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Valency states of Yb, Eu, Dy and Ti ions in $\text{Li}_2\text{B}_4\text{O}_7$ glasses

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Abstract

Absorption and emission spectra of Eu and Dy, Yb and Ti ions in $\text{Li}_2\text{B}_4\text{O}_7$ glasses grown in oxygen and hydrogen gas atmospheres were measured for valency states and lattice-sites analysis. For the $\text{Li}_2\text{B}_4\text{O}_7$ glass doped with Eu^{2+} , Eu^{3+} and Dy^{3+} ions which were grown in oxidizing and reducing atmospheres, absorption and emission bands due to these ions were investigated before and after γ -irradiation. For the Yb^{3+} -doped $\text{Li}_2\text{B}_4\text{O}_7$ glass, a weak, broad band was observed near the sharp 976.3 nm absorption band. The origin of this band is discussed in comparison with other glasses. Moreover, irradiation experiments using γ -rays were also performed in order to investigate the possibility of valency change of Yb ions. It was found that Ti^{4+} ions, which are produced under oxidizing atmosphere, change to Ti^{3+} ions after γ -irradiation with a dose of 10^5 Gy. An additional absorption band observed at about ~ 500 nm is due to the Ti^{3+} ions accompanied by charge-compensating vacancy and does not give any emission.

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1. Introduction

Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) is a congruently melting compound with a melting point of 917 °C. Single crystals of this material are used as substrates for surface acoustic wave (SAW) devices. The material has a temperature-independent acoustic wave velocity and a relatively high electromechanical coupling coefficient for SAW. Polycrystals of $\text{Li}_2\text{B}_4\text{O}_7$ containing a small amount of impurity ions (called dopants, hereafter) also

find applications in thermoluminescent dosimeters [1].

Owing to the small ionic radii of lithium and boron atoms, it is impossible to introduce dopants into $\text{Li}_2\text{B}_4\text{O}_7$ single crystals at high concentrations. A relatively high viscosity of molten lithium tetraborate, like of other borates, is a source of serious problems during single crystal growth of this material. On the other hand, this viscosity allows us to obtain the material in a form of glass containing much larger amounts of dopants than in case of single crystals [2,3].

One of the most investigated impurity ions also in these glasses is chromium, and the large number of review articles and papers testifies to the high

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level of interest in this field [4,5], even in connection with the development of lasers. Unfortunately, in Cr³⁺ doped Li₂B₄O₇ glass, a broad excited state absorption (ESA) band arises. This ESA band overlaps with the Cr³⁺ emission bands, resulting in reducing the possibility of laser action. The published results [4] have also shown that Cr ions can enter the Li₂B₄O₇ lattice at two lattice sites: at the octahedral coordinate site as Cr³⁺ and at the tetrahedral coordinate site as Cr⁶⁺ in the [CrO₄]²⁻ complex. It has been shown that the ratio of Cr⁶⁺ to Cr³⁺ ion concentration decreases with increasing the doped Cr concentration. Cobalt ion is very intensively investigated for its possible application for laser non-linear absorbers [4,8].

Jayasankar et al. have investigated energy levels of Pr³⁺ [6] and Tm³⁺ [7] doped Li₂B₄O₇ glasses. They stated that energy levels in LBO glasses are more or less similar to other glasses and are generally greater than those in aqua-ion and crystals. Most of the energy values of the levels decrease from glasses to aqua-ion, to crystals. The results have shown that the various spectroscopic properties of the excited states are subject to ligand environment.

In this paper, we point out the possibility of easily hosting impurity ions Yb, Eu, Dy, and Ti in a Li₂B₄O₇ glassy matrix. The study of doping with Eu and Dy is performed simultaneously with a check on possible energy transfer from Eu²⁺ to Dy³⁺ ions. The purpose of this work is also to investigate possible lattice sites and valency states of Yb, Eu, Dy and Ti ions in Li₂B₄O₇ glasses.

