

RESEARCH INTO PHASE FORMATION AND SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE Sb_2Se_3 -GaSe SYSTEM ALLOYS

I.I. Aliyev¹, N.A. Mammadova¹, F.M. Sadigov²

¹ Acad. M. Nagiyev Institute of Catalysis and Inorganic Chemistry of ANAS,
113, H. Javid Ave., AZ 1043, Baku, Azerbaijan; e-mail: aliyevimir@rambler.ru

² Baku State University
23, Z. Khalilov str., AZ-1148 Baku, Azerbaijan

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Abstract: Behavior of interaction in the Sb_2Se_3 -GaSe system was explored and a phase diagram constructed using the complex methods of physical and chemical analysis: differential thermal (DTA), X-ray phase (XRD), microstructural analysis (MSA), as well as the measurement of micro hardness and density. It found that in the system Sb_2Se_3 -GaSe two congruently melting compounds of the GaSb_4Se_7 and GaSb_2Se_4 compositions are formed at 515 °C and 490 °C, respectively. It revealed that the GaSe-based solubility in solid state is 4 mol. % Sb_2Se_3 ; but if based on Sb_2Se_3 – it is 5 mol. % GaSe. Three eutectics are formed in the system with composition appropriate of 43 and 60 mol. % Sb_2Se_3 and melts at 470, 425 and 450°C, respectively.

Keywords: system, congruent, eutectic, solidus, liquidus.

Introduction

It is known that chalcogenides of III B subgroup elements, as well as multicomponent phases on their basis are reputed to be perspective substances used in the development of photoelectric devices [1-3].

In literature [4-7], it is known that chalcogenides of antimony Sb_2X_3 (X-S, Se, Te) and solid solutions on their basis are used as materials for a p-branch of thermoelectric coolers. From this standpoint, the study of interaction between chalcogenides Sb_2Se_3 and GaSe is of scientific and practical significance. In literature [8-10] some systems were studied using chalcogenides of antimony.

The objective of the work is to study the phase formation and some physical and chemical properties of Sb_2Se_3 -GaSe system alloys.

Note that the Sb_2Se_3 compound is obtained with open for maximums and melts congruently at 617°C, crystallized in a rhombic syngony with lattice parameters: $a = 11,633$; $b = 11,780$; $c = 3,985$ Å, space group Pbnm-D_{2h}^{16} density $\rho = 5,843$ g/cm³ and micro hardness $H_{\mu} = 1200$ MPa [11].

Gallium monoselenide GaSe melts congruently at 960°C and is crystallized in a hexagonal syngony with lattice parameters: $a = 3,755$; $c = 15,94$ Å, $Z = 4$, space group $\text{P6}_3/\text{mmc-D}_{6h}^4$, density $\rho = 5,03$ g/cm³ and micro hardness 300 MPa [12].

Experimental part

Initial components of the Sb_2Se_3 -GaSe system were synthesized by melting elements of high purity in quartz ampoules vacuumed up to 0.133 Pa at 700-1100°C. Note that antimony Sb-000, selenium -B4 and gallium 99.999% were used as initial elements. To obtain equilibrium state, alloys were annealed at 400°C for 350 hrs.

Equilibrium alloys were studied in line with methods of differential and thermal (DTA), X-ray phase, microstructural (MSA) analyses, as well as measurement of micro hardness and determination of density.

DTA of alloys of the system was conducted using «TEMASKON-2» with a heating rate of 10 deg./min. Calibration chrome-aluminum thermocouple are used, Al_2O_3 is served as a standard.

X-ray phase analysis was conducted on D2 PHASER using CuK α -radiation, Ni-filter. MSA of alloys of the system was investigated through the use of a metallographic microscope MIM-8 with GOI paste polished specimens. The microstructure was revealed by an etchant with the HNO₃(conc) composition: H₂O₂ =1 : 1. the etching time was 20 sec.

Micro hardness of alloys of the system was measured using PMT-3 at loads of 0.10 and 0.20 N. Density of alloys of the system was determined using pycnometer method while toluene was used as a working liquid.

Results and discussion

Alloys of system Sb₂Se₃-GaSe are obtained in the form of light grey compact ingots. Resistance to air, water and organic solvents was studied. Strong mineral acids (HCl, HNO₃) decompose them well.

Thermal analysis of the Sb₂Se₃-GaSe system alloys shows that two endothermic effects relating to solidus and liquidus were found on thermograms of alloys.

