

Synthesis and optical spectroscopy of the lithium tetraborate glasses, doped with terbium and dysprosium

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A series of the Tb- and Dy-doped glasses with $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ (or $\text{Li}_2\text{B}_4\text{O}_7\text{:Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7\text{:Dy}$) composition were synthesised and their spectroscopic properties were investigated. The $\text{Li}_2\text{B}_4\text{O}_7\text{:Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7\text{:Dy}$ glasses of high chemical purity and optical quality were obtained from corresponding polycrystalline compounds in the air using standard glass technology. The Tb and Dy impurities were added to $\text{Li}_2\text{B}_4\text{O}_7$ composition in the form of Tb_2O_3 and Dy_2O_3 oxide compounds in amounts of 0.5 and 1.0 mol%. The electron paramagnetic resonance (EPR), luminescence excitation and emission spectra of the $\text{Li}_2\text{B}_4\text{O}_7\text{:Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7\text{:Dy}$ glasses were investigated. On the basis of EPR and photoluminescence spectra analysis it was shown that the Tb and Dy impurities are incorporated in the $\text{Li}_2\text{B}_4\text{O}_7$ glass network as Tb^{3+} ($4f^8$, 7F_6) and Dy^{3+} ($4f^9$, $^6H_{15/2}$) ions, exclusively. All observed transitions of the Tb^{3+} and Dy^{3+} centres in the luminescence excitation and emission spectra were identified. The luminescence kinetics shows single exponential decay for Tb^{3+} and Dy^{3+} centres in $\text{Li}_2\text{B}_4\text{O}_7$ glasses. The lifetime values for main emission transitions of the Tb^{3+} and Dy^{3+} centres in the $\text{Li}_2\text{B}_4\text{O}_7$ glasses containing 0.5 and 1.0 mol% Tb_2O_3 and Dy_2O_3 are determined at $T = 300$ K. Peculiarities of optical properties and local structure of the Tb^{3+} and Dy^{3+} centres in the $\text{Li}_2\text{B}_4\text{O}_7\text{:Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7\text{:Dy}$ glasses as well as their potential applications have been discussed.

Keywords: tetraborate glass synthesis and structure, Tb^{3+} centre, Dy^{3+} centre, electron paramagnetic resonance (EPR), optical absorption, luminescence, decay kinetics, local structure.

1. Introduction

Crystalline and glassy (or vitreous) borate compounds, undoped and doped with rare-earth and transition elements, are very promising materials for quantum electronics

and non-linear optics [1, 2], scintillators and thermoluminescent (TL) dosimeters [3–5] as well as γ and neutron detectors [6–8]. This also concerns lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) single crystals, which are characterised by extremely high radiation stability [9, 10], good TL properties [4–8] and high transparency in a wide spectral range from vacuum UV to far IR [11]. Rare-earth ions such as Eu^{3+} , Eu^{2+} , Er^{3+} , Nd^{3+} , Tm^{3+} , Sm^{3+} , Yb^{3+} , *etc.*, show high luminescence efficiency in a variety of host materials with emission in a broad spectral range and widely used as activator centres in laser and luminescent materials [12, 13], including borate and tetraborate crystals and glasses with different chemical compositions [14–27]. In particular, compounds activated with Tb^{3+} and Dy^{3+} are considered as effective luminescent materials in green and yellow–blue spectral ranges, respectively.

Investigations into the electron and local structure of the paramagnetic impurity and luminescence centres as well as the intrinsic point defects in glasses and other disordered compounds is an interesting problem of solid state physics and spectroscopy of functional materials. The electron paramagnetic resonance (EPR) and optical spectroscopy allow to investigate the electron and local structure of the paramagnetic and luminescence centres in single crystals and disordered solids, including glasses. A clear interpretation of EPR and optical spectra and derivation from experimental spectra of the electron and local structure of the luminescence and paramagnetic centres in glasses need structural and spectroscopic data for their crystalline analogies [28, 29]. The borate compounds represent appropriate host materials for investigation the nature and structure of the luminescence and paramagnetic centres, because practically all borates, including tetraborates, can be obtained in both crystalline and glassy phases. Furthermore, the glassy tetraborate compounds are most perspective in comparison with their crystalline analogies from a technological point of view, because the growth of tetraborate single crystals is a difficult, long-term and, as a consequence, very expensive process. Besides, very low velocity of the crystals growth and high viscosity of the melt lead to problems with doping of tetraborate crystals by transition and rare-earth elements. These problems are absent in borate glasses.

At present the luminescent properties of Tb-doped borate compounds are published only in several papers. The paper [8] reports on the synthesis, and the optical and luminescence properties as well as some scintillation characteristics at the registration of neutrons ($E_n \leq 10$ MeV) and ^{60}Co γ radiation of the undoped and Tb, Cu, Ce, Sm, Eu, Tm, and Yb doped lithium tetraborate glasses. Luminescence excitation and emission spectra of the $\text{LiCaBO}_3:\text{M}^{3+}$ ($\text{M}^{3+} = \text{Eu}^{3+}$, Sm^{3+} , Tb^{3+} , Ce^{3+} , Dy^{3+}) polycrystalline compounds as promising phosphors for white light emitted diodes (LED) are investigated in [27]. Paper [30] reported on the synthesis and luminescence properties of the Eu^{3+} , Eu^{2+} , and Tb^{3+} centres in $\text{SrB}_4\text{O}_7:\text{Eu}$, Tb new phosphors. It was found that the valence state of Eu is influenced by Tb and the relative intensity of the Eu^{2+} emission in comparison with Eu^{3+} emission increases when Tb^{3+} is incorporated in $\text{SrB}_4\text{O}_7:\text{Eu}$ [30].

