Chem. Chem. Technol., 2017,
Vol. 11, No. 2, pp. 138–143

Chemistry

PHASE EQUILIBRIA IN THE AS_2SE_3-$TL_3AS_2S_3SE_3$ SYSTEM AND PROPERTIES OF ALLOYS

Imir Aliyev[1, *], Ceyran Ahmedova[2, *], Abdin Farzaliyev[1]

https://doi.org/10.23939/chcht11.02.138

Abstract. The As_2Se_3-$Tl_3As_2S_3Se_3$ system was studied using differential thermal analysis, powder X-ray diffraction, as well as microhardness and density measurements and its phase diagram was constructed. The studied system contains a new quaternary compound $TlAs_2Se_3S$, which crystallizes in tetragonal structure. The temperature dependence of the electrical conductivity of alloys was studied.

Keywords: chalcogenides, phase diagram, semiconductors, solidus, glass formation.

1. Introduction

Arsenic chalcogenides and alloys based on them are known to be IR transparent and are widely used in optical information processing systems, in particular, in elements of acousto-optic lines and targets of vidicon video camera tubes [1-6]. Therefore, the search for new vitreous compound semiconductors based on As_2S_3 and As_2Se_3 is an urgent and interesting topic in both theoretical and practical aspects. Therefore, the important features and application areas of glassy alloys that can be obtained in As_2Se_3-$Tl_3As_2S_3Se_3$ system have been researched per the physico-chemical parameters. Previously, we investigated some quasi-binary sections of the As-Tl-S-Se quaternary system [7–10].

The purpose of this work was to study the chemical interaction and glass formation in the As_2Se_3-$Tl_3As_2S_3Se_3$ system. The compounds As_2Se_3 and $Tl_3As_2S_3Se_3$ have the following properties: As_2Se_3 is a vitreous semiconductor that melts congruently at 653 K and crystallizes in the monoclinic system with the unit cell parameters a = 1.2053, b = 0.989, c = 0.4277 nm, β =90°28′ (space group $P2_1/n$) [11]. The density and microhardness of crystalline As_2Se_3 are $\rho = 4.618 \cdot 10^3$ kg/m^3 and $H\mu$ = 1280 MPa, respectively, and those of vitreous As_2Se_3 – $5.10 \cdot 10^3$ kg/m^3 and $H\mu$ = 760 MPa, respectively [12].

The compound $Tl_3As_2S_3Se_3$ was obtained in the vitreous state. It melts congruently at 553 K and crystallizes in the tetragonal system with the unit cell parameters a = 1.120, c = 0.923 nm, Z = 4 [13].

2. Experimental

The interaction in the As_2Se_3-$Tl_3As_2S_3Se_3$ section was investigated within the 0–100 mol % $Tl_3As_2S_3Se_3$ concentration range. Intermediate alloys were prepared from the As_2Se_3 and $Tl_3As_2S_3Se_3$ constituents in quartz ampoules evacuated to 0.133 Pa at 523–1073 K. Thermal annealing was used to crystallize glassy alloys. Cooling rates were 40–50 K/h. Physicochemical analyses of As_2Se_3–$Tl_3As_2S_3Se_3$ system alloys were performed both as glassy and crystalline state.

The phase diagram was constructed using the data of differential thermal analysis, X-ray powder diffraction, microstructural analysis, as well as microhardness and density measurements.

Thermal curves were recorded on a ”Termoscan-2” low-frequency temperature recorder at the heating rate of 10 K/min. Temperature measurements of phase transformations were carried out by the combined chromel-alumel-thermocouples. Heating and cooling of the alloys were performed in tubular electrical resistance furnaces.

Recording thermograms were carried out under vacuum. Alloys of the investigated system were heated and annealed in Stepanova evacuated sealed quartz vessels, which was placed in the hole of a steel block. Al_2O_3 was used as etalon.

X-ray powder diffraction patterns were recorded on “D2 PHASER” diffractometer (Cu K_α radiation). The microhardness was measured with “Thixomet Smart-Drive” microhardness meter under loads chosen by studying the microhardness of each of the phases. The microstructure of the alloys ware examined with an MIM-8 microscope. The etchant used was 10 ml conc.

