ELSEVIER

A solvothermal synthesis and characterization of a new open-framework $K_4Ag_2Ge_3S_9 \cdot H_2O$

Yonglin An,[a,]* Ling Ye,[b] Min Ji,[a] Xin Liu,[a] Baiyin Menghe,[a] and Cuiying Jia[a]

[a] *Department of Chemistry, Dalian University of Technology, Dalian 116024, China*
[b] *Key Laboratory for Supramolecular Structure and Materials of the Ministry of Education on Jilin University, Changchun 130023, China*

Abstract

A novel framework $K_4Ag_2Ge_3S_9 \cdot H_2O$ was synthesized solvothermally in the presence of a chelating agent of $HSCH_2CH(SH)CH_2OH$. Its structure was determined by single-crystal X-ray diffractometry. This material crystallizes in the orthorhombic space group $Pna2(1)$ (No. 33) with $a = 14.4524(4)$ Å, $b = 9.6339(3)$ Å, $c = 16.5636(9)$ Å, $z = 4$, $R_1 = 0.0292$, $wR_2 = 0.0624$ for all data. The structure comprises of adamantane-like clusters $[AgGe_3S_9]^{5-}$ linked by $Ag+$ ions to form a open-framework, and potassium ions and water molecules are located in the channels. Its IR and thermal properties were investigated.
© 2004 Elsevier Inc. All rights reserved.

Keywords: Solvothermal synthesis; Quaternary thiogermanate; Framework

1. Introduction

Open-framework chalcogenides are potentially useful materials for separation, ion exchange, catalysis and optical application [1–3]. They can be prepared with a variety of inorganic and organic structure directing cations. In these compounds the thio-anionic clusters are often found to serve as structural building units, which usually go through self-condensation or are connected by transition metal from solution to form frameworks [4–9]. Because the less soluble transition metal chalcogenides prefers to form during the synthesis, it is usually difficult to synthesize quaternary chalcogenides, or to obtain pure phases of the compounds even if they could be synthesized [10,11]. So far, solvo(hydro)thermal reaction have produced many binary and ternary chalcogenides; however, the number of known quaternary chalcogenides prepared via this route is very limited [12].

With an aim to synthesize new quaternary chalcogenides, we have developed a mild synthetic route to these types of chalcogenides [13,14]. In this publication we report a solvothermal synthesis of $K_4Ag_2Ge_3S_9 \cdot H_2O$ in the presence of a chelating agent $HSCH_2CH(SH)CH_2OH$, this new compound have a framework structure consisting of clusters $[AgGe_3S_9]^{5-}$ bridged by 3-coordinated Ag^+ ions, and potassium ions and water molecules reside within the openings of this framework.

2. Experimental

The synthesis of $K_4Ag_2Ge_3S_9 \cdot H_2O$ was carried out as following: 0.0320 g of GeS_2, synthesized according to Maclachlan et al. [15], 0.0090 g of $AgNO_3$ and 0.0650 g of K_2CO_3 were put into a glass tube, to which 0.4 ml of a ethanol/$HSCH_2CH(SH)CH_2OH$ mixed solvent with volume ratio: ethanol/$HSCH_2CH(SH)CH_2OH$ = 2:1 was added, then 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; cubic colorless crystals were obtained with 70% yield based on silver.

*Corresponding author. Tel.: +86-411-8470-7372; fax: +86-411-8470-1400.

E-mail address: ylan@dlut.edu.cn (Y. An).

Powder X-ray diffraction (XRD) was performed using a Shimadzu XRD-6000 diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5418$ Å) and operating at 40 kV and 20 mA.

Energy dispersive spectroscopy (EDS) was made on a JEOL JSM-5600LV scanning electronic microscope. A Mettler Toledo DSC/822 and TGA/SDTA851 system were used to carry out the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in nitrogen with a heating rate of $10°C\,min^{-1}$.

IR spectra were recorded on a Nicolet Avatar 360 spectrometer in a range of temperature from room temperature to 250°C, KBr pellet technique was used.

