Electronic Supplementary Material

Realizing high thermoelectric performance of Cu & Ce co-doped p-type polycrystalline SnSe via inducing nanoprecipitation arrays

Yi QIN[a], Tao XIONG[a,b], Jian-feng ZHU[a],Yan-ling YANG[a], Hong-rui REN[b], Hai-long HE[b,*], Chun-ping NIU[b], Xiao-han LI[a], Mei-qian XIE[a], Ting ZHAO[a,*]

a School of Material Science and Engineering, Shaanxi Key Laboratory of Green Preparation and Functionalization for Inorganic Materials, Shaanxi University of Science and Technology, Xi'an, 710021, China

b State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China

*Corresponding Authors.

E-mail: H.-L. He, hhlong@mail.xjtu.edu.cn;

T. Zhao, zhaoting@sust.edu.cn

Section S1. The research of Cu and Ce co-doped SnSe powder microstructure with the change of *x*, *y* values.

We synthesized Cu and Ce doping SnSe powders from *x*, *y* = 0 to 0.02 as shown in Fig. S1 (a) to (g). As the increase of *x* and *y* values, more and more microbelts as well as nanoprecipitations appear in the powders. When *x*, *y* = 0.02, nanoprecipitation disappear and form separate $SnSe_2$ phase. Thus, we choose *x*, *y* = 0.01 as our main researched values. In addition, as shown in (h), which the *x* value equals 0 and *y* value equals 0.01, show many pores appear in the surface of SnSe, indicating why the nanoprecipitation can emerge in our synthesized powders.

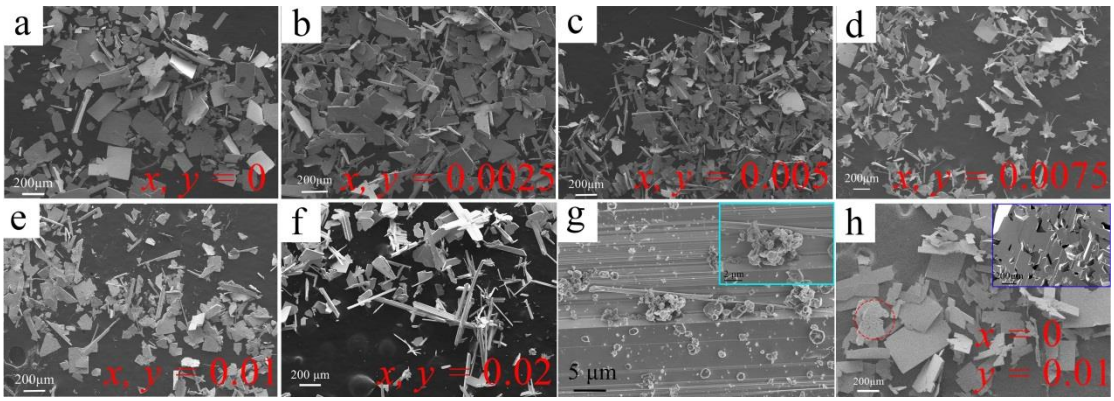

Fig. S1. The SEM micrograph of $Cu_xCe_ySn_{1-x-y}Se$ (x, y = 0 to 0.02). (a) x, y = 0, (b) x, y = 0.0025, (c) x, y = 0.005, (d) x, y = 0.0075, (e) x, y = 0.01， (f) x, y = 0.02, (g) SEM images of a section of typical microbelt taken from magnified (f), (h) x=0, y=0.01.

Section S2. Calculation of Lorenz number (L) for Cu/Ce-doping nanoprecipitation SnSe

The Lorenz numbers (L) are calculated via single parabolic band model (SPB). The values of L for Spark Plasma Sintering (SPS) bulks are decreasing with the entire temperature range (from 1.68 to 1.5×10^{-8} V^2 K^{-2}), revealing that nanoprecipitation play a vital role in strengthening phonon scattering at the low temperature and the material of SnSe is a conventional thermoelectric material. The values of κ largely depend on the phonon scattering at high temperature due to the different scattering means. The calculation for Lorenz numbers and Pisarenko plot is shown in details below of Eqs. (S1)-(S7) [1-4].

$$S = \frac{k_b}{e}\left[\frac{\left(\lambda+\frac{5}{2}\right)F_{\lambda+\frac{3}{2}}\ \eta}{\left(\lambda+\frac{3}{2}\right)F_{\lambda+\frac{1}{2}}\ \eta}-\eta\right] \tag{S1}$$

$$n = \frac{1}{e \cdot R_H} \frac{(2m^* k_b T)^{\frac{3}{2}}}{3\pi\hbar^3} \cdot \frac{\left(r+\frac{3}{2}\right) \cdot F^2_{r+\frac{1}{2}} \ \eta}{\left(2r+\frac{3}{2}\right) \cdot F_{2r+\frac{1}{2}} \ \eta} \tag{S2}$$

$$\mu = \left[\frac{e\pi\hbar^4 C_l}{\sqrt{2} \ k_b T^{\frac{3}{2}} E^2_{def} \ m^{*\frac{5}{2}}} \right] \frac{\left(2r+\frac{3}{2}\right) F_{2r+\frac{1}{2}} \ \eta}{\left(r+\frac{3}{2}\right)^2 F_{r+\frac{1}{2}} \ \eta} \tag{S3}$$

