



Excitation and photoluminescence spectra of single- and non-single-phased phosphors based on LaInO_3 doped with Dy^{3+} , Ho^{3+} activators and Sb^{3+} probable sensitizer

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ABSTRACT

Single-phased $\text{La}_{0.95}\text{Ln}_{0.05}\text{InO}_3$ ($\text{Ln} = \text{Dy}, \text{Ho}$), $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$, LaInO_3 ceramic samples as well as the $\text{La}_{0.95}\text{Ln}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ ($\text{Ln} = \text{Dy}, \text{Ho}$), $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ samples with additional impurity LaSbO_3 phase were prepared by solid-state reactions method. Their excitation and photoluminescence (PL) spectra were measured at room temperature. It was established that PL bands intensity of spectra obtained for samples of nominal composition $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ is much higher than that of single-phase $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ solid solutions. It may be probably explained by sensitizing effect of Sb^{3+} ions on Dy^{3+} , Ho^{3+} ions photoluminescence. Although it can't be excluded that the reason could be higher PL of Dy^{3+} and Ho^{3+} ions in impurity matrix than in LaInO_3 -based matrix. It was observed in the PL spectrum of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ sample that under the excitation by $\lambda_{\text{ex}} = 320 \text{ nm}$ an intense simultaneous emission of blue, green and yellow light took place.

1. Introduction

There is a significant number of works devoted to the excitation (absorption) and photoluminescence (PL) spectra of perovskite-type solid solutions based on YAlO_3 , LaAlO_3 , CaTiO_3 and other oxide compounds doped with Ho^{3+} , Dy^{3+} , Tb^{3+} ions [1–9]. In [9] it was noted that due to the low intensity of the excitation (absorption) bands of rare earth ions their PL quantum yield is significantly lower than 100%. Therefore a search of sensitizers that lead to a significant increase of rare earth ions PL intensity is actual. Among these ions there are Bi^{3+} , Sb^{3+} ions as well as $3d$ -elements ions such as Mn^{3+} , Cr^{3+} . In past ten years much attention was drawn to the study of excitation and PL spectra of LaInO_3 -based solid solutions doped with rare earth ions Pr^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} and Bi^{3+} ions that can emit visible light [10–14]. In [12] it was shown that Bi^{3+} ions located in La^{3+} ions sublattice of LaInO_3 doped with Eu^{3+} are a sensitizer for Eu^{3+} ions PL. Sb^{3+} ions have the $5s^2$ electronic configuration similar to that of Bi^{3+} ions ($6s^2$). Therefore one can expect that Sb^{3+} ions should also be good sensitizers for some rare earth-ions PL. There is a

number of studies on the luminescence properties of Bi^{3+} , Sb^{3+} ions in LnBO_3 ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Gd}, \text{Lu}$) orthoborates with Bi^{3+} , Sb^{3+} ions located in the sublattice of Ln^{3+} ions [15–20]. It was found that the Bi^{3+} ions act as a sensitizer for Eu^{3+} ions PL in $(\text{Y}, \text{Gd})\text{BO}_3$ matrix and absorbed energy transfer from the Bi^{3+} to Eu^{3+} includes Gd^{3+} . It occurs through the following chain $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+} \dots \text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$ [16,17]. In [18] PL properties of YBO_3 doped with Eu^{3+} , Sb^{3+} ions were investigated. The authors [18] stated that the energy absorbed by Sb^{3+} ions did not transfer to the Eu^{3+} ions. This means that Sb^{3+} ions in this case are not sensitizer but play the role of second activator together with Eu^{3+} ions. Note that the reference data on luminescent properties of Sb^{3+} ions in the In^{3+} ions sublattice of LaInO_3 are absent.

In this regard, in the present study we investigated the excitation and PL spectra of single- and non-single-phased ceramic samples based on LaInO_3 perovskite prepared by solid-state reactions method and doped with Dy^{3+} , Ho^{3+} ions, pairs of ions $\text{Dy}^{3+}\text{-Sb}^{3+}$, $\text{Ho}^{3+}\text{-Sb}^{3+}$, three ions $\text{Dy}^{3+}\text{-Ho}^{3+}\text{-Sb}^{3+}$.

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2. Experimental

$\text{La}_{0.95}\text{Ln}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Ln}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ ($\text{Ln} - \text{Dy, Ho}$), $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ and LaInO_3 ceramic samples were synthesized by solid-state reactions method using mixture of La_2O_3 , Dy_2O_3 , Ho_2O_3 , In_2O_3 , Sb_2O_3 oxides. All reagents had a “chemically pure” qualification. La_2O_3 , Dy_2O_3 , Ho_2O_3 oxides were preheated in air at 1273 K for 1 h. Stoichiometric amounts of the reagents were mixed with the addition of ethanol, ground in planetary mill (“Pulverizette Fritch”) in cups with zirconia balls and then pressed in pellets ($D = 25 \text{ mm}$, $h = 5\text{--}7 \text{ mm}$). The pellets were sintered at 1523 K for 6 h on the Al_2O_3 substrate. The pellets of different composition were not in contact with each other. In order to prevent the pellet-substrate interaction the pellets were separated from the substrate by thin powder layer of the same composition. Then the pellets were ground, milled and pressed in bars ($5 \times 5 \times 30 \text{ mm}$). The bars were finally sintered at 1523 K for 6 h. The bars were 30 mm length and they were used for thermal expansion investigation. Their parts were then used for PL and magnetic properties measurements. The samples prepared were characterized by powder X-ray diffraction (XRD) analysis (Bruker D8 Advance) at room temperature using $\text{CuK}\alpha$ radiation. Crystal structure parameters of the investigated samples were calculated using RTP program. Excitation and emission spectra were recorded at 300 K using automatic spectrofluorimeter SDL-2 in Physics Institute of National Academy of Sciences of Belarus. Xe-lamp DKsSh-120 was used as excitation source. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of ceramic samples were measured on a retrofitted spectroscopic unit SDL-2 (LOMO, Soviet Union), which consisted of a high throughput MDR-12 monochromator for excitation and an MDR-23 monochromator for detection. Inverse linear dispersion values monochromators 2.4 and 1.3 nm/mm. The excitation and detection axes were at an angle of 90° . A DKsSh-120 xenon lamp was used as the excitation source. The light signal passing through the monochromator was detected by photon counting using a cooled FE’U-100 and FE’U-62 photomultipliers (230–800 and 600–1200 nm ranges). In the near infrared photodetectors used as InGaAs-photodiodes IGA-050-TE2-H (900–1700 nm) and IGA2.2-030-TE2-H (900–2800 nm) company “Electro-Optical Systems Inc” (Canada, USA). The amplified signal from the photodiodes was directed to the main amplifier with a Lock-in nanovoltmeter type 232B synchrodetector (Poland, United States). The samples were rods having 5–7 mm length and $5 \times 5 \text{ mm}^2$ section. The angle between the plane of the rod and the axis of the detector system was 30° . The validity of the comparison of the intensities of the emission from the different samples was provided by permanent angle between the plane of the sample and the registration axis, equal power of excitation source and constant (or changed discretely) spectrometer sensibility during all spectra measurements. Registration conditions above make it possible to compare spectra intensities (especially maximum intensities) of different samples using the same intensity scale. SEM-images of ceramic samples were obtained with scanning electronic microscope JEOL JSM – 5610LV with assistance of Energy Dispersive X-ray Spectrometer JED 22 – 01.

3. Results and discussion

X-ray diffraction patterns of LaInO_3 , $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ samples prepared (Fig. 1a) show that all the samples were single-phase and had the structure of orthorhombically distorted perovskite. According to [21,22] orthorhombically distorted perovskite structure of LaInO_3 belongs to the $Pnma$ space group symmetry, for which the ratio of the parameters a , b , c of the unit cell is determined by the inequality $c < b/\sqrt{2} < a$. However, there is a number of papers where it is considered that orthorhombically distorted perovskite structure of the indates PrInO_3 [23], NdInO_3 [24], SmInO_3 [25], EuInO_3 [26], DyInO_3 [27] belongs to the $Pbmn$ space group symmetry. Here the ratio of the unit cell parameters a , b , c is determined by the inequality $a < c/\sqrt{2} < b$. Our

studies of $\text{PrInO}_3\text{--LaInO}_3$, $\text{NdInO}_3\text{--LaInO}_3$, $\text{SmInO}_3\text{--LaInO}_3$ binary systems showed that they formed a continuous series of solid solutions $\text{Pr}_{1-x}\text{La}_x\text{InO}_3$, $\text{Nd}_{1-x}\text{La}_x\text{InO}_3$, $\text{Sm}_{1-x}\text{La}_x\text{InO}_3$ [28] ($0 \leq x \leq 1$). X-ray diffraction patterns of all these solid solutions were identical. This shows that orthorhombically distorted perovskite structure of the indates PrInO_3 , NdInO_3 , SmInO_3 , LaInO_3 belongs to the same space group symmetry. In this regard in our paper the determination of hkl indexes of X-ray reflections of the investigated solid solutions was made by the corresponding hkl reflections of indate NdInO_3 with the $Pbmn$ space group symmetry [24]. The calculated a , b , c parameters of the studied samples are shown in the Table 1. Their analysis shows that the a , b , c parameters of various solid solutions differ slightly. For LaInO_3 and all the samples obtained the ratio values of the parameters a , b , c are determined by inequality $a < c/\sqrt{2} < b$ which according to the literature data [29] is realized for gadolinium orthoferrite GdFeO_3 . X-ray diffraction patterns of samples of nominal composition $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (Fig. 1b) in addition to the main phase with a perovskite structure show low intensity reflex ($d = 3.111 \text{ \AA}$, $2\theta = 28.70^\circ$) for $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ sample of impurity phase. The same reflex also presented at X-ray diffraction pattern of the sample with $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ nominal composition that was additionally calcined in air at 1523 K for 6 h. This reflex probably refers to the phase of $\text{La}_{1-y}\text{Dy}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$, $\text{La}_{1-y}\text{Ho}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$, $\text{La}_{1-2y}\text{Dy}_y\text{Ho}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$ solid solutions based on LaSbO_3 [30]. Those solutions could form during the synthesis of the samples with $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ nominal composition. The ratio of intensities of reflexes with highest intensity of the impurity phase ($2\theta = 28.90^\circ$) and the main phase ($2\theta = 30.65^\circ$) shows that for example in the $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ sample the amount of impurity phase based on LaSbO_3 is about 5% to the main LaInO_3 phase amount. Fig. 1c shows the SEM-images of $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, and $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ ceramic samples. It can be clearly seen that all the samples are composed of spherical and ellipsoid particles with sizes around 0.5–2.5 μm . No signs of impurity phase could be seen. The morphology of the samples with different composition changes slightly.

