Elementary Processes of Energy Transfer in the Lithium Borate Crystals Doped with Ce and Eu[1]

I.N. Ogorodnikov, V.A. Pustovarov, S.I. Omelkov, A.V. Tolmachev * and R.P. Yavetskiy *

Ural State Technical University, Mira Street19, Ekaterinburg, 620002, Russia, Phone, Fax, E-mail: ogo@dpt.ustu.ru
* Institute for Single Crystals NAS of Ukraine, Lenin Avenue 60, Kharkiv, 61001, Ukraine

Abstract – The paper presents the results of a study of the electronic excitation dynamics, fast luminescence and energy transport in the lithium-gadolinium borate crystals $Li_6Gd(BO_3)_3$ (LGBO) doped with Ce and Eu, the Mg-modified LGBO crystals $Li_{5.7}Mg_{0.15}Gd(BO_3)_3$:Eu, and $Li_6Eu(BO_3)_3$ crystals. Efficient energy transfer between rare-earth ions $Gd^{3+} \rightarrow Ce^{3+}$, $Gd^{3+} \rightarrow Eu^{3+}$ due to resonant mechanism and also at the expense of electron-hole recombination has been observed. Fast decay kinetics of Ce^{3+}-centers activator luminescence under intraband and 'band-to-band' excitations.

1. Introduction

The lithium-gadolinium borate single crystals $Li_6Gd(BO_3)_3$ (LGBO) are of interest first of all as potential optical material for neutron detection by means of scintillation method [1,2]. Due to considerable amount of boron atoms per elementary cell, large capture section for warm neutrons by isotope ^{10}B, great amount of emitted energy per absorbed neutron (total energy is about 2.8 MeV) borate compounds are promising materials for neutron registration in $^{10}B(n,\alpha)^7Li$ reaction. The presence of Li atoms in LGBO allows also use of $^6Li(n,\alpha)^3H$ reaction, which has advantages upon detection of low energy neutrons. Besides, in composition of LGBO there are isotopes of $^{155,157}Gd$, nuclei of which have great capture section for warm neutrons with energy below several keV.

Currently for these crystals primary data on defects, radiation-stimulated processes [5,6], luminescence [7] and scintillation properties [1] have been obtained. For instance, it is known, that radioluminescence of LGBO:Ce crystals is characterized by one exponential component with time constant $\tau \approx 21$ ns, light yield S is about 1000 photon/MeV at wavelength 395 nm, energy resolution R=26% for ^{238}Pu [8]. Maximum value of light yield is achieved at Ce impurity concentration in LGBO crystal 1.6–1.7 mass. % [9].

Present study touches the problem of researching processes of transfer and transformation of electronic excitations energy in the lithium borates (LGBO:Ce, LGBO:Eu, $Li_{5.7}Mg_{0.15}Gd(BO_3)_3$:Eu, $Li_6Eu(BO_3)_3$) by means of low-temperature luminescence VUV spectroscopy with the time-resolution under selective synchrotron radiation (SR) excitation.

2. Experimental details

The lithium-gadolinium borate crystals $Li_6Gd(BO_3)_3$ doped with Ce and Eu, the Mg-modified LGBO crystals $Li_{5.7}Mg_{0.15}Gd(BO_3)_3$:Eu, and $Li_6Eu(BO_3)_3$ crystals were researched in this paper. The samples were prepared in the form of plane-parallel transparent plates $7 \times 7 \times 1$ mm^3. All the examined APb_2X_5 crystals were grown by Czohralsky method in air atmosphere in the Institute for Single Crystals NASU (Kharkiv, Ukraine) [3,4,10–12].