[1] Institute of Catalysis and Inorganic Chemistry named after acad. M.F. Nagiyev of Azerbaijan National Academy of Sciences, H. Javid ave, 113, Baku, Az1143, Azerbaijan
[2] Faculty of Arts and Sciences, Chemistry Department, Adiyaman University, Turkey
[*] *aliyevimir16@gmail.com;cahmedova@yahoo.com*

HNO_3 : 5 ml H_2O_2, the etching time was 20 s. The densities of the alloys were determined picnometrically with toluene as a filler.

The electrical conductivity of the alloys was measured by a standard bridge technique using samples in the shape of rectangular parallelepipeds. The experimental error was estimated at 2.7–3.0 %.

3. Results and Discussion

Alloys of the As_2Se_3-$Tl_3As_2S_3Se_3$ system had the form of dense, dark-black ingots. Alloys with 0–30 mol % of As_2Se_3 are stable in air, organic solvents and poorly soluble in mineral acids. Alloys with 30–100 mol % of $Tl_3As_2S_3Se_3$ are well soluble in concentrated mineral acids (HNO_3 and H_2SO_4). All alloys of the system are well soluble in alkalis (NaOH and KOH). For crystallization the glassy alloys were annealed for 720 h at their crystallization temperature. The system As_2Se_3-$Tl_3As_2S_3Se_3$ alloys were studied before and after annealing.

The DTA curves for annealed alloys show softening (glass transition) temperatures *Tg*. After long (720 h) annealing, the softening temperatures (398–453 K) disappear from the DTA curves, while features relating to solidus and liquidus were retained (Tables 1, 2).

Table 1 shows that the softening temperature of glassy alloys change from 398 to 453 K. Alloys with As_2Se_3-$Tl_3As_2S_3Se_3$ system before annealing are in fact one nontransparent phase. Individual phases in the alloys are very diffuse, and it is difficult to determine exact boundaries of solid solutions. After annealing the individual phases are well visible in the structure of glassy sampler.

Microhardness measurements on cast alloys of the As_2Se_3-$Tl_3As_2S_3Se_3$ system show two sets of values (Tables 1, 2). One set corresponds to the microhardness of α-phase (As_2Se_3 based solid solution): $H\mu$ = 1300–1350 MPa, r = (4.62–5.20)·10^3 kg/m^3. The other one refers to β-phase ($Tl_3As_2S_3Se_3$ based solid solution): $H\mu$ = 1050–1100 MPa, r = (6.50–7.05)·10^3 kg/m^3. After annealing of the As_2Se_3-$Tl_3As_2S_3Se_3$ alloys, the microhardness of α-phase was 760–780 MPa, r = = (5.10–5.60)·10^3 kg/m^3; that of the β-phase was 880–900 MPa and r = (6.80–7.18)·10^3 kg/m^3.

The above given data shows, that microhardness values of glasses are higher than the relevant crystals. Density values for glasses are lower than for the relevant crystals. To determine the glass formation region in the system, alloys were subjected to powder X-ray diffraction analysis before and after annealing. Before annealing 20, 33.3, 50 and 100 mol % $Tl_3As_2Se_3Se_3$ alloys do not show diffraction peaks (Fig. 1). After annealing strong peaks appear in the diffraction patterns of these alloys (Fig. 2). This implies that all glassy alloys are completely crystalline after annealing.

Table 1

Composition, DTA results, microhardness, and density determination (glassy form) for alloys of As_2Se_3-$Tl_3As_2S_3Se_3$ system

