Synthesis and Optical Spectroscopy of Borate Glasses, Doped with Terbium and Dysprosium

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Abstract. *The high optical quality glasses 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 have been obtained. By electron paramagnetic resonance (EPR) and optical spectroscopy it was shown that the Tb and Dy impurities are incorporated in the CaB_4O_7 and $LiCaBO_3$ glass network as Tb^{3+} ($4f^8$, $^7F_6$) and Dy^{3+} ($4f^9$, $^6H_{15/2}$) ions, exclusively. All observed f – f transitions of Tb^{3+} and Dy^{3+} centres in optical absorption, luminescence excitation and emission spectra have been identified. Luminescence kinetic shows single exponential decay for Tb^{3+} and Dy^{3+} centres in the CaB_4O_7 and $LiCaBO_3$ glasses. Lifetimes for main emitting levels of Tb^{3+} and Dy^{3+} centres in all investigated glasses were determined at T = 300 K. Spectroscopy shows that obtained glasses are promising luminescent materials.*

Key words: borate glass synthesis, Tb^{3+} centre, Dy^{3+} centre, luminescence, decay kinetics.

I. Introduction

Rare-earth ions show high luminescence efficiency in a variety host compounds including borates and widely used as activator centres in laser and luminescent materials [1]. In particular, borate crystals and glasses activated with Tb^{3+} and Dy^{3+} are considered as effective luminescent materials in green and yellow-blue spectral ranges, respectively. The borate glasses are most perspective in comparison with their crystalline analogies, because the borate single crystals growth is difficult, expensive and long-term. Beside this, low velocity of crystals growth and high viscosity of melt leads to problems with rare-earth doping of borate crystals.

The luminescence properties of Tb- and Dy-doped borate compounds and their potential applications are described in number papers [2-5]. Particularly, in [3] it was reported about synthesis, luminescence properties and scintillation characteristics at registration of neutrons ($E_n \leq 10$ MeV) and ^{60}Co γ-radiation of the un-doped and Tb, Cu, Ce, Sm, Eu, Tm, and Yb doped lithium tetraborate ($Li_2B_4O_7$) glasses. In [4] it was shown that the $LiCaBO_3$:M^{3+} (M = Eu, Sm, Tb, Ce, Dy) polycrystalline compounds are promising phosphors for white light emitted diodes (LED). In [5] by optical and EPR spectroscopy it was shown that Tb and Dy impurities are incorporated in 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 kinetic shows single exponential decay for both Tb^{3+} and Dy^{3+} centres in the $Li_2B_4O_7$ glass network [5].

In this work the luminescence excitation, emission and luminescence kinetic of the CaB_4O_7 and $LiCaBO_3$ glasses doped with Tb and Dy are investigated.

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II. Experimental

The glasses with CaB_4O_7:Tb, $LiCaBO_3$:Tb, CaB_4O_7:Dy, and $LiCaBO_3$:Dy compositions were obtained in the air from corresponding polycrystalline compounds using corundum crucibles and standard glass technology. For synthesis of the CaB_4O_7:Tb, $LiCaBO_3$:Tb, CaB_4O_7:Dy, and $LiCaBO_3$:Dy polycrystalline compounds were used carbonates ($CaCO_3$, Li_2CO_3) and boric acid (H_3BO_3) of high chemical purity. The Tb and Dy were added to raw materials as Tb_2O_3 and Dy_2O_3 in amounts 0.5 and 1.0 mol. %. Solid-state synthesis of CaB_4O_7:Tb, $LiCaBO_3$:Tb, CaB_4O_7:Dy, and $LiCaBO_3$:Dy compounds were carried out using multi-step heating process. Large samples of the Tb- and Dy-doped CaB_4O_7 and $LiCaBO_3$ glasses of high optical quality were obtained by fast cooling of melts, heated more than 100 K higher that the melting temperature for exceeding glass transition points.

The luminescence excitation and emission spectra as well as luminescence kinetic were registered at room temperature using a HORIBA spectrofluorometer (model FluoroMax-4). The EPR spectra were registered using radiospectrometers RADIOPAN (SE/X-2013 and SE/X-2013 models).

