Supplementary Information

High Thermoelectric and Mechanical Performance Achieved by Hyperconverged Electronic Structure and Low Lattice Thermal Conductivity in GeTe through CuInTe₂ alloying

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Samples	Rhombohedral unit cell		Pseudo cubic unit cell	
	a [Å]	c [Å]	a ₁ [Å]	α ₁ [°]
GeTe	4.169	10.661	5.984	88.333
Ge _{0.95} Bi _{0.05} Te	4.192	10.629	5.999	88.666
(Ge _{0.94} Bi _{0.05} Te _{0.99})(CuInTe ₂) _{0.005}	4.192	10.627	5.998	88.674
(Ge _{0.93} Bi _{0.05} Te _{0.98})(CuInTe ₂) _{0.01}	4.197	10.603	5.998	88.808
(Ge _{0.91} Bi _{0.05} Te _{0.96})(CuInTe ₂) _{0.02}	4.202	10.582	5.999	88.932
(Ge _{0.89} Bi _{0.05} Te _{0.94})(CuInTe ₂) _{0.03}	4.201	10.577	5.997	88.941

Table S1. The lattice parameters of samples based on the rhombohedral and pseudo cubic unit cells.

The calculation equations for the lattice parameter based on the pseudo cubic unit cell:1

$$a_1 = \frac{\sqrt{12a^2 + c^2}}{3} \tag{1}$$

$$\sin\frac{\alpha_1}{2} = \frac{3}{2} \frac{1}{\sqrt{3 + \left(\frac{c}{2a}\right)^2}}$$
(2)



Fig. S1. SEM image from the fracture surface of pristine GeTe, showing the herringbone structure.



Fig. S2. SEM image and corresponding EDS mapping from the fracture surface for a) $(Ge_{0.93}Bi_{0.05}Te_{0.98})(CuInTe_2)_{0.01}$ and b) $(Ge_{0.89}Bi_{0.05}Te_{0.94})(CuInTe_2)_{0.03}$.



Fig. S3. a) BSE image and b) line scan results of EPMA analysis in $(Ge_{0.89}Bi_{0.05}Te_{0.94})(CuInTe_2)_{0.03}$.



Fig. S4. Microstructures observation in $(Ge_{0.93}Bi_{0.05}Te_{0.98})(CuInTe_2)_{0.01}$ sample. a) Lowmagnification HAADF image and corresponding EDS mappings of Ge, Te, Bi, Cu, and In. b) Enlarged HAADF image of the red-square area in a) and corresponding EDS mappings of Ge, Te, Bi, Cu, and In.



Fig. S5. (a) Bright-field TEM micrograph of $CuInTe_2$ precipitate in $(Ge_{0.93}Bi_{0.05}Te_{0.98})(CuInTe_2)_{0.01}$ sample and (b) contrast-adjusted image of a) for a clear distinction.



Fig. S6. Schematic diagram to explain the crystal orientation relationship between GeTe matrix and CuInTe₂ precipitate in SAED of Fig 2i.



Fig.S7. pDOS of cubic Ge₁₅InTe₁₆. The hybridization of 's' orbitals of In along with 'p' orbitals of Te and Ge leads to increase in the DOS near the Fermi level corresponding to the resonance states exhibited in the electronic structure of In doped GeTe.



Fig.S8. Electronic structure and pDOS of rhombohedral (a and b) Ge_8Te_8 ; (c and d) $Ge_5BiInCuTe_8$. The increase in the DOS near Fermi level corresponds to the resonance states in the electronic structure of $Ge_5BiInCuTe_8$.

The Debye-Callaway model

According to the Debye-Callaway model,^{2–4} the lattice thermal conductivity (κ_{latt}) can be defined as the sum of the spectral lattice conductivity ($\kappa_s(f)$) at different phonon frequencies (f), can be expressed as:

$$\kappa_{latt} = \int \kappa_s(f) df = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/t} \tau_{tot}(x) \frac{x^4 exp^{[in]}(x)}{\left[\exp\left(x\right) - 1\right]^2} dx$$
(3)

where k_B is Boltzmann's constant, v_s is the sound velocity, \hbar is the reduced Plank constant, T is absolute temperature, θ_D is Debye temperature, $\tau_{tot}(x)$ is the total phonon relaxation time of the participating phonon scattering processes, and $x = \hbar f/k_B T$ is reduced phonon frequency.