2. Experimental

The synthesis of lithium tetraborate was carried out from lithium carbonate Li₂CO₃, and boric oxide H₃BO₃ (Merck, extra pure) in platinum crucibles in air. After reaction of the starting materials at 950 °C, the obtained compound was overheated to 1150 °C to remove traces of water and carbon dioxide, which were present in the melt. Because of B₂O₃ losses, due to evaporation, 1 mol% surplus of H₃BO₃ was added to the starting composition. After rapid cooling below 550 °C,

Table 1

Material	Growth conditions	FAE [nm]
LBO:Eu,Dy	In oxygen gas flow	270
LBO:Eu,Dy	In argon gas flow	340
LBO:Eu,Dy	In hydrogen gas flow	355
LBO:Yb	In oxidizing atmosphere	210
LBO:Ti	In oxidizing atmosphere	300
LBO:Ti	In hydrogen gas flow	310
LBO	In oxidizing atmosphere	190

the melt formed glass which did not show any tendency to crystallise.

When Li₂B₄O₇ (LBO) glasses containing Ti₂O₃ are grown under hydrogen or argon gas flow (i.e. in reducing atmosphere), they become light-violet colored, while when Li₂B₄O₇ glasses containing TiO₂ are grown under air or oxygen gas flow (i.e. in oxidizing atmosphere), they become almost transparent. The Li₂B₄O₇ glasses containing Yb₂O₃ when grown in oxidizing atmosphere, also become almost transparent. The glasses doped with Eu and Dy ions grown in oxidizing atmosphere showed up to be transparent. The same result was obtained for the glasses grown in reducing atmosphere.

The following Li₂B₄O₇ glasses were obtained: glass doped with Ti³⁺ (1.25 wt.%) and Ti⁴⁺ (1.25 wt.%), glass with Yb³⁺ (0.6 wt.%), and glass with Eu²⁺ (2 wt.%) and Dy³⁺ (2 wt.%). Doping with Eu and Dy in LBO glass gives a characteristic change in the short-wave absorption edge value (fundamental absorption edge—FAE) (see Table 1).

The glass samples were cut as 10 × 10 mm parallel plates with a thickness of about 1 mm. The samples were irradiated by gamma photons immediately after the growth process. The gamma source of ⁶⁰Co with a strength of 1.5 Gy/s was used. The gamma doses applied were up to 10⁶ Gy. Optical transmission was measured before and after γ -irradiation using a LAMBDA-900 Perkin-Elmer spectrophotometer in UV-VIS-IR range. Values of $\Delta K(\lambda)$ due to the irradiation were calculated according to the formula:

$$\Delta K(\lambda) = \frac{1}{d} \cdot \ln \frac{T_1}{T_2}, \quad (1)$$

where K is absorption, $\Delta K(\lambda)$ is additional absorption, λ is wavelength, d is sample thickness, and T_1 and T_2 are transmissions of the sample

measured before and after the irradiation, respectively. Low temperature absorption spectra of the glasses were measured in a spectral region of 3100–200 nm with a Cary-5E spectrophotometer. The spectral resolution was fixed at 0.2 nm.

Fluorescence spectra were obtained in the 200–800 nm range using a Perkin–Elmer LS-5B spectrofluorimeter. Radioluminescence spectra were obtained in the 200–850 nm range by excitation with X-rays generated in DRON (35 kV/25 mA) and using an ARC Spectra Pro-500i spectrograph (diffraction grating Hol-UV 1200 g/mm and diffraction grating brighten up at 500 nm 1200 g/mm, 0.5 mm slits) and a Hamamatsu R928 (1000 V) photomultiplier.

