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Electronic Supplementary Information

Fermi-surface dynamics and High thermoelectric performance along the out-of-plane direction in *n*-type SnSe crystal

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Experimental Details

Preparation details and the possible faults: The repeatability of single crystal SnSe is poor because of the harsh preparation conditions and poor mechanical properties. Firstly, we seal the fused materials into a double quartz tube. Since the thermal expansion coefficient of sample and the quart tube are different, the inner quartz tube will break during the cooling process, so a second quartz tube is needed to isolate the air to prevent the samples from being oxidized. Then materials are melted again in the vertical furnace, and slowly cool down. SnSe crystal starts nucleating when the temperature drops to near the melting point. If there is only one nucleation point, the probability of forming a single crystal with better quality is higher. But the reality is that many external factors, such as temperature, vibration, and so on, cause crystals to nucleate in different place leading to sample preparation failure, a typical example is the formation of multiple crystals with irregular directions. The period of slow cooling in vertical furnace is about two weeks. Finally, each crystal needs to be cut into strips and flakes according to the direction. In the process of cutting, the sample is very easy to cleavage, resulting in sample scrap. So, it is difficult to get a high-quality single crystal that can fully be used to measure different properties. Ultimately, it can take several months to get complete date of one sample.

Sample cutting: The SnSe single crystals are cut along in-plane and out-of-plane directions by a diamond wire cutting machine. The cutting wire width is about 0.14 mm, moreover, considering the poor mechanical properties of SnSe single crystals, the cutting speed is controlled at 0.1mm/min to reduce the breakage of samples in cutting process. The samples are cut into 9mm × 2mm × 2mm bars to measure electrical properties and φ10mm × 1.5mm disks to measure thermal properties.

Structure characterization: The structure information of SnSe single crystals are characterized via X-ray diffraction (XRD, Bruker D8, Germany), the section and polished surfaces of samples are observed by scanning electron microscope (SEM, Quanta FEG 250, FEI Co.). The energy dispersive spectrometer (EDS, Oxford Instruments, Britain) attached SEM is used to determine the compositions of samples and the distributions of elements. Transmission electron microscopy (TEM, Tecnai F20) is used to observe the microstructure of samples.

Electrical properties measurements: The Seebeck coefficient S and electrical conductivity σ are measured using a ULVAC instrument (ZEM-3, Japan) simultaneously in a helium atmosphere from 300 K to 813 K. The hall coefficient R_H are measured using a physical propertied measurement system (PPMS-9, Quantum Design,USA) in magnet fields ranging from –5 T to 5 T at room temperature. And the hall carrier concentration n and hall mobility μ are calculated via $n=1/(eR_H)$ and $\mu=\sigma R_H$, respectively.

Thermal properties measurements: The thermal conductivity is calculated from the formula $\kappa=\rho DC_p$, where ρ is the density, D is the thermal diffusivity and C_p is the heat capacity. The thermal diffusivity D from 300 K to 813 K is measured by a laser-flash system (LFA-457, Netzsch, Germany), the density ρ is measured using Archimedes method and the heat capacity C_p is obtained from previous work.[1]

Measurement uncertainties: The uncertainty of Seebeck coefficient S and electrical conductivity σ measurements from systematic error, respectively are 3% and 5%. The combined uncertainly for the total thermal conductivity κ is about 16% calculated by formula: $\frac{d\kappa}{\kappa}=\sqrt{(\frac{d\rho}{\rho})^2+(\frac{dC_p}{C_p})^2+(\frac{dD}{D})^2}$ (1% for the density ρ, 5% for the specific heat C_p[1] and 15% for the thermal diffusion D). Ultimately, the uncertainty of the ZT value is estimated to be within 18%. The computational formula involved is as follows: $\frac{d(ZT)}{ZT}=\sqrt{(2\times\frac{dS}{S})^2+(\frac{d\sigma}{\sigma})^2+(\frac{d\kappa}{\kappa})^2}$.

Density functional theory calculations: Band structure calculations are performed using the density functional theory method as implemented in the VASP code.[2,3] The exchange-correlation energy is in the form of Perdew-Bruke-Ernzerhof (PBE).[4] The cutoff energy for plane-wave basis set is 500 eV, and 6 × 10 × 10 Γ-centered k-points grids is used for the Brillouin zone integrations. The Fermi surface is plotted with the programs Wannier90[5] and Xcrysden.[6]

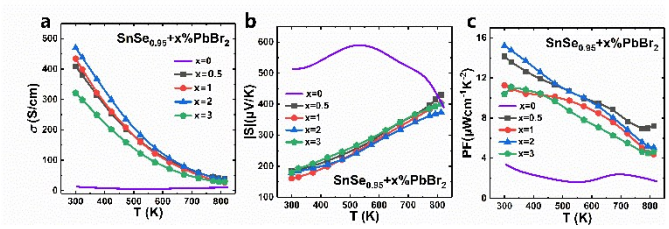

Figure S1. Temperature-dependent electrical properties of $SnSe_{0.95}$ + x%$PbBr_2$(x = 0, 0.5, 1, 2 and 3) along in-plane direction: (a) Electrical conductivity; (b) Seebeck coefficient; (c) Power factor.