III. Results and Discussion

A. Spectroscopy of $LiCaBO_3$:Tb and CaB_4O_7:Tb Glasses

The Tb impurity can be incorporated in the structure of oxide crystals and glasses as paramagnetic Tb^{4+} ($4f^7$, $^8S_{7/2}$) and non-paramagnetic Tb^{3+} ($4f^8$, $^7F_6$) ions. In all investigated glasses the EPR spectra of Tb^{4+} ions were not observed.

Emission and luminescence excitation spectra of the $LiCaBO_3$:Tb and CaB_4O_7:Tb glasses are similar. Emission spectra of all Tb-doped glasses exhibit bands belonging to the $^5D_3 \rightarrow {}^7F_J$ (J = 0 ÷ 6) and $^5D_4 \rightarrow {}^7F_J$ (J = 0 ÷ 6) transitions of Tb^{3+} showed for $LiCaBO_3$:Tb glasses in Fig. 1.

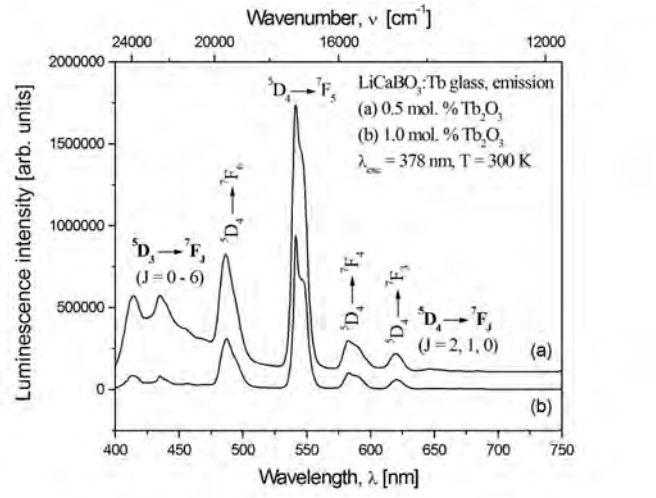

Fig. 1. Emission spectra of the Tb^{3+} centres in $LiCaBO_3$:Tb glasses.

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In the luminescence excitation spectra of all obtained glasses doped with Tb are observed several weakly-resolved and unresolved bands belonging to the Tb^{3+} $f - f$ transitions, which are shown for CaB_4O_7:Tb glasses in Fig. 2.

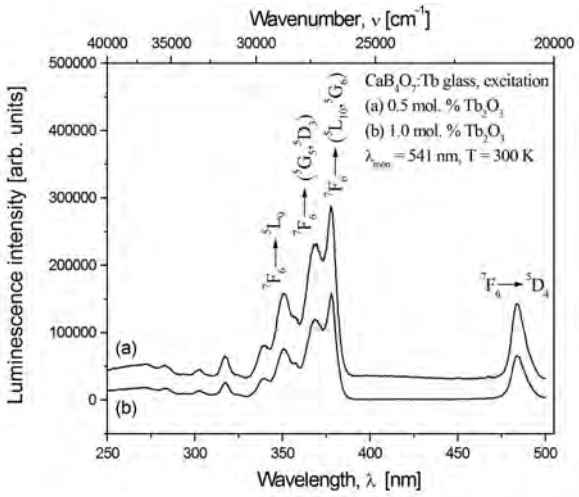

Fig. 2. Luminescence excitation spectra of Tb^{3+} in CaB_4O_7:Tb glasses.

Luminescence kinetics for most intense green emission band ($^5D_4 \rightarrow {}^7F_5$ transition) of the Tb^{3+} centres in both investigated glasses show single exponential decay with lifetimes τ = 2.4 ms and τ = 2.35 ms for samples containing 0.5 and 1.0 mol. % Tb_2O_3, respectively. The lowering of lifetime with increasing Tb_2O_3 content in the investigated glasses is related to influence of $Tb^{3+} - Tb^{3+}$ interaction [6].

