

# Optical spectra and luminescence kinetics of the Sm<sup>3+</sup> and Yb<sup>3+</sup> centres in the lithium tetraborate glasses

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Optical absorption, luminescence excitation, and emission spectra as well as luminescence kinetics of the Sm- and Yb-doped glasses with lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) composition were investigated and analysed. The Sm- and Yb-doped lithium tetraborate glasses of high optical quality were obtained in air from corresponding polycrystalline compounds according to standard glass synthesis technology. The Sm and Yb impurities were added to the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> compound in the form of Sm<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> oxides in amount of 0.4 mol%. Using optical and electron paramagnetic resonance spectroscopy it was shown that the Sm and Yb impurities are incorporated into the lithium tetraborate glass network as Sm<sup>3+</sup> (4f<sup>5</sup>, <sup>6</sup>H<sub>5/2</sub>) and Yb<sup>3+</sup> (4f<sup>13</sup>, <sup>2</sup>F<sub>7/2</sub>) ions, exclusively. All of the observed transitions in the absorption and luminescence spectra of Sm<sup>3+</sup> and Yb<sup>3+</sup> centres were identified. The luminescence kinetics of the Sm<sup>3+</sup> and Yb<sup>3+</sup> centres in the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> glass are characterised by a single exponential decay. Decay constants for the main emission transitions of the Sm<sup>3+</sup> and Yb<sup>3+</sup> centres in the lithium tetraborate glass were obtained at *T* = 300 K. Incorporation peculiarities and optical spectra of Sm<sup>3+</sup> and Yb<sup>3+</sup> ions in the lithium tetraborate glass have been discussed in comparison with other borate glasses and crystals.

Keywords: borate glasses, Sm<sup>3+</sup> centre, Yb<sup>3+</sup> centre, optical absorption, luminescence, decay kinetics, local structure.

## 1. Introduction

The borate, in particular tetraborate crystals, are characterised by extremely high radiation stability [1, 2] and high transparency in the wide spectral range from vacuum

ultraviolet (VUV) to far infrared (IR). The rare-earth ions, such as  $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Yb}^{3+}$ , *etc.*, show high luminescence efficiency in a variety of host materials with emission in a wide spectral range, in particular the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  ions give a red and IR characteristic emission bands [3, 4], respectively. Therefore, the rare-earth activator ions are widely used in different luminescent materials [3, 4], including borate crystals and glasses [5, 6].

In connection with their attractive spectroscopic and luminescence properties, the undoped and doped borate crystals and glasses are promising materials for different technical applications: scintillators and tissue-equivalent materials for thermoluminescence (TL) dosimeters [7, 8],  $\gamma$  and neutron detectors [9, 10], lasers [11] and second harmonic generation media [12]. Obtaining tetraborate single crystals is technologically difficult, time-consuming and, consequently, very expensive. Besides, very low crystal growth rate and high viscosity of the melt lead to problems with doping, particularly with the rare-earth doping of tetraborate crystals. Therefore, from the technological point of view the glassy (or vitreous) tetraborate compounds are most perspective in comparison with their crystalline analogies. On the other hand, the study of electron and local structure of the luminescence centres in complex oxide glasses is an interesting problem of quantum electronics and solid state physics. Thus, synthesis and spectroscopic investigations of rare-earth doped tetraborate crystals and glasses are fundamental as far as real-life applications are concerned.

Methods of optical and electron paramagnetic resonance (EPR) spectroscopy allow investigating the electron and local structure of the impurity luminescence and paramagnetic centres in crystals and glasses. For interpretation of optical and EPR spectra in complex glasses need corresponding spectroscopic and structural data for their crystalline analogies [13, 14]. Practically all borate compounds, including tetraborates, can be obtained in both crystalline and glassy states. Therefore, borates are good candidates for studying the electron and local structure of luminescence and paramagnetic centres in them.

