



Spectroscopic properties of the Ce-doped borate glasses



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ABSTRACT

The EPR, optical absorption and photoluminescence (emission and excitation) spectra as well as decay kinetics of a series of the Ce-doped glasses with Li₂B₄O₇, LiKB₄O₇, CaB₄O₇, and LiCaBO₃ compositions have been investigated and analysed. The borate glasses were obtained from the corresponding polycrystalline compounds in the air atmosphere, using standard glass technology. The EPR signals of the isolated Ce³⁺ and pair Ce³⁺–Ce³⁺ centres, coupled by magnetic dipolar and exchange interactions were registered at liquid helium temperatures. The characteristic for glass host broad bands corresponding to the 4*f* → 5*d* transitions of the Ce³⁺ centres have been observed in the optical absorption and photoluminescence (emission and excitation) spectra. The obtained luminescence decay curves can be satisfactorily described by exponential function with lifetimes in the 19.8–26.1 ns range, which depend on the basic glass composition. The local structure of Ce³⁺ centres in the investigated glasses has been considered and discussed.

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1. Introduction

In recent years, the study of borate crystals and glasses represents considerable interest due to their attractive optical and physical properties and wide practical applications. In particular, the borate compounds, un-doped and doped with rare-earth and transition elements, are very promising materials for nonlinear optics, quantum electronics and laser technology [1–3], scintillators and thermoluminescent dosimeters [4,5], detectors and transformers of the ionising radiation [6,7], and many other applications [8].

From the technological point of view the glassy (or vitreous) borate compounds are more promising materials than their crystalline analogues because the growth of borate single crystals is a difficult, long-term and, consequently, very expensive process. Hence, borate glasses represent potential materials due to low cost production, high chemical and physical stability, and good solubility of doping rare-earth and transition elements.

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have been very promising due to its relatively high light output and short luminescence decay time. Thus, Ce³⁺-doped glasses are used as efficient phosphors in the near UV, violet, and blue spectral regions and fast scintillators for detection of the X- and γ-rays as well as neutrons [9,10]. Beside wide practical applications the Ce³⁺ ions can be used as a probe of the local crystal field, ion-lattice, and ion–ion interactions [11].

It should be noted that cerium can be incorporated into oxide glasses in two valence states, Ce³⁺ and Ce⁴⁺, and their ionic equilibrium depends on the conditions of glass formation and the type and composition of glass system [12]. Tetravalent (Ce⁴⁺) ions not show luminescence due to closed electronic shell, whereas a broad charge transfer (Ce⁴⁺ + e⁻ → Ce³⁺) band appears in the UV–Vis region of the optical absorption spectra [13].

The Ce³⁺ ions (4*f*¹ electron configuration) show efficient luminescence in the UV–Vis spectral region due to allowed 5*d*–4*f* transitions. The emission occurs from the lowest crystal field component of the 5*d* configuration to the ²F_{5/2} and ²F_{7/2} levels of the 4*f* configuration, separated around 2000 cm⁻¹ due to spin–orbit coupling [14]. The wavelength position of the 5*d*–4*f* transitions depends strongly on the nature and structure of host through the crystal-field splitting of the 5*d* configuration and widely varies from near UV to red regions [15]. The decay time of the Ce³⁺ emission is very short (10⁻⁷–10⁻⁸ s) due to parity and

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spin-allowed $5d-4f$ transitions [14].

Optical properties of the Ce-doped lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) crystal and glass were investigated in Ref. [16]. The Ce-doped $\text{Li}_2\text{B}_4\text{O}_7$ single crystal show emission peaked at 365 nm and two excitation bands at 260 and 330 nm, whereas in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Ce}$ glass emission band peaked at 350 nm are efficiently excited around 290 nm. Similar luminescence band around 400 nm with decay time 36 ns appears under both 275 and 345 nm excitation in the $\text{Ca}_3(\text{BO}_3)_2$ crystals [17]. The emission of Ce-doped PbB_4O_7 glass-ceramics excited at 350 nm shows one broad band with maximum at 480 nm [18].

