Supplementary Material for

Enhanced Thermoelectric Properties of Cu_xSe ($1.75 \leq x \leq 2.10$) during Phase Transitions

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Calculation of thermal conductivity during the phase transition[1]

The thermal diffusivity measured by laser flash method is calculated from the specimen thickness and the time required for the rear face temperature rise to reach a percentage of its maximum value[1], this could be expressed using equation S1.

$$\lambda = 0.13879 * L^2 * \frac{1}{t_{1/2}} \quad \text{(S1)}$$

Here, λ is the thermal diffusivity, L is the thickness of the sample and $t_{1/2}$ is the half-rise time which represents the time required from the initiation of the plus for the rear face temperature to reach half ΔT_{max}. During a phase transition, extra energy is absorbed from the heat flow to change the crystal structure, the half-rise time of a material during phase transitions could be overlooked. Then the measured thermal diffusivity calculated using equation S1 is underestimated, which should be corrected before further calculation.

To calculate the real thermal conductivity κ during the phase transition, the true λ_0 and C_{p0} without the contribution of phase transition should be used.

$$\kappa_{\text{Real}} = C_{p0} * d * \lambda_0 \quad \text{(S2)}$$

The general heat conduction expression for one-dimensional phase transition is[2]

$$\frac{\kappa}{C_{p0}d}\cdot\frac{\partial^2 T}{\partial x^2}-\frac{\partial T}{\partial t}-\frac{\Delta H}{C_{p0}}\cdot\frac{\partial a}{\partial t}=0 \qquad \text{(S3)}$$

The third term in equation S3 is the energy change due to the phase transition[3]. The temperature dependent mole fraction of high temperature β-phase (a) using the phase transition kinetics equations is given by

$$\frac{da}{dt}=B\cdot(a_{eq}-a) \qquad \text{(S4)}$$

$$B=A\cdot n\cdot\exp(-\frac{E}{RT})\cdot\frac{(1-a_{eq})^{n-1}}{a_{eq}} \qquad \text{(S5)}$$

Here, B refers to the speed of the phase transition, which could be obtained by fitting the heat flow curves with different heating rates. The fitting curves and fitting parameters are given in **Figure S**6 and **Table S**2, respectively. With equations S4 and S5, we can use the phase transition speed B to solve equation S3.

$$B\cdot(\frac{\kappa}{C_{p0}d}\frac{\partial^2 T}{\partial x^2}-\frac{1+C_{pt}/C_{p0}}{1}\frac{\partial T}{\partial t})+\frac{\kappa}{C_{p0}d}\frac{\partial^3 T}{\partial x^2\partial t}-\frac{\partial^2 T}{\partial t^2}=0 \qquad \text{(S6)}$$

Based on equation S6, the approximate solution of the relationship between λ_0 and λ_m is:

$$\frac{\lambda_m}{\lambda_0}\approx\frac{1}{1+C_{pt}/C_{p0}}+\frac{C_{pt}/C_{p0}}{1+C_{pt}/C_{p0}}\cdot e^{-\frac{1.81\cdot B\cdot L^2}{\lambda_0\cdot\pi^2}\cdot\frac{1+C_{pt}/C_{p0}}{1}} \qquad \text{(S7)}$$

Then the true κ during phase transitions could be solved using equation S2.

