Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary Information

Multiple Synergistic Effects Induced by Ge Doping Enhance the Thermoelectric Performance of n-Type PbTe

Jiaxing Luo,[a#] Xiaobo Tan,[a#] Qian Deng,[b#] Ruiheng Li,[a] Fan Feng,[a] Zhilong Zhao,[a] Liwei Lin,[a] and Ran Ang[a,c,d*]

[a]Key Laboratory of Radiation Physics and Technology, Ministry of Education, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064, China

[b]Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

[c]College of Physics, Sichuan University, Chengdu 610064, China

[d]Institute of New Energy and Low-Carbon Technology, Sichuan University, Chengdu 610065, China

#Jiaxing Luo, Xiaobo Tan, and Qian Deng contributed equally to this work.

*Corresponding author and Email: rang@scu.edu.cn (R.A)

Single Kane Band (SKB) Model

The density-of-state (DOS) effective mass (m^*), Lorenz number (L), and other transport parameters were derived within the framework of the single Kane band (SKB) model. The relevant expressions are as follows[1, 2]:

Seebeck coefficient:

$$S = \frac{k_\mathrm{B}}{e}\left[\frac{{}^{1}F^{1}_{-2}}{{}^{0}F^{1}_{-2}} - \eta\right] \qquad \text{(eq. S1)}$$

Hall carrier density:

$$n_\mathrm{H} = \frac{1}{A}\left[\frac{2m^* k_\mathrm{B} T}{\hbar^2}\right]^{3/2} {}^{0}F^{2/3}_{0} \qquad \text{(eq. S2)}$$

Hall factor:

$$A = \frac{3K(K+2)}{(2K+1)^2}\frac{{}^{0}F^{1/2}_{-4}\,{}^{0}F^{3/2}_{0}}{\left({}^{0}F^{1}_{-2}\right)^2} \qquad \text{(eq. S3)}$$

Lorenz number:

$$L = \left(\frac{k_\mathrm{B}}{e}\right)^2\left[\frac{{}^{2}F^{1}_{-2}}{{}^{0}F^{1}_{-2}} - \left(\frac{{}^{1}F^{1}_{-2}}{{}^{0}F^{1}_{-2}}\right)^2\right] \qquad \text{(eq. S4)}$$

Carrier mobility:

$$\mu_\mathrm{H} = \frac{2\pi\hbar^4 e C_l}{m_\mathrm{I}^*\left(2m^* k_\mathrm{B} T\right)^{3/2}\Xi^2}\frac{3\,{}^{0}F^{1}_{-2}}{{}^{0}F^{3/2}_{0}} \qquad \text{(eq. S5)}$$

Generalized Fermi integral:

$${}^{n}F^{m}_{l}(\eta,\alpha) = \int_0^\infty \left(-\frac{\partial f}{\partial \varepsilon}\varepsilon^n\right)(\varepsilon + \varepsilon^2\alpha)^m (1 + 2\varepsilon\alpha)^l \, d\varepsilon \qquad \text{(eq. S6)}$$

Here, k_B is the Boltzmann constant, $\varepsilon = E/k_\mathrm{B}T$ and $\eta = E_\mathrm{F}/(k_\mathrm{B}T)$ represent the reduced carrier energy and reduced chemical potential, respectively, with E_F being the Fermi energy. The generalized Fermi integral is denoted as ${}^{n}F^{m}_{l}(\eta,\alpha)$. m^* and m_I^* are the density-of-states effective mass and inertial effective mass, respectively, K is the anisotropy factor ($K = 3.6$ for n-type PbTe),[3] Ξ is the deformation potential of materials, C_l is the average longitudinal elastic constant ($C_l = 7 \times 10^{10}$ Pa for n-type PbTe).[4]

Calculation of Average PF_{avg} and zT_{avg}

The average power factor (PF_{avg}) and average figure of merit (zT_{avg}) over specified temperature ranges were determined using the following equations[5]:

$$PF_{\mathrm{avg}} = \frac{\int_{T_{\mathrm{c}}}^{T_{\mathrm{h}}} PF dT}{T_{\mathrm{h}} - T_{\mathrm{c}}} \quad \text{(eq. S7)}$$

$$zT_{\mathrm{avg}} = \frac{\int_{T_{\mathrm{c}}}^{T_{\mathrm{h}}} zT dT}{T_{\mathrm{h}} - T_{\mathrm{c}}} \quad \text{(eq. S8)}$$