During studying microstructure of alloys of the system it found that on the basis of initial components there are limited areas of homogeneity. To determine areas of solid solutions on the basis of Sb₂Se₃, alloys containing 2, 5, 7 and 10 mol% GaSe were synthesized. Obtained alloys were annealed for 520 hrs. at 200 and 300°C and hardened in icy water. Then microstructural analysis was conducted. It revealed that the solubility on the basis of Sb₂Se₃ at room temperature is 5 mol % GaSe, but at 470°C it is 10 % GaSe. Solid solutions on the basis of GaSe stretch up to 4 mol % GaSe.

Two compounds of the GaSb₄Se₇ and GaSb₂Se₄ compositions congruently melting at 515 and 490°C are formed in the system Sb₂Se₃-GaSe. The existence of compounds was confirmed using DTA, X-ray phase analysis, MSA analysis methods, microhardness and density measurements.

On thermo-grams of GaSb₄Se₇ and GaSb₂Se₄ compounds there is a single endothermic effect at 515 and 490°C which indicates their congruent melting. Figure 1 shows microstructure of alloys of eutectics, compounds GaSb₄Se₇ and GaSb₂Se₄. Microstructure (fig. 1 and c) of compounds GaSb₄Se₇ and GaSb₂Se₄ was studied after annealing for 750 hrs. at 450°C.

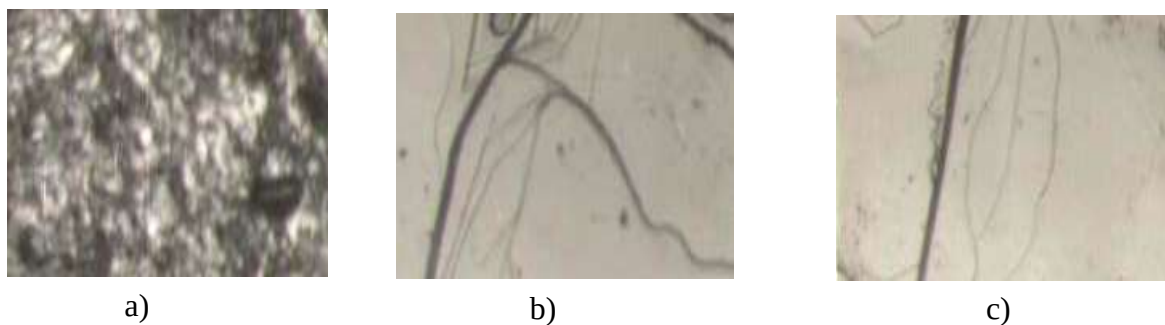


Fig.1. Microstructure of eutectics (a) and GaSb₄Se₇ (b) and GaSb₂Se₄ (c) compounds.
a) -15 mol. % GaSe (eutectics), b)- GaSb₄Se₇, c)- GaSb₂Se₄.

According to X-ray phase analysis, inter-planar distances and intensities of diffraction peaks of initial alloys 20; 33,33; 50 and 70 mol. % GaSe (Fig.2) were calculated.