Debye temperature (θ_D) and Debye frequency (f_D) are calculated by

$$\theta_D = \frac{2\pi\hbar}{k_B} \left(\frac{3N}{4\pi V}\right)^{1/3} v_s \tag{4}$$

$$f_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3} v_s \tag{5}$$

where N is the number of atoms in a unit cell, V is the volume of a unit cell.

According to Matthiessen's rule, $\tau_{tot}(x)$ is the reciprocal sum of the relaxation times at a certain f, given by:

$$\tau_{tot}^{-1} = \sum \tau_{intrinsic}^{-1} + \sum \tau_{extrinsic}^{-1}$$
(6)

where $\tau_{intrinsic}$ is the intrinsic process, including the Umklapp process (τ_{U}) and the normal process (τ_{N}), and $\tau_{extrinsic}$ is the extrinsic scattering, including the grain boundary scattering (τ_{GB}), the point defect scattering (τ_{PD}), and the nanoprecipitate phonon scattering (τ_{NP}). Umklapp process (τ_{U}) based on the second-order perturbation theory:⁵

$$\tau_{U}^{-1} = \frac{\hbar \gamma^{2} f^{2} T}{M_{av} v_{s}^{2} \theta_{D}} exp^{[m]} (-\frac{\theta_{D}}{3T})$$
(7)

where γ is Grüneisen parameter, M is average atomic mass. Normal process (τ_N):

$$\tau_N^{-1} = \beta \tau_U^{-1} \tag{8}$$

where β is the temperature-dependent ratio of the normal process to the Umklapp process. Grain boundary scattering (τ_{GB}):

$$\tau_B^{-1} = \frac{\nu_s}{D} \tag{9}$$

where *D* is the average grain size of polycrystalline materials.

Point defect scattering $(^{T_{PD}})$:

$$\tau_{PD}^{-1} = \frac{V_{av} f^4}{4\pi v_s^3} \Gamma$$
(10)

where V_{av} is the average atomic volume in a unit cell, Γ is the point defect scattering parameter.

 Γ can be calculated by:⁶

$$\Gamma = x(1-x) \left[\left(\frac{\Delta M}{M} \right)^2 + \varepsilon \left(\frac{a_{disorder} - a_{pure}}{a_{pure}} \right)^2 \right]$$
(11)

where x is the doping fraction, $\Delta M/M$ is the ratio of change of atomic mass, ε is a phenomenological parameter for fitting, $a_{disorder}$ and a_{pure} represent the lattice parameter of disordered and pure alloys.

Nanoprecipitate phonon scattering (τ_{NP}):

$$\tau_{NP}^{-1} = v_s \left[\left(2\pi R_{NP} \right)^{-1} + \left(\pi R_{NP}^{2} \frac{4}{9} \left(\frac{\Delta \rho}{\rho} \right)^2 \left(\frac{fR_{NP}}{v_s} \right)^4 \right)^{-1} \right]^{-1} N_{NP}$$
(12)

where R_{NP} and N_{NP} are the radius and number density for the nanoprecipitate, ρ and $\Delta \rho$ are the matrix density and the density difference between the matrix and nanoprecipitate.

Parameters	Description	Values	Reference
β	Ratio of normal and Umklapp process	0.3	7
γ	Grüneisen parameter	2.19	8
ε	Phenomenological parameter	82	9
v_s	Sound velocity [m s ⁻¹]	1967	10
М	Average atomic mass [kg]	1.66 × 10 ²⁵	Calculated
V _{av}	Average atomic volume in a unit cell [m ³]	2.68 × 10 ⁻²⁹	Calculated
ρ	Matrix density [g cm ⁻³]	6	10
Δho	Density difference [g cm ⁻³]	0.1	11
R _{NP}	Radius for the nanoprecipitate [nm]	1.76	This work
N _{NP}	Number density of nanoprecipitate [m ⁻³]	6.15×10^{18}	This work

Table S2. Parameters for the Debye-Callaway modelling.

