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Isothermal section of the Ag_2S–PbS–GeS_2 system at 300 K and the crystal structure of Ag_2PbGeS_4

Yu. Kogut[a], A. Fedorchuk[b], O. Zhbankov[a], Ya. Romanyuk[c], I. Kityk[d], L. Piskach[a], O. Parasyuk[a,*]

[a] Department of Inorganic and Physical Chemistry, Volyn State University, 13 Voli Avenue, 43025 Lutsk, Ukraine
[b] Department of Inorganic and Organic Chemistry, Lviv National University of Veterinary Medicine and Biotechnologies, 50 Pekarska St., 79010 Lviv, Ukraine
[c] EMPA, Swiss Federal Laboratories for Materials Testing and Research, 8600 Dubendorf, Switzerland
[d] Electrical Engineering Department, Czestochowa University of Technology, Al. Armii Krajowej 17/19, 42-200 Czestochowa, Poland

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ABSTRACT

The isothermal section of the Ag_2S–PbS–GeS_2 system at room temperature was investigated by XRD. The existence of two quaternary compounds, Ag_2PbGeS_4 and $Ag_{0.5}Pb_{1.75}GeS_4$, was confirmed, and the phase equilibria between the binary system components and the ternary and the quaternary compounds were determined. The crystal structure of Ag_2PbGeS_4 was studied using the single crystal X-ray diffraction. It was established that Ag_2PbGeS_4 crystallizes in an own structural type in non-centrosymmetric space group *Ama*2 with the lattice parameters $a = 1.02390(4)$ nm, $b = 1.02587(5)$ nm, $c = 0.67701(3)$ nm.

1. Introduction

Recently, we performed an analysis of the quasi-ternary systems A^I_2X–$B^{II}X$–$C^{IV}X_2$ (where A^I is Cu, Ag; B^{II} is Zn, Cd, Hg; C^{IV} is Si, Ge, Sn and X is S, Se, Te) [1] to examine the formation of intermediate compounds. It was determined that the compounds with the equimolar component ratio described by the $A^I_2B^{II}C^{IV}X_4$ formula are the most numerous. These compounds crystallize primarily in an orthorhombic (space group (S.G.) $Pmn2_1$ or $Cmc2_1$) or a tetragonal (S.G. $I\bar{4}2m$ or $I\bar{4}$) structure that are derived from the wurtzite or sphalerite structure, respectively, and are characterized by the tetrahedral coordination of atoms. The compounds of such composition do not exist for C^{IV} = Pb (though several $A^I_2FePbX_4$ compounds were reported [2]). However, as the most typical oxidation state of lead is +2, it was suggested to test its position as a B^{II} element. In the copper-containing systems, only one compound, Cu_2PbSiS_4, was discovered that crystallizes in the trigonal structure (S.G. $P3_221$, $a = 0.60565$ nm, $c = 1.51841$ nm) [3].

Testing the possible variations of the silver-containing compositions, we discovered the existence of a quaternary compound Ag_2PbGeS_4. Presently, we report the investigation of the isothermal section of the Ag_2S–PbS–GeS_2 system and the determination of the Ag_2PbGeS_4 crystal structure by X-ray single crystal method. The quasi-ternary system was not studied before; however, the existence of another quaternary compound was reported, $Ag_{0.5}Pb_{1.75}GeS_4$, which crystallizes in a cubic space group $I\bar{4}3d$, $a = 1.40291$ nm [4].

Two congruently melting compounds exist at the side system Ag_2S–GeS_2. Ag_2GeS_3 crystallizes in S.G. $Cmc2_1$, $a = 1.179$ nm, $b = 0.7064$ nm, $c = 0.6338$ nm [5,6], and a dimorphous Ag_8GeS_6 [7,8]. The high-temperature (HT) modification of the argyrodite has *fcc* structure ($a = 1.070$ nm) [9]. The structure of the low-temperature (LT) modification as determined by Eulenberger [10] is orthorhombic (S.G. $Pna2_1$, $a = 1.5149$ nm, $b = 0.7476$ nm, $c = 1.0589$ nm). The existence of another incongruent phase was also reported. Its composition is given as Ag_4GeS_4 in [6], and its structure is described as triclinic; the authors of [11] give the composition as $Ag_{10}Ge_3S_{11}$, that crystallizes in a monoclinic structure (S.G. *Cc* or *C*2*c*). We have confirmed the latter composition, and have determined by single crystal X-ray diffraction that $Ag_{10}Ge_3S_{11}$ crystallizes in S.G. *Cc* with unit cell parameters $a = 2.6244(4)$ nm, $b = 0.65020(5)$ nm, $c = 2.5083(4)$ nm, $\beta = 109.910(1)^\circ$ [12]. Both ternary compounds $PbGeS_3$ and Pb_2GeS_4 that are known in the PbS–GeS_2 system crystallize in the monoclinic S.G. $P2_1/c$ with the lattice parameters $a = 0.7224$ nm, $b = 1.0442$ nm, $c = 0.6825$ nm, $\beta = 105.7^\circ$ [13] and $a = 0.7974$ nm, $b = 0.8925$ nm, $c = 1.0876$ nm, $\beta = 114.2^\circ$ [14] respectively. No intermediate phases were found in the Ag_2S–PbS system [15].