B. Spectroscopy of CaB_4O_7:Dy and $LiCaBO_3$:Dy Glasses

The Dy impurity can be incorporated in the structure of oxide compounds as non-paramagnetic Dy^{2+} ($4f^9$, $^7F_6$) and paramagnetic Dy^{3+} ($4f^9$, $^6H_{15/2}$). In all investigated Dy-doped glasses at liquid helium temperatures were observed EPR spectra of Dy^{3+} centres. The emission and luminescence excitation spectra of the $LiCaBO_3$:Dy and CaB_4O_7:Dy glasses are closely similar. Emission spectra of all Dy-doped glasses exhibit exclusively $f - f$ transitions of Dy^{3+} centres, which are identified for CaB_4O_7:Dy glasses in Fig. 3.

In the luminescence excitation spectra of obtained glasses doped with Dy were observed 7 well-resolved characteristic bands belonging to the Dy^{3+} $f - f$ transitions, which are identified for $LiCaBO_3$:Tb glasses in Fig. 4.

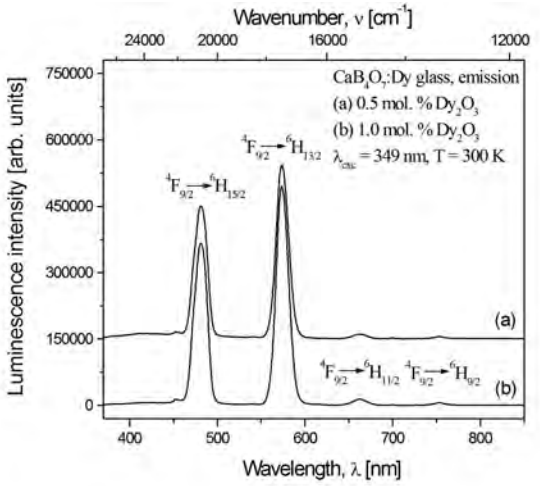

Fig. 3. Emission spectra of the Dy^{3+} centres in CaB_4O_7:Dy glasses.

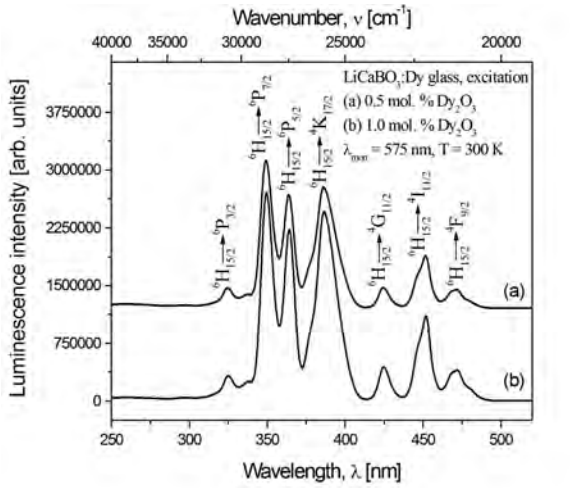

Fig. 4. Luminescence excitation spectra of Dy^{3+} in $LiCaBO_3$:Dy glasses.

Luminescence kinetics for most intense yellow emission band ($^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition) of the Dy^{3+} centres in both glasses show single exponential decay with the following lifetimes: τ = 680 μs and 649 μs ($LiCaBO_3$:Dy), τ = 706 μs and 702 μs (CaB_4O_7:Dy) for samples containing 0.5 and 1.0 mol. % Dy_2O_3, respectively. In both glasses the $Dy^{3+} - Dy^{3+}$ interaction also reveals with increasing Dy concentration.

IV. Conclusions

The observed luminescence spectra and single exponential decay curves in the investigated glasses correspond to one type of the Tb^{3+} and Dy^{3+} centres in the glass network with slightly different crystal field parameters that reveals as inhomogeneous broadening of the spectral lines. Presented results show that CaB_4O_7 and $LiCaBO_3$ glasses activated with Tb^{3+} and Dy^{3+} ions are perspective luminescent materials for green and yellow-blue regions, respectively.

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