Structural nature of $^7$Li and $^{11}$B sites in the nonlinear optical material LiB$_3$O$_5$ using static NMR and MAS NMR

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HIGHLIGHTS

• The structural nature of the nonlinear optical properties of LiB$_3$O$_5$.
• Single-crystal NMR and MAS NMR.
• The 3-coordinated trigonal and 4-coordinated tetragonal.
• The spin-lattice relaxation time in rotating frame $T_{1r}$.

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ABSTRACT

The structural nature of the nonlinear optical properties of LiB$_3$O$_5$ is analyzed using single-crystal nuclear magnetic resonance (NMR) and magic angle spinning (MAS) NMR. The 3-coordinated trigonal [B(1) and B(2)] and 4-coordinated tetragonal [B(3)] sites are distinguished using the spectrum and the spin-lattice relaxation time in rotating frame $T_{1r}$, which was obtained from the $^{11}$B MAS NMR. Moreover, the $T_1$ and $T_{1r}$ values for $^7$Li and $^{11}$B are compared, and the activation energies were obtained. The $T_{1r}$ values of the boron nuclei in LiB$_3$O$_5$ show no significant changes. These results may be closely related to the largest second-order nonlinear optical coefficient.

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1. Introduction

Borate crystals such as LiB$_3$O$_5$, LiCsB$_6$O$_{10}$, Li$_2$B$_4$O$_7$, BiB$_3$O$_6$, and BaB$_2$O$_4$ have received a great deal of attention with regard to the generation of ultraviolet (UV) light using wavelength conversion because of their excellent nonlinear optical (NLO) properties in the UV region [1–3]. Among these crystals, lithium triborate LiB$_3$O$_5$ possesses good nonlinear-optical, acousto-optical, and physical properties that promise a wide variety of practical applications [4–6]. Many research papers have also discussed, in particular, the bond parameter methods, anharmonic oscillator models, and the bond charge model [7–10]. Chen’s group [2] recognized that borate compounds have numerous structural types since boron atoms may have either 3- or 4-coordination. They also suggested that the large second-order susceptibility in such molecules is mainly attributed to the $\pi$-conjugated orbital system of an acenitric planar organic molecule with charge transfer between the donor and acceptor substituent groups [11,12]. Owing to this complex structural nature of borate compounds, the selection of structural types that enhance the NLO effect is not straightforward.

There are relatively small numbers of papers on nuclear magnetic resonance (NMR) studies of LiB$_3$O$_5$. Matsuo et al. [13] studied the $^7$Li nuclear relaxation time and line intensities against temperature using both crystal and glass phases of LiB$_3$O$_5$. According to their result, the dominant contribution to the relaxation rate at low temperature was from the spin-phonon interaction, and the relaxation above 580 K was caused by the diffusion of Li ions. In addition, the quadrupole parameters of $^7$Li and $^{11}$B in LiB$_3$O$_5$ crystals were evaluated by NMR experiments in previous reports [14,15]. For $^7$Li nuclei, the quadrupole coupling constant $e^2Q/\hbar = 143 \pm 1$ kHz and asymmetry parameter $\eta = 0.6 \pm 0.1$ [14].
Further, three types of quadrupole parameters were also discussed for the $^{11}$B in LiB$_3$O$_5$ crystals \[15\]: the $e^2Q/Qh$ and $\eta$ are as follows: B(1): $e^2Q/Qh = 2.615 \pm 0.005$ MHz, $\eta = 0.266 \pm 0.005$, B(2): $e^2Q/Qh = 2.690 \pm 0.004$ MHz, $\eta = 0.204 \pm 0.003$, B(3): $e^2Q/Qh = 0.176 \pm 0.003$ MHz, $\eta = 0.584 \pm 0.003$.

