Supporting Information

Large enhancement of electrical transport properties of SnS in the out-of-plane direction by n-type doping: a combined ARPES and DFT study

Juan Cui[1,2], Chaoyu Chen[3], Wenke He[4], José Avila[3], Li-Dong Zhao[4], Maria C. Asensio[3,*], Jiaqing He[2], and Yue Chen[1,*]

[1]Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China. *E-mail: yuechen@hku.hk
[2]Department of Physics, Southern University of Science and Technology, Shenzhen, 518055, China.
[3]ANTARES Beamline, Synchrotron SOLEIL & Universite Paris-Saclay, L'Orme des Merisiers, Saint Aubin-BP 48, 91192 Gif sur Yvette Cedex, France. *Email: asensio@synchrotron-soleil.fr
[4]School of Materials Science and Engineering, Beihang University, Beijing, 100191, China.

ARPES

All the ARPES measurements were performed at beamline ANTARES,[1,2] synchrotron SOLEIL. Samples were cleaved in ultrahigh vacuum at room temperature and measured by ARPES at room temperature. The angle and energy resolutions of the ARPES measurements are set as ~ 0.1° and ~ 20 meV. The photon energy-dependent ARPES experiments were performed with photon energy varying from 100 eV to 135 eV. The k_z is calculated by $k_z = 0.152\sqrt{E_{kin}\cos^2\vartheta + V_0}$. V_0 was determined in a semiempirical approach.

Computational methods

DFT calculations were conducted using the Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP).[3] A plane wave cutoff energy of 400 eV was used and an energy convergence criterion of 10^{-6} eV was applied. A *k*-point mesh generated by Monkhorst-Pack scheme[4] with a density of $2\pi\times0.03$ Å^{-1} was adopted. A 3×3×1 supercell containing 72 atoms was constructed with one Sn or S atom substituted by a doping atom, corresponding to a concentration of about 2.8%. To compare with the experimental measurements, band structure of pristine SnS was calculated with HSE06[5] hybrid functional. For doped systems, the PBE functional was used to calculate the electronic structures. The electrical transport properties were computed by applying the Boltzmann transport theory implemented in BoltzTraP[6] with a dense *k*-point mesh density of $2\pi\times0.01$ Å^{-1}. For direct comparison with the band structure of pristine SnS, the effective band structures of doped systems were obtained using a recently developed band unfolding technique.[7,8] The band structures of supercells were unfolded onto the primitive cell by calculating the spectral weight $P_{\vec{K}m}(\vec{k}_i) = \sum_n \left|\langle \vec{K}m|\vec{k}_i n\rangle\right|^2$, where $P_{\vec{K}m}(\vec{k}_i)$ is the probability of finding a set of

pristine cell states $|\vec{k}_i n\rangle$ contributing to the supercell states $|\vec{K} m\rangle$.[9,10] Before effective band structure calculations, atomic positions of the doped supercells were relaxed.