A crystal with dimension $0.30 \times 0.15 \times 0.11\,mm^3$ was used in the single-crystal diffraction measurements at room temperature on a Rigaku RAXIS_RAPID diffractometer with graphite monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). An absorption correction was performed using the program by Higashi [16]. A total of 2238 reflections were collected, 2238 reflections unique and 2054 reflections with $I>2\sigma(I)$. The structure were solved by the direct method with SHELXS 97 and refined by SHELXTL 97 [17]. All non-hydrogen atomic positions were located in Fourier maps and refined anisotropically based on F^2. 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-412868. Experimental details for the structure determination are presented in Table 1. The final atomic coordinates and the selected bond distances and bond angles are presented in Tables 2 and 3, respectively.

3. Results and discussion

Our research showed that the presence of $HSCH_2CH(SH)CH_2OH$ is essential for the synthesis of $K_4Ag_2Ge_3S_9 \cdot H_2O$, otherwise silver sulfide is always formed, and $K_4Ag_2Ge_3S_9 \cdot H_2O$ cannot be obtained. $HSCH_2CH(SH)CH_2OH$ appears to serve as a mineralizer in this solvothermal synthesis, not simply as a solvent, because $HSCH_2CH(SH)CH_2OH$ can form stable and soluble chelates with silver under alkaline conditions. A pure phase of $K_4Ag_2Ge_3S_9 \cdot H_2O$ was obtained by the above-mentioned method, and it does not dissolve in polar organic solvents such as alcohols and pyridine, but hydrolyzes slightly in water.

A composition analysis by EDS indicates the presence of K, Ag, Ge and S in a 3.6:2.0:3.1:8.5 molar ratio, which is consistent with that expected from the crystal structure analysis.

The thermal properties of $K_4Ag_2Ge_3S_9 \cdot H_2O$ were investigated by DSC-TGA combined with variable

Table 1
Crystal data and structure refinement for $K_4Ag_2Ge_3S_9 \cdot H_2O$

Formula weight	896.47
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $Pna2(1)$
Unit cell dimensions	$a = 12.4524(4)$ Å, $\alpha = 90°$
	$b = 9.6339(3)$ Å, $\beta = 90°$
	$c = 16.5636(9)$ Å, $\gamma = 90°$
Volume	$V = 1987.06$ Å^3
Z, Calculated density	4, 2. 997 Mg m^{-3}
Absorption coefficient	8.189 mm^{-1}
F(0 0 0)	1680
Crystal size	$0.30 \times 0.15 \times 0.11$ mm^3
Theta range for data collection	2.45–27.46°
Limiting. indices	$0 \leqslant h \leqslant 16, 0 \leqslant k \leqslant 12, -21 \leqslant l \leqslant 0$
Reflections collected/unique	2238/2238[R (int) = 0.034]
Completeness to $\theta = 27.46°$	95%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2238/1/167
Goodness-of-fit on F^2	1.152
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0265, wR_2 = 0.0619$
R indices (all data)	$R_1 = 0.0292, wR_2 = 0.0624$
Largest diff. peak and hole	1.768 and -0.872 e Å^{-3}

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $K_4Ag_2Ge_3S_9 \cdot H_2O$

	x	y	z	U_{eq}
Ag(1)	9242(1)	4512(1)	4146(1)	34(1)
Ag(2)	7494(1)	5756(1)	5832(1)	37(1)
Ge(1)	11648(1)	5650(1)	5216(1)	19(1)
Ge(2)	11497(1)	2146(1)	4314(1)	16(1)
Ge(3)	11688(1)	5180(1)	2997(1)	17(1)
S(1)	9946(2)	5993(2)	5334(2)	33(1)
S(2)	7228(1)	4911(2)	4394(1)	20(1)
S(3)	9978(2)	5537(20	2818(2)	30(1)
S(4)	9768(1)	1958(2)	4243(2)	26(1)
S(5)	12098(2)	3396(2)	5361(1)	22(1)
S(6)	12320(1)	4911(2)	4394(1)	20(1)
S(7)	12565(2)	6694(2)	6145(1)	29(1)
S(8)	7356(2)	4027(2)	1090(2)	50(1)
S(9)	12155(2)	2945(2)	3127(2)	21(1)
K(1)	450(2)	7016(2)	1090(2)	50(1)
K(2)	12406(2)	−724(2)	2513(2)	39(1)
K(3)	4952(2)	6574(3)	4127(3)	68(1)
K(4)	5307(2)	7411(3)	7099(2)	64(1)
O(1)	4794(9)	5127(11)	5762(8)	90(3)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

