Electronic Supplementary Information

Syntheses, crystal structures and photocurrent responses of Cs$_2$Ag$_2$Sb$_2$S$_5$ and CsAgSb$_4$S$_7$ with thiourea as a mineralizer

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1. Synthesis

All of the reactants were purchased from commercial agency and were used without any purification. The reactants were sealed in a Pyrex glass tube (about 10% filling volume) at air atmosphere, and then the glass tube was placed in a stainless-steel autoclave (about 80% filling volume of water), and finally heated at 180 °C for 5 days. After cooling to room temperature naturally, the products were washed with absolute ethyl alcohol, and then pure crystals were obtained. Detailed synthesis conditions and basic information of compounds are shown in Table 1.

Table S1. The synthesis conditions and basic information of compounds **1** and **2**.

Compound	Reactants	Color	EDS analyses	Morphology
$Cs_2Ag_2Sb_2S_5$ (**1**)	Cs_2CO_3 24.1 mg $AgNO_3$ 5.9 mg Sb_2S_3 7.4 mg S powder 2.1 mg thiourea 15.2 mg 1,3-dap 400 mg H_2O 60 mg	Orange red	$Cs_{2.0}Ag_{1.8}Sb_{1.9}S_{5.1}$	
$CsAgSb_4S_7$ (**2**)	Cs_2CO_3 17.7 mg $AgNO_3$ 5.8 mg Sb_2S_3 16.3 mg S powder 2.1 mg thiourea 14.9 mg 1,3-dap 200 mg H_2O 200 mg	Red	$Cs_{1.0}Ag_{0.8}Sb_{3.6}S_{7.0}$	

2. Characterizations and theoretical calculation

The crystal morphologies and elemental analyses of compounds **1** and **2** were accomplished on Thermo Fisher scanning electronic microscope (SEM) equipped with EDS analysis. The SEM images and EDS results of the two compounds are displayed in Fig. S1 and Fig. S2. Powder X-ray diffraction (PXRD) analysis was investigated on a D8 ADVANCE instrument with Cu *Kα* (λ = 1.5418 Å) radiation (2θ = 5~65°, scanning speed of 5°/min). The diffraction data of the title compounds were collected on a Bruker XRD D8 VENTURE diffractometer equipped with Liquid Ga-target (λ = 1.34137 Å) at 150(2) K. The structures were obtained by using direct methods and full-matrix least-squares fitting on F^2 using SHELXL-2017 program package.[1, 2] The UV-vis diffuse reflectance experiment was investigated using SHIMADZU UV2600 spectrophotometer with $BaSO_4$ as a reference (with the wave length ranging from 200 to 800 nm). The band gaps of the title compounds were evaluated by converting the data of reflectance spectra to absorbance spectra by the Kubelka-Munk function.

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R}$$
(1)

In the above equation of Kubelka-Munk function, *K*, *S*, and *R* represent absorption coefficient, scattering coefficient, and reflectance, respectively.

The photocurrent response experiments of the compounds were carried out on a CHI660E electrochemical workstation with a standard three-electrode system (reference / counter / working electrodes). The 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. The Ag/AgCl and platinum sheet were employed as reference and counter electrodes, respectively; ITO glasses coated with sample were used as the working electrodes. The photocurrent response was measured by regular switches (every 50 seconds) under simulated solar light illumination (300 W Xe lamp).

Density functional theory (DFT) calculations with the periodic boundary conditions were carried out using a plane wave based on Castep program in Materials Studio 2019.[3, 4] The hybrid functional (HSE) used in this work combines Hartree-Fock and DFT exchange conditions, which is considered a practical solution to the energy

band problem. Therefore, Heyd-Scuseria-Ernzerhof (HSE 03) method was used to calculate the band gaps, total density of states (TDOS), and partial density of states (PDOS), with the aim to avoid the underestimate of band gaps than the actual values.[5-7] HSE mainly modified the short range exchange interaction by mixing a part of the Hartree-Fock exchange. Therefore, the band gap of the semiconductor can be successfully calculated using eq 2.

