Electronic Supplementary Information

Syntheses, structures, and photocatalytic properties of open-framework Ag-Sn-S compounds

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1. Experiments and Characterizations

EDS analyses were performed using the EDS-equipped Quanta 450 scanning electronic microscope (SEM). Single crystals diffraction data were collected on Bruker Smart APEX II diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. The crystal structures were all solved by direct methods [1], and all atomic positions and displacement parameters were performed in Fourier maps and refined anisotropically based on F^2 using SHELXL-2017 [2]. Powder X-ray diffraction (PXRD) were performed on Smart-Lab 9KW instrument with Cu Kα (λ = 1.5418 Å) radiation at room temperature. The data were collected in the range of 2θ = 5-50° and a scanning speed of 5° per minute. The ultraviolet-visible (UV-vis) reflectance spectra of the compounds were measured at room temperature using Hitachi U3900 spectrophotometer, and $BaSO_4$ as a reference in the wavelength range from 200 to 800 nm.

The photocatalytic activities of the as-synthesized samples were investigated by photodegradation of methylene blue (MB) in a CEL-LAB500 photochemical reactor (CEAULIGHT Co. Ltd., China). A 500 W Xe lamp equipped with a 420 nm cut-off filter employed as light source. In brief, 20 mg of catalyst was suspended in 40 mL of MB aqueous solution (20 mg/L) and magnetically stirred for 60 min to reach adsorption/desorption equilibrium before the photocatalytic degradation reaction. In the process of adsorption and light irradiation, 3 mL of the suspension was sampled at selected timespans and centrifuged to remove the catalyst. The residual concentration of MB was monitored by measuring the maximum absorbance with a UV-vis spectrophotometer at 554 nm.

The photoelectric response experiments were performed on a CHI660E electrochemical workstation using a standard three-electrode configuration. The sample was ground into powders and coated onto ITO glasses (about 2 cm^2 effective area) which employed as the working electrodes. A Pt sheet was used as the counter electrodes. A saturated Hg/Hg_2Cl_2 was used as the reference electrodes. A 500 W Xe lamp equipped with a 420 nm cut-off filter was employed as light source. The light source located 25 cm away from the surface of the ITO electrode. 0.2 M Na_2SO_4 aqueous solution was chosen as the supporting electrolyte.

2. Synthetic procedures

Compounds **2-4** can also be synthesized by the following method.

$K_2Ag_2SnS_4$ (**2**) can be synthesized at 200 °C by mixing Ag (6.0 mg), Sn (4.0 mg), S (15.0 mg), K_2CO_3 (8.0 mg), about 300 mg ethylenediamine, and 60 mg deionized water in a Pyrex-glass tube for 8 days.

$Rb_2Ag_2SnS_4$ (**3**) can be synthesized using the same procedure with **2** except using 9.0 mg Rb_2CO_3 instead of K_2CO_3.

$Cs_2Ag_2SnS_4$ (**4**) can be synthesized at 200 °C by mixing Ag (6.0 mg), Sn (3.0 mg), S (19.0 mg), Cs_2CO_3 (9.0 mg), about 420 mg ethylenediamine, and 60 mg deionized water in a Pyrex-glass tube for 8 days.

3. PXRD Patterns

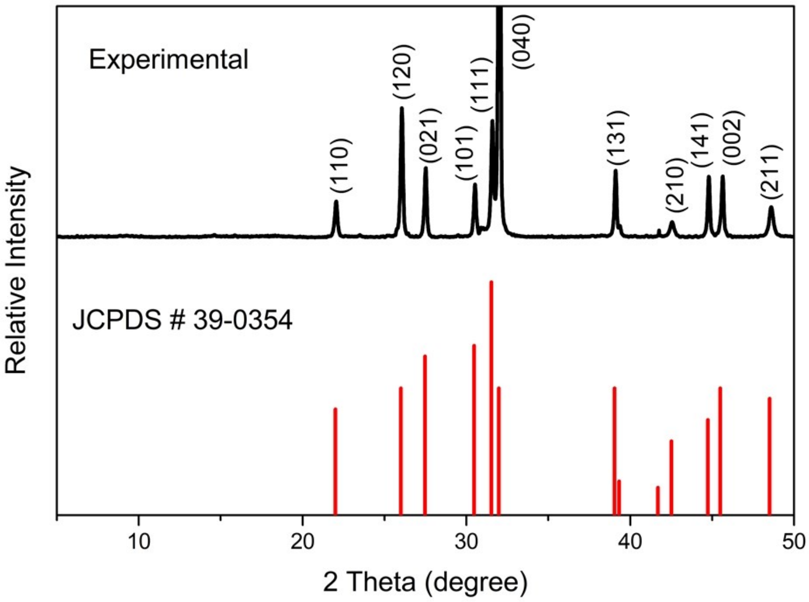

Figure S1. Experimental PXRD pattern of SnS.

