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Judd–Ofelt analysis and radiative properties of the Sm^{3+} centres in $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ glasses

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ABSTRACT

The spectroscopic and luminescence properties of a series Sm-doped $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ borate glasses are investigated using optical absorption, photoluminescence, and decay kinetics techniques as well as Judd–Ofelt (J–O) analysis. Borate glasses of high chemical purity and optical quality, doped with Sm_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 J–O intensity parameters have been calculated using the spectral intensities of the Sm^{3+} absorption bands. Radiative properties such as transition probabilities, branching ratios, stimulated emission cross-sections, and radiative lifetimes are estimated for $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, and 11/2) emission transitions of the Sm^{3+} ions. The luminescence kinetics of the Sm^{3+} centres are characterised by slightly non exponential decay with lifetime values, which depend on the basic glass composition and Sm impurity concentration. The measured lifetimes were compared with those calculated and quantum efficiencies have been estimated. The obtained high quantum efficiencies of emission transitions (~70%) and high quantum yields of luminescence (~14%) of the Sm^{3+} centres show that the investigated borate glasses belong to perspective luminescent and laser materials.

1. Introduction

In recent years, the study of borate glasses presents considerable interest due to their interesting structural, optical, and physical properties [1–8]. 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, high thermal stability, 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 lasers, energy transformers, telecommunication, biomedicine, display devices, sensors, etc. [9]. Wide practical applications of the rare-earth doped glasses and crystals stimulate the search of new materials and investigation of their luminescence properties.

The intensity of transitions of the rare-earth ions can be calculated using the Judd–Ofelt (J–O) theory [10,11]. This theory defines a set of 3 phenomenological parameters (Ω_2, Ω_4, and Ω_6), which are sensitive to the local environment of the rare-earth ions in the crystal lattice or glass network. The Ω_2, Ω_4, and Ω_6 intensity parameters can be used for calculation of the radiative transition probabilities for spontaneous emission, radiative lifetimes of the excited state, branching ratios, and stimulated emission cross-sections of the various emission lines. All these data are essentially required in order to obtain the best ion-host configuration and improve the luminescence efficiency of specific electronic transitions in the developing materials for lasers and other optical devices.

The Sm-doped oxide glasses, in particular, the borate glasses are efficient luminescent materials with high emission quantum yield at room temperature and high thermal and chemical stability in the air [12]. The photoluminescence spectra of the Sm^{3+} centres in glasses and crystals reveal intense characteristic green, orange, and red emission bands, which correspond to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ emission transitions and can be used in new light sources, fluorescent display devices,

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UV-sensors, and visible lasers [13–16]. The large energy gap between the metastable $^4G_{5/2}$ state and the next lower level of the Sm^{3+} ions has the advantage that their multiphonon relaxation rate is quite low and hence quantum efficiency is relatively high [17].

Spectroscopic and luminescence properties of the Sm^{3+} ions already have been investigated in a various glass hosts [13–28], such as borate [18], lithium borate [19,20], lithium fluoroborate [20], lithium aluminoborate [13,14], lithium calcium borate [21], lithium lead borate [21], lithium calcium barium borate [22], lithium zinc borate [23], lead fluoroborate [24], sodium fluoroborate [16,25], lithium strontium bismuth borate [17], bismuth borate [26], zinc bismuth borate [27], and zinc alumino bismuth borate [28] glasses.

In order to obtain suitable characteristics for practical applications, the influence of glass host as well as impurity concentration is essential. Variation of structural properties of the alkali or alkaline earth borate glasses [4] allows investigating the relationship between the glass composition, impurity concentration and luminescent efficiency. 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 [4–8].

The present article reports the spectroscopic properties of a series Sm-doped borate glasses with $Li_2B_4O_7$, CaB_4O_7, and $LiCaBO_3$ compositions, obtained by optical absorption, photoluminescence, and decay kinetics techniques. In order to predict radiative properties such as radiative transition probabilities, radiative lifetimes, branching ratios, and emission cross-sections the detailed J–O analysis has been carried out. The present work mainly is focused on the search of suitable Sm^{3+}-doped glassy-like luminescent materials, which exhibit superior optical and radiative properties.

2. Experimental details

2.1. The glass synthesis and samples preparation

The Sm-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–$0.5B_2O_3$) compositions were obtained in the air atmosphere from the corresponding polycrystalline compounds according to standard glass synthesis method and technological conditions, which are described in [4]. 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.