ARPES results on X-Γ-Y plane

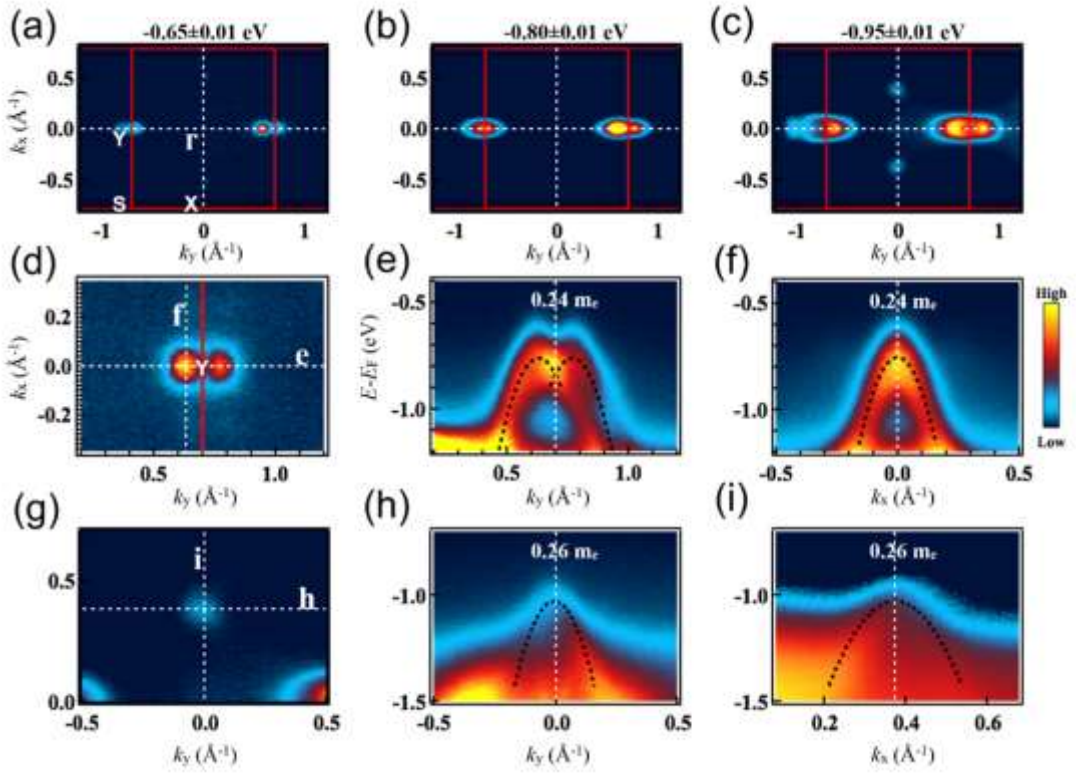

Figure S1 ARPES CEC mapping and band dispersion of SnS at X-Γ-Y plane. (a-c) ARPES CECs of X-Γ-Y plane integrated from different energy windows as indicated for each panel. Red rectangles indicate the first BZ boundaries. (d) Location of VBM 1 by zooming spectra of panel (a) around the Y high symmetry point. (e-f) Band dispersion of VBM 1 along Γ-Y and Γ-X directions, respectively. (g) Location of VBM 3. (h-i) Band dispersion of VBM 3 along Γ-Y and Γ-X directions, respectively. White dashed lines in (d) and (g) indicate the momentum cuts where dispersions shown in (e), (f), (h) and (i) are extracted. Black dashed lines in (e), (f), (h) and (i) are curve-fitted dispersions.

Results of Sb-doped SnS

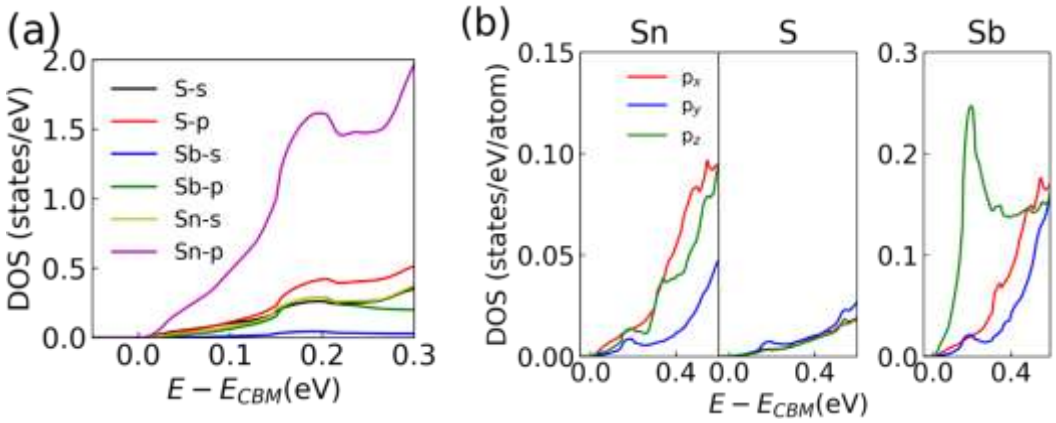

Figure S2 The projected electronic density of states of Sb-doped SnS.

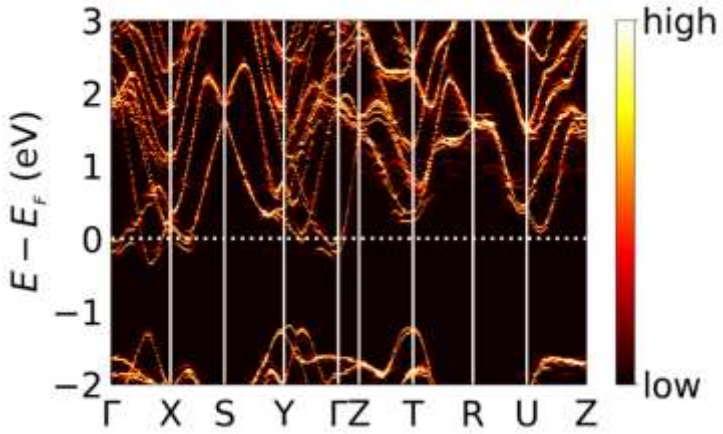

Figure S3 Effective band structure of Sb-doped SnS calculated from DFT. Fermi level is located at 0 eV.

