Glass formation region and X-ray analysis of the glassy alloys in AgGaSe$_2$+GeS$_2$⇔AgGaS$_2$+GeSe$_2$ system

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Abstract. A region of glass formation was found during melt quenching from 1273 K in the AgGaSe$_2$+GeS$_2$⇔AgGaS$_2$+GeSe$_2$ system. It is localized along the binary GeSe$_2$-GeS$_2$ system. Characteristic parameters (T_g, T_c, T_m) were determined for the glassy alloys, and T_{gr} and K_G were calculated using them. The radial distribution functions were calculated using the integral Fourier transformation based on X-ray scattering curves. The average interatomic distances within the first and second coordination spheres were determined.

Keywords: glassy alloy; radial distribution function; average interatomic distances; coordination sphere.

1. Introduction

Glassy chalcogenide alloys (GCAs) attract attention of many researchers. These materials have low infrared absorption, high refractive index, high solubility of the rare-earth elements in the chalcogenide matrix of the alloy, technological simplicity of production and chemical resistivity to aggressive media [1-4]. Therefore, GCAs of suitably adjusted compositions may be used for the development of optical amplifiers, powerful diode lasers and telecommunication applications. The alloy compositions can be varied substantially if a wide glass formation region is observed. We investigated the boundaries of the glass formation region in the ternary reciprocal system AgGaSe$_2$+GeS$_2$⇔AgGaS$_2$+GeSe$_2$. The change of composition can lead to substantial variations of physical properties of glasses because the matrix of glassy materials is sensitive media to some electrically and optically active modifiers. Specifically, silver atoms in the glassy matrix behave as electrically active modifiers influencing the electric conductivity of glass [5]. The glass structure is a basic factor that determines the entire set of its physical properties. The most reliable method in studying the glass structure is diffraction measurement, particularly X-ray diffraction (XRD). In this work, the dependence of the structure of glassy alloys in the reciprocal system AgGaSe$_2$+GeS$_2$⇔AgGaS$_2$+GeSe$_2$ on the S/Se content ratio was investigated using XRD methods.

2. Experimental techniques

Alloys were synthesized from high-purity elements (Ag – 99.997 wt%, Ga – 99.997 wt%, Ge – 99.997 wt%, Se – 99.997 wt%, S – 99.999 wt%) in evacuated silica ampoules in two stages. The free volume of container was thermostabilized using string asbestos for the prevention of vapour phase condensation losses. After evacuation, the final pressure in ampoules was ~0.1 Pa. At the first stage, the synthesis was carried out in the flame of oxygen-gas burner for the bonding of elemental sulfur. The ampoules were placed in a shaft furnace and heated at the rate 20 K/h to the maximum temperature 1273 K. The samples were held at the maximum temperature for 10 hours. The synthesis was finished by quenching the alloys from 1273 K into 25 % saline solution at room temperature. The obtained glasses were monolithic blocks, with color changing from yellow (for high sulfur content) to dark-red (high selenium content). The glassy state of the alloys was established by X-ray phase (DRON 4-13 diffractometer, CuK$_\alpha$, MoK$_\alpha$ radiation, Bragg-Brentano geometry) and microstructure (MMU-3 microscope) analysis. The determination of characteristic temperatures (T_g, T_c, T_m – glass transition, crystallization and melting points, respectively) was carried out using VDTA 8M3 thermograph. The W-Re 0.05/W-Re 0.2 thermocouple was used for temperature control.

3. Results and discussion

3.1. The determination of the glass formation region

The diffraction patterns of alloys that are localized in the vicinity of the boundaries of the glass formation region are presented in Fig. 1.

