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Mild Solvothermal Syntheses and Characterization of Layered Copper Thioantimonates(III) and Thioarsenate(III)

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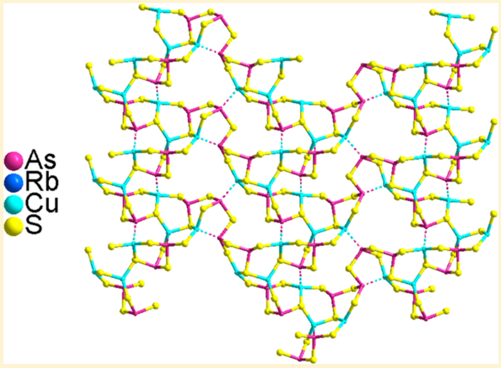
Supporting Information

ABSTRACT: The new copper thioantimonates(III) and thioarsenate(III) $\mathrm{Rb_2Cu_2Sb_2S_5}$ (**1**), $\mathrm{Cs_2Cu_2Sb_2S_5}$ (**2**), and $\mathrm{Rb_8Cu_6As_8S_{19}}$ (**3**) have been synthesized solvothermally. Compound **1** contains a $[\mathrm{Cu_2SbS_3}]$ net to which $[\mathrm{Sb_2S_4}]$ chains adhere through Cu−S bonds and Sb−Cu interactions to give a layered structure. In compound **2**, the layer is formed by edge-sharing tetrahedral $\mathrm{CuS_4}$ chains linked by dimeric $[\mathrm{Sb_2S_5}]$ units. The layered structure in compound **3** is constructed by helical chains built from $[\mathrm{Cu_3S_7}]$ moieties and dimeric $[\mathrm{As_2S_5}]$ units which are further connected by tetrameric $[\mathrm{As_4S_9}]$ groups. Their optical and thermal properties have been investigated.



■ INTRODUCTION

During the past few decades, substantial syntheses of microporous chalcogenides have been conducted due to their complex architectures and potentialities in technical applications.[1] The synthetic research on thioantimonate(III) and thioarsenate(III) frameworks has been extensive because the stereochemical effect of lone electron pairs and the various coordinations of $\mathrm{Sb^{III}}$ and $\mathrm{As^{III}}$ by sulfur atoms can give rise to large structural and compositional diversities.[2] Recently, considerable attention have been paid to the incorporation of transition-metal ions into the group 15 sulfides to search for novel chalcogenide materials.[3]

Among the transition-metal ions, $\mathrm{Ag^+}$, $\mathrm{Cu^+}$, and $\mathrm{Hg^{2+}}$ appear to be more readily to form part of a network of group 15 sulfides. For example, a series of mercury thioantimonates(III) $[\mathrm{1,2\text{-}dapH}][\mathrm{HgSbS_3}]$ (dap = diaminopropane),[4a] $[\mathrm{(Me)_2NH_2}]_2[\mathrm{HgSb_8S_{14}}]$,[4a] and $[\mathrm{Ni(en)_3}]_{0.5}[\mathrm{HgSbS_3}]$[4a] and mercury thioarsenates(III) such as $[\mathrm{(Me)_4N}][\mathrm{HgAs_3S_6}]$[4b] and $[\mathrm{(Ph)_4P}]_2[\mathrm{Hg_2As_4S_9}]$[4b] have been reported.[4] Some silver/copper group 15 sulfides, e.g. $[\mathrm{C_2N_2H_9}][\mathrm{Ag_2SbS_3}]$,[5b] $[\mathrm{C_2N_2H_9}]_2[\mathrm{Ag_5Sb_3S_8}]$,[5b,c] have also been synthesized in the presence of organic cations or transition-metal complexes as the templates.[5] Representative examples of copper-containing compounds are $[\mathrm{C_4N_2H_{12}}]_{0.5}[\mathrm{CuSb_6S_{10}}]$,[6a] $\mathrm{RCu_2SbS_3}$ (R= amine)[6b] and $[\mathrm{C_4N_3H_{14}}][\mathrm{Cu_3Sb_2S_5}]$,[6b] $[\mathrm{C_6N_4H_{20}}]_{0.5}[\mathrm{Cu_3Sb_2S_5}]$,[6b] $[\mathrm{Ni(dap)_2}][\mathrm{Cu_4Sb_2S_6}]$ and $[\mathrm{Ni(dien)_2}][\mathrm{CuSb_3S_6}]$ (dien = diethylenetriamine),[6c] $[\mathrm{enH}][\mathrm{Cu_3As_2S_5}]$,[6d] and $[\mathrm{Ni(dap)_3}]_4[\mathrm{Cu_2As_{10}^{II,III}S_{18}}]$.[6e]