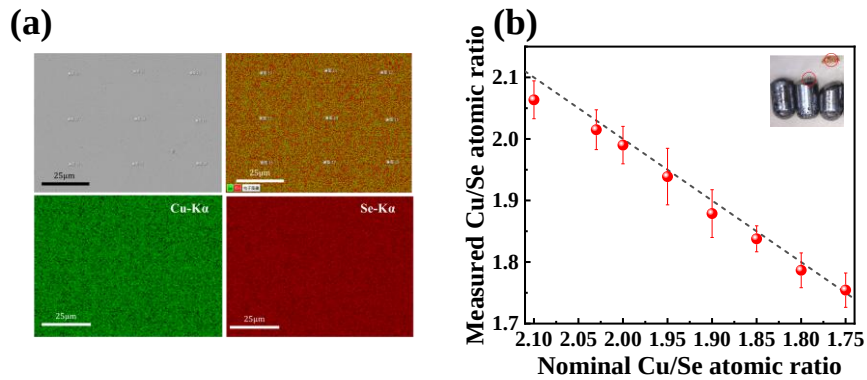

Figure S1. **(a)** Secondary electron (SE) image and elemental energy dispersive spectroscopy (EDS) mapping for Cu_2Se. **(b)** Nominal Cu/Se atomic ratio *vs* measured Cu/Se atomic ratio for Cu_xSe (x=1.75, 1.80, 1.85, 1.90, 1.95, 2.00, 2.03 and 2.10) samples. 9 points are randomly selected to obtain the mean value and the error bar is shown in the figure. The inset shows the ingots after annealing.

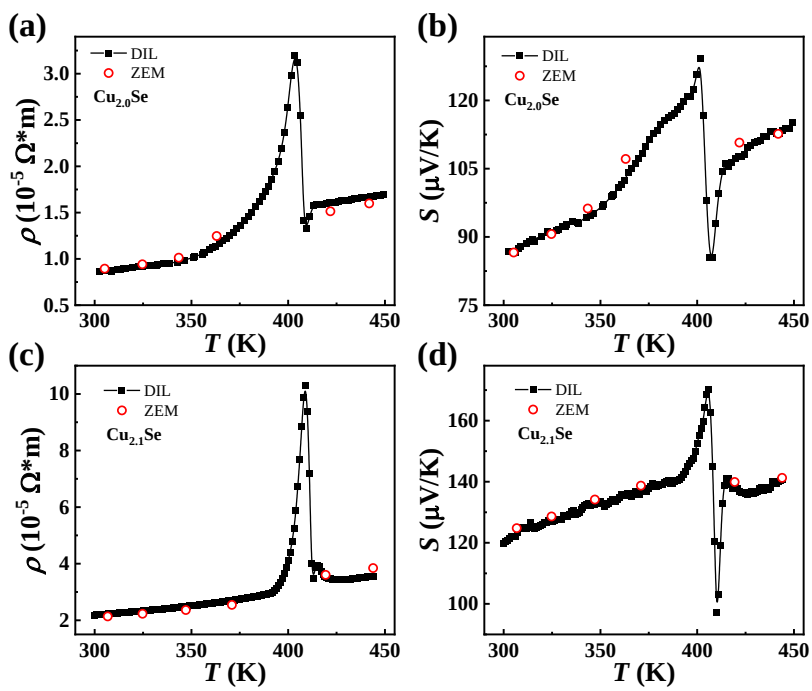

Figure S2. Electrical resistivity (ρ) and Seebeck coefficient (S) measured by DIL (black square) and ULVAC ZEM-3 system (red circle) for $Cu_{2.00}Se$ and $Cu_{2.10}Se$

