

## PHASE EQUILIBRIUM OF La – Ga – Se AND DIELECTRIC SPECTROSCOPY OF SINGLE-CRYSTAL LaGaSe<sub>3</sub>

S.N. MUSTAFAEVA\*, M.M. ASADOV\*\*, \*\*\*, V.F. LUKICHEV\*\*\*\*

\*Institute of Physics, Ministry of Science and Education of Azerbaijan, Baku, AZ-1143

Azerbaijan, 131 G. Javid Ave

e-mail: solmust@gmail.com

\*\*Nagiyev Institute of Catalysis and Inorganic Chemistry, Ministry of Science and Education of Azerbaijan, Baku, AZ-1143 Azerbaijan, 113 G. Javid Ave.

e-mail: mirasadov@gmail.com

\*\*\*Scientific Research Institute of Geotechnological Problems of Oil, Gas and Chemistry, Baku, AZ-1010 Azerbaijan, 20 Azadliq Ave

\*\*\*\*Valiev Institute of Physics and Technology Institute, Russian Academy of Sciences, Moscow, 117218 Russia, 34 Nakhimovskiy Ave

It is shown that the grown LaGaSe<sub>3</sub> single crystal crystallizes in the hexagonal syngony with space  $P6_3/mmc$  and lattice parameters  $a = 3.722 \text{ \AA}$  and  $c = 15.721 \text{ \AA}$ . Taking into account the properties of binary selenides, the standard enthalpy of formation of the ternary compositions LaGaSe<sub>3</sub> and La<sub>6</sub>Ga<sub>10/3</sub>Se<sub>14</sub> was calculated, which were used to triangulate the La – Ga – Se system. Based on the  $T - x$  phase diagrams of the boundary systems La – Ga, La – Se and Ga – Se the enthalpy of formation of ternary phases, an isothermal cross section of the La – Ga – Se system in the solid state were constructed.

The frequency dispersion of the dielectric coefficients and conductivity of LaGaSe<sub>3</sub> has been studied. The nature of dielectric losses and the hopping mechanism of charge transfer in LaGaSe<sub>3</sub> are established. The parameters of localized states are calculated, such as the density of states near the Fermi level and their energy spread, the average time and distance of hops. The concentration of deep traps responsible for ac conduction in LaGaSe<sub>3</sub> was also determined.

**Keywords:** phase equilibrium, ternary La – Ga – Se, single-crystal LaGaSe<sub>3</sub>, dielectric characteristics, ac-conductivity parameters

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### 1. INTRODUCTION

Binary and complex chalcogenide compounds of rare earth elements (lanthanides) based on compositions La<sub>2</sub>X<sub>3</sub> (X = S, Se) [1,2] and semiconductors Ga<sub>2</sub>X<sub>3</sub> (X = S, Se) [3,4] are of practical interest. The presence of  $3d$ ,  $4f$  elements in ternary compounds, for example, La – Ga – X systems, makes them promising materials in the field of nonlinear optics and electronics. In particular, sulfide glasses of the La – Ga – S (LGS) system are laser materials with a wide transmission window in the IR range. LGS has a high glass transition temperature  $T_g = 580 \text{ }^\circ\text{C}$  and can be used in high temperature applications [5].

The double phase diagrams of the state of the systems La – Ga [6], La – Se [7,2], Ga – Se [8,3,4], limiting the La – Ga – Se ternary system, have been studied. But the properties of the phases in the La – Ga – Se ternary system have not been sufficiently studied.

State diagram of the system La<sub>2</sub>Se<sub>3</sub> – Ga<sub>2</sub>Se<sub>3</sub> presented in [9]. Alloys were studied by X-ray phase, thermal, chemical analysis and electrophysical measurements. The formation of one compound with the composition LaGaSe<sub>3</sub> was indicated. The melting temperature of the composition LaGaSe<sub>3</sub> is  $1120 \text{ }^\circ\text{C}$ . LaGaSe<sub>3</sub> has a hexagonal syngony with cell parameters  $a = 10.32 \text{ \AA}$ ,  $c = 6.28 \text{ \AA}$ . The paper [10] also indicated

the formation of one ternary compound, but with a different stoichiometric composition La<sub>6</sub>Ga<sub>10/3</sub>Se<sub>14</sub>. It is shown that this intermediate phase melts at  $1170 \text{ }^\circ\text{C}$  and has a hexagonal syngony with lattice parameters  $a = 10.53 \text{ \AA}$ ,  $c = 6.39 \text{ \AA}$ .

In a similar sulfide system La<sub>2</sub>S<sub>3</sub> – Ga<sub>2</sub>S<sub>3</sub> [11], the formation of a compound with a composition of 1:1 was also indicated. The LaGaS<sub>3</sub> compound has a monoclinic structure and the following lattice parameters (space group  $P2_1/c$ , № 14),  $a = 10.33(9) \text{ \AA}$ ,  $b = 12.82(6) \text{ \AA}$ ,  $c = 10.56(4) \text{ \AA}$ ,  $\gamma = 98.90(7) \text{ }^\circ$ ,  $V = 1381.6 \text{ \AA}^3$ ,  $Z = 12$ . In the LaGaS<sub>3</sub> structure, gallium atoms have tetrahedral coordination (GaS<sub>4</sub>). One lanthanum atom La(1) is nine-coordinated with sulfur atoms [La(1)S<sub>9</sub>], and the other two La(2) and La(3) are eight-coordinated with [La(2)S<sub>8</sub>], [La(3)S<sub>8</sub>]. The LaGaS<sub>3</sub> phase has the  $\beta$  – LaGaS<sub>3</sub> polymorph, which crystallizes in  $Pna2_1$  (№ 33);  $a = 10.405(1) \text{ \AA}$ ,  $b = 21.984(2) \text{ \AA}$ ,  $c = 6.0565(5) \text{ \AA}$ ,  $V = 1385.3(2) \text{ \AA}^3$  and  $Z = 12$  [12]. Also known is the La<sub>6</sub>Ga<sub>3.33</sub>S<sub>14</sub> composition phase (hexagonal syngony; Ce<sub>6</sub>Al<sub>3.33</sub>S<sub>14</sub> type) [13].

