INVESTIGATION OF PHYSICO-CHEMICAL, X-RAY AND ELECTROPHYSICAL PROPERTIES OF THE OBTAINED PHASES IN THE Ga_2Sr-SrSe SYSTEM

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Using methods of physicochemical analysis (DTA, XRF, MSA, as well as density and microhardness measurements), the chemical interaction in the Ga_2Sr-SrSe system was studied and its T-x phase diagram was constructed. It has been established that the Ga_2Sr-SrSe system is a quasi-binary section of the Sr-Ga-Se ternary system and belongs to the eutectic type. In the Ga_2Sr-SrSe system, there are limited regions of solid solutions based on the initial components at room temperature. Microstructural analysis showed that at room temperature, solid solutions based on the Ga_2Sr compound reach 5 mol % SrSe, and based on SrSe-3.5 mol % Ga_2Sr. The composition of the eutectic formed between the Ga_2Sr and SrSe compounds is 25 mol % SrSe, at a temperature of 850°C. The lattice parameters were calculated as a result of X-ray diffraction analysis of solid solutions $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03), respectively: for the SrSe compound, a=6.243 Å (SrSe) and for alloys solid solutions, a=6.263 Å (1 % Ga_2Sr), a=6.275 Å (2 % Ga_2Sr), a=6.298 Å (3 % Ga_2Sr). The temperature dependence of electrical conductivity and thermo-EMF of solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03) on composition was studied.

Keywords: system, phase, quasi-binary, eutectic, microhardness
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INTRODUCTIONS

It is known from the literature that chalcogenides of the main elements of subgroup II and ternary phases obtained on their basis are used as energy converters [1-6]. The chemical interaction of chalcogenides of elements of the calcium subgroup with gallium chalcogenides produces compounds containing $A^{II}MeX_2$, $A^{II}Me_2X_4$, $A^{II}Me_4X_7$ (A^{II}–Ca,Sr,Ba; Me-Ga, In, X-S,Se, Te) [7-10]. Indium chalcogenides form compounds such as $InMeX_2$, $InMe_2X_4$ (Me-Ca,Sr,Ba) [11-15]. Systems based on strontium and barium chalcogenides have been little studied. Compounds like $A^{II}MeX_2$, $A^{II}Me_2X_4$ exhibit strong luminescent properties due to the action of activators [16-20].

Previously, we studied a number of internal cross sections of the Ca-Ga(In)-Se ternary system [21-24]. The Ga_2Sr-SrSe system has not been studied.

The purpose of this work is to study the nature of chemical interaction in the Ga_2Sr-SrSe system, construct its phase diagram and detect areas of solid solution.

The intermetallic compound Ga_2Sr melts with an open maximum at 1045°C and crystallizes in the hexagonal system, lattice parameter: a = 4.344; c = 4.732 Å, sp. gr. P6/mmm [25]. The SrSe compound melts congruently at 1600°C and crystallizes in the cubic syngony, lattice parameter: a = 6.243 A, sp. gr. Fm3m, density ρ = 4.50 g/cm^3 [26].

EXPERIMENTAL PART

Alloys of the Ga_2Sr-SrSe system was synthesized from Ga_2Sr and SrSe components in quartz ampoules, evacuated to a pressure of 0.133 Pa, in the temperature range 1100-1200°C. To achieve an equilibrium state, the alloys of the system were subjected to annealing at a temperature of 700°C for 240 hours. Equilibrium alloys were studied by methods of physicochemical analysis (DTA, XRD, MSA, as well as density and microhardness measurements).

Differential-thermal analysis of the samples was carried out on a Kurnakov pyrometer NTR-73. Al_2O_3 was used as a standard; the heating rate was 10°/min.

X-ray phase analysis was performed on a D2 PHASER X-ray diffractometer. A CuKα cathode and a Ni filter were used as irradiators. Microhardness was calculated using a PMT-3 metallographic microscope. Microstructure analysis was carried out using a MIM-8 microscope. The density of the samples was determined by the pycnometric method using toluene as a filler.

The electrical conductivity and thermo-EMF of the solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03) were measured in weak electric and magnetic fields (E < 10 V/cm, H < 10 kG) using a UA-1-51 electrometric amplifier using the traditional direct current method [27,28].

