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$K_2Ag_6Sn_3S_{10}$: A Quaternary Sulfide Composed of Silver Sulfide Layers Pillared by Zigzag Chains ${}^{1}_{\infty}[SnS_3]^{2-}$

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A novel framework $K_2Ag_6Sn_3S_{10}$ was synthesized solvothermally and characterized by single-crystal diffraction. The framework comprises ${}^{2}_{\infty}[Ag_6SnS_4]^{2+}$ cationic layers pillared by ${}^{1}_{\infty}[SnS_3]^{2-}$ zigzag chains formed by vertex-sharing SnS_4 tetrahedra, and potassium ions are located in 1D channels. This compound crystallizes in the orthorhombic *Pbcn* space group with $a = 24.0201(2)$ Å, $b = 6.4017(3)$ Å, $c = 13.3056(4)$ Å, $Z = 4$. Its thermal and optical properties are studied.

Chalcogenides possess a very diverse and interesting structural chemistry, and exhibit useful physical and chemical properties which are promising for applications in modern technologies.[1] In recent years, the syntheses of binary and ternary chalcogenides have been extensively investigated using high-temperature solid state, intermediate-temperature flux, and low-temperature solvothermal techiques, but relatively little is known about quaternary chalcogenides which may also exhibit interesting properties.[2−5] Syntheses of new quaternary chalcogenides are becoming an active area of solid state chemistry.[2,4,5] Up to now most known quaternary chalcogenides are prepared using the molten alkali-metal polychalcogenide flux technique; however, low-temperature solvo(hydro)thermal reactions have produced a limited number of quaternary chalcogenides.[6] In principle, the mild solvothermal technique is especially suitable for synthesis of new solids. With an aim to synthesize new quaternary chalcogenides, we began systematically solvothermal syntheses of tin- and germanium-containing quaternary chalcogenides due to their considerable potentiality to form interesting new structures,which may result from Ge and Sn unique or flexible coordination behavior (e.g., 4 for Ge; 4, 5, 6 for Sn) and various condensation ways of thiostannate and thiogermanate anions by edge or vertex sharing.[7−12] In this publication, we report the preparation, crystal structure, and optical and thermal properties of $K_2Ag_6Sn_3S_{10}$. This novel framework $K_2Ag_6Sn_3S_{10}$ comprises silver-rich cationic layers ${}^{2}_{\infty}[Ag_6SnS_4]^{2+}$ pillared by ${}^{1}_{\infty}[SnS_3]^{2-}$ zigzag chains.

The synthesis of $K_2Ag_6Sn_3S_{10}$ was as follows: 0.010 g of Sn, 0.045 g of $AgNO_3$, 0.089 g of K_2CO_3, and 0.012 g of sulfur were put into a glass tube, to which 0.4 mL of an ethanol/$HSCH_2CH(SH)CH_2OH$ mixed solvent with volume ratio ethanol/$HSCH_2CH(SH)CH_2OH$ = 3:1 was added. The glass tube was sealed (reagents filled about 10% of the tube), placed into a Teflon-lined stainless steel autoclave, and heated at 120 °C for 5 days. The products were washed with ethanol and water, respectively, and dark-red needlelike crystals were obtained in 70% yield based on silver. At ambient temperature this compound does not dissolve in water and common polar organic solvents such as alcohols and pyridine. EDS indicated the presence of four elements, K, Ag, Sn, S with a ratio of 2.0:6.3:3.2:10.1, which is very close to the chemical formula determined by the single-crystal diffraction. Our research showed that the presence of $HSCH_2CH(SH)CH_2OH$ is essential for the synthesis; otherwise silver sulfide will form, and $K_2Ag_6Sn_3S_{10}$ will not be obtained. $HSCH_2CH(SH)CH_2OH$ appears to serve as a mineralizer in the synthesis, not simply as a solvent; $HSCH_2CH(SH)CH_2OH$ is a chelating agent, which can form a stable and soluble chelate with Ag^+ under alkaline conditions. By the above method, pure $K_2Ag_6Sn_3S_{10}$ was obtained.

A single crystal with dimensions of $0.45 \times 0.08 \times 0.04$ mm^3 was used in the diffraction measurements on a Rigaku RAXIS-RAPID diffractometer equipped with graphite monochromatized Mo Kα radiation. The diffraction data were collected at room temperature by the ω-scan method. The θ range for data collection was from 1.70° to 27.45°. A total of 1604 reflections ($0 \le h \le 31$, $0 \le k \le 4$, $0 \le l \le 17$)

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $K_2Ag_6Sn_3S_{10}$

AgS_4 tetrahedra		AgS_3 trigonal pyramids		SnS_4 tetrahedra	
Ag(1)−S(1)	2.511(2)	Ag(2)−S(3)	2.473(3)	Sn(1)−S(1)	2.321(2)
Ag(1)−S(3)	2.468(3)	Ag(2)−S(4)	2.595(3)	Sn(1)−S(2)	2.437(3)
Ag(1)−S(4)	2.741(3)	Ag(2)−S(5)	2.545(3)	Sn(1)−S(2)	2.443(2)
Ag(1)−S(5)	2.643(5)	Ag(3)−S(3)	2.650(3)	Sn(1)−S(4)	2.377(2)
		Ag(3)−S(4)	2.467(3)	Sn(2)−S(3)	2.401(3)
		Ag(3)−S(5)	2.476(3)	Sn(2)−S(3)	2.402(3)
				Sn(2)−S(5)	2.381(3)
				Sn(2)−S(5)	2.381(3)
S−Ag−S	92.93(8)−129.91(8)	S−Ag−S	146.57(8)−102.60(9)	S−Sn−S	98.33(8)−117.07(8)

were collected which give 1604 unique reflections, and 1269 observed reflections ($I > 2\sigma(I)$). An absorption correction was performed using a program described by Higashi.[13] The crystal structure was solved by SHELXS-97 and refined by SHELXL-97.[14,15] Selected bond lengths and angles of $K_2Ag_6Sn_3S_{10}$ are listed in Table 1.