It follows from the analysis of these that the phase relationships in the La<sub>2</sub>Se<sub>3</sub> – Ga<sub>2</sub>Se<sub>3</sub> system have not been precisely established. Triangulation of the La – Ga – Se ternary system has also not been carried out. In addition, single crystals and the physical properties of samples of this ternary system are almost not studied.

The purpose of the work is the thermodynamic analysis of the La – Ga – Se system, the identification of the lattice parameters of the grown single crystal LaGaSe<sub>3</sub>, the study of the electrical properties of the samples in alternating electric fields of the radio frequency range.

The study of the dielectric properties and electrical conductivity of La – Ga – Se system crystals at direct and alternating current can provide information on the parameters of charge transfer and on localized states in the band gap.

The frequency dependence of electrophysical parameters is important for establishing the mechanism of electrical conductivity on alternating current. The mechanism of charge transfer in La – Ga – Se system single crystals has not yet been studied.

## 2. EXPERIMENTAL PART

### 2.1. Growing a single crystal

Methods for the synthesis and growth of crystals of chalcogenide phases are known. In particular, lanthanum chalcogenides are obtained by the method of solid-phase synthesis [12]. LaGaSe<sub>3</sub> crystals were synthesized by the solid-phase synthesis method by using pure ready-made starting chemical elements La (Alfa Aesar China (Tianjin) Co., Ltd., 99.9%), Ga (Sinopharm Chemical Reagent Co., Ltd., 99.99%) and Se (Sinopharm Chemical Reagent Co., Ltd., 99.99%). A stoichiometric mixture of elements with a total mass of about 300 mg La, Ga and Se (molar ratio 1:1:3) was weighed and placed in a graphite crucible. The crucible loaded with components was placed in a quartz ampoule, which was sealed to 10<sup>-3</sup> Pa.

The ampoule with the components was placed in a tubular electric furnace with controlled temperature. The furnace temperature was raised to 450 °C and the ampoule was held for 10 h. Then the furnace temperature was raised to 1100 °C for 20 h. The ampoule was kept for 120 h, then cooled to 820 °C for 2 h and kept for 120 hours. Finally, the ampoule was cooled to room temperature for 72 hours. Dark red LaGaSe<sub>3</sub> crystals were obtained. The resulting compound was stable in air for a long time.

The completion of the synthesis of LaGaSe<sub>3</sub> polycrystals and their individuality were controlled by X-ray diffraction (XRD) analysis. XPA of powder crystal samples was carried out on a D8-ADVANCE diffractometer in the mode 0.5° < 2θ < 80° (Cu Kα radiation; λ = 1.5418 Å) at 40 kV and 40 mA.

The growth of the LaGaSe<sub>3</sub> single crystal was carried out by the Bridgman-Stockbarger method. The pre-synthesized LaGaSe<sub>3</sub> ingot was loaded into a graphitized double quartz ampule with a tapered end. The ampoule was pumped out to a residual pressure of 10<sup>-3</sup> Pa and placed in a two-temperature furnace. The temperature in the furnace in the first zone (melt zone) was maintained at 1120–1170 °C, and in the second zone (crystal annealing zone) at 1100–1120 °C.

The ampoule with the melt was kept in the furnace for 24 h, and then the ampoule was lowered through the crystallization front into the crystal annealing zone at a

rate of 0.1–0.2 mm/h at a temperature gradient of 20–30 K/cm. The resulting crystals were annealed for 150 h. LaGaSe<sub>3</sub> single crystals 10 mm in diameter and up to 50 mm long were grown.

### 2.2. Measurement technique

Single-crystal LaGaSe<sub>3</sub> samples for electrical measurements were made in the form of flat capacitors. Silver paste was used as contacts to the LaGaSe<sub>3</sub> samples. The thickness of single-crystal samples was 0.3 cm.

The dielectric coefficients of LaGaSe<sub>3</sub> single crystal samples were measured by the resonance method [14] using a Q-factor meter BM-560 [15]. The frequency range of the alternating electric field was 5 × 10<sup>4</sup>–3.5 × 10<sup>7</sup> Hz. Electrical measurements of the samples were carried out in a shielded chamber. All dielectric measurements were carried out at 298 K.

The dielectric properties of materials, which describe their interaction with an electric field, is determined by the known equations

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad (1)$$

$$\varepsilon' = \varepsilon_r \varepsilon_0 \quad (2)$$

$$\varepsilon'' = \varepsilon' \operatorname{tg} \delta. \quad (3)$$

where  $\varepsilon'$  is the real part of the permittivity,  $\varepsilon''$  is the imaginary part of the permittivity (dielectric loss factor),  $\varepsilon_r$  is the relative permittivity,  $\varepsilon_0 = 8.85 \times 10^{-12}$  F/m is the electrical constant,  $\delta$  is the dielectric loss angle.

The amplitude of the alternating electric field applied to the samples on the measuring device corresponded to the Ohmic region of the current-voltage characteristic. The accuracy of determining the resonant values of capacitance and quality factor  $Q = 1 / \operatorname{tg} \delta$  of the measuring circuit corresponded to the errors of the device. The calibration of the device capacitor had an accuracy of ± 0.1 pF. The reproducibility of the resonance position was ± 0.2 pF in terms of capacitance, and ± 1.0–1.5 divisions of the scale in terms of quality factor. The largest deviations from the average values were 3–4% for the permittivity ( $\varepsilon'$ ) and 7% for  $\operatorname{tg} \delta$ .

