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CHARACTER OF INTERACTION AND GLASS FORMATION IN THE $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ SYSTEM

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Abstract. The character of the interaction in the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system was studied by the methods of DTA, RFA, MSA, and also by measuring the microhardness and determining the density. State diagram of the system was constructed. It was established that the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system is partially a quasibinary section of the quaternary As, Tl//Se, Te system. One congruently melting compound $TlAs_2Se_2Te_2$ is formed in the system at 548 K. Solid solutions based on $TlAs_2Se_3Te$ at room temperature reach up to 10 mol % $TlAs_2Te_3Se$, and solid solutions on the basis of $TlAs_2Te_3Se$ are practically not detected. All the samples obtained are vitreous.

Keywords: congruently, eutectic, quasi-binary, solid solutions, chalcogenides.

1. Introduction

It is known that arsenic chalcogenides and their alloys are IR transparent and widely used in optical information processing systems, in particular, in elements of acousto-optical devices and targets for video codes [1-3].

In the recent years, ternary and more complex systems involving arsenic chalcogenides and other metal chalcogenides have been widely used as semiconductor and luminescent material in electronic engineering [4, 5].

In the literature on the interaction of arsenic and thallium chalcogenides, much information is available on ternary and quaternary systems [6-11]. The system $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ is investigated for the first time. The purpose of this work is to study the nature of the chemical interaction and glass formation in the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system, as well as the detection of semiconductor phases.

The $TlAs_2Se_3Te$ compound melts congruently at 498 K and crystallizes in a hexagonal system with lattice parameters: a = 10.66; c = 9.05 Å, ρ = 6.78·10^3 kg/m^3 [12]. The $TlAs_2Te_3Se$ compound melts incongruently at 513 K and crystallizes in tetragonal system with lattice parameters: a = 10.83; c = 9.32 Å, ρ = 7.4·10^3 kg/m^3 [12].

2. Experimental

The alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system were synthesized by an ampoule method in a single-temperature vertical furnace at 773-973 K. Taking into account the peritectic nature of the $TlAs_2Te_3Se$ formation, in order to achieve completeness of reaction, the quaternary compound was annealed below the peritectic temperature (503 K) for 500 h.

Interaction in the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system was studied by differential thermal (DTA), X-ray diffraction (XRD), microstructural (MSA) analyses, as well as microhardness and density determination.

DTA scans were made using a TERMOSCAN-2 thermal analyzer, calibrated chromel-alumel thermocouples, and Al_2O_3 as a reference substance. The heating rate was 10 K/min. X-ray diffraction patterns were studied on a D-2 PHASER model diffractometer using Cu_α -radiation with a Ni-filter. The microstructure of the alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system was examined with a metallographic MIM-8 microscope on pre-etched sections, polished with GOI paste. The microstructure was revealed by an etchant with the composition of 10 ml conc. NaOH : 5 ml of C_2H_5OH = 1:1, etching time 20 s. The microhardness of the alloys was studied at the PMT-3 installation at 0.15 loads. The densities of the system alloys were determined by a pycnometric method, toluene was used as the working fluid.

3. Results and Discussion

The samples obtained are compact and black in color. At room temperature, all samples of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system are resistant to air organic solvents and mineral acids. When heated, mineral

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acids (HNO_3, H_2SO_4) and alkalis (NaOH, KOH) decompose them. Annealing of the alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system was carried out at 453 and 523 K for 740 h. Crystallization of the glassy alloys was monitored by periodic studies of DTA, XRD, density determination, and microhardness measurements.

DTA results show that almost all fixed on the heating and cooling curves are irreversible. On the thermograms of the system alloys, three series of softening point values (T_g) were found. For $TlAs_2Se_3Te$, T_g = 423 K, for $TlAs_2Se_2Te_2$ T_g = 383 K and for $TlAs_2Te_3Se$ T_g = 408 K.

To determine the region of glass formation, XRD, MCA, microhardness measurements, and determination of the density of alloys of the system before and after annealing were carried out.

The MSA of the alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system shows that all the alloys are glassy. After annealing, the thermograms of the alloys from the glass region lack softening temperatures. The microstructures of these alloys show that, in addition to alloys containing 0–10 mol % of $TlAs_2Te_3Se$ and 50 mol % of $TlAs_2Te_3Se$, all alloys are two-phase and three-phase alloys.

