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Spectroscopy of the CaB_4O_7 and $LiCaBO_3$ glasses, doped with terbium and dysprosium

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ABSTRACT

A series of borate glasses of high optical quality with CaB_4O_7:Tb, $LiCaBO_3$:Tb, CaB_4O_7:Dy, and $LiCaBO_3$:Dy compositions containing 0.5 and 1.0 mol% Tb_2O_3 and Dy_2O_3 impurity compounds were obtained from corresponding polycrystalline compounds using standard glass technology. By electron paramagnetic resonance (EPR) and optical spectroscopy it was shown that the Tb and Dy impurities are incorporated as Tb^{3+} ($4f^8$, $^7F_6$) and Dy^{3+} ($4f^9$, $^6H_{15/2}$) ions in the Ca and Li(Ca) sites of CaB_4O_7 and $LiCaBO_3$ glasses network, respectively. The luminescence excitation and emission spectra as well as luminescence kinetics of the Tb^{3+} and Dy^{3+} centres in the CaB_4O_7 and $LiCaBO_3$ glasses have been investigated and analysed in comparison with obtained earlier results for Tb^{3+} and Dy^{3+} centres in the $Li_2B_4O_7$ glasses. All observed *f*–*f* transitions of the Tb^{3+} and Dy^{3+} centres in the luminescence excitation and emission spectra have been identified. Luminescence kinetics show single exponential decay for Tb^{3+} and Dy^{3+} centres in the CaB_4O_7 and $LiCaBO_3$ glass network. The lifetime values for the main emitting levels of the Tb^{3+} and Dy^{3+} centres in all investigated glasses were determined at room temperature and their dependencies on the basic glass compositions and impurity concentrations are discussed. The obtained results show that the CaB_4O_7 and $LiCaBO_3$ glasses are promising luminescent materials, operating in green and yellow–blue spectral regions, when activated with Tb^{3+} and Dy^{3+} ions, respectively.

1. Introduction

The investigation of electron and local structure of the impurity luminescence and paramagnetic centres including intrinsic point defects in glasses and other disordered compounds is still an attractive and interesting problem of modern solid state physics and spectroscopy of the functional materials. The rare-earth ions (Eu^{3+}, Eu^{2+}, Er^{3+}, Nd^{3+}, Tm^{3+}, Sm^{3+}, Yb^{3+}, etc.) show high luminescence efficiency in the UV–vis–IR spectral ranges in a variety host compounds and can be used as activator centres in laser and luminescent materials, including borate crystals and glasses with different compositions [1–6]. In particular, the borate compounds activated with Tb^{3+} and Dy^{3+} are considered as effective luminescent materials for green and yellow–blue spectral ranges, respectively.

The electron paramagnetic resonance (EPR) and optical spectroscopy allows investigating the electron and local structure of the paramagnetic and luminescence centres in single crystals and glasses. Clear interpretation of EPR and optical spectra and derivation from experimental spectra electron and local structure of the luminescence and paramagnetic centres in glasses needs structural and spectroscopic data for their crystalline analogies [7–9]. The borate compounds represent appropriate host materials for different practical applications and investigation of the nature and structure of luminescence and paramagnetic centres in them, because practically all borates can be obtained in both crystalline and glassy (or vitreous) phases. Furthermore, from a technological point of view, the vitreous borate compounds are most perspective in comparison with their crystalline analogies, because the growth of borate single crystals is a difficult, expensive and long-term process. Besides this, the very low velocity of the borate crystals growth and the high viscosity of the melt lead to problems with doping of the borate crystals by rare-earth and transition elements. These problems are absent in the borate glasses.