## 3. RESULTS AND DISCUSSION

### 3.1. Structure

The diffraction patterns taken on powder samples from different parts of the single crystal corresponded to the hexagonal structure (Fig. 1). Unit cell parameters calculated by the least squares method from the reflections of 2θ angles. It has been established that the compound LaGaSe<sub>3</sub> crystallizes in the hexagonal syngony with the space group  $P6_3/mmc$ ;  $a = 3.722$  Å and  $c = 15.72$  Å. These parameters differ from the hexagonal parameters given in [9]. The crystal lattice of LaGaSe<sub>3</sub> is deformed in the direction of the  $c$ -axis of the crystal. Such a deformation of the cell may be due to a significant difference in the ionic and/or atomic radii of Ga and La: (Ga<sup>3+</sup> 0.62; Ga 1.41 Å), respectively (La<sup>3+</sup> 1.17; La 1.95 Å).

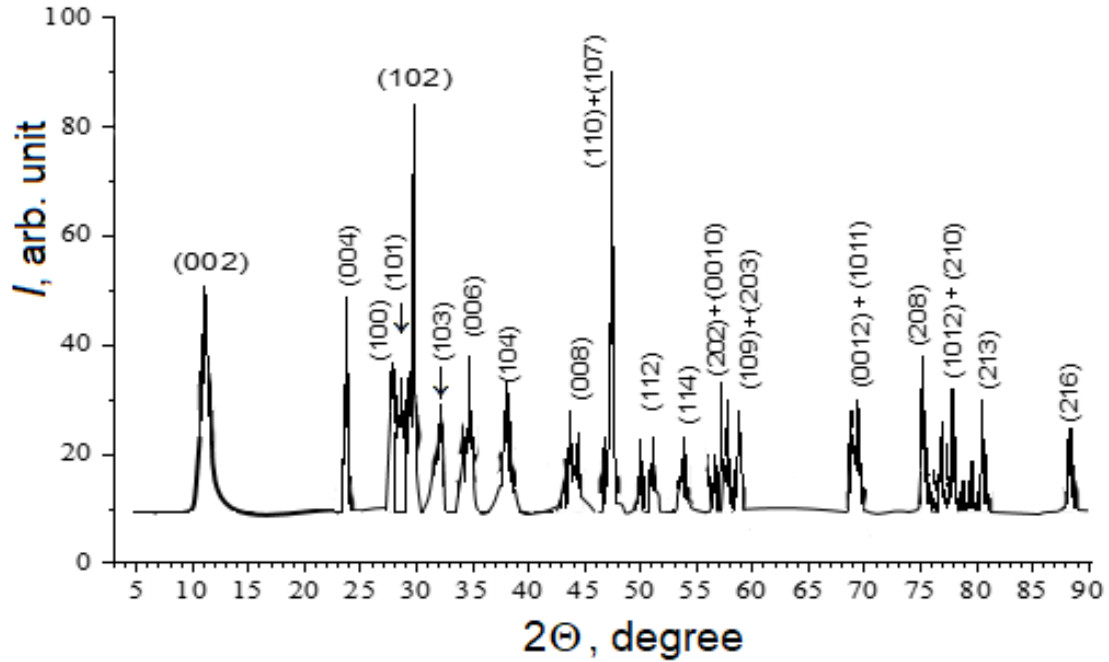


Fig. 1. X-ray diffraction pattern of the LaGaSe<sub>3</sub> powder sample with the component ratio La<sub>2</sub>Se<sub>3</sub>: Ga<sub>2</sub>Se<sub>3</sub> = 1:1.

### 3.2. Binary systems

The ternary system La – Ga – Se consists of binary boundary systems La – Ga, Ga – Se and La – Se. From the analysis of the phase diagrams of binary systems, it follows that they are characterized by the formation of several binary compounds. The coordinates of the connections of binary systems are shown in Figs. 2a,b,c.

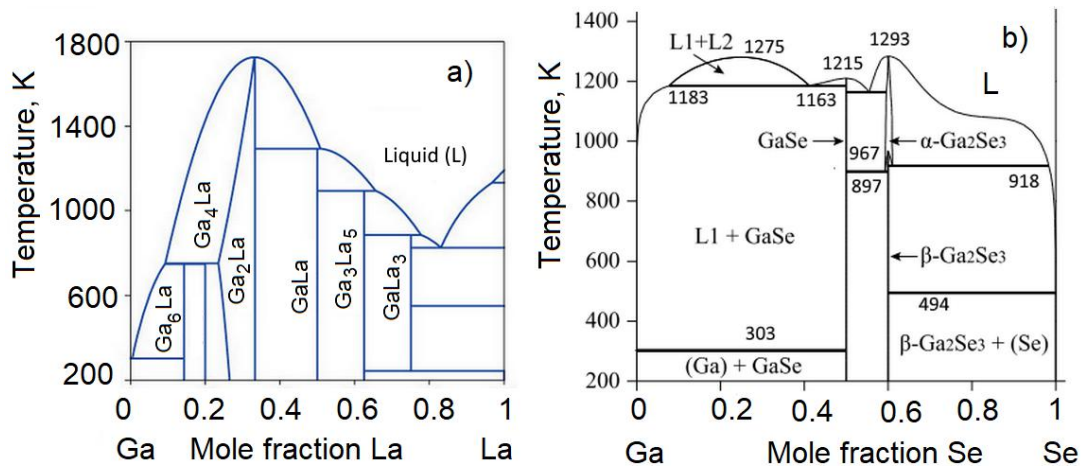
As can be seen, the phase diagrams involving lanthanum are more complex than the diagram of the Ga – Se system. In addition, in the La – Ga, La – Se diagrams, it is necessary to take into account the phase transitions of lanthanum. The average values of phase transitions for lanthanum are:  $\alpha \rightarrow \beta$  563 ± 38 K,  $\beta \rightarrow \gamma$  1133 ± 6 K, and the melting point  $T_m = 1189 \pm 2$  K.

