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Luminescence properties and quantum efficiency of the Eu-doped borate glasses

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ABSTRACT

The luminescence and radiative properties of the Eu-doped borate glasses with $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ basic compositions have been investigated and analysed. The borate glasses of high chemical purity and optical quality, doped with Eu_2O_3 in amounts of 0.5 and 1.0 mol. % were obtained from the corresponding polycrystalline compounds in the air atmosphere using standard glass synthesis technology. The spectroscopic and radiative properties of obtained Eu-doped glasses were studied using electron paramagnetic resonance (EPR), optical absorption, photoluminescence (excitation and emission spectra, decay kinetics) techniques, and modified Judd–Ofelt analysis. The photoluminescence spectra of the Eu-doped borate glasses reveal intense emission bands, which correspond to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0 \div 4$) transitions of Eu^{3+} ions. The observed luminescence decay curves are satisfactory described in the framework of single exponential approximation with lifetimes, which lie in the 2.04 ÷ 2.26 ms range. The Judd–Ofelt intensity parameters (Ω_λ) for Eu^{3+} centres in the investigated glasses were calculated from their luminescence emission spectra. Radiative lifetimes and internal quantum efficiencies were estimated for observed emission transitions of the Eu^{3+} centres in the investigated glasses. External quantum yield of luminescence was measured experimentally via an absolute method. The high calculated internal quantum efficiency (~50%) and relatively high measured external quantum yield (~11%) of the Eu^{3+} luminescence show that the $Li_2B_4O_7$:Eu, CaB_4O_7:Eu, and $LiCaBO_3$:Eu glasses belong to perspective luminescent materials.

1. Introduction

In recent years, the study of borate glasses presents considerable interest due to their interesting optical, structural, and physical properties [1–9]. This interest caused by the fact that the glassy (or vitreous) borate compounds are more promising materials than their crystalline analogues due to simple and inexpensive producing technology and high coefficient of incorporation of the rare-earth ions.

Attractive optical properties and high luminescence efficiency of the rare-earth doped materials opened new possibilities for their different practical application e.g. in new light sources, lasers, display and telecommunication devices, energy transformers, sensors, *etc.* [10,11]. Wide practical applications of the rare-earth doped glasses and crystals stimulate the search of new materials and detailed investigation of their luminescence properties.

The Eu-doped oxide glasses, in particular, borate glasses are efficient luminescent materials with high emission quantum yield and high thermal and chemical stability in the air [1]. In order to obtain suitable characteristics for practical applications, the influence of glass host as well as impurity concentration is essential. Special interest from scientific and practical points of view present borate glasses with $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ compositions, which are similar to the well-known crystalline analogues [7–9].

In general case the europium impurity can be incorporated into the structure of oxide compounds in two valence states: Eu^{3+} ($4f^6$, $^7F_0$) and Eu^{2+} ($4f^7$, $^8S_{7/2}$). Both ions, Eu^{3+} and Eu^{2+}, are characterised by efficient photoluminescence [11].

The luminescence of Eu^{3+} ions arises from the $4f - 4f$ intra-configurational transitions. The emission spectra of trivalent europium consist of several sharp bands, which belong to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0 \div 6$) transitions. Luminescence of Eu^{3+} ions are localised in the red spectral range and characterised by lifetimes in the

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order of several milliseconds [11,12]. The fine structure and the relative intensities of Eu^{3+} transitions in the absorption and luminescence spectra can be used as probe the local environment of the Eu^{3+} ions in different compounds [12].

Emission spectra of divalent europium usually consist of a broad band that belongs to $4f^65d^1 \rightarrow 4f^7$ interconfigurational transition. Wavelength position of Eu^{2+} emission strongly depends on the host composition and can vary from ultraviolet up to yellow spectral range. The lifetime value of the Eu^{2+} luminescence equals a few microseconds [11,12].

Up to now, the optical and luminescent properties of the glassy Eu-doped borate compounds with different chemical compositions have been extensively investigated and published in number papers [13–21]. In particular, were reported the spectroscopic properties of Eu-doped lithium borate [13–15], lithium fluoroborate [13], calcium borate [16,17], lithium calcium borate [16], strontium borate [18,19], lanthanum borate [20], and zinc borate [21] glasses. Usually, the optical absorption, excitation and emission spectra of investigated borate glasses are presented in these papers. It should be noted that all abovementioned referenced data show presence of Eu^{3+} ions, exclusively.

Reduction of Eu^{3+} ions to the divalent state in borate compounds was studied in Refs. [22–27]. Particularly, it was demonstrated that the synthesis conditions and host-matrix properties crucially determine the valence state of europium and the luminescence characteristics of the relevant material [22–27]. It should be noted that Eu^{3+} ions can be obtained in borate crystals growing in the air atmosphere [23,24]. Obtaining of Eu^{2+} ions in borate glasses is a more complicated task and need special synthesis conditions [25,26]. Only a small part of Eu^{3+} ions can be transformed to the Eu^{2+} state during glass synthesis in the reducing atmosphere [27].