The peculiarities of solid-phase reactions during $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ samples synthesis were analyzed. It was found that the probability of intermediate DySbO_3 , HoSbO_3 , LaSbO_3 compounds and $\text{La}_{1-y}\text{Dy}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$, $\text{La}_{1-y}\text{Ho}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$, $\text{La}_{1-2y}\text{Dy}_y\text{Ho}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$ solid solutions formation is much lower than that of LaInO_3 compound and the solid solutions on its base. Hence, a small amount (less than 5%) of impurity phase of LaSbO_3 -based solid solutions in a samples of nominal composition $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ could lead only to negligible Dy^{3+} , Ho^{3+} , Sb^{3+} ions transition to the impurity phase. Therefore, impurity phase existence in Sb^{3+} containing samples only insignificantly decreases pre-set Dy^{3+} , Ho^{3+} , Sb^{3+} ions concentration in LaInO_3 -based solid solutions. This conclusion is confirmed by Table 1 data showing that crystal structure parameters a , b and crystal cell volume V of obtained LaInO_3 -based phosphors samples are slightly lower than that of undoped LaInO_3 . That decrease is due to the ionic radii. The ionic radius of Sb^{3+} ion is 0.02 \AA lower than that of In^{3+} ($r_{\text{In}^{3+}} = 0.92 \text{ \AA}$ [31]). The ionic radii of Dy^{3+} , Ho^{3+} are 0.16 and 0.18 \AA lower than that of La^{3+} , respectively ($r_{\text{La}^{3+}} = 1.04 \text{ \AA}$ [31]). That proves that during $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ synthesis Dy^{3+} , Ho^{3+} and Sb^{3+} ions were placed into crystal structure of LaInO_3 matrix and only insignificant part of them transferred to the LaSbO_3 -based impurity phase.

Fig. 2 shows the excitation spectra of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$. At monitoring of the Dy^{3+} emission spectra we took two wavelength values: $\lambda_{\text{mon}} = 482 \text{ nm}$ (Fig. 2a) and $\lambda_{\text{mon}} = 576 \text{ nm}$ (Fig. 2b) which were chosen in accordance with its PL maxima (Fig. 3). Excitation spectra have the most intense excitation bands in the wavelength range of 250–460 nm with maximum at $\lambda = 273 \text{ nm}$ ($\nu = 36360 \text{ cm}^{-1}$). Other excitation bands with maxima at $\lambda = 323, 349, 363, 388, 426, 454 \text{ nm}$ have much

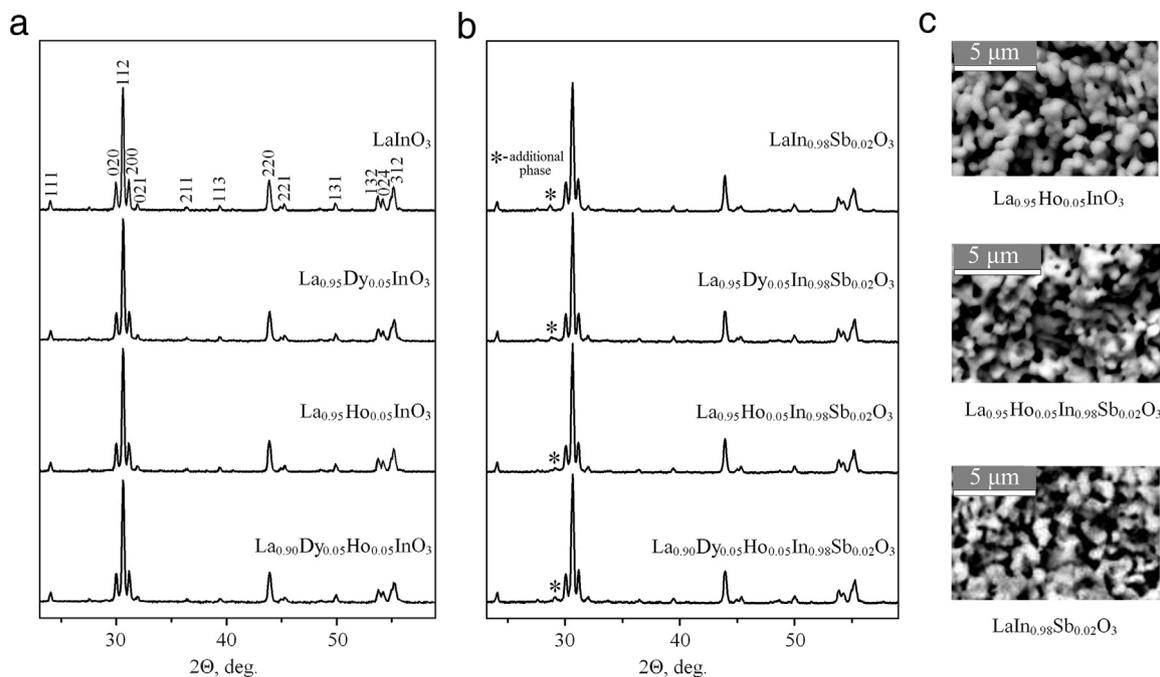


Fig. 1. X-ray diffraction patterns of LaInO_3 , $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ (a); $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (b); SEM-images of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ and $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ ceramic samples (c).

Table 1

Cell parameters (a , b , c), cell volume (V) and orthorhombical distortion degree (ϵ) for LaInO_3 -based samples doped with Dy^{3+} , Ho^{3+} , Sb^{3+} .

Composition	Cell parameters					$c/\sqrt{2}$, Å
	a , Å	b , Å	c , Å	V , Å ³	$\epsilon = (b - a) / a$, %	
LaInO_3	5.738	5.953	8.227	281.0	3.75	5.817
$\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$	5.724	5.942	8.233	280.0	3.81	5.822
$\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$	5.727	5.940	8.239	280.3	3.72	5.826
$\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$	5.727	5.940	8.230	279.9	3.72	5.819
$\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$	5.735	5.937	8.234	280.3	3.52	5.822
$\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$	5.728	5.940	8.228	280.0	3.70	5.818
$\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$	5.731	5.935	8.237	280.1	3.56	5.824
$\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$	5.726	5.934	8.234	279.8	3.63	5.822

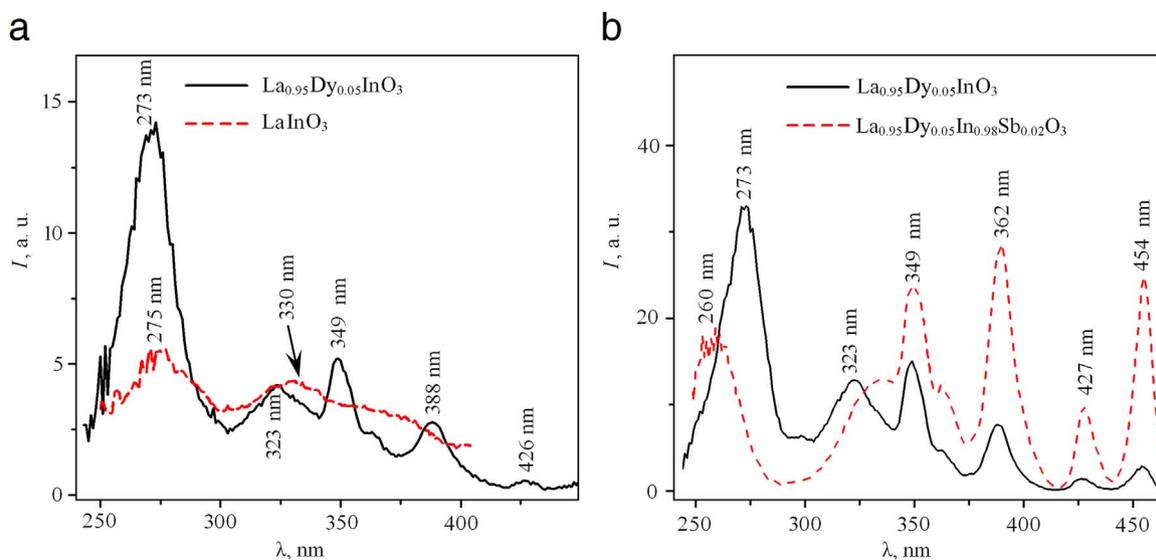


Fig. 2. Excitation spectra of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ (at $\lambda_{\text{mon}} = 482$ nm), LaInO_3 (at $\lambda_{\text{mon}} = 433$ nm) (a), $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (at $\lambda_{\text{mon}} = 576$ nm) (b).

