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Intrinsic luminescence of un-doped borate glasses

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ABSTRACT

The nature of intrinsic luminescence in the un-doped borate glasses of different compositions has been investigated using spectroscopic methods including photoluminescence, optical absorption, electron paramagnetic resonance (EPR), and thermally stimulated luminescence (TSL). The un-doped borate glasses with $\text{Li}_2\text{B}_4\text{O}_7$, LiKB_4O_7 , CaB_4O_7 , and LiCaBO_3 basic compositions were obtained from corresponding polycrystalline compounds in the air with usage the standard technology of glasses. Three different broad emission bands in the UV–Visible spectral range have been observed under different wavelength of photoexcitation. The luminescence kinetics of the observed emission bands have been registered and analysed. The nature and possible mechanisms of the intrinsic luminescence in the investigated borate glasses are considered and discussed based on the obtained results and referenced data.

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 [1,2], scintillators and thermoluminescent dosimeters [3,4], detectors and transformers of the ionising radiation [5,6], as well as many other applications [7]. From the technological point of view, the glassy borate compounds are more promising materials than their crystalline analogues. Growth technology of the borate single crystals is a difficult, long-term and very expensive process, whereas large high quality samples of borate glasses can be obtained in a simple, fast and inexpensive way [8].

Intrinsic luminescence is an important and useful property for a number of compounds, because has been widely used in scintillators and thermoluminescent detectors. Besides this, the intrinsic luminescence can participate in the efficient transfer of the excitation energy to the impurity luminescence centres including rare-earth and transition ions. Hence, the study of intrinsic luminescence represents important scientific and practical interests. The intrinsic luminescence in solids is a complicated phenomenon. At present time, there are different mechanisms, which can be responsible for intrinsic luminescence. Generally, the intrinsic luminescence is related with recombination processes of the excited charge carriers, radiative annihilation of excitons, and/or presence of point defects in hosts.

Up to now the intrinsic luminescence was studied in the $\text{Li}_2\text{B}_4\text{O}_7$ [9,10], LiB_3O_5 [10], CaB_2O_4 [11], SrB_2O_4 [11], $\text{Ba}_3\text{Lu}(\text{BO}_3)_3$ [12], YBO_3 [13], LuBO_3 [13], and $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ [14] borate crystals. Let us consider the main obtained results. The intrinsic luminescence in the range of 3.5 eV was observed at 295 K and 9.6 K in the LiB_3O_5 and $\text{Li}_2\text{B}_4\text{O}_7$ crystals [10]. This luminescence is characterised by three exponential decay components ($\tau_{f1} < 1$ ns, $\tau_{f2} = 8.5$ ns, and $\tau_s > 250$ ns) and is caused by radiative annihilation of self-trapped excitons (STEs) [10]. The emission bands at 3.19 eV and 3.65 eV in the un-doped MB_2O_4 ($M = \text{Ca}, \text{Sr}$) alkaline earth metaborates [11] as well as at 339 nm in the $\text{Ba}_3\text{Lu}(\text{BO}_3)_3$ [12] crystal were also ascribed to STEs.

The intrinsic luminescence band with maximum in the range of 260–270 nm and lifetimes 2.58 ns, 7.14 ns, and 11.09 ns caused by annihilation of STEs was observed in the YBO_3 , $\text{Lu}_{0.65}\text{Y}_{0.35}\text{BO}_3$, and LuBO_3 crystals [13]. Quenching of the intrinsic luminescence band in few times has been observed with temperature increasing from 10 to 300 K [13]. The broad luminescence band with maximum at 425–450 nm due to the presence of defects in the crystal structure of borates also was noticed in [13]. In the $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ crystal, it was observed intrinsic photoluminescence band at 3.28 eV attributed to radiative annihilation of STEs and the emission band at 2.68 eV that is related to defects [14]. Photoexcitation at 4.1 eV causes STEs luminescence with exponential decay kinetics that consists of two lifetime components, 1.8 ns and 6.5 ns [14]. Excitation by photons with energies of 6.8 eV leads to luminescence band at 2.68 eV with lifetimes in the micro- and millisecond range [14]. Hence, fast intrinsic luminescence in borate crystals observed in the UV–Visible range have

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been attributed to the luminescence of self-trapped excitons (STEs). Discussion about the nature of defects responsible for observed slow intrinsic luminescence in [13,14] was not presented.

