DFT CALCULATION OF ELECTRONIC PROPERTIES, ENTHALPY OF FORMATION OF $LaGaX_3$ ($X = S, Se$) AND TRIANGULATION IN $La - Ga - X$ SYSTEMS

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The electronic properties of ternary semiconductor compounds of $La - Ga - X$ ($X = S, Se$) systems were calculated by the DFT SGGA method. The standard enthalpies of formation and structural parameters of the ternary compounds $LaGaSe_3$ and $La_3Ga_{1.67}X_7$ were also calculated. Quasi-binary phase diagrams are adapted, in which two compounds $LaGaSe_3$and $La_3Ga_{1.67}X_7$ are formed. Triangulation of $La - Ga - X$ systems was carried out on the basis of thermodynamic data and the results of analysis of $T - x$ diagrams of binary and quasi-binary subsystems. The grown $LaGaSe_3$ single crystals have a hexagonal structure with space group $P6_3/mmc$ and lattice parameters a = 3.722 Å and c = 15.72 1 Å.

Keywords: DFT SGGA method, phase formation, $La - Ga - X$ ($X = S, Se$) ternary system, calculation, enthalpies of formation, structure, $LaGaX_3$, $La_3Ga_{1.67}X_7$.
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1. INTRODUCTION

Binary and ternary lanthanide chalcogenides based on La_2X_3($X = S, Se$) [1] and semiconductors Ga_2X_3($X = S, Se$) [2] are of practical interest. The presence of $3d$, $4f$ elements in $La - Ga - X$ ternary compounds make them promising materials for 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 relatively high glass transition temperature T_g= 580 °C and can be used in high temperature applications [3]. Binary phase diagrams of $La - Ga$ [4], $La - X$ [4], $Ga - X$ [2,4], limiting the $La - Ga - X$ system are known. They form binary compounds of various compositions. Intermediate phases are also formed in the $La - Ga - X$ ternary system. For example, along the $La_2X_3 - Ga_2X_3$ cuts, compounds of $LaGaX_3$ and $La_3Ga_{1.67}X_7$ [5,6] composition are formed. However, the properties of these compositions of the $La - Ga - X$ phases have not been sufficiently studied.

In the $La_2S_3 - Ga_2S_3$ system [5], compounds of $LaGaS_3$ and $La_3Ga_{1.67}S_7$ composition are formed. The $\alpha - LaGaS_3$ compound has a monoclinic structure and the following lattice parameters (space group $P2_1/c$, № 14), a = 10.33(9) Å, b = 12.82(6) Å, c = 10.56(4) Å, γ = 98.90 (7)°, V = 1381.6 Å^3, Z = 12. In the $\alpha - LaGaS_3$ structure, gallium atoms have tetrahedral coordination with sulfur atoms (GaS_4). And individual lanthanum atoms are linked to sulfur atoms in three different coordinations. Out of every three lanthanum atoms, one lanthanum atom La(1) is nine-coordinated [$La(1)S_9$], and the other two La(2) and La(3) are eight-coordinated [$La(2)S_8$], [$La(3)S_8$] with sulfur atoms. The $\alpha - LaGaS_3$ phase has the $\beta - LaGaS_3$ polymorph, which crystallizes in $Pna2_1$ (№ 33); a = 10.405(1) Å, b = 21.984(2) Å, c = 6.0565(5) Å, V = 1385.3(2) Å^3 и Z = 12 [7]. The $La_3Ga_{1.67}S_7$ phase has a hexagonal structure of the $Ce_3Al_{1.67}S_7$ type.