Components, mol %		Thermal effects, K	Density, 10^3·kg/m^3	Microhardness, MPa		
As_2Se_3	$Tl_3As_2S_3Se_3$			α	$TlAs_2Se_3S$	b
				P = 0.15 N		
100	0.0	453, 653	4.62	1300	–	–
97	3.0	448, 598, 638	4.69	1350	–	–
95	5.0	448, 563, 633	4.76	1350	–	–
90	10	443, 513, 618	4.90	1350	–	–
85	15	443, 513, 558	5.08	1350	–	–
80	20	438, 513	5.20	–	–	–
75	25	438, 513,553	5.32	–	860	–
70	30	438, 513, 573	5.85	–	860	–
66.6	33.3	438, 578	6.15	–	860	–
60	40	433, 493, 573	6.20	–	850	–
50	50	418, 493, 548	6.25	–	840	–
40	60	408, 493, 508	6.30	–	840	–
35	65	403, 493	6.38	–	–	
30	70	403, 493, 503	6.50	–	–	1060
20	80	398, 498, 523	6.67	–	–	1070
15	85	398, 508, 533	6.75	–	–	1100
10	90	398, 523, 543	6.90	–	–	1100
5.0	95	398, 528, 548	6.95	–	–	1080
3.0	97	403, 533, 553	6.98	–	–	1080
0.0	100	408. 553	7.05	–	–	1050

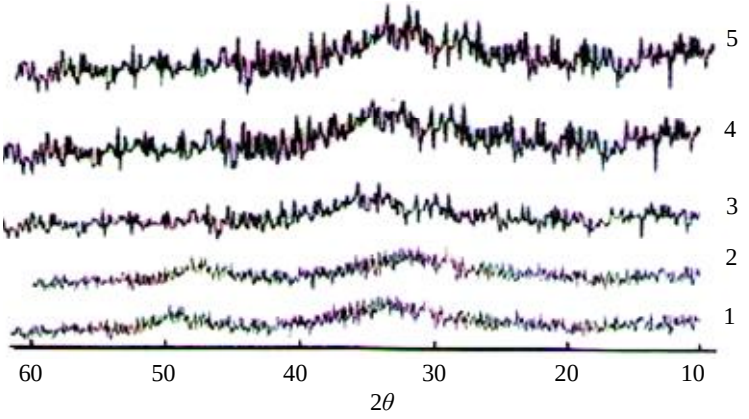

Fig. 1. X-ray powder diffraction patterns of glassy alloys of As_2Se_3-$Tl_3As_2S_3Se_3$ system: As_2Se_3 (1); 20 (2); 33.3 (3); 50 (4) and 100 mol % $Tl_3As_2S_3Se_3$ (5)

Table 2

Composition, **DTA results, microhardness, and** density **determination** (**crystalline) for alloys of As_2Se_3- $Tl_3As_2S_3Se_3$** system

Components, mol %		Thermal effects, K	Density, 10^3·kg/m^3	Microhardness, MPa		
As_2Se_3	$Tl_3As_2S_3Se_3$			*α*	$TlAs_2Se_3S$	*b*
				P = 0.10 N		
100	0.0	653	5.10	760	–	–
97	3.0	598, 638	5.20	780	–	–
95	5.0	563, 633	5.32	780	–	–
90	10	513, 618	5.42	780	–	–
85	15	513, 558	5.54	780	–	–
80	20	513	5.60	eutectic	eutectic	–
75	25	513, 553	5.82	–	740	–
70	30	513, 573	6.24	–	730	–
66.6	33.3	578	6.49	–	720	–
60	40	493, 573	6.54	–	740	–
50	50	493, 548	6.58	–	740	–
40	60	493, 498	6.62	–	740	–
35	65	493	6.70	–	eutectic	eutectic
30	70	493, 503	6.80	–	–	900
20	80	498, 523	6.80	–	–	900
15	85	508, 533	6.90	–	–	900
10	90	523, 543	6.98	–	–	900
5.0	95	528, 548	7.05	–	–	890
3.0	97	533, 553	7.10	–	–	880
0.0	100	553	7.18	–	–	880

The structure of alloys was studied also by microscopic method. The results of microstructural analysis showed that all obtained alloys are glassy. Before annealing, the alloy microstructure under the microscope appears dark in the form of a single phase. To find a new phase and range of solid solutions the alloys with the concentration range of 0–33 mol % $Tl_3As_2S_3Se_3$ were annealed at 440 K, and alloys with the concentration range of 33–100 mol % of $Tl_3As_2S_3Se_3$ were annealed at 430 K for 800 h. After alloys crystallization the microscopic analysis was performed. As a result of the microstructural analysis we found a limited region of the solid solution and one new compound of the composition $TlAs_2Se_3S$.