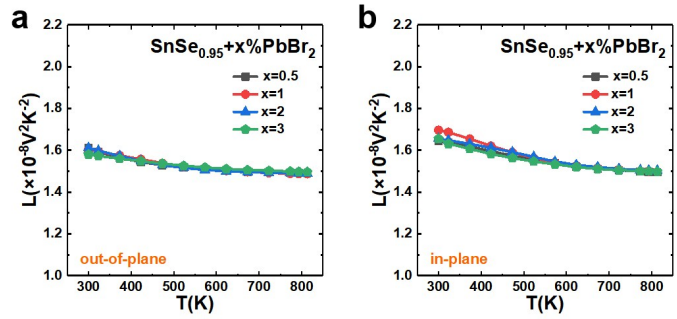

Figure S2. Lorenz numbers as a function of temperature for $SnSe_{0.95}$ + x%$PbBr_2$(x = 0.5, 1, 2 and 3) for both directions: (a) out-of-plane direction; (b) in-plane direction.

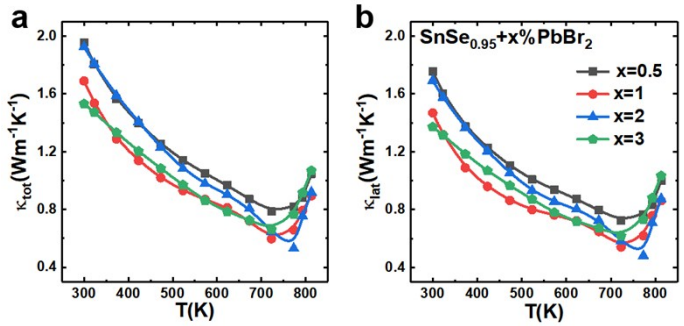

Figure S3. The thermal properties as a function of temperature for $SnSe_{0.95}$ + x%$PbBr_2$(x = 0.5, 1, 2 and 3) along the in-plane direction: (a) Total thermal conductivity and (b) lattice thermal conductivity.

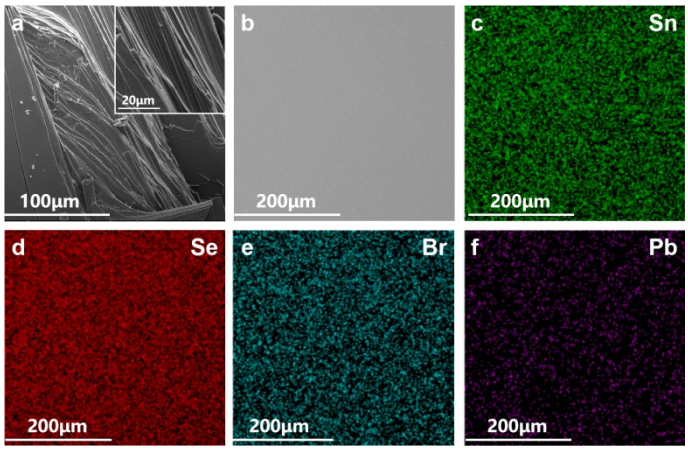

Figure S4. SEM images of $SnSe_{0.95}$ + 3%$PbBr_2$: (a) and (b) are the fractured surface morphologies; (c-f) The matching Sn, Se, Br and Pb are uniformly distributed in the area shown in (b).

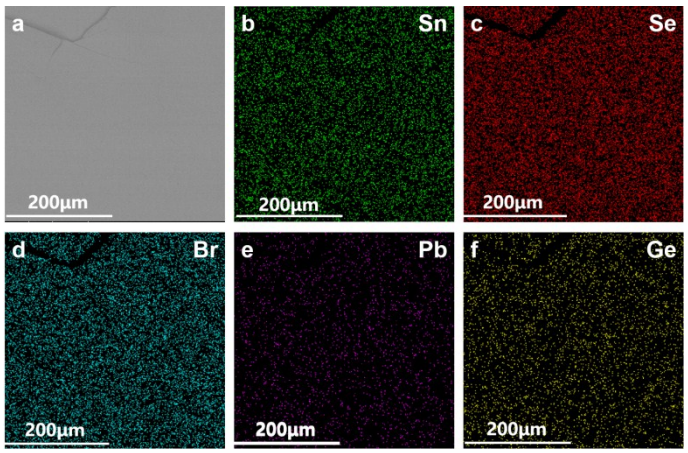

Figure S5. SEM images of $Sn_{0.99}Ge_{0.01}Se_{0.95}$ + 3%$PbBr_2$: (a) the polished surface morphologies; (b-f) The matching Sn, Se, Br, Pb and Ge are uniformly distributed in the area shown in (a).