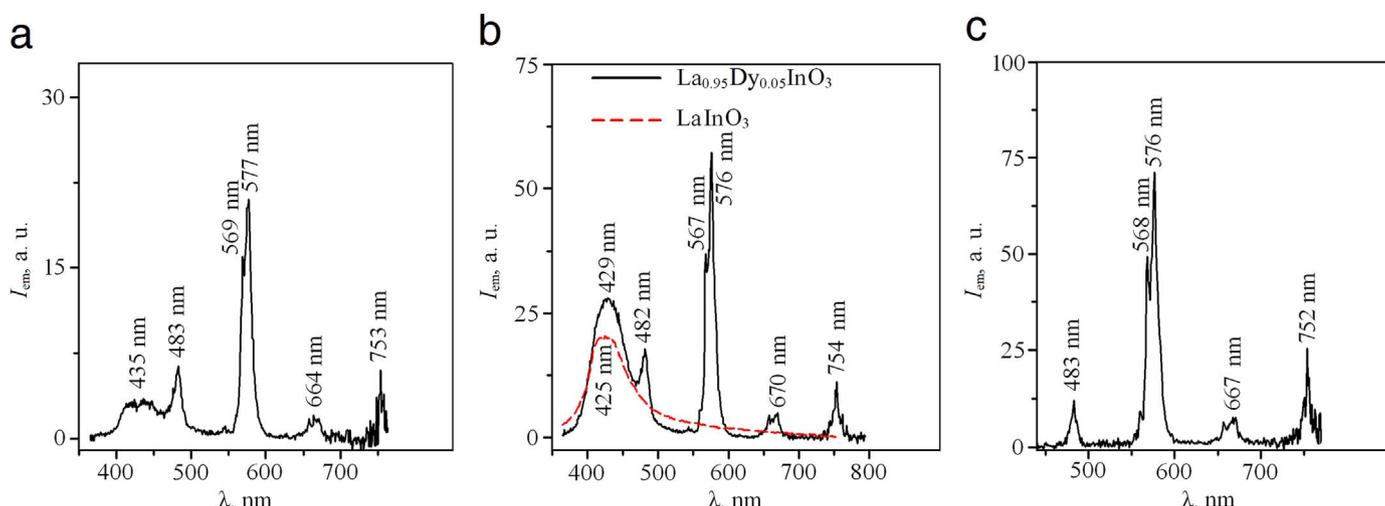


Fig. 3. Photoluminescence spectra of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ at $\lambda_{\text{ex}} = 275$ nm (a), $\lambda_{\text{ex}} = 320$ nm (b), $\lambda_{\text{ex}} = 390$ nm (c); LaInO_3 at $\lambda_{\text{ex}} = 330$ nm (b).

Table 2

The maxima of wavelength of excitation bands (λ), their inverse values ($\nu = 1/\lambda$) for $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ at $\lambda_{\text{mon}} = 482$ nm and 576 nm; $f-f$ transitions, causing the excitation bands, their energy intervals for $\text{Gd}_{0.97}\text{Dy}_{0.03}\text{AlO}_3$ at $\lambda_{\text{mon}} = 577$ nm [1].

$\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$		$\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$		$f-f$ transition (energy interval, cm^{-1}) in $\text{Gd}_{0.97}\text{Dy}_{0.03}\text{AlO}_3$ at $\lambda_{\text{mon}} = 577$ nm [1]
$\lambda_{\text{mon}} = 482$ nm	$\lambda_{\text{mon}} = 576$ nm	$\lambda_{\text{mon}} = 482$ nm	$\lambda_{\text{mon}} = 576$ nm	
λ , nm	ν , cm^{-1}	λ , nm	ν , cm^{-1}	
273	36630	273	36630	
323	30960	323	30960	${}^6H_{15/2} \rightarrow {}^5P_{3/2}$ (30675)
349	28653	349	28653	${}^6H_{15/2} \rightarrow {}^6P_{7/2}$ (28409)
363	27548	362	27624	${}^6H_{15/2} \rightarrow {}^6P_{5/2}$ (27322)
388	25773	388	25773	${}^6H_{15/2} \rightarrow {}^4I_{13/2}$ (25840)
426	23474	426	23474	${}^6H_{15/2} \rightarrow {}^4G_{11/2}$ (23419)
–	–	454	22026	${}^6H_{15/2} \rightarrow {}^4I_{15/2}$ (22173)

lower intensity. Basic parameters (λ , ν) of excitation bands for $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ solid solution with orthorhombically distorted perovskite structure excitation bands are shown in Table 2. Data of Table 2 are in good agreement with the data given in the work [1] for the GdAlO_3 -based solid solution with orthorhombically distorted perovskite structure where 3 mol. % of Gd^{3+} ions are substituted by Dy^{3+} ions. According to [1] the excitation maxima of Dy^{3+} ion in $\text{Gd}_{0.97}\text{Dy}_{0.03}\text{AlO}_3$ solid solution at 326, 352, 366, 387, 427, 451 nm are due to $f-f$ electron transitions of Dy^{3+} ion from ${}^6H_{15/2}$ ground level to ${}^5P_{3/2}$, ${}^6P_{7/2}$, ${}^6P_{5/2}$, ${}^4I_{13/2}$, ${}^4G_{11/2}$, ${}^4I_{15/2}$ excited levels respectively. Analysis of the Table 2 data shows that the wavenumbers ($\nu = 1/\lambda$) of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ excitation bands differ insignificantly from the values of the $f-f$ transitions energy intervals responsible for the excitation band of $\text{Gd}_{0.97}\text{Dy}_{0.03}\text{AlO}_3$ [1]. Hence, range excitation band of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ solid solution in 320–460 nm wavelength is due to the same $f-f$ transitions as for $\text{Gd}_{0.97}\text{Dy}_{0.03}\text{AlO}_3$. However, it should be noted that the excitation bands in wavelength range 300–400 nm with maxima at $\lambda = 323, 349, 388$ nm for $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ overlap with a broad excitation band of undoped LaInO_3 sample with excitation maximum at $\lambda = 330$ nm (Fig. 2a). This fact shows that the intensity of these excitation bands is due not only to $f-f$ electrons transitions of Dy^{3+} ions in $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, but also to In^{3+} ions. The nature of the excitation band of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ with maximum at $\lambda = 273$ nm (electronic transitions of Dy^{3+} or In^{3+} ions) is not clear. It should be noted that the similar excitation band ($\lambda_{\text{max}} = 275$ nm) but with significantly lower intensity was observed in excitation spectrum of the undoped LaInO_3 (Fig. 2a). It agrees well with [32], where it was shown that the undoped LaInO_3 absorption band with maximum at $\lambda = 278$ nm is due to charge transfer from $2p$ -level of O^{2-} ions to $5s$ - and $5p$ -

levels of In^{3+} ions in InO_6 octahedra. Hence, the excitation band of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ with $\lambda_{\text{max}} = 273$ nm is mainly due to the electronic transitions of Dy^{3+} ions and partly of In^{3+} ions.

Fig. 3 shows the PL spectra of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ at $\lambda_{\text{ex}} = 275, 320, 390$ nm. The most intense narrow PL band has a maximum at $\lambda = 577$ nm and bands of a lower intensity with maxima at $\lambda = 435, 483, 664, 753$ nm (Fig. 3a). Basic parameters (λ , ν) of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ PL bands are shown in the Table 3. PL spectra of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ (Fig. 3) show that Dy^{3+} ions introduced into the crystal lattice of LaInO_3 excited by near UV (275, 320 nm) and visible violet (390 nm) light emit yellow light (577 nm) of significant intensity as well as blue (435, 483 nm) and red (664, 752 nm) light with significantly less intensity. According to [1] and the data of Table 3 PL maxima of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ solid solution at $\lambda = 483, 577, 664, 753$ nm (Fig. 3a) are due to the f -electron transitions of Dy^{3+} on the excited level ${}^4F_{9/2}$ to lower levels ${}^6H_{15/2}$, ${}^6H_{13/2}$, ${}^6H_{11/2}$, ${}^6F_{11/2} + {}^6H_{9/2}$, respectively. PL band of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ with maxima at 435 nm (Fig. 3a) and 429 nm (Fig. 3b) also presents in the PL spectrum of undoped LaInO_3 ($\lambda_{\text{ex}} = 330$ nm) with maximum at $\lambda = 425$ nm (Fig. 3b), but this band is absent in PL spectrum with $\lambda_{\text{ex}} = 390$ nm (Fig. 3c). These data show that the PL band of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ with maxima at $\lambda = 429$ –435 nm is due to electronic transitions of both Dy^{3+} and In^{3+} ions.

In [33] we investigated the excitation spectrum for $\lambda_{\text{mon}} = 450$ nm and PL spectrum for $\lambda_{\text{ex}} = 320$ nm of the sample having nominal composition $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$. It was found that in excitation spectrum of $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ there is a single band with $\lambda_{\text{max}} = 324$ nm. In PL spectrum of this sample there is also a single band with $\lambda_{\text{max}} = 430$ nm. These values for the sample with nominal composition of $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ differ insignificantly from those of undoped LaInO_3

Table 3

The maxima of wavelengths of photoluminescence bands (λ), their inverse values ($\nu = 1/\lambda$) for $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ at $\lambda_{\text{ex}} = 275$ nm, $\lambda_{\text{ex}} = 320$ nm, $\lambda_{\text{ex}} = 390$ nm; $f-f$ transitions, causing the photoluminescence bands, their energy intervals for $\text{Gd}_{0.97}\text{Dy}_{0.03}\text{AlO}_3$ at $\lambda_{\text{ex}} = 352$ nm [1].