In contrast, quaternary transition-metal group 15 sulfides that contain alkali-metal ions are still uncommon. Most of them have been prepared at high temperature or/and high pressure.[7] For example, several quaternary sulfides such as $\mathrm{Na_2CuSbS_3}$,[7g] $\mathrm{KCu_2AsS_3}$, and $\mathrm{KCu_4AsS_4}$[7e] were obtained via supercritical methods. Our previous research has shown that $\mathrm{CsCu_2AsS_3}$[8] and $\mathrm{KCu_2AsS_3}$[7e] have different layered structures, although the stoichiometries of the anionic layers are the same in both compounds. The structural difference may result from the structure-directing agents or synthetic conditions. $\mathrm{CsCu_2AsS_3}$[8] was synthesized under mild conditions, while a potassium analogue was obtained in a supercritical ethylenediamine system. Therefore, there is a great possibility to access new quaternary sulfides under mild synthetic conditions. Although we have successfully synthesized the group 15 sulfides $\mathrm{A_3Ag_9Sb_4S_{12}}$ (A = K, Rb, Cs),[9] $\mathrm{CsM_2AsS_3}$ (M = Ag, Cu),[8,9] $\mathrm{KCu_4AsS_4}$,[8] etc. under mild conditions using thiophenol as a mineralizer, limited research on syntheses of sulfides has been conducted due to the toxic nature of thiophenol.

Recently, we found that a large excess of sulfur could decrease synthetic temperature of several thioargentates effectively.[10] In an attempt to further this strategy, $\mathrm{Rb_2Cu_2Sb_2S_5}$ (**1**), $\mathrm{Cs_2Cu_2Sb_2S_5}$ (**2**), and $\mathrm{Rb_8Cu_6As_8S_{19}}$ (**3**) were obtained under mild solvothermal conditions.

■ EXPERIMENTAL SECTION

All reagents were commercially available and used as received. A Quanta 450 instrument was used for EDS analyses. A D/MAX-2400 instrument with Cu Kα radiation ($\lambda = 1.5418$ Å) was used for PXRD measurements at 40 kV and 100 mA. A JASCO V-570 UV−vis−NIR instrument was used to record UV−vis diffuse-reflectance spectra. A Metter Toledo Star instrument was used to study thermal behaviors (TGA and DSC) under a $\mathrm{N_2}$ atmosphere (40 mL $\mathrm{min^{-1}}$) with a heating rate of 10 °C $\mathrm{min^{-1}}$.

Syntheses. Syntheses of title compounds were carried out through similar procedures. The reactants were sealed in a thick glass tube in

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air (ca. 10% filling), and then the tube was placed in an autoclave which was heated to 160 °C (145 °C for **3**) for 5 days prior to cooling to room temperature naturally. The products were washed several times with ethanol and deionized water and dried under ambient conditions.

$Rb_2Cu_2Sb_2S_5$ (**1**) was synthesized from 5 mg of Cu powder, 10 mg of Sb powder, 12 mg of S powder, 12 mg of Rb_2CO_3, 300 mg of 1,2-diaminopropane, and 90 mg of methanol aqueous solution (50 wt %). The Cu/Sb/S/Rb_2CO_3 molar ratio is 0.08/0.082/0.375/0.052. Red rodlike crystals were obtained in 36% yield (based on copper).

$Cs_2Cu_2Sb_2S_5$ (**2**) was synthesized from 5 mg of Cu powder, 10 mg of Sb powder, 16 mg of S powder, 10 mg of Cs_2CO_3, 300 mg of 1,2-diaminopropane, and 60 mg of H_2O. The Cu/Sb/S/Cs_2CO_3 molar ratio is 0.08/0.082/0.5/0.031. Red rodlike crystals were obtained in 32% (yield based on copper).

$Rb_8Cu_6As_8S_{19}$ (**3**) was synthesized from 4 mg of Cu powder, 15 mg of As_2S_3, 10 mg of S powder, 12 mg of Rb_2CO_3, 400 mg of 1,2-diaminopropane, and 110 mg of methanol aqueous solution (50 wt %). The Cu/As_2S_3/S/Rb_2CO_3 molar ratio is 0.063/0.061/0.312/0.052. Orange needlelike crystals were obtained in 56% yield (based on copper).