$$E_{XC}^{HSE} = \alpha E_X^{\text{exact},SR}(\mu) + (1-\alpha)E_X^{PBE,SR}(\mu) + E_X^{PBE,LR}(\mu) + E_C^{PBE} \tag{2}$$
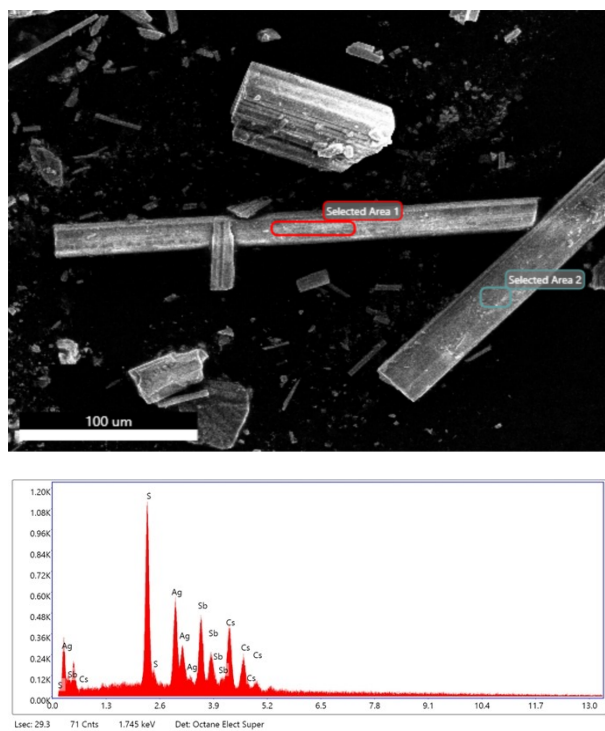
3. SEM images and EDS analyses

Figure S1. SEM image and EDS analysis of compound **1**. (Cs: Ag: Sb: S=2.0: 1.8: 1.9: 5.1)
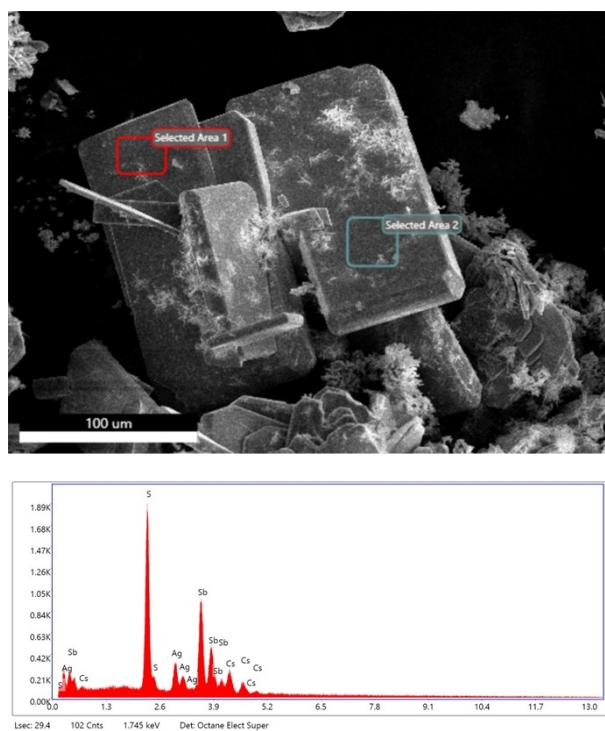
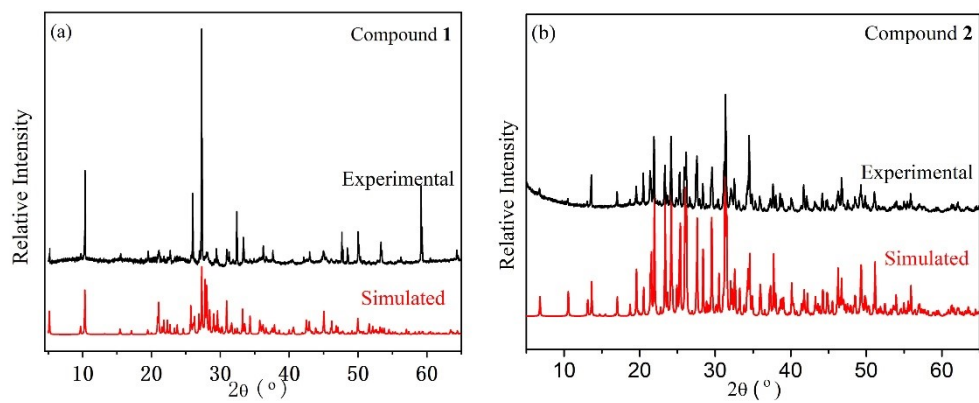Figure S2. SEM image and EDS analysis of compound **2**. (Cs: Ag: Sb: S=1.0: 0.8: 3.6: 7.0)