RESULTS AND ITS DISCUSSION

Alloys of the Ga_2Sr-SrSe system have the form of a compact mass in the temperature range of 900-1000°C and are dark gray substances. When the alloys of the system are left in the open air for a long time, they absorb air moisture and undergo hydrolysis. The alloys of the system dissolve well in strong mineral acids (HNO_3, H_2SO_4).

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Based on the results of differential thermal analysis, it was established that two endothermic effects are observed in the thermograms of alloys of the Ga_2Sr-SrSe system. Based on the results of microstructural analysis, it was found that the solubility at room temperature in the Ga_2Sr-SrSe system based on Ga_2Sr is 5 mol. % SrSe, and based on SrSe-3.5 mol % Ga_2Sr. In Fig. 1 shows the microstructures of alloys of the Ga_2Sr-SrSe system with a content of 5, 25, 60 and 97 mol % SrSe.

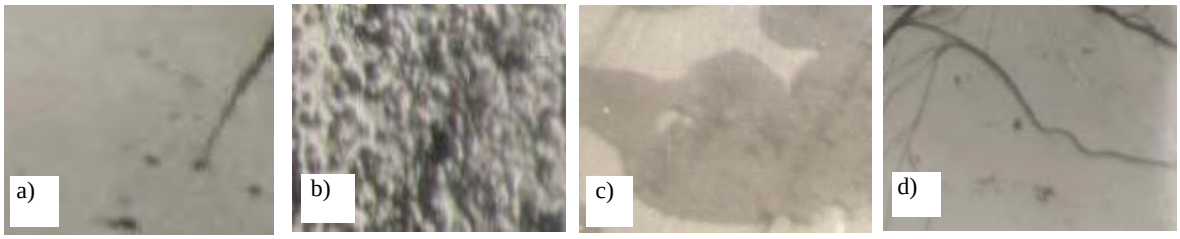

Fig. 1. Microstructures of alloys of the Ga_2Sr-SrSe system. a) -5, b) -25, c) -60, d) -96.5 mol % SrSe