In the La – Ga and La – Se binary systems, six compounds are formed in each (Figs. 2a,c), and in the

Ga – Se system, two intermediate phases are formed: GaSe and Ga<sub>2</sub>Se<sub>3</sub> (Fig. 2b).

Note that the physical properties of semiconductor compounds of the Ga – Se system have been studied relatively more than compounds of the La – Se system. GaSe has a layered crystal structure and is characterized by anisotropy of properties. The Ga<sub>2</sub>Se<sub>3</sub> compound has two polymorphic modifications:  $\alpha$  – Ga<sub>2</sub>Se<sub>3</sub> (structure type ZnS) and  $\beta$  – Ga<sub>2</sub>Se<sub>3</sub> (structure type Ga<sub>2</sub>Se<sub>3</sub>). The temperature of the polymorphic transition  $\alpha \rightarrow \beta$  is 967 K, and  $T_m = 1293$  K.

Table 1 shows crystallographic data for binary and ternary selenides found in the La – Ga – Se system.



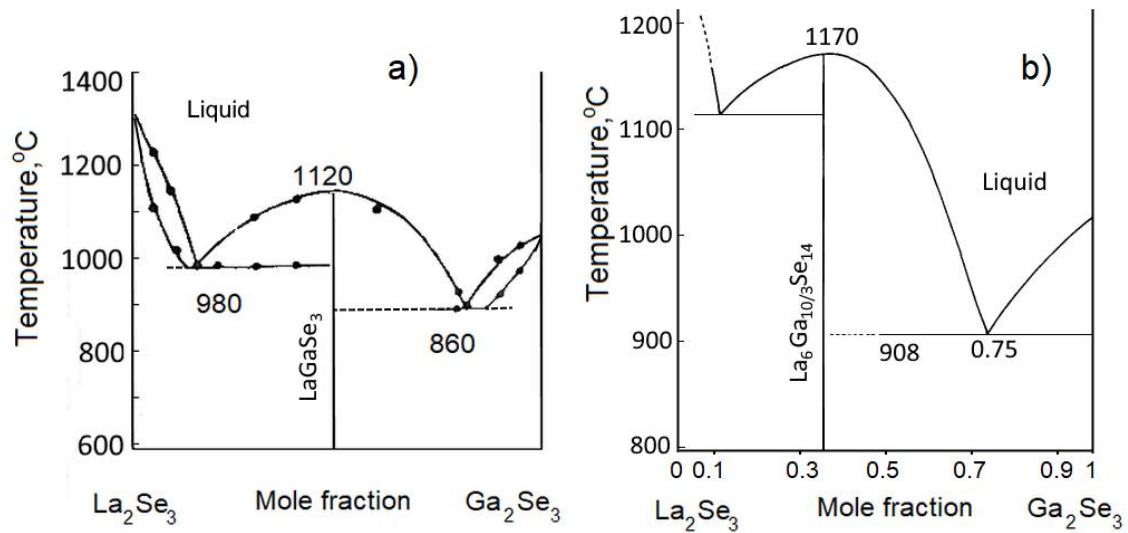


Fig. 2. Phase diagrams of binary systems: a) La – Ga [6], b) Ga – Se [4], c) La – Se [7], d) La – Se [This work].

Table 1.

Crystallographic data for the compounds of La – Ga – Se system

Compound	Structure type	Space group	Cell parameters, Å			Ref.
			<i>a</i>	<i>b</i>	<i>c</i>	
La <sub>2</sub> Se <sub>3</sub>	Th <sub>3</sub> P <sub>4</sub>	<i>I</i> – 43 <i>d</i>	9.0521			[16]
β – Ga <sub>2</sub> Se <sub>3</sub>	Ga <sub>2</sub> Se <sub>3</sub>	<i>Cc</i>	6.6608	11.6516	6.6449	[17]
α – Ga <sub>2</sub> Se <sub>3</sub>	ZnS	<i>F</i> – 43 <i>m</i>	5.463			[18]
α – LaGaSe <sub>3</sub>	LaGaSe <sub>3</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	10.399	12.826	10.564	[19]
β – LaGaSe <sub>3</sub>	Ag <sub>8</sub> SiS <sub>6</sub>	<i>P</i> <i>na</i> 2 <sub>1</sub>	10.15	21.9835	6.0565	[12,13]
La <sub>3</sub> Ga <sub>1.67</sub> Se <sub>7</sub>	La <sub>3</sub> CuSiS <sub>7</sub>	<i>P</i> 6 <sub>3</sub>	10.67		6.10	[10]
LaGaSe <sub>3</sub>			10.32		6.28	[9]
LaGaSe <sub>3</sub>	GaS	<i>P</i> 6 <sub>3</sub> / <i>mmc</i>	3.722		15.72	This work

### 3.3. Enthalpy of formation

Gibbs free energy ( $G$ ) or thermodynamic potential, as is known, characterizes the change in the internal energy of the system during a chemical reaction. Those. the quantity  $G$  is the total potential chemical energy of the system. In reactions, the change in free energy shows what part of the total internal energy of the system is used for chemical transformations. The  $G$  value allows to set the possibility of a chemical reaction occurring under given conditions ( $P, V, T$ ), where  $P$  is pressure,  $V$  is volume,  $T$  is temperature. With this in mind, the thermodynamic potential  $G$  is written as:  $G = U + PV - TS$ , where  $U$  is the internal energy, which is a function of the entropy  $S$  and the generalized coordinates of the system  $x_1, x_2 \dots$ . In an isobaric process occurring in the system at constant pressure and mass of matter enthalpy  $H = U + PV$ .

The Helmholtz free energy ( $F$ ), like  $G$ , is also a thermodynamic potential. The decrease in  $F$  in a quasi-static isothermal process is equal to the work done by the system on external bodies:  $F = U - TS$ . Then the Gibbs potential is  $G = H - TS = F + PV = U + PV - TS$ .

