

# The $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3-\text{Si}(\text{Ge})\text{S}_2$ systems and crystal structure of quaternary sulfides $\text{Ag}_2\text{In}_2\text{Si}(\text{Ge})\text{S}_6$

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## Abstract

Isothermal sections of quasi-ternary systems  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3-\text{Si}(\text{Ge})\text{S}_2$  at 298 K were constructed using XRD results. Vertical sections  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3$ ,  $\text{AgInS}_2-\text{SiS}_2$ ,  $\text{AgIn}_5\text{S}_8-\text{Ag}_{1.57}\text{SiS}_{2.79}$  were investigated in the  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3-\text{SiS}_2$  system. Two new quaternary compounds were discovered in the systems,  $\text{Ag}_2\text{In}_2\text{SiS}_6$  (melts incongruently at 1133 K) and  $\text{Ag}_2\text{In}_2\text{GeS}_6$ . Both compounds crystallize in the monoclinic structure (structural type  $\text{Ag}_2\text{In}_2\text{GeS}_6$ , space group  $Cc$ ) with lattice parameters  $a = 1.21379(3)$  nm,  $b = 0.71681(2)$  nm,  $c = 1.21171(4)$  nm,  $\beta = 109.252(2)^\circ$  and  $a = 1.22089(4)$  nm,  $b = 0.72115(3)$  nm,  $c = 1.21978(5)$  nm,  $\beta = 109.508(2)^\circ$ , respectively. Atomic parameters were refined in the isotropic approximation to  $R_1 = 0.0746$ ,  $R_p = 0.1256$  ( $\text{Ag}_2\text{In}_2\text{SiS}_6$ );  $R_1 = 0.0657$ ,  $R_p = 0.1189$  ( $\text{Ag}_2\text{In}_2\text{GeS}_6$ ).

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## 1. Introduction

Phase equilibria in the quasi-ternary systems  $\text{Ag}_2\text{X}-\text{B}^{\text{III}}_2\text{X}_3-\text{C}^{\text{IV}}\text{X}_2$  ( $\text{B}^{\text{III}} = \text{Ga, In}$ ;  $\text{C}^{\text{IV}} = \text{Si, Ge, Sn}$ ;  $\text{X} = \text{S, Se}$ ) were partially investigated [1–5]. The results show that nearly all compounds form at the  $\text{AgB}^{\text{III}}\text{X}_2-\text{C}^{\text{IV}}\text{X}_2$  sections with a 2:1 ratio for the quaternary phases  $\text{Cu}_2\text{In}_2\text{SiS}_6$  (space group (SG)  $Cc$ ) [6],  $\text{Ag}_2\text{In}_2\text{SiS}_6$  (SG  $Cc$ ) [7],  $\text{Ag}_2\text{In}_2\text{GeSe}_6$  (SG  $Cc$ ) [8]; and 1:1 ratio for the phases  $\text{AgGaGeS}_4$  (SG  $Fdd2$ ) [3],  $\text{AgInSnS}_4$  (SG  $Fd\bar{3}m$ ) [9],  $\text{Ag}_{0.735}\text{InGeSe}_4$  (SG  $P\bar{4}2c$ ) [10],  $\text{AgInSnSe}_4$  [5]. Only one compound,  $\text{AgGaGe}_3\text{Se}_8$  (SG  $Fdd2$ ) [11], corresponds to the ratio of 1:3. Acentricity of the crystal structure of these chalcogenides is one of the reasons to forecast their possible application as non-linear optical materials. Quality single crystals of large size were obtained for the compounds  $\text{AgGaGeS}_4$  (melting point 1135 K),  $\text{AgGaGe}_3\text{Se}_8$  (993 K) [3,11–17]. The studies of physical properties [15–17] show that they have improved non-linear optical properties compared to their ternary analogues  $\text{AgGaS}_2$  and  $\text{AgGaSe}_2$  (transparency region widens, birefringence increases, laser radiation resistance is doubled, etc.). Therefore the goal of this work is the search for new qua-

ternary compounds in the systems  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3-\text{Si}(\text{Ge})\text{S}_2$ , the study of their crystal structure and the construction of certain vertical sections to determine the conditions for the growth of the single crystals of these phases.

## 2. Bibliographic information on the quasi-binary systems

The crystallographic parameters and the melting points of the initial compounds and of the intermediate compounds of the quasi-binary systems are summarized in Table 1 [18–37]. The  $\text{Ag}_2\text{S}-\text{SiS}_2$  and  $\text{Ag}_2\text{S}-\text{GeS}_2$  systems were studied repeatedly, therefore the literature data on the crystal structure of the ternary compounds and phase diagrams of these systems are quite dissimilar. According to Ref. [31], three compounds form in the system  $\text{Ag}_2\text{S}-\text{SiS}_2$ : argyrodite  $\text{Ag}_8\text{SiS}_6$  that melts congruently at 1231 K and has a phase transition at 526 K,  $\text{Ag}_{10}\text{Si}_3\text{S}_{11}$  that corresponds to the incongruent melting type at 1034 K, and an equimolar composition  $\text{Ag}_2\text{SiS}_3$  that has an open melting maximum at 985 K. The system is divided by the intermediate phases into four sub-systems that exhibit a eutectic interaction between  $\text{Ag}_2\text{S}$  and  $\text{Ag}_8\text{SiS}_6$  (1085 K), a peritectic interaction between  $\text{Ag}_8\text{SiS}_6$  and  $\text{Ag}_{10}\text{Si}_3\text{S}_{11}$  (1034 K), a eutectic interaction between  $\text{Ag}_{10}\text{Si}_3\text{S}_{11}$  and  $\text{Ag}_2\text{SiS}_3$  (970 K), and  $\text{Ag}_2\text{SiS}_3$

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Table 1  
Crystallographic parameters and melting points of the compounds of the quasi-ternary systems  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3-\text{Si}(\text{Ge})\text{S}_2$

Compounds	Space group	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	<i>T<sub>m</sub></i> (K)	Reference
$\alpha$ - $\text{Ag}_2\text{S}$	$P2_1/c$	0.4231	0.6930 ( $\beta = 125^\circ 48'$ )	0.9526	450 <sup>a</sup>	[18]
$\beta$ - $\text{Ag}_2\text{S}$	$I4\bar{3}m$	0.486	–	–	860 <sup>a</sup>	[19]
$\gamma$ - $\text{Ag}_2\text{S}$	$Fd\bar{3}m$	0.626	–	–	1111	[20]
$\alpha$ - $\text{GeS}_2$	$P2_1/c$	0.672	1.6101 ( $\beta = 90^\circ 88'$ )	1.1436	865	[21]
$\beta$ - $\text{GeS}_2$	$Pc$	0.6875	2.2550 ( $\beta = 120^\circ 45'$ )	0.6869	1113	[22]
$\text{SiS}_2$	$labm$	0.9583	0.5614	0.5547	1373	[23]
$\alpha$ - $\text{In}_2\text{S}_3$	$I4_1/amd$	0.7623	–	3.236	1027 <sup>a</sup>	[24,25]
$\beta$ - $\text{In}_2\text{S}_3$	$Fd\bar{3}m$	1.0774	–	–	693 <sup>a</sup>	[24–26]
$\gamma$ - $\text{In}_2\text{S}_3$	$P\bar{3}m1$	0.3806	–	0.9044	1363	[24,25]
	$R\bar{3}c$	0.651	–	17.570		[24]
$\text{Ag}_2\text{SiS}_3$	$P1$	1.15662 ( $\alpha = 89^\circ 999'$ )	0.66568 ( $\beta = 91^\circ 748'$ )	0.66709 ( $\gamma = 90^\circ 000'$ )	1223	[27–29]
$\alpha$ - $\text{Ag}_8\text{SiS}_6$	$Pna2_1$	1.5024	0.7428	1.0533	526 <sup>a</sup>	[27–30]
$\beta$ - $\text{Ag}_8\text{SiS}_6$	–	–	–	–	983	[27–29]
$\text{Ag}_{10}\text{Si}_3\text{S}_{11}$	$P\bar{1}$	1.24114 ( $\alpha = 78^\circ 92'$ )	1.3476 ( $\beta = 77^\circ 61'$ )	0.6459 ( $\gamma = 68^\circ 71'$ )	1034 <sup>b</sup>	[31,32]
$\alpha$ - $\text{Ag}_2\text{GeS}_3$	$Cmc2_1$	1.1791	0.7079	0.6344	580 <sup>a</sup>	[33]
$\beta$ - $\text{Ag}_2\text{GeS}_3$	–	–	–	–	921 <sup>b</sup>	[33]
$\alpha$ - $\text{Ag}_8\text{GeS}_6$	$Pna2_1$	1.5149	0.7476	1.0589	493 <sup>a</sup>	[34]
$\beta$ - $\text{Ag}_8\text{GeS}_6$	–	–	–	–	1223	[35]
$\text{Ag}_{10}\text{Ge}_3\text{S}_{11}$	$Cc$	2.6244	0.65020 ( $\beta = 109^\circ 91'$ )	2.5083	989 <sup>b</sup>	[35]
$\text{AgIn}_5\text{S}_8$	$Fd\bar{3}m$	1.08265	–	–	1360	[36,37]
$\alpha$ - $\text{AgInS}_2$	$I\bar{4}2d$	0.58760	–	1.12007	935 <sup>a</sup>	[36]
$\beta$ - $\text{AgInS}_2$	$Pna2_1$	0.69972	0.82733	0.66939	1130 <sup>b</sup>	[36]

