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TITLE: Optical Properties of Li2B4O7 Glasses Doped with Rare-Earths and Transition Metal Ions

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Optical properties of $Li_2B_4O_7$ glasses doped with rare-earths and transition metal ions

S.M. Kaczmarek[a], Cz. Koepke[b], M. Grinberg[c], A. Majchrowski[d], K. Wiśniewski[b], M. Czuba[a]

[a] Institute of Optoelectronis, Military University of Technology, 2 Kaliski Str., 00-908 Warsaw, Poland
[b] Institute of Physics, N. Copernicus University, Grudziądzka 5/7, 87-100 Toruń, Poland
[c] Institute of Experimental Physics, University of Gdańsk, Wita Stwosza 57, 80-952 Gdańsk, Poland
[d] Institute of Physics, Military University of Technology, 2 Kaliski Str., 00-908 Warsaw, Poland

ABSTRACT

Absorption and emission spectra of Cr, Eu and Dy ions in $Li_2B_4O_7$ glasses melted in oxygen and hydrogen were measured for valency states and excited states analysis. It was stated that the presence of Cr^{6+} ion is limited by composition of the starting mixture and atmosphere of the melting and that this ion arises as $Cr^{6+}O_4$ complex. The 308 nm line excites the $Li_2B_4O_7$:Cr glass within the highest absorption peak which can be ascribed to the following charge transfer transition: $Cr^{6+}O_4(3d^02p^6)\rightarrow Cr^{5+}O^-(3d^12p^5)$. Under gamma irradiation $Cr^{6+}O_4$ complex of $3d^0$ configuration can be disintegrated giving additional absorption bands of Cr^{3+} and may be Cr^{4+} centers at tetrahedral sites. One of these additional absorption bands is responsible for 430 nm emission.

Keywords: $Li_2B_4O_7$, absorption and emission spectra, gamma irradiation.

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, a peculiar temperature dependence of the quantum efficiency [6].

Lithium tetraborate ($Li_2B_4O_7$ or LBO) 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 electromechanical coupling coefficient for SAW. Polycrystals of $Li_2B_4O_7$ with some dopants find also applications in thermoluminescent personal dosimeters [7].

Owing to small ionic radii of lithium and boron it is impossible to introduce dopants into $Li_2B_4O_7$ single crystals at high levels. Relatively high viscosity of molten lithium tetraborate, like other borates, is a source of serious problems during single crystals 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 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, 8], even in connection with the development of lasers. Europium and dysprosium doped glasses exhibit wide application in gamma dosimetry and as scintillators.

In this paper we point out the possibility of hosting easily impurity ions: Cr, Eu, Dy in a $Li_2B_4O_7$ glassy matrix. The purpose of this work is also to investigate possible valency states and excited states of Cr, Eu and Dy ions in $Li_2B_4O_7$ glasses.

2. EXPERIMENTAL PROCEDURE

2.1. Glass preparation

The synthesis of lithium tetraborate was carried out from lithium carbonate Li_2CO_3, and boric oxide H_3BO_3 (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 B_2O_3 losses, due to evaporation, 1 mol% surplus of H_3BO_3 was added to the starting composition. After rapid cooling below 550°C the melt formed glass which did not show any tendency to crystallise. Prolonged heating of obtained glass at

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*Further author information
S. M. K. (correspondence): Email: skaczmar@wat.waw.pl.; Telephone: (022) 6859019

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temperatures higher than 600°C led to its crystallisation and subsequent formation of polycrystalline material. Cr_2O_3 was dissolved in lithium tetraborate at the level of 0.13 mol% and 2.5 mol%. The addition of chromium oxide, Cr_2O_3, caused green coloration of the glass. The glasses were obtained in oxidizing atmosphere.

Almost completely transparent $Li_2B_4O_7$ glasses doped with Eu, Dy were obtained in oxidizing and reducing atmosphere of hydrogen.

The following $Li_2B_4O_7$ glasses were obtained: doped with Cr (0.13 wt. % and 2.5 wt. %), and Eu, Dy (2wt.%, 2wt.%).

2.2. Absorption and photoluminescence measurements

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

$$\Delta K(\lambda)=(1/d)\ln(T_1/T_2) \qquad (1)$$

where K is the absorption, λ 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.

