Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Enhanced thermoelectric performance of layered SnS crystals: the synergetic effect of temperature and carrier concentration

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1. Calculation of transport coefficients in Boltzmann theory

As mentioned in the context, we calculated the transport coefficients based on Boltzmann transport theory within the constant scattering-time approximation, using the BOLTZTRAP program [ref. S1]. Here, we made a brief summary of the formalism and the more detailed information can be seen in ref. S1. In this approach, the temperature and doping-level-dependent thermopower $S(T, \mu)$ is obtained from

$$S_{\alpha\beta} = \sum_{\gamma} \left(\sigma^{-1}\right)_{\alpha\gamma} \nu_{\beta\gamma} \tag{S1}$$

where σ is the electronic conductivity given by

$$\sigma_{\alpha\beta}(T, \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[- \frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \tag{S2}$$

and

$$\nu_{\alpha\beta}(T, \mu) = \frac{1}{e T \Omega} \int \sigma_{\alpha\beta}(\varepsilon) (\varepsilon - \mu) \left[- \frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \tag{S3}$$

Here the $\varepsilon_{i,k}$ is the electron-band energies (band index i), f_{μ} is the Fermi distribution function, μ is the chemical potential which depends on doping level and temperature, T, and Ω is the volume. Energy projected conductivity tensors can be calculated by

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N} \sum_{i,k} \sigma_{\alpha\beta}(i, k) \delta(\varepsilon - \varepsilon_{i,k}) \tag{S4}$$

where N is the number of k-points sampled. These transport distributions can be obtained using the k-dependent conductivity tensor

$$\sigma_{\alpha\beta}(i, k) = e^2 \tau_{i,k} \upsilon_{\alpha}(i, k) \upsilon_{\beta}(i, k) \tag{S5}$$

where $\tau_{i,k}$ is the scattering time and the $\upsilon_{\alpha}(i, k)$ are the components of the band velocities, $v_i(k) = \nabla_k \varepsilon_i(k)/\hbar$, which are obtained from the band structure. The BoltzTrap code does this by taking the analytic gradient of a symmetry-adapted Fourier

interpolation of the band energies [ref. S1]. The integrals in Eqs. (S2)-(S3) are performed in the subroutine FERMIINTEGRALS.

2. The anisotropy of Seebeck coefficient and electrical conductivity in SnS

Fig. S1 shows the Seebeck coefficient and the electrical conductivity at 800 and 900 K along different crystallographic directions, for both *p*-type and *n*-type. Here, we used 800 K data to represent the *Pnma* phase, while 900 K data for the *Cmcm* phase. In Fig. S1 it is easily found for both *p*-type and *n*-type, the anisotropy of both the Seebeck coefficient and electrical conductivity behaves in different ways. As shown in Fig. S1(a), at heavy doping, the anisotropy of the Seebeck coefficient becomes lower for the *Pnma* phase whereas tends to be higher for the *Cmcm* phase. Of note, for *p*-type in the *Cmcm* phase (see Fig. S1(a3)), the S_x increases with increasing carrier concentration at low doping (below 10^{19} cm^{-3}), in contrast to the usual situation. This may be due to the bipolar effect. In terms of the electrical conductivity (see Fig. S1(b)), for *p*-type, we detected a strong anisotropy between the three axes, with $\sigma_y > \sigma_z > \sigma_x$ for both the *Pnma* phase and *Cmcm* phases. For *n*-type, the electrical conductivity shows a small anisotropy, especially for the *Pnma* phase. Therefore, the TE performance of SnS would be anisotropic for both *p*- and *n*-type.