3. Results and discussion

Ti³⁺-doped crystals have attracted interest in view of their potentials as tunable solid-state laser materials. There are a lot of materials showing strong absorption and emission bands due to ²T₂–²E transition of Ti³⁺ ions, e.g. Ti³⁺:Al₂O₃ [9], Ti³⁺:YAl₃(BO₃)₄ and Ti³⁺:GdAl₃(BO₃)₄ [10]. Some of them, moreover, exhibit the presence of Ti³⁺/Ti⁴⁺ pairs (Ti³⁺:Al₂O₃) that limit emission

properties of Ti³⁺ ions. We tried to produce Ti³⁺ and Ti⁴⁺ by growing Ti³⁺-doped Li₂B₄O₇ glass under oxidizing and reducing atmosphere. We found the appearance of Ti⁴⁺ in the case of oxidizing atmosphere, while the presence of not only Ti³⁺ but also of Ti³⁺/Ti⁴⁺ pairs in the case of reducing atmosphere was detected (see curve 1 in Fig. 2).

Fig. 1 shows the room temperature absorption spectra of Ti-doped Li₂B₄O₇ glasses grown in oxidizing and reducing atmosphere. In the two glasses, an intense absorption rise is observed at about 300 nm. It can be seen that curve 1 does not exhibit any absorption band in the about 300–2000 nm region. This suggests that Ti enters only as Ti⁴⁺ ions in TiO₂-doped Li₂B₄O₇, because absorption bands due to charge transfer from the valence band to the Ti⁴⁺ ion appear to be at the ultraviolet region (wavelengths shorter than 350 nm) as expected from the cases of YAlO₃, Li₄Ge₂O₁₂ and Y₂SiO₂ [11,12]. Contrary to the glasses grown in oxidizing atmosphere, the Ti₂O₃-doped glass grown in reducing atmosphere showed a wide, double structured band at 500 nm.

In Fig. 2 the low temperature absorption spectrum of Ti₂O₃-doped glass (curve 1) is shown. Two absorption bands are observed at about 495 and

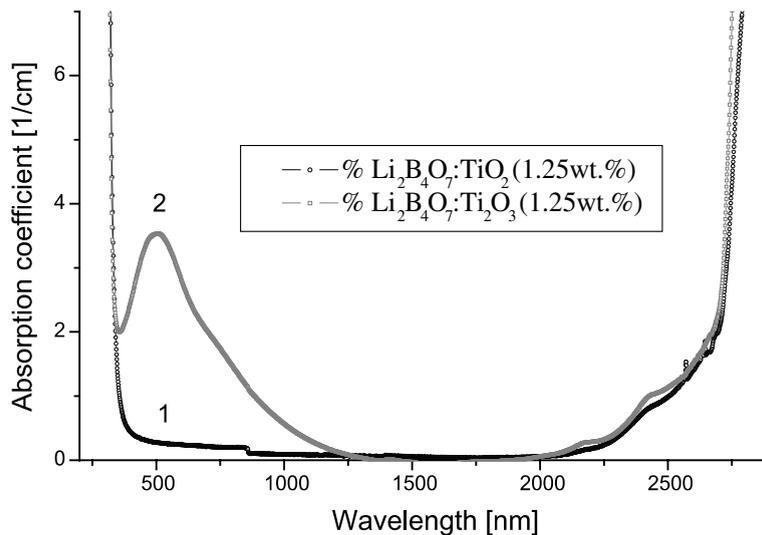


Fig. 1. Room temperature absorption spectra of TiO₂ doped (oxidizing atmosphere) Li₂B₄O₇ glass (1) and Ti₂O₃ (reducing atmosphere) doped Li₂B₄O₇ glass (2).

