Functional Materials 11, No.2 (2004) © 2004 — Institute for Single Crystals

Activator centers in $Li_6Gd(BO_3)_3$:Ln (Ln = Ce, Eu) single crystals

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Received September 10, 2003

The activator centers in $Li_6Gd(BO_3)_3$ single crystals doped by Ce and Eu have been investigated. Two types of activator centers in $Li_6Gd(BO_3)_3$:Ce single crystals and one activator center type in $Li_6Gd(BO_3)_3$:Eu ones have been established. The optical characteristics of activator centers have been determined.

Изучены активаторные центры в монокристаллах перспективного сцинтилляционного материала — литий-гадолиниевого бората $Li_6Gd(BO_3)_3$, активированного европием или церием. Методами оптического поглощения, фото- и рентгенолюминесценции установлено наличие двух типов центров в кристаллах $Li_6Gd(BO_3)_3$:Ce и одного типа центров в кристаллах $Li_6Gd(BO_3)_3$:Eu. Определены характеристики активаторных центров.

Borate compounds are materials of good prospects to use in scintillation technique, quantum electronics and as phosphors. Their attractiveness is due to a number of physicochemical characteristics defined by the crystal structure peculiarities. The practical application of rare-earth borates is based on the spectroscopic properties of Ln activator ions [1–3]. In [1], the data have been reported on a promising compound $Li_6Gd(BO_3)_3$:Ce (LGBO:Ce) for neutron detection. However, there is no information in literature on optical centers formed by activator ion in this crystal. In this work, the activator centers are considered. The main activator centers and their characteristics are determined in LGBO single crystals activated by two rare-earth elements (Ce and Eu).

The questions associated with Ce and Eu valence in LGBO single crystals are to be considered in this connection. It is usually believed [4] that a rare-earth activator having bivalent stable states will have a highest state if its electronegativity χ is lower than that of host cation being replaced. For example, in CaF_2 crystals, europium has the Eu^{2+} charge state, while it has the Eu^{3+} one in CdF_2, because $\chi_{Cd} = 1.4$ eV $> \chi_{Eu} \cong \chi_{Ca} = 1.04$ eV. Considering the χ values for cerium, europium, and gadolinium [5] we get that in LGBO:Ce, $\chi_{Ce} \le \chi_{Gd}$ (1.08 and 1.11, respectively), thus, the Ce^{4+} charge state is more preferable than Ce^{3+} one. In LGBO:Eu, $\chi_{Eu} \le \chi_{Gd}$ (1.01 and 1.11), i.e. most likely europium will have Eu^{3+} state in the host. Thus, there is the problem of excess positive charge compensation in LGBO:Ce crystals. In the end, however, the charge state of rare-earth element in a host will be determined by the growth conditions and/or post-growth heat treatment [6].

An overlap of Gd^{3+} emission with $4f$–$5d$ absorption band of Ce^{3+} (λ = 320, 350 nm) is observed in LGBO:Ce crystal spectra. This results in the energy transfer from Gd^{3+} host ion to the activator and Ce^{3+} luminescence peaked at λ = 395 nm. The excitation photoluminescence spectrum of LGBO:Ce crystals is shown in Fig. 1. Ce^{3+}

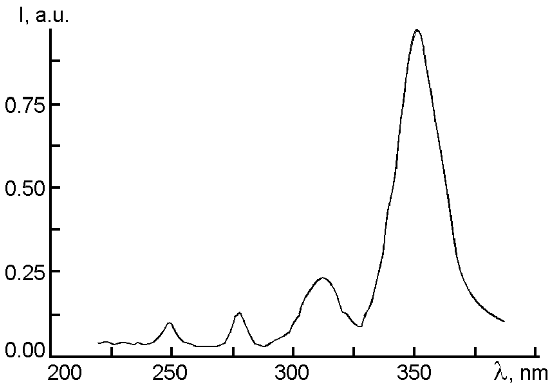

Fig. 1. Excitation spectrum of Ce^{3+} emission at λ = 395 nm for $Li_6Gd_{0.955}Ce_{0.045}(BO_3)_3$ single crystal.