At the present time the luminescence properties of Tb- and Dy-doped borate compounds and their potential applications are described in a number of papers [10–21]. Particularly, in [10] the synthesis of the SrB_4O_7:Eu, Tb polycrystalline phosphors and luminescence properties of the Eu^{3+}, Eu^{2+}, and Tb^{3+} centres in them was described. It was found that the valence state of Eu is influenced by Tb and the relative intensity of the Eu^{2+} emission in comparison with Eu^{3+} emission is increased when Tb^{3+} is incorporated in the SrB_4O_7:Eu compound [10]. In [11] the synthesis, optical and luminescence properties of the un-doped and Tb, Cu, Ce, Sm, Eu, Tm, and Yb doped lithium tetraborate ($Li_2B_4O_7$) glasses and their scintillation characteristics for registration of the neutrons ($E_n \leq 10$ MeV) and the ^{60}Co γ radiation were reported. Luminescence excitation and emission spectra of the $LiCaBO_3$:M^{3+} ($M^{3+} = Eu^{3+}$, Sm^{3+}, Tb^{3+}, Ce^{3+}, Dy^{3+}) polycrystalline compounds as promising phosphors for white light emitted diodes (LED) are investigated in [12]. The

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compositional and temperature dependences of the optical and fluorescence properties of Dy^{3+} centres in borate glasses with (95 − x) B_2O_3–x Na_2O–5 CaO compositions were investigated and analysed using the Judd–Ofelt theory in [13]. Optical properties and their anomalous temperature variations in [13] are discussed combined with the change of radiative decay rate of the Dy^{3+} ions in borate glasses. In [14] spectroscopic properties of lithium borate ((99 − x) Li_2CO_3 + x H_3BO_3 + 1 Dy_2O_3, where x = 39.5, 49.5, 59.5, and 69.5) and lithium fluoroborate (xLi_2CO_3 + (49.5 − x) LiF + 49.5 H_3BO_3 + 1 Dy_2O_3, where x = 24.75, and 0) glasses were investigated and analysed using the Judd–Ofelt theory and dependencies of Dy^{3+} spectral characteristics due to compositional changes of the glasses are examined. In [15] using optical absorption spectra analysis it was shown that Dy impurity is incorporated in the $Li_2B_4O_7$ glasses melted in oxygen and hydrogen as Dy^{3+} ions. In [16] the fluorescence properties of Dy^{3+} ions with two concentrations (1.0 and 0.1 mol%) have been investigated in a variety of borate and fluoroborate glasses modified with Li, Zn, and/or Pb. Particularly, in [16] it was shown that emission decay curves for glasses containing 0.1 and 1.0 mol% Dy^{3+} are characterised by single exponential and non-exponential decay, respectively, and decreasing trend in lifetimes of the $^4F_{9/2}$ level has been observed when the glass composition contain modifiers in the LiF → Li_2O → ZnO → PbO order. Optical absorption, fluorescence and photoacoustic spectra of Dy^{3+}-doped oxyfluoroborate glass has been investigated in [17], particularly the lifetime and fluorescence yield of the $^4F_{9/2}$ level for different concentrations of Dy^{3+} have been measured and analysed. In [18] the synthesis of Dy-doped boroaluminasilicate glasses in the air and optical absorption, emission and excitation spectra of the Dy^{3+} ions in these glasses were reported. In [19] the results of X-ray diffraction, differential scanning calorimetry, and spectroscopic investigations of the Bi_2O_3–ZnF_2–B_2O_3–Li_2O–Na_2O glasses containing 1.0 mol% Dy^{3+} and Pr^{3+} were presented and analysed. The Dy-doped oxychloroborate glasses of the B_2O_3–$PbCl_2$–PbO–Al_2O_3–WO_3 system were investigated in [20] by X-ray diffraction, Raman, FT-IR, absorption, and luminescence spectroscopy. In [21] by optical and EPR spectroscopy it was shown that the Tb and Dy impurities are incorporated in the Li sites of the $Li_2B_4O_7$ glass structure as Tb^{3+} ($4f^8$, $^7F_6$) and Dy^{3+} ($4f^9$, $^6H_{15/2}$) ions. The luminescence kinetics show single exponential decay for Tb^{3+} and Dy^{3+} centres in $Li_2B_4O_7$ glass and their lifetimes decrease with increasing Tb and Dy concentrations [21].