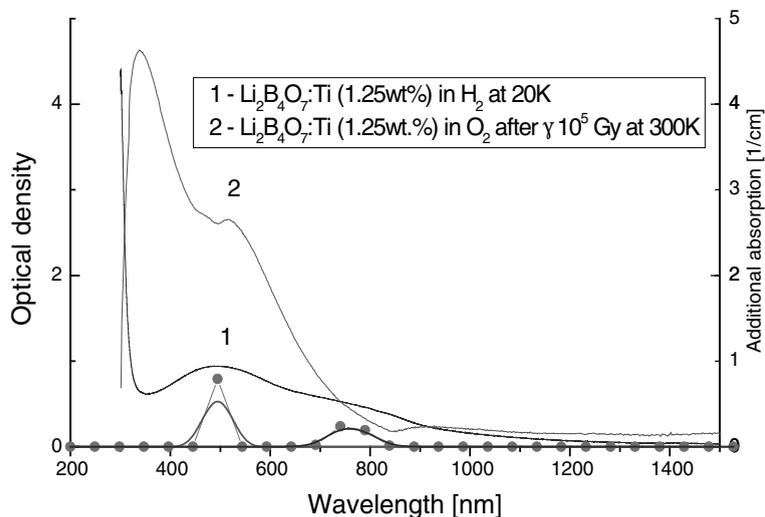


Fig. 2. Absorption spectra of Ti_2O_3 doped glass at 20 K (1) and TiO_2 doped glass after γ -irradiation with a dose of 10^5 Gy at 300 K (2).

750 nm, which are due to Ti^{3+} and Ti^{4+} ions. The 495 nm band is attributed to the ${}^2\text{T}_2\text{-}{}^2\text{E}$ transition of Ti^{3+} and the second, weaker 750 nm band, is attributed to $\text{Ti}^{3+}/\text{Ti}^{4+}$ pairs. The experimental results discussed here show that the absorption bands of Ti^{3+} are slightly shifted to longer wavelengths relative to benchmark system $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$. This follows from slightly weaker octahedral crystal field term at octahedral site in $\text{Li}_2\text{B}_4\text{O}_7$ glass compared to the Al^{3+} site in Al_2O_3 .

Curve 2 of Fig. 2 shows the absorption spectrum of a TiO_2 -doped glass after γ -irradiation with a dose of 10^5 Gy. Irradiation with γ -ray leads to a change of glass coloration to violet. As is seen from the figure, the 750 nm band disappears but two additional bands appear at 320 and 450 nm after γ -irradiation. The 495 nm band does not disappear even after irradiation. The 320 nm band is suggested to be due to a F-type color center. We suppose that Ti^{4+} ions, which are produced under the oxidizing atmosphere, change to Ti^{3+} ions by γ -ray irradiation with a dose of 10^5 Gy. The Ti^{3+} ions are produced by capturing of electrons, which are generated by γ -irradiation, by Ti^{4+} ions, i.e. $\text{Ti}^{4+} + e \rightarrow \text{Ti}^{3+}$. It is suggested that the 450 nm absorption band is due to center related with Ti^{3+} . Taking into account that (1) the 450 nm band is close to the 495 nm band due to the isolated Ti^{3+}

ions and (2) in TiO_2 -doped $\text{Li}_2\text{B}_4\text{O}_7$, where Ti^{4+} ions are present, charge-compensating vacancies are produced, it is suggested that the 450 nm band is attributed to Ti^{3+} ions accompanied by charge-compensating vacancy. This is the reason why we cannot observe any emission due to Ti^{3+} ions.

Fig. 3 shows the photoluminescence (PL) and radioluminescence (RL) spectra of Eu- and Dy-doped $\text{Li}_2\text{B}_4\text{O}_7$ glass grown in oxidizing (curve 1) and reducing (curve 2) atmosphere. Two different types of emission bands are observed: an intense and broad Eu^{2+} emission band is observed at about 440 nm in the case of the reducing atmosphere of growth as shown in curve 2 in addition to relatively weak Dy^{3+} emission bands at 470 and 570 nm, while an intense, sharp Eu^{3+} emission bands are observed at about 595, 615, 650 and 700 nm in the case of the oxidizing atmosphere of growth. The 470 and 570 nm emission bands are attributed to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transitions in Dy^{3+} , respectively, while the 595, 615, 650 and 700 nm emission bands are attributed to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1, {}^7\text{F}_2, {}^7\text{F}_3$ and ${}^7\text{F}_4$ transitions in Eu^{3+} . Intense RL bands due to Dy^{3+} are observed in addition to relatively weak Eu^{2+} emission band in the glass grown in reducing atmosphere (curve 1 of Fig. 3). This indicates that Eu^{2+} ions are converted from Eu^{3+} ions by reducing atmosphere,