Thermoelectric Module Calculation

Ignoring contact resistance, the parameters for device calculation are as follows:

Internal resistance:

$$R_{in} = N\left(\frac{L}{A_p}\bar{\rho}_p + \frac{L}{A_n}\bar{\rho}_n\right) \quad \text{(eq. S9)}$$

Where N is the number of thermocouple pairs; L is the leg length; A_p and A_n are the cross-sectional areas, respectively; $\bar{\rho}_p$ and $\bar{\rho}_n$ represent the average electrical resistivities.

Open-circuit voltage:

$$V_{oc} = N\left(T_h - T_c\right)\left(\bar{S}_p - \bar{S}_n\right) \quad \text{(eq. S10)}$$

Open-circuit current:

$$I = \frac{V_{oc}}{2R_{in}} \quad \text{(eq. S11)}$$

Output power:

$$P = \frac{V_{oc}^2}{4R_{in}} \quad \text{(eq. S12)}$$

Open-circuit heat flow:

$$Q_{oc} = N\left(\frac{A_p}{H}\overline{\kappa}_p + \frac{A_n}{H}\overline{\kappa}_n\right)\Delta T \quad \text{(eq. S13)}$$

Total heat flow:

$$Q_{input} = Q_{oc} - \frac{R_{in}I^2 + N(\beta_p + \beta_n)T_h I}{2} + N\left[S_p(T_h) - S_n(T_h)\right]T_h I \quad \text{(eq. S14)}$$

Conversion efficiency:

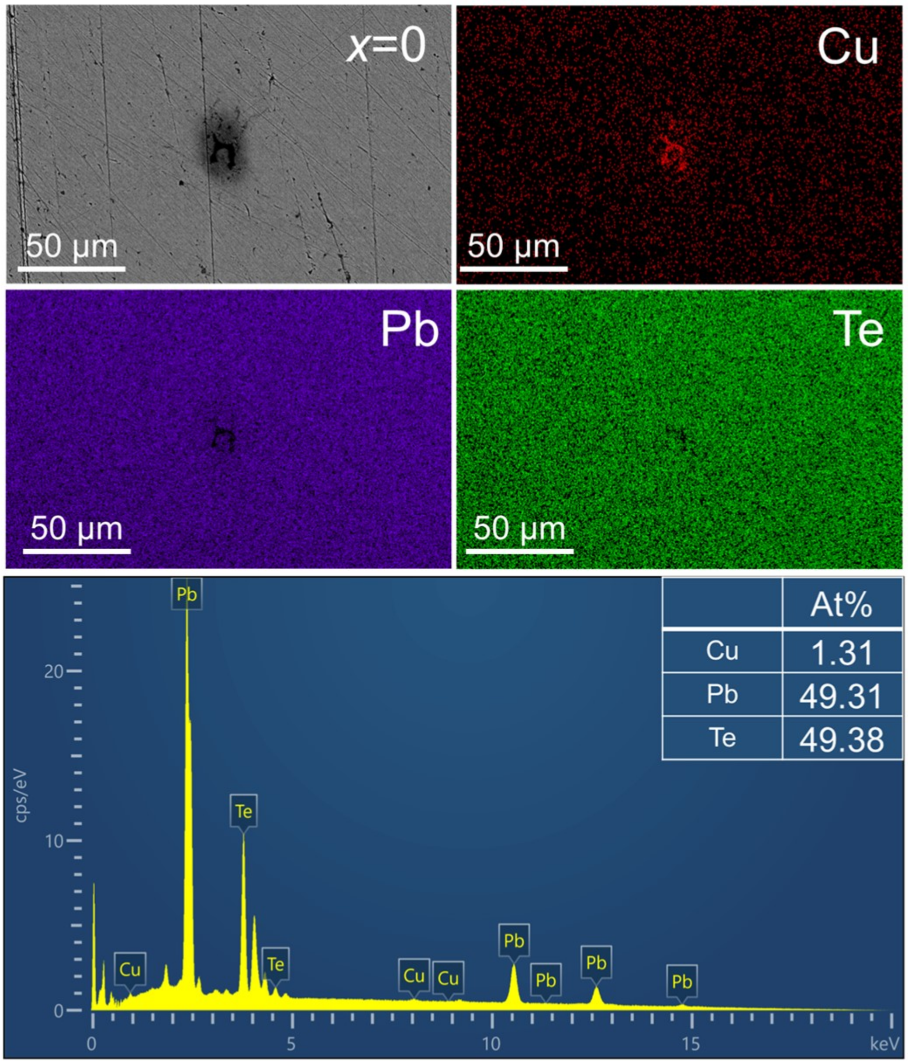
$$\eta = \frac{P}{Q_{input}} \quad \text{(eq. S15)}$$

