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SYNTHESIS, MAGNETIC AND LUMINESCENT PROPERTIES OF $Nd_{1-x}La_xGaO_3$ ($0.7 \le x \le 1.0$) SOLID SOLUTIONS

$Nd_{1-x}La_xGaO_3$ ($0.7 \le x \le 1.0$) solid solutions were synthesized by the ceramic method, their crystal structure, magnetic and luminescent properties were investigated. The solid solutions investigated behave as paramagnetics in temperature region of 5–300 K. Calculated values of Nd^{3+} ion effective magnetic moment in solid solutions investigated are lower than theoretical. There probably exists „partial freezing" of orbital moment of Nd^{3+} ions by the crystal field of the orthorhombically distorted perovskite structure of $Nd_{1-x}La_xGaO_3$ gallates. It is shown that $Nd_{0.1}La_{0.9}GaO_3$ is an efficient phosphor with IR-emission, so it is prospective for use in IR-LEDs.

Introduction. Compounds of rare earth and other metals oxides with perovskite structure occupy a special place among modern and promising materials widely used in electronics and chemical industry [1–3]. In particular, lanthanum and other rare earth elements (Ln) scandates, gallates, indates, aluminates and their solid solutions with perovskite structure ($LnMO_3$, M = Al, Sc, Ga, In) are promising materials for of active laser elements [4–6]. Indium and gallium compounds containing rare-earth ions are also good photo- and cathodoluminescent phosphors [7, 8], which can be used for white LEDs.

If paramagnetic ions of rare earth elements in $LnAlO_3$, $LnGaO_3$, $LnInO_3$ are partially substituted by isovalent diamagnetic La^{3+} ions there will be observed magnetic dilution of rare-earth ions, resulting in decrease in their interaction and in growing influence of the crystal field on the spin-orbital interaction. That leads to a so-called "partial freezing" of rare earth ions orbital moment. As far as we know such studies are absent in literature despite their great scientific and practical importance.

The aim of the present work is to synthesize by the ceramic technique $Nd_{1-x}La_xGaO_3$ solid solutions, where paramagnetic Nd^{3+} ions are substituted by diamagnetic La^{3+} ions to obtain high degree of magnetic dilution and to investigate magnetic and luminescent properties of solid solutions synthesized.

Experimental technique. Polycrystalline samples of $Nd_{1-x}La_xGaO_3$ (x = 0,7–1,0), solid solutions being the subject of study, were prepared by ceramic method from oxides Nd_2O_3 (99.99% REO), La_2O_3 (ЛаО-Д), Ga_2O_3. Hygroscopic La_2O_3 and Nd_2O_3 oxides had been calcined at 1,273 K for 1 hour before weighting.

Gallium oxide Ga_2O_3 was obtained by thermal combustion of $Ga(NO_3)_3 \cdot 5H_2O$ nitrate (chemichally pure) as it is described in work [9]. From the X-ray diffraction pattern (Fig. 1) one can see that the sample of gallium oxide obtained was single-phased and had crystal structure of monoclinic β-Ga_2O_3 [10].

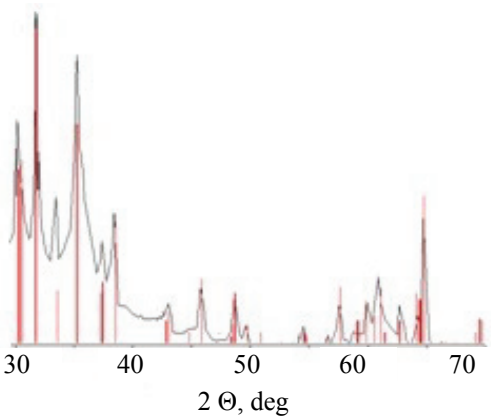


Fig. 1. Powder XRD pattern of obtained gallium oxide sample (lines stand for β-Ga_2O_3 XRD pattern [10])

Stoichiometric amounts of starting materials were mixed and milled in a planetary mill Pulverizette 6 with addition of ethanol. The resulting mixture was pressed under a pressure of 50–75 MPa into tablets of 25 mm diameter and 5.7 mm height. Tablets were sintered in air in an electric resistance furnace for 4 hours at 1,473 K, then crushed, milled, pressed into bars of 30 mm length and 5×5 mm^2 cross section. Bars were sintered in air in an electric resistance furnace for 4 hours at 1,523 K.

