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Phase diagram of the Ag_2Se–As_2Se_3 system and crystal structure of the $AgAs_3Se_5$ compound

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The phase diagram of the quasi-binary Ag_2Se–As_2Se_3 system was constructed using differential-thermal and X-ray phase analyses. The crystal structure of the ternary $AgAs_3Se_5$ compound (space group $R\bar{3}m$, a = 0.38195(1) nm, c = 5.0082(2) nm, R_I = 0.0868) was investigated using X-ray powder diffraction. The Se atoms form a close-packed arrangement with the layers stacked in the sequence *ABC*. The atoms of a statistical mixture *M* (0.5Ag+0.5As) and the remaining As atoms occupy 4/5 of the octahedral interstices.

Semiconductors / Phase diagram / Crystal structure / X-ray powder diffraction

The quasi-binary Ag_2Se–As_2Se_3 system is interesting due to the formation of the semiconductor Ag_3AsSe_3 and the compound $AgAsSe_2$ [1]. Since the sulfur analogs of these compounds are natural minerals with interesting optical properties, the investigation of the compounds in the Ag–As–Se system is an important step in the search for new materials for optoelectronics [2].

The polythermal section of the Ag_2Se–As_2Se_3 system was proposed for the first time in [3]. It was found that the system is quasibinary. In addition the formation of two ternary compounds at the compositions Ag_3AsSe_3 and $AgAsSe_2$ was established. The Ag_3AsSe_3 compound forms according to a peritectic reaction at 673 K, whereas the $AgAsSe_2$ compound melts congruently at 683 K. The possibility of a polymorphic transformation of $AgAsSe_2$ at 658 K was also suggested in [3]. The crystal structure of the Ag_3AsSe_3 compound (space group $R3c$, a = 1.1298 nm, c = 0.8757 nm) was determined in [4]. The crystal structure of the high-temperature modification of $AgAsSe_2$ (space group $R\bar{3}m$, a = 0.3915 nm, c = 2.0375 nm) was reported in [5]. The X-ray powder diffraction pattern of the low-temperature modification of $AgAsSe_2$ was indexed in a tetragonal unit cell (a = 1.2548 nm, c = 1.1140 nm) [5]. New results of investigations of the $AgAsSe_2$ compound were reported in [6].

The formation of three compounds: Ag_3AsSe_3, $AgAsSe_2$ and $AgAs_3Se_5$, in the Ag_2Se–As_2Se_3 system was established in [7]. The $AgAs_3Se_5$ compound (unknown structure) forms according to the peritectic reaction L + $AgAsSe_2$ ↔ $AgAs_3Se_5$ at 643 K and forms together with As_2Se_3 a eutectic at 90 mol.% As_2Se_3 and 630 K. The $AgAsSe_2$ compound was found to melt congruently at 673 K, but no polymorphic transformation was observed. The peritectic reaction L + Ag_2Se ↔ Ag_3AsSe_3 at 663 K was also observed in [7].

The in part contradictory information found in the literature on the Ag_2Se–As_2Se_3 system motivated us to reinvestigate its phase diagram. The polythermal section of the Ag_2Se–As_2Se_3 system and the crystal structure of the $AgAs_3Se_5$ compound are presented here.

Experimental

14 samples were prepared for the investigation of the phase diagram of the Ag_2Se–As_2Se_3 system. The alloys were prepared by sintering the elemental constituents of purity better than 99.999 wt.% in an evacuated quartz ampoule. The synthesis was carried out in a tube resistance furnace. The ampoules were first heated with a rate of 25 K per hour up to 1200 K and then kept at this temperature for 5 hours. Afterwards the samples were slowly cooled (5 K per hour) down to 520 K and annealed at this temperature for 600 hours. Subsequently the ampoules were quenched in cold water.

X-ray powder diffraction patterns for phase analysis were recorded using a DRON-4-13 powder diffractometer (CuK_α radiation, $10° \le 2\theta \le 90°$, step scan mode with a step size of 0.05° and counting time of 1 s per data point). The X-ray powder diffraction

Table 1 DTA results of the Ag_2Se–As_2Se_3 system.

