

Interaction of the components in the $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system

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The isothermal section of the quasi-ternary $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system at 520 K was constructed using differential-thermal and X-ray phase analyses. The existence of a quaternary compound, $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ (space group $R\bar{3}m$, $a = 0.38118(1)$ nm, $c = 3.9724(3)$ nm) with incongruent type of melting at 690 K, was established. The Se atoms in the structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound are stacked in a close-packed arrangement with the layers in the sequence ABC. A statistical mixture of cations ($0.333\text{Ag}+0.167\text{Sn}+0.500\text{As}$) occupy one half of the octahedral interstices. The remaining As atoms are distributed over the other octahedral interstices.

Semiconductors / Phase equilibria / Isothermal section / Crystal structure / X-ray powder diffraction

1. Introduction

The binary compounds Ag_2Se , SnSe_2 and As_2Se_3 melt congruently at 1170, 930 and 648 K [1], respectively, and can be considered as the components of a quasi-ternary system. The $\text{Ag}_2\text{Se}-\text{SnSe}_2$ polythermal section of the ternary Ag–Sn–Se system has been investigated in [2,3], but information on the quasi-binary $\text{SnSe}_2-\text{As}_2\text{Se}_3$ system is absent in the literature. The $\text{Ag}_2\text{Se}-\text{As}_2\text{Se}_3$ system has been investigated in [4-6]. The authors of [6] confirmed the existence of the compounds Ag_3AsSe_3 and AgAsSe_2 that were reported in [4,5] and discovered the compound AgAs_3Se_5 with unknown structure.

The isothermal section of the quasi-ternary $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system at 520 K and the crystal structure of the new quaternary compound $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ are presented and discussed in this paper.

2. Experimental details

111 samples were prepared for the investigation of the interaction between the components in the $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system. The alloys were prepared by sintering mixtures of the elemental constituents of purity better than 99.999 wt.% in an evacuated quartz ampoule. The synthesis was carried out in a tubular resistance furnace. The ampoules were first heated with a rate of 25 K per hour up to 1100 K and then kept at this temperature for 2 hours. Afterwards the samples were slowly cooled (5 K per

hour) down to 520 K and annealed at this temperature for 600 hours. Finally the ampoules were quenched in cold water.

X-ray powder diffraction patterns of the samples were recorded using a DRON-4-13 powder diffractometer (CuK_α radiation, $10^\circ \leq 2\theta \leq 90^\circ$, step scan mode with a step size of 0.05° and counting time of 1 s per data point). Phase analysis was carried out. The X-ray powder diffraction pattern of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ sample used for the crystal structure determination was recorded on a DRON-4-13 powder diffractometer (CuK_α radiation, $10^\circ \leq 2\theta \leq 100^\circ$, step scan mode with a step size of 0.05° and counting time of 20 s per data point). The crystal structure was determined using the CSD program [7].

The alloys of the $\text{SnSe}_2-\text{As}_2\text{Se}_3$ system were investigated by differential-thermal analysis (Paulik–Paulik–Erdey system derivatograph, Pt/Pt-Rh thermocouple) (DTA) and partly by metallography (“Leica VMHT Auto” metal microscope).

3. Results

3.1. The quasi-binary systems

The lack of literature data on the $\text{SnSe}_2-\text{As}_2\text{Se}_3$ system motivated our investigation of this section. Results of the investigation of 16 samples in the $\text{SnSe}_2-\text{As}_2\text{Se}_3$ system are shown in Fig. 1 and Table 1. The diagram is of the eutectic type with the eutectic point situated at 19 mol.% SnSe_2 and 640 K. No significant solid solubility ranges were detected for the initial components (<1 mol. %).

Table 1 DTA results of $\text{SnSe}_2-\text{As}_2\text{Se}_3$ system.