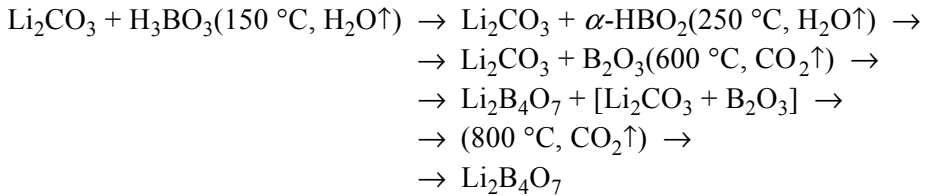
Optical and luminescence properties of Dy-doped borate glasses with different compositions are described in [27, 31–37]. In paper [27] the excitation and emission spectra of the $\text{LiCaBO}_3:\text{Dy}^{3+}$ polycrystalline phosphors are investigated and proposed to be used in a UV chip with $\text{LiCaBO}_3:\text{Dy}^{3+}$ phosphor for white LED. In paper [31] the compositional and temperature dependences of the optical and fluorescence properties of the Dy^{3+} centres in borate glasses with $(95 - x)\text{B}_2\text{O}_3 - x\text{Na}_2\text{O} - 5\text{CaO}$ composition were investigated and analysed using the Judd–Ofelt theory. Optical properties and their anomalous temperature variations are discussed in [31], combined with a change of a radiative decay rate of the Dy^{3+} ions in borate glasses. In [32] the spectroscopic properties of lithium borate $((99 - x)\text{Li}_2\text{CO}_3 + x\text{H}_3\text{BO}_3 + 1\text{Dy}_2\text{O}_3$, where $x = 39.5, 49.5, 59.5$, and 69.5) and lithium fluoroborate $(x\text{Li}_2\text{CO}_3 + (49.5 - x)\text{LiF} + 49.5\text{H}_3\text{BO}_3 + 1\text{Dy}_2\text{O}_3$, where $x = 24.75$ and 0) glasses were investigated and analysed using the Judd–Ofelt theory, and the dependences of Dy^{3+} spectral characteristics due to the compositional changes of the glasses were examined. In paper [33], using an optical absorption spectra analysis, it was shown that Dy impurity is incorporated in the $\text{Li}_2\text{B}_4\text{O}_7$ glasses melted in oxygen and hydrogen as Dy^{3+} ions. In [34] the fluorescence properties of Dy^{3+} ions with two concentrations (1.0 and 0.1 mol%) were investigated in a variety of borate and fluoroborate glasses modified with Li, Zn, and/or Pb. Particularly, in [34] it was shown that the emission decay curves for glasses containing 0.1 and 1.0 mol% Dy^{3+} are characterised by single exponential and non-exponential decay, respectively, and a decreasing trend in the lifetimes of the ${}^4F_{9/2}$ level was observed when the glass composition contained modifiers in the $\text{LiF} \rightarrow \text{Li}_2\text{O} \rightarrow \text{ZnO} \rightarrow \text{PbO}$ order. Optical absorption, fluorescence and photoacoustic spectra of Dy^{3+} -doped oxyfluoroborate glass were studied in [35], particularly the lifetime and fluorescence yield of the ${}^4F_{9/2}$ level for different concentration of Dy^{3+} was measured and analysed. Paper [36] reported on the synthesis of Dy-doped borosilicate glasses in the air and the optical absorption, emission and excitation spectra of the Dy^{3+} ions in these glasses. In [37] the results of X-ray diffraction, differential scanning calorimetric, and spectroscopic investigations of the $\text{Bi}_2\text{O}_3 - \text{ZnF}_2 - \text{B}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O}$ glasses containing 1.0 mol% Dy^{3+} and Pr^{3+} were presented and analysed. The Dy-doped oxychloroborate glasses of $\text{B}_2\text{O}_3 - \text{PbCl}_2 - \text{PbO} - \text{Al}_2\text{O}_3 - \text{WO}_3$ system were studied in [38] by X-ray diffraction, Raman, FT-IR, absorption and luminescence spectroscopy.

From the available reference data it was concluded that EPR and optical spectra of the Tb- and Dy-doped borate glasses were studied insufficiently. In particular the spectroscopic properties of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ tetraborate glasses as well as the electron and local structure of Tb and Dy luminescence centres in the tetraborate glass network were not satisfactorily investigated up to now. Therefore, the aim of this work is to investigate the spectroscopic properties of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ glasses as well as the electron and local structure of the Tb and Dy luminescence centres, using the reference structural data for $\text{Li}_2\text{B}_4\text{O}_7$ crystal and the glass, and spectroscopic data for other borate glasses doped with Tb and Dy.