In [10, 15–17], optical and spectroscopic properties of doped lithium tetraborate crystals and glasses, obtained in air, were investigated and perspectives of their applications for scintillators in neutron detectors, TL dosimeters and laser media were considered. In [10, 15, 16] it was shown by means of optical spectroscopy that the rare-earth impurities, particularly Sm and Yb, are incorporated into the  $\text{Li}_2\text{B}_4\text{O}_7$  glass and crystal structure, in general, as trivalent ions, which are characterised by high efficient luminescence at room temperature. In [16], by EPR spectroscopy it was shown that the Yb impurity is incorporated into the  $\text{Li}_2\text{B}_4\text{O}_7$  glass and crystal as  $\text{Yb}^{3+}$  ions, located in the  $\text{Li}^+$  and, probably  $\text{B}^{3+}$  or interstitial sites of the structure. Optical spectroscopy shows the presence of  $\text{Yb}^{2+}$  centres in the  $\gamma$ -irradiated  $\text{Li}_2\text{B}_4\text{O}_7$  crystal [16]. According to [17], no  $\text{Yb}^{3+}$  bands were observed in optical absorption spectra of the “as-grown” in air  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  crystals and absorption bands, peaked near 198, 234, and 280 nm in these crystals were assigned to  $\text{Yb}^{2+}$  centres. In lithium

borate glasses, there were also observed the  $\text{Yb}^{2+}$  centres with characteristic broad absorption band near UV region and emission in the 520–540 nm spectral range [10].

As we can see from the above referenced data, optical and luminescence properties of the Sm- and Yb-doped glasses with  $\text{Li}_2\text{B}_4\text{O}_7$  composition have not been systematically investigated up to now and electron and local structure of Sm and Yb luminescence centres in them have not been finally established. The present paper reports the synthesis and optical spectroscopy of the  $\text{Li}_2\text{B}_4\text{O}_7$  glasses, doped by Sm and Yb. The electron and local structure of Sm and Yb luminescence centres in the lithium tetraborate glass and crystal have been discussed based on referenced structural and spectroscopic data and the results obtained.

## 2. Glass synthesis, characterisation, and experimental equipment

The Sm- and Yb-doped glasses with lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) compositions were obtained in air from corresponding polycrystalline compounds according to standard glass technology. For solid state synthesis of the  $\text{Li}_2\text{B}_4\text{O}_7$  polycrystalline compounds there were used the  $\text{Li}_2\text{CO}_3$  carbonate and boric acid ( $\text{H}_3\text{BO}_3$ ) of high chemical purity (99.999%). The Sm and Yb impurities were added into the  $\text{Li}_2\text{B}_4\text{O}_7$  composition in the form of  $\text{Sm}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  oxide compounds in the amount of 0.4 mol%. The Sm- and Yb-doped lithium tetraborate glasses were obtained by fast cooling of the corresponding melt, heated more than 100 K above the melting temperature ( $T_{\text{melt}} = 1190$  K) for exceeding the glass transition point.

Our undoped lithium tetraborate glasses are characterised by high transparency in the 330–2500 nm spectral range (Fig. 1a). According to [10], undoped lithium borate glasses are transparent in the 281–2760 nm region, whereas nominally-pure  $\text{Li}_2\text{B}_4\text{O}_7$  single crystals reveal high transparency in a very wide (167–3200 nm) spectral range [17]. The Sm- and Yb-doped glass samples obtained are almost uncoloured and characterised by high optical quality. In Sm- and Yb-doped glasses with  $\text{Li}_2\text{B}_4\text{O}_7$  composition, characteristic optical spectra were observed, which are presented in Figs. 1–7 and discussed in Section 3.

The non-controlled and rare-earth paramagnetic impurities in the glasses obtained were registered by EPR technique with the use of 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 and liquid helium temperatures. The microwave frequency was measured with the help of the Hewlett–Packard microwave frequency counter of the 5350 B type and DPPH  $g$ -marker ( $g = 2.0036 \pm 0.0001$ ). Practically, in all undoped and rare-earth doped glasses with  $\text{Li}_2\text{B}_4\text{O}_7$  composition, two characteristic EPR signals were observed, with  $g_{\text{eff}} = 4.29 \pm 0.01$  and  $g_{\text{eff}} = 2.00 \pm 0.01$ . The integral intensity of the signal with  $g \cong 4.29$  is more than 100 times greater than that of  $g \cong 2.00$ . According to [18, 19] both observed EPR signals were assigned to the  $\text{Fe}^{3+}$  ( $3d^5$ ,  ${}^6S_{5/2}$ ) non-controlled

