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Spectral characteristics and energy transfer $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ in $LuBO_3(Ce, Tb, Eu)$ compound

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The structure, IR, luminescence, and luminescence excitation spectra of Ce^{3+}, Tb^{3+}, and Eu^{3+} ions in $Lu_{1-2x}Ce_xEu_xBO_3$ and $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ solid solutions were studied. The minimum „threshold" distance between Ce^{3+} and Eu^{3+} ions was estimated, at which there is no charge transfer between these ions, leading to the quenching of Ce^{3+} and Eu^{3+} luminescence. It is shown that in $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ compounds, the range of Ce and Eu concentrations of 0.2−0.25 at.% is optimal for obtaining the maximum luminous intensity of this compound.

Keywords: phosphors for LEDs, rare earth orthoborates, X-ray diffraction analysis, IR spectroscopy, luminescence spectra.

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1. Introduction

In recent years, active research is being conducted to create light-emitting diode sources of „white" light. The most widespread scheme for generation of „white" light is proportional mixing of blue, green and red luminescence from three luminophores, luminescence being excited by one ultraviolet light-emitting diode (UVL). The use of three different materials as luminophores complicates the technological chain for production of light-emitting sources of „white" light. Therefore, it is interesting to find a luminophore that simultaneously contains a blue, green and red luminescence centers and emits „white" light upon UVL excitation. Such luminescence centers can be Ce^{3+}, Tb^{3+} and Eu^{3+} ions in compounds of rare-earth elements' borates. Lutetium borate $LuBO_3$ has two stable structural modifications: vaterite and calcite [1–3]. At the same time, orthoborates $REBO_3$ (where RE — Gd, Tb, Eu, Y) have only one structural modification — vaterite [2]. The lutetium ion in calcite and vaterite structures is surrounded by six and eight oxygen atoms, respectively [3].

The luminescence spectrum (LS) for the calcite modification of lutetium borate, alloyed with Ce^{3+} ions, has two wide bands in the wavelength range of 350−450 nm with the maxima at $\lambda_{\max} \sim 370$ and ~ 410 nm. The LS for vaterite modifications $REBO_3(Ce)$, where RE — Lu, Tb, Gd, Y also had wide bands (380−470 nm) with $\lambda_{\max} \sim 395$ and ~ 425 nm. Cerium luminescence in the calcite and vaterite modifications of rare-earth ions' borates is conditioned by the permitted transitions $5d \rightarrow 4f$ in Ce^{3+} centers [4–7].

The spectrum of luminescence excitation of cerium ions in rare-earth elements' borates, corresponding to the permitted transitions $4f \rightarrow 5d$ in Ce^{3+} ions, contains a wide band of 290−360 nm with the maximum at $\lambda_{\mathrm{ex}} \sim 340$ nm for the calcite modification and the band of 310−390 nm with the maximum at $\lambda_{\mathrm{ex}} \sim 370$ nm for the vaterite modification.

The largest intensity in the luminescence spectrum for rare-earth ions' borates, alloyed with Tb^{3+} — $REBO_3$ (Tb), where RE — Lu, Eu, Tb, Gd, Y have narrow bands with $\lambda_{\max} = 541.8$ and 549.5 nm for the calcite modification and $\lambda_{\max} = 542.3$ nm for the vaterite modification, corresponding to the transition $^5D_4 \rightarrow {}^7F_5$ [8–10].

The luminescence spectrum for europium-alloyed lutetium borate, having the calcite structure, has two narrow bands with $\lambda_{\max} \sim 590$ and ~ 596 nm (electron transition $^5D_0 \rightarrow^7 F_1$) [10–12]. The luminescence spectrum for the vaterite modification $REBO_3(Eu)$, where RE — Lu, Y, Gd contains three bands: in the wavelength region of 588−596 nm (electron transition $^5D_0 \rightarrow {}^7F_1$), 608−613 and 624−632 nm ($^5D_0 \rightarrow {}^7F_2$). Each of these bands consists of several narrow lines [8,11–12].

Thus, blue luminescence is typical for cerium-alloyed borates. Green luminescence is observed in terbium-containing borates. Orange and red luminescence is respectively typical for calcite and vaterite modifications of europium-alloyed borates. Therefore, a fundamental possibility to generate „white" light emission exists in case of certain cerium, terbium and europium concentrations in the compounds $RE_{1-x-y-z}Ce_xTb_yEu_zBO_3$, where RE — Lu, Y, Gd upon simultaneous excitation of Ce^{3+}, Tb^{3+} and Eu^{3+} ions.

As is known, dipole transitions between the states of free ions RE^{3+}, pertaining to one configuration, in our case the $4f^n$-configuration, are prohibited by parity [13,14]. This prohibition is partially removed under the action of a crystalline field, which enables transitions between the states of the $4f^n$-electron configuration. However, luminescence intensity due to such transitions remains very low. For instance, luminescence intensity of Tb^{3+} ions in borate $LuBO_3(Tb)$ in case of their resonant excitation in the band, corresponding to the prohibited electron transition $\lambda_{ex} = 378$ nm ($^7F_6 \to {}^5D_3$) is more than in 10 times lesser than in case of excitation in the short-wave bands ($\lambda_{ex} = 220-290$ nm) that correspond to the permitted transition $4f^8 \to 4f^7 5d^1$.

It should be noted that when electron excitation energy is transferred from one center (donor — D) to another one (acceptor — A), luminescence intensity of acceptor A may considerably increase [15,16]. Electron excitation energy is transferred not by the process of photon emission–adsorption, but as a result of radiationless energy transfer due to Coulomb interaction between the donor and acceptor (Ferster mechanism of energy transfer). Two conditions must be met for fulfilling the energy transfer process: 1) donor emission spectrum (D) must be in the spectral range of acceptor absorption (A); 2) distance between the donor and acceptor shall be not more than the („threshold“) distance R. It should be noted that energy transfer in various compounds takes place when distances between the donor and acceptor are in the range of $5-50$ Å [16–21].

Electron excitation energy transfer was studied for a whole range of compounds alloyed with different rare-earth ions. For instance, luminescence intensity of Tb^{3+} in samples of $LaPO_4(Ce,Tb)$ increases as a result of energy transfer from Ce^{3+} to Tb^{3+} [16]. Energy transfer from Gd^{3+} to Eu^{3+} is observed in compounds $Gd_{1-x}Eu_xBO_3$ and $Lu_{0.99-x}Gd_xEu_{0.01}BO_3$ [22,10].

The papers [23–25] studied the energy transfer from Ce^{3+} to Tb^{3+} in lutetium, yttrium and gadolinium orthoborates. It was showed that luminescence intensity of Tb^{3+} ions in $REBO_3(Ce,Tb)$ compounds, where RE — Lu, Y, Gd with excitation by light that corresponds to the maximum of luminescence excitation of Ce^{3+} ions ($\lambda_{ex} \sim 340$ and ~ 370 nm for the calcite and vaterite modifications, respectively), is in many times (in more than ~ 40 times) greater than luminescence intensity of Tb^{3+} ions in case of their resonant excitation ($\lambda_{ex} = 378$ nm). Such considerable increase in terbium ions' luminescence intensity is related to a high efficiency of electron excitation energy transfer from Ce^{3+} ions to Tb^{3+} (η). Value of η can be determined by comparing the luminescence intensities of Ce^{3+} ions in the studied compounds in case of absence and presence of Tb^{3+} ions in them. Value of η for $LuBO_3(Ce,Tb)$, $YBO_3(Ce,Tb)$ and $GdBO_3(Ce,Tb)$ is equal to $\sim 80\%$ [23–25]. Attention should be paid to the fact that efficiency of energy transfer from Ce^{3+} ions to Tb^{3+} in the $Ba_3Gd(PO_4)_3(Ce,Tb)$ compound $\eta \sim 79\%$ [26] is close to values of η for cerium- and terbium-alloyed borates of lutetium, yttrium and gadolinium.

The maximum („threshold“) distance (R), at which excitation can be transferred from cerium to terbium, for borates $YBO_3(Ce,Tb)$ and $LuBO_3(Ce,Tb)$ is equal to ~ 16 and ~ 18 Å respectively [23–25]. It should be noted that the value of R for the compound $Ba_3Gd(PO_4)_3(Ce,Tb)$ is ~ 16 Å [26]. Close values of „threshold“ distances at which energy is transferred from Ce^{3+} to Tb^{3+}, as well as values for efficiency of energy transfer from Ce^{3+} to Tb^{3+}, for various compounds means that the energy transfer from Ce^{3+} to Tb^{3+} is virtually independent from the matrix where cerium and terbium ions are located.