X-ray diffraction patterns of powder samples of $Nd_{1-x}La_xGaO_3$ (x = 0.7–1.0) solid solutions were obtained on a D8 ADVANCE diffractometer using CuK_α-radiation in the range of 2Θ angles 20–80°. Crystal structure parameters of the investigated

compounds were determined using RTP program and data of International Centre for Diffraction Data (ICDD JCPDS) [11, 12].

Specific magnetization (σ_{sp}) in magnetic fields up to 14 T and specific magnetic susceptibility (χ_{sp}) in the temperature range 6–300 K in magnetic field of 0.8 T of $Nd_{1-x}La_xGaO_3$ samples were measured by vibrational method with universal high-field measuring system (Cryogenic Ltd, London, 4IS) in SSPA "Scientific and Practical Materials Research Centre of NAS of Belarus".

Photoluminescence and excitation spectra were obtained with automatic spectrofluorimeter СДЛ-2, consisting of excitation monochromator МДР-12 and registration monochromator МДР-23 of Institute of Physics of NAS of Belarus.

Main part. Due to the results of X-ray analysis $Nd_{1-x}La_xGaO_3$ solid solutions ($0.7 \le x \le 1.0$) were single-phased and crystallized in orthorhombically distorted perovskite structure.

In $Nd_{1-x}La_xGaO_3$ solid solutions increasing the substitution level x of Nd^{3+} ions by La^{3+} ions with larger on 0.005 nm ionic radii [13], leads to gradual increase of crystal lattice parameters a, c and unit cell volume V (Table 1) while crystal lattice parameter b stays almost changeless (Table 1). Crystal lattice parameters of obtained $LaGaO_3$ (Table 1) correlate well with reference data [12].

X-ray density of $Nd_{1-x}La_xGaO_3$ ceramic samples was calculated with the following formula:

$$\rho_{XRD} = 4M / (N_A \cdot V), \qquad (1)$$

where 4 – number of formula units in the elementary cell; M – molar mass of the formula unit, g/mol; N_A – Avogadro constant ($N_A = 6.022 \cdot 10^{23}$ mol^{-1}); V – elementary cell volume, cm^3.

X-ray density of $Nd_{1-x}La_xGaO_3$ ceramic samples gradually decreases with increase in substitution level x of Nd^{3+} ions by La^{3+} ions with larger ionic radii and lower atomic mass (Table 1). In present work as well as in work [13] for $LaGaO_3$ crystal lattice parameters ratio $a > b$ was established, while for $NdGaO_3$ the ratio is $b > a$. This explains the fact that the orthorhombic distortion degree of $Nd_{1-x}La_xGaO_3$ solid solutions with $x = 0.7$–1.0 ($\varepsilon = (b - a)/a$)) is negative (Table 1).

Dependences of reciprocals of specific magnetic susceptibility value for gallate содержащего 1 mol of Nd^{3+} ions on temperature (Fig. 2) were obtained using temperature dependences of molar magnetic susceptibility of $Nd_{1-x}La_xGaO_3$ ($x = 0.7$; 0.8; 0.9) samples and temperature dependence of molar magnetic susceptibility of diamagnetic $LaGaO_3$. All the dependences in Fig. 2 in the 20–170 K temperature range obey Curie – Weiss law and coincide with each other what means that effective magnetic moment of Nd^{3+} ions in solid solutions investigated has practically no dependence on x.

For temperature ranges where specific magnetic susceptibility obeys Curie – Weiss law equations of $1/\chi_{sp}$ linear dependence on T ($1/\chi_{sp} = a + bT$) were defined by the least squares method. Specific Curie constants ($C_{sp} = 1/b$) and Weiss constants ($\Theta = -a/b$) were calculated using a and b coefficients. Molar Curie constant (C_m) values were determined by multiplying C_{sp} on molar mass of the $Nd_{1-x}La_xGaO_3$ compound appropriate.

