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The Ag_2S–ZnS–GeS_2 system: Phase diagram, glass-formation region and crystal structure of Ag_2ZnGeS_4

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ABSTRACT

Isothermal section of the quasi-ternary system Ag_2S–ZnS–GeS_2 at 298 K was investigated by X-ray phase analysis. The existence of a quaternary compound Ag_2ZnGeS_4 was discovered, and its crystal structure was determined using X-ray powder method (Cu_2FeSnS_4 structure type, space group $I\bar{4}2m$, $a = 0.574996(9)$ nm, $c = 1.03434(3)$ nm, $c/a = 1.799$ and $R_I = 0.0495$). The glass-formation region in the system was investigated. It is localized along the Ag_2S–GeS_2 system, and the maximum amount of ZnS in the glass phase is 12 mol.%.

1. Introduction

The investigation of the phase diagram of the Ag_2S–ZnS–GeS_2 system is the continuation of the study of the quasi-ternary systems of the type $A^I{}_2X$–$B^{II}X$–$C^{IV}X_2$, where A^I–Cu, Ag; B^{II}–Zn, Cd, Hg; C^{IV}–Si, Ge, Sn and X–S, Se, Te. Some of the results of our investigation of such systems are summarized in Ref. [1]. It was shown that the most common formula of the compounds that form in these systems is $A^I{}_2B^{II}C^{IV}X_4$; such compounds crystallize primarily in either of the non-centrosymmetric space groups $I\bar{4}2m$ or $Pmn2_1$ and are of interest as potential materials for non-linear optics and optoelectronics.

Phase diagrams of the bounding quasi-binary systems were investigated earlier. The systems Ag_2S–ZnS [2] and ZnS–GeS_2 [3] are of the eutectic type. The absence of either intermediate phases or solid solubility of the components is typical of both systems. The Ag_2S–GeS_2 system and the crystal structure of the compounds that form in it were investigated repeatedly [4–14]. The latest paper [14] that presents the Ag_2S–GeS_2 phase diagram reports three compounds: Ag_8GeS_6 (space group $Pna2_1$, $a = 1.5137$ nm, $b = 0.7483$ nm and $c = 1.0590$ nm), Ag_4GeS_4 (triclinic, $a = 0.9072$ nm, $b = 1.412$ nm, $c = 0.3346$ nm, $\alpha = 95.90^\circ$, $\beta = 92.63^\circ$ and $\gamma = 74.96^\circ$) and Ag_2GeS_3 (space group $Cmc2_1$, $a = 1.179$ nm, $b = 0.7064$ nm, $c = 0.6338$ nm). Ag_2GeS_3 and Ag_8GeS_6 melt congruently at 921 K and 1223 K; they are dimorphous, with the phase transition temperatures of 579 K and 500 K, respectively. Ag_4GeS_4 forms in a peritectic reaction $L + Ag_8GeS_6 \Leftrightarrow Ag_4GeS_4$ at 1013 K. Recently, we confirmed the composition of the compound $Ag_{10}Ge_3S_{11}$ [15]. It was determined by the single crystal method that it crystallizes in the monoclinic structure (space group Cc, $a = 2.6244(4)$ nm, $b = 0.65020(5)$ nm, $c = 2.5083(4)$ nm, $\beta = 109.910(1)^\circ$ and own structure type) which agrees well with Ref. [10]. This quasi-binary system is also of interest due to a large concentration range of the existence of glassy state; according to Refs. [16,17] the range extends from 45 mol.% to 100 mol.% GeS_2. Properties of the glasses were studied [13,18–20], and high ionic conductivity was reported.

The Ag_2S–ZnS–GeS_2 system was not studied in detail. A phase diagram of the section Ag_8GeS_6–ZnS [21] was investigated earlier; it is of the eutectic type, with the invariant point coordinates 1201 K and 42 mol.% ZnS. In this paper we present the results of the investigation of the isothermal section of the quasi-ternary system at 298 K, the determination of the glass-formation region, and the crystal structure of the new quaternary phase Ag_2ZnGeS_4.

