† Supporting information

Grain size optimization for high-performance polycrystalline SnSe thermoelectrics

Kunling Peng[a,b], Hong Wu[a,b], YanCi Yan[a,b], Lijie Guo[a], Guoyu Wang [*b,c], Xu Lu[*a], Xiaoyuan Zhou[*a]

[a] College of Physics, Chongqing University, Chongqing 401331, People's Republic of China. E-mail: xiaoyuan2013@cqu.edu.cn, luxu@cqu.edu.cn.

[b] Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, People's Republic of China. E-mail: guoyuw@cigit.ac.cn.

[c] University of Chinese Academy of Sciences, Beijing, 100004, China

1 Crystal structure

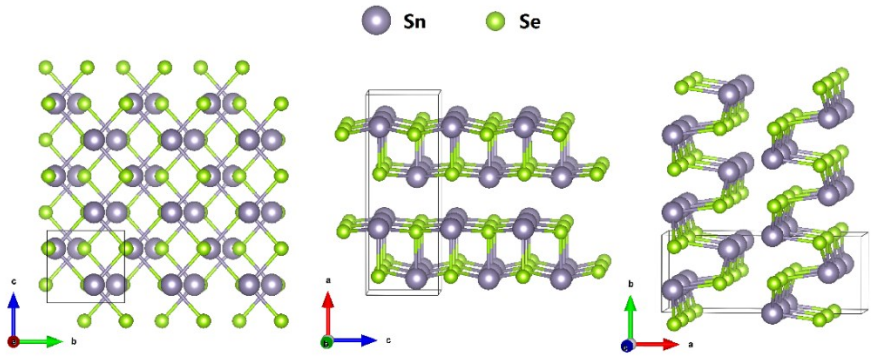
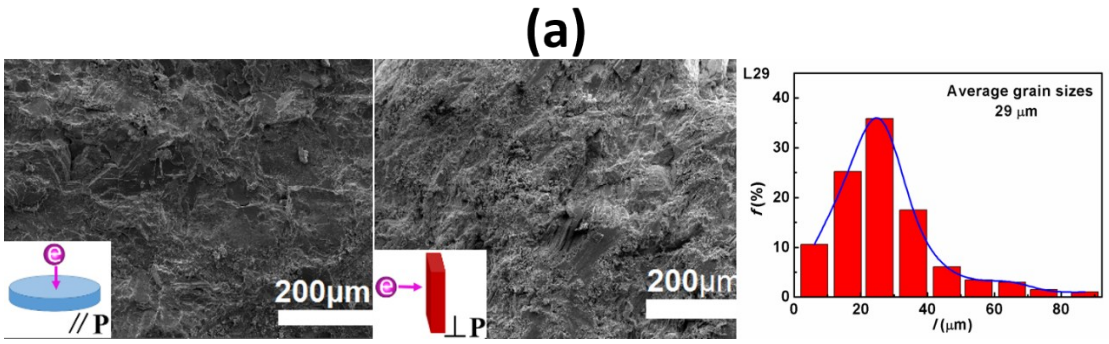


Figure S1. The crystal structure of SnSe with *Pnma* space group.