#	Phase composition (mol.%)		Temperature (K)	
	SnSe_2	As_2Se_3	Liquid	Solid
1	100	0	920	-
2	90	10	892	633
3	80	20	866	634
4	70	30	846	634
5	60	40	828	635
6	50	50	810	643
7	40	60	802	645
8	30	70	769	640
9	25	75	703	643
10	20	80	657	634
11	18	82	650	640
12	15	85	655	643
13	12	88	655	640
14	10	90	657	646
15	5	95	658	640
16	0	100	660	-

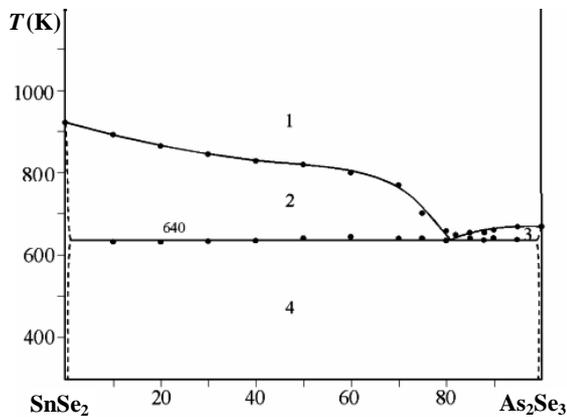


Fig. 1 Phase diagram of the $\text{SnSe}_2-\text{As}_2\text{Se}_3$ system (1 - L; 2 - L+ SnSe_2 ; 3 - L+ As_2Se_3 ; 4 - $\text{SnSe}_2+\text{As}_2\text{Se}_3$).

The formation of the Ag_3AsSe_3 , AgAsSe_2 and AgAs_3Se_5 compounds in the $\text{Ag}_2\text{Se}-\text{As}_2\text{Se}_3$ system was observed, in good accordance with the results of [5]. The formation of Ag_8SnSe_6 in the $\text{Ag}_2\text{Se}-\text{SnSe}_2$ system was also confirmed.

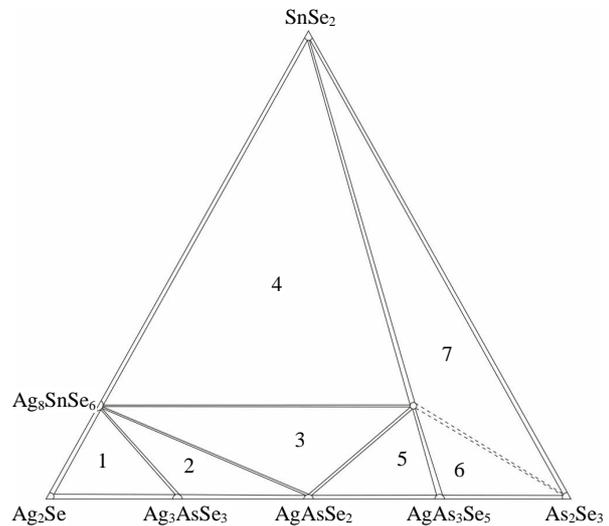


Fig. 2 Isothermal section of the quasi-ternary $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system at 520 K.

1. $\text{Ag}_2\text{Se}-\text{Ag}_8\text{SnSe}_6-\text{Ag}_3\text{AsSe}_3$;
2. $\text{Ag}_8\text{SnSe}_6-\text{Ag}_3\text{AsSe}_3-\text{AgAsSe}_2$;
3. $\text{Ag}_8\text{SnSe}_6-\text{AgAsSe}_2-\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$;
4. $\text{Ag}_8\text{SnSe}_6-\text{SnSe}_2-\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$;
5. $\text{AgAsSe}_2-\text{Ag}_2\text{SnAs}_6\text{Se}_{12}-\text{AgAs}_3\text{Se}_5$;
6. $\text{AgAs}_3\text{Se}_5-\text{Ag}_2\text{SnAs}_6\text{Se}_{12}-\text{As}_2\text{Se}_3$;
7. $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}-\text{SnSe}_2-\text{As}_2\text{Se}_3$.

Table 2 Results of the crystal structure determination of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound.

Empirical formula	$\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$
Number of formula units per unit cell	1
Space group	$R\bar{3}m$ (No. 166)
a (nm)	0.38118(2)
c (nm)	3.9724(3)
Cell volume (nm^3)	0.4999(9)
Number of atoms per unit cell	21
Calculated density (g/cm^3)	5.751
Radiation and wavelength (nm)	CuK_α 0.154178
Diffractometer	DRON-4-13
Mode of refinement	Full profile
Number of atom sites	5
R_f	0.0893
R_p	0.1665
Texture axis and parameter	[0 0 1] 0.432(9)

Table 3 Atomic coordinates and isotropic displacement parameters for $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$.

