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Crystal structure of the Ag_2SiS_3 compound

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ABSTRACT

The crystal structure of the ternary compound Ag_2SiS_3 was determined on the basis of X-ray powder diffraction. The compound belongs to a new structure type, space group $P2_1/c$, $a = 0.66709(1)$, $b = 0.66567(2)$, $c = 1.31748(3)$ nm, and $\beta = 118.658(1)°$. Ag_2SiS_3 contains isolated $[Si_2S_6]$ anionic units consisting of pairs of edge-shared tetrahedra. The Ag atoms are situated in the interstices formed by these fragments.

1. Introduction

The phase diagram of the quasi binary Ag_2S–SiS_2 system was studied by several research groups [1–4] but the results agree only poorly. The existence of two ternary compounds is indicated in phase diagram represented in Ref. [1]: Ag_8SiS_6 (SG $Pna2_1$, $a = 1.5001$, $b = 0.7405$, and $c = 1.0539$ nm [2]) and $Ag_{10}Si_3S_{11}$ (SG $P\bar{1}$, $a = 1.2414$, $b = 1.3476$, $c = 0.6459$ nm, $\alpha = 78.92°$, $\beta = 77.61°$, and $\gamma = 68.71°$ [3]). The diffraction patterns of the samples from the range of 5–60 mol.% Ag_2S annealed at 673 K and 873 K contained the reflections of an un-identified phase that was not shown at the phase diagram [1]. The authors of Ref. [4] did not obtain the $Ag_{10}Si_3S_{11}$ phase, indicating the Ag_2SiS_3 composition instead. The most complete version of the diagram which contains all three compounds was proposed in Ref. [2]. The eventual lattice parameters of the monoclinic unit cell of Ag_2SiS_3 were given there as $a = 0.9614$, $b = 0.5555$, $c = 0.6722$ nm, and $\beta = 94.68°$ [2].

2. Experimental

The synthesis of the sample of the Ag_2SiS_3 composition was performed by co-melting the stochiometric amounts of pure elemental components (99.99%) in a vacuum-sealed quartz ampoule. The preliminary synthesis in the flame of oxygas burner flame to complete bonding of the elementary sulfur was performed. The ampoule was heated slowly (20 K/h) to 1373 K, kept at the maximum temperature for 6 h with the vibration mixing and cooled at the rate of 10 K/h to 673 K. The sample was annealed at this temperature for 300 h, and after that was quenched into water.

The X-ray powder diffraction pattern was collected by DRON 4-13 diffractometer using Ni-filtered CuK_α radiation. Powder diffraction pattern was recorded in the 2θ range of 10–100° with 0.05° step and counting time 20 s per data point. All crystallographic calculations were performed using WinCSD [5] and Platon [6] software packages and Structure Tidy program [7].

3. Results

The indexing of the diffraction pattern with parameters $a = 0.9614$, $b = 0.5555$, $c = 0.6722$ nm, and $\beta = 94.68°$ [2] failed. The diffraction pattern of the compound was indexed using the automatic mode of the WinCSD program. The best fit was obtained for the triclinic cell with parameters $a = 1.15662(6)$, $b = 0.66572(4)$, $c = 0.66706(3)$ nm, $\alpha = 90.01(1)°$, $\beta = 91.748(3)°$, $\gamma = 90.01(1)°$ (number of reflection = 530, $R_I = 0.0653$, and $R_P = 0.0939$). The determination of the structure model was performed in the assumption of the space group $P1$ or $P\bar{1}$ by separating in the Patterson electronic map the position of heavy atoms (silver) in the 0 0 0 and ½ ½ ½ sites. The positions of the remaining atoms were located from the Fourier electronic map. In the refinement of the model, the best values of the fit factors ($R_I = 6.44\%$ and $R_p = 10.11\%$) were obtained for the space group $P1$.

The presented unit cell parameters show that the metrics of the lattice corresponds to the monoclinic symmetry. The search for additional symmetry elements for the transition to a monoclinic space group was performed using the Addsym program, a part of the Platon package. It was established that the atom placement corresponds to the space group $P2_1/c$ with the transformation of the

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Table 1
Parameters of the crystal structure determination for Ag_2SiS_3.