Based on the results of physicochemical analysis of the samples, we constructed the phase diagram of the As_2Se_3-$Tl_3As_2S_3Se_3$ system (Fig. 3). The As_2Se_3-$Tl_3As_2S_3Se_3$ system is a quasi-binary section of the quaternary system As-Tl-S-Se.

The $TlAs_2Se_3S$ compound was obtained with the ratio of 2:1. This compound $TlAs_2Se_3S$ melts congruently at 578 K. In the As_2Se_3-$Tl_3As_2S_3Se_3$ system As_2Se_3-based solid solutions are formed up to 4 mol % $Tl_3As_2S_3Se_3$ and $Tl_3As_2S_3Se_3$-based solid solutions are formed up to 16 mol % As_2Se_3.

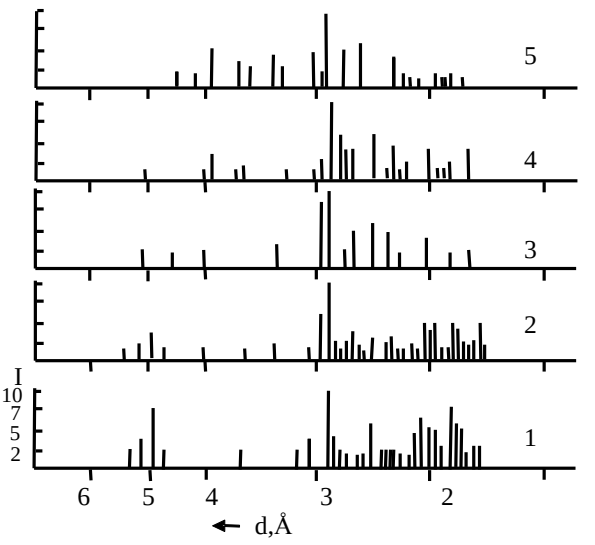

Fig. 2. X-ray Powder Diffraction Pattern scan line system diagram of alloys of As_2Se_3-$Tl_3As_2S_3Se_3$ system: As_2Se_3 (1); 20 (2); 33.3 (3); 50 (4) and 100 mol % $Tl_3As_2S_3Se_3$ (crystalline) (5)