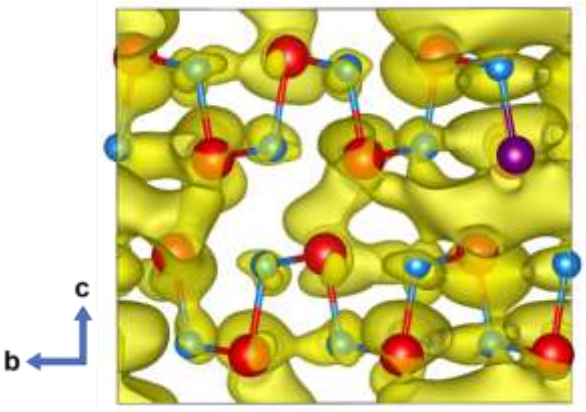

Figure S4 Decomposed charge density corresponding to the bottom of conduction bands at a carrier concentration of $-10^{20}/cm^3$ for Sb-doped SnS. Sn, S and Sb atoms are colored by red, blue and purple, respectively. The value of isosurface is equal to 3 $\times 10^{-5}$ e/bohr^3.

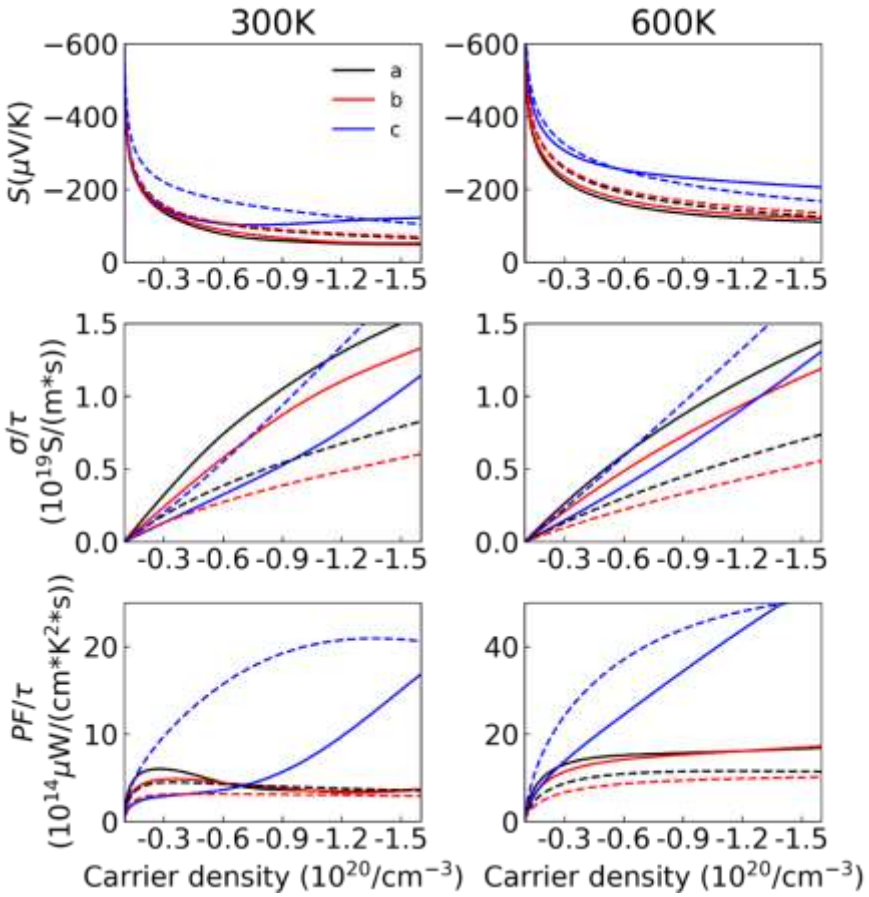

Figure S5 Seebeck coefficients (upper), electrical conductivity normalized by the relaxation time (middle), and power factor normalized by the relaxation time (bottom) of pristine (solid curves) and Sb-doped SnS (dashed curves) at 300 K and 600 K.

References

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