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Article

Syntheses and Characterization of a Series of Silver−Thioantimonates(III) and Thioarsenates(III) Containing Two Types of Silver−Sulfur Chains

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Three framework silver−thioantimonates, $K_3Ag_9Sb_4S_{12}$(**1**), $Rb_3Ag_9Sb_4S_{12}$(**2**), and $Cs_3Ag_9Sb_4S_{12}$(**3**), and one layered silver−thioarsenate, $CsAg_2AsS_3$(**4**), have been synthesized solvothermally in the presence of thiophenol as a mineralizer. Compounds **1**, **2**, and **3** are isostructural and contain infinite silver−sulfur chains $[Ag_9S_{12}]^{15-}$. These chains are connected to one another by the antimony atoms to generate wide channels along the [001] direction where the alkali metal cations reside. The structure of **4** consists of helical chains $[Ag_2S_3]^{4-}$ linked by the arsenic atoms to form layers with potassium ions between the layers.

Introduction

Thioantimonates and thioarsenates are now a substantial subclass of solid-state chalcogenometalates that are undergoing a rapid resurgence of academic interest because of the richness of diversity of their intrinsic structure. The majority of them involve ternary systems associated with alkali metals ions and/or organic counterions.[1] Of particular interest are the thioantimonates(III) and thioarsenates(III) which contain pyramidal $[AsS_3]^{3-}$ and $[SbS_3]^{3-}$ ainons that undergo a variety of condensation and ring closure reactions into extended structures giving rise to various structure types.[2]

Recently, increasing interest in this field is the incorporation of transition metal ions to enrich the structural diversity and chemical and physical properties of the chalcogenometalate compounds. In most cases, the transition metal ions coordinate with various amines to form complex cations acting as space fillers[3] or charge−compensating ions,[4] and resulting in low dimensional structural characteristics of these materials. A rare example $[Co(en)_3]CoSb_4S_8$[5] was synthesized in superheated ethylenediamine and possesses a purely inorganic framework containing transition metal ions, in which the Co atoms connect the SbS_2^- chains to give polar $[CoSb_4S_8]^{2-}$ layers. The late transition metals appear to be more readily incorporated into the inorganic framework than their early series. Thus, one class of materials, silver−thioantimonates(III) and thioarsenates(III), attracts our attention because of various coordinations of silver by sulfur atoms (e.g., 2, 3, 4), diverse linkages of silver−sulfur polyhedra through vertices or edges and even complex argentophilic interactions. The following $[C_2N_2H_9][Ag_2SbS_3]$,[6] $[C_2N_2H_9]_2[Ag_5Sb_3S_8]$,[6,8] $[C_6N_4H_{20}]_2$-$[Ag_5Sb_3S_8]$,[7] and $[C_4N_2H_{14}][Ag_3Sb_3S_7]$[8] have been synthesized under solvothermal conditions, in which the polyamine

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plays a structure directing role and has a marked influences on the structure of the final products. A further example, $KAg_3As_2S_5$,[9] was obtained by the methanothermal method and shows condensation of the pyramidal $[AsS_3]^{3-}$ units.

Mineralizers, such as hydroxide or fluoride ions,[10] added to the reaction mixtures in the correct quantities are often vital for crystallization of the desired molecular sieve products. In addition to helping solubilize the starting materials under the reaction conditions, fluoride itself can play a structure-directing role and is intimately involved in template ordering in certain materials. This arouses us to search for suitable mineralizer to increase the solubility of silver sulfide and obtain new compositions in the synthesis of silver−thioantimonates and thioarsenates. In preceding papers, we have demonstrated that $HSCH_2CH(SH)CH_2OH$ is an excellent mineralizer for the synthesis of silver−thiogermanates and thiostannates[11] under mild solvothermal conditions. Recently, we found that thiophenol(PhSH) can dissolve silver sulfide under amine alkaline conditions, and two layered silver−thioantimonates(III), KAg_2SbS_3 and $K_2Ag_3Sb_3S_7$,[12] have been synthesized solvothermally in the presence of thiophenol as a mineralizer. In an attempt to extend this work, we obtained three open framework silver−thioantimonates, $K_3Ag_9Sb_4S_{12}$ (**1**), $Rb_3Ag_9Sb_4S_{12}$ (**2**), and $Cs_3Ag_9Sb_4S_{12}$ (**3**), and one layered silver−thioarsenate, KAg_2AsS_3 (**4**).