#	Phase composition (mol.%)		Temperature (K)			
	Ag_2Se	As_2Se_3	liquid	subliquid	solid	subsolid
1	100	0	1170			418
2	90	10	983		660	418
3	80	20	808		660	418
4	75	25	758		660	
5	70	30	698		655	
6	60	40	672	658	655	
7	50	50	683	658		
8	40	60	678	658	645	
9	30	70	665	658	644	
10	25	75	657		644	
11	20	80	649	644	635	
12	10	90	638			
13	5	95	648		635	
14	0	100	652			

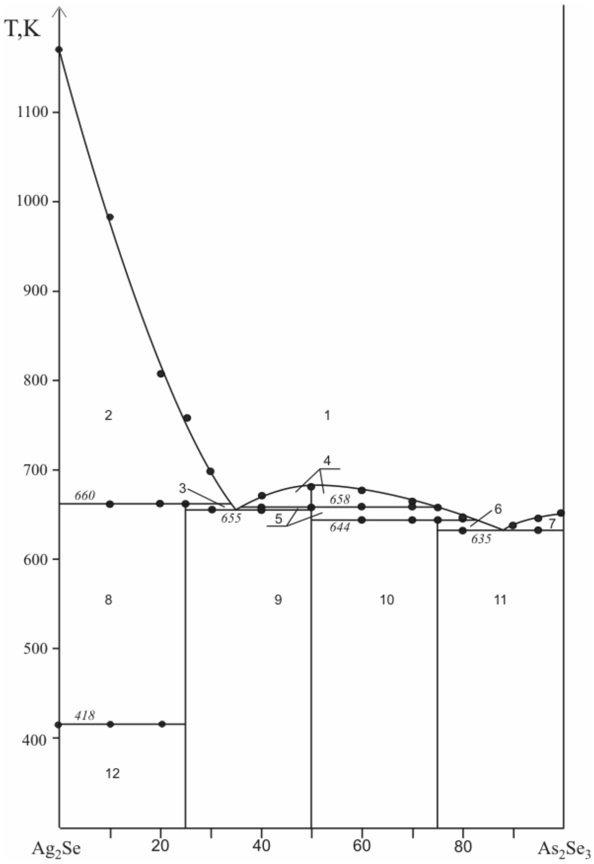

Fig. 1 Phase diagram of the Ag_2Se–As_2Se_3 system
1 – L; 2 – L + β-Ag_2Se;
3 – L + Ag_3AsSe_3; 4 – L + β-$AgAsSe_2$;
5 – L + α-$AgAsSe_2$; 6 – L + $AgAs_3Se_5$;
7 – L + As_2Se_3; 8 – β-Ag_2Se + Ag_3AsSe_3;
9 – Ag_3AsSe_3 + α-$AgAsSe_2$;
10 – α-$AgAsSe_2$ + $AgAs_3Se_5$;
11 – $AgAs_3Se_5$ + As_2Se_3;
12 – α-Ag_2Se + Ag_3AsSe_3.

pattern of the $AgAs_3Se_5$ sample used for the crystal structure determination was also recorded on a DRON-4-13 powder diffractometer (CuK_α radiation, $10° \leq 2\theta \leq 100°$, step size 0.05°, counting time 20 s per data point). The crystal structure determination was performed using the CSD program [8].

Results and discussion

Ag_2Se–As_2Se_3 system: The results of our investigation of the Ag_2Se–As_2Se_3 system are shown in Fig. 1. The formation of three compounds, Ag_3AsSe_3, $AgAsSe_2$ and $AgAs_3Se_5$, was confirmed. The temperatures of the nonvariant processes are similar to those reported in [7] (Table 1). However, a polymorphic transformation of $AgAsSe_2$ at 658 K was observed.

Crystal structure of the $AgAs_3Se_5$ compound: Several single crystals selected from a sample of composition $AgAs_3Se_5$ were tested. The quality of these single crystals was not good for X-ray single crystal investigation. For this reason the crystal structure of the $AgAs_3Se_5$ compound was studied by 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 determined. All the anion positions are fully occupied. The first cation position is occupied by a mixture of randomly distributed Ag and As atoms (0.5Ag+0.5As). The second cation position is occupied exclusively by As atoms. The composition of the statistical mixture (M)

Table 2 Results of the crystal structure determination of the $AgAs_3Se_5$ compound.

