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A Solvothermal Synthesis and the Structure of $(NH_4)_2Ag_6Sn_3S_{10}$

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A novel framework, $(NH_4)_2Ag_6Sn_3S_{10}$, was synthesized solvothermally and characterized by single-crystal X-ray diffraction. The framework comprises silver-rich cationic layers, $[Ag_6SnS_4]^{2+}$, pillared by $[SnS_3]^{2-}$ zigzag chains formed by vertex-sharing SnS_4 tetrahedra; NH_4^+ ions are located in 1D channels.

During the past few years, solvo- or hydrothermal techniques have been successfully applied to the syntheses of new and fascinating multinary chalcogenides. The new compounds show interesting structural features as well as physical properties,[1–3] such as semiconductors, photoconductivity, catalysis, and ion-exchange capability. Recently, two types of polythiostanntes with $[Sn_3S_7]^{2-}$[4–8] and $[Sn_4S_9]^{2-}$[8–11] were synthesized by a hydrothermal reaction using Sn or SnS_2 and S_8 as reactants and amine or tetraalkylammonium hydroxide as mineralizers. The dimeric anion $[Sn_2S_6]^{4-}$ is a precursor of $[Sn_3S_7]^{2-}$, which can be obtained from an aqueous solution of $[Sn_2S_6]^{4-}$ simply by precisely controlling the pH through bubbling CO_2 into the motherliquor.[6,8] The dimeric anion is the predominant tin-contaning species in synthetic systems of Sn/S/amine and a basic building block for the SnS-*n* framework.[8]

One of the active studies in solid-state chemistry is to prepare new chalcogenides at relatively low temperature. Our approach to this problem is to use $HSCH_2CH(SH)CH_2OH$ as a reaction mineralizer. We have been extending this idea to prepare a number of quaternary chalcogenides.[12–15] Recently, although we successfully synthesized $K_2Ag_6Sn_3S_{10}$,[14] the analogues of smaller Na^+ and larger Rb^+ could not be obtained under the same reaction conditions. It can be concluded the size of the template's ionic radius is one of the most important factors in solvothermal synthesis. Our study was to determine whether NH_4^+ can template the same tin sulfide open-framework as K^+,[14] because the K^+ and the NH_4^+ ionic radii are very similar. Here, we report on the preparation, crystal structure and thermal properties of $(NH_4)_2Ag_6Sn_3S_{10}$. This novel framework, $(NH_4)_2Ag_6Sn_3S_{10}$, comprises silver-rich cationic layers of $[Ag_6SnS_4]^{2+}$ pillared by $[SnS_3]^{2-}$ single zigzag chains.

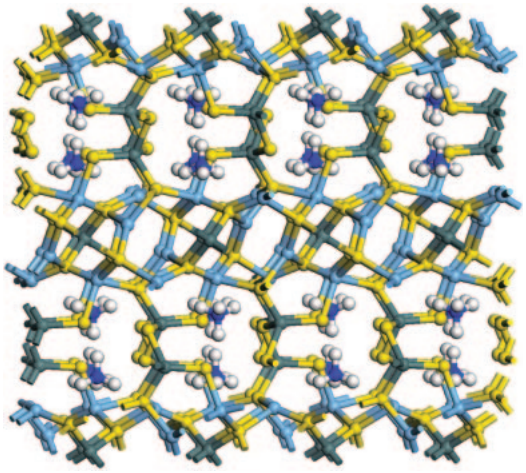

Fig. 1. View down [010] of $(NH_4)_2Ag_6Sn_3S_{10}$ showing 1D channels, and the connection of cationic layers, $[Ag_6SnS_4]^{2+}$, by a zigzag chain, $[SnS_3]^{2-}$. Yellow, S; blue, Ag; white, H; gray, Sn.

EDS indicated the presence of three elements (Ag, Sn, S) with a ratio of 18.47:9.33:28.62, which is close to the chemical formula determined by the single-crystal X-ray diffraction. The material contains cationic layers of $[Ag_6SnS_4]^{2+}$, into which Sn^{4+} ions are incorporated, and coordinated tetrahedrally by sulfur atoms with Sn–S bond lengths ranging from 2.3830(17) Å to 2.4007(17) Å and S–Sn–S angles between 109.12(9)° and 112.80(6)°; Ag ions are coordinated tetrahedrally and trigonal-pyramidally by sulfur atoms, respectively (Fig. 1). AgS_4 units are seriously distorted tetrahedral with the Ag–S bond length ranging from 2.4828(19) Å to 2.7602(19) Å and S–Ag–S angles between 92.38(6)° and 132.88(6)°. AgS_3 trigonal pyramids are also distorted with the Ag–S bond length ranging from 2.4716(19) Å to 2.6471(19) Å and S–Ag–S angles between 100.40(6)° and 147.08(7)°; S atoms in the layers are coordinated tetrahedrally by Ag or Sn atoms. Interestingly, the layers are connected further by $[SnS_3]^{2-}$ single zigzag chains to a novel framework (Fig. 1), and each tetrahedron of SnS_4 in the chains is distorted with the Sn–S bond length ranging from 2.3217(18) Å to 2.4382(18) Å and S–Sn–S angles between 98.80(5)° and 115.93(7)°, 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 NH_4^+ ions are arranged in columns in the large 1D channels, as depicted in Fig. 1. The H atom of NH_4^+ ions occupy two different crystallographic sites, which can be confirmed by IR spectroscopy. The IR spectrum of $(NH_4)_2Ag_6Sn_3S_{10}$ has two different absorption peaks due to NH stretching modes at 3063 and 2902 cm^{-1}, respectively; the peaks at 1617 and 1358 cm^{-1} correspond to the bond-bending frequencies of the different NH bonds, due to the formation of hydrogen bonds (N–H···S); also the absorption peak of the NH stretching frequencies are smaller than these for amines. In known that synthetic quaternary sulfides, 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-

