Supporting Information

Enhancing thermoelectric performance of Cu1.8S by Sb/Sn co-doping and incorporating multiscale defects to scatter heat-carrying phonons

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1. Density ρ, heat capacity C_p and thermal diffusivity

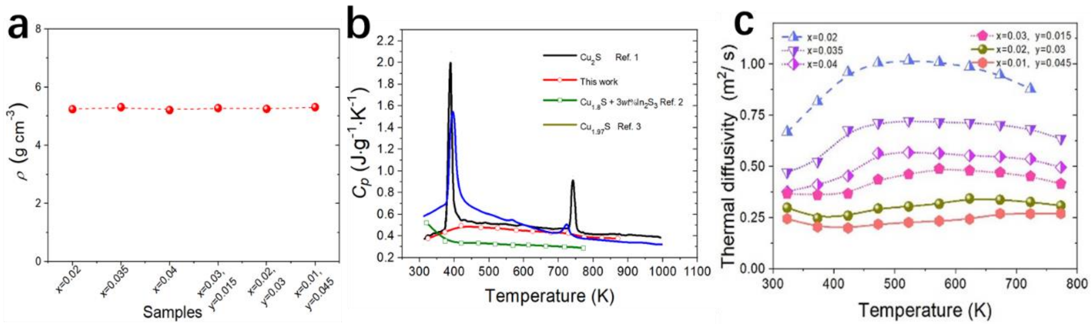

Fig. S1. a) density ρ, temperature dependence of **b)** heat capacity C_p and **c)** thermal diffusivity.[1-3]

2. The SEM images of all samples.

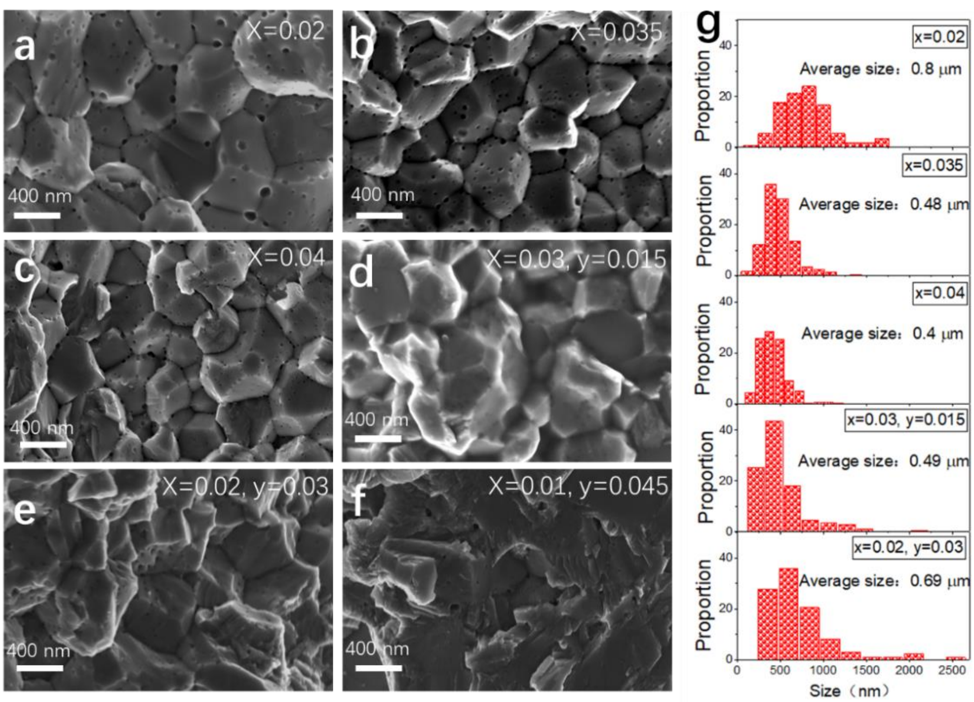

Fig.S2. a) - f) the typical SEM cross-sectional images of all samples. **g)** the distribution of grain sizes based on the SEM images. Because the grains of the sample $Cu_{1.8}Sb_{0.01}Sn_{0.045}S$ are linked together and can not be distinguished clearly, the distribution of grain size has not been counted. However, it can be clearly seen that the average grain size of the $Cu_{1.8}Sb_xSn_yS$ samples increases with the increase of Sn content.

3. Calculated electrical thermal conductivity κ_e and lattice thermal conductivity κ_l

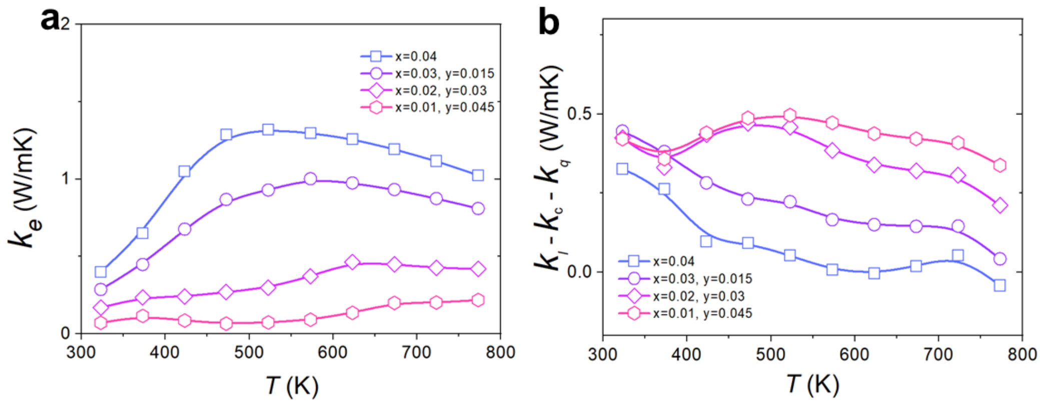

Fig.S3. Temperature dependence of **a)** electrical thermal conductivity κ_e and **b)** apparent lattice thermal conductivity *(κ_l - κ_c - κ_q)*.