2.3. Excited state absorption investigations

The excited state absorption (ESA) spectra were measured using a setup which utilized a RD-EXC-150/25 XeCl excimer laser (308 nm) as a source of excitation, a Hamamatsu Xe flash lamp as a source of probe beam and ORIEL InstaSpec II photodiode array detector coupled to MultiSpec 1/8 m spectrograph in the detection branch. The setup operated in pulsed regime and transverse geometry (like in [9]).

3. RESULTS AND DISCUSSION

3.1 Absorption and photoluminescence

3.1. 1 Absorption and the additional absorption measurements

Figs 1-5 show absorption spectra of representative samples obtained at 300K.

In the case of pure $Li_2B_4O_7$ glass (Fig. 1, curve 1) the range of transparency origins 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 $5*10^4$ Gy.

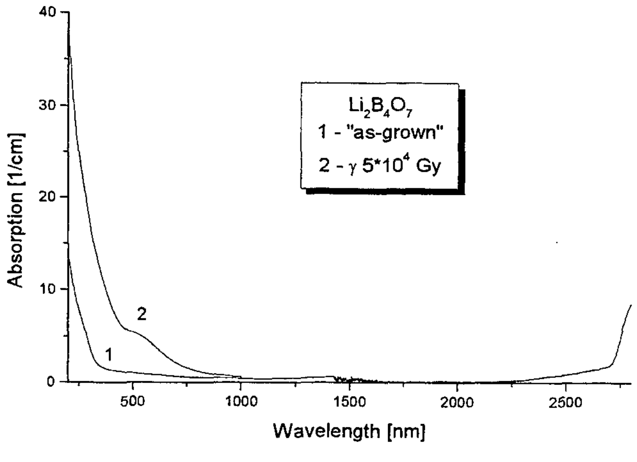


Fig. 1. Absorption of $Li_2B_4O_7$ glass before (1) and after (2) γ-irradiation with a dose of $5*10^4$ Gy

In the 0.15wt% chromium doped $Li_2B_4O_7$ glass (Fig. 2a and 2b, curve 1) we observe Cr^{3+} and Cr^{6+} ions spectra. FAE of the glass is equal to 245 nm and lattice absorption origin at 2700 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 parity forbidden $^4A_2$-$^4T_1$ transition and the latter to the spin-allowed but parity-forbidden $^4A_2$-$^4T_2$ transition. The Cr^{6+} ion has strong absorption band centered at 358 nm and a weak one at 318 nm. It seems that these bands refer to $Cr^{6+}O_4$ complex of $3d^0$ configuration rather than to Cr^{6+} ion [5]. Curve 2 shows absorption of the glass after 10^5 Gy γ-rays while curve 3 the additional absorption. There are seen at least two bands in the additional absorption centered at about 297 and 450 nm. Curve 4 in Fig. 2b shows the absorption of highly doped with Cr (2.5wt.%) $Li_2B_4O_7$ glass. One can see that in case of high doping only 614 nm band due to $^4A_2$-$^4T_2$ transition in Cr^{3+} ions is present.

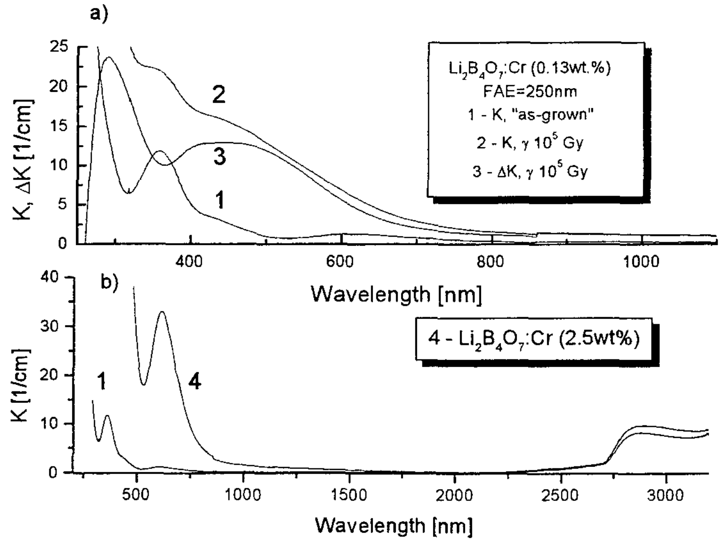
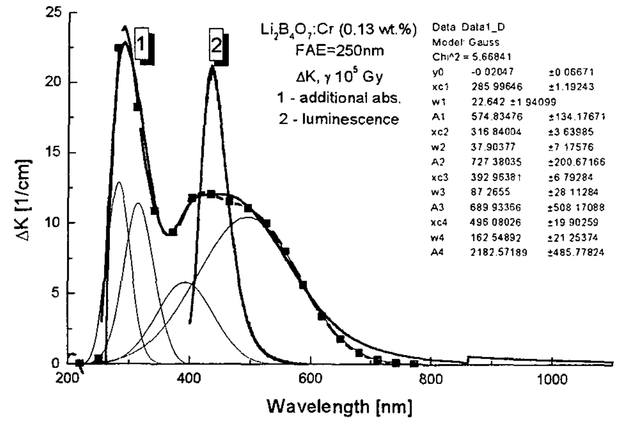


