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Spectroscopy of the Er-doped lithium tetraborate glasses

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ABSTRACT

The electron paramagnetic resonance (EPR), optical absorption, and luminescence (emission and excitation) spectra as well as luminescence kinetics of the Er-doped glasses with $Li_2B_4O_7$ composition were investigated and analysed. The high optical quality glasses with $Li_2B_4O_7$:Er composition containing 0.5 and 1.0 mol.% Er_2O_3 were obtained from corresponding polycrystalline compound by standard glass synthesis. The EPR spectroscopy in the 4.2–300 K temperature range and optical spectroscopy at 300 K show that the Er impurity is incorporated into the network of $Li_2B_4O_7$ glass as Er^{3+} ($4f^{11}$, $^4I_{15/2}$) ions, exclusively. The local structure of the Er^{3+} luminescence centres in Li sites of the glass network is proposed. Based on the standard Judd–Ofelt theory the oscillator strength (P_{cal}) and experimental oscillator strength (P_{exp}) for observed absorption transitions as well as phenomenological intensity parameters (Ω_2, Ω_4, Ω_6) for Er^{3+} centres in the $Li_2B_4O_7$:Er glass containing 1.0 mol.% Er_2O_3 were calculated. Spectroscopic parameters of relevance for laser applications, including emission probabilities of transitions (W_r), branching ratios (β), and radiative lifetime (τ_{rad}) have been calculated for main observed emission transitions of the Er^{3+} centres in $Li_2B_4O_7$:Er glasses. Experimental and calculated lifetimes were compared and quantum efficiency (η) for green ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition) and infrared ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition) emission bands has been estimated.

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1. Introduction

Spectroscopic investigations of the Er-doped crystals and glasses are related to their wide applications as active elements of the Er^{3+} lasers, amplifiers and up-converters in optical fibres for telecommunication [1–6]. The Er^{3+} ($4f^{11}$, $^4I_{15/2}$) ions in crystals and glasses exhibit green, red, near infrared (NIR) and infrared (IR) Stokes emission bands, which can be used for laser generation [1,2], particularly for eye-safe laser emission at $\lambda_{max} \cong 1.5\ \mu m$ ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition) and $\lambda_{max} \cong 2.9\ \mu m$ ($^4I_{11/2} \rightarrow {}^4I_{13/2}$) with a low threshold action [5,6]. Furthermore, within the Er^{3+} energy level scheme several up-conversion processes can take place resulting in the visible anti-Stokes emission [1,2,7–9]. In particular, the Er^{3+}-doped oxide glasses and compositionally-disordered crystals are perspective materials for active elements for up-converted visible (green) laser with light emitting diode (LED) pumping in the 800–980 nm spectral range [10]. In these reasons, the optical

properties of Er-doped oxide crystals and glasses have been intensively investigated [3–12]. However, in contrast to crystals with well-defined structure, the features of electron paramagnetic resonance (EPR) and optical spectra as well as local structure of the Er^{3+} ions in oxide glasses and crystals with disordered structure, particularly in the borate glasses are studied insufficiently.

The borate glasses with different basic compositions, activated with transition and rare-earth ions are very promising luminescent materials for different applications including laser technology [13–16], because they are characterised by high transparency in wide spectral range, relatively low melting point, high thermal and radiation stability, and good solubility of the transition and rare-earth ions [13,17–19]. The borate glasses of different composition activated with Er^{3+} ions can also be considered as promising luminescent and laser materials in the visible and IR spectral ranges. The results of spectroscopic investigation of the Er-doped borate glasses of different compositions are published in the number of papers [20–29]. First our results of spectroscopic investigation of the $Li_2B_4O_7$:Er glasses have been presented in [30]. Our preliminary results of the EPR and optical spectroscopy of the $Li_2B_4O_7$:Er and other ($LiCaBO_3$:Er and CaB_4O_7:Er) glasses have been reported in [31,32], but the obtained results were not published yet.