$\lambda_{\text{ex}} = 275$ nm		$\lambda_{\text{ex}} = 320$ nm		$\lambda_{\text{ex}} = 390$ nm		$f-f$ transition (energy interval, cm^{-1}) in $\text{Gd}_{0.97}\text{Dy}_{0.03}\text{AlO}_3$ at $\lambda_{\text{ex}} = 352$ nm [1]
λ , nm	ν , cm^{-1}	λ , nm	ν , cm^{-1}	λ , nm	ν , cm^{-1}	
435	22989	429	23310	–	–	
483	20704	482	20747	483	20704	${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (20747)
569	17575	567	17637	568	17606	${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (17331)
577	17331	576	17361	576	17361	
664	15060	670	14925	667	14993	${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ (14771)
753	13280	754	13263	752	13298	${}^4F_{9/2} \rightarrow {}^6F_{11/2} + {}^6H_{9/2}$ (13459) [2]

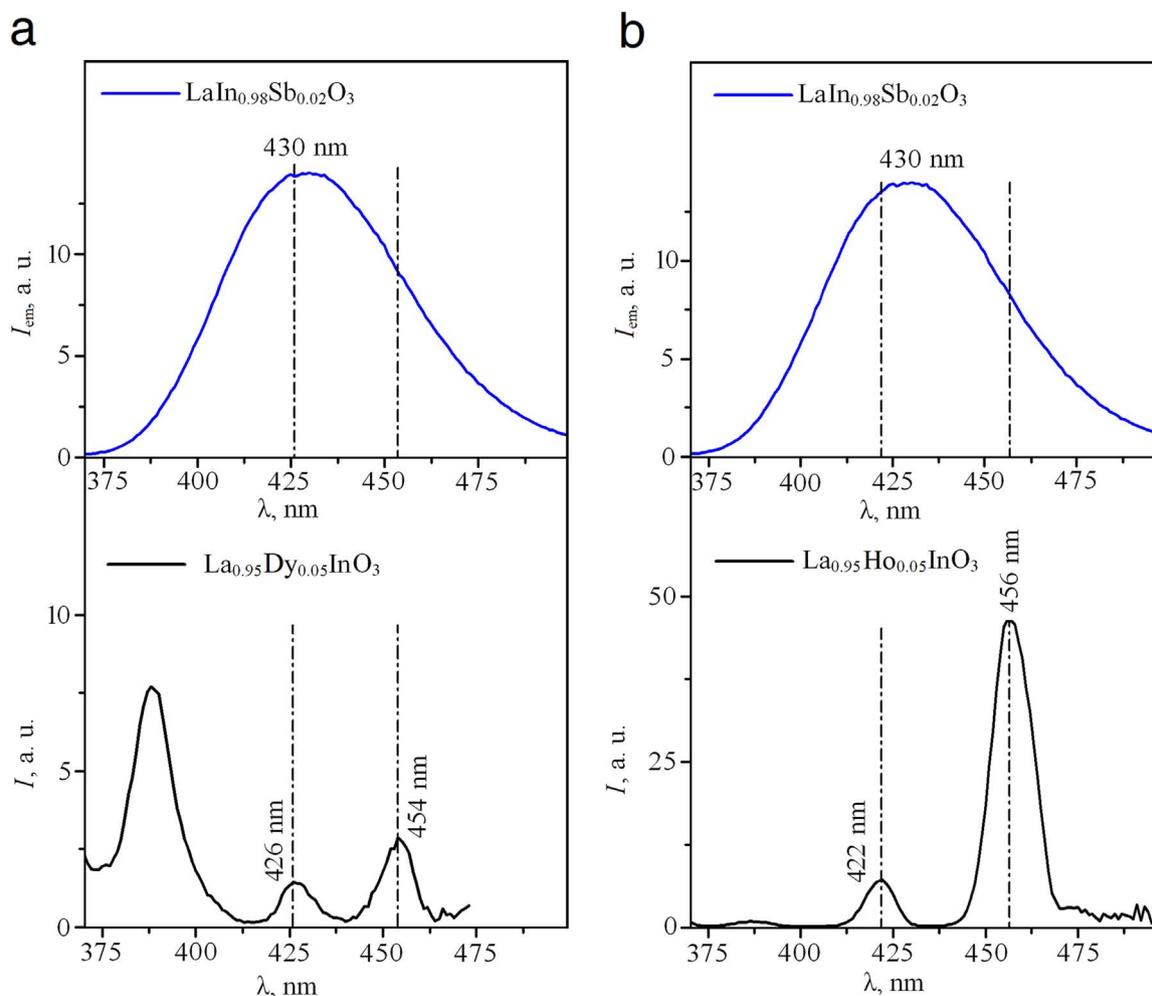


Fig. 4. The overlap of photoluminescence bands (I_{em}) for $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ at $\lambda_{ex} = 320$ nm, and excitation bands (I) for $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ at $\lambda_{mon} = 576$ nm (a) and $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ at $\lambda_{mon} = 543$ nm (b).

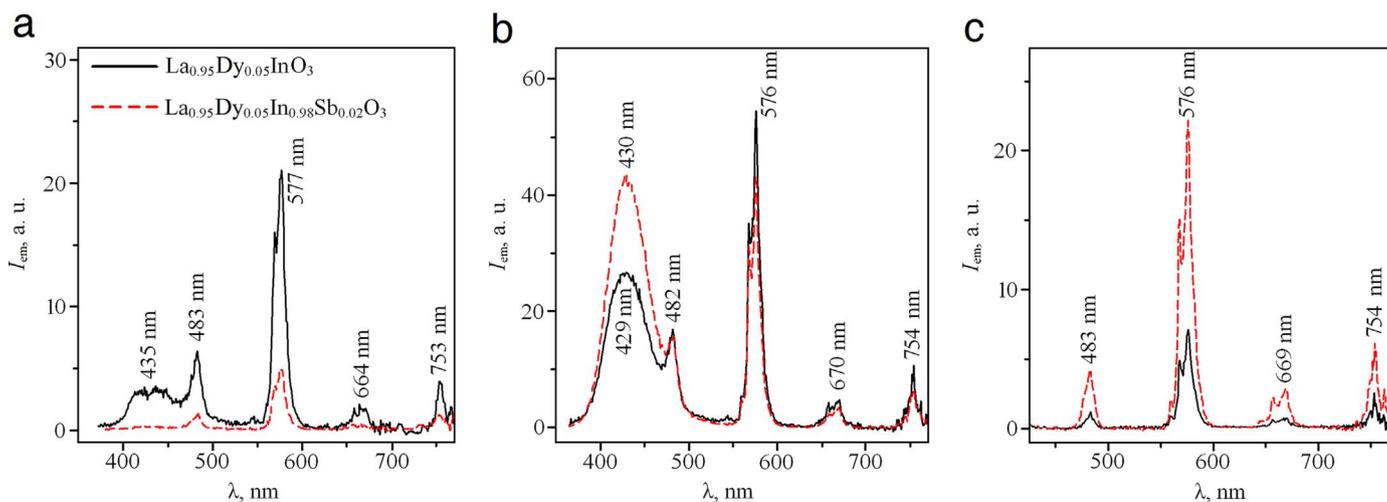


Fig. 5. Photoluminescence spectra of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ and $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ at $\lambda_{ex} = 275$ nm (a), $\lambda_{ex} = 320$ nm (b), $\lambda_{ex} = 390$ nm (c).

($\lambda = 330$ nm, Fig. 2a and $\lambda = 425$ nm, Fig. 3b, respectively). Excitation and PL spectra analysis shows that for $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ and $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ samples the sensitizer's PL band overlaps the activator's excitation (absorption) band, hence the main sensitization condition is obeyed [34]. Fig. 4a shows that PL band of $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ sample overlaps two excitation bands with maxima of 426, 454 nm of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ solid solution. So for a Sb^{3+} - Dy^{3+} pair of ions the

main sensitization condition is fulfilled and for that reason the energy absorbed by Sb^{3+} ions can be transferred to Dy^{3+} ions and it could lead to an increase in Dy^{3+} ion PL intensity. Comparison of the PL spectra obtained for $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ and $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ at $\lambda_{ex} = 275$, 320, 390 nm (Fig. 5a, b, c, respectively) shows that only PL spectrum for $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ containing only insignificant part of Dy^{3+} and Sb^{3+} ions in impurity phase at $\lambda_{ex} = 390$ nm (Fig. 5c)