2. Experimental

The isothermal section of the Ag_2S–PbS–GeS_2 system was investigated on 110 alloys (the large number was caused by the parallel studies of the vertical sections).

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* Corresponding author. Tel.: +380 3322 49972; fax: +380 3322 41007.
E-mail address: oleg@univer.lutsk.ua (O. Parasyuk).

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Table 1
Results of the crystal structure determination of Ag_2PbGeS_4.

Compound	Ag_2PbGeS_4
Number of formula units per unit cell	4
Space group	*Ama*2(40)
a (nm)	1.02390(4)
b (nm)	1.02587(5)
c (nm)	0.67701(3)
Cell volume (nm^3)	0.71112(9)
Number of atoms in the cell	32.0
Calculated density (g/cm^3)	5.8257(8)
Absorption coefficient (1/cm)	1046.16
Radiation and wavelength	Mo-Kα 0.071073 nm
Diffractometer	STOE IPDS
Mode of refinement	$F(h\,k\,l)$
Restrictions	$F(h\,k\,l) > 4.00\,\mathrm{sig}(F)$
Extinction formalism	Sheldrick-2 0.0006(1)
Number of atomic sites	6
Number of free parameters	43
2θ and $\sin\theta/\lambda$ (max.)	58.27 and 0.685
Number of measured reflections	576
Reflections used in refinement	489
R_F, R_w	0.0375, 0.0419
Goodness of fit	1.050
Scale factor	1.581(2)

The alloys were prepared by co-melting the high-purity elements (at least 99.99 wt.% purity) in evacuated quartz ampoules. At the preliminary stage the ampoules with the batches were heated in an oxygen-gas burner flame under the visual observation of the process to achieve the maximum bonding of the elementary sulfur. Then the ampoules were placed in a shaft-type furnace and heated to 1270 K at the rate of 50 K/h. They were held at this temperature for 6 h with periodic vibration followed by slow cooling to the annealing temperature (670 K) at the rate of 10 K/h. The annealing was held for 250 h followed by cooling to room temperature at the rate of 10 K/h.

We were not able to preserve by quenching the HT modification of argyrodites $Ag_8C^{IV}X_6$, in this research or other related studies [16,17]. The HT-$Ag_8C^{IV}X_6$ compounds have large solid solution ranges, that are easily recorded by DTA, but that cannot be quenched. Therefore the equilibria at room temperature with the LT modification of Ag_8GeS_6 are presented in this paper.

The crystal structure was studied by the single crystal technique using STOE IPDS diffractometer (Mo-Kα-radiation), with parameters and the crystallographic data presented in Table 1. The structural computations were performed using CSD program package [18]. The analysis of systematic extinctions of the obtained data set evidenced the possibility of the following space groups: a centrosymmetric *Cmcm* and non-centrosymmetric $Cmc2_1$ and *Ama*2. For all possible groups, using the Patterson synthesis we established the position of the heaviest atom, in our case Pb, that was localized in the 0 0 0 position in each case. Further on, the Fourier analysis was used to localize the position of the remaining atoms. After the refinement of the model, the best position separation and the best value of the goodness factor were achieved for the space group *Ama*2.

