UDC 546.87′24 + 662′24

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

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Received 28.04.2019

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.*
DOI: 10.32737/2221-8688-2019-3-403-407

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 chancogenides 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 ρ= 5,843 g/cm^3 and micro hardness Hμ= 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 $P6_3/mmc$-D^4_{6h}, density ρ = 5,03 g/cm^3 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 CuKα-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 HNO_3 (conc) composition: H_2O_2 =1 : 1. ehe 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 Sb_2Se_3-GaSe are obtained in the form of light grey compact ingots. Resistance to air, water and organic solvents was studied. Strong mineral acids (HCl, HNO_3) decompose them well.

Thermal analysis of the Sb_2Se_3-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 Sb_2Se_3, 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 Sb_2Se_3 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 $GaSb_4Se_7$ and $GaSb_2Se_4$ compositions congruently melting at 515 and 490°C are formed in the system Sb_2Se_3-GaSe. The existence of compounds was confirmed using DTA, X-ray phase analysis, MSA analysis methods, microhardness and density measurements.

On thermo-grams of $GaSb_4Se_7$ and $GaSb_2Se_4$ 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 $GaSb_4Se_7$ and $GaSb_2Se_4$. Microstructure (fig. 1 and c) of compounds $GaSb_4Se_7$ and $GaSb_2Se_4$ was studied after annealing for 750 hrs. at 450°C.

a) b) c)

Fig.1. Microstructure of eutectics (a) and $GaSb_4Se_7$ (b) and $GaSb_2Se_4$ (c) compounds.
a) -15 mol. % GaSe (eutectics), b)- $GaSb_4Se_7$, c)- $GaSb_2Se_4$.