Using the reference data [6] and the results of investigations for 35 alloys along the five sections, the location of the glass formation region and its boundaries were determined (Fig. 2). The region is stretched along the GeS_2–$GeSe_2$ side. The glass formation regions along the investigated sections are as follows: 98-100 mol.% of $GeSe_2$ along the $AgGaSe_2$-$GeSe_2$ section, 90-100 mol.% of $GeSe_{1.5}S_{0.5}$ along the $AgGaSe_{1.5}S_{0.5}$-$GeSe_{1.5}S_{0.5}$ section, 84-100 mol.% of GeSeS along the AgGaSeS-GeSeS section, 84-100 mol.% of $GeSe_{0.5}S_{1.5}$ along the $AgGaSe_{0.5}S_{1.5}$-$GeSe_{0.5}S_{1.5}$ section, 86-100 mol.% of GeS_2 along the $AgGaS_2$-GeS_2 section.

Using obtained results for the glasses of the $AgGaGe_{19}S_{40}$-$AgGaGe_{19}Se_{40}$ section in the $AgGaSe_2$+GeS_2⇔$AgGaS_2$+$GeSe_2$ system, the values of the reduced glass formation temperature T_{gr} and K_G parameter were calculated (Table 1).
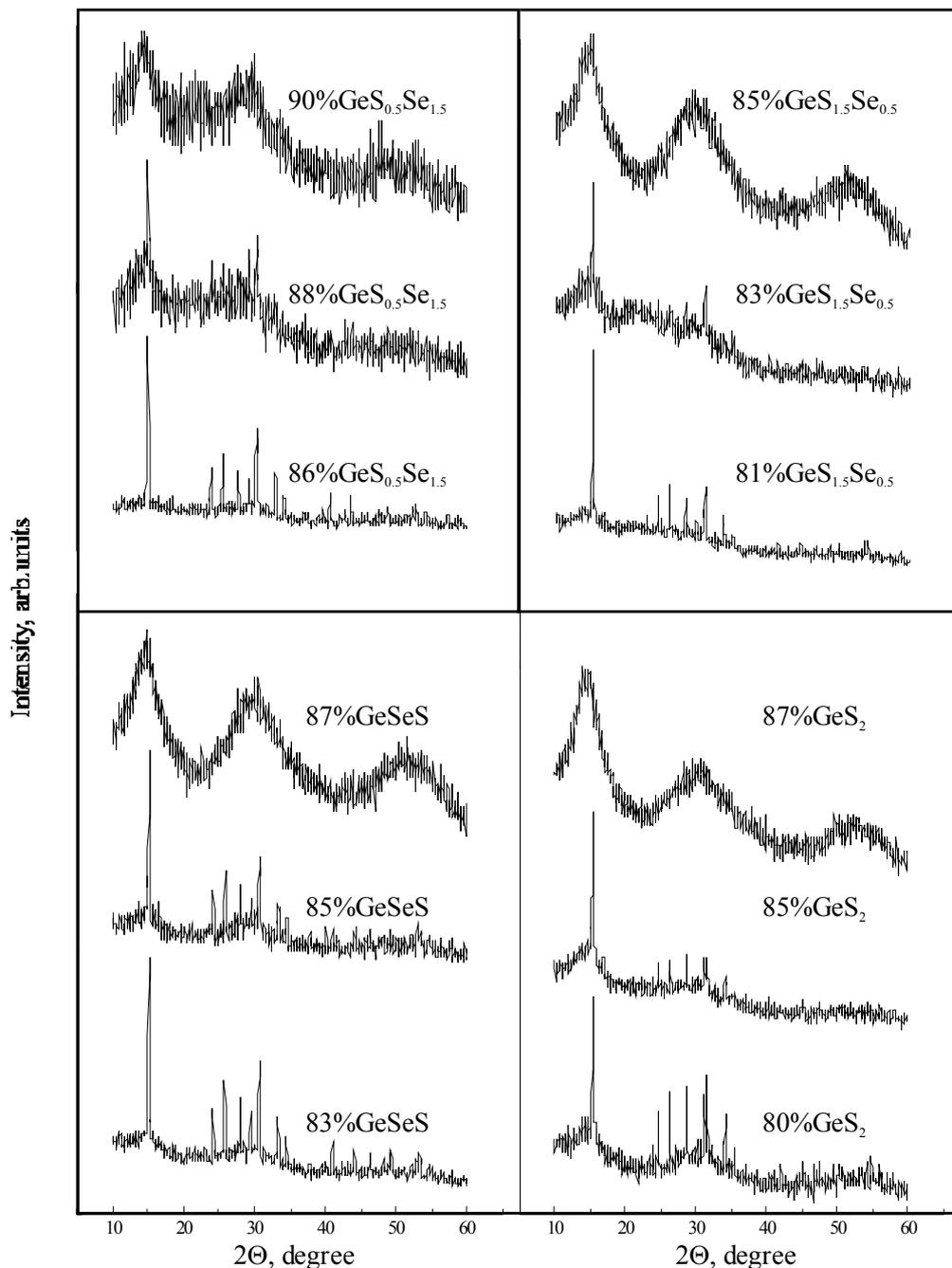
Fig. 1. Difraction patterns of the alloys of the $AgGaSe_2$+GeS_2⇔$AgGaS_2$+$GeSe_2$ system.

