

PACS: 78.40.-q; 78.55.-m; 78.70.En

Luminescence and radiation-induced defects in $\text{Li}_2\text{B}_4\text{O}_7:\text{Eu}$ single crystals

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Abstract. Thermostimulated luminescence (TSL) of $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Eu}$ single crystals in the temperature range 290-650K has been studied. Lithium tetraborate (LTB) doped with europium has been found to favour a further increase of the light sum storage of electron-captured centres. Radiation-induced defects and their participation in recombination process in LTB:Eu are considered. Suggestions about character of Eu site in the host lattice based on the photoluminescence spectral data are discussed. The electron structure of LTB crystals measured by XPS method is presented.

Keywords: lithium tetraborate, single crystal, photoluminescence, thermostimulated luminescence, radiation-induced defect.

Paper received 24.06.00; revised manuscript received 30.06.00; accepted for publication 12.07.00.

1. Introduction

Lithium tetraborate $\text{Li}_2\text{B}_4\text{O}_7$ (LTB) is well known as material of promise for thermoluminescent dosimetry and attracts attention of researchers from many countries [1-3]. The thermoluminescent properties of this crystal have been profoundly investigated during last years, but there are still many problems which are to be solved. In particular, there are few works considering color and TSL centres in $\text{Li}_2\text{B}_4\text{O}_7$ single crystals [3,4]. It is difficult to determine the structure of those centres, and it is reasonable to reach some accordancy in results obtained by different methods. It is known that doping with rare-earth elements enhances the thermoluminescence intensity [5].

In this work, we have studied the possibility to enhance the LTB thermostimulated luminescence efficiency by Eu doping and discuss the structure of TSL centres in LTB single crystals. The question of the dopant inclusion into the crystal lattice is also discussed.

2. Experimental

LTB single crystals were grown by Czochralski method. The crystal parameters were similar to those of perfect LTB crystals [6]. Doped crystals possess optical inhomogeneity regions. The Eu content was 0.06% by mass, according to atomic-emission spectral analysis data. Transparent samples $10 \times 10 \times 2 \text{ mm}^3$ were produced with optical c-axis along the 2 mm dimension.

Crystal samples were irradiated by radionuclide *b*-source (Sr:Y)-90 with activity 2 Ci (dose = 2.5×10^6 Gy). TSL was investigated within 290-650 K temperature range using a FEU-79 cooled-cathode PMT, the sample heating rate was approximately 20 K/min. Absorption spectra of additively colored crystals was measured by means of a SPECORD M40 spectrophotometer at room temperature.

Electron structure of the crystals was studied by X-ray photoelectron spectroscopy (XPS) using an XPS-800 spectrometer (KRATOS) with non-monochromatic $\text{Al } K_{\alpha}$ emission. The sample charging effect was accounted for,

and the spectra were calibrated on the binding energy using C1s line (285 eV). The studies were performed on the freshly-cleaved surface of an LTB crystal. The quantitative analysis made using L1s, B1s, O1s lines has shown that the sample surface has the stoichiometric composition.

3. Results and discussion

We investigated excitation and photoluminescence spectra of LTB:Eu sample (Fig. 1). It has been determined that Eu ions in the LTB crystal are in the trivalent state. The photoluminescence spectrum is characterized by the presence of forbidden electric and magnetic $^5D_0 \rightarrow ^7F_0$ transition. The shift of the Eu^{3+} luminescence spectrum bands to longer wavelengths with respect to the free ion ones as well as the presence of a small $^5D_0 \rightarrow ^7F_0$ band are due to the crystal lattice field influence on the doping ion [7]. The observed splitting character of $^5D_0 \rightarrow ^7F_1$ band and $^5D_0 \rightarrow ^7F_2$ ones in the LTB:Eu $^{3+}$ luminescence spectrum allows to conclude that the symmetry of the Eu^{3+} ion is monoclinic [8]. It can be realized either when the dopant substitutes the Li^+ cation or when it is arranged in the chains of Li tetrahedrons.

Three intense peaks at 414, 473, 548 and one weak peak at 365 K were observed on the TSL curve of LTB (Fig. 2, a). This corresponds to the levels of 0.83, 0.96, 1.0 and 0.73 eV energy, respectively [9]. LTB single crystals show no optical absorption bands at wavelengths 200-900 nm [1]. The absorption spectra of LTB:Eu possess absorption bands of Eu^{3+} -ion. After irradiation, the samples take a slightly yellowish colour. Optical spectra (Fig. 2, a) show a weak absorption peak at 235 nm and a broad band in the region of 260-375 nm. The complex band was divided into four individual bands at 235, 285, 321 and 352 nm. Absorption bands at 321 nm and 352 nm were interpreted in [10] as those related to F^+ - and F^- -

centers, respectively. Absorption peaks at 235 nm and 285 nm could be assigned to the trapping levels of O^- -center. In this center model, the trapped hole is localized on the p -orbital of oxygen, bridging the three- and four-coordinated boron ions in the vicinity of the negatively charged stabilizing defects, for example, a lithium vacancy [11,12]. The observed TSL maxima are caused by recombination luminescence of the main radiation-induced point defects: oxygen vacancies neighboring the alkali ions trap one or two electrons and likely O^- -centers.

No additional TSL peaks were observed for doped single crystals in the studied temperature range (Fig. 2, b). The doping by Eu^{3+} results in an increased intensity of two peaks at 473 and 548 K. The doping results also in an increased height of 321 nm optical band due to F^+ -center and of 352 nm one assigned to F^- -center [13]. Only one 285 nm optical band related likely to O^- -center observed in LTB:Eu $^{3+}$.

