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PHYSICAL AND CHEMICAL PROPERTIES OF SOLID SOLUTIONS BASED ON LANTHANUM INDATE DOPED BY Nd^{3+} , Cr^{3+} , Mn^{3+} IONS

$\text{La}_{1-x}\text{Nd}_x\text{InO}_3$ ($x = 0.007; 0.02; 0.05$); $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{1-y}\text{M}_y\text{O}_3$ ($M = \text{Cr}^{3+}, \text{Mn}^{3+}; y = 0.005$), $\text{LaIn}_{1-y}\text{M}_y\text{O}_3$ ($M = \text{Cr}^{3+}, \text{Mn}^{3+}; y = 0.01$) solid solutions were obtained by solid-phase route. Their crystal structure, FT-IR spectra, thermal expansion were investigated. Additionally for named solid solutions complex thermal analysis was carried out. It was found that all samples were single-phased and had the structure of orthorhombically distorted perovskite and the lattice parameters vary slightly due to the small content of doping ions. There were absorption bands of $\text{La}(\text{Nd})\text{-O}$ and $\text{In}(\text{Cr}, \text{Mn})\text{-O}$ stretching vibrations on the FT-IR spectra. The frequencies and intensities of the absorption bands were similar for obtained solid solutions. There were no anomalies caused by phase transitions at temperature dependences of elongation. The curves obtained by differential scanning calorimetry had no thermal effects. Total weight loss in the temperature range of 300–1,265 K did not exceed 0.14 wt %. These results indicate that the solid solutions based on LaInO_3 are thermally stable and have a linear coefficient of thermal expansion no greater than $(8.3\text{--}8.4) \cdot 10^{-6} \text{ K}^{-1}$.

Key words: solid-phase method, lanthanum indate, X-ray diffraction, FT-IR spectroscopy, thermal expansion, complex thermal analysis.

Introduction. The phosphor based on LaInO_3 doped with ions of rare-earth elements are promising for those in FED-displays (field emission displays), as well as for creating white light LEDs [1–2]. In [3] the physical and chemical properties of $\text{La}_{1-x}\text{Nd}_x\text{InO}_3$ solid solutions with the Nd^{3+} ion content of more than 10 mol. % have been studied. When preparing photoluminescent phosphors on the basis of lanthanum indate or lanthanum gallate, ions of rare earth elements (Pr^{3+} , Nd^{3+} , Sm^{3+}) in their crystal lattice in quantity not exceeding 5 mol. % were introduced. However, magnetic properties as well as their IR spectra, thermal expansion and the thermal stability are not fully investigated. The present work is aimed at investigating the effect of doping lanthanum indate, LaInO_3 , with Nd^{3+} , Cr^{3+} , Mn^{3+} , ions in the quantity not exceeding 5 mol. %, on crystal structure, IR absorption spectra, thermal expansion and thermal stability.

The main part. $\text{La}_{1-x}\text{Nd}_x\text{InO}_3$ ($x = 0.007, 0.02, 0.05$); $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{0.995}\text{Cr}_{0.005}\text{O}_3$; $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{0.995}\text{Mn}_{0.005}\text{O}_3$; $\text{LaIn}_{0.99}\text{Cr}_{0.01}\text{O}_3$; $\text{LaIn}_{0.99}\text{Mn}_{0.01}\text{O}_3$ solid solutions were received from oxides of lanthanum (La_2O_3), indium (In_2O_3), neodymium (Nd_2O_3), manganese (Mn_2O_3), and chromium (Cr_2O_3) by using solid phase method. All reagents had a “chemically pure” qualification. Lanthanum and neodymium oxides was precalcinated during 1 h in air at the temperature of 1273 K. Powders of the oxides, taken in the specified molar ratios were mixed and milled in a planetary mill “Pulverizette 6” with the addition of ethanol (the material of glass and grinding balls being ZrO_2). The resulting mixture (with ethanol added) was pressed under pressure of 50–75 MPa into tablets with a diameter of 25 mm and a height of

