PHASE EQUILIBRIUM AND X-RAY ANALYSIS OF SOLID SOLUTION ALLOYS IN THE In-SrSe SYSTEM

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Abstract

The nature of chemical interaction in the In-SrSe system was studied and its phase diagram was constructed using physicochemical methods of analysis (DTA, X-ray diffraction, microstructural analysis, as well as density and microhardness measurements). It was found that the In-SrSe system is a quasi-binary section of the In-Sr-Se ternary system and belongs to the eutectic type. A degenerate eutectic is formed between In and SrSe, the temperature of which is 150°C. In the In-SrSe system, solid solutions based on the SrSe compound make up 5 at. % In. The dependence of the microhardness of the alloys on the composition was studied. It was found that there are two types of microhardness values in the system. The microhardness value of 150 MPa corresponds to the microhardness of the In element, and the value (1240-1270) MPa corresponds to the microhardness of the α-solid solution based on SrSe. The dependence of the melt densities on the composition changes monotonically. An X-ray structural analysis of the solid solution alloy $(SrSe)_{1-x}(In)_x$ (x=0.02; 0.05) was performed and the lattice parameters were calculated. In the system, 95 and 98 mol. % SrSe solid solution alloys based on the SrSe compound crystallize in a cubic syngony with lattice parameters *a*=6.257 Å and *a*=6.274 Å, respectively.

Keywords: alloy, system, solid solution, microhardness, quasibinary.

Introduction

In the literature, the elements of the main II subgroup have high reactivity. In the literature [1–4], ternary systems involving calcium chalcogenides were studied. Since strontium chalcogenides are very difficult to obtain and study, the ternary system with their participation has been little studied. The authors of [5–8] studied the following systems: SrS–GaS, SrSe–GaSe (InSe), and SrSe–Ga_2Se_3 (In_2Se_3). In the SrX–MeX systems (Me=Ga,In; X=S,Se,Te), compounds containing $SrMeX_2$, $SrMe_2X_4$, and $SrMe_4X_7$ are formed. Materials with luminescent properties were obtained by adding rare earth elements as activators to compounds containing $CaMeX_2$, $CaMe_2X_4$, and $CaMe_4X_7$ [9–11]. A number of internal sections of the ternary system Ca-Ga(In)-Se(Te) were studied by us earlier [12–19]. Most of these systems are quasi-binary or partially quasi-binary. The In-SrSe system was studied for the first time.

The aim of this work is to study the nature of chemical interactions in the In-SrSe system, construct a phase diagram and identify solid solution regions using X-ray diffraction. The In-SrSe system is studied for the first time. The In element melts at 156ºC and crystallizes in the tetragonal system with lattice parameters *a*=3.252; *c*=4.946 Å, density d=7.36 g/cm^3 [20]. The SrSe compound melts congruently at 1600ºC, crystallizes in the cubic syngony, lattice parameter: *a*= 6.243 Å, sp. gr. Fm3m, density ρ=4.50 g/cm^3 [21].

Experimental part

To synthesize In-SrSe system alloys from element compounds, SrSe was first synthesized. The Sr element is retained in oil because it oxidizes when in contact with air. To synthesize the SrSe compound, Sr and Se are calculated in stoichiometric composition. First, Se is weighed and poured into a quartz ampoule, and the Sr element is degreased in a vacuum using a BOX setup. Then it is weighed on scales and placed in an ampoule with selenium, the air is pumped out to a pressure of 0.133 Pa and the neck is sealed, melting it in an arc flame. It should be noted that excess temperature during synthesis melts and destroys the quartz ampoule, releasing a large amount of energy. Thus, SrSe is synthesized as follows. The ampoule with the substance is placed in a furnace, the temperature is increased to the melting point of indium (156°C) and maintained for 2 days, while the process is continued with constant stirring. Strontium gradually begins to transform into SrSe. At the next stage, the temperature in the furnace is increased to 300°C and maintained for 24 hours.

At the next stage, the furnace temperature was increased to 1200°C for 2 hours, and then the temperature was reduced to 1000°C and maintained for 3 hours. After synthesis, the sample was obtained in the form of a heterogeneous powder. To obtain the full composition of the SrSe compound, the sample was finely ground and pressed to 200 atm. and obtained in the form of a tablet. Then, the sample was subjected to a solid-phase reaction in an evacuated quartz ampoule at a temperature of 800°C for 100 hours. The composition of the SrSe compound was refined using X-ray diffraction analysis. Then, alloys of the In-SrSe system were synthesized from the In and SrSe components at a temperature of 1000-1200°C in an ampoule with air suction to

a pressure of 0.133 Pa. The synthesized alloys were homogenized at a temperature of 350°C for 150 hours.

