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Enhanced thermoelectric performance of Sn-doped Cu_3SbS_4

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1. Representative TEM images of Sn-doped Cu_3SbS_4

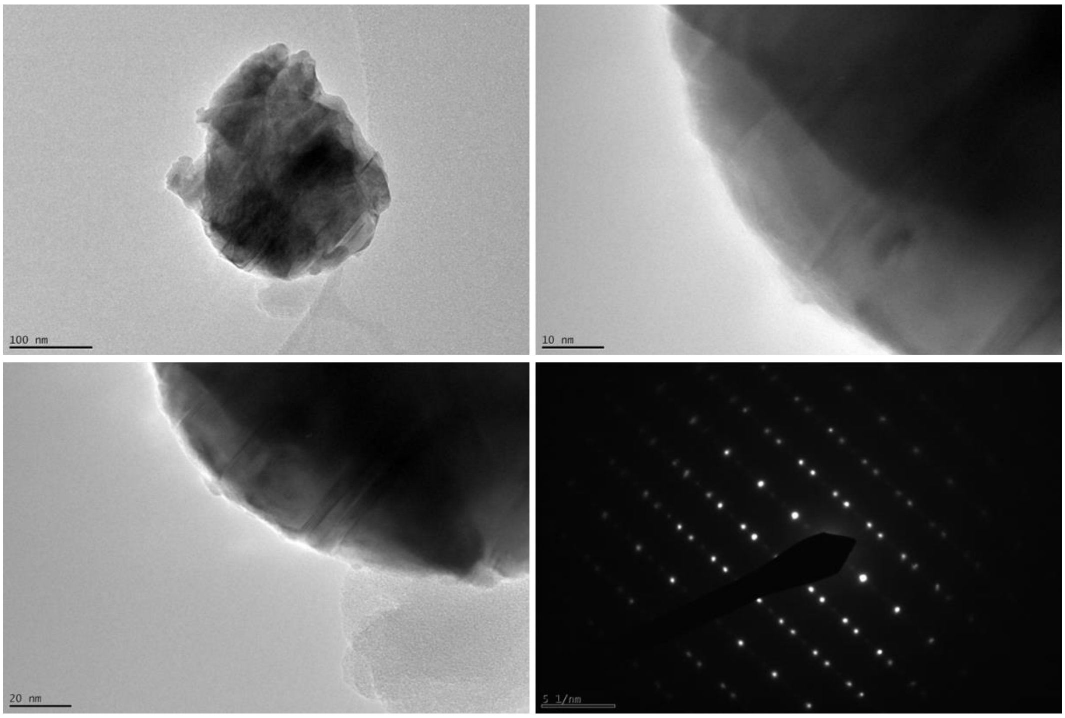

Figure S1. Representative TEM images of Sn-doped Cu_3SbS_4 samples.

2. SPB Calculations

The single parabolic band (SPB) model is based on Boltzmann transport equation and the relaxation time approximation, which is widely used to in thermoelectric materials.[1] In the SPB model, the Seebeck coefficient (α), the Hall carrier concentration (n_H), the

Hall mobility (μ_H), and the Lorenz number (L) can be written as Equation (1), (2), (3) and (4).

$$\alpha = \frac{k_B}{e}\left[\frac{(2+r)F_{1+r}(\eta)}{(1+r)F_r(\eta)} - \eta\right] \qquad (1)$$

$$n_H = \frac{8\pi(2k_B T m^*)^{3/2}}{3h^3}\frac{(1+r)^2 F_r^{\,2}(\eta)}{(1/2+2r)F_{2r-1/2}(\eta)} \qquad (2)$$

$$\mu_H = \mu_0 \frac{(1/2+2r)F_{2r-1/2}(\eta)}{(1+r)F_r(\eta)} \qquad (3)$$

$$L = \left(\frac{k_B}{e}\right)^2\left[\frac{(1+r)(3+r)F_r(\eta)F_{2+r}(\eta) - (2+r)^2 F_{r+1}^2(\eta)}{(1+r)^2 F_r^{\,2}(\eta)}\right] \qquad (4)$$

Where k_B is the Boltzmann constant, e is the elementary charge, r is the scattering factor (In this work, the acoustic phonon scattering is assumed to be dominant for charge carrier transport, $r = 0$.), h is the Planck constant, m^* is the density-of-state effective mass, μ_0 is the mobility parameter, $F_i(\eta) = \int_0^\infty \frac{x^i dx}{1+\exp(x-\eta)}$ is the Fermi integral and η is the reduced chemical potential. According to Equations (1) and (2), the Pisarenko line (α versus n) was plotted by adjusting m^* at room temperature to fit the experimental data. The powder factor ($PF=\alpha^2\sigma=\alpha^2 n_H e\mu_H$) dependence of carrier concentration at 573 K was calculated using Equations (1), (2) and (3) and μ_0 of 8 $cm^2V^{-1}s^{-1}$ was used in the calculation. L was calculated based on measured α by using Equation (1) and (3), and the results are showing in Figure S2.

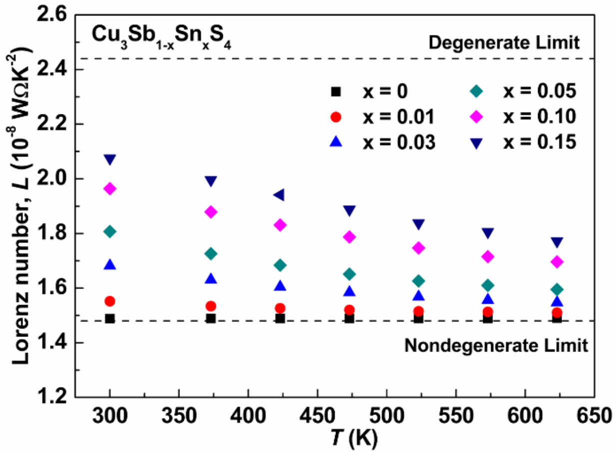

Figure S2. Calculated Lorenz number in the $Cu_3Sb_{1-x}Sn_xS_4$ system as a function of temperature using SPB model with the assumption of acoustic phonon scattering.

Reference.

1. D. M. Rowe, *Thermoelectrics and its energy harvesting*, CRC Press, Boca Raton, FL, 2012.