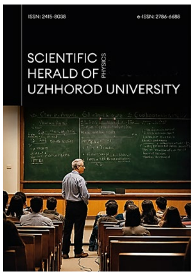
Scientific Herald of Uzhhorod University
Series "Physics"
Journal homepage: https://physics.uz.ua/en
Issue 55, 3002–3008
Received: 27.10.2023. Revised: 14.01.2024. Accepted: 06.03.2024



DOI: 10.54919/physics/55.2024.300or2

Luminescence properties of Eu^{3+} ions in glassy lithum tetraborate matrix

Pavlo Danyliuk
Uzhhorod National University
88000, 54 Voloshyna Str., Uzhhorod, Ukraine

Aleksandr Gomonai*
Institute of Electron Physics of the National Academy of Sciences of Ukraine
88017, 21 Universytetska Str., Uzhhorod, Ukraine

Pavlo Puga
Uzhhorod National University
88000, 54 Voloshyna Str., Uzhhorod, Ukraine

Anna Gomonai
Institute of Electron Physics of the National Academy of Sciences of Ukraine
88017, 21 Universytetska Str., Uzhhorod, Ukraine

Vasyl Rizak
Uzhhorod National University
88000, 54 Voloshyna Str., Uzhhorod, Ukraine

Abstract

Relevance. Luminescent properties of materials doped with rare-earth ions have garnered significant interest due to their applications in various fields, including optoelectronics and photonics. Glassy lithium tetraborate (LTB) represents a promising matrix for hosting such ions, offering tunable luminescence properties.

Purpose. The purpose of this study was to investigate the concentration dependence of the luminescence spectrum of glassy LTB doped with europium oxide within the spectral range of 300-750 nm.

Methodology. Glassy samples of LTB activated by europium oxide were synthesized via a high-temperature process and characterized using photoluminescence (PL) spectroscopy. The PL spectra were recorded in the specified spectral range under excitation by a titanium-sapphire laser. The experimental setup provided insights into the luminescence behavior of the samples at different Eu^{3+} ion concentrations.

Results. The concentration dependence of the photoluminescence spectra of glassy lithium tetraborate $Li_2B_4O_7$ activated by europium oxide Eu_2O_3 was investigated in the spectral range of 300-750 nm. The intense emission observed in the wavelength region of 570-720 nm is attributed to the intra-configurational electronic *f–f* transitions between the excited multiplet levels ^5D and the ground multiplet ^7F of the Eu^{3+} ion.

Conclusions. The observed transitions, forbidden by selection rules, indicated J-mixing effects. The study highlights the potential of Eu-activated LTB glass for optoelectronic applications and provides insights into the underlying luminescence mechanisms.

Keywords: rare-earth doping; photoluminescence spectroscopy; europium ions; emission spectra; glassy materials.

Suggested Citation:
Danyliuk P, Gomonai A, Puga P, Gomonai A, Rizak V. Luminescence properties of Eu^{3+} ions in glassy lithum tetraborate matrix. *Sci Herald Uzhhorod Univ Ser Phys.* 2024;(55):3002-3008. DOI: 10.54919/physics/55.2024.300or2

*Corresponding author

Introduction

The spectroscopic properties of lanthanide ions make them practically indispensable as luminescence activators in the synthesis of materials that can be successfully applied in various fields of science, technology, medicine, and dosimetry [1-3]. Depending on the synthesis conditions and matrix components, lanthanides can significantly enhance the characteristics of optical materials as dopants [4-6]. One of the interesting materials that has been the subject of intensive research due to its attractiveness for use as an optical material is lithium tetraborate (LTB) in various aggregate states [7, 8]. Glass, single crystals, and polycrystals of LTB are promising objects for information display and transmission devices, various light sources [9-11], including lasers [12], frequency converters, scintillators, thermoluminescent dosimeters, gamma, and neutron detectors [13-15].

On the other hand, the electronic and local structures associated with dopant-related luminescent centers in crystals, glasses, and other disordered compounds present an interesting problem in solid-state physics and spectroscopy of functional materials. Dopant ions of lanthanides incorporated into LTB typically exist as trivalent ions, which interact with electron and hole trapping centers of the matrix and occupy mutually distant positions within its framework, acting as thermodynamically stable optical centers that promote their own luminescence [16].