The alloys in the equilibrium state were studied by differential- thermal analysis (DTA), X-ray diffraction (XRD), microstructure (MSA), as well as determination of density and microhardness.

Differential-thermal analysis (DTA) was carried out on a low-frequency Kurnakov pyrometer. The heating rate of the alloys was 10°C/min. Chromel-alumel was used as a thermocouple.

X-ray structural analysis of the alloys was carried out on a D2 PHASER X-ray diffractometer. A CuKα electrode was used as an irradiator. Microhardness was measured using a PMT-3 metallographic microscope. During the measurements, the dependence of microhardness on weight was studied.

Microstructural analysis (MSA) was carried out on an MIM-8 microscope. For this, the alloys were polished to a shine and their structure was examined under a microscope. To clarify the phase boundaries, a solution of 5 ml HNO_3 + 5 ml H_2O_2 was used as a etching agent. The densities of the alloys of the system were determined by the pycnometric method, using toluene as a filling solution.

Results and discussion

Alloys were synthesized to study the phase equilibrium in the In-SrSe system. The synthesized alloys have a silvery color in the concentration range of 0–30 mol. % SrSe, gradually changing from gray to black as the amount of the SrSe compound increases. The behavior of the system's alloys under the influence of the external environment was studied. Indium-rich alloys do not change in air, water and organic solvents, but alloys containing 30–100 mol.% SrSe gradually hydrolyze when exposed to open air for a long time, absorbing moisture from the air. All In-SrSe systems dissolve well in strong acids (HCl, HNO_3). The equilibrium alloys were studied using physico-chemical analysis methods.

As a result of differential thermal analysis, two endothermic effects are present on the thermograms of the alloys. To clarify the results of differential thermal analysis, a microstructural analysis of the alloys was carried out. It was found that in the In-SrSe system there is a single-phase and a two-phase field.

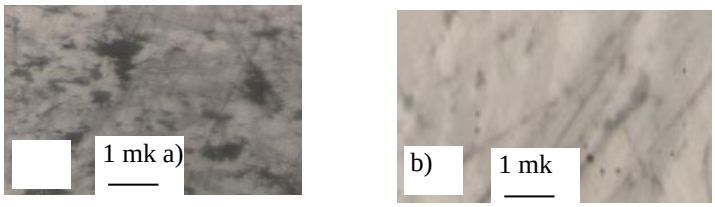

Fig. 1.
Microstructure of In-SrSe system alloys.
a) - 50 mol. %, b) -95 mol. % SrSe.

Difference-thermal analysis showed that the thermograms of the alloys exhibit two endothermic effects. To clarify the results of differential thermal analysis, microstructural analysis of the alloys was performed. It was found that the In-SrSe system has a single-phase and a two-phase field. Figure 1 shows the microstructure images of alloys containing 50 and 95 mol. % SrSe. As can be seen from Figure 1a, the alloy with a concentration of 50 mol. % SrSe is two-phase. The alloy with 95 mol. % SrSe is a solid solution alloy based on SrSe and is single-phase (Fig. 1b).

X-ray structural analysis of In-SrSe alloys was carried out for alloys containing 50, 95 and 98 mol. % SrSe and compared with the X-ray diffraction patterns of the initial components (Fig. 2). It was found that the diffraction maxima observed in the diffraction pattern of the 50 mol. % SrSe alloy consist of a mixture of diffraction lines of the initial components. The diffraction patterns of alloys containing 95 and 98 mol. % SrSe do not differ much in intensity and interplanar distances from the diffraction lines of the SrSe compound. This indicates that these alloys are solid solution alloys based on SrSe.