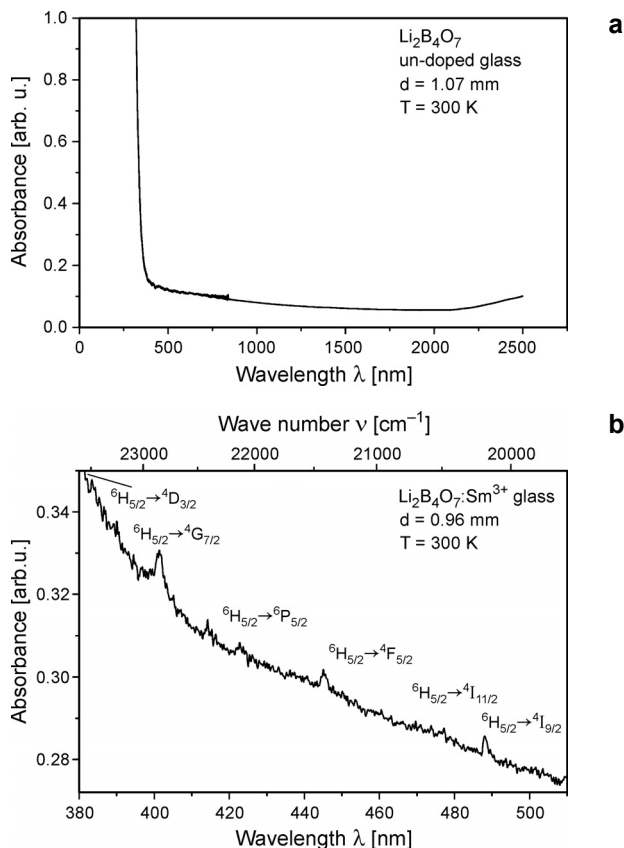


Fig. 1. Optical absorption spectra of the undoped (a) and Sm-doped ( $\text{Sm}_2\text{O}_3$  content – 0.4 mol%) (b) glasses with  $\text{Li}_2\text{B}_4\text{O}_7$  composition, recorded at  $T = 300$  K.

impurity ions in octahedral and/or tetrahedral sites of the glass network. Weak EPR signals of the non-controlled  $\text{Mn}^{2+}$  ( $3d^5$ ,  $6S_{5/2}$ ) ions, characteristic of glassy state [18, 19] were also observed in Sm- and Yb-doped samples.

Optical absorption spectra were recorded with a Varian spectrophotometer (model 5E UV-VIS-NIR). Luminescence and excitation spectra were acquired with a Dongwoo (model DM711) scanning system consisting of an excitation monochromator with 150 mm focal length and emission monochromator having a 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 reference source. The  $\text{Yb}^{3+}$  emission spectra were measured using a 1m GDM 1000 double grating monochromator with a spectral bandwidth of  $2\text{ cm}^{-1}$  and detected by a photomultiplier with S-20 or S-1 spectral response. The resulting signal was analysed by a Stanford (model SRS 250) boxcar integrator and stored in a personal computer. Decay curves were recorded with a Tektronix (model TDS 3052) digital oscilloscope. Excitation was provided by a Continuum Surelite I Optical Parametric Oscillator

(OPO) pumped by a third harmonic of an Nd:YAG laser and the emitted light was filtered using a GDM grating monochromator (focal length – 1000 mm). All optical measurements were performed at room temperature.

### 3. Results and discussion

#### 3.1. The $\text{Sm}^{3+}$ centres in the $\text{Li}_2\text{B}_4\text{O}_7$ glass

The Sm impurity in oxide crystals and glasses reveals  $\text{Sm}^{3+}$  ( $4f^5$ ,  $^6H_{5/2}$ ) and  $\text{Sm}^{2+}$  ( $4f^6$ ,  $^7F_0$ ) ions with characteristic optical absorption, luminescence and EPR spectra. In the obtained  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glasses only  $\text{Sm}^{3+}$  optical and EPR spectra were observed. This result correlates with the previous referenced data for  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass and corresponding crystal [10, 15].

