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GLASS AND PHASE FORMATION IN Sm – As – Se AND Eu – As – Se SYSTEMS

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Abstract. The Sm – As – Se and Eu – As – Se systems have been studied by the methods of physicochemical analysis (Differential thermal (DTA), X-ray phase (XRF) and micro-structural (MSA) analyzes, measurement of microhardness and electrophysical properties). $LnAs_4Se_7$, $LnAs_2Se_4$, $Ln_3As_4Se_9$, and $LnAsSe_3$ (where Ln - Sm, Eu) types of compounds were found in the systems. The nature of the formation of the obtained compounds is considered. Physical properties of these compounds have been studied. The parameters of their crystal lattices were calculated and it was found that they crystallize in the rhombic system. The boundaries of glass formation regions in the systems were established in different cooling modes. The electrical conductivity of the glasses was measured. It was found that the studied glasses have "p" type conductivity. Formation of new structural units in glasses is assumed. Phase diagrams of some quasi-binary sections are presented.

Keywords: *chalcogenide glasses, phase diagrams, glass formation region, semiconductors.*

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1. Introduction

It is known, chalcogenide glassy semiconductors (CGSs) based on arsenic chalcogenides are widely used in electronic engineering as photosensitive materials for targets of cathode ray devices (Ilyasly *et al.*, 1977, 1978, 1986; Khiminets, 1982; Rustamov *et al.*, 1995). In optoelectronics, acousto-optic materials are prepared on the basis of them (Ilyasly, *et al.*, 2018; Yan, 2019).

In this work, obtaining reliable materials with optical and photoelectric properties is based on the use of the relationship between the phase diagram and the glass structure, as well as the extent of glass formation regions in the systems under study (Ilyasly *et al*, 2018; 2002; 2021; 2022; 2023; Wang *et al*, 2015; Henderson-Sapir *et al*, 2016; Khudiyeva *et al*, 2016; Gahramanova, 2020; Alıyev *et al*, 2022).

In the ternary systems Sm – As – Se and Eu – As – Se, glass formation regions have been discovered. It has been established that in the Sm – As – Se system, depending on the cooling rate, it is 3.2 and 5.3 wt.% of the total mass of the triangle. In the Eu – As – Se system, depending on the cooling rate, it constitutes 3 and 3.8 wt.% of the total mass of the triangle.

In the ternary systems Sm – As – Se and Eu – As – Se along the sections As_2Se_3-Ln, As_2Se_3-LnSe, As_2Se-Ln_2Se_3 (where Ln - Sm, Eu) compounds $LnAs_4Se_7$, $LnAs_2Se_4$,

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$Ln_3As_4Se_9$, and $LnAsSe_3$. are formed. The parameters of their crystal lattices have been calculated. The electrical conductivity of the glasses was measured by the compensation method in the temperature range 570-720 K. It was found that the studied glasses have "p" type conductivity.

The AsSe - Sm, AsSe - Eu sections of these ternary systems were also re-examined. SmAsSe and EuAsSe compounds were found in the systems, the melting points of which are 1395 K and 1425 K, respectively.

2. Experiments and results

Alloys of the ternary systems have been studied along various quasi- and non-quasi-binary sections both in glassy and crystalline states. Samarium, europium, arsenic and selenium of the corresponding grades Sm-A1, Eu- A1, As-A5 and Se-B4 were used for the synthesis of alloys of the system. Synthesis was carried out step by step, at the first stage the furnace temperature was raised to 450–500 K, and then to 1000 K and held for 3 hours, and then cooled to room temperature at different rates.

The initial samples after evacuation of the ampule were placed in an oven and the oven was heated to 650-750 K for 8-10 hours, and then the temperatures were raised to 1200 K. At this temperature the ampules were kept for 5 hours and the ampule with the oven were slowly cooled to room temperature.