XRD cast alloys of the system showed that on the diffractograms of alloys containing 20, 40 and 70 mol % of $TlAs_2Te_3Se$, no diffraction maxima were observed (Fig. 1a). After annealing on the diffractograms of the above alloys, intense diffraction maxima appear (Fig. 1b).

Given the conchoidal fracture, the presence of thermal effects of softening temperatures on thermograms, the absence of diffraction maxima in diffractograms and finally, the absence of crystalline inclusions, one can judge glasses.

Thus, it was found that all the alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system under ordinary conditions are obtained in the glassy form. Based on the physico-chemical analysis, a phase diagram of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system was constructed (Fig. 2). It was established that a compound of the composition $TlAs_2Se_2Te_2$ and a melting incoherent at 548 K is formed in the system. Using the methods of physical and chemical research, the existence of the $TlAs_2Se_2Te_2$ compound was confirmed.

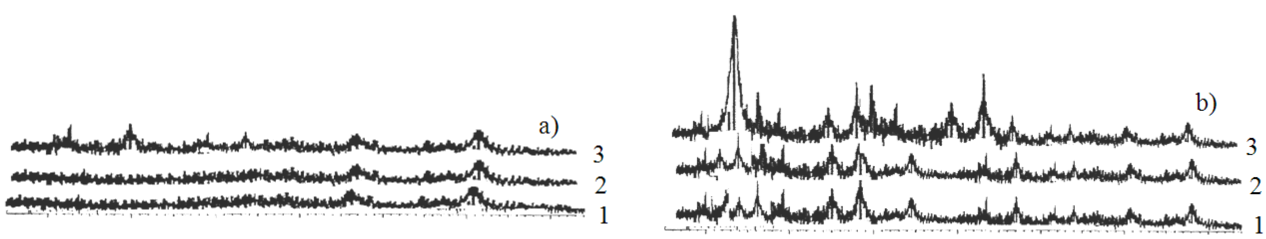

Fig. 1. Diffractograms of alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system containing 20 (1), 40 (2) and 70 (3) mol % of $TlAs_2Te_3Se$ before (a) and after (b) annealing

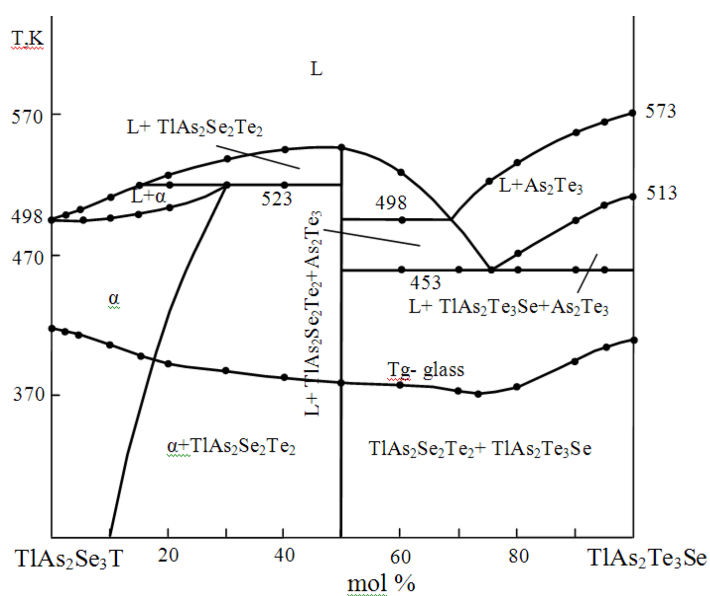

Fig. 2. Phase diagram of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system

Table 1

Composition, DTA results, microhardness measurements and determination of the density of alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system before annealing