The present article reports the luminescence properties of a series Eu-doped borate glasses with $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ compositions. The fine structure and the relative intensities of observed transitions were used in order to characterise the local environment of Eu^{3+} ion in the investigated borate glasses. The present work also is focused on the evaluation of internal quantum efficiency and external quantum yield of the Eu-doped borate glasses.

2. Experimental details

2.1. Glass synthesis and samples preparation

The Eu-doped borate glasses with $Li_2B_4O_7$ ($Li_2O - 2B_2O_3$), CaB_4O_7 ($CaO - 2B_2O_3$), and $LiCaBO_3$ ($0.5Li_2O - CaO - 0.5B_2O_3$) composition were obtained in the air atmosphere from the corresponding polycrystalline compounds according to standard glass synthesis method and technological conditions, which are described in Ref. [28]. Quantitative composition of the $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ glasses can be also written as $33.33Li_2O - 66.66B_2O_3$, $33.33CaO - 66.66B_2O_3$, and $25Li_2O - 50CaO - 25B_2O_3$, respectively.

Carbonates (Li_2CO_3 and $CaCO_3$) and boric acid (H_3BO_3) of high chemical purity (99.999%, Aldrich) were used for solid-state synthesis of the polycrystalline compounds. The europium impurity was added to the raw materials as Eu_2O_3 oxide of chemical purity (99.99%) in amounts of 0.5 and 1.0 mol. %.

Solid-state synthesis of the polycrystalline borate compounds was performed using multi-step chemical reactions [28], which can be described by the following equations:

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

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

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

$$CaCO_3 + 2B_2O_3 = CaB_4O_7 + CO_2\uparrow\ (900\,^{\circ}C) \tag{4}$$

$$Li_2CO_3 + 2CaCO_3 + B_2O_3 = 2LiCaBO_3 + 3CO_2\uparrow\ (700\,^{\circ}C) \tag{5}$$

Large samples of the Eu-doped $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ glasses were obtained by fast cooling of the corresponding melts, heated more than 100 K above the melting points ($T_{melt} = 917\,^{\circ}C$ (1190 K), 980 °C (1253 K), and 777 °C (1050 K) for $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ compounds, respectively) for blocking the crystallisation process [28]. For EPR investigations the glass samples were cut to the approximate size of $(5 \times 3 \times 2)\ mm^3$. The glass samples for optical measurements were cut and polished to the approximate size of $(10 \times 5 \times 2)\ mm^3$.

2.2. Experimental equipment

The optical absorption spectra were recorded with usage Cary 5000 ("Agilent Technologies") UV–Vis–NIR spectrophotometer. The luminescence (excitation and emission) spectra and the luminescence decay curves were registered in the UV and visible spectral ranges at T = 300 K using a FluoroMax–4 ("Horiba") spectrofluorimeter. Quantum yield was measured using Hamamatsu Absolute PL quantum yields measurement system (model C9920-02G). The X-ray diffraction (XRD) studies were carried out with usage computer controlled X-ray diffractometer of DRON-3 type. The paramagnetic impurities in the investigated glasses were detected with the EPR technique using modernised X-band radiospectrometer SE/X-2013 ("RADIOPAN", Poland).

3. Results and discussion

3.1. XRD and EPR characterisation

The X-ray diffraction patterns of the $Li_2B_4O_7$:Eu, CaB_4O_7:Eu, and $LiCaBO_3$:Eu glasses containing 1.0 mol. % Eu_2O_3 are shown in Fig. 1. The absence of discrete sharp peaks in the XRD patterns confirms disordered glassy (or vitreous) structure of the investigated glasses.

The europium impurity can be incorporated into the structure of different oxide compounds as paramagnetic Kramers Eu^{2+} ($4f^7$, $^8S_{7/}$

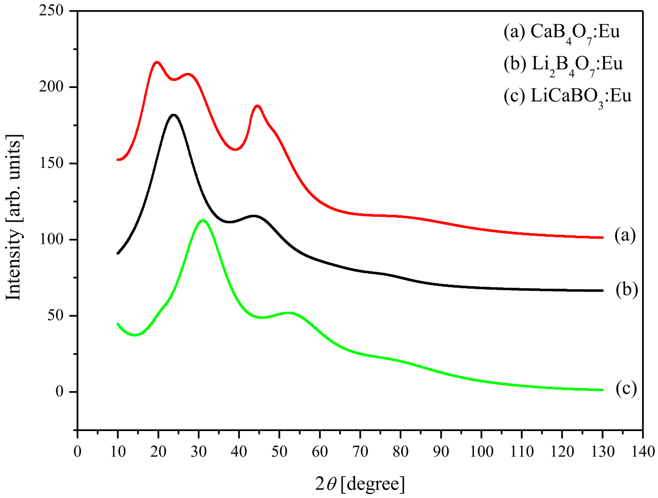

Fig. 1. The XRD patterns of the CaB_4O_7:Eu (a), $Li_2B_4O_7$:Eu (b), and $LiCaBO_3$:Eu (c) glasses containing 1.0 mol. % Eu_2O_3.