2. Experimental

Phase diagram of the Ag_2S–ZnS–GeS_2 system at 298 K was constructed from the results of the investigation of 47 alloys; their chemical and phase composition is shown in Fig. 1. The batches of 1 g were synthesized from high-purity elements (at least 99.99 wt.% of the principal component) in evacuated quartz containers. The synthesis was carried out in several stages. At the first stage the evacuated ampoules were heated in the oxygen-gas burner flame to complete bonding of elementary sulfur. Then the containers were placed in a shaft-type furnace and heated to the maximum temperature of 940–1420 K (based on the data on the phase diagrams of the bounding systems) at the rate of 50 K h^{-1}. The cooling process was also stepwise. The alloys were cooled to 670 K at the rate of 10 K h^{-1}. At this temperature they were

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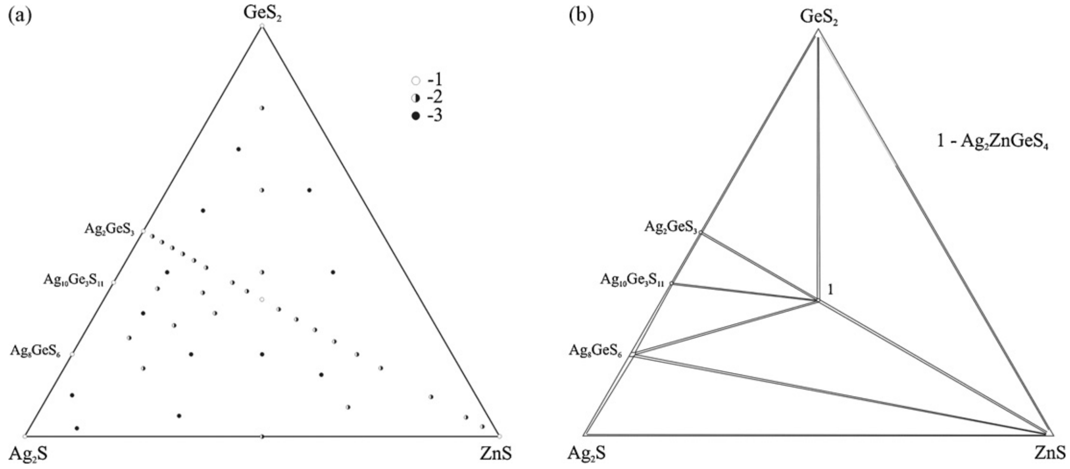

Fig. 1. Alloy compositions (a) and isothermal section (b) of the quasi-ternary system Ag_2S–ZnS–GeS_2 at 298 K: 1, single-phase alloys; 2, two-phase alloys and 3, three-phase alloys.

annealed for 800 h. Then the alloys were cooled to 420 K at the same rate and then to room temperature with the furnace turned off. The third stage was applied to the alloys with ZnS content over 70 mol.% which were non-homogeneous after the two stages. These alloys were crushed in an agate mortar to fine powder, pressed into pellets and heated in evacuated ampoules to 1420 K. They were then cooled to 420 K at the rate of 10 K h^{-1} with intermediate exposure to 1170 K for 48 h and to 670 K for 800 h. The synthesis ended in the inertial cooling of the furnace to room temperature.

The synthesis of the glasses utilized previously synthesized alloys that were repacked into ampoules of special construction of thin-wall (0.8 mm) quartz, evacuated, and heated (heating rate 50 K h^{-1}) in a shaft-type furnace to 1270 K. The alloys were held at this temperature for 10 h to homogenize the melts, and then quenched into saturated saline solution. The cooling rate during quenching is estimated as $\geq$200 K/s. Obtained glasses exhibit a characteristic shine. Their color deepens from orange for high GeS_2 content to red for 60 mol.% GeS_2 or less.