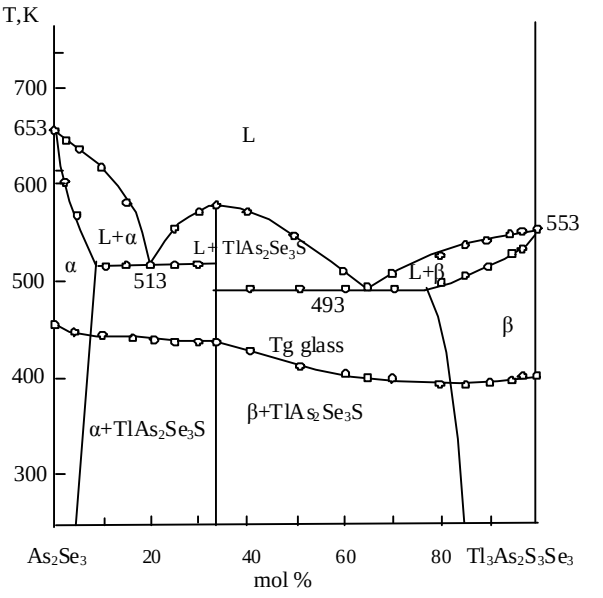

Fig. 3. Phase diagram of the As_2Se_3-$Tl_3As_2S_3Se_3$ system

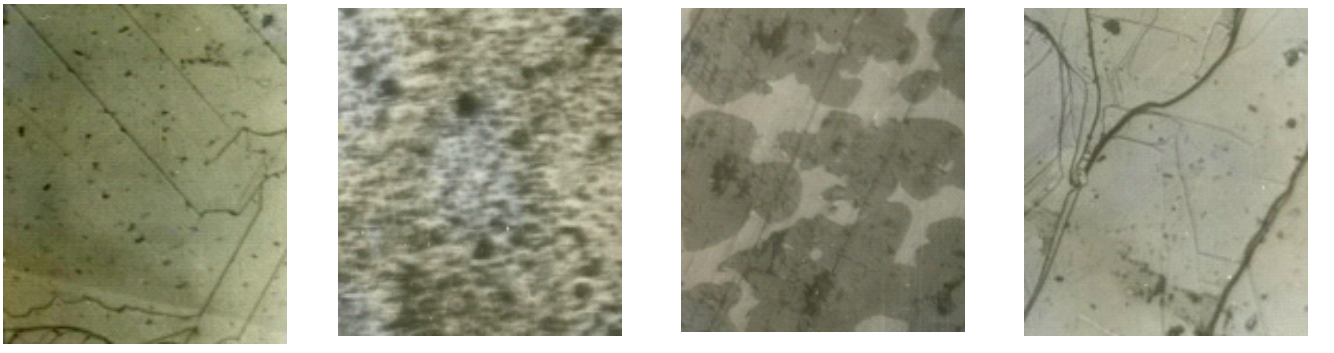

Fig. 4. The microstructure of alloys in the As_2Se_3-$Tl_3As_2S_3Se_3$ system: 5 (a); 20 (b); 50 mol % $Tl_3As_2S_3Se_3$ (c) and $TlAs_2Se_3S$ (compound) (d)

Table 3

The interplanar spacings (*d*, Å), *hkl* indices, and relative peak intensities in the XRD pattern of $TlAs_2Se_3S$

Intensity	$d_{exp.}$	$d_{calc.}$	*hκl*
18	5.0834	5.0898	200
15	4.5606	4.5596	001. 210
20	4.0005	3.8461	211
30	3.3605	3.3844	221
85	3.0585	3.0400	003
100	2.8606	2.8205	222
25	2.7503	2.7176	302
50	2.6697	2.6243	312
60	3.5206	2.5375	400
40	2.3702	2.3769	411
18	2.2804	2.2798	004
18	2.1199	2.1186	332
36	2.0399	2.0298	430
18	1.8240	1.8239	005
25	1.6720	1.6727	414

The liquidus of the As_2Se_3-$Tl_3As_2S_3Se_3$ system includes three primary crystallization fields: α-phase (As_2Se_3-based solid solutions), $TlAs_2Se_3S$, and β-phase ($TlAs_2Se_3S$- based solid solutions).

At $Tl_3As_2S_3Se_3$ concentration interval of 0–20 mol % the two-phase region ($L+\alpha$) is formed between the liquidus and solidus curves.

Two eutectic points of the system As_2Se_3-$Tl_3As_2S_3Se_3$ have coordinates 513 K and 20 mol % $Tl_3As_2S_3Se_3$ and 493 K and 65 mol % $Tl_3As_2S_3Se_3$, respectively. In Fig. 4 the microstructures of various alloys of the system are given. The microstructure of the alloy indicates: a) the glassy monophase solid solutions; b) eutectic; c) the two-phase region; d) compound $TlAs_2Se_3S$.

There is a relationship between the glass formation and the character of the phase diagram in the system. This area is located in the concentration range of 0–20 mol % $Tl_3As_2S_3Se_3$. Within $Tl_3As_2S_3Se_3$ concentration of 20–65 mol %, the structure is determined by the structure of $Tl_3As_2S_3Se_3$ glasses. The crystallization ability of glasses was investigated as a function of temperature, time and composition.

It was known that crystallization of the glass corresponding to the compound in the system occurs easily, unlike crystallization of the glasses of eutectic composition. There is no detailed information in literature about it.

The difficulty is mainly explained by the fact that crystallization of eutectic composition at the eutectic point crystallization temperature is very close to softening. Therefore, at the slightest deflection temperature, glass crystallization does not occur. With the introduction of the second component $Tl_3As_2S_3Se_3$ in the glass As_2Se_3 form small crystals and the glass crystallizes easily. Metallic bond formation adversely affects the formation of glass.