Here, T_h and T_c are the hot-side and cold-side temperatures, respectively; $\overline{S}_n$ and $\overline{S}_p$ are the average Seebeck coefficients; $\overline{\kappa}_n$ and $\overline{\kappa}_p$ are the average thermal conductivities; β_n and β_p are the Thomson correction coefficients, defined as:

$$\beta_n = \frac{T_c}{T_h}\left[\left[S_n(T_c) - \overline{S}_n\right] + \left[\overline{S}_n - S_n(T_h)\right]\right] \quad \text{(eq. S16)}$$

$$\beta_p = \frac{T_c}{T_h}\left[\left[\overline{S}_p - S_p(T_c)\right] + \left[S_p(T_h) - \overline{S}_p\right]\right] \quad \text{(eq. S17)}$$

Supplementary details



	At%
Cu	1.31
Pb	49.31
Te	49.38

Fig. S1 Microstructure and elemental distribution of the $Cu_{0.002}PbTe$ (x = 0) sample with SEM image at a scale bar of 50 μm and corresponding EDS elemental mapping.

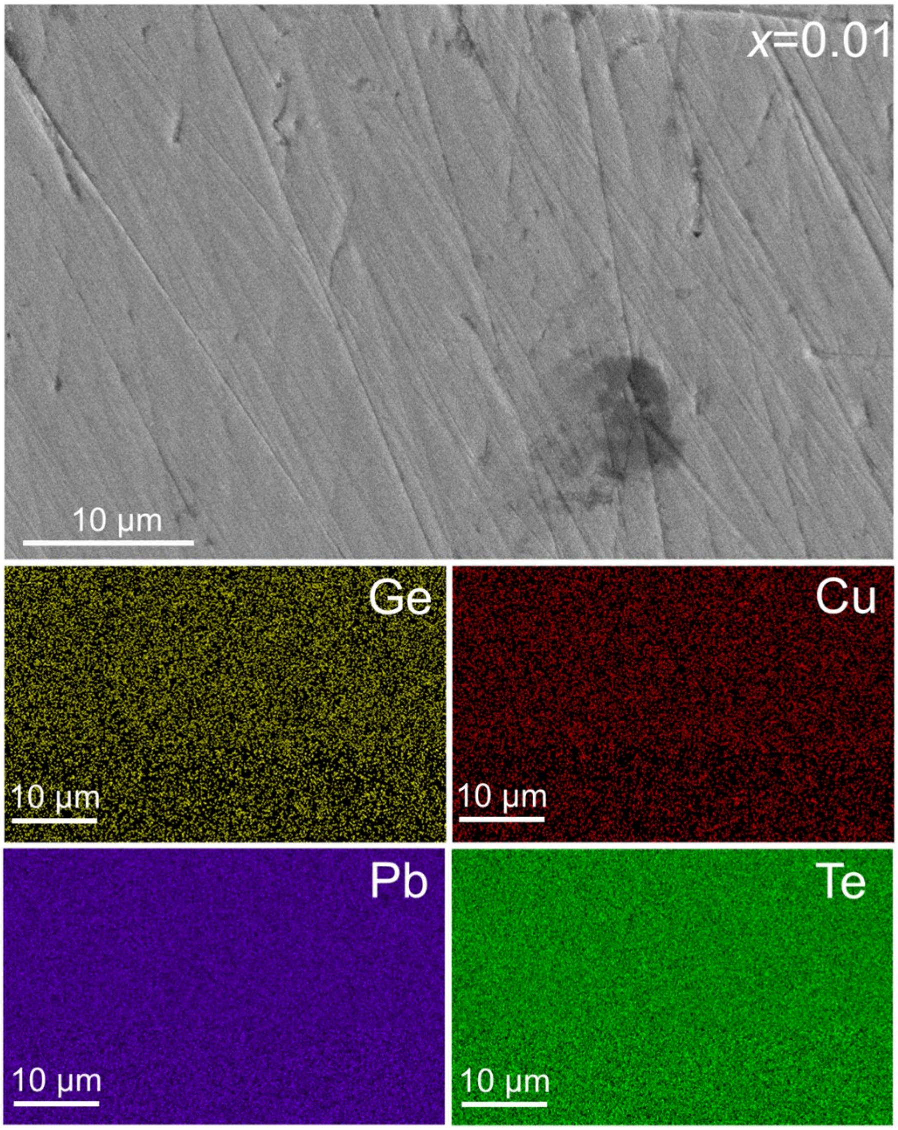


Fig. S2 Microstructure and elemental distribution of the $Cu_{0.002}Pb_{0.99}Ge_{0.01}Te$ ($x = 0.01$) sample with SEM image at a scale bar of 10 μm and corresponding EDS elemental mapping.

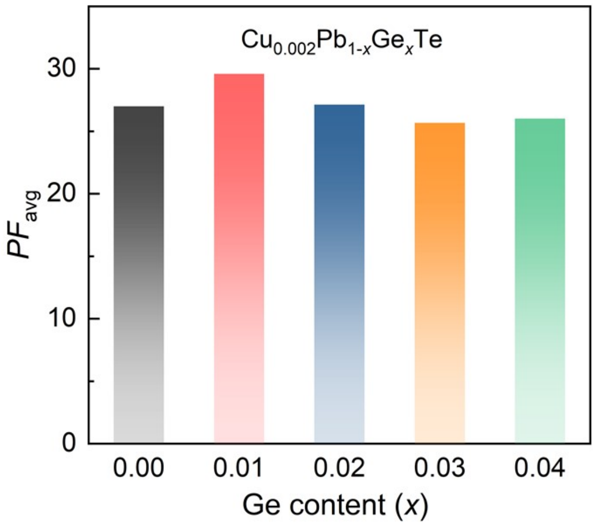


Fig. S3 Average power factor (PF_{avg}) of $Cu_{0.002}Pb_{1-x}Ge_xTe$ (x = 0-0.04) with varying Ge content.