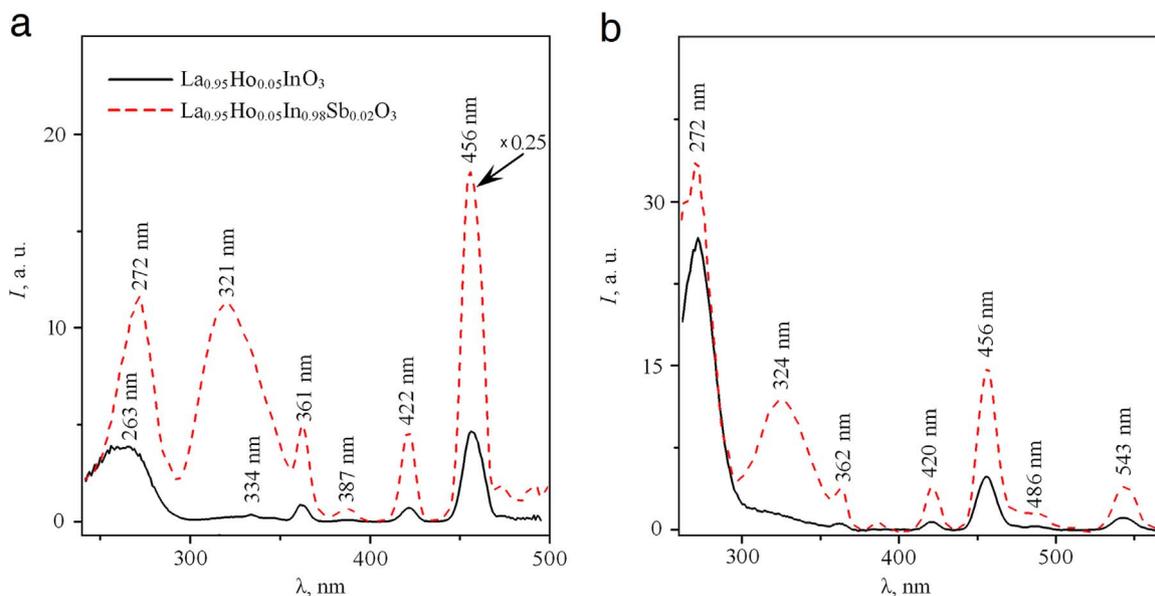


Fig. 6. Excitation spectra of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ and $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ at $\lambda_{\text{mon}} = 544$ nm (a) and $\lambda_{\text{mon}} = 1198$ nm (b).

shows higher intensity of all bands than that of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ solid solution containing no Sb^{3+} ions. In PL spectra at $\lambda_{\text{ex}} = 320$ nm (Fig. 5b) presence of Sb^{3+} ions increases intensity only of a band with $\lambda_{\text{max}} = 429$ nm. The lack of PL intensity increase of $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ sample in comparison with $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ solid solution after the excitation at $\lambda_{\text{ex}} = 275$ nm (Fig. 5a) may be explained by absence of PL excitation (absorption) band of Sb^{3+} ions at this λ_{ex} [33]. Hence, we can suppose that Sb^{3+} ions in crystal lattice of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ are good sensitizer of Dy^{3+} ions PL only after the excitation at $\lambda_{\text{ex}} = 390$ nm. Although one can't exclude that increasing of PL intensity for sample with nominal composition $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ in comparison with that of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ solid solution could happen because of probable higher PL intensity of Dy^{3+} and Sb^{3+} ions placed in $\text{La}_{1-y}\text{Dy}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$ impurity phase than in LaInO_3 -based main phase.

Excitation spectrum (Fig. 6a, $\lambda_{\text{mon}} = 544$ nm) of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ solid solution shows that in 250–500 nm wavelength range the most intense bands are the bands with maxima at $\lambda = 263$ and 456 nm. In the excitation spectrum of the $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ obtained at $\lambda_{\text{mon}} = 1198$ nm (Fig. 6b) the most intense band has a peak at $\lambda = 272$ nm and a band with a maximum at $\lambda = 456$ nm has a significantly lower intensity than band with a maximum at $\lambda = 272$ nm. The intensity of the remaining excitation bands with a maximum at $\lambda = 334, 361, 387, 422$ nm is small. The basic parameters (λ, ν) of the excitation bands of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ are given in the Table 4. That data show that the wave numbers (ν) of the excitation bands for $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ in the wavelength range 250–570 nm differ slightly from the values of energy intervals for $f-f$ transitions causing excitation (absorption) bands of solid solutions $\text{La}_{0.96}\text{Ho}_{0.04}\text{AlO}_3, \text{Y}_{0.96}\text{Ho}_{0.04}\text{AlO}_3$ [3,4] where 4 mol. % of the ions $\text{La}^{3+}, \text{Y}^{3+}$ ions are substituted by Ho^{3+} ions. Consequently, in the examined wavelength interval corresponding excitation bands for the $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ are due to the same $f-f$ transitions as for $\text{La}_{0.96}\text{Ho}_{0.04}\text{AlO}_3, \text{Y}_{0.96}\text{Ho}_{0.04}\text{AlO}_3$ [3,4]. Thus excitation bands of Ho^{3+} ions with maxima at wavelengths 334, 361, 387, 422, 456, 486, 543 nm are due to the same $f-f$ transitions of Ho^{3+} ions from ground level 5I_8 to corresponding excited levels $^3K_6 + ^3F_4, ^3H_6 + ^3D_2, ^5G_4 + ^3K_7, ^5G_5, ^5G_6, ^5F_3, ^5F_4 + ^5S_2$ as in $\text{La}_{0.96}\text{Ho}_{0.04}\text{AlO}_3, \text{Y}_{0.96}\text{Ho}_{0.04}\text{AlO}_3$. However, as for the $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, for $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ it is not definitely established which electronic transitions of Ho^{3+} or In^{3+} ions are due to the excitation band with a maximum at $\lambda = 263$ nm (Fig. 6a) and $\lambda = 272$ nm (Fig. 6b) on the excitation spectra obtained at $\lambda_{\text{mon}} = 544$ and 1198 nm, respectively.

b

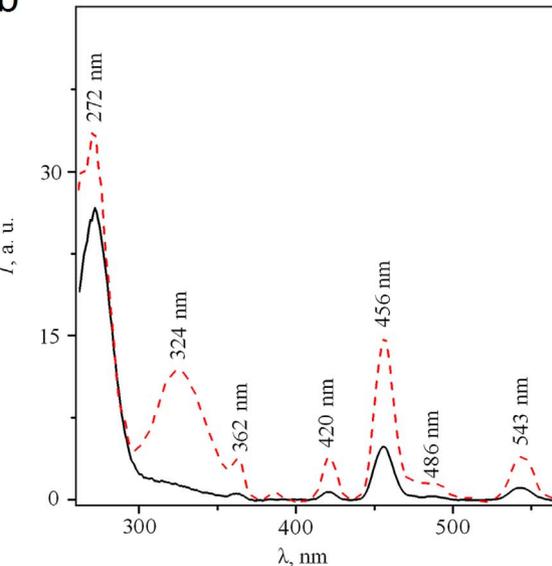


Table 4

The maxima of wavelengths of excitation bands (λ), their inverse values ($\nu = 1/\lambda$) for $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ at $\lambda_{\text{mon}} = 544$ nm and 1198 nm; $f-f$ transitions, causing the excitation bands, their energy intervals [3,4].

$\lambda_{\text{mon}} = 544$ nm		$\lambda_{\text{mon}} = 1198$ nm		$f-f$ transition (energy interval, cm^{-1}) [3,4]
λ , nm	ν , cm^{-1}	λ , nm	ν , cm^{-1}	
263	38023	272	36765	
334	29940	–	–	$^5I_8 \rightarrow ^3K_6 + ^3F_4$ (30120)
361	27701	362	27624	$^5I_8 \rightarrow ^3H_6 + ^3D_2$ (27624)
387	25840	–	–	$^5I_8 \rightarrow ^5G_4 + ^3K_7$ (25773)
422	23697	420	23810	$^5I_8 \rightarrow ^5G_5$ (23866)
456	21929	456	21930	$^5I_8 \rightarrow ^5G_6$ (22124)
–	–	486	20576	$^5I_8 \rightarrow ^5F_3$ (20576)
–	–	543	18416	$^5I_8 \rightarrow ^5F_4 + ^5S_2$ (18519)

Probably, this excitation band for Ho^{3+} ions $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ as for Dy^{3+} ions in $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ is mainly due to the electronic transitions of Ho^{3+} ions and partially of In^{3+} ions. It should be noted that such an intense excitation band with a maximum at $\lambda = 255$ and 268 nm [10] is present in the excitation spectra of $\text{La}_{0.998}\text{Pr}_{0.002}\text{InO}_3$ and $\text{La}_{0.98}\text{Sm}_{0.02}\text{InO}_3$. According to [10], this band for the solid solution containing Pr^{3+} ions is due to the electron transition $4f^2 \rightarrow 4f 5d$ of Pr^{3+} ions, whereas for solid solution doped with Sm^{3+} ions it is due to the charge transfer from the sublevel $2p$ of oxygen O^{2-} ions to the $4f$ sublevel of Sm^{3+} ions.