Thus, the thermodynamic potentials, which are functions of the corresponding variables, are the canonical equations of state for a given system. More precisely, thermodynamic potentials are functions:  $= U(S, V)$ ,  $H = H(S, P)$ ,  $F = F(T, V)$ ,  $G = G(T, P)$ . Knowledge of these functions allows obtaining information about the properties of the system. They are valid for equilibrium states. In nonequilibrium states of the system, these equations are not satisfied.

The thermodynamic method Calphad (Calculation of Phase Diagrams) allows one to calculate phase equilibria in multicomponent systems. In this case, the thermodynamic properties of both binary and multicomponent systems are taken into account. Various software products (ThermoCalc, MTDATA, FactSage) and paid databases are used in the calculations.

The thermodynamic properties of phases in ternary or quaternary systems can also be estimated using semi-empirical geometric or polynomial models [20]. In such models, the properties of the ternary system are calculated through a combination of the properties of three boundary binary systems, taking into account the weight coefficients of the properties.

Excess thermodynamic functions are the excess of some property of a real solution over the corresponding

property of an ideal solution of the same composition for the same  $T$  and  $P$ :  $g_{\text{general}}^E = g_{\text{general}}(\text{real solution}) - g_{\text{general}}(\text{ideal solution})$ , thermodynamic property of the system, superscript  $E$  denotes the excess of the function.

Excessive thermodynamic characteristics (excess Gibbs energy  $G^E$  of mixing, enthalpy of mixing  $H^E$  and excess entropy  $S^E$ ) of binary systems ( $i - j, i - k, j - k$ ) allow us to estimate the degree of deviation of the properties of the ternary system ( $i - j - k$ ) from the ideal behavior ( $G^E = 0$ ). If  $G^E > 0$ , then positive deviations of properties from ideality occur in the system, and when  $G^E < 0$ , negative deviations from ideality occur due to intermolecular interaction.

The partial excess Gibbs energies  $\Delta G_i^E(x_i, T)_P$  of boundary binary systems make it possible to calculate

the properties of a ternary system at different temperatures and compositions. The excess Gibbs energy in the ternary and corresponding binary systems are related by the equation

$$\Delta G_{ijk}^E = W_{ij}\Delta G_{ij}^E + W_{jk}\Delta G_{jk}^E + W_{ik}\Delta G_{ik}^E \quad (4)$$

where  $\Delta G_{ijk}^E$  and  $\Delta G_{ij}^E, \Delta G_{jk}^E, \Delta G_{ik}^E$  are the excess Gibbs energy in the ternary and corresponding binary systems at the same ratio of the molar fractions of these components as in the ternary system, respectively,  $W_{ij}, W_{jk}, W_{ik}$  are the weight coefficients of the components of the corresponding binary systems. The weight coefficient formulas in the geometric models and the mass triangle models are given in Table 2.

Table 2.

Weight coefficients in known semi-empirical models for calculating thermodynamic properties in a ternary system

Model	$W_{ij}$ in geometrical model	$W_{ij}$ in mass triangle model
Kohler (1960)	$W_{i(ij)} = (x_i + x_j)^2$	$W_{i(ij)}^M = (x_i + x_j)/2$
Toop (1965)	$\begin{cases} W_i = W_k = x_j/(x_j + x_k) \\ W_j = (x_j + x_k)^2 \end{cases}$	$\begin{cases} W_i^M = W_k^M = x_j/(x_j + x_k) \\ W_j^M = 0 \end{cases}$
Muggianu-Jacob (1977)	$W_{i(ij)} = 4x_i x_j / (1 + x_i - x_j) / (1 - x_i + x_j)$	
Hillert (1980)	$\begin{cases} W_i = W_k = x_j/(x_j + x_k) \\ W_j = 4x_i x_j / (1 + x_j - x_k) / (1 - x_j + x_k) \end{cases}$	$\begin{cases} W_i^M = W_k^M = x_j/(x_j + x_k) \\ W_j^M = 0 \end{cases}$
Luck-Chou (1987)	$W_{i(ij)} = x_i x_j / (x_i x_j + x_j x_k)$	$W_{i(ij)}^M = x_i x_j / (x_i x_j + x_j x_k + x_i x_k)$

Despite the fact that alloys of binary boundary systems in La – Ga – Se have been studied for a long time, information on the thermodynamic characteristics of ternary phases is not known. The stability of intermetallic and selenide phases in the La – Ga – Se system was evaluated by calculating the enthalpy of phase formation. The enthalpies of formation of intermediate phases under standard conditions are negative.

The enthalpies of formation of binary compounds La<sub>2</sub>Se<sub>3</sub> and Ga<sub>2</sub>Se<sub>3</sub> at 298 K obtained from experimental data have relatively high absolute values:  $-\Delta_f H_{298}^0(\text{La}_2\text{Se}_3) = 933.03 \pm 20.92$  kJ/mol [1, 2],  $-\Delta_f H_{298}^0(\text{Ga}_2\text{Se}_3) = 397.5 \pm 37.65$  kJ/mol [21].

The standard enthalpies of formation  $\Delta_f H_{298}^0$  calculated by us for the ternary phases of the La – Ga – Se system, taking into account the averaged data  $\Delta_f H_{298}^0$  for binary compounds, are given in Table 3.

Table 3.