The maximum luminescence intensity of Tb^{3+} (I_{Tb}) ions in borates $LuBO_3(Ce,Tb)$ and $YBO_3(Ce,Tb)$ in case of excitation in the band that corresponds to the maximum of luminescence excitation of Ce^{3+} ions, is observed at the concentrations of $0.5-1$ at.% of Ce^{3+} ions and ~ 10 at.% of Tb^{3+} ions [24,25]. Luminescence intensity of Tb^{3+} ions in the compounds $LuBO_3(Ce,Tb)$ and $YBO_3(Ce,Tb)$ remains virtually unchanged at concentrations of Ce^{3+} ions in the interval of $0.25-1.0$ at.%. At the same time, these compounds have a strong dependence of luminescence intensity of Tb^{3+} ions (I_{Tb}) on their concentration: I_{Tb} decreases $\sim$ in 2 times in relation to the maximum value upon an increase in Tb^{3+} concentration to ~ 20 at.% [24,25].

Transfer of electron excitation energy from Tb^{3+} ions to Eu^{3+} was observed in a number of compounds: in molybdates [27] and tungstates [28] of rare-earth elements, in samples of $Tb(OH)_3(Eu)$, $SrTiO_3(Tb,Eu)$ [29,30] and orthoborates $MeBO_3(Tb,Eu)$, where Me = Y, Gd, La, In [31,32]. The highest efficiency of energy transfer (η) from Tb^{3+} to Eu^{3+} was observed in the samples of $Tb(OH)_3:Eu^{3+}$. When the concentration of Eu^{3+} ions increased from 0.03 to 3 mol.%, the value of η increases in these samples from 67 to 99% [29].

Thus, successive transfer of electron excitation energy from Ce^{3+} to Tb^{3+} and from Tb^{3+} to Eu^{3+} ($Ce^{3+} \to Tb^{3+} \to Eu^{3+}$) may take place in the compounds $REBO_3(Ce,Tb,Eu)$, where RE = Lu, Gd, Y in case of excitation in a single band only — the band of absorption of Ce^{3+} ions ($\lambda_{ex} \sim 340$ and ~ 370 nm for the calcite and vaterite modifications, respectively). Thereat, luminescence of all alloying additives must be observed: blue luminescence of Ce^{3+} ions, as well as green luminescence of Tb^{3+} ions (having a high color purity) and orange or red luminescence of Eu^{3+} ions. It can be anticipated that the high efficiency of energy transfer from Ce^{3+} ions to Tb^{3+} and from Tb^{3+} to Eu^{3+} will ensure a considerable increase in europium luminescence intensity, similarly to the above-mentioned increase in luminescence intensity of terbium ions as a result of energy transfer from Ce^{3+} to Tb^{3+}. However, this set of alloying optically-active luminescence centers, which is seemingly optimal for increasing the intensity of orange or red luminescence, as well as for obtaining of „white“ light, has an essential disadvantage. As already noted in the pioneering papers [33,34], in many compounds, including cerium- and europium-alloyed borates, the charge is transferred from Ce^{3+} to Eu^{3+} (metal-metal charge transfer (MMCT)) according to the scheme $Ce^{3+} + Eu^{3+} \rightarrow Ce^{4+} + Eu^{2+}$. This process quenches the luminescence of these activators [33,34].

As shown in [35], attenuation of the MMCT process (recharge of Ce^{3+} and Eu^{3+}) takes place upon a significant increase in concentration of Tb^{3+} ions to 50–60 mol.%. Thereat, Tb^{3+} ions act as a buffer that reduces the interaction of Ce^{3+} and Eu^{3+} ions. A marked increase in the Tb^{3+} concentration made it possible to observe simultaneous luminescence of three activators as a result of energy transfer according to the scheme $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ in a whole range of compounds simultaneously alloyed with Ce^{3+}, Tb^{3+} and Eu^{3+} ions: $Na_2Y_2B_2O_7$ [36], $YSiO_5$ [37], YBO_3, $GdBO_3$ and $LuBO_3$ [35,38,39]. It should be noted that the need for such a high content of Tb^{3+} ions for reducing the MMCT process between Ce^{3+} and Eu^{3+} has still not been understood [39].

With such high concentrations of Tb^{3+} ions (50–60 mol.%) in borates of rare-earth elements alloyed with Ce^{3+} and Tb^{3+}, the luminescence intensity of Tb^{3+} ions (I_{Tb}) decreases considerably [24,25,31]. For instance, luminescence intensity of Tb^{3+} ions in the compound $Lu_{0.99-y}Ce_{0.01}Tb_yBO_3$ with the concentration of Tb^{3+} ions equal to 50 mol.% decreases in approximately 3 times in relation to the maximum, observed at the Tb^{3+} concentration of ~ 9 mol.% [24,38]. Moreover, the papers [10,12] have found that a solid solution consisting of orthoborate $LuBO_3$, which has two stable structural modifications (calcite and vaterite), and orthoborates $REBO_3$ (RE = Eu, Gd, Tb, Y and Dy), which have one structural modification (vaterite), at concentrations of rare-earth ions, which substitute lutetium, above 15–20 at.% crystallizes only in the vaterite structure. Therefore, with the terbium concentrations of $\sim 50\%$ the compound $Lu_{0.5-x-z}Ce_xTb_{0.5}Eu_zBO_3$ has only one structural modification (vaterite) characterized, as was already noted, only by red luminescence of Eu^{3+} ions [8,10–12]. At the same time, the orange luminescence of Eu^{3+} ions [8,10–12], typical for the calcite modification, must also be present in order to expand the possibilities of formation of emission color shades, e.g., to generate various shades of „white" light.

This paper suggests a different method for attenuation of the MMCT process — recharge of Ce^{3+} and Eu^{3+} ions in orthoborates that contain Ce^{3+} and Eu^{3+}, which is based on reducing the concentrations of Ce^{3+} and Eu^{3+} ions to the optimal values. It should be noted that luminescence intensities of these activators can decrease when the cerium and terbium concentration decreases. However, luminescence intensity of Ce^{3+} ions, e.g., in the $CaAlBO_4(Ce)$ compound remains virtually constant in the cerium concentration range of 0.05–0.2 mol.% [40]. Moreover, luminescence intensity of Tb^{3+} ions in the samples of $Lu_{0.85-x}Ce_xTb_{0.15}BO_3$, as already noted, upon excitation in the absorption band of Ce^{3+} ions is virtually independent of Ce^{3+} concentration in the range of 0.25–1.0 at.%. [24]. This important circumstance makes it possible to use small concentrations of Ce^{3+} and Eu^{3+} ions, at which the process MMCT is attenuated, in order to obtain high integral luminescence intensities of orthoborates $Lu_{1-x-y-z}Ce_xTb_yEu_zBO_3$.

This paper studies a change in luminescence intensity of Ce^{3+} ions in the samples of $Lu_{1-x}Ce_xBO_3$ and $Lu_{1-2x}Ce_xEu_xBO_3$ at $0.0005 \leq x \leq 0.01$ (depending on presence and absence of Eu^{3+} ions). The optimal concentrations of Ce^{3+} and Eu^{3+} ions, at which luminescence intensity of Ce^{3+} ions is maximal in these samples, were determined. It was showed that in case of the optimal concentrations of Ce^{3+} and Eu^{3+} ions there is effective energy transfer according to the scheme $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$. The method suggested in this paper for attenuation of the recharge of Ce^{3+} and Eu^{3+} ions, which does not depend on concentration of Tb^{3+} ions, makes it possible to change the concentration of Tb^{3+} in order to obtain samples of $Lu_{1-2x-y}Ce_xTb_yEu_xBO_3$ in the calcite or vaterite phase.

2. Experimental procedures

2.1. Sample synthesis

The studied polycrystalline samples of lutetium borate having the composition $Lu_{1-x-y-z}Ce_xTb_yEu_zBO_3$ were synthesized by the reaction of interaction of rare-earth elements' oxides with molten sodium tetraborate at the temperature of 970°C. The initial reagents were aqueous solutions of rare-earth elements' nitrates and crystalline borax, taken in stoichiometric ratios

$$2(1-x-y-z)Lu(NO_3)_3 + 2xCe(NO_3)_3$$
$$+ 2yTb(NO_3)_3 + 2zEu(NO_3)_3 + Na_2B_4O_7 = Na_2B_2O_4$$
$$+ 2Lu_{1-x-y-z}Ce_xTb_yEu_zBO_3 + 1.5 \cdot O_2 \uparrow + 6NO_2 \uparrow .$$

The initial components were combined with addition of water and thoroughly ground in an agate mortar, then the aqueous suspensions were dried with weak heating. The obtained powder was annealed at the temperature of 500°C for one hour, thoroughly ground and pressed into tablets at the pressure of 300 MPa. Then the tablets underwent high-temperature annealing at 970°C for 2 h. In order to separate the lutetium orthoborate polycrystals, the obtained products were treated with hydrochloric acid having the concentration of 6 wt.% for 15 min, then filtered, washed with water, alcohol and dried at 120°C for 1 h.