In this work, which is a continuation of our previous studies on the optical properties of lanthanide ions, specifically Tb^{3+}, Er^{3+}, and Eu^{3+}, incorporated into the glassy matrix $Li_2B_4O_7$ [17-20], the photoluminescent properties of glassy LTB activated by europium oxide at various concentrations were investigated under UV irradiation. The trivalent europium ion has a relatively simple electronic structure with a non-degenerate ground state $4f^{6}\,{}^7F_0$ and is characterized by a high luminescence quantum yield in the red spectral region, predominantly attributed to transitions from the ${}^5D_0$ excited state to lower levels of the ${}^7F$ ground multiplet [21]. The relatively simple Stark structure of the lower energy levels of Eu^{3+} significantly simplifies the interpretation of spectra and enables the study of the nature of luminescence in different matrices.

In the vast majority of studies on the luminescent properties of $Li_2B_4O_7$:Eu glass available in the literature to date, a sufficiently high concentration (≥0.5 mol.%) of dopant Eu^{3+} ions has been used (see, for example, [22-24]). In this work, samples of $Li_2B_4O_7$:Eu with much lower dopant concentrations (0.001 and 0.003 wt.%) were also investigated.

Materials and Methods

The glassy samples of lithium tetraborate activated by europium oxide used in this study were synthesized in platinum crucibles in air at a temperature of 950°C from molten high optical quality single crystal $Li_2B_4O_7$ and Eu_2O_3 as an activator. The obtained melt was heated to a temperature of 1050°C and then rapidly cooled to 550°C. At this temperature, the melt was maintained for three hours, after which it was cooled to room temperature in the switched off furnace. The glass obtained in this way showed no tendency to crystallize. The experimental samples consisted of plane-parallel plates measuring 8×5×2.5 mm, with their surfaces polished to the 8-10 roughness grade.

During the experiment, the photoluminescence (PL) spectra of glassy LTB with europium oxide concentrations of 0.001, 0.003, 0.5, and 1.0 wt.% were investigated in the spectral range of 300-750 nm. The excitation of the samples' luminescence was performed using the third harmonic of a titanium-sapphire laser CF 131A with a wavelength of 260 nm. The laser operated in a pulsed-periodic mode with a repetition frequency of 10 Hz and pulse duration of 10 ns.

The energy of the laser pulses was approximately 20 μJ. The laser beam was oriented parallel to the entrance slit of the monochromator MS 7504i. The fluorescence zone image was projected with a 1:1 scaling onto the entrance slit of the monochromator using a quartz lens with a focal length of 75 mm. The spectral resolution of the monochromator was 2 nm. Time-integrated luminescence spectra were recorded by a CCD camera HS 101H and a PC.

Results and Discussion

The measured photoluminescence (PL) spectra of glassy LTB for various concentrations of europium oxide in the spectral range of 550–750 nm are shown in Fig. 1. It should be noted that Figure 1 does not include the sub-550 nm wavelength region because no significant fluorescence signal was detected in that region. As seen, with an increase in activator concentration from 0.001 wt.% (Figure 1a) to 1.0 wt.% (Figure 1d), the fluorescence intensity increases by approximately 20 times. At the same time, the structure of the fluorescence spectrum remains practically unchanged. Comparison of the spectra obtained by us with the PL spectrum of stoichiometric glassy LTB indicates that the observed structure is due to electronic transitions in the spectrum of the trivalent europium ion [20].

According to S.K. Sharma *et al.* [25], for lanthanide ions (in this case Eu^{3+}), whose inner optically active 4*f*-shell (in this case $4f^6$) is relatively well shielded from the influence of surrounding ions in the matrix by external $5s^2$- and $5p^6$-shells, a case of weak crystal field is realized. Therefore, the splitting of energy levels by the crystal field is much smaller than the multiplet splitting caused by spin-orbit interaction. As a result, the centroid position of the 4*f* multiplets depends significantly less on the specific matrix [26, 27]. Therefore, when interpreting PL spectra, we relied on data on the energy positions of Eu^{3+} ion levels both in the free state and in various matrices [28-30].