The PL spectra in the wavelength range 320–2020 nm at $\lambda_{\text{ex}} = 275, 333, 362, 455$ nm are shown in Fig. 7. From Fig. 7b, d one can see that the most intense PL band is a band with a maximum at 1964–1966 nm. Another bands that are in the IR-region (with the maximum at 1197 nm (Fig. 7b) and 1195 nm (Fig. 7d)) and in green region of the spectrum (with the maximum of the PL at 543, 544 nm) have less intensities. The intensity of the rest PL bands with a maximum at $\lambda = 428, 584, 653, 756$ nm is insignificant. Basic parameters (λ, ν) of PL bands for $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ are given in the Table 5. In this table on the basis of the published data [4–6] $f-f$ transitions causing PL bands of Ho^{3+} ions introduced into the crystal lattice of $\text{YAlO}_3, \text{LaAlO}_3$ with a perovskite structure are also presented. The values of the energy intervals of $f-f$ transitions of electrons for Ho^{3+} ions in solid solutions based on aluminates YAlO_3 and LaAlO_3 differ insignificantly from the values of the wave numbers of Ho^{3+} ions for PL bands of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ (Table 5). Consequently, PL bands of Ho^{3+} ions in $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ PL

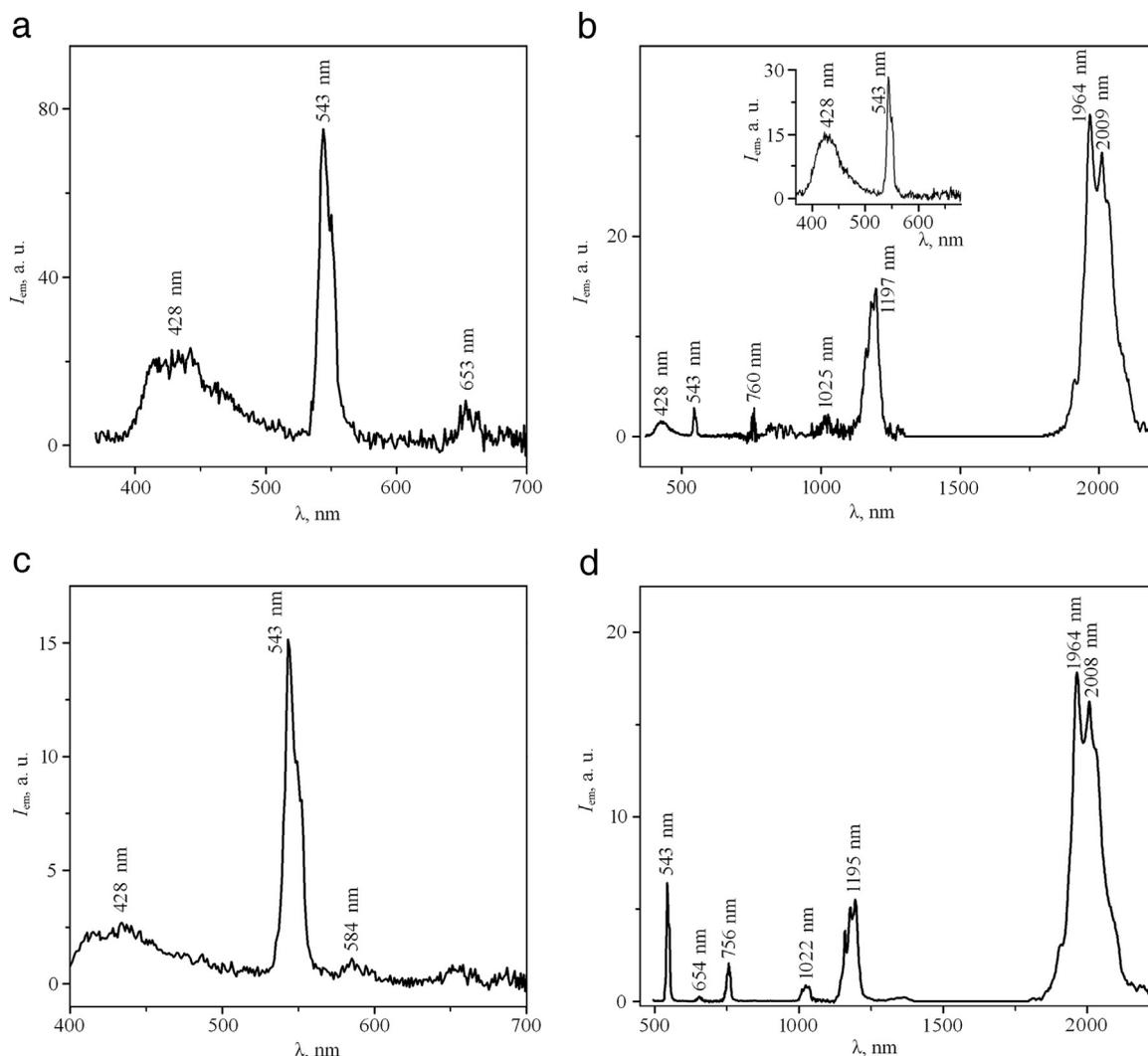


Fig. 7. Photoluminescence spectra of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ at $\lambda_{\text{ex}} = 275$ nm (a), $\lambda_{\text{ex}} = 333$ nm (b), $\lambda_{\text{ex}} = 362$ nm (c), $\lambda_{\text{ex}} = 455$ nm (d).

are due to the same $f-f$ transitions as it takes place for Ho^{3+} in solid solutions based on YAlO_3 and LaAlO_3 (Table 5). However, it should be noted that the broad PL band with maximum at 428 nm is present not only in PL spectra of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ (Fig. 7a, b, c) and undoped LaInO_3 (Fig. 3b), but also in the PL spectra of aluminates YAlO_3 and LaAlO_3 , doped with Ho^{3+} [4–6], where the In^{3+} ions are absent. Consequently, the PL band with a maximum at $\lambda = 428$ nm for

$\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ is due to the electronic transitions of Ho^{3+} ions and partially In^{3+} ions.

Fig. 4b shows that PL band with a maximum at $\lambda = 430$ nm for sample of nominal composition $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ overlaps with the excitation bands with maxima at $\lambda = 422, 456$ nm for $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ solid solution. Therefore, for Ho^{3+} , Sb^{3+} ions in sample of nominal composition $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ the main condition of sensitiza-

Table 5

The maxima of wavelengths of photoluminescence bands (λ), their inverse values ($\nu = 1/\lambda$) for $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ at $\lambda_{\text{ex}} = 275$ nm, $\lambda_{\text{ex}} = 333$ nm, $\lambda_{\text{ex}} = 362$ nm, $\lambda_{\text{ex}} = 455$ nm; $f-f$ transitions, causing the photoluminescence bands, their energy intervals [4–6].

$\lambda_{\text{ex}} = 275$ nm		$\lambda_{\text{ex}} = 333$ nm		$\lambda_{\text{ex}} = 362$ nm		$\lambda_{\text{ex}} = 455$ nm		$f-f$ transition (energy interval, cm^{-1}) [4–6]
λ_{lum} , nm	ν_{lum} , cm^{-1}							
428	23364	428	23364	428	23364	–	–	$^5\text{S}_2 + ^5\text{F}_4 \rightarrow ^5\text{I}_8$ (18564)
544	18382	543	18416	543	18416	543	18416	
550	18182	550	18182	549	18215	549	18215	$^5\text{G}_4 \rightarrow ^5\text{I}_6$ (17083)
–	–	–	–	584	17123	–	–	
653	15314	–	–	–	–	654	15291	$^5\text{F}_5 \rightarrow ^5\text{I}_8$ (15509)
–	–	760	13158	–	–	756	13228	$^5\text{S}_2 \rightarrow ^5\text{I}_7$ (13332)
–	–	1025	9757	–	–	1022	9785	$^5\text{F}_5 \rightarrow ^5\text{I}_7$ (10277)
–	–	1162	8606	–	–	1160	8621	$^5\text{I}_6 \rightarrow ^5\text{I}_8$ (8767)
–	–	1180	8475	–	–	1179	8482	
–	–	1197	8354	–	–	1195	8368	
–	–	1966	5086	–	–	1964	5092	$^5\text{I}_7 \rightarrow ^5\text{I}_8$ (5232)
–	–	2009	4978	–	–	2008	4980	