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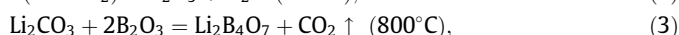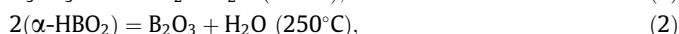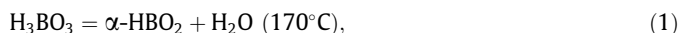
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In this paper the results of EPR and optical spectroscopy as well as local structure of the Er^{3+} centres in glasses with $Li_2B_4O_7:Er$ composition have been presented and analysed.

2. Experimental details

2.1. The synthesis of the borate glasses and samples preparation

The $Li_2B_4O_7:Er$ glasses of high optical quality were obtained in the air from corresponding polycrystalline compound according to standard glass technology [30–33]. For solid state synthesis of the $Li_2B_4O_7$ polycrystalline compound were used the Li_2CO_3 carbonate and boric acid (H_3BO_3) of high chemical purity (Aldrich, 99.999%). The Er impurity was added to the raw materials as Er_2O_3 compound of chemical purity (99.99%) in amounts of 0.5 and 1.0 mol.%. Solid-state synthesis of the $Li_2B_4O_7$ polycrystalline borate compound was carried out using multi-step heating reactions [33], which can be described for $Li_2B_4O_7$ by the following chemical equations:

$$H_3BO_3 = \alpha\text{-}HBO_2 + H_2O \ (170°C), \tag{1}$$

$$2(\alpha\text{-}HBO_2) = B_2O_3 + H_2O \ (250°C), \tag{2}$$

$$Li_2CO_3 + 2B_2O_3 = Li_2B_4O_7 + CO_2 \uparrow \ (800°C), \tag{3}$$

Large samples of the $Li_2B_4O_7:Er$ glasses were obtained by fast cooling of the corresponding melted compounds, heated to more than 100 K above the melting points (T_{melt} = 917 °C (1190 K) for $Li_2B_4O_7$ compound) to make the crystallisation process impossible [33]. The mechanical stresses in the obtained glasses were eliminated by thermal annealing of the samples in 680–730 K temperature range [33].

For EPR investigation the obtained glasses were cut to the approximate size of $3 \times 2 \times 2 \ mm^3$. The glass samples for optical absorption and luminescence measurements were cut and polished to the approximate size of $5 \times 4 \times 2 \ mm^3$.

2.2. The experimental equipment and short characterisation of the glass samples

The X-ray diffraction (XRD) studies of the obtained samples were carried out using the X-ray diffractometer of DRON-3 type (CuK$_\alpha$ line, λ = 1.544 Å). The XRD diffractograms had been measured in the range of $10° < 2\theta < 110°$ by step scanning of 0.015° and rate of 2°/min.

Commercial computer controlled X-band spectrometers RADIO-PAN (models SE/X-2013 and SE/X-2544), operated in the high-frequency (100 kHz) modulation mode of magnetic field were used for EPR spectra registration at room temperature (RT). The paramagnetic impurities in $Li_2B_4O_7:Er$ glasses at low temperatures were detected using the X-band EPR spectrometer BRUKER (model ELEXSYS E-500) completed with helium-flow cryostat (OXFORD Instruments).

The optical absorption spectra were registered at RT using "Varian" (model 5E UV–VIS–NIR) spectrophotometer. Resolution of the spectrophotometer did not exceed 0.2 nm in the UV–VIS and 0.8 nm in the NIR regions. 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 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 range against reference source.

The luminescence decay curves were recorded with a Tektronix (model TDS 3052) digital oscilloscope at RT. Excitation was provided by a Continuum Surelite I Optical Parametric Oscillator (OPO) pumped by a third harmonic of an Nd:YAG laser

(λ = 355 nm) and the emitted light was filtered using a grating monochromator (GDM type) with 1000 mm focal length. The visible emission was detected using a Hamamatsu R928 photomultiplier and an EG&G InSb detector was used to detect luminescence in the NIR region.