temperature in situ IR and powder XRD. The DSC and TGA results of $K_4Ag_2Ge_3S_9 \cdot H_2O$ show an endothermal transition peaked around 280°C with a corresponding weight loss of 2.8%. This thermal transition is attributed to the dehydration, the higher weight loss than the theoretical value (2.0%) is due to partially hydrolysis of the sulfide during dehydration. A powder XRD study shows the framework collapses to an amorphous material after the dehydration. A series of thermal transitions occur in a range of 320–500°C

Table 3
Bond lengths (Å) and bond angles (°) for $K_4Ag_2Ge_3S_9 \cdot H_2O$

Ag(1)–S(4)	2552(2)
Ag(1)–S(2)	2.570(5)
Ag(1)–S(3)	2.579(3)
Ag(1)–S(1)	2.583(3)
Ag(2)–S(7)	2.513(2)
Ag(2)–S(8)	2.553(2)
Ag(2)–S(2)	2.539(2)
Ge(1)–S(1)	2.154(2)
Ge(1)–S(7)	2.164(2)
Ge(1)–S(5)	2.255(2)
Ge(1)–S(6)	2.273(2)
Ge(2)–S(4)	2.164(2)
Ge(2)–S(2)	2.184(3)
Ge(2)–S(5)	2.240(2)
Ge(2)–S(9)	2.266(2)
Ge(3)–S(3)	2.178(2)
Ge(3)–S(8)	2.200(2)
Ge(3)–S(6)	2.360(2)
Ge(3)–S(9)	2.240(2)
S(2)–Ge(2)	2.184(3)
S(7)–Ag(2)	2.513(2)
S(8)–Ge(3)	2.200(2)
Ag(2)–S(2)–Ag(1)	94.01(7)
Ge(3)–S(9)–Ge(2)	108.44(9)
Ge(1)–S(1)–Ag(1)	100.37(9)
Ge(2)–S(5)–Ge(1)	110.62(9)
Ge(2)–S(2)–Ag(2)	113.70(9)
Ge(3)–S(6)–Ge(1)	110.48(8)
Ge(3)–S(3)–Ge(1)	99.86(9)
Ge(2)–S(4)–Ge(1)	100.25(7)
Ge(1)–S(7)–Ag(2)	106.78(9)

Symmetry transformation used to generate equivalent atoms: #1: $x + 1/2, -y + 3/2, z$; #2: $x + 1, -y + 1, z$; #3: $-x + 1, -y + 1, z - 1/2$; #4: $x - 1/2, -y + 1/2, z$; #5: $x + 1/2, -y + 3/2, z$; #6: $-x + 2, -y + 1, z + 1/2$.

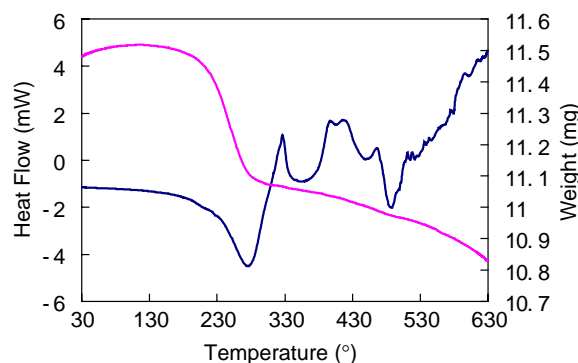

Fig. 1. DSC–TGA curves of $K_4Ag_2Ge_3S_9 \cdot H_2O$.