2. Experimental details

2.1. The glass synthesis and samples preparation

Tetraborate glasses with $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ (or LTB:Tb and LTB:Dy) compositions were obtained in the air from corresponding polycrystalline compounds according to a standard glass synthesis using technological conditions, developed by the authors. For the solid state synthesis of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ polycrystalline compounds, the Li_2CO_3 carbonate and boric acid (H_3BO_3) of high chemical purity (99.999%) were used. The Tb and Dy impurities were added to the $\text{Li}_2\text{B}_4\text{O}_7$ composition in the form of Tb_2O_3 and Dy_2O_3 oxide compounds in the amounts of 0.5 and 1.0 mol%. The solid-state synthesis of the $\text{Li}_2\text{B}_4\text{O}_7$ polycrystalline compound was carried out using the multi-step heating process, which can be described by the following reaction:



Finally, the large samples of $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ glasses were obtained by fast cooling of the corresponding melt, heated to more than 100 K above the melting temperature ($T_{\text{melt}} = 1190\text{ K}$ for $\text{Li}_2\text{B}_4\text{O}_7$ compound) for exceeding the glass transition point. Two types of crucibles, graphite (C) and corundum ceramic (Al_2O_3), were used to obtain tetraborate glasses. The quality of the obtained glasses is practically independent of the type of crucibles. The samples for optical investigations were cut and polished to an approximate size of $5\times 4\times 2\text{ mm}^3$.

2.2. Experimental methods, equipment and samples characterisation

The non-controlled and activator (Tb and Dy) paramagnetic impurities in the obtained LTB:Tb and LTB:Dy glasses were registered by EPR technique using modernised commercial X-band spectrometers of the SE/X-2013 and SE/X-2544 types (RADIOPAN, Poznań, Poland), operating in the high-frequency (100 kHz) modulation mode of magnetic field at room temperature (RT). Microwave frequencies were measured with the use the Hewlett Packard microwave frequency counter of the 5350 B type and DPPH g -marker ($g = 2.0036 \pm 0.0001$).

The luminescence excitation and emission spectra as well as luminescence kinetics were registered in the UV–VIS spectral range at RT. The emission and luminescence excitation spectra were acquired with a Dongwoo (model DM711) scanning system consisting of an excitation monochromator with 150 mm focal length and an emission

monochromator having 750 mm focal length equipped with a photomultiplier and an InGaAs detector. Spectral response of the whole emission system was calibrated in the 400–800 nm spectral region against a reference source. The resulting signal was analysed by a Stanford (model SRS 250) boxcar integrator and stored in a personal computer. Luminescence decay curves were recorded with a Tektronix (model TDS 3052) digital oscilloscope at $T = 300$ K. Excitation was provided by a Continuum Surelite I optical parametric oscillator (OPO) pumped by a third harmonic of a Nd:YAG laser ($\lambda = 355$ nm) and the emitted light was filtered using a GDM grating monochromator (focal length – 1000 mm). Luminescence excitation and emission spectra as well as decay curves also were registered using a HORIBA spectrofluorometer (model FluoroMax-4).

The obtained samples of the LTB:Tb and LTB:Dy glasses were characterised by high optical quality. In the Tb- and Dy-doped lithium tetraborate glasses were observed characteristic for glassy compounds luminescence excitation and emission spectra, which are presented and discussed below in the Sections 3.1 and 3.2, respectively.

It should be noted that in all Tb- and Dy-doped glasses with $\text{Li}_2\text{B}_4\text{O}_7$ compositions the EPR signals with $g_{\text{eff}} \cong 4.3$ and $g_{\text{eff}} \cong 2.0$ signed as Fe^{3+} (1) and Fe^{3+} (dip), respectively, were observed (Fig. 1). In Tb- and Dy-doped glasses, the integrated intensity of Fe^{3+} (1) signal with $g_{\text{eff}} \cong 4.3$ is larger (approximately 10–20 times) than the integrated intensity of the Fe^{3+} (dip) signal with $g_{\text{eff}} \cong 2.0$ (Fig. 1). According to [39, 40], the EPR signal with $g_{\text{eff}} \cong 4.3$ is characteristic for glassy compounds and belongs to isolated Fe^{3+} ($3d^5$, ${}^6S_{5/2}$) non-controlled impurity ions, localised in the octahedral and/or tetrahedral sites of the glass network with a strong rhombic distortion. The presence of the Fe^{3+} (1) signals with $g_{\text{eff}} \cong 4.3$ clearly demonstrates

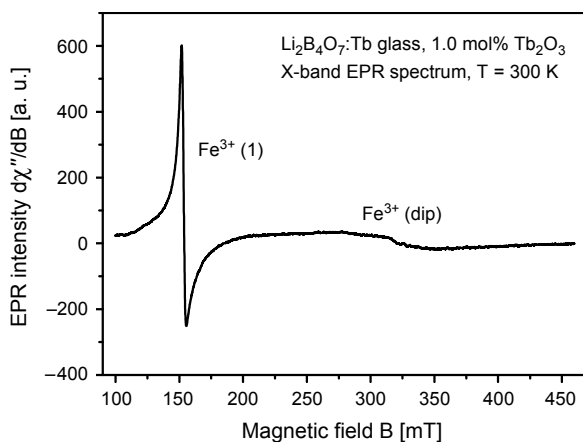


Fig. 1. The X-band EPR spectrum of the $\text{Li}_2\text{B}_4\text{O}_7$:Tb glass containing 1.0 mol% Tb_2O_3 , registered at $T = 300$ K.

the classical glass structure of the investigated $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ compounds. Broad EPR signal Fe^{3+} (dip) with $g_{\text{eff}} \cong 2.0$ is related to the $\text{Fe}^{3+}-\text{Fe}^{3+}$ pair centres, coupled by magnetic dipolar interaction [39].