4. PXRD

Fig. S3. The experimental and simulated XRD patterns of compounds **1** (a) and **2** (b).

5. Crystal data and structural refinement

Table S2. Crystal data and structural refinement of compounds **1** and **2**.

Compound	1	2
Empirical formula	$Cs_2Ag_2Sb_2S_5$	$CsAgSb_4S_7$
Formula weight	885.36	952.20
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C2/c*
a (Å)	10.7773(15)	26.150(6)
b (Å)	6.9250(10)	8.8407(19)
c (Å)	34.247(5)	12.134(3)
β (°)	90	97.616(6)
Volume (Å^3)	2555.9(6)	2780.5(10)
Z	8	8
D_c (g·cm^{-3})	4.602	4.549
Absorption coefficient (mm^{-1})	13.578	12.643
F (000)	3088	3344
θ range (°)	1.19-28.50	1.57-26.38
Index ranges	$-14 \leq h \leq 11$ $-9 \leq k \leq 7$ $-45 \leq l \leq 31$	$-32 \leq h \leq 32$ $-10 \leq k \leq 10$ $-14 \leq l \leq 15$
Reflections collected/unique	17547 / 3142	11622 / 2815
Goodness-of-fit on F^2	1.072	1.068
R_{int}	0.0634	0.0697
Final R indices [I>2σ(I)]	$R_1 = 0.0505$ $\omega R_2 = 0.2245$	$R_1 = 0.0462$ $\omega R_2 = 0.1245$
R indices (all data)	$R_1 = 0.0559$ $\omega R_2 = 0.2318$	$R_1 = 0.0482$ $\omega R_2 = 0.1265$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å^{-3})	3.915, -4.176	3.032, -3.315
CCDC numbers	2339991	2322137

$R_1 = \sum||F\text{o}| - |F\text{c}||/\sum|F\text{o}|$, $\omega R_2 = [\sum\omega(F\text{o}^2 - F\text{c}^2)^2/\sum\omega(F\text{o}^2)^2]^{1/2}$.

6 Selected bond lengths and angles

Table S3 Selected bond lengths (Å) and angles (°) for $Cs_2Ag_2Sb_2S_5$ (**1**).

Lengths (Å)		Bond Angles (°)	
Ag(1)-S(5)#4	2.492(3)	S(5)#4-Ag(1)-S(3)#9	123.36(9)
Ag(1)-S(3)#9	2.530(3)	S(5)#4-Ag(1)-S(5)#1	107.78(8)
Ag(1)-S(5)#1	2.581(3)	S(3)#9-Ag(1)-S(5)#1	114.91(10)
Ag(2)-S(4)	2.550(4)	S(4)-Ag(2)-S(4)#2	107.75(9)
Ag(2)-S(4)#2	2.585(3)	S(4)-Ag(2)-S(1)#3	108.92(10)
Ag(2)-S(1)#3	2.624(3)	S(4)#2-Ag(2)-S(1)#3	110.50(10)
Ag(2)-S(3)#2	2.626(3)	S(4)-Ag(2)-S(3)#2	117.55(10)
Sb(1)-S(1)	2.372(3)	S(4)#2-Ag(2)-S(3)#2	94.69(9)
Sb(1)-S(2)#2	2.486(3)	S(1)#3-Ag(2)-S(3)#2	116.18(10)
Sb(1)-S(2)	2.509(3)	S(1)-Sb(1)-S(2)#2	95.17(10)
Sb(2)-S(4)#1	2.398(3)	S(1)-Sb(1)-S(2)	102.53(10)
Sb(2)-S(3)#3	2.435(3)	S(2)#2-Sb(1)-S(2)	93.02(8)
Sb(2)-S(5)#1	2.443(3)	S(4)#1-Sb(2)-S(3)#3	99.65(10)
		S(4)#1-Sb(2)-S(5)#1	101.46(11)
		S(3)#3-Sb(2)-S(5)#1	98.28(10)