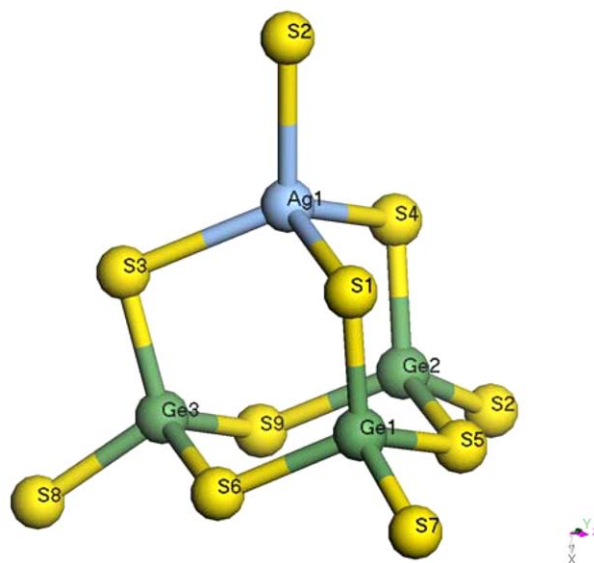Fig. 2. Geometric details of the linkage of GeS_4, AgS_4 and atom labeling in an adamantane-like cluster $[AgGe_3S_9]^{5-}$.

with a smaller weigh loss (Fig. 1), these transitions may be associated with dehydroxylation and sublimation of components in the sample. In situ IR results show the intensity of an absorption at $3258.47\,cm^{-1}$, attributed to water stretching mode, decreases gradually with increasing temperature, and new absorptions at 3740 and $1515\,cm^{-1}$, which are attributed to hydroxyl groups due to the hydrolysis, appear around 75°C, and increase gradually with the increasing temperature.

This structure contains adamantane-like clusters $[AgGe_3S_9]^{5-}$ as building units as shown in Fig. 2. In an adamantane-like cluster $[AgGe_3S_9]^{5-}$, there are three tetrahedrally coordinated Ge atoms, geometries of GeS_4 units are distorted: $Ge(1)S_4$ with Ge–S bond distances ranging from 2.154(2) to 2.273(2) Å, S–Ge–S angles from 103.92(9)° to 112.56(9)°; $Ge(2)S_4$ with Ge–S bond distances from 2.164(2) to 2.266(2) Å, S–Ge–S angles from 102.13(8)° to 118.96(7)°; $Ge(3)S_4$ with Ge–S bond distances from 2.178(2) to 2.240(2) Å, S–Ge–S angles from 101.84(8)° to 114.74(9)°; These tetrahedra share corners each other to form a unique cluster $Ge_3S_9^{6-}$, which share S atoms further with a tetrahedral $Ag(1)S_4$,

