CHEMICAL SCIENCES

INVESGATION OF INTERACTION AND GLASS FORMATION IN THE $Tl_3As_2Se_6$-$TlAs_2Se_3S$ SYSTEM

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Abstract

Using physicochemical methods of analysis (DTA, X-ray diffraction, micstructural analysis, as well as determination of density and microhardness), the chemical interaction and glass formation in the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system were studied, and its phase diagram was constructed. It was found that the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system is a non-quasi-binary section of the quaternary Tl-As-S-Se system. In the $Tl_3As_2Se_6$-based system, the solid solution region at room temperature is 5 mol %, and on the basis of $TlAs_2Se_3S$, the solid solutions are 3 mol %. Since the initial components of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system are glassy, all alloys of the system are glassy.

Keywords: glass, phase, system, solid solution, liquidus.

Introduction

The components of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system are obtained from the compounds As_2Se_3, TLS and TlSe. These compounds are materials with functional properties. It is known that arsenic chalcogenides and glassy alloys based on them are photosensitive semiconductor materials of the visible wavelength range and are used in various fields of photoelectronics [1-8].

Thallium chalcogenides and new phases based on them are photosensitive materials and are widely used as energy converters [9-11]. From this point of view, the study of chemical interaction and phase equilibrium between $Tl_3As_2Se_6$ and $TlAs_2Se_3S$, which form the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system, has scientific and practical significance. Systems consisting of internal sections of the As, Tl//S, Se quaternary system have been previously studied by us [12-15].

The aim of this work is to construct its phase diagram by studying the physicochemical interaction and glass formation in the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system.

The $Tl_3As_2Se_6$ compound melts incongruently at 245°C, the microhardness in the crystalline state is 1250 MPa, in the glass 1080 MPa [16]. The $TlAs_2Se_3S$ compound is a glassy material with congruent melting at 305°C, with microhardness and density, respectively: $H\mu$ = 840 MPa and ρ = 6.82 g/cm^3 [17].

Experimental part

The alloys of the system were obtained by joint melting of $Tl_3As_2Se_6$ and $TlAs_2Se_3S$ compounds in a sealed quartz ampoule with air suction to a pressure of 0.133 MPa. . During the synthesis, the temperature was first smoothly increased to 600°C and maintained by vibration for 5 hours, then the furnace temperature was reduced to 400°C and maintained for 24 hours. The next day, the temperature was brought to 200°C by cooling at a rate of 100°C per hour, and then cooled by switching off. The alloys of the $Tl_3As_2Se_6$ and $TlAs_2Se_3S$ system were studied by DTA, X-ray diffraction, MSA analysis, as well as by determining the density and microhardness.

Differential-thermal analysis was performed on a low-frequency pyrometer THERMOSCAN-2. Chromel-alumel was used as a thermocouple, the heating rate was 5°C/min. X-ray phase analysis of the alloys was performed on a D2 PHASER X-ray diffractometer. CuKα radiation and a Ni filter were used as an anode. Microstructure analysis was performed on a MIM-8 microscope. A solution of 10 ml of 0.1 HC1 + 5 ml of H_2O_2 was used as an etchant to detect the phase boundary in the samples. Microhardness was measured on a PMT-3 metallographic microscope. Density was determined by the pycnometric method, toluene was used as a filler.

Results and discussion

The synthesized alloys are dense, black shiny substances. The alloys of the system are resistant to water and air. Samples rich in the $Tl_3As_2Se_6$ compound are relatively poorly soluble in mineral acids, while the $TlAs_2Se_3S$ compound is practically insoluble. They dissolve well only in heated HNO_3 acid and gradually in alkaline solutions (NaOH, KOH).

The synthesized samples were kept at 170 °C for 850 hours for crystallization. Crystallization was monitored using physicochemical analysis methods. Some physicochemical properties of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system alloys in glass and crystalline form are given in Tables 1 and 2.

Table 1.
Composition of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system alloys, DTA results, microhardness and density measurements (in glass form)

Composition, mol %		Thermal effects,ºC	Density, q/cm³	Mikrohardness, MPa			
$Tl_3As_2Se_6$	$TlAs_2Se_3S$			α	$TlAs_2Se_4$	$Tl_3As_2S_3Se_3$	β
				P=0,15 N			
100	0.0	145. 245	7.40	1250	–	–	–
95	5.0	140. 230. 245	7.40	1280	–	–	–
90	10	140. 225. 240	7.25	1280	–	–	–
80	20	135. 190. 225. 235	7.15	1270	1150	1050	–
70	30	135. 190. 225. 230	6.97	1250	1130	1060	–
60	40	140. 190. 215. 245	6.90	1250	1100	1050	–
50	50	130. 190. 265	6.80	–	1100	1050	–
45	55	130. 190. 225. 275	6.72	–	–	–	–
40	60	130. 190. 240. 280	6.67	–	–	1050	–
35	65	135. 250. 285	6.60	–	1100	1050	–
30	70	140. 205. 270	6.56	–	–	–	–
20	80	150. 205. 250. 270	6.49	–	–	–	880
10	90	155. 230. 250. 290	6.42	–	–	–	880
5,0	95	160. 270. 300	6.30	–	–	–	870
0,0	100	165. 305	6.25	–	–	–	840