Optical properties of the Ce^{3+} -doped phosphate, borate, silicate and germanate glasses were investigated and analysed in Ref. [19]. It was found that highest intensity of the excitation and emission bands were observed in borate glasses in comparison with other three glass systems. Fluorescence spectra of Ce^{3+} in silicate, borate, and phosphate glasses excited at 266 nm show asymmetric broad band with maximum between 280 and 500 nm that depend on glass composition [20]. According to [21], the luminescence properties of Ce^{3+} in silica-based (borosilicate, phosphosilicate, borophosphosilicate) glasses are strongly affected by presence of B and P former elements. Decay times equal 54 ns and 58 ns for Ce-doped silicate and borosilicate glasses. For borophosphosilicate and phosphosilicate glasses the lifetime values lowering from 32 to 29 ns and from 29 to 25 ns, respectively, while Ce molar ratio increases from 10^{-4} to 10^{-2} [21].

In the $x\text{CeO}_2-20\text{PbO}-(80-x)\text{B}_2\text{O}_3$ glass was observed broad emission bands peaked at 482 and 514 nm under excitation at 380 nm [22]. Photoluminescence spectrum of the Ce-doped lithium-alumino-borate glass upon 290 nm excitation exhibit a broad band at 360 nm with lifetimes 25 ± 2 ns [23]. The fluorescence spectrum of barium-sodium borate glass shows weakly-resolved band at 367 nm upon 306 nm excitation [24]. Also one broad emission band at 338 nm with lifetime $\tau = 28.5$ ns was observed upon 270 nm excitation in the Ce-doped $57.5\text{Li}_2\text{O}-5\text{B}_2\text{O}_3-37.5\text{P}_2\text{O}_5$ glass [25]. Under excitation at 347 nm, the photoluminescence spectrum of the $\text{NaCaBO}_3:0.01\text{Ce}^{3+}$ powder sample shows an asymmetric emission band that extends from 350 to 550 nm with a maximum at 427 nm [26]. Similar results were obtained in Ref. [27] for $\text{LiCaBO}_3:\text{Ce}^{3+}$ polycrystalline compounds, in which the emission spectrum upon 365 nm excitation shows one asymmetric band at 428 nm.

Analysis of the available referenced data shows that spectroscopic and luminescence properties of the lithium and calcium borate glass are studied insufficiently. In particular, very limited studies have been done for Ce-doped $\text{Li}_2\text{B}_4\text{O}_7$ glass, whereas $\text{LiKB}_4\text{O}_7:\text{Ce}$, $\text{CaB}_4\text{O}_7:\text{Ce}$, and $\text{LiCaBO}_3:\text{Ce}$ glasses have not been investigated yet. Therefore, the main aim of this work is an investigation of the features of the spectroscopic and luminescence properties of a series borate glasses with $\text{Li}_2\text{B}_4\text{O}_7:\text{Ce}$, $\text{LiKB}_4\text{O}_7:\text{Ce}$, $\text{CaB}_4\text{O}_7:\text{Ce}$, and $\text{LiCaBO}_3:\text{Ce}$ compositions and different Ce concentrations as well as determination of the electron and local structures of the Ce luminescence centres in those glasses using EPR and optical spectroscopy methods, supported by corresponding X-ray diffraction (XRD) structural data.

2. Experimental details

2.1. The glass synthesis and samples preparation

The Ce-doped borate glasses with $\text{Li}_2\text{B}_4\text{O}_7$ ($\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$), LiKB_4O_7 ($0.5\text{Li}_2\text{O}-0.5\text{K}_2\text{O}-2\text{B}_2\text{O}_3$), CaB_4O_7 ($\text{CaO}-2\text{B}_2\text{O}_3$), and LiCaBO_3 ($0.5\text{Li}_2\text{O}-\text{CaO}-0.5\text{B}_2\text{O}_3$) were obtained in the air atmosphere from corresponding polycrystalline compounds according to the standard glass synthesis method and technological

conditions according to [28]. For solid-state synthesis of the polycrystalline compounds were used carbonates (Li_2CO_3 , K_2CO_3 , CaCO_3) and boric acid (H_3BO_3) of high chemical purity (99.999%, Aldrich). The cerium impurity was added to the raw materials as Ce_2O_3 oxide of chemical purity (99.99%). Solid-state synthesis of the polycrystalline borate compounds was performed using multi-step heating reactions, presented elsewhere [28,29].