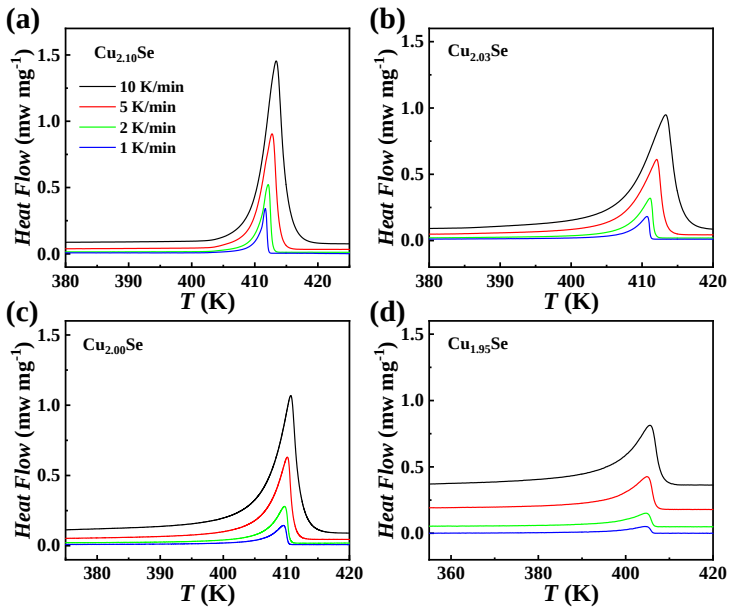

Figure S3. Heat flow curves for $Cu_{2.10}Se$, $Cu_{2.03}Se$, $Cu_{2.00}Se$ and $Cu_{1.95}Se$ measured by DSC with different heating rates (1.0, 2.0, 5.0 and 10 K/min).

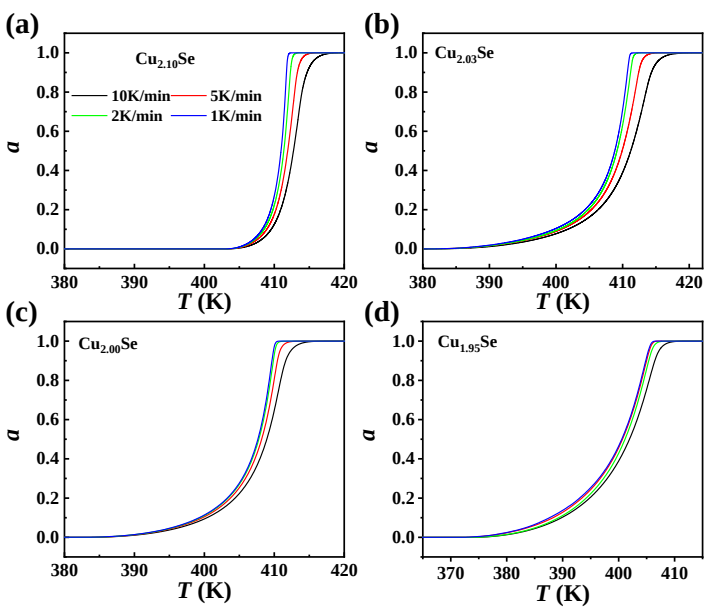

Figure S4. Temperature dependence of mole fraction of high temperature β-phase at different heating rates (1.0, 2.0, 5.0 and 10 K/min) for **(a)** $Cu_{2.10}Se$, **(b)** $Cu_{2.03}Se$ **(c)** $Cu_{2.00}Se$ and **(d)** $Cu_{1.95}Se$.

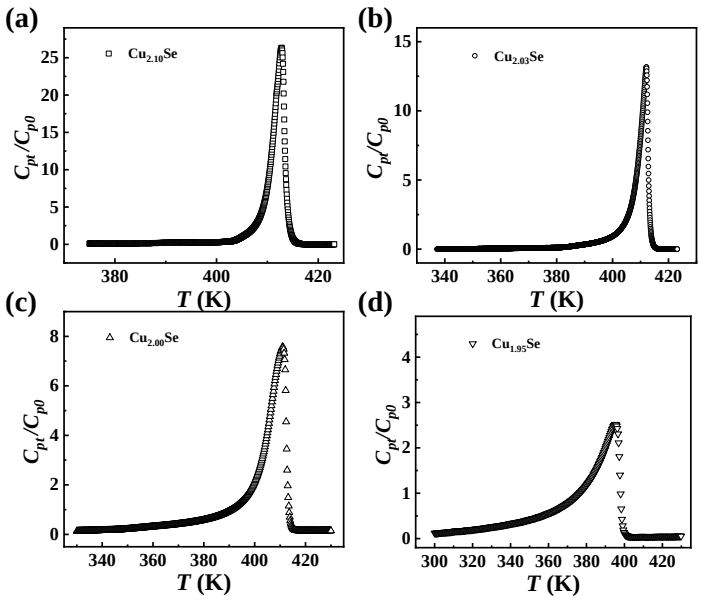

Figure S5. C_{pt}/C_{p0} for Cu_xSe ($1.95 \leq x \leq 2.10$) during the phase transition. The heat capacity is measured with a heating rate of 5 K min^{-1}.