Single-Crystal X-ray Diffraction. A Bruker Smart APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used for data collections at 296 K. The structures of the title compounds were solved by direct methods using SHELXS-97 and refined against F^2 using SHELXL-97.[11] Crystal data and structure refinement details for **1**−**3** are given in Table 1.

■ RESULTS AND DISCUSSION

$Rb_2Cu_2Sb_2S_5$ (**1**) has a layered structure, in which the layers are separated by charge-balancing Rb^+ cations. Each layer consists of two parts: a $[Sb_2S_4]$ chain and a $[Cu_2SbS_3]$ net. The chain is composed of trigonal-pyramidal $Sb(2)S_3$ units linked by vertex sharing (Figure 1, top). The $[Cu_2SbS_3]$ net is constructed by tetrahedral $Cu(1)S_4$ units and pyramidal $Cu(2)S_3$ units. These units share vertices to form a two-dimensional crownlike structure, while the Sb(1) ions are located in the chambers through the Sb(1)−S bond (Figure 1, bottom).

Table 1. Crystal Data and Structure Refinement Details

	1	2	3
empirical formula	$Rb_2Cu_2Sb_2S_5$	$Cs_2Cu_2Sb_2S_5$	$Rb_8Cu_6As_8S_{19}$
fw	701.82	796.7	2273.50
temp/K	296(2)	296(2)	296(2)
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1$
Flack factor			0.013(14)
a/Å	16.5448(12)	7.4013(2)	11.876(3)
b/Å	10.3545(7)	8.5533(2)	9.1984(19)
c/Å	6.6128(4)	9.8390(2)	19.792(5)
α/deg		91.9590(1)	
β/deg	99.952(4)	92.2180(1)	95.985(17)
γ/deg		101.8830(1)	
V/Å^3	1115.81(13)	608.49(3)	2150.3(9)
Z	4	2	2
calcd density/Mg m^{-3}	4.178	4.348	3.511
abs coeff/mm^{-1}	18.089	14.534	18.951
F(000)	1256	700	2076
2θ(max)/deg	50.00	50.00	50.00
index range	$-19 \leq h \leq 19$ $-12 \leq k \leq 12$ $-7 \leq l \leq 7$	$-8 \leq h \leq 8$ $-9 \leq k \leq 10$ $-11 \leq l \leq 11$	$-14 \leq h \leq 14$ $-10 \leq k \leq 9$ $-23 \leq l \leq 23$
no. of collected/unique rflns (R(int))	5690/1942 (0.1384)	5690/2133 (0.0400)	10869/6779 (0.0557)
no. of data/restraints/params	1942/0/101	2133/0/101	6779/1/370
GOF on F^2	1.102	1.086	0.991
final R indices ($I > 2\sigma(I)$)	R1 = 0.0637	R1 = 0.0266	R1 = 0.0541
	wR2 = 0.1773	wR2 = 0.0672	wR2 = 0.1079
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	2.092, −3.136	1.346, −1.207	2.263, −1.237

In tetrahedral $Cu(1)S_4$ units, the Cu(1)-S distances range from 2.3422(4) to 2.4397(4) Å with the S−Cu(1)−S angles ranging from 96.781(2) to 114.910(6) °. However, in the pyramidal $Cu(2)S_3$ units, the Cu(2)−S distances are between 2.2805(4) and 2.3450(5) Å with the S−Cu(2)−S angles ranging from 111.626(1) to 121.396(1)°. There are two kinds of pyramidal SbS_3 units in compound **1**. The main difference concerns the coordination environment of S atoms: each S atom of the $Sb(1)S_3$ units in the net adopts a μ_3-pyramidal geometry to bond one Sb(1) and two Cu atoms; each S atom of the $Sb(2)S_3$ units in the chain adopts a μ_2-V shaped mode to link two Sb(2) or one Sb(2) and one Cu(1). The Sb(1)−S and Sb(2)−S distances range from 2.4024(4) to 2.4720(4) Å and from 2.3740(4) to 2.5050(4) Å, respectively.