2.2. Research methods

X-ray diffraction studies of the samples were conducted using a Siemens D-500 diffractometer (emission of $CuK\alpha_1$, $\lambda = 1.5406$ Å). The range of angles 2θ is from 10 to 140°. Phase analysis of the samples and calculation of lattice parameters were performed using the Match and PowderCell 2.4 programs.

Samples' IR-spectra of absorption were measured in a Fourier-spectrometer VERTEX 80v in the spectral range of 400−5000 cm^{-1}, resolution being 2 cm^{-1}. For measurements, the orthoborate samples were ground in an agate mortar, and then were applied in a thin layer onto a crystalline polished substrate KBr.

The sample morphology was studied using a Supra 50VP X-ray microanalyzer with an add-on for EDS INCA (Oxford).

Photoluminescence spectra and luminescence excitation spectra were studied on a unit that consisted of a light source: lamp DKSSh-150, two monochromators MDR-4 and MDR-6 (spectral range 200−1000 nm, dispersion 1.3 nm/mm). Luminescence was recorded by means of photomultiplier FEU-106 (spectral sensitivity range 200−800 nm) and an amplification system. Monochromator MDR-4 was used to study the samples' luminescence excitation spectra, monochromator MDR-6 was used to study luminescence spectra.

Spectral and structural characteristics, as well as samples' morphology were studied at room temperature.

3. X-Ray diffraction studies

Orthoborates $Lu_{1-x}Ce_xBO_3$ and $Lu_{1-z}Eu_zBO_3$, as well as $Lu_{1-x-z}Ce_xEu_zBO_3$ (synthesized at 970°C) with $x, z \le 0.01$ are single-phase and have the calcite structure $R\bar{3}c$, sp. gr. № 167 [12,23]. As an example, Fig. 1, (spectra *1* and *2*) gives the diffraction patterns for the samples of $Lu_{0.998}Ce_{0.002}BO_3$ and $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$. According to the X-ray phase analysis data, the sample of $Lu_{0.9}Ce_{0.005}Tb_{0.09}Eu_{0.005}BO_3$ is also single-phase and has the calcite structure (Fig. 1, spectrum *3*). The samples of $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$, $Lu_{0.9075}Ce_{0.0025}Tb_{0.09}BO_3$, $Lu_{0.91}Tb_{0.09}BO_3$ and $Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3$ (Fig. 1, spectra *4−7*) are two-phase; in addition to the calcite phase, they contain a small amount of the vaterite phase $C2/c$ (sp. gr. № 15 [41]) — 2, 3.5, 5 and 9.5%, respectively (Table 1). The lines that correspond to the vaterite phase are marked in Fig. 1 with the symbol „v".

Table 1. Dependences of calcite and vaterite phase content on concentration of Ce^{3+}, Tb^{3+} and Eu^{3+} in orthoborates $Lu_{1-x-y-z}Ce_xTb_yEu_zBO_3$

Ce, at.%	Tb, at.%	Eu, at.%	Calcite, %	Vaterite, %
0.2	0	0	100	0
0	9	0	95	5
0.2	0	0.2	100	0
0.12	9	0	100	0
0.25	9	0	96.5	3.5
0.2	9	0.2	98	2
0.25	9	0.25	90.5	9.5
0.5	9	0.5	100	0

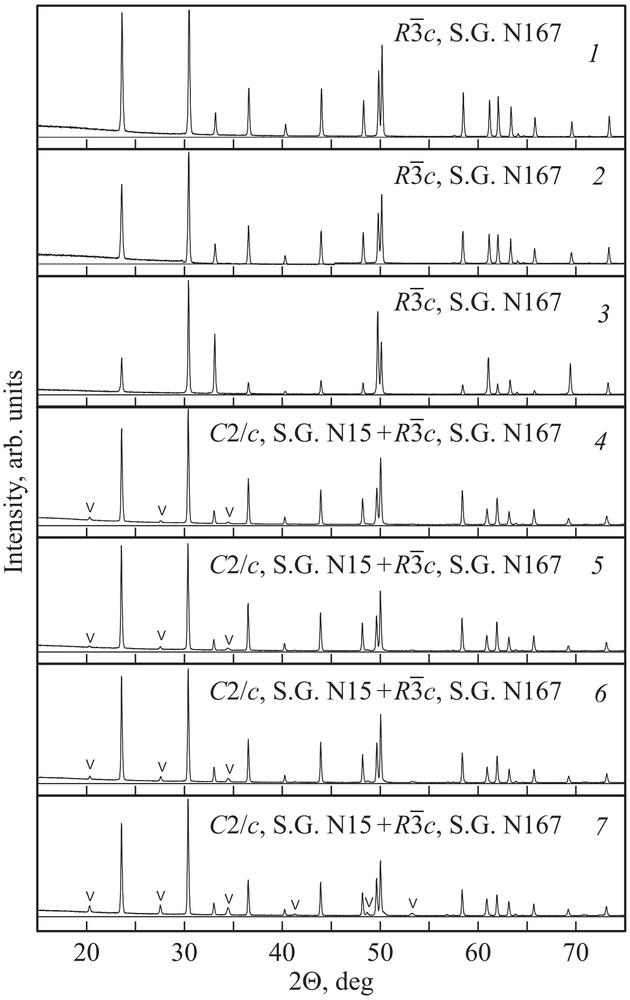

Figure 1. Diffraction patterns for samples. *1* — $Lu_{0.998}Ce_{0.002}BO_3$; *2* — $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$; *3* — $Lu_{0.9}Ce_{0.005}Tb_{0.09}Eu_{0.005}BO_3$; *4* — $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$; *5* — $Lu_{0.9075}Ce_{0.0025}Tb_{0.09}BO_3$; *6* — $Lu_{0.91}Tb_{0.09}BO_3$; *7* — $Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3$.

4. Sample morphology

As seen from Fig. 2, *a, b, c*, the size of microcrystals of orthoborates $Lu_{0.998}Ce_{0.002}BO_3$, $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$ and $Lu_{0.9}Ce_{0.005}Tb_{0.09}Eu_{0.005}BO_3$ is ∼ 10−20 μm. These samples, according to the X-ray phase analysis data (Table 1), have a calcite structure. A small amount of fine microcrystals, having a size ∼ 1−2 μm, is observed in the other studied orthoborates that chiefly have a calcite structure but contain a small amount of vaterite, along with microcrystals sized ∼ 10−20 μm. As an example, Fig. 2, *d, e, f* shows the morphology of the microcrystals in compounds $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$, $Lu_{0.91}Tb_{0.09}BO_3$ and $Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3$, which contain 2, 5 and 9.5% of the vaterite phase respectively (Table 1).

The study by X-ray phase analysis and IR-spectroscopy of a fine microcrystal array in orthoborates $Lu_{0.91}Gd_{0.08}Eu_{0.01}BO_3$ has showed that the microcrystals

