu, C. Chang, D. Feng, Y. Xiao, X. Zhang, Y. Pei, L. Zheng, D. Wu, S. Gong,
Y. Chen, J. He, M. G. Kanatzidis and L.-D. Zhao, *Energy Environ. Sci.*, 2015, *8*, 3298–3312.

15 X. Xu, J. Cui, Y. Yu, B. Zhu, Y. Huang, L. Xie, D. Wu and J. He, *Energy Environ. Sci.*, 2020, 13, 5135–5142.

16 A. Banik, T. Ghosh, R. Arora, M. Dutta, J. Pandey, S. Acharya, A. Soni, U. V. Waghmare and K. Biswas, *Energy Environ. Sci.*, 2019, *12*, 589–595.

17 X. Zhang, D. Y. Wang, H. J. Wu, M. J. Yin, Y. L. Pei, S. K. Gong, L. Huang, S. J. Pennycook, J. Q. He and L.-D. Zhao, *Energy Environ. Sci.*, 2017, *10*, 2420–2431.

18 A. Banik, B. Vishal, S. Perumal, R. Datta and K. Biswas, *Energy Environ. Sci.*, 2016, 9, 2011–2019.

- 19 A. F. May, E. S. Toberer, A. Saramat and G. J. Snyder, *Phys. Rev. B*, 2009, *80*, 1–12.
- 20 J. R. Sootsman, R. J. Pcionek, H. J. Kong, C. Uher and M. G. Kanatzidis, *Chem. Mater.*, 2006, *18*, 4993–4995.
- 21 M. Zhou, Z. M. Gibbs, H. Wang, Y. Han, L. Li and G. J. Snyder, *Appl. Phys. Lett*, 2016, *109*, 042102.
- 22 G. Tan, L. D. Zhao, F. Shi, J. W. Doak, S. H. Lo, H. Sun, C. Wolverton, V. P. Dravid,
- C. Uher and M. G. Kanatzidis, J. Am. Chem. Soc., 2014, 136, 7006-7017.
- 23 B. Gao, J. Tang, F. Meng and W. Li, J. Materiomics, 2019, 5, 111-117.
- 24 D. Sarkar, T. Ghosh, A. Banik, S. Roychowdhury, D. Sanyal and K. Biswas, *Angew. Chem., Int. Ed.*, 2020, *59*, 11115–11122.
- 25 Q. Zhang, R. Wang, K. Song, X. Tan, H. Hu, Z. Guo, G. Wu, P. Sun, G.-Q. Liu and J. Jiang, *Nano Energy*, 2022, *94*, 106940.
- 26 M. Manikandan, A. Amudhavalli, R. Rajeswarapalanichamy and K. Iyakutti, *Solid State Communications*, 2019, *291*, 36–42.
- 27 P. Jood, M. Ohta, A. Yamamoto, M. Kanatzidis, Joule, 2018, 2, 1339–1355.
- 28 T. Xing, Q. Song, P. Qiu, Q. Zhang, M. Gu, X. Xia, J. Liao, X. Shi, L. Chen, *Energy Environ. Sci.* 2021, *14*, 995–1003.
- 29 D. Sarkar, M. Samanta, T. Ghosh, K. Dolui, S. Das, K. Saurabh, D. Sanyal, K. Biswas, *Energy Environ. Sci.*, 2022, *15*, 4625–4635.