photoluminescence is excited in the bands at λ = 245–250, 270–280 nm corresponding to the $^8S_{7/2}$–^6D_j and $^8S_{7/2}$–^6I_j transitions of Gd^{3+} ion and at λ = 320, 350 nm corresponding to the 4*f*–5*d* transitions of Ce^{3+} ion. Moreover, a peak at λ = 300 nm (Fig. 2, curve 1) appears in the LGBO:Ce crystal absorption spectrum. This peak is associated with the charge transfer $Ce^{4+} + O^{2-} \rightarrow Ce^{3+} + O^-$ (electron transfer from 2*p* orbital of oxygen to empty 4*f* shell of cerium) [7]. The intensity of the λ = 300 nm peak depends on Ce^{3+}/Ce^{4+} ratio in the host crystal. According to the chemical analysis data, the Ce^{3+}/Ce^{4+} ratio in the crystal is 1:4 and can vary depending on the growth conditions.

The absorption spectrum of LGBO:Eu^{3+} crystal (Fig. 2) comprises a broad band in the UV region and lines corresponding to *f*–*f* transitions of Gd^{3+} and Eu^{3+} ions. The band peaked at λ = 250 nm is a charge transfer one and corresponds to the electron transfer from 2*p* orbital of oxygen to empty 4*f* shell of europium ion: $Eu^{3+} + O^{2-} \rightarrow Eu^{2+} + O^-$ [8]. Under excitation in the Gd^{3+} absorption band (λ = 245–250, 270–280 nm), LGBO: Eu^{3+} crystals exhibit red luminescence. This evidences the transfer of excitation energy from Gd^{3+} to Eu^{3+}. The emission spectrum of LGBO:Eu^{3+} consists of the peak at λ = 313 nm (Gd^{3+} emission) and the group of lines between 575 and 720 nm corresponding to transitions from the first excited state $^5D_0$ to the ^7F_j (j = 0–4) levels of Eu^{3+} ion (Fig. 3). As the europium concentration increases, the Gd^{3+} emission intensity at λ = 313 nm decreases. In the photoluminescence spectrum of $Li_6Gd_{0.97}Eu_{0.03}(BO_3)_3$ crystal, the Gd^{3+} emission is not observed, i.e. the full energy transfer from Gd^{3+} to Eu^{3+} occurs at europium concentration 3 at.%.

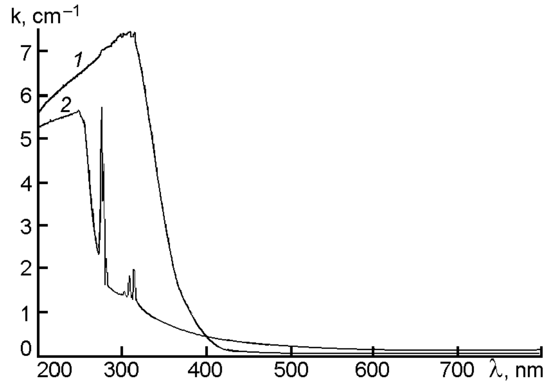

Fig. 2. Absorption spectra of single crystals: $Li_6Gd_{0.955}Ce_{0.045}(BO_3)_3$ (*1*); $Li_6Gd_{0.99}Eu_{0.01}(BO_3)_3$ (*2*).

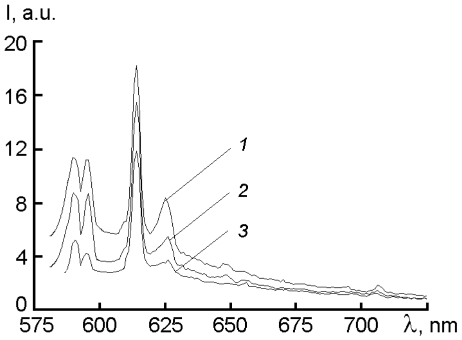

Fig. 3. $Li_6Gd_{1-x}Eu_x(BO_3)_3$ single crystals luminescence spectra of at excitation by λ = 276 nm: $x = 0.03$ (*1*); $x = 0.01$ (*2*); $x = 0.003$ (*3*).