3. Results and discussion

3.1. Isothermal section of the Ag_2S–PbS–GeS_2 system at 300 K

The chemical and the phase composition of the investigated alloys and the resulting isothermal section of the Ag_2S–PbS–GeS_2 system at 300 K are shown in Fig. 1. We had reported previously that the Ag_8GeS_6–PbS section is one of the triangulating sections of the system [16]. This section is of the eutectic type, with the invariant point coordinates 72 mol.% PbS and 951 K. The existence of the $Ag_{0.5}Pb_{1.75}GeS_4$ phase was confirmed, and another quaternary compound Ag_2PbGeS_4 was discovered. The $Ag_{0.5}Pb_{1.75}GeS_4$ compound crystallizes in the cubic S.G. $I\bar{4}3d$ with the unit cell parameter $a = 1.40277(1)$ nm, which agrees well with the single crystal data [4].

According to XRD data, the existence of 10 three-phase fields was determined in the system. The numbering of the fields and the phases that form are listed in Table 2. Additionally, 19 two-phase equilibria of binary, ternary and quaternary compounds were identified in the system. No significant solid solution ranges (over 2 mol.%) were found.

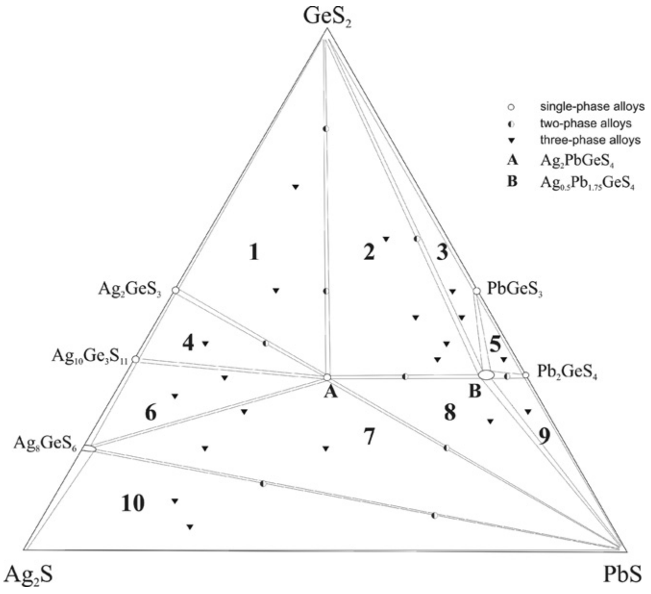

Fig. 1. Isothermal section of the Ag_2S–PbS–GeS_2 system at 300 K.

Table 2
Three-phase fields in the isothermal section of the Ag_2S–PbS–GeS_2.

Field number in Fig. 1	Phases that exist in the field
1	Ag_2GeS_3, GeS_2, Ag_2PbGeS_4
2	Ag_2PbGeS_4, $Ag_{0.5}Pb_{1.75}GeS_4$, GeS_2
3	$Ag_{0.5}Pb_{1.75}GeS_4$, GeS_2, $PbGeS_3$
4	Ag_2GeS_3, $Ag_{10}Ge_3S_{11}$, Ag_2PbGeS_4
5	$PbGeS_3$, Pb_2GeS_4, $Ag_{0.5}Pb_{1.75}GeS_4$
6	Ag_8GeS_6, $Ag_{10}Ge_3S_{11}$, Ag_2PbGeS_4
7	Ag_8GeS_6, Ag_2PbGeS_4, PbS
8	$Ag_{0.5}Pb_{1.75}GeS_4$, Ag_2PbGeS_4, PbS
9	$Ag_{0.5}Pb_{1.75}GeS_4$, Pb_2GeS_4, PbS
10	Ag_2S, Ag_8GeS_6, PbS

Testing a possible homogeneity region of the $Ag_{0.5}Pb_{1.75}GeS_4$ compound, we synthesized 18 alloys with 2 mol.% step around its composition (not shown in Fig. 1 for simplification). A small homogeneity region extends from the stoichiometric composition to the side of Pb_2GeS_4. The diffraction patterns of other alloys exhibited a residual reflection of GeS_2 or the triplet, characteristic of PbS; the alloys from the field 5 also were three-phase samples.

Table 3
Atomic positions and atomic displacement parameters for the Ag_2PbGeS_4 structure.