Optical absorption spectra of the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glasses in the visible spectral range, registered at room temperature consist of several very weak absorption bands (Fig. 1b). In the luminescence excitation spectrum of the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass (Fig. 2) at room temperature there were also observed several weakly-resolved bands that correspond to  $\text{Sm}^{3+}$  optical absorption transitions (Fig. 1b). In accordance with energy levels diagram and referenced data [20, 21], the observed weak absorption and luminescence excitation bands centred about 345, 362, 377, 405, 421, 463, 476, 490 nm were assigned to appropriate electronic  $f-f$  transitions within  $\text{Sm}^{3+}$  ion from  $^6H_{5/2}$  ground state to the following terms of excited states:  $^3H_{7/2}$ ,  $^4F_{9/2}$ ,  $^4D_{3/2}$ ,  $^4G_{7/2}$ ,  $^6P_{5/2}$ ,  $^4F_{5/2}$ ,  $^4I_{11/2}$ , and  $^4I_{9/2}$ , respectively (Fig. 1b and Fig. 2). One can notice that bands corresponding to the  $^6H_{5/2} \rightarrow ^3H_{7/2}$  and  $^6H_{5/2} \rightarrow ^4F_{9/2}$  transitions of the  $\text{Sm}^{3+}$  centres were not well revealed in the optical absorption (Fig. 1b), but clearly observed in the luminescence excitation spectrum (Fig. 2). The intense absorption below 350 nm (Fig. 1b) may result from the  $\text{O}^{2-} \rightarrow \text{Sm}^{3+}$  charge transfer band [22] and fundamental

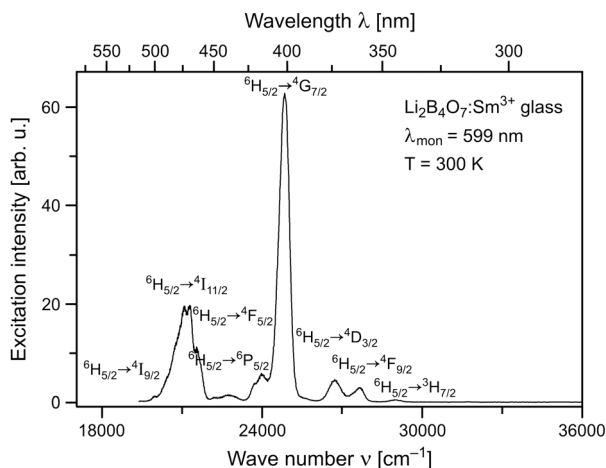


Fig. 2. The luminescence excitation spectrum of  $\text{Sm}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass, monitored at  $\lambda_{\text{mon}} = 599$  nm and  $T = 300$  K.

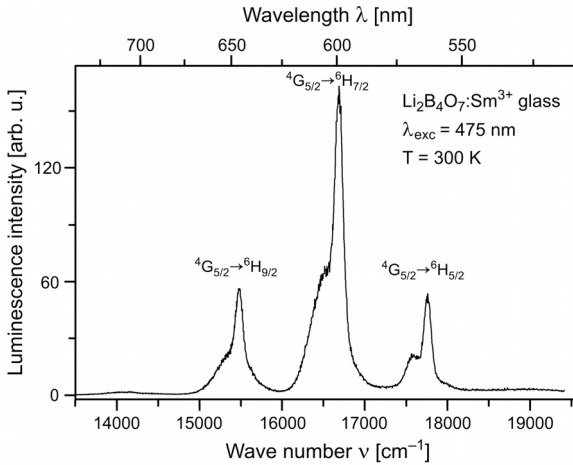


Fig. 3. The luminescence spectrum of  $\text{Sm}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}^{3+}$  glass, obtained under excitation with  $\lambda_{\text{exc}} = 475$  nm and recorded at  $T = 300$  K.

absorption of the  $\text{Li}_2\text{B}_4\text{O}_7$  glass host (Fig. 1a). Thus, the Sm impurity is incorporated into the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass network as  $\text{Sm}^{3+}$  ions, exclusively, because characteristic optical absorption and luminescence excitation spectra of  $\text{Sm}^{2+}$  [21] ions were not observed.

