Li$_2$B$_4$O$_7$ glasses doped with Cr, Co, Eu and Dy

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Abstract

Absorption and emission spectra of Cr, Co, Eu and Dy ions in Li$_2$B$_4$O$_7$ glasses melted in oxygen and hydrogen were measured for valency states analysis. It was stated that the presence of Cr$^{3+}$ ion is limited by composition of the starting mixture and atmosphere of the melting and that this ion arises as Cr$^{6+}$O complex. Independently of the above factors in all the glasses there were present Cr$^{4+}$ ions. Under $\gamma$-irradiation Cr$^{6+}$-O$^-$ complex of 3d$^0$ configuration can be disintegrated giving additional absorption band of Cr$^{3+}$ and may be Cr$^{4+}$ and higher valency centers. Corresponding photoluminescence is centered at about 430 nm. Absorption of Li$_2$B$_4$O$_7$:Co glasses obtained in oxygen atmosphere reveals Co$^{2+}$ and Co$^{3+}$ ions which does not give any emission in the UV-VIS and near-infrared region of luminescence spectrum. The content and optical characteristics of Eu$^{2+}$ and Eu$^{3+}$-doped Li$_2$B$_4$O$_7$ glasses are dependent of the growth atmosphere. © 2001 Published by Elsevier Science B.V.

1. Introduction

In the last four decades a great effort has been devoted to the study of glasses containing transition metal and rare-earth impurities [1–5]. Glasses as laser hosts have advantages such as mass production at low cost and form fibers more easily than single crystals. The emission properties in the glasses are characterized by broader emission spectra, a radiation lifetime with a non-exponential decay law, and a peculiar temperature dependence of the quantum efficiency [6].

Lithium tetraborate (Li$_2$B$_4$O$_7$) is a congruently melting compound with a melting point 917 °C. Single crystals of this material are used as substrates for surface acoustic wave (SAW) devices. The material has cuts with temperature stability of acoustic wave velocity and relatively high electro-mechanical coupling coefficient for SAW. Polycrystals of Li$_2$B$_4$O$_7$ with some dopants also find applications in thermoluminescent personal dosimeters [7,8].

Owing to small ionic radii of lithium and boron it is impossible to introduce dopants into Li$_2$B$_4$O$_7$ single crystals at high levels. Relatively high viscosity of molten lithium tetraborate, like other borates, is a source of serious problems during single crystal growth of this material. On the other hand this viscosity allows to obtain the material in a form of glass containing much higher amounts of dopants than in the case of single crystals.

One of the most investigated impurity ions also in glasses is chromium, and the large number of review articles and papers testifies to the high level of interest in this field [4,5,9], even in connection with the development of lasers. Also cobalt ion is very intensively investigated for its possible application for laser nonlinear absorbers [10]. Europium and dysprosium-doped glasses exhibit wide
application in gamma dosimetry and as scintillators.

In this paper we point out the possibility of easily hosting impurity ions: Cr, Co, Eu, Dy in a Li₂B₂O₇ glassy matrix. The purpose of this work is also to investigate possible valency states of Cr, Co, Eu and Dy ions in Li₂B₂O₇ glasses.

2. Experimental procedure

2.1. Glass preparation

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 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. Cr₂O₃ was dissolved in lithium tetraborate at the level of 0.15 mol%. After rapid cooling below 550 °C the melt formed glass which did not show any tendency to crystallize. Prolonged heating of obtained glass at temperatures higher than 600 °C led to its crystallization and subsequent formation of polycrystalline material.

The addition of chromium oxide, Cr₂O₃, caused green coloration of the glass. The addition of cobalt oxide, Co₂O₃, caused blue coloration. The glasses were obtained in oxidizing atmosphere.

Almost completely transparent Li₂B₂O₇ glasses doped with Eu, Dy were obtained in oxidizing and reducing atmosphere of hydrogen.

The following Li₂B₂O₇ glasses were obtained: doped with Cr (0.13 and 2.5 wt%), Co²⁺ (10 wt%) and Eu, Dy (2 wt%, 2 wt%).