5–7 mm, which were dried in air at room temperature and then calcined at 1,523 K in air for 6 h. In order to avoid the possible (during the synthesis and sintering) interacting of tablets with the substrate material (Al_2O_3) the specimens were separated from the substrate with a thin buffer layer of batch mixture having the same composition as the tablets. The cooling of specimens from the sintering to room temperature proceeded slowly, at the same time as the furnace cooled, the cooling rate being $2\text{--}5 \text{ K} \cdot \text{min}^{-1}$. After preliminary calcining the tablets were crushed, milled, pressed with the addition of small quantity of ethanol into bars being 30 mm in length and $5 \times 5 \text{ mm}^2$ in cross section, which were calcined at the temperature of 1,523 K in air for 6 h on aluminum oxide substrates. X-ray diffraction patterns were obtained on a D8 ADVANCED diffractometer of the Bruker company using CuK_α radiation at room temperature in the angle range of $2\Theta = 20\text{--}80^\circ$ (step angle being $2\Theta - 0.03^\circ$, and exposure at each point – 3 s). To identify the solid solutions obtained the information of the card index of the International Centre for Diffraction Data (ICDD JCPDC) was used. The crystal structure parameters (a , b , c and unit cell volume V) of the obtained solid solutions based on lanthanum indate, LaInO_3 , was determined using X-ray structure tabular processor (RTP) applying the values of interplanar distances and Miller indices for 12–15 reflexes. The error in the determination of unit cell parameters did not exceed $\pm 0.001 \text{ \AA}$.

Infrared spectra of the synthesized solid solutions in the range of wave numbers $250\text{--}900 \text{ cm}^{-1}$ were recorded in KBr produced mixtures by using NEXUS infrared interferometer spectrometer by THERMO NICOLET. The mass of the sample

of the investigated solid solution with lanthanum indate as the base was ≈ 1 mg – about 0.1% by mass of KBr. The accuracy of determining the frequency of oscillation did not exceed ± 2 cm^{-1} .

The thermal expansion of the ceramic samples of solid solutions based on lanthanum indate was investigated in the temperature range of 350–850 K by using a quartz dilatometer with a vertical quartz pusher with IGM micron indicator (lever-gear multiturn head with a scale division of 0.001 mm in dynamic mode at heating-cooling speeds of 3–5 $\text{K} \cdot \text{min}^{-1}$). Heating and cooling were carried out in air in an electroresistance furnace. The specimens were rectangular parallelepipeds of $5 \times 5 \times 30$ mm in size. The error of determining the relative elongation of the specimens did not exceed 0.1%. The average linear coefficient of thermal expansion (α) of the specimens was calculated using the least square method. The error α was 1–5% for different specimens and temperature intervals.

The curves of differential scanning calorimetry (DSC), thermogravimetric and differential thermogravimetric analysis (TG, DTG) were read at the derivatograph TGA / DSC1 / 1600 produced by company METTLER TOLEDO Instruments (Switzerland). The changes were carried out in static air atmosphere over the temperature range of 300–1265 K using Al_2O_3 as a reference. At a linear heating mode of $10^\circ/\text{min}$, mass of the powdered sample was 65 mg.

Analysis of X-ray diffraction patterns (Fig. 1) showed that the indate specimens obtained are single-phase and have a crystalline structure of orthorhombically distorted perovskite. Due to the fact that literature data on the Miller indices of planes (hkl) of the LaInO_3 unit cell are contradictory, the (hkl) X-ray diffraction maxima data for indate neodymium NdInO_3 were used [4], to define as in [3] it is established that in the system of $\text{LaInO}_3 - \text{NdInO}_3$ a continuous series of $\text{La}_{1-x}\text{Nd}_x\text{InO}_3$ ($0.1 \leq x \leq 0.9$) solid solutions with crystal structure of the orthorhombic distorted perovskite of the GdFeO_3 type ($a < c / \sqrt{2} < b$) [5] is formed.