whose Ag–S bond distances range from 2.552(2) to 2.583(3) Å, and S–Ag–S angle from 97.30(7)° to 115.18(7)°, to form an adamantane-like cluster $[AgGe_3S_9]^{5-}$. The adamantane-like clusters are linked through $Ge(2)S_4$ sharing S(2) with $Ag(1)S_4$ of adjacent clusters in turn to form a zigzag chain of the clusters along [1 0 0], and these zigzag chains are joined through trigonal pyramidally coordinated Ag(2) ions to a framework as depicted in Figs. 3 and 4, respectively. Each tetrahedron in $[AgGe_3S_9]^{5-}$ shares corners with $Ag(2)S_3$ trigonal pyramids, as a consequence sulfur atoms have two types of coordination by the metal atoms, S(2) is 3-coordinated by Ge(2), Ag(1) and Ag(2) with S(2)–Ge(2) 2.184(3) Å, S(2)–Ag(1) 2.570(5) Å, S(2)–Ag(2) 2.539(2) Å. Except this type of coordination of sulfur atom, sulfur atoms are 2-coordinated by Ge and Ag (or Ge) atoms in the anionic framework. The potassium ions and water molecules are located in the channels. The water molecule is trigonally coordinated
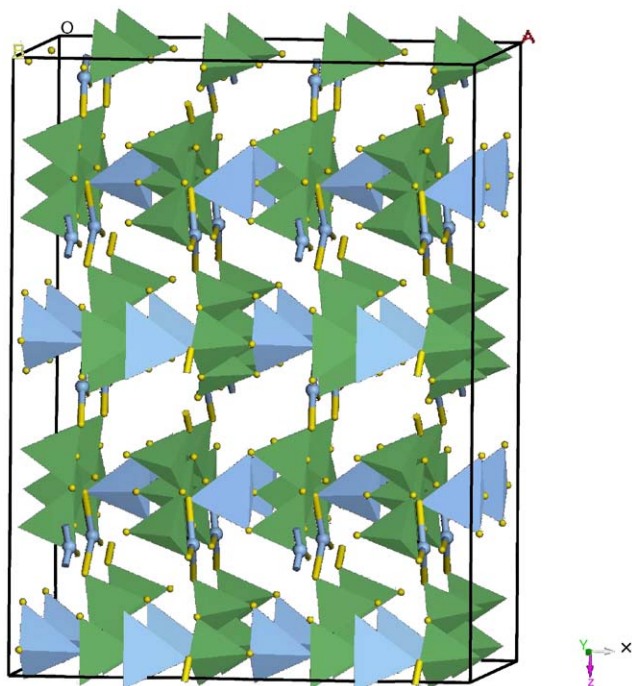
Fig. 3. View down [0 1 0] of the 3D framework of $K_4Ag_2Ge_3S_9 \cdot H_2O$ showing channels running parallel to the b-axis.
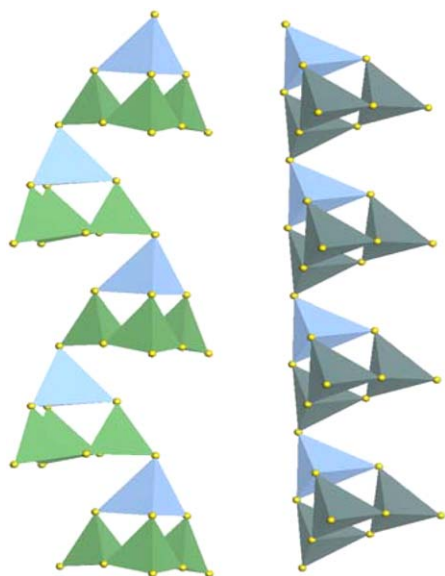
Fig. 4. Comparison between chains of adamantine-like cluster in $K_4Ag_2Ge_3S_9 \cdot H_2O$ (left) and $K_4Ag_2Sn_3S_9 \cdot 2H_2O$ (right). Green, GeS_4; gray, SnS_4; blue, AgS_4; yellow, sulfur.

by potassium ions with bond distances from 3.052 to 3.183 Å.

The adamantane-like building unit $[AgGe_3S_9]^{5-}$ is different with a adamantine-like $Ge_4S_{10}^{4-}$ found in known synthetic quaternary germanium sulfide frameworks [6–8,18,19], the former can be considered as formed by replacing one Ge^{4+} in a $Ge_4S_{10}^{4-}$ by a tetrahedral Ag^+, such a replacement between ions with

significantly different charge implies strong covalent character of the Ag–S and Ge–S bonds which reduce the effect of ionic charge on the substitution. A considerable covalent property of Ge–S bonds also can be reflected from edge-sharing linkage between GeS_4 tetrahedra in some thiogermanates and germanium sulfides [20].