2.2. Absorption and photoluminescence measurements

The samples were polished to the thickness of about 1 mm. They were irradiated by gamma photons immediately after growth process. The ⁶⁰Co gamma source with a power of 1.5 Gy/s was used. Optical transmission was measured before and after γ treatment using LAMBDA-900 Perkin–Elmer spectrophotometer in UV–VIS range and FT–IR-1725 in the IR range. Additional absorption was calculated according to the formula:

\[ \Delta K(\lambda) = (1/d) \ln(T_1/T_2), \]

where \( K \) is the absorption, \( \lambda \) is the wavelength, \( d \) is the sample thickness and \( T_1 \) and \( T_2 \) are transmissions of the sample before and after a treatment, respectively.

Photoluminescence (PL) was recorded using Perkin–Elmer spectrofluorimeter from 200–900 nm and He–Ne laser excitation of 630 nm.

3. Results

3.1. Absorption and the additional absorption measurements

Figs. 1–6 shows absorption spectra of representative samples obtained at 300 K.

In the case of pure Li₂B₂O₇ glass (Fig. 1, curve 1) the range of transparency originate at 190 nm (fundamental absorption edge – FAE) and ends at about 2700 nm (lattice absorption). Curve 2 shows absorption of this glass after γ-irradiation with a dose of 5 × 10⁴ Gy.

In the 0.15 wt% chromium-doped Li₂B₂O₇ glass (Fig. 2(a) and (b), curve 1) we observe Cr³⁺ and Cr⁶⁺ ion spectra. FAE of the glass is equal to 245 nm and lattice absorption originate at 2700 nm.

![Fig. 1. Absorption of Li₂B₂O₇ glass before (1) and after (2) γ-irradiation with a dose of 5 × 10⁴ Gy.](image)
Fig. 2. Absorption before (1) and after $\gamma$-irradiation (2) and additional absorption (3) of Li$_2$B$_2$O$_4$:Cr (0.13 wt%) glass, and absorption of Li$_2$B$_2$O$_4$:Cr (2.5 wt%) glass (4).

Fig. 3. Gauss distribution of the additional absorption in $\gamma$ $10^5$ Gy irradiated Li$_2$B$_2$O$_4$:Cr (0.13 wt%) glass (1) and photoluminescence of the glass (2) excited with 260 nm.

The Cr$^{3+}$ ion has two absorption bands centered at about 430 and 614 nm due to d–d transition: the former was attributed to the spin-allowed but purity forbidden $^4A_2-^4T_1$ transition and the latter to the spin-allowed but parity-forbidden $^4A_2-^4T_2$ transition. The Cr$^{5+}$ ion has strong absorption band centered at 358 nm and a weak one at 318 nm. It seems that these bands refer to Cr$^{5+}$–O$^-$ complex of 3d$^0$ configuration rather than to Cr$^{5+}$ ion [5]. Curve 2 shows absorption of the glass after $10^5$ Gy $\gamma$-rays while curve 3 the additional ab-

Fig. 4. Absorption spectrum of Li$_2$B$_2$O$_4$:Co (10 wt%) glass.

Fig. 5. The absorption of Li$_2$B$_2$O$_4$:Eu, Dy (2 wt%, 2 wt%) glass obtained in oxygen atmosphere at 300 K before (1) and after (2) $\gamma$-irradiation with a dose of $10^4$ Gy.

Fig. 6. Absorption of Li$_2$B$_2$O$_4$:Eu, Dy (2 wt%, 2 wt%) glass obtained in hydrogen atmosphere.
sorption. There are at least two bands seen in the additional absorption centered at about 297 and 450 nm. Curve 4 in Fig. 2(b) shows the absorption of highly doped with Cr (2.5 wt%) Li$_2$B$_4$O$_7$ glass. One can see that in the case of high doping only 614 nm band due to $^4$A$_2$–$^3$T$_2$ transition in Cr$^{3+}$ ions is present.

Detailed analysis using the fitting with Gauss curves has shown that there are at least four bands in the additional absorption centered at about 285, 316, 392 and 496 nm (Fig. 3) which are responsible for 297 and 450 nm additional absorptions. Three of them seem to correspond to previously described color centers in Li$_2$B$_4$O$_7$ glasses. Fourth, at about 392 nm, seems to be responsible for 430 nm emission observed after 260 nm excitation. This broad-band 450 nm additional absorption may be due to $^4$A$_2$–$^4$T$_2$, $^4$T$_1$ transitions in Cr$^{3+}$ and/or $^3$A$_2$–$^3$T$_2$, $^3$T$_1$–$^3$T$_2$ transitions in Cr$^{3+}$ [10]. Parameters of the fitting are listed in a table inside the figure.