Obtained alloys were investigated by X-ray powder method using DRON 4-13 diffractometer, CuK_α radiation. The glassy alloys of the quasi-ternary system additionally underwent differential thermal analysis (Paulik–Paulik–Erdey derivatograph, Pt/Pt–Rh thermocouple). The computation of the crystal structure was performed using CSD software package [22].

3. Results

3.1. The isothermal section of the quasi-ternary system

Isothermal section of the quasi-ternary system Ag_2S–ZnS–GeS_2 at 298 K that was constructed according to the results of X-ray phase analysis is presented in Fig. 1. Three ternary compounds Ag_8GeS_6, $Ag_{10}Ge_3S_{11}$ and Ag_2GeS_3 were identified in the bounding system Ag_2S–GeS_2. Obtained values of unit cell parameters agree with the literature data [10,14]. The existence of a new quaternary phase Ag_2ZnGeS_4 was discovered which crystallizes in the tetragonal stannite structure. The compound forms equilibria with all ternary compounds and the system components, except Ag_2S which is cut off by the section Ag_8GeS_6–ZnS.

The results of the investigation of quasi-ternary systems $A^I{}_2S$–$B^{II}S$–GeS_2 [1,23–26] show that the formation of a compound is typical for the equivalent ratio of all three components. A tendency to the increase of the number of compounds with the substitution of B^{II} element (Zn to Cd to Hg) is marked out; this correspondingly complicates the picture of the phase equilibria. Such tendency is observed in both silver- and copper-containing systems. Both Cu_2S–ZnS–GeS_2 [1] and Ag_2S–ZnS–GeS_2 systems contain only one compound of equi-molar composition. Analogous systems with CdS exhibit two intermediate phases each. The same number of compounds is found in the Cu_2S–HgS–GeS_2 system [25] (another one exists at higher temperatures [26]); and the largest number of compounds (4) was discovered in the Ag_2S–HgS–GeS_2 system [24]. Another particularity common to zinc- and cadmium-containing systems is the formation of equilibria between the ternary phases $A^I{}_8GeS_6$ and ZnS or CdS.

3.2. Glass-formation in the Ag_2S–ZnS–GeS_2 system

The composition and the state of obtained alloys are shown in Fig. 2. The region of the glass existence on the Ag_2S–GeS_2 side in our experiment extends from 100 mol.% to 48 mol.% GeS_2, which agrees well with other researchers [16,17]. The maximum amount of zinc sulfide that can be introduced into glass is 12 mol.% in 60–70 mol.% GeS_2 range. The glass-formation region narrows with higher content of the glass-forming element.

Similar extent of the glass-formation region was observed in the related system Ag_2S–CdS–GeS_2 where the maximum amount of the modifier CdS was 15 mol.%. However, in the Ag_2S–HgS–GeS_2 system the glass-formation region crosses the entire concentration triangle for the germanium disulfide concentration over 50 mol.% [27]. The likely reasons are the much higher ionicity of the bonds in ZnS and CdS compared to HgS and the existence of a large glass-formation region at the bounding side HgS–GeS_2 where it extends from 50 mol.% to 100 mol.% GeS_2 [28].

