Inorg. Chem. **2003**, *42*, 4248–4249

Inorganic Chemistry

Communication

A Solvothermal Synthesis and the Structure of $K_4Ag_2Sn_3S_9 \cdot 2KOH$

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Received February 19, 2003

A novel layered $K_4Ag_2Sn_3S_9 \cdot 2KOH$ was synthesized solvothermally. A mixture of ethanol and $HSCH_2CH(SH)CH_2OH$ was used for the synthesis. The $HSCH_2CH(SH)CH_2OH$ plays an important role and appears to serve as a mineralizer for the solvothermal reaction. A layer comprises $Sn_3S_9^{6-}$ clusters linked by Ag^+ ions and possesses two types of 1D channels in which potassium ions are located. The compound crystallizes in the monoclinic $P2(1)/m$ space group [$a = 7.8071(2)$ Å, $b = 27.3508(1)$ Å, $c = 10.5008(2)$ Å, $\alpha = 90°$, $\beta = 103.874(1)°$, $\gamma = 90°$, $Z = 4$]. Its crystal structure, composition analysis, and IR are presented.

Novel framework structures capable of occluding inorganic guests are of interest for their potential for molecular sieving, catalysis, ion exchange, and ion conduction. By building upon experience with the hydrothermal synthesis of zeolites,[1,2] the compositional and structural range of materials capable of forming open frameworks has increased greatly over the past decade. For example, metal chalcogenide framework materials can be prepared with a variety of inorganic and organic structure directing cations.[3−5] Thioanionic clusters are often found to serve as structural building units in these metal−chalcogenide open-framework materials; these clusters usually go through self-condensation or are connected by transition metal ions from solution to form frameworks.[6−13] Because less soluble transition metal chalcogenides prefer to form during the synthesis by the solution route, it is usually difficult to synthesize quaternary chalcogenides, or to obtain pure phases of these compounds even if they could be synthesized.[14,15] Therefore the number of known synthetic quaternary chalcogenides is surprisingly small.

With an aim to synthesize new quaternary chalcogenides, we have developed a mild synthetic route to these types of chalcogenides. In this publication we report a novel solvothermal synthesis of layered $K_4Ag_2Sn_3S_9 \cdot 2KOH$ in the presence of chelating agent $HSCH_2CH(SH)CH_2OH$. This novel layered compound $K_4Ag_2Sn_3S_9 \cdot 2KOH$ comprises tin sulfide clusters $Sn_3S_9^{6-}$ linked by Ag^+ ions.

The synthesis of $K_4Ag_2Sn_3S_9 \cdot 2KOH$ was as follows: 0.026 g of Sn, 0.015 g of $AgNO_3$, 0.089 g of K_2CO_3, and 0.017 g of sulfur were put into a glass tube, to which 0.4 mL of ethanol/ $HSCH_2CH(SH)CH_2OH$ mixed solvent with volume ratio ethanol/$HSCH_2CH(SH)CH_2OH$ = 2:1 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 yellowish chunky crystals were obtained. At ambient temperature this compound does not dissolve in water and some polar organic solvents such as alcohols and pyridine. A composition analysis by an energy-dispersive spectrum collected by scanning electron microscope indicated the presence of K, Ag, Sn, and S in a 5.3:2.0:2.9:8.3 molar ratio, which is consistent with that expected from the following crystal structure determination. Our research showed that the presence of $HSCH_2CH(SH)CH_2OH$ is essential for the synthesis; otherwise silver sulfide will always form, and $K_4Ag_2Sn_3S_9 \cdot 2KOH$ will not be obtained. $HSCH_2CH(SH)CH_2OH$ appears to serve as a mineralizer in this solvothermal synthesis, not

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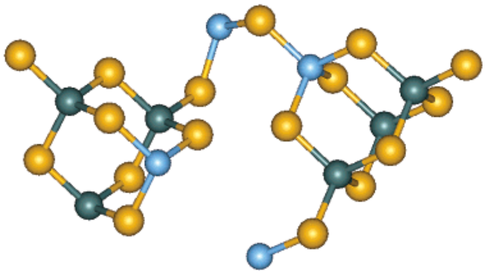

Figure 1. Geometric details of coordination about Sn and Ag in $K_4Ag_2Sn_3S_9 \cdot 2KOH$: Ag, blue ball; Sn, gray ball; S, yellow ball.