Experimental Section

Materials and Physical Measurements. All chemicals and solvents were reagent-grade materials and were used as received without further purification. EDS analysis of the compounds **1**, **2**, **3**, and **4** were performed using JSM-5600LV. The K:Ag:Sb:S molar ratio in compounds **1**, **2**, and **3** are close to 3:9:4:12. The Cs:Ag:As:S molar ratio in compound **4** is 1:2.1:1.1:3.2. The UV−vis spectra of **1**, **2**, **3**, and **4** were measured in the solid at room temperature using a JASCO V-570UV/VIS/NIR double-beam, double-monochromator spectrophotometer and wavelength range from 200 to 800 nm. The thermal behavior (TGA and DSC) of the compounds **1**, **2**, **3**, and **4** were carried out by Metter Toledo Star under a flow of nitrogen (40 mL/min) from 50 to 550 °C at heating rate of 10 °C/min.

Synthesis of Compounds 1−4. For **1**, the compound was prepared using $AgNO_3$ (0.026 g, 0.15 mmol), Sb (0.012 g. 0.10 mmol), S (0.010 g, 0.31 mmol), K_2CO_3 (0.014 g, 0.10 mmol), about 0.3 mL mixed solvent of thiophenol/pyridine (v/v = 1:3), and 0.2 mL of ethylenediamine. The mixture was sealed in a Pyrex glass tube with ca. 10% filling at air atmosphere, placed in a stainless-steel autoclave, and then heated at 145 °C for 6 days. After cooling naturally to ambient temperature, the products were washed with ethanol and water, respectively, and red block crystals were obtained in 41% yield based on silver. Compounds **2** and **3** were obtained with a procedure similar to the synthesis of **1**, except for applying Rb_2CO_3 (0.023 g, 0.010 mmol) and Cs_2CO_3 (0.023 g, 0.07 mmol) instead of K_2CO_3. Red block crystals were obtained in 52% and 74% yields based on silver, respectively. For **4**, the compound was synthesized using AgSPh (0.031 g, 0.015 mmol), As (0.005 g, 0.07 mmol), S (0.013 g, 0.4 mmol), Cs_2CO_3 (0.029 g, 0.09 mmol), about 0.3 mL mixed solvent of glycol/pyridine (v/v = 1:3), and 0.2 mL ethylenediamine after 7 days at 150 °C. Yellow crystals were obtained in 62% yield based on silver. All compounds are stable in air and water.

Table 1. Crystal Data and Structure Refinement for Compounds **1**−**4**

compound	**1**	**2**	**3**	**4**
formula	$K_3Ag_9Sb_4S_{12}$	$Rb_3Ag_9Sb_4S_{12}$	$Cs_3Ag_9Sb_4S_{12}$	$CsAg_2AsS_3$
fw	1959.85	2098.96	2241.28	519.75
crystal system	tetragonal	tetragonal	tetragonal	monoclinic
space group	$I4/m$	$I4/m$	$I4/m$	$P2(1)/c$
a (Å)	10.8844(8)	10.9396(3)	11.0356(4)	10.0357(16)
b (Å)				8.3893(11)
c (Å)	11.5046(18)	11.6137(9)	11.8076(9)	9.2176(14)
β (deg)				107.034(5)
V (Å^3)	1363.0(3)	1389.87(12)	1437.98(13)	742.01(19)
Z	2	2	2	4
T (K)	293(2)	293(2)	293(2)	293(2)
D_c (g/cm^3)	4.776	5.015	5.176	4.653
2θ/(max), deg	49.98	49.94	49.94	49.96
total reflns	2567	3093	3530	2211
unique reflns	625	640	672	1254
GOF	1.079	1.031	1.096	1.056
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0494, 0.1162	0.0474, 0.1396	0.0485, 0.1148	0.0770, 0.2053
$R1$, $wR2$ (all data)	0.0502, 0.1168	0.0495, 0.1418	0.0486, 0.1148	0.0776, 0.2064
$\delta(F)/e$ Å^{-3}	−1.190/2.074	−1.346/1.977	−1.633/2.369	−1.558/2.249