3. Results and discussion

3.1. Spectroscopy of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ glasses

The terbium impurity, generally, can be incorporated in the structure of different compounds as non-paramagnetic Tb^{3+} ($4f^8$, 7F_6) and paramagnetic Tb^{4+} ($4f^7$, $^8S_{7/2}$) ions. The paramagnetic Tb^{4+} ions can be registered by the EPR technique even at room temperature. In the $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ glasses, the EPR spectrum of the Tb^{4+} centres was not observed (Fig. 1). Thus, the terbium impurity is incorporated into the lithium tetraborate glass network as Tb^{3+} ions, exclusively.

The Tb^{3+} impurity centres in crystals and glasses are revealed in their characteristic optical spectra. Presented below luminescence excitation and emission spectra of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ glasses confirm the incorporation of Tb impurity into the lithium tetraborate glass network in trivalent (Tb^{3+}) state. This result correlates with the reference data for Tb-doped lithium tetraborate [8] and other borate glasses, obtained in the air [27, 30]. The $4f-4f$ transitions of Tb^{3+} ions only weakly appear in the UV–VIS optical absorption spectra of LTB:Tb glasses, but are very well observed in their luminescence excitation and emission spectra (Figs. 2 and 3). In accordance with the energy levels diagram [41] and reference data [42, 43], the observed luminescence excitation bands were assigned to appropriate electronic $4f-4f$ transitions within Tb^{3+} ion from 7F_6 ground state to the following terms of excited states: 5L_9 , 5G_5 , 5D_3 , $^5L_{10}$, 5G_6 , and 5D_4 (Fig. 2). Weak resolution of some bands in

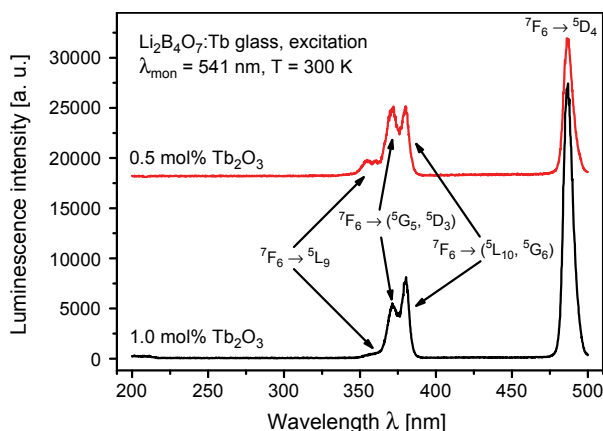
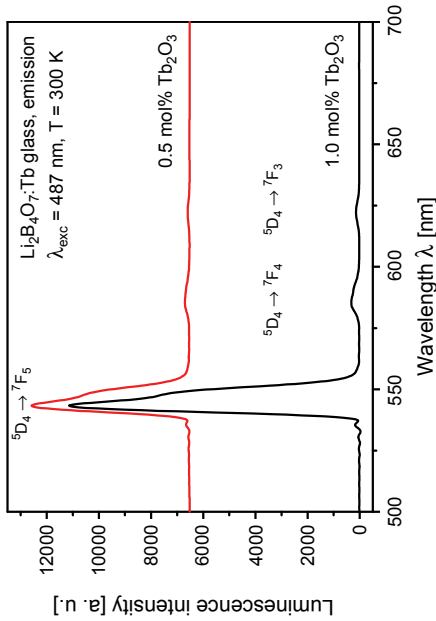
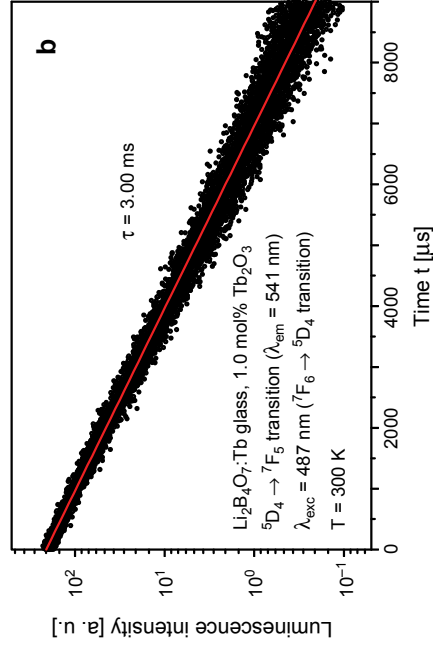
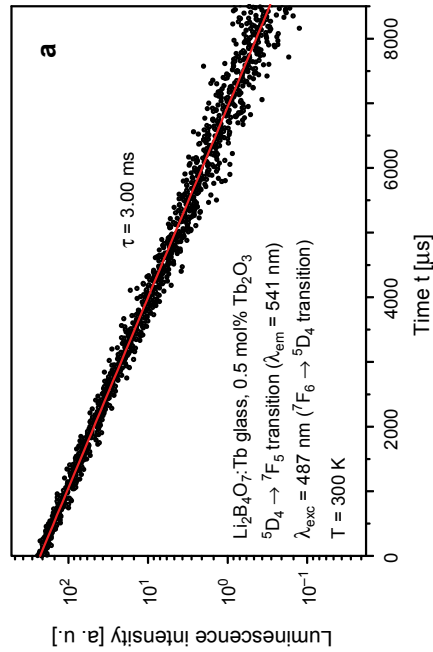