The reduced glass formation temperature $T_{gr} = T_g/T_m$, that should be equal to ~0.67, for the cooling rates of 10-100 K/s, according to [7], characterizes glass formation ability. If $T_{gr} < 0.57$, then glasses can be obtained only at rather hard quenching conditions. The Hruby parameter K_G [8] also characterizes a tendency to glass formation, and have been used in practice. This parameter relates glass-formation (T_g) and melting (T_m) temperatures to the temperature of crystallization beginning from the region of supercooled melt (T_c): $K_G = (T_c - T_g)/(T_m - T_c)$. The obtained results indicate high affinity of alloys to glass formation in the investigated system.

○ glass   ◑ glass and crystals   ● crystals
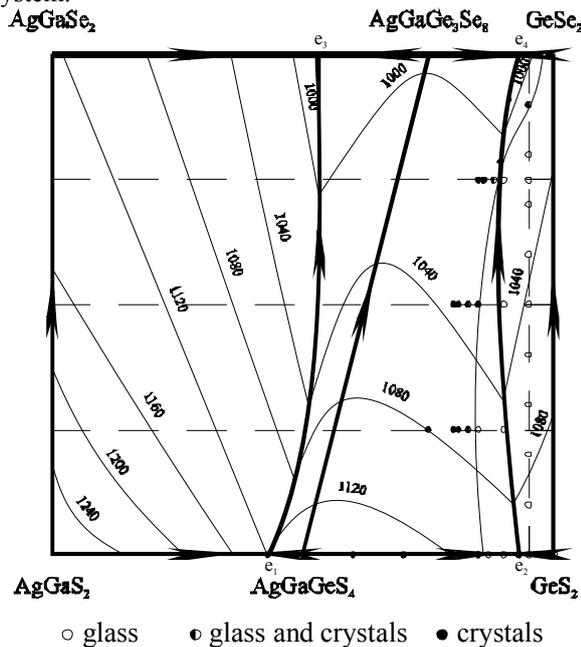
Fig. 2. Liquidus surface projection and the glass formation region of the AgGaSe$_2$+GeS$_2$⇔AgGaS$_2$+GeSe$_2$ system.

Table 1. Temperature parameters of glassy alloys in the AgGaSe$_2$+GeS$_2$⇔AgGaS$_2$+GeSe$_2$ system.

Composition, mol.%			T_g	T_c	T_m	T_{gr}	K_G
AgGaS$_2$	GeSe$_2$	GeS$_2$	K				
5	–	95	707	763	1107	0.638	0.162
5	10	85	712	773	1089	0.653	0.193
5	20	75	761	813	1058	0.719	0.212
5	30	65	703	807	1043	0.674	0.440
5	40	55	686	783	1034	0.663	0.386
5	50	45	681	786	1031	0.660	0.428
5	60	35	674	777	1022	0.659	0.420
5	70	25	666	768	1016	0.655	0.411
5	80	15	663	725	1015	0.653	0.213

3.2. X-ray diffraction analysis of the glass structure

The composition of the glassy alloys that were studied by XRD is shown in Table 2.