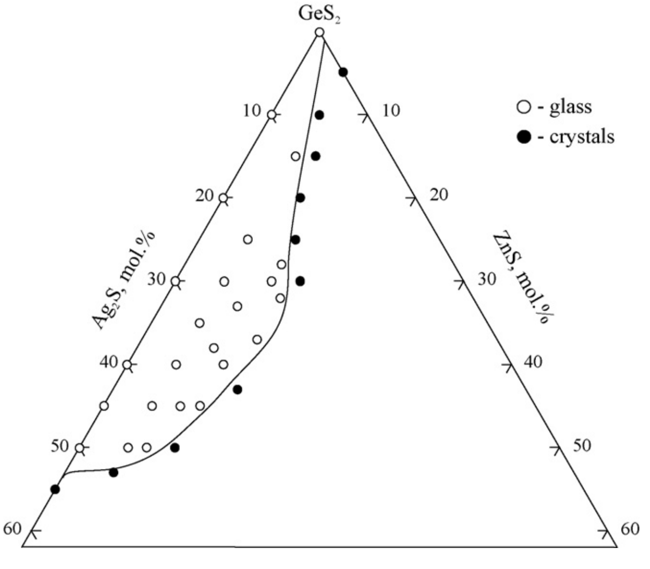

Fig. 2. Glass-formation region in the quasi-ternary system Ag_2S–ZnS–GeS_2.

Table 1
Compositions of the glassy alloys of the quasi-ternary system Ag_2S–ZnS–GeS_2 and characteristic temperatures: glass formation (T_g), crystallization (T_c) and melting point (T_m).

No.	Composition, mol.%			T_g, K	T_c, K	T_m, K	T_{gr}, K
	Ag_2S	ZnS	GeS_2				
3-1	45	–	55	550	642, 664, 689	853	0.64
3-2	40	–	60	552	646, 689	885	0.62
3-3	35	–	65	549	658, 688	974	0.56
3-4	30	–	70	546	659, 688	1038	0.53
3-5	10	–	90	553	663, 690	1063	0.52
3-6	25	5	70	548	660, 672, 689	930	0.59
3-7	35	10	55	571	654, 690	975	0.59
3-8	30	10	60	563	633	989	0.57
3-9	20	10	70	562	623, 632, 688	1065	0.53
3-10	37	8	55	571	652	951	0.60
3-11	20	12	68	571	627	1056	0.54
3-12	43	7	50	564	643, 688	983	0.57
3-13	25	12	63	572	684	1029	0.56

The characteristic temperatures of obtained glassy alloys were determined. The glass formation and the crystallization temperatures and melting point are listed in Table 1, along with the calculated values of the reduced glass-formation temperature T_{gr}.

The glass-formation temperature varies only narrowly for obtained glasses, likely because the amounts of zinc sulfide that can be sustained by the glassy state are quite moderate. The T_g values increase slightly from ∼550 K for the side system Ag_2S–GeS_2 to ∼570 K for the glasses with the highest concentration of ZnS reached (10–12 mol.%). The variations of the crystallization temperature are likewise minor.

Only the glasses on the Ag_2S–GeS_2 side with high Ag_2S content follow “the two-thirds rule” fairly closely. On the contrary, the majority of alloys are characterized by low values of the reduced glass-formation temperature, near the limits of this criterion ($T_{gr} \geq 0.6$). This was also observed in the Ag_2S–HgS–GeS_2 system [27] and is explained by the high affinity of GeS_2 and its alloys to crystallization. Indeed, certain alloys could not be obtained in the glassy state without fail every time and required repeated quenching.

3.3. *The crystal structure of Ag_2ZnGeS_4 compound*

The crystal structure of the Ag_2ZnGeS_4 compound was investigated by the X-ray powder method. The set of the experimental intensities of the diffraction reflections in the 2Θ range 10–100° with scan step 0.05° and the exposure of 20 s in each point was recorded using DRON 4-13 diffractometer (CuKα radiation). The conditions of the X-ray experiment and the crystallographic parameters of the structure are given in Table 2. The diffraction pattern of obtained compound was indexed in the assumption of the tetragonal body-centered cell with the parameters $a = 0.574996(9)$ nm and $c = 1.03434(3)$ nm. Such metrics indicates the possibility that our compound is isostructural with analogous compounds with Cu_2FeSnS_4 structure. The refinement of the profile and structure parameters in the selected model resulted in the goodness factor value $R_I = 0.0495$. The calculated diffraction pattern agrees well with the experimental one (Fig. 3).