Fig. 2. The luminescence excitation spectra of Tb^{3+} centres in $\text{Li}_2\text{B}_4\text{O}_7:\text{Tb}$ glasses containing 0.5 and 1.0 mol% Tb_2O_3 , registered at $\lambda_{\text{mon}} = 541 \text{ nm}$ ($^5D_4 \rightarrow ^7F_5$ transition) and $T = 300 \text{ K}$.



▼ Fig. 3. The emission spectra of the Tb^{3+} centres in the $Li_2B_4O_7:Tb$ glasses containing 0.5 and 1.0 mol% Tb_2O_3 , registered under excitation with $\lambda_{exc} = 487$ nm (${}^7F_6 \rightarrow {}^5D_4$ transition) at $T = 300$ K.



▲ Fig. 4. The luminescence decay curves for Tb^{3+} centres (${}^5D_4 \rightarrow {}^7F_5$ transition, $\lambda_{max} = 541$ nm), registered at $T = 300$ K under excitation with $\lambda_{exc} = 487$ nm (${}^7F_6 \rightarrow {}^5D_4$ transition) in the $Li_2B_4O_7:Tb$ glasses containing 0.5 mol% (a) and 1.0 mol% (b) Tb_2O_3 . Solid lines present the results of the single exponential fit.

the Tb^{3+} luminescence excitation spectra is related to inhomogeneous broadening, caused by structural disordering of the glass host. The LTB:Tb glasses, excited with $\lambda_{\text{exc}} = 487$ nm, exhibit strong band peaked at 543 nm (green luminescence) and two weak bands with maxima around 586 nm and 623 nm (yellow luminescence), which corresponds to the ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_4$, ${}^5D_4 \rightarrow {}^7F_3$ emission transitions of Tb^{3+} centres (Fig. 3). Other emission bands of the Tb^{3+} centres, corresponding to the ${}^5D_4 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) transitions, are very weak and can be observed at liquid nitrogen temperatures [42]. The high-energy emission bands giving blue luminescence, which correspond to the ${}^5D_4 \rightarrow {}^7F_6$ and ${}^5D_3 \rightarrow {}^7F_J$ ($J = 0-6$) transitions, were not investigated in this work.

The luminescence kinetics for the most intense green emission band (${}^5D_4 \rightarrow {}^7F_5$ transition) of Tb^{3+} centres shows single exponential decay with the lifetime value of $\tau = 3.0$ ms, obtained at $T = 300$ K for LTB:Tb glasses containing 0.5 and 1.0 mol% Tb_2O_3 (Figs. 4a and 4b, respectively). The lifetime values for ${}^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} centres in LTB:Tb glasses are close to those obtained for other Tb^{3+} -doped glasses [38, 42]. The same lifetime value for LTB:Tb glasses with different Tb^{3+} concentration clearly demonstrates that the Tb^{3+} - Tb^{3+} interaction is absent or negligible even in the LTB:Tb sample with relatively high Tb concentration (1.0 mol%). This result shows homogeneous distribution of the Tb^{3+} centres without pairing and clustering [43] in the lithium tetraborate glass network.

3.2. Spectroscopy of the $\text{Li}_2\text{B}_4\text{O}_7$:Dy glasses

The dysprosium impurity can be incorporated in the structure of different crystalline and glassy compounds as paramagnetic Dy^{3+} ($4f^9$, ${}^6H_{15/2}$) and non-paramagnetic Dy^{2+} ($4f^8$, 7F_6) ions. The electron structure of Dy^{2+} and Tb^{3+} ions is the same ($4f^8$, 7F_6). In the investigated $\text{Li}_2\text{B}_4\text{O}_7$:Dy glasses only Dy^{3+} optical spectra were observed (Figs. 5 and 6). These results show good correlation with the reference data for

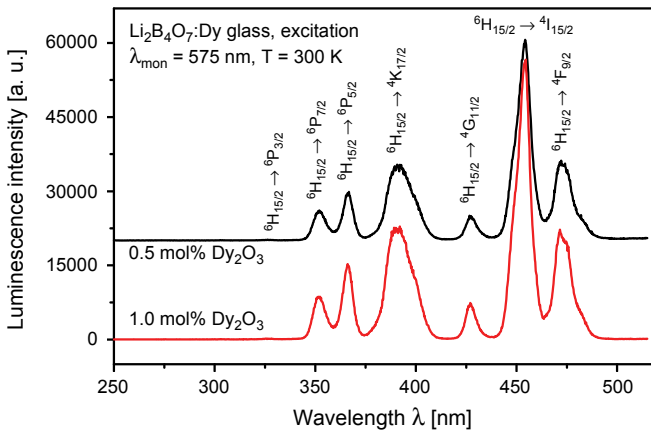


Fig. 5. The luminescence excitation spectra of Dy^{3+} centres in $\text{Li}_2\text{B}_4\text{O}_7$:Dy glasses containing 0.5 and 1.0 mol% Dy_2O_3 , registered at $\lambda_{\text{mon}} = 575$ nm (${}^4F_{9/2} \rightarrow {}^6F_{13/2}$ transition) and $T = 300$ K.