Table 2. Composition of glassy alloys in the AgGaSe$_2$+GeS$_2$⇔AgGaS$_2$+GeSe$_2$ system.

Composition, mol.%			Composition, at.%				
AgGaS$_2$	GeSe$_2$	GeS$_2$	Ag	Ga	Ge	S	Se
5	–	95	1.6	1.6	31.2	65.6	0.0
5	10	85	1.6	1.6	31.2	59.0	6.6
5	20	75	1.6	1.6	31.2	52.5	13.1
5	30	65	1.6	1.6	31.2	45.9	19.7
5	40	55	1.6	1.6	31.2	39.4	26.2
5	50	45	1.6	1.6	31.2	32.8	32.8
5	60	35	1.6	1.6	31.2	26.2	39.4
5	70	25	1.6	1.6	31.2	19.7	45.9
5	80	15	1.6	1.6	31.2	13.1	52.5

Unlike many authors [9-11] that investigated physico-chemical properties of chalcogenide glasses depending on the metal component (Ag) content, we concentrated on the investigation of amorphous chalcogenide alloys at a constant percentage of Ag, Ga, Ge atoms by replacing S with Se atoms in the glass matrix.

The smoothed curves of the intensity of the scattered X-rays are shown in Fig. 3. They have three basic maxima. The most intense sharp first scattering peak lies at the wave vector $s = 1.08$ Å^{-1}. The position of the first scattering peak depends on the glass composition. The increase of the Se atom concentration, beginning from $x = 13.1$ (Fig. 3), leads to the shift of the position of the scattering peak towards higher values of the wave vector that reaches the value 1.33 Å^{-1}. This indicates the structural change in the boundaries of the first coordination sphere. The change is presumably due to the increase of the content of Se atoms (with higher atomic radius $r = 0.0918$ nm) that substitute S atoms ($r = 0.0810$ nm).

Based on the X-ray scattering intensity curves, the radial distribution function (RDF) of the atomic density was calculated using the integral Fourier transformation [12]:

$$RDF(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_{s_{min}}^{s_{max}} s\,i(s)\,e^{-\alpha^2 s^2} \sin(rs)\,ds ,$$