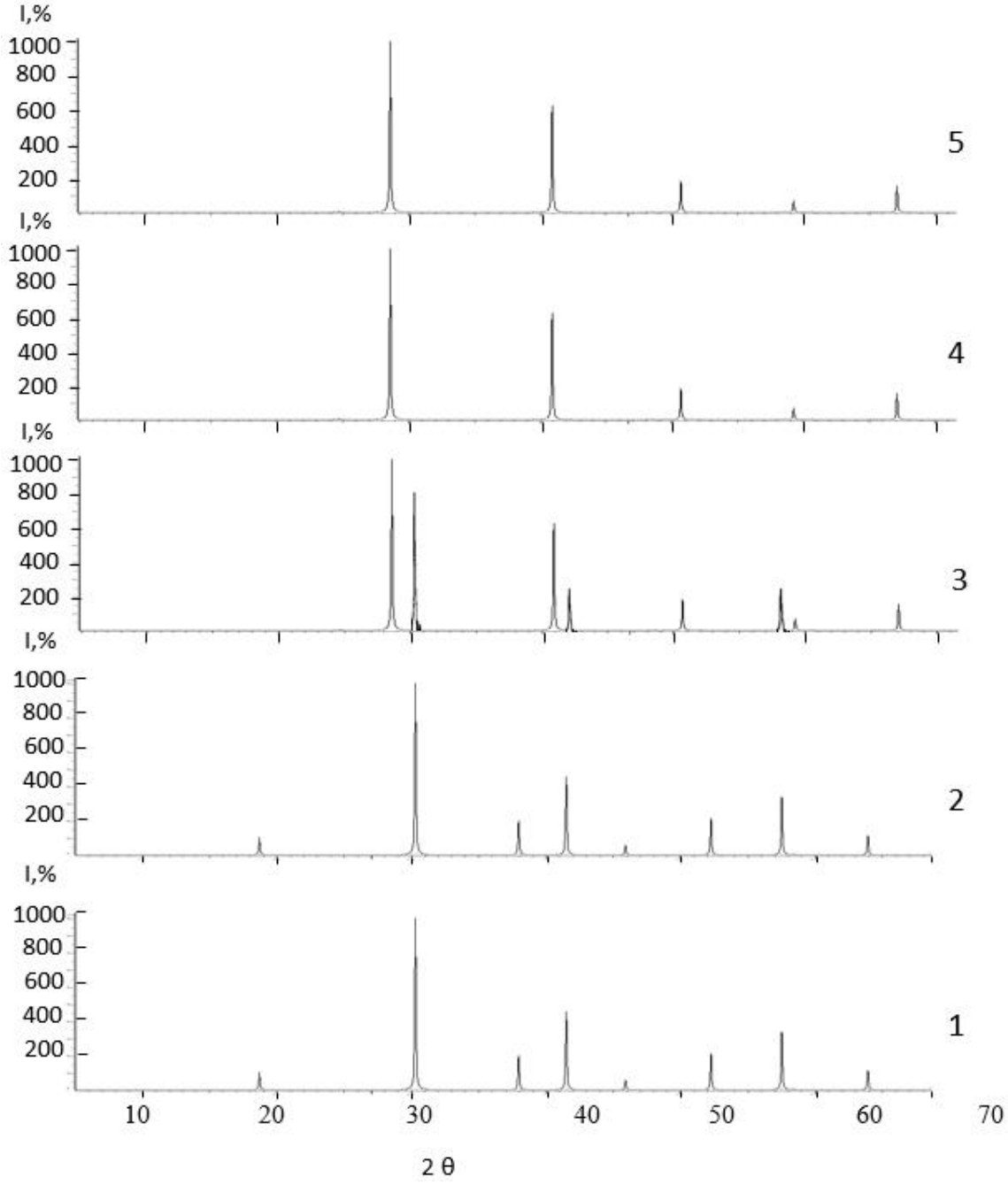

Fig. 2. X-ray diffraction patterns of alloys of the Ga_2Sr–SrSe system.
1- Ga_2Sr, 2-5, 3-60, 4-96.5; 5–100 mol % SrSe.

As can be seen from fig. 1, single-phase alloys containing 5 and 96.5 mol % SrSe are solid solution alloys based on Ga_2Sr and SrSe compounds, respectively. Alloy with SrSe content 25 mol % has a eutectic composition, and the sample with an SrSe content of 60 mol % - two-phase.

To confirm the correctness of differential thermal and microstructural analyses, X-ray phase analysis of alloys containing 5, 60 and 96.5 mol % SrSe (Fig. 2).

The diffraction maxima in the diffraction patterns of the alloys are identical to the diffraction patterns of the Ga_2Sr and SrSe compounds. That is, samples 5 and 96.5 are solid solution alloys based on Ga_2Sr and SrSe compounds, respectively. The diffraction pattern of the sample shows 60 mol % SrSe diffraction lines are a mixture of diffraction lines of the main components, i.e. it is a two-phase alloy. As a result of X-ray phase analysis, the results of DTA and MSA analyzes are confirmed.

As a result of physicochemical analysis methods, a T-x phase diagram of the Ga_2Sr–SrSe system was constructed (Fig. 3). The phase diagram of the system is quasi-binary, eutectic type. Cocrystallization of Ga_2Sr and SrSe compounds ends at the double eutectic point, composition 25 mol % SrSe, temperature 850°C.

The liquidus of the Ga_2Sr–SrSe system is limited by the monovariant equilibrium curves of an α-solid solution based on the Ga_2Sr compound and a β-solid solution based on the SrSe compound. Below the solidus line, single-phase (α) alloys crystallize in the region of 0–5 mol % SrSe, two-phase (α+β) alloys – in the range of 5–96.5 mol % SrSe, and single-phase (β) alloys crystallize in the region of 96.5-100 mol % SrSe.