Photoluminescence (PL) spectra, PL excitation spectra and the decay kinetics of PL were measured at 10 K and 290 K at the SUPERLUMI station of HASYLAB using SR [13]. For selective excitation of PL by SR in the energy range 3.7–27 eV 2m-vacuum monochromator, equipped by removable Al and Pt-gratings was used. PL spectra in the energy range from 1.5 eV to 6.2 eV were measured using 0.3 m ARC Spectra Pro-300i monochromator, R6358P (Hamamatsu) photomultiplier and CCD. Within PL spectra with time resolution registration method of time windows was used. For study of spectra and kinetics of luminescence under X-ray excitation it was used the synchrotron radiation of storage VEPP-3 in the Nuclear Physics Institute of SB RAS (Novosibirsk). Pulses had Gauss form (σ=430 ps), and energy 3–60 keV. In this case for registration of spectra and decay kinetics of luminescence the electron-optical chronography method with time reolution on the basis of dissector as LI-602 was used [14].

3. Results and Discussion

The PL emission spectra of LGBO comprises from both the broad bands and narrow intense lines. Alongside with the typical luminescence of the Ce^{3+} and Eu^{3+} activators we revealed the luminescent manifestation of the host lattice due to the radiative transitions in the Gd^{3+} ion. The Gd^{3+} PL emission can be selectively excited over the broad energy range starting from $hv < E_g \approx 9$ eV and continuing to $hv > E_g$. At the higher excitation energy range ($hv > 2E_g$) the photon multiplication process manifests itself in the PL excitation spectra.

On the basis of the detail analysis of the PL emission and PL excitation (Figs. 1, 2) spectra for Ce^{3+}, Eu^{3+} and Gd^{3+} ions in LGBO we revealed an efficient channel of the resonance energy transfer from the
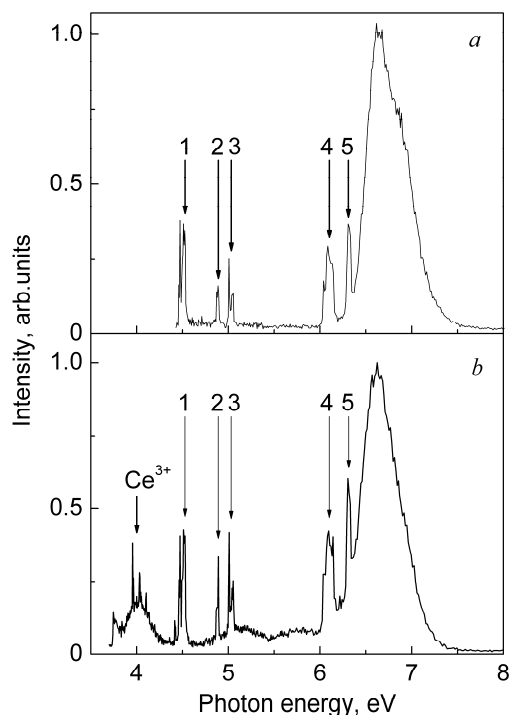
Fig. 1. The PL excitation spectra of the 3.02eV – (a) and 3.97eV – (b) emission bands measured for LGBO:Ce at room temperature. Arrows indicate the transitions of Gd^{3+}: $^8S_{7/2} \rightarrow ^6I$ – (1), $^8S_{7/2} \rightarrow ^6D_{9/2}$ – (2), $^8S_{7/2} \rightarrow ^6D_{1/2,7/2,3/2,5/2}$ – (3), $^8S_{7/2} \rightarrow ^6G_{7/2}$ – (4), $^8S_{7/2} \rightarrow ^6G_{3/2,13/2}$ – (5)
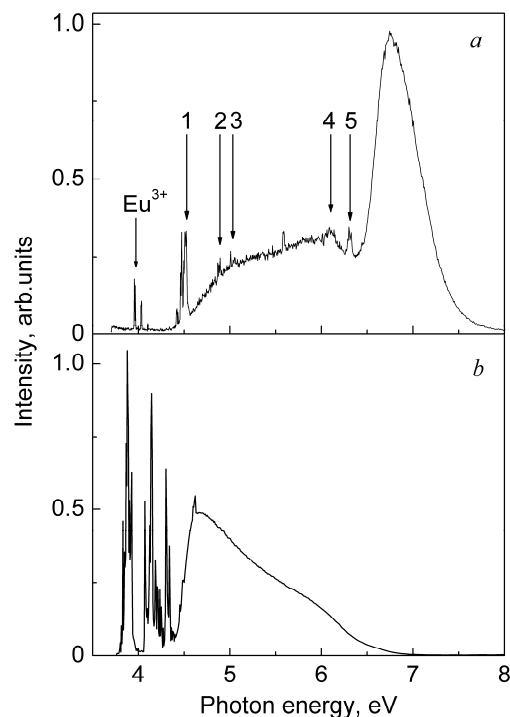