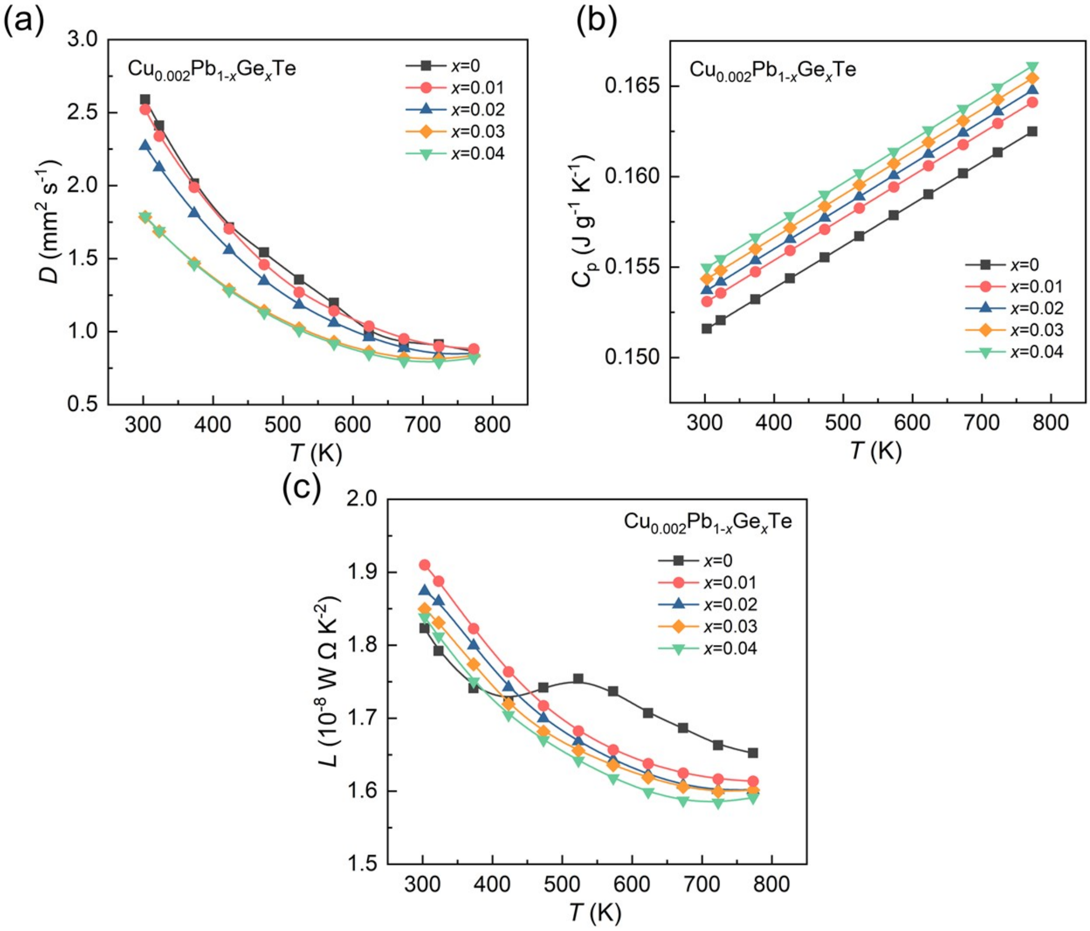


Fig. S4 Temperature-dependent (a) thermal diffusivity (*D*), (b) heat capacity (C_p), (c) Lorenz number (*L*) of $Cu_{0.002}Pb_{1-x}Ge_xTe$ (x = 0-0.04).

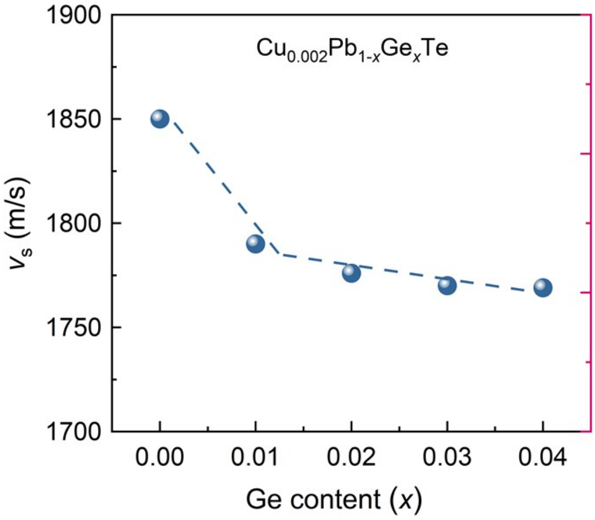