Atom	Position	x/a	y/b	z/c	Occupation ^a	$B_{\text{iso}} \times 10^2$ (nm^2)
M	$6c$	0	0	0.8826(1)	0.333Ag 0.167Sn 0.500As	0.7(1)
As	$6c$	0	0	0.6400(2)	0.5	2.4(4)
Se1	$3a$	0	0	0	1	1.2(3)
Se2	$3b$	0	0	1/2	1	0.7(2)
Se3	$6c$	0	0	0.2508(1)	1	1.8(3)

^a The site occupations were not refined.

3.2. Isothermal section of the quasi-ternary $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system at 520 K

The isothermal section of the quasi-ternary $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system at 520 K is shown in Fig. 2. The formation of a new quaternary compound, $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$, was established. This compound melts congruently at 690 K. Two-phase equilibria exist between the quaternary $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ and the ternary Ag_8SnSe_6 , AgAsSe_2 , and AgAs_3Se_5 , and the binary SnSe_2 and As_2Se_3 compounds. Two-phase $\text{Ag}_8\text{SnSe}_6-\text{Ag}_3\text{AsSe}_3$ and $\text{Ag}_8\text{SnSe}_6-\text{AgAsSe}_2$ equilibria are also observed. Seven three-phase fields exist in the $\text{Ag}_2\text{Se}-\text{SnSe}_2-\text{As}_2\text{Se}_3$ system at 520 K. No significant solubility of the third (fourth) component in the binary (ternary) compounds was detected (<1–2 mol.%).

3.3. Crystal structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound

The crystal structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound was investigated using X-ray powder diffraction. The peaks of the X-ray powder diffraction pattern were indexed on the basis of a hexagonal unit cell with the

lattice parameters listed in Table 2. The extinctions were found to be consistent with the space group $R\bar{3}m$. By assuming space group $R\bar{3}m$ we were able to extract a plausible structural model from the powder X-ray intensities by means of direct methods and difference Fourier syntheses. Preferred orientation was taken into account during the refinement procedure. Two cation positions and three anion positions were found. All anion positions are fully occupied. The first cation position was found to be occupied by a random distribution of Ag, Sn and As atoms (0.333Ag+0.167Sn+0.500As), the second position by As atoms alone (0.5As). The composition of the statistical mixture (M) and the occupation factor of the As site were fixed according to the nominal composition of the sample. Some results of the crystal structure determination are summarized in Table 2, whereas the atomic coordinates and isotropic displacement parameters are given in Table 3. The observed, calculated and difference diffraction patterns for $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ are shown in Fig. 3.