Fig. 2. The PL excitation spectra of the 2.02 eV emission band measured for LGBO:Eu at room temperature (a) and for $Li_6Eu(BO_3)_3$ at 10K (b). Arrows indicate the transitions of Gd^{3+}: $^8S_{7/2} \rightarrow ^6I$ – (1), $^8S_{7/2} \rightarrow ^6D_{9/2}$ – (2), $^8S_{7/2} \rightarrow ^6D_{1/2,7/2,3/2,5/2}$ – (3), $^8S_{7/2} \rightarrow ^6G_{7/2}$ – (4), $^8S_{7/2} \rightarrow ^6G_{3/2,13/2}$ – (5)

Gd^{3+} host ion to the either Eu^{3+} or Ce^{3+} activator ions in LGBO:Eu and LGBO:Ce, respectively. This channel is characterized by an enlargement of time-constant of the Ce^{3+} PL decay kinetics from 25 ns (direct photoexcitation) to several microseconds (excitation at the Gd^{3+} band).

PL excitation spectra of LGBO:Ce and LGBO:Eu are presented (Figs. 1, 2). Identification of Gd^{3+} bands in these spectra is made on the basis of extended J. Dicke's diagram [15]. In excitation spectrum of Ce^{3+} it is observed relatively broad band in energy range 4.0 eV, then a number of narrow bands and intensive broad band in the range 6.7 eV are manifested in PL excitation spectrum within energy increasing. In excitation spectrum of Eu^{3+} (2.02 eV) there are revealed narrow peaks at 4.5, 4.88, 5.03, 6.09, 6.3 eV on the background of broad band. Under excitation above 7.5 eV the luminescence yield in both crystals is rapidly decrease.

In modified lithium borate crystals, containing Eu ions, it was revealed the PL similar to that one for LGBO:Eu. In Fig. 2b PL excitation spectra at 2.02 eV in $Li_6Eu(BO_3)_3$ crystals at 10 K, in Fig. 3 – PL excitation spectra at 2.02 eV и 3.97 eV for $Li_{5.7}Mg_{0.15}Gd(BO_3)_3$:Eu crystals at 10 K.

The 2.02 eV PL excitation broad band locating at 5–6 eV in all the Eu-containing crystals (Figs. 2, 3) can be tentatively assigned to the Eu–O charge transfer band. This is in a good agreement with the results of theoretical calculations [16].

The PL excitation broad band locating at 6.5–6.7 eV was only observed in the crystals containing Gd^{3+} ions (Figs. 1–3). We tentatively assign this band to the Gd–O charge transfer band. It should be noted that the theoretical calculations [16] predicted an energy of 9.8 eV for a charge transfer O^{2-} to Gd^{3+}. However, the hybridization of the boron and oxygen orbitals, usually occurring in borates, can be responsible for the observed reduction the charge transfer energy for O^{2-} to Gd^{3+} transition in the examined borate crystals.

4. Conclusion

Luminescence corresponding radiative transitions in Ce^{3+}, Eu^{3+} и Gd^{3+} ions in LGBO crystals is efficiently excited in the broad energy range.