Alloys of the $La_2Se_3 - Ga_2Se_3$ system were studied by X-ray thermal chemical analysis and electrophysical measurements [6]. The formation of $LaGaSe_3$ compound with a melting point of 1120 °C was indicated. $LaGaSe_3$ has a hexagonal syngony with cell parameters a = 10.32 Å, c = 6.28 Å. In the $La_2Se_3 - Ga_2Se_3$ system, a compound with $La_3Ga_{1.67}Se_7$ composition is formed, which melts at 1170 °C. This compound has a hexagonal syngony with lattice parameters a = 10.53 Å, c = 6.39 Å. It follows from a brief review of the $La - Ga - X$ systems that the phase relationships in the system have not been precisely established, and triangulation has not been carried out either. In addition, the issues of synthesis, the growth of single crystals, and the physical properties of ternary compounds and samples are little understood.

Information is also known about the structural [7,8], physicochemical [9] and dielectric properties [10] of ternary phases of $La-Ga-X$ systems.

The purpose of this work is to calculate the electronic and crystal structures, as well as the enthalpy

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of formation of $LaGaX_3$ ternary compounds of chalcogenides of the $La-Ga-X$ (S, Se) systems. In addition to these, isothermal cross sections of $La-Ga-X$ ternary systems in the solid state were constructed, and the lattice parameters of the grown $LaGaSe_3$ single crystal were analyzed.

2. METHODICAL PARTS

2.1 Synthesis and crystal growth

$LaGaSe_3$ polycrystals were synthesized by solid phase synthesis [7]. The pure 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.) were used, 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 with the components was placed in a quartz ampoule, which was sealed to 10^{-3} Pa. The ampoule containing the components was placed in a temperature-controlled tubular electric synthesis furnace. The temperature of the furnace with the ampoule was first raised to 450 °C and held for 10 h. Then the temperature was raised to 1100 °C for 20 h and kept for 120 h. The oven was then cooled to room temperature over 72 h. Dark red $LaGaSe_3$ polycrystals were obtained in this way. The resulting compound was stable in air for a long time.

The growth of the $LaGaSe_3$ single crystal was carried out by the Bridgman–Stockbarger (BS) method. The pre-synthesized $LaGaSe_3$ ingot was loaded into a graphitized double quartz ampule with a tapered end. The ampoule was pumped out to a residual pressure of 10^{-3} Pa and placed in a two-temperature furnace of a single crystal growth unit. 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 $LaGaSe_3$ melts in the two-zone BS furnace was kept in the hot zone for 2 h, after which the ampoule was lowered into the cold zone at a rate of 0.1–0.2 mm/h. The temperature gradient between the hot and cold zones of the furnace was 20–30 K/cm. The resulting $LaGaSe_3$ single crystals were annealed for 150 h. The single crystals grown had a diameter of 10 mm and a length of 50 mm.

2.2 DFT calculations

Using density functional theory (DFT), we calculated the crystal and electronic structures, as well as the thermodynamic properties of ternary compounds of $La-Ga-X$ systems. The method for calculating the electronic and thermodynamic properties of ternary chalcogenide semiconductors was similar to that described by us earlier in works [11-14].

3. RESULTS AND DISCUSSION

3.1 Crystal structure

The diffraction patterns taken on powder samples from different parts of the single crystal corresponded to the hexagonal structure. Unit cell parameters calculated by the least squares method from the reflections of 2θ angles. To determine the lattice parameters, powders were prepared from $LaGaSe_3$ single crystals. X-ray diffraction patterns of powder samples corresponded to the hexagonal structure. The $LaGaSe_3$ compound crystallizes in a structure with space group $P6_3/mmc$. The unit cell parameters were a = 3.722 Å and c = 15.72 Å. These lattice parameters differ from known data (Table 1).

Table 1.

Crystallographic data for the compounds of $La-Ga-S(Se)$ system

Compound	Structure type	Space group	Cell parameters, Å			Ref.
			a	b	c	
$\alpha-LaGaS_3$	$LaGaS_3$	$P2_1/c$	10.399	12.826	10.564	[8]
$\beta-LaGaS_3$	Ag_8SiS_6	$Pna2_1$	10.15	21.9835	6.0565	[7]
$La_3Ga_{1.67}Se_7$	La_3CuSiS_7	$P6_3$	10.67		6.10	[6]
$LaGaSe_3$			10.32		6.28	[9]

It follows from the X-ray diffraction data that the crystal lattice of the resulting $LaGaSe_3$ was deformed in the direction of the c-axis of the crystal. The deformation of the cell can be associated with a large difference in the ionic radii of the components Ga (Ga^{3+}0.62 Å) and La (La^{3+}1.17 Å).