Let the peculiarities of LGBO crystal structure be considered. The regular LGBO structure consists of gadolinium and lithium polyhedrons. The distances between gadolinium cations and oxygen anions in gadolinium polyhedrons shaped as chain clusters extended along the *b* direction are within 0.2351 to 0.2556 nm. Lithium cations are coordinated with four and five oxygen anions, the Li–O distance being of 0.1875 to 0.2428 nm. Boron forms only boron-oxygen triangles unbound to each other but linking the gadolinium and lithium polyhedrons. The B–O distances range from 0.1369 to 0.1398 nm. The distances between gadolinium cations and the nearest lithium and boron ones are 0.265 to 0.322 nm and 0.274 to 0.286 nm, respectively. Comparison of Gd^{3+} (0.128 nm), Eu^{3+} (0.122 nm) and Ce^{3+} (0.102 nm) ionic radii for coordination number 8 allows the suggestion that the activator ions enter pre-

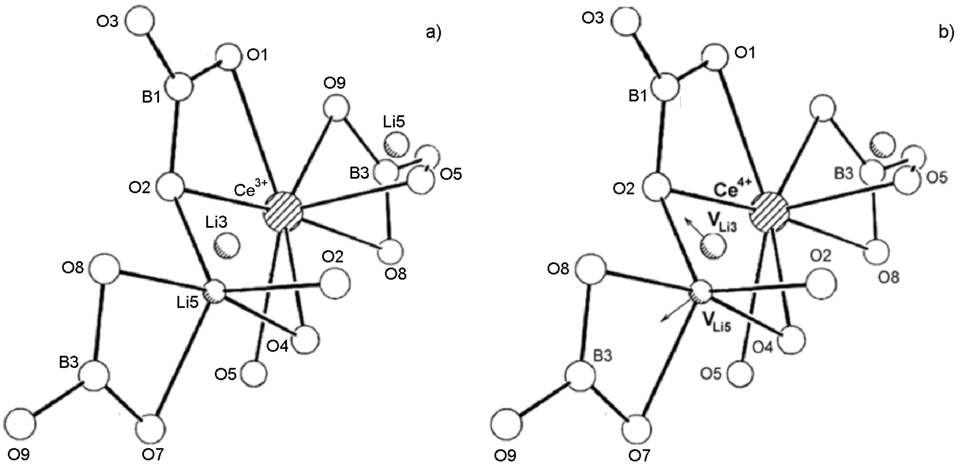

Fig. 4. Activator centers in LGBO:Ce single crystals: $Ce_{Gd}{}^{3+}$ (1); $Ce_{Gd}{}^{4+}$, V_{Li} (2); the arrows show more probable position of lithium vacancies for charge compensation.

dominantly the gadolinium sites. The introduction of cerium as Ce^{4+} needs the excess positive charge compensation. The compensation may be realized due to formation of lithium or boron vacancies in the nearest coordination sphere of Ce^{4+} activator. But the lithium vacancy creation seems to be more probable [9]. A similar effect is observed in $Li_2B_4O_7$:Ln single crystals [3]. The analysis of absorption and luminescence spectra of LGBO:Ce and LGBO:Eu crystals and their structure allows to consider the existence of two types of activator centers in LGBO:Ce crystals and one activator center in LGBO:Eu crystals. Those are $Ce_{Gd}{}^{3+}$, i.e., Ce^{3+} being in the Gd^{3+} site of the crystal lattice (first type activator center, Fig. 4,a); $Ce_{Gd}{}^{4+}$, V_{Li}, i.e., Ce^{4+} being in the Gd^{3+} site of the crystal lattice, the excess positive charge being compensated by lithium vacancy V_{Li} (second type activator center, Fig. 4, 2); $Eu_{Gd}{}^{3+}$ i.e., Eu^{3+} being in the Gd^{3+} site of the crystal lattice. The $Ce_{Gd}{}^{3+}$ and $Eu_{Gd}{}^{3+}$ activator centers are seen to be similar to one another and do not need any charge compensation. The positive charge compensation is necessary in $Ce_{Gd}{}^{4+}$ V_{Li} activator center. In this case, the electric neutrality equation can be written as $[Li_{6-x}\square_x][Gd_{1-x}Ce_x{}^{4+}]$ $[B_3][O_9]$, where [] is the crystal lattice site, □ is a vacancy. Two components, $\tau_1 = 5$ ns and $\tau_2 = 24$ ns, characterize the decay of $Ce_{Gd}{}^{3+}$ activator center photoluminescence while the single component $\tau_1 = 1$ ms characterizes the decay of one.