Under intraband (direct) photoexcitation ($h\nu < E_g \approx 9$ eV) typical Ce^{3+}, Eu^{3+} и Gd^{3+} ions luminescence spectra are observed. Matching Ce^{3+}, Eu^{3+} и Gd^{3+} ions PL and PL excitation spectra (Figs. 2–3) we may conclude that in LGBO crystals efficient channel of resonant energy transfer from matrix ion Gd^{3+} to Eu^{3+} or Ce^{3+} activator ions.
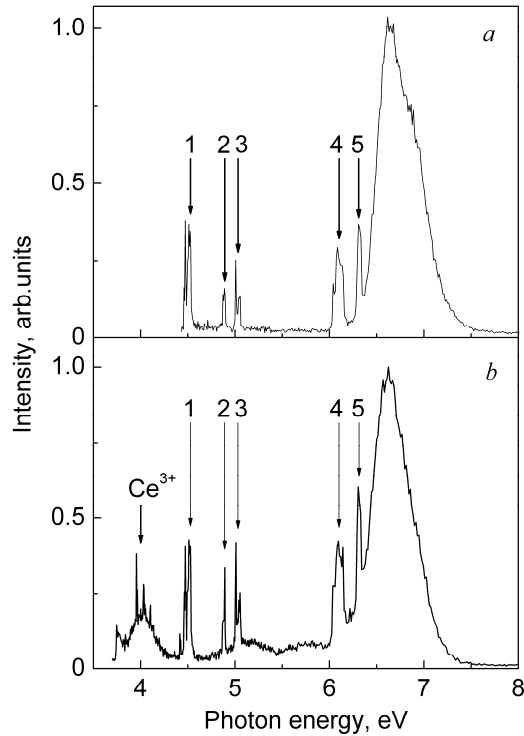
Fig. 3. The PL excitation spectra of the 2.02eV – (a) and 3.97eV – (b) emission bands measured for $Li_{5.7}Mg_{0.15}Gd(BO_3)_3$:Eu at 10K

Fig. 4.: Time-resolved PL excitation spectra in LGBO:Ce crystals at 290 K ($E_m = 3.02$ eV), measured in time window with width Δt=30 нс, delayed relatively excitation pulse on σ=4.2 ns – (a) and in LGBO:Eu ($E_m = 2.02$ eV, Δt=90 ns, δ=60 ns) – (b)

For interpretation of broad 5–6 eV and 6.7 eV bands in the PL excitation spectra in LGBO crystals it is necessary to use data of theoretical calculations. According to [16], energy of charge transfer between ligand oxygen, mainly forming, probably, as for other borates, the valence band top, and Eu impurity ion in oxides ($O^{2-} \rightarrow Eu^{3+}$ или $Eu^{3+} + O^{2-} \leftrightarrow Eu^{2+} + O^-$) is about 5.0 eV. On the grounds of this data, the broad 5–6 eV and 6.7 eV bands, observed in the PL excitation spectra in all considered lithium borates, containing Eu ions: LGBO:Eu, $Li_6Eu(BO_3)_3$ (Fig. 2) and $Li_{5.7}Mg_{0.15}Gd(BO_3)_3$:Eu (Fig. 3), should be interpreted as band of Eu-O charge transfer.