Eu^{3+} acts as an electron trap [14]. The electron capture by Eu^{3+} can take place resulting in the Eu^{2+} due to its high electron affinity. This ion state has a very short lifetime and electron is released already at room temperature and captured by the matrix electron traps - oxygen vacancies. This consideration can explain the observed increasing of TSL peaks in doped crystals connected with F^+ - and F^- -center decay.

The XPS spectrum near the valence band is shown in Fig. 3 (see also [15]). The data presented allow to conclude that the valence band width is 9-10 eV. In [16], the LTB electron structure has been calculated using the quantum-chemical self-consistent cluster method. The calculation results agree well with the experimental spectrum and show that it is just oxygen atoms that contribute mainly to the electron state density near the valence band top. The investigation into the LTB crystal electron structure confirm our previous data on the involving of oxygen atoms in the emissive recombination processes.

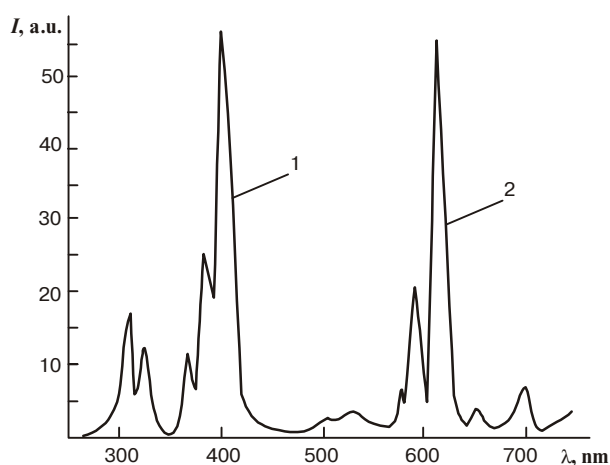


Fig. 1. The excitation (1) and photoluminescence (2) spectra of $\text{Li}_2\text{B}_4\text{O}_7:\text{Eu}$.

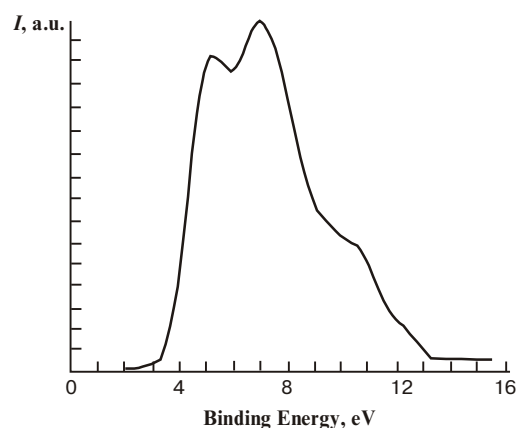


Fig. 2. XPS spectrum of $\text{Li}_2\text{B}_4\text{O}_7$ single crystals.

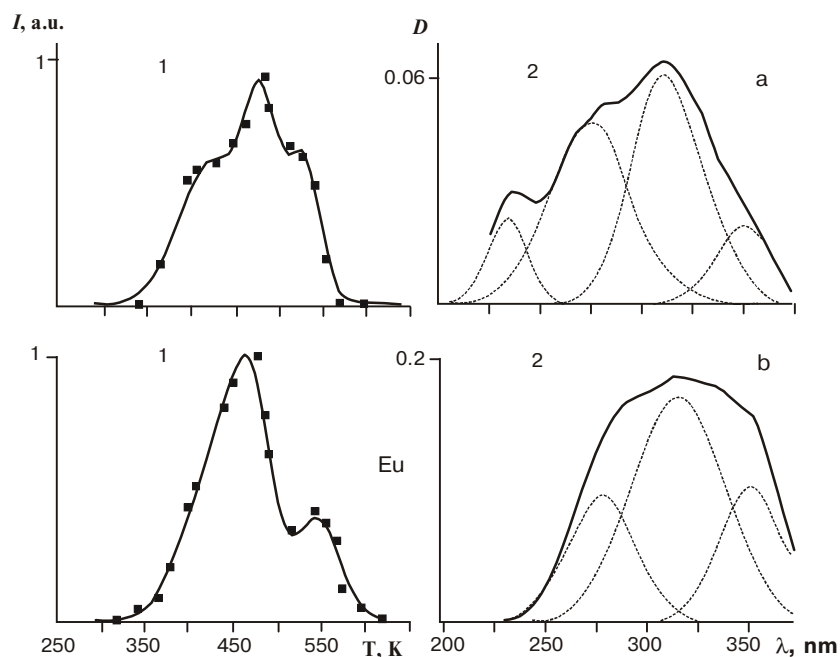


Fig. 3. Thermoluminescence data (1) and absorption spectra (2) of additively colored LTB (a) and LTB:Eu (b) single crystals.

Conclusions

LTB:Eu crystals are characterized by intense photoluminescence in the region of 580-700 nm. Europium is present in the crystal in the trivalent state. The luminescence spectrum of LTB:Eu³⁺ allows to conclude the symmetry of the Eu³⁺ ion to be monoclinic one. It can be realized either when the dopant substitutes the Li⁺ cation or when it is arranged in the region of Li tetrahedrons chain. Doping by Eu results in an increased height of the 321 nm optical band due to F⁺-center and the 352 nm one are assigned to F-center. The observed TSL maxima are caused by recombination luminescence of the main radiation-induced point defects: oxygen vacancies neighboring the alkali ions having trapped one or two electrons.

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