In the frame of dipole-dipole approximation, the energy transfer probability P_{dd} from Gd^{3+} host ion to activators (Ce^{3+} and Eu^{3+}) and critical transfer radius R_c were estimated according to [10]:

$$P_{dd} = \tag{1}$$

$$= \frac{3\hbar^4 c^4 \int \sigma(E)dE}{4\pi n^4 \tau_0 R^6}\left(\frac{\varepsilon_0}{\varepsilon_{eff}\sqrt{k}}\right)^4 \int \frac{F_d(E)F_a(E)dE}{E^4} =$$

$$= K_c R^{-6},$$

$$R_c = (K_c \tau_0)^{1/6}, \tag{2}$$

where $\hbar$ is the Plank constant; c, light speed; n, the reflection index; τ_0, the decay time; R, distance between the donor and acceptor; E, energy; $\int \sigma(E)dE$, the integrated absorption cross section which we can get from the acceptor absorption spectrum; $F_d(E)$ and $F_a(E)$, spectra of donor luminescence and acceptor absorption, respectively. R_c is the critical transfer radius. The multiplier $(\varepsilon_0/\varepsilon_{eff}\sqrt{k})^4$ is assumed to be equal to 1 [10]. For $Gd^{3+} \rightarrow Ce^{3+}$ transfer, we get $P_{dd} \sim 10^8$ s^{-1} and $R_c \sim 5$ E. Comparison of R_c and Gd–Gd distances in the chain (3.88 E) and that between the chains (6.68 E) allows us to conclude that the $Gd^{3+} \rightarrow Ce^{3+}$ energy transfer occurs most probably within the Gd-chain. In other words, the energy transfer from Gd^{3+} to Ce^{3+} can occur only from two nearest Gd^{3+} ions. This makes it possible to introduce rather high Ce^{3+} concentrations into LGBO crystals without concentration quenching of luminescence. In the case of LGBO:Eu^{3+} crystals, we obtain $P_{dd} \sim 3{\cdot}10^4$ s^{-1} and $R_c \sim 7$ E. Thus, the excitation energy can be transferred from Gd^{3+} ion to nearest Eu^{3+} ions both within a chain and between neighboring chains. It is to note that exact determination of one-dimension or three-dimension $Gd^{3+} \to Eu^{3+}$ energy transfer is hampered at room temperature by a number of principal difficulties [11].

Thus, the activator center models have been proposed for LGBO single crystals doped by cerium and europium. Two types of activator centers in LGBO:Ce single crystals and one activator centers in LGBO:Eu single crystals have been established. In the frame of dipole-dipole approximation, the energy transfer parameters from Gd^{3+} host ion to activators ($Ce_{Gd}{}^{3+}$ and $Eu_{Gd}{}^{3+}$) and critical transfer radius R_c have been estimated.

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Активаторні центри у монокристалах $Li_6Gd(BO_3)_3$:Ln (Ln = Ce, Eu)

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Вивчено активаторні центри у монокристалах перспективного сцинтиляційного матеріала — литій-гадолінієвого бората $Li_6Gd(BO_3)_3$, активованого європієм та церієм. Методами оптичного поглинання, фото- та рентгенолюмінесценції встановлено наявність двох типів центрів у кристалах $Li_6Gd(BO_3)_3$:Ce та одного типу центрів у кристалах $Li_6Gd(BO_3)_3$:Eu. Визначено характеристики активаторних центрів.