EXCITON LUMINESCENCE OF CRYSTALS LiB_3O_5

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Abstract. This paper presents the results of a study of luminescent properties of the lithium triborate crystals - LiB_3O_5 (LBO). The study was carried out mainly through the measurements of the excitation and luminescence spectra for the nominally pure LBO crystals of various crystallographic orientations taken over the broad spectral (1.2 eV–10.5 eV) and temperature (8 K–500 K) ranges. The optical spectroscopy of LBO in the vicinity of the fundamental absorption edge was made as well. On the base of these experimental results, we concluded that the broad-band LBO luminescence at 3.5 eV–4.5 eV can be excited effectively either by photons from the energy range higher than 7.5 eV, or through the recombination processes, or by exposure with the corpuscular and roentgen radiation. The paper discusses the origin of the LBO luminescence and attributes it to the radiative decay of the relaxed electronic excitations.

1   INTRODUCTION

Considerable recent attention has been focused on a study of the electronic excitation dynamics in non-linear crystals of borates of some alkali metals: among them $\beta-BaB_2O_4$ (BBO), LiB_3O_5 (LBO), CsB_3O_5 (CBO) and $Li_2B_4O_7$. From the viewpoint of practical implementations, these crystals have found a wide utility in modern laser techniques as non-linear optical units and materials for integrated optical wave-guides. Some of these crystals ($\beta-BaB_2O_4$ (1), $Li_2B_4O_7$(2)) exhibit a fairly bright short-wavelength luminescence attributed either to a radiative annihilation of self-trapped excitons, or to a decay electronic excitations (EE) on the lattice defects. Luminescence of these crystals share the common properties that the luminescence can be effectively excited either by photons with energy over the long-wavelength fundamental absorption edge (FAE) region, or through the recombination processes.

In this regard LBO is kept in the shade until very recent times. Bearing in mind an elevated stability of its optical properties as well as a wide transparency band extended from 159 nm to 3500 nm (3), a compensation for a deficiency in this field may be of importance. Since the bright ultraviolet (UV) luminescence of LiB_3O_5 (LBO) was observed for the first time (4), it was the subject of extensive research. The current state of the art for the LBO luminescence was given, *e.g.*, in Refs. (5, 6). However, not so much is known about the luminescence origin, and dynamics of electronic excitations in LBO. In fact, some properties of this luminescence depend on the lattice defects, whereas the others are usually inherent in an intrinsic emission. In this connection, the main goal of the current work is to throw new light on the origin of the LBO luminescence. The paper presents the results of a study of the excitation, emission and time-response of the LBO luminescence over the broad spectral (1–10.5 eV), temperature (8–500 K) and decay-time ranges as well as some optical properties of LBO in the vicinity of fundamental absorption edge.

2   EXPERIMENTAL DETAILS

All the examined LBO crystals of a high optical quality were grown by the advanced flux method. As grown crystals, weighing usually 70–120 g, were cut square to the **X** or **Z** crystallographic axes and polished in the form of a plane-parallel plate measuring $10 \times 10 \times 1$ mm^3. The samples are marked as LBO$\perp$**X** and LBO$\perp$**Z**, respectively. A detailed description of the instrumentation has been given elsewhere (5, 6). Luminescent and optical measurements were made by the use of the experimental set-up incorporating the VMR-2 vacuum monochromator, the FEU-142 and FEU-106 photomultipliers in a photon counting mode, the VMF-25 hydrogen discharge lamp, the large-aperture MDR-2 grating monochromator and the LiF-window vacuum chamber equipped with a cryostat operating over the 8–600 K temperature region. The roentgenoluminescence spectra were taken using the X-rays tube with Cu-anode, operating at 40 kV. All the final luminescence and excitation spectra were corrected. The measurements were carried out using the on-line computer, connected via CAMAC type equipment with the experimental set-up.

