Anisotropic properties of self-flux grown LiB\textsubscript{3}O\textsubscript{5} single crystals

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Abstract

In this paper, we report the existence of anisotropic behavior along the crystallographic axes in optical, electrical and thermal properties of lithium tri borate, a recently developed vacuum UV-NLO material. The variation of refractive index with the wavelength along the crystallographic axes was investigated by prism coupling method. The results of impedance spectroscopy measurement reveal the presence of a strong anisotropy in ionic conductivity and dielectric constant along the axes and also show the super-ionic conduction behavior along the \( c \)-axis with the activation energy of \( \Delta \sim 0.20 \) eV. A thermo-mechanical study in the temperature range of 300–900 K indicates the existence of a strong variation in the linear thermal expansion coefficient (positive value along the \( a \)-axis, and negative value along the \( c \)-axis) of LiB\textsubscript{3}O\textsubscript{5} crystals.

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1. Introduction

In recent years, borate crystals with B–O bonds have played an important role in the field of frequency conversion, optical parametric oscillation and amplifications [1]. Among them, LiB\textsubscript{3}O\textsubscript{5} (LBO) is a recently developed UV non-linear optical crystal with a wide transparency (160 nm–2.6 \( \mu \)m), a moderate NLO coefficient (1.4 pm/V) and high mechanical and chemical stability. It also possesses a high optical damage resistance (25 GW/cm\textsuperscript{2}, 1064 nm, 0.1 ns) [2] than any other inorganic oxide crystals, which makes it an important candidate in the field of high power laser devices [3]. Single crystal growth of LBO has been investigated by many researchers in the recent past using self and modified solvents [4–6] and optimized the critical growth parameters to yield inclusion free crystals [4,7–9]. However, it is reported that the LBO crystals are prone to crack during growth as well as against high power laser radiation due to the presence of anisotropic thermal gradient/stress [10]. Furthermore, the optical damage resistance of NLO materials is strongly influenced by their electrical conductivity [11]. Hence, it is worthwhile to study the physical, thermal and electrical characteristics for engineering this material suitable for device applications. The non-linear optical [7,12] and other physical properties like, Raman spectra, hardness, density, elastic and piezoelectric constants have been studied intensively by researchers [3,10,12]. In spite of these studies, there are only a few studies on electrical and thermal properties of LBO crystals [13,14]. Nevertheless, there has not been a comprehensive report on the dielectric relaxation and the existence of quasi-one dimensional ionic conduction/
dielectric nature in flux-grown LBO crystals. Taking this into account, it was aimed to grow high quality LBO crystals by self-flux method and to characterize their anisotropic behavior in thermal expansion coefficient, ionic conductivity and dielectric constant properties along the crystallographic axes.

2. Experimental

LBO crystals were grown by top seeded solution growth (TSSG) technique using B₂O₃ as solvent. The nucleation thermodynamics of LBO/B₂O₃ system and the detailed growth procedure of LBO are described elsewhere [15]. The grown crystals were cut into rectangular shape along the crystallographic axes and polished to optical quality. Specimens were subjected to optical transmission/absorption measurements (transmittance ~ 60% at 190 nm) and the dependence of optical absorption coefficient (α) with the wavelength has been investigated using the McLean’s formula. The variations of refractive index with the wavelength and the Vickers’s micro hardness values have also been evaluated along the axes [15]. For the electrical measurements, specimens were electroded with silver paste on opposite sides to ensure good electrical contact. The ionic conductivity and dielectric constant measurements have been performed using a computer controlled HP Impedance analyzer in the frequency range of 100 Hz–10 MHz and in the temperature range of 300–570 K with a heating rate of 1 K/min. A PM100 piezo tester was used to measure the piezoelectric coefficient (d₃₃) of LBO crystals along the c-axis. The thermal expansion coefficients of LBO crystal along the crystallographic axes were calculated using the thermo-mechanical analyzer (Model-MAC-5000). Measurements have been performed in the temperature range of 300–870 K with a heating/cooling rate of 2 K/min.

3. Results and discussion

According to the Nernst–Einstein [16] relation the ionic conductivity (σ) is given by

$$\sigma = \frac{N(Ze)^2a^2}{2k_B T} \Gamma_0 \exp\left(\frac{-\Delta}{k_B T}\right) f$$  \hspace{1cm} (1)

where, N is the number of charge carriers, Ze is the charge of the carriers (Z=1 for LBO), a is the hopping distance of mobile ion, Γ₀ is the hopping rate, f is a correlation factor (value ~1) and Δ is the activation energy, that defines the nature of conduction mechanism in solids, which is closely related and affected by the interaction between the mobile ions and the frameworks. The Eq. (1) can be re-written in a simple form as

$$\sigma T = A \exp\left(\frac{-\Delta}{k_B T}\right)$$  \hspace{1cm} (2)

where $A = (N(Ze)^2a^2)/(2k_B T) \Gamma_0 f$. This implies that the relation between log (σT) and 1/T gives a linear relation and the slope is equal to (-Δ/k_B) from which, the activation energy (Δ) can be measured.