Fig. S5 Room-temperature average sound velocity (v_s) as a function of Ge doping content.

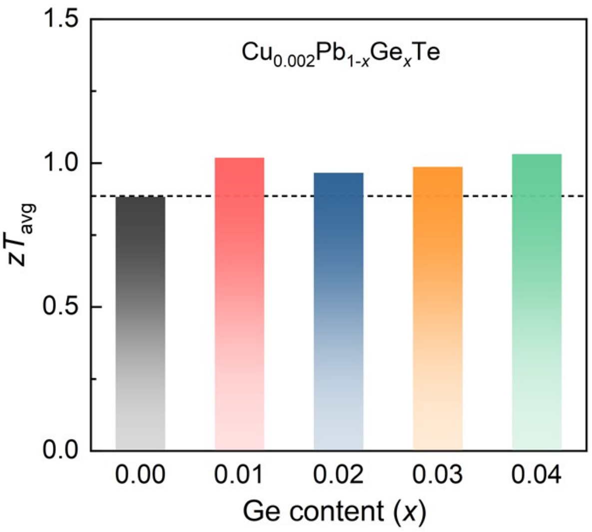


Fig. S6 Average figure of merit (zT_{avg}) of $Cu_{0.002}Pb_{1-x}Ge_xTe$ (x = 0-0.04) with varying Ge content.