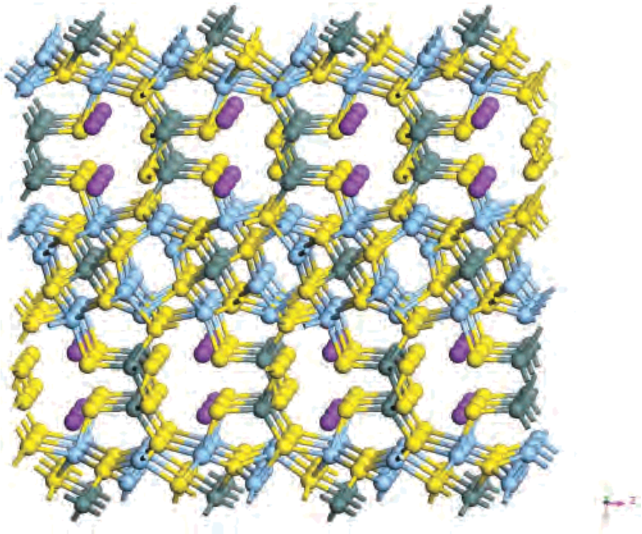

Figure 1. View down [010] of $K_2Ag_6Sn_3S_{10}$ showing 1D channels, and connection of cationic layers ${}^{2}_{\infty}[Ag_6SnS_4]^{2+}$ by zigzag chain ${}^{1}_{\infty}[SnS_3]^{2-}$: yellow, S; purple, K; blue, Ag; gray, Sn.

The material contains cationic layers ${}^{2}_{\infty}[Ag_6SnS_4]^{2-}$, into which Sn^{4+} ions are incorporated, and coordinated tetrahedrally by sulfur atoms with Sn−S bond lengths ranging from 2.381(3) to 2.401(3) Å and S−Sn−S angles between 107.68(8)° and 111.65(8)°; Ag ions are coordinated tetrahedrally and trigonal pyramidally by sulfur atoms, respectively (Figure 1). AgS_4 units are seriously distorted tetrahedra with Ag−S bond lengths ranging from 2.468(3) to 2.741(3) Å and S−Ag−S angles between 92.93(9)° and 129.91(8)°; AgS_3 trigonal pyramids are also distorted with Ag−S bond lengths ranging from 2.467(3) to 2.650(3) Å, and S−Ag−S angles between 102.60(9)° and 146.57(8)°. S atoms in the layers are coordinated tetrahedrally by Ag or Sn atoms; the angles of Ag−S−Ag (or Sn) vary from 95.93(9)° to 120.66(7)°. Interestingly the layers are connected further by ${}^{1}_{\infty}[SnS_3]^{2-}$ single zigzag chains to a novel framework, and each tetrahedron of SnS_4 in the chains is distorted with Sn−S bond lengths ranging from 2.321(2) to 2.443(2) Å and S−Sn−S angles between 98.33(8)° and 117.07(8)°, and shares two S atoms with Ag ions in a layer. These bridging S atoms connect with one or three silver atoms, respectively. This novel pillaring results in two types of 1D channels along the *b* axis, and all potassium ions are arranged in columns in the larger 1D channels, as depicted in Figure 1. In known synthetic quaternary chalcogenides, thioanionic clusters of main group metals are usually found to be linked by transition metal ions; however, the case of transition metal thio-cationic layers to be linked by main group thio-anions is very rare. Silver sulfide layers are never found in known quaternary silver-containing chalcogenides, in which silver ions usually exist in the form of isolated Ag^+ or uncommon Ag_2^{2+}, acting as a "binder" of the thio-anionic clusters.[11,16,17] Recently the interconnection of single chains into single layers was reported for synthetic gallate $Sr_3Ga_4O_9$,[18] but to our knowledge this unusual pillared layer structure has never been observed in chalcogenides prior to this work.

The thermal stability of this compound was investigated by DSC−TGA and powder XRD. DSC−TG analyses were carried out in nitrogen with a heating rate of 10 °C/min. The results show only one sharp endothermic transition at 519 °C with a very small weight loss. The powder XRD confirmed that an amorphous phase forms after this thermal transition. The title compound was also characterized by UV−vis reflectance spectroscopy. The reflectance data were converted to the adsorption data using the Kubelka−Munk functions.[19] The absorption spectrum shows a steep absorption edge from which a band gap of 1.8 eV was derived; therefore the compound is a narrow-gap semiconductor.

In conclusion, $K_2Ag_6Sn_3S_{10}$ possesses a new and unusual structure. The successful synthesis of $K_2Ag_6Sn_3S_{10}$ suggests the possibility of synthesizing more new quaternary chalcogenides by the solvothermal method.

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Supporting Information Available: One X-ray crystallographic file in CIF format, DSC−TG curves, and UV−vis reflectance spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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