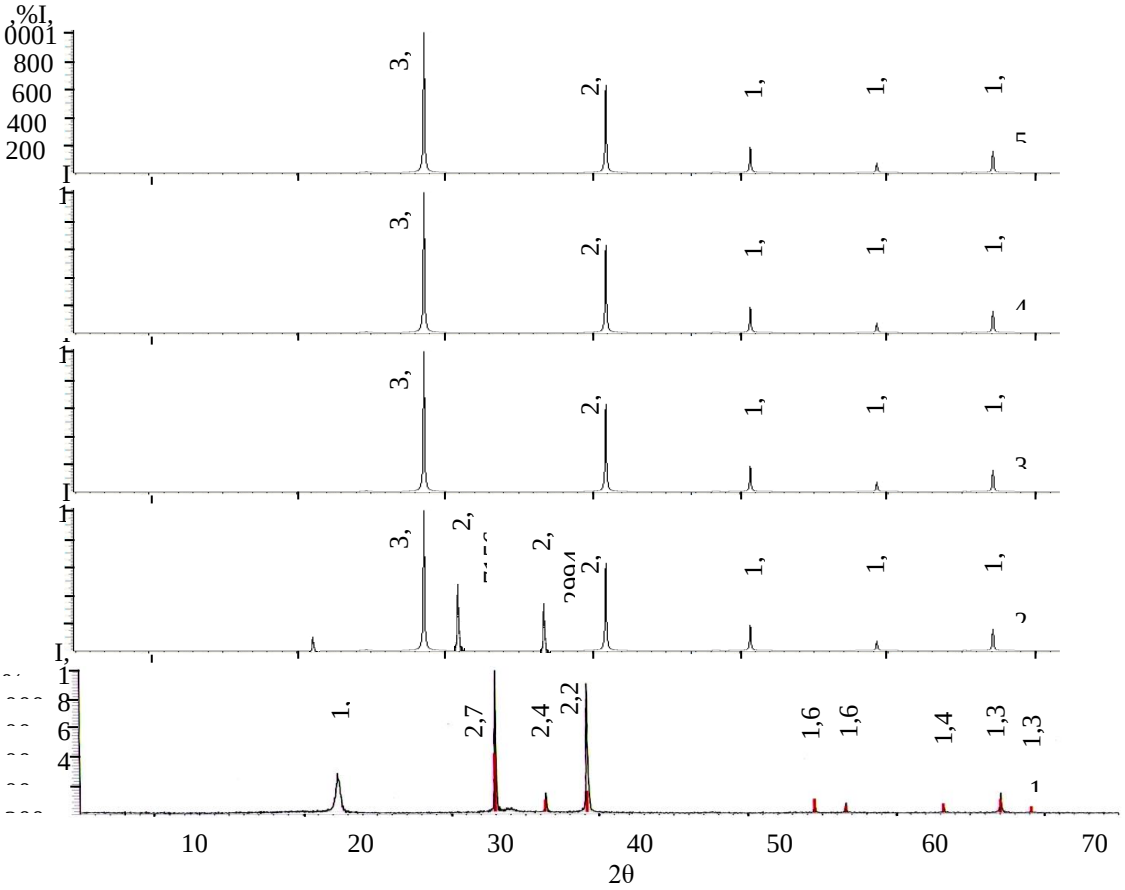

Fig. 2. Diffraction patterns of alloys of the In - SrSe system.
1-In, 2-50 mol. %, 3-95 mol. %. 4-98 mol. %, 5-100 mol. % SrSe.

As a result of X-ray structural analysis of 95 and 98 mol. % SrSe solid solution alloys based on the SrSe compound, their crystal lattice parameters were calculated (Table 1). Solid solution alloys based on the SrSe compound with a content of 95 and 98 mol. % SrSe crystallize in the cubic syngony as SrSe with lattice parameters a=6.257 Å and a=6.274 Å, respectively.

Table 1.

X-ray data of SrSe-based solid solution alloys in the In-SrSe system

SrSe			98 % SrSe- 2 % In			95 % CaSe- 5 % In		
I,%	d, Å	hkl	I,%	d, Å	hkl	I,%	d, Å	hkl
100	3,1168	200	100	3,1280	111	100	3,1373	111
64	2,2053	220	64	2,2124	200	64	2,2184	200
20	1,7999	222	20	2,1,8063	220	18	1,8110	220
8	1,5588	400	8	1,5642	311	6	1,5684	311
16	1,3950	420	16	1,3980	222	14	1,4029	222

Based on the results of complex physicochemical analysis, a phase diagram of the In – SrSe system was constructed (Fig. 3).