Interpretation the impurity centers PL excitation spectra in LGBO:Ce и LGBO:Eu crystals only on the grounds of theoretical calculations are not so uniquely. So, data [16] predict the energy of transitions between ligand oxygen and Gd ion ($O^{2-} \rightarrow Gd^{3+}$ или $Gd^{3+} + O^{2-} \leftrightarrow Gd^{2+} + O^-$) as about 9.8 eV. On the one hand, 6.7 eV observed band can correspond to formation of bound excitonic states, existence of which was observed early experimentally in some lithium borates [17]. However for LGBO crystals such interpretation can be argued so far because of absence of spectroscopic data on research of fundamental absorption edge.
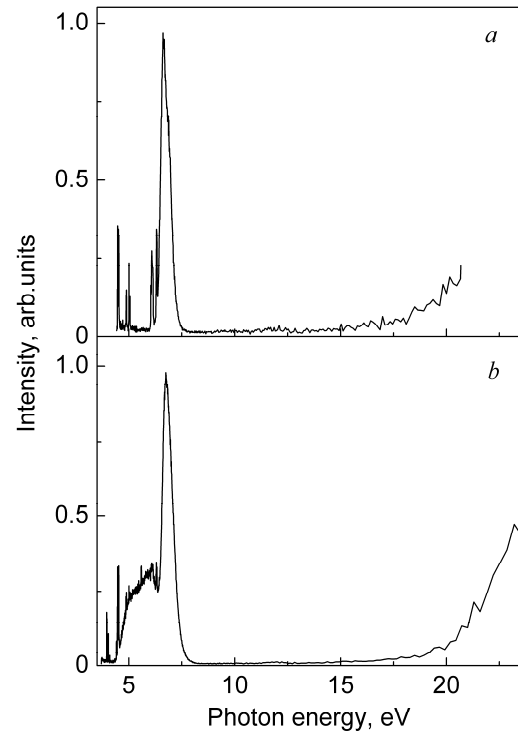
On the other hand, in some oxide crystals, for instance, in YPO_4, the charge transfer band is located at lower energies than $4f^{n-1}5d$ transitions of Eu^{3+} ions. Therefore $4f^n \leftrightarrow 4f^{n-1}5d$ transitions of Eu^{3+} ions can be also observed, but in the VUV range. In connection with this fact, 6.7 eV band in the Eu^{3+} PL excitation spectra can be related with $4f^n \leftrightarrow 4f^{n-1}5d$ interconfiguration transitions of Eu^{3+} ions [18].

However in our opinion 6.7 eV band in the Eu^{3+} PL excitation spectra should be interpreted as charge transfer band ($O^{2-} \rightarrow Gd^{3+}$), in spite of the fact that its low energy shift (about 3 eV) relatively calculated data [16] is considerable. The possible reason of this shift can be hybridization of atomic orbitals of oxygen and boron within valence band formation of crystal. In some crystals, containing Gd ions it was found in the VUV spectral region the similar broad excitation band, interpreted as band of charge transfer $O^{2-} \rightarrow Gd^{3+}$: $GdAl_3(BO_3)_4$:Eu (8.2 eV), $Ca_4GdO(BO_3)_3$:Eu (6.7 eV), Gd_2SiO_5:Eu (6.8 eV) и $GdAlO_3$:Eu (7.3 eV) [19].

Our experimental data are a solid argument in favor of this interpretation (Figs. 1–3). From these data it follows that 6.7 eV band in the activator PL excitation spectra is observed only for crystals, containing Gd^{3+} ions. At the same time in $Li_6Eu(BO_3)_3$ crystals, not containing Gd^{3+} ions, this band is not found (Fig. 2).

From impurity luminescence excitation spectra, measured with time resolution in the broad energy range (Fig. 4) we can say that their yields are very low in the range of 8–17 eV. Taking into account the assessment of $E_g \approx 9$ eV [4,9], it should be related such kind of PL excitation spectra in the 'band-to-band' excitation region with large nonradiative energy losses of electron excitations because of their high mobility.

It is observed the increase of PL yield in the excitation energy range $h\nu > 2E_g$ (Fig. 4). It can indicate the manifestation of photon multiplication in these crystals due to generation of secondary electron-hole pairs by hot carriers, and as a result we usually have an increase of PL yield under excitation by photons with $h\nu > 2E_g$. High yield of Eu^{3+} and Ce^{3+} impurity luminescence in LGBO under excitation by X-ray radiation, formatting high energy electron-hole pairs, is definite assumption of this fact and besides, this high yield indicates the efficient energy transfer by means of electron-hole mechanism.