Fig. 4 shows the absorptions in Li$_2$B$_4$O$_7$ glass doped with 10 wt% of Co. As one can see strong absorption bands are observed in visible and infrared parts of the absorption spectrum. The main features of spectrum consist of a double band in the IR region (800–2500 nm) and a triple band in the visible region (400–750 nm). The latter absorption band is responsible for blue color of the sample. We notice also the strong absorption in the far IR, and in the UV region (not indicated in figure). All these absorption bands, due to their mixed structure seem to be transitions in Co$^{2+}$–Co$^{3+}$ mixed system [11].

Fig. 5 presents the absorption (1) from two ground states: Dy$^{3+}$–$^6$H$_{15/2}$ and Eu$^{3+}$–$^7$F$_0$ of Li$_2$B$_4$O$_7$:Eu, Dy (2 wt%, 2 wt%) glass. As one can see FAE in this case is equal to 270 nm. Refraction coefficient is equal to 1.58. Curve 2 shows the absorption after γ-irradiation with a dose of 10$^5$ Gy. Fig. 6 shows the absorption of Dy$^{3+}$ from $^6$H$_{15/2}$ ground state and Eu$^{2+}$ transitions 4f$^7$–4f$^6$5d$^1$ [12]. FAE is equal to about 355 nm and refraction coefficient 1.62.

3.2. Photoluminescence measurements

Fig. 7 presents photoluminescence of Li$_2$B$_4$O$_7$:Cr glasses excited with 630 nm He–Ne laser. As one can see γ-irradiation leads to the increase in Cr$^{3+}$ PL intensity.

Fig. 8 shows excitation–emission spectra of Li$_2$B$_4$O$_7$:Cr (0.13 wt%) glass after γ-exposure with a dose of 10$^5$ Gy (a) and emission from Li$_2$B$_4$O$_7$:Cr (2.5 wt%) glass (b) under 270 nm excitation. As one can see emission at 430 nm is due to excitation at 362 and 385 nm. This same type of
emission is observed also in the case of high doping of the glass with Cr (Fig. 8(b)).

The emission from Li₂B₂O₇:Co (10 wt%) glass was not observed up to 1700 nm. It may be due to the fact that usual emission bands of Co²⁺ ions arises over 2.2 μm. Moreover, emission in the visible range of emission spectrum may be quenched by non-radiative transitions between Co³⁺ and Co²⁺ ions [11]. The shape of the emission spectrum from Li₂B₂O₇:Eu, Dy (2 wt%, 2 wt%) glass strongly depend on the type of growth atmosphere. Fig. 9 shows characteristic emissions for the two basic cases of the obtained glasses: oxidizing (a) and reducing (b) atmospheres [12].

4. Discussion

As one can see in Fig. 1 the absorption spectrum of pure Li₂B₂O₇ glass shows a transmission range larger than that of other glasses [1]. The relevant feature of the glass, as it takes place also in the case of other glasses, is its high susceptibility to γ-irradiation. Wide, almost non-structural additional absorption in the UV–VIS and NIR of the absorption spectrum (190–1000 nm) is seen with weakly distinguished bands centered at about: 250, 360 and 530 nm.

