ADVANCED MATERIALS

Supporting Information

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Are Cu_2Te-Based Compounds Excellent Thermoelectric Materials?

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Supporting Information

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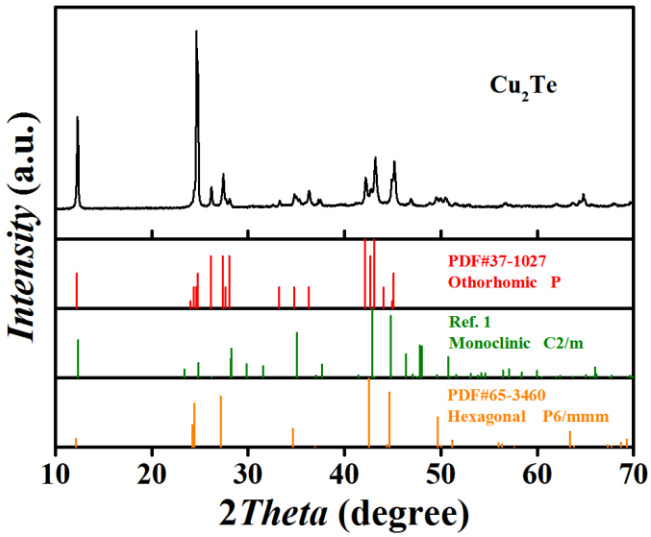

Figure S1. Powder X-ray diffraction pattern of Cu_2Te at room temperature

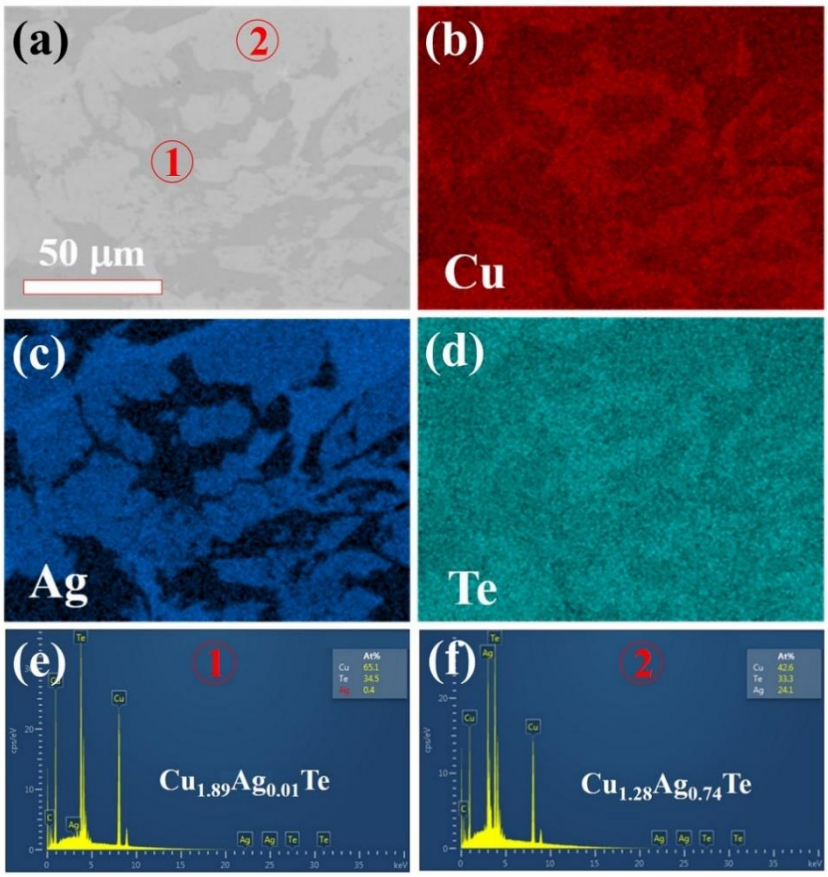

Figure S2. (a) Backscattered electron microscopy (BSE) image and **(b, c, d)** corresponding elemental energy-dispersive X-ray spectroscopy (EDS) mapping for Cu_2Te+35%Ag_2Te at room temperature. **(e, f)** Quantitative EDS results for the areas denoted in figure (a). The solubility of Ag in Cu_2Te is quite low at room temperature, which is in accordance with previous reports. Besides the cationic elements, it is very surprising that the anion element Te is also not homogenously distributed. The concentration of Te in CuAgTe phases is obviously higher than that in Cu_2Te phases. The quantitatively EDS analysis reveals that Cu_2Te phases are Cu deficient while CuAgTe phases are Te deficient, which implies that Cu_2Te is p-type conduction while CuAgTe is n-type conduction.

