Supporting Materials

Equivalent doping of Te leads to optimized electrical and thermal transport properties in thermoelectric $Cu_2MnSnSe_4$ alloys

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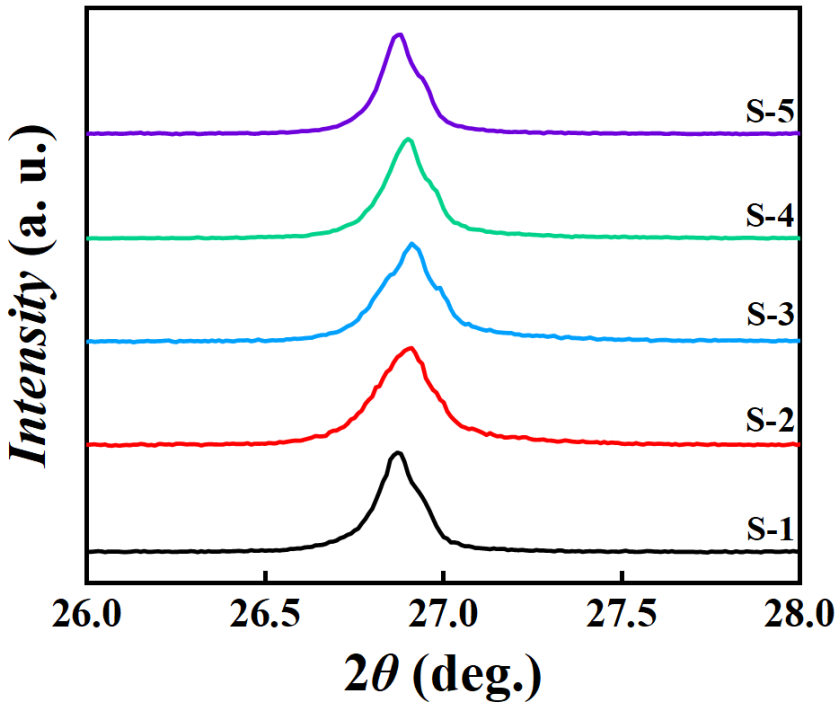

Figure S1. Local amplifications of the XRD patterns for all samples.