X-ray Crystallography. Single crystals of **1**, **2**, **3**, and **4** were mounted on a Bruker Smart APEX II diffractometer equipped with graphite monochromitized Mo Kα radiation (λ = 0.71073 Å). Intensity data were collected by the narrow frame method at 293 K. All structure solutions were performed with direct methods using SHELXS-97.[13] Further details are given in Table 1. Structure refinement was done against F^2 using SHELXL-97.[14] All non-hydrogen atoms were refined with anisotropic displacement parameters. Important bond lengths and angles are listed in Table 2.

Results and Discussion

Crystal Structures. Compound **1** crystallizes in the tetragonal space group $I4/m$ with two formula units in the unit cell and has a three-dimensional anionic framework, $[Ag_9Sb_4S_{12}]^{3-}$, containing channels in which the

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Table 2. Ranges of Bond Distances (Å) and Angles (deg) in Compounds **1** and **4**

	1	4
Ag(1)−S	2.886(3)	2.414(9)−2.452(9)
Ag(2)−S	2.495(3)−2.557(3)	2.476(10)−2.591(10)
Sb−S	2.409(4)−2.434(3)	
As−S		2.213(9)−2.278(9)
S−Ag(1)−S	97.64(4), 137.24(11)	155.9(4)
S−Ag(2)−S	111.26(10)−128.72(10)	113.5(3)−124.7(3)
S−Sb−S	97.10(14) −98.83(9)	
S−As−S		96.4(3)−106.6(4)

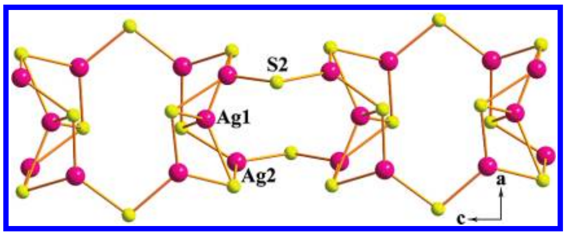

Figure 1. View along the [010] direction of the silver−sulfur chain formed from linkage through bridging sulfur atoms of 8-membered Ag_4S_4 rings adopting a boatlike conformation in compound **1**: Ag, pink; S, yellow.

potassium cations reside. In anionic framework, the atoms Ag(2) and S(2) are located on general positions whereas all other unique atoms are on special positions. The Ag(2) atom has a nearly trigonal planar coordination by three sulfur atoms with the Ag−S bond distances ranging from 2.495(3)−2.557(3) Å and S−Ag−S angles between 111.26(10) and 128.72(10)° (Table 2), comparable to values in the literature for silver sulfur in trigonal planar coordination.[15] The Ag(1) atom exhibits a regular tetrahedral coordination, with a long Ag−S bond of 2.886(3) Å and S(2)−Ag(1)−S(2) angles of 97.64(4) and 137.24(11)°.

Vertex-sharing of four $Ag(2)S_3$ units produces 8-membered Ag_4S_4 rings adopting a boatlike conformation. These boats are linked through bridging sulfur atoms to form infinite silver−sulfur chains $[Ag_8S_{12}]^{16-}$ directed along [001]. Interestingly, the Ag(1) atom is embedded in the boats resulting chain of stoichiometry $[Ag_9S_{12}]^{15-}$, and each Ag(1) atom has contacts with eight atoms of boat, located at the center of the boat (Figure 1). The Ag(2)−Ag(1)−Ag(2) angles are 97.178(15) and 138.60(4)°, and the Ag(1)−Ag(2) separation is 2.7914(12) Å, which is similar to Ag−Ag distances in monovalent silver compounds in which there are significant $d^{10}-d^{10}$ interactions.[16]

