The point radiation defects in $Li_6YB_3O_9$:Eu^{3+} single crystals

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The point radiation defects in $Li_6YB_3O_9$:Eu^{3+} single crystals have been studied. The irradiation of $Li_6YB_3O_9$:Eu^{3+} single crystals with beta particles has been found to cause a valence state change ($Eu^{3+} \rightarrow Eu^{2+}$) in some fraction of europium ions being detected by decrease of Eu^{3+} photoluminescence integral intensity, as well as formation of O^- hole centers resulting in appearance of a radiation induced broad absorption band in the $\lambda = 320$–500 nm range. Two models of hole centers in $Li_6YB_3O_9$:Eu^{3+} crystals (O^- isolated ion or BO_3^{2-} complex ion) have been proposed.

Изучены точечные радиационные дефекты в монокристаллах $Li_6YB_3O_9$:Eu^{3+}. Установлено, что облучение монокристаллов $Li_6YB_3O_9$:Eu^{3+} бета-частицами приводит к изменению зарядового состояния части ионов европия $Eu^{3+} \rightarrow Eu^{2+}$, фиксируемого по снижению интегральной интенсивности фотолюминесценции ионов Eu^{3+}, а также к формированию дырочных O^--центров, что вызывает появление широкой полосы наведенного оптического поглощения в области длин волн $\lambda = 320$–500 нм. Предложены две модели дырочного центра в кристаллах $Li_6YB_3O_9$:Eu^{3+}: изолированный ион O^- или комплексный BO_3^{2-} ион.

The $Li_6REB_3O_9$ (RE=Y, Gd) double lithium and rare earth orthoborates find application as red phosphors in plasma display panels [1–3], scintillation detectors for thermal neutron registration in the mixed neutron-gamma fields [4, 5], or as active solid state laser media [6–8]. The $Li_6YB_3O_9$ (LYBO) crystal belongs to the monoclinic system, $P2_1/c$ space group, and is characterized by the following parameters: $a = 7.18192(7)$, $b = 16.4247(2)$, $c = 6.64193(5)$ Å, $\beta = 105.2857(7)°$, $V = 748.74(2)$ Å^3. The LYBO crystal structure is formed by lithium and yttrium polyhedrons combined by planar BO_3 groups in a three-dimensional composite network. Utilization of LYBO crystals in laser and scintillation devices implies intense processes of radiation defect formation in the material. However, no sufficient attention was given so far to studies of the radiation-induced defects in $Li_6REB_3O_9$ (RE = Y, Gd) crystals. The main thermoluminescent properties of LYBO:Ce^{3+} and LYBO:Ce^{3+},Sm^{3+} powders were studied before [9, 10]. However, using of polycrystalline powders to study processes of radiation defects formation does not allow to propose physically correct models of point radiation defects. In [11–13], the radiation induced processes in $Li_6GdB_3O_9$:Ce^{3+} (LGBO:Ce^{3+}) and $Li_{6-x}Na(Mg)_xGdB_3O_9$:Ce^{3+} single crystals have been reported. However, the presence of cerium ions in two valence states (Ce^{3+} and Ce^{4+}) and low thermostimulated luminescence (TSL) yield cause some difficulties in interpretation of the radiation processes in the crystals studied.