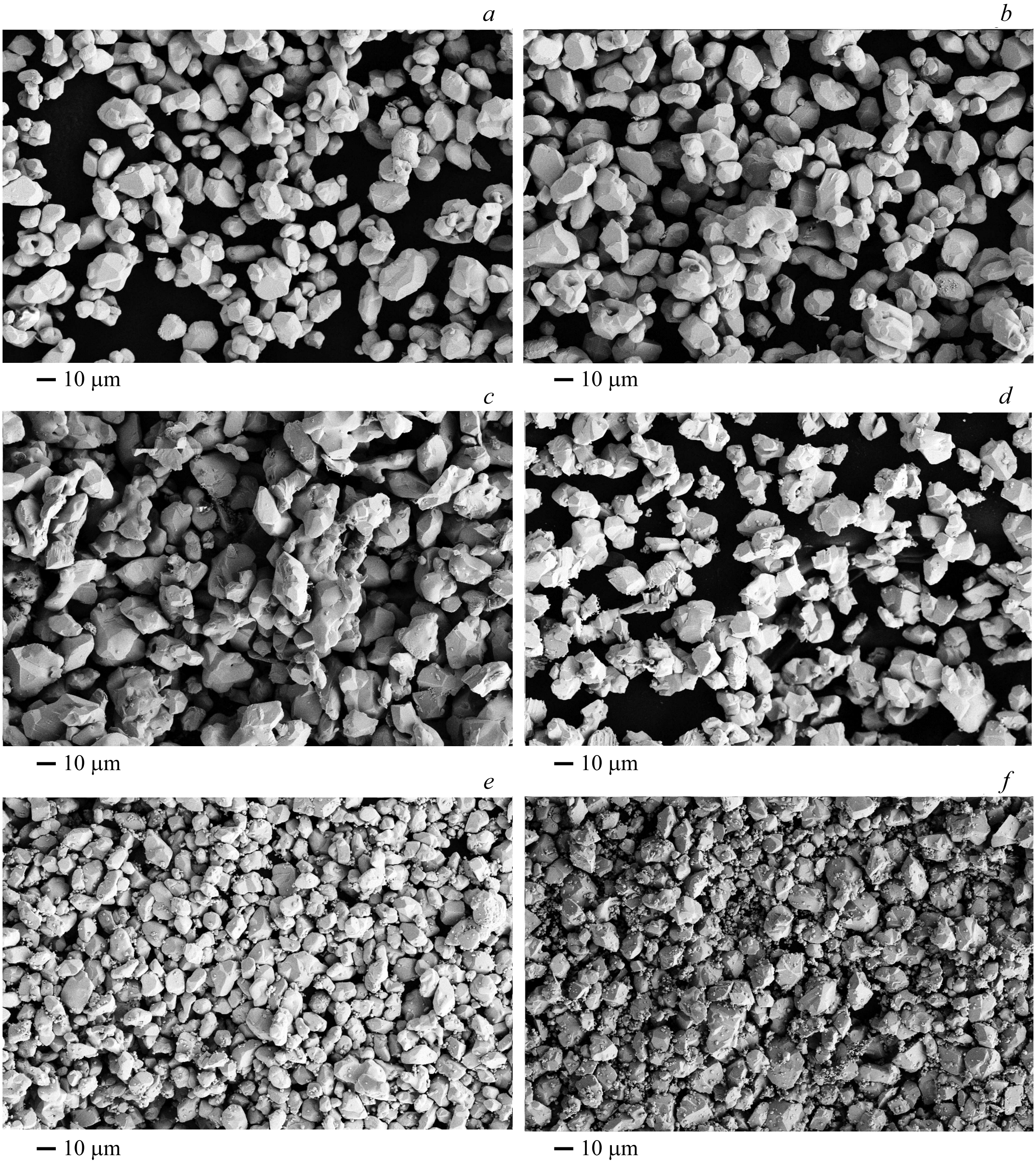

Figure 2. Morphology of orthoborates. *a* — $Lu_{0.998}Ce_{0.002}BO_3$; *b* — $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$; *c* — $Lu_{0.9}Ce_{0.005}Tb_{0.09}Eu_{0.005}BO_3$; *d* — $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$; *e* — $Lu_{0.91}Tb_{0.09}BO_3$; *f* — $Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3$.

sized $1-2\,\mu$m have a vaterite structure [42]. It can be also assumed that microcrystals sized $1-2\,\mu$m in the compounds, the morphology of which is given in Fig. 2, *d, e, f*, also have a vaterite structure.

5. Results of IR-spectroscopy

IR-spectra of orthoborate $LuBO_3$, which has two crystalline modifications (calcite and vaterite), were studied in several papers [10,43]. A significant difference of the IR-spectra in the region of fluctuations of B–O bonds due to a different coordination number (c. n.) for boron atoms (c. n. $= 3$ and 4 for the calcite and vaterite phase, respectively) makes it possible to use the IR-spectroscopy method for identification of the $LuBO_3$ crystalline structure.

Figure 3 shows the IR-spectra for the compounds of different compositions based on lutetium orthoborate $LuBO_3$ alloyed with rare-earth elements Ce, Tb, Eu.

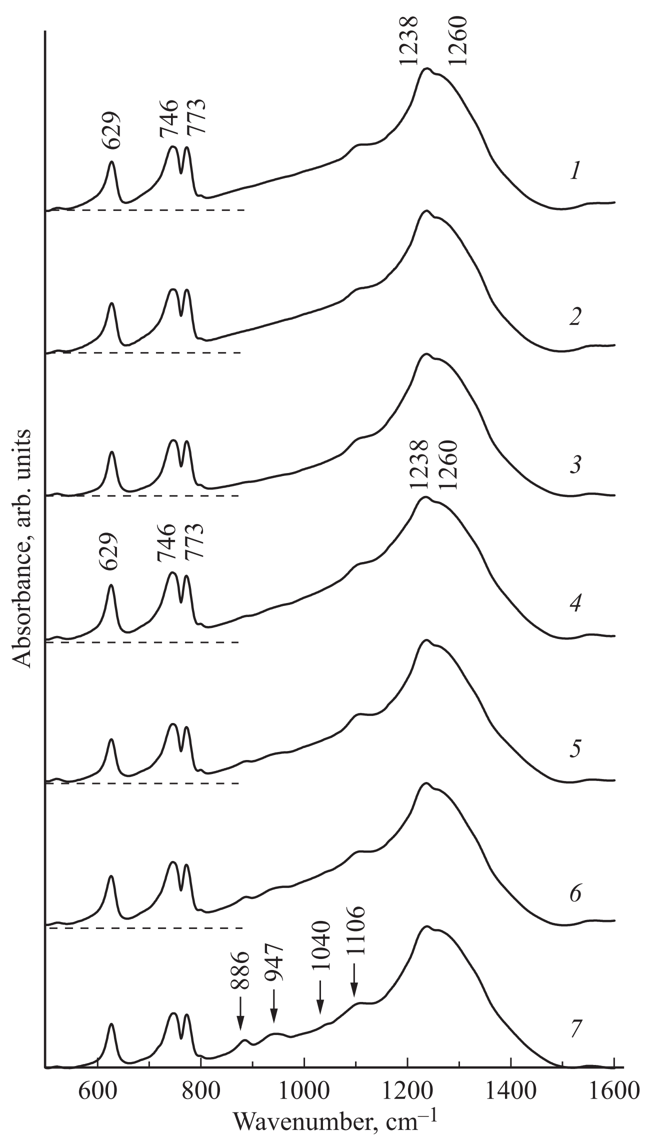

Figure 3. IR-spectra of orthoborates. *1* — $Lu_{0.998}Ce_{0.002}BO_3$; *2* — $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$; *3* — $Lu_{0.90}Ce_{0.005}Tb_{0.09}Eu_{0.005}BO_3$; *4* — $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$; *5* — $Lu_{0.9075}Ce_{0.0025}Tb_{0.09}BO_3$; *6* — $Lu_{0.91}Tb_{0.09}BO_3$; *7* — $Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3$. The zero values of ordinate axes for the spectra *1–6* are showed by dashed line.

The spectra for the samples of $Lu_{0.998}Ce_{0.002}BO_3$, $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$ and $Lu_{0.90}Ce_{0.005}Tb_{0.09}Eu_{0.005}BO_3$ (Fig. 3, spectra *1, 2, 3*) have intensive bands of 629, 746, 773 and 1238 with an arm of 1260 cm^{-1}, respectively typical for bending and stretching vibrations for B–O bonds in the calcite structure [42–44]. These samples, according to the X-ray phase analysis data, have a calcite structure and are single-phase. The IR-spectra for the samples of $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$, $Lu_{0.9075}Ce_{0.0025}Tb_{0.09}BO_3$, $Lu_{0.91}Tb_{0.09}BO_3$ and $Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3$ (Fig. 3, spectra *4–7*), along with intensive bands that correspond to the calcite phase, have weak bands near 886, 947, 1040 and 1106 cm^{-1}, marked with arrows (Fig. 3, spectrum *7*). Similar bands were observed in the IR-spectra of two-phase $LuBO_3$ samples alloyed with rare-earth ions RE = Eu, Tb, Gd, Dy. They appeared in the samples of $Lu_{1-x}RE_xBO_3$ with $0 < x \leq 0.15$ [10]. The spectral position of the weak bands corresponds to the stretching vibrations of B–O bonds in the vaterite structure [43,44,8,10]. Their intensity increases with an increase in the amount of the vaterite phase in the specimens (Fig. 3, spectra *4–7*). These samples, according to the X-ray phase analysis data, contain a small amount of the vaterite phase — 2, 3.5, 5, 9.5%, respectively (Table 1). It should be noted that the spectra for the samples with a calcite structure (Fig. 3, spectra *1, 2, 3*) have an absorption band ~ 1100 cm^{-1}, which is not typical for the calcite phase. The analysis of NMR-spectra for samples of $LuBO_3$, outlined in [44], makes it possible to suggest that this band appears in the samples' spectra (Fig. 3, spectra *1, 2, 3*) due to the presence of BO_4 groups in the calcite phase.