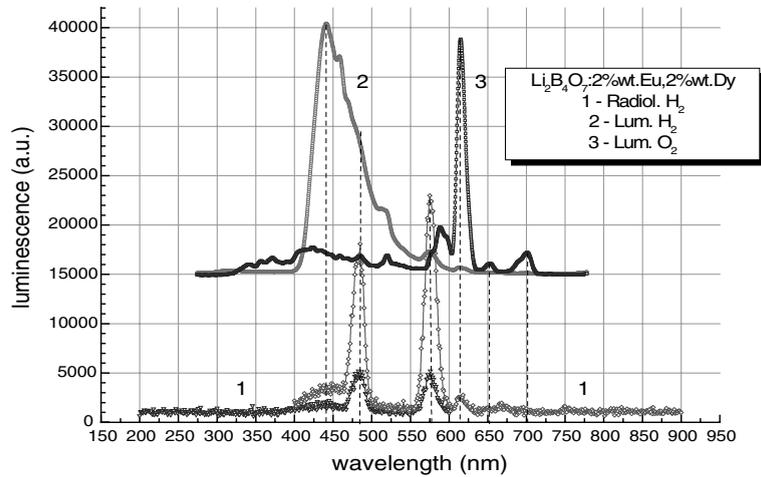


Fig. 3. Photoluminescence (PL) spectra of Eu and Dy doped $\text{Li}_2\text{B}_4\text{O}_7$ glass obtained in oxidizing atmosphere (3) and reducing atmosphere (2) and radioluminescence (RL) spectra (curve 1). The additional curve is an enlarged spectrum of curve 1.

while Eu^{3+} ions are converted from Eu^{2+} ions by oxidizing atmosphere. It is observed that emission bands due to both Eu^{2+} and Eu^{3+} ions are observed in glasses grown in not only reducing atmosphere but also oxidizing atmosphere although their intensity ratio depends on the growth condition. Therefore it is confirmed that Eu^{2+} and Eu^{3+} ions coexist in $\text{Li}_2\text{B}_4\text{O}_7$ glass, where Eu^{2+} and Eu^{3+} are located at tetrahedral and octahedral sites, respectively.

We made another measurement of the PL spectrum for the Eu- and Dy-doped glass grown in the reducing atmosphere using excitation with 266 nm laser. The results are presented in Fig. 4 where PL was obtained by excitation with 260 nm light from Xe-lamp. In addition to the 440 nm broad emission band due to Eu^{2+} , several sharp bands due to Dy^{3+} and Eu^{3+} are observed in the visible spectral region. The intense bands at about 470 and 570 nm are attributed to Dy^{3+} . Emission band due to Eu^{3+} is observed at 615 nm. The relative Dy^{3+} emission intensity compared with the Eu^{2+} emission is higher than in the case of curve 2 of Fig. 3. This can be explained as follows. Dy^{3+} has absorption bands in 400–500 nm range, which overlap with the 440 nm broad Eu^{2+} emission band. Therefore it is suggested that the Dy^{3+} emission was due to energy transfer from Eu^{2+} to Dy^{3+} . The high-power 266 nm laser gives rise to