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

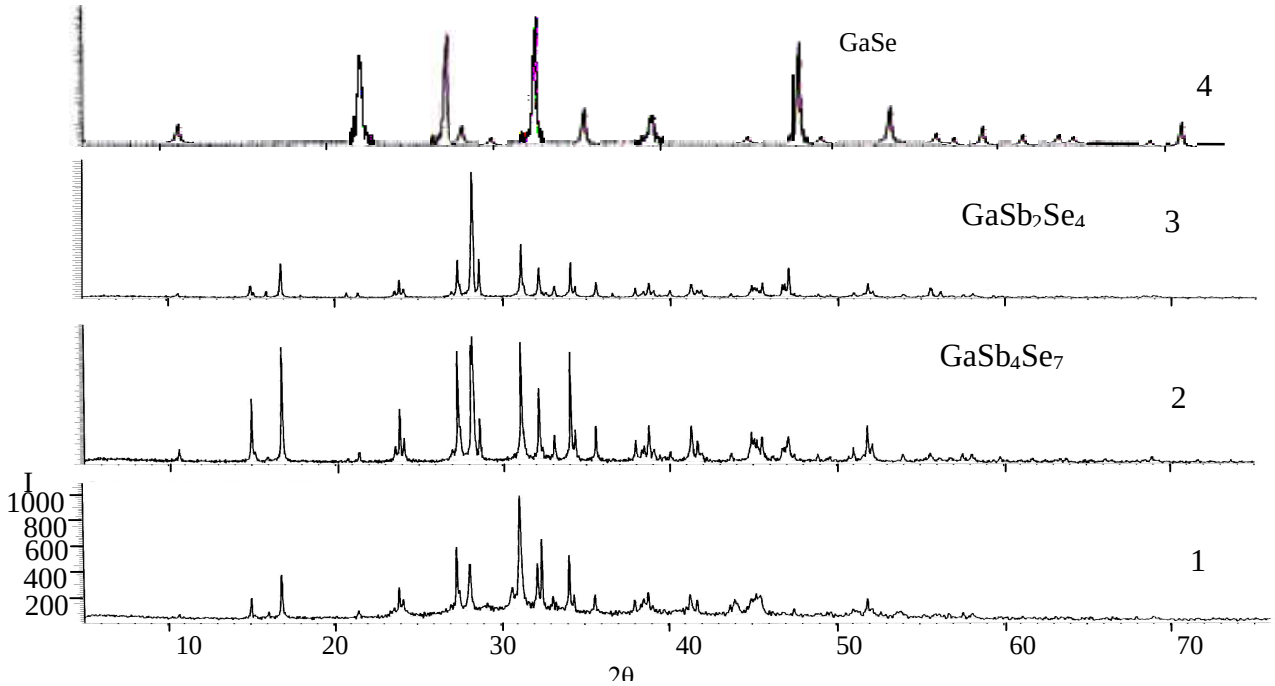

Fig.2. Diffractograms of alloys of the system Sb_2Se_3-GaSe.
1- Sb_2Se_3 2-20, 3- 33,33 ($GaSb_4Se_7$), 4- 50 ($GaSb_2Se_4$), 5-70 , 6- 100 mol. % GaSe.

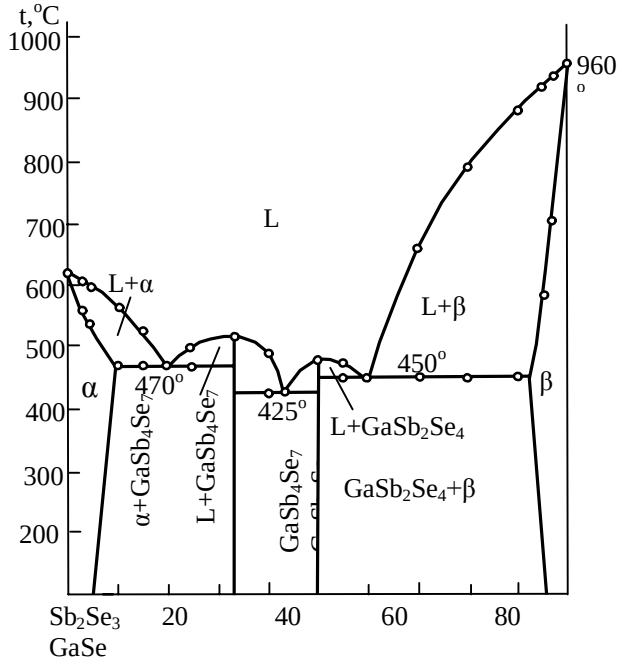

Fig. 3. Phase diagram of the Sb_2Se_3-GaSe system.

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 Sb_2Se_3-GaSe system alloys

Composition, mol %		Thermal effects, ˚C	Density, 10^3kg/m^3	Micro hardness of phases, MPa			
Sb_2Se_3	GaSe			α	$GaSb_4Se_7$	$GaSb_2Se_4$	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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Sb_2Se_3-GaSe SİSTEMİNDƏ FAZAƏMƏLƏGƏLMƏ VƏ ƏRİNTİLƏRİN FİZİKİ-KİMYƏVİ XASSƏLƏRİNİN TƏDQİQİ

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Fiziki-kimyəvi analizin kompleks metodları: diferensial-termiki (DTA), rentgenfaza (RFA), mikroquruluş (MQA) analizi və eləcə də mikrobərkliyin və sıxlığın təyini vasitəsilə Sb_2Se_3-GaSe sistemi tədqiq edilmiş və faza diaqramı qurulmuşdur. Müəyyən edilmişdir ki, Sb_2Se_3-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 и 60 mol % Sb_2Se_3, temperaturları isə uyğun olaraq 470, 425 и 450°C-dir.
Açar sözlər: *sistem, konqruyent, evtektika, solidus, likvidus.*

ИССЛЕДОВАНИЕ ФАЗООБРАЗОВАНИЯ И НЕКОТОРЫХ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ СПЛАВОВ СИСТЕМЫ Sb_2Se_3-GaSe

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Комплексными методами физико-химического анализа: дифференциально-термического (ДТА), рентгенофазового (РФА), микроструктурного (МСА) анализа, а также измерением микротвердости и плотности изучен характер взаимодействия в системе Sb_2Se_3-GaSe и построена фазовая диаграмма. Установлено, что в системе Sb_2Se_3-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.*