3.2 Ab initio calculations

DFT PBE-GGA calculations of the electronic structure of a- and b-$LaGaS_3$ modifications were previously carried out in work [7] with the WIEN2k software package. The following electronic configurations of La, Ga, S were used: La, [Xe]$5d^1 6s^2$; Ga, [Ar]$3d^{10}4s^2 4p^1$; S, [Ne]$3s^2 3p^4$. The values of atomic radii are taken equal to 2.50 au. for La, 2.06 a.u. for Ga and 2.06 a.u. for S. Convergence of self-consistent iterations was carried out for points inside the Brillouin zone with an accuracy of 0.0001 Ry at a cutoff of -7 Ry between the valence and ground states. Figures 1 and 2 show the structures of two modifications of the compound $\alpha-LaGaS_3$ (space group $P2_1/c$, no. 14) (Figure 1) [8] and $\beta-LaGaS_3$ (space group $Pna2_1$; no. 33; lattice parameters a = 10.405(1) Å, b = 21.984(2) Å, c = 6.0565(5) Å, V = 1385.3(2) $Å^3$ and Z = 12 (Figure 2) [7].

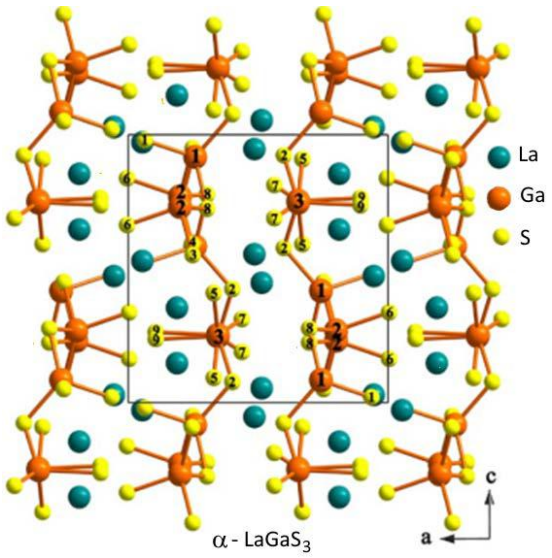

Fig. 1. Structure of $\alpha - LaGaS_3$ viewed along the *b*-axis.

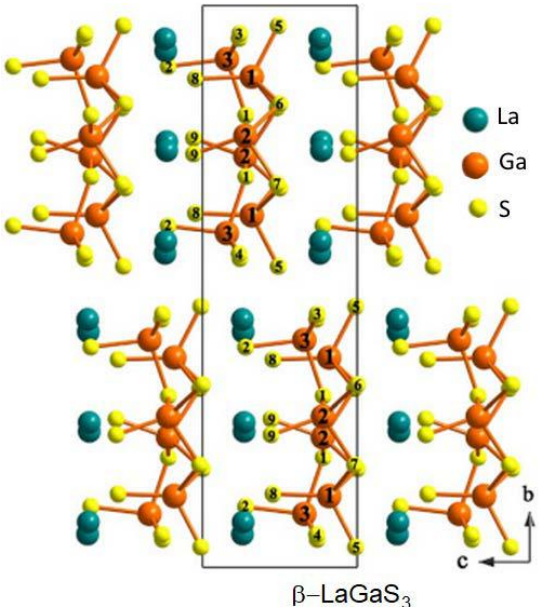

Fig. 2. Structure of $\beta - LaGaS_3$ viewed along the *a*-axis.

The results of calculations of the electronic structure of α- and $\beta - LaGaS_3$ are shown in Figures 3,a,b [7].