In this study, the mechanisms underlying the NLO properties of LiB$_3$O$_5$ are discussed from the static NMR and magic angle spinning (MAS) NMR. We investigate the structural nature of lithium in LiB$_3$O$_5$ by performing $^7$Li single-crystal NMR and MAS NMR. Moreover, we use the same method to study the structural nature of 3-coordinated BO$_3$ and 4-coordinated BO$_4$. Here, the $^{11}$B MAS NMR spectrum and the spin-lattice relaxation times in the rotating frame $T1r$ for the 3-coordinated BO$_3$ and 4-coordinated BO$_4$ are distinguished. To obtain detailed information about the environments of lithium and the three borons, it is necessary to measure the spin-lattice relaxation times of the $^7$Li and $^{11}$B nuclei in the laboratory frame ($T1$) and in the rotating frame ($T1p$), respectively. Our results can be used in framing guidelines for the investigation and development of NLO materials.

2. Crystal structure

LiB$_3$O$_5$ single crystals are orthorhombic with four formula units per unit cell. The space group and point group are $Ia$ and $C2/c$, respectively, and the lattice constants are $a = 8.447$ Å, $b = 7.3789$ Å, and $c = 5.1408$ Å \[16\]. Fig. 1 shows a projection of the LiB$_3$O$_5$ structure onto the ab-plane. The main structural unit of LiB$_3$O$_5$ consists of two crystallographically distinct boron–oxygen triangles and one boron–oxygen tetrahedron: the boron atoms are located within coordination polyhedra of two types, the 3-coordinate triangles [B(1) and B(2)] and the 4-coordinate tetrahedron [B(3)]. The B(1) and B(2) atoms lie within planar triangles formed by the oxygen, and the B(3) atoms within the oxygen tetrahedra. The average nearest neighbor distance of B(1)–O is 1.3692 Å, of B(2)–O is 1.3773 Å, and of B(3)–O is 1.473 Å. There are four Li atoms in a cell, and they are surrounded by four oxygen atoms in a considerably distorted tetrahedron \[17,18\]. The Li–O distance is rather longer than the B–O distance and ranges from 1.9887 to 2.1722 Å with a distorted tetrahedral coordination \[18\].

3. Experimental method

The LiB$_3$O$_5$ single crystals used in the present work were synthesized by the top-seeded slow-cooling method \[12\] at CASIX in China. The NMR signals of the $^7$Li and $^{11}$B nuclei in LiB$_3$O$_5$ single crystals were measured using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute. The static magnetic field was 9.4 T, the central radio frequencies, $\omega_0/2\pi$, for the $^7$Li nuclei were set to 155.51 MHz, and those for the $^{11}$B nuclei were set to 128.34 MHz. The spin-lattice relaxation times in the laboratory frame $T1r$ were measured using $(\pi/2)_\text{sat} - \tau - \pi/2$ pulse sequences. The nuclear magnetizations $M(t)$ of the $^7$Li and $^{11}$B nuclei at time $t$ after the $(\pi/2)_\text{sat}$ pulses were determined from each saturation recovery sequence following the pulse. The width of the $\pi/2$ pulse for $^7$Li and $^{11}$B was 1.65 and 0.5 μs, respectively.

In addition, MAS NMR experiments were performed using a Bruker DSX 400 FT NMR spectrometer to obtain the spin-lattice relaxation time in the rotating frame $T1p$. The $^7$Li and $^{11}$B MAS NMR measurements were performed at Larmor frequencies of 155.51 and 128.34 MHz, respectively. The samples were placed in a 4-mm cross-polarization (CP)/MAS probe as powders. The MAS rate for $^7$Li and $^{11}$B was set as 5 and 13 kHz, respectively, in order to minimize the spinning sideband overlap. The width of the $\pi/2$ pulse for $^7$Li and $^{11}$B was 3.33 and 2.5 μs, respectively, corresponding to spin-locking field strengths of 75.07 and 100 kHz. The $^7$Li and $^{11}$B spin-lattice relaxation times in the rotating frame $T1p$ were measured by applying the spin-locking pulses. The temperature-dependent NMR measurements were carried out over the temperature range of 180–420 K. The samples were maintained at constant temperatures by controlling the nitrogen gas flow and heater current.

