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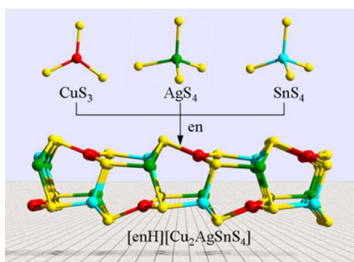
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[enH][Cu₂AgSnS₄]: A Quaternary Layered Sulfide Based on Cu-Ag-Sn-S Composition

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A new copper-silver-thiostannate, [enH][Cu₂AgSnS₄] (**1**), which features a quaternary two dimensional anionic [Cu₂AgSnS₄]⁻ layer, has been solvothermally synthesized.

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COMMUNICATION

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A new copper-silver-thiostannate, [enH][Cu₂AgSnS₄] (**1**), has been successfully synthesized under solvothermal condition. Compound **1** features a quaternary two dimensional anionic [Cu₂AgSnS₄]⁻ layer, where Cu⁺ adopt a trigonal coordination and Ag⁺ has a tetrahedral configuration. The photoelectrochemical studies indicate that **1** is photoactive and exhibits p-type semiconductor characteristics under visible light illumination.

Metal chalcogenides represent an important type of semiconductors due to their excellent performance in the areas of photoelectric, thermoelectric, non-linear optics, ionic conductivities, and photocatalysis.^[1] The fascinating properties of these materials are determined by their structures and compositions. Therefore, multinary metal chalcogenides with variable structures are highly desirable for on-demand tuning their properties. A popular approach to prepare multinary metal chalcogenides is to insert transition metal sulfide into main group chalcogenide blocks to form heterometallic secondary building units (SBUs) or clusters.^[2]

Chalcogenidostannates have rich structural chemistry because Sn⁴⁺ ions can flexibly coordinate with different number of chalcogen ions (4, 5, or 6), and the subsequent primary building units can be condensed to form complex SBUs via edge or corner sharing.^[3] On the other hand, transition metal ions Cu⁺/Ag⁺ can also form various coordination modes with chalcogen ions (S²⁻, Se²⁻, Te²⁻) ranging from linear, trigonal to tetrahedral geometries.^[4] Thus, incorporation of low-valence transition metal Cu⁺/Ag⁺ ions into chalcogenidostannates could allow the generation of a variety of heterometallic chalcogenides based on ternary Cu/Ag-Sn-Q components with diverse architectures and interesting properties. Actually, numerous pure inorganic copper/silver-chalcogenidostannates have been synthesized under high-temperature solid state reactions or molten alkali metal polychalcogenide flux conditions, such as, Ln₃MnSnQ₇ (Ln = Y, La-Nd, Sm, Gd-Ho; M = Cu, Ag; Q = S, Se),^[5] Ba₃Cu₂Sn₃Se₁₀,^[6] A_xM₂SnQ₄ (A = K, Rb, Sr, Ba; M = Cu, Ag; x = 1, 2; Q = S, Se, Te),^[6-7] A₂Cu₂Sn₂Q₆ (A = Na, K, Rb, Cs; Q = S, Se).^[7c] Among these quaternary chalcogenides, compounds A_xM₂SnQ₄ exhibit variable anionic [M₂SnQ₄]²⁻ frameworks caused by different condensation ways of MQ₄ and SnQ₄ tetrahedrons. For example, K₂Cu₂SnS₄ and K₂Ag₂SnSe₄ have similar two dimensional anionic layers,^[7c, 7e] while AM₂SnQ₄ (A = Sr, Ba, M = Cu, Ag; Q = S, Se) features a three dimensional anionic framework.^[6, 7a-7b]