Atom coordinates and temperature displacement parameters are presented in Table 3; interatomic distances and coordination numbers of atoms in the structure are given in Table 4; selected valence angles in the Ag_2ZnGeS_4 structure are listed in Table 5.

The Ag_2ZnGeS_4 structure is a 3D network of the closest packing of sulfur atoms in which the cation atoms occupy one half of tetrahedral voids (Fig. 4). All atoms in the Ag_2ZnGeS_4 structure have tetrahedral surrounding. The structure can be derived from the cubic sphalerite structure by doubling the unit cell along *c* axis. The cation-centered tetrahedra are oriented in the same direction

Table 2
Results of the crystal structure refinement of Ag_2ZnGeS_4.

Compound	Ag_2ZnGeS_4
Number of formula units per unit cell	2
Space group	$I\bar{4}2m$
Pearson’s symbol	*tI16*
a (nm)	0.574996(9)
b (nm)	0.574996(9)
c (nm)	1.03434(3)
c/*a*	1.799
Cell volume (nm^3)	0.34198(2)
Number of atoms in the cell	16
Calculated density (g/cm^3)	4.6799(3)
Absorption coefficient (1/cm)	659.23
Radiation and wavelength (nm)	Cu 0.154178
Diffractometer	Powder DRON 4-13
Mode of refinement	Full profile
Number of atomic sites	4
Number of free parameters	14
2Θ and $\sin\Theta/\lambda$ (max)	119.02 and 0.559
R_I, R_P	0.0495 and 0.0937
Texture axis and parameter	[0 0 1] and 0.7914

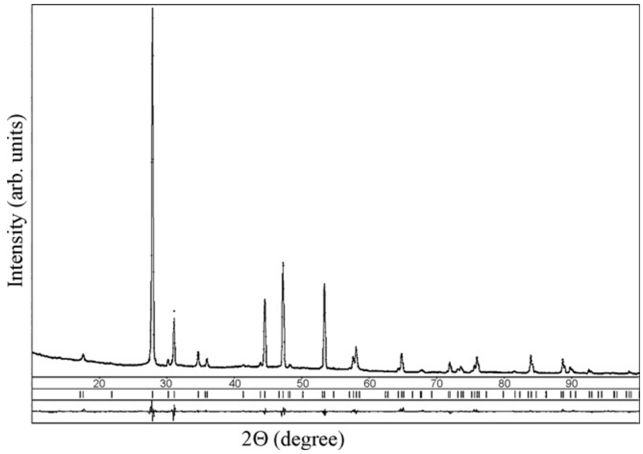

Fig. 3. Experimental and theoretical diffraction patterns of the Ag_2ZnGeS_4 compound and their difference.

Table 3
Atomic coordinates and isotropic temperature factors for the Ag_2ZnGeS_4 compound.

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	$B_{iso} \times 10^2$, nm^2
Ag	*2*(*b*)	0	0	1/2	1.08(4)
M*	*4*(*d*)	0	1/2	1/4	1.13(4)
Ge	*2*(*a*)	0	0	0	3.53(9)
S	*8*(*i*)	0.2317(6)	*x*	0.1328(8)	2.80(8)

M* = 0.50 Ag + 0.50 Zn.

Table 4
Interatomic distances δ (nm) and coordination numbers (CN) of the atoms in the Ag_2ZnGeS_4 structure.

Atoms	δ (nm)	CN
Ag		
4S	0.2578(5)	4
M*		
4S	0.2372(5)	4
Ge		
4S	0.2332(5)	4
S		
1Ge	0.2332(5)	4
2M*	0.2372(5)	
1Ag	0.2578(5)	

M* = 0.50 Ag + 0.50 Zn.

Table 5
Valence angles (°) for Ag_2ZnGeS_4 compound.