Due to the fact that ions Nd^{3+} 0.05 Å are smaller than ionic radius of La^{3+} , as established in [3], the increase in the content of Nd^{3+} ions in the solid solution $\text{La}_{1-x}\text{Nd}_x\text{InO}_3$ from $x = 0.1$ to 0.9 leads to a decrease of the parameter a of the unit cell in Å 0.078, the parameter b – is 0.028 Å, the parameter c – is 0.073 Å. It follows that an increase in the degree of substitution x in LaInO_3 ions La^{3+} with ions Nd^{3+} on the magnitude of 0.1 leads to a decrease in, for example, parameter a of the unit cell of the orthorhombic perovskite structure at approximately 0.0097 Å, and the increase in the degree of substitution x by 0.01 leads to a decrease of the parameter a approximately of 0.001 Å.

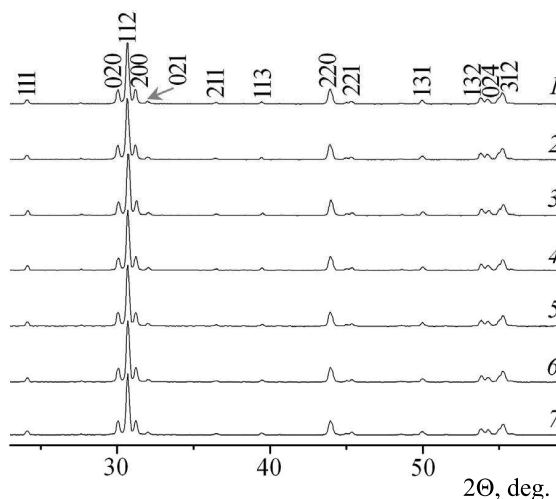


Fig. 1. X-ray diffraction patterns of solid solutions:

- 1 – $\text{La}_{0.993}\text{Nd}_{0.007}\text{InO}_3$; 2 – $\text{La}_{0.98}\text{Nd}_{0.02}\text{InO}_3$;
- 3 – $\text{La}_{0.95}\text{Nd}_{0.05}\text{InO}_3$; 4 – $\text{LaIn}_{0.99}\text{Cr}_{0.01}\text{O}_3$;
- 5 – $\text{LaIn}_{0.99}\text{Mn}_{0.01}\text{O}_3$;
- 6 – $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{0.995}\text{Cr}_{0.005}\text{O}_3$;
- 7 – $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{0.995}\text{Mn}_{0.005}\text{O}_3$

It is found (Table) that the degree of substitution of x ions of La^{3+} with Nd^{3+} ions in LaInO_3 increasing from $x = 0.007$ to 0.050 results in the reduction of the a , b , c parameters of the orthorhombically distorted perovskite unit cell by 0.008, 0.006 and 0.006 Å, respectively. This agrees well with the data obtained in [3]. The volume of the unit cell indate obtained decreases from 280.2 Å³ for $\text{La}_{0.993}\text{Nd}_{0.007}\text{InO}_3$ to 279.3 Å³ for $\text{La}_{0.95}\text{Nd}_{0.05}\text{InO}_3$.

Mn^{3+} and Cr^{3+} ions in the solid solution replace the In^{3+} ions in the corresponding LaInO_3 sublattice. The concentration of the ions concerned being negligible, the lattice parameters also change slightly with introduction of Cr^{3+} or Mn^{3+} ions, not with standing relatively large difference of ionic radii (difference of ionic radii of indium and chromium is 0.28 Å, and indium and manganese – 0.22 Å) (see Table).

The absolute values of the degree of orthorhombic distortion ε ($\varepsilon = (b - a) / a$) for the solid indate solutions obtained vary slightly. The sign of orthorhombic distortion degree is constant, which agrees with the data for the system of $\text{La}_{1-x}\text{Nd}_x\text{InO}_3$ ($0 \leq x \leq 1$) solid solutions, studied in [3].

The comparison of the IR spectra of all the solid solution obtained (Fig. 2) shows that over the investigated range of wave numbers (250–650 cm^{-1}), they differ slightly. The IR spectra have absorption bands caused by the stretching vibration of the $\text{In}(\text{Cr}, \text{Mn})\text{O}$ (543–550, 490–494 cm^{-1}), and $\text{La}(\text{Nd})\text{O}$ (389–400, 348–353 cm^{-1}) [6].

The absorption bands frequencies of all the solid solutions obtained on the basis of lanthanum indate agree well with the data obtained for LaInO_3 in [3].