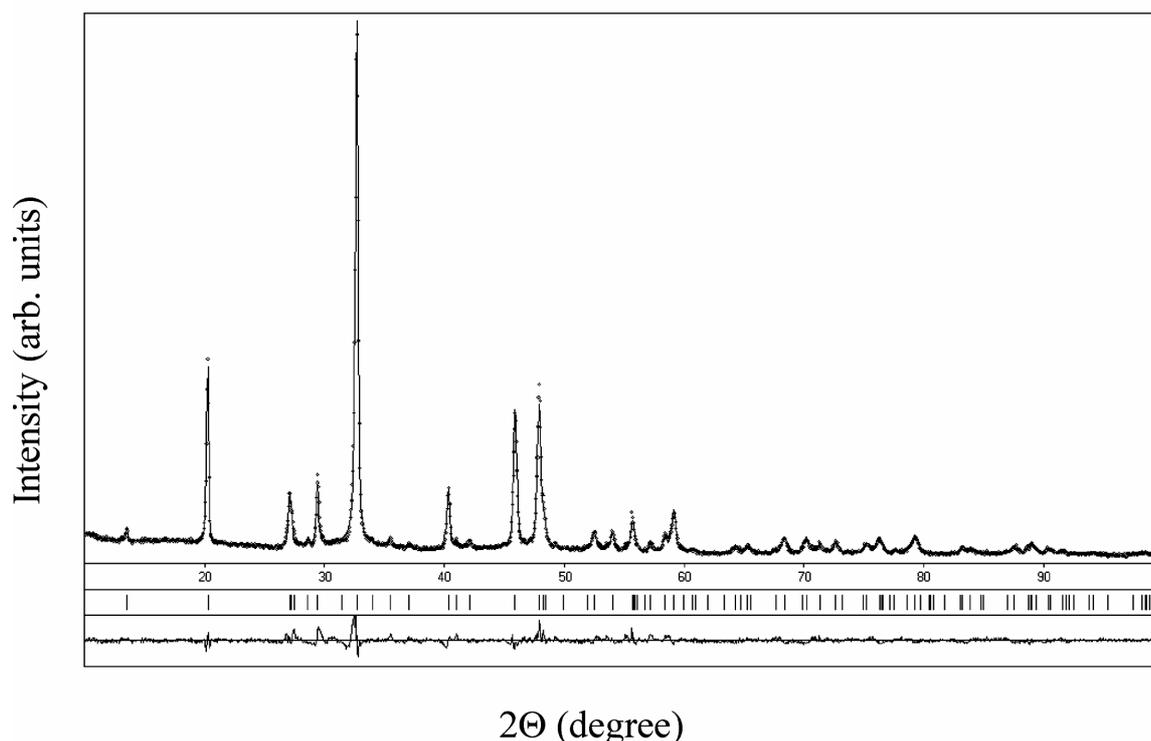


Fig. 3 Observed, calculated and difference diffraction patterns for $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ (Cu $K\alpha$).

Table 4 Interatomic distances δ (nm) and coordination numbers (c.n.) of the atom sites in $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$.

Atoms		δ (nm)	c.n.
M^a	- 3Se3	0.2600(4)	6
	- 3Se2	0.2944(3)	
As	- 3Se1	0.2443(4)	3
Se1	- 6As	0.2443(4)	6
Se2	- 6M	0.2944(3)	6
Se3	- 3M	0.2600(4)	3

^a $M = 0.333\text{Ag} + 0.167\text{Sn} + 0.500\text{As}$

A projection of the crystal structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound onto the (1120) plane, the coordination polyhedra of the M (a), As (b), Se1 (c), Se2 (d) and Se3 (e) atoms and the decomposition of the structure into atomic layers of hexagonal topology formed by Se are shown in Fig. 4.

Interatomic distances and coordination numbers of the atoms in the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ structure are given in Table 4. The interatomic distances agree well with the sum of the respective ionic radii [8].

The atoms of the statistical mixture M ($0.333\text{Ag} + 0.167\text{Sn} + 0.500\text{As}$) are surrounded by six Se atoms forming an octahedron. The As atoms from the As site have three neighbors. The coordination polyhedron is a triangle, non-coplanar with the As atom. The sites Se1 and Se2 are surrounded by six cations (octahedron), the site Se3 by three cations (non-coplanar triangle).

The Se atoms in the structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound are stacked in a close-packed arrangement with the layers in the sequence ...ABC... (cubic close packing) (Fig. 4). The atoms of the statistical mixture M ($0.333\text{Ag} + 0.167\text{Sn} + 0.500\text{As}$) occupy one half of the octahedral interstices. The other As atoms are distributed over the remaining octahedral interstices, occupying half of these. The M atoms are located close to the centres of the octahedra (Fig. 5a), whereas the As atoms are shifted from the centers of the octahedra. Since three Se atoms are located at significantly longer distances than the other three Se atoms, actually a triangular surrounding should be considered for the As atoms (Fig. 5b).