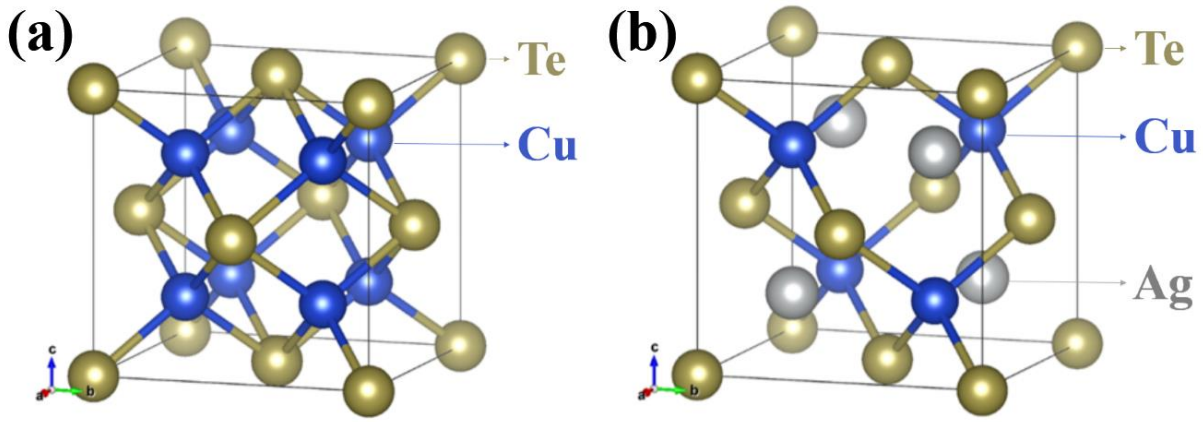

Figure S3. Crystal structures of Cu_2Te and CuAgTe used for defect formation energy calculations. In the CuAgTe crystal structure, both Cu and Ag atoms occupy half of 8c sites. This model is on behalf of the case where Cu and Ag have uniform distributions.

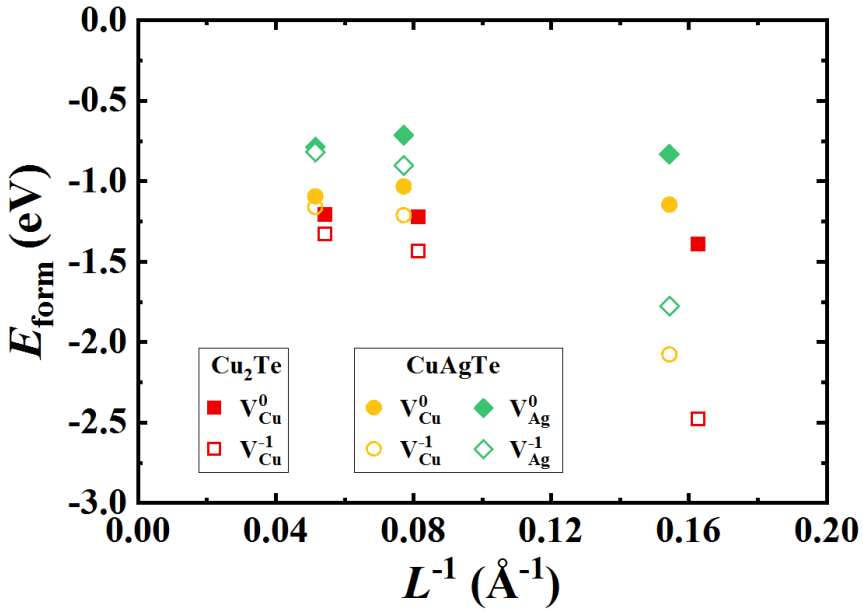

Figure S4. Vacancy formation energies as a function of the reciprocal of supercell size based on defect calculations for 1×1×1, 2×2×2 and 3×3×3 supercells. *L* is the side length of the supercells. For charged defect, the electron potential is set to the valence band maximum. The electrostatic potential of defected system is aligned to that of bulk.