Methods of differential thermal (DTA), X-ray phase (XRF) and micro-structural (MSA) analyzes (MIM microscope - 7 and MIN - 8), measurement of microhardness (PMT-3 microhardness tester) and electrophysical properties, studied the nature of the physicochemical interaction in the systems. In the study of the high-temperature part, the installation VDTA 987 was used. DTA was performed using the PDS-021 installation (a two-coordinate self-feeding potentiometer), "Thermoscan-2" using chromel/alumel thermocouple. After the separation of glassy alloys, the electrophysical properties were measured by the compensation method.

Glass formation in the Sm–As–Se system

Alloys of the Sm–As–Se system have been studied along various quasi- and non-quasi-binary sections both in glassy and crystalline states. They were synthesized by the above method and cooled to room temperature in different modes.

At a cooling rate of 10 degrees per minute, glassy alloys are obtained with different percentages of Sm in the sections As_2Se_3-Sm, As_2Se_3-SmSe, As_2Se_3-Sm_2Se_3. It has been established that samarium is present in As_2Se_3 and AsSe in both the ionized and non-ionized states. The boundary of the glass formation region in the ternary system Sm - As - Se has been determined by studying individual sections emanating from glass-forming compounds, and some ternary alloys of various regions close to the As - Se binary system.

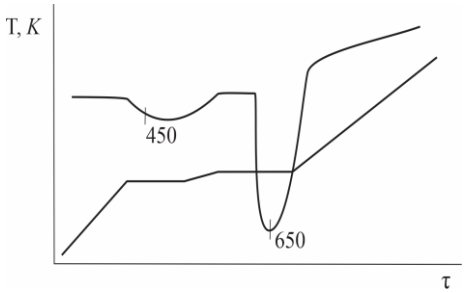


Fig. 1. Thermogram of glassy As_2Se_3

Some alloys based on the glass-forming compound As_2Se_3 have been synthesized and studied in the As_2Se_3-Sm section. On the thermograms of As_2Se_3 (Fig.1) and the synthesized alloys, some endo- and exothermic effects are observed, presented in Table 1. The area of glass formation reaches 5 mol. % Sm.

Table 1. Some physical-chemical properties of glasses of the As_2Se_3- Sm system

No	Composition of alloys, mol %		Composition of alloys, at %			Thermal effects T,K			Density d, 10^3 kg/m^3	Microhardness H_μ, MPa
	As_2Se_3	Sm	Sm	As	Se	T_g	$T_{cr.}$	$T_{melt.}$		
1	100	0	0	40	60	450	-	650	4,50	1300
2	99	1	0,2	39,9	59,9	460	510	645	4,58	1380
3	97	3	0,6	39,7	59,6	470	500	640	4,65	1475
4	95	5	1,0	39	59,4	480	495	635	4,70	1490

Alloys based on the glass-forming compound As_2Se_3 of the As_2Se_3-SmSe section have been synthesized and studied (Table 2).

It has been established that the region of glass formation based on the glass-forming compound As_2Se_3 reaches 0-15 mol.% SmSe. The thermograms of these glassy alloys revealed 3 thermal effects corresponding to T_g, $T_{cr.}$, and T_{melt} (Fig.2). Unlike As_2Se_3, the appearance of T_{cr} in alloys means that they partially crystallize during differential thermal analysis.

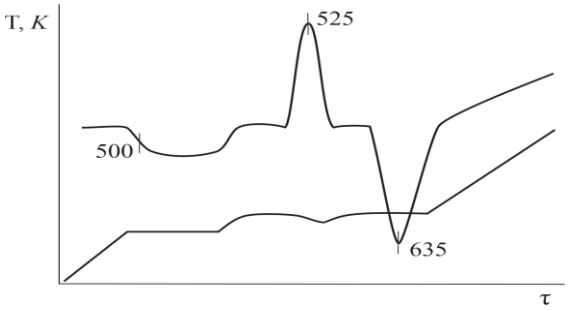


Fig.2. Thermogram of the As_2Se_3 - SmSe system alloy containing 10 mol.% SmSe

Some physicochemical properties of glasses are given in Table. 2. On the thermograms of the synthesized alloys, some endo- and exothermic effects are observed.