Considering the above referenced data it was concluded that the optical and luminescence properties of Tb- and Dy-doped borate glasses with different compositions are widely investigated at the present time. But, spectroscopic properties as well as electron and local structure of the luminescence centres in the CaB_4O_7:Tb, $LiCaBO_3$:Tb, CaB_4O_7:Dy, and $LiCaBO_3$:Dy glasses were not investigated up until now. The technology of synthesis and preliminary results of optical spectroscopy of the CaB_4O_7 and $LiCaBO_3$ glasses doped with Tb and Dy firstly were presented in [22]. In this paper the luminescence excitation and emission spectra as well as luminescence kinetics of the CaB_4O_7 and $LiCaBO_3$ glasses doped with Tb and Dy are investigated in detail and analysed in comparison with corresponding data for $Li_2B_4O_7$:Tb, $Li_2B_4O_7$:Dy and other borate glasses, doped with Tb and Dy. The local structure of Tb^{3+} and Dy^{3+} centres in the CaB_4O_7 and $LiCaBO_3$ glasses is also proposed.

2. Experimental details

The glasses with CaB_4O_7:Tb, $LiCaBO_3$:Tb, CaB_4O_7:Dy, and $LiCaBO_3$:Dy compositions of high optical quality and chemical purity were obtained in the air from corresponding polycrystalline compounds using corundum crucibles and standard glass technology set-up, described in [22,23]. For the synthesis of the CaB_4O_7, $LiCaBO_3$, CaB_4O_7, and $LiCaBO_3$ polycrystalline compounds, carbonates ($CaCO_3$, Li_2CO_3) and boric acid (H_3BO_3) of high chemical purity (99.999%, Aldrich) were used. The Tb and Dy impurities were added to the raw materials as Tb_2O_3 and Dy_2O_3 oxide compounds (99.999%, Aldrich) in amounts of 0.5 and 1.0 mol%. Solid-state synthesis of the polycrystalline borate compounds was carried out using a multi-step heating process [23], which can be described for CaB_4O_7 and $LiCaBO_3$ compounds by the following chemical reactions

$$H_3BO_3 = \alpha - HBO_2 + H_2O\uparrow(170°C), \quad (1)$$

$$2\alpha - HBO_2 = B_2O_3 + H_2O\uparrow(250°C), \quad (2)$$

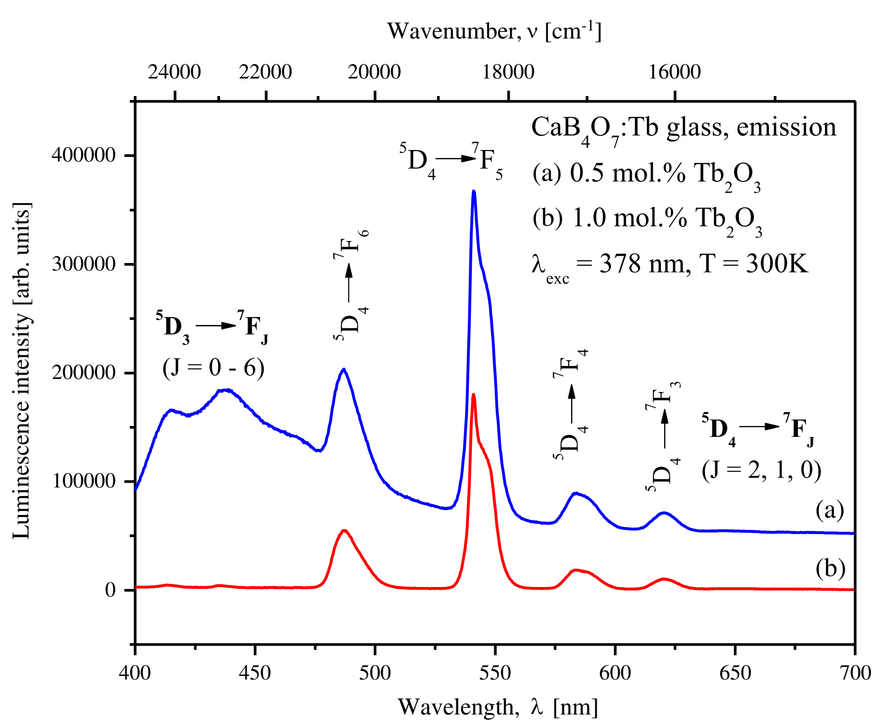

Fig. 1. The emission spectra of the Tb^{3+} centres in the CaB_4O_7:Tb glasses.