CHEMICAL SCIENCES

PHYSICOCHEMICAL STUDY OF INTERACTION AND GLASS FORMATION IN THE As_2Se_3-$TlGaSe_2$ SYSTEM

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Abstract

The chemical interaction and glass formation in the As_2Se_3-$TlGaSe_2$ system were studied using physicochemical methods of analysis: differential thermal analysis (DTA), X-ray phase analysis (XRD), microstructural analysis (MSA), as well as density and microhardness measurements, and its phase diagram was constructed. It was found that the phase diagram of the As_2Se_3-$TlGaSe_2$ system is quasi-binary and eutectic. The composition of the binary eutectic formed in the system is 20 mol % $TlGaSe_2$, the temperature is 270°C. According to the results of microstructural analysis in the system based on the As_2Se_3 compound, the region of solid solutions reaches 3 mol % $TlGaSe_2$ at room temperature. Solid solutions based on the $TlGaSe_2$ compound reach 8 mol % As_2Se_3. It was found that in the As_2Se_3-$TlGaSe_2$ system, 20 mol % $TlGaSe_2$ of the glass formation region based on the As_2Se_3 compound is formed upon slow cooling.

Keywords: system, phase equilibrium, quasi-binary, density, glass transition.

Introduction

Arsenic chalcogenides of the As_2X_3 (X-S,Se) type are glassy semiconductor substances. Arsenic chalcogenides and glassy and crystalline compounds based on them are widely used in color TVs and memory centers for their photosensitive [1-6], luminescent [7], and acousto-optic [8,9] properties. Glass fibers based on arsenic sulfide and selenide compounds [10-12] are used to transmit light in the mid-IR range and are used as a compact nonlinear medium providing Raman amplification [13], and laser regeneration [14]. The $TlGaSe_2$ compound is a light-sensitive semiconductor compound [15,16]. Previously, we studied systems of the As_2X_3-$GaGaX_2$ (X-S,Se,Te) type [17-19].

The aim of this work is to study the chemical interaction and glass formation in the As_2Se_3-$TlGaSe_2$ system and to construct its phase diagram.

The As_2Se_3 compound melts congruently at 380°C and crystallizes in the monoclinic syngony with the lattice parameters: a = 12.053; b = 9890; c = 4.277 Å, α = 90º28/, sp. gr. $P2_1/n$ has a density ρ = 4.62 g/cm^3 in glass, microhardness $H\mu$ = 1400 MPa and a density ρ = 5.21 g/cm^3 in crystalline form, microhardness $H\mu$ = 75 MPa [20]. The $TlGaSe_2$ compound melts congruently at 817°C and crystallizes in the tetragonal syngony with the lattice parameters: a = 7.62 Å; c = 30.5 Å, z = 16, density and microhardness, respectively, ρ = 6.47 g/cm^3, $H\mu$ = 820 MPa [21, 22].

Experimental part

The components As_2Se_3 and $TlGaSe_2$ of the As_2Se_3-$TlGaSe_2$ system were synthesized from high-purity elements: As-99.999%, Tl-000, Ga-99.998%, Se-99.999% by the ampoule method. Then, alloys of the As_2Se_3-$TlGaSe_2$ system were synthesized from the components As_2Se_3 and $TlGaSe_2$ by melting in quartz ampoules in the temperature range of 600-1000°C under a pressure of 0.133 Pa. After the synthesis, the alloys were subjected to heat treatment at a temperature of 250°C for 240 hours to bring them to equilibrium. Then the alloys of the As_2Se_3-$TlGaSe_2$ system were studied by the methods of physicochemical analysis: differential thermal analysis (DTA), X-ray phase analysis (XRD), microstructural analysis (MSA), as well as methods of measuring density and microhardness.

Differential-thermal analysis (ДТА) was performed on a TERMOSKAN-2 thermograph. The Al_2O_3 compound was taken as standard, the heating rate was 5 degr./min. X-ray phase analysis was performed on an X-ray diffractometer brand D2-PNASER. CuKα-radiation and Ni-filter were used during the research.

Microstructural analysis (MSA) was performed on a MIM-8 microscope. To do this, alloys were polished and given a shine, and their structure was examined under a microscope. To clarify phase boundaries, 10 ml of NaOH solution + 5 ml of C_2H_5OH solution were taken as an etchant. Microhardness was measured with a metallographic hardness tester PMT-3. Measured concentration dependence of microhardness for each phase. The density of the samples was determined by the pycnometric method, and toluene was used as the filling solution.

Results and discussion

In the As_2Se_3-$TlGaSe_2$ system, glass formation regions are formed on the basis of As_2Se_3 during slow cooling in the concentration range of 0-20 mol % $TlGaSe_2$. Alloys with 20-30 mol % $TlGaSe_2$ are a glass-crystalline mixture. Glassy alloys containing 0-20 mol % $TlGaSe_2$ were subjected to heat treatment at 250°C for 500 hours for crystallization. Alloys of the As_2Se_3-$TlGaSe_2$ system were studied by physicochemical analysis methods.