Additively calculated standard enthalpies of formation  $\Delta_f H_{298}^0$  of the phases of the La – Ga – Se system

Compound	$-\Delta_f H_{298}^0, \text{kJ/mol}$	
	experiment	calculation
La <sub>2</sub> S <sub>3</sub>	1179.9 ± 16.74 [1]	
La <sub>2</sub> Se <sub>3</sub>	933 ± 21 [22]	
Ga <sub>2</sub> S <sub>3</sub>	502.5 ± 8.37 [23]	
$\alpha$ – Ga <sub>2</sub> Se <sub>3</sub>	384.93 ± 16.74 [23]	
$\alpha$ – LaGaS <sub>3</sub>		1786
LaGaSe <sub>3</sub>		1360
La <sub>3</sub> Ga <sub>1.67</sub> Se <sub>7</sub>		3508

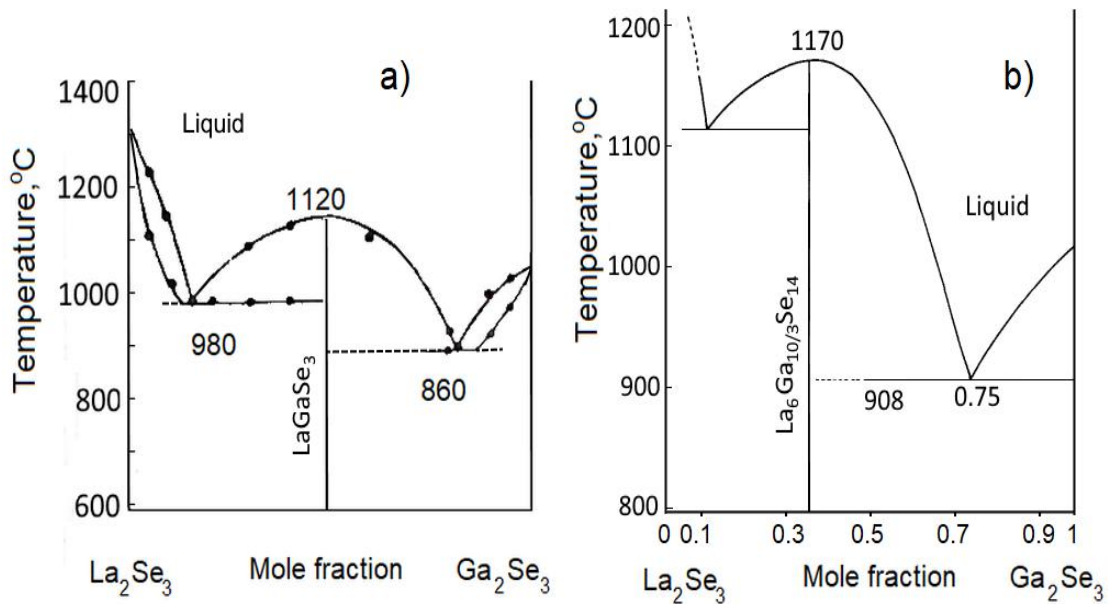


Fig. 3. Phase diagram of the  $\text{Ga}_2\text{Se}_3 - \text{La}_2\text{Se}_3$  system: a) [9], b) [10].

If we take into account deviations from the additive values  $\Delta_f H_{298}^0$  of binary phases, then it is obvious that for real ternary phases  $\Delta_f H_{298}^0$  will be even smaller. This is due to the fact that the formation of a ternary phase from binary compounds in a chemical reaction occurs due to a decrease in the Gibbs free energy ( $\Delta_f G_T^0$ ) of the system. In this case,  $\Delta_f G_T^0$  of the ternary phase must obviously be less than the  $\Delta_f G_T^0$  calculated additively from  $\Delta_f G_T^0$  of binary compounds. The above is also true for the value  $\Delta_f H_{298}^0$  of the ternary phases.

### 3.4. La – Ga – Se system

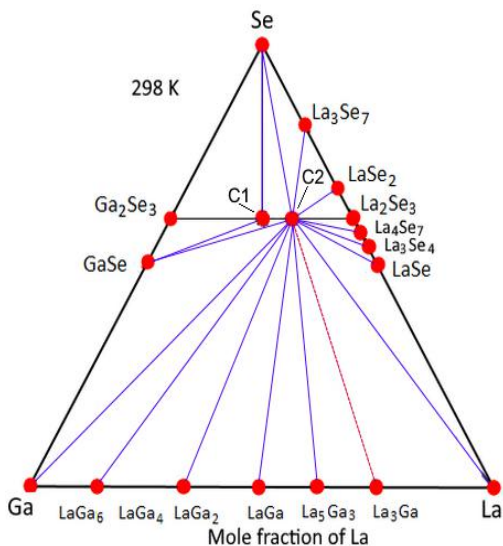


Fig. 4. Phase relations in the La – Ga – Se system at 298 K. C1– $\text{LaGaSe}_3$ , C2– $\text{La}_3\text{Ga}_{1.67}\text{Se}_7$ .

The intermediate phases of the compositions  $\text{LaGaSe}_3$  (Fig. 3a) and  $\text{La}_3\text{Ga}_{1.67}\text{Se}_7$  (Fig. 3b) determine the stability of cuts in the solid state of the La – Ga – Se system.

Fig. 4 shows the phase relations of the La – Ga – Se system constructed by us in the subsolidus region.

### 3.5. Dielectric Properties

Fig. 5 shows the frequency dependence of the real component of the complex permittivity ( $\epsilon'$ ) of the  $\text{LaGaSe}_3$  sample.

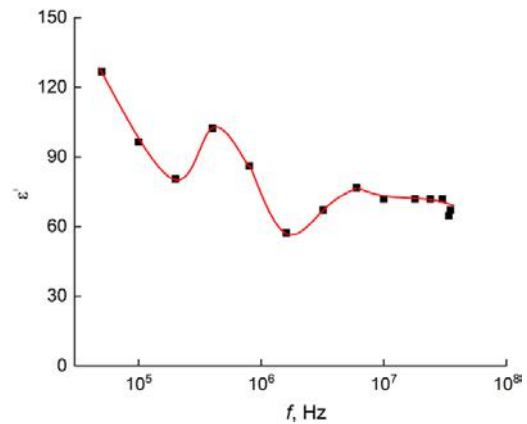


Fig. 5. Frequency dispersion of the real component of the complex permittivity of a  $\text{LaGaSe}_3$  single crystal.