Recent researches have already demonstrated that solvothermal synthesis could provide a much milder and softer synthetic conditions for the construction of chalcogenide frameworks consisting of Cu/Ag-Sn-Q systems, in which various organic amines can act as templates or structure-directing agents. Examples include, discrete clusters as [enH]₂[Ln(en)₄(CuSn₃S₉)]·0.5en (Ln = La, Ce),^[8] and [enH]₄[Ln(en)₄]₂[Cu₆Sn₆S₂₀]]·3en (Ln = Nd, Gd, Er),^[8] one dimensional chains (e.g. [DBUH][CuSnS₃],^[9] [1,4-dabH₂][M₂SnS₄] (M = Cu, Ag),^[9-10] and A₃AgSn₃Se₈ (A = K, Rb)^[11]), two dimensional layers (e.g. [dienH₂][Cu₂Sn₂S₆],^[12] [DBNH]₂[Cu₆Sn₂S₈],^[13] K₄Ag₂Sn₃S₉·2KOH,^[14] K₂Ag₆Sn₃S₁₀,^[15] [enH₂][Ag₂SnS₄],^[16] and [Mn(en)₃][Ag₆Sn₂Te₈]^[17]), and three dimensional frameworks ([enH₂]₂[Cu₈Sn₃S₁₂],^[18] [enH]₃[Cu₇Sn₄S₁₂],^[18a] and [(Me)₂NH₂]_{0.75}[Ag_{1.25}SnSe₃]^[19]). In recent years, some new synthetic strategies have been explored for the preparation of metal chalcogenides, such as ionothermal and surfactant-thermal techniques.^[11c, 20] A new silver-selenidostannate features two dimensional anionic [AgSn₁₂Se₂₈]⁷⁻ layer have been ionothermally synthesized.^[21]

Although copper/silver-chalcogenidostannates can exhibit diverse configurations, most of these compounds contain only one type of group 11 metals (Cu or Ag), namely ternary chalcogenide materials, and to the best of our knowledge, no quaternary chalcogenidostannate contains both copper and silver metals with different coordination modes has been reported till now. In our continuous research efforts in the exploration of multinary chalcogenidostannates,^[20g, 22] we are increasingly interested in developing quaternary chalcogenides based on Cu-Ag-Sn-S composition. In this contribution, we report a novel thiometallate, [enH][Cu₂AgSnS₄] (**1**), which features a quaternary two dimensional anionic [Cu₂AgSnS₄]⁻ layer containing both Cu⁺ and Ag⁺ ions. Moreover, the Cu⁺ and Ag⁺ ions adopt different coordination modes with S²⁻ ions (trigonal for Cu⁺ and tetrahedral for Ag⁺). The photoelectrochemical studies indicate that **1** displays p-type semiconducting behavior under visible light illumination (λ > 400 nm).

Red ribbon-like crystals of compound **1** were prepared by reacting Cu₂S, Ag, Sn, and S in a mixed solvent of ethylenediamine and octylamine (v:v=2:1) at 160 °C for 7 days. When octylamine was replaced with another surfactant PEG-400 (poly(ethylene glycol)-400), big crystals of **1** can also be obtained. However, when surfactants (PEG-400 or octylamine) were removed from the reaction, only small crystals of **1** with

much lower yield were obtained. This result indicates that the surfactants may be helpful to grow the large and high quality crystals of **1**.

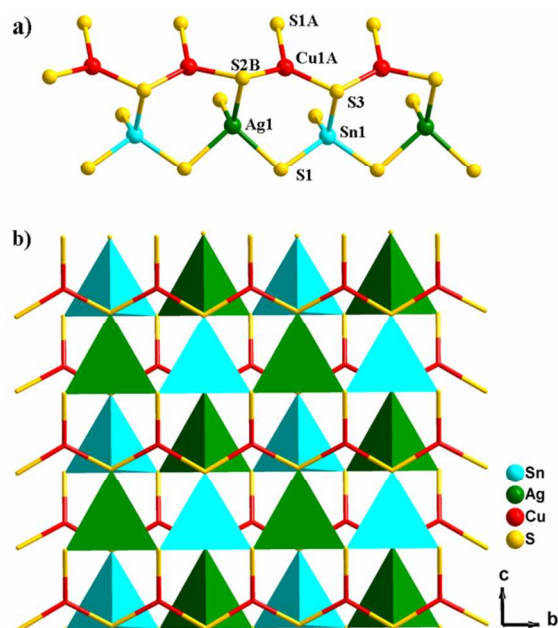


Fig. 1 (a) A double $[\text{Cu}_2\text{AgSnS}_8]$ chain was made up by the condensation of single $[\text{Cu}_2\text{S}_4]$ chain and $[\text{AgSnS}_6]$ chain, symmetry code: A, $1/2 - x, -y, 1/2 + z$; B, $1/2 - x, -y, -1/2 + z$. (b) View of the quaternary anionic $[\text{Cu}_2\text{AgSnS}_4]^-$ layer along a -axis, SnS_4 , green tetrahedrons, AgS_4 , turquoise tetrahedrons.

