CHEMICAL SCIENCES

PHYSICO-CHEMICAL INVESTIGATION OF PHASE EQUILIBRIUM AND GLASS FORMATION IN THE As_2Se_3-$TlGaS_2$ SYSTEM

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Abstract

Phase equilibrium and glass transition in the As_2Se_3-$TlGaS_2$ system were studied by methods of physico-chemical analysis: differential thermal analysis (DTA), X-ray diffraction analysis (XRD), microstructural analysis (MSA), as well as density and microhardness measurements; its phase diagram was constructed. It has been established that the As_2Se_3-$TlGaS_2$ system is a quasi-binary part of the quasi-ternary system As_2Se_3-Ga_2S_3-Tl_2S and belongs to the eutectic type. The composition of the binary eutectic formed in the system is 15 mol % $TlGaS_2$, temperature is 290°C. Based on the results of microstructural analysis, it was established that in the As_2Se_3-$TlGaS_2$ system, solid solutions based on As_2Se_3 containing 2.5 mol % $TlGaS_2$ at room temperature, and based on $TlGaS_2$ solid solutions is 6.5 mol % As_2Se_3. The glass formation region based on As_2Se_3 extends to 25 mol % $TlGaS_2$ with slow cooling.

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

Introduction

It is known that arsenic chalcogenides are semiconductor compounds obtained in glass form under normal conditions. Recently there has been some interest in complex chalcogenide compounds. First of all, the broad study of the chemistry and physics of arsenic chalcogenide compounds is associated with the expansion of their practical application.

Arsenic chalcogenides and compounds based on them, as well as glassy alloys, are materials with high photoelectric [1-6], luminescent [7,8] and acousto-optical [9] properties. In recent years, chalcogenide fibers [10–12] based on As_2S_3 and As_2Se_3 have been used to transmit light in the mid-IR range and have found application as a compact nonlinear medium allowing Raman amplification [13] and laser lasing [14]. Compounds of the $TlGaX_2$ (X-S.Se,Te) type are also photosensitive materials and are widely studied [15-17]. A number of systems including $TlGaX_2$ compounds have been studied in the literature [18–22].

The purpose of this work is to construct a T-x phase diagram and identify regions of solid solutions based on the study of phase equilibria and glass transition in the As_2Se_3-$TlGaS_2$ system.

The As_2Se_3 compound melts congruently at 381°C and crystallizes in a monoclinic syngony with a lattice parameter a = 12.053; b=9890; c=4.277 Å, α=90°28′, sp.gr. P21/n has a glass density ρ=4.62 g/cm^3, microhardness Hμ=140 MPa, crystal density ρ=5.21 g/cm^3, microhardness Hμ=75 MPa [23]. The $TlGaS_2$ compound melts congruently at 905°C and crystallizes in the tetragonal syngony, lattice parameters: a = 7.29 Å, c = 29.90 Å, z = 16, density 5.64 g/cm^3, microhardness 700 MPa [24].

Experimental part

Alloys of the As_2Se_3-$TlGaS_2$ systems were synthesized from the As_2Se_3 and $TlGaS_2$ components by fusing in quartz ampoules in the temperature range 700-1000°C at a pressure of 0.133 Pa. After synthesis, the alloys were subjected to heat treatment at a temperature of 280°C for 240 hours to homogenize them. Then the alloys of the As_2Se_3-$TlGaS_2$ system were studied by methods of physicochemical analysis: differential thermal analysis (DTA), X-ray diffraction (XRD), microstructural analysis (MSA), as well as methods of measuring density and microhardness.

Differential-thermal analysis (DTA) was carried out using a TERMOSCAN-2 thermograph. The Al_2O_3 compound was taken as standard, the heating rate was 5 min/min.

X-ray phase analysis was performed on a D2-PhASER X-ray diffractometer. The study used CuKα radiation and a Ni filter. Microstructural analysis (MSA) was carried out on a MIM-8 microscope. To do this, the alloys were polished and given shine, and their structure was examined under a microscope. To clarify the phase boundaries, a solution of 10 ml KOH + 5 ml C_2H_5OH was used as an etchant. Microhardness was measured with a PMT-3 metallographic hardness tester. The compositional dependence of microhardness for each phase was measured. The density of the samples was determined by the pycnometric method; Toluene was used as a filling solution.