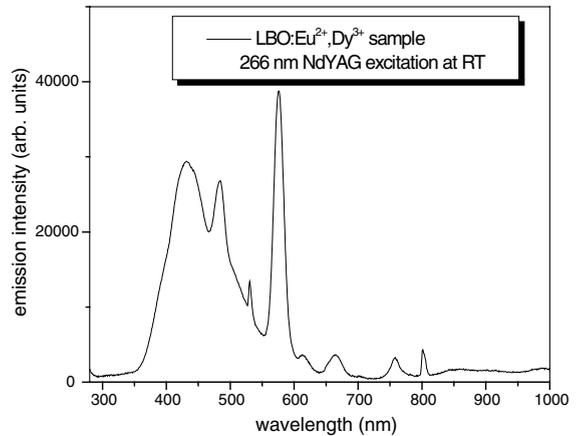


Fig. 4. High resolution PL spectrum of Eu^{2+} , Dy^{3+} doped $\text{Li}_2\text{B}_4\text{O}_7$ glass. For excitation, a 266 nm fourth harmonic of Nd:YAG laser was used. Two sharp peaks at 532 and 800 nm are due to the scattered light from the laser used for excitation.

much intense Eu^{2+} emission than the excitation with 260 nm light from lamp. As a result, energy transfer to Dy^{3+} is achieved efficiently in the case of laser excitation as seen in Fig. 4.

Fig. 5 shows the PL curves for Eu and Dy doped glass before (1) and after (2) γ -irradiation with a dose of 10^5 Gy. The intensive sharp line centered at 520 nm is the second harmonic line (excitation was performed for a wavelength of 260

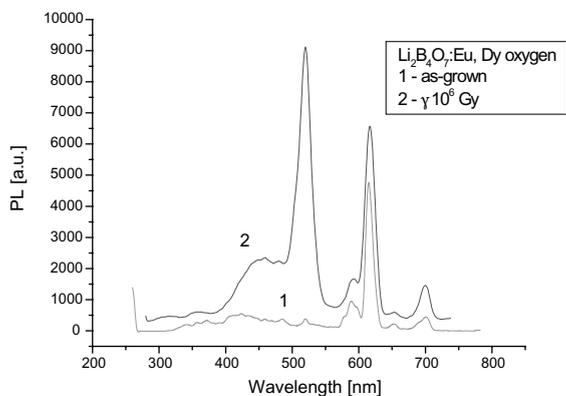


Fig. 5. PL spectra of Eu^{2+} , Dy^{3+} doped $\text{Li}_2\text{B}_4\text{O}_7$ glass before (1) and after (2) γ -irradiation with a dose of 10^5 Gy.

nm). As one can see, γ -irradiation changes the relative intensity of PL in the range of 430 nm that corresponds to Eu^{2+} emission. This may be due to the increase in content of Eu^{2+} centers by the Compton electron capture of the type: $\text{Eu}^{3+} + e^- \rightarrow \text{Eu}^{2+}$. The spectroscopy of Eu emission for the glass was analyzed elsewhere [4].

Fig. 6 presents the results of additional absorption measurements after γ -irradiation of pure $\text{Li}_2\text{B}_4\text{O}_7$ glass (curves 5, 6), doped with Eu and Dy (curves 1, 2) and doped with Yb (curves 3, 4). Two doses of gamma quanta were applied: 10^4 and 10^5 Gy for pure glass and 10^5 and 10^6 Gy for doped

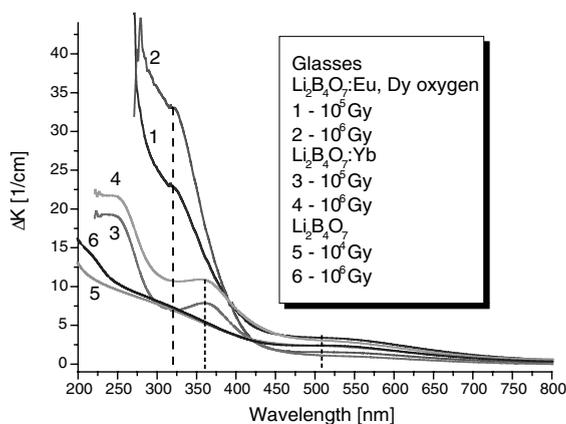


Fig. 6. Additional absorption bands after γ -irradiation: pure glass, doses 10^4 Gy (5) and 10^5 Gy (6); doped with Eu and Dy, doses 10^5 Gy (1) and 10^6 Gy (2) and doped with Yb, doses 10^5 Gy (3) and 10^6 Gy (4).