<sup>a</sup> Phase transformation temperature.

<sup>b</sup> Decomposition temperature.

and  $\text{SiS}_2$  form a eutectic at 860 K. The compositions of the ternary compounds of the  $\text{Ag}_2\text{S}-\text{GeS}_2$  section correspond to the compositions in the silicon-containing system [38,39].  $\text{Ag}_8\text{GeS}_6$  has a congruent melting character at 1213 K and a phase transition at 473 K,  $\text{Ag}_2\text{GeS}_3$  undergoes a eutectoid decomposition at 593 K,  $\text{Ag}_{10}\text{Ge}_3\text{S}_{11}$  is not represented at the phase diagram in Ref. [31] though its existence is mentioned in Ref. [35] and its crystal structure was investigated.

The information on the investigation of the  $\text{In}_2\text{S}_3-\text{GeS}_2$  and  $\text{In}_2\text{S}_3-\text{SiS}_2$  sections is limited. The formation of intermediate ternary phases in these systems is absent [40]. The eutectic interaction between the system components dominates, and their phase diagrams belong to Type V of Roozeboom classification [41].

The phase diagram of the  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3$  system is ambiguously described in the literature. The formation type of  $\text{AgInS}_2$  provokes many contradictions. In Ref. [42], where the phase diagram of the  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3$  system is presented, the invariant horizontal lines corresponding to the  $\text{AgInS}_2$  phase transition are not shown, though the polymorphism of this ternary chalcogenide was confirmed. The investigation of the  $\text{AgGaS}_2-\text{AgInS}_2$  system in Ref. [43] discovered continuous solid solubility of the system components. The phase diagram of such system corresponds to Roozeboom Type I, consequently  $\text{AgInS}_2$  has congruent type of melting, which in turn disagrees with Refs. [42,44] where it was established that  $\text{AgInS}_2$  forms in a peritectic reaction. The authors of Ref. [45] indicate the existence of a ternary compound  $\text{AgIn}_{11}\text{S}_{17}$  that is not represented at the phase diagram. Two ternary compounds exist in the  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3$  system,  $\text{AgInS}_2$  [46] and  $\text{AgIn}_5\text{S}_8$  [47–49] with the tetragonal (SG  $I42d$ ) and the cubic (SG  $Fd\bar{3}m$ ) structure, respectively.  $\text{AgInS}_2$

melts incongruently at 1130 K, and the liquidus curve at the stoichiometric point passes at 1150 K. On the contrary, the data obtained in Ref. [47] indicate that this phase has an open melting maximum at 1150 K. The investigation of the crystal structure of  $\text{HT-AgInS}_2$  established that this modification crystallizes in the orthorhombic structure (SG  $Pna2_1$ ) [48]. The compound  $\text{In}_2\text{S}_3$  is trimorphous, therefore the phase diagram of the binary system  $\text{In}-\text{S}$  [50] has two horizontal lines at 687 and 1023 K. The studies [51–54] were devoted to analysis of the crystal structure of various  $\text{In}_2\text{S}_3$  modifications.  $\alpha$ - $\text{In}_2\text{S}_3$  has tetragonal structure (SG  $I4amd$ ), though in Refs. [51,54] the authors describe it as  $\beta$ - $\text{In}_2\text{S}_3$ . The symmetry of  $\beta$ - $\text{In}_2\text{S}_3$  corresponds to the cubic structure (SG  $Fd\bar{3}m$ ) [53];  $\gamma$ - $\text{In}_2\text{S}_3$  forms a layered packing, and its trigonal unit cell corresponds to SG  $P\bar{3}m1$  [51]. Both  $\alpha$ - $\text{In}_2\text{S}_3$  and  $\beta$ - $\text{In}_2\text{S}_3$  may be obtained at room temperature [50]. The phenomenon of the stabilization of  $\beta$ - $\text{In}_2\text{S}_3$  may be explained as follows: since all compounds with the spinel structure have the ratio of cations to anions as 3:4, except  $\text{In}_2\text{S}_3$  where it is 2:3, the stabilization of  $\beta$ - $\text{In}_2\text{S}_3$  to room temperature is accompanied by an increase in cation deficiency, therefore the phase composition does not conform to the stoichiometry of the binary compound. The melting point of  $\gamma$ - $\text{In}_2\text{S}_3$  is 1363 K. All these facts cause an interest in the re-investigation of the quasi-binary system  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3$ .

### 3. Experimental

A total of 85 and 64 alloys were synthesized for the investigation of the  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3-\text{SiS}_2$  and  $\text{Ag}_2\text{S}-\text{In}_2\text{S}_3-\text{GeS}_2$  systems, respectively (Fig. 1). High-purity elements (at least 99.99 wt.% purity) were used as the starting materials. The 2 g batches were placed in quartz containers which were evacuated to the residual pressure of  $\sim 10^{-2}$  Pa. The synthesis was performed in a shaft-type

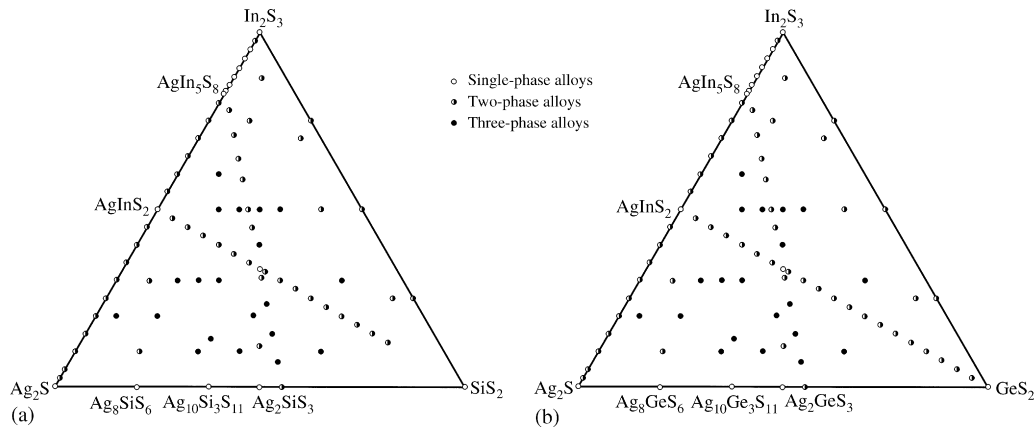


Fig. 1. Phase and chemical composition of the investigated alloys of the  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{SiS}_2$  (a) and  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{GeS}_2$  (b) systems.

furnace using a single-temperature method by the gradual heating (at the rate of 10 K/h) to 1370 K with an intermediate exposure to 820 K for 24 h. The alloys were held at the maximum temperature for 3 h and then cooled to room temperature at the same rate of 10 K/h.

XRD investigation of all synthesized alloys utilized a DRON 4–13 diffractometer using  $\text{Cu K}\alpha$  radiation. X-ray reflection sets for the structure investigation were recorded in the  $10$ – $100^\circ$  range ( $\theta/2\theta$  scanning) with the scan step of  $0.05^\circ$  and 30 s exposure at a point. The computation of the crystal structure was performed using CSD program package [55].

