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PHASE EQULIBRIA IN THE $NdAs_2Se_4$-Nd_2Se_3 SYSTEM

A.Q. Khudiyeva[1], T.M.Ilyaslı[1], I.I.Aliyev[2], S.A.Mehdiyeva[2]

[1]Baku State University, e-mail aynur.khudiyeva@yahoo.com
[2]Acad. M.F. Nagiyev Institute of Catalysis and Inorganic Chemistry
National Academy of Sciences of Azerbaijan
Baku, G. Javid ave. 113, e-mail: aliyevimir@rambler.ru

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***Abstract**: The $NdAs_2Se_4$-Nd_2Se_3 system was investigated by methods of differential thermal (DTA), X-ray phase (XRF), microstructural (MSA) analysis, as well as microhardness and density measurements, and a T-x phase diagram was constructed. It has been established that this system is a non-quasi-binary section of the ternary Nd-As-Se system. Above the solidus temperature (675^0C) the $NdAs_2Se_4$-Nd_2Se_3 system is not quasi-binary, and below the solidus is stable. In the $NdAs_2Se_4$-Nd_2Se_3 system solid solutions based on the initial components are practically not detected.*

***Keywords:** system, quasi-binary, solid solution, syngony, microhardness, density.*
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Introduction

Arsenic chalcogenides and related alloys have photoelectric, acoustic-optical properties [1-4]. As is known, rare-earth chalcogenides and ternary phases, as well as solid solutions obtained from them are also photoelectric, luminescent semiconductor materials with magnetic properties. These materials are widely used in various areas of the electronics industry [5-7].

From this point of view, it was interesting to investigate the physicochemical interaction of arsenic chalcogenides with neodymium chalcogenides. The search for new photosensitive and thermoelectric materials is both of scientific and practical importance. Earlier, we studied chemical interactions of arsenic chalcogenides with rare-earth chalcogenides [8–10].

The purpose of the work is to study the phase equilibria and the construction of the phase diagram of the $NdAs_2Se_4$-Nd_2Se_3 system.

The Nd_2Se_3 compound melts congruently at 1700°C and is crystallized in a cubic system like Th_3P_4 with the unit cell parameters: a = 8.871 Å, sp.gr. I43d-T^6_d, density ρ = 6.69 g/sm^3 [11].

The $NdAs_2Se_4$ compound melts congruently at 675°C and is crystallized in a tetragonal system with lattice parameters: a = 12.62; c = 7.42 Å, Z = 7, $\rho_{pukn.}$ = 5.75 g/sm^3; ρ_{X-ray} = 5.99. g/sm^3.

Experimental part

To study the phase equilibria in the $NdAs_2Se_4$-Nd_2Se_3 system, alloys were synthesized in a wide concentration range. The synthesis of ternary alloys of the system under consideration was carried out through fusing the $NdAs_2Se_4$ and Nd_2Se_3 components into quartz ampoules having been evacuated to 0.133 Pa at a temperature of 800-1200°C. To homogenize the alloys, annealing was performed at 450°C for 200 h. The alloys of the $NdAs_2Se_4$-Nd_2Se_3 system were studied by means of differential thermal (DTA), X-ray phase (XRD), micro-structural (MCA) analyses, and microhardness measurement and density determination.

DTA alloys of the system were carried out on a TERMOSKAN-2 device with an accuracy of 3-5°C, a chromel-alumel thermocouple, and calcined Al_2O_3 served as the standard. Heating rate of 9 degrees/min. X-ray phase analysis was performed on an X-ray instrument of the D2 PHASER model through the use of CuKα radiation with a Ni filter. The micro-structural analysis of alloys was carried out using an MIM-8 microscope. In the study of alloy microstructure, an etchant of composition 1 N HNO_3 + HF = 2:1 was used, the etching time was 20 s. The microhardness of the phases was measured on a PMT-3 instrument with an accuracy of 5 %, and the density of the samples was determined by the pycnometric method.