Under excitation of the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass with  $\lambda_{\text{exc}} = 475$  nm that corresponds to  ${}^6\text{H}_{5/2} \rightarrow {}^4\text{I}_{11/2}$  luminescence excitation transition (Fig. 2) at room temperature there were observed intense characteristic reddish-orange emission bands originating from  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$  ( $J = 5/2, 7/2, 9/2$ ) transitions of the  $\text{Sm}^{3+}$  ions (Fig. 3). In crystalline compounds, each  $\text{Sm}^{3+}$  emission band corresponds to  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$  transitions in the luminescence spectrum, and is split to several separate components, which practically are unresolved in the  $\text{Li}_2\text{B}_4\text{O}_7$  glass (Fig. 3). Thus, from the emission spectrum (Fig. 3) we can see only one type of the  $\text{Sm}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass network with complex unresolved emission bands.

The observed optical absorption and luminescence spectra of the  $\text{Sm}^{3+}$  ions in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass are similar to those obtained earlier for the  $\text{Sm}^{3+}$  ions in lithium tetraborate glasses [10, 15] and other borate glasses with different compositions [22–24]. The linewidth and resolution of the  $\text{Sm}^{3+}$  optical absorption and luminescence bands in  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glasses were practically not changed at lowering temperature up to liquid nitrogen, which is the evidence of their inhomogeneous broadening. The inhomogeneous broadening of spectral lines is characteristic of luminescence centres in glasses and is related to disordering of the local neighbourhood around centres in a glass network.

The luminescence decay curve of  $\text{Sm}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass for the most intense emission band corresponds to the  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$  transition ( $\lambda_{\text{max}} = 599$  nm) and was registered at  $T = 300$  K (Fig. 4). The observed decay curve has been satisfactorily fitted by a single exponential model with lifetime value

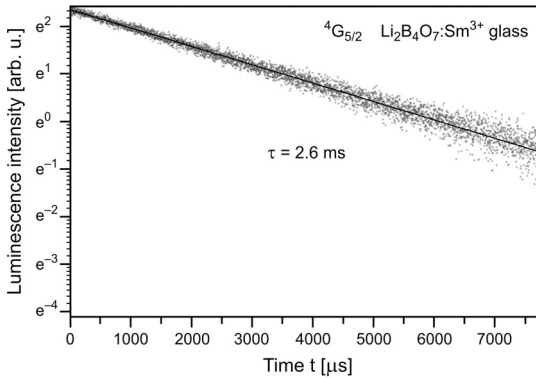


Fig. 4. The luminescence decay curve of  $\text{Sm}^{3+}$  centres for  ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$  transition ( $\lambda_{\text{max}} = 599$  nm), registered at  $T = 300$  K. Solid line – result of a single exponential fit.

$\tau = 2.6$  ms in the  ${}^4G_{5/2}$  emitting level (Fig. 4) that corresponds to one type of  $\text{Sm}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass network. One can notice that the obtained lifetime value is characteristic of  ${}^4G_{5/2}$  level of the  $\text{Sm}^{3+}$  luminescence centres and close to  $\text{Sm}^{3+}$  lifetimes in other complex oxide glasses [25], particularly in borate glasses with different compositions [22–24]. The local structure of  $\text{Sm}^{3+}$  luminescence centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  crystal and glass is considered and discussed in Section 3.3.

### 3.2. The $\text{Yb}^{3+}$ centres in the $\text{Li}_2\text{B}_4\text{O}_7$ glass

The Yb impurity can be incorporated in oxide crystals and glasses as  $\text{Yb}^{3+}$  ( $4f^{13}, {}^2F_{7/2}$ ) and  $\text{Yb}^{2+}$  ( $4f^{14}, {}^1S_1$ ) ions with characteristic optical absorption, luminescence and EPR spectra. In the investigated glasses with  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  composition only  $\text{Yb}^{3+}$  optical and EPR spectra were observed. This result shows good agreement with previous referenced data for Yb-doped lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$ ) glass [15, 16], but does not correlate with results obtained for Yb-doped lithium borate glasses [10] and  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  crystals [17], which show the presence of  $\text{Yb}^{2+}$  centres, exclusively.