The construction of the vertical sections used the results of differential thermal analysis of the alloys (a Paulik–Paulik–Erdey derivatograph). Temperature was controlled by a Pt/Pt–Rh thermocouple,  $\text{Al}_2\text{O}_3$  was used as a standard. Temperature measurement uncertainty is  $\pm 5$  K. The thermograph was calibrated by measuring the melting points of Sn (505 K), Cd (594 K), Te (723 K), Sb (904 K), NaCl (1074 K), Ge (1209 K), Ag (1236 K), Cu (1356 K). The heating rate was 10 K/min. The cooling process was recorded in the inertial mode.

## 4. Results and discussion

### 4.1. Phase diagram of the $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ system

The phase diagram of the  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$  system constructed by us is presented in Fig. 2. The melting point of  $\text{AgIn}_5\text{S}_8$  is 1360 K. This ternary sulfide crystallizes in the spinel structure and has a wide homogeneity region from 81 to 96 mol.%  $\text{In}_2\text{S}_3$  as determined by the change of unit cell parameters (Fig. 3). The diffraction pattern of the alloy with 97.5 mol.%  $\text{In}_2\text{S}_3$  contained additional reflections that correspond to the tetragonal structure of  $\alpha$ - $\text{In}_2\text{S}_3$ . Thus the  $\text{AgIn}_{11}\text{S}_{17}$  compound [43] is, in fact, a solid solution based on  $\text{AgIn}_5\text{S}_8$  as its composition belongs to the homogeneity region of this phase. The coordinates of the eutectic of  $\text{AgIn}_5\text{S}_8$  and HT- $\text{In}_2\text{S}_3$  are 1336 K and 95 mol.%  $\text{In}_2\text{S}_3$ .

$\beta$ - $\text{In}_2\text{S}_3$  and  $\text{AgIn}_5\text{S}_8$  form a continuous solid solution series therefore the phase  $\text{AgIn}_5\text{S}_8$  may be considered as a berthollide with a shifted melting maximum that corresponds to the composition  $\text{In}_2\text{S}_3$ . A similar situation is observed in the binary system In–S [50].

The formation of HT- $\text{AgInS}_2$  occurs in a peritectic reaction  $\zeta + \text{L} \Leftrightarrow \text{HT-}\text{AgInS}_2$  at 1130 K. The interaction of  $\text{Ag}_2\text{S}$  and HT- $\text{AgInS}_2$  is of eutectic type with the eutectic coordinates 13 mol.%  $\text{In}_2\text{S}_3$  and 943 K. A minor solid solution range of HT- $\text{Ag}_2\text{S}$  is observed ( $<2$  mol.%), the extent of which increases somewhat with temperature and reaches  $\sim 8$  mol.% at the eutectic temper-

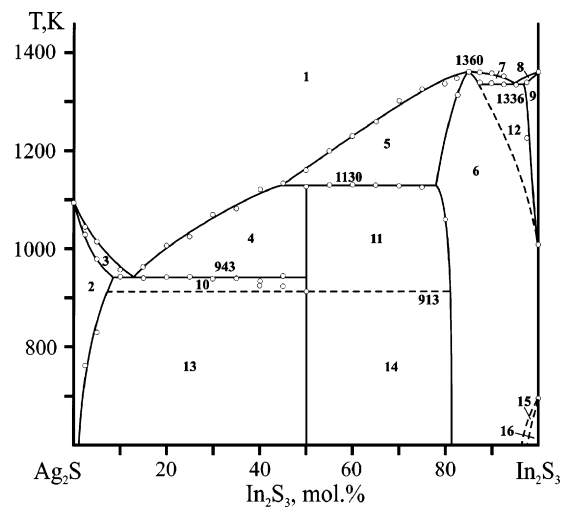


Fig. 2. Phase diagram of the system  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ : (1) L, (2)  $\alpha'$ , (3) L +  $\alpha'$ , (4) L + HT- $\text{AgInS}_2$ , (5) L +  $\zeta$ , (6)  $\zeta$ , (7) L +  $\zeta$ , (8) L +  $\beta''$ , (9)  $\beta''$ , (10)  $\alpha'$  + HT- $\text{AgInS}_2$ , (11) HT- $\text{AgInS}_2$  +  $\zeta$ , (12)  $\zeta$  +  $\beta''$ , (13)  $\alpha'$  + LT- $\text{AgInS}_2$ , (14) LT- $\text{AgInS}_2$  +  $\zeta$ , (15)  $\zeta$  +  $\beta$ , (16)  $\beta$ .

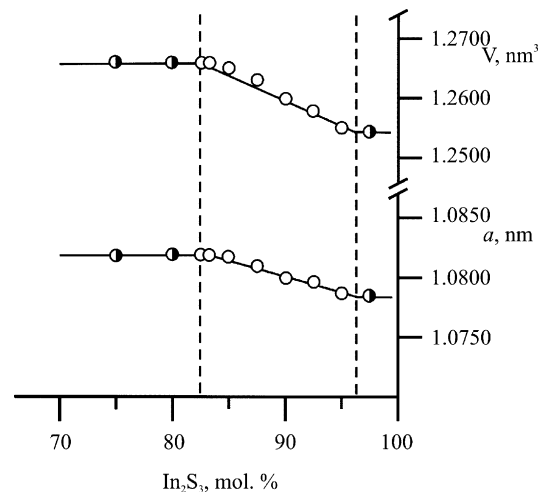


Fig. 3. Change of the lattice parameters within the homogeneity region of the  $\text{AgIn}_5\text{S}_8$  compound.

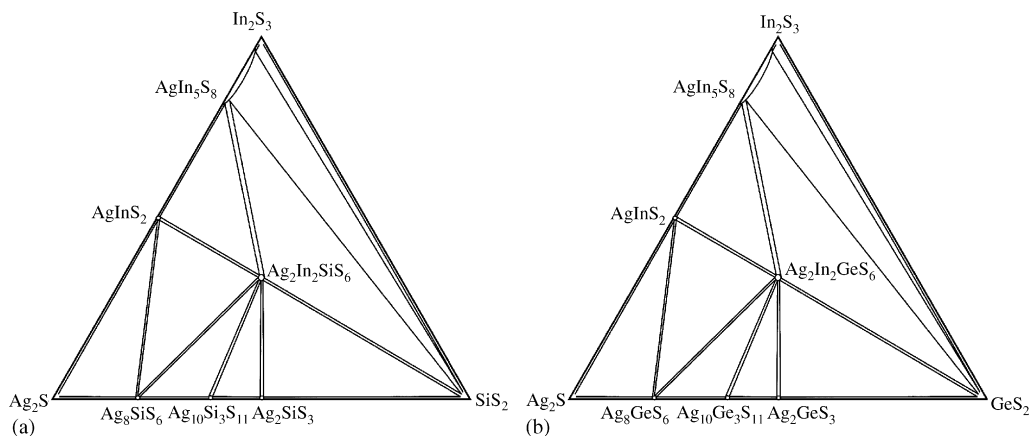


Fig. 4. Isothermal section of the  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{SiS}_2$  (a) and  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{GeS}_2$  (b) systems at room temperature.

ature. The phase transition of HT- $\text{AgInS}_2$  to LT- $\text{AgInS}_2$  takes place at 913 K.

4.2. Isothermal section of the  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{Si(Ge)S}_2$  systems at room temperature

The  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{Si(Ge)S}_2$  systems are composed of binary normal-valency sulfides, of which  $\text{Ag}_2\text{S}$  and  $\text{In}_2\text{S}_3$  possess polymorphism (Table 1), but only their low-temperature modifications were recorded in this work. The composition of alloys used for the determination of the phase equilibria is shown in Fig. 1. Five ternary compounds exist at room temperature in each of the investigated systems, their compositions, crystallographic data and melting points are given in Table 1. The quaternary compounds existing in these systems form equilibria with all available ternary sulfides (Fig. 4). The intermediate phase, in either system, forms an equilibrium with

only one binary chalcogenide,  $\text{SiS}_2$  or  $\text{GeS}_2$ , respectively. The interaction of  $\text{Ag}_2\text{In}_2\text{Si(Ge)S}_6$  with  $\text{Ag}_2\text{S}$  or  $\text{In}_2\text{S}_3$  is impossible due to the existence of equilibria  $\text{Ag}_8\text{Si(Ge)S}_6$ – $\text{AgInS}_2$  and  $\text{AgIn}_5\text{S}_8$ – $\text{Si(Ge)S}_2$ . A significant homogeneity region is observed only for  $\text{AgIn}_5\text{S}_8$  where it is localized along the  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$  section in either system.