The obtained $LiB_4O_7:Er$ samples show typical glassy-like XRD pattern similar as for Sm-doped borate glasses [19] without any discrete sharp peaks that confirm their disordered glass structure. One can notice that the un-doped $Li_2B_4O_7$ glasses are transparent approximately in the 300–2500 nm spectral region. The Er-doped $Li_2B_4O_7$ glasses are almost uncoloured and characterised by a high optical quality. The Er dopant concentrations in the obtained glasses have been proved by X-ray energy dispersive spectroscopy (EDS) using scanning electron microscope REMMA-102-02 (Selmi, Ukraine). The EDS of investigated glasses confirms the presence of the Er_2O_3 impurity in amounts about 0.5 and 1.0 mol.% for corresponding $Li_2B_4O_7$ glasses. Thus, the coefficient of incorporation of the Er impurity into the lithium tetraborate glass network is close to unity.

3. Results and discussion

3.1. The EPR spectra of $Li_2B_4O_7:Er$ glasses

The erbium impurity can be incorporated into the structure of different oxide compounds such as paramagnetic Kramers Er^{3+} ($4f^{11}$, $^4I_{15/2}$) and/or non-Kramers Er^{2+} ($4f^{12}$, $^3H_6$) ions, which can reveal in their characteristic EPR, optical absorption and luminescence spectra. The EPR spectra of the non-S-state Kramers rare-earth ions (Ce^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+}, Yb^{3+}) in glasses and other disordered compounds were not satisfactorily studied yet. According to [34], the X-band EPR spectra of the non-S-state Kramers rare-earth ions in zeolites, which belong to disordered polycrystalline compounds, consist of extremely broad asymmetric signals, which can be observed only at liquid helium temperature (T = 4.2 K). Up to now the Er^{3+} EPR spectra in oxide glasses were reported only in several papers [35–37]. In [35] it was shown that EPR spectra of Er^{3+} ions in the $Na_2O–SiO_2$ and $PbO–SiO_2$ glasses at T = 4.2 K consist of the resonance signals with g = 8.5–8.6 and g = 7.6–6.8, respectively. Broad EPR signal at about 80 mT due to Er^{3+} ions was observed in the $Na_2O–GeO_2$ glasses at liquid-helium temperature [36]. The EPR signal with g = 8.62947 ± 0.0759 observed at liquid helium temperatures in soda-lime silicate glasses of the compositions (in mol.%) (65-x)SiO_2:25Na_2O:10CaO:xEr_2O_3 (where x = 0.02, 0.05, 0.1, 0.3, 0.5, 1, 2, 3, 4, and 5) was assigned to the Er^{3+} ions [37]. Before our work the referenced data on EPR spectroscopy of the Er^{3+} ions in borate glasses were absent.

In the EPR spectra of our un-doped and doped with transition and rare-earth elements borate glasses at RT observed intense sharp signal with effective g-factor $g_{eff} \cong 4.26$ and relatively weak signal with $g_{eff} \cong 2.00$ [17,38,39]. Sharp EPR signal with $g_{eff} \cong 4.26$ is characteristic of glassy compounds and belongs to the single (isolated) Fe^{3+} ($3d^5$, $^6S_{5/2}$) non-controlled impurity ions, localised in octahedral and/or tetrahedral sites of the glass network with a strong rhombic distortion [40–43], whereas the EPR signal with $g_{eff} \cong 2.00$ belongs to the Fe^{3+} isolated ions in the glass network sites with nearly cubic local symmetry [40,43] or $Fe^{3+} – Fe^{3+}$ pair centres and their small clusters, coupled by magnetic dipolar and exchange interactions [17,39].

In EPR spectra of the $Li_2B_4O_7:Er$ glasses at liquid helium temperatures, besides the Fe^{3+} EPR signals with $g_{eff} \cong 4.26$ and $g_{eff} \cong 2.00$, there are observed additional EPR signals with $g_{eff} \cong 9.78$ and $g_{eff} \cong 2.01$ (Fig. 1). The increase of Er_2O_3 content in the glass composition leads to increasing the integral intensity of EPR signals with $g_{eff} \cong 9.78$ (see Fig. 1, spectra a and b). The asymmetric broad