Atom	Position	x/a	y/b	z/c	$B_{eq.} \times 10^2$ (nm^2)
Pb	4a	0	0	0.0000(3)	2.91(3)
Ag	8c	0.1053(2)	0.3781(2)	0.0185(5)	5.78(7)
Ge	4b	1/4	0.2015(2)	0.4807(4)	0.76(6)
S1	4b	1/4	0.3862(6)	0.6499(9)	1.58(14)
S2	4b	1/4	0.5406(6)	0.1983(9)	1.88(15)
S3	8c	0.4275(4)	0.1992(4)	0.2945(7)	2.04(11)

$B_{eq.} = 1/3[B_{11}a^{*2}a^2 + \cdots + 2B_{23}b^*c^*bc\cos\alpha]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pb	3.65(5)	2.88(4)	2.19(4)	−0.30(4)	0	0
Ag	5.73(11)	5.53(10)	6.08(14)	−2.84(9)	−3.26(12)	1.72(13)
Ge	0.61(9)	0.81(9)	0.86(11)	0	0	0.24(10)
S1	1.6(2)	1.5(2)	1.6(3)	0	0	0.1(2)
S2	2.3(3)	1.9(3)	1.4(3)	0	0	0.4(2)
S3	1.9(2)	2.2(2)	2.0(2)	0.5(2)	0.5(2)	−0.1(2)

$T = \exp[-1/4(B_{11}a^{*2}h^2 + \cdots + 2B_{23}b^*c^*kl)]$

Table 4
Interatomic distances δ (nm) and coordination numbers (C.N.) of the atoms in the Ag_2PbGeS_4 structure.

Atoms		δ (nm)	C.N.	Atoms		δ (nm)	C.N.
Pb	- 2S3	0.2950(5)	8	S1	- 1Ge	0.2214(6)	5
	- 2S1	0.2991(3)			- 2Ag	0.2904(6)	
	- 2S2	0.3301(4)			- 2Pb	0.2991(3)	
	- 2S3	0.3465(5)					
Ag	- 1S3	0.2498(5)	4	S2	- 1Ge	0.2212(7)	5
	- 1S2	0.2541(6)			- 2Ag	0.2541(6)	
	- 1S3	0.2640(5)			- 2Pb	0.3301(4)	
	- 1S1	0.2904(6)					
Ge	- 2S3	0.2212(5)	4	S3	- 1Ge	0.2212(5)	5
	- 1S2	0.2212(7)			- 1Ag	0.2498(5)	
	- 1S1	0.2214(6)			- 1Ag	0.2640(5)	
					- 1Pb	0.2950(5)	
					- 1Pb	0.3465(5)	

3.2. *Crystal structure of a new quaternary compound Ag_2PbGeS_4*

According to the structure computation results that are presented in Table 1, Ag_2PbGeS_4 has an orthorhombic structure which contains isolated tetrahedra GeS_4, and Pb and Ag countercations. This non-centrosymmetric phase (space group *Ama*2) has two formula units per unit cell, with the unit cell volume of $0.71112\,nm^3$. The standardized atom coordinates and their displacement parameters in the Ag_2PbGeS_4 structure are listed in Table 3, the interatomic distances and the coordination numbers of atoms are given in Table 4. All interatomic distances are equal to or somewhat smaller than the sum of the respective atomic radii.

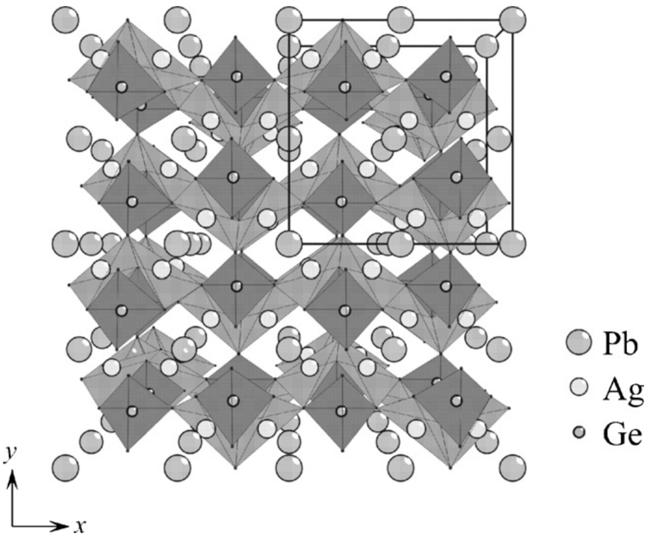

Fig. 3. Packing of the AgS_4 and GeS_4 tetrahedra in the Ag_2PbGeS_4 structure.