The frequency dependence of real and imaginary parts of dielectric constant measured along the a- and c-axes is shown in Fig. 1(a) and (b), respectively. Since the dielectric and the ionic conduction behavior along the a- and b-axes are very similar, b-axis part is not included. From the Fig. 1(a), a broad relaxation peak can be observed in the real part of the dielectric constant in the frequency range of 10⁴–10⁶ Hz and it is pronounced more in the imaginary part. However, there is no broad anomaly appearing either in real or imaginary part of dielectric constant measured along the...
c-axis (Fig. 1(b)). In addition, along the c-axis the dielectric constant (real and imaginary) is characterized by the large dispersion at low frequencies and it vanishes completely for frequencies higher than \( \sim 10^3 \) Hz, and thereafter remains constant. The temperature dependence of real and imaginary dielectric constants measured for various frequencies along the a- and c-axes is shown in Fig. 2(a) and (b), respectively. The imaginary part is shown as an inset. As shown in Fig. 2(a), the dielectric constants (real and imaginary) along the a-axis increases linearly with temperature as compared to the c-axis, where the behavior is little different. The effect of temperature is independent of frequencies at temperatures up to 330 K, thereafter even at higher frequencies the temperature effect is more evident. From the \( \varepsilon'' \) shown in Fig. 2(a) and (b), one can see that at all measuring frequencies, \( \varepsilon'' \) increases monotonically above 350 K. This confirms to the well-known fact that \( \varepsilon'' \) is related to the ionic conductivity \( \sigma \) as \( \varepsilon'' = \varepsilon_0 \sigma \), where \( \omega \) is the frequency and \( \varepsilon_0 \) is the vacuum permittivity [17]. The \( \varepsilon'' \) increases gradually because the electrical conductivity increases above 350 K. The measured real and imaginary dielectric constant values along the a-axis are few orders of magnitude lower than that of the c-axis, which clearly indicates that the electrical conductivity (\( \sigma \)) along the a-axis should be lower that that of the c-axis. The measured dielectric constant values are summarized in Table 1.

Fig. 3 shows the frequency dependence of ionic conductivity (\( \sigma \)) along the c- and a-axes measured at various temperatures. The latter one is shown as an inset. Similar to the dielectric constant phenomenon, the ionic conductivity along the a-axis linearly increases with frequency and independent of temperatures as compared to the c-axis, where it shows dispersion at frequencies lower than \( \sim 10^3 \) Hz and independent thereafter. The magnitude of the ionic conductivity measured along the c-axis (\( \sigma_c \sim 1.0815 \times 10^{-2} \) S/cm, at \( T \sim 373 \) K, \( f = 50 \) kHz) is higher than that of value measured along the a-axis (3.4840 \( \times 10^{-7} \) S/cm). The temperature dependence of ionic conductivity measured for selected frequencies along the a- and c-axes have been derived from Eq. (1) and depicted in Fig. 4(a) and (b), respectively. Along a-axis (Fig. 4(a)), the ionic conductivity (\( \sigma \)) linearly increases with temperature and the corresponding activation energy (\( \Delta \)) was calculated by fitting the conductivity data with the Arrhenius relation of Eq. (1). It is noted that for all the selected frequencies the measured activation energy (\( \Delta \)) is \( \sim 0.0347 \) eV, which indicates that the conduction mechanism is probably due to the localized motion of Li\(^+\) ions.
instead of Arrhenius-type conduction mechanism. Whereas, along the c-axis (Fig. 4(b)), it exhibit two characteristic regions with different slopes, and hence dispersion in activation energies. The measured activation energy ($\Delta \sim 0.02$–$0.08$ eV) at low temperature region is few orders of magnitude lower than that of high temperature region ($\Delta \sim 0.175$–$0.215$ eV) and the values are given in Table 1. We note that the values measured at high temperature region are close to the super-ionic conductors [18,19]. The piezoelectric constant ($d_{33}$) of LBO crystal along the c-axis has been measured at a frequency of 100 Hz and it was found to be $d_{33} \sim 7.12$ pC/N, which is comparable to the literature data ($d_{33} \sim 9.4$ pC/N) [13].