Thus, it is found that increasing the content Nd^{3+} ion in $\text{La}_{1-x}\text{Nd}_x\text{InO}_3$ solid solutions from $x = 0.007$ to 0.050 in frequency and intensity of the absorption bands In–O bonds decrease from 548 to 543 cm^{-1} .

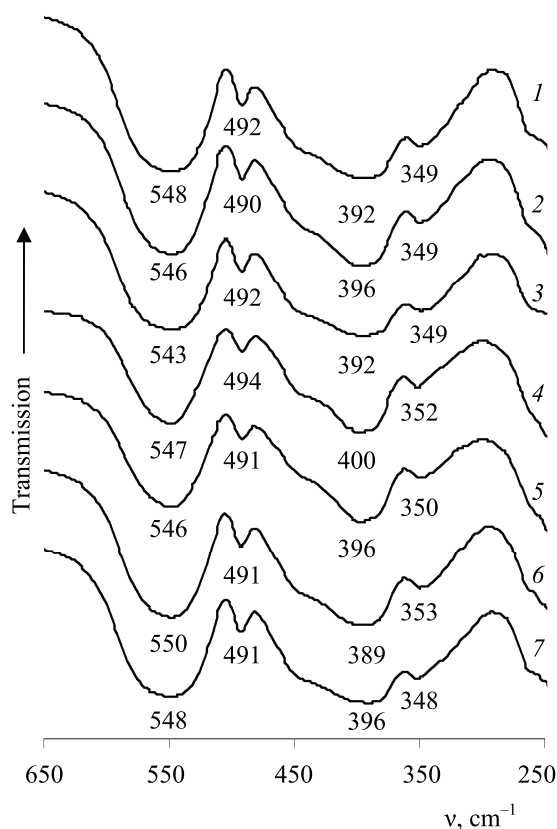


Fig. 2. IR absorption spectra of solid solutions:

- 1 – $\text{La}_{0.993}\text{Nd}_{0.007}\text{InO}_3$;
 2 – $\text{La}_{0.98}\text{Nd}_{0.02}\text{InO}_3$; 3 – $\text{La}_{0.95}\text{Nd}_{0.05}\text{InO}_3$;
 4 – $\text{LaIn}_{0.99}\text{Cr}_{0.01}\text{O}_3$; 5 – $\text{LaIn}_{0.99}\text{Mn}_{0.01}\text{O}_3$;
 6 – $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{0.995}\text{Cr}_{0.005}\text{O}_3$;
 7 – $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{0.995}\text{Mn}_{0.005}\text{O}_3$

The change of the La(Nd)–O bonds absorption bands frequencies is within the error of the measurement method ($\pm 2 \text{ cm}^{-1}$).

On adding extra 0.5 mol. % of Cr^{3+} or Mn^{3+} ions to solid solution of $\text{La}_{0.95}\text{Nd}_{0.05}\text{InO}_3$ frequencies of the absorption bands stretching vibrations of the In(Cr, Mn)–O bonds increase from 543 to 550 and 548 cm^{-1} , respectively. The frequency change of the La(Nd)–O bonds absorption bands does not differ greatly from the accuracy of the measurement.

When introducing into LaInO_3 1 mol. % Cr^{3+} or Mn^{3+} ions IR absorption spectra of the resulting solid solutions do not differ from the spectra of LaInO_3 [3].

The temperature dependences of the relative elongation $\Delta l / l_0$ of the ceramic specimens on the basis of lanthanum indate, doped with Nd^{3+} ions

(Fig. 3) obtained by dilatometric method show that in the temperature range of 350–850 K the relative elongation $\Delta l / l_0$ increases almost linearly with increasing temperature.