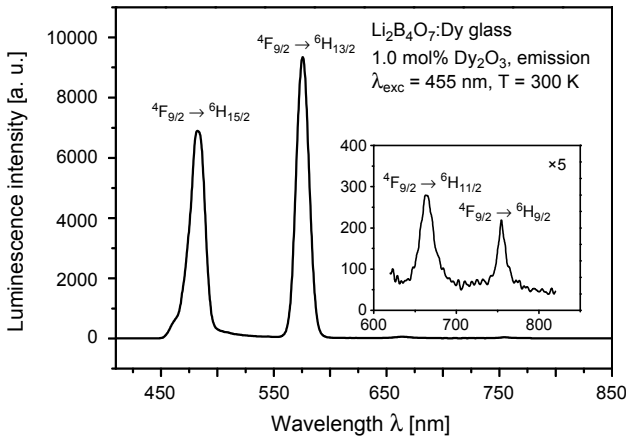


Fig. 6. The emission spectrum of Dy^{3+} centres in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ glass containing 1.0 mol% Dy_2O_3 , registered under excitation with $\lambda_{\text{exc}} = 455$ nm (${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$ transition) at $T = 300$ K.

other Dy-doped glasses, in particular for borate glasses with different compositions, obtained in air [15, 27, 31–38]. One can notice that the EPR spectra of Dy^{3+} paramagnetic ions can be observed only at liquid helium temperatures and were not investigated in this work.

The luminescence excitation and emission spectra of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ glasses containing 0.5 and 1.0 mol% Dy_2O_3 show characteristic bands belonging to the $4f-4f$ transitions of Dy^{3+} ions (Figs. 5 and 6). Particularly, in the luminescence excitation spectra of the emission band, peaked at 575 nm in the LTB:Dy glasses at RT six characteristic bands were observed, which according to [31, 32, 35, 38, 41] correspond to the following transitions of Dy^{3+} ions: ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{7/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{5/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{K}_{17/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{G}_{11/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{9/2}$ (Fig. 5). The band corresponds to the ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{3/2}$ transition only weakly appears in the luminescence excitation spectra. In the LTB:Dy glasses under photoexcitation with $\lambda_{\text{exc}} = 455$ nm that corresponds to the ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$ transition (Fig. 5) at RT two characteristic emission bands were observed, peaked at 575 nm (yellow luminescence) and 482 nm (blue luminescence), which corresponds to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ transitions of Dy^{3+} centres (Fig. 6). It should be noted that weak red bands around 670 and 760 nm, which corresponds to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2}$ transitions, are also revealed in Dy^{3+} emission spectrum (see insert in Fig. 6). The luminescence excitation and emission spectra of Dy^{3+} ions are characterised by inhomogeneous broadening of spectral lines, caused by structural disordering of LTB glasses, which points to the existence of a number of types of Dy^{3+} centres in glass network with slightly-different local environment and crystal field parameters.

The luminescence kinetics of yellow emission band (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) of the Dy^{3+} centres can be satisfactorily described by single exponential decay with the lifetime of $\tau = 850$ μs for LTB:Dy glass containing 0.5 mol% Dy_2O_3 and $\tau = 800$ μs for LTB:Dy glass containing 1.0 mol% Dy_2O_3 (Fig. 7). The obtained