In [14], we have for the first time reported TSL and radiation-induced absorption in the LGBO:Eu^{3+} single crystals irradiated with beta particles from a ^{90}Sr:^{90}Y source. The purpose of this work was to
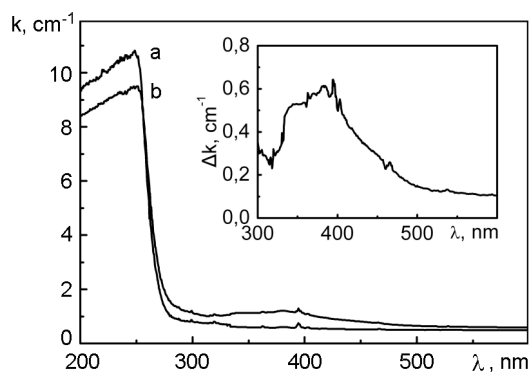
Fig. 1. Absorption spectra of $Li_6YB_3O_9:Eu^{3+}$ single crystal: prior to irradiation (a); after β-irradiation ($D = 10^6$ rad) (b). Inset: differential absorption spectrum of irradiated and non-irradiated $Li_6YB_3O_9:Eu^{3+}$ crystals.
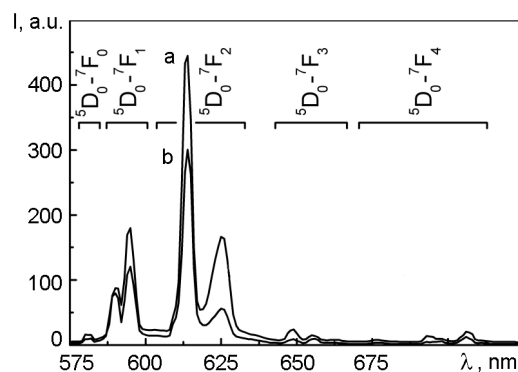

Fig. 2. Photoluminescence spectra of $Li_6YB_3O_9:Eu^{3+}$ crystal ($\lambda_{ex.} = 395$ nm): prior to irradiation (a); after β-irradiation ($D = 10^6$ rad) (b).

study the point radiation defects created by ionizing radiation in LYBO:Eu^{3+} single crystals which are isostructural to LGBO:Eu^{3+}.

The LYBO:Eu^{3+} (3 at. %) compound was obtained by solid state reaction at $T = 973$–1023 K for 24 hours. Chemical purity grade H_3BO_3, high purity grade Li_2CO_3, Y_2O_3 (99.99 %) and Eu_2O_3 (99.988 %) were used as the starting materials. The phase composition of the obtained samples was controlled by the X-ray phase analysis (XPA) using a Siemens D500 powder diffractometer (Cu Kα emission). LYBO:Eu^{3+} single crystals were grown by the Czochralski technique according to the procedure [15]. Europium concentration in the grown crystals was determined to be 0.62 at. % by atomic emission spectroscopy with arc excitation. The absorption spectra were recorded using a Specord M40 UV-VIS double-beam spectrophotometer. The photoluminescence spectra were obtained using a SDL-2 (LOMO) automated complex. The samples were irradiated with β-particles (^{90}Sr:^{90}Y source, 1 Curie activity; the average electron energy 0.2–0.7 MeV) at room temperature.

The undoped LYBO crystals are transparent within the 176–900 nm range, the band gap being 7.04 eV (56,800 cm^{-1}) [9]. Doping with europium causes the appearance of a wide charge transfer band (CTB) in the UV, and several narrow lines in the visible spectral region corresponding to the $4f$–$4f$ transitions of Eu^{3+} ions (Fig. 1, a). The intense CTB with a maximum at $\lambda = 249$ nm corresponds to the electron transport from the oxygen $2p$ orbital to an unoccupied $4f$ orbital of europium ion: $Eu^{3+} + O^{2-} \leftrightarrow Eu^{2+} + O^{-}$ [3].

The photoluminescence of LYBO:Eu^{3+} crystals is presented by a group of lines between 575 and 725 nm which correspond to transitions from the first excited level $^5D_0$ to the ^7F_J ($J = 0$ to 4) levels of Eu^{3+} ions (Fig. 2). The $^5D_0 \rightarrow {}^7F_2$ electric dipole transitions (with a maximum at $\lambda = 613$ nm) are predominant. The emission and excitation spectra are found to be in a good agreement with the data from [1–3]. The luminescence of Eu^{3+} ions in the "green" wavelength range connected with transition from the higher $^5D_1$ levels to the ^7F_J levels is quenched by high frequency vibrations of borate groups.