Empirical formula	$AgAs_3Se_5$
Number of formula units per unit cell	3
Space group	$R\bar{3}m$ (No. 166)
a (nm)	0.38195(1)
c (nm)	5.0082(6)
Cell volume (nm^3)	0.63273(6)
Number of atoms per unit cell	27
Calculated density (g/cm^3)	5.7267
Radiation and wavelength (nm)	Cu 0.154178
Diffractometer	DRON-4-13
Mode of refinement	Full profile
Number of atom sites	5
Profile function	Pseudo-Voigt
R_I	0.0868
R_P	0.1484
Texture axis and parameter	[001] 0.396(8)

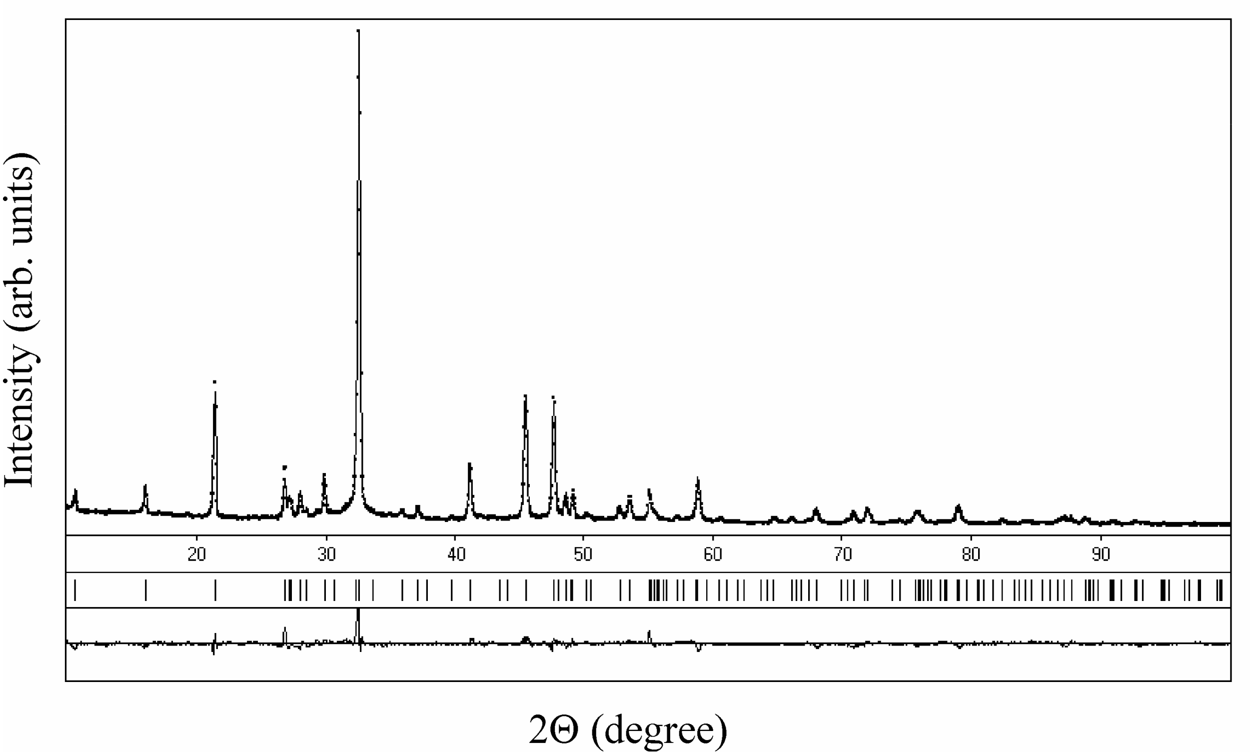

Fig. 2 Experimental and calculated diffraction diagrams and the corresponding difference diagram for $AgAs_3Se_5$.

was fixed at the value required to satisfy the charge balance. 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 experimental and calculated diffraction diagrams, and the corresponding difference diagram are shown in Fig. 2.

A projection of the crystal structure of the $AgAs_3Se_5$ compound on the $(11\bar{2}0)$ plane, the coordination polyhedra of the M (a), As (b), Se1 (c), Se2 (d) and Se3 (e) sites, and the decomposition of the structure into Se atomic layers of hexagonal topology are shown in Fig. 3. Interatomic distances and coordination numbers of the atoms are given in Table 4. The interatomic distances agree well with the sum of the ionic radii [9]. Each atom of the statistical mixture M (0.5Ag+0.5As) is surrounded by six Se atoms forming an octahedron. Each As atom has also six neighbors and the coordination polyhedron is an octahedron. The sites Se1 and Se2 are surrounded by six cations (octahedron), Se3 by three cations (non coplanar triangle).

The Se atoms in the structure of the $AgAs_3Se_5$ compound form a close-packed arrangement with the

Table 3 Atomic coordinates and isotropic displacement parameters for $AgAs_3Se_5$.