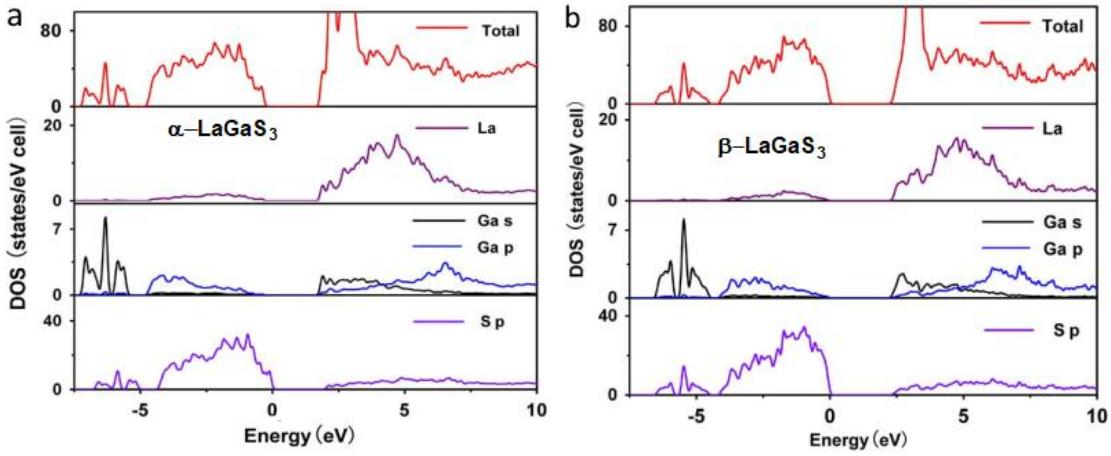

Fig. 3. Total and partial density of states of (a) $\alpha - LaGaS_3$; (b) $\beta - LaGaS_3$.

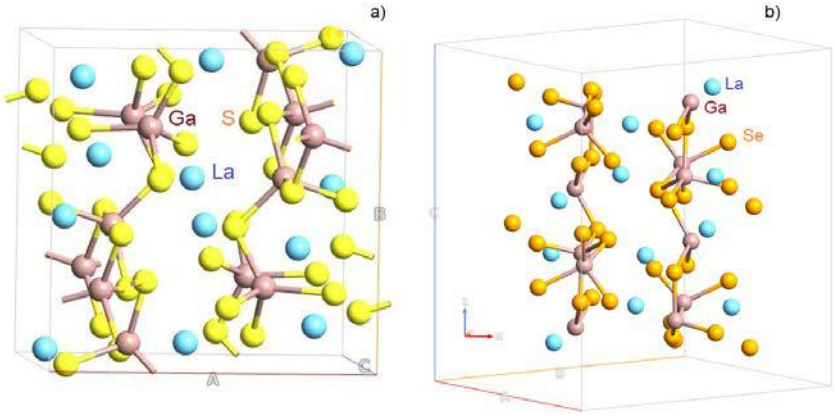

Fig. 4. Structures of $LaGaS_3$ (a) and $LaGaSe_3$ (b), viewed down the *c*-direction.

We carried out DFT SGGA calculations of the electronic structure of $LaGaS_3$ and $LaGaSe_3$ ternary chalcogenides using the method described in [11-14]. The following electronic formulas for the configurations of atoms included in these compounds were used: La, [Xe]$5d^16s^2$; Ga, [Ar]$3d^{10}4s^24p^1$; S, [Ne]$3s^23p^4$; Se, [Ar] $3d^{10}4s^24p^4$

The band structure and electron density of states in these ternary compounds are calculated. Our DFT SGGA calculations show that compounds $\alpha - LaGaS_3$ (E_g = 1.90 eV), $LaGaSe_3$ (Figure 4) and $La_3Ga_{1.67}Se_7$ are semiconductors.