Neodymium ions effective magnetic moment ($\mu_{ef, Nd3+}$) was calculated with the following formula:

$$\mu_{ef.\,Nd^{3+}} = \sqrt{\frac{7.997\,C_m}{1-x}}, \qquad (2)$$

where $7.997 = 3k / N_A\mu_B^2$, k – Boltzmann constant; N_A – Avogadro constant; μ_B – Bohr magneton.

Values of Weiss constant (Θ), and effective magnetic moment of Nd^{3+} ions ($\mu_{ef, Nd3+}$) in $Nd_{1-x}La_xGaO_3$ solid solutions are presented in Table 2. Error of effective magnetic moment of Nd^{3+} ions $\mu_{ef\,Nd3+}$ and Weiss constant Θ calculation was about 1–3%.

Effective magnetic moment of Nd^{3+} ions ($\mu_{ef, Nd3+}$) in $Nd_{1-x}La_xGaO_3$ gallates with $0.7 \le x \le 0.9$ varies slightly in the range of (2.94–3.03) μ_B and is lower than theoretical value of the effective spin-orbital magnetic moment of Nd^{3+} ions that is equal to 3.62 μ_B. So we can suppose that in $Nd_{1-x}La_xGaO_3$ solid solutions with high degree of madnetic dilution of paramagnetic Nd^{3+} ions by diamagnetic La^{3+} ions occurs «partial freezing» of orbital magnetic moment of Nd^{3+} ions by crystal field of orthorhombically distorted perovskite structure.

.Table 1

Crystal lattice parameters a, b, c, unit cell volume V, orthorhombical distortion degree ε and X-ray density ρ_{XRD} of $Nd_{1-x}La_xGaO_3$ gallates

Compound	Crystal lattice parameters					ρ_{XRD}, g/cm^3
	a, nm	b, nm	c, nm	$V \cdot 10^3$, nm^3	$\varepsilon \cdot 10^2$	
$NdGaO_3$ [11]	0.54276	0.54979	0.7708	230.00	1.30*	7.57*
$Nd_{0,3}La_{0,7}GaO_3$	0.5501	0.5488	0.7757	234.16	–0.23	7.32
$Nd_{0,2}La_{0,8}GaO_3$	0.5512	0.5484	0.7767	234.76	–0.52	7.29
$Nd_{0,1}La_{0,9}GaO_3$	0.5518	0.5491	0.7760	235.10	–0.48	7.27
$LaGaO_3$	0.5519	0.5493	0.7782	235.57	–0.47	7.24
$LaGaO_3$ [12]	0.55243	0.54925	0.77745	235.9*	–0.58*	7.23*

Note. Values marked with * were calculated in the present work using literature data.

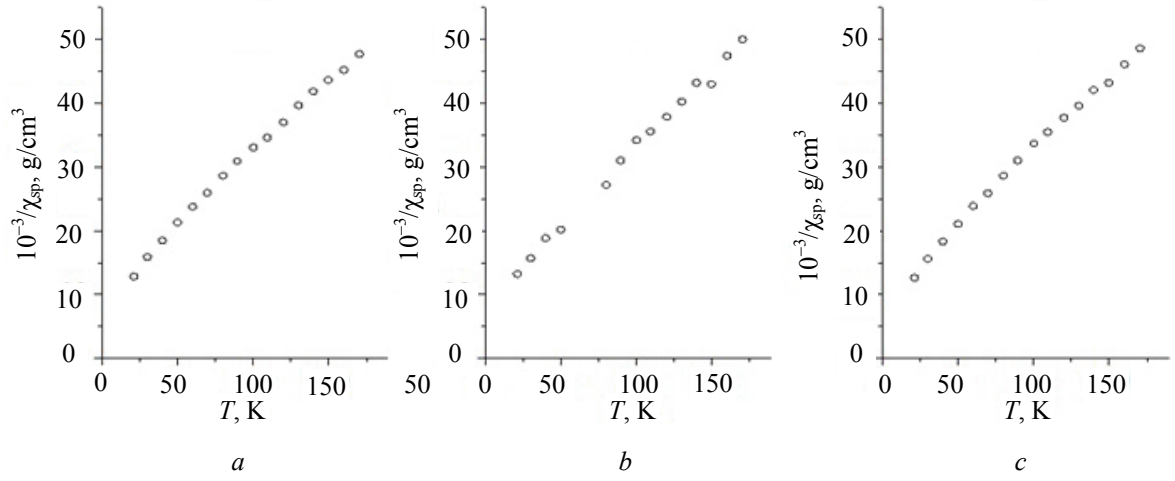


Fig. 2. Dependences of $1/\chi_{sp}$ of gallate with 1 mol of Nd^{3+} ions on temperature for different samples of $Nd_{1-x}La_xGaO_3$: *a* – $x = 0.7$; *b* – $x = 0.8$; *c* – $x = 0.9$