$$\kappa_{tatol} = \kappa_e + \kappa_l - \kappa_c - \kappa_q = LT\sigma + \kappa_l - \kappa_c - \kappa_q \quad (1)$$

The κ_c and κ_q correspond to the reduced lattice thermal conductivity of phonons scattered by carriers and liquid-like Cu^+ behavior. The *L* was calculated by SPB model. *r* is selected to be -1/2 due to the hypothetical acoustic phonon scattering mechanism. The computational equations are as follows.

$$L = \left(\frac{\kappa_B}{e}\right)^2 \left\{\frac{(r+7/2)F_{r+5/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \left[\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)}\right]^2\right\} \quad (2)$$

$$\alpha = \pm\left(\frac{\kappa_B}{e}\right)^2 \left[\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta\right] \quad (3)$$

$$n = \frac{2(2\pi m^* \kappa_B T)^{3/2}}{\hbar^{3/2}} F_{r+1/2}(\eta) \quad (4)$$

$$F_s(\eta) = \int_0^\infty \frac{x^s dx}{1 + exp(x-\eta)} \quad (5)$$

4. The thermal cycle testing of $Cu_{1.8}Sb_{0.02}Sn_{0.03}S$ sample.

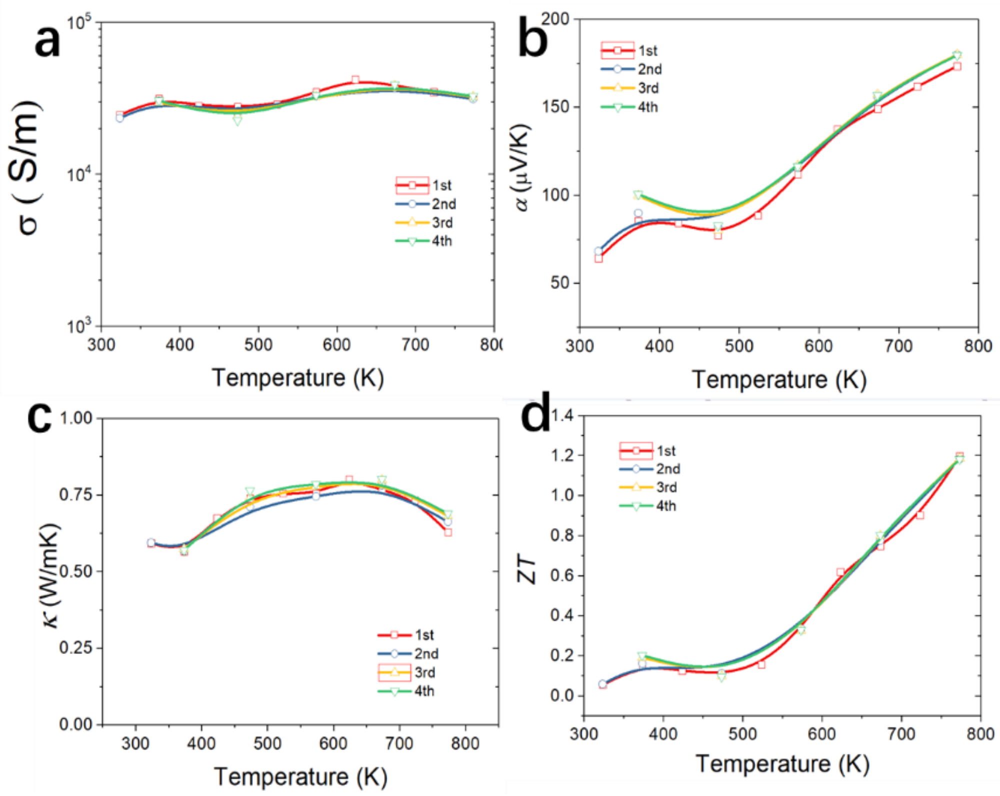

Fig. S4. Temperature dependence of TE properties of $Cu_{1.8}Sb_{0.02}Sn_{0.03}S$ in cyclic test.

Reference

1. Y. He, T. Day, T. Zhang, H. Liu, X. Shi, L. Chen and G. J. Snyder, *Adv Mater*, 2014, **26**, 3974-3978.
2. Z. H. Ge, X. Chong, D. Feng, Y. X. Zhang, Y. Qiu, L. Xie, P. W. Guan, J. Feng and J. He, *Materials Today Physics*, 2019, **8**, 71-77.
3. L. Zhao, X. Wang, F. Y. Fei, J. Wang, Z. Cheng, S. Dou, J. Wang and G. J. Snyder, *Journal of Materials Chemistry A*, 2015, **3**, 9432-9437.