As can be seen from the concentration dependences of the alloys (Table 2), with an increase in the concentration of samarium chalcogenide, the values of T_g, $T_{cr.}$, d and H_μ increase.

Table 2. Some physicochemical properties of glasses of the As_2Se_3- SmSe system

No	Composition of alloys, mol %		Composition of alloys, at %			Thermal effects T,K			Density d, 10^3 kg/m^3	Microhardness H_μ, MPa
	As_2Se_3	SmSe	Sm	As	Se	T_g	$T_{cr.}$	$T_{melt.}$		
1	100	0	0	40	60	450	-	650	4,50	1300
2	99	1	0,2	39,8	60	460	510	640	4,53	1360
3	97	3	0,6	39,5	59,9	470	500	635	4,65	1470
4	95	5	1,0	39,2	59,8	480	495	625	4,67	1550
5	90	10	2,1	38,7	59,6	500	525	635	4,70	1700
6	85	15	2,6	37,9	59,5	520	530	515	4,79	1800

Some alloys based on the glass-forming compound As_2Se_3 were synthesized and studied in the As_2Se_3-Sm_2Se_3 section. On the thermograms of the synthesized alloys of the As_2Se_3-Sm_2Se_3 system, some endo- and exothermic effects are observed, presented in Table 3.

Table 3. DTA data for alloys of the As_2Se_3- Sm_2Se_3 system

No	Composition of alloys, mol %		Composition of alloys, at %			Thermal effects, T,K		
	As_2Se_3	Sm_2Se_3	Sm	As	Se	T_g	$T_{cr.}$	$T_{melt.}$
1	100	0	0	40	60	450	-	650
2	99	1	0,22	39,88	59,9	455	480	645
3	97	3	0,6	39,4	59,0	465	495	640
4	95	5	1,0	39,2	59,8	480	510	615
5	93	7	2,10	38,3	59,6	490	520	610
6	90	10	2,60	37,9	59,6	500	550	590
7	88	12	2,61	37,89	59,5	505	555	595

Each chemical composition corresponds to a certain value of T_g, as a result of isothermal annealing, the effects corresponding to T_g disappear. The glasses obtained are soluble in nitric acid and in alkalis.

Based on the results of the study of individual sections, as well as some ternary alloys, the boundaries of glass formation regions in the ternary system Sm - As - Se were determined in two cooling modes. It has been established that the region of glass formation in the system upon cooling at a rate of 10 deg/min and 10^2 deg/min are 3.2 and 5.3 wt. %, respectively, of the total area of the triangle (Fig.3).

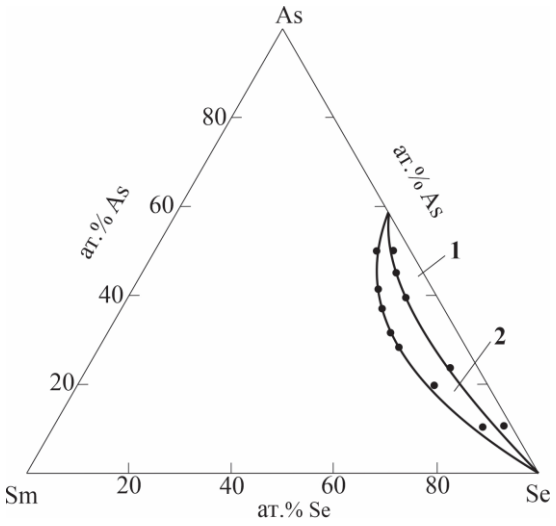


Fig. 3. The region of glass formation in the ternary system Sm – As – Se
1- at a cooling rate of ~10 deg/min; 2- at a cooling rate of 10^2 deg/min

Glass formation in the Eu – As – Se system

In the system, the region of glass formation is adjacent to the As-Se side and is extended along the As_2Se_3 - EuSe section. The system was studied by sections and ternary alloys located near As_2Se_3, AsSe, and Se.