Table 1.
Composition of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system alloys, DTA results, microhardness and density measurements (in crystalline form)

Composition, mol %		Thermal effects,ºC	Density, q/cm³	Mikrohardness, MPa			
$Tl_3As_2Se_6$	$TlAs_2Se_3S$			α	$TlAs_2Se_4$	$Tl_3As_2S_3Se_3$	β
				P=0,10 N			
100	0.0	245	7.80	1080	–	–	–
95	5.0	230. 245	7.78	1100	–	–	–
90	10	225. 240	7.70	1100	–	–	–
80	20	190. 225. 235	7.52	1120	920	890	–
70	30	190. 225. 230	7.40	1100	900	970	–
60	40	190. 215. 245	7.25	1090	910	870	–
50	50	190. 265	7.15	1080	910	–	–
45	55	190. 225. 275	7.05	Eutek.	Eutek.	Evuek.	–
40	60	190. 240. 280	6.95	–	900	–	–
35	65	250. 285	6.82	–	900	–	–
30	70	205. 270	6.79	–	Eutek.	Eutek.	Eutek.
20	80	205. 250. 270	6.62	–	–	870	820
10	90	230. 250. 290	6.54	–	–	–	820
5.0	95	270. 300	6.45	–	–	–	800
0,0	100	305	6.40	–	–	–	780

Differential-thermal analysis of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system shows that softening temperatures are observed on the thermograms of alloys before heat treatment. Thermal effects are almost always very small and mixed. The fact that the temperature Tg (140-165°C) does not increase monotonically and takes different values indicates the complexity of the composition. In order to distinguish phases, microstructural analysis of glassy and crystalline samples was carried out. One of the ways to better detect phases is etching with a chemical solution. Annealing allows us to identify the size, shape and distribution of phases in the alloy. The main condition is the formation of different phase relief. In this case, it is not important which phase has the highest dissolution rate inside the alloy. To determine the composition of the obtained samples, they were crystallized and their microstructure was studied. It was found that in areas close to the main components, single-phase and two-phase alloys are found. It was found that three-phase alloys exist in the concentration range of 15-80 mol % $TlAs_2Se_3S$ (Fig. 1). The alloy with a concentration of 5 mol % shown in the figure is a solid solution alloy based on the compound

$Tl_3As_2Se_6$. Samples of 10 and 40 mol % are two-phase and three-phase alloys.

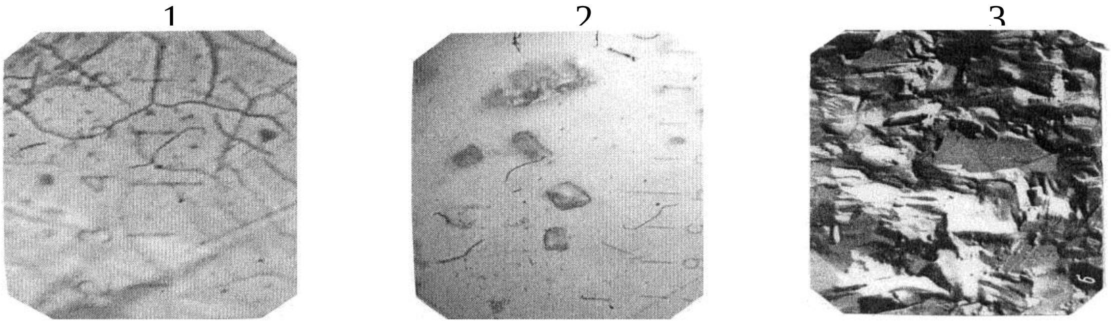

Fig. 1. Microstructures of alloys of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system. (×340): 1-5, 2 -10, 3-40 mol % $TlAs_2Se_3S$.

An X-ray structural analysis of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ alloys was performed. It was found that no diffraction maxima were obtained on the diffraction patterns of the samples before heat treatment. Figure 2 shows the X-ray patterns of $TlAs_2Se_3S$ samples with a content of 20, 50 and 80 mol % $TlAs_2Se_3S$ in the glassy state. This indicates that all the obtained alloys are glassy.