It is seen from Fig.5 that a significant dispersion  $\epsilon'$  is observed in the entire studied frequency range. The experimentally observed decrease in the permittivity of a single crystal with an increase in frequency from  $5 \times 10^4$  to  $3.5 \times 10^7$  Hz indicates relaxation dispersion.

Fig. 6 shows the frequency dependence of the imaginary component of the complex permittivity ( $\epsilon''$ ) of a  $\text{LaGaSe}_3$  single crystal. The dispersion curve  $\epsilon''(f)$  was characterized by a rather noticeable decrease in the entire studied frequency range. At  $f = 5 \times 10^4$  Hz, the value of  $\epsilon''$  of the  $\text{LaGaSe}_3$  single crystal was almost 6 times higher than the value of  $\epsilon''$  at  $3.5 \times 10^7$  Hz.

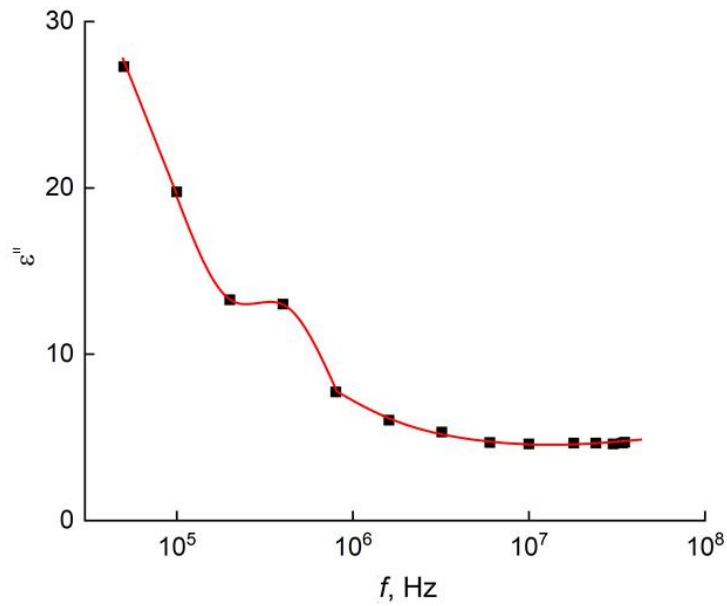


Fig. 6. Frequency dispersion of the imaginary component of the complex permittivity of a LaGaSe<sub>3</sub> single crystal.

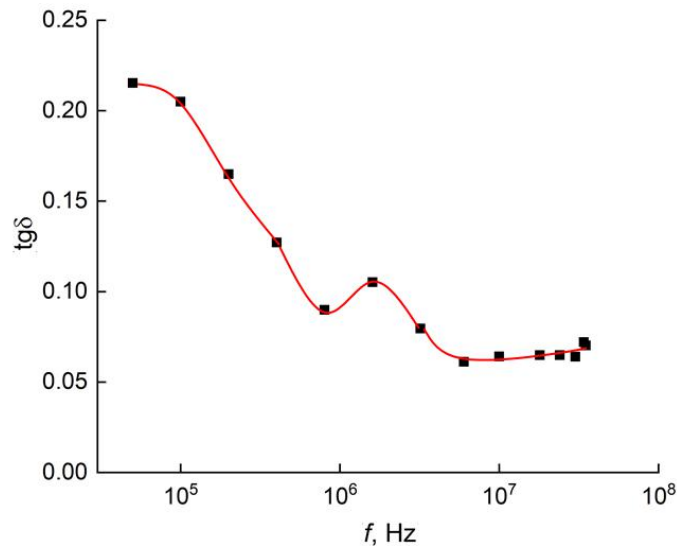


Fig. 7. Frequency dependence of the dielectric loss tangent in a LaGaSe<sub>3</sub> single crystal.

The frequency dependence of the dielectric loss tangent ( $\text{tg}\delta$ ) in the studied LaGaSe<sub>3</sub> single crystals is shown in Fig. 7. The decrease in  $\text{tg}\delta$  with increasing frequency in LaGaSe<sub>3</sub> single crystals indicate a loss of through conduction.

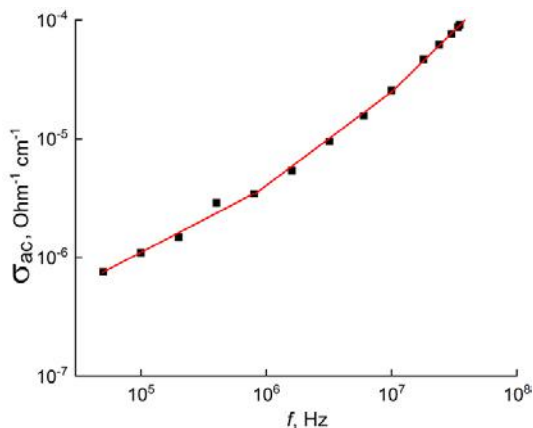


Fig. 8. Frequency-dependent ac conductivity of a LaGaSe<sub>3</sub> single crystal at 300 K.

Fig. 8 shows the experimental results of studying the frequency-dependent ac-conductivity of the LaGaSe<sub>3</sub> single crystal at 300 K. In the frequency range  $5 \times 10^4 - 8 \times 10^5$  Hz, the ac-conductivity of the LaGaSe<sub>3</sub> single crystal varied according to the law  $\sigma_{ac} \sim f^{0.6}$ , and at  $f = 8 \times 10^5 - 10^7$  Hz  $\sigma_{ac} \sim f^{0.8}$ . At  $f > 10^7$  Hz, a linear dependence  $\sigma_{ac} \sim f$  took place.