Identification of the observed structure in the PL spectrum is provided in Table 1. The data from the study by E.R. Smith *et al.* [31], where the largest number of transitions between Stark sublevels of multiplets ${}^5D$ and ${}^7F$ was observed, are also presented there. As seen, all identified transitions are intra-configurational $f \rightarrow f$ transitions between levels of the ${}^5D$ and ${}^7F$ multiplets of the same parity. For the free Eu^{3+} ion, such transitions are forbidden according to Laporte's rule. However, for the ion embedded in the matrix, this prohibition is lifted due to the mixing of 4*f*- and 5*d*- configurations under the influence of the matrix crystal field. Additionally, the mixing of wave functions of levels with different total angular momentum J values leads to transitions satisfying the condition $\Delta J \leq 6$. In the case where the transition occurs from a level with J=0 or to a level with J=0, this condition becomes ΔJ=2, 4, 6 [21]. These are the so-called induced electric dipole transitions, which, in terms of intensity, are significantly inferior to ordinary electric dipole transitions. It should also be noted that for the Eu^{3+} ion in the matrix, magnetic dipole f-f transitions satisfying the condition ΔJ=0, ±1 is possible (the transition 0→0 is forbidden).

Let's delve more deeply into the structure associated with the luminescence of the Eu^{3+} ion in the LTB matrix. In Figure 1, a set of vertical segments connected by a vertical line represents the wavelengths of transitions between Stark sublevels of multiplets ^5D and ^7F [31]: $^5D_0 \to {}^7F_{0\text{-}4}$ (lower row) and $^5D_1 \to {}^7F_{3,4}$ (upper row).

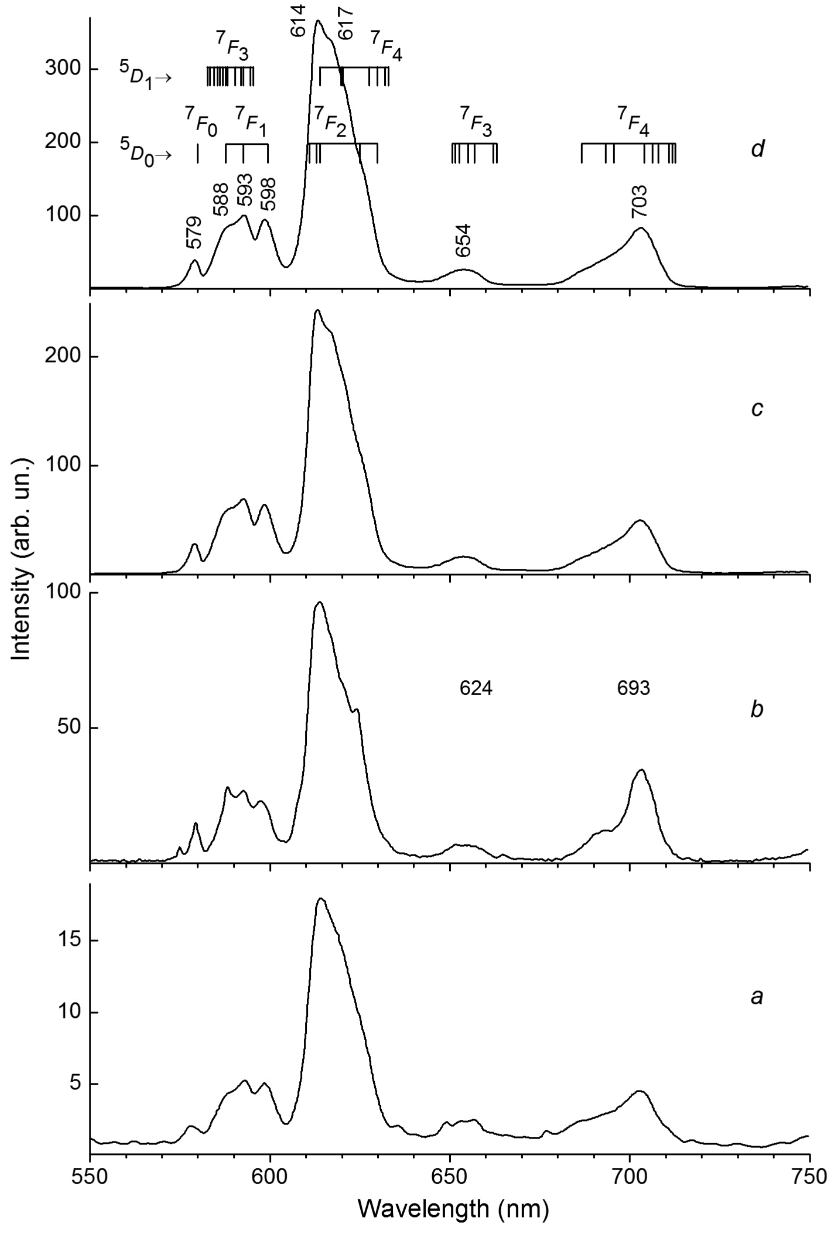


Figure 1. Photoluminescence spectra of glassy LTB activated by europium oxide at different concentrations: 0.001 (a), 0.003 (b), 0.5 (c), and 1.0 (d) wt.%