Table 2

Weiss constants (Θ) and Nd^{3+} ions effective magnetic moment ($\mu_{ef,\ Nd3+}$) in temperature range of Curie – Weiss law implementation for the $Nd_{1-x}La_xGaO_3$ gallates

$Nd_{1-x}La_xGaO_3$, x	$\mu_{ef\ Nd3+}$, μ_B	Θ, K
0.7	3.03	–41.4
0.8	2.94	–35.0
0.9	2.99	–39.0

Analysis of Table 2 data shows that the values of Weiss constant of $Nd_{1-x}La_xGaO_3$ solid solutions are negative. This allows us to suppose that solid solutions investigated transfer to антиферромагнитное state if the temperature is below 1 K, like it occurs for $NdInO_3$ [14].

Field dependences of magnetization of one formula unit of $Nd_{1-x}La_xGaO_3$ at 5 and 300 K in magnetic fields up to 14 T are displayed at Fig. 3 *a*, *b*, respectively. At 300 K increase in magnetic field up to 14 T results in linear magnetization increase, and at 5 K a tendency to saturation is observed.

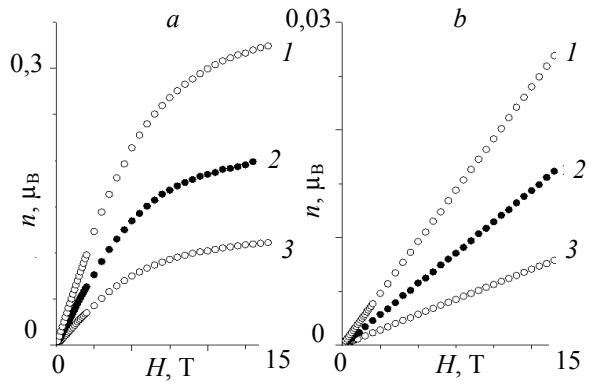


Fig. 3. Magnetization dependences on magnetic field at 5 K (*a*) и 300 K (*b*) for $Nd_{1-x}La_xGaO_3$ with different x: $x = 0.7$ (*1*); 0.8 (*2*); 0.9 (*3*)

Values of magnetic moment of Nd^{3+} ions (μ_{Nd3+}) in $Nd_{1-x}La_xGaO_3$ at 5 K in magnetic field up to 14 T, were calculated for 1 mol of Nd^{3+} ions by formula (3) and presented in Table 3:

$$\mu_{Nd3+} = n / (1 - x), \quad (3)$$

where n – calculated in Bohr magnetons magnetization for one $Nd_{1-x}La_xGaO_3$ formula unit.

Neutron diffraction study of $NdInO_3$ showed that below 1 K there occurs antiferromagnet ordering of Nd^{3+} ions magnetic moment in $g_y a_x$ configuration and at 0.280 K magnetic moment of Nd^{3+} ions is equal to (2.9 ± 0.2 μ_B) [14].