The alloys of the sections As_2Se_3-Eu, As_2Se_3-EuSe and As_2Se_3-Eu_2Se_3 were synthesized and studied similarly to the alloys of systems with the participation of samarium. The glass formation region in the As_2Se_3-Eu section reaches 4 at.% Eu. The obtained black glasses are dissolved in concentrated nitric acid and alkalis. Measurement of microhardness and determination of density showed that the values of density and microhardness increase with increasing concentration of Eu and its chalcogenides relative to As_2Se_3.

The glass transition temperature determined from the thermograms of the alloys indicates an increase in its values when Eu and its chalcogenides are introduced into its composition.

According to the thermograms of glasses of the As_2Se_3-Eu, As_2Se_3-EuSe systems, T_g, $T_{cr.}$, $T_{melt.}$ were determined, the values of which are given in Tables 4 and 5.

Table 4. Some physical-chemical properties of glasses of the As_2Se_3- Eu system

No	Composition of alloys, mol %		Composition of alloys, at %			Thermal effects T,K			Density d, 10^3 kg/m^3	Microhardness H_μ, MPa
	As_2Se_3	Eu	Eu	As	Se	T_g	$T_{cr.}$	$T_{melt.}$		
1	100	0	0,0	40	60	450	-	650	4,58	1300
2	99	1	0,2	39,9	59,9	456	520	645	4,61	1350
3	97	3	0,6	39,7	59,6	465	515	640	4,70	1390
4	95	5	1,0	39	59,4	470	500	635	4,83	1250

Table 5. Some physical-chemical properties of glasses of the As_2Se_3- EuSe system

No	Composition of alloys, mol %		Thermal effects T,K			Density d, 10^3 kg/m^3	Microhardness H_μ, MPa	Results of MSA
	As_2Se_3	EuSe	T_g	$T_{cr.}$	$T_{melt.}$			
1	100	0	450	-	650	4,58	1300	Single-turbid phase
2	99	1	457	507	645	4,65	1350	Single-turbid phase
3	97	3	465	510	645	4,68	1380	Single-turbid phase
4	95	5	4875	515	630	4,75	1420	Single-turbid phase
5	93	7	490	520	590	4,81	1450	Single-turbid phase
6	90	10	510	535	555	5,10	1580	Single-turbid phase
7	85	15	518	540	560	5,25	1590	Crystalline glass

The glasses of this system, as well as the glasses of the As_2Se_3-SmSe system, partially crystallize during DTA. All the concentration dependences of glass properties show a monotonic increase (Table 4). Density varies within the range of 4.50 - 5.10 kg/m^3. Microhardness - 1300 -1600 MPa, glass transition temperature varies within 723-783K. The value $\Delta T = T_{cr} - T_g$, which determines the ability of glasses to crystallize, for the glasses of the system is 310-360 K.

Glass formation in the As_2Se_3-Eu_2Se_3 section was studied in two cooling regimes. Table 6 shows the properties of glasses obtained by cooling at a rate of 10 deg/min. There is a monotonous increase in the values of the concentration properties (Table 6). On the thermograms of alloys from the region of glasses, 2 endothermic and 1 exothermic effects are observed. Endothermic effects correspond to the glass transition and melting temperatures; the exothermic effect corresponds to the crystallization temperatures of glasses.

Table 6. Some physicochemical properties of glasses of the As_2Se_3- Eu_2Se_3 system

No	Composition of alloys, mol %		Thermal effects T,K			Density d, 10^3 kg/m^3	Microhardness H_μ, MPa	Results of MSA
	As_2Se_3	Eu_2Se_3	T_g	$T_{cr.}$	$T_{melt.}$			
1	100	0	450	-	650	4,58	1300	Single-turbid phase
2	99	1	457	507	645	4,65	1350	Single-turbid phase
3	97	3	465	510	645	4,70	1380	Single-turbid phase
4	95	5	485	515	630	4,85	1420	Single-turbid phase
5	93	7	490	520	590	4,87	1450	Single-turbid phase
6	90	10	485	555	650	5,15	1580	Crystalline glass

With the introduction of elemental europium into the composition of As_2Se_3 up to 3 at %, glassy alloys are obtained. In this case, the chemical interaction can be represented as follows: first of all, selenium will react with europium, and secondly with arsenic. Such a conclusion can be drawn from the estimate of the binding energy and from the standard values of the enthalpy. This value is for As_2Se_3 ΔH^0_{298}=54 kcal/mol, for Eu_2Se_3 ΔH^0_{298}=23.0 kcal/mol, and for EuSe ΔH^0_{298}=26 kcal/mol. When interacting with arsenic selenides, we obtain $As_2Se_3 + Eu = Eu_2Se_3 + As$.