The bands of minimal intensity with peaks at 579 nm and 654 nm are attributed to transitions $^5D_0 \to {}^7F_0$ and $^5D_0 \to {}^7F_3$, respectively. Their low intensity is due to the fact that both transitions are forbidden by the selection rules for J (ΔJ=2, 4, 6). The observation of these transitions in the PL spectra is related to J-mixing, whereby the wave functions of the $^7F_0$ and $^7F_3$ states contain admixtures of states with J=2, 4, 6. The significant width of the band with a peak at 654 nm is associated with the splitting of the $^7F_3$ level into Stark sublevels under the influence of the matrix field and their broadening at room temperature (Table 1).

Table 1. Identification of the PL spectra structure

Wavelength (nm)	Transition	[31]	Wavelength (nm)	Transition	[31]
579	$^5D_0\rightarrow{}^7F_0$	580.6	624	$^5D_0\rightarrow{}^7F_2$	625.0
588	$^5D_1\rightarrow{}^7F_3$	582.6		$^5D_1\rightarrow{}^7F_4$	627.5
	$^5D_1\rightarrow{}^7F_3$	583.3		$^5D_1\rightarrow{}^7F_4$	629.8
	$^5D_1\rightarrow{}^7F_3$	584.5		$^5D_0\rightarrow{}^7F_2$	629.8
	$^5D_1\rightarrow{}^7F_3$	585.4		$^5D_1\rightarrow{}^7F_4$	632.0
	$^5D_1\rightarrow{}^7F_3$	586.1		$^5D_1\rightarrow{}^7F_4$	632.9
	$^5D_1\rightarrow{}^7F_3$	586.9	654	$^5D_0\rightarrow{}^7F_3$	650.6
	$^5D_0\rightarrow{}^7F_1$	587.8		$^5D_0\rightarrow{}^7F_3$	651.5
	$^5D_1\rightarrow{}^7F_3$	587.8		$^5D_0\rightarrow{}^7F_3$	652.6
	$^5D_1\rightarrow{}^7F_3$	588.3		$^5D_0\rightarrow{}^7F_3$	655.0
593	$^5D_1\rightarrow{}^7F_3$	590.3		$^5D_0\rightarrow{}^7F_3$	656.9
	$^5D_1\rightarrow{}^7F_3$	591.9		$^5D_0\rightarrow{}^7F_3$	662.0
	$^5D_0\rightarrow{}^7F_1$	592.6		$^5D_0\rightarrow{}^7F_3$	663.0
	$^5D_1\rightarrow{}^7F_3$	592.6	693	$^5D_0\rightarrow{}^7F_4$	686.7
	$^5D_1\rightarrow{}^7F_3$	594.5		$^5D_0\rightarrow{}^7F_4$	693.3
	$^5D_1\rightarrow{}^7F_3$	595.3		$^5D_0\rightarrow{}^7F_4$	695.6
598	$^5D_0\rightarrow{}^7F_1$	599.4	703	$^5D_0\rightarrow{}^7F_4$	704.1
614	$^5D_0\rightarrow{}^7F_2$	611.0		$^5D_0\rightarrow{}^7F_4$	706.3
	$^5D_0\rightarrow{}^7F_2$	613.0		$^5D_0\rightarrow{}^7F_4$	707.9
	$^5D_0\rightarrow{}^7F_2$	613.9		$^5D_0\rightarrow{}^7F_4$	710.8
	$^5D_1\rightarrow{}^7F_4$	613.9		$^5D_0\rightarrow{}^7F_4$	711.9
617	$^5D_1\rightarrow{}^7F_4$	619.7		$^5D_0\rightarrow{}^7F_4$	712.6
	$^5D_1\rightarrow{}^7F_4$	620.2			