Calculation for $^{ZT_{eng}}$ and $^{\eta(ZT_{eng})}$

Kim *et al.* have proposed the engineering figure of merit $(ZT)_{eng}$ and the maximum efficiency η_{max} based on cumulative temperature-dependent properties, which are realistic indicators related to the large temperature difference, given by:¹²

$$(ZT)_{eng} = Z_{eng}\Delta T = \frac{\left(\int_{T_c}^{T_h} S(T)dT\right)^2}{\int_{T_c}^{T_h} \rho(T)dT \int_{T_c}^{T_h} \kappa(T)dT} \Delta T = \frac{(PF)_{eng}}{\int_{T_c}^{T_h} \kappa(T)dT} \Delta T$$
(13)

$$\eta_{max} = \eta_c \frac{\sqrt{1 + (ZT)_{eng} (\hat{a}/\eta_c - 1/2)} - 1}{\hat{a} (\sqrt{1 + (ZT)_{eng} (\hat{a}/\eta_c - 1/2)} + 1) - \eta_c}$$
(14)

 $\hat{a} = S(T_h)\Delta T / \int_{T_c}^{T_h} S(T) dT$ where $\eta_c = (T_h - T_c) / T_h$ is Carnot efficiency, is a dimensionless intensity

factor of the Thomson effect, and $S(T_h)$ is the Seebeck coefficient at the hot-side temperature T_{h} .

References

- C. Zhu, F. Luo, J. Wang, S. Zhang, J. Wang, H. Liu and Z. Sun, *J. Mater. Chem. C*, 2022,
 10, 9052–9061.
- 2 J. Callaway and H. C. Von Baeyer, *Phys. Rev.*, 1960, **120**, 1149–1154.
- 3 D. Bessas, I. Sergueev, H. C. Wille, J. Peron, D. Ebling and R. P. Hermann, *Phys. Rev. B* -*Condens. Matter Mater. Phys.*, 2012, **86**, 1–9.
- 4 M. Hong, T. C. Chasapis, Z. G. Chen, L. Yang, M. G. Kanatzidis, G. J. Snyder and J. Zou, ACS Nano, 2016, **10**, 4719–4727.
- 5 D. T. Morelli, J. P. Heremans and G. A. Slack, *Phys. Rev. B Condens. Matter Mater. Phys.*, 2002, **66**, 1953041–1953049.
- 6 G. Tan, L. D. Zhao and M. G. Kanatzidis, *Chem. Rev.*, 2016, **116**, 12123–12149.
- J. Li, Y. Xie, C. Zhang, K. Ma, F. Liu, W. Ao, Y. Li and C. Zhang, ACS Appl. Mater.
 Interfaces, 2019, 11, 20064–20072.
- 8 Y. Gelbstein, J. Davidow, E. Leshem, O. Pinshow and S. Moisa, *Phys. Status Solidi Basic Res.*, 2014, **251**, 1431–1437.
- 9 D. Wu, L. Xie, X. Xu and J. He, *Adv. Funct. Mater.*, 2019, **29**, 1806613.
- M. Hong, Z. G. Chen, L. Yang, Y. C. Zou, M. S. Dargusch, H. Wang and J. Zou, *Adv. Mater.*, 2018, **30**, 1705942.
- M. Li, Y. Luo, G. Cai, X. Li, X. Li, Z. Han, X. Lin, D. Sarker and J. Cui, J. Mater. Chem. A, 2019, 7, 2360–2367.
- 12 H. S. Kim, Z. M. Gibbs, Y. Tang, H. Wang and G. J. Snyder, *APL Mater.*, 2015, **3**, 041506.