Large samples of borate glasses with $\text{Li}_2\text{B}_4\text{O}_7:\text{Ce}$, $\text{LiKB}_4\text{O}_7:\text{Ce}$, $\text{CaB}_4\text{O}_7:\text{Ce}$, and $\text{LiCaBO}_3:\text{Ce}$ compositions were obtained by fast cooling of the corresponding melts, heated more than 100 K above the melting points ($T_{\text{melt}} = 917$ °C (1190 K), 807 °C (1080 K), 980 °C (1253 K), and 777 °C (1050 K) for $\text{Li}_2\text{B}_4\text{O}_7$, LiKB_4O_7 , CaB_4O_7 , and LiCaBO_3 compounds, respectively) to make the crystallisation process impossible [28]. The glass samples for optical measurements were cut and polished to the approximate size of $8 \times 5 \times 2$ mm³. For EPR investigation the glass samples were cut to the approximate size of $3 \times 2 \times 2$ mm³.

2.2. Experimental equipment and samples characterisation

The paramagnetic impurities in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Ce}$, $\text{LiKB}_4\text{O}_7:\text{Ce}$, $\text{CaB}_4\text{O}_7:\text{Ce}$, and $\text{LiCaBO}_3:\text{Ce}$ glasses were detected in the 4.2–50 K temperature range using the X-band EPR spectrometer Bruker (model ELEXSYS E-500) completed with helium-flow cryostat (Oxford Instruments).

The optical absorption spectra of the investigated glasses were recorded with usage Shimadzu UV–Vis spectrophotometer (model UV-2450). The luminescence excitation and emission spectra were registered in the UV and visible spectral ranges using a Horiba spectrofluorimeter (model FluoroMax-4).

The luminescence kinetics was investigated using the special equipment for time-resolved luminescence [30]. The experimental setup consists of laser system as the excitation source, which includes the PL 2143 A/SS laser and the parametric optical generator PG 401/SH that generates 30 ps laser pulses with frequency 10 Hz. The detection part consists of the spectrograph 2501S (Bruker Optics) and the Hamamatsu Streak Camera (model C4334-01).

The investigated Ce-doped borate glasses are almost uncoloured and characterised by a high optical quality. The nominal cerium concentrations in the obtained glasses have not been proved analytically, but our previous investigation [29] has shown that the incorporation coefficient of rare-earth impurities into the borate glass network is close to unity.

The X-ray diffraction studies were carried out using computer controlled X-ray diffractometer (model DRON-3) with monochromatic $\text{Cu K}\alpha$ line. The XRD patterns of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Ce}$, $\text{LiKB}_4\text{O}_7:\text{Ce}$, $\text{CaB}_4\text{O}_7:\text{Ce}$, and $\text{LiCaBO}_3:\text{Ce}$ borate glasses are shown in Fig. 1. The obtained XRD patterns confirm disorder glass structure of the investigated samples.

3. Results and discussion

3.1. EPR spectroscopy of the Ce-doped borate glasses

The Ce impurity can be incorporated in the structure of oxide crystals and glasses as Ce^{3+} ($4f^1$, $^2F_{5/2}$) paramagnetic Kramers ions and Ce^{4+} ($[\text{Xe}]4f^0$, 1S_0) non-paramagnetic ions. So, only Ce^{3+} ions can be observed by EPR spectroscopy. Registration and identification of the Ce^{3+} centres in the EPR spectra of glasses is not easy due to the following reasons. First, the spin-lattice relaxation times of the rare-earth ions (with exception of the S-state Kramers $4f^7$ ($^8S_{7/2}$) ions – Eu^{2+} , Gd^{3+} , Tb^{4+}) are very short for observation EPR lines at room and liquid nitrogen temperatures. Second, the experimental g -factor values for Ce^{3+} ions in crystal fields of different symmetry vary in a wide range, as reported for single crystal

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