Source: compiled by the authors

The maximum intensity in the investigated PL spectra is exhibited by a broad asymmetric band with a peak at 614 nm and features at 617 nm and 624 nm. It is attributed to transitions $^5D_0\rightarrow{}^7F_2$ and $^5D_1\rightarrow{}^7F_4$, which are allowed by the selection rules for J (ΔJ=2, 4, 6 and $\Delta J\leq 6$, respectively). The significant width and asymmetry of this band, particularly towards longer wavelengths, are associated with the splitting of the $^7F_2$, $^7F_4$, and $^5D_1$ levels into Stark sublevels and their broadening at room temperature. It is noteworthy that the induced electric dipole transition $^5D_0\rightarrow{}^7F_2$ is a so-called "hypersensitive" transition, the intensity of which significantly depends on the local symmetry of the Eu^{3+} ion and the nature of the ligand. Even with slight deviations from inversion symmetry at the cationic site, such a transition manifests in the fluorescence spectrum as the most intense band. The high intensity of the transition $^5D_0\rightarrow{}^7F_2$ in our case indicates the low symmetry of the Eu^{3+} ions in the glassy $Li_2B_4O_7$ matrix.

The wide structured band with peaks at 593 nm and 598 nm, and a feature at 588 nm, is attributed to transitions $^5D_0\rightarrow{}^7F_1$ and $^5D_1\rightarrow{}^7F_3$. The significant width of this band is associated with the splitting of the $^5D_1$, $^7F_1$, and $^7F_3$ levels into Stark sublevels due to the matrix field and their broadening at room temperature. It is worth noting that the transition $^5D_0\rightarrow{}^7F_1$, unlike the transition $^5D_1\rightarrow{}^7F_3$, is a magnetic dipole transition. Therefore, in our opinion, its contribution to the intensity of the observed band is somewhat smaller than that of the induced electric dipole transition $^5D_1\rightarrow{}^7F_3$, allowed by the selection rules for J ($\Delta J\leq 6$). Some confirmation of this is provided by the intensity ratio of the Stark sublevels of transitions $^5D_1\rightarrow{}^7F_3$ and $^5D_0\rightarrow{}^7F_1$ in the La_2O_3:Eu^{3+} matrix [27].

The wide band that is asymmetric toward shorter wavelengths and has a peak intensity at 703 nm and a feature at 693 nm is attributed to the induced electric dipole transition $^5D_0\rightarrow{}^7F_4$, allowed by the selection rules for J (ΔJ=2, 4, 6). In terms of intensity, it is comparable to the previously discussed band caused by transitions $^5D_0\rightarrow{}^7F_1$ and $^5D_1\rightarrow{}^7F_3$ and is approximately four times less intense than the most intense band corresponding to induced electric dipole transitions $^5D_0\rightarrow{}^7F_2$ and $^5D_1\rightarrow{}^7F_4$. The significant width and asymmetry of this band are related to the splitting of the $^7F_4$ level into Stark sublevels and their broadening at room temperature. In addition, all observed fluorescence bands exhibit additional broadening due to the irregular distribution of Eu^{3+} ions in the glassy $Li_2B_4O_7$ matrix.

It should be noted that upon irradiation of the glassy TBL samples with laser radiation at a wavelength of 260 nm, additionally to the $^5D_0$ and $^5D_1$ levels, higher-lying levels were also excited, including $^5D_2$ and $^5D_3$. Part of the possible radiation transitions from these levels to the ground term ^7F falls within the investigated range of 300-750 nm. As mentioned earlier, no visible luminescence was detected in the spectral range <550 nm. This indicates the absence or very low efficiency of radiation transitions $^5D_{2,3}\rightarrow{}^7F$ in this spectral region. Therefore, in our opinion, the contribution of such transitions to the observed structure of the luminescence spectrum in the range of 550–750 nm is also insignificant.

Overall, the luminescence spectra of glassy $Li_2B_4O_7$:Eu investigated in this study are in good agreement with the luminescence spectra obtained by other authors [22-24], as well as with the X-ray luminescence spectra investigated by us earlier [20].

Conclusions

The concentration dependence of the luminescence spectrum of glassy LTB doped by europium oxide in the spectral range of 300-750 nm has been studied. Intense luminescence was observed in the wavelength range of 550-750 nm, while no noticeable emission was detected in the <550 nm spectral range. As the activator concentration increased from 0.001 wt.% to 1.0 wt.%, the luminescence intensity increased by approximately 20 times, while the spectral structure remained almost unchanged.