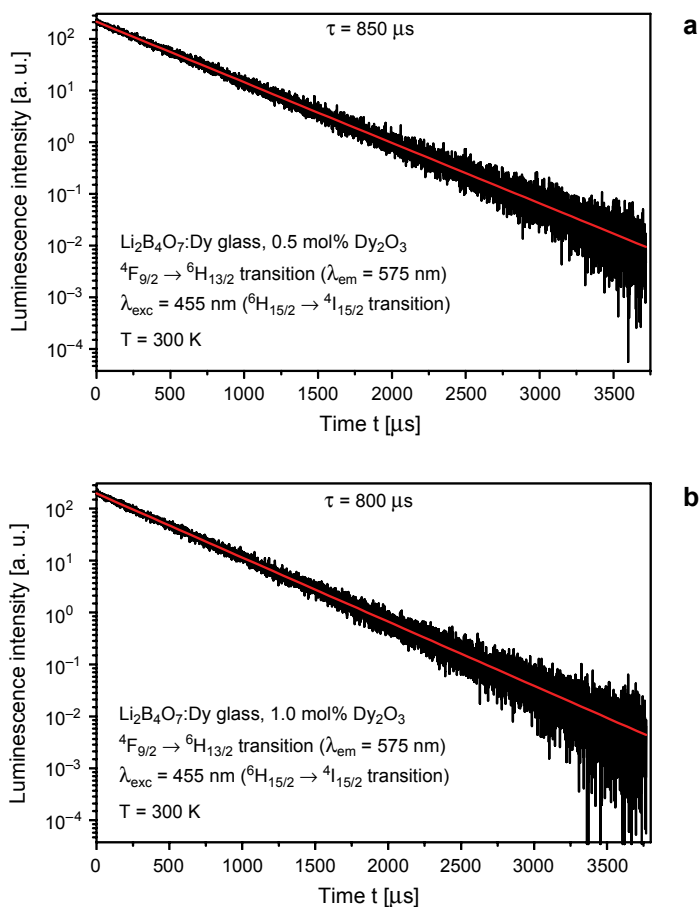


Fig. 7. The luminescence decay curves for Dy^{3+} centres (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, $\lambda_{\text{max}} = 575$ nm), registered at $T = 300$ K under excitation with $\lambda_{\text{exc}} = 455$ nm (${}^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition) in glasses with $\text{Li}_2\text{B}_4\text{O}_7:\text{Dy}$ composition containing 0.5 mol% (a) and 1.0 mol% (b) Dy_2O_3 . Solid lines present the results of the single exponential fit.

lifetime values are similar to those obtained for Dy^{3+} centres in other borate glasses with different compositions [31, 32, 34, 35, 38]. The lowering of luminescence lifetime with increasing Dy_2O_3 content is related to the influence of $\text{Dy}^{3+}-\text{Dy}^{3+}$ interaction in the LTB glass host. The observed decay curves correspond to one type of Dy^{3+} centres with slightly different parameters, which is exhibited as inhomogeneous broadening of spectral lines.

3.3. The local structure of Tb^{3+} and Dy^{3+} centres in the $\text{Li}_2\text{B}_4\text{O}_7$ glass network

The incorporation peculiarities and local structure of the Tb^{3+} and Dy^{3+} luminescence centres in the tetraborate glass network are considered basing on the $\text{Li}_2\text{B}_4\text{O}_7$ crystal [44] and glass [45] structure analysis as well as our direct EXAFS (extended X-ray

absorption fine structure) study of the L_3 -edge of rare-earth impurity ions [46]. In paper [46] it was shown that the local structure (first coordination shell) of rare-earth impurities in crystal and glass with the same composition, particularly in crystals and glasses of the $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system, is closely similar.

The $\text{Li}_2\text{B}_4\text{O}_7$ crystal belongs to the $4mm$ point group and $I4_1cd$ (C_{4v}) space group of tetragonal symmetry ($a = b = 9.479 \text{ \AA}$, $c = 10.286 \text{ \AA}$) [44]. The B^{3+} ions occupy threefold- and fourfold-coordinated sites with average $\text{B}^{3+}\text{-O}^{2-}$ bonds equal to 1.373 and 1.477 \AA , respectively and the Li^+ ions are located in the fourfold-coordinated distorted tetrahedra with $\text{Li}^+\text{-O}^{2-}$ distances which lie in the 1.97–2.14 \AA range (Fig. 8). According to [44], the number of nearest oxygen anions (coordination number to oxygen N) with the $\text{Li}^+\text{-O}^{2-}$ distances equal to 2.63, 2.85, and 2.88 \AA are 5, 6, and 7, respectively. The statistical distribution of $\text{Li}^+\text{-O}^{2-}$ distances for different coordination numbers ($N = 4\text{--}7$) leads to the so-called “positional disorder” in the $\text{Li}_2\text{B}_4\text{O}_7$ crystal lattice. Basing on the crystal structure data [44], we can suppose that trivalent rare-earth impurity ions (RE^{3+}) in the $\text{Li}_2\text{B}_4\text{O}_7$ crystal occupy Li^+ sites of the lattice due to extremely small ionic radius of the B^{3+} ions (0.23 \AA). So, the Tb^{3+} and Dy^{3+} ions are expected to incorporate in Li^+ sites of the $\text{Li}_2\text{B}_4\text{O}_7$ crystal lattice, because the Li^+ , Tb^{3+} , and Dy^{3+} ionic radii are close and equal approximately to 0.76, 1.04, and 0.97 \AA , respectively. Owing to positional disorder, the RE^{3+} luminescence centres in the Li^+ sites of $\text{Li}_2\text{B}_4\text{O}_7$ crystal lattice will be characterised by slightly different spectroscopic parameters, which leads to inhomogeneous broadening of spectral lines.