3.3 Enthalpy of formation

The enthalpies of formation of binary compounds La_2Se_3 and Ga_2Se_3 at 298 K obtained from experimental data have relatively high values: $-\Delta_f H^0_{298}(La_2Se_3)$ = 933.03 ± 20.92 kJ/mol, $-\Delta_f H^0_{298}(Ga_2Se_3)$ = 397.5 ± 37.65 kJ/mol. The standard enthalpies of formation calculated by us for ternary phases were [$-\Delta_f H^0_{298}$, kJ/mol]: 1786 ($\alpha - LaGaS_3$), 1360 ($LaGaSe_3$), 3508 ($La_3Ga_{1.67}Se_7$). If we take into account deviations from the $\Delta_f H^0_{298}$ additive values of binary compounds of ternary systems, then for ternary compounds $\Delta_f H^0_{298}$ values 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 ($\Delta_f G^0_T$) of the system. In this case, $\Delta_f G^0_T$ of the ternary phase must be less than the $\Delta_f G^0_T$ calculated additively from $\Delta_f G^0_T$ of binary compounds. The above is also true for the $\Delta_f H^0_{298}$ value of the ternary phases.

3.4 Triangulation La − Ga − S(Se) system

The rules for singular triangulation of triple diagrams are known and a number of conclusions of practical interest follow from them. The following dependencies exist between individual compounds during singular triangulation, regardless of the nature of the melting of the compounds (or their formation in the solid state):

$$R = e = M + 3S \quad (1)$$

$$T = E = 1 + M + 2S \quad (2)$$

where R is the number of quasi-binary cuts, e is the number of saddle points of double eutectics on these cuts, M is the number of double chemical compounds, S is the number of ternary chemical compounds, T is the number of elementary eutectic diagrams, equal to the number of triple eutectic points E in these systems.

The quasi-binary phase diagrams of systems $La_2S_3 - Ga_2S_3$ [5] and $La_2Se_3 - Ga_2Se_3$ [10] that we adapted are shown in Figures 5 a, b.

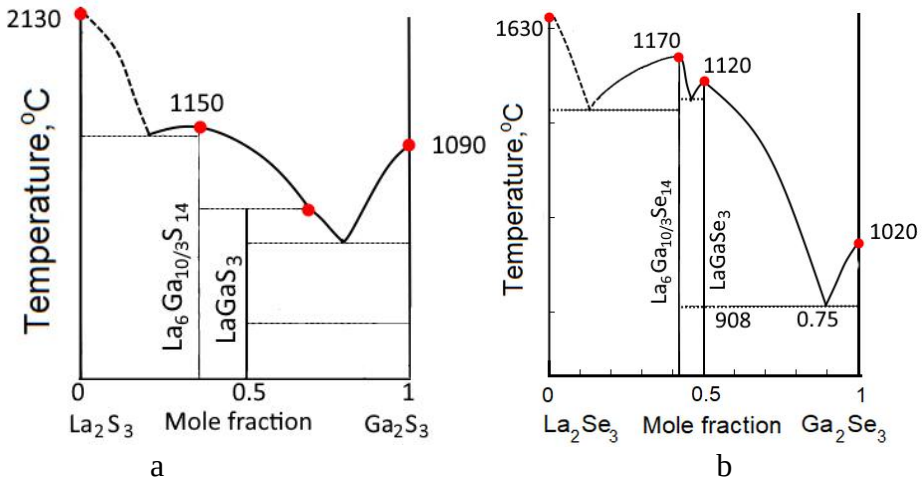

Fig. 5. The quasi-binary phase diagrams of systems $La_2S_3 - Ga_2S_3$ (a) and $La_2Se_3 - Ga_2Se_3$ (b.)

The division of ternary diagrams $La-Ga-X$ with several double ($La_{1-x}X_x$ and $La_{1-x}Ga_x$) and two ternary (C_1, C_2) chemical compounds is shown in Figure 5. As can be seen from the figures, in ternary systems the quasi-binary cuts intersect at the concentration triangles. In this case, the compositions of the alloys corresponding to their points of intersection correspond to ternary chemical compounds.