The undoped LYBO single crystals was found to be radiation resistant, no changes in optical absorption spectrum being detected after β-irradiation up to $D \sim 10^7$ rad dose [16]. Irradiation of LYBO:Eu^{3+} crystals with β-particles results in a decrease of the CTB absorption coefficient, appearance of a wide non-elementary band of induced optical absorption in the 320–500 nm range (Fig. 1, b), and in a decreased integral photoluminescence intensity of Eu^{3+} ions (Fig. 2, b). After the irradiation, LYBO:Eu^{3+} samples become yellow. It is known that irradiation of rare-earth doped crystals results often in changed valence state of rare-earth ions, which can be detected by electron paramagnetic resonance spectra, optical absorption and photoluminescence ones. Hence we ascribe the observed radiation-induced changes to transition of some fraction of Eu^{3+} ions into divalent state: $Eu^{3+} \rightarrow Eu^{2+}$. The arising excess charge may be compensated by local distortion of the borate group or by structural defect in the second coordination sphere.
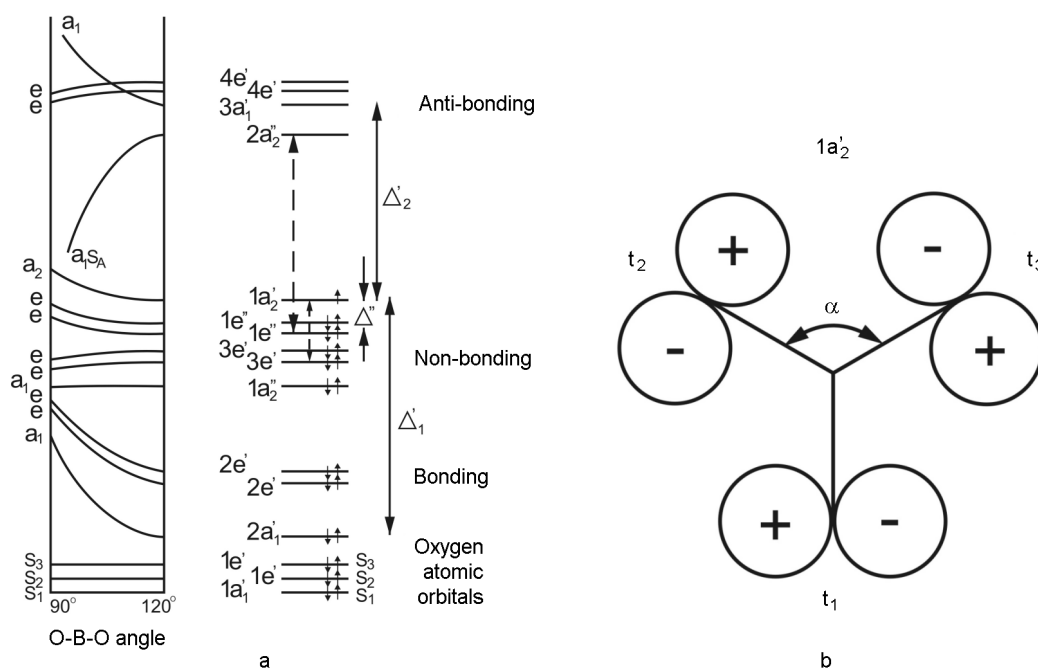
Fig. 3. Molecular orbital energy levels for a planar BO_3^{2-} ion. The allowed optical transitions are represented by dashed lines (a); the $1a_2'$ molecular orbital for planar BO_3^{2-} ion. The angle α is 120° for undistorted molecules (b) [26].

The induced absorption spectrum is presented by wide structureless band in the $\lambda = 300-500$ nm region (inset in Fig. 1). The radiation-induced optical absorption bands have been observed in many oxides and this absorption was ascribed to holes trapped at O^{2-} ions. We suppose that the radiation-induced coloration of LYBO:Eu^{3+} single crystals is connected with formation of O^- hole centers. The model of O^- hole center in an oxide material includes also an adjacent acceptor defect, such as a vacancy or an impurity ion [17]. For example, for lithium triborate LiB_3O_5, it has been clearly demonstrated that radiation-induced lithium vacancy positioned in the second coordination sphere is a charge compensating defect binding the hole of the O^- center [18, 19]. We suggest that excess charge of O^- center in LYBO:Eu^{3+} crystal is compensated by lithium vacancies, too. During the O^- centers formation, the lattice distortion usually causes localization of holes at one of the oxygen site. These holes thus form small polarons bound to an acceptor. According to a modern concept, optical properties of O^- centers can be correctly described within the small polaron model [20]. The typical features of bound small polarons are wide absorption bands, high oscillator strengths ($f = 0.1$), excited states tunneling splits. Although some borates, for instance

LiB_3O_5, demonstrate optical absorption which is not typical of bound hole polarons [20]; nevertheless, we believe that the radiation-induced absorption of LYBO:Eu^{3+} crystal is the small polaron absorption.