Four of these infinite $[Ag_9S_{12}]^{15-}$ chains are connected to one another by the antimony atoms to yield a square channel with a size of 5.7 × 5.7 Å^2 (the Ag−Ag distances) along the [001] direction where the K cations are located (Figure 2). Each face of the channel may be regarded as the fusion of infinite $[Ag_4Sb_3S_7]^-$ and $[Ag_4Sb_4S_8]^{2-}$ chains in the ac or bc planes (Figure 3). The $[Ag_4Sb_3S_7]_\infty^-$ chain is formed by the condensation of 8-membered $Ag_2Sb_2S_4$ rings along the Sb(1)−S(1) edge while the $[Ag_4Sb_4S_8]_\infty^{2-}$ chain is generated by the condensation of 6-membered Ag_2SbS_3 rings and 10-membered Ag_4SbS_5 rings along the Ag(2)−S(2) edge, and all these rings are formed by vertex-linking of $Sb(1)S_3$ and $Ag(2)S_3$ units. The Sb(1) atom is in a trigonal pyramidal environment of sulfur atoms and has an additional S atom at a longer distance of 3.668 Å.

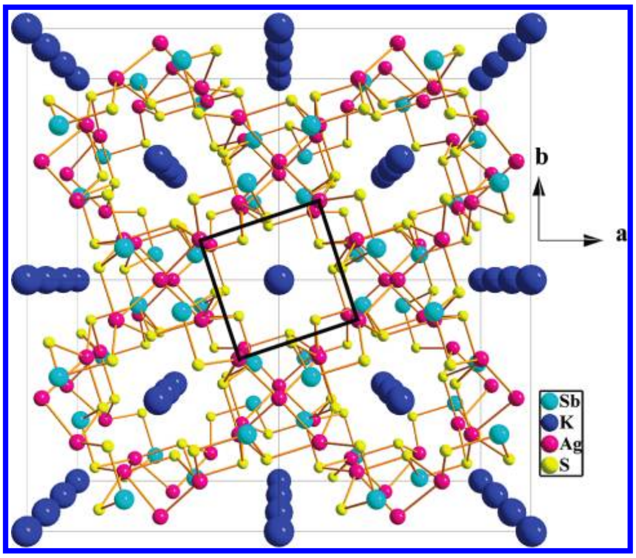

Figure 2. Linkage of the chains by the antimony atoms in compound **1** to generate wide channels along the [001] direction where the K cations reside.

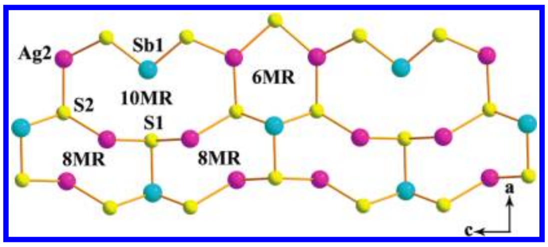

Figure 3. Face of square channel showing the fusion of infinite $[Ag_4Sb_3S_7]^-$ and $[Ag_4Sb_4S_8]^{2-}$ chains.

Compounds **2** and **3** are isostructural with **1** and have a contiguous anionic covalent framework containing channels which provide the necessary void spaces for two kinds of alkali metal cations environments. The potassium cation is illustrated here as a example. An interesting feature is that the coordination environment for K(1) is square prismatic with bond length of 3.401 Å (3.472 Å for Rb, 3.567 Å for Cs), and such a coordination mode of alkali metal is not found in chalcogenides and chalcogenometalates. The crystallographically unique potassium atom, K(2), is eight coordinate to sulfur, in distorted square prismatic, with bond distances that average 3.379 Å (3.446 Å for Rb, 3.549 Å for Cs). Although the distances of alkali metal with sulfur is different, the size of channels is nearly equivalent for compounds **1**−**3**.