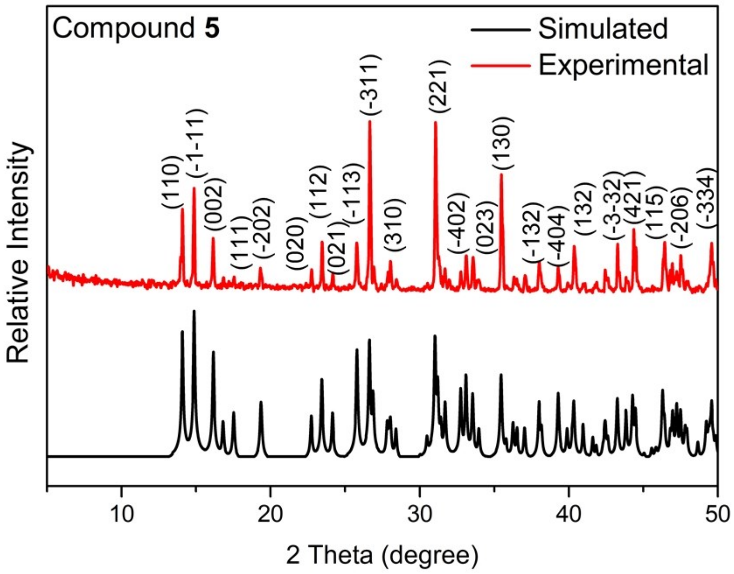

Figure S2. Simulated and experimental PXRD pattern of compound **5**.

4. Crystal Structures

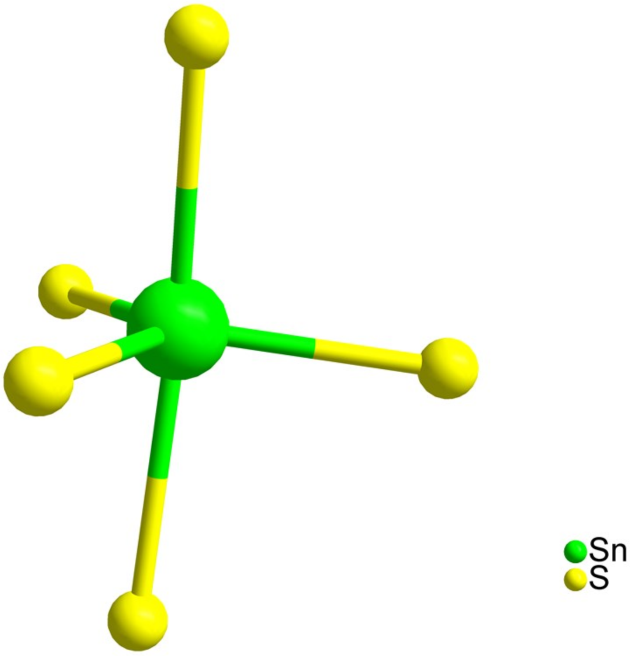

Fig. S3. SnS_5 trigonal bipyramids in compound **5**.

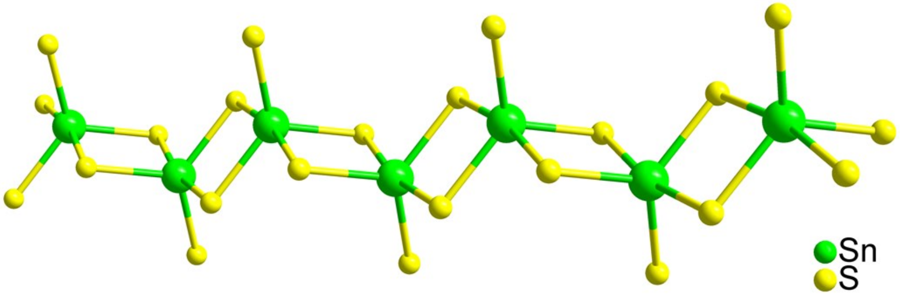

Fig. S4. $[SnS_3]_n^{2n-}$ chain in compound **5**.