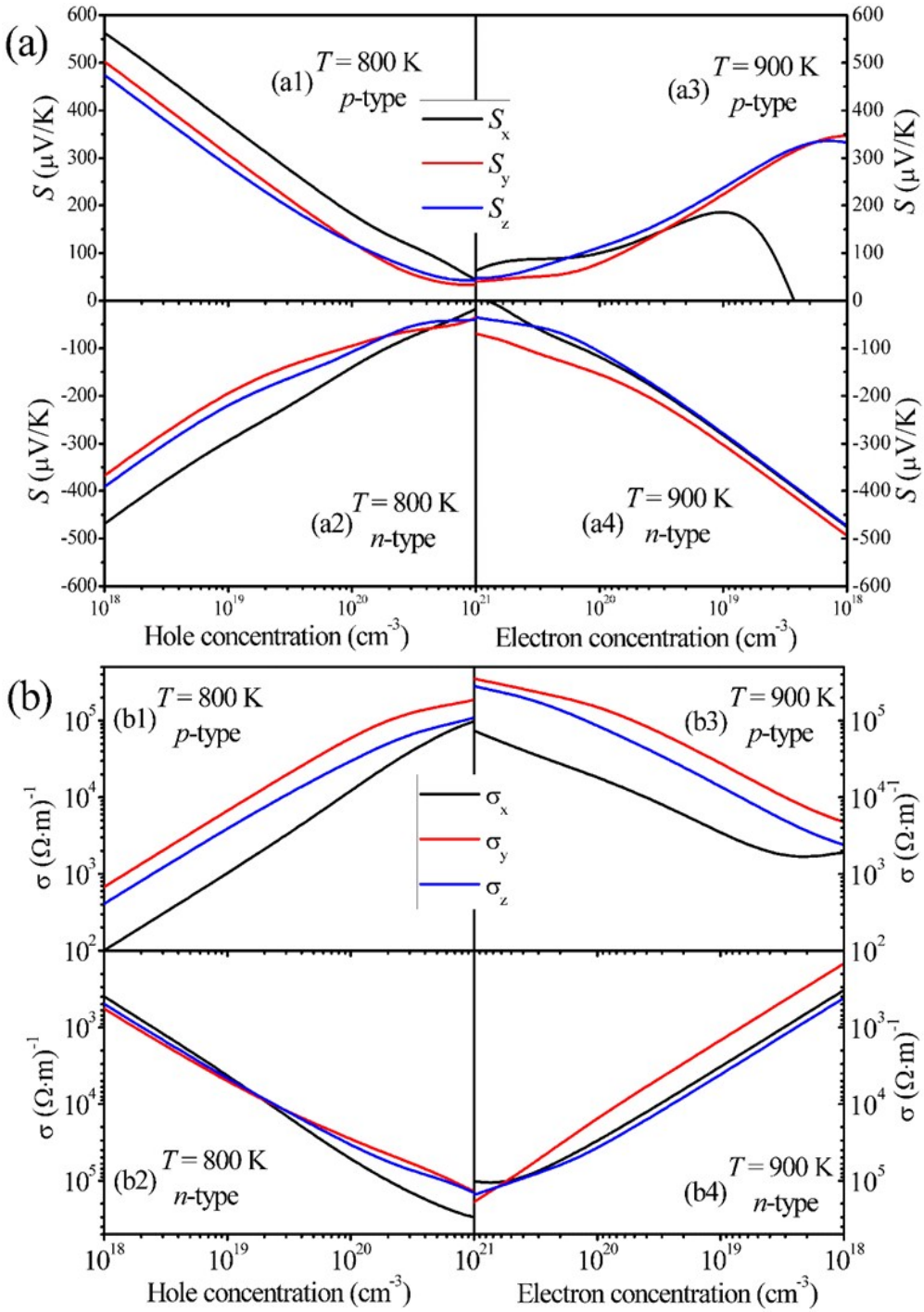

Fig. S1 Seebeck coefficients (a) and electric conductivities (b) of the *Pnma* and *Cmcm* phases along different axial directions. Note: (1) 800 K data stands for the *Pnma* phase and 900 K data for the *Cmcm* phase; (2) the x, y, and z directions denote the *a*, *b* and *c* axes of the *Pnma* phase and the *b*, *c*, and *a* axes of the *Cmcm* phase, respectively.

References:

[S1]. G. K. H. Madsen and D. J. Singh, *Comput Phys Commun*, 2006, **175**, 67.