Room temperature optical absorption and luminescence spectra of the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass show spectra typical of  $\text{Yb}^{3+}$  (Figs. 5 and 6). The absorption spectrum consists of a strong peak centred at 970 nm and an unstructured broadband restricted from 875 to 1100 nm associated with the  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$  transition within the  $\text{Yb}^{3+}$  ions electronic  $f-f$  levels (Fig. 5). The  ${}^2F_{5/2}$  excited level is separated from the  ${}^2F_{7/2}$  ground level by about  $10000\text{ cm}^{-1}$ . Therefore, under resonant photoexcitation of the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass with  $\lambda_{\text{exc}} = 970$  nm ( $10700\text{ cm}^{-1}$ ) that corresponds to  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$  absorption transition (Fig. 5) there was observed a characteristic emission spectrum of  $\text{Yb}^{3+}$  centres, which consists of unresolved zero-line peak at 970 nm and broadband in the 950–1020 nm spectral range ( ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$  transition) (Fig. 6). The observed absorption and emission spectra show one type of  $\text{Yb}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass network.

The observed optical absorption and emission spectra of  $\text{Yb}^{3+}$  ions in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass (Figs. 5 and 6) are very similar to corresponding  $\text{Yb}^{3+}$  optical

spectra, observed in other borate glasses [26, 27] and disordered borate crystals with different compositions [28, 29]. The linewidth and resolution of the  $\text{Yb}^{3+}$  optical absorption and emission bands in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass did not practically change with temperature decreasing to that of liquid nitrogen, which is the evidence of their inhomogeneous broadening characteristic of luminescence centres in disordered hosts.

The luminescence decay curve of  $\text{Yb}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass for  ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$  emission transition ( $\lambda_{\text{max}} = 970 \text{ nm}$ ) is satisfactorily described in the framework of a single exponential decay with lifetime  $\tau = 484 \mu\text{s}$  in the  ${}^2F_{5/2}$  level at  $T = 300 \text{ K}$  (Fig. 7). One can notice that the obtained lifetime value is similar to the  $\text{Yb}^{3+}$  lifetimes in borate glasses and crystals with different compositions [26, 27]

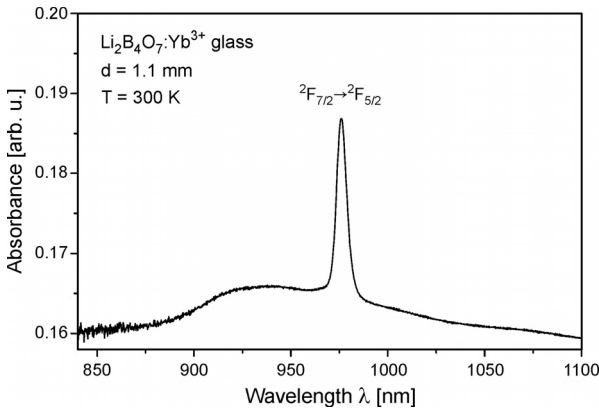


Fig. 5. The optical absorption spectrum of the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass, containing 0.4 mol% of  $\text{Yb}_2\text{O}_3$ , recorded at  $T = 300 \text{ K}$ .

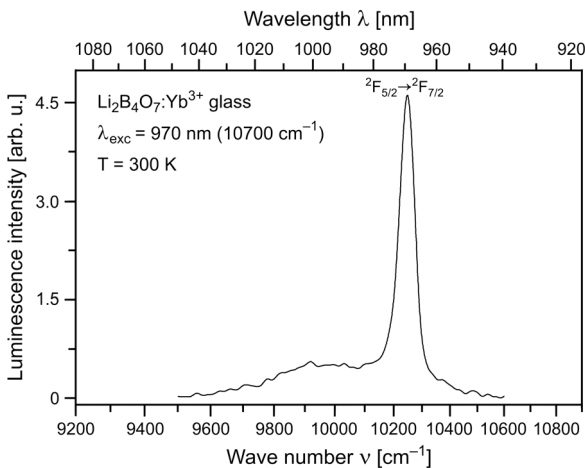


Fig. 6. The luminescence spectrum of  $\text{Yb}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass, obtained under excitation with  $\lambda_{\text{exc}} = 970 \text{ nm}$  ( $\nu = 10700 \text{ cm}^{-1}$ ) and recorded at  $T = 300 \text{ K}$ .