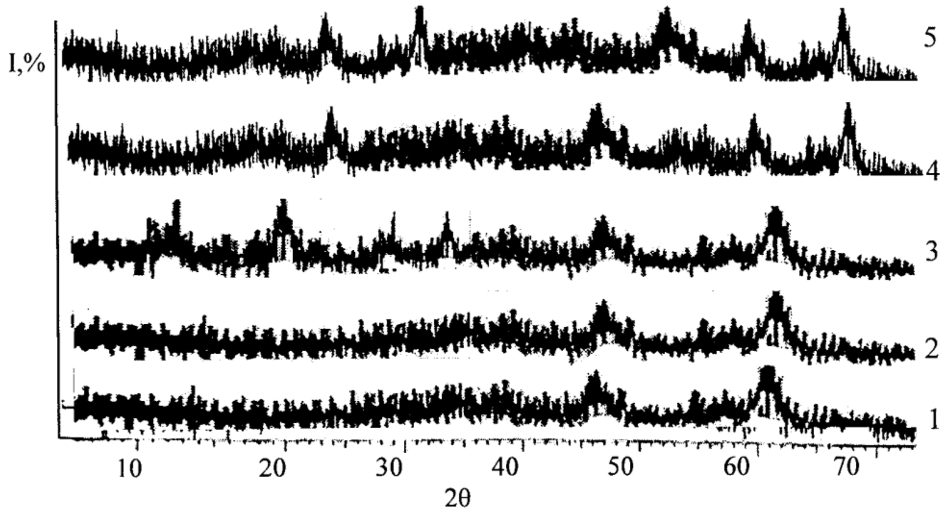

Fig. 2. Diffraction patterns of glassy alloys of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system.
1- $Tl_3As_2Se_6$, 2-20, 3-50, 4-80, 5- 100 mol % $TlAs_2Se_3S$

X-ray analysis after heat treatment shows that diffraction lines of sufficiently high intensity appear on the X-ray images of the samples. Thus, X-ray analysis, like the above-mentioned methods of analysis, shows that a complex interaction occurs in the system. When measuring the microhardness of the alloys of the system, four different, relatively close values were obtained. The following values of microhardness and density of glass were obtained. The values of microhardness $H\mu$ = (1250-1280) MPa and density ρ = (7.15-7.40) g/cm^3 of the α-solid solution obtained on the basis of the combination $Tl_3As_2Se_6$, $H\mu$ = (1100-1150) MPa, ρ = (6.90-7.15) g/cm^3 of the $TlAs_2Se_4$ compound, $H\mu$ = (1050-1060) MPa, ρ = (6.56-6.80) g/cm^3 of the $Tl_3As_2S_3Se_3$ compound and $H\mu$ = (840-880) MPa, ρ = (6.25-6.56) g/cm^3 correspond to the values of microhardness and density of the β-solid solution obtained on the basis of the $TlAs_2Se_3S$ compound.

Based on the results of physicochemical analysis methods, a phase diagram of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system was constructed (Fig. 3).