The intrinsic luminescence was very well studied for some simple oxide compounds with disordered structure. In particular, broad luminescence band with microsecond lifetime has been observed at 1.9 eV in the silica (SiO₂) and at 2.4 eV in the alumina (Al₂O₃) [15,16]. The observed luminescence bands in the silica and alumina are caused by intrinsic defects [15,16].

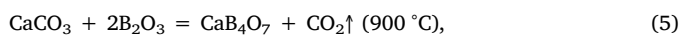
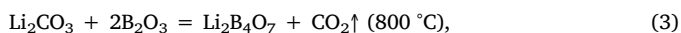
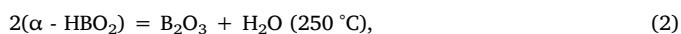
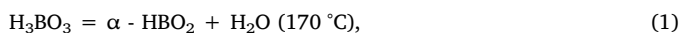
The amount of referenced data that provide information about intrinsic luminescence in glasses is strongly limited. Broad phosphorescence band around 500 nm it was observed in the GeO₂–B₂O₃–ZnO glass upon excitation about 300 nm [17]. Glasses of the CaO–Ga₂O₃–GeO₂ system under UV-excitation at 290 nm show broad emission band in the 350–500 nm spectral region with a maximum at about 430 nm [18]. The nature of intrinsic luminescence in the glasses of CaO–Ga₂O₃–GeO₂ system under synchrotron excitation at T=8 K was investigated in [19]. The luminescence emission spectrum of the Ca₃Ga₂Ge₃O₁₂ glass consists of intense band peaked near 450 nm and two weak bands located near 570 nm and 760 nm [19]. Two bands with maxima about 500 nm and 580 nm were observed in the luminescence spectrum of the Ca₃Ga₂O₆ glass [19]. The luminescence decay curves of all observed emission bands in [19] were described in the framework of two-exponential model with lifetimes in the nanoseconds range. The recombination mechanism of intrinsic luminescence in the CaO–Ga₂O₃–GeO₂ glasses was proposed in [19].

Analysis of the available literature shows that intrinsic luminescence of borate glasses is studied insufficiently. Up to now, there are no reference data, which report intrinsic luminescence in the lithium and calcium borate glasses. Therefore, the main aim of this work is an investigation of the intrinsic luminescence in a series of un-doped alkaline and alkaline-earth borate glasses. The presence of intrinsic luminescence in borate glasses was briefly noted in our articles devoted to spectroscopic researches of the Sm- and Ce-doped borate glasses [20,21]. In this article, the intrinsic luminescence has been detailed studied in the un-doped borate glasses with Li₂O–2B₂O₃, 0.5Li₂O–0.5K₂O–2B₂O₃, CaO–2B₂O₃, 0.5Li₂O–CaO–0.5B₂O₃ compositions, which are identical to the compositions of well-known crystalline analogues Li₂B₄O₇, LiKB₄O₇, CaB₄O₇, and LiCaBO₃, respectively.