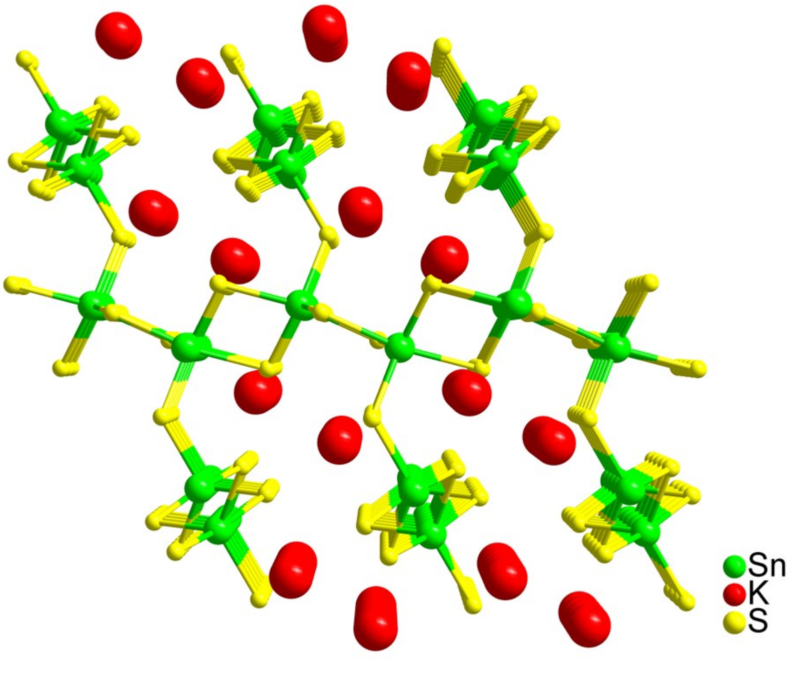

Fig. S5. Crystal structure of compound **5** viewing along from the [101] direction.

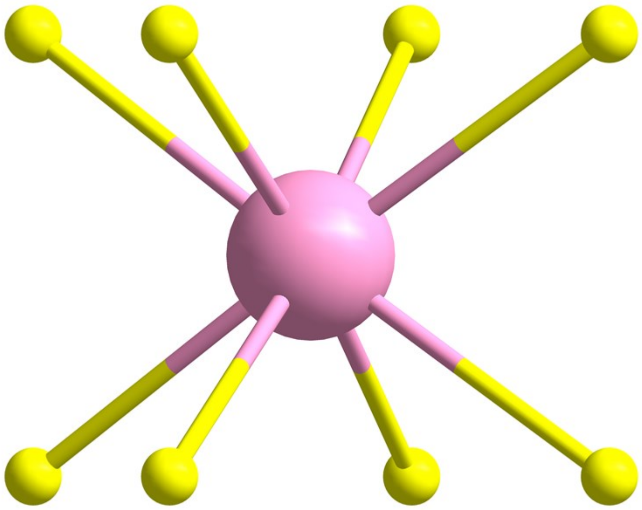

Fig. S6. Coordination environment of Cs$^+$ ions in compound **4**.

5. Theoretical Calculation

The band gaps, total density of states (TDOS) and partial density of states (PDOS) were calculated by Density functional theory (DFT). The common generalized-gradient approximation (GGA) and local density approximation (LDA) methods usually underestimate the band gaps [3]. In this paper, we use the combination of Heyd-Scuseria-Ernzerhof (HSE) and Perdew-Burke-Ernzerhof (PBE) methods to obtain reliable band gap values [4-6]. By introducing a part of Hartree-Fock exchange, HSE can modify the short-range exchange interaction. The calculated band gaps of the two compounds can be obtained by the following equation [3].

$$E_{XC}^{HSE} = \alpha E_X^{\mathrm{exact},SR}(\mu) + (1-\alpha) E_X^{PBE,SR}(\mu) + E_X^{PBE,LR}(\mu) + E_C^{PBE} \quad (1)$$

In equation (1), α represents the proportion of Hartree-Fock precise exchange interaction that introduced [51]. The parameter α is 0.25, which means 25% of Hartree-Fock in the short-range interaction. Monkhorst-Pack method was applied to calculate the single point energy. We calculated the single point energy when the singular value of *k*-point meshes increasing from 1 × 1 × 1 to 21 × 21 × 21. When the *k*-point mesh increases to 5 × 5 × 5, the error of single point energy was less than 0.0001eV, which can be considered as energy convergence. In consideration of lowering the calculation cost of hybrid functional HSE06, the 5 × 5 × 5 *k*-point mesh was used to calculate the band gaps and the DOSs.

The configurations for generating pseudo potentials were K $3p^6 4s^1$, Cs $5p^6 6s^1$, Ag $4d^{10} 5s^1$, Sn $5s^2 5p^2$, and S $3s^2 3p^4$. Vienna Ab initio Simulation Package (VASP) was used to calcaulate the DOSs [7]. In the calculation, the other calculating parameters and convergent criteria were set by the default values.

6. References

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