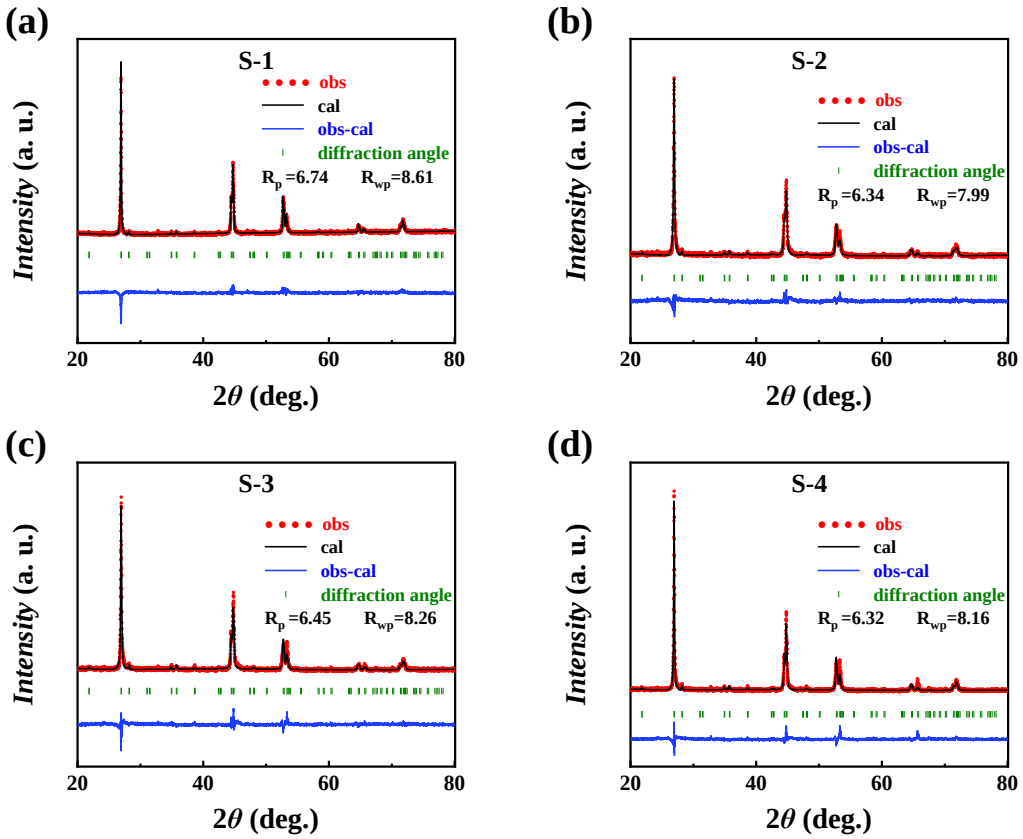

Figure S2. Rietveld refinement of (a) S-1, (b) S-2, (c) S-3, (d) S-4.

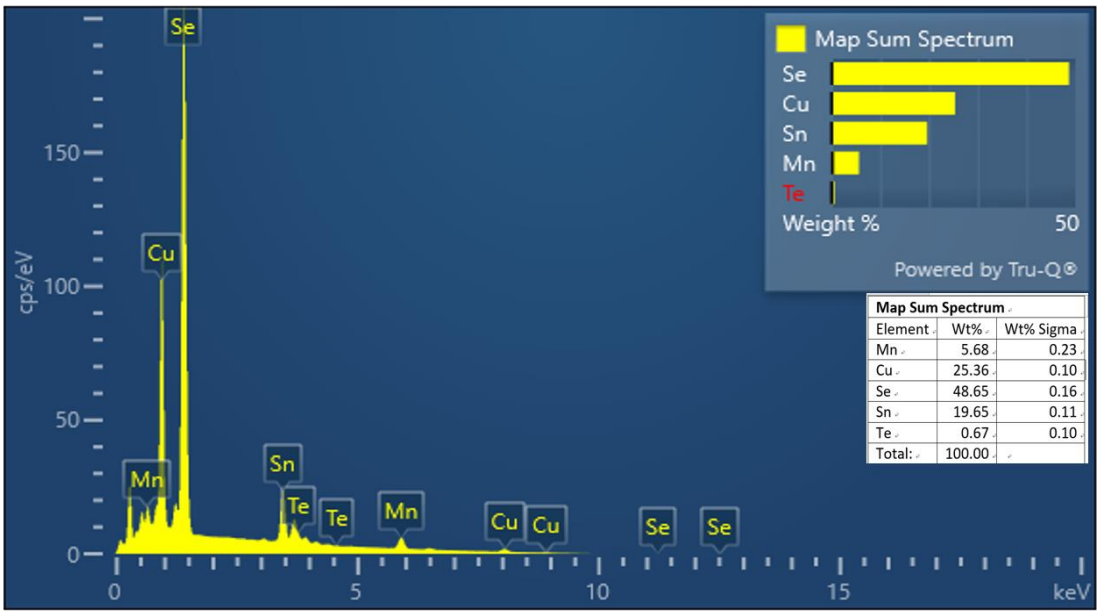

Figure S3. The atomic percentage of each element for S-5. (EDS result)

