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**CHARACTER OF INTERACTION AND GLASS FORMATION IN THE
AsSe–NdAs₂Se₄ SYSTEM****T.M.Ilyasly¹, A.G.Khudiyeveva¹, I.I.Aliyev², M.G.Shakhbazov³**¹*Baku State University**aynur.khudiyeveva@yahoo.com*²*M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan*
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The character of the chemical interaction and glass formation in the AsSe–NdAs₂Se₄ system was studied by physico-chemical analysis methods (DTA, RFA, MSA), as well as by measuring the microhardness and density, and a state diagram of this system was plotted. It is established that the AsSe–NdAs₂Se₄ system is partially quasi-binary section of the As–Nd–Se ternary system. Solid solutions on the basis of the starting components have not been practically established. In the system with slow cooling, the glass formation region on the basis of AsSe reaches 15 mol% NdAs₂Se₄, and 20 mol% NdAs₂Se₄ in the quenching regime on ice water.

Keywords: microhardness, system, phase diagram, eutectic, density.

Semiconductor materials on the basis of arsenic chalcogenides as photosensitive materials are transparent in the IR spectrum and are widely used in the electronics industry [1–5]. Chalcogenides of neodymium and their alloys refer to promising substances for the development of magnetic and thermoelectric materials [6]. Therefore, the study of the interaction between the chalcogenides AsSe and NdAs₂Se₄ is of scientific and practical importance. The last years with participation of arsenic chalcogenides there are studied ternary and quaternary systems [7–11].

In the present paper, we offer the synthesis conditions and the results of investigating the certain physico-chemical properties of the AsSe–NdAs₂Se₄ system alloys.

As₂Se₃ is a glassy semiconductor, melts at 315⁰C [12], and crystallizes in a monoclinic symmetry with unit cell parameters: $a = 6.69$, $b = 13.86$, $c = 11.00$ Å, $\beta = 113^{\circ}2'$ (Ave P2₁/n) [13], microhardness $H\mu = 1060$ MPa and density $\rho = 5.30$ g/sm³.

Compound NdAs₂Se₄ melts incongruently at 675⁰C and crystallizes in tetragonal system with lattice parameters: $a = 12.62$, $c = 7.42$ Å, $Z = 7$, $\rho = 5.75$ g/sm³, $\rho = 5.99$ g/sm³.

Experimental part

The alloys of the system were synthesized from AsSe and NdAs₂Se₄ components in quartz ampoules evacuated to 0.1333 Pa at 500–900⁰C.

To achieve an equilibrium state, the alloys were annealed at 200⁰C for 350 hours.

The alloys of the system were investigated by differential thermal (DTA), X-ray diffraction (XRD) and microstructural (MSA) analyses, as well as by measuring microhardness and density.

Differential thermal analysis was carried out in the thermograph "Termoskan-2". The Al₂O₃ compound was used as a reference, and the heating rate was 10⁰C/min.

X-ray phase analysis was performed on a D2 PHASER X-ray diffractometer. For the study CuK α radiation and Ni filter were used.

MSA alloys of pre-etched polishing, polished with GOI paste was performed on a metallographic microscope MIM-8, KOH: C₂H₅OH=2:1, etching time 20 s was used at studying the microstructure of the alloys. The microhardness of the alloys of the AsSe–NdAs₂Se₄ system was measured on a PMT-3 device at loads of 0.10 and 0.15 N.

The density of the alloys was determined by a pycnometric method, toluene was used as the working fluid.

Results and discussion

AsSe riched alloys are obtained in a glassy state. The obtained ingots are dense, in the concentration range 0–25 mol% NdAs_2Se_4 – dark black color. The alloys of the AsSe– NdAs_2Se_4 system are resistant to air, water and organic solvents. Concentrated mineral acids (H_2SO_4 , HNO_3) and alkali (NaOH , KOH) decompose them.

All alloys in the AsSe– NdAs_2Se_4 system were investigated before and after annealing. To plot the phase diagram of the AsSe– NdAs_2Se_4 system, the data of the physico-chemical analysis of the samples after annealing were used.

DTA alloys of the AsSe– NdAs_2Se_4 system before annealing showed that on the thermograms of the samples in the concentration range of 0–25 mol% NdAs_2Se_4 there are softening temperatures (T_g), varying within 170–180°C (Table 1). An annealing was carried out at 190°C for 540 h to crystallize the vitreous alloys.

DTA alloys after annealing showed that the heating curves of the annealed samples showed no softening point (Table 2). This proves that all the glassy alloys after annealing are completely crystallized.

MSA alloys of the AsSe– NdAs_2Se_4 system were carried out before and after annealing. The study of the microstructure of alloys showed that all of them in the solid state are biphasic.

Two series of values of microhardness of the alloys of the system was obtained (Tables 1, 2). For vitreous alloys, the value of the microhardness varies within the range $H\mu = 1060$ –1150 MPa. After annealing, the microhardness values for the same alloy region were 780–880 MPa.