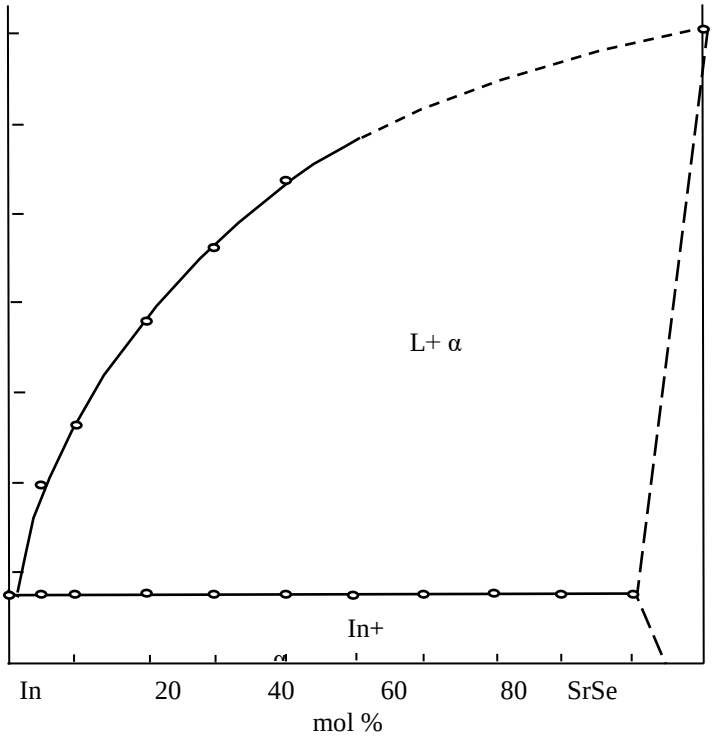

Fig. 3. Phase diagram of the In – SrSe system.

It was found that the In – SrSe system is a quasi-binary section of the Sr-In-Se ternary system. In the In – SrSe system, a degenerate eutectic is formed on the SrSe side, the temperature of which is 150°C. In the system, the In and SrSe components form a degenerate eutectic between themselves, the content is ~3 mol SrSe, the temperature is 150 °C. In the system, solid solutions based on SrSe reach up to 5 mol. % In at room temperature. In the range of SrSe concentrations in the system from 3 to 100 mol. %, crystals of the α-solid solution based on SrSe begin to precipitate along the liquidus curve. Below the liquidus curve, there is a two-phase region consisting of L + α. In the range of SrSe concentrations in the system of 3–95 mol. % below the solidus line, two-phase alloys consisting of (In+α) crystallize.

The dependence of the density and microhardness of the In – SrSe system on the composition is given in Table 2. As a result of measuring the microhardness of the alloys of the system, two types of microhardness values were obtained. The microhardness value of 150 MPa corresponds to the microhardness of In, and the value (1240-1250) MPa corresponds to the microhardness of the SrSe compound. The dependence of the densities of the alloys of the system on the composition changes monotonically.

Cədvəl 2.

In–SrSe sisteminin ərintilərinin tərkibi, DTA, mikrobərkliklərinin və sıxlıqlarının tərkibdən asılılığı

Composition, mol %		Thermal effects. ºC	Density, q/cm^3	Microhardness , MPa	
In	SrSe			In	α
				P=0,10 N	P=0,15 N
100	0,0	156	7,36	150	-
95	5,0	150,400	7,20	150	-
90	10	150,525	7,05	150	-
80	20	150,760	6,79	150	-
70	30	150,925	6,50	150	-
60	40	150,1130	6,22	150	1250
50	50	150	5,98	-	1250
40	60	150	5,64	-	1250
30	70	150	5,36	-	1250
20	80	150	5,07	-	1250
10	90	150	4,79	-	1250
0,0	100	1600	4,50	-	1240

Conclusion

As a result of complex physicochemical studies, a phase diagram of the In-SrSe system was constructed. The phase diagram of the system is quasi-binary, of the degenerate eutectic type, with a composition of ~3 mol. % SrSe and a temperature of 150°C. Based on the results of microstructural analysis, it was found that a uniform field based on SrSe is observed in the system. In the In-SrSe system, a solid solution with a concentration of 5 mol. % In was obtained at room temperature based on the SrSe compound. The dependence of the density and microhardness of the alloys of the system on the composition was studied. X-ray structural analysis of the solid solution alloys $(SrSe)_{1-x}(In)_x$ (x=0.02; 0.05) was carried out and the lattice parameters were calculated. It was found that 95 and 98 mol. % SrSe of solid solution alloys based on the SrSe compound crystallize in a cubic syngony with lattice parameters *a*=6.257 Å and *a*=6.274 Å, respectively.

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