4.3. Phase diagram of the  $\text{AgInS}_2$ – $\text{SiS}_2$  systems

The phase diagram of the  $\text{AgInS}_2$ – $\text{SiS}_2$  system is shown in Fig. 5. Since  $\text{AgInS}_2$  forms in a peritectic reaction  $\zeta + \text{L} \rightleftharpoons \delta'$ , the diagram features a field of primary crystallization of  $\text{AgIn}_5\text{S}_8$ . A compound  $\text{Ag}_2\text{In}_2\text{SiS}_6$  forms peritectically in the system at the ratio of initial compounds of 2:1 at 1133 K. The interaction of  $\text{Ag}_2\text{In}_2\text{SiS}_6$  and  $\text{SiS}_2$  is of the eutectic type, the eutectic coordinates are 57 mol.%  $\text{SiS}_2$  and 1097 K. The homogeneity region of the chalcopyrite phase is <5 mol.%  $\text{SiS}_2$ . The  $\text{AgInS}_2$  polymorphism is the reason for the peritectoid process  $\delta + \text{Ag}_2\text{In}_2\text{SiS}_6 \rightleftharpoons \delta'$  at 1011 K. At lower temperatures, the section is quasi-binary, where the intermediate quaternary phase is in equilibrium with either  $\text{AgInS}_2$  or  $\text{SiS}_2$ .

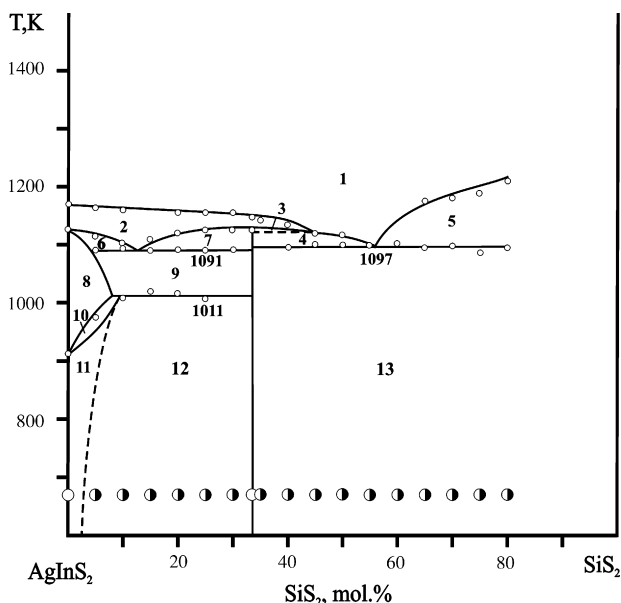


Fig. 5. Phase diagram of the  $\text{AgInS}_2$ – $\text{SiS}_2$  section: (1) L, (2)  $\text{L} + \zeta$ , (3)  $\text{L} + \zeta + \text{Ag}_2\text{In}_2\text{SiS}_6$ , (4)  $\text{L} + \text{Ag}_2\text{In}_2\text{SiS}_6$ , (5)  $\text{L} + \text{SiS}_2$ , (6)  $\text{L} + \zeta + \delta'$ , (7)  $\text{L} + \zeta + \text{Ag}_2\text{In}_2\text{SiS}_6$ , (8)  $\delta'$ , (9)  $\delta' + \text{Ag}_2\text{In}_2\text{SiS}_6$ , (10)  $\delta' + \delta$ , (11)  $\delta$ , (12)  $\delta + \text{Ag}_2\text{In}_2\text{SiS}_6$ , (13)  $\gamma + \text{SiS}_2$ .

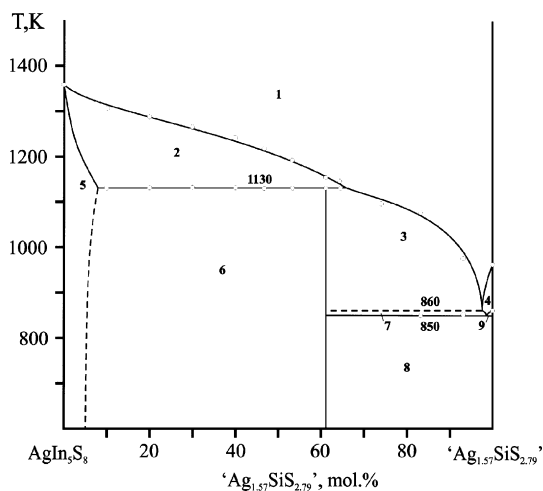


Fig. 6. Phase diagram of the  $\text{AgIn}_5\text{S}_8$ – $\text{Ag}_{1.57}\text{SiS}_{2.79}$  section: (1) L, (2)  $\text{L} + \zeta$ , (3)  $\text{L} + \text{Ag}_2\text{In}_2\text{SiS}_6$ , (4)  $\text{L} + \text{Ag}_2\text{SiS}_3$ , (5)  $\zeta$ , (6)  $\zeta + \text{Ag}_2\text{In}_2\text{SiS}_6$ , (7)  $\text{L} + \text{Ag}_2\text{In}_2\text{SiS}_6 + \text{Ag}_2\text{SiS}_3$ , (8)  $\text{Ag}_2\text{In}_2\text{SiS}_6 + \text{Ag}_2\text{SiS}_3 + \text{SiS}_2$ , (9)  $\text{L} + \text{Ag}_2\text{SiS}_3 + \text{SiS}_2$ .

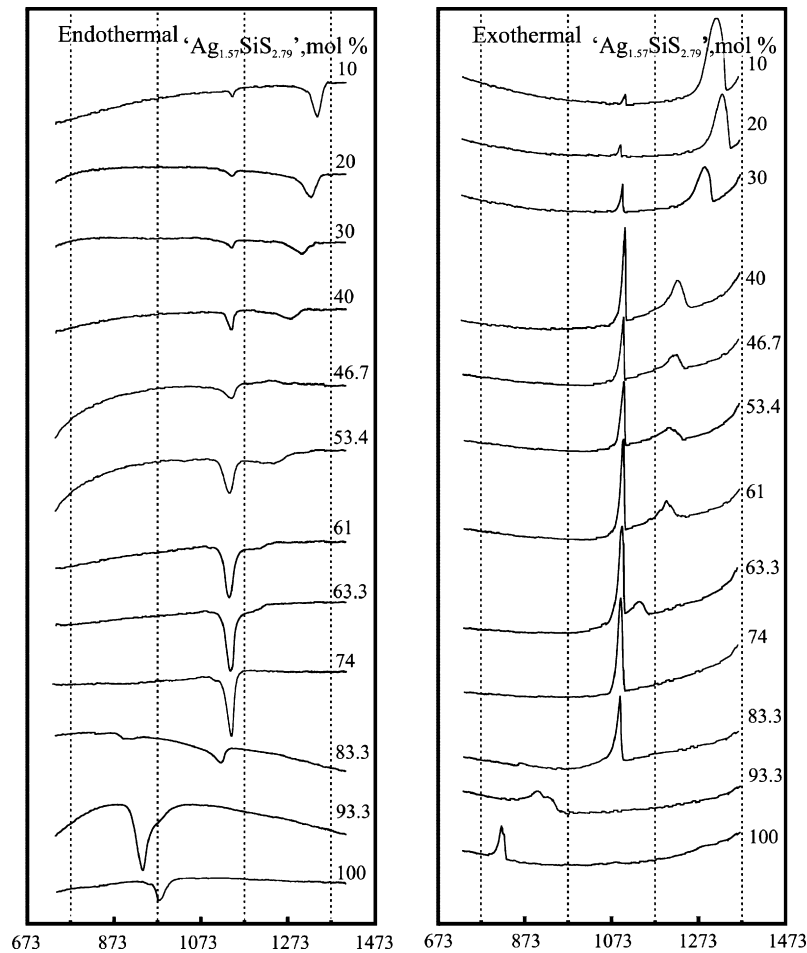


Fig. 7. Thermograms of the alloys of the  $\text{AgIn}_5\text{S}_8$ – $\text{Ag}_{1.57}\text{SiS}_{2.79}$  section.