X-ray analysis of the alloys of the AsSe– NdAs_2Se_4 system was carried out to confirm the results of DTA and MSA. Before annealing the alloys in the range concentration of 0–25 mol% NdAs_2Se_4 the intense diffraction maxima was not observed (Figure 1, a). After annealing, diffraction patterns of the same alloys show intense diffraction peaks (Figure 1, b).

Fig. 1. Diffractograms of alloys of the AsSe– NdAs_2Se_4 system before annealing (*a*) and after annealing (*b*): 1 – 10 mol%, 2 – 15 mol% NdAs_2Se_4 .

Fig. 2. Phases diagram of the system AsSe–NdAs₂Se₄.

On the basis of the physico-chemical analysis, a phase diagram of the AsSe–NdAs₂Se₄ system is constructed (Figure 2). As can be seen from Figure 2, the AsSe–NdAs₂Se₄ system is a partially nonquasi-binary section of ternary As–Nd–Se system but is stable in subsolidus.

Liquidus of the system consists of curves

of primary crystallization of AsSe and NdAs₂Se₄. Above the solidus temperature (240°C) in the concentration range 0–20 mol% NdAs₂Se₄ there are three-phase regions of L+AsSe+NdSe, and in the range of 20–100 mol% L+NdSe+NdAs₂Se₄. Below the solidus line, the two-phase alloys AsSe+NdAs₂Se₄ crystallize.

Table 1. Composition, DTA results, microhardness, and density determination (glassy form) for glass alloys of the AsSe–MnSe system

Mole %		Thermal events during heating, °C	Density, g/cm ³	Microhardness, MPa	
AsSe	NdAs ₂ Se ₄			AsSe	NdAs ₂ Se ₄
				<i>P</i> =0.10 N	<i>P</i> =0.20 N
100	0.0	170, 315	5.30	1060	–
95	5.0	170, 240, 270, 300	5.32	1100	–
90	90	175, 240, 270, 280	5.46	1120	–
85	15	175, 240, 305	5.54	1150	–
80	20	180, 240, 360	5.60	1150	1825
75	25	180, 240, 275, 400	5.65	–	1830
70	30	240, 310, 470	5.70	–	1840

Table 2. Composition, DTA results, microhardness, and density determination (crystalline) for glass alloys of the AsSe–MnSe system

Mole percent %		Thermal events during heating, °C	Density g/cm ³	Microhardness, MPa	
AsSe	NdAs ₂ Se ₄			AsSe	NdAs ₂ Se ₄
				<i>P</i> =0,10 N	<i>P</i> =0,20 N
100	0.0	315	5.48	780	–
95	5.0	240, 270, 300	5.52	790	–
90	90	240, 270, 280	5.56	870	–
85	15	240, 305	5.59	880	–
80	20	240, 360	5.64	880	1825
75	25	240, 275, 400	5.69	–	1830
70	30	240, 310, 470	5.75	–	1840

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AsSe–NdAs₂Se₄ SİSTEMİNDƏ QARŞILIQLI TƏSİR VƏ ŞÜŞƏMƏLƏGƏLMƏ

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Fiziki-kimyəvi analiz metodları (DTA, RFA, MQA, eləcə də sıxlığın və mikrobərkliyin ölçülməsi) vasitəsilə AsSe–NdAs₂Se₄ sistemində kimyəvi qarşılıqlı təsirin xarakteri tədqiq edilmiş və onun faza diaqramı qurulmuşdur. Müəyyən edilmişdir ki, AsSe–NdAs₂Se₄ kəsiyi As–Sb–Se sisteminin qismən kvazibinar kəsiyidir. Sistemdə ilkin komponentlər əsasında bərk məhlul sahəsi praktiki olaraq aşkar edilməmişdir. Sistemdə yavaş soyudulma zamanı AsSe əsasında 15 mol% NdAs₂Se₄ şüşə sahəsi əmələ gəlir, buzlu suda birbaşa soyudulma zamanı isə şüşə sahəsi 20 mol% NdAs₂Se₄ təşkil edir.

Açar sözlər: mikrobərklik, sistem, faza diaqramı, evtektika, sıxlıq.

ХАРАКТЕР ВЗАИМОДЕЙСТВИЯ И СТЕКЛООБРАЗОВАНИЯ В СИСТЕМЕ AsSe–NdAs₂Se₄

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Методами физико-химического анализа (ДТА, РФА, МСА), а также измерением микротвердости и плотности изучен характер химического взаимодействия и стеклообразования в системе AsSe–NdAs₂Se₄ и построена диаграмма состояния. Установлено, что система AsSe–NdAs₂Se₄ является частично квазибинарным сечением тройной системы As–Nd–Se. Твердые растворы на основе исходных компонентов практически не установлены. В системе при медленном охлаждении область стеклообразования на основе AsSe доходит до 15 мол% NdAs₂Se₄, а в режиме закалки в ледяной воде – 20 мол% NdAs₂Se₄.

Ключевые слова: микротвердость, система, фазовые диаграмма, эвтектика, плотность.