Fig. 2. Absorption before (1) and after γ-irradiation (2) and additional absorption (3) of $Li_2B_4O_7$:Cr (0.13wt.%) glass, and absorption of $Li_2B_4O_7$:Cr (2.5wt.%) glass (4)



Data Data1_D
Model Gauss
Chi^2 = 5.66841

y0	-0 02047	±0 06671
xc1	285 99646	±1.19243
w1	22.642 ±1 94099	
A1	574.83476	±134.17671
xc2	316 84004	±3 63985
w2	37.90377	±7 17576
A2	727 38035	±200.67166
xc3	392 96381	±6 79284
w3	87 2655	±28 11284
A3	689 93366	±508 17088
xc4	496 08026	±19 90259
w4	162 54892	±21 25374
A4	2182.57189	±485.77824

Fig. 3. Gauss distribution of the additional absorption in γ 10^5 Gy irradiated $Li_2B_4O_7$:Cr (0.13wt.%) glass (1) and photoluminescence of the glass (2) excited with 260 nm.

Detailed analysis using the fitting with Gauss curves have shown that there are at least four bands in the additional absorption centered at about 285 nm, 316 nm, 392 nm and 496 nm (Fig. 3) which are responsible for 297 nm and 450 nm additional absorptions. Three of them seem correspond to previously described color centers in $Li_2B_4O_7$ glasses. Fourth, at about 392 nm, seems to be responsible for 430 nm emission observed after 260 nm excitation. This broad-band 450 nm

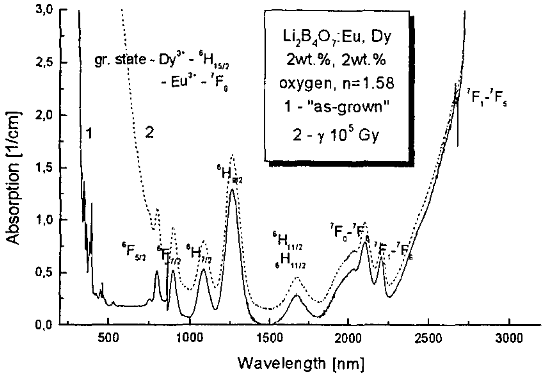


Fig. 4. The absorption of $Li_2B_4O_7$:Eu, Dy (2wt.%, 2wt.%) glass obtained in oxygen atmosphere at 300K before (1) and after (2) γ-irradiation with a dose of 10^5 Gy

additional absorption may be due to $^4A_2$-$^4T_2$, $^4T_1$ transitions in Cr^{3+} and/or $^3A_2$-$^3T_2$, $^3T_1$-$^3T_2$ transitions in Cr^{4+} [10]. Parameters of the fitting are listed in a table inside the figure.

Fig. 4 presents the absorption (1) from two ground states: Dy^{3+} – $^6H_{15/2}$ and Eu^{3+} – $^7F_0$ of $Li_2B_4O_7$:Eu, Dy (2wt.%, 2wt.%) glass. As one can see FAE in this case is equal to 270 nm. Refraction coefficient is equal to 1.58. Curve 2 show the absorption after γ-irradiation with a dose of 10^5 Gy. Fig. 5 shows the absorption of Dy^{3+} from $^6H_{15/2}$ ground state and Eu^{2+} transitions $4f^7$-$4f^65d^1$ [11]. FAE is equal to about 355 nm and refraction coefficient 1.62.