Single crystal X-ray diffraction analysis showed that compound **1** crystallizes in the orthorhombic space group $Pnma$, and features a two-dimensional quaternary anionic $[\text{Cu}_2\text{AgSnS}_4]^-$ layer. However, the protonated ethylenediamine cations are highly disordered in the structure and could not be fully located from the difference-Fourier maps. In the inorganic $[\text{Cu}_2\text{AgSnS}_4]^-$ layer of **1**, each Cu1 atom is coordinated with three S atoms (S1, S2, S3) to generate a $[\text{CuS}_3]$ trigonal plane, which connects to each other via corner-sharing S2 and S3 atoms to form a $[\text{Cu}_2\text{S}_4]$ chain (Figure S1). All the Ag1 and Sn1 atoms adopt tetrahedral coordination geometry by bonding to two S1 atoms, one S2 atom, and one S3 atom to form the $[\text{AgS}_4]$ and $[\text{SnS}_4]$ tetrahedrons, respectively. A $[\text{AgSnS}_6]$ chain was made up by alternately fusing $[\text{AgS}_4]$ and $[\text{SnS}_4]$ tetrahedrons at vertex-sharing S1 atoms (Figure S2). Then, the single $[\text{Cu}_2\text{S}_4]$ chain and $[\text{AgSnS}_6]$ chain are linked together by sharing S2 and S3 atoms to produce a double chain $[\text{Cu}_2\text{AgSnS}_8]$ (Figure 1a), which further condenses with the adjacent $[\text{Cu}_2\text{AgSnS}_8]$ chains along c -axis to form the anionic $[\text{Cu}_2\text{AgSnS}_4]^-$ layer (Figure 1b). The adjacent layers are stacked in an ABAB sequence along the a -axis, where highly disordered ethylenediamine cations are located between the layers (Figure S3). The interlayer distance is estimated to be 9.87 Å. In the structure of **1**, the Cu-S bond lengths are in the ranges of 2.2702(15) to 2.2728(15) Å, which are comparable with the previously reported Cu-S bond lengths.^{18a} The Ag-S bond lengths range from 2.583(3) to 2.6152(19) Å, which are similar to those reported in the literature.¹⁵ The distinct differences between Cu-S and Ag-S bond lengths were helpful for the identification of Cu and Ag metal sites in the structure, since both Cu and Ag atoms

could adopt trigonal or tetrahedral coordination mode with S atoms. Subsequent energy dispersive X-ray spectroscopy studies confirmed the Cu-Ag-Sn-S composition of **1**. Compound **1** represents the first quaternary thioannate containing both copper and silver metals with different coordination modes.

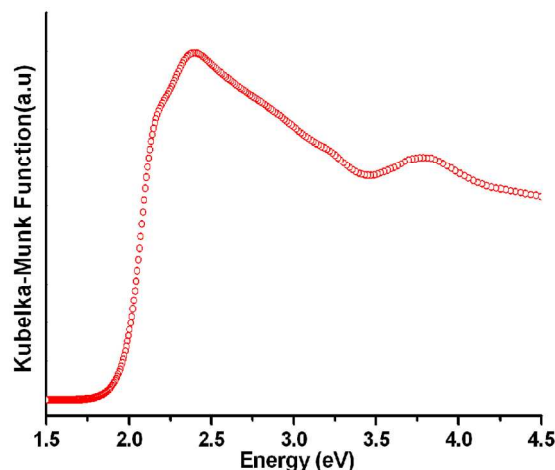


Fig. 2 Solid state optical absorption spectrum of **1**.