The experimental data suggest that two types of hole centers could be created in borates: isolated hole centers [19, 21], or hole centers based on borate anionic group [22-24]. In any case, O^- center formation is accompanied by significant lattice distortion, the average distance from O^- center to an acceptor defect increasing by 30-40 % as compared to regular crystal lattice. In the LYBO crystal structure, all the boron atoms are coordinated by three oxygen atoms and form planar BO_3 groups which occupy three independent positions [25]. Therefore, we have assumed formation of isolated O^- hole centers (the hole is trapped mainly at an oxygen ion), or BO_3^{2-} ions (the hole is uniformly distributed upon the orbitals of three oxygen ions which coordinate the defect) in irradiated LYBO:Eu^{3+} single crystals.

The radiation-induced absorption of these centers can be described as follows. In the case of O^- center, the absorption is due to transition from the local level of the center to the valence band levels. Such transitions present a photoinduced hole transfer from one to another oxygen atom near the defect

and can be referred to as charge transfer transitions in a sense. In the case of BO_3^{2-} center, the absorption is caused by transitions between the ground and excited states of the BO_3^{2-} ion; the uncoupled electron is located at the $1a'_2$ orbital which consists of $2p$ atomic orbitals of three oxygen atoms (Fig. 3) [26].

The maximum of induced absorption band attributed to isolated O^- centers in borate crystals is observed at $\lambda = 360$ nm for LiB_3O_5 [27] and at $\lambda = 365$ nm for $Sr_2B_5O_9Br:Ce^{3+}$ crystals [21]. These wavelengths are close to the value of 365 to 380 nm obtained in our experiment for $LYBO:Eu^{3+}$ (inset in Fig. 1). At the same time, the BO_3^{2-} ions being very stable at room temperature cause absorption in a relatively long-wavelength spectral region $\lambda = 500-700$ nm for $CaCO_3$ and $\lambda = 550-950$ nm for 25 mol. % $K_2B_2O_4$ + 75 mol. % K_2CO_3 [26]. Thus, the induced absorption of $LYBO:Eu^{3+}$ single crystals is most probably caused by the O^- center formation, i.e. the hole is trapped predominantly at one oxygen atom and does not belong to the whole BO_3 planar borate group. This conclusion agrees qualitatively with the remarkable difference in the B–O distances in the BO_3-triangles (from 1.343(2) Å to 1.389(2) Å) as compared to typical values B–O = 1.37 Å, and with low point symmetry of oxygen atoms, that make localization of the hole at one oxygen ion more energy favorable. For comparison, in the alkaline earth oxides, the hole localization at one oxygen ion provides a gain of 2.3 eV in the system kinetic energy, while in the case of hole distribution upon six oxygen atom the kinetic energy is lowered only by 1.0 eV [28].

The presence of intense radiation-induced absorption band has stimulated our search for luminescent manifestations of radiation defects. However, the selective optical stimulation of $LYBO:Eu^{3+}$ crystals by the monochromatic light in the $\lambda = 360-425$ nm range results only in characteristic luminescence of Eu^{3+} ions caused by direct photoexcitation thereof. The transition of even a small fraction of europium ions into divalent state should be manifested in the luminescence spectra, since the oscillator strengths ratio for the $4f^7 \rightarrow 4f^65d$ allowed dipole-dipole transitions of Eu^{2+} ions and $4f-4f$ forced dipole-dipole transitions of Eu^{3+} ions is $f(Eu^{2+}):f(Eu^{3+}) \approx 1:10^{-4}$. However, we have not found any luminescence of the Eu^{2+} ions. Perhaps the luminescence

of Eu^{2+} ions in LYBO crystals is quenched by photoionization processes. In particular, this mechanism is responsible for degradation of scintillation response of some cerium activated oxide crystals [29].