Ag	
106.5(2)	S/S
115.6(2)	S/S
106.5(2)	S/S
106.5(2)	S/S
115.6(2)	S/S
106.5(2)	S/S
Ge	
110.3(2)	S/S
107.8(2)	S/S
110.3(2)	S/S
110.3(2)	S/S
107.8(2)	S/S
110.3(2)	S/S
M*	
118.5(2)	S/S
105.2(2)	S/S
105.2(2)	S/S
105.2(2)	S/S
105.2(2)	S/S
118.5(2)	S/S
S	
110.6(2)	Ge/M*
110.6(2)	Ge/M*
111.7(2)	Ge/Ag
118.0(2)	M*/M*
102.7(2)	M*/Ag
102.7(2)	M*/Ag

M* = 0.50 Ag + 0.50 Zn.

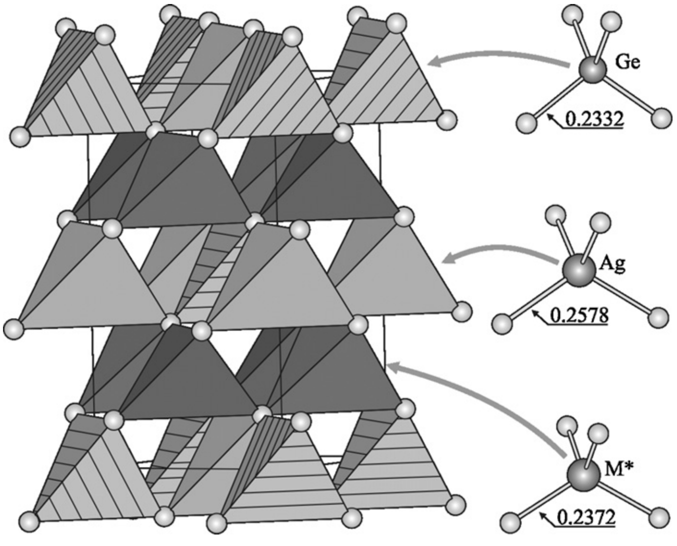

Fig. 4. Packing of the tetrahedra of sulfur atoms around the atoms of cations in the Ag_2ZnGeS_4 structure.

and are joined by the corners (each corner is shared by four tetrahedra). Silver atoms occupy the crystallographic site 2(*b*), i.e. the one that is occupied by B^{II} atoms in other quaternary compounds $A^{I}_2B^{II}C^{IV}X_4$; conversely, the statistical mix of Ag and Zn atoms in 1:1 ratio occupies the crystallographic site 4(*d*) that typically belongs to A^I atoms. The positions of other atoms are equivalent to the analogous compounds. This particular arrangement of atoms in the crystallographic sites was required for the best values of fit factor and temperature displacement parameters. An attempt to arrange the atoms of metallic components Ag and Zn in an ordered variant, Ag in 4(*d*) site and Zn in 2(*b*) site, leads to inadequate values of temperature parameters, namely that of Ag is >5, and that of Zn is <0. The refinement in the assumption of the statistical distribution of metallic components in the site 4(*d*) and silver in the site 2(*b*) led to the site occupation presented in Table 3.

Each of sulfur atoms is surrounded by two atoms M(Ag + Zn) and by one atom each of silver and germanium. The distances Ag–S are somewhat smaller than the sum of ionic radii ($r(Ag^+) = 0.114$ nm and $r(S^{2-}) = 0.170$ nm [29]) and are close to those reported for other compounds (Ag_2CdGeS_4 0.2522–0.2570 nm [24] or Ag_2HgGeS_4 0.237–0.263 nm [25]). Weighted average radius (WAR) for M(Ag + Zn), calculated as WAR = $(\Sigma r_i n_i)/\Sigma n_i$ [30] ($r(Zn^{2+}) = 0.074$ nm [29]), is 0.089 nm. Consequently, the interatomic distance M–S is also somewhat smaller than the sum of ionic radii (0.259 nm).

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