The packing of the M - and As-centered octahedra in the structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound is shown in Fig. 6. A similar arrangement of Ag- and As-centered octahedra is observed in the structure of the AgAsSe_2 compound (space group $R\bar{3}m$,

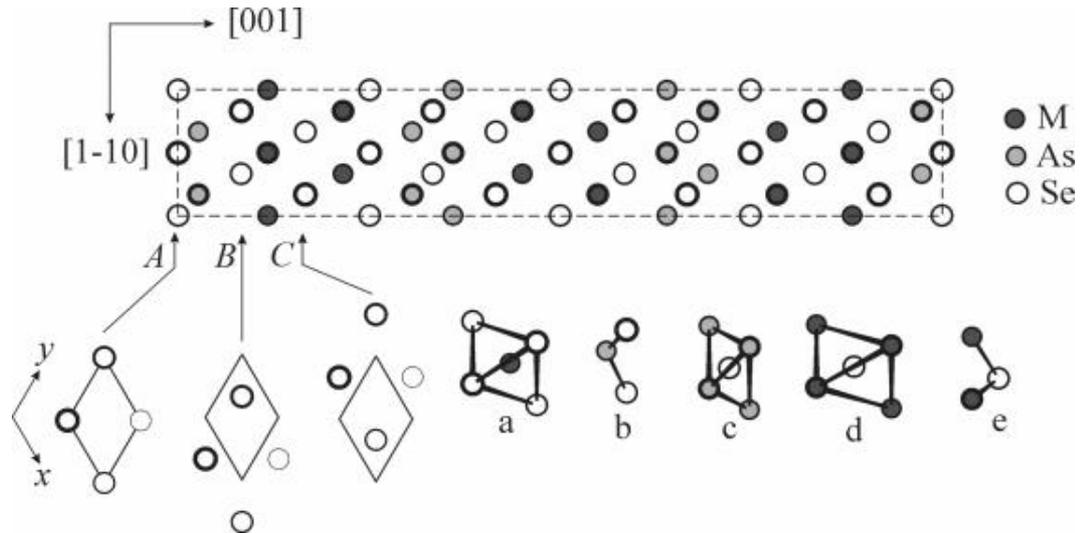


Fig. 4 Projection of the crystal structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound onto the (1120) plane, the coordination polyhedra of the M (a), As (b), Se1 (c), Se2 (d) and Se3 (e) atoms and the decomposition of the structure into Se layers of hexagonal topology.

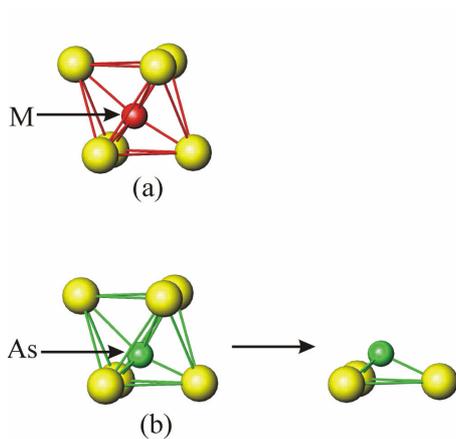


Fig. 5 The polyhedra centered by M (a) and As alone (b) in the structure of the $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ compound.

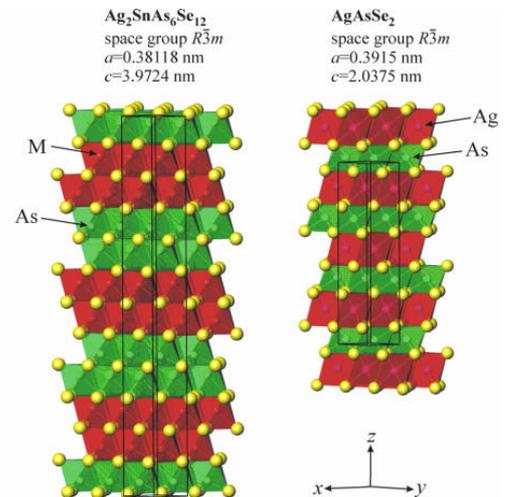


Fig. 6 The packing of M -, Ag- and As-centered octahedra in the structures of $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ and AgAsSe_2 .

$a = 0.3915 \text{ nm}$, $c = 2.0375 \text{ nm}$) [5] (Fig. 6). The structure of $\text{Ag}_2\text{SnAs}_6\text{Se}_{12}$ is an $a \times b \times 2c$ superstructure of AgAsSe_2 . Both crystal structures are superstructures of the NaCl-type structure (space group $Fm\bar{3}m$).

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