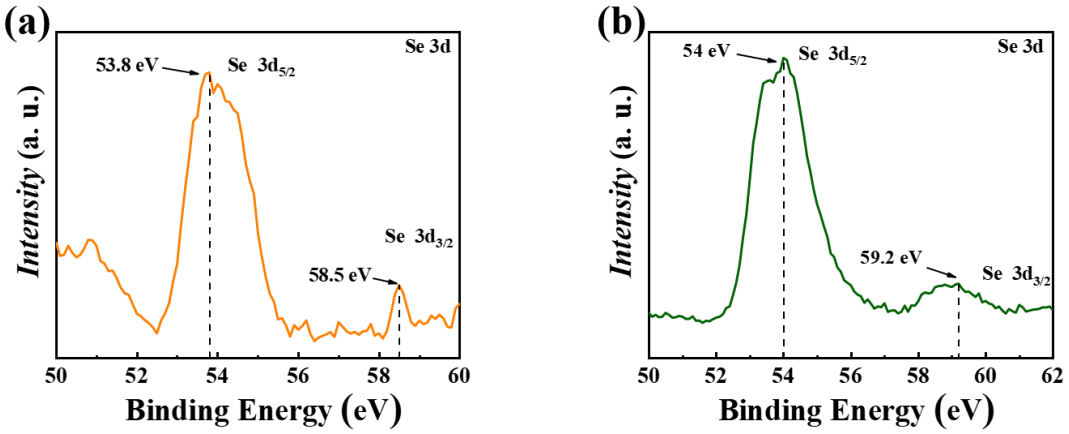

Figure S4. Se XPS peaks for the S-2 (a) and S-5 (b).

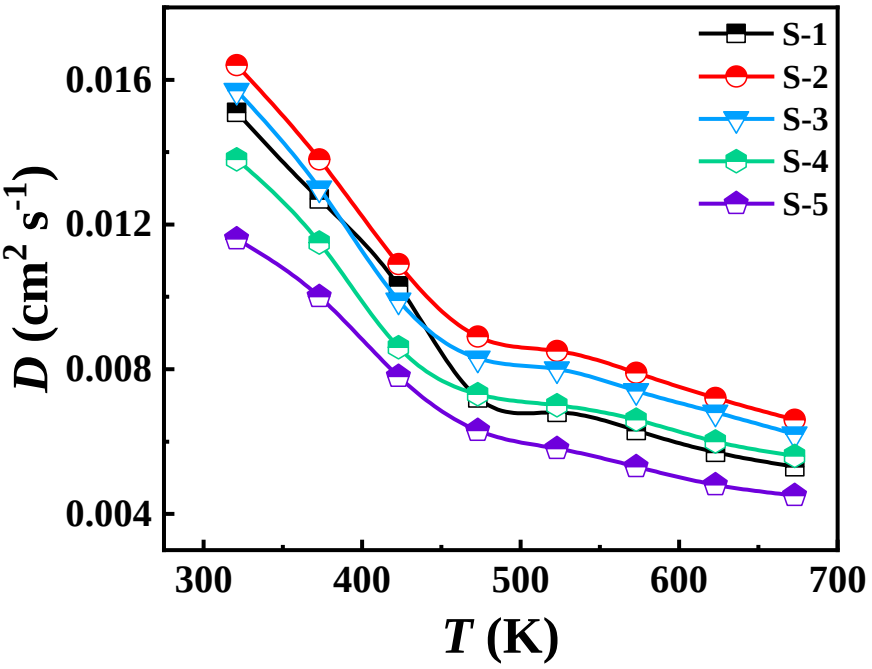

Figure S5. Thermal diffusion coefficients (*D*) of all samples.

