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PHASE EQUILIBRIUM IN THE Ga_2Se_3 – CoSe SYSTEM

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Using differential thermal, X-ray phase, microstructural analyzes and microhardness measurements, we studied the phase equilibrium in the Ga_2Se_3 – CoSe system in the entire concentrated region and constructed its phase diagram. It has been established that the phase diagram refers to eutectic types with monotectics. The eutectic crystallizes at 1000°C and 10 mol% CoSe . Liquid phase delamination occurs in the concentration range from 15 to 85 mol% CoSe and 1030°C. There are no intermediate compounds formed in the system.

Keywords: *system, phase equilibrium, delamination, phase transition, cobalt selenide.*

doi

Introduction

Ga_2Se_3 is a defective compound formed with an open maximum at 1020°C. In the crystal lattice of this sphalerite-type compound, 1/3 of the space occupied by gallium is empty, and its crystallochemical formula is written as $\text{Ga}_{0.666}[\]_{0.333}\text{Se}$ [1, 2]. The large number of own defects leads to a high concentration of charge carriers in this compound ($\sim 10^{20}$ – 10^{21}) cm^{-3} , and therefore alien impurity atoms in it are not electroactive. On the other hand, due to a large number of specific defects its thermal conductivity reduces, that leads to an increase in the cost of its thermoelectricity [2]. Defective structure of the compound may affect the nature of its interaction with other chalcogenides and the kinetics of the process. It is accidental because on the basis of Ga_2Se_3 and other similar compounds type $\text{A}_2^{\text{III}}\text{B}_3^{\text{IV}}$ there has been obtained a number of compounds of more complex composition, as well alien elements [1, 3–6].

Finally, structural defects have a significant effect on many mechanical and physical parameters of solids. For example, the effect of defects on the electrical conductivity, photoconductivity, plasticity, density, etc. of a substance. varies. In fact, Ga_2Se_3 and such compounds with a special structural defects are insensitive to many elements in terms of electrical

conductivity. However, it is known that transition elements, especially 3d-transition elements, have a significant effect on their electrophysical and magnetic properties. It should be noted that the nature of the interaction of various 3d-transition elements with indium and gallium chalcogenides of formula $\text{A}_2^{\text{III}}\text{B}_3^{\text{IV}}$ varies sharply [6]. For example, the presence of a FeGa_2Se_4 compound in the Ga_2Se_3 – FeSe system has been confirmed in the corresponding phase diagrams [7, 8]. However, a compound with a similar composition in the presence of nickel was not found in the Ga_2Se_3 – NiSe system, it was confirmed that the phase diagram of this system is monotectic-eutectic and layered in liquid alloys over a wide concentration range [6, 9]. It should be noted that a similar situation is repeated in similar systems in the presence of sulfur. That is, the presence of FeGa_2S_4 is confirmed in the corresponding phase diagram [10–12] and it is noted that alloys containing 50 mol% Ga_2S_3 and 50 mol% CoS (NiS) are two-phase [6, 13, 14]. However, in many studies such two-phase compounds have been presented as compounds [15–17]. Thus, FeGa_2S_4 (Se_4) compounds have don't cobalt and nickel analogues. In contrast, in Ga_2S_3 (Se_3)– CoS (NiS) systems, stratification is observed in liquid alloys containing 50 mol% CoS (NiS).

The authors of [18] also show the presence of CoGa_2Se_4 compound in the Ga_2Se_3 – CoSe system. The authors of [19] show that intermediate phase is not formed in the Ga_2Se_3 – CoSe system. Unfortunately is found in sometimes contradictory information the literature.

Experimental part

The purpose of this article is to re-examine the Ga_2Se_3 – CoSe system and determine the true existence of a compound containing CoGa_2Se_4 by the classical methods of physical-chemical analysis.

Samples of the system were synthesized by melting of highly pure elements (gallium grade Ga-000, cobalt grades are carbonyl, selenium grade OSCH 17-3) in evacuated (~ 0.1 Pa) and sealed quartz ampoules. During synthesis, the temperature was gradually raised to 1100°C and maintained by stirring periodically for 6 hours. Samples were cooled slowly (~ 6 deg/min) to room temperature and kept to heat treatment processing at 800°C for 100 hours.

As a result of the synthesis, completely melted gray, monolithic samples that do not adhere to the quartz ampoule are obtained. The samples are divided into two approximately equal parts. The first part is taken for X-ray diffraction and MSA. The second part is crushed into small pieces, filled into special quartz ampoules for DTA, vacuumed and sealed.

Thermograms of the samples were taken

on a two-coordinate potentiometer H 307/1 with the help of a chromel/alumel thermocouple. Calcined Al_2O_3 powder was used as a standard. Thermograms mainly show two series of thermal effects (1030 and 1000°C). The thermogram of the stoichiometric CoSe compound has only one thermal effect, its melting point (1055°C), that corresponds to the thermal analysis of cobalt monoselenide made of carbonyl cobalt [20].