The optical absorption spectrum for compound **1** was converted from the solid-state UV-Vis diffuse reflectance data by using the Kubelka-Munk function. As shown in Figure 2, the sharp absorption edge revealed the band gap of 1.96 eV for **1**, which suggests that compound **1** is a semiconductor. The band gap of **1** displays a slightly red shift compared with that of the reported $\text{Rb}_2\text{Cu}_2\text{SnS}_4$ (2.08 eV),^[7c] and exhibits a blue shift compared with that of $\text{K}_2\text{Ag}_6\text{Sn}_3\text{S}_{10}$ (1.80 eV),^[15] which may be attributed to the differences in structural characteristics and components. Thermogravimetric analysis (TGA) was used to study the thermal property of **1** in a N_2 atmosphere from 30 to 500 °C (Figure S6 in the Supporting Information). The TGA curve of **1** undergoes a main weight loss step of 11.3%, which consists with the loss of one ethylenediamine molecule (11.2%) per formula unit.

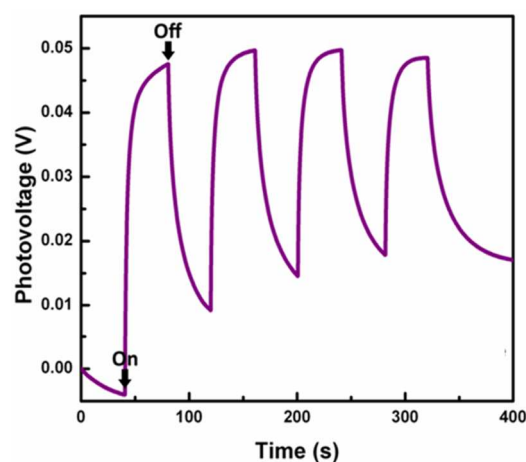


Fig. 3 Photovoltage responses of **1**/FTO electrode upon chopped AM 1.5 G light illumination.

The photoelectrochemical behavior of **1** was investigated in a three-electrode set-up.^[1d, 23] As shown in Figure 3, the photovoltage profile of **1**/FTO electrode indicates that compound

1 is active towards visible light illumination ($\lambda > 400$ nm), and exhibits p-type semiconductor characteristics as positive photovoltage responses were observed. This material shows highly repeatable photovoltage responses of ~ 40 mV during the on-off cycles of illumination. We also carried out the photocurrent measurement under biased condition, with an applied voltage of -0.3 V vs. Ag/AgCl. A photocurrent density of ~ 300 nA/cm² was obtained during the on-off cycles of illumination (Figure S7).

In conclusion, we have successfully synthesized a new two dimensional copper-silver-thiostannate under solvothermal conditions, which represents the first quaternary chalcogenidostannate containing both copper and silver metals with different coordination modes. In the structure of quaternary anionic [Cu₂AgSnS₄] layer, Cu⁺ and Ag⁺ ions adopt trigonal and tetrahedral configurations, respectively. Compound **1** can act as a p-type semiconductor under visible light illumination ($\lambda > 400$ nm). Our success in synthesizing **1** could offer a new route for the construction of quaternary metal chalcogenides with novel diverse structures and interesting properties.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, additional figures, powder X-ray diffraction patterns, energy-dispersive X-ray spectra, TGA curves, and crystallographic data (CIF), CCDC number: 995740. See DOI: 10.1039/b000000x/

‡ Synthesis of [enH][Cu₂AgSnS₄] (**1**): A mixture of Cu₂S (0.13 mmol, 0.020 g), Ag (0.25 mmol, 0.027 g), Sn (0.24 mmol, 0.028 g), S (3.94 mmol, 0.126 g), ethylenediamine (2 ml), and octylamine (1 ml) was sealed into an autoclave equipped with a Teflon liner (20 ml) and heated at 160 °C for 7 days. After cooling to room temperature, red ribbon-like crystals of **1** were obtained by filtration with yield of 34.5% (based on Sn). Crystal data for [enH][Cu₂AgSnS₄] (**1**): $M = 543.07$, Orthorhombic, $Pnma$, $a = 19.7256(11)$ Å, $b = 7.8544(4)$ Å, $c = 6.5083(4)$ Å, $V = 1008.35(10)$ Å³, $Z = 4$, $\mu = 9.293$ mm⁻¹, 3469 reflections measured, 1172 unique ($R_{int} = 0.0283$), 1025 observed ($I > 2\sigma(I)$), $R_1 = 0.0369$, $wR_2 = 0.1164$, $GOF = 1.046$.

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