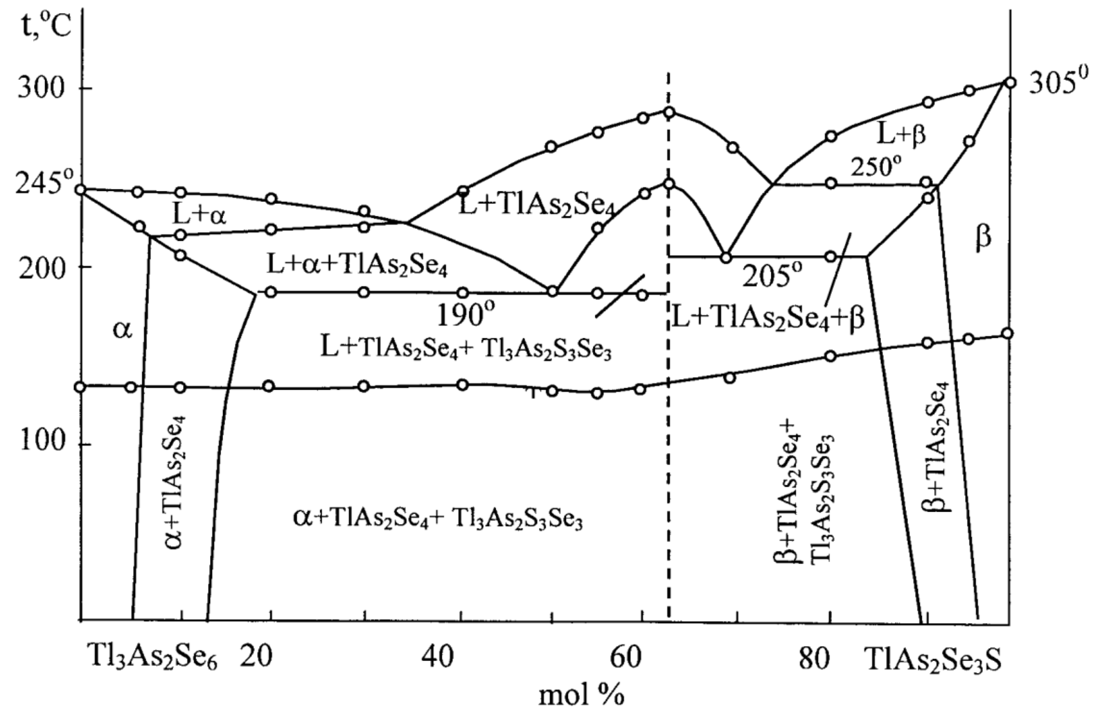

Fig. 3. Phase diagram of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system.

During the study of the quasi-ternary system As_2S_3-As_2Se_3-TlS(Se), it was found that the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system is non-quasi-binary, passing through the regions of two subordinate triangles As_2Se_3-$Tl_3As_2S_3Se_3$-$T1As_2Se_4$ and $TlAs_2Se_4$-$Tl_3As_2S_3Se_3$-$Tl_3As_2Se_6$. $Tl_3As_2Se_6$-$TlAs_2Se_3S$ crosses the three-phase field, crossing the triangle $TlAs_2Se_4$-$Tl_3As_2S_3Se_3$-$Tl_3As_2Se_6$. At this time, in the range of 0–63 mol % $TlAs_2Se_3S$, the liquid of this part of the system is limited by the initial crystallization curves of the $TlAs_2Se_4$ compound with an α-solid solution. The combined crystallization of both phases ends with a double eutectic. At this point, a three-phase equilibrium L↔α+$TlAs_2Se_4$ occurs. In the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system based on the compound $Tl_3As_2Se_6$, the solid solution region at room temperature is 5 mol % $TlAs_2Se_3S$, and based on the compound $Tl_3As_2Se_6$ up to 3 mol % $TlAs_2Se_3S$.

The composition of the eutectic is ~35 mol% $TlAs_2Se_3S$, the melting point is 225°C. In this region, the phases (L+α) and (L+$TlAs_2Se_4$) are located below the liquids lines. Below the liquidus line, there are two-phase and three-phase regions, (L+$TlAs_2Se_4$) and (L+$TlAs_2Se_4$+ $Tl_3As_2S_3Se_3$). Below the solidus line, as a result of double precipitation, alloys consisting of three-phase (α+$T1As_2Se_4$+$Tl_3As_2S_3Se_3$) alloys crystallize. In the ternary eutectic, a four-phase equilibrium is formed: L↔ α+$TlAs_2Se_4$+$Tl_3As_2S_3Se_3$.

The rest of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system passes through the region of the As_2Se_3-$Tl_3As_2S_3Se_3$-$TlAs_2Se_4$ hardness triangle. At the intersection point, the $Tl_3As_2S_3Se_3$ and $TlAs_2Se_4$ phases are formed. In the concentration range of the system of 53–100 mol % $TlAs_2Se_3S$, the liquidus region is surrounded by the curves of primary crystallization of $TlAs_2Se_4$ and the β-solid solution. Their cocrystallization is completed by a binary eutectic of the composition ~73 mol % $TlAs_2Se_3S$ with a melting point of 250°C. At this point, invariant equilibrium occurs: L ↔ β + $TlAs_2Se_4$. Below the liquids line, in the range of 73–90 mol % $TlAs_2Se_3S$, phases consisting of a mixture of L + β + $TlAs_2Se_4$ are formed. As a result of reprecipitation, the liquid phase completely dissolves, passes into the solid phase, and three-phase alloys consisting of (β+$TlAs_2Se_4$+$TlAs_2Se_3S$) crystallize below the solidus line.

Conclusion

Thus, the phase diagram of the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system was constructed using physicochemical analysis methods. This system is a non-quasi-binary part of the quasi-ternary As_2S_3-As_2Se_3-TlSe system. Based on the initial components, a limited area of solid solutions is obtained in the system. Upon normal cooling, all alloys of the system were obtained in the form of glass. In the $Tl_3As_2Se_6$-$TlAs_2Se_3S$ system, the area of the solid solution at room temperature is 5 mol % based on the $Tl_3As_2Se_6$ compound and 3 mol % based on $TlAs_2Se_3S$. The softening and crystallization temperatures of the obtained chalcogenide glasses were determined.

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