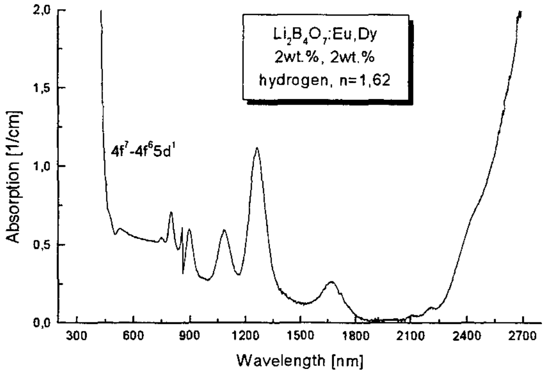


Fig. 5. Absorption of $Li_2B_4O_7$:Eu, Dy (2wt.%, 2wt.%) glass obtained in hydrogen atmosphere

3.1.2. Photoluminescence measurements

Fig. 6 presents photoluminescence of $Li_2B_4O_7$:Cr glasses excited with 630 nm He-Ne laser. As one can see gamma irradiation leads to the increase in Cr^{3+} PL intensity.

Fig. 7 shows excitation-emission spectra of $Li_2B_4O_7$:Cr (0.13wt.%) glass after γ-exposure with a dose of 10^5 Gy (a) and emission from $Li_2B_4O_7$:Cr (2.5wt.%) glass (b) under 270 nm excitation. As one can see emission at 430 nm is due to excitation at 362 nm and 385 nm. This same type of emission is observed also in case of high doping of the glass with Cr (Fig. 7b).

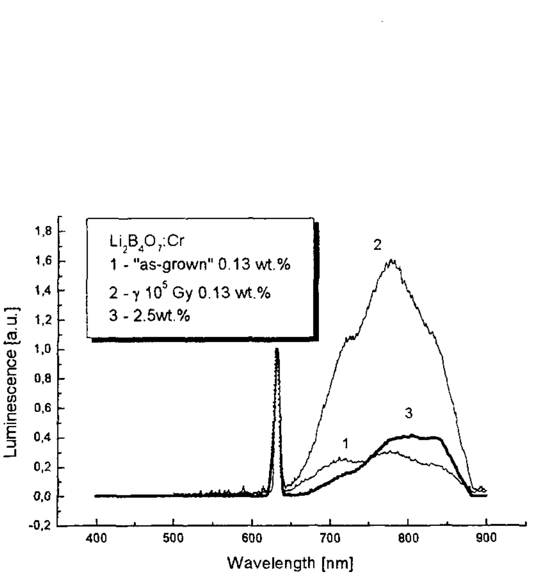


Fig. 6. Photoluminescence of $Li_2B_4O_7$:Cr glasses excited by 630 nm He-Ne laser: 0.13wt.%Cr "as-grown" (1), 0.13wt.%Cr γ-irradiated with a dose of 10^5 Gy and 2.5wt.%Cr (3)

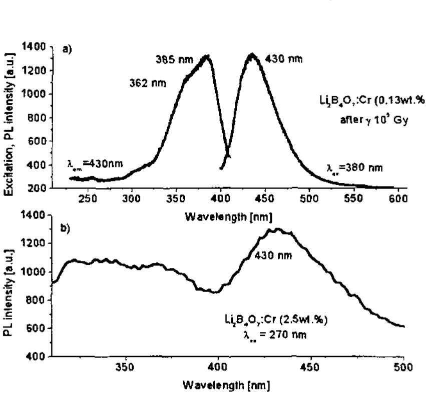


Fig. 7. Excitation-emission spectra of $Li_2B_4O_7$:Cr (0.13wt.%) glass after γ-exposure with a dose of 10^5 Gy (a) and emission from $Li_2B_4O_7$:Cr (2.5wt.%) glass (b) under 270 nm excitation

The shape of emission spectrum from $Li_2B_4O_7$:Eu, Dy (2wt.%, 2wt.%) glass strongly depend on the type of growth atmosphere. Fig. 8 shows characteristic emissions for the two basic cases of the obtaining of the glasses: oxidizing (a) and reducing (b) atmospheres [11].