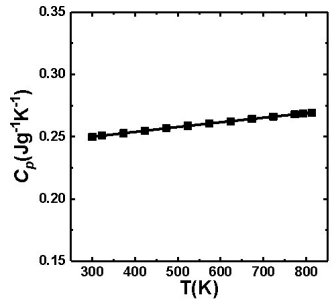

Figure S6. Specific heat capacity for SnSe single crystal, and the data is from previous work.[1]

Figure S7. The obtained SnSe single crystals.

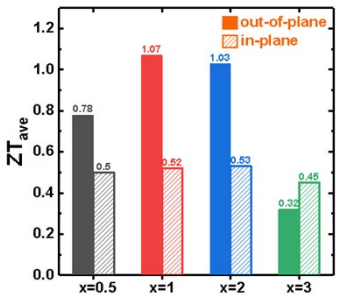

Figure S8. ZT_{ave} of $SnSe_{0.95}$ + x%$PbBr_2$(x = 0, 0.5, 1, 2 and 3) samples.

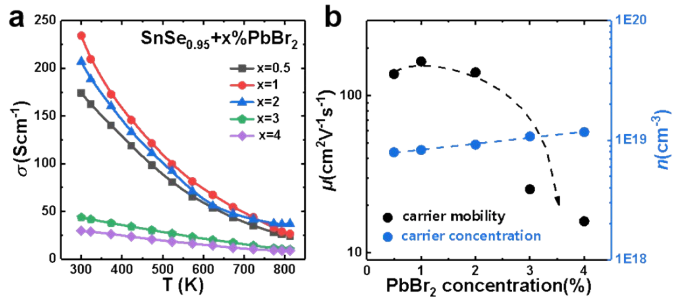

Figure S9. Electrical transport properties of $SnSe_{0.95}$ + x%$PbBr_2$ (x = 0.5, 1, 2, 3 and 4): a) electrical conductivity; b) carrier mobility and concentration.

Table S1. Lattice parameters for $SnSe_{0.95}$ + x%$PbBr_2$ (x = 0.5, 1, 2 and 3) and $Sn_{0.99}Ge_{0.01}Se_{0.95}$+3%$PbBr_2$.

Samples	Lattice parameter(Å)		
	a	*b*	*c*
$SnSe_{0.95}$ + 0.5%$PbBr_2$	11.4984	4.1560	4.4402
$SnSe_{0.95}$ + 1%$PbBr_2$	11.5036	4.1523	4.4432
$SnSe_{0.95}$ + 2%$PbBr_2$	11.5086	4.1593	4.4388
$SnSe_{0.95}$ + 3%$PbBr_2$	11.5122	4.1597	4.4390
$Sn_{0.99}Ge_{0.01}Se_{0.95}$ + 3%$PbBr_2$	11.4835	4.1496	4.4214

Table S2. The obtained carrier concentration n, electrical conductivity σ, and carrier mobility μ for $SnSe_{0.95}$ + x%$PbBr_2$ (x = 0.5, 1, 2 and 3) along in-plane direction.

Sample	*n* (cm^{-3})	σ ($S\ cm^{-1}$)	μ ($cm^2\ V^{-1}\ s^{-1}$)
$SnSe_{0.95}$ + 0.5%$PbBr_2$	0.71×10^{19}	408.74	359.69
$SnSe_{0.95}$ + 1%$PbBr_2$	0.89×10^{19}	434.48	304.14
$SnSe_{0.95}$ + 2%$PbBr_2$	1.05×10^{19}	469.85	277.21
$SnSe_{0.95}$ + 3%$PbBr_2$	0.97×10^{19}	321.67	209.09

References

[1] C. Chang, M. Wu, D. He, Y. Pei, C. F. Wu, X. Wu, H. Yu, F. Zhu, K. Wang and Y. Chen, *Science*, 2018, **360**, 778-783.
[2] P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
[3] G. Kresse and D. Joubert, *Phys. Rev. B,* 1999, **59**, 1758-1775.
[4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77**, 3865-3868.
[5] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt and N. Marzari, *Comput. Phys. Commun.,* 2008, **178**, 685-699.
[6] A. Kokalj, *Comput. Mater. Sci.,* 2003, **28**, 155-168.