#### 4.4. Phase diagram of the $\text{AgIn}_5\text{S}_8$ – $\text{Ag}_{1.57}\text{SiS}_{2.79}$ system

A more detailed study of the formation of  $\text{Ag}_2\text{In}_2\text{SiS}_6$  and the refinement of the equilibria described in Section 4.2 required the construction of a vertical section shown in Fig. 6. The concentration range was selected to connect the stoichiometric compositions of the compounds  $\text{AgIn}_5\text{S}_8$  and  $\text{Ag}_2\text{In}_2\text{SiS}_6$ . According to the phase diagram in Fig. 5,  $\text{Ag}_2\text{In}_2\text{SiS}_6$  forms in a peritectic interaction of  $\text{AgIn}_5\text{S}_8$  and L at 1130 K (the sample thermograms clearly exhibit a peak that increases with the decrease of the  $\text{AgIn}_5\text{S}_8$  concentration in the system and reaches its maximum at the stoichiometric composition of the quaternary compound (Fig. 7). The part of the diagram from 61 to 100 mol.%  $\text{Ag}_{1.57}\text{SiS}_{2.79}$  is non-quasi-binary. The crystallization in this concentration range (at 850 K) ends in the formation of three phases  $\text{Ag}_2\text{In}_2\text{SiS}_6$ ,  $\text{Ag}_2\text{SiS}_3$ ,  $\text{SiS}_2$ , according to the ternary eutectic process.

#### 4.5. Partial liquidus surface projection of the quasi-ternary system $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{SiS}_2$

Using the investigated sections, we can approximate a part of the liquidus surface projection in the fields of primary crystallization of  $\text{AgIn}_5\text{S}_8$  and  $\text{Ag}_2\text{In}_2\text{SiS}_6$  following a method applied

for the analysis of the  $\text{Li}_3\text{NbO}_4$ – $\text{KNbO}_3$ – $\text{Nb}_2\text{O}_5$  system in Ref. [56]. We can affirm the existence of a peritectic reaction  $\text{L} + \zeta \rightleftharpoons \delta' + \text{Ag}_2\text{In}_2\text{SiS}_6$  (Fig. 8) at 1091 K, though the invariant point coordinates require more precise definition. Point U is the

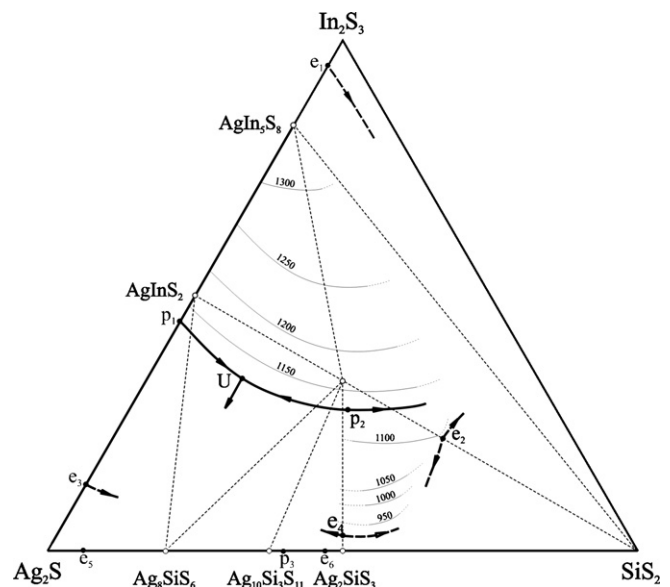


Fig. 8. Partial liquidus surface projection of the  $\text{Ag}_2\text{S}$ – $\text{In}_2\text{S}_3$ – $\text{SiS}_2$  system near  $\text{Ag}_2\text{In}_2\text{SiS}_6$ .



convergence point of the monovariant lines emerging from the binary peritectics  $p_1$  and  $p_2$ .

The field of primary crystallization of  $\text{Ag}_2\text{In}_2\text{SiS}_6$ , due to the incongruent type of its formation, is shifted from the stoichiometric composition to lower  $\text{In}_2\text{S}_3$  content. Metallographic analysis of alloys from the region between  $\text{Ag}_2\text{In}_2\text{SiS}_6$  and  $\text{Ag}_2\text{SiS}_3$  and the existence of a stable equilibrium between these compounds (Fig. 4) lead to the conclusion on the formation of a binary eutectic of  $\text{Ag}_2\text{In}_2\text{SiS}_6$  and  $\text{Ag}_2\text{SiS}_3$ . Monovariant lines emerging from the point  $e_4$  would show the decrease of temperature to either side of it, according to the rule of Rhines [41,57]. The position of the point  $e_4$ , though is also required more accurate definition, is shifted to  $\text{Ag}_2\text{SiS}_3$  (on the  $\text{Ag}_2\text{In}_2\text{SiS}_6$ – $\text{Ag}_2\text{SiS}_3$  section) as seen from the data on the  $\text{AgIn}_5\text{S}_8$ – $\text{Ag}_{1.57}\text{SiS}_{2.79}$  section (Fig. 6). The field of primary crystallization of  $\text{Ag}_2\text{In}_2\text{SiS}_6$  is promising for the selection of starting compositions for its single crystal growth.

#### 4.6. Crystal structure refinement of $\text{Ag}_2\text{In}_2\text{SiS}_6$ and $\text{Ag}_2\text{In}_2\text{GeS}_6$

$\text{Ag}_2\text{In}_2\text{SiS}_6$  and  $\text{Ag}_2\text{In}_2\text{GeS}_6$  crystallize in the monoclinic space group  $Cc$ . The basis model for the computation of the crystal structure of the quaternary phases was the structure of the  $\text{Ag}_2\text{In}_2\text{GeSe}_6$  compound [8]. Six positions of selenium were occupied by sulfur, in case of  $\text{Ag}_2\text{In}_2\text{SiS}_6$  Ge was changed to Si, the positions of other atoms remained unchanged. The computation under such initial conditions led to satisfactory results as shown in the values of the fit factors and profile factors. The conditions of XRD study and the results of the calculation of the unit cell parameters of the quaternary phases are listed in Table 2.

Table 2

Results of the crystal structure determination of the  $\text{Ag}_2\text{In}_2\text{SiS}_6$  and  $\text{Ag}_2\text{In}_2\text{GeS}_6$  compounds

Formula	$\text{Ag}_2\text{In}_2\text{SiS}_6$	$\text{Ag}_2\text{In}_2\text{GeS}_6$
Space group	$Cc$	$Cc$
$a$ (nm)	1.21379(3)	1.22089(4)
$b$ (nm)	0.71681(2)	0.72115(3)
$c$ (nm)	1.21171(4)	1.21978(5)
$\beta$ ( $^\circ$ )	109.252(2)	109.508(2)
Cell volume ( $\text{nm}^3$ )	0.9953(1)	1.0123(1)
Number of atoms in cell	44.0	44.0
Calculated density ( $\text{g}/\text{cm}^3$ )	4.4430(4)	4.6604(6)
Absorption coefficient ( $\text{cm}^{-1}$ )	811.93	823.14
Radiation and wavelength (nm)		Cu $K\alpha$ and 0.154185
Diffractometer		Powder DRON 4–13
Mode of refinement		Full profile
Number of atom sites	11	11
Number of free parameters	46	46
$R_1$ and $R_p$	0.0746 and 0.1256	0.0657 and 0.1189
Texture axis and parameter	[001] and 1.232(9)	[001] and 1.33(3)

Experimental, calculated and differential XRD spectra shown in Fig. 9 agree well. The atom coordinates and isotropic temperature parameters for the compounds are presented in Table 3. The number of atoms per unit cell, due to hidden symmetry operations, is 22, i.e. the unit cell contains 2 formula units of  $\text{Ag}_2\text{In}_2\text{SiS}_6$  or  $\text{Ag}_2\text{In}_2\text{GeS}_6$ , respectively.