The reference literature on binary systems [21] states that there is a polymorphic transition at $\sim 640.5^\circ\text{C}$. In this study, the stoichiometric CoSe thermogram shows no thermal effect other than the melting process.

Results and its discussion

Diffraction patterns of CoSe and intermediate samples of the system were drawn on a D2 PHASER diffractogram using monochromatic CuK_α rays. X-ray reflexes determined from a diffractogram of CoSe with a stoichiometric composition gradually cooled to room temperature are the same as those shown in [20]. The reflexes observed in the diffractograms of the intermediate components show that the samples of the system are two-phase (consisting of primary compounds) (Table 1). Reflexes belonging only to Ga_2Se_3 are observed to move to a slightly larger angle, that may be due to the solution based on Ga_2Se_3 . In intermediate samples, CoSe -specific reflexes remain unchanged in angle.

Table 1. Observed reflections in the diffraction pattern of samples of the Ga_2Se_3 – CoSe system

Ga_2Se_3		50 mol% Ga_2Se_3 + 50 mol% CoSe		CoSe	
d_a , nm*	I_{nis}	d_a , nm	I_{nis}	d_a , nm	I_{nis}
		0.508	6	0.508	13
0.314	35	0.314	20		
				0.300	4
0.271	6	0.271	2		
		0.268	45	0.268	100
		0.238	5	0.238	12
				0.202	2
0.192	100	0.192	60		
		0.184	7	0.184	15
		0.180	21	0.180	46
		0.174	3	0.174	9
0.164	10	0.164	6		
0.159	5	0.159	2		
		0.145	10	0.145	22
		0.133	7	0.133	17

Ga_2Se_3 – phase equilibrium of the CoSe system (a) and dependence of microhardness on composition (b).

Microstructure analysis and microhardness measurements were performed on a PMT-3 device. Phase liquefaction is observed in the samples in the liquid state, the heavier phase accumulates in the lower part of the samples. Here, the microhardness of the CoSe phase is 4850 MPa under load 50 g and the microhardness of the Ga_2Se_3 phase under load 20g was set equal to 3160MPa.

Based on the results of the study, a phase diagram of the Ga_2Se_3 – CoSe system was constructed (Figure).

Conclusion

As can be seen, the system is a monotectic eutectic type. Eutectic crystallizes at 10 mol% CoSe and at 1000°C. The monotectic process takes place at 85 mol% CoSe and 1030°C, and stratification in the liquid alloy covers a range of 15–85 mol% concentration. The area of a solid solution based on Ga_2Se_3 can be up to 5 mol% CoSe at eutectic temperature. However, at room temperature, the limit of α -solid solution is less

than 1 mol% CoSe . Cobalt monoselenide-based solubility is practically non-existent.

Thus, the results of our research confirm the conclusions of the authors of the work [19]. That is, the Ga_2Se_3 – CoSe system does not form a new intermediate phase, including a compound containing CoGa_2Se_4 .

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$\text{Ga}_2\text{Se}_3\text{--CoSe}$ SİSTEMİNDƏ FAZA TARAZLIĞI

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Differensial termiki (DTA), rentgen faza, mikroquruluş və mikrobərkliyin ölçülməsi üsulları ilə $\text{Ga}_2\text{Se}_3\text{--CoSe}$ sisteminin bütün quruluş sahələrində faza tarazlığı tədqiq edilmiş və sistemin faza diaqramı qurulmuşdur. Məlum olmuşdur ki, sistemin faza diaqramı monotektikalı evtektik tiplidir. Sistemin evtektikası 1000°C və 10 mol% CoSe tərkibdə kristallaşır. Maye fazada təbəqələşmə geniş qatılıq intervalında (15–85 mol% CoSe) və 1030°C temperaturda baş verir. Sistemdə yeni birləşmə aşkar edilməmişdir.

Açar sözlər: sistem, faza tarazlığı, təbəqələşmə, faza keçidi, kobalt selenid.

ФАЗОВОЕ РАВНОВЕСИЕ В СИСТЕМЕ $\text{Ga}_2\text{Se}_3\text{--CoSe}$

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Методами дифференциально-термического, рентгенофазового, микроструктурного анализов и измерением микротвердости исследовано фазовое равновесие в системе $\text{Ga}_2\text{Se}_3\text{--CoSe}$ во всей концентрированной области и построена её фазовая диаграмма. Установлено, что фазовая диаграмма относится к эвтектическим типам с монотектикой. Эвтектика кристаллизуется при 1000°C и 10 мол% CoSe. расщавление фаз в жидком состоянии происходит в интервале концентраций от 15 до 85 мол.% CoSe и 1030°C . В системе не образуются промежуточные соединения.

Ключевые слова: система, фазовое равновесие, расщавление, фазовый переход, селенид кобальта.