$$L = \left(\frac{k_b}{e}\right)^2 \left\{ \frac{\left(r+\frac{7}{2}\right) \cdot F_{r+\frac{5}{2}} \ \eta}{\left(r+\frac{3}{2}\right) \cdot F_{r+\frac{1}{2}} \ \eta} - \left[\frac{\left(r+\frac{5}{2}\right) F_{r+\frac{3}{2}} \ \eta}{\left(r+\frac{3}{2}\right) F_{r+\frac{1}{2}} \ \eta} \right]^2 \right\} \tag{S4}$$

$$S = \frac{8\pi^2 k_B^2}{3e\hbar^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3} \tag{S5}$$

Where η, k_b, e, r, R_H, C_l, E_{def}, $\hbar$ and L are the reduce Fermi level, the Boltzmann constant, the electron charge, the scattering factor (r = -1/2 for acoustic phonon scatter) [3], the Hall coefficient, the elastic constant for longitudinal vibrations, the deformation potential coefficient, the reduced plank constant and the Lorenz number, respectively.

$$C_l = \nu_l^2 \rho \tag{S6}$$

Where the ν_l represent the longitudinal sound velocity and taken as 3350 $m \cdot s^{-1}$ in this work [5]. $F_i(\eta)$ is the Fermi integral exhibited as:

$$F_i \ \eta \ = \int_0^\infty \frac{x^i}{1+e^{x-\eta}} dx \tag{S7}$$

Section S3. The calculated band structure and DOS of pure SnSe.

Fig. S2 shows the calculated results of electronic band structure and density of state (DOS) for pure SnSe. It is obviously that SnSe has a

complex electronic structure with indirect bandgap. The calculated value is 0.59 eV which belong to wide bandgap semiconductor. The calculated results are within the margin of error that can be as the reference.

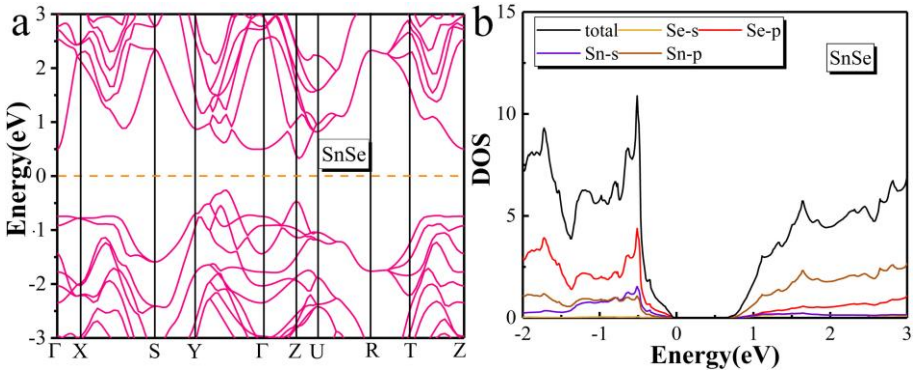

Fig. S2. Calculated electronic band structure (a), density of state (DOS) (b) of pure SnSe

Section S4. The ZT values of temperature-dependent for parallel sintering samples.

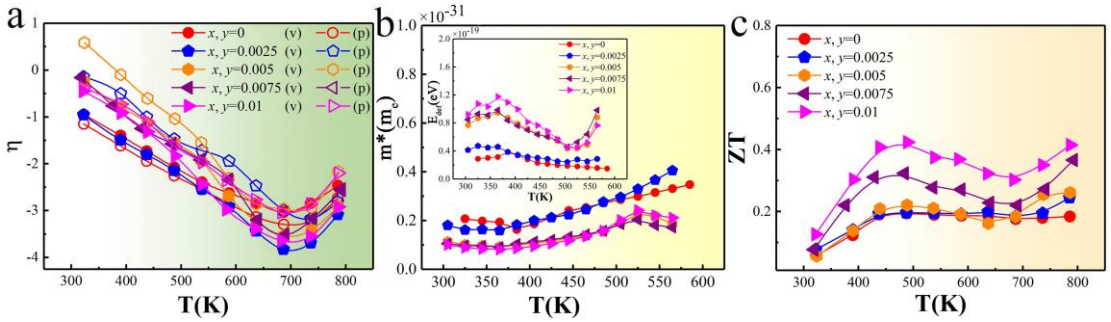

Fig. S3. The temperature-dependent of (a) reduced Fermi level (η), (b) Effective mass (m*) corresponding deformation potential coefficient shown in inset, (c) ZT values with the increase of *x*, *y* values along parallel to the sintering pressure.

In order to calculate the parameter of electric properties, the reduce Fermi level is calculated and plotted in Fig. S3(a). Fig. S3(b) shows the calculation of effective mass and deformation potential coefficient [6-9]. The trend is the same as carrier concentration and mobility. Fig. S3(c) demonstrates the ZT values along parallel to the sintering pressure that obviously indicate the lower values than perpendicular direction.

Reference

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