Results and its discussion

Alloys of the $NdAs_2Se_4$-Nd_2Se_3 system in the concentration range 0-60 mol % Nd_2Se_3 are obtained in the form of compact ingots. Alloys in the range of 60-100 mol % Nd_2Se_3 are non-uniform. Therefore, in this range the samples were ground into powder at 200 atm. pressed into a tablet and exposed to heat treatment at 800°C for 100 hours.

The alloys of the $NdAs_2Se_4$-Nd_2Se_3 system in the form of ingots are resistant to air and water. Powdered samples are exposed to hydrolysis with prolonged exposure to air. They are well soluble in nitric acid HNO_3. Homogenized alloys were examined by methods of physical and chemical analysis. Note that the thermograms of the system alloys have three endothermic effects. Proceeding from the results of micro-structural analysis of alloys, it found that the alloys of the $NdAs_2Se_4$-Nd_2Se_3 system in the solid state are two-phased. In the system based on the initial components, solid solutions are not practically installed.

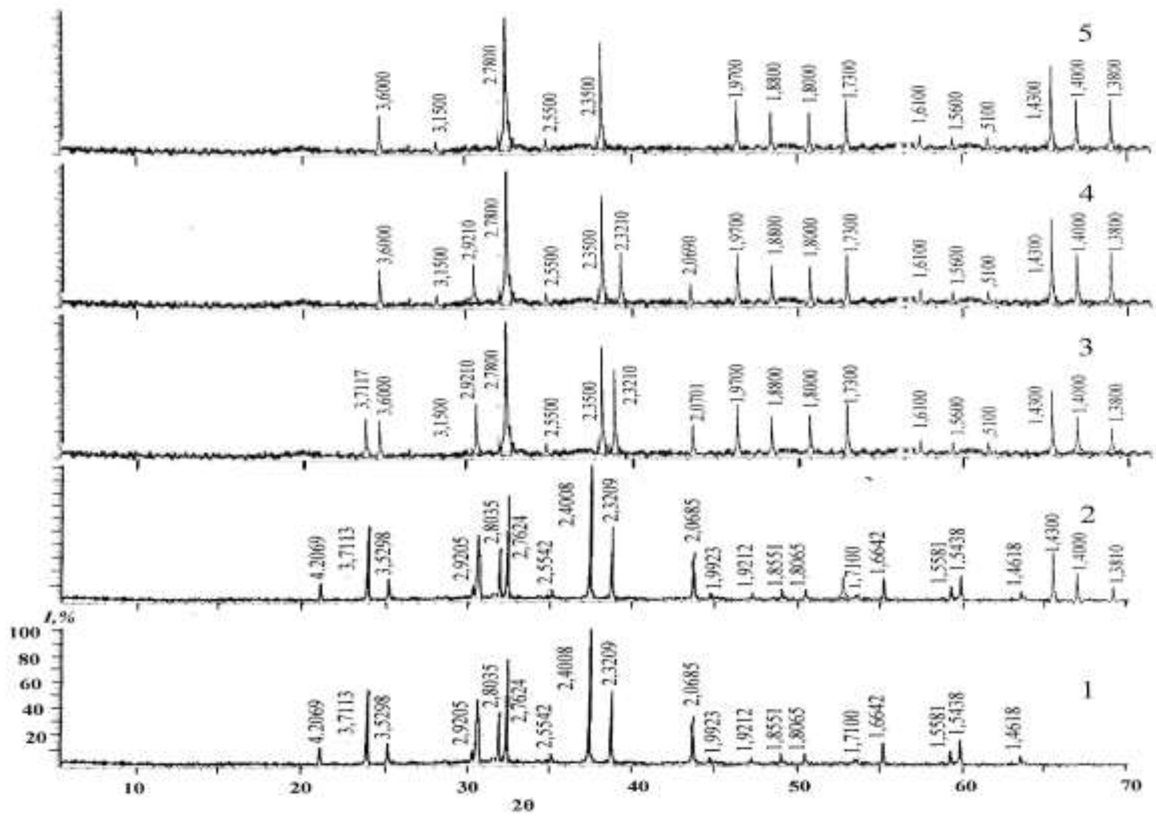

Fig.1. Diffractograms of the alloys $NdAs_2Se_4$-Nd_2Se_3 system.
1- $NdAs_2Se_4$, 2- 30, 3-50, 4-70, 5-100 mol % Nd_2Se_3.