Results and its discussion

Alloys of the As_2Se_3-$TlGaS_2$ system with a concentration of 0-25 mol % $TlGaS_2$ are glassy, and the remaining alloys are crystalline substances. Glassy alloys based on the As_2Se_3 compound in the range of 0-25 mol % $TlGaS_2$ was heat treated at 220°C for 580 hours for crystallization. Then the alloys of the system were studied by methods of physicochemical analysis.

The results of differential-thermal analysis show that the endothermic effects obtained from the thermograms of the alloys are accompanied by a softening temperature Tg in the glass region. Two endothermic effects are observed in the thermograms of alloys.

As a result of microstructural analysis of the alloys, it was established that near the As_2Se_3 and $TlGaS_2$ compounds, single-phase alloys are present in the system, and the remaining alloys are two-phase. Microstructures of alloys of the As_2Se_3-$TlGaS_2$ system containing 20, 60 and 92.5 mol % $TlGaS_2$ are presented in Fig. 1.

Fig. 1. Microstructures of alloys of the As_2Se_3-$TlGaS_2$ system.
1-20 mol %, 2-60 mol %, 93.5 mol % $TlGaS_2$.

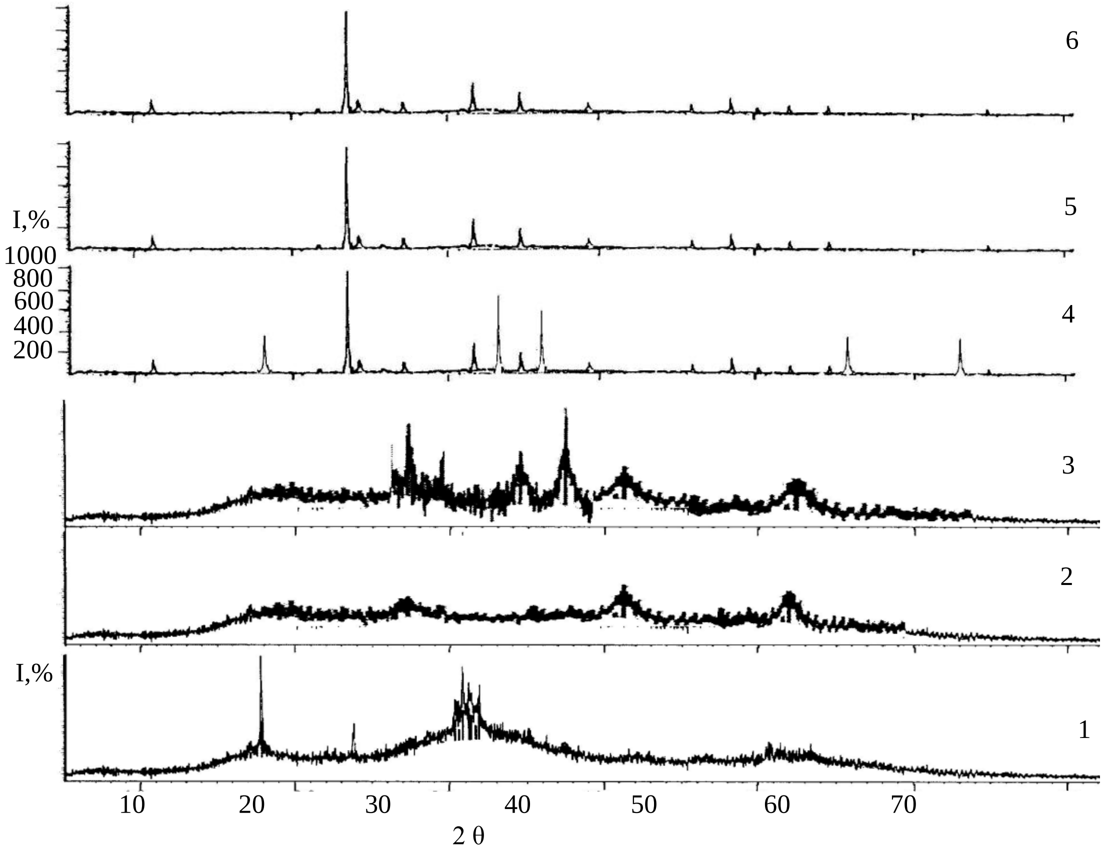

Fig. 2. Diffraction patterns of alloys of the As_2Se_3-$TlGaS_2$ system.
1- As_2Se_3, 2- 10, 3-25, 4-60, 5- 93, 6-100 mol % $TlGaS_2$.