glasses. As one can see, two wide additional absorption bands arise after γ -irradiation of pure glass: one centered at 320 nm and the other at 520 nm. The nature of these bands demands further investigations. The same type of bands can be observed for the glass doped with Eu and Dy, although the intensity of the first band is much higher in the case of doped glass. For Yb-doped glass, beside the 520 nm band, two additional different bands are observed at 274 and 375 nm. Intensities of these bands increase with increasing the dose of γ -rays.

Figs. 7 and 8 show the absorption spectra of $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$ (0.6 wt.%) glass: "as grown" (1), after γ -irradiation with a dose of 10^5 Gy (2) and after γ -irradiation with a dose of 10^6 Gy (3). In the 850–1100 nm range, no essential change in the intensity of Yb absorption is observed (see Fig. 7). This statement and also the large value of the 2851 nm absorption (charge compensation) suggest a distorted octahedral coordination of Yb^{3+} ion in $\text{Li}_2\text{B}_4\text{O}_7$ lattice. Moreover, as can be seen from Fig. 8, there is some change in the symmetry of Yb^{3+} ions in the sites (shifting of the peak maximum towards higher wavelengths) after γ -irradiation with a dose of 10^6 Gy. This confirms that the octahedral environment of Yb ion is strongly distorted. The 274 nm and 375 nm additional absorption bands (Fig. 6) seem to be connected with the valency change of Yb^{3+} ion ($\text{Yb}^{3+} + e^- \rightarrow$

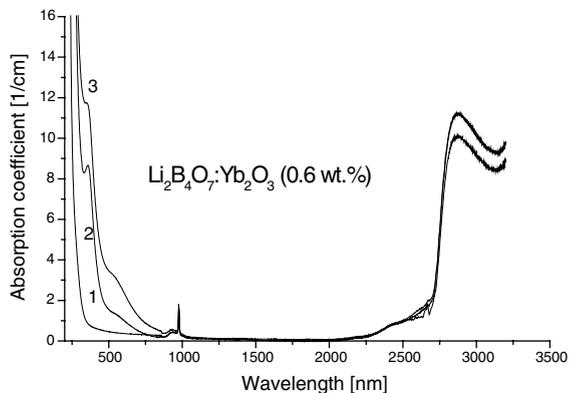


Fig. 7. Absorption spectrum of $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}_2\text{O}_3$ (0.6 wt.%) glass: "as grown" (1), after γ -irradiation with a dose of 10^5 Gy (2) and after γ -irradiation with a dose of 10^6 Gy (3).

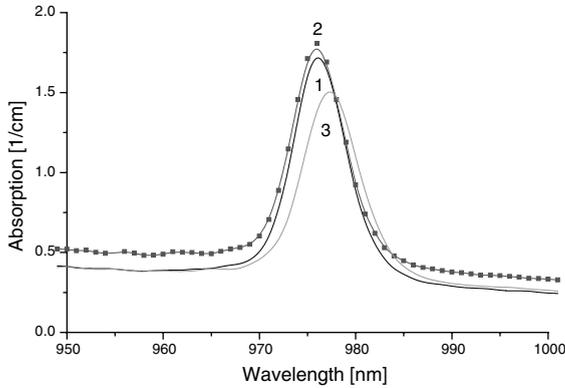


Fig. 8. Absorption spectra in the range 950–1000 nm for the same samples as in Fig. 7.