Interatomic distances Si–S and certain Ag–S and In–S distances in the  $\text{Ag}_2\text{In}_2\text{SiS}_6$  compound that are given in Table 4 are shorter than the sums of respective ionic radii ( $r_{\text{S}^{2-}} = 0.155$  nm,  $r_{\text{Ag}^{1+}} = 0.074$  nm,  $r_{\text{In}^{3+}} = 0.076$  nm,  $r_{\text{Si}^{4+}} = 0.040$  nm,  $r_{\text{Ge}^{4+}} = 0.053$  nm [58]). The distances  $\delta(\text{Ag–S})$ ,  $\delta(\text{In–S})$ ,  $\delta(\text{Si–S})$  in the compounds

Table 3

Crystallographic positions in the  $\text{Ag}_2\text{In}_2\text{SiS}_6$  and  $\text{Ag}_2\text{In}_2\text{GeS}_6$  structures

Atom	Position	$x$	$y$	$z$	$B_{\text{iso}} \times 10^2$ ( $\text{nm}^2$ )
$\text{Ag}_2\text{In}_2\text{SiS}_6$					
Ag1	4a	0.3960(6)	0.5859(5)	0.2700(6)	1.07(9)
Ag2	4a	0.5938(6)	0.2029(4)	0.4201(6)	1.00(8)
In1	4a	0.4223(6)	0.0943(5)	0.0749(6)	1.05(9)
In2	4a	0.2389(6)	0.0643(4)	0.2704(6)	1.07(9)
Si1	4a	0.1665(14)	0.745(2)	0.0140(14)	0.7(2)
S1	4a	0.353(2)	0.779(2)	0.0521(13)	1.5(3)
S2	4a	0.4202(12)	0.2460(13)	0.2469(12)	1.2(3)
S3	4a	0.1044(10)	–0.009(2)	0.0682(10)	0.9(3)
S4	4a	0.0844(10)	0.2706(13)	0.3202(13)	1.6(3)
S5	4a	0.2992(13)	0.2297(13)	0.8792(14)	0.7(2)
S6	4a	0.6312(10)	0.029(2)	0.0857(10)	1.3(3)
$\text{Ag}_2\text{In}_2\text{GeS}_6$					
Ag1	4a	0.3952(5)	0.5885(5)	0.2577(6)	1.17(9)
Ag2	4a	0.6012(5)	0.2090(4)	0.4132(5)	1.14(8)
In1	4a	0.4130(5)	0.0968(5)	0.0590(6)	1.06(9)
In2	4a	0.2333(5)	0.0595(4)	0.2582(5)	0.77(9)
Ge1	4a	0.1650(6)	0.7580(8)	0.0012(7)	0.94(9)
S1	4a	0.3617(14)	0.7661(15)	0.0601(13)	1.1(3)
S2	4a	0.4026(13)	0.2167(12)	0.2413(12)	0.8(2)
S3	4a	0.0876(11)	0.020(2)	0.0386(12)	0.9(3)
S4	4a	0.0979(11)	0.2713(15)	0.2897(15)	1.4(3)
S5	4a	0.2933(13)	0.2317(14)	0.8780(14)	1.2(2)
S6	4a	0.6287(10)	0.0076(14)	0.0958(10)	0.5(3)

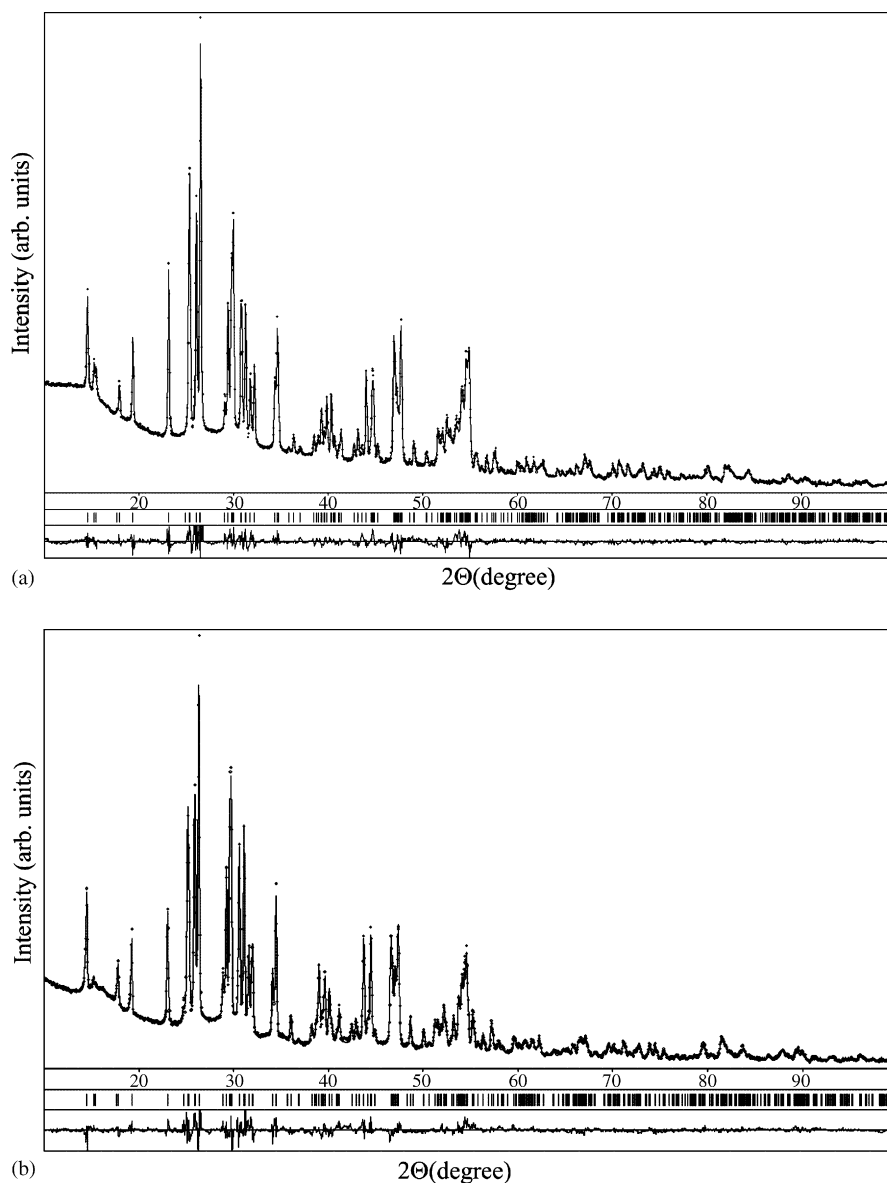


Fig. 9. Experimental and calculated diffraction patterns and corresponding difference diagrams for the  $\text{Ag}_2\text{In}_2\text{SiS}_6$  (a) and  $\text{Ag}_2\text{In}_2\text{GeS}_6$  (b) compounds.

$\text{Ag}_2\text{In}_2\text{SiS}_6$ ,  $\text{Ag}_2\text{In}_2\text{GeS}_6$  correlate to the respective distances in known compounds, e.g.  $\delta(\text{Ag}-\text{S}) = 0.255 \text{ nm}$  ( $\text{AgInS}_2$ ) [36],  $\text{In}-\text{S} = 0.2464 \text{ nm}$  ( $\text{CuInS}_2$ ) [59];  $\text{Si}-\text{S} = 0.2133 \text{ nm}$  ( $\text{SiS}_2$ ) [60].

The tetrahedral voids of the anionic sub-lattice of sulfur are partially occupied by silver, indium and silicon atoms. The coordination polyhedra of all cations are nearly regular tetrahedra that are connected by their tops. The tetrahedra of the same cations may be considered as isolated ones, they are paired for silver and indium atoms and are separately located for silicon. The quaternary phases  $\text{Ag}_2\text{In}_2\text{Si}(\text{Ge})\text{S}_6$  belong to cation-deficient compounds [61]. The ratio of cations to anions is  $\approx 0.83$ , therefore sulfur has both tetrahedral and trigonal surrounding. The latter, however, can be described as the tetrahedral one with a vacancy ( ) in the place of one of the cations. One formula unit (11 atoms) in the structure contains one vacancy which is 9.09% of the number of atoms. The second coordination spheres of sulfur atoms S1, S3, S4, S6 are icosahedra which

allows one to attribute phases  $\text{Ag}_2\text{In}_2\text{Si}(\text{Ge})\text{S}_6$  to a large class of icosahedral compounds [62,63]. These polyhedra form a layered packing where they are edge-shared. Icosahedra layers are connected by the tops. Atoms S2 and S5 coordinate 17 other sulfur atoms of various sorts.