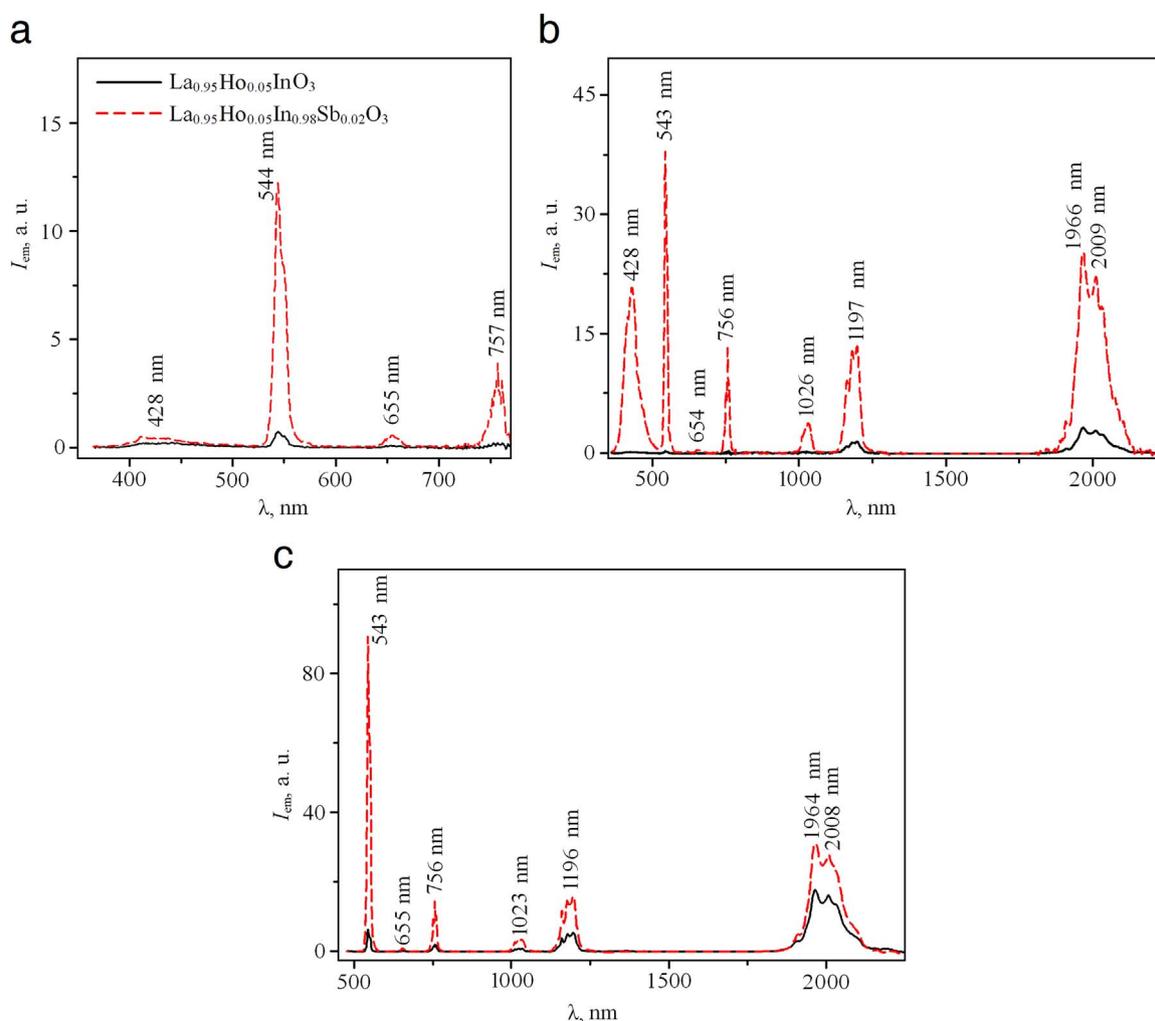


Fig. 8. Photoluminescence spectra of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ and $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ at $\lambda_{\text{ex}} = 275$ nm (a), $\lambda_{\text{ex}} = 333$ nm (b), $\lambda_{\text{ex}} = 455$ nm (c).

tion is realized. According to this condition the PL band of the sensitizer must overlap with the absorption (excitation) band of activator. In this regard, it can be assumed that the ions Sb^{3+} , introduced into the crystal lattice of the solid solution $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$, will influence sensitization of PL for Ho^{3+} ions. If comparing the PL spectra of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ solid solution and sample with nominal composition $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (Fig. 8) obtained at $\lambda_{\text{ex}} = 275, 333, 455$ nm, it can be seen that intensity of all PL bands of solid solution containing only insignificant part of Ho^{3+} and Sb^{3+} ions in impurity phase $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ sample is significantly higher than that of the solid solution with no Sb^{3+} ions. Therefore Sb^{3+} ions introduced in the of In^{3+} ions sublattice of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ are probably good PL sensitizer of Ho^{3+} ions. As a result of this sensitization effect of Sb^{3+} ions on the PL of Ho^{3+} ions intensity of PL band for Ho^{3+} ions with a maximum at $\lambda = 543$ nm increases in several times in the spectra obtained at $\lambda_{\text{ex}} = 275, 333, 455$ nm. It should be noted that PL spectra of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ (Fig. 7b, d) has the most intense PL band with a maximum at $\lambda = 1966$ nm (IR region). But in PL spectra for sample of nominal composition of $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ the most intense band is the band with a maximum at $\lambda = 543$ nm (Fig. 8b, c). In the PL spectrum ($\lambda_{\text{ex}} = 455$ nm) of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ (Fig. 7d) the ratio of the peak intensity of the band with a maximum at 543 nm to the value of the peak intensity of the band with a maximum at 1966 nm is equal to 0.36. However, for the PL spectrum ($\lambda_{\text{ex}} = 455$ nm) of $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ such a ratio of peak intensities for the bands with maxima at a $\lambda = 543$ nm and 1966 nm is equal to 2.84. Since in sample of nominal composition $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ ions Ho^{3+}

and Sb^{3+} are in different sublattices and their concentration is small whereas concentration of In^{3+} ions is large then the probability of a direct transfer of the energy absorbed by Sb^{3+} ions directly to the Ho^{3+} ions is small. In this regard, it can be assumed that the energy absorbed at excitation of Sb^{3+} ions are not directly transferred to the Ho^{3+} ions. At first, the energy is transferred to the In^{3+} ions and then along the chain $\text{Sb}^{3+} \rightarrow \text{In}^{3+} \dots \text{In}^{3+} \rightarrow \text{Ho}^{3+}$ to the Ho^{3+} ions. Thus, In^{3+} ions are an intermediary of transfer of the absorbed by Sb^{3+} ions energy to the Ho^{3+} ions. For In^{3+} ions maxima of PL and PL excitation bands are close to the corresponding values of the maxima for Sb^{3+} ions (Figs. 2a and 3b, [33]). Previously, such a transfer mechanism of the energy absorbed by sensitizer ions (Bi^{3+}) to the activator ions (Eu^{3+}) was proposed for the $\text{Y}_{1-x}\text{Gd}_x\text{BO}_3$ matrix in [17]. However one can't exclude that as for Dy^{3+} ions such PL intensity increasing of sample having nominal composition $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ in comparison with that of $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ solid solution is due to higher PL intensity of Ho^{3+} and Sb^{3+} ions in $\text{La}_{1-y}\text{Ho}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$ impurity matrix than in LaInO_3 -based matrix. In accordance to that it is possible that PL intensity of samples containing both Ho^{3+} and Sb^{3+} ions is predominantly due to impurity phase PL, but not that of main phase. However early we determined that for $\text{Tb}^{3+}, \text{Sb}^{3+}$ ions in sample with nominal composition $\text{La}_{0.93}\text{Tb}_{0.07}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ the main condition of sensitization is not realized because the PL band of the Sb^{3+} ions does not overlap with the excitation band of Tb^{3+} ions. Thus the presence of Sb^{3+} ions here leads nowhere PL intensity amplification for Tb^{3+} ions. This fact confirms our conclusion that for $\text{Dy}^{3+}\text{-Sb}^{3+}, \text{Ho}^{3+}\text{-Sb}^{3+}$ pairs Sb^{3+} ions act as a sensitizer of $\text{Dy}^{3+}, \text{Ho}^{3+}$ PL because for this

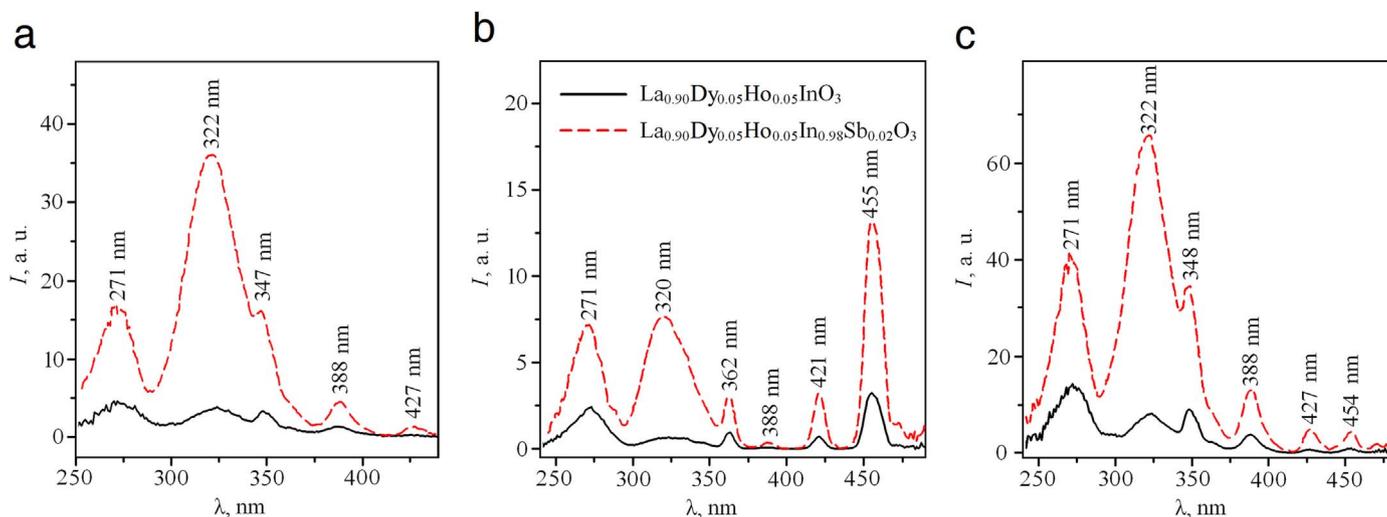


Fig. 9. Excitation spectra of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ and $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ at $\lambda_{\text{mon}} = 482$ nm (a), $\lambda_{\text{mon}} = 543$ nm (b), $\lambda_{\text{mon}} = 576$ nm (c).

pairs of ions the main condition of sensitization is realized.

Fig. 9 shows the excitation spectra of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ solid solution and sample of nominal composition of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ obtained at $\lambda_{\text{mon}} = 482$, 543, 576 nm which correspond to the maxima of PL bands of Dy^{3+} ions ($\lambda = 483$, 576 nm, Fig. 3) and Ho^{3+} ($\lambda = 543$ nm, Fig. 7) ions. Each of the three excitation spectra of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ contains bands with maxima at $\lambda = 271$, 320–322, 426–427 nm, which are present also in excitation spectra of $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$ (Fig. 2) and $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$ (Fig. 6). From excitation spectra of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ and $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (Fig. 9) one can see that the introduction of little less than 2 mol% of Sb^{3+} ions in crystal lattice of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ sample leads to a significant increase in the intensity of the Dy^{3+} and Ho^{3+} ions excitation bands.