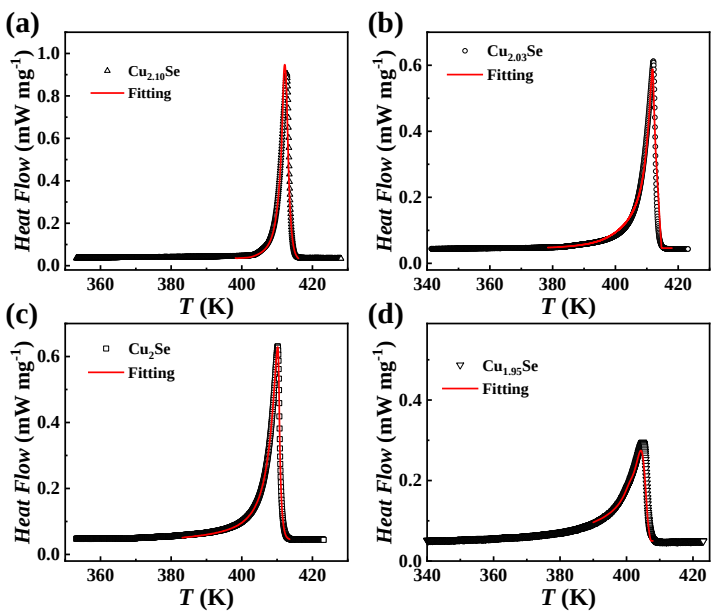

Figure S6. Heat Flow measured with a heating rate of 5 K min^{-1}. The symbols represent the experiment data, and the red lines are fitted by the equations S3 and S4 with the fitting parameters listed in **Table S**2

Table S1. The critical temperature T_p measured with a heating rate of 1 K min^{-1} and the offset of critical temperature ΔT_p measured with heating rates of 2 K min^{-1}, 5 K min^{-1}, and 10 K min^{-1} for Cu_xSe (x =1.85, 1.90, 1.95, 2.00, 2.03 and 2.10) samples.

Materials	T_p **(K)**	ΔT_p **(K)**		
	1K min^{-1}	**2K min^{-1}**	**5K min^{-1}**	**10K min^{-1}**
$Cu_{2.10}Se$	411.65	0.5	1.1	1.9
$Cu_{2.03}Se$	410.70	0.4	1.4	2.6
$Cu_{2.00}Se$	409.45	0.3	0.6	1.2
$Cu_{1.95}Se$	404.45	0.2	0.4	1.1
$Cu_{1.90}Se$	376.25	0.3	0.6	1.2
$Cu_{1.85}Se$	362.55	-0.1	0.0	0.1

Table S2. DSC Fitting parameters using phase transition kinetics equations S3 and S4. n is the reaction order, A is the pre-exponential factor, E is the activation energy.

Materials	E **[kJ mol^{-1}]**	***Log(A)***	***n-1***
$Cu_{2.10}Se$	636	79	0.078
$Cu_{2.03}Se$	253	31	0.065
$Cu_{2.00}Se$	247	30	0.024
$Cu_{1.95}Se$	171	28	0.097

References

[1]. Astm E 1991 *Annual book of ASTM standards* **15**, 750

[2]. Chen H, Yue Z, Ren D, Zeng H, Wei T, Zhao K, Yang R, Qiu P, Chen L, Shi X 2018 *Adv. Mater.* **31**

[3]. Incropera F P, DeWitt D P, Bergman T L, Lavine A S *Fundamentals of heat and mass transfer* 1996 (New York: Wiley Press)