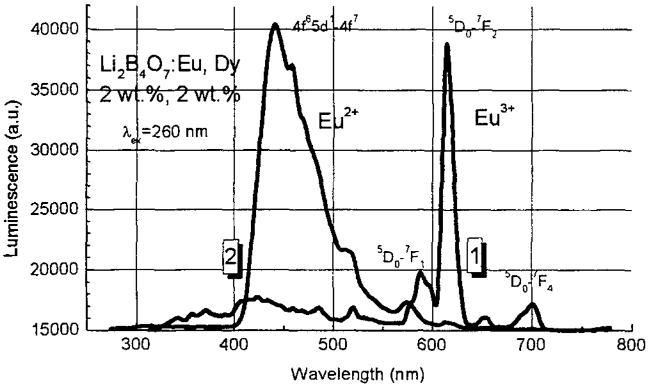


Fig. 8. Emission spectra of $Li_2B_4O_7$:Eu, Dy (2wt.%, 2wt.%) glasses obtained in oxidizing (1) and reducing (2) atmosphere

3.1.3. Discussion

As one can see in Fig. 1 the absorption spectrum of pure $Li_2B_4O_7$ glass shows a transmission range larger than of other glasses[1]. The relevant feature of the glass, as it take place also in case of other glasses, is its high susceptibility to gamma 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 nm, 360 nm and 530 nm.

As one can see from Fig. 2 some changes under gamma radiation may be positive one. Our experimental data cannot be interpreted in terms of Cr^{3+} alone, but have to be analyzed in view of the coexistence of Cr ions of different valences. Low chromium doped $Li_2B_4O_7$ glass shows presence of Cr^{3+} and Cr^{6+} ions. The former like exist octahedrally coordinated while the latter tetrahedrally coordinated. The former give well known emission, which is clearly seen in Fig. 6 for λ_{ex}=630 nm of He-Ne laser. The latter does not give emission because $Cr^{6+}O_4$ complex of $3d^0$ configuration seem to be responsible for the 318 and 358 nm absorption. But under gamma irradiation with a dose of 10^5 Gy $Cr^{6+}O_4$ complex disintegrates giving additional absorption connected with the above mentioned, specific for $Li_2B_4O_7$ color centers and 392 nm band which may be attributed to $^3A_2$-$^3T_2$, $^3T_1$-$^3T_2$ transitions in Cr^{4+} and/or $^4A_2$-$^4T_2$, $^4T_1$ transitions in Cr^{3+} (Fig. 3). Emission spectrum of the gamma irradiated glass reveal an increase in PL intensity of Cr^{3+} ions (Fig. 6), while excitation-emission spectra presented in Fig. 7a suggests presence of other luminescence center. It was previously reported that the Cr^{4+} ion exists in aluminate based glasses [12]. The mechanism of forming Cr^{4+} ions was detail discussed in [5] based on point defects in the glasses. It was stated that Cr^{4+} is observed only in glasses in which oxygen excess defects such as super oxide ion radicals and peroxy linkages are observed. It is possible that in our case $Cr^{6+}O_4$ complex disintegrates simultaneously to Cr^{4+} and Cr^{3+}. But it demand more and detailed investigations.

Highly doped with chromium $Li_2B_4O_7$ glasses show presence only $^4A_2$-$^4T_2$ absorption band (Fig. 2b) although 430 nm emission is also observed (Fig. 7b). Analyzing low and high doping in case of $Li_2B_4O_7$ 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 Cr^{3+} and Cr^{6+} vary systematically with basicity in the silicate and borate glasses.

Europium [11] and dysprosium co-doping characterizes dependency of Eu valence on growth atmosphere. As one can see in Fig. 4 absorption of $Li_2B_4O_7$: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 $Li_2B_4O_7$:Eu, Dy glass obtained in reducing atmosphere of hydrogen (Fig. 5) well known transitions of Dy^{3+} ions are seen in the absorption spectrum and the new one $4f^7$-$4f^65d^1$ of Eu^{2+} ions. Emission of both types Eu ions is clearly seen in Fig. 8. As it follows from emission measurements both types of Eu ions exists in both types of the obtained glasses, but one of them dominates giving characteristic emission.

3.2 Excited state absorption measurements of Cr:LBO (0.15wt.%) glass

The ESA spectrum of the Cr:LBO (0.15wt.%) glass sample is presented in figure 9. As it is seen, there is no chance to fit this ESA spectrum by a single Gaussian function, whereas two Gaussians {one relatively narrow (2800 cm^{-1}) and another much broader (8200 cm^{-1})} fit the spectrum perfectly. This strongly suggests that the observed ESA under UV excitation consists of transitions to two distinctly defined excited states.