PL spectra for single phase $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ sample, and the sample of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ nominal composition (Fig. 10) clearly show that the introduction of Sb^{3+} ions in $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ sample leads to significant amplification of all Dy^{3+} , Ho^{3+} PL bands intensity. The main part of Sb^{3+} ions goes to the main LaInO_3 -based phase and only negligible amount could transfer to LaSbO_3 -based phase. It was found that the ratio of the intensities of the bands of simultaneous radiation by Dy^{3+} , Ho^{3+} ions depends on the excitation wavelength (λ_{ex}). So on the PL spectrum at $\lambda_{\text{ex}} = 320$ nm for $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (Fig. 10b) there is a significant simultaneous emission of blue ($\lambda_{\text{max}} = 429$ nm), green ($\lambda_{\text{max}} = 543$ nm), yellow ($\lambda_{\text{max}} = 576$ nm) light and red light ($\lambda_{\text{max}} = 756$ nm) with less intensity. In the PL spectrum of this sample at $\lambda_{\text{ex}} = 361$ nm (Fig. 10c) the most intense band is a band of green light emission ($\lambda_{\text{max}} = 543$ nm) whereas the intensity of blue ($\lambda_{\text{max}} = 430$ nm) and yellow ($\lambda_{\text{max}} = 576$ nm) light bands is much lower. However, the PL spectra of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (Fig. 10d) obtained at $\lambda_{\text{ex}} = 455$ nm contain intense bands of Ho^{3+} ions PL, and the intensity of the PL of Dy^{3+} ions bands including yellow light radiation band ($\lambda = 576$ nm) is small. It should be noted that the excitation bands with maxima at 454 nm (Fig. 5a) or 456 nm (Fig. 5b) are present on the excitation spectra of both Dy^{3+} and Ho^{3+} ions, respectively. Therefore, in the PL spectra at $\lambda_{\text{ex}} = 455$ nm for $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ PL bands both Dy^{3+} and Ho^{3+} ions should present. However, these PL spectra practically contain no PL bands of Dy^{3+} ions. Earlier in [2] a cross-relaxation mechanism of concentration quenching of Dy^{3+} ions PL was proposed for their content in the crystal structure of LaAlO_3 perovskite above 3 mol%. According to this work, f -electrons of Dy^{3+} ions at exposure under light with $\lambda = 458$ nm go from the ground level ${}^6H_{15/2}$ to the

excited level ${}^4I_{15/2}$ and then they have radiationless transitions to the level ${}^4F_{9/2}$. This excited Dy^{3+} ion transfers part of its excess energy to another Dy^{3+} ion nonradiatively transferring its f -electrons from the ground to the excited level ${}^6H_{5/2}$. Probably, such a mechanism of cross-relaxation of concentration quenching of Dy^{3+} ions PL is also observed in PL spectra at $\lambda_{\text{ex}} = 455$ nm for $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ (Fig. 10d).

4. Conclusion

Room temperature excitation and PL spectra of single-phased $\text{La}_{0.95}\text{Ln}_{0.05}\text{InO}_3$ ($\text{Ln} = \text{Dy}, \text{Ho}$), $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$, LaInO_3 ceramic samples as well as the $\text{La}_{0.95}\text{Ln}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ ($\text{Ln} = \text{Dy}, \text{Ho}$), $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ samples with additional impurity LaSbO_3 were measured. The spectra show that PL band for sample with nominal composition $\text{LaIn}_{0.98}\text{Sb}_{0.02}\text{O}_3$ ($\lambda_{\text{max}} = 430$ nm) overlaps with the excitation band for $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$. Consequently, for these solid solutions, the main condition of sensitization PL of Dy^{3+} , Ho^{3+} ions by Sb^{3+} ions in LaInO_3 -based solid solutions takes place. It is established that the introduction of less than 2 mol% Sb^{3+} ions in $\text{La}_{0.95}\text{Dy}_{0.05}\text{InO}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{InO}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ leads to a significant increase in the PL bands intensity of Dy^{3+} , Ho^{3+} ions. Probably such a significant PL intensity increase for the sample with nominal composition $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ could be caused by sensitizing effect of Sb^{3+} on Dy^{3+} , Ho^{3+} photoluminescence. It was suggested that the excess energy transfer of Sb^{3+} ions to the Dy^{3+} , Ho^{3+} ions takes place along the chain $\text{Sb}^{3+} \rightarrow \text{In}^{3+} \dots \text{In}^{3+} \rightarrow \text{Ho}^{3+}$ (Dy^{3+}). However one can't exclude that increasing of PL band intensity for samples containing Sb^{3+} ions in comparison with that of for samples containing no Sb^{3+} ions is due to probable higher PL bands intensity of Dy^{3+} (Ho^{3+}) and Sb^{3+} ions in impurity phase matrix than at their arrangement in LaInO_3 -based matrix of the main phase. That $\text{La}_{1-y}\text{Dy}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$, $\text{La}_{1-y}\text{Ho}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$, $\text{La}_{1-2y}\text{Dy}_y\text{Ho}_y\text{Sb}_{1-z}\text{In}_z\text{O}_3$ impurities could form during solid state synthesis of the samples of $\text{La}_{0.95}\text{Dy}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.95}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$, $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ nominal composition. The impurity amount in those Sb^{3+} containing samples was estimated to be 19 times lower than that of the main LaInO_3 -based phase. So the predominant part of PL intensity could be referred to Dy^{3+} , Ho^{3+} ions in LaInO_3 phase, but not in the impurity phase. It was found that the PL spectrum of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ sample at $\lambda_{\text{ex}} = 320$ nm contains simultaneously intense emission of blue, green and yellow light.

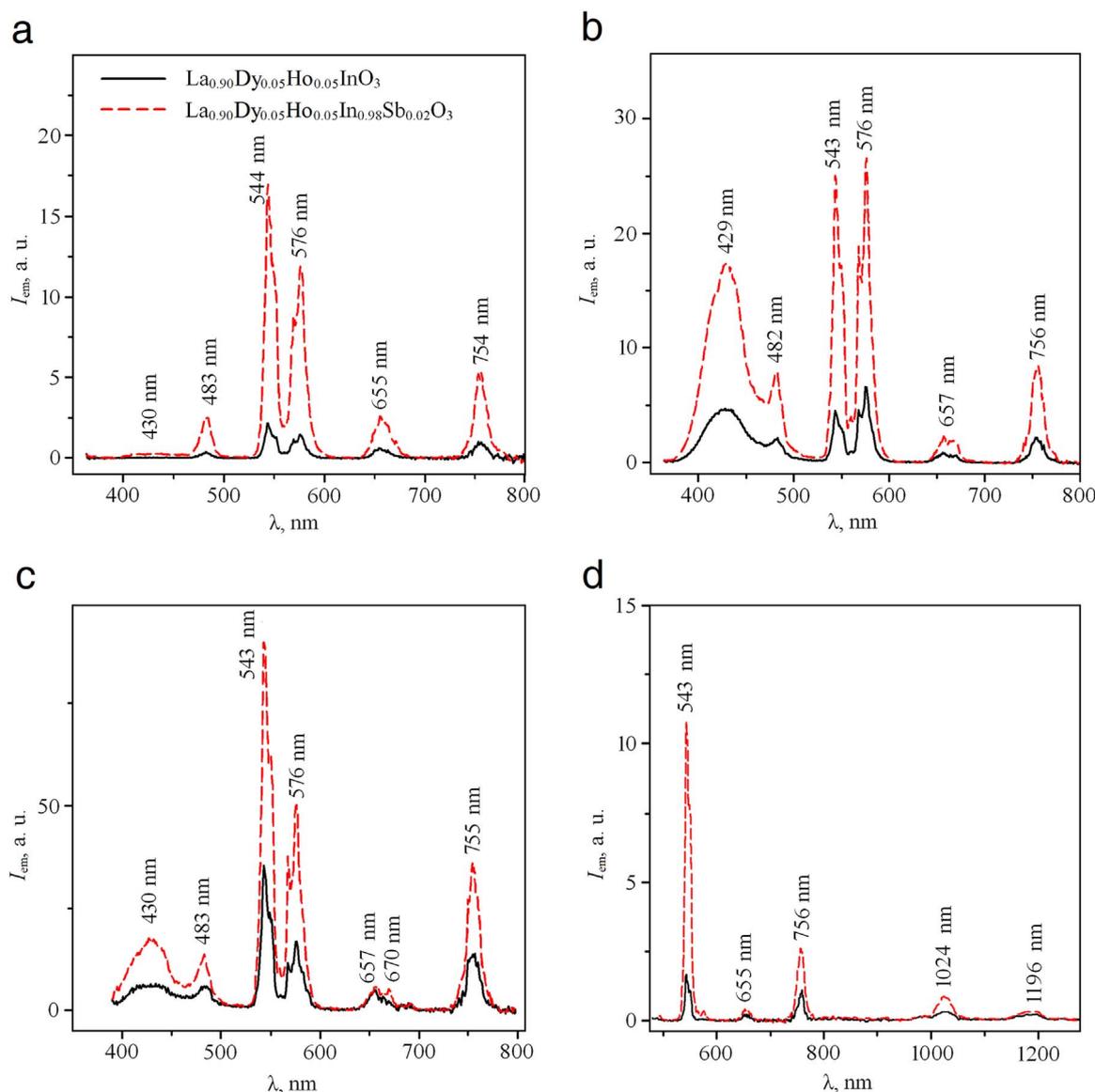


Fig. 10. Photoluminescence spectra of $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{InO}_3$ and $\text{La}_{0.90}\text{Dy}_{0.05}\text{Ho}_{0.05}\text{In}_{0.98}\text{Sb}_{0.02}\text{O}_3$ at $\lambda_{\text{ex}} = 275$ (a), $\lambda_{\text{ex}} = 320$ nm (b), $\lambda_{\text{ex}} = 361$ nm (c), $\lambda_{\text{ex}} = 455$ nm (d).

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