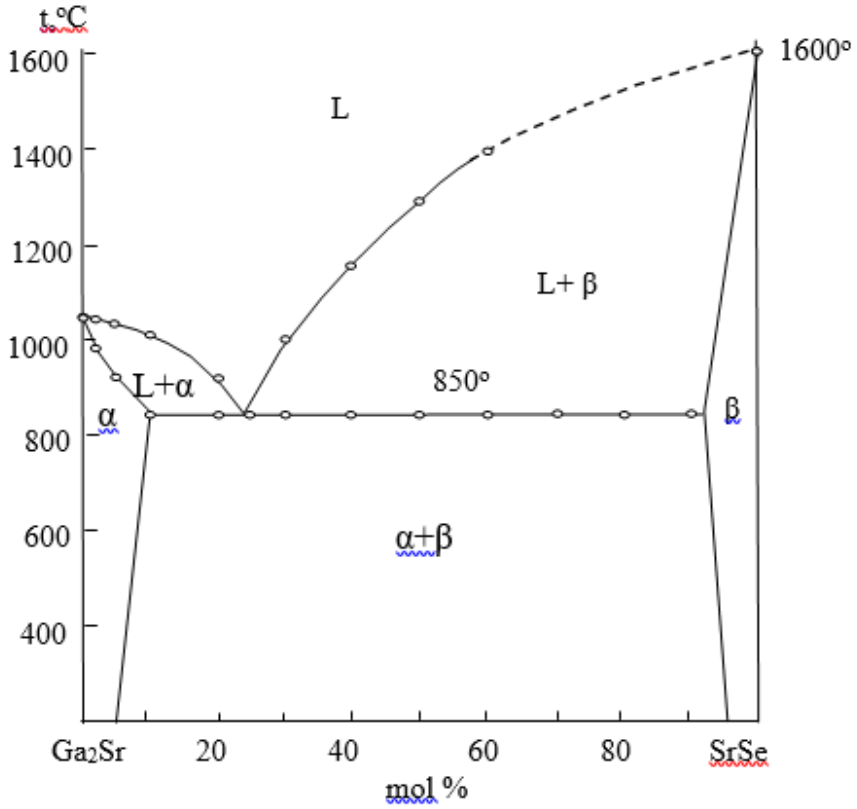

Fig. 3. T-x phase diagram of the Ga_2Sr–SrSe system.

Table 1.

Compositions of alloys of the Ga_2Sr–SrSe system, results of DTA, microhardness and density measurements

Composition, mol %		Thermal effects, °C	Density, q/cm^3	Microhardness, MPa	
Ga_2Sr	SrSe			α	β
				P=0,20 N	P=0,15 N
100	0,0	1045	4,80	2250	-
98	2,0	980,1040	4,82	2300	
95	5,0	920,1030	4,84	2300	-
90	10	850,1010	4,81	2300	-
80	20	850.925	4,75	2300	-

75	25	850	4,72	Eutec.	Eutec.
70	30	850,1000	4,71	-	-
60	40	850,1150	4,68	-	1290
50	50	850,1240	4,65	-	1290
40	60	850,1400	4,62	-	1290
30	70	850,	4,60	-	1290
20	80	850,	4,55	-	1290
10	90	850,	4,53	-	1280
0,0	100	1600	4,50	-	1250

In table table 1 shows some physicochemical properties of alloys of the Ga_2Sr–SrSe system. As a result of determining the microhardness of alloys of the Ga_2Sr–SrSe system, two different microhardness values were obtained. The microhardness value (2250-2300) MPa corresponds to the microhardness of α-solid solutions based on Ga_2Sr, and the other value (1250-1290) MPa corresponds to the microhardness of β-solid solution based on SrSe.

X-ray data of SrSe compound and alloys of the Ga_2Sr–SrSe system containing 1, 2 and 3 mol % Ga_2Sr are given in table 2.

Table 2.

X-ray data of solid solution alloys $(Ga_2Sr)_{1-x}(SrSe)_x$ (x=0.01; 0.02; 0.03)

SrSe a=6,243 Å				1 % Ga_2Sr-99 % SrSe a=6,263 Å			
I,%	$d_{eks.}$, Å	$d_{cal.}$,Å	hkl	I,%	$d_{eks.}$, Å	$d_{cal.}$,Å	hkl
100	3,1218	3,1219	200	100	3,1332	3,1326	200
50	2,2072	2,2075	220	50	2,215	2,214	220
20	2,1939	2,1937	222	20	2,2148	2,2146	222
10	1,5610	1,5608	400	10	1,5665	1,5665	400
15	1,3965	1,3960	420	15	1,4010	1,4005	420
2 % Ga_2Sr-98 % SrSe a=6,275 Å				3 % Ga_2Sr-97 % SrSe a=6,298 Å			
I,%	$d_{eks.}$, Å	$d_{cal.}$,Å	hkl	I,%	$d_{eks.}$, Å	$d_{cal.}$,Å	hkl
100	3,1391	3,1388	200	100	3,1501	3,1497	200
50	2,2192	2,2189	220	50	2,2270	2,2272	220
20	1,8123	1,8116	222	18	1,8183	1,8181	222
10	1,5691	1,5688	400	10	1,5753	1,5746	400
15	1,4038	1,4031	420	12	1,4085	1,4083	420