Polyhedral representation of the Ag_2PbGeS_4 structure projection and the coordination polyhedra of atoms are shown in Fig. 2. The coordination surrounding of Pb, the heaviest atom, is characterized by eight sulfur atoms forming a two-capped trigonal prism. Such surrounding of the Pb atoms is observed also in a quaternary compound Cu_2PbSiS_4 [3]. The Pb–S distances ranging from 0.2950(5)–0.33465(5) nm in Ag_2PbGeS_4 are similar to those in Cu_2PbSiS_4 (0.3011–0.3222 nm) [3] and $PbGa_2S_4$ compounds (0.2790–0.3276 nm) [19]. Smaller-sized cations Ag and Ge are surrounded by the tetrahedra of sulfur atoms. The AgS_4 tetrahedra are rather distorted unlike to GeS_4 tetrahedra which are practically regular. The interatomic distances Ag–S agree well with the respective distances in known compounds $Ag_{0.5}Pb_{1.75}GeS_4$ (0.2710 nm) [4] or KAg_2SbS_4 (0.2603 nm) [20]. The Ge–S distances also correlate quite well to the distances in the similar compounds Ag_2CdGeS_4

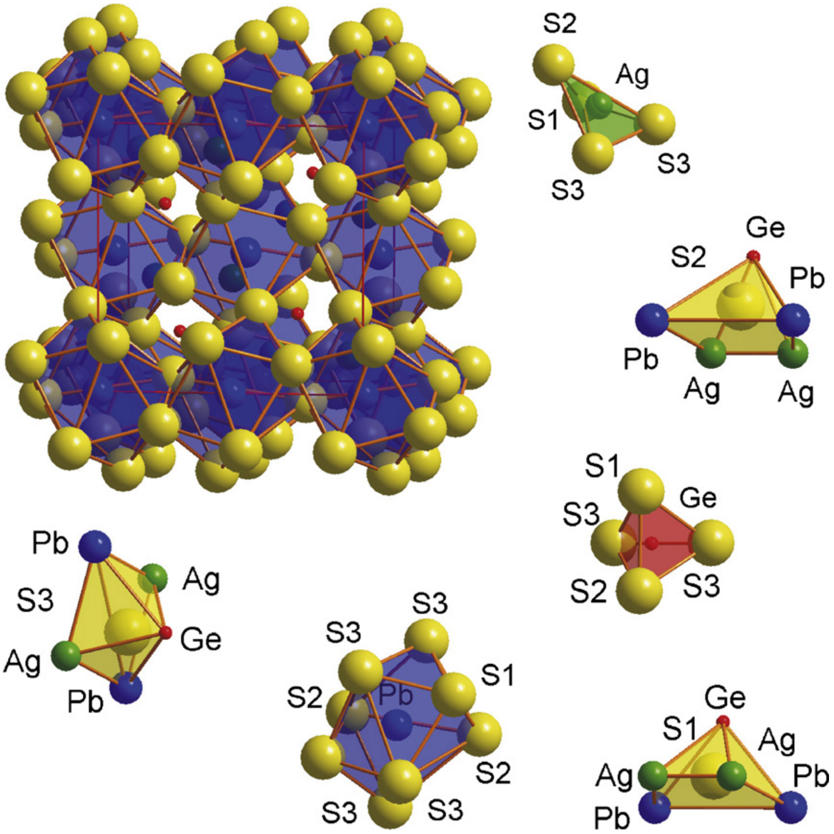

Fig. 2. Polyhedral representation of the Ag_2PbGeS_4 structure and the coordination polyhedra of atoms.