A layered packing of sulfur atoms can be seen in the  $\text{Ag}_2\text{In}_2\text{Si}(\text{Ge})\text{S}_6$  structure. The layers alternate every  $0.25 \cdot b$  in the  $[010]$  direction, with pentagon-trigonal networks forming at  $0.25 \cdot b$  and  $0.75 \cdot b$ , and exclusively trigonal networks existing at  $0 \cdot b$  and  $0.5 \cdot b$ . In two cases the described networks are slightly corrugated. Discussing general order of atoms, non-coplanar hexagonal formations can be seen that combine to form distorted networks that are represented in the fragments of structure shown in Fig. 10.

Icosahedral compounds are widespread among intermetallic compounds that are called Laves' phases. Some of the first chalcogenides with such structure were  $\text{Cd}_4\text{GeS}_6$  [64],

Table 4  
Interatomic distances  $\delta$  (nm) and coordination numbers (CN) of the atoms in the  $\text{Ag}_2\text{In}_2\text{SiS}_6$  and  $\text{Ag}_2\text{In}_2\text{GeS}_6$  compound structures

$\text{Ag}_2\text{In}_2\text{SiS}_6$			$\text{Ag}_2\text{In}_2\text{GeS}_6$		
Atoms	$\delta$ (nm)	CN	Atoms	$\delta$ (nm)	CN
Ag1–S5	0.243(2)	4	Ag1–S5	0.257(2)	4
Ag1–S2	0.2481(11)		Ag1–S1	0.264(2)	
Ag1–S4	0.2536(15)		Ag1–S2	0.2692(10)	
Ag1–S1	0.287(2)		Ag1–S4	0.2715(15)	
Ag2–S2	0.245(2)	4	Ag2–S3	0.2524(14)	4
Ag2–S6	0.2528(12)		Ag2–S5	0.256(2)	
Ag2–S5	0.274(2)		Ag2–S2	0.262(2)	
Ag2–S3	0.2809(12)		Ag2–S6	0.2648(13)	
In1–S2	0.2359(14)	4	In1–S5	0.241(2)	4
In1–S1	0.2399(14)		In1–S2	0.2429(15)	
In1–S6	0.2539(14)		In1–S1	0.2467(12)	
In1–S5	0.254(2)		In1–S6	0.2600(14)	
In2–S5	0.2466(12)	4	In2–S4	0.2374(14)	4
In2–S3	0.2510(13)		In2–S2	0.243(2)	
In2–S4	0.2610(14)		In2–S5	0.2523(13)	
In2–S2	0.265(2)		In2–S3	0.2691(15)	
Si1–S6	0.189(2)	4	Ge1–S3	0.2224(14)	4
Si1–S3	0.211(2)		Ge1–S6	0.2265(13)	
Si1–S1	0.217(3)		Ge1–S1	0.227(2)	
Si1–S4	0.223(2)		Ge1–S4	0.244(2)	
S1–Si1	0.217(3)	3	S1–Ge1	0.227(2)	3
S1–In1	0.2399(14)		S1–In1	0.2467(12)	
S1–Ag1	0.287(2)		S1–Ag1	0.264(2)	
S2–In1	0.2359(14)	4	S2–In1	0.2429(15)	4
S2–Ag2	0.245(2)		S2–In2	0.243(2)	
S2–Ag1	0.2481(11)		S2–Ag2	0.262(2)	
S2–In2	0.265(2)		S2–Ag1	0.2692(10)	
S3–Si1	0.211(2)	3	S3–Ge1	0.2224(14)	3
S3–In2	0.2510(13)		S3–Ag2	0.2524(14)	
S3–Ag2	0.2809(12)		S3–In2	0.2691(15)	
S4–Si1	0.223(2)	3	S4–In2	0.2374(14)	3
S4–Ag1	0.2536(15)		S4–Ge1	0.244(2)	
S4–In2	0.2610(14)		S4–Ag1	0.2715(15)	
S5–Ag1	0.243(2)	4	S5–In1	0.241(2)	4
S5–In2	0.2466(12)		S5–In2	0.2523(13)	
S5–In1	0.254(2)		S5–Ag2	0.256(2)	
S5–Ag2	0.274(2)		S5–Ag1	0.257(2)	
S6–Si1	0.189(2)	3	S6–Ge1	0.2265(13)	3
S6–Ag2	0.2528(12)		S6–In1	0.2600(14)	
S6–In1	0.2539(14)		S6–Ag2	0.2648(13)	

$\text{Cd}_4\text{SiS}_6$ ,  $\text{Hg}_4\text{SiS}_6$ ,  $\text{Hg}_4\text{GeS}_6$  [65,66]. A quaternary analogue of such phases is the  $\text{Ag}_2\text{In}_2\text{GeSe}_6$  compound that was discovered in Ref. [8]. Later,  $\text{LT-Ag}_2\text{In}_2\text{SiSe}_6$  compound was added to the isostructural series [7]. The genesis of ternary and quaternary “icosahedral” compounds is exemplified for  $\text{Cd}_4\text{GeS}_6$  and  $\text{Ag}_2\text{In}_2\text{GeS}_6$  (Fig. 11). Unlike the ternary compound  $\text{Cd}_4\text{GeS}_6$ , in  $\text{Ag}_2\text{In}_2\text{GeS}_6$  two of  $4a$  positions of Cd atoms are occupied with Ag atoms, two others—with In atoms, the occupation of other crystallographic positions is equivalent. The change in position occupation may be pictured as follows:  $\text{Cd1} \rightarrow \text{Ag1}$ ;  $\text{Cd2} \rightarrow \text{In2}$ ;  $\text{Cd3} \rightarrow \text{In1}$ ;  $\text{Cd4} \rightarrow \text{Ag2}$ . The representatives of this structure type have the packing of 24 chalcogene atoms per unit

cell. Since the symmetry of the location of the crystal lattice points is described by the monoclinic structure, the cleavage plane of the unit cell is (0.5 0 0). Such atom placement can be viewed as a pseudo-cubic cell with periods  $a_c \approx b_m\sqrt{2}$ , therefore one may expect a transformation of the monoclinic structure into the cubic one at higher temperature. As investigations show, the prevailing majority of “icosahedral” compounds undergo phase transitions, e.g.  $\text{Ag}_2\text{In}_2\text{SiSe}_6$ ,  $\text{Ag}_2\text{In}_2\text{GeS}_6$ , etc. The formation of the  $\text{Ag}_2\text{In}_2\text{C}^{\text{IV}}\text{X}_6$  ( $\text{C}^{\text{IV}} = \text{Si, Ge}$ ;  $\text{X} = \text{S, Se}$ ) compounds may be discussed by analyzing ratios of the tetrahedral radii of the cations and the volumes of the tetrahedral units in the structure of ternary cadmium chalcogenides and their quaternary analogues.



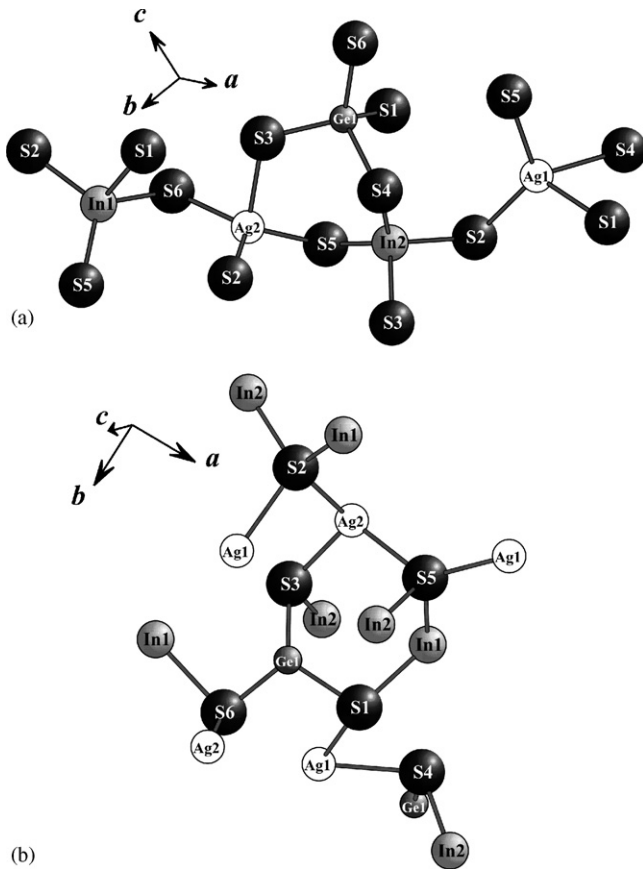


Fig. 10. Structure fragments illustrating cationic (a) and anionic (b) surrounding in  $\text{Ag}_2\text{In}_2\text{GeS}_6$ .