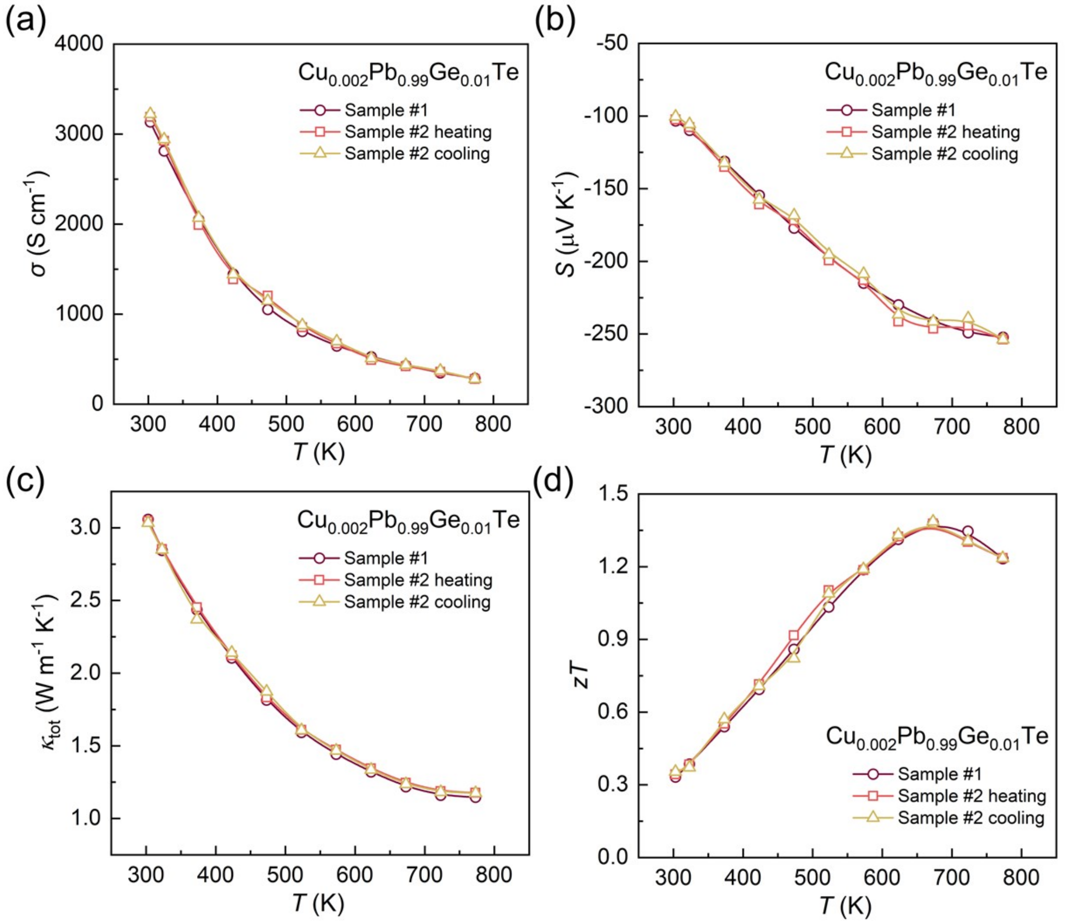


Fig. S7 Repeated measurements of temperature-dependent (a) electrical conductivity (σ), (b) Seebeck coefficient (S), (c) total thermal conductivity (κ_{tot}), and (d) figure of merit zT for n-type $Cu_{0.002}Pb_{0.99}Ge_{0.01}Te$.