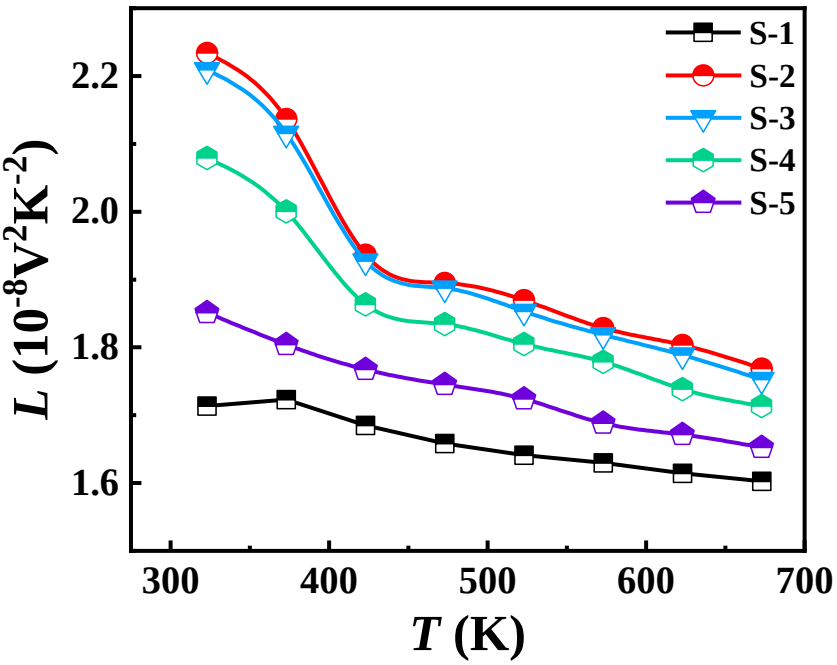

Figure S6. Calculated Lorentz number (L = 1.5+exp (-|S| / 116)) of all samples.

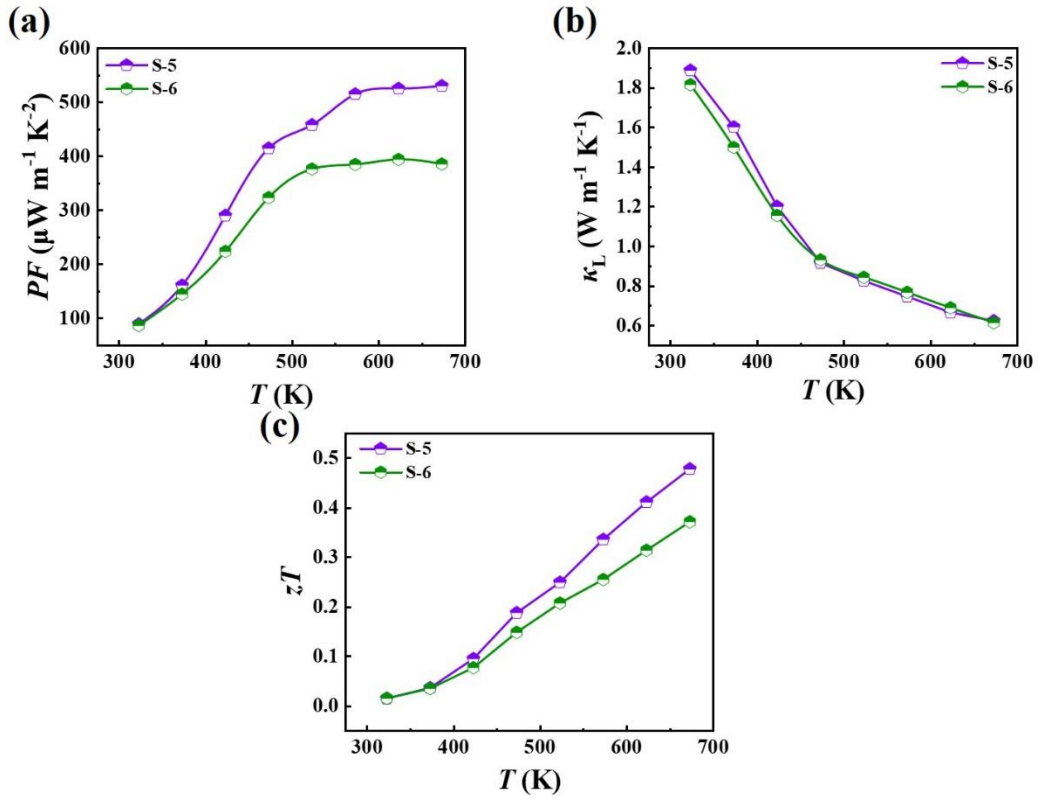

Figure S7. Temperature dependences of (a) the power factor *PF*, (b) the lattice thermal conductivity (κ_L) and (c) the dimensionless figure of merit (zT) for S-5 and S-6.