It follows from the experiment that band-type ac-conductivity ( $\sigma_{ac}$ ) in semiconductors and dielectrics is mainly frequency-independent up to  $10^{10} - 10^{11}$  Hz. The experimental dependence  $\sigma_{ac} \sim f^{0.8}$  of sample LaGaSe<sub>3</sub> observed by us indicates that  $\sigma_{ac}$  is due to charge carrier hops between states localized in the band gap. These can be states localized near the edges of allowed bands or states localized near the Fermi level. In experiments, the conductivity over states near the Fermi level dominates over the conductivity over states near the edges of allowed bands.

Therefore, the law  $\sigma_{ac} \sim f^{0.8}$  obtained by us testifies to the hopping mechanism of charge transfer

through states localized in the vicinity of the Fermi level [24,25]:

$$\sigma_{ac}(f) = \frac{\pi^3}{96} e^2 k T N_F^2 a_L^5 f \left[ \ln \left( \frac{\nu_{ph}}{f} \right) \right]^4, \quad (5)$$

where  $e$  is the electron charge;  $k$  is the Boltzmann constant;  $N_F$  is the density of states near the Fermi level;  $a_L = 1/\alpha$  – localization radius;  $\alpha$  is the decay constant of the wave function of the localized charge carrier  $\psi \sim e^{-\alpha r}$ ;  $\nu_{ph}$  is the phonon frequency.

According to formula (5), ac-conductivity depends on frequency as  $f [\ln(\nu_{ph}/f)]^4$ , i.e. at  $f \ll \nu_{ph}$ , the value of  $\sigma_{ac}$  is approximately proportional to  $f^{0.8}$ . Using formula (5), the experimentally found values of  $\sigma_{ac}(f)$  were used to calculate the density of states at the Fermi level. The calculated  $N_F$  value for the LaGaSe<sub>3</sub> single crystal was  $N_F = 4.3 \times 10^{18} \text{ eV}^{-1} \cdot \text{cm}^{-3}$ . When calculating  $N_F$ , the value  $a_L = 34 \text{ \AA}$  was taken for the localization radius [25]. And the value of  $\nu_{ph}$  for LaGaSe<sub>3</sub> is taken equal to  $10^{12} \text{ Hz}$ .

According to the theory of hopping conduction on alternating current, the average hopping distance ( $R$ ) is determined by the following formula [24]:

$$R = \frac{1}{2\alpha} \ln \left( \frac{\nu_{ph}}{f} \right). \quad (6)$$

In formula (6), the value of  $f$  corresponds to the average frequency at which  $f^{0.8}$  is observed - the law. The value of  $R$  calculated by formula (6) for the LaGaSe<sub>3</sub> single crystal was  $207 \text{ \AA}$ . This value of  $R$  is approximately 6 times greater than the average distance between charge carrier localization centers in a LaGaSe<sub>3</sub> single crystal.

The value of  $R$  allowed by the formula

$$\tau^{-1} = \nu_{ph} \cdot \exp(-2\alpha R) \quad (7)$$

determine the average hopping time in a LaGaSe<sub>3</sub> single crystal:  $\tau = 1.85 \times 10^{-7} \text{ s}$ .

According to the formula:

$$\Delta E = \frac{3}{2\pi R^3 \cdot N_F} \quad (8)$$

in LaGaSe<sub>3</sub> the spread of states localized near the Fermi level was estimated:  $\Delta E = 0.013 \text{ eV}$ .

And according to the formula:

$$N_t = N_F \cdot \Delta E \quad (9)$$

the concentration of deep traps in LaGaSe<sub>3</sub>, which are responsible for ac-conductivity at alternating current, was determined:  $N_t = 5.6 \times 10^{16} \text{ cm}^{-3}$ .

## 4. CONCLUSION

A dark red LaGaSe<sub>3</sub> single crystal was grown in the La – Ga – Se system. According to XRD data, LaGaSe<sub>3</sub> crystallizes in the hexagonal syngony with space group  $P6_3/mmc$  and lattice parameters  $a = 3.722 \text{ \AA}$  and  $c = 15.72 \text{ \AA}$ . The crystal lattice of LaGaSe<sub>3</sub> is deformed in the direction of the c-axis of the crystal. The enthalpy of formation of LaGaSe<sub>3</sub> has been calculated. Compared to LaGaSe<sub>3</sub>, its sulfide analog LaGaS<sub>3</sub> has a higher absolute enthalpy of formation. An isothermal cross section of the La – Ga – Se ternary system at 298 K is constructed. In the isothermal cross section of the La<sub>3</sub>Ga<sub>1.67</sub>Se<sub>7</sub> and LaGaSe<sub>3</sub> phases are in equilibrium with the binary compounds of the La – Ga, La – Se and Ga – Se boundary systems.

The study of the frequency dependences of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) components of the complex permittivity, dielectric loss tangent, and ac-conductivity ( $\sigma_{ac}$ ) in the frequency range  $f = 5 \times 10^4 - 3.5 \times 10^7 \text{ Hz}$  of single crystal LaGaSe<sub>3</sub> showed the following.

In the indicated frequency range, relaxation dielectric dispersion took place in LaGaSe<sub>3</sub> and losses of through conduction were observed. At  $f = 8 \times 10^5 - 10^7 \text{ Hz}$  in LaGaSe<sub>3</sub> single crystals, the frequency dependence of the conductivity obeyed the regularity  $\sigma_{ac} \sim f^{0.8}$ , which is characteristic of the hopping mechanism of charge transfer along states localized near the Fermi level.

The following parameters were calculated: density of states ( $N_F = 4.3 \times 10^{18} \text{ eV}^{-1} \cdot \text{cm}^{-3}$ ) and their energy spread ( $\Delta E = 0.013 \text{ eV}$ ), average time ( $\tau = 1.85 \times 10^{-7} \text{ s}$ ) and distance ( $R = 207 \text{ \AA}$ ) jumps of charge carriers in a LaGaSe<sub>3</sub> single crystal.

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## Conflict of interest

The authors declare that they have no conflicts of interest.

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