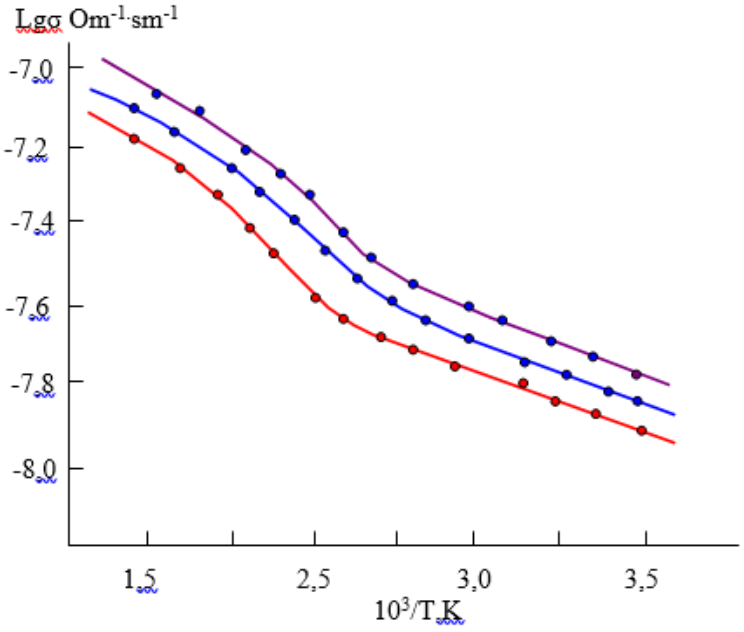

Fig. 4. The dependence of electrical conductivity of solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03) on composition and temperature was studied. 1-1 mol. %, 2-2 mol. %, 3-3 mol. % Ga_2Sr.

To study the electrophysical properties of solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03) containing 1; 2; 3 mol. % Ga_2Sr, they were synthesized in the temperature range of 1100-1200 °C. The samples were subjected to heat treatment at a temperature of 700°C for 100 hours for homogenization. Then the samples were shaped as a parallelepiped with dimensions of 1.2 x 1.0 x 0.8 cm^3 and physical measurements were carried out. The temperature dependence of the electrical conductivity of solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)x$ (x=0.01; 0.02; 0.03) is shown in Figure 4.

With the introduction of 1; 2; 3 mol. % Ga_2Sr in the SrSe compound, the electrical conductivity, as is typical for semiconductors, increases depending on the composition and temperature.

For solid solution alloys with concentrations of 1; 2; 3 mol. % Ga_2Sr, impurity conductivity occurs in the temperature range of 300–450 K. Intrinsic conductivity begins at a temperature of 450 K. That is, electrons and holes participate in conductivity at this time.

As can be seen from Figure 4, for the samples containing 1; 2; 3 mol. % Ga_2Sr, the logarithmic values of electrical conductivity at room temperature were lgσ=-7.92 $Om^{-1}\cdot cm^{-1}$, lgσ=-7.85 $Om^{-1}\cdot cm^{-1}$ and lgσ=-7.78 $Om^{-1}\cdot cm^{-1}$, respectively. At 650 K, for the samples containing 1; 2; 3 mol. % Ga_2Sr, the logarithmic values of electrical conductivity were lgσ=-7.18 $Om^{-1}\cdot cm^{-1}$, lgσ=-7.10 $Om^{-1}\cdot cm^{-1}$ and lgσ=-7.05 $Om^{-1}\cdot cm^{-1}$, respectively.