2 SEM image



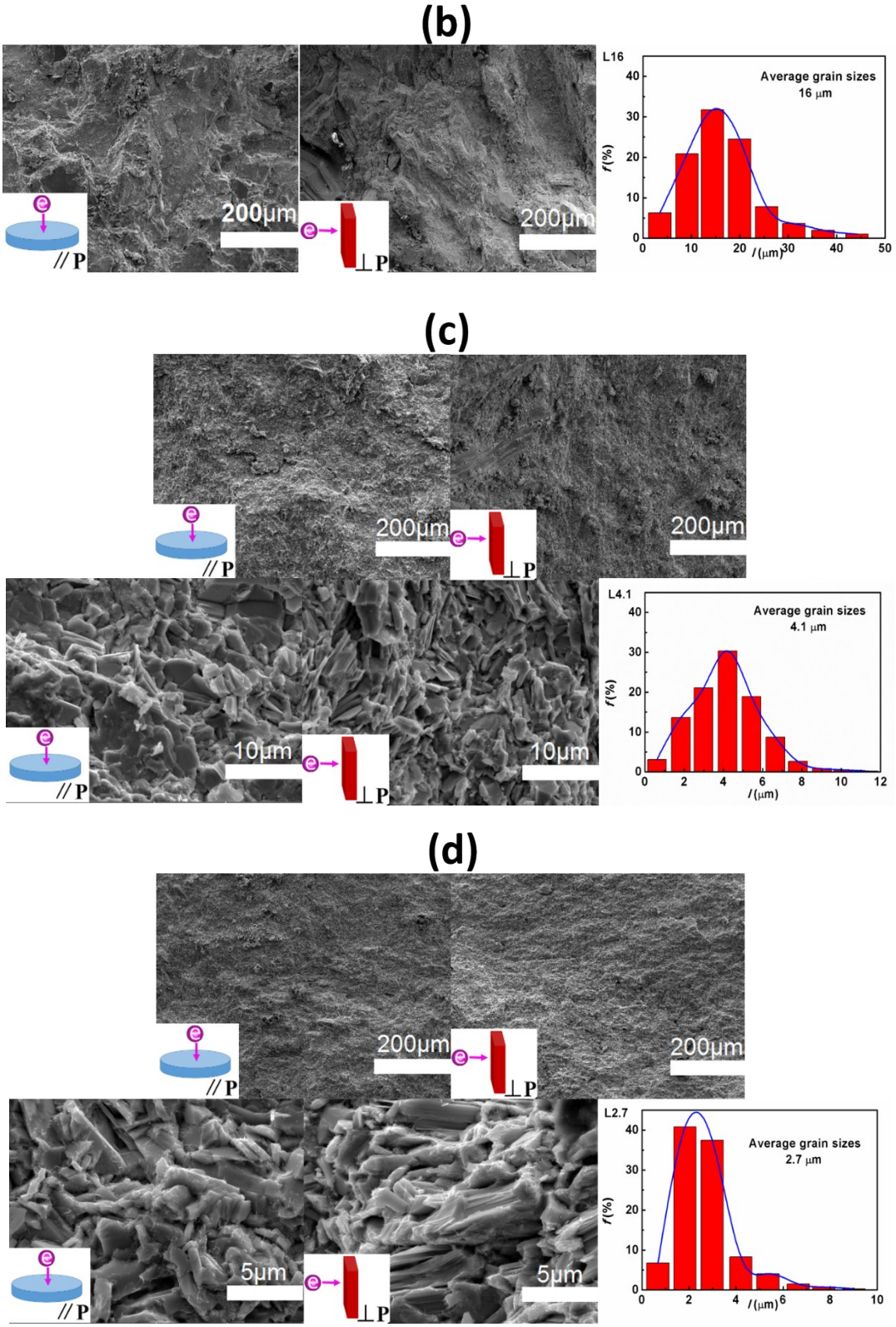


Figure 2S. The SEM image of (a) sample L29, (b)L16, (c)L4.1 and (d)L2.7. The Nominal component of all samples is $Sn_{0.97}Na_{0.03}Se$. The average grain sizes are roughly determined from those SEM images.

3 the electrical properties stability

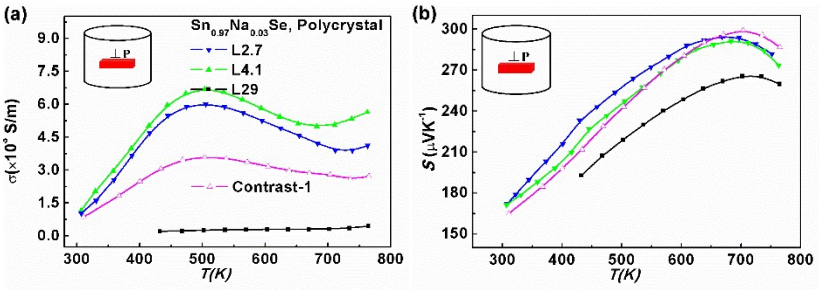


Figure 3S. (a) and (b) are the results of stability test of all samples perpendicular to pressing direction, except the sample L16 because of its huge resistance after three month. All data in this Figure are obtained after three months. The results indicate that the electrical conductivity of the samples with ball-milling is quite stable, while that of the samples without ball-milling deteriorates significantly compared with the data measured previously.

4 The thermal transport properties

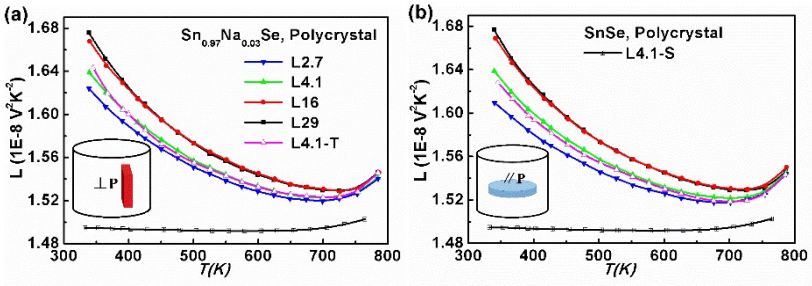


Figure S4. The Lorenz number as a function of temperature for each sample.