6. Luminescence spectra and luminescence excitation spectra for $LuBO_3(Ce, Tb, Eu)$

6.1. Luminescence spectra and luminescence excitation spectra for $LuBO_3(Ce, Eu)$

The luminescence spectra (LS) for Ce^{3+} ions and luminescence excitation spectra (LES) for the main luminescence bands of Ce^{3+} ions in lutetium orthoborates, alloyed with cerium only and simultaneously with cerium and europium, coincide in the interval of Ce^{3+} and Eu^{3+} ions' concentrations of 0.05–1.0 at.%. As an example, Figs. 4 and 5 give LS and LES for Ce^{3+} ions in the samples of $Lu_{0.9975}Ce_{0.0025}BO_3$ and $Lu_{0.995}Ce_{0.0025}Eu_{0.0025}BO_3$. The luminescence spectra for Ce^{3+} ions contain two wide bands with the maxima at $\lambda_{\max} \sim 370$ and ~ 407 nm, coinciding with the luminescence spectra for Ce^{3+} ions, being in the calcite modification of $LuBO_3(Ce)$. The LS for Ce^{3+} ions are conditioned by the permitted electron transitions $4f^05d^1 \to 4f^1(^2F_{5/2})$ and $4f^05d^1 \to 4f^1(^2F_{7/2})$ in Ce^{3+} ions [4,23]. The luminescence excitation spectra for Ce^{3+} ions in lutetium borates, alloyed only with Ce^{3+} and simultaneously with Ce^{3+} and Eu^{3+}, have a wide band with the maximum at $\lambda_{ex} \sim 340$ nm and an arm at ~ 307 nm (Fig. 5, spectra *1* and *2*). These spectra coincide with the LES for the calcite modification of cerium-alloyed lutetium borate, and correspond to the permitted transitions $4f \to 5d^1$ in Ce^{3+} ions [4,23]. Luminescence intensities of Ce^{3+} ions ($\lambda_{\max} = 407$ nm) under excitation by light, corresponding to the maximum of the excitation band for Ce^{3+} ($\lambda_{ex} \sim 340$ nm), in the samples of lutetium borate alloyed only with Ce^{3+} (I_{Ce}) and simultaneously with Ce^{3+} and Eu^{3+} — $I_{Ce}(Eu)$, at the concentration of Ce^{3+} and Eu^{3+} in the interval of 0.05–1.0 at.% are given in Table 2 and in Fig. 6. When the concentration of

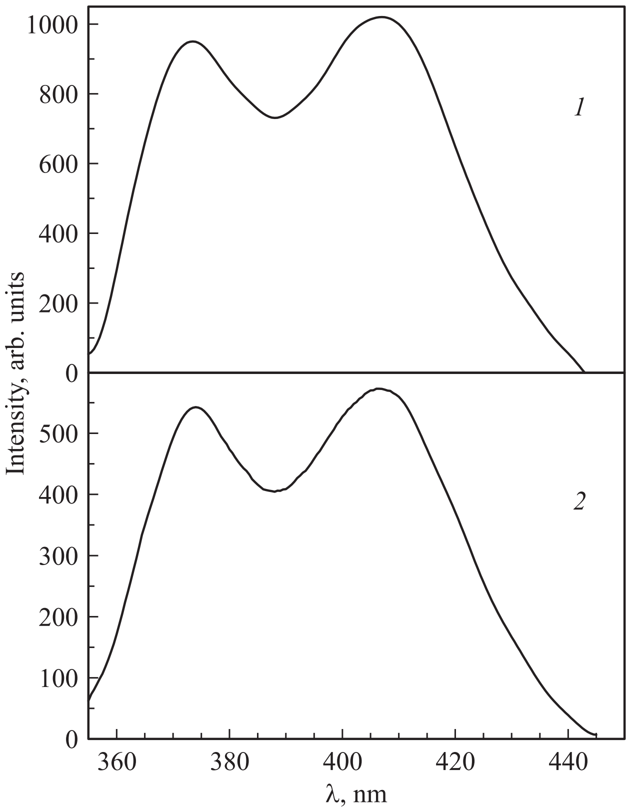

Figure 4. Samples' luminescence spectra. *1* — $Lu_{0.9975}Ce_{0.0025}BO_3$; *2* — $Lu_{0.995}Ce_{0.0025}Eu_{0.0025}BO_3$. Excitation by light with $\lambda_{ex} = 340$ nm.

Ce^{3+} ions increases from 0.05 to 0.25 at.%, luminescence intensity I_{Ce} in the samples of $LuBO_3(Ce)$ increases in ~ 2.5 times and attains the maximum value at ~ 0.5 at.%, and then starts decreasing. A quick drop in I_{Ce} takes place in case of Ce^{3+} concentrations > 1.0 at.%. Luminescence intensity in the samples of $LuBO_3(Ce)$ in the region of Ce^{3+} concentrations 0.2–1.0 at.% changes insignificantly (Table 2, Fig. 6, curve *1*).

In case of simultaneous alloying of $LuBO_3$ with Ce^{3+} and Eu^{3+} ions (in equal atomic fractions), luminescence intensity of cerium ions $I_{Ce}(Eu)$ at first increases upon an increase in their concentrations and attains the maximum when Ce^{3+} and Eu^{3+} concentrations are ~ 0.2 at.%, and then it starts decreasing (Table 2, Fig. 6, curve *2*). Luminescence intensities of Ce^{3+} ions in the samples of $LuBO_3$, alloyed only with Ce^{3+}, and simultaneously with Ce^{3+} and Eu^{3+}, concentrations of Ce^{3+} and Eu^{3+} activators being 0.05 at.%, almost coincide. When concentrations of Ce^{3+} and Eu^{3+} increase, differences between I_{Ce} and $I_{Ce}(Eu)$ increase, and in case of Ce^{3+} and Eu^{3+} ion concentrations equal to 1 at.% the luminescence intensity of Ce^{3+} (I_{Ce}) is in ~ 6 times higher than $I_{Ce}(Eu)$ (Table 2, Fig. 6). The coincidence of the luminescence intensities of Ce^{3+} ions in lutetium borate, alloyed with cerium only (I_{Ce}), and simultaneously with Ce^{3+} and Eu^{3+} ($I_{Ce}(Eu)$)

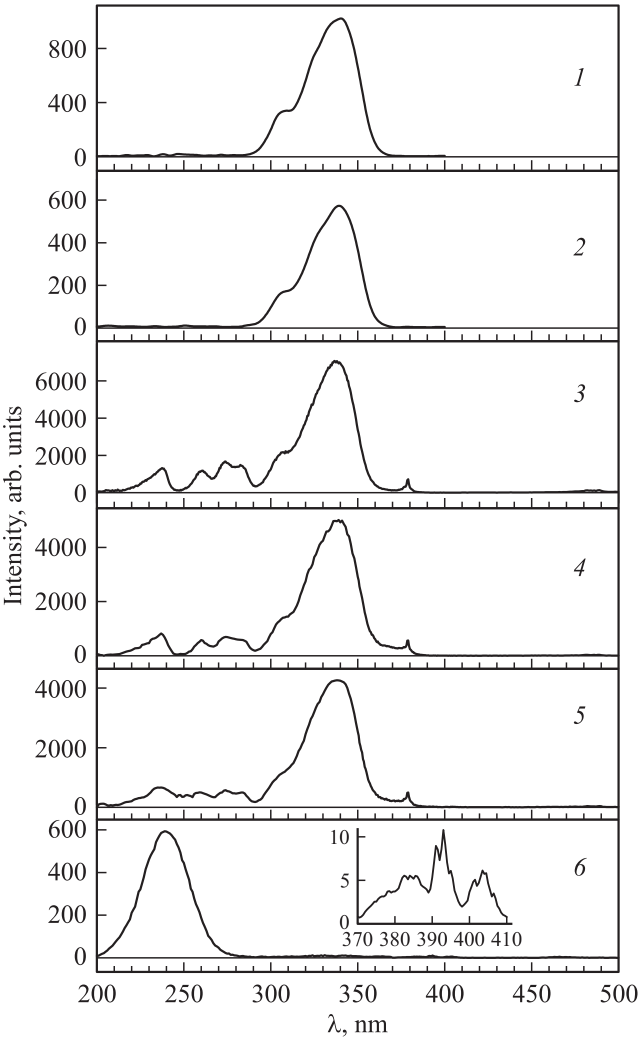

Figure 5. Samples' luminescence excitation spectra. *1* — $Lu_{0.9975}Ce_{0.0025}BO_3$; *2* — $Lu_{0.995}Ce_{0.0025}Eu_{0.0025}BO_3$; *3* — $Lu_{0.9088}Ce_{0.0012}Tb_{0.09}BO_3$; *4* — $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$; *5* — $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$; *6* — $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$; *1, 2* — $\lambda_{max} = 407$ nm; *3, 4* — $\lambda_{max} = 541.8$ nm; *5, 6* — $\lambda_{max} = 589.8$ nm.