Considering the thermodynamic data of binary compounds and the data calculated by us for the ternary phases of $LaGaX_3$ and $La_3Ga_{1.67}X_7$, we triangulated $La-Ga-X$ ternary systems (Figure 6a,b). The compositions of the ternary phases link the conodes with the binary compounds of the La–Ga–Se system.

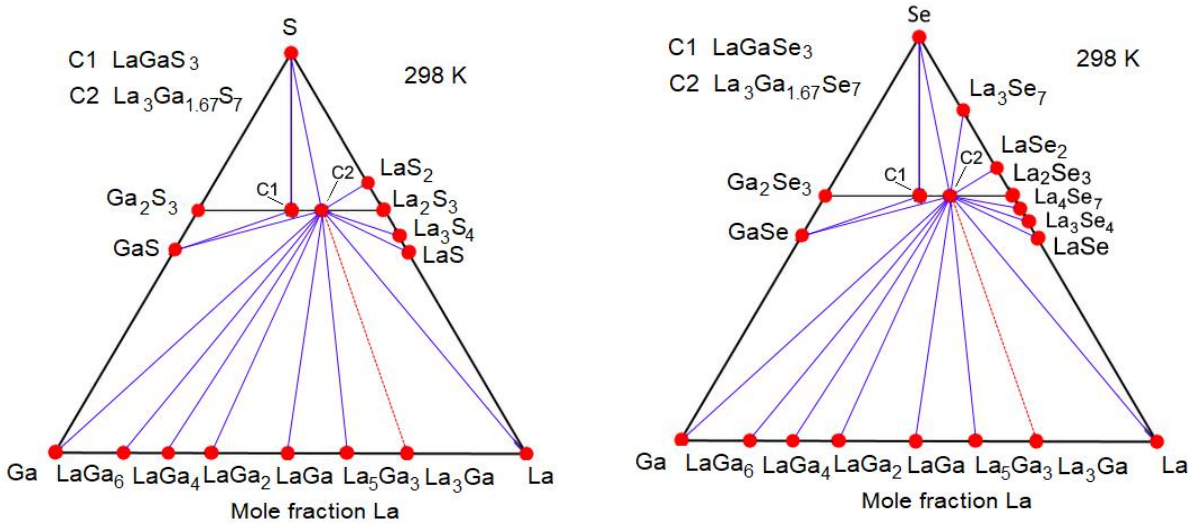

Fig. 6. Phase relations in the La–Ga–S (a) and La–Ga–Se(b) systems at 298 K.

4. CONCLUSION

Quasi-binary phase diagrams of the $La_2S_3-Ga_2S_3$ and $La_2Se_3-Ga_2Se_3$ systems adapted by us were used to construct the La-Ga-X concentration triangles. Based on the phase diagrams of these systems, the growth temperatures of single crystals were established. A dark red $LaGaSe_3$ single crystal was grown by directional crystallization. $LaGaSe_3$ crystallizes in the hexagonal system with space group $P6_3/mmc$ and lattice parameters a = 3.722 Å and c = 15.72 Å. These parameters differ from known data (a = 10.32 Å and c = 6.28 Å). DFT SGGA method calculated electronic properties show that the compounds $\alpha-LaGaS_3$ (E_g = 1.90 eV), $LaGaSe_3$ and $La_3Ga_{1.67}Se_7$ are semiconductors. The enthalpy of formation ($\Delta_f H^0_{298}$) of $\alpha-LaGaS_3$, $LaGaSe_3$, and $La_3Ga_{1.67}X_7$ compounds was calculated. The $\Delta_f H^0_{298}$ values were -1786, -1360, and -3508 kJ/mol, respectively. In the isothermal cross section of the $La-Ga-X$ ternary system constructed by us at 298 K, the compositions of the ternary phases of $LaGaX_3$ and $La_3Ga_{1.67}X_7$ are in equilibrium with the compositions of the corresponding binary compounds of the boundary systems.

Conflict of interest

The authors declare that they have no conflict of interest

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