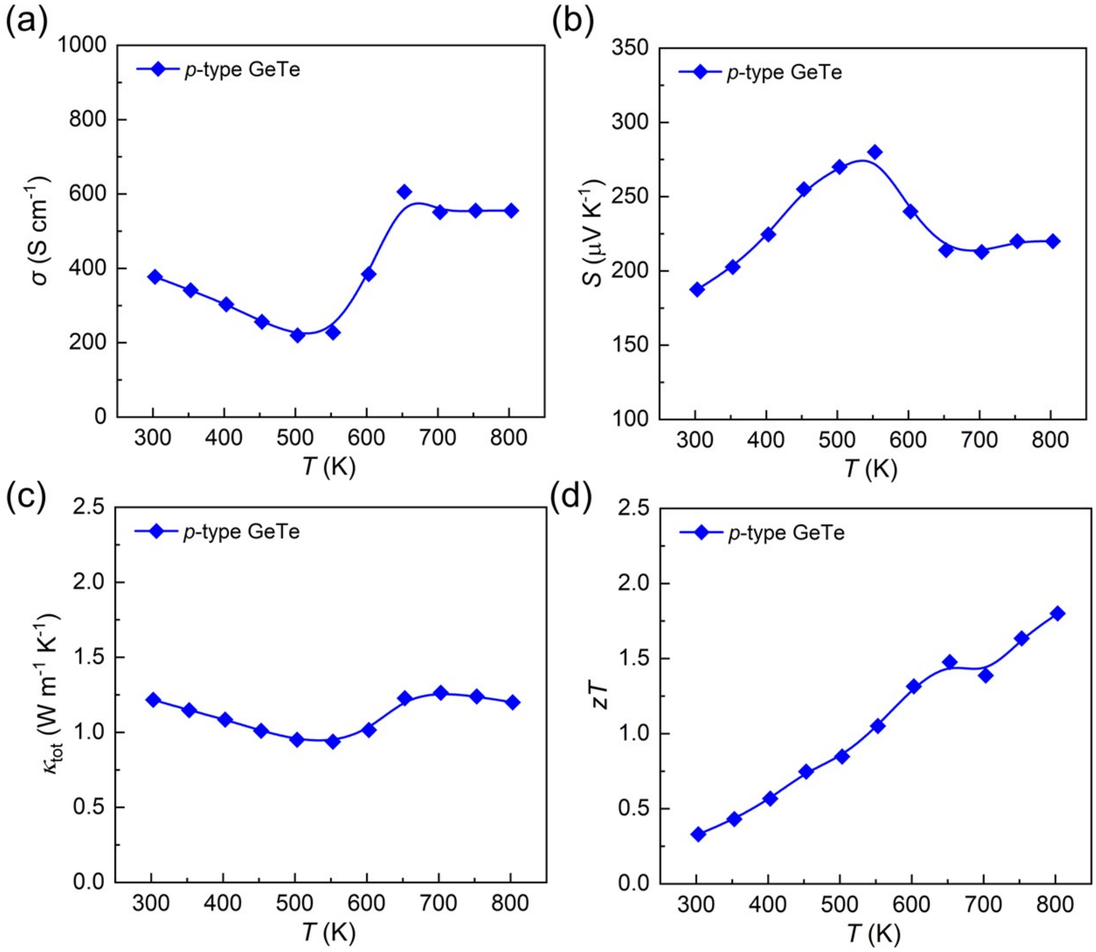


Fig. S8 Thermoelectric performance of p-type $Ge_{0.83}Zr_{0.02}Pb_{0.15}Te$-3%Cu for the simulation calculation. Temperature-dependent (a) electrical conductivity (σ), (b) Seebeck coefficient (S), (c) total thermal conductivity (κ_{tot}), and (d) figure-of-merit zT.

Table S1 Density of sintered $Cu_{0.002}Pb_{1-x}Ge_xTe$ samples in this work.

Composition	Measure density (g cm^{-3})	Relative density (%)
$x = 0$	8.059	98.28
$x = 0.01$	7.920	96.59
$x = 0.02$	8.010	97.68
$x = 0.03$	8.156	99.46
$x = 0.04$	8.028	97.90

References

1. E. O. Kane, *J. Phys. Chem. Solids*, 1957, **1**, 249-261.
2. Y. I. Ravich, B. A. Efimova and V. I. Tamarchenko, *Phys. Status Solidi B*, 1971, **43**, 453-469.
3. H. A. Lyden, *Phys. Rev.*, 1964, **135**, A514-A521.
4. Y. Pei, Z. M. Gibbs, A. Gloskovskii, B. Balke, W. G. Zeier and G. J. Snyder, *Adv. Energy Mater.*, 2014, **4**, 1400486.
5. J. Zhu, R. Li, X. Tan, Q. Sun, G. Su, S. Huo, P. Song, M. Hong and R. Ang, *J. Am. Chem. Soc.*, 2025, **147**, 37555-37564.