Compound **4**, $CsAg_2AsS_3$, crystallizes in the monoclinic space group $P2(1)/c$ with four formula units in the unit cell and contains a novel layered anionic framework separated by cesium cations. Each layer is a complex structure consisting of silver ions linked in a complicated fashion by a series of trigonal AsS_3^{3-} groups, and the primary building units are one trigonal AsS_3 pyramid,

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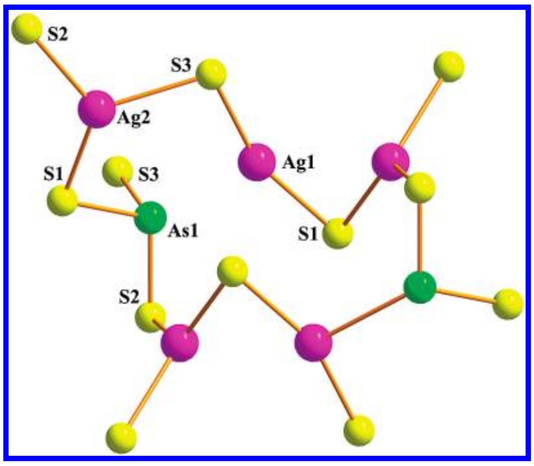

Figure 4. Local coordination of the framework atom in compound **4** showing primary building units.

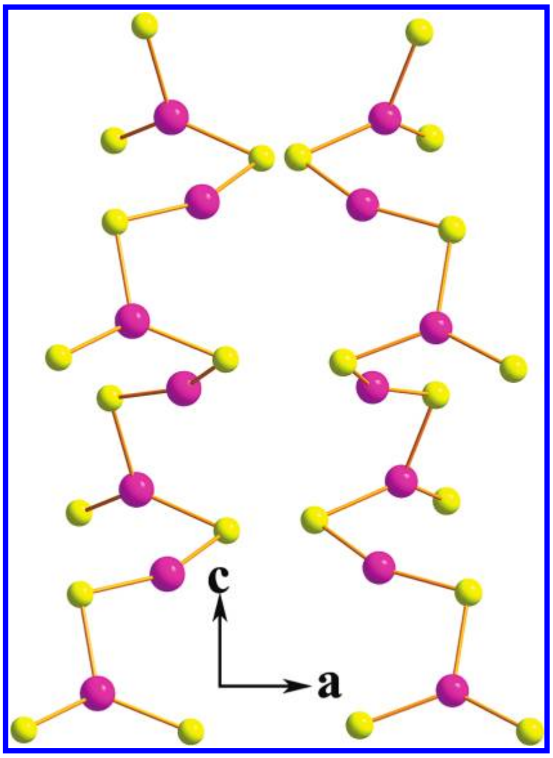

Figure 5. Left- and right-handed helical silver−sulfur chains in compound **4**: Ag, pink; S, yellow.

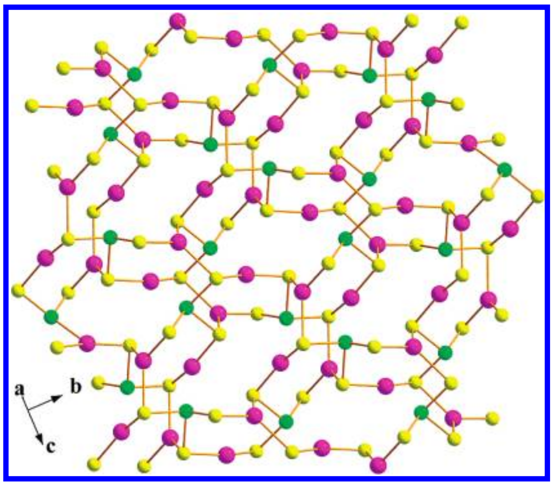

Figure 6. Linkage of the left- and right-handed helical chains by the arsenic atoms to form the [Ag$_2$AsS$_3$]$^-$ layer: Ag, pink; As, green; S, yellow.

one AgS$_2$, and one AgS$_3$ moiety (Figure 4). The Ag(1) atom is a nearly linear coordinated by two sulfur atoms with the Ag−S bond distances of 2.414(9) and 2.452(9) Å and an S(1)−Ag(1)−S(3) angle of 155.9(4)° whereas Ag(2) is a nearly trigonal planar environment of three sulfur atoms with the Ag−S bond distances ranging from 2.476(10) to 2.591(10) Å and S−Ag−S angles between 113.5(3) and 124.7(3)°.