To confirm the results of differential thermal and micro-structural analysis, X-ray phase analysis of alloys with a content of 30, 50 and 70 mol % Nd_2Se_3 is required. On the basis of the experimentally calculated inter-planar distances and line intensities, the initial compounds and intermediate alloys were compared. The results of radiographs of alloys containing 30, 50 and 70 mol % Nd_2Se_3 are shown in Fig. 1. As can be seen from Fig. 1, the diffraction patterns of the alloys of the $NdAs_2Se_4$-Nd_2Se_3 system consist of a mixture of diffraction lines of the initial components. This indicates that the alloys of the system are two-phased.

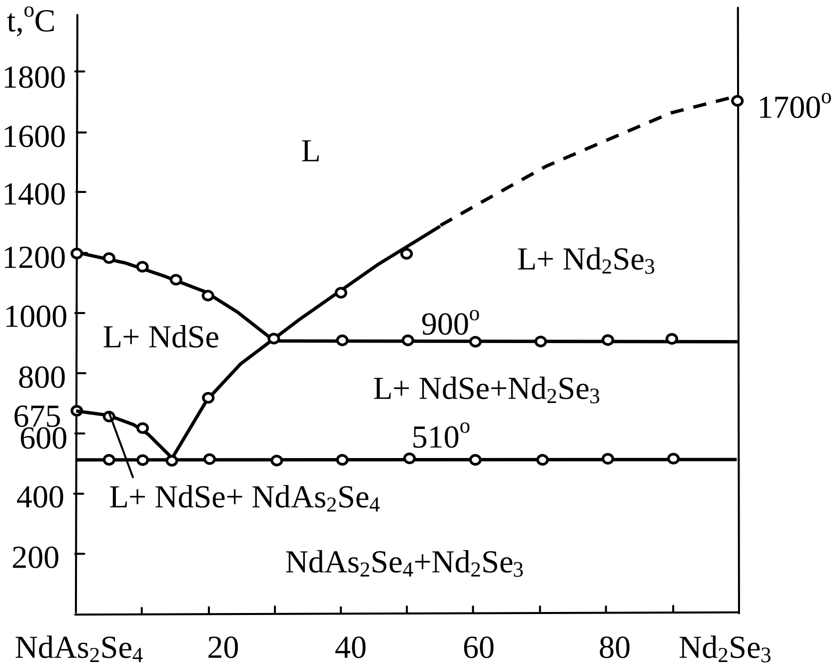

Fig. 2. Phase diagram of the $NdAs_2Se_4$-Nd_2Se_3 system.