3   EXPERIMENTAL RESULTS

Figure 1 presents the optical absorption (OA) spectra of LBO measured in the vacuum UV spectral region. From these spectra it follows that from 7.5 eV and on, unirradiated LBO crystals exhibit a monotonous e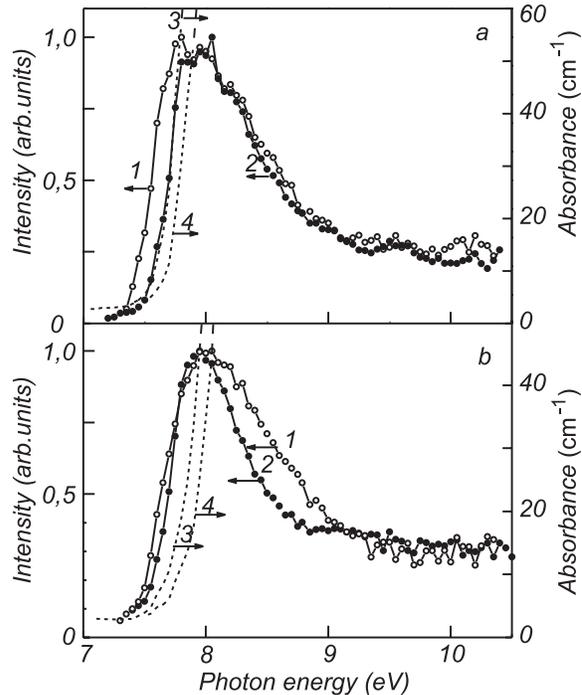xponential rise of optical density, correlating with FAE. No optical absorption bands were found below this energy over all the optical transparency band. We revealed that the real position of FAE depends not only on temperature, but on crystallographic orientation of a sample as well. In doing so, LBO at room temperature has a spectral position of FAE about 100 meV below that of crystal at 78 K. At the same time, all samples of LBO$\perp$**X** demonstrate a spectral position of FAE about 150 meV below that of LBO$\perp$**Z** (Fig. 1).

Exposure of LBO by photons over the energy region above than 7.5 eV results in excitation of the broad band photoluminescence (PL) in the 2.5–4.5 eV spectral region (Fig. 2). The excitation spectrum of this PL exhibits a clearly defined spectral band at 7.9–8.0 eV. In doing so, its long-wavelength slope is represented as a steeply rising curve at 7.5–7.9 eV. Further, we can observe the gradually slopped curve, which transform to the horizontal line, comprising 20–25% of the maximum. This level remains almost unchanged over the 9.5–10.5 eV spectral region (Fig. 1). From Fig. 1 it follows that the excitation spectrum profile depends not only on a temperature,
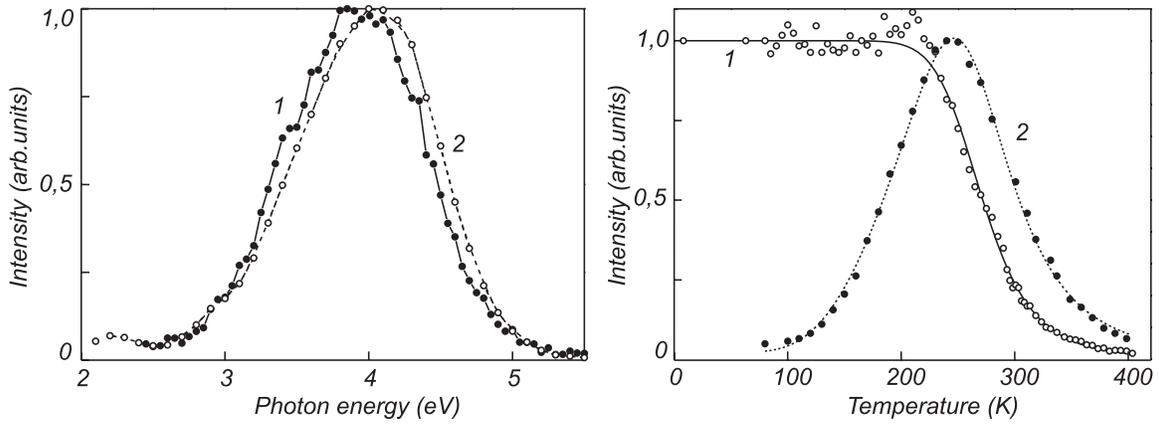

Figure 1: The luminescence excitation spectra (1,2) and spectra of the optical absorption (3,4) of crystals of LBO$\perp$**X** – (*a*) and LBO$\perp$**Z** – (*b*) at 290 K (1,3) and 78 K (2,4).