Atom	Position	*x/a*	*y/b*	*z/c*	Occupation	$B_{iso}\times10^2$ (nm^2)
M	6*c*	0	0	0.11128(8)	0.5Ag+0.5As	1.6(1)
As	6*c*	0	0	0.2963(1)	1	2.3(1)
Se1	3*a*	0	0	0	1	0.5(2)
Se2	6*c*	0	0	0.60063(9)	1	0.6(2)
Se3	6*c*	0	0	0.1971(1)	1	1.4(2)

Table 4 Interatomic distances δ(nm) and coordination numbers (c.n.) of the atoms in $AgAs_3Se_5$.

Atoms		δ(nm)	c.n.
M [a]	- 3Se3	0.2534(3)	6
	- 3Se2	0.3164(4)	
As	- 3Se2	0.2641(4)	6
	- 3Se1	0.2881(4)	
Se1	- 6As	0.2881(4)	6
Se2	- 3As	0.2641(4)	6
	- 3*M*	0.3161(4)	
Se3	- 3*M*	0.2534(3)	3

[a] *M* = 0.5Ag + 0.5As

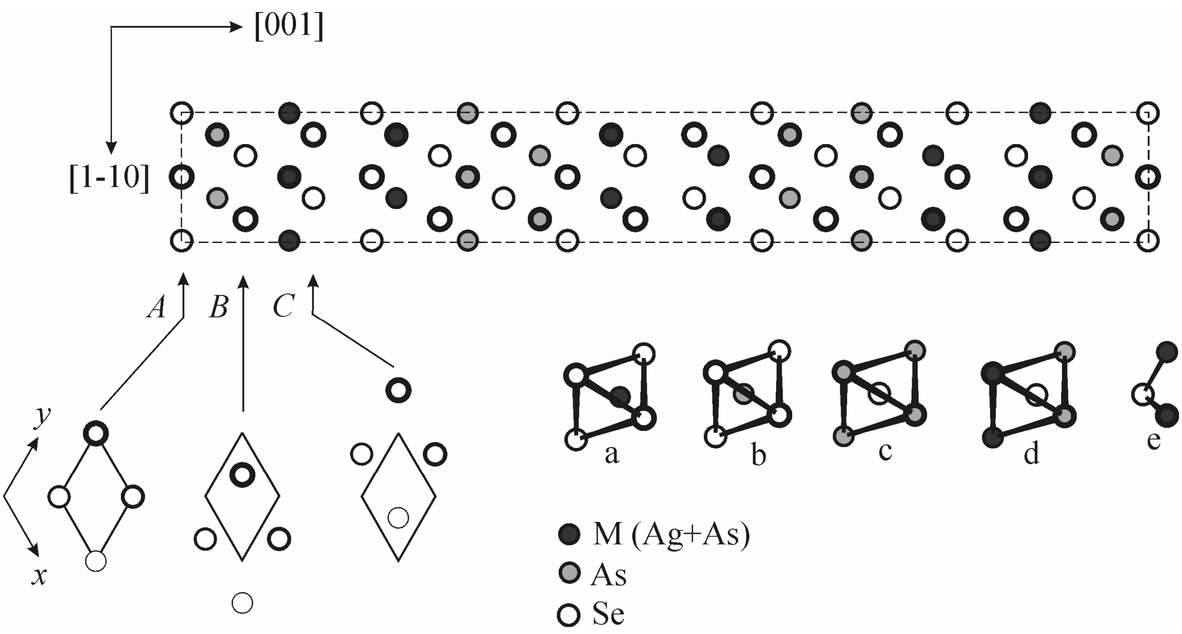

Fig. 3 Projection of the crystal structure of the $AgAs_3Se_5$ compound on the (11$\bar{2}$0) plane, the coordination polyhedra of the *M* (a), As (b), Se1 (c), Se2 (d) and Se3 (e) atoms and decomposition of the structure into atomic Se layers of hexagonal topology.