The results of differential thermal analysis of the As_2Se_3-$TlGaSe_2$ system in the concentration range of 0-20 mol % $TlGaSe_2$ before heat treatment show that the thermograms of alloys accompanied by a softening temperature of Tg = 180-195°C are characteristic of glasses.

After crystallization, glassy alloys in the range of 0-20 mol % $TlGaSe_2$ lose their softening temperature, and endothermic effects characteristic of crystals are observed instead. Tables 1 and 2 show a number of macroparameters of alloys in the range of 0-30 mol % $TlGaSe_2$ in the glass and crystalline states.

As a result of the analysis of the microstructure of the alloys, it was found that there is a limited solubility region based on the initial components of the system. Fig. 1 shows the microstructures of alloys of the As_2Se_3-$TlGaSe_2$ system with a content of 20, 50, and 92 mol % $TlGaSe_2$. The sample with a concentration of 20 mol % $TlGaSe_2$ is a glassy alloy, which is a matte single-phase phase. The sample of 50 mol % $TlGaSe_2$ is a two-phase field alloy. The single-phase sample with a content of 92 mol % $TlGaSe_2$ is a solid solution based on the compound $TlGaSe_2$.

Fig. 1. Microstructures of alloys of the As_2Se_3-$TlGaSe_2$ system.
1-20 mol %, 2-50 mol %, 92 mol % $TlGaSe_2$.

Table 1.

Composition of glassy alloys of the As_2Se_3-$TlGaSe_2$ system, DTA, results of determination of microhardness and density (in the case of glass)

Composition, mol %		Thermal effects, ˚C	Density, 10^3 kq/m^3	Microhardness, MPa	
As_2Se_3	$TlGaSe_2$			α	$TlGaSe_2$
				P=0,20 N	
100	0.0	180.380	4.62	1400	glass
97	3.0	180.320.380	4.65	1420	-
95	5.0	190.270.375	4.68	1450	-
90	10	190.270. 365	4.74	1470	-
85	15	195. 270.300	4.90	1470	-
80	20	195. 270	4.99	1470	-
75	25	195. 270.375	5.07	1470	glas-krustal
70	30	195. 270.435	518	1470	830

Table 1.

Composition of glassy alloys of the As_2Se_3-$TlGaSe_2$ system, DTA, results of determination of microhardness and density (in crystalline state)

Composition, mol %		Thermal effects, ˚C	Density, 10^3 kq/m^3	Microhardness, MPa	
As_2Se_3	$TlGaSe_2$			α	$TlGaSe_2$
				P=0,20 N	
100	0.0	380	5.21	750	crustal
97	3.0	320.380	5.25	800	-
95	5.0	270.375	5.30	830	-
90	10	270. 365	5.33	850	-
85	15	270.300	540	860	-
80	20	270	5.46	Eutec.	Eutec.
75	25	270.375	5.52	-	840
70	30	270.435	5.60	-	830

X-ray phase analysis of alloys containing 10, 20 and 30 mol % $TlGaSe_2$ from the glass area of the As_2Se_3-$TlGaSe_2$ system was performed (Fig. 2). It was determined that the alloys containing 10 and 20 mol % $TlGaSe_2$ are glassy, and no diffraction lines were obtained in their diffractograms. The sample containing 30 mol % $TlGaSe_2$ is an alloy made of glass-crystal material