The identified features observed in the luminescence spectrum of Eu-activated LTB glass are attributed to transitions $^5D_0 \to {}^7F_{0\text{–}4}$ and $^5D_1 \to {}^7F_{3,4}$ in the Eu^{3+} ion spectrum. The significant width of the observed bands is associated with the splitting of levels $^5D_1$ and $^7F_{0\text{–}4}$ into Stark sublevels due to the matrix field effect and their broadening due to the irregular distribution of Eu^{3+} ions in the glassy LTB matrix.

The most intense feature in the luminescence spectrum is the band at 614 nm, attributed to the so-called “hypersensitive” induced electric dipole transition $^5D_0 \to {}^7F_2$. Its dominance suggests the absence of an inversion center around the Eu^{3+} ion in the $Li_2B_4O_7$ glass matrix. The least intense bands are those resulting from transitions $^5D_0 \to {}^7F_0$ (579 nm) and $^5D_0 \to {}^7F_3$ (654 nm), which are forbidden by the selection rules for J (ΔJ=2, 4, 6). The presence of these transitions in the luminescence spectra is a result of J-mixing, where the wave functions of states $^7F_0$ and $^7F_3$ contain admixtures of states with J=2, 4, 6.

The luminescence spectra obtained at low concentrations of Eu^{3+} ions indicate a sufficiently high luminescence yield. A decrease in impurity concentration by a factor of 10^3 leads to a reduction in the luminescence intensity of the most intense band (614 nm) by only 20 times.

Acknowledgements

None.

Conflict of Interest

None.

References

[1] Sanyal B, Goswami M, Shobha S, Prakasan V, Krishnan M, Ghosh SK. Thermoluminescence and electron paramagnetic resonance study on rare earth/transition metal doped lithium borate glasses for dosimetry applications. *J Lumin.* 2019;216: 116725. DOI: 10.1016/j.jlumin.2019.116725.

[2] Padlyak BV, Drzewiecki A, Padlyak TB, Adamiv VT, Teslyuk IM. Resonant excited UV luminescence of the Gd^{3+} centres in borate glasses, co-doped with Gd and Ag. *Opt Mater.* 2018;79:302–309. DOI: 10.1016/j.optmat.2018.03.050.

[3] Vallejo MA, Elias JA, Honorato M, *et al*. Silver nanoparticles enhance thermoluminescence and photoluminescence response in $Li_2B_4O_7$ glass doped with Dy^{3+} and Yb^{3+}. *J Fluoresc.* 2020;30(1):143-150. DOI: 10.1007/s10895-019-02479-w.

[4] Kindrat II, Padlyak BV, Lisiecki R, Adamiv VT. Spectroscopic and luminescent properties of the lithium tetraborate glass co-doped with Nd and Ag. *J Alloys Compd.* 2021;853: 157321. DOI: 10.1016/j.jallcom.2020.157321.

[5] Elkelany EA, Hassan MA, Samir A, Abdel-Ghany AM, El-Bahnasawy HH, Farouk M. Optical and Mössbauer spectroscopy of lithium tetraborate glass doped with iron oxide. *Opt Mater.* 2021;112: 110744. DOI: 10.1016/j.optmat.2020.110744.

[6] Kindrat I, Padlyak B, Kukliński B, Drzewiecki A, Adamiv VT. Effect of silver co-doping on enhancement of the Sm^{3+} luminescence in lithium tetraborate glass. *J Luminesc.* 2019;213:290-296. DOI: 10.1016/j.jlumin.2019.05.045.

[7] Marzouk ZG, Dhingra A, Burak Ya, Adamiv V, Teslyuk I, Dowben PA. Long carrier lifetimes in crystalline lithium tetraborate. *Mater Let.* 2021;297:129978. DOI: 10.1016/j.matlet.2021.129978.

[8] Santiago M, Lavat A, Caselli E, *et al.* Thermoluminescence of strontium tetraborate. *Phys Status Solidi (a).* 1998;167(1):233-236. DOI: 10.1002/(SICI)1521-396X(199805)167:1%3C233::AID-PSSA233%3E3.0.CO;2-3.

[9] Prokić M. Dosimetric characteristics of $Li_2B_4O_7$:Cu,Ag,P solid TL detectors. *Radiat Prot Dosimetry*. 2002;100(1-4):265-268. DOI: 10.1093/oxfordjournals.rpd.a005863.

[10] Dubovik MF, Korshikova TI, Oseledchik YuS, *et al.* Thermostimulated luminescence of SrB_4O_7 single crystals and glasses. *Funct Mater.* 2005;12(4):685-688. Available from: http://functmaterials.org.ua/contents/12-4/fm124-14.pdf.