layers stacked in the sequence *ABC* (cubic close packing) (Fig. 3). The atoms of the statistical mixture *M* (0.5Ag+0.5As) occupy 2/5 of the octahedral interstices. The atoms from the As site occupy another 2/5 of the octahedral interstices, whereas the remaining 1/5 of the octahedral interstices are vacant. The packing of the *M*- and As-centered octahedra in the structure of $AgAs_3Se_5$ is shown in Fig. 4. A similar arrangement of Ag- and As-centered octahedra is observed in the structure of $AsAsSe_2$ (space group $R\bar{3}m$, a = 0.3915 nm, c = 2.0375 nm) [5] (Fig. 4). The Se atoms in the structure of $AgAsSe_2$ are also stacked in a close-packed arrangement with the layers in the sequence *ABC*, but all the octahedral interstices are occupied. The Ag atoms occupy half of the octahedral interstices, and the As atoms are located in the remaining ones. The structure of $AgAs_3Se_5$ is an $a \times b \times 5/2c$ superstructure to $AgAsSe_2$. The $AgAs_3Se_5$ and $AgAsSe_2$ compounds are also superstructures of the NaCl type of structure (space group $Fm\bar{3}m$). The structure of $Ag_2SnAs_6Se_{12}$ (space group $R\bar{3}m$, a = 0.38118 nm, c = 3.9724 nm) [10] (Fig. 4) is

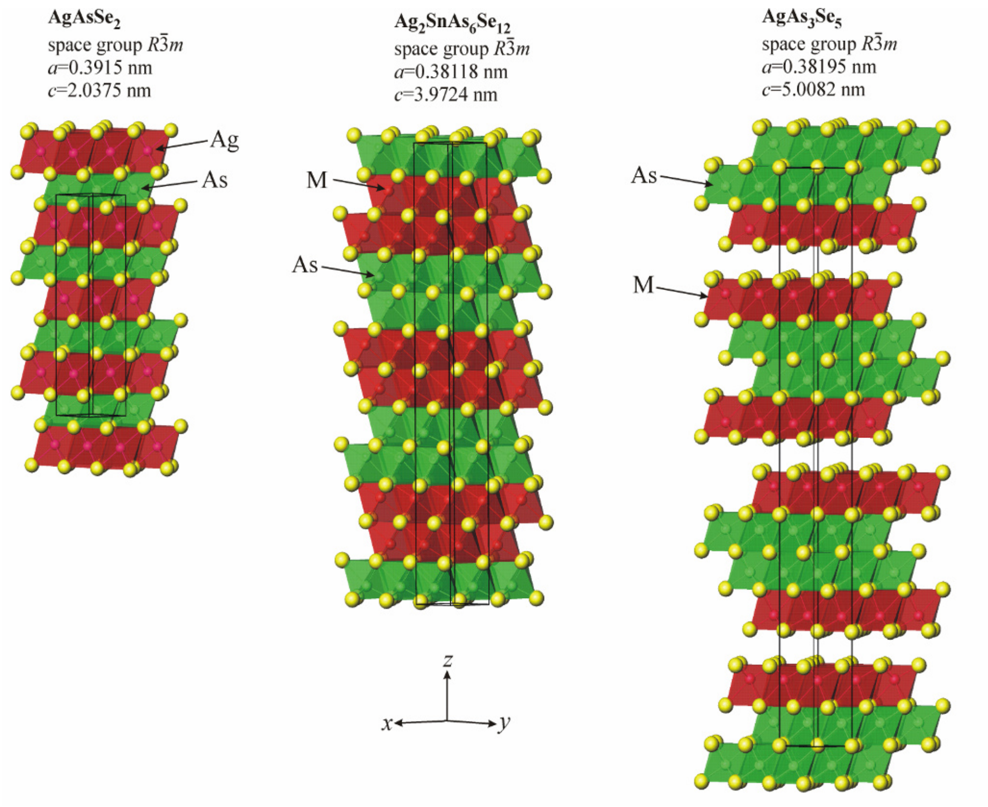

Fig. 4 Stacking of *M*-, Ag- and As-centered octahedra in the structures of the $AsAsSe_2$, $Ag_2SnAs_6Se_{12}$ and $AgAs_3Se_5$ compounds.

intermediate between the structures of $AgAsSe_2$ and $AgAs_3Se_5$. The Se atoms in $Ag_2SnAs_6Se_{12}$ are also stacked in a close-packed arrangement with layers in the sequence *ABC*. The atoms of a statistical mixture *M* (2Ag+1Sn+3As) occupy half of the octahedral interstices, whereas 50% of the remaining octahedral interstices are occupied exclusively by As atoms in statistical disorder.

The structures of the $AgAsSe_2$, $Ag_2SnAs_6Se_{12}$ and $AgAs_3Se_5$ compounds represent a series of superstructures of NaCl with the cell parameters a, b, nc ($a = b \sim 0.4$ nm, $c \sim 1.0$ nm). The compounds $AgAsSe_2$, $Ag_2SnAs_6Se_{12}$ and $AgAs_3Se_5$ are realized at $n = 2$, 4 and 5, respectively.

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