Such an approach was used in Refs. [67,68]; it is used for the tetrahedral compounds exclusively [69]. Cadmium in ternary compounds has the size intermediate between that of Ag and In. Consequently, the formation of quaternary “icosahedral” compounds requires the cations to be commensurate with the cations of the ternary analogues.

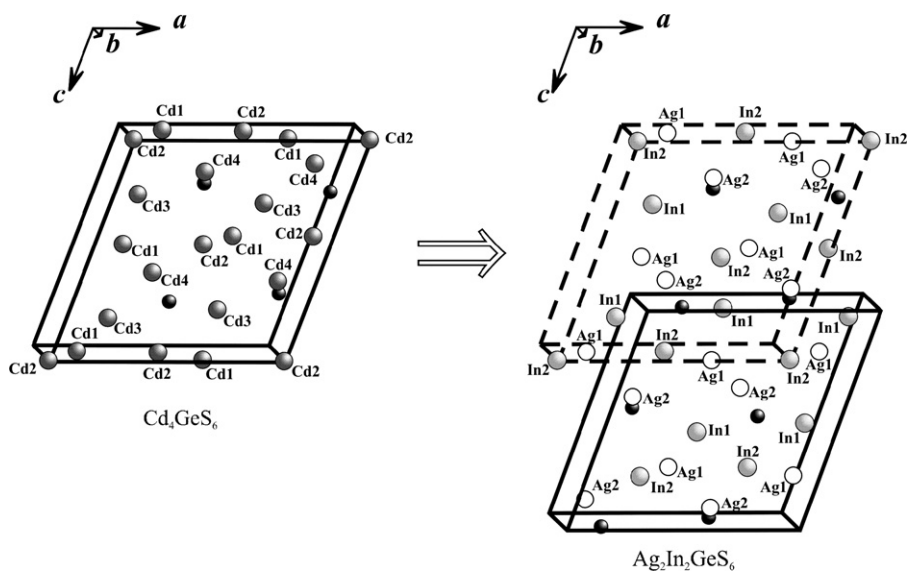


Fig. 11. Genesis of the  $\text{Cd}_4\text{GeS}_6$  and  $\text{Ag}_2\text{In}_2\text{GeS}_6$  structures.

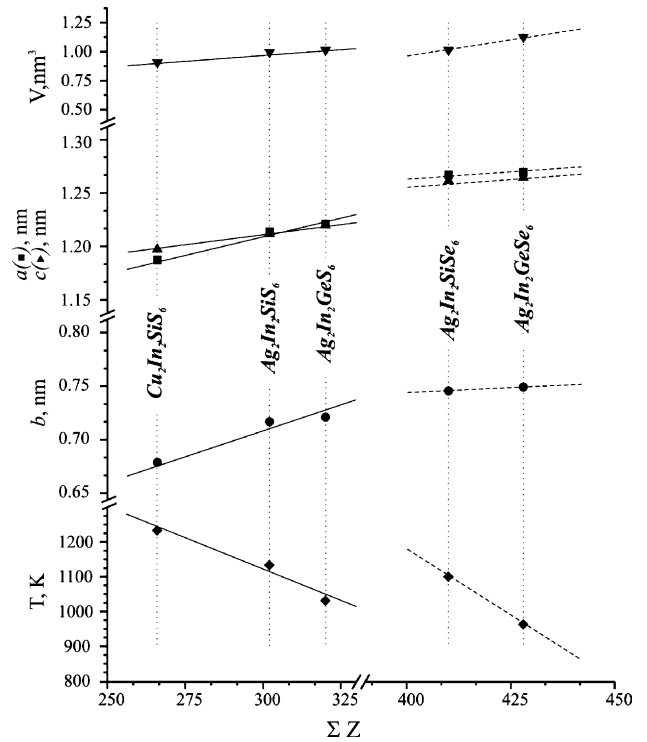


Fig. 12. Graphic dependences of unit cell parameters ( $a, b, c$ ), maximum temperatures of the existence ( $T$ ) and volumes of elementary parallelepiped ( $V$ ) on the sum of atomic numbers ( $\Sigma Z$ ) of the constituent atoms in the  $\text{A}_{1/2}\text{In}_2\text{C}^{\text{IV}}\text{X}_6$  compounds.

Currently, five complex chalcogenides of the  $\text{A}_{1/2}\text{In}_2\text{C}^{\text{IV}}\text{X}_6$  type with the monoclinic structure are known. Their crystallographic parameters and melting points (or decomposition temperature) are given in Table 5. The compound stability increases with the molecular weight, as do the structure stability and the absence of polymorphism (re-ordering at higher temperature).  $\text{Cu}_2\text{In}_2\text{SiS}_6$  is stable in a small temperature range ( $\sim 130$  K), with a eutectoid decomposition below 1107 K into

Table 5  
Crystallographic parameters of quaternary “icosahedral” compounds and their melting points

Compound	$\sum Z$	$a$ (nm)	$b$ (nm)	$c$ (nm)	$V$ (nm <sup>3</sup> )	$T_m$ (K)	Reference
Cu <sub>2</sub> In <sub>2</sub> SiS <sub>6</sub>	266	1.18725	0.67880	1.19718	0.90533	1233	[6]
Ag <sub>2</sub> In <sub>2</sub> SiS <sub>6</sub>	302	1.21379	0.71681	1.21171	0.9953	1133	[ <sup>a</sup> ]
Ag <sub>2</sub> In <sub>2</sub> GeS <sub>6</sub>	320	1.22089	0.72115	1.21978	1.0123	1031	[ <sup>a</sup> ]
Ag <sub>2</sub> In <sub>2</sub> SiSe <sub>6</sub>	410	1.26683	0.74565	1.26133	1.1246	1100	[7]
Ag <sub>2</sub> In <sub>2</sub> GeSe <sub>6</sub>	428	1.2692	0.7492	1.2644	1.1333	963	[8]

<sup>a</sup> This work.

two phases, CuInS<sub>2</sub> and SiS<sub>2</sub>. The compounds Ag<sub>2</sub>In<sub>2</sub>SiS<sub>6</sub> and Ag<sub>2</sub>In<sub>2</sub>GeS<sub>6</sub> form in peritectic reactions. Though melting congruently, Ag<sub>2</sub>In<sub>2</sub>SiSe<sub>6</sub> is dimorphous, with the thermal effect of the phase transition occurring at 1030 K. Of the listed compounds, only Ag<sub>2</sub>In<sub>2</sub>GeSe<sub>6</sub> has an open melting maximum. Polymorphism is absent in Ag<sub>2</sub>In<sub>2</sub>GeSe<sub>6</sub> and Ag<sub>2</sub>In<sub>2</sub>SiS<sub>6</sub>. The geometric dimensions of the unit cell (Fig. 12) and its volume also regularly increase with the sum of atomic numbers (molecular weight) of the compound. The dependence of the maximum temperature of the existence of the crystalline phase (melting or decomposition point) A<sub>2</sub>In<sub>2</sub>C<sup>IV</sup>X<sub>6</sub> on the sum of atomic numbers of the compound illustrates “double periodicity” (Fig. 12). There is no gradual transition from sulfides to selenides, though the nature of decrease is observed in either case.

## 5. Conclusions

The character of the phase equilibria in the Ag<sub>2</sub>S–In<sub>2</sub>S<sub>3</sub>–Si(Ge)S<sub>2</sub> systems was established in this study. Investigated vertical sections make possible the selection of the conditions of single crystal growth of the newly discovered non-centrosymmetric quaternary sulfides Ag<sub>2</sub>In<sub>2</sub>SiS<sub>6</sub> and Ag<sub>2</sub>In<sub>2</sub>GeS<sub>6</sub>. The use of our preparative methods gives no hints for the existence of AgIn<sub>11</sub>S<sub>17</sub> as an individual compound. The crystal structure of the found compounds was studied by the powder diffraction method. A comparative analysis of the crystal-chemical parameters and melting points in the series of new isostructural “icosahedral” phases was performed.

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