Space group	$P2_1/c$
a (nm)	0.66709(1)
b (nm)	0.66567(2)
c (nm)	1.31748(3)
β (°)	118.658(1)
Cell volume (nm^3)	0.51337(4)
Pearson symbol	mP24
Radiation and wavelength	CuK$_\alpha$, 0.154185 nm
Calculated density (g/cm^3)	4.3988(4)
Absorption coefficient (1/cm)	741.35
Diffractometer	Powder DRON 4-13
Mode of refinement	Full profile
Number of atom sites	6
Number of refined parameters	30
2θ and $\sin\theta/\lambda$ (max)	99.71 and 0.496
R_I, R_p	0.0493, 0.0814
Texture axis and parameter	[0 0 1] and 1.0567(4)

Table 2
Atomic coordinates and isotropic displacement parameters for the Ag_2SiS_3 structure.

Atom	x/a	y/b	z/c	B_{iso} ($\times 10^2$ nm^2)
Ag1	0.2242(5)	0.5203(3)	0.2515(2)	1.68(11)
Ag2	0.4871(5)	0.3941(4)	0.1132(2)	2.45(12)
Si1	0.840(2)	0.1498(13)	−0.0070(7)	0.5(5)
S1	0.8764(15)	0.2997(11)	0.1436(8)	0.6(4)
S2	0.8504(14)	−0.1689(11)	0.0181(7)	0.4(4)
S3	0.557(2)	0.2468(10)	−0.1578(8)	0.7(4)

Table 3
Standardized atomic coordinates (Structure Tidy program) for Ag_2SiS_3.

Atom	x/a	y/b	z/c
Ag1	0.2242(5)	0.4797(3)	0.2515(2)
Ag2	0.5129(5)	0.1059(4)	0.3868(2)
Si1	0.160(2)	0.1498(13)	0.0070(7)
S1	0.1236(15)	0.2003(11)	0.3564(8)
S2	0.1496(14)	0.6689(11)	0.4819(7)
S3	0.443(2)	0.2468(10)	0.1578(8)

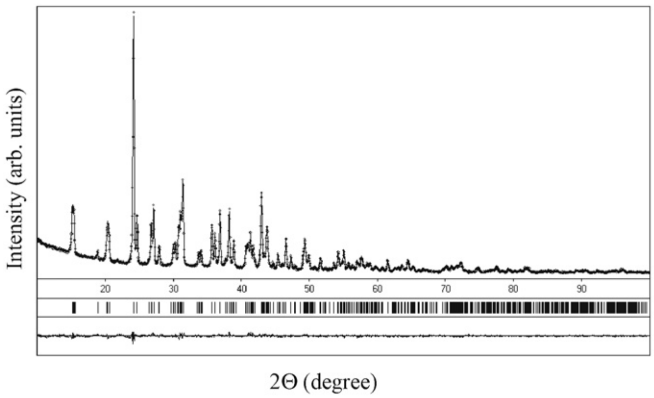

Fig. 1. Experimental, calculated powder diffraction patterns and their difference diagram for the Ag_2SiS_3. Tildes correspond to the calculated reflection position.

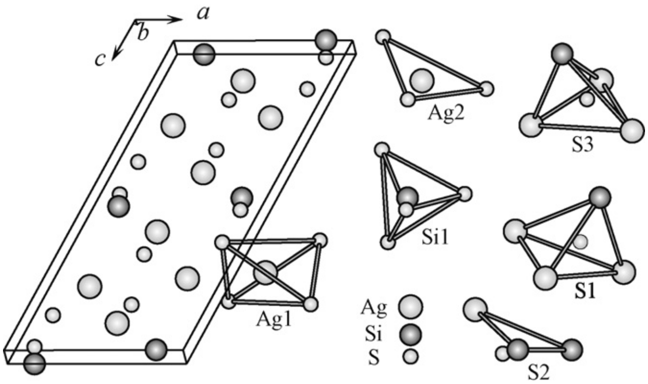

Fig. 2. Unit cell projection of the Ag_2SiS_3 structure along [0 1 0] and the coordination of the atoms.

cell according to the transformation matrix:

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & -1 \end{pmatrix}$$

and the origin shift by (−0.2246 −0.5117 −0.2515). The results of the final refinement of the Ag_2SiS_3 crystal structure in space group $P2_1/c$ are given in Table 1. The atomic coordinates and the atomic displacement parameters refined in the isotropic approximation are listed in Table 2. To avoid the negative coordinates standardization of the structure model were performed using Structure Tidy program. Standardized coordinates of atoms for Ag_2SiS_3 listed in Table 3. The interatomic distances and the coordination numbers of the atoms in the reported crystal structure are listed in Table 4. The experimental and the calculated diffraction patterns and their difference for the Ag_2SiS_3 compound are presented in Fig. 1. The projection of the unit cell of the Ag_2SiS_3 compound along [0 1 0] plane and the coordination polyhedra of the atoms are presented in Fig. 2.

All atoms in the structure of Ag_2SiS_3 are located in the general position 4(e) which corresponds to the Pearson symbol $mP24$ and Wyckoff sequence e^6. The interatomic distances are comparable with the sum of the ionic radii $r(Ag^+) = 0.100$ nm, $r(Si^{4+}) = 0.026$, and $r(S^{2-}) = 0.184$ nm [8]. A contraction of interatomic distances is likely related to the formation of the covalent bonding. The calculated Ag–S (0.2529–0.2792 nm) and Si–S distances (0.2081–0.2143 nm) are comparable with those reported for Ag_8SiS_6: δ(Ag–S) = 0.2384–0.2774 nm, and δ(Si–S) = 0.2092–0.2129 nm [9].

Table 4
Interatomic distances (δ) and coordination numbers (CN) of atoms in the crystal structure of Ag_2SiS_3.

Atoms		δ (nm)	CN	Atoms		δ (nm)	CN
Ag1	S1	0.2529(10)	4	S1	Si1	0.2129(13)	4
	S1	0.2590(9)			Ag2	0.2510(11)	
	S3	0.2640(10)			Ag1	0.2529(10)	
	S3	0.2792(10)			Ag1	0.2590(9)	
Ag2	S1	0.2510(11)	3	S2	Si1	0.2143(15)	3
	S3	0.2512(8)			Si1	0.2143(11)	
	S2	0.2563(9)			Ag2	0.2563(9)	
Si1	S3	0.2081(13)	4	S3	Si1	0.2081(13)	4
	S2	0.2129(13)			Ag2	0.2512(8)	
	S1	0.2143(15)			Ag1	0.2640(10)	
	S2	0.2143(11)			Ag1	0.2792(10)	

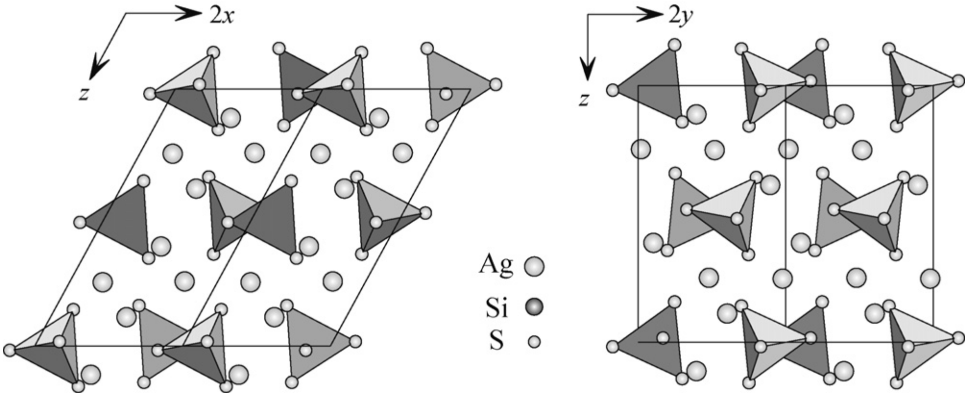

Fig. 3. Crystal structure of Ag_2SiS_3 with emphasised $[Si_2S_6]$ units (projection along [0 1 0] and [1 0 0]).