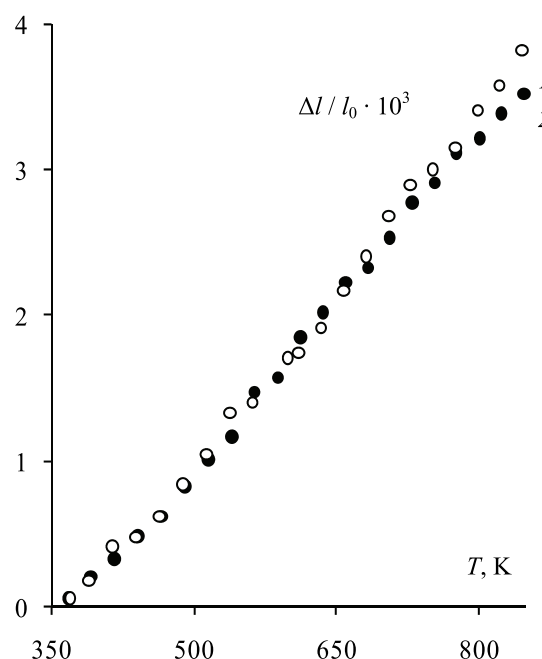


Fig. 3. Temperature dependences of relative elongation $\Delta l / l_0$ of solid solutions:
 1 – $\text{La}_{0.993}\text{Nd}_{0.007}\text{InO}_3$; 2 – $\text{La}_{0.98}\text{Nd}_{0.02}\text{InO}_3$

This indicates that in the investigated solid solutions based on lanthanum indate there are not changes over the temperature range mentioned.

According to the obtained temperature dependences of the relative elongation of the ceramic specimens of solid solutions investigated using the method of least squares calculated average values of coefficients of linear thermal expansion α of these samples are calculated. It is established that due to the low content of Nd^{3+} ions in the investigated solid solutions based on lanthanum indate LaInO_3 their coefficients of linear thermal expansion are practically the same and have the values of $(8.3\text{--}8.4) \cdot 10^{-6} \text{ K}^{-1}$, which agrees well with in [3] the value of $8.65 \cdot 10^{-6} \text{ K}^{-1}$ obtained for solid solution $\text{La}_{0.7}\text{Nd}_{0.3}\text{InO}_3$.

On DSC curves (Fig. 4) for the studied solid solutions on the basis of lanthanum indate ($\text{La}_{0.95}\text{Nd}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Nd}_{0.05}\text{In}_{0.995}\text{Cr}_{0.005}\text{O}_3$) there are no thermal effects, which confirms the absence of any phase transitions in the examined samples over the studied temperature range. On TG curves, there is a slight mass loss with a deviation from linear dependence, indicating the increase in the rate of loss of mass, the maximum value of which (the least value on the DTG curve) is reached at a certain temperature T_1 .

Composition	Lattice parameters					ρ_{Xrd} , g/cm ³	$c/\sqrt{2}$, E
	a , Å	b , Å	c , Å	V , Å ³	$\varepsilon = (b - a) / a$		
La _{0.993} Nd _{0.007} InO ₃	5.732	5.943	8.226	280.2	0.0368	7.16	5.817
La _{0.98} Nd _{0.02} InO ₃	5.736	5.944	8.229	280.6	0.0363	7.15	5.819
La _{0.95} Nd _{0.05} InO ₃	5.724	5.937	8.220	279.3	0.0372	7.18	5.812
LaIn _{0.99} Cr _{0.01} O ₃	5.725	5.937	8.225	279.5	0.0370	7.16	5.816
LaIn _{0.99} Mn _{0.01} O ₃	5.724	5.938	8.225	279.6	0.0374	7.16	5.816
La _{0.95} Nd _{0.05} In _{0.995} Cr _{0.005} O ₃	5.726	5.941	8.225	279.8	0.0375	7.16	5.816
La _{0.95} Nd _{0.05} In _{0.995} Mn _{0.005} O ₃	5.727	5.943	8.221	279.8	0.0376	7.16	5.813
LaInO ₃ [3]	5.712	5.933	8.220	278.5	0.0387	7.20	5.812
NdInO ₃ [3]	5.631	5.897	8.133	270.1	0.0472	7.55	5.751