Fig. 5 shows the variation of thermal expansion coefficient of LBO crystal measured along the c- and a-axes. Inset figure shows the expanded view of thermal expansion along the a-axis. Wei et al. [14] have earlier studied the thermal expansion of LBO crystals by high temperature X-ray diffraction measurements and observed the existence of positive and negative expansions along the a-, b- and c-axes, respectively. Similarly, as seen from Fig. 5, a week positive linear thermal expansion was observed along the a-axis (up to $T \sim 650$ K) compared to a strong negative linear thermal expansion along the c-axis. The average linear thermal expansion coefficients measured in the temperature range of 300–650 K along the crystallographic a- and c-axes are $1.03 \times 10^{-5}$ and $-3.494 \times 10^{-5}$ K$^{-1}$, respectively. Apparently, the results reveal that the variation of thermal expansion coefficient along

Table 1
Dielectric constant and activation energies of LBO crystal

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\varepsilon_r$, $T \sim 300$ K</th>
<th>$\varepsilon_r$, $T \sim 425$ K</th>
<th>$\Delta$(eV), $f=1$ kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250 kHz</td>
<td>1 MHz</td>
<td>250 kHz</td>
</tr>
<tr>
<td>c-axis</td>
<td>16.176</td>
<td>15.541</td>
<td>53.759</td>
</tr>
<tr>
<td>a-axis</td>
<td>12.086</td>
<td>11.884</td>
<td>13.725</td>
</tr>
</tbody>
</table>

Fig. 4. Plot of log ($\varepsilon T$) vs 1000/$T$ for LBO crystal. (a) Along a-axis; (b) along c-axis.

Fig. 5. Variation of thermal expansion with temperature along the axes. Inset shows the expand view along a-axis.
the $a$- and $c$-axes is anisotropic, which leads to thermal stress and thus generate cracks on the growing crystal.

The reason for the anisotropic behavior in ionic conductivity, activation energies and thermal expansion coefficients of LBO along the axes is mainly due to the structural characteristics and the transport mechanism of Li$^+$. The structure of LBO crystal is constructed by the (B$_3$O$_7$)$_{5^-}$ anion rings (contains [BO$_3$] triangle and [BO$_4$] tetrahedral) and are linked by the bridging oxygen atoms, which are the apices shared by the three-fold coordinated BO$_3$ triangle and four-fold coordinated BO$_4$ tetrahedral [10, 14, 20]. These anion rings constitute a three-dimensional framework (channel) along the $c$-axis and loosely bonded Li$^+$ ions are located inside the framework and would hop easily into the neighboring vacancy site from the occupied site through the channels by little interaction with frameworks, which is responsible for the large value of ionic conductivity along the $c$-axis. Whereas, the hopping motion of Li$^+$ ions along the $a$-axis is restricted by the frameworks and hence lowers the ionic conductivity. It is worth mentioning here that the conductivity variation observed in $a$-axis (Fig. 4(a)) at high temperature is presumed to be a result of the large interaction of thermally activated Li$^+$ ions with the frameworks, while increasing the temperature. Furthermore, prior to the hopping motion at high temperature from occupied site to vacancy site, Li$^+$ ions also exhibit a localized motion and thus lattice relaxation, which causes the broad non-Debye type peaks [21] observed in dielectric constant spectra (real and imaginary) along the $a$-axis. A disturbance observed in dielectric constant measurements along $a$-axis at frequencies near to 1 MHz is ascribed to piezo-resonance. The variation of thermal expansion coefficient along the axes is explained as follows: In general, the framework formed by the basic structural unit (B$_3$O$_7$)$_{5^-}$ of LBO exist along the $c$-axis. While increasing the temperature, the direction of structural unit changes and tends to be parallel to $a$--$b$ plane, which may be responsible for the positive expansion along the $a$-axis and contraction (negative expansion) along the $c$-axis. It is also believed that the increase of temperature decreases the bond angle of B–O–B as oxygen atoms are the apices shared by the BO$_3$ triangle and BO$_4$ tetrahedral in B$_3$O$_7$ anionic ring.

4. Conclusion

The temperature and frequency dependence of ionic conductivity, dielectric constant of self-flux grown LBO crystal along the crystallographic $a$- and $c$-axes has extensively been studied and found that hopping motion of Li$^+$ ions and ion–lattice interaction are responsible for the existence of anisotropic nature and relaxation peaks. The measured ionic conductivity along the $c$-axis is higher than that of $a$-axis and further exhibits a superionic conduction behavior with activation energy of $\Delta \sim 0.20$ eV. Thermo-mechanical results reveal the presence of positive and negative expansion coefficients along the $a$- and $c$-axes, respectively. In conclusion, the dielectric, ionic conductivity and thermal expansion studies confims the existence of a strong anisotropy in flux-grown LBO crystals.

References