where ρ_0 is the mean atomic density that includes the partial contribution of each sort of atoms and $e^{-\alpha^2 s^2}$ is the convergence factor. For the investigated samples $\alpha^2 = 0.014$. The α^2 constant was chosen so that $i(s)\,e^{-\alpha^2 s^2}$ function at $s = s_{max}$ is equal to 0.1 of the initial value. The $i(s)$ calculation includes the following factors: the atomic distribution function f^2 with a partial contribution of each sort of atoms; incoherent scattering; correction for polarization.
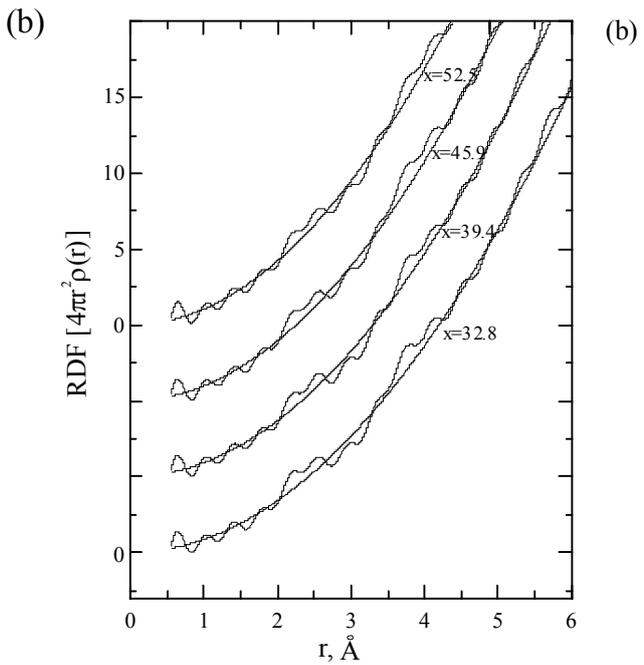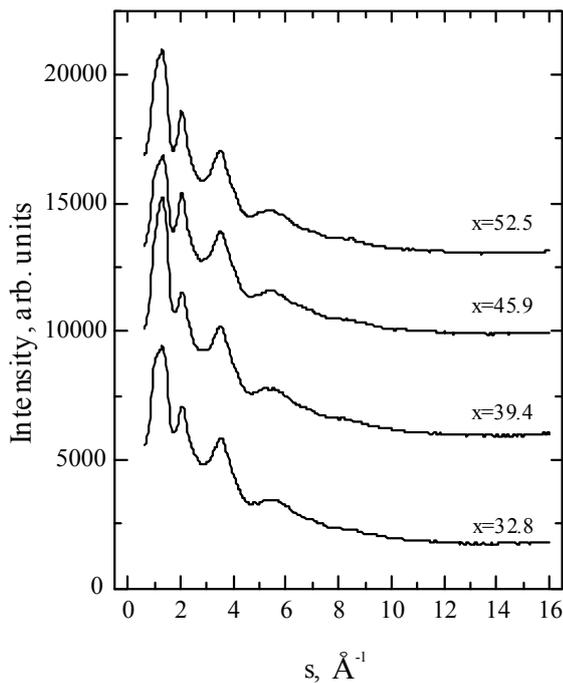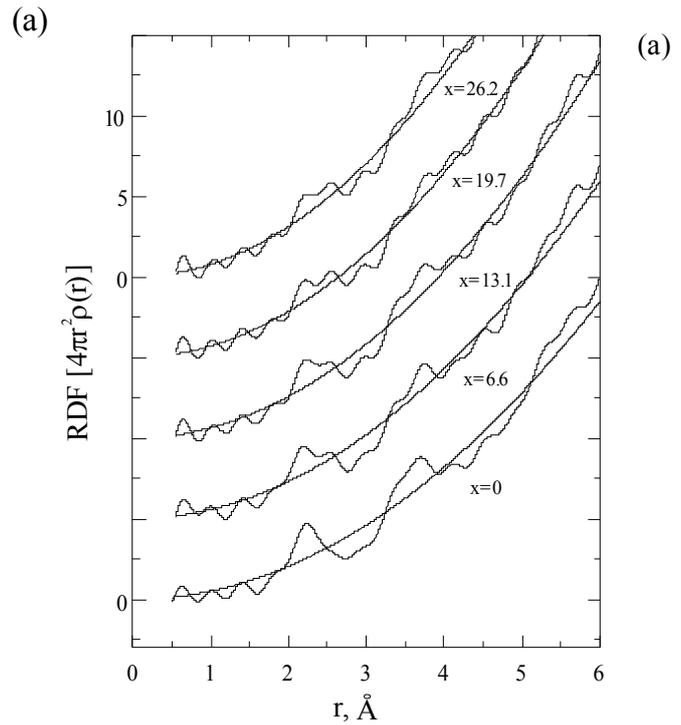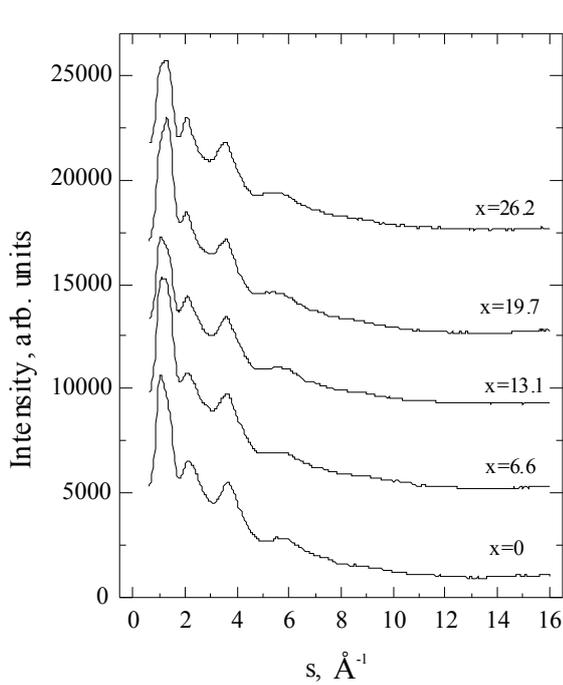
Fig. 3. X-ray scattering intensities of the glassy alloys of the $AgGaSe_2+GeS_2 \Leftrightarrow AgGaS_2+GeSe_2$ system (x – at% of Se).