The calculated Lorenz number are calculated from a parabolic band model (SPB) which is defined as[S1]

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

with the Fermi integral

$$F_n(\eta) = \int_0^\infty \frac{\xi^n}{1+e^{\xi-\eta}} d\xi$$

where η is the reduced Fermi energy from the Seebeck coefficient given by equation

$$S = \pm \frac{k_B}{q} \left[\eta - \frac{\left(r+\frac{5}{2}\right)F_{r+\frac{3}{2}}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+\frac{1}{2}}(\eta)} \right]$$

Here, q is the electron charge, κ_B the Boltzmann constant, r (= -1/2) the scattering factor.

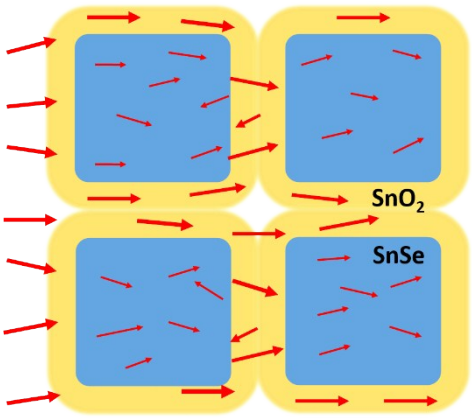


Figure 5S. The schematic diagram of thermal transport process in a sample with a thin oxidied/amorphoue layer on grain boundaries.

The blue part designates the SnSe matrix and the yellow area stands for a thin oxidied/amorphoue layer around grain boundaries (like SnO_2). The phonon transport capability of SnO_2 is believed to be higher than that of the matrix due to the ultra-high lattice thermal conductivity of SnO_2 (~98 $Wm^{-1}K^{-1}$ @ RT) as compared to doped SnSe single crystal (2.0 $Wm^{-1}K^{-1}$ @ RT). Thus, the lattice thermal conductivity of polycrystalline samples with a thin oxidied/amorphoue layer on grain boundaries is considered to be higher than that of the doped single crystal with the same composition.

5 The calculation of average zT

First, the fitting curve was fitted from the data of zT value according to the below equation:

$$zT(T) = \sum_{i=0}^{5} C_i T^i$$

where T is absolute temperature, C_i is the fitting constants for each power of T. And the average zT is calculated by

$$zT_{ave} = \frac{\int_{T_{min}}^{T_{max}} zT(T)\, dT}{T_{max} - T_{min}}$$

where T_{min} and T_{max} are the minimum and maximum temperature, respectively in the required temperature range.

All the average zT in this study are based on the above method and two example are shown Figure 6S.

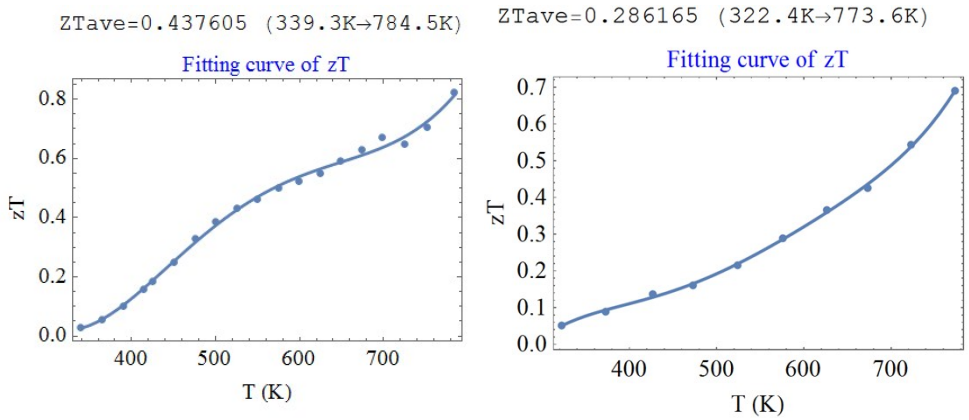


Figure 6S. The calculated average zT of L4.1 sample (left) and SnSe-1%Na reported by Wei *et al*[S2] (right).

Supplementary References

S1. T. Dahal, Q. Jie, Y. C. Lan, C. F. Guo and Z. F. Ren, *Phys. Chem. Chem. Phys.*, 2014, 16, 18170-18175.

T. R. Wei, G. J. Tan, X. M. Zhang, C. F. Wu, J. F. Li, V. P. Dravid, G. J. Snyder and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2016, 138, 8875-8882.