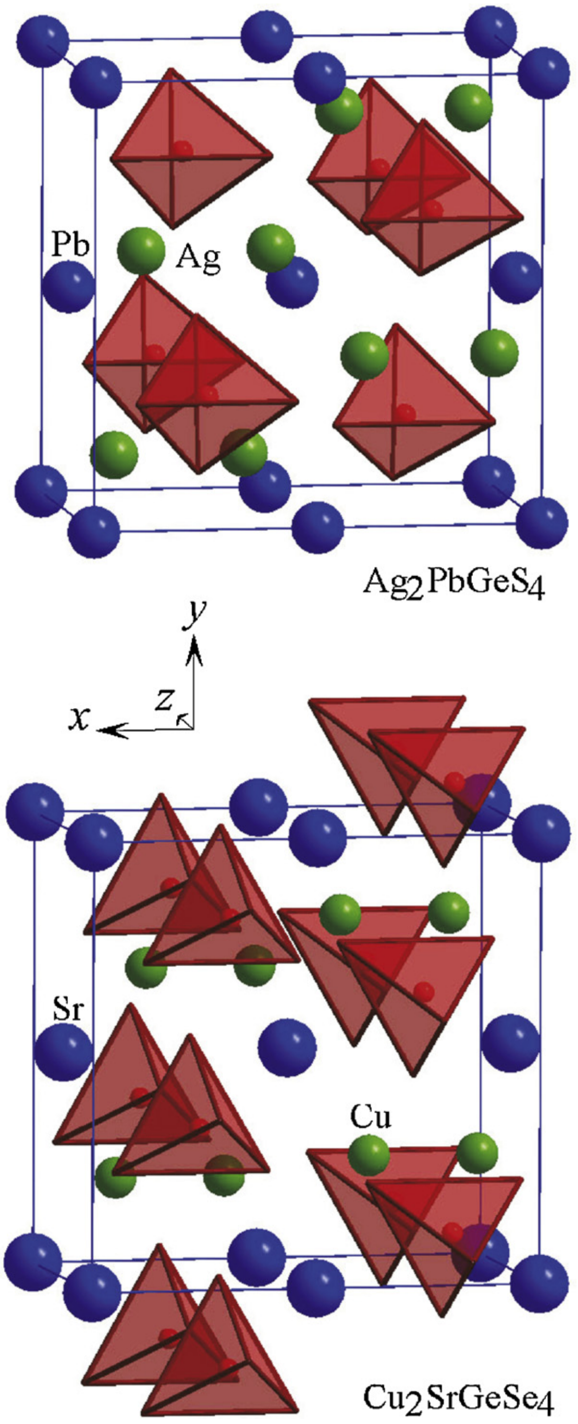

Fig. 4. Packing of the Ge-centered tetrahedra in the structures of the Ag_2PbGeS_4 and $Cu_2SrGeSe_4$ compounds.

(0.2179–0.2246 nm) [21] and α-Pb_2GeS_4 (0.2210–0.2248 nm) [22]. Finally, sulfur atoms are coordinated by five cation atoms (two atoms of Pb and Ag each and one Ge). They form a tetragonal pyramid for S1 and S2 atoms the base of which in both cases is composed by Pb and Ag atoms paired in the rectangle corners. Ge atoms are situated in the pyramid tops, therefore these polyhedra, in addition to being distorted in the base, have also flattened tops. The similar situation is observed for S3 atoms but the cations of the base are situated diagonally. The diagonal formed by Pb atoms is somewhat dropped below the rectangle plane which tranforms the polyhedron into a heavily distorted trigonal bipyramid.

Lead atoms form eight covalent bonds Pb–S of which two are formed by sharing electrons, and the remaining six by the donor–acceptor mechanism; free electron pair does not exhibit stereochemical activity. Such nature of bonding causes strong polarizing effect by the PbS_8 clusters because the charges of sulfur atoms are not compensated by a single lead atom. The residual electrostatic forces thus cause a shift of Ag^+ ions from the geometrical center of a regular tetrahedron AgS_4 which in turn causes the distortion of the coordination surrounding of silver atoms and of their thermal ellipsoids. Thus, Ag^+ ions compensate, to some extent, the residual electrostatic charge of the PbS_8 clusters. That the GeS_4 tetrahedra are not distorted is likely related to practically total shielding of much smaller Ge^{4+} cations by their counter-ions.

The structure of the $Cu_2SrGeSe_4$ compound is the closest to the investigated (space group *Ama*2, $a = 1.0807$ nm, $b = 1.0735$ nm, $c = 0.6541$ nm) [23]. Isolated GeS_4 tetrahedra connected by the AgS_4 tetrahedra can be marked out in the structure. The structure of the compound is formed by the infinite corrugated layers of corner- and edge-shared AgS_4 tetrahedra connected by the GeS_4 tetrahedra and the PbS_8 two-capped trigonal prisms (Fig. 3). The packing of the Ge-centered polyhedra in both structures is presented in Fig. 4 (standardized atom coordinates were used). Both structures are characterized by the layers of the tetrahedra along the *b* axis. The corners of the GeS_4 tetrahedra in the Ag_2PbGeS_4 structure face the same direction in both layers, whereas in the $Cu_2SrGeSe_4$ structure they are oriented in the opposite directions. It is worth noting that in the packing of the GeS_4 tetrahedra, the Ag_2PbGeS_4 structure is related to the $Ag_{0.5}Pb_{1.75}GeS_4$ structure [4].

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