Since the solubility limit of the Ga_2Sr compound in SrSe is not large (3.5 mol. %), it is very likely that the band structure of the obtained solid solutions is similar to the structure of SrSe. Based on this assumption, using the parameters of the zones, it is possible to calculate the electrical conductivity of the "heavy" (σ_1) and "light" (σ_2) holes and the reduced level of chemical potential (ή*) using the formulas; $\sigma= \sigma_1+ \sigma_2$

$$\sigma_1 = 2e\left(\frac{2\pi m_0 KT}{h^2}\right)^{3/2} \cdot F_0(\eta^*)\mu_{01}\left(\frac{m_1}{m_0}\right)^{3/2}$$

$$\sigma_2 = 2e\left(\frac{2\pi m_0 KT}{h^2}\right)^{3/2} \cdot F_0(\eta^* - \Delta)\mu_{01}\left(\frac{m_2}{m_0}\right)^{3/2}$$

Where e- is the electron charge, m_0- is the mass, K -is the Boltzmann constant, h- is the Planck constant, F_0- is the Fermi integral.

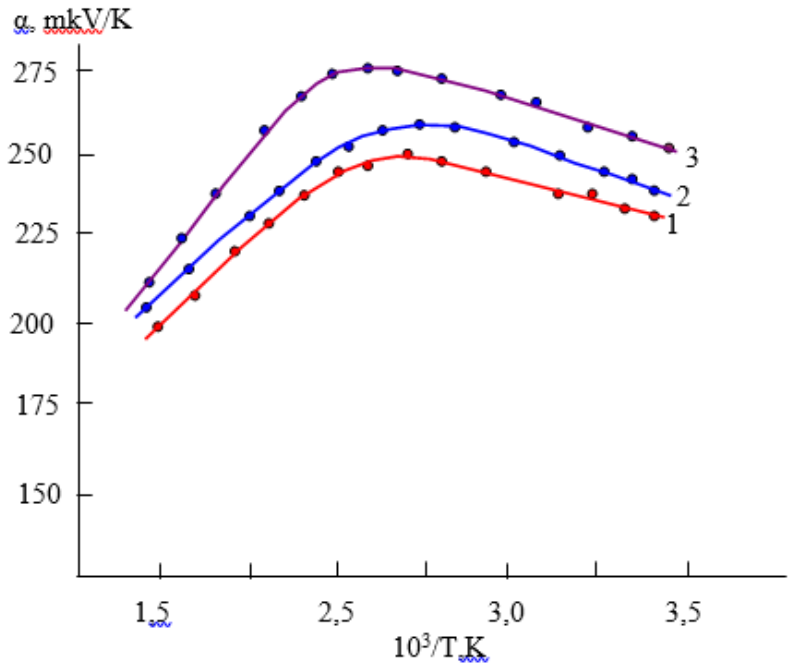

Fig. 5. Dependence of thermo-EMF of solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03) on composition and temperature. 1-1 mol. %, 2-2 mol. %, 3-3 mol. % Ga_2Sr.

Fig. 5 shows the temperature dependences of thermo-EMF of solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03) on composition and temperature. It follows that the thermo-EMF coefficient increases from room temperature to the transition temperature to intrinsic conductivity, and decreases in the intrinsic region. The temperature change in the thermo-EMF coefficient is in good agreement with the change in electrical conductivity of the specified solid solution alloys.

CONCLUSION

Using complex methods of physicochemical analysis, the chemical interaction in the Ga_2Sr–SrSe system was studied and its T-x phase diagram was constructed. The phase diagram of the system is quasi-binary, eutectic type. Eutectic coordinates: 25 mol % SrSe, temperature 850°C. In the Ga_2Sr–SrSe system at room temperature, solid solutions based on the Ga_2Sr compound reach 5 mol % SrSe, and based on SrSe-3.5 mol % Ga_2Sr. The lattice parameters were calculated as a result of X-ray diffraction analysis of solid solutions $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03). X-ray diffraction analysis of samples containing 1, 2 and 3 mol % Ga_2Sr, shows that these samples crystallize in the cubic syngony. The crystal lattice parameters increase accordingly in the following order: for the SrSe compound a = 6.243 Å and for solid solution alloys a = 6.263 Å (1 % Ga_2Sr) and a = 6.275 (2 % Ga_2Sr), a = 6.298 Å (3 % Ga_2Sr). The dependence of electrical conductivity and thermo-EMF of solid solution alloys $(SrSe)_{1-x}(Ga_2Sr)_x$ (x=0.01; 0.02; 0.03) on composition and temperature was studied.

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