

SUPPLEMENTARY DATA

Intrinsic defect formation and effect of transition metals doping on transport property in ductile thermoelectric material α -Ag₂S: First-principles study

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I. Checking the effect of the mixing parameter and screening parameter of the hybrid functional on bandgap energy in α -Ag₂S

Hybrid functionals are the combination between DFT exchange-correlation energy functional and a portion of exact exchange from Hartree – Fock (HF) theory. Here, we used hybrid functional in the form of Heyd – Scuseria – Ernzerhof or HSE06 method for investigation:

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\omega) + (1-\alpha) E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}}$$

where α is the mixing parameter; ω is screening parameter; E_x is the exchange functional; E_c is the correlation functional; SR and LR stand for the short-range and long-range parts of Coulomb potential. The mixing parameter α and screening parameter ω are chosen to be 0.25 and 0.2 for HSE06 standard, respectively. However, the bandgap energy in α -Ag₂S predicted by HSE06 is quite overestimated, which is double value compared to the experimental data. Usually, we can reproduce bandgap energy via controlling parameters α and ω . We have checked the effect of α and ω on E_g and the results are shown in **Fig. I**. It can be seen that experimentally reported

bandgap can be obtained by changing the two parameters. However, we recommend not to use this approach for calculations in a large supercell because it is massively time-consuming.

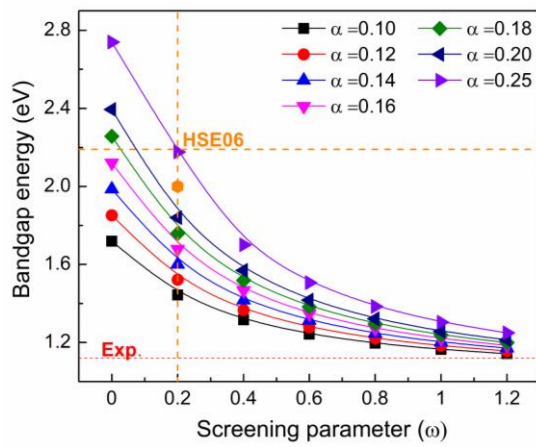


Fig. I. Bandgap energy dependence on α and ω in hybrid functional method

II. Band structure of α -Ag₂S using functional GGA-PBE

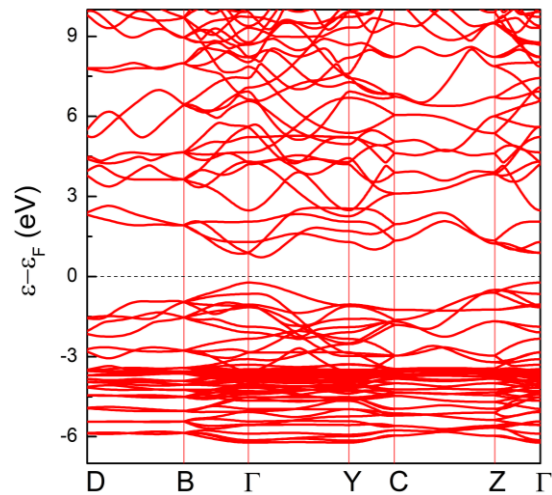


Fig. II. Band structure of α -Ag₂S using GGA-PBE shows the displacement of CBM from center of BZ

III. Atomic configuration around sulfur vacancy:

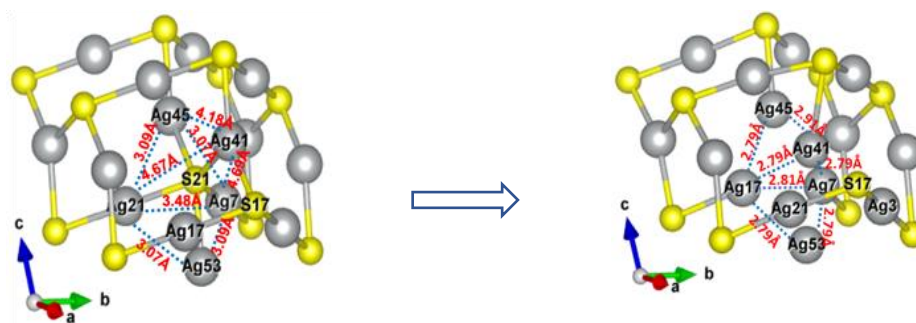


Fig. III. After removing the sulfur (S21) atom, the surrounding silver atoms tend to move closer together to form a silver cluster. Their bond lengths decrease from 3.09 Å to 2.79 Å, which is smaller than the shortest Ag-Ag bonds in the Ag fcc-bulk (about 2.87 Å).