Yb^{2+}) located at different than octahedral lattice sites [13,14].

Fig. 9 shows the absorption spectra of $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}^{3+}$ glass at 14 and 300 K. One can clearly see an absorption band in the 900–1200 nm region. It is attributed to the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition in Yb^{3+} . This absorption band consists of a sharp and intense line at 976.3 nm and a broad and weak band at the high-energy side of the 976.3 nm line. Such a sharp and intense Yb^{3+} line has been observed in various single crystals (see, e.g. [15–19]). Therefore, this 976.3 nm line in LBO glass is attributed to the zero-phonon line as in the case of crystals. The broad side bands at the low energy side of the

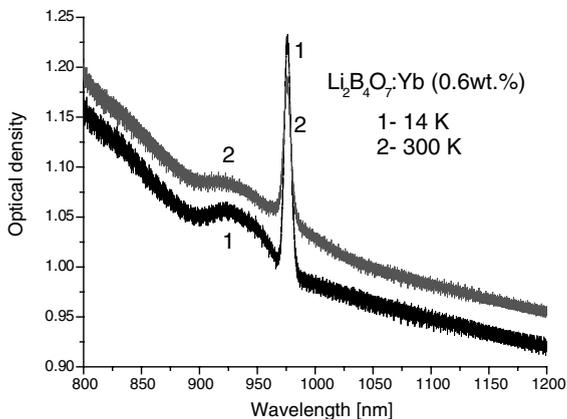


Fig. 9. Absorption spectra of $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}^{3+}$ (0.6 wt.%) glass at 14 and 300 K.

zero-phonon line are also observed in various crystals. Unlike the case of single crystals, the observed broad band is much weaker. In crystals, the broad band consists of several components, which are due to transitions from the lowest level of the ${}^2\text{F}_{7/2}$ ground state to several Stark split levels of the ${}^2\text{F}_{5/2}$ excited states [15–19]. Such a fine structure, however, has not been observed in our glasses. Additionally, the 976.3 nm band has a half width of 6.4 nm at room temperature. This band width is much broader than those of the corresponding zero-phonon bands observed in single crystals (e.g. the zero-phonon band has a half width of about 2.3 nm in GdCOB [15], 2.4 nm in YCOB [16] and LaCOB [18] at room temperature). Therefore it is suggested that the non-structured broad band is due to the presence of Yb^{3+} ions with various site symmetries in the glass. The zero-phonon band becomes considerably narrow in crystals with decreasing temperature, but the 976.3 nm band slightly becomes narrow. This is consistent with the presence of Yb^{3+} ions with various site symmetries.

4. Conclusions

Unlike the case of glass containing Eu^{3+} and Dy^{3+} ions (oxidizing atmosphere), the emission bands due to not only Eu^{2+} but also Dy^{3+} were observed by 266 nm excitation (hydrogen atmosphere). This indicates energy transfer from Eu^{2+} to Dy^{3+} .

In the $\text{Li}_2\text{B}_4\text{O}_7$ glass doped with the Yb^{3+} sharp 976.3 nm absorption line is observed due to the transition ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$. Under γ -irradiation Yb^{3+} ions change their valency and some of them the symmetry of environment. Irradiation with gamma quanta and low temperature measurements confirm the arising of Yb^{3+} ions in LBO glass at different lattice sites.

In the $\text{Li}_2\text{B}_4\text{O}_7$ glass doped with Ti ions we found appearance of Ti^{4+} in the case of oxidizing atmosphere, while we found presence of not only Ti^{3+} but also $\text{Ti}^{3+}/\text{Ti}^{4+}$ pairs in the case of reducing atmosphere. In the latter case low temperature measurements have shown two overlapping bands at about 495 and 750 nm; the 495 nm band is due

to the 2T_2 - 2E transition of Ti^{3+} and the second weaker 750 nm band is caused by Ti^{3+}/Ti^{4+} pairs.

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