4. Experimental results and discussion

We describe recovery laws for quadrupole relaxation process in $^7$Li($I = 3/2$) and $^{11}$B($I = 3/2$) nuclear spin systems. The temperature dependence of the spin-lattice relaxation time in the laboratory frame $T1$ is indicative of a system in which the relaxation is dominated by fluctuations in the electric field gradient (EFG) tensor, driven by a thermally activated motion. For $I = 3/2$, the relaxation transition probabilities can be described by the equations \[19,20\]:

$$W_1 = \frac{1}{12} \left[ \frac{eQ}{\kappa} \right]^2 \int_{-\infty}^{\infty} \left\{ V(1)(0)V_{-1}(t) \right\} \exp(i\omega t) dt$$

$$W_2 = \frac{1}{12} \left[ \frac{eQ}{\kappa} \right]^2 \int_{-\infty}^{\infty} \left\{ V(2)(0)V_{-2}(t) \right\} \exp(i\omega t) dt,$$

where $W_1$ and $W_2$ denote the transition probabilities corresponding to the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ transitions, respectively.

When the central line is at saturation, its recovery functions for the $^7$Li and $^{11}$B transitions are given by the equation:

$$M(t) - M(\infty) = 0.5 \left[ \exp(-2W_1t) + \exp(-2W_2t) \right]$$

where $M(t)$ is the nuclear magnetization corresponding to the central transition at time $t$ after saturation. The spin–lattice relaxation rate is then given by the equation:

$$1/T1 = 0.4(W_1 + 4W_2)$$

The spin-lattice relaxation times in the rotating frame $T1p$ for $^7$Li and $^{11}$B in LiB$_3$O$_5$ were measured at several temperatures. The $T1p$ values could be obtained by Fourier-transforming the FID following the end of spin locking and by repeating the experiments for various periods of time $t$. All the magnetization traces obtained for $^7$Li and $^{11}$B were fitted with the following single exponential function \[21,22\]:

![Fig. 1. Crystal structure of LiB$_3$O$_5$ projected on the ab-plane.](image-url)
4.1. Spin-lattice relaxation time of $^{11}$B in LiB$_3$O$_5$ single crystals using single-crystal NMR

$^{11}$B is a quadrupolar nucleus with a nuclear spin of 3/2. When this nucleus is located in a non-zero EFG, it gives 21 resonance lines for the case in which the nuclear quadrupole interaction perturbs the Zeeman energy levels. One of them is the central transition line and the other two are satellite lines. If the local symmetry around the boron atoms is not cubic, a boron atom gives three resonance lines. Thus, the 4 boron atoms per unit cell in LiB$_3$O$_5$ give a total of 24 satellite lines. These 24 satellite lines of the $^{11}$B nucleus degenerate into 12 in each plane as shown in Fig. 2(a). Here, the central resonance lines of $^{11}$B overlap, and only one resonance line is visible. On the other hand, the rotation patterns of the $^{11}$B NMR spectra were reported previously [15] in three mutually perpendicular planes, and instead of one set (two satellites) of resonance lines for $^{11}$B, there is one central transition line and two satellite resonance lines were reported previously [15] in three mutually perpendicular planes, and instead of one set (two satellites) of resonance lines for $^{11}$B, there is one central transition line and two satellite resonance lines.

The spin-lattice relaxation time in the rotating frame $T_{1p}$ is given by $T_{1p} = 1/W$.

Although the quadrupole parameters of the three types of $^{11}$B are distinguished from the data for the rotation patterns of the $^{11}$B NMR spectra in mutually perpendicular planes, the spin-lattice relaxation times in the laboratory frame $T_1$ for the central resonance line B(1), B(2), and B(3) cannot be distinguished. The $^{11}$B $T_1$ were measured at a Larmor frequency of 128.34 MHz, and were obtained using the saturation recovery method for only one central resonance line. The magnetizations for the $^{11}$B nuclei were measured at several temperatures. The recovery traces for the central resonance line of $^{11}$B with dominant quadrupole relaxation can be expressed as combinations of two exponential functions, as given in Eq. (2). $T_1$ was determined directly from the slope of the plot of log $\left(\frac{M(t)}{M(0)}\right)$ versus temperature.