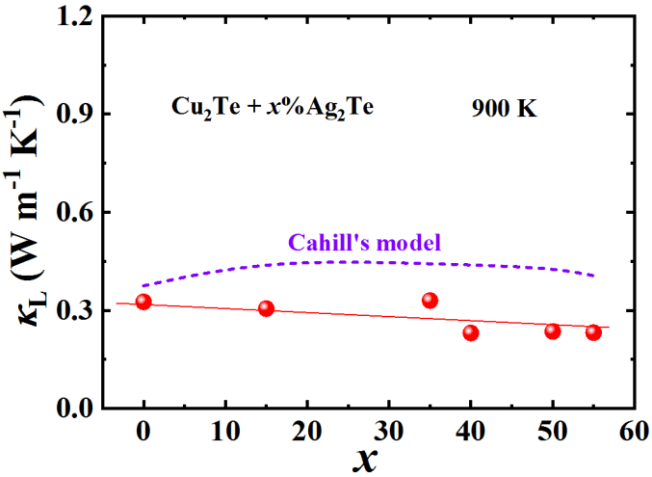

Figure S5. Lattice thermal conductivity κ_L as a function of Ag_2Te content at 900 K. The purple dashed line represents the minimum lattice thermal conductivity (κ_{min}) estimated by the Cahill's model.[1] The minimum lattice thermal conductivity κ_{min} for a normal solid can be expressed as

$$\kappa_{min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_i \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \qquad \text{(S1)} \ ,$$

where v_i is the speed of sound, Θ_i $(= v_i(\hbar/k_B)(6\pi^2 n)^{1/3})$ is the cutoff frequency, and n is the number density of atoms. This model assumes that a material has a completely disordered structure with three phonon modes (one longitudinal and two transverse) taken into account. The calculated κ_{min} values for Cu_2Te + x% Ag_2Te (x = 0, 15, 35, 40, 50, and 55) are around 0.4 W m^{-1} K^{-1}.

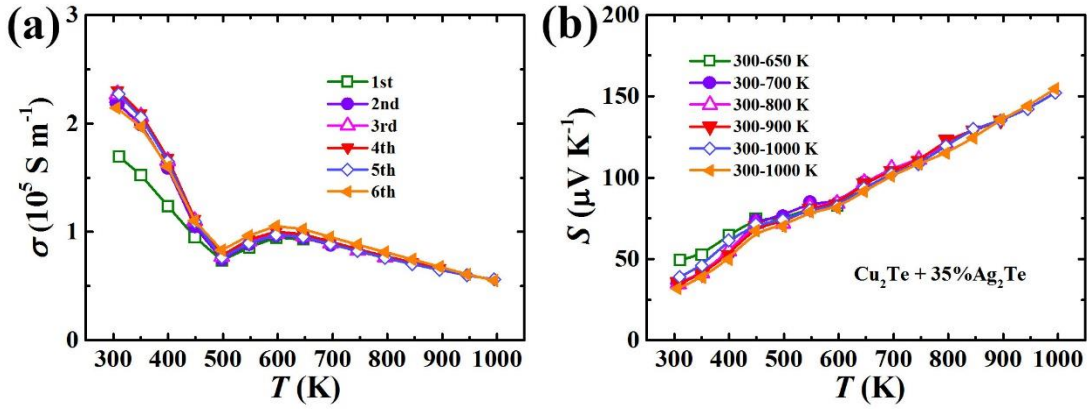

Figure S6. Repeatability test on the electrical transport properties for Cu_2Te + 50% Ag_2Te. The measurements were repeated six cycles at different cycling temperatures.

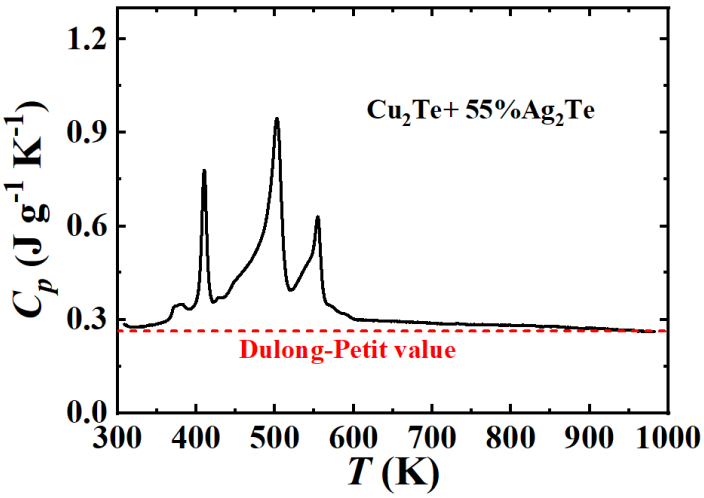

Figure S7. Temperature dependent heat capacity at constant pressure (C_p) for Cu_2Te + 55% Ag_2Te sample. The dashed line represents the theoretical heat capacity at constant volume (C_v) derived from Dulong-Petit law. The C_p is significantly changed during phase transitions.[2, 3] But the measured C_p values at high temperature are very close to the value estimated by the Dulong-Petit law.