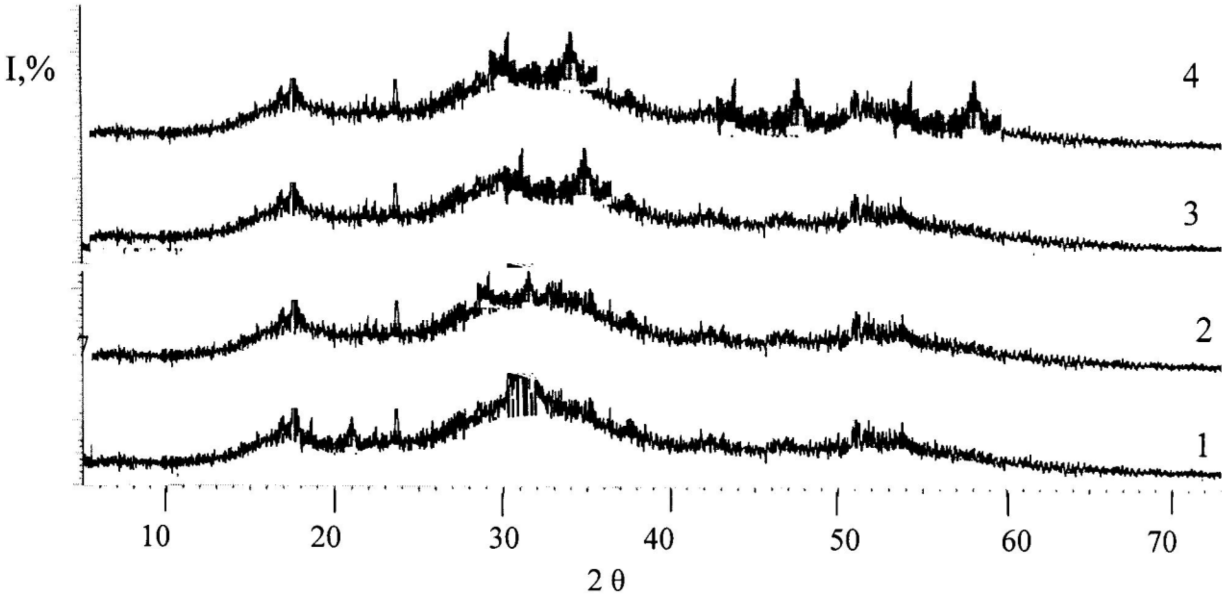

Fig. 2. Diffraction patterns of alloys of the As_2Se_3-$TlGaSe_2$ system.
1- As_2Se_3, 2- 10, 3-20, 4-30 mol % $TlGaSe_2$.

Thus, the X-ray phase analysis confirms the results of the DTA and MSA analyses.

Based on the results of the physicochemical analysis methods, a phase diagram of the As_2Se_3-$TlGaSe_2$ system was constructed (Fig. 3). The phase diagram of the system is quasi-binary, eutectic type. Joint crystallization of As_2Se_3 and $TlGaSe_2$ compounds ends with a double eutectic, composition 20 mol % $TlGaSe_2$, temperature 270°C.

The liquidus of the As_2Se_3-$TlGaSe_2$ system consists of monovariant equilibrium curves of the α-solid solution formed on the basis of the As_2Se_3 compound and the β-solid solution based on $TlGaSe_2$, which are in equilibrium with the liquid.

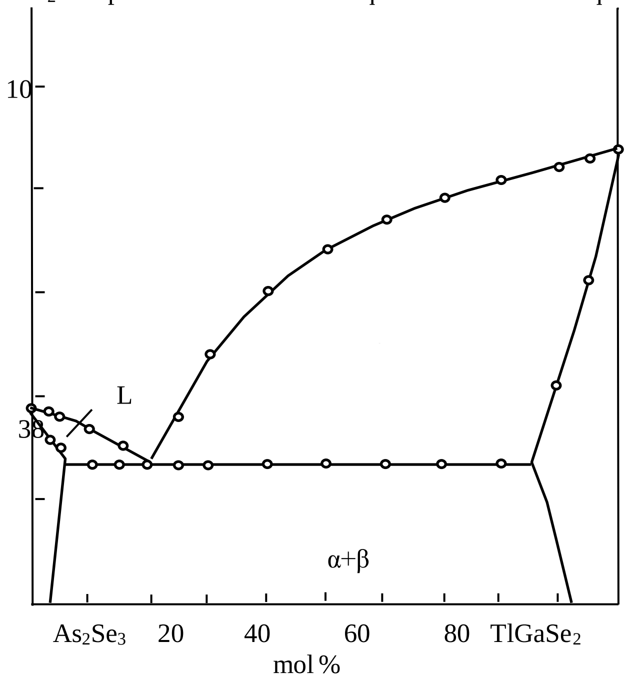

Fig.3. Phase diagram of the As_2Se_3-$TlGaSe_2$ system.

In the system at room temperature, based on the compound As_2Se_3, solid solutions reach 3 mol % $TlGaSe_2$, and based on the compound $TlGaSe_2$ - up to 8 mol % As_2Se_3. In the As_2Se_3-$TlGaSe_2$ system, two-phase alloys consisting of (α+β) crystallize below the solidus line.

The dependence of the microhardness of the As_2Se_3-$TlGaSe_2$ system lloys on the composition was studied and it was found that there are two different values of microhardness. The microhardness of alloys with a glass area of 0–20 mol % $TlGaSe_2$ varies within (1400–1470) MPa, and their density – within 4.62–5.18 g/cm^3 (Table 1). The microhardness of the α-solid solution alloys based on the crystalline compound As_2Se_3 of all alloys of the system varies within (750–860) MPa (Table 2), and the microhardness value (820–840) MPa corresponds to the microhardness of β-solid solutions based on $TlGaSe_2$.

Conclusion

The phase equilibrium and glass formation in the As_2Se_3-$TlGaSe_2$ system were studied using a set of physicochemical analysis methods: differential thermal analysis (DTA), X-ray diffraction (XRD), microstructural analysis (MSA), as well as density and microhardness measurements, and its phase diagram was constructed. It was found that the As_2Se_3-$TlGaSe_2$ phase diagram is quasi-binary and eutectic. The binary eutectic formed between the As_2Se_3 and $TlGaSe_2$ compounds has a composition of 20 mol % $TlGaSe_2$ and a temperature of 270°C. It was determined that the area of the solid solution based on the As_2Se_3 compound at room temperature is 3 mol % $TlGaSe_2$, and based on the $TlGaSe_2$ compound, the solubility is 8 mol % As_2Se_3. In the As_2Se_3-$TlGaSe_2$ system, the glass area was determined to be 20 mol % $TlGaSe_2$ based on the As_2Se_3 compound under slow cooling.

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