A sample with a concentration of 20 mol % $TlGaS_2$ is a glassy alloy which is a matte single phase. A sample containing 60 mol % $TlGaS_2$ is a two-phase alloy. Single-phase sample containing 93.5 mol % $TlGaS_2$, are solid solutions based on the $TlGaS_2$ compound.

X-ray phase analysis of alloys of the As_2Se_3-$TlGaS_2$ system containing 10, 25, 60 and 93.5 mol % $TlGaS_2$ are presented in Fig. 2. It has been established that alloys containing 10 and 25 mol % $TlGaS_2$, are glassy; no diffraction lines were obtained in their diffraction patterns. Diffraction lines in the diffraction pattern of the alloy 60 mol % $TlGaS_2$ are a mixture of diffraction lines of the original components, i.e. it is a two-phase alloy. X-ray diffraction pattern of the alloy 93.5 mol % $TlGaS_2$ is identical to the $TlGaS_2$ compound, i.e. the sample is a solid solution based on the $TlGaS_2$ compound.

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

The T-x phase diagram of the As_2Se_3-$TlGaS_2$ system was constructed based on the results of physicochemical analysis methods (Fig. 3). The phase diagram of the system is quasi-binary, eutectic type. The composition of the eutectic formed between the compounds As_2Se_3 and $TlGaS_2$ is 15 mol % $TlGaS_2$, temperature 280°C.

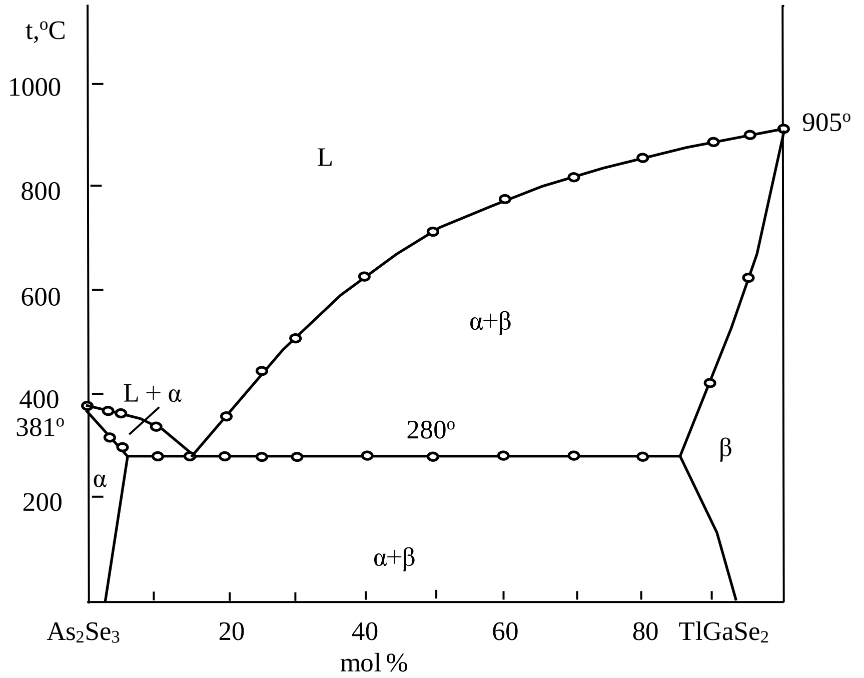

Fig.3. T-x phase diagram of the As_2Se_3-$TlGaS_2$ system.