As one can see from Fig. 2 some changes under γ-radiation may be a positive one. Our experimental data cannot be interpreted in terms of Cr³⁺ alone, but have to be analyzed in view of the co-existence of Cr ions of different valences. Low chromium-doped Li₂B₂O₇ glass shows presence of Cr³⁺ and Cr⁶⁺ ions. The former exists tetrahedrally coordinated while the latter octahedrally coordinated. The former gives well-known emission, which is clearly seen in Fig. 7 for λₑₓ = 630 nm of He–Ne laser. The latter does not give emission because Cr⁶⁺O⁻ complex of 3d⁰ configuration seem to be responsible for the 318 and 358 nm absorption. But under γ-irradiation with a dose of 10⁵ GyCr⁶⁺O⁻ complex disintegrates giving additional absorption connected with the above mentioned, specific for Li₂B₂O₇ color centers and 392 nm band which may be attributed to ³A₂−³T₂, ³T₁−³T₂ transitions in Cr⁴⁺ and/or ⁴A₂−⁴T₂, ⁴T₁ transitions in Cr³⁺ (Fig. 3). Emission spectrum of the gamma irradiated glass reveal an increase in PL intensity of Cr³⁺ ions (Fig. 7), while excitation–emission spectra presented in Fig. 8(a) suggest presence of other luminescence center. It was previously reported that the Cr⁴⁺ ion exists in aluminate-based glasses [13]. The mechanism of forming Cr⁴⁺ ions was discussed in detail in [5] based on point defects in the glasses. It was stated that Cr⁴⁺ is observed only in glasses in which oxygen excess defects such as super oxide ion radicals and peroxide linkages are observed. It is possible that in our case Cr⁶⁺ O⁻ complex disintegrates simultaneously to Cr⁴⁺, Cr³⁺ or higher valency states of Cr. But it demands more and detailed investigations.

Highly doped with chromium Li₂B₂O₇ glasses show presence only ⁴A₂−⁴T₂ absorption band (Fig. 2(b)) although 430 nm emission is also observed (Fig. 8(b)). Analyzing low and high doping in case of Li₂B₂O₇ glass one can state that there exists compositional dependence of the valency states of Cr ions in the glasses. In [5] it was stated that the contents of Cr³⁺ and Cr⁶⁺ vary systematically with basicity in the silicate and borate glasses.

As one can see from Fig. 4 high doping (10 wt%) of Li₂B₂O₇ glasses with cobalt is possible. Wide absorption bands seen in the visible as well as IR parts of the absorption spectrum suggest presence of both Co²⁺ and Co³⁺ ions which can interchange excitation energy not giving any emission [11].

Europium [12] and dysprosium co-doping characterizes dependency of Eu valence on growth
atmosphere. As one can see in Fig. 5 absorption of Li$_2$B$_4$O$_7$:Eu, Dy glass obtained in oxidizing atmosphere shows many transitions from ground state of Dy$^{3+}$(6H$_{15/2}$) and ground state of Eu$^{3+}$(7F$_{0}$) to higher states. Gamma irradiation does not change a valence of the impurities, but leads to strong additional absorption in the range 270–1000 nm. In case of Li$_2$B$_4$O$_7$:Eu, Dy glass obtained in reducing atmosphere of hydrogen (Fig. 6) well-known transitions of Dy$^{3+}$ ions are seen in the absorption spectrum and the new one 4f$^7$–4f$^6$5d$^1$ of Eu$^{3+}$ ions. Emission of both types of Eu ions is clearly seen in Fig. 9. As it follows from emission measurements both types of Eu ions exist in both types of the obtained glasses, but one of them dominates giving characteristic emission.

5. Conclusions

It was shown that in case of Li$_2$B$_4$O$_7$ glasses high doping with transition metal and rare-earth element impurities is possible. Obtained compounds are of good optical quality, giving clear luminescence especially for Cr$^{3+}$ and Eu$^{3+}$ and Eu$^{2+}$ ions.

It was stated that the presence of Cr$^{6+}$ ion is limited by composition of the starting mixture and atmosphere of the melting (oxidizing). Independently on the above factors in all the glasses there were present Cr$^{3+}$ ions. Under $\gamma$-irradiation Cr$^{6+}$O$_4$ complex of 3d$^0$ configuration can be disintegrated giving additional absorption band of Cr$^{3+}$ and may be Cr$^{4+}$ and higher valence ions. Photoluminescence of the latter center is centered at about 430 nm. $\gamma$-irradiation leads to arising of strong additional absorption in the range of 190–1000 nm with weakly distinguished bands peaked at about: 250, 360 and 530 nm.

Absorption of Li$_2$B$_4$O$_7$:Co glasses obtained in oxygen atmosphere reveals Co$^{2+}$ and Co$^{3+}$ ions which does not give any emission in the UV–VIS and near-infrared region of luminescence spectrum.

The content and optical characteristics of Eu$^{2+}$ and Eu$^{3+}$-doped Li$_2$B$_4$O$_7$ glasses are dependent of the growth atmosphere.

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