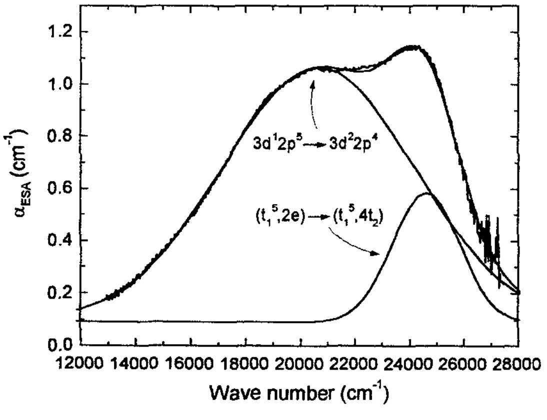


Fig. 9. Experimental ESA spectrum obtained for 308 nm excitation, fit by two Gaussians, and assignation of the contributing ESA bands.

The single configuration coordinate (SCC) diagram can be used to reproduce a characteristic ESA spectrum comparable to that obtained with 308 nm excitation (figure 9). To achieve this, certain assumption has to be made, namely - the existence of additional excited electronic manifold, strongly coupled to the lattice, not detectable in the ground state absorption (GSA) spectrum. Such a state can be related to the $3d^22p^4$ electronic configuration of the central ion - ligand system. The $3d^22p^4$ excited electronic configuration origins from the consecutive excitation of two electrons from the valence band (made mostly of ligands orbitals) to the d orbitals of the central ion. The resulting SCC diagram is presented in Fig. 10 together with definitions of energies taken from the experiment. It shows two positions of the state $|3\rangle$ ($3d^22p^4$) (dashed and solid) corresponding to two qualitatively different situations described in the caption.

Considering the nature of the electronic configurations which the SCC diagram is constructed from, one should remember that $Cr^{6+}O_4$ centre is a typical d^0 complex (of approximated T_d symmetry). Then it is possible to write formally the electronic configuration of the central ion-ligand system as $3d^02p^6$ [13].

4. CONCLUSIONS

It was shown that in case of $Li_2B_4O_7$ glasses it is possible high doping with transition metal and rare-earth element impurities. Obtained compounds are good optical quality, giving clear luminescence especially for Cr^{3+} and Eu^{3+} and Eu^{2+} ions.

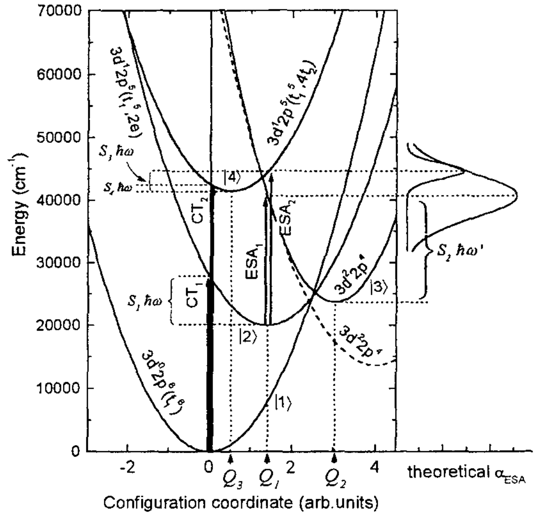


Fig. 10 SCC diagram quantitatively reproducing the ESA spectrum obtained with 308 nm excitation. Right side of the figure shows two Gaussian ESA spectra (of the widths corresponding to the respective relaxation energies) whose composition fits the experiment. The dashed parabola corresponds to the $3d^22p^4$ state of linear coupling to the lattice i.e. with the same phonon energy as all remaining states ($\eta\omega = 250$ cm^{-1}). The solid parabola of the $3d^22p^4$ state corresponds to the different phonon energy $\eta\omega' = 400$ cm^{-1}.

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. The 308 nm line excites the $Li_2B_4O_7$:Cr (0.13 wt.%) glass within the highest absorption peak which can be ascribed to the following charge transfer transition: $Cr^{6+}O_4(3d^02p^6) \rightarrow Cr^{5+}O^-(3d^12p^5)$. 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+} ions. There arises luminescence 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 nm, 360 nm and 530 nm.

The content and optical characteristics of Eu^{2+} and Eu^{3+} doped $Li_2B_4O_7$ glasses are dependent of the growth atmosphere.

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