Calculation section:

The average sound velocity (v_a), Poisson ration (v_p), Grüneisen parameter (γ), Debye temperatures (θ_D) and mean free path of phonons (l_{ph}) are calculated by:

$$v_a = \left(\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right)^{-1/3} \quad \text{(Equation S1)}$$

$$v_p = \frac{1-2(v_t/v_l)^2}{2-2(v_t/v_l)^2} \quad \text{(Equation S2)}$$

$$\gamma = \frac{3}{2}\left(\frac{1+v_p}{2-3v_p}\right) \quad \text{(Equation S3)}$$

$$\theta_D = \frac{v_a}{k_B}\left(\frac{6\pi^2}{V}\right)^{1/3} \quad \text{(Equation S4)}$$

$$l_{ph} = \frac{3\kappa_L}{\rho C_p v_a} \quad \text{(Equation S5)}$$

In equations (S1 - S5), v_t is the transverse sound velocity, v_l is the longitudinal sound velocity, V is the volume per atom, k_B is the Boltzmann constant, κ_L is the experimental lattice thermal conductivity at 323 K, ρ is the experimental density and C_p is the specific heat at constant pressure.

Phonon relaxation time can be expressed as

$$\tau_c^{-1} = \tau_U^{-1} + \tau_N^{-1} + \tau_{GB}^{-1} + \tau_{PD}^{-1}$$

where τ_U^{-1}, τ_N^{-1}, τ_{GB}^{-1} and τ_{PD}^{-1} are the relaxation times due to the scattering of Umklapp processes, Normal processes, grain boundary and point defects.

$$\tau_U^{-1} = \frac{\gamma^2}{M v_a^2 \theta_D}\omega^2 T exp\left(-\frac{\theta_D}{3T}\right) \quad \text{(Equation S6)}$$

$$\tau_N^{-1} = \beta \tau_U^{-1} \quad \text{(Equation S7)}$$

$$\tau_{GB}^{-1} = \frac{v_a}{\lambda} \quad \text{(Equation S8)}$$

$$\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi v_a^3}\Gamma \quad \text{(Equation S9)}$$

In equations (S6 - S9), γ is the Grüneisen parameter, ω is the phonon frequency, M is the average atomic mass of crystal, v_a is the average sound velocity, θ_D is the Debye temperatures, β is the Ratio of N- to U- processes, λ is the average grain size, V is the

average volume of atom and Γ is the total disorder parameter.

The mass fluctuation parameter (Γ_M) and the strain fluctuation parameter (Γ_S) are calculated by:

$$\Gamma_M = \frac{\sum_{i=1}^{n} c_i (\frac{\overline{M}_i}{\overline{\overline{M}}})^2 \Gamma_M^i}{\sum_{i=1}^{n} c_i} \quad \text{(Equation S10)}$$

$$\Gamma_M^i = \sum_k f_i^k \, (1 - \frac{M_i^k}{\overline{M}_i})^2 \quad \text{(Equation S11)}$$

$$\Gamma_S = \frac{\sum_{i=1}^{n} c_i (\frac{\overline{M}_i}{\overline{\overline{M}}})^2 \varepsilon \Gamma_r^i}{\sum_{i=1}^{n} c_i} \quad \text{(Equation S12)}$$

$$\Gamma_r^i = \sum_k f_i^k \, (1 - \frac{r_i^k}{\bar{r}_i})^2 \quad \text{(Equation S13)}$$

and the $\overline{M}_i$, $\bar{r}_i$, $\overline{\overline{M}}$, ε are calculated by:

$$\overline{M}_i = \sum_k f_i^k M_i^k \quad \text{(Equation S14)}$$

$$\bar{r}_i = \sum_k f_i^k r_i^k \quad \text{(Equation S15)}$$

$$\overline{\overline{M}} = \frac{\sum_{i=1}^{n} c_i \overline{M}_i}{\sum_{i=1}^{n} c_i} \quad \text{(Equation S16)}$$

$$\varepsilon = \frac{2}{9} (\frac{6.4\gamma(1+\nu_p)}{1-\nu_p})^2 \quad \text{(Equation S17)}$$

In equations (S10 - S17), c_i is the relative degeneracies of the respective sites, f_i^k is the fractional occupation of the k^{th} atom on the i_{th} sublattice, $\overline{M}_i$ is the average mass of atoms on the i_{th} sublattice, $\bar{r}_i$ is the average radius of atoms on the i_{th} sublattice, $\overline{\overline{M}}$ is the average atomic mass of the compound, ε is the anharmonic parameter.