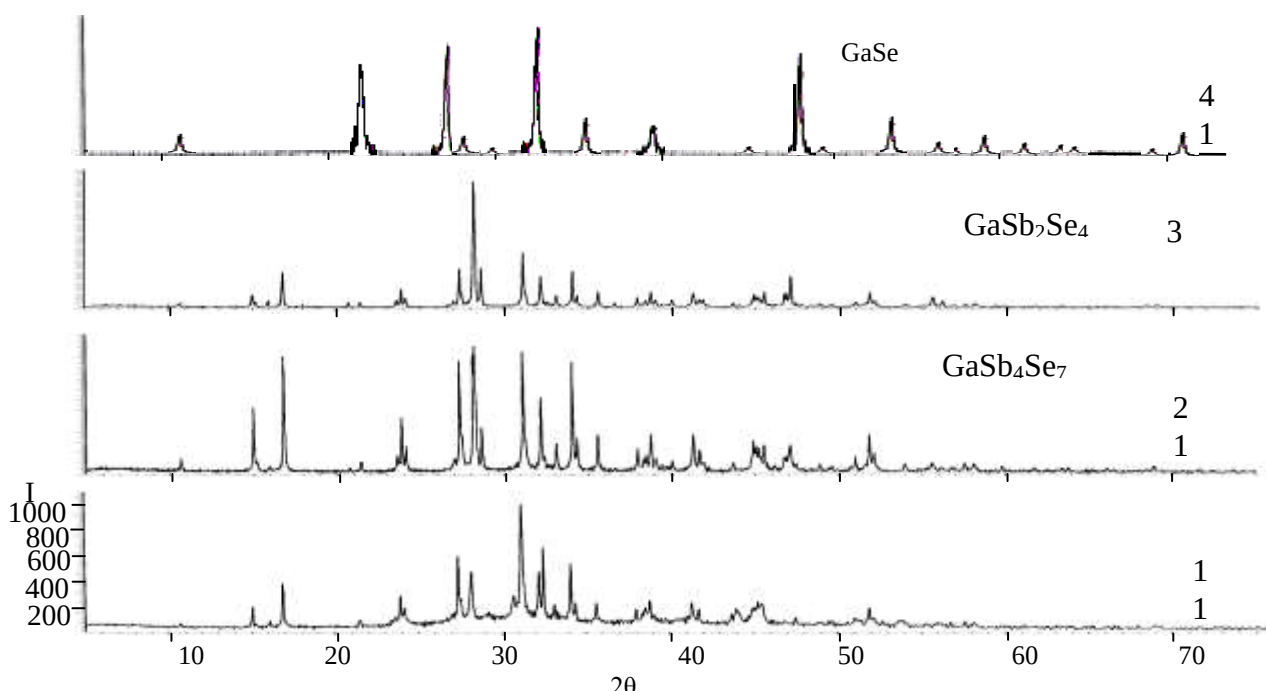


Fig.2. Diffractograms of alloys of the system Sb_2Se_3 -GaSe.

1- Sb_2Se_3 2-20, 3- 33,33 (GaSb_4Se_7), 4- 50 (GaSb_2Se_4), 5-70 , 6- 100 mol. % GaSe.

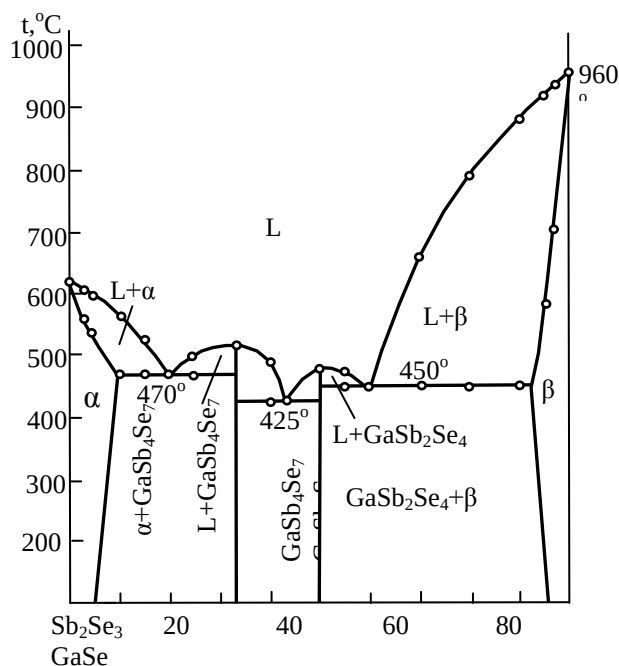


Fig. 3. Phase diagram of the Sb_2Se_3 -GaSe system.

It found that diffraction peaks of alloys 33.33; 50 mol % GaSe revealed on diffraction pattern differ from diffraction peaks of initial compounds.

According to physical and chemical analysis, the state diagram of the Sb_2Se_3 -GaSe system was constructed (Fig. 3). Part of liquidus in the concentration range of 0-20 mol % GaSe corresponds to primary separation of α -phase (solid solutions based on Sb_2Se_3), concentration limits of 20-43 mol % GaSe crystals of new phase GaSb_4Se_7 are separated from liquid, primary crystallization of the phase GaSb_2Se_4 occurs in the range of 43-60 mol % GaSe, finally, β -phases (solid solutions based on GaSe) are crystallized in concentration range of 60-100 mol % GaSe .

It should be added that microhardness of alloys in the system was measured using PMT-3 loaded up to 0.15 N. Results of micro hardness measurement of alloys are cited in Table to

show that four rows of values are found in the system. For the α -phase, the microhardness varies within (1200–1250) MPa. In the concentration range of 20-43 mol. % GaSe a new value of microhardness (1350-1400) MPa is revealed to indicate the microhardness of the new phase GaSb₄Se₇. In the range of 43-60 mol. % GaSe the microhardness value (1500-1530) MPa is in accord with the new GaSb₂Se₄ phase. For the GaSe compound, the microhardness values are 300 MPa.