Possibility of energy transfer in researched crystals at the expense of electron-hole mechanism give us an opportunity on manifestation efficient recombination processes within studying thermal stimulated luminescence (TSL). Really, in the paper [5] for LGBO:Ce crystal it was found at T=426 K electron TSL peak, for which kinetics has first order, activation energy is 0.82 eV and frequency factor is about 100 MHz. According to data [5] TSL peak at 426 K is due to electron delocalization F^+-center with latter radiative recombination on scheme $Ce^{4+} + e^- \rightarrow (Ce^{3+})^* \rightarrow Ce^{3+} + h\nu$. Our results on research TSL of crystals under X-ray photon excitation confirm these experimental data for LGBO:Ce crystals and besides show the presence of efficient centers of capture in LGBO:Eu too.

References

[1] Czirr J. B., MacGillivray G. M., MacGilivray R. R., Seddon P. J., Nucl. Instrum. Meth. Phys. Res. A, **424**, 15 (1999).

[2] Eijk, van C. W. E., Radiat. Measurements, **38**, 337 (2004).

[3] Baumer V. N., Grinyov B. V., Dubovik M. F., Dolzhenkova E. F., Korshikova T. I., Tolmachev A. V., Shekhovtsov A. N., Poverkhnost, **5**, 62 (2002).

[4] Shekhovtsov A. N., Tolmachev A. V., Dubovik M. F., Dolzhenkova E. F., Korshikova T. I., Grinyov B. V., Baumer V. N., Zelenskaya O. V., J. Cryst. Growth, **242**, 167 (2002).

[5] Baumer V. N., Dubovik M. F., Grinyov B. V., Korshikova T. I., Tolmachev A. V., Shekhovtsov A. N., Radiat. Measurements, **38**, 359 (2004).

[6] Yavetskiy R., Dubovik M., Tolmachev A., Tarasov V., Phys. Status Solidi (c), **2**, 268 (2005).

[7] Garapon C. T., Jacquier B., Chaminade J. P., Fouassier C., J. Luminesc., **34**, 211 (1985).

[8] Chernikov V. V., Dubovik M. F., Gavrilyuk V. P., Grinyov B. V., Grin' L. A., Korshikova T. I., Shekhovtsov A. N., Sysoeva E. P., Tolmachev A. V., Zelenskaya O. V., Nucl. Instrum. Meth. Phys. Res. A, **498**, 424 (2003).

[9] Chaminade J. P., Viraphong O., Guillen F., IEEE Trans. Nucl. Sci., **48**, 1158 (2001).

[10] Baumer V. N., Grinyov B. V., Dolzhenkova E. F., Dubovik M. F., Korshikova T. I., Tolmachev A. V., Shekhovtsov A. N., Materialovedenie, **7**, 48 (2004).

[11] Yavetskiy R. P., Dolzhenkova E. F., Dubovik M. F., Korshikova T. I., Tolmachev A. V., J. Cryst. Growth, **276**, 485 (2005).

[12] Dubovik M. F., Gayduk O. V., Grinyov B. V., Korshikova T. I., Tolmachev A. V., Shekhovtsov A. N., Yavetskiy R. P., Functional materials, **11**, 247 (2004).

[13] Zimmerer G., Nucl. Instrum. Meth. Phys. Res. A, **308**, 178 (1991).

[14] Pustovarov V. A., Zinin É, Krymov A. L., Shulgin B. V., Rev. Sci. Instrum., **63**, 3521 (1992).

[15] Wegh R. T., Meijerink A., Lamminmäki R.-J., Hölsä J., J. Luminesc., **87–89**, 1002 (2002).

[16] Belsky A., Krupa J. C., Displays, **19**, 185 (2000).

[17] Ogorodnikov I. N., Pustovarov V. A., Kruzhalov A. V., Isaenko L. I., Kirm M., Zimmerer G., Fiz. Tv. Tela, **42**, 454 (2000).

[18] Pieterson, van L. Charge transfer and $4f^n \leftrightarrow 4f^{n-1}5d$ luminescence of lantanide ions. PhD Thesis. Utrecht: Utrecht University, 225 p. (2001)

[19] Wang Y. H., Endo T., Guo X., Murakami Y., Ushirozawa M., J. Soc. Inform. Display, **12**, 495 (2004).