Table 3

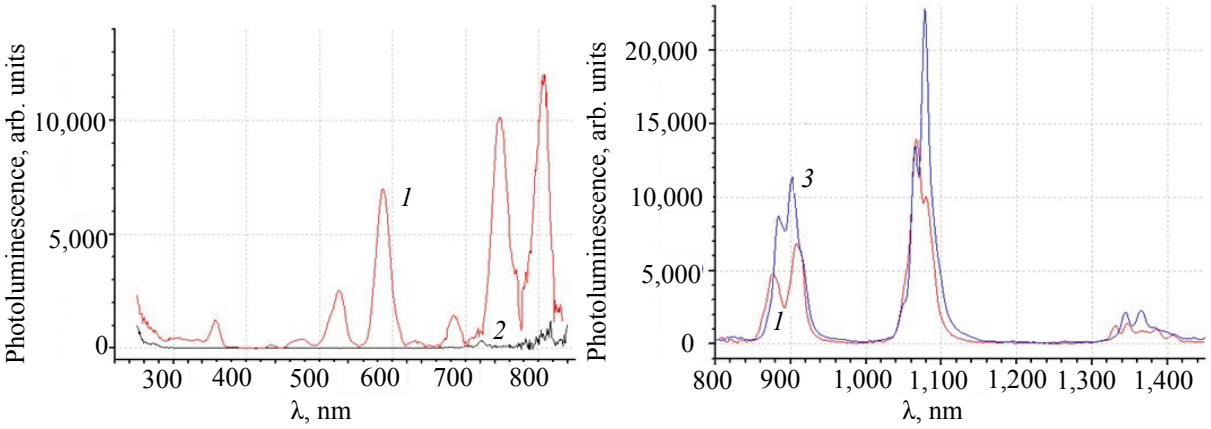
Magnetization (n) and magnetic moment of Nd^{3+} ions (μ_{Nd3+}) in $Nd_{1-x}La_xGaO_3$ at 5 K in magnetic field 14 T

$Nd_{1-x}La_xGaO_3$, x	n, μ_B	μ_{Nd3+}, μ_B
0.7	0.11	1.11
0.8	0.20	1.00
0.9	0.32	1.08

Fig. 4, *a* presents excitation spectra of $Nd_{1-x}La_xGaO_3$ gallates with $x = 0,9$; 0,8. Maximum excitation intensity was observed for sample with c $x = 0.9$ (Nd^{3+} ion 10 mol. %). For photoluminescence spectra $\lambda_{ex} = 585$ nm was chosen (Fig. 4 *b*).

Photoluminescence spectrum of $Nd_{0.1}La_{0.9}GaO_3$ sample with $\lambda_{ex} = 585$ nm contains wide bands in of 870–930, 1,040–1,110, 1,320–1,380 nm related to IR-region. Photoluminescence maxima for $Nd_{0.1}La_{0.9}GaO_3$ sample and studied before in [15] $Nd_{0.1}La_{0.9}InO_3$ sample are almost the same. The explanation may be due to the equal influence of $LaInO_3$ and $LaGaO_3$ crystal field C_S symmetry on Nd^{3+} ion.

Table 3 data analysis shows that magnetic moment of Nd^{3+} ions (μ_{Nd3+}) in $Nd_{1-x}La_xGaO_3$ at 5 K in magnetic field of 14 T is quite lower than the value from [14] or the theoretical value of effective spin-orbital magnetic moment $\mu_{rf\ Nd3+} = 3.62$ μ_B.



a *b*

1 − $Nd_{0,1}La_{0,9}GaO_3$; *2* − $Nd_{0,2}La_{0,8}GaO_3$; *3* − $Nd_{0,1}La_{0,9}InO_3$

Fig. 4. Excitation spectra of $Nd_{0,1}La_{0,9}GaO_3$ and $Nd_{0,2}La_{0,8}GaO_3$ solid solutions with λ_{reg} = 910 nm (*a*) and photoluminescence spectra of $Nd_{0,1}La_{0,9}InO_3$ and $Nd_{0,1}La_{0,9}GaO_3$ solid solutions with λ_{ex} = 585 nm (*b*)

As radiation of Nd^{3+} ions in $LaInO_3$ and $LaGaO_3$ with perovskite structure refer to near IR-region, this kind of phosphors can be used in IR-LEDs manufacturing. IR-LEDs spheres of application are optical instrumentations, remote control devices, opto-switching devices, wireless links [16, 17].

Conclusion. $Nd_{1-x}La_xGaO_3$ ($0.7 \le x \le 1.0$) solid solutions were synthesized by ceramic method, their crystal structure, magnetic and luminescent properties were investigated. It was supposed that in $Nd_{1-x}La_xGaO_3$ solid solutions with $0.7 \le x \le 0.9$ occurs "partial freezing" of orbital magnetic moment of Nd^{3+} ions by crystal field of orthorhombically distorted perovskite structure. It was shown that $Nd_{0.1}La_{0.9}GaO_3$ galate is effective IR-phosphor prospective for IR-LEDs.

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