IV. The directional anisotropy of Seebeck coefficient:

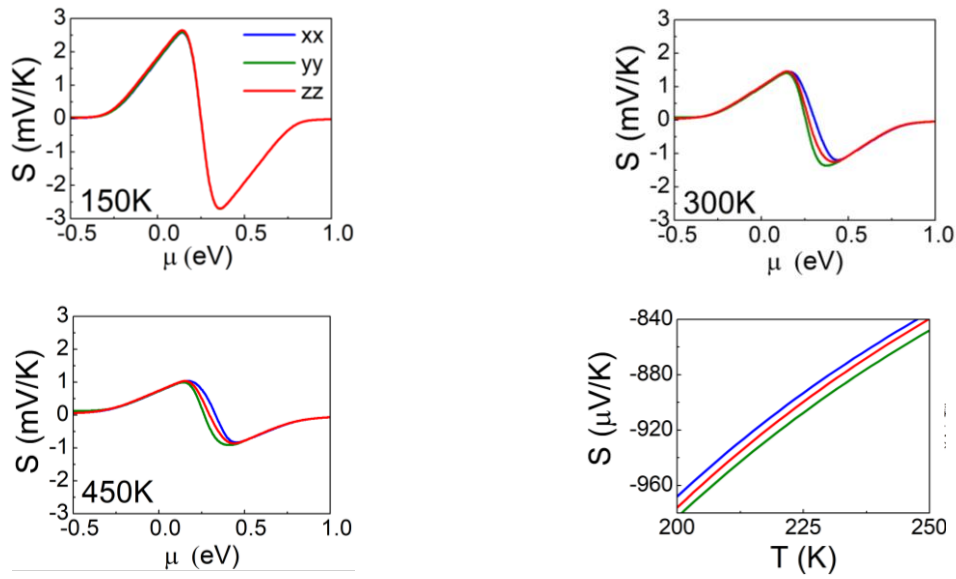
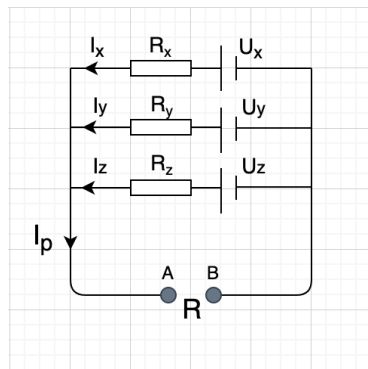


Fig. IV. Anisotropic nature of the Seebeck coefficients in α -Ag₂S are expressed as a function of the chemical potential. Here, we consider three representative temperatures: 150K, 300K, and 450K (phase transition to β -Ag₂S occurs when the temperature is higher than 453K). Temperature-dependent Seebeck coefficients are also illustrated with deviations in value of about 10 μ V/K in different directions at $n = 10^{14}$ cm⁻³.

V. The average value of Seebeck coefficient for anisotropic materials:

In material systems with cubic symmetry, the dependence of Seebeck coefficient (S) on the crystal direction is negligible. However, in systems with different lattice parameters in each direction, the transport coefficients depend strongly on it (i.e., they are anisotropic). Therefore, it is necessary to quantify these values as an average value to compare with experimental data. Here, a simple circuit model is used to determine the average Seebeck coefficient in different directions. It should be noted that this formula is not always suitable for averaging, especially for systems with non-symmetric tensors. In the case of Ag₂S system, the off-diagonal components are very small values only about 1% of diagonal components in magnitude. Therefore, we can safely ignore them in calculation of average Seebeck coefficient in this system by the following formula:



$$R_x = \frac{3L}{\sigma_{xx}S}; \quad U_x = S_{xx}\Delta T; \quad U_{AB} = I_p R = S_{poly}\Delta T;$$

$$U_{AB} = I_p R = U_x - I_x R_x = U_y - I_y R_y = U_z - I_z R_z$$

$$I_p = \frac{U_{AB}}{R} = I_x + I_y + I_z$$

$$\Leftrightarrow \frac{U_{AB}}{R} = \frac{U_x - U_{AB}}{R_x} + \frac{U_y - U_{AB}}{R_y} + \frac{U_z - U_{AB}}{R_z}$$

$$\Rightarrow U_{AB} = \frac{\frac{U_x}{R_x} + \frac{U_y}{R_y} + \frac{U_z}{R_z}}{\frac{1}{R} + \frac{1}{R_x} + \frac{1}{R_y} + \frac{1}{R_z}} = \frac{\frac{(S_{xx}\Delta T)}{(3L/\sigma_{xx}S)} + \frac{(S_{yy}\Delta T)}{(3L/\sigma_{yy}S)} + \frac{(S_{zz}\Delta T)}{(3L/\sigma_{zz}S)}}{\frac{\sigma_{xx}S}{3L} + \frac{\sigma_{yy}S}{3L} + \frac{\sigma_{zz}S}{3L}} \Rightarrow S_{poly} = \frac{S_{xx}\sigma_{xx} + S_{yy}\sigma_{yy} + S_{zz}\sigma_{zz}}{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}$$