According to structural data for $\text{Li}_2\text{B}_4\text{O}_7$ crystal [44] and glass [45], the RE^{3+} ions can be incorporated into the Li^+ sites of the glass network (Fig. 8). The local

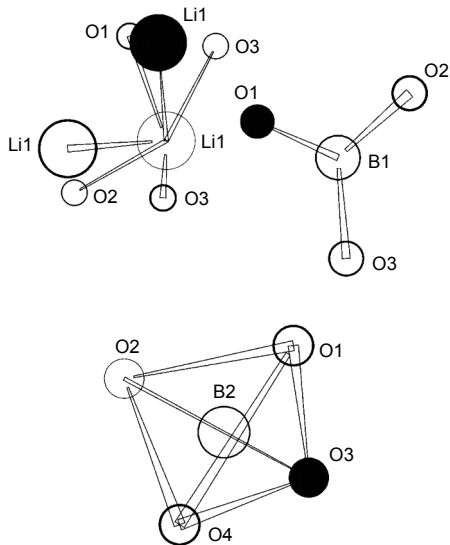


Fig. 8. The proposed model of local environment for RE^{3+} (Tb^{3+} and Dy^{3+}) impurity centres in the $\text{Li}_2\text{B}_4\text{O}_7$ glass network. For Li1 sites, which are occupied by RE^{3+} ions, only 4 oxygen atoms ($\text{O1}\text{--}\text{O4}$) of the first coordination sphere are shown, limited by $r \leq 0.214 \text{ nm}$ [44, 45].

environment of RE³⁺ (Tb³⁺ and Dy³⁺) centres in the Li₂B₄O₇ glass network also consists of O²⁻ anions with statistically distributed structural parameters (RE³⁺-O²⁻ interatomic distances and coordination numbers to oxygen) in the first coordination shell (positional disorder) which is exhibited in the inhomogeneous broadening of their spectral lines. Additionally, a glass network is characterised by continual disturbance of the short-range order that destroys the middle- and long-range order. This glassy-like disordering of the second (cationic) coordination sphere around the luminescence centres leads to the additional inhomogeneous broadening of spectral lines. As a result, optical spectra of the Tb³⁺ and Dy³⁺ centres in the Li₂B₄O₇ glass are characterised by stronger inhomogeneous broadening than that in the corresponding crystal. Because the local structure of the oxide crystals and corresponding glasses with the same composition according to [46] is closely similar we can state that the Tb³⁺ and Dy³⁺ centres are located in the Li⁺ sites of Li₂B₄O₇ glass network.

4. Conclusions

Large samples of the Tb- and Dy-doped lithium tetraborate glasses of high optical quality and chemical purity were obtained by the standard glass synthesis, according to technological conditions developed by authors. On the basis of the EPR, optical spectroscopy and structural data analysis, the following was shown:

1. The terbium and dysprosium impurities are incorporated into the Li₂B₄O₇ glass network as Tb³⁺ (4*f*⁸, ⁷F₆) and Dy³⁺ (4*f*⁹, ⁶H_{15/2}) ions, exclusively and they form the Tb³⁺ and Dy³⁺ luminescence centres with characteristic luminescence excitation and emission spectra.

2. All transitions of the Tb³⁺ and Dy³⁺ centres, observed in the UV-VIS optical spectra, have been identified. Optical spectra of the Tb³⁺ and Dy³⁺ centres in the Li₂B₄O₇ glass network are quite similar to the Tb³⁺ and Dy³⁺ optical spectra, observed in other complex borate glasses and characterised by essential inhomogeneous broadening of spectral lines.

3. Luminescence decay curves for Tb³⁺ centres (⁵D₄ → ⁷F₅ transition, λ_{max} = 541 nm) in the Li₂B₄O₇:Tb glasses containing 0.5 and 1.0 mol% Tb₂O₃ are satisfactorily described by single exponential decay with the lifetime value of τ = 3.0 ms at T = 300 K that is typical for ⁵D₄ level of Tb³⁺ centres in other borate glasses. The influence of the Tb³⁺-Tb³⁺ interaction on the lifetime value was not revealed in the Li₂B₄O₇:Tb glass containing 1.0 mol% Tb₂O₃.

4. Luminescence decay curves for Dy³⁺ centres (⁴F_{9/2} → ⁶H_{13/2} transition, λ_{max} = 575 nm) in the Li₂B₄O₇:Dy glasses containing 0.5 and 1.0 mol% Dy₂O₃ are satisfactorily described by single exponential decay with τ = 850 and 800 μs, respectively, obtained at T = 300 K. These results correlate with the corresponding data for Dy³⁺ centres in other borate glasses with different composition. The lowering of the lifetime value with increasing Dy³⁺ concentration is related to Dy³⁺-Dy³⁺ interaction in the LTB glass network.

5. The Tb^{3+} and Dy^{3+} luminescence centres are localised in the Li^+ sites, coordinated by O^{2-} positionally disordered anions in the LTB glass network. The charge compensation at $RE^{3+} \rightarrow Li^+$ heterovalence substitution can be carried out by cation vacancies, V_{Li}^- and V_B^{3-} , presented in the tetraborate glass network.

6. The multi-site character of the Tb^{3+} and Dy^{3+} luminescence centres in the glass with $Li_2B_4O_7$ composition is related to the presence of Li^+ sites in their structure with different coordination numbers ($N = 4-7$) and statistically distributed $RE^{3+}-O^{2-}$ distances (positional disorder) that leads to statistical distribution of spectroscopic parameters of the Tb^{3+} and Dy^{3+} and appears in the inhomogeneous broadening of their spectral lines.

7. Basing on the obtained results, it could be suggested that the investigated LTB glasses, activated with Tb^{3+} and Dy^{3+} , are promising luminescent materials for green and yellow–blue spectral regions, respectively.

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