Individuality of $TlAs_2Se_3S$ compound was confirmed by DTA, XRD, density determination, and measurement of microhardness.

For the $TlAs_2Se_3S$ compound in vitreous state the microhardness $H\mu$ = 860 MPa and $\rho = 6.15 \cdot 10^3$ kg/m^3 while a microhardness of the crystalline state is equal to 720 MPa with a specific of $\rho = 6.49 \cdot 10^3$ kg/m^3.

It was established that the maximum obtained on diffractograms of the compound $TlAs_2Se_3S$ for intensities and interplanar spacing differ from the initial components. This proves formation of new compound $TlAs_2Se_3S$ in the system As_2Se_3-$Tl_3As_2S_3Se_3$. By the results of X-ray powder diffraction analysis, it was found that $TlAs_2Se_3S$ crystallizes in tetragonal crystal system with unit cell parameters: a= 1.015; c = 0.921 nm; Z = 6; $\rho_{pic.} = 6.49 \cdot 10^3$ kg/m^3; $\rho_{rent.} = 6.52 \cdot 10^3$ kg/m^3.

The interplanar spacings (d, E), hkl indices and relative peak intensities in the XRD pattern of the $TlAs_2Se_3S$ compound are presented in Table 3.

Electrical conductivity of As_2Se_3-$Tl_3As_2S_3Se_3$ glasses was studied at the temperatures of 300–350 K (Fig. 5). The samples used were in the form of a parallelepiped. According to our data, electrical conductivity of As_2Se_3 at room temperature is $8.2 \cdot 10^{-11}$ Om^{-1}·m^{-1}, and the band gap is 1.68 eV, which agrees with the literature data. The temperature dependence of the electrical conductivity of alloys containing 5, 10 and 15 mol % $Tl_3As_2S_3Se_3$ are linear. The temperature dependence of the electrical conductivity of the samples 5, 10 and 15 mol % $Tl_3As_2S_3Se_3$ composition shows that the conductivity increase with the addition of a second component that appears due to the increase of metallization of chemical bond. With increasing temperature, the conductivity of the studied glasses increases significantly.

The results of measurements of the electrical conductivity of the alloys glasses system As_2Se_3-$Tl_3As_2S_3Se_3$ 5, 10, 15 mol % $Tl_3As_2S_3Se_3$ in the temperature ranges of 290–350 K are shown in Fig. 5. Temperature dependence of the electrical conductivity shows that in As_2Se_3-$Tl_3As_2S_3Se_3$ system glassy alloys in all temperature ranges are semiconductor conductivity. The conductivity of the glassy alloys varies from $8.2 \cdot 10^{-11}$ to $1.8 \cdot 10^{-8}$ Om^{-1}·m^{-1} with addition of 5, 10, 15 mol % $Tl_3As_2S_3Se_3$ into the compound As_2Se_3.

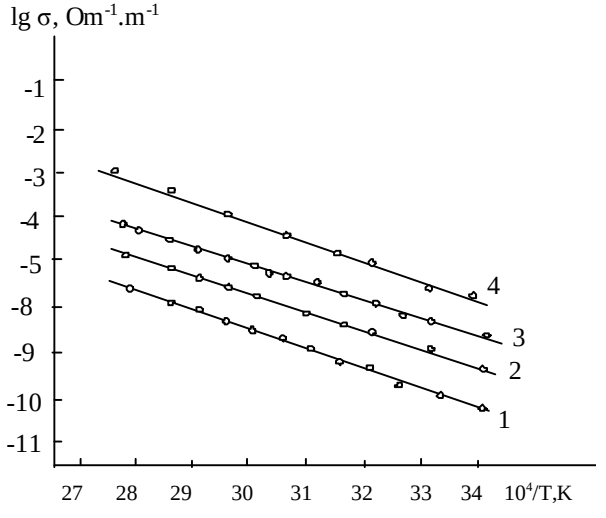

Fig. 5. The temperature dependence of the electrical conductivity of glass As_2Se_3-$Tl_3As_2S_3Se_3$ system: As_2Se_3 (1); 5 (2); 10 (3) and 15 mol % $Tl_3As_2S_3Se_3$ (4)