Table S4 Selected bond lengths (Å) and angles (°) for $CsAgSb_4S_7$ (**2**).

| Lengths (Å)		Bond Angles (°)	
Ag(1)-S(7)#1	2.504(3)	S(7)#1-Ag(1)-S(7)#4	137.31(5)
Ag(1)-S(7)#4	2.523(3)	S(7)#1-Ag(1)-S(3)	105.99(8)
Ag(1)-S(3)	2.675(3)	S(7)#4-Ag(1)-S(3)	97.87(8)
Ag(1)-S(4)#4	2.879(2)	S(7)#1-Ag(1)-S(4)#4	99.08(8)
Sb(1)-S(6)#8	2.442(2)	S(7)#4-Ag(1)-S(4)#4	95.18(8)
Sb(1)-S(5)	2.444(2)	S(3)-Ag(1)-S(4)#4	125.11(8)
Sb(1)-S(1)#11	2.583(2)	S(6)#8-Sb(1)-S(5)	102.97(8)
Sb(2)-S(7)	2.413(2)	S(6)#8-Sb(1)-S(1)#11	92.95(8)
Sb(2)-S(4)#4	2.476(2)	S(5)-Sb(1)-S(1)#11	90.26(8)
Sb(2)-S(5)#2	2.528(2)	S(7)-Sb(2)-S(4)#4	92.19(8)
Sb(3)-S(2)	2.467(2)	S(7)-Sb(2)-S(5)#2	89.00(8)
Sb(3)-S(1)#4	2.483(2)	S(4)#4-Sb(2)-S(5)#2	95.73(7)
Sb(3)-S(4)	2.549(2)	S(2)-Sb(3)-S(1)#4	94.90(8)
Sb(4)-S(3)	2.432(2)	S(2)-Sb(3)-S(4)	93.14(8)
Sb(4)-S(2)	2.505(2)	S(1)#4-Sb(3)-S(4)	92.84(7)
Sb(4)-S(6)	2.587(3)	S(3)-Sb(4)-S(2)	98.62(8)
		S(3)-Sb(4)-S(6)	89.37(8)
		S(2)-Sb(4)-S(6)	90.86(8)

7. Optical properties
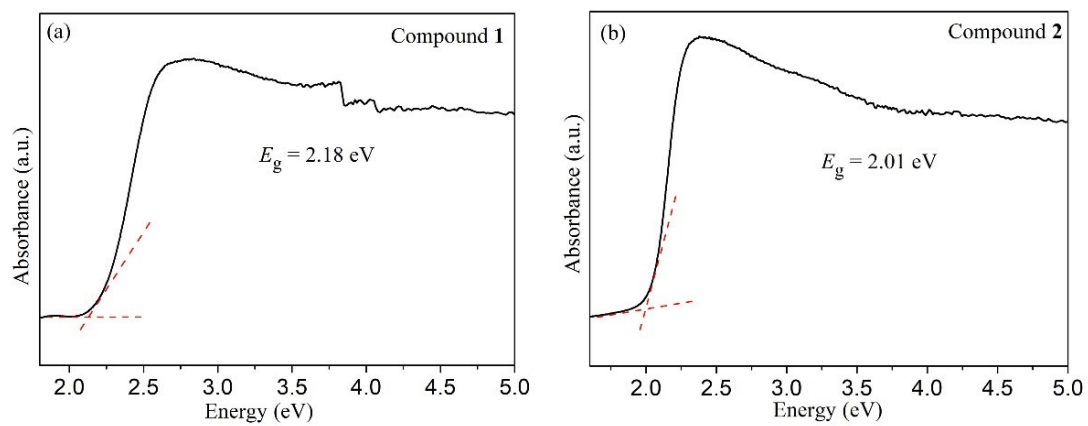
Figure S4. UV-vis absorption spectra of compounds **1** (a) and **2** (b).

8. Reference

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