Figure 2: Spectra of the luminescence of LBO at 290 K under photoexcitation at 7.7 eV (1) and under excitation by X-rays (2).

Figure 3: Temperature dependencies of the photoluminescence of unirradiated LBO under photoexcitation at E_{ex} =7.7 eV (1), and roentgenoluminescence (2). Open circles represent the experimental data, solid lines represent assumed theoretical plots.

but on a crystallographic orientation as well. For example, the excitation spectra of the LBO$\perp$**X** and LBO$\perp$**Z** crystals at 78 K are almost the same in profile and they are represented by the well resolved band at 8.0 eV with full width of about 0.8 eV. On the contrary, at room temperature both spectra are subject to the 200 meV broadening. In doing so, the excitation spectrum in LBO$\perp$**Z** broads towards the short-wavelength side, whereas the spectrum in LBO$\perp$**X** broads towards the opposite side of the excitation band.

The emission band of PL can be fitted by a gaussian with E_m=4.0 eV and full width of 1.2 eV (Fig. 2). It should be noted that this emission band remains almost unchanged in profile on variation of energy of exciting photons over all the 7.7–10.5 eV spectral region. Figure 2 demonstrates also a spectrum of the LBO X-rays luminescence, which closely matches the spectrum of PL. More over, we found no significant change of the PL spectral band profile on cooling to 8 K. A temperature dependence of PL was studied over the 8–600 K temperature region. From Fig. 3 it follows that this PL obeys the Mott's law with an activation energy E_a=290 meV and frequency factor ω=2.4$\cdot 10^5$ s^{-1}. A temperature quenching of PL begin on heating above 240 K. Taking into account a temperature shift of the excitation spectrum of PL, the temperature behavior of PL was found to be the same for various energies of exciting photons. A completely different type of situation occurs in the roentgenoluminescence of LBO. Spectra of this luminescence closely match in profile that for PL. However, its temperature behavior is quite different. In the temperature region above 240 K the X-rays luminescence is subjected to a temperature quenching coincident with that for PL, whereas below this temperature the X-rays luminescence decreases in intensity by 20–25 times (Fig. 3). This is due to the process of localization of charge carriers on the trapped electron (B^{2+}) and hole (O$^-$) centers marked by the annealing temperatures of 130 K and 210 K, respectively. Notably, spectra of both the hole (130 K) and electron (210 K) recombination luminescence are almost the same and they are coincident with that for PL. Time response of this luminescence can be fitted by the fast exponential component with τ=1.2 ns, and by several components in the microsecond time-range. We revealed that the LBO luminescence is strongly polarized (60–70%).

4 DISCUSSION

On the analysis of the experimental results, several facts have engaged our attention primarily: among them a large Stokes shift of PL, ranging up to about 4 eV, and the observed consistency between a drastic increase in the optical density of LBO at photon energy above 7.5 eV and a profile of the long-wavelength slope of the excitation spectrum of PL, Fig. 1. We believe that this decrease in optical density of LBO over the spectral range above 7.5 eV is due to the fundamental absorption of LBO. In fact, although the exact value of E_g remains to be a debated topic to the present day, a large body of the experimental and theoretical assessments of E_g on the basis of the spectral position of FAE converge on the value of 7.75–7.80 eV (3, 7, 8).

At the same time, a band simulation of the LBO electronic structure (9) predicts E_g=7.37 eV in the Γ–Γ direction. This has no contradiction with results of a study of the LBO reflection spectra over the 6–12 eV spectral region and with quantum chemical simulations carried out on the basis of these spectra (10).

In this connection, from the experimental data shown in Fig. 1) we can conclude that the most long-wavelength edge of the fundamental optical absorption of LBO manifests itself in the photon energy region above 7.7 eV or 7.9 eV depending on the crystallographic orientation of a sample. This correlates well with the value of 7.78 eV obtained previously for the non-oriented samples of LBO and taken as the E_g assessment for LBO (3). More over, from an extended analysis of FAE at various temperatures (Fig. 1) it follows that the edge profile can be well fitted by the Lorentz curve. A rough estimate of the optical density at the maximum of this band approximated 10^4 cm^{-1}. The magnitude of this value is fairly elevated. Such properties of LBO may testify that the exciton-like electronic excitations can exist in the vicinity of its FAE and, probably, overlap the inter-band transitions.