Fig. 4. Radial distribution functions of the atomic density of the glassy alloys of the $AgGaSe_2+GeS_2 \Leftrightarrow AgGaS_2+GeSe_2$ system (x – at% of Se).

The calculated dependences of RDF are presented in Fig. 4. The estimation of the main structural parameters, i.e. distances to the nearest atoms, was made using the position of RDF maxima. From the curve that corresponds to $x = 0$ one can isolate the first coordination sphere (FCS) that is typical for GeS_2 and is localized at the distance of 2.22 Å.

The coordination sphere with the maximum at that position corresponds to the Ge-S interactions [9, 12, 13] and indicates the existence of the GeS_4 tetrahedra. A shoulder to the left of basic maximum in the limits of the FCS indicates a possible existence of some number of Ge–O bonds caused by uncontrollable presence of oxygen atoms [14]. As the number of Se atoms

increases, beginning from $x = 6.6$, the decrease of the basic maximum in the FCS limits and its split into two maxima is observed. The position of the latter is 2.52 Å for low selenium concentrations (6.6-13.1 at.%). It is supposed that this maximum corresponds to the superposition of several maxima that are due to the interactions Ge–Se (2.36 Å [12]), Ag–S (2.58-2.63 Å [9, 10]), and depends on the S/Se content ratio. With further increase of the content of Se atoms, the substitution of S with Se atoms in the glass matrix takes place, therefore both maxima in the FCS shift towards higher r values, reaching 2.27 Å for the first maximum and 2.58 Å for the second one. The shift of the maxima in the FCS is due to the increase of the number of Ge–Se, Ag–Se bonds for which the average interatomic distance is longer than for Ge–S, Ag–S, respectively [9, 11, 12].

The second coordination sphere (SCS) is presented by the wide non-symmetric maximum that is located in the $r = 3.1$-3.9 Å range. A shoulder to the left that extends from 3.4 to 3.6 Å (Fig. 2, $x = 0 - 26.2$) is due to homopolar S–S interactions that is located at 3.55 Å according to Ref. [12]. The SCS maximum for the $x = 0$ is observed at 3.7 Å, and shifts towards higher values during the Se content increase (obviously due to the Se–Se bonds), reaching 3.81 Å (at $x = 32.8$). The maximum diffuses with the further increase of the Se content, turning into a low plateau and becomes practically noteless on the RDF curve. The wide SCS peak is probably a combination of contribution from several interactions. This maximum is due to Ag–Ge (3.69-3.73 Å [14]) interaction and also second order of Ag–Ag (3.7 Å [9]) and Se–Se (3.89 Å [11]) interactions that are difficult to distinguish.

As can be observed in Fig. 4 ($x = 0$), well developed FCS indicates that the GeS_4 tetrahedra are the dominant structure groups in the glassy alloy. The introduction of Se atoms leads to loosening of the structure that is formed on the basis of GeS_4 tetrahedra and weakening the Ge–S interactions as well as strengthening the Ge–Se bonds.

4. Conclusions

Boundaries of the glass formation region were determined under melt quenching of alloys in the $AgGaSe_2 + GeS_2 \Leftrightarrow AgGaS_2 + GeSe_2$ system from 1273 K. The radial distribution functions of the atomic density for the glassy alloys were calculated using the integral Fourier transformation based on X-ray scattering curves. The average interatomic distances within the first and second coordination spheres were determined. The increase of the interatomic distances with the Se content increase is due to the replacement of S atoms with Se atoms in the glass matrix of the alloys.

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