An anionic layer is formed by interconnection of $[Sb_2S_4]$ chains and the $[Cu_2SbS_3]$ net through the coordination of S(3) to Cu(1) and Sb(2)−Cu(2) interactions (Figure 2). The lone electron pair of Sb(2) always points toward Cu(2), and the separation between Cu(2) and Sb(2) is 2.8130(2) Å, which is close to that in A_2CuSbS_3 (A = Na, K) (2.808/2.8554 Å).[7g,h]

In compound **1**, Rb^+ cations are located between adjacent anionic layers. Rb(1) adopts a distorted -pentagonal-bipyramidal coordination mode by S atoms, and the average Rb(1)−S distance is 3.409 Å. Rb(2) is eight-coordinated by S atoms with an averaged Rb(2)−S distance of 3.473 Å.

$Cs_2Cu_2Sb_2S_5$ (**2**) is isomorphic with $Cs_2Cu_2Sb_2Se_5$,[12] which is constructed by edge-sharing tetrahedral CuS_4 chains with bridging dimeric $[Sb_2S_5]$ moieties. Although the layer in compound **2** has the same stoichiometry as in compound **1**, their crystal structures are different.

In a dimeric $[Sb_2S_5]$ moiety, each Sb is coordinated pyramidally by S with Sb−S ranging from 2.3736(2) to 2.5142(2) Å. The dimeric $[Sb_2S_5]$ moieties link adjacent tetrahedral CuS_4 chains through vertex sharing (Figure 3).

In each tetrahedral CuS_4 chain, the Cu−S distances range from 2.3259(2) to 2.4624(2) Å and from 2.277(2) to 2.639(2) Å, respectively, with the S−Cu−S angles between 99.15(5) and 126.68(7)°. $[Cu_2Sb_2S_5]^{2-}$ anionic layers are separated by the cationic double layers formed by Cs^+ and stack along the b axis. Each Cs^+ is eight-coordinated by S atoms with Cs−S distances ranging from 3.4324(2) to 3.9386(1) Å.

Bensch et al. have solvothermally synthesized the series of copper thioantimonates(III) $[H_2R]_{0.5}[Cu_2SbS_3]$ with the same layered structure by using a series of organic diamines.[6b] The results indicate that amines have a weak structure-directing effect, which is also proved by our experimental results. During the syntheses of compounds **1** and **2** in the diaminopropane system, amine-templated copper thioantimonates(III) were never obtained. The structural difference between **1** and **2** indicates the relatively strong structure-directing effect of alkali-metal ions, considering the interaction between cationic templates and anionic layers.

Our attempt to prepare sodium and potassium analogues in a similar fashion was not successful. An amorphous phase was always obtained when sodium was used as the structure-directing agent; in the case of potassium, the product is $KSbS_2$. However, the layered compounds A_2CuSbS_3 (A = Na, K) have

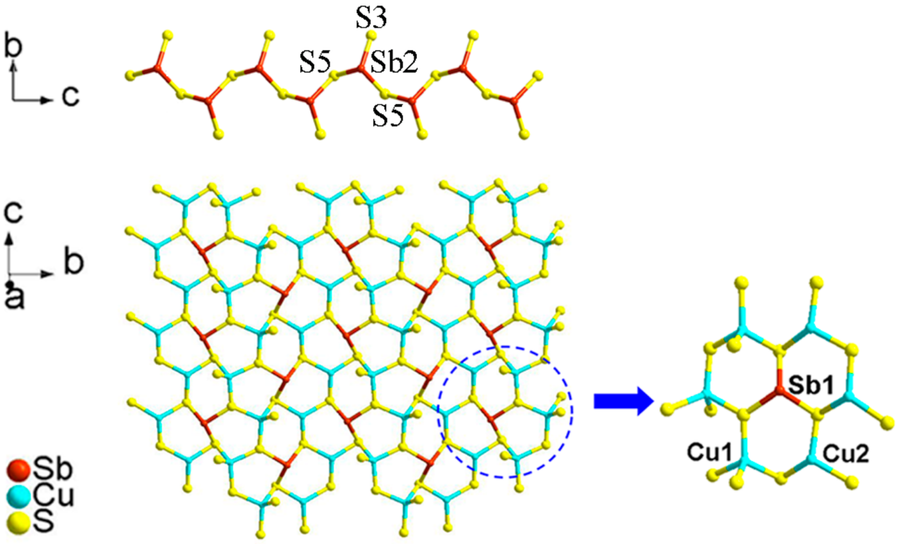

Figure 1. (top) Chain formed by vertex-sharing Sb(2)S_3 units. (bottom) [Cu_2SbS_3] net constructed by tetrahedral Cu(1)S_4, pyramidal Cu(2)S_3, and Sb(1)S_3 units.