For solid-state synthesis of the polycrystalline compounds were used carbonates (Li_2CO_3 and $CaCO_3$) and boric acid (H_3BO_3) of high chemical purity (99.999%, Aldrich). The samarium impurity was added to the raw materials as Sm_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 heating reactions [4], which can be described by the following chemical equations:

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

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

$$Li_2CO_3 + 2B_2O_3 = Li_2B_4O_7 + CO_2\uparrow \ (800\ ^\circ C) \quad (3)$$

$$CaCO_3 + 2B_2O_3 = CaB_4O_7 + CO_2\uparrow \ (900\ ^\circ C) \quad (4)$$

$$Li_2CO_3 + 2CaCO_3 + B_2O_3 = 2LiCaBO_3 + 3CO_2\uparrow \ (700\ ^\circ C) \quad (5)$$

Large samples of the Sm-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 °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) to make the crystallisation process impossible [4]. Two types of crucibles, graphite (C) and corundum ceramic (Al_2O_3), were used for producing of borate glasses. Optical quality of the obtained glasses practically was independent of the type of crucibles. The glass samples for optical investigations were cut and polished to the approximate size of $5 \times 4 \times 2\ mm^3$.

2.2. Experimental equipment and glass samples characterisation

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 Sm dopant concentrations in the obtained glasses have been proved by X-ray energy dispersive spectroscopy (EDS) using REMMA-102-02 ("Selmi") scanning electron microscope. The EDS of investigated glasses confirms the presence of Sm_2O_3 in amounts 0.5 and 1.0 mol.% for corresponding samples. Thus, the coefficient of incorporation of the samarium impurities into the borate glass network is close to unity.

The X-ray diffraction (XRD) studies were carried out using the computer controlled X-ray diffractometer of DRON-3 type with monochromatic Cu Kα line. The XRD diffractograms had been recorded in the range of $10° < 2\theta < 110°$ by step scanning of 0.015° and rate of 2°/min. The XRD patterns of the $Li_2B_4O_7$:Sm, CaB_4O_7:Sm, and $LiCaBO_3$:Sm glasses containing 1.0 mol.% Sm_2O_3 are shown in Fig. 1. The absence of discrete sharp peaks in the XRD patterns confirms the disorder glassy structure of the investigated samples.

The obtained Sm-doped borate glasses are almost uncoloured and characterised by a high optical quality. The refractive indices have been measured within 400–700 nm spectral range for $Li_2B_4O_7$:Sm, $LiCaBO_3$:Sm, and CaB_4O_7:Sm glasses at selected wavelengths using liquid immersion method. The data were fitted by least squares to the Sellmeier equations and were used in J–O calculations. The densities of the $Li_2B_4O_7$:Sm, $LiCaBO_3$:Sm, and CaB_4O_7:Sm glasses containing 1.0 mol.% Sm_2O_3 were measured by the Archimedes method. The thickness (d), density (ρ), average molar mass ($\overline{M}$), refractive index (n) and reflection loss ($R = ((n-1)/(n+1))^2$) at λ = 589.3 nm as well as Sellmeier

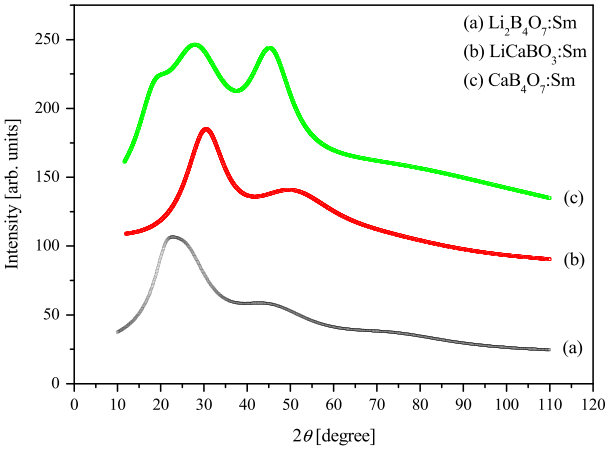

Fig. 1. The XRD patterns of the $Li_2B_4O_7$:Sm (a), $LiCaBO_3$:Sm (b), and CaB_4O_7:Sm (c) glasses containing 1.0 mol.% Sm_2O_3, registered at T = 300 K.