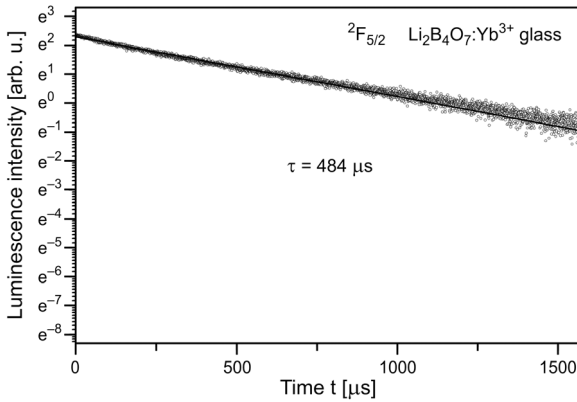


Fig. 7. The luminescence decay curve of  $\text{Yb}^{3+}$  centres for  ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$  transition ( $\lambda_{\text{max}} = 970 \text{ nm}$ ), registered at  $T = 300 \text{ K}$ . Solid line – result of a single exponential fit.

and other oxide glasses [30, 31]. Particularly, in [30] it was shown that the  $\text{Yb}^{3+}$  decay time strongly depends on Yb concentration and luminescence kinetics can be described by a double exponential model with slow (190–1250  $\mu\text{s}$ ) and fast (6–300  $\mu\text{s}$ ) decay times, which was assigned to the  $\text{Yb}^{3+}$  isolated and  $\text{Yb}^{3+}\text{--Yb}^{3+}$  pair centres, respectively. Thus, the luminescence kinetics of  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}^{3+}$  glasses shows one type of isolated  $\text{Yb}^{3+}$  centres in the glass network. The local structure of  $\text{Yb}^{3+}$  luminescence centres in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  crystal and glass is considered in Section 3.3.

### 3.3. The local structure of $\text{Sm}^{3+}$ and $\text{Yb}^{3+}$ centres in the $\text{Li}_2\text{B}_4\text{O}_7$ crystal and glass

Let us consider the incorporation peculiarities and local structure of the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  luminescence centres in the  $\text{Li}_2\text{B}_4\text{O}_7$  crystal and corresponding glass with the same ( $\text{Li}_2\text{O--}2\text{B}_2\text{O}_3$ ) composition. The  $\text{Li}_2\text{B}_4\text{O}_7$  crystal belongs to a  $4mm$  point group and  $I4_1cd$  ( $C_{4v}$ ) space group of tetragonal symmetry ( $a = b = 9.479 \text{ \AA}$ ,  $c = 10.286 \text{ \AA}$ ). The  $\text{B}^{3+}$  ions occupy threefold- and fourfold-coordinated sites with average  $\text{B}^{3+}\text{--O}^{2-}$  bonds equal to 1.373 and 1.477  $\text{ \AA}$ , respectively [32]. According to [32], the  $\text{Li}^+$  ions are located in the fourfold-coordinated distorted tetrahedra with  $\text{Li}^+\text{--O}^{2-}$  distances in the range 1.97–2.14  $\text{ \AA}$ . The numbers 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  $\text{ \AA}$  are 5, 6, and 7, respectively [32]. The statistical distribution of  $\text{Li}^+\text{--O}^{2-}$  distances for different coordination numbers ( $N = 4\text{--}7$ ) leads to so-called “positional disorder” in the  $\text{Li}_2\text{B}_4\text{O}_7$  crystal lattice. Based on the crystal structure data we can suppose that trivalent rare-earth impurity ions,  $\text{RE}^{3+}$ , in the  $\text{Li}_2\text{B}_4\text{O}_7$  crystal occupy  $\text{Li}^+$  sites of the lattice due to extremely small ionic radius of the  $\text{B}^{3+}$  ions (0.23  $\text{ \AA}$ ). So, the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  ions are expected to incorporate in  $\text{Li}^+$  sites of the  $\text{Li}_2\text{B}_4\text{O}_7$  crystal lattice, because the  $\text{Li}^+$ ,  $\text{Sm}^{3+}$ , and  $\text{Yb}^{3+}$  ionic radii are close and approximately equal to 0.76, 0.958, and 0.868  $\text{ \AA}$ , respectively. Owing to positional disorder, the  $\text{RE}^{3+}$  luminescence centres in  $\text{Li}^+$  sites of the  $\text{Li}_2\text{B}_4\text{O}_7$  lattice are characterised by slightly different spectroscopic parameters and the weak inhomogeneous broadening of spectral lines.