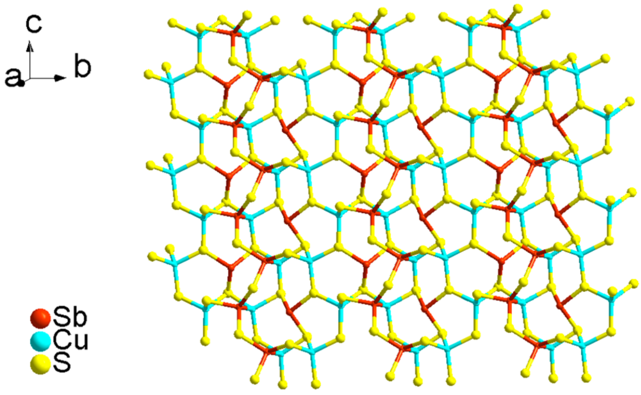

Figure 2. [$Cu_2Sb_2S_5$]$^{2-}$ layer formed by linkage of infinite [Sb_2S_4] chains and a [Cu_2SbS_3] net.

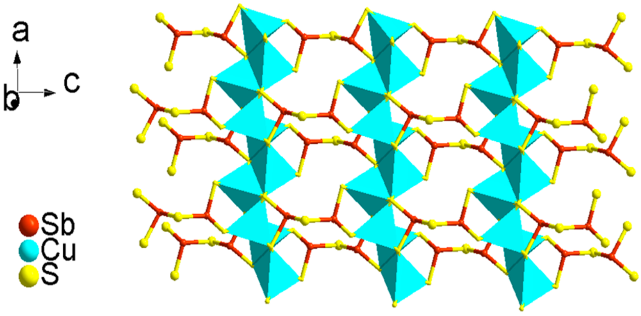

Figure 3. [$Cu_2Sb_2S_5$]$^{2-}$ anionic layer in **2**.

been synthesized by supercritical or flux methods.[7g,h] These results reveal that alkali-metal ions not only can be used as structure-directing agents but also play a crucial role in the crystallization of sulfides.

We explored the solvothermal reaction system A−Cu−As−S (A = alkali metal) in a similar way and obtained the layered compounds $K_2Cu_2As_2S_5$ and $Rb_8Cu_6As_8S_{19}$ (**3**). $K_2Cu_2As_2S_5$ is isomorphic with compound **1**.[13] It is perhaps still impossible to put forward a clear mechanism for the self-assembly of simple building units into complex structures, but there is no doubt that structure-directing agents control the organization processes. In addition, a particular network may be generated by using different structure-directing agents, as mentioned above for thioantimonates. Alternatively, a given template can be applied to access different structure types. This observation is provided by the varying structures of $K_2Cu_2As_2S_5$,[13] KCu_2AsS_3,[7e] and KCu_4AsS_4,[8] all of which are directed by the K^+ cation.

The versatile template effect of alkali-metal cations is also reflected in the fact that $Rb_8Cu_6As_8S_{19}$ (**3**) has a novel layered structure. The anionic layer in $Rb_8Cu_6As_8S_{19}$ (**3**) consists of helical chains formed by edge sharing of the [Cu_3S_7] moieties and dimeric [As_2S_5] units. The helical chains run along the 2_1 screw axis parallel to the *b* axis, which are strictly alternating and are further connected by tetrameric [As_4S_9] groups (Figures 4 and 5).

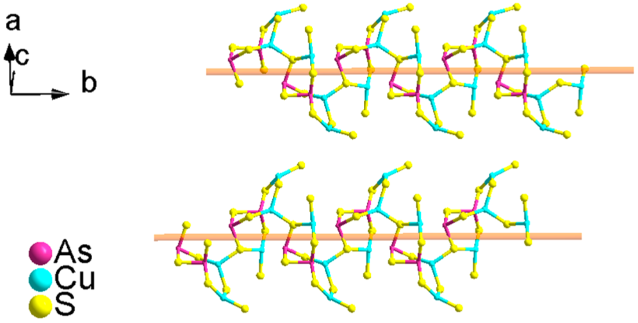

Figure 4. Helical chains running along the 2_1 screw axis parallel to the *b* axis in **3**.

Each Cu atom is in a pyramidal coordination environment with the Cu−S distances between 2.288(5) and 2.368(6) Å (S−Cu−S angles range from 101.26(2) to 124.52(2)°). Each As atom bonds to three S atoms in a pyramidal mode, and the bond distances and angles are close to the reported values.[7e,8] As in the compound $K_2Cu_2As_2S_5$, there are also Cu−As interactions with distances of 2.414(3)−2.703(3) Å in compound **3**.