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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.[12,16,17] The thermal behaviors of the title compound were measured between temperatures of 30 and 610 °C by the DSC-TGA method under nitrogen. The compound is decomposed at 280 °C, accompanied by one endothermic peak in the DSC curve. The corresponding loss of 4.3% is in accordance with the complete mass loss of two NH_3 and H_2S (Calcd: 4.7%). The second mass loss of 7.1% (Calcd: 7.5%) is attributed to a partial loss of sulfide species at 609 °C, accompanied by one endothermic peak in the DSC curve. The residue is a mixture of SnS and Ag_2S; the formation of SnS may be explained by the reduction of Sn(IV) to Sn(II) accompanied by the oxidation of S(-II) to S(-I).[18]

Experimental

Preparation. The synthesis of $(NH_4)_2Ag_6Sn_3S_{10}$ was as follows: 0.023 g of Sn, 0.033 g of $AgNO_3$, 0.126 g of $(NH_4)_2CO_3$, and 0.025 g of sulfur were put into a glass tube, to which 0.5 mL of a mixed solvent with a volume ratio of pyridine/$HSCH_2CH(SH)CH_2OH$ = 2:1 was added. The glass tube was sealed, placed into a Teflon-lined stainless steel autoclave, and heated at 120 °C for 7 days. The products were washed with ethanol and water, respectively, and dark-red needlelike crystals were obtained. At ambient temperature this compound did not dissolve in water and common polar organic solvents, such as alcohols and pyridine.

X-ray Crystallography. A single crystal with dimensions of $0.2 \times 0.15 \times 0.10$ mm^3 was used in diffraction measurements on a Rigaku RAXIS-RAPID diffractometer equipped with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The diffraction data were collected at room temperature by the ω-scan method. The θ range for data collection was from 3.04° to 28.26°. A total of 2950 reflections were collected, which gave 2451 unique reflections, and 2266 observed reflections [$I > 2\sigma(I)$]. An absorption correction was performed using a program described by Higashi.[19] The crystal structure was solved by SHELXS-97 and refined by SHELXTL-97. The crystallographic parameters are as follows: MW = 1360.07, crystal system orthorhombic, space group *Pbcn*, $a = 23.8579(13)$ Å, $b = 6.4875(4)$ Å, $c = 13.3992(7)$ Å, $V = 2073.9(2)$ Å^3, $Z = 4$, μ(Mo Kα) = 10.078 mm^{-1}, $R = 0.0477$, $Rw = 0.1265$, for all reflections $R = 0.0513$ and $Rw = 0.1301$. Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-415212.

Measurements. IR spectra were recorded with a Nicolet Avatar 360 spectrometer in dry KBr pellets. Differential scanning calorimetry (DSC) and thermogravimetry (TG) analyses were conducted on a Metter Toledo TGA/SDTA851 and DSC/822 System. The samples were heated under a nitrogen stream of 40 mL/min at a heating rate of 10 °C/min. Energy dispersive spectroscopy (EDS) was made on a JEOL JSM-5600LV scanning electron microscope (SEM).

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20 Selected bond length (Å) and angles (°): S1–Sn2 2.4007(17), S1–Ag3 2.4716(19), S1–Ag1 2.4828(19), S1–Ag2 2.6471(19), Sn1–S3 2.3217(18), Sn1–S5 2.3883(17), Sn1–S4 2.4382(18), Sn2–S2 2.3830(17), Ag1–S3 2.540(2), Ag1–S2 2.6031(18), Ag1–S5 2.7602(19), Ag2–S5 2.4821(18), Ag2–S2 2.4857(18), Ag3–S5 2.569(2), S2–Ag3 2.5785(19), S3–Sn1–S5 114.46(7), S3–Sn1–S4 115.93(7), S5–Sn1–S4 102.09(6), S3–Sn1–S4 111.01(7), S5–Sn1–S4 113.35(7), S4–Sn1–S4 98.80(5), S2–Sn2–S2 109.12(9), S2–Sn2–S1 107.08(6), S2–Sn2–S1 112.80(6), S2–Sn2–S1 112.80(6), S2–Sn2–S1 107.08(6), S1–Sn2–S1 108.05(9), S1–Ag1–S3 120.32(7), S1–Ag1–S2 132.88(6), S3–Ag1–S2 98.66(6), S1–Ag1–S5 92.38(6), S3–Ag1–S5 98.60(6), S2–Ag1–S5 107.85(6), S5–Ag2–S2 147.08(7), S5–Ag2–S1 104.22(6), S2–Ag2–S1 100.40(6), S1–Ag3–S5 130.01(7), S1–Ag3–S2 128.33(7), S5–Ag3–S2 101.39(6).