[11] Furetta C, Prokic M, Salamon R, Prokic V, Kitis G. Dosimetric characteristics of tissue equivalent thermoluminescent solid TL detectors based on lithium borate. *Nucl Instrum Methods Phys Res A*. 2001;456(3):411-417. DOI: 10.1016/S0168-9002(00)00585-4.

[12] Can N, Karali T, Townsend PD, Yildiz F. TL and EPR studies of Cu, Ag and P doped $Li_2B_4O_7$ phosphor. *J Phys D: Appl Phys.* 2006;39:2038-2043. DOI: 10.1088/0022-3727/39/10/009.

[13] Senguttuvan N, Ishii M, Shimoyama M, *et al*. Crystal growth and luminescence properties of $Li_2B_4O_7$ single crystals doped with Ce, In, Ni, Cu and Ti ions. *Nucl Instrum Methods Phys Res A*. 2002;486(1-2):264-267. DOI: 10.1016/S0168-9002(02)00714-3.

[14] Ishii M, Kuwano Y, Asaba S, *et al*. Luminescence of doped lithium tetraborate single crystals and glass. *Radiat Meas.* 2004;38(4-6):571-574. DOI: 10.1016/j.radmeas.2004.03.017.

[15] Zadneprovski BI, Eremin NV, Paskhalov AA. New inorganic scintillators on the basis of LBO glass for neutron registration. *Funct Mater.* 2005;12(2):261-268. Available from: http://functmaterials.org.ua/contents/12-2/fm122-14.pdf.

[16] Collins R, Durrant JP, He M, Layfield RA. Electronic structure and magnetic properties of rare-earth organometallic sandwich compounds. *Handbook Phys Chem Rare Earth.* 2019;55:89-121. DOI: 10.1016/bs.hpcre.2019.05.002.

[17] Puga PP, Puga GD, Popovych KP, *et al*. Optical absorption and X-ray luminescence of glasslike lithium tetraborate activated by terbium oxide. *Glass Phys Chem.* 2012;38(2):190-195. DOI: 10.1134/S1087659612020071.

[18] Puga PP, Popovych KP, Danilyuk PS, *et al*. X-ray luminescence of polycrystalline Tb_2O_3-doped $Li_2B_4O_7$. *Inorg Mater.* 2012;48(10):1033-1038. DOI: 10.1134/s0020168512100081.

[19] Danilyuk PS, Puga PP, Gomonai AI, Krasylynec VN, Volovich PN, Rizak VM. X-ray luminescence and spectroscopic characteristics of Er^{3+} ions in a glassy lithium tetraborate matrix. *Opt Spectr.* 2015;118(6):924-929. DOI: 10.1134/S0030400X15060089.

[20] Danilyuk PS, Krasylynec VN, Gomonai AI, Puga GD, Rizak VM, Turok II. X-ray fluorescence of Eu^{3+} ions in glassy and polycrystalline lithium tetraborate. *Glass Phys Chem.* 2018;44(1):1-6. DOI: 10.1134/S1087659618010066.

[21] Binnemans K. Interpretation of europium(III) spectra. *Coord Chem Rev.* 2015;295:1-45. DOI: 10.1016/j.ccr.2015.02.015.

[22] Padlyak BV, Kindrat II, Protsiuk VO, Drzewiecki A. Optical spectroscopy of $Li_2B_4O_7$, CaB_4O_7 and $LiCaBO_3$ borate glasses doped with europium. *Ukr J Phys Opt.* 2014;15(3):103-117. DOI: 10.3116/16091833/15/3/103/2014.

[23] Kumaresh A, Kumar RA, Ravikumar N, *et al*. Structural and photoluminescence studies on europium-doped lithium tetraborate ($Eu:Li_2B_4O_7$) single crystal grown by microtube Czochralski (μT-Cz) technique. *Chinese Phys B.* 2016;25(5):058105. DOI: 10.1088/1674-1056/25/5/058105.

[24] Secu M, Secu CE. Processing and optical properties of eu-doped chloroborate glass-ceramic. *Crystals*. 2020;10(12):1101. DOI: 10.3390/cryst10121101.

[25] Sharma SK, Behm T, Köhler T, Beyer J, Gloaguen R, Heitmann J. Library of UV-visible absorption spectra of rare earth orthophosphates, $LnPO_4$ (Ln=La-Lu, except Pm). *Crystals*. 2020;10(7):593. DOI: 10.3390/cryst10070593.