Table 1. Crystal Data for $K_4Ag_2Sn_3S_9 \cdot 2KOH^a$

empirical formula	$K_4Ag_2Sn_3S_9 \cdot 2KOH$	Z	4
space group	$P2(1)/m$ (No. 11)	V	2176.82 Å^3
unit cell		fw	1128.97
a	7.8071(2) Å	wavelength	0.71073 Å
b	27.3508(11) Å	density (calcd)	3.445 g/cm^{-3}
c	10.5008(2) Å	abs coeff	7.167 mm^{-1}
α	90°	R	0.0359
β	103.874(11)°	R_w	0.0854
γ	90°	R (all data)	0.0426
		R_w (all data)	0.0873

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (0.0292P)^2 + 18.3310P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $K_4Ag_2Sn_3S_9 \cdot 2KOH$

AgS_4 tetrahedra		AgS_3		SnS_4 tetrahedra	
Ag(2)−S(7)	2.5634(1)	Ag(1)−S(1)	2.4433(1)	Sn(1)−S(3)	2.3296(1)
Ag(2)−S(5)	2.5859(1)	Ag(1)−S(6)	2.5333(1)	Sn(1)−S(6)	2.3580(1)
Ag(2)−S(4)	2.5958(1)	Ag(1)−S(4)	2.5347(1)	Sn(1)−S(2)	2.4085(1)
Ag(2)−S(3)	2.6724(1)	Ag(1)−S(4)		Sn(1)−S(9)	2.4660(1)
S−Ag−S	95.85(5)−118.69(6)	S−Ag−S	101.74(5)−128.91(6)	S−Sn−S	95.85(5)−118.16(6)

simply as a solvent, because $HSCH_2CH(SH)CH_2OH$ is a chelating agent, which can form stable and soluble chelates with heavy metals such as silver and mercury under the alkaline conditions. By the above method, a pure $K_4Ag_2Sn_3S_9 \cdot 2KOH$ was obtained.

A 0.37 × 0.35 × 0.22 mm^3 specimen 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 crystal structure was solved by SHELXS-97 and refined by SHELXS-97. An absorption correction was performed using a program described by Higashi.[16] The crystal data are listed in Tables 1 and 2.

The material contains $AgSn_3S_9^{5-}$ adamantane-like clusters, in which the tetrahedral SnS_4 and AgS_4 are distorted to different extents in comparison with regular tetrahedra. The adamantane-like clusters are connected by 3-coordinated Ag cations to form a layered network (Figure 1). Interestingly the layer has a hollow structure in which two types of 1D channels along the [101] direction exist (Figure 2). Some potassium ions are in these two 1D channels. These layers are perpendicular to the b axis with an interlayer distance $b/2$. All of the OH^- and the rest of the K^+ ions are located between the layers. The OH^- ions occupy two different crystallographic sites; these can also be confirmed by IR spectroscopy. An IR spectrum of $K_4Ag_2Sn_3S_9 \cdot 2KOH$ has two sharp adsorption peaks due to OH stretching modes at 3514 and 3356 cm^{-1}, respectively. It means that these two types of OH^- have very different O−H bond lengths which are usually difficult to obtained from crystallographic data because of the very small scattering factor of the hydrogen atom. From the IR results we can conclude that the bond lengths of O−H are larger than those in gaseous alkali hydroxide molecules or matrix-isolated alkali hydroxide, in which the IR adsorptions of OH are usually near 3600 cm^{-1}.[17,18] The structure of this material is unique, and not reported previously.

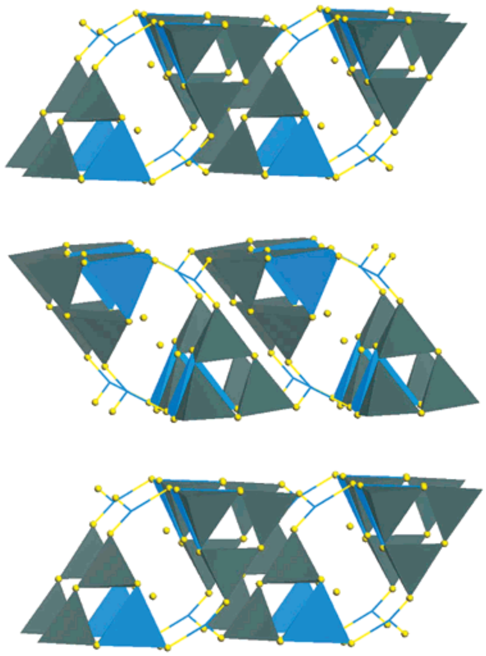

Figure 2. View down [101] of the layered $K_4Ag_2Sn_3S_9 \cdot 2KOH$ showing the layer with 1D channels, and connection of clusters $Sn_3S_9^{6-}$ by two types of Ag^+ ions: AgS_4, blue; SnS_4, gray; S, yellow.

In conclusion, we have shown that $HSCH_2CH(SH)CH_2OH$ is a very effective mineralizer for solvothermal synthesis of $K_4Ag_2Sn_3S_9 \cdot 2KOH$. It forms a stable and soluble chelate with Ag^+ under alkaline conditions. The successful synthesis of $K_4Ag_2Sn_3S_9 \cdot 2KOH$ suggests the possibility of synthesizing new quaternary chalcogenides, subsequently obtaining new chalcogenide materials by this novel method.

Acknowledgment. We thank the National Science Foundation of China for supporting this work (20071006).

Note Added after ASAP Posting: Due to a production error, the word adamantane was misspelled once in the version of this Communication posted on June 12, 2003. It is correctly spelled in the version posted on June 19, 2003.

Supporting Information Available: One X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034186P

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