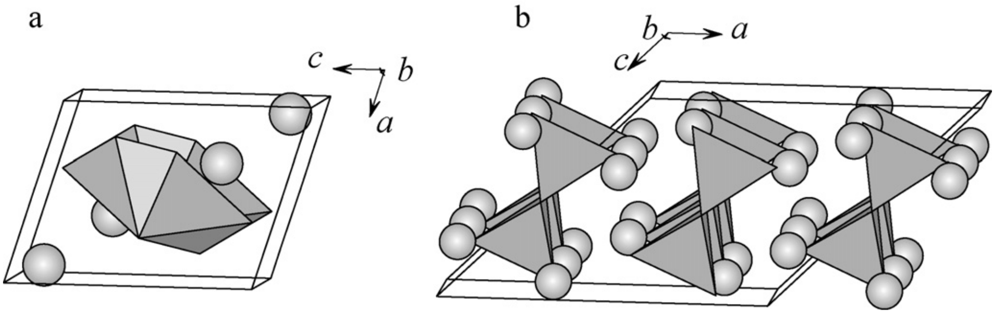

Fig. 4. Dimeric complexes $[Sn_2Se_6]$ in the crystal structures of the Rb_2SnSe_3 (a) and Cs_2SnSe_3 (b) compounds.

The Ag2 atoms have an uncommon coordination number 3 for the cations of 4-electron normal-valence chalcogenides which is compensated by the three-coordinated S2 atom. The valence angles S–Ag2–S range from 115.4(3) to 123.5(3)° that correspond to the coordination in a slightly distorted coplanar triangle.

The crystal lattice of the Ag_2SiS_3 compound (Fig. 3) is composed of isolated $[Si_2S_6]$ units consisting of pairs of edge-shared tetrahedra. The Si–Si distance is 0.2861(14). The isolated structural units $[Si_2S_6]$ form blocks parallel to the *XY* plane. The Ag1 atoms are located in the middle between the blocks and possess tetrahedral surrounding, while the Ag2 atoms are drawn out by the polarization of the blocks and have triangular surrounding. A described spatial placement of the atoms allows us to suggest a strong anisotropy of the ionic component of the electric conductivity (with Ag^+ ions as charge carriers). The ionic conductivity along the *XY* plane should be higher than in other directions.

The formation of dimeric thiosilicate anionic units $[Si_2S_6]$ in the Ag_2SiS_3 crystal structure sets this compound apart from the class of normal-valence tetrahedral semiconductors with valence electron concentration of 4 electrons per atom. The structures in this class belong to the non-centro-symmetric space groups that are derived from the structure types of sphalerite (ZnS) or zincite (ZnO); the cationic tetrahedra are corner-shared only. For example, in crystal structure of Cu_2SiS_3 (SG *Cc*, $a = 0.6332$, $b = 1.1230$, $c = 0.6273$ nm, and $\beta = 107.49^\circ$ [10]) and Ag_2GeS_3 (SG $Cmc2_1$, $a = 1.1791$, $b = 0.7079$, and $c = 0.6344$ nm [11]) corner-shared tetrahedra SiS4 or GeS4 forms infinite zigzag chains stretched along the 3-fold pseudo-axis. The $Cu_5Si_2S_7$ structure (SG *Bb*, $a = 1.6216$, $b = 0.9597$, $c = 0.6317$ nm, and $\gamma = 92.38(5)^\circ$ [12]) forms a different motif: the anionic units $[Si_2S_7]$ consisting of pairs of edge-shared tetrahedra are isolated, similar to the structural units $[Si_2S_6]$ in the Ag_2SiS_3 structure.

The structure units $[Si(Ge,Sn)_2S(Se)_6]$ are observed in the structure types of Tl_2GeS_3 (SG $P\bar{1}$) [13] (and isostructural Tl_2SiSe_3, Tl_2GeSe_3, Tl_2SnSe_3 [14]), Rb_2SnSe_3 (Fig. 4a) (SG $P\bar{1}$) [15], Cs_2SnSe_3 (SG $C2/m$) (Fig. 4b) [16], $KAuSnS_3$ (SG $P4/mcc$) [17], and $K_2Y_4Sn_2S_{11}$ (SG $P4/ncc$) [18]. One should note that all the listed crystal structures are centrosymmetrical which is likely related to the low polarization ability of the anionic units $[Si(Ge,Sn)_2S(Se)_6]$; the single-charged cations possess octahedral coordination surrounding in these structures.

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