The liquidus of the As_2Se_3-$TlGaS_2$ system consists of the initial crystallization curves of the α-solid solution formed based on the As_2Se_3 compound and the β-solid solution based on $TlGaS_2$. In the system at room temperature, the solubility based on the As_2Se_3 compound reaches 2.5 mol % $TlGaS_2$, and solid solutions based on the $TlGaS_2$ compound is 6.5 mol % As_2Se_3. In the As_2Se_3-$TlGaS_2$ system, two-phase alloys consisting of (α+β) crystallize below the solidus line.

The dependence of the microhardness of alloys of the As_2Se_3-$TlGaS_2$ system on composition has been studied and it has been established that there are two different values of microhardness. Some physicochemical properties of alloys 0–25 mol % $TlGaS_2$ in the glass area is given in Table 1. Some physicochemical properties of the system after heat treatment of alloys of the As_2Se_3 system at a temperature of 220°C for 580 hours are given in Table 2. The microhardness of glassy alloys based on the As_2Se_3 composition varies in the range (1400-1470) MPa, and their density is in the range of 4.62-5.40 g/cm_3 (Table 1). The microhardness of α-solid solutions based on the As_2Se_3 crystalline state of all alloys of the system varies within the range of (750-830) MPa, and the microhardness value (700-780) MPa corresponds to the microhardness of β-solid solutions based on $TlGaS_2$ (Table 2). After crystallization of alloys containing 0–25 mol % $TlGaS_2$ the softening temperature disappears, but the temperature effect of liquidus and solidus remains.

Table 1.

Composition of alloys of the As_2Se_3-$TlGaS_2$ system, results of DTA, measurements of density and microhardness (glassy state)

Composition, mol %		Thermal effecns, °C	Density, q/sm^3	Microhardness, MPa	
As_2Se_3	$TlGaS_2$			α	β
				P=0,10 N	P=0,15 N
100	0.0	140,381	4,62	1400	–
97	3,0	140,320,380	4,65	1450	–
95	5,0	145,290,375	4,67	1470	–
90	10	150,280,370	4,72	1470	–
85	15	150,280	4,77	1470	–
80	20	155,280,340	4,83	1470	–
75	25	155,280,440	4,87	1470	780

Table 2.

Composition of alloys of the As_2Se_3-$TlGaS_2$ system, results of DTA, density and microhardness measurements (in crystalline form)

Composition, mol %		Thermal effecns, °C	Density, q/sm^3	Microhardness, MPa	
As_2Se_3	$TlGaS_2$			α	β
				P=0,10 N	P=0,15 N
100	0.0	381	5,21	750	–
97	3,0	320,380	5,23	790	–
95	5,0	290,375	5,25	830	–
90	10	280,370	5,26	830	
85	15	280	5,27	Eutek.	Eutek.
80	20	280,340	5,30	–	780
75	25	280,440	5,33	–	780
70	30	280,510	5,34	–	780
60	40	280,625	5,38	–	780
50	50	280,710	5,42	–	780
40	60	280,775	5,46	–	780
30	70	280,815	5,51	–	780
20	80	280,850	5,55	–	780
10	90	420,880	5,62	–	780
5,0	95	625,900	5,66	–	750
0,0	100	905	5,64	–	700

Conclusion

Phase equilibrium and glass formation in the As_2Se_3-$TlGaS_2$ system were studied using complex methods of physical and chemical analysis: differential thermal analysis (DTA), X-ray diffraction analysis (XRD), microstructural analysis (MSA), as well as measuring microhardness and density and constructing its phase diagram. It has been established that the phase diagram of the As_2Se_3-$TlGaS_2$ system is quasi-binary and eutectic. The binary eutectic formed between the compounds As_2Se_3 and $TlGaS_2$ has a composition of 15 mol % and temperature 280°C. It has been established that the area of the solid solution at room temperature based on the As_2Se_3 compound is 2.5 mol % $TlGaS_2$, and the solubility based on the $TlGaS_2$ compound is 6.5 mol % As_2Se_3. During slow cooling in the As_2Se_3-$TlGaS_2$ system based on As_2Se_3, the glass transition region expands to 25 mol % $TlGaS_2$.

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