4. Conclusions

The phase diagram of the system was plotted. It was established that it is a quasi-binary section of the

quaternary As-Tl-S-Se system. At the ratio of the components 2:1 in the system one quaternary compound of composition $TlAs_2Se_3S$ was found. The $TlAs_2Se_3S$ melts congruently at 578 K and crystallizes in tetragonal structure symmetry with the unit cell parameters a = 1.015 nm, c = 0.912 nm, Z = 6, ρ_{pik} = $6.49 \cdot 10^3$ kg/m^3, $\rho_{rent.}$ = $6.52 \cdot 10^3$ kg/m^3. The As_2Se_3-based solid solution in the system extends to 12 mol % $Tl_3As_2S_3Se_3$ and $Tl_3As_2S_3Se_3$-based solid solution extends to 16 mol % As_2Se_3. In the system two eutectic points at 20 and 65 mol % $Tl_3As_2S_3Se_3$ and the temperature of 513 and 493 K, respectively, are formed. All alloys of the system were obtained in the glassy state. The temperature dependence of the electrical conductivity of alloys As_2Se_3-$Tl_3As_2S_3Se_3$ was studied.

References

[1] Sati D., Kumar R., Mehra M.: Turk. J. Phys., 2006, **30**, 519.
[2] Lovu M., Shutov S., Rebeja S. *et al.*: J. Optoelectron. Adv. Mater., 2000, **2**, 53.
[3] Hineva T., Petkova T., Popov C. *et al.*: J. Optoelectron. Adv. Mater., 2007, **9**, 326.
[4] Littler I., Fu L., Magi E. *et al.*: Opt. Express, 2006, **14**, 8088. http://dx.doi.org/10.1364/OE.14008088
[5] Kandpal S., Kushwaha R.P.S.: PRAM ANA J. Phys., 2007, **69**, 481.
[6] Babaev A., Muradov R., Sultanov S., Askhabov A.: Neorgan. Materialy, 2008, **44**, 1187.
[7] Aliyev I., Aliyev E.: 8th Eur. Conf. Solid State Chem. Norway, Oslo 2001, 215 .
[8] Farzaliev A., Aliev I., Aliev O., Aliyev I.: V Int. Conf. "Amorphous and microcrystalline semiconductors". Russia, St.Petrsburg 2006, 203.
[9] Veliev C., Aliev I., Mamedova A.: Russ. J. Inorg. Chem., 2007, **52**, 312. http://dx.doi.org/10.1134/S0036023607020234
[10] Aliev I., Bagieva M., Babanly M. *et al.*: Russ. J. Inorg. Chem, 2011, **56**, 498. http://dx.doi.org/10.1134/S0036023611030028
[11] Liakishev N. (Ed.): Diahramy Sostoianyia Dvoinykh Metallycheskykh System. Mashinostroenie, Moskva 2001, T.3.
[12] Chernov A.: Ph.D. thesis, Institute of General and Inorganic Chemistry, Moskva 1970.
[13] Aliyev I.: Doct. thesis. Fiziko-khimicheskie osnovy polucheniia novykh materialov v khalkohenidnykh systemakh arsenia s khalkohenidami indiia i tallia. Baku 1992.

Received: August 10, 2016 / Revised: September 22, 2016 / Accepted: January 12, 2017

ФАЗОВІ РІВНОВАГИ В СИСТЕМІ As_2Se_3-$Tl_3As_2S_3Se_3$ І ВЛАСТИВОСТІ СПЛАВІВ

Анотація. *За допомогою диференціального термічного аналізу, порошкової рентгенівської дифракції, а також вимірювань мікротвердості і щільності була вивчена система As_2Se_3-$Tl_3As_2S_3Se_3$ і побудовано її фазову діаграму. Встановлено, що система містить нову четвертинну сполуку $TlAs_2Se_3S$, яка кристалізується в тетрагональну структуру. Досліджено температурна залежність електропровідності сплавів.*

Ключові слова: *халькогеніди, фазова діаграма, напівпровідник, солідус, склоутворення.*