4.2. Spin-lattice relaxation time of $^{11}$B in LiB$_3$O$_5$ using MAS NMR

The structural analysis of the $^{11}$B in LiB$_3$O$_5$ was carried out by the MAS NMR method. The $^{11}$B MAS NMR spectrum of LiB$_3$O$_5$ at room temperature is shown in Fig. 3(a). The central lines for the three kinds of $^{11}$B in the static NMR cannot be distinguished. However, the $^{11}$B MAS NMR spectrum consists of two peaks at chemical shifts $\delta$ of $-18.60$ and $-7.21$ ppm. This indicates the presence of chemically different $^{11}$B nuclei. The signal at the chemical shift of $-18.60$ ppm is assigned to the 4-coordinated tetragonal BO$_4$ [B(3)] and the signal at the chemical shift of $-7.21$ ppm is assigned to the 3-coordinated trigonal BO$_3$ [B(1) and B(2)]. The chemical shifts were assigned to B(1), B(2), and B(3) using the $^{11}$B MAS spectrum reported by Hansen et al. [23,24]. The weaker and stronger signals represent the $^{11}$B NMR lines for the 3-coordinated B(1) and B(2) and the 4-coordinated B(3) borons, respectively, as shown in Fig. 3(a).

The $^{11}$B spin-lattice relaxation times in the rotating frame $T_{1p}$ were also measured at several temperatures. The spin-lattice relaxation times in the laboratory frame $T_1$ for B(1), B(2), and B(3) cannot be distinguished, whereas those for B(1), B(2), and B(3) in the rotating frame $T_{1p}$ can be distinguished. The nuclear magnetization recovery traces obtained for B(1), B(2), and B(3) were described by a single exponential function of Eq. (4): the recovery traces exhibited a single exponential decay at all temperatures. The slopes of the recovery traces are nearly same at each temperature. The temperature dependences of the $^{11}$B $T_{1p}$ is shown in Fig. 3(b). The $T_{1p}$ of the 3-coordinated [B(1) and B(2)], and 4-coordinated B(3) shows similar trends, and the $T_{1p}$ value of B(3) is longer than that of B(1) and B(2). The $T_{1p}$ value, which differs from $T_1$, is nearly constant with temperature. The $E_a$ obtained from the slope of the $T_1$ versus inverse temperature curve is 6.73 kJ mol$^{-1}$.

4.3. Spin-lattice relaxation time of $^7$Li in LiB$_3$O$_5$ using single-crystal NMR and MAS NMR

$^7$Li is a quadrupole nucleus with a nuclear spin of 3/2. Just as for $^{11}$B, there is one central transition line and two satellite resonance
An NMR spectrum of $^7\text{Li}$ at room temperature is shown in Fig. 4 (a). The zero point of the $x$-axis shows the resonance frequency, 155.51 MHz, of the $^7\text{Li}$ nucleus. Instead of the two satellite resonance lines of the $^7\text{Li}$ nucleus, four satellite resonance lines are obtained in the case of the LiB$_3$O$_5$ crystal. Here, the Li spectrum of the two groups is due to the magnetically different sites. The rotation patterns of the $^7\text{Li}$ NMR spectra measured in the crystallographic ab-, bc-, and ca-planes at room temperature were reported previously [14]. From these results, the nuclear quadrupole coupling constant and the asymmetry parameter for the $^7\text{Li}$ nucleus in a LiB$_3$O$_5$ crystal were obtained; the quadrupole coupling constant, $e^2qQ/h$ was $143 \pm 1$ kHz, and the asymmetry parameter $\eta$ was $0.6 \pm 0.1$ at room temperature [14]. The EFG tensors of Li are not axially symmetric, consistent with the crystal structure. The spectra for the two groups of Li(1) and Li(2) have different orientations, and originate from magnetically different sites.