Thus, the X-ray analysis confirms the results of the DTA analysis and microstructure. Proceeding from the results of physicochemical analysis methods, the phase diagram of the $NdAs_2Se_4$-Nd_2Se_3 system was constructed (Fig.2). The $NdAs_2Se_4$ compound melts incongruently; therefore, above 675°C it decomposes by the reaction: $NdAs_2Se_4 \leftrightarrow L + NdSe$. The liquidus system consists of primary crystallization curves of the NdSe and Nd_2Se_3 compounds in the concentration range 0-30 mol % Nd_2Se_3 from the liquid stand primary crystals NdSe. In the range of 0-15 mol % Nd_2Se_3 during the secondary crystallization, three-phase regions are formed: (L+NdSe+$NdAs_2Se_4$). The starting crystals of the Nd_2Se_3 compound from the liquid are separated in the range of 30-100 mol. % Nd_2Se_3. Another three-phase region (M+NdSe+Nd_2Se_3) was found in the range of 15-100 mol % Nd_2Se_3. In the system below, the solidus line, two-phase alloys ($NdAs_2Se_4$+Nd_2Se_3) crystallize. The $NdAs_2Se_4$-Nd_2Se_3 system intersects the mono-variant double eutectic lines at 900°C and the composition of 30 mol % Nd_2Se_3. The system undergoes peritectic transformation by the reaction: $L+NdSe \leftrightarrow NdAs_2Se_4$. Some physical-chemical properties of alloys of the $NdAs_2Se_4$-Nd_2Se_3 system are listed in Table. 1. From Table 1 it can be seen that two microhardness values are detected in the system. Of these, the first corresponds to the microhardness of $NdAs_2Se_4$ (1860-1870) MPa, and the value (2300-2340) MPa corresponds to the microhardness of Nd_2Se_3.

Table 1. Composition, results of DTA, measurements of microhardness and density determination of alloys of the $NdAs_2Se_4$-Nd_2Se_3 system.

Content, mol %		Thermal effects, °C	Density, q/sm^3	Microhardness, MPa	
$NdAs_2Se_4$	Nd_2Se_3			$NdAs_2Se_4$	Nd_2Se_3

				P=0.15 H	P=0.20 H
100	0,0	675, 1200	5,75	1860	-
95	5,0	510,650, 1190	5,80	1870	-
90	10	510,625, 1150	5,86	1870	-
85	15	510,1100	5,92	1860	
80	20	510,720,1060	5,97	1860	-
70	30	510, 900	6,02	1860	-
60	40	510,900,1070	6,12	1860	-
50	50	510,900,1210	6,26	-	-
40	60	510,900	6,30	-	2340
30	70	510,900	6,45	-	2340
20	80	510,900	6,55	-	2340
10	90	510,900	6,60	-	2340
5,0	95	510,900	6,64	-	2330
0,0	100	1700	6,69	-	2300

References

1. Fuyuki Shimojol, Shıııji Munejiril, Kozo Hoshinol, Zempo Y. Temperature dependence of the atomic structure of liquid As_2Se_3: ab initio molecular dynamics simulations. *J. Phys.: Condens. Matter*. 2000, vol.12, no. 28, pp. 6161 -6165.
2. Hari P., Cheneya C., Luepkea G., Singha S., Tolka N., Sanghera J.S., Aggarwal D. Wavelength selective materials modification of bulk As_2S_3 and As_2Se_3 by free electron laser irradiation. *Journal of Non-Crystalline Solids*. 2000, vol. 270, pp. 265-268.
3. Dinesh Chandra SATI, Rajendra KUMAR, Ram Mohan MEHRA. Influence of Thickness Oil Optical Properties of a: As_2Se_3 Thin Films. *Turk J. Phys*. 2006, vol. 30, pp. 519- 527.
4. Lovu M., Shutov R., Rebeja S., Colomeyco E., Popescu M. Effect of metal additives on photo darkening kinetics in amorphous films. *Journal of Optoelectronics and Advanced Materials*. 2000, vol. 2, issue 1, pp. 53-58.
5. Burdiyan I.I., Senokosov E.A., Kosyuk V.V., Pynzar R.A. The effect of holmium (Ho) impurity on the photovoltaic properties of As_2Se_3 and $(As_2S_3)_{0.3}(As_2Se_3)_{0.7}$. *Physics and technology of semiconductors*. 2006, vol. 40, no. 10, pp.1250-1253. (In Russian).
6. Yarembash E.I., Eliseev A.A. Chalcogenides of rare earth elements. Moscow: Nauka Publ., 1975, 260 p.
7. Fu Quang, Paul Brazis, Carl R. Kannewuef, James A. Ibers. Syntheses, Structures, and Physical Properties of LnAsTe (Ln=La, Pr, Sm, Gd, Dy, Er). *J. Inorg. Chem*. 2000, vol. 39, pp. 3176-3180.
8. Aliyev I.I., Hasanquliyeva Sh.A., Ilyasly T.M., Mehdiyeva S.A. Phase equilibriums and glass formation in the As Se- $MnAs_2Se_4$ system. *Chemical Problems*. 2014, no. 2, pp. 119-12.
9. Rustamov P.G., Ilyasov T.M., Najafov A.I. As2Se3-NdSe System State Diagram. *Russian Journal of Inorqanic Chemistry*. 1988, vol.33, no.5, pp. 1253-1255.
10. Ilyasli T.M., Khudiyeva A.G., Aliyev I.I. Glas formation and propetes of glasses based