According to the results of the studied sections and alloys, the glass formation region in the Eu-As-Se system has been determined (Fig. 4). It has been established that the region of glass formation in the system upon cooling at a rate of 10 deg/min and 10^2 deg/min are 3 and 3.8 wt.% %, respectively, of the total area of the triangle.

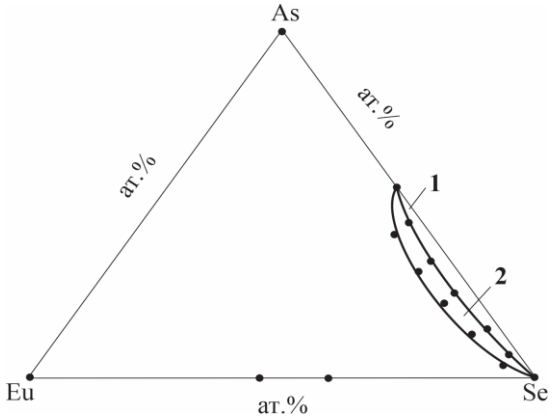
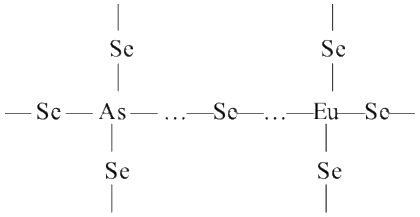


Fig.4. Glass formation region in the Eu-As-Se system
1- at a cooling rate of ~10 deg/min; 2- at a cooling rate of 10^2 deg/min

An increase in the value of the concentration properties suggests that, in addition to $AsSe_{3/2}$, new structural units are formed in glasses.

The introduction of europium into glassy As_2Se_3 can lead to the formation of coordinate bonds of the following type



and the formation of tetrahedral structural sites of $EuAsSe_{8/2}$. The introduction of europium into arsenic selenide leads to a slight increase in the density, microhardness, and glass transition temperatures (Table 6), which confirms the formation of new structural units.

Phase diagrams of the As_2Se_3-SmSe and As_2Se_3-Sm_2Se_3 sections

The isothermal treatment led to the crystallization of glasses of the Sm – As – Se and Eu – As – Se systems. After crystallization and bringing the alloys to an equilibrium state, they were re-investigated by methods of physicochemical analysis. Heat treatment was carried out for 600 hours at a temperature of 550 K.

X-ray diffraction (XRD) analysis of system alloys containing 33.3 mol. % SmSe, 50 mol. % SmSe and 60 mol. % SmSe showed that new diffraction lines appear on the diffraction patterns. Based on the XRD results, hkl, interplanar spacings, and unit lattice parameters of the $SmAs_4Se_7$, $SmAs_2Se_4$, and $Sm_3As_4Se_9$ compounds formed in the As_2Se_3-SmSe section were calculated (Fig. 5).