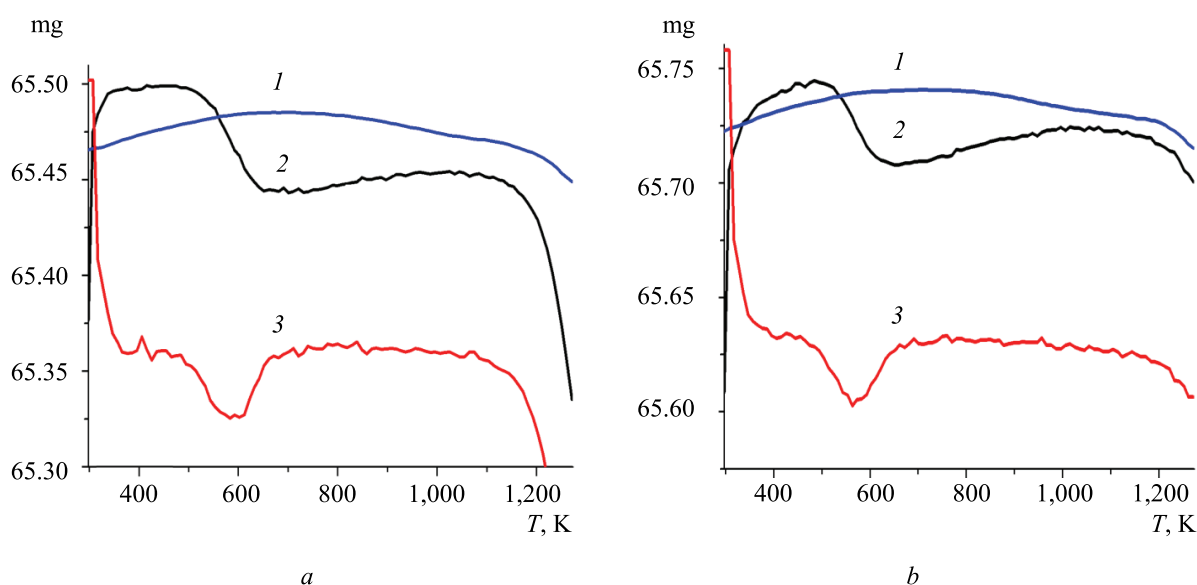


Fig. 4. DSC (1), TG (2) and DTG (3) curves for solid solutions La_{0.95}Nd_{0.05}InO₃ (a), La_{0.95}Nd_{0.05}In_{0.995}Cr_{0.005}O₃ (b)

The total mass loss in the temperature range of 300–1265 K for all studied specimens is not more than 0.14 wt %.

And for all the solid solutions there is a slight increase in mass (less than 0.1%) in the temperature range of 300–490 K and 660–1060 K. Probably the nature of these minor mass fluctuations for La_{0.95}Nd_{0.05}InO₃ and La_{0.95}Nd_{0.05}In_{0.995}Cr_{0.005}O₃ solid solutions is the same, but in the present paper it has not been established.

Conclusion. By using the solid-phase method solid solutions based on lanthanum indiate, LaInO₃, doped with Nd³⁺, Cr³⁺, Mn³⁺ ions, (the content of doping ions being less than 5 mol. %) were obtained from the appropriate oxides. The crystal structure, IR

spectra, thermal expansion of the solid solution specimens obtained were studied. The influence of the nature and quantity of the doping elements on the lattice parameters, on the frequency of the absorption bands, the average linear coefficient of thermal expansion were determined, comprehensive differential thermal analysis being carried out.

It is determined that indiate specimens are single-phase and have the crystal structure of the orthorhombically distorted perovskite of the GdFeO₃ type ($a < c/\sqrt{2} < b$). The unit cell parameters of the crystal lattice of solid solutions La_{1-x}Nd_xInO₃ with increasing content of Nd³⁺ ions from $x = 0.007$ to 0.050 K change slightly. Adding to the solid solution La_{0.95}Nd_{0.05}InO₃ additional

0.5 mol. % Cr^{3+} or Mn^{3+} ions does not have a significant influence on the parameters a, b and c. In the IR spectra, the stretching vibrations of In(Cr, Mn)–O and La(Nd)–O bonds for different compositions vary slightly. Thermal stability of

solid solutions based on lanthanum indiate, LaInO_3 , and the absence of phase transitions of the first kind in the temperature range of 350–850 K point to their practical use being promising over a wide range of operating temperatures.

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