on As_2S_3. *Chemical senses*. 2016, vol. 41, issue 9(2), pp. 968-977.
11. Physico-chemical properties of semiconductor substances. Handbook. Moscow: Nauka Publ., 1979, 340 p.

$NdAs_2Se_4$-Nd_2Se_3 SİSTEMİNDƏ FAZA TARAZLIĞI

A.Q. Xudiyeva[1], T.M.İlyaslı[1], İ.İ.Əliyev[2], S.A.Mehdiyeva[2]

[1]*Bakı Dövlət Universiteti*
AZ 1148 Bakı, Z.Xəlilov küç., 23; e-mail:aynur.khudiyeva@yahoo.com
[2]*AMEA-nın akad. M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu*
AZ 1143, Bakı, H.Cavid pr., 113; e-mail: aliyevimir@rambler.ru

Fiziki-kimyəvi analiz (DTA, MQA, RFA, eləcə də mikrobərkliyin və sıxlığın təyini) metodları vasitəsilə $NdAs_2Se_4$-Nd_2Se_3 sistemində faza tarazlığı tədqiq edilmiş və onun T-x faza diaqramı qurulmuşdur. Müəyyən edilmişdir ki, $NdAs_2Se_4$-Nd_2Se_3 sistemi Nd-As-Se üçlü sisteminin qismən qeyri-kvazibinar kəsiyidir. Solidus temperaturundan yuxarıda (675°C) $NdAs_2Se_4$-Nd_2Se_3 sistemi qeyri-kvazibinar, aşağıda isə stabil kəsik kimi özünü göstərir. $NdAs_2Se_4$-Nd_2Se_3 sisteminin ilkin komponentləri əsasında həllolma sahəsi praktiki olaraq təyin edilməmişdir.
***Açar sözlər**: sistem, qeyri-kvazibinar, bərk məhlul, sinqoniya, mikrobərklik, sıxlıq*

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ $NdAs_2Se_4$-Nd_2Se_3

А.Г. Худиева[1], Т.М. Ильяслы[1], И.И. Алиев[2], С.А. Мехтиева[2]

[1]*Бакинский государственный университет*
AZ 1148 Баку, ул. З.Халилова, 23; e-mail:aynur.khudiyeva@yahoo.com
[2]*Институт катализа и неорганической химии им. акад. М.Нагиева*
Национальной АН Азербайджана
AZ 1143 Баку, пр.Г.Джавида, 113; e-mail: aliyevimir@rambler.ru

Методами физико-химического анализа (ДТА, РФА, МСА а также определением плотности и измерением микротвердости) исследовано фазовое равновесие и построена T-x диаграмма системы $NdAs_2Se_4$-Nd_2Se_3. Установлено, что разрез $NdAs_2Se_4$-Nd_2Se_3. является неквазибинарным сечением тройной системы Nd-As-Se. Выше температуры солидуса (675°C) система $NdAs_2Se_4$-Nd_2Se_3 является неквазибинарной, а ниже линии солидуса система стабильна. В системе $NdAs_2Se_4$-Nd_2Se_3 на основе исходных компонентов твердые растворы практически не обнаружены.
***Ключевые слова:** система, неквазибинарный, твердый раствор, сингонии, микротвердость, плотность.*