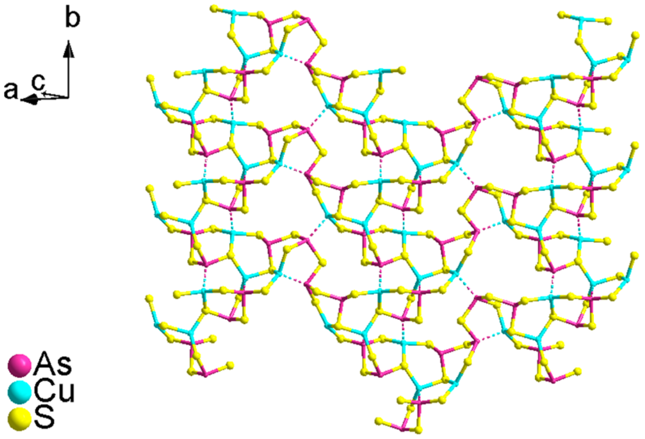

Figure 5. Linkage of building units to form a $[Cu_6As_8S_{19}]^{8-}$ anionic layer in **3**.

The Rb^+ cations lie between the anionic layers. Rb(3) and Rb(8) are eight-coordinated by S atoms with an average Rb−S distance of 3.576 Å. The rest of the Rb^+ cations are seven-coordinated by S atoms, forming a distorted-capped-octahedral coordination with an average Rb−S distance of 3.500 Å.

Optical Properties and Thermal Analyses. Powder samples were used to study UV−vis diffuse reflectance spectra. The absorption spectra were calculated by the Kubelka−Munk function from the reflectance spectra. From the absorption spectra of **1** and **2**, band gaps of 1.6 eV are estimated (Figure 6). A band gap of 1.8 eV is found for **3** (Figure 7). The results confirmed that these compounds are semiconductors.

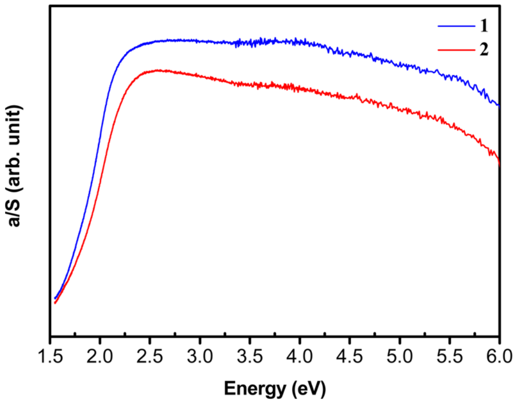

Figure 6. UV−vis spectra of compounds **1** and **2**.

The thermal properties were investigated by TG-DSC. The TG results show that all of the compounds have no weight loss. The DSC curve of compound **1** displays an endothermic peak and exothermic peaks at 350 and 450 °C, respectively. For compounds **2** and **3**, endothermic phase transitions occur at 383 and 172 °C, respectively.

CONCLUSION

Three copper thioantimonates(III) and thioarsenate(III) have been obtained under mild solvothermal conditions. Their different layered structures indicate that alkali-metal cations are a type of efficient structure-directing agent; therefore, it is anticipated that new copper group 15 sulfides can be obtained through an appropriate choice of alkali-metal cations. This mild solvothermal route offers a new possibility to access new quaternary sulfides containing copper.

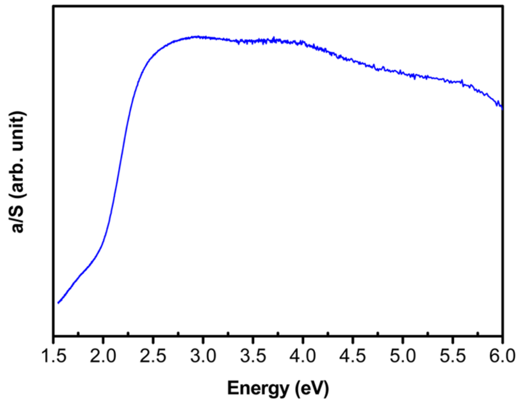

Figure 7. UV−vis spectrum of compound **3**.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving packing diagrams, EDS data, PXRD patterns, DSC curves, selected bond lengths and angles, and crystallographic data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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