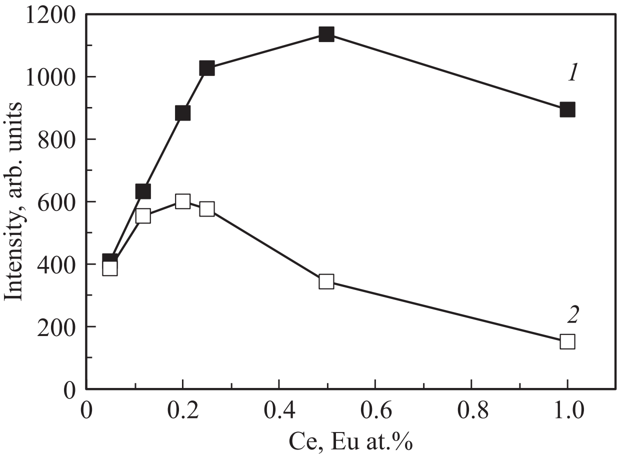

Figure 6. Dependences of luminescence intensities of Ce^{3+} ions in samples $Lu_{1-x}Ce_xBO_3$ (I_{Ce}) and $Lu_{1-2x}Ce_xEu_xBO_3$ ($I_{Ce}(Eu)$) on concentration of Ce^{3+} and Eu^{3+} 1. I_{Ce}; 2. $I_{Ce}(Eu)$.

Table 2. Dependences of luminescence intensities of Ce^{3+} ions ($\lambda_{max} = 407$ nm) upon excitation by light with $\lambda_{ex} \sim 340$ nm on concentration of Ce^{3+} and Eu^{3+} ions in the compounds $Lu_{1-x}Ce_xBO_3$ (I_{Ce}) and $Lu_{1-2x}Ce_xEu_xBO_3$ ($I_{Ce}(Eu)$)

Ce, at.%	0.05	0.05	0.12	0.12	0.2	0.2	0.25	0.25	0.5	0.5	1.0	1.0
Eu, at.%	0	0.05	0	0.12	0	0.2	0	0.25	0	0.5	0	1.0
I_{Ce}, $I_{Ce}(Eu)$, arb. units.	399	383	633	550	878	595	1020	573	1130	339	892	149

Note. I_{Ce} is the luminescence intensity of Ce^{3+} ions in the absence of Eu^{3+} ions. $I_{Ce}(Eu)$ is the luminescence intensity of Ce^{3+} ions with presence of Eu^{3+} ions.

means that when concentrations of Ce^{3+} and Eu^{3+} are 0.05 at.%, the charge is not transferred from Ce^{3+} to Eu^{3+} (metal–metal charge transfer (MMCT)) according to the scheme $Ce^{3+} + Eu^{3+} \to Ce^{4+} + Eu^{2+}$ [33,34]. This occurs, most probably, because at the concentrations of 0.05 at.% the Ce^{3+} and Eu^{3+} ions are located at a distance greater than the „threshold"from each other (R_{CT}), at which the charge is not transferred from Ce^{3+} to Eu^{3+}.

Ionic radii of Ce^{3+} and Eu^{3+} activators (1.081 and 0.987 Å) are greater than the ionic radius of Lu^{3+} (0.867 Å) [45], therefore, the activator ions that substitute the Lu^{3+} ions, generate same-type separating stresses in the $LuBO_3(Ce, Eu)$ microcrystal, and are located in the sample randomly at the maximum possible distance from each other. If concentration of one of the activators, e.g. Eu^{3+}, is greater than concentration of Ce^{3+}, then (with a random arrangement of activators) a Ce^{3+} ion will be located between the neighboring Eu^{3+} ions, distance between which R_{Eu} is lesser than between Ce^{3+} ions (R_{Ce}). Distance between Ce^{3+} and Eu^{3+} ions in this case will be equal to half the minimum distance between same-type ions. Therefore, in order to reduce the impact of charge transfer between Ce^{3+} and Eu^{3+} ions on luminescence intensity of these ions, lutetium borate should be alloyed with an identical number of Ce^{3+} and Eu^{3+} ions.

As already noted, when concentrations of Ce^{3+} and Eu^{3+} ions are 0.05 at.%, the charge is not transferred between these ions. Based on the given threshold value of activator concentrations and taking into account the fact that the parameters of an elementary cell in the calcite modification of lutetium borate are equal to $a = 4.9153$ Å, $c = 16.212$ Å (PDF 72-1053), while an elementary cell contains six Lu atoms [46], it follows from the simple calculations that the „threshold" distance between Ce^{3+} and Eu^{3+} ions in the compound $LuBO_3(Ce, Eu)$ is equal to $R_{CT} \sim 26$ Å.

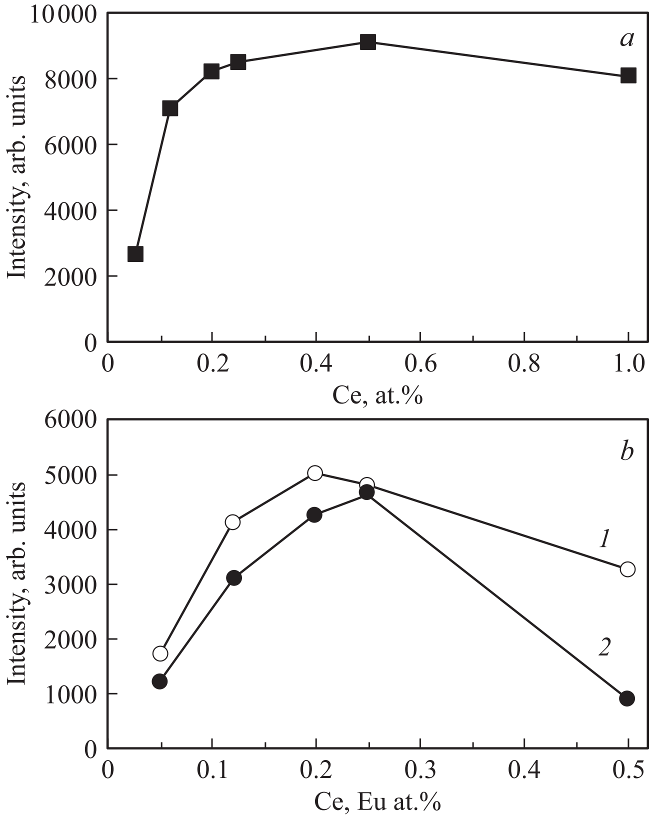

Figure 7. Dependences of luminescence intensities of orthoborates $Lu_{0.91-x}Ce_xTb_{0.09}BO_3$ and $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ on activator concentration. *a* — Change in luminescence intensity of Tb^{3+} ions ($\lambda_{max} = 541.8$ nm) from concentration of Ce^{3+} ions in the samples of $Lu_{0.91-x}Ce_xTb_{0.09}BO_3$. *b* — Change in luminescence intensity of Tb^{3+} ions ($\lambda_{max} = 541.8$ nm) (curve *1*) and Eu^{3+} ions ($\lambda_{max} = 589.8$ nm) (curve *2*) from concentration of Ce^{3+} and Eu^{3+} ions in the samples of $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$; $\lambda_{ex} = 340$ nm.

6.2. Dependence of spectral characteristics of $LuBO_3(Ce, Tb, Eu)$ on alloying additive concentration

As shown in the papers [24,38], the maximum luminescence intensity of Tb^{3+} ions in orthoborates $LuBO_3(Ce, Tb)$ is observed at the Tb^{3+} concentration of 9–10 at.%, that's why the study of luminescence spectra and luminescence excitation spectra for the compounds $LuBO_3(Ce, Tb, Eu)$ in this paper was conducted chiefly at the Tb^{3+} concentration of 9 at.%. Concentration of Ce^{3+} and Eu^{3+} ions varied from 0.025 to 1 at.%.

The greatest intensity in the luminescence spectrum for the samples of $Lu_{0.91-x}Ce_xTb_{0.09}BO_3$, at $0.0005 \le x \le 0.01$ is observed for two bands with $\lambda_{max} = 541.8$ and 549.5 nm ($^5D_4 \to ^7F_5$), typical for the calcite modification of lutetium borate alloyed with Tb^{3+} ions [8–10]. The luminescence excitation spectra

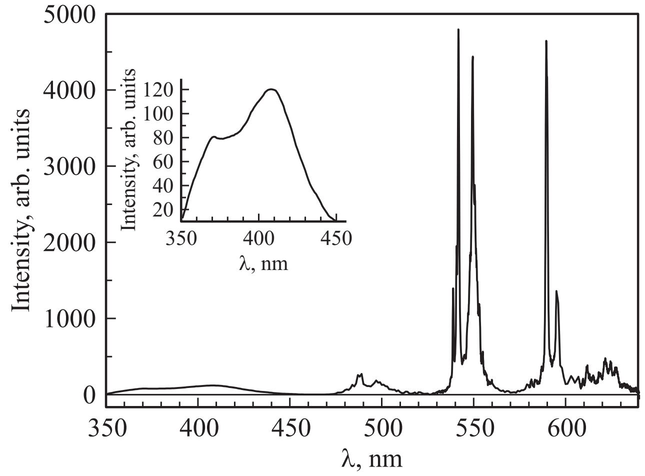

Figure 8. Luminescence spectrum for orthoborate $\mathrm{Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3}$, $\lambda_{\mathrm{ex}} = 340$ nm.

of these bands for the samples of $\mathrm{Lu_{0.91-\mathit{x}}Ce_\mathit{x}Tb_{0.09}BO_3}$ in the studied range of $\mathrm{Ce^{3+}}$ concentrations are similar. Figure 5, spectrum *3*, as an example, gives the LES for $\mathrm{Tb^{3+}}$ ions (bands with $\lambda_{\max} = 541.8$ nm) in orthoborate $\mathrm{Lu_{0.9088}Ce_{0.0012}Tb_{0.09}BO_3}$.