The local environment of  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7$  glass network also consists of  $\text{O}^{2-}$  anions with statistically-distributed structural parameters ( $\text{RE}^{3+}-\text{O}^{2-}$  interatomic distances and coordination numbers) in the first coordination shell (positional disorder) that is revealed in the inhomogeneous broadening of the optical absorption and luminescence bands. Additionally, a glass network is characterised by continual disturbance of the short-range order that destroys middle- and long-range order. This glassy-like disorder in the second (cationic) coordination sphere around the luminescence centres leads to the additional inhomogeneous broadening of spectral lines. As a result, the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  optical spectra in glasses with  $\text{Li}_2\text{B}_4\text{O}_7$  composition are characterised by strong inhomogeneous broadening. Because the local structures of oxide crystals and corresponding glasses with the same composition are very similar [13, 14, 33] we can suppose that the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  centres are also located in  $\text{Li}^+$  sites of the  $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$  glass network. This suggestion needs confirmation by the direct EXAFS (extended X-ray absorption fine structure) investigation of Sm and Yb impurity  $L_3$ -edge in the crystal and glass with  $\text{Li}_2\text{B}_4\text{O}_7$  composition that will be a subject of future work.

#### 4. Conclusions

The Sm- and Yb-doped lithium tetraborate glasses ( $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  and  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$ ) of high optical quality and chemical purity were obtained by standard glass synthesis in air according to technology developed by the authors. On the basis of optical spectroscopy data analysis we have shown the following:

1. The samarium and ytterbium impurities are incorporated into the  $\text{Li}_2\text{B}_4\text{O}_7$  glass network as  $\text{Sm}^{3+}$  ( $4f^3$ ,  $^4I_{9/2}$ ) and  $\text{Yb}^{3+}$  ( $4f^{13}$ ,  $^2F_{7/2}$ ) ions, exclusively, and form the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  luminescence centres with characteristic optical absorption and luminescence spectra.

2. All the observed UV–VIS–IR transitions of the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  centres in optical absorption and luminescence spectra have been identified. Optical spectra of the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  centres in the  $\text{Li}_2\text{B}_4\text{O}_7$  glass network are quite similar to the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  optical spectra, observed in other complex borate glasses and disordered crystals and are characterised by inhomogeneous broadening of spectral lines.

3. The luminescence kinetics of the  $\text{Sm}^{3+}$  centres for the  $^4G_{5/2} \rightarrow ^6H_{7/2}$  transition ( $\lambda_{\text{max}} = 599$  nm) in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Sm}$  glass containing 0.4 mol% of Sm is satisfactorily described by a single exponential decay with lifetime  $\tau = 2.6$  ms at  $T = 300$  K that is typical of the  $^4G_{5/2}$  level of  $\text{Sm}^{3+}$  centres in other borate glasses.

4. The luminescence kinetics of the  $\text{Yb}^{3+}$  centres for  $^2F_{5/2} \rightarrow ^2F_{7/2}$  transition ( $\lambda_{\text{max}} = 970$  nm) in the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Yb}$  glass containing 0.4 mol% of Yb is satisfactorily described by a single exponential decay with  $\tau = 484$   $\mu\text{s}$  at  $T = 300$  K that correlates with corresponding data for  $\text{Yb}^{3+}$  centres in other borate glasses.

5. It was supposed that the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  luminescence centres are localised in the  $\text{Li}^+$  sites, coordinated by  $\text{O}^{2-}$  positionally-disordered anions in the  $\text{Li}_2\text{B}_4\text{O}_7$  glass network that is also characteristic of crystals with the same composition and

other borate glasses and disordered crystals. The multisite character of the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  luminescence centres in the glass and crystal with  $\text{Li}_2\text{B}_4\text{O}_7$  is related to the presence of  $\text{Li}^+$  sites in their structure with different coordination numbers ( $N = 4-7$ ) and statistically-distributed  $\text{RE}^{3+}-\text{O}^{2-}$  distances (positional disorder), which leads to distribution of  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  spectroscopic parameters and is revealed in the inhomogeneous broadening of their spectral lines.

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