Table. Results of DTA, measurement of micro hardness and density of the Sb₂Se₃-GaSe system alloys

Composition, mol %		Thermal effects, °C	Density, 10 ³ kg/m ³	Micro hardness of phases, MPa			
Sb ₂ Se ₃	GaSe			α	GaSb ₄ Se ₇	GaSb ₂ Se ₄	β
				P=0,15 H			
100	0.0	617	5.84	1200	-	-	-
97	3.0	560,610	5.82	1230	-	-	-
95	5.0	520,590	5.80	1250	-	-	-
90	10	470,565	5.74	1250	-	-	-
85	15	470,520	5.68	-	-	-	-
80	20	570	5.65	Eutec.	Eutec.	-	-
75	25	470,500	5.64	-	-	-	-
70	30	470,510	5.60	-	1350	-	-
66,6	33.3	515	5.63	-	1400	-	-
60	40	425,480	5.55	-	1400	-	-
57	43	425	5.50	-	Eutec.	Eutec.	-
50	50	490	5.52	-	-	1500	-
45	55	450,475	5.41	-	-	1530	-
40	60	450	5.35	-	-	Eutec.	Eutec.
30	70	450,655	5.23	-	-	-	370
20	80	450,770	5.19	-	-	-	370
10	90	450,875	5.16	-	-	-	370
5,0	95	580,940	5.12	-	-	-	370
3,0	97	700,945	5.08	-	-	-	350
0,0	100	960	5.03	-	-	-	300

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$\text{Sb}_2\text{Se}_3\text{-GaSe}$ SİSTEMİNDƏ FAZAƏMƏLƏGƏLMƏ VƏ ƏRİNTİLƏRİN FİZİKİ-KİMYƏVİ XASSƏLƏRİNİN TƏDQİQİ

I.I. Əliyev¹, N.A. Məmmədova¹, F.M. Sadıqov²

¹AMEA-nın acad. M.Nağıyev ad. Kataliz və Qeyri-Üzvi Kimya İnstitutu
AZ 1043, Bakı, H. Cavid pr.113; e-mail: aliyevimir@rambler.ru

²Bakı Dövlət Universiteti
AZ-1148 Bakı, Z.Xəlilov küç., 23

Fiziki-kimyəvi analizin kompleks metodları: diferensial-termiki (DTA), rentgenfaza (RFA), mikroquruluş (MQA) analizi və eləcə də mikrobərkliyin və sıxlığın təyini vasitəsilə $\text{Sb}_2\text{Se}_3\text{-GaSe}$ sistemi tədqiq edilmiş və faza diaqramı qurulmuşdur. Müəyyən edilmişdir ki, $\text{Sb}_2\text{Se}_3\text{-GaSe}$ sistemində iki - GaSb_4Se_7 və GaSb_2Se_4 tərkibli uyğun olaraq, 515°C və 490°C -də konqruyent əriyən birləşmələr alınmışdır. Sistemdə GaSe əsasında 4 mol % Sb_2Se_3 həll olduğu halda, Sb_2Se_3 birləşməsi əsasında isə 5 mol % GaSe həll olduğu aşkar edilmişdir. Sistemdə əmələ gələn üç evtektikanın tərkibi 20; 43 u 60 mol % Sb_2Se_3 , temperaturları isə uyğun olaraq 470, 425 u 450°C -dir.

Açar sözlər: sistem, konqruyent, evtektika, solidus, likvidus.

ИССЛЕДОВАНИЕ ФАЗООБРАЗОВАНИЯ И НЕКОТОРЫХ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ СПЛАВОВ СИСТЕМЫ $\text{Sb}_2\text{Se}_3\text{-GaSe}$

И.И. Алиев¹, Н.А. Мамедова¹, Ф.М. Садыгов²

¹Институт катализа и неорганической химии Национальной АН Азербайджана
AZ 1043 Баку, пр.Г.Джавида,113; e-mail: aliyevimir@rambler.ru

²Бакинский государственный университет
AZ-1148 Баку, у. 3. Халилова, 23

Комплексными методами физико-химического анализа: дифференциально-термического (DTA), рентгенофазового (РФА), микроструктурного (МСА) анализа, а также измерением микротвердости и плотности изучен характер взаимодействия в системе $\text{Sb}_2\text{Se}_3\text{-GaSe}$ и построена фазовая диаграмма. Установлено, что в системе $\text{Sb}_2\text{Se}_3\text{-GaSe}$ образуются два конгруэнтно плавящихся соединения GaSb_4Se_7 и GaSb_2Se_4 при температурах 515°C и 490°C соответственно. Установлено, что растворимость на основе GaSe в твердом состоянии составляет 4 мол. % Sb_2Se_3 , а на основе Sb_2Se_3 - 5 мол. % GaSe . В системе образуются три эвтектики, состав которых отвечает 20; 43 и 60 мол. % Sb_2Se_3 при температурах 470, 425 и 450°C соответственно.

Ключевые слова: система, конгруэнтный, эвтектика, солидус, ликвидус.