The structural analysis of the $^7\text{Li}$ in LiB$_3$O$_5$ was carried out by the MAS NMR method. The $^7\text{Li}$ MAS NMR spectrum of LiB$_3$O$_5$ at room temperature is shown in Fig. 4 (b). The $^7\text{Li}$ MAS NMR spectrum consists of one peak at a chemical shift of $-0.85$ ppm. The spinning sidebands are marked with asterisks. The signals for Li(1) and Li(2) obtained by MAS NMR do not split because the Li nuclei are chemically equivalent, even though they are magnetically different.

The spin-lattice relaxation time in the laboratory frame, $T_1$, was measured by applying $(\pi/2)_\text{sat}$ − $\pi/2$ pulse sequences. The recovery traces of the magnetization of the crystals were measured at several different temperatures. The value of $T_1$ was measured at the central resonance line. $T_1$ for Li(1) and Li(2) cannot be distinguished because of the overlap of the central resonance line of Li(1) and Li(2). The recovery traces of Li have a single exponential function. Thus, the spin-lattice relaxation time is determined from

![Fig. 3. (a) $^{11}\text{B}$ MAS NMR spectrum [B(1) and B(2) in 3-coordinate BO$_3$, and B(3) in 4-coordinate BO$_4$] in LiB$_3$O$_5$ at room temperature. The spinning sidebands are marked with asterisks, and (b) Temperature dependences of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ for 3-coordinate B(1) and B(2), and 4-coordinate B(3) in LiB$_3$O$_5$.](image)

![Fig. 4. (a) $^7\text{Li}$ single-crystal NMR spectrum in the LiB$_3$O$_5$ crystals. The static magnetic field $B_0$ is parallel to the b + 25°-axis in ac-plane. (b) $^7\text{Li}$ MAS NMR spectrum in LiB$_3$O$_5$ at room temperature. The spinning sidebands are marked with asterisks.](image)

![Fig. 5. Temperature dependences of the spin-lattice relaxation time in the laboratory frame $T_1$, and in the rotating frame $T_{1\rho}$ for $^7\text{Li}$ in LiB$_3$O$_5$.](image)
a fit of the recovery pattern given by Eq. (2). Here, $W_1$ and $W_2$ have the same values in the recovery traces and thus, the recovery traces of Li have a single exponential function: when $W_1 = W_2$, $T_1 = 5/\left[2(W_1 + 4W_2)\right] = 1/(2W_1)$. The relaxation time was determined directly from the slope of the log $[M(\infty)/M(t)/M(\infty)]$ versus time ($t$) plot. The results of the temperature dependence of $T_1$ of $^7$Li in this single crystal are shown in Fig. 5. At room temperature, $T_1$ has a large value of 559 s. The relaxation time decreases with increasing temperature and appears to be proportional to temperature in the temperature range from 180 to 400 K. The $E_a$ obtained from the slope of the $T_1$ versus inverse temperature curve is 1.21 kJ mol$^{-1}$.

The $^7$Li spin-lattice relaxation times in the rotating frame $T_{1p}$ were measured at several temperatures. Although the quadrupole parameters for the two types of $^7$Li are distinguished from data for the rotation patterns of the $^7$Li NMR spectra in mutually perpendicular planes, the spin-lattice relaxation times in the rotating frame, $T_{1p}$, cannot be distinguished for Li(1) and Li(2) because of the chemical equivalence. The nuclear magnetization recovery traces obtained for $^7$Li were described by the single exponential function of Eq. (4). The result of the temperature dependence of $T_1$ for $^7$Li is shown in Fig. 5. At room temperature, $T_{1p}$ has a short value of 1.43 s. The relaxation time $T_{1p}$ is nearly constant with increasing temperature, and $E_a$ has a very small value, 0.09 kJ mol$^{-1}$.