2. Experimental details

2.1. The glass synthesis and samples preparation

The un-doped borate glasses with Li₂B₄O₇ (Li₂O–2B₂O₃), LiKB₄O₇ (0.5Li₂O–0.5K₂O–2B₂O₃), CaB₄O₇ (CaO–2B₂O₃), and LiCaBO₃ (0.5Li₂O–CaO–0.5B₂O₃) compositions were obtained in the air atmosphere from corresponding borate compounds according to standard glass synthesis and technological conditions presented in [8]. For solid-state synthesis of the borate compounds were used carbonates (Li₂CO₃, K₂CO₃, CaCO₃) and boric acid (H₃BO₃) of high chemical purity (99.999%, Aldrich). Solid-state synthesis of the borate compounds was performed using multi-step heating reactions [8], which can be described by the following chemical equations:



Large samples of high quality borate glasses with Li₂B₄O₇, LiKB₄O₇, CaB₄O₇, and LiCaBO₃ compositions were obtained by fast cooling of the corresponding melts, heated more than 100 K above the melting points (T_{melt} = 917 °C (1190 K), 807 °C (1080 K), 980 °C (1253 K), and 777 °C (1050 K) for Li₂B₄O₇, LiKB₄O₇, CaB₄O₇, and LiCaBO₃ compounds, respectively) for blocking of the crystallisation process [8]. The glass samples for optical measurements were cut and polished to the approximate size of 10 × 7 × 2 mm³.

2.2. Experimental methods and equipment

The luminescence excitation and emission spectra were registered in the UV and visible spectral ranges at T=300 K using commercial HORIBA spectrofluorimeter (model FluoroMax-4). The optical absorption spectra were recorded with usage Shimadzu UV–Vis spectrophotometer (model UV-2450).

The luminescence kinetics was investigated using the special equipment for time-resolved luminescence described in [22,23]. Long-pass optical filters were used during registration of luminescence spectra. Cut-on wavelength was about 10–20 nm longer than used excitation wavelengths. Spectral bandwidth of excitation light not exceeds 6 nm. Spectral resolution of detection part varies from 0.5 to 0.02 nm depending on spectral range. Time resolution of detection part is 2 ps for 1 ns range. Pulse width equals 89 fs.

The X-ray diffraction studies were carried out using computer controlled X-ray diffractometer (model DRON-3) with monochromatic Cu K α line ($\lambda = 1.5406 \text{ \AA}$). The paramagnetic centres in the un-doped borate glasses, irradiated by X and γ rays were detected using modernised X-band EPR spectrometer RADIOPAN (model SE/X-2013). The thermally stimulated luminescence (TSL) of the X- and γ -irradiated borate glasses was registered with usage ZMR-3 monochromator and FEU-39A photomultiplier tube.

3. Results and discussion

3.1. The XRD and optical absorption of the un-doped borate glasses

The XRD patterns of the obtained un-doped Li₂B₄O₇ and LiCaBO₃ samples are presented in Fig. 1. The absence of discrete sharp peaks in the XRD patterns confirms disordered glass structure of the obtained materials. The observed broad bands at low scattering angles (see Fig. 1) are associated with the short-range order of atoms in the glass network. The registered XRD data were Fourier-transformed in order to obtain the corresponding pair distribution functions for deriving average interatomic distances in the network of investigated glasses. Detailed results of the XRD data analysis for un-doped borate glasses have been published in [8].

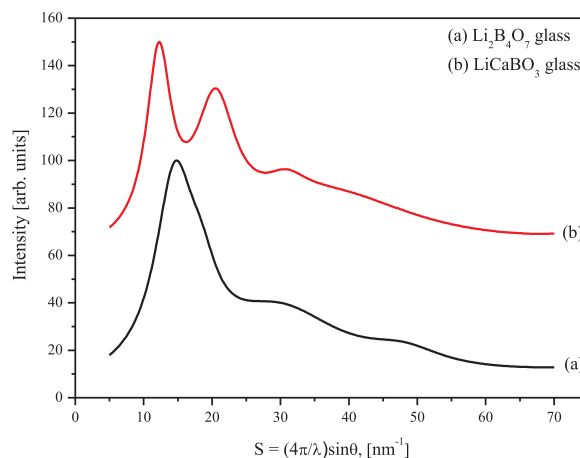


Fig. 1. The XRD patterns of the Li₂B₄O₇ (a) and LiCaBO₃ (b) glasses.

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