Composition, mol %		Thermal effects, K	Density, 10^3 kg/m^3	Microhardness, MPa		
$TlAs_2Se_3Te$	$TlAs_2Te_3Se$			α	$TlAs_2Se_2Te_2$	$TlAs_2Te_3Se$
				P = 0.15 N		
100	0	423, 498	6.55	820	–	–
97	3.0	418, 503	6.57	830	–	–
95	5.0	413, 498, 503	6.61	880	–	–
90	10	408, 508, 518	6.65	920	–	–
85	15	403, 508, 523	6.67	920	–	–
80	20	398, 513, 523, 533	6.72	920	–	–
70	30	393, 523, 538	6.80	–	1100	–
60	40	388, 523, 543	6.86	–	1100	–
50	50	383, 548	6.95	–	1060	–
40	60	383, 453, 493, 533	6.97	–	1080	–
30	70	378, 453	6.99	–	–	–
25	75	473, 453, 528	7.00	–	–	–
20	80	383, 453, 473, 538	7.04	–	–	890
10	90	398, 453, 493, 563	7.08	–	–	900
5.0	95	408, 453, 508, 568	7.10	–	–	900
0.0	100	413, 513, 573	7.12	–	–	870

Table 2

Composition, DTA results, microhardness measurements and density determination of alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system after annealing

Composition, mol %		Thermal effects, K	Density, 10^3·kg/м^3	Microhardness, MPa		
$TlAs_2Se_3Te$	$TlAs_2Te_3Se$			α	$TlAs_2Se_2Te_2$	$TlAs_2Te_3Se$
				P = 0.15 N		
100	0	498	6.78	680	–	–
97	3.0	503	6.80	690	–	–
95	5.0	498, 503	6.83	700	–	–
90	10	508, 518	6.87	700	–	–
85	15	508, 523	6.89	740	–	–
80	20	513, 523, 533	6.93	740	–	–
70	30	523, 538	6.97	eutect.	eutect.	–
60	40	523, 543	7.05	–	800	–
50	50	548	7.12	–	760	–
40	60	453, 493, 533	7.12	–	770	–
30	70	453	7.14	–	770	–
25	75	453, 528	7.15	–	–	–
20	80	453, 473, 538	7.17	–	–	600
10	90	453, 493, 563	7.18	–	–	600
5.0	95	453, 508, 568	7.20	–	–	600
0.0	100	513, 573	7.20	–	–	570

From the measurements of the microhardness of cast alloys of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system, three series of values are different (Tables 1, 2). The first one corresponds to the microhardness of the dark α-phase (solid solutions based on $TlAs_2Se_3Te$, 820–920 MPa), the microhardness value within 1060–1100 MPa corresponds to the new phase of $TlAs_2Se_2Te_2$, and the microhardness value within 870–900 MPa corresponds to the $TlAs_2Te_3Se$ compound. After annealing, the microhardness for α-solid solutions is 680–740 MPa, for $TlAs_2Se_2Te_2$ it is equal to 760–800 MPa, and for $TlAs_2Te_3Se$ – to 570–600 MPa.

The density of vitreous alloys before and after annealing differs markedly (Tables 1, 2). In the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system, the boundaries of solid solutions based on $TlAs_2Se_3Te$ are extending up to 10 mol % $TlAs_2Se_3Te$, and on the basis of $TlAs_2Te_3Se$

solid solutions are practically not detected. To clarify the region of glass formation in the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system, XRD was carried out before and after annealing.

The liquidus of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system consists of three branches of primary crystallization of the α-phase (solid solutions based on $TlAs_2Se_3Te$), a new phase of $TlAs_2Se_2Te_2$ and $TlAs_2Te_3Se$.

In the concentration range of 0–30 mol % $TlAs_2Te_3Se$, the primary crystallization of the α-phase takes place along the liquidus line. Within the range of 15–70 mol % $TlAs_2Te_3Se$, the phase is first released from the liquid, and in the range of 70–100 mol % $TlAs_2Te_3Se$ the As_2Te_3 compound is released from the liquid. Above the temperature of 513 K, the $TlAs_2Te_3Se$ compound decomposes according to the reaction: $TlAs_2Te_3Se \leftrightarrow L+As_2Te_3$.