Distinctively, a helical [Ag$_2$S$_3$]$^{4-}$ chain is created that follows the 2$_1$ screw axis by vertex-linking of the AgS$_2$ and AgS$_3$ units (Figure 5). The left- and right-handed helical chains are above and below and strictly alternating due to the *c*-glide symmetry. And these helical chains are connected by the arsenic atoms to form the [Ag$_2$AsS$_3$]$^-$ layer (Figure 6). The coordination sphere of the arsenic atom consists of three As−S bonds (2.213(9)−2.278(9) Å) completed by a longer As(1)−Ag(1) contact of 2.834(4) Å. The latter may be responsible for a slight distortion of the linear AgS$_2$ coordination mode. Within the anionic layer, the interchain Ag(1)−Ag(2) distances of 3.037(5) and 3.298(5) Å are considerably longer than the Ag−Ag separation of 2.89 Å in elemental Ag. Thus, no bonding d^{10}−d^{10} interactions can be expected.

It is noteworthy that the anionic framework of compound **4** has the same stoichiometry of anions found in RCu$_2$SbS$_3$[17] (R = amine), [C$_2$N$_2$H$_8$]$_{0.5}$[Cu$_2$SbSe$_3$],[18] [C$_2$N$_2$H$_9$][Ag$_2$SbS$_3$],[6] KAg$_2$SbS$_3$,[12] and KCu$_2$AsS$_3$[19] but very different structures due to the presence of diverse primary building units. The only crystallographically independent Cs$^+$ cation in **4** is 8-fold-coordinated by S atoms (3.432(9)−3.760(10) Å) and forms an irregular coordination polyhedron.

Mineralizer Effect. A range of chalcogenometalates containing silver have been prepared under organic amine and supercritical ammonia conditions.[6−9,20] To synthesize new compositions, however, the addition of suitable mineralizer is often necessary to aid in the discovery of these compositions and to prepare compounds exhibiting novel structure types. In our laboratory, we found that thiophenol can dissolve silver sulfide under amine alkaline conditions. This thiophenol content is possibly beneficial to the formation of chalcogenides containing transition metal silver as thiophenol can act as a mineralizer when present in only reactant quantities. In the syntheses of **1**, **2** and **3**, our research showed that

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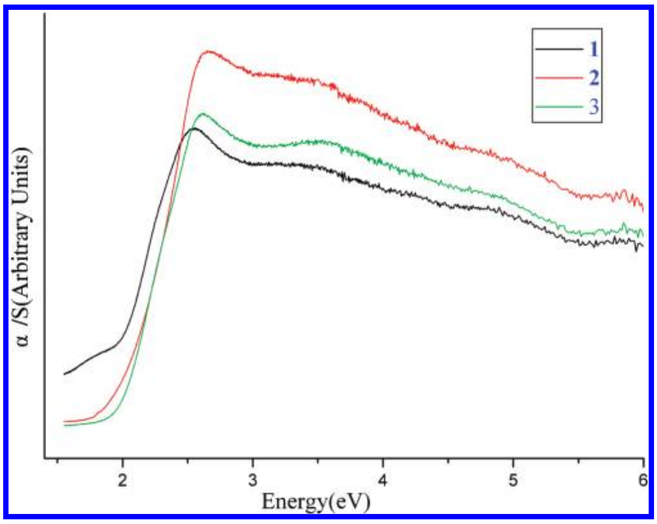

Figure 7. UV−vis spectra of **1**−**3**.