$K_4Ag_2Sn_3S_9 \cdot 2H_2O$ [13], which was incorrectly reported as $K_4Ag_2Sn_3S_9 \cdot 2KOH$, also contains adamantane-like clusters $[AgSn_3S_9]^{5-}$ as building units, possesses a double-layered structure. A double layer also comprises of adamantine-like clusters chains, in which the linkage of the cluster is the same as that in $K_4Ag_2Ge_3S_9 \cdot H_2O$ except a straight chain of clusters in the compound instead of a zigzag one in the title compound due to different orientation of the clusters as shown in Fig. 4. The nearest chains alternate with opposite apical directions of the tetrahedra to form a double row of the chains, which are cross-linked by trigonal pyramidally coordinated Ag^+ to a double layer. From above structural discussion, it can be seen that the difference of these two structures are only due to different orientation of clusters, which results in the zigzag chains in the title compound, and straight chains in the Sn analogue. The transition from a layered structure to a framework structure of quaternary chalcogenide are observed in other systems, usually the transition derives from the counterions effect, and involves changes of linkage or coordination environment of anionic framework [21]. The interesting structural transition reported here results from the different orientation of building units.

4. Conclusion

We have shown that $HSCH_2CH(SH)CH_2OH$ is very effective mineralizer for the solvothermal synthesis of $K_4Ag_2Ge_3S_9 \cdot H_2O$. This method appears to be of general utility, the successful synthesis of a novel framework $K_4Ag_2Ge_3S_9 \cdot H_2O$ suggests the possibility of accessing more new chalcogenides materials by variations of chelating agents, counterions, transition—and main-group metals.

References

[1] R.L. Bedard, L.D. Vail, S.T. Wilson, E.M. Flanigen, US Patent 4,880,761,1989.

[2] R.L. Bedard, L.D. Vail, S.T. Wilson, E.M. Flanigen, US Patent 4,933,068,1990.

[3] J.B. Parise, Y. Ko, J. Rijssenbeck, D.M. Nellis, K. Tan, S. Koch, J. Chem. Soc. Chem. Commun. (1994) 527.

[4] D.M. Nellis, K. Tan, Y. Ko, S. Koch, J.B. Parise, J. Chem. Soc. Chem. Commun. (1995) 541.

[5] J.Y. Pivan, O. Achak, M. Louer, D. Louer, Chem. Mater. 6 (1994) 827.

[6] J.B. Parise, K. Tan, J. Chem. Soc. Chem. Commun. (1996) 1687.

[7] O.M. Yaghi, Z. Sun, A. Richardson, T.L. Groy, J. Am. Chem. Soc. 116 (1994) 807.

[8] K. Tan, A. Darovsky, J.B. Parise, J. Am. Chem. Soc. 117 (1995) 7039.

[9] K. Tan, Y. Ko, J.B. Parise, A. Darovsky, Chem. Mater. 8 (1996) 448.

[10] G.L. Schimek, W.T. Pennington, P.T. Wood, J.W. Kolis, J. Solid State Chem. 123 (1996) 277.

[11] J.H. Liao, M.G. Kanatzadis, Chem. Mater. 5 (1993) 1561.

[12] W.S. Sheldrick, M. Wachhold, Coord. Chem. Rev. 176 (1998) 211.

[13] Y. An, M. Ji, M. Baiyin, X. Liu, C. Jia, D. Wang, Inorg. Chem. 42 (2003) 4248.

[14] Y. An, M. Baiyin, X. Liu, M. Ji, C. Jia, G. Ning, Inog. Chem. Commun. 7 (2004) 114.

[15] M.J. Maclachlan, S. Petrov, R.L. Bedard, I. Manners, G.A. Ozin, Angew. Chem. Int. Ed. Engl. 37 (1998) 2076.

[16] T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan, 1995.

[17] (a) G.M. Sheldrick, SHELXS97, Program for Crystal Structure Determination, University of Gottingen, Germany, 1997;
(b) G.M. Sheldrick, SHELXTL97, Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.

[18] C.L. Bowes, A.J. Lough, A. Malek, G.A. Ozin, S. Petrov, D. Young, Chem. Ber. 129 (1996) 283.

[19] C.L. Bowes, W.U. Huynh, S.J. Kirkby, A. Malek, G.A. Ozin, S. Petrov, M. Twardowski, D. Young, Chem. Mater. 8 (1996) 2147.

[20] G. Dittmar, H. Schafer, Acta Crystallogr. B31 (1975) 2060.

[21] G.A. Marking, J.A. Hanko, M.G. Kanatzidis, Chem. Mater. 10 (1998) 1191.