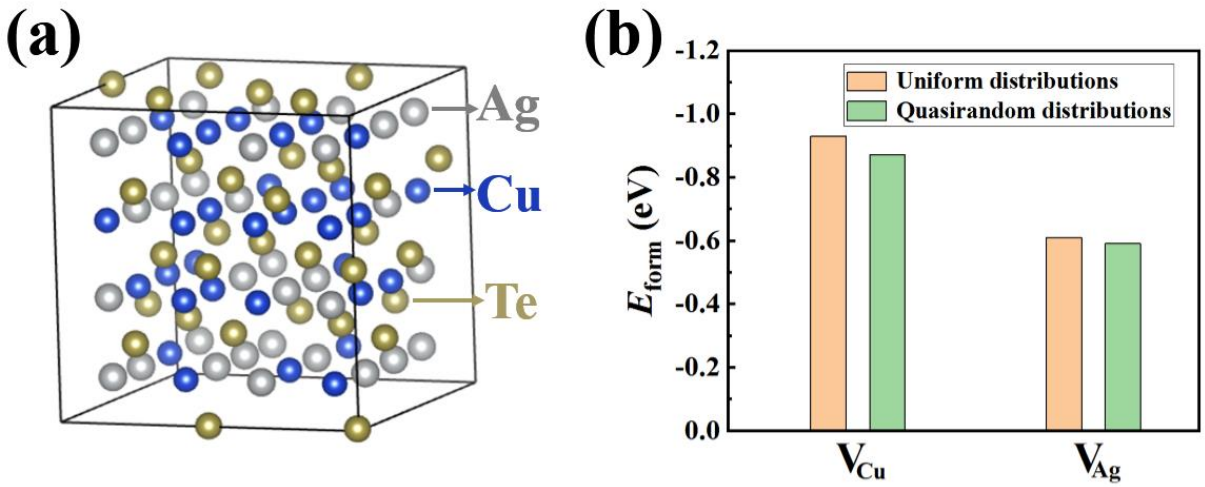

Figure S8. (a) Special Quasirandom Structure (SQS) of CuAgTe generated by "mcsqs" code of the Alloy Theoretic Automated Toolkit (ATAT). (b) Comparison of the defect formation energy for uniform distribution (Fig. S3b) and quasirandom distribution (Fig. S8a) of Cu and Ag in CuAgTe.

Single Parabolic Band Model

Based on the Fermi statistics, the Seebeck coefficient S can be expressed as

$$S = \frac{k_B}{e}\left[\frac{(2+\lambda)F_{\lambda+1}(\eta)}{(1+\lambda)F_{\lambda}(\eta)} - \eta\right] \quad , (S2)$$

where k_B is the Boltzmann constant, e is the electron charge, λ is the scattering factor (0 for acoustic phonon scattering), and η (=E_F/k_BT) is the reduced Fermi energy. The Fermi integrals

are given by $F_m(\eta) = \int_0^\infty \frac{x^m dx}{1+\exp(x-\eta)}$, where x is the reduced carrier energy. The Hall carrier concentration p can also be expressed as a function of Fermi integrals

$$p = 4\pi \left(\frac{2m^* k_B T}{h^2}\right)^{3/2} \frac{F_{1/2}(\eta)}{r_H} \quad , (S3)$$

$$r_H = \frac{3}{4}\frac{F_{1/2}(\eta)F_{-1/2}(\eta)}{{F_0}^2(\eta)} \quad , (S4)$$

where m^* is the electronic effective mass, h is the Planck constant and r_H is the Hall factor. The Hall mobility μ for acoustic phonon scattering in the non-degenerate limit can be expressed as

$$\mu = \frac{1}{2}\frac{F_{-1/2}(\eta)}{F_0(\eta)} \cdot \mu_0 \quad , (S5)$$

where μ_0 represents the drift mobility. Thus the electrical conductivity σ can be obtained by

$$\sigma = pe\mu = \frac{16\sqrt{2}\pi e k_B^{3/2} T^{3/2} F_0(\eta)}{3h^3} \mu_0 m^{*3/2} \quad . (S6)$$

Through Equation S2 and Equation S6, we can calculate the *S*-σ (Seebeck coefficient *vs* electrical conductivity) relation if $\mu_0 m^{*3/2}$ (also called weighted mobility) is given.

References

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