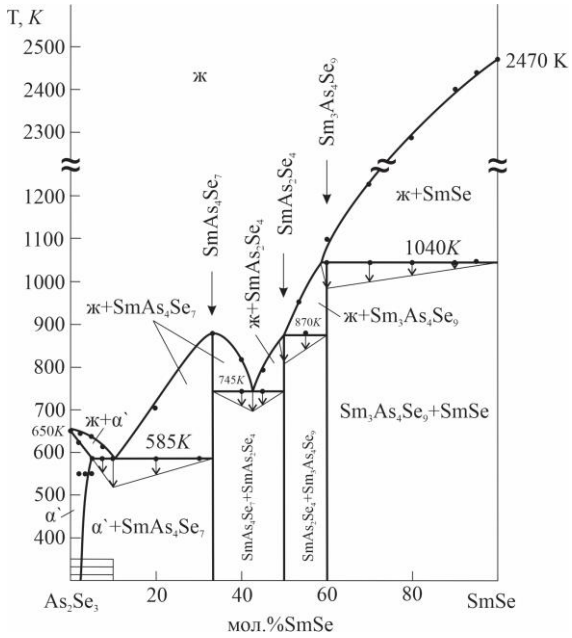


Fig. 5. Phase diagram of the As_2Se_3-SmSe section. ▭ - region of glass formation in the As_2Se_3-SmSe section

The MSA data, measurements of microhardness and density confirmed that in the system at a ratio of components of 1:1 a new phase of composition $SmAsSe_3$ is formed and its microhardness is 1100 MPa. Based on the results of physical and chemical analysis, a state diagram of the As_2Se_3-Sm_2Se_3 system was constructed (Fig. 6).

The phase diagrams of systems with europium are similar to the presented diagrams with the participation of samarium.

The As_2Se_3-EuSe and As_2Se_3-Eu_2Se_3 systems were studied by the authors and the data are presented in the works (Ilyasly T.M., *et al.*, 2016). Compounds of composition $EuAs_4Se_7$, Eu As_2Se_4, $Eu_3As_4Se_9$, and $EuAsSe_3$ are formed in these systems.

The $EuAs_4Se_7$ and $Eu_3As_4Se_9$ compounds melt congruently at 848 and 1010 K, respectively. The $EuAs_2Se_4$ compound is formed at 858 K by the peritectic reaction L +

$Eu_3As_4Se_9 \leftrightarrow EuAs_2Se_4$. $EuAsSe_3$ compound is formed at 1030 K by the peritectic reaction $L + Eu_2Se_3 \leftrightarrow EuAsSe_3$.

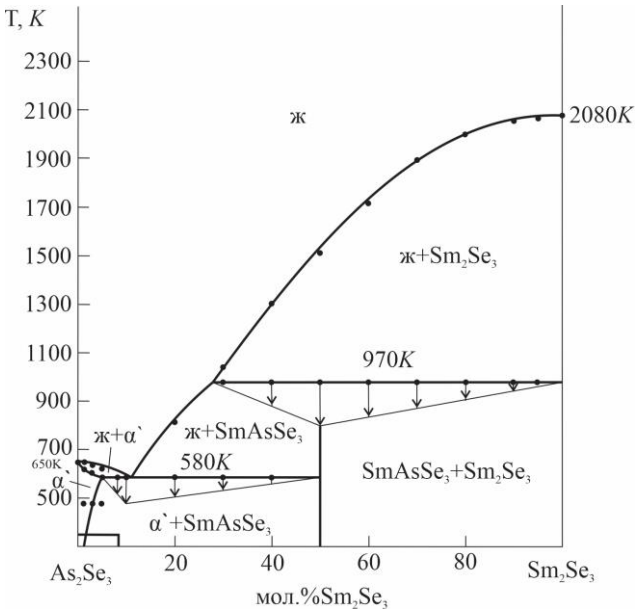


Fig. 6. Phase diagram of the As_2Se_3-Sm_2Se_3 section. ⌙ - region of glass formation in the As_2Se_3-Sm_2Se_3 section

3. Conclusion

The boundaries of glass formation regions in the Sm – As – Se and Eu – As – Se systems have been determined. $LnAs_4Se_7$, $LnAs_2Se_4$, $Ln_3As_4Se_9$, and $LnAsSe_3$ types of compounds were found in the As_2Se_3-Ln, As_2Se_3-LnSe and As_2Se_3-Ln_2Se_3 systems. The lattice parameters of the resulting compounds were calculated and it was found that they crystallize in the orthorhombic system. Obtained data of the physical properties of glasses and compounds showed that they are high-resistivity semiconductors with a predominant "p"-type conductivity.

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