Let us consider possible mechanisms of point radiation defects formation in $LYBO:Eu^{3+}$ single crystals. Irradiation of $LYBO:Eu^{3+}$ with beta particles can displace lithium ions from their regular crystallographic positions and create lithium vacancies. Such defects may stabilize O^- hole trapped centers [19]. The O^- centers in $LYBO:Eu^{3+}$ crystals may arise created either due to impact mechanism, or to "re-charge" of intrinsic (growth) lithium vacancies. The latter are created during $LYBO:Eu^{3+}$ crystal pulling as a result of Li and B species evaporation [30]. The threshold displacement energy of lithium atoms by impact mechanism has the lowest value as compared to other constituent elements (yttrium, boron) which form LYBO compound. According to theoretical predictions, the displacement energy required to create one lithium vacancy in a complex oxide material, for example, $LiNbO_3$, is 5 to 26 eV. Yttrium atoms have a larger ionic radius and charge as compared to lithium ones, and seem to be hardly displaced from their crystallographic positions. On the other hand, only one lithium vacancy is necessary to compensate the excess charge of an O^- hole center. The creation probability of boron vacancies in LYBO crystal very low due to high covalence degree of the B–O bounds. In LYBO crystal structure, lithium polyhedrons form two-dimensional network [25], resulting in appearance of ionic conductivity in this crystal [31]. Furthermore, lithium sublattice of LYBO compound is mobile to some extent and this also points on the possibility of radiation-induced displacement of lithium ions. The presence of radiation-induced defects in $LYBO:Eu^{3+}$ crystals allows one to expect effective recombination processes resulting in TSL. Indeed, in [16], we have found for $LYBO:Eu^{3+}$ crystal the TSL peak at $T = 450-480$ К connected with decomposition of hole centers. This peak is characterized by first order kinetics and its activation energy is 1.2 eV.

To conclude, the point radiation defects in $Li_6YB_3O_9:Eu^{3+}$ single crystals have been studied. The radiation-induced optical absorption of $Li_6YB_3O_9:Eu^{3+}$ crystals in the $\lambda = 320-500$ nm range has been ascribed to bound small polaron absorption. It has been shown that irradiation of $Li_6YB_3O_9:Eu^{3+}$ sin-

gle crystals with beta particles results in transition of some europium ions into divalent state $Eu^{3+} \rightarrow Eu^{2+}$, and in formation of O^- hole centers. Two models of hole centers in $Li_6YB_3O_9{:}Eu^{3+}$ crystals, namely O^- isolated ion or $BO_3{}^{2-}$ complex ion, have been proposed. It has been determined that formation of isolated O^- centers is more probable as compared to hole centers based on anionic borate group. It has been assumed that the excess charge of O^- centers in $Li_6YB_3O_9{:}Eu^{3+}$ crystals is most probably compensated by radiation induced or growth lithium vacancies.

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Точкові радіаційні дефекти у монокристалах $Li_6YB_3O_9{:}Eu^{3+}$

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Розглянуто точкові радіаційні дефекти у монокристалах $Li_6YB_3O_9{:}Eu^{3+}$. Встановлено, що опромінення монокристалів $Li_6YB_3O_9{:}Eu^{3+}$ бета-частинками спричиняє зміну валентного стану частини іонів європію $Eu^{3+} \rightarrow Eu^{2+}$, що проявляється у зниженні інтегральної інтенсивності фотолюмінесценції іонів Eu^{3+}, а також утворення діркових O^--центрів, що викликає появу широкої полоси індукованого оптичного поглинання в області довжин хвиль $\lambda = 320{-}500$ нм. Запропоновано дві моделі діркового центру у кристалах $Li_6YB_3O_9{:}Eu^{3+}$: ізольований іон O^- або комплексний $BO_3{}^{2-}$ іон.