Therefore, in the range of 75–100 mol % $TlAs_2Te_3Se$ below the liquidus line, there are three-phase mixtures ($L + As_2Te_3 + TlAs_2Te_3Se$). Within 0–10 mol % below the solidus line, single-phase alloys (α) crystallize, in the range of 10–50 mol % $TlAs_2Te_3Se$ crystallizes biphase alloys (α + $TlAs_2Se_2Te_2$), and in the range of 50–100 mol % $TlAs_2Te_3Se$ alloys crystallize ($TlAs_2Te_3Se$ + $TlAs_2Se_2Te_2$).

4. Conclusions

The phase diagram of the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system was studied by DTA, RFD, and MSA methods, as well as by measuring of microhardness and density determination, and by constructing state diagram. It is established that the $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ system is a partially quasi-binary section of the quaternary system As, Tl//Se, Te. In the system at 548 K one congruent-melting compound $TlAs_2Se_2Te_2$ is formed. Solid solutions based on $TlAs_2Se_3Te$ at room temperature reach 10 mol % $TlAs_2Te_3Se$, and solid solutions on the basis of $TlAs_2Te_3Se$ are practically not detected. All the samples obtained are vitreous.

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References

[1] Hari P., Cheneya C., Luepkea G. *et al.*: J. Non-Crystal. Solid., 2000, 270, 265. https://doi.org/10.1016/S0022-3093(00)00072-7
[2] Iovu M., Shutov C., Rebeja S., Colomeyco E.: J. Optoelectron. Adv. Mater., 2000, 2, 53.
[3] Littler I., Fu L., Mägi E. *et* al.:J. Opt. Express, 2006, 14, 8088. https://doi.org/10.1364/OE.14.008088
[4] Hineva T., Petkova T.,Popov C. *et al.*: J. Optoelectron. Adv. Mater., 2007, **9**, 326.
[5] Babaiev A., Muradov R., Sultanov S., Askhabov A.: Neorg. Materialy, 2008, **44**, 1319.
[6] Aliyev I., Ahmedova C., Farzaliyev A.: Chem. Chem. Technol., 2017, **11**, 138. https://doi.org/10.23939/chcht11.02.138
[7] Aliyev I., Babanly M., Farzaliev A.: XI Int. Conf. on the Physics and Technology of Thin Films. Ukraine, Ivano-Frankivsk, 7-12 May 2007, 86.
[8] Aliyev I., Aliyev I.G., Farzaliev A., Veliev D.: Rus. J. Inorg. Chem., 2008, **53**, 962. https://doi.org/10.1134/S00.6023608060259
[9] Veliev D., Aliyev I., Mamedova A.: Zh. Neorg. Khim., 2007, **52**, 312.
[10] Farzaliev A., Aliyev I., Aliyev O., Aliyev I.G.: Chem. Problems, 2006, **2**, 269. https://doi.org/10.1134/S0036023607020234
[11] Vorobyev Yu., Velikova N., Kirilenko V., Shchelkov R.: Neorg. Materialy, 1987, **23**, 1110.
[12] Aliyev I.: Doct. thesis. Physicochemical basis for obtaining new materials in chalcogenide systems of arsenic with indium and thallium chalcogenides. Baku 1992.

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ХАРАКТЕР ВЗАЄМОДІЇ ТА СКЛОУТВОРЕННЯ В СИСТЕМІ $TlAs_2Se_3Te$–$TlAs_2Te_3Se$

***Анотація**. Характер взаємодії в системі $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ досліджено за допомогою диференційного термічного, рентгеноструктурного та мікроструктурного методів, а також внаслідок вимірювання мікротвердості та визначення густини. На основі одержаних результатів побудовано діаграму стану. Встановлено, що ділянка $TlAs_2Se_3Te$–$TlAs_2Te_3Se$ частково є квазібінарною секцією четвертинної системи As, Tl//Se, Te. Показано, що за температури 548 K у системі утворюється одна конгруентноплавка сполука $TlAs_2Se_2Te_2$. Визначено, що область розчинності твердих розчинів на основі $TlAs_2Se_3Te$ за кімнатної температури досягають 10 % мол. $TlAs_2Te_3Se$, а сполуки на основі $TlAs_2Te_3Se$ практично не спостерігаються. Показано, що всі отримані зразки склоподібні.*

***Ключові слова:** конгруентно, евтектичні, квазібінарні, тверді розчини, халькогеніди.*