[26] Martin NC, Zalubas R, Hagan L. *Atomic energy levels: The rare-Earth elements*. Washington: US-RDS-NBS 60, 1978. Avaialble from: https://nvlpubs.nist.gov/nistpubs/Legacy/NSRDS/nbsnsrds60.pdf.

[27] Moune OK, Porcher P, Caro P. A new analysis of the fluorescence spectrum of Eu^{3+} in A-type La_2O_3. *J Solid State Chem*. 1983;50(1):41-50. DOI: 10.1016/0022-4596(83)90231-1.

[28] Carnall WT, Fields PR, Rajnak K. Electronic energy levels of the trivalent lanthanide aquo ions. IV. Eu^{3+}. *J Chem Phys*. 1968;49(15):4450-4455. DOI: 10.1063/1.1669896.

[29] Liu L, Shao X, Zhang Z, Liu J, Hu Y, Zhu C. Spectral properties and self-reduction of Eu^{3+} to Eu^{2+} in aluminosilicate oxyfluoride glass. *RSC Adv*. 2023;13(34):23708-23715. DOI: 10.1039/D3RA03689H.

[30] Hölsä J, Porcher P. Free ion and crystal field parameters for REOCl: Eu^{3+}. *J Chem Phys*. 1981;75(5):2108-2117. DOI: 10.1063/1.442314.

[31] Smith ER, Gruber JB, Wellenius P, Muth JF, Everitt HO. Spectra and energy levels of Eu^{3+} in cubic phase Gd_2O_3. *Phys Status Solidi B*. 2010;247(7):1807-1813. DOI: 10.1002/pssb.200945602.

Люмінесцентні властивості іонів Eu^{3+} у склоподібній матриці тетраборату літію

Павло Данилюк
Ужгородський національний університет
88000, вул. Волошина, 54, м. Ужгород, Україна

Олександр Гомонай
Інститут електронної фізики Національної академії наук України
88017, вул. Університетська, 21, м. Ужгород, Україна

Павло Пуга
Ужгородський національний університет
88000, вул. Волошина, 54, м. Ужгород, Україна

Анна Гомонай
Інститут електронної фізики Національної академії наук України
88017, вул. Університетська, 21, м. Ужгород, Україна

Василь Різак
Ужгородський національний університет
88000, вул. Волошина, 54, м. Ужгород, Україна

Анотація

Актуальність. Люмінесцентні властивості матеріалів, легованих рідкісноземельними іонами, викликають значний інтерес завдяки їхньому застосуванню в різних галузях, зокрема в оптоелектроніці та фотоніці. Склоподібний тетраборат літію є перспективною матрицею для розміщення таких іонів, що дає змогу регулювати властивості люмінесценції.

Мета. Метою цієї роботи було дослідити концентраційну залежність спектра люмінесценції склоподібного тетраборату літію, легованого оксидом європію, в спектральному діапазоні 300-750 нм.

Методологія. Склоподібні зразки тетраборату літію, активовані оксидом європію, були синтезовані за допомогою високотемпературного процесу і охарактеризовані за допомогою фотолюмінесцентної спектроскопії. Спектри фотолюмінесцентної спектроскопії реєстрували в заданому спектральному діапазоні при збудженні титан-сапфіровим лазером. Експериментальна установка дозволила дослідити поведінку люмінесценції зразків при різних концентраціях іонів Eu^{3+}.

Результати. Досліджено концентраційну залежність спектрів фотолюмінесценції склоподібного тетраборату літію $Li_2B_4O_7$, активованого оксидом європію Eu_2O_3, у спектральному діапазоні 300-750 нм. Інтенсивне випромінювання, що спостерігається в області довжин хвиль 570-720 нм, пов'язане з внутрішньоконфігураційними електронними f-f переходами між збудженими мультиплетними рівнями ^5D і основним мультиплетом ^7F іона Eu^{3+}.

Висновки. Спостережувані переходи, заборонені правилами відбору, вказують на ефекти J-змішування. Дослідження підкреслює потенціал Eu-активованого скла тетраборату літію для оптоелектронних застосувань і дає уявлення про механізми люмінесценції, що лежать в основі цього явища.

Ключові слова: рідкісноземельне легування; фотолюмінесцентна спектроскопія; іони європію; емісійні спектри; склоподібні матеріали.