The LES for this compound has four short-wave bands $\lambda_{\mathrm{ex}} \sim 237$, 260, 273 and 284 nm in the wavelength range $\lambda_{\mathrm{ex}} = 220{-}290$ nm (transition $4f^8 \to 4f^7 5d^1$) and a narrow resonance band $\lambda_{\mathrm{ex}} = 378$ nm $({}^7F_6 \to {}^5D_3)$, which coincide with the positions of the bands in LES for $\mathrm{Tb^{3+}}$ ions in the calcite modification $\mathrm{LuBO_3(Tb)}$ [8–10]. However, the greatest intensity is showed by the band $\lambda_{\mathrm{ex}} \sim 340$ nm that coincides with the excitation band for $\mathrm{Ce^{3+}}$ ions (Fig. 5, spectrum *1*). Thus, luminescence of $\mathrm{Tb^{3+}}$ ions in the compound $\mathrm{LuBO_3(Ce, Tb)}$ arises upon excitation of $\mathrm{Ce^{3+}}$ ions, unambiguously meaning the transfer of electron excitation energy from $\mathrm{Ce^{3+}}$ ions to $\mathrm{Tb^{3+}}$. As seen from Table 3 and Fig. 7, *a*, luminescence intensity of $\mathrm{Tb^{3+}}$ ions in the sample of $\mathrm{Lu_{0.91-\mathit{x}}Ce_\mathit{x}Tb_{0.09}BO_3}$ attains the maximum at $x = 0.005$ and changes insignificantly at $\mathrm{Ce^{3+}}$ concentrations of 0.12–1 at.%. Luminescence intensity of $\mathrm{Tb^{3+}}$ ions decreases abruptly if $\mathrm{Ce^{3+}}$ concentrations are more than 1 at.% and less than 0.12 at.%.

Thus, the following conclusions can be made based on the studies presented in Sections 6.1 and 6.2. The optimal concentration of $\mathrm{Ce^{3+}}$ and $\mathrm{Eu^{3+}}$ ions, at which the greatest luminescence intensity of $\mathrm{Ce^{3+}}$ ions in compounds $\mathrm{Lu_{1-2\mathit{x}}Ce_\mathit{x}Eu_\mathit{x}BO_3}$ is observed, is 0.12–0.25 at.%. At the same time, the maximum luminescence intensity of $\mathrm{Tb^{3+}}$ ions in the samples of $\mathrm{Lu_{0.91-\mathit{x}}Ce_\mathit{x}Tb_{0.09}BO_3}$ is observed when $\mathrm{Ce^{3+}}$ concentration is 0.5 at.%, and decreases slightly when $\mathrm{Ce^{3+}}$ concentration is 0.12–0.5 at.%. Therefore, it can be assumed that the optimal concentration of $\mathrm{Ce^{3+}}$ and $\mathrm{Eu^{3+}}$ ions in the samples of $\mathrm{Lu_{0.91-2\mathit{x}}Ce_\mathit{x}Tb_{0.09}Eu_\mathit{x}BO_3}$ is also in the interval of 0.12–0.5 at.%.

Table 3. Dependences of luminescence intensities of $\mathrm{Ce^{3+}}$ ions ($\lambda_{\max} = 407$ nm) ($\mathrm{I_{Ce}}$) and $\mathrm{Tb^{3+}}$ ions ($\lambda_{\max} = 541.8$ nm) ($\mathrm{I_{Tb}}$) on concentration of $\mathrm{Ce^{3+}}$ in the compound $\mathrm{Lu_{0.91-\mathit{x}}Ce_\mathit{x}Tb_{0.09}BO_3}$ upon excitation by light with $\lambda_{\mathrm{ex}} \sim 340$ nm

Ce, at.%	0.05	0.12	0.2	0.25	0.5	1.0
$\mathrm{I_{Ce}}$, arb. units.	98	133	176	214	226	180
$\mathrm{I_{Tb}}$, arb. units.	2627	7066	8204	8487	9087	8063

Table 4. Dependences of luminescence intensities of $\mathrm{Ce^{3+}}$ ($\mathrm{I_{Ce}}$), $\mathrm{Tb^{3+}}$ ($\mathrm{I_{Tb}}$) and $\mathrm{Eu^{3+}}$ ($\mathrm{I_{Eu}}$) ions in the compound $\mathrm{Lu_{0.91-2\mathit{x}}Ce_\mathit{x}Tb_{0.09}Eu_\mathit{x}BO_3}$ on concentration of $\mathrm{Ce^{3+}}$ and $\mathrm{Eu^{3+}}$ upon excitation by light with $\lambda_{\mathrm{ex}} = 340$ nm

Ce, at.%	0.05	0.12	0.2	0.25	0.5
Eu, at.%	0.05	0.12	0.2	0.25	0.5
$\mathrm{I_{Ce}}(\lambda = 407\,\mathrm{nm})$, arb. units.	92	115	125	120	102
$\mathrm{I_{Tb}}(\lambda = 541.8\,\mathrm{nm})$, arb. units.	1718	4093	5009	4796	3254
$\mathrm{I_{Eu}}(\lambda = 589.8\,\mathrm{nm})$, arb. units.	1199	3081	4261	4646	889

The luminescence spectra (LS) for orthoborates $\mathrm{Lu_{0.91-2\mathit{x}}Ce_\mathit{x}Tb_{0.09}Eu_\mathit{x}BO_3}$ with $0.12 \le x \le 0.5$ upon excitation in the excitation band of $\mathrm{Ce^{3+}}$ ions ($\lambda_{\mathrm{ex}} = 340$ nm) contain bands typical for the luminescence of $\mathrm{Ce^{3+}}$, $\mathrm{Tb^{3+}}$ and $\mathrm{Eu^{3+}}$ ions that substitute the $\mathrm{Lu^{3+}}$ ions in the calcite modification of $\mathrm{LuBO_3}$. As an example, Fig. 8 gives a luminescence spectrum for orthoborate $\mathrm{Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3}$ with $\lambda_{\mathrm{ex}} = 340$ nm. It contains wide bands with $\lambda_{\max} \sim 370$ and ~ 407 nm $(5d^1 \to 4f^1)$, corresponding to the luminescence of $\mathrm{Ce^{3+}}$, bands of 488; 497 nm $({}^5D_4 \to {}^7F_6)$ and 541.8; 549.5 nm $({}^5D_4 \to {}^7F_5)$, conditioned by luminescence of $\mathrm{Tb^{3+}}$, as well as bands with $\lambda_{\max} = 589.8$ and 595.7 nm, typical for the luminescence of $\mathrm{Eu^{3+}}$ ions $({}^5D_0 \to {}^7F_1)$. Thus, luminescence of $\mathrm{Tb^{3+}}$ and $\mathrm{Eu^{3+}}$ ions in the compound $\mathrm{Lu_{0.91-2\mathit{x}}Ce_\mathit{x}Tb_{0.09}Eu_\mathit{x}BO_3}$ upon excitation in the absorption band of $\mathrm{Ce^{3+}}$ ions means a transfer of electron excitation energy first from $\mathrm{Ce^{3+}}$ ions to $\mathrm{Tb^{3+}}$, and then from $\mathrm{Tb^{3+}}$ ions to $\mathrm{Eu^{3+}}$ according to the scheme $\mathrm{Ce^{3+} \to Tb^{3+} \to Eu^{3+}}$.

