Dynamics of electronic excitations and localized states in LiB₃O₅

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Abstract

The paper presents the results of study of dynamics of electronic excitations and their interaction with the localized states for non-linear crystals LiB₃O₅ (LBO). The results were gained mainly by the use of spectroscopy of transient optical absorption under excitation with an electron beam. Origin of the absorption centers, and role of the localized states in the electronic excitation dynamics of LBO are discussed. © 1998 Elsevier Science B.V. All rights reserved.

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Orthorhombic crystal LiB₃O₅ (LBO) (C₄ᵥ, Pna₂₁ symmetry group) combines successfully an elevated radiation resistance in optical properties (up to 25 GW cm⁻² for the 100 ps laser pulses at λ = 1064 nm [1]) and fairly high magnitude of the non-linear coefficients. The initial unirradiated samples of LBO are transparent over the broad spectral range 159-3500 nm. Owing to these properties, LBO is cited as a versatile optical material, enjoying various applications in the short-wavelength laser optics. In Ref. [2] we have reported about the fast (τ = 1.2 ns) polarized luminescence of LBO. The current paper presents the results of study of both the stable and transient optical absorption of LBO under excitation with an electron beam. The experimental details were described in Refs. [3,4]. All the examined LBO crystals were grown by V. Maslov and L. Olkhovaya through the use of the advanced flux method [5].

We have found that irradiation of LBO at 77 K with an electron beam (Φ = 5 × 10¹⁵ cm⁻², Eₑ = 150 keV, τ = 7 ns) results in a creation of stable radiation-induced defects. They manifest themselves in the optical absorption (OA) spectra over the broad spectral range 2.5-7.0 eV (Fig. 1). A heating to the room temperature causes a thermal bleaching of the crystal. Analysis of the spectral-band profile yields four overlapped Gaussians G₁...G₄ (Fig. 1, Table 1).

The plot of the thermal bleaching demonstrates two well-defined stages in the temperature regions 120-140 K and 190-230 K. The first of them is characterized by a 50% decrease in optical density, whereas the final thermal annealing occurs in the second temperature region. In addition, these temperatures are typical for the relaxation processes in LBO: thermal decay of the trapped electron center B⁺⁺ (first temperature region), and decay of the trapped hole center O⁻ (second region) [6]. Notably, the thermal bleaching plot match almost exactly that for the non-isothermal decay of the paramagnetic center O⁻. From Ref. [7] it follows

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that the trapped hole is localized on the p-orbital of oxygen, bridging the three- and four-coordinated boron ions, in the vicinity of the negatively charged stabilizing defects, for example, a lithium vacancy. This allows us to attribute the radiation-induced optical absorption of LBO to the trapped hole center O\(^-\). This center may play a twofold role. On the one hand, we can expect the optical transitions inside the O\(^-\) center, between the anion p-orbitals split by the crystalline field. These transitions were revealed experimentally in some oxides, for example, in BeO [8]. However, they are forbidden by the selection rules and result usually in a weak OA in the relatively long-wavelength spectral region. On the other hand, one can envisage the transitions from the local level of the O\(^-\) center onto the valence band (VB) states. In this connection, it is of importance to compare the radiation-induced optical absorption spectrum of LBO with density of the one-electron states (DOS) of VB calculated previously for LBO [9] and with a diagram of the one-electron energies of the molecular orbitals calculated for the cluster \([\text{B}_3\text{O}_5]^-\) as it is found in Ref. [9].

Table 1

<table>
<thead>
<tr>
<th>Sub-band</th>
<th>(E_m) (eV)</th>
<th>FWHM (eV)</th>
<th>(I_m) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(G_1) (OA)</td>
<td>2.18</td>
<td>0.82</td>
<td>1.2</td>
</tr>
<tr>
<td>(G_2)</td>
<td>3.67</td>
<td>1.25</td>
<td>62</td>
</tr>
<tr>
<td>(G_3)</td>
<td>4.76</td>
<td>1.76</td>
<td>81</td>
</tr>
<tr>
<td>(G_4)</td>
<td>6.20</td>
<td>1.32</td>
<td>49</td>
</tr>
<tr>
<td>(G_1) (TOA)</td>
<td>2.24</td>
<td>0.82</td>
<td>52</td>
</tr>
<tr>
<td>(G_2)</td>
<td>3.75</td>
<td>1.26</td>
<td>77</td>
</tr>
<tr>
<td>(G_3)</td>
<td>4.89</td>
<td>1.73</td>
<td>54</td>
</tr>
</tbody>
</table>

Note: \(E_m\) is a spectral position of the maximum. \(I_m\) is the intensity at the maximum of the band, arb. units normalized to 100 at the maximum intensity of the complex band.

Fig. 1. (a) Spectra of the radiation-induced optical absorption of LBO at 77 K after irradiation with an electron beam. (1), elementary sub-bands of OA \((G_1 \ldots G_4)\) and DOS of the LBO valence band calculated in Ref. [9] (2). (b) Diagram of the one-electron states of the molecular orbitals of the cluster \([\text{B}_3\text{O}_5]^-\) as it is found in Ref. [9].

![Fig. 1](image1)

Excitation of LBO with an electron beam at 290 K does not create a stable radiation-induced optical absorption, but it results only in the transient optical absorption (TOA). Fig. 2 demonstrates the spectrum of TOA measured at 290 K immediately after termination of the excitation pulse. The appropriate analysis of the spectral band profile (Table 1) demonstrates the elementary Gauss-type sub-bands matched almost exactly that for the

![Fig. 2](image2)
stable optical absorption spectra at 77 K. By this is meant that the optical transitions for both the stable and transient optical absorption of LBO are almost identical.

Decay of the optical density $D(t)$ at 290 K (Fig. 3) obeys a complex law, which can be approximated by three components with the intensity ratios at 3.5 eV−1:1.49:0.37.

$$D(t) = D_0 \exp\left(-t/\tau_0\right) + D_1 \exp\left(-t/\tau_1\right) + D_2/(1 + a \cdot t),$$  

(1)

where $\tau_0 = 1.2 \pm 0.2 \mu$s, $\tau_1 = 33 \pm 3 \mu$s, $a^{-1} = 4.0 \pm 0.4$ ms are the time-constants for the decay components. Fig. 2 demonstrates also a spectral consistency of the predicted components $D(E)$. Notably, the 'intermediate component' $D_1$ gives the main contribution into the spectral bands $G_2$ and $G_3$. At the same time, both the 'fast' ($D_0$) and 'slow' ($D_2$) components of TOA are grouped mainly in the spectral region of the $G_2$ band.

Thus, a study of the stable and transient optical absorption of LBO allows us to conclude that its origin is associated with the optical transitions from the local level of the trapped hole center $O^-$ onto the valence band states.

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References