Although we have found no luminescence manifestation of such excitations over the spectral region in the vicinity of FAE in LBO at 8 K as opposed to the alkali-halide crystals and some binary oxides, *e.g.* BeO (11), this hypothesis is supported by a great deal of evidence. In fact, the luminescence excitation spectrum in LBO is situated in the spectral region of FAE, its profile, temperature behavior, wide emission band and large Stokes shift are typical of the exciton luminescence observed in various crystals. In this connection, the LBO luminescence can be attributed either to a radiative annihilation of relaxed exciton-like electronic excitations, as in crystals BBO (1) and $Li_2B_4O_7$ (12), or to a decay of relaxed excitons localized on the insignificant lattice distortions.

To date a large body of research of the LBO electronic structure have been available: among them not only the results of the band (3, 7, 9, 13) and cluster (8) calculations, but the results of the roentgen photoelectron spectroscopy of LBO as well (3, 14). All the results bear witness to the fact that the LBO valence band (VB) is formed, mainly, by the anion orbitals. In doing so, the boron ions contribute to formation of the valence and conduction band states only insignificantly, whereas the lithium ions demonstrate no contribution to formation of the VB states at all. As a result, the electronic states of LBO are determined, mainly, by the localized boron–oxygen bonds. From the calculation it follows that the LBO bands exhibit an insignificant dispersion in the K-space. In particular, VB has a mini-slits over all range of the wave-vector variation. Hence, an effective mass of the charge carriers is fairly big, and it may run as high as 0.73 m_e, 0.89 m_e and 0.69 m_e for the Γ–X, Γ–S,

and Γ–Z directions of the conduction band (CB), respectively (9). From the analysis of the allowed electronic transitions from the upper valence band on the lower conduction band it follows that they are determined by the electronic structure of the boron-oxygen clusters, and this situation is typical for a sequence of various borates: among them LBO, CBO and BBO. The recent calculation of the electronic structure of the mentioned crystals by the use of the linearized augmented plane-wave method (13) demonstrated that the valence band top in all these crystals is formed predominantly by the oxygen orbitals, and a contribution from the boron atoms is almost negligible. In doing so, the most low energy transition in LBO can proceed from VB onto the CB states formed by the hybridized orbitals of both the three coordinated boron and oxygen atoms determined the conduction band bottom. In the other borates (CBO and BBO), contrastingly, the conduction band bottom is formed by the cation states, and transitions from the oxygen valence band states onto the cation conduction band states are fairly ineffective. The transitions become more pronounced only for the photons with energy higher by 1 eV than that for the conduction band bottom, because the mixed boron–oxygen orbitals are involved there in formation of the final state of the interband transition in both CBO and BBO.

Taking into account all the mentioned facts, namely, position of the luminescence excitation spectrum on the spectral region of the fundamental optical absorption of LBO, more effective excitation of luminescence in the long-wavelength slope of FAE, large Stokes shift, specific temperature behavior of the roentgeno- and photoluminescences, and excitation of this luminescence in thermally stimulated recombination processes, it may be deduced that the LBO luminescence is intrinsic in origin, it is due to radiative annihilation of the relaxed exciton-like electronic excitations, which can be formed either by a direct excitation, or through the recombination processes with participation of the lattice defects B^{2+} and O^-.

5   CONCLUSION

Thus, the results of a study of the photoluminescence and excitation spectra of LBO suggest that the broad-band photoluminescence at 3.75–3.8 eV is an intrinsic luminescence of LiB_3O_5, and this luminescence is due to the radiative annihilation of the relaxed exciton-like electronic excitation. From the practical viewpoint this luminescence may be of importance for non-destructive testing of the LiB_3O_5-based optical units, operating usually under high-power laser irradiation.

ACKNOWLEGMENT

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KEY WORDS

Exciton luminescence, lithium triborate (LiB_3O_5), non-linear crystals, spectra of luminescence and excitation.