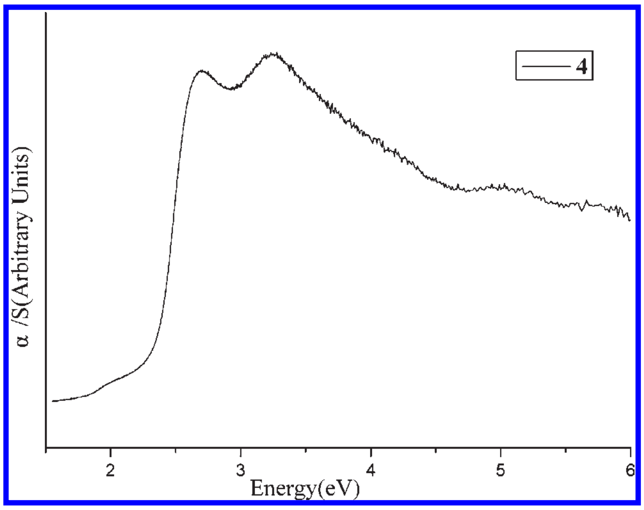

Figure 8. UV−vis spectra of compound **4**.

thiophenol is essential for the synthesis due to thiophenol appears to act as a mineralizer, not simply as a solvent; otherwise, products will not be obtained. We attempted to use $HSCH_2CH(SH)CH_2OH$ instead of thiophenol to serve as a mineralizer, but a large quantity of silver sulfide were formed probably due to hydrogenosulfide (HS^-) fall off under higher temperature. Since the solvothermal reactions were carried out for the synthesis of **4**, and we have failed to carry out the same reactions with $AgNO_3$, $AgSO_4$, and AgSCN in place of AgSPh, we believe that PhS^- groups play a mineralizing role.

Optical Properties and Thermal Analyses. The thermal behavior of **1**, **2**, **3**, and **4** was investigated by DSC−TGA under a flow of nitrogen (40 mL/min) from 50 to 550 °C at a heating rate of 10 °C/min. The results of **1**, **2**, **3**, and **4** show endothermic melting transition centered approximately at 413, 446, 423, and 372 °C, respectively, and without weight loss. A second heating and cooling cycle for all four compounds showed no transitions up to 500 °C, and the X−ray powder patterns confirmed that the residues of these compounds were amorphous. The UV−vis reflectance spectroscopy measurements on **1**, **2**, **3**, and **4** confirmed that they are wide−bandgap semiconductors. The optical absorption spectrum of **1**, **2**, and **3** exhibit steep absorption edges, revealing the same optical bandgaps of 2.0 eV (Figure 7). The spectrum of **4** shows a absorption edge with a corresponding bandgap of 2.7 eV (Figure 8). These intense absorption are probably due to charge−transfer transitions from a primarily sulfur−based filled valence band to a mainly silver−based empty conduction band.

Conclusion

In summary, three open framework silver−thioantimonates and one layered silver−thioarsenate have been obtained by the solventothermal reactions and contain two types of infinite silver−sulfur chains. In compounds **1**−**3**, four of the $[Ag_9S_{12}]^{15-}$ chains are connected to one another by the antimony atoms to form a square channel in which the alkali metal cations reside, but the radii of alkali metal cations do not affect the size of channel. Compound **4** possesses left- and right-handed helical $[Ag_2S_3]^{4-}$ chains, and these chains are linked by the arsenic atoms to generate an anionic layer.

In the syntheses of **1**−**4**, thiophenol serves as a mineralizing agent to avoid the forming of silver sulfide under amine alkaline conditions. This offers a new possible protocol for other main-group metals to construct diverse new quaternary chalcogenides containing transition metal silver. Further investigations on such systems may also yield a series of chalcogenide materials with interesting features and useful properties.

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Supporting Information Available: DSC curves and CIF. This material is available free of charge via the Internet at http://pubs.acs.org. CSD 420840, 421090, 420841, and 421091 contain the supplementary crystallographic data for **1**, **2**, **3**, and **4**, respectively.