### Table 1

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Bond-length (Å)</th>
<th>$e^2qQ/h$ (kHz)</th>
<th>$\eta$</th>
<th>$T_1$ (sec)</th>
<th>$E_a$ ($T_1$) (kJ/mol)</th>
<th>$T_{1p}$ (sec)</th>
<th>$E_a$ ($T_{1p}$) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-coordinated B(1)</td>
<td>1.3692</td>
<td>2615</td>
<td>0.266</td>
<td>1181$^1$</td>
<td>6.73$^1$</td>
<td>0.50 $\times$ 10$^{-3}$</td>
<td>0.17</td>
</tr>
<tr>
<td>3-coordinated B(2)</td>
<td>1.3713</td>
<td>2690</td>
<td>0.204</td>
<td>1181$^1$</td>
<td>6.73$^1$</td>
<td>0.50 $\times$ 10$^{-3}$</td>
<td>0.17</td>
</tr>
<tr>
<td>4-coordinated B(3)</td>
<td>1.473</td>
<td>176</td>
<td>0.584</td>
<td>1181$^1$</td>
<td>6.73$^1$</td>
<td>12.52 $\times$ 10$^{-3}$</td>
<td>1.79</td>
</tr>
<tr>
<td>Li</td>
<td>1.9887–2.1722</td>
<td>143</td>
<td>0.6</td>
<td>559</td>
<td>1.21</td>
<td>1.43</td>
<td>0.09</td>
</tr>
</tbody>
</table>

*a $T_1$ for B(1), B(2), and B(3) from NMR experiment cannot be distinguished.

5. Conclusion

We propose NMR studies as a microscopic tool for evaluating and identifying LiB$_3$O$_5$ among NLO borate materials. $^{11}$B NMR spectroscopy is a well-established analytical tool in several areas of the diverse structural chemistry of boron. Although the quadrupole parameters of three borons [B(1), B(2), and B(3)] were reported using single-crystal NMR, $T_1$ of the three kinds of bonds cannot be distinguished. In addition, Li(1) and Li(2) corresponding to two resonance lines in the Li nucleus cannot be distinguished by static NMR. Therefore, the structural nature of lithium and the three borons in LiB$_3$O$_5$ were investigated by MAS NMR. The B(1), B(2), and B(3) sites obtained from the $^{11}$B MAS NMR are distinguished by the spectrum and $T_{1p}$. The $T_1$ and $T_{1p}$ values for lithium and boron in LiB$_3$O$_5$ are compared, as shown in Table 1. The $T_{1p}$ value for 3-coordinated B(1) and B(2) is shorter than that of 4-coordinated B(3). This result is consistent with the boron–oxygen distances. The $T_1$ of $^{11}$B slowly decreases with increasing temperature, whereas the $T_{1p}$ of $^{11}$B, which differs from $T_1$, is nearly constant. However, Li(1) and Li(2) corresponding to two resonance lines in the Li nucleus cannot be distinguished by MAS NMR. The reason is that although Li(1) and Li(2) are magnetically inequivalent, they are chemically equivalent. In addition, $T_1$ and $T_{1p}$ of Li are nearly constant with increasing temperature. Finally, $E_a$ was obtained for $^7$Li and $^{11}$B. The $E_a$ for the molecular motions obtained from $T_1$ of $^{11}$B are larger than that for the molecular motions obtained from $T_{1p}$ of $^{11}$B. In fact, $T_{1p}$ is affected by slower molecular motions as compared with $T_1$, and so the $T_{1p}$ measurements provide additional information that can be used for a more reliable check on various models of motion.

Consequently, the boron sites for the trigonal 3-coordinated BO$_3$ and the tetrahedral 4-coordinated BO$_4$ were distinguished by the $^{11}$B MAS NMR spectrum and $T_{1p}$. No significant changes were seen in the $T_{1p}$ at the $^7$Li and $^{11}$B nuclei in LiB$_3$O$_5$. Therefore, the local symmetry around the $^7$Li and $^{11}$B atoms is insensitive with respect to changes in temperature. We made an attempt to find the relationship between the NMR parameters and NLO structural features. This research may help explain the structure–property relationships in most known NLO crystals of various structural types and to establish guidelines for identifying and developing new NLO materials.

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