The intensities of the luminescence principal bands for the compounds $\mathrm{Lu_{0.91-2\mathit{x}}Ce_\mathit{x}Tb_{0.09}Eu_\mathit{x}BO_3}$ depending on $\mathrm{Ce^{3+}}$ and $\mathrm{Eu^{3+}}$ concentration are given in Table 4. As seen from the table, an increase in $\mathrm{Ce^{3+}}$ and $\mathrm{Eu^{3+}}$ concentrations causes an increase in luminescence intensities of $\mathrm{Tb^{3+}}$ ($\mathrm{I_{Tb}}$) ions ($\lambda_{\max} = 541.8$ nm) and $\mathrm{Eu^{3+}}$ ($\mathrm{I_{Eu}}$) ions ($\lambda_{\max} = 589.8$ nm). The maximum luminescence intensity of $\mathrm{Tb^{3+}}$ $\mathrm{I_{Tb}} = 5009$ arb. units. is observed when concentrations of $\mathrm{Ce^{3+}}$, $\mathrm{Eu^{3+}}$ are 0.2 at.%, while the largest luminescence intensity of $\mathrm{Eu^{3+}}$ $\mathrm{I_{Eu}} = 4646$ arb. units. — when concentrations of $\mathrm{Ce^{3+}}$, $\mathrm{Eu^{3+}}$ are 0.25 at.%. With further increase in cerium and europium concentrations, luminescence intensities of Tb^{3+} and Eu^{3+} ions decrease, while luminescence intensity of Ce^{3+} ions changes insignificantly. Due to the presence of a small amount of the vaterite phase in certain compounds of $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$, the luminescence spectra for these samples have weak bands in the wavelength range of 600−635 nm that correspond to the luminescence of Eu^{3+} ions, being in the vaterite modification of lutetium borate. Thus, the luminescence spectrum for orthoborates $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ at $0.0005 < x < 0.005$ has blue, green and orange-red luminescence, ratio between the intensities of which changes when the concentrations of Ce^{3+} and Eu^{3+} ions change.

It should be noted that luminescence intensity of Tb^{3+} ions upon excitation by light with $\lambda_{\text{ex}} \sim 340$ nm in the samples of $Lu_{0.91-x}Ce_xTb_{0.09}BO_3$, which contain 0.5, 0.25, 0.2, and 0.12 at.% of Ce^{3+}, is 9087, 8487, 8204 and 7066 arb. units., respectively (Table 3, Fig. 7, *a*). The total luminescence intensity of Tb^{3+} and Eu^{3+} ions in the samples of $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$, which contain 0.5, 0.25, 0.2, and 0.12 at.% of Ce^{3+} and Eu^{3+}, is 4143, 9442, 9270 and 7174, respectively (Table 4). Thus, the total luminescence intensity of Tb^{3+} and Eu^{3+} ions in the samples, containing 0.25, 0.2, and 0.12 at.% of Ce^{3+} and Eu^{3+}, was even slightly higher than the luminescence intensity of Tb^{3+} ions in the compounds $Lu_{0.91-x}Ce_xTb_{0.09}BO_3$, where the charge is not transferred from Ce^{3+} to Eu^{3+}. Such a high luminescence intensity of terbium and europium ions in orthoborates $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ is related to the high efficiency of electron excitation energy transfer from Ce^{3+} ions to Tb^{3+} and from Tb^{3+} ions to Eu^{3+}.

It should be noted that the compounds $Y_{0.493}Ce_{0.002}Tb_{0.5}Eu_{0.005}BO_3$ [35], $Y_{1.48}Ce_{0.01}Tb_{0.5}Eu_{0.01}SiO_5$ [37], $Gd_{0.68}Ce_{0.01}Tb_{0.3}Eu_{0.01}$ [38] had a significant increase in red illumination upon excitation in the absorption band of Ce^{3+} ions ($\lambda_{\text{ex}} \sim 365$ nm).

A considerable increase of orange luminescence in the compounds $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ ($0.0005 < x < 0.005$) in relation to the compounds $Lu_{1-2x}Ce_xEu_xBO_3$ upon excitation by light in the absorption band of Ce^{3+} ions ($\lambda_{\text{ex}} = 340$ nm) is also observed in this paper.

The excitation spectrum of the luminescence main band for Eu^{3+} ions (589.8 nm) in the compound $Lu_{0.996}Ce_{0.002}Eu_{0.002}BO_3$ is given in Fig. 5, spectrum *6*. It is seen from this figure that luminescence intensity of Eu^{3+} ions upon excitation in the resonance band I_{Eu} ($\lambda_{\text{ex}} \sim 394$ nm ($^7F_0 \to ^5L_6$)) is very small ~ 10 arb. units. At the same time, luminescence intensity of Eu^{3+} ions in the compound $Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$ upon excitation in the excitation band of Ce^{3+} ions ($\lambda_{\text{ex}} \sim 340$ nm) is 4261 arb. units., which is more than ~ 100 times greater than the luminescence intensity of Eu^{3+} ions upon resonant excitation. A similar process was observed, as stated in the introduction, in the compounds $LuBO_3(Ce,Tb)$ [23–25]. Luminescence intensity of Tb^{3+} ions upon excitation of these samples by light, corresponding to the maximum of luminescence excitation for Ce^{3+} ions ($\lambda_{\text{ex}} \sim 340$ nm), is more than ~ 40 times greater than the luminescence intensity of Tb^{3+} ions upon their resonant excitation ($\lambda_{\text{ex}} = 378$ nm). Such considerable increase in terbium luminescence intensity is related to a high efficiency of electron excitation energy transfer from Ce^{3+} ions to Tb^{3+} ions, which is $\sim 80\%$. A similar reason is probably accountable for the multiple increase of luminescence intensity of Eu^{3+} ions upon excitation in the band that corresponds to the maximum of luminescence excitation for Ce^{3+} ions, as compared with the resonant excitation of Eu^{3+} ions.

Color coordinates CIE (x, y) were determined (on the CIE color chart of 1931) for orthoborates having the largest luminescence intensity upon excitation by light with $\lambda_{\text{ex}} \sim 360$ nm:

$Lu_{0.90}Ce_{0.005}Tb_{0.09}Eu_{0.005}BO_3$ — $x = 0.3373$, $y = 0.5418$,
$Lu_{0.905}Ce_{0.0025}Tb_{0.09}Eu_{0.0025}BO_3$ — $x = 0.4706$, $y = 0.4865$,
$Lu_{0.906}Ce_{0.002}Tb_{0.09}Eu_{0.002}BO_3$ — $x = 0.3459$, $y = 0.5204$,
$Lu_{0.9076}Ce_{0.0012}Tb_{0.09}Eu_{0.0012}BO_3$ — $x = 0.4306$, $y = 0.5177$.

7. Conclusion

This paper outlines the studies of structure, morphology, IR-spectra, luminescence spectra and luminescence excitation spectra of Ce^{3+}, Tb^{3+} and Eu^{3+} ions in solid solutions $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ with $0.0005 < x < 0.005$. It has been showed that in the compounds $Lu_{1-2x}Ce_xEu_xBO_3$ with $x \leq 0.0005$ there is no charge transfer from Ce^{3+} to Eu^{3+} (metal−metal charge transfer (MMCT)) according to the scheme $Ce^{3+} + Eu^{3+} \to Ce^{4+} + Eu^{2+}$, which quenches the luminescence of Ce^{3+} and Eu^{3+}. We estimated the „threshold" distance between Ce^{3+} and Eu^{3+} (R_{CT}) ions, beyond which the charge is not transferred between these ions ($R_{\text{CT}} \sim 26$ Å).

A method is suggested to attenuate the MMCT process in orthoborates that contain Ce^{3+} and Eu^{3+}, which is based on reduction of Ce^{3+} and Eu^{3+} ion concentrations to the optimal values.

It has been established that luminescence intensity of Ce^{3+} ions in the compounds $Lu_{1-2x}Ce_xEu_xBO_3$ is the maximum at $x = 0.002$−0.0025. The maximum luminescence intensity of Tb^{3+} ions ($\lambda_{\max} = 541.8$ nm) ($I_{\text{Tb}} = 9087$ arb. units.) in the compounds $Lu_{0.91-x}Ce_xTb_{0.09}BO_3$ is observed at $x = 0.005$. At the same time, in the range of $0.002 \leq x \leq 0.005$ I_{Tb} decreases only by $\sim 10\%$ (Table 3).

It has been showed that the maximum luminescence intensity of Tb^{3+} ions ($I_{\text{Tb}} = 5009$ arb. units.) in the compounds $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ is observed when concentrations of Ce^{3+}, Eu^{3+} are 0.2 at.%, while the maximum luminescence intensity of Eu^{3+} ions ($I_{\text{Eu}} = 4646$ arb. units.) — when concentrations of Ce^{3+}, Eu^{3+} are 0.25 at.%. The range of cerium and europium concentrations of 0.2−0.25 at.% is the optimal one for attaining the maximum luminescence intensity of Tb^{3+} and Eu^{3+} ions.

Given the high luminescence intensity, radiation and chemical resistance of borates, their high heat conductivity, the compound $Lu_{0.91-2x}Ce_xTb_{0.09}Eu_xBO_3$ with $0.002 \leq x \leq 0.005$ can be considered an efficient luminophore for light-emitting diodes.

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Conflict of interest

The authors declare that they have no conflict of interest.

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