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# Crystal Structure of Lithium Triborate, $LiB_3O_5$

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# $LiB_3O_5$의 결정구조

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**Abstract**

Single crystals of lithium triborate, $LiB_3O_5$ ($M_r$=119.37), have been grown and their structure was determined by the single crystal x-ray diffraction technique. The space group was determined to be $Pna2_1$ (No. 33) with $a$=8.432(1) Å, $b$=7.364(1) Å, $c$=5.110(1) Å, $\alpha=\beta=\gamma=$ 90.00°, $V$=317.3(6) Å$^3$, $Z$=4, $D_x$=2.50 gcm$^{-3}$, Mo$K\alpha_1$, $\lambda$=0.71069 Å, $\mu$=0.23/mm, F(000)=232, $T$=293 K. The structure was refined to $R$=0.0222 and $wR$=0.0582 for 510 unique reflections by the single crystal diffraction.

**요 약**

Lithium triborate, $LiB_3O_5$($Mr$=119.37), 단결점을 상단 종자정 용액법으로 성장시켰으며, 결정구조를 X-선 회절법으로 연구하였다. 결정계는 사방정계이며 공간군은 $Pna2_1$(No. 33)이다. 단위포의 상수는 $a$=8.432(1) Å, $b$=7.364(1) Å, $c$=5.110(1) Å, $\alpha=\beta=\gamma$=90.00°, $V$=317.3(6) Å$^3$, $Z$=4, $D_x$=2.50 gcm$^{-3}$, Mo$K\alpha_1$, $\lambda$=0.71069 Å, $\mu$=2.3/cm, F(000)=232, $T$=293 K 이었다. 최종 구조의 오차인자는 510개 회절 점에서 각각 R=0.0222과 wR=0.0582 이었다.

## 1. Introduction

Li-B-O system has numerous types of boron-oxygen compounds. This is because the boron atom have either three or four coordination. This gives the various properties of lithium borate compound. Lithium borate compounds have a unique combination of nonlinear-optical, acousto-optical and physical properties which promise a wide variety of practical applications.[1] So x-ray diffraction studies have been reported during last decade.[2,3] Among this, $LiB_3O_5$ is of special interests which is advantageous in frequency conversion of high power pulse lasers.[3] This property is deeply connected with the structure of $LiB_3O_5$. In this paper, we report on the result of the structure analysis of $LiB_3O_5$.

## 2. Experimental

All the growth experiments were carried out in a home-made TSSG furnace with a Kanthal A1 heating element controlled by a programmable PID controller. The axial temperature gradient in solution was controlled by varying the position of a crucible in the growth furnace. The solution composition was varied from Li : B=1 : 4 to Li : B=1 : 4.4 by mole ratio. $Li_2B_4O_7$ and $H_3BO_3$ powders were selected as starting materials to prepare a 110 g charge after decomposition. A 70

cc platinum crucible was filled with pre-mixed powder melt in specially designed charging furnace. The solution was heated to 950°C in the growth furnace, homogenized completely in 12 hours and then cooled down to the saturation temperature. A seed crystal fixed to a platinum seed holder was dipped into solution and the temperature was maintained for 24 hours. Then the furnace was slowly cooled down at a rate of 0.96°C/day until the end of the growth. During the growth, the crystal was uni-directionally rotated at a rate of 20 or 50 rpm. All the crystals were grown in air atmosphere without $N_2$ flow nor humidity control. After cooling down by 5°C, the grown crystal was pulled up from the solution and cooled down to room temperature for about 2 days.

**Table 1. Experimental and refinement details**

| | |
|---|---|
| *Crystal data* | |
| $LiB_3O_5$ | Mo $K\alpha_1$ radiation |
| $M_r$=477.48 | $\lambda$=0.71069 Å |
| Tetragonal | Cell parameters from 25 |
| P $na2_1$ | reflections |
| a=8.431(1) Å | $\alpha$=90.00° |
| b=7.364(1) Å | $\beta$=90.00° |
| c=5.109(1) Å | $\gamma$=90.00° |
| V=317.28 Å | $2\theta$=20-30° |
| Z=4 | T=293 K |
| $D_x$=2.50 g/cm$^3$ | sphere |
| $\mu$=0.23 mm$^{-1}$ | 0.7 mm (diameter) |
| *Data collection* | |
| Enraf Nonius CAD4 | 510 observed reflections |
| diffractometer | [I>2$\sigma$(I)] |
| $\omega/\theta$ scans | $R_{int}$=0.00 |
| Scan width(°) 0.8+0.35tan$\theta$ | $\theta_{max}$=30.0° |
| Absortion collection; | h=-11~11 |
| psi-scan | k=0~10 |
| intensity decay: none | l=0~7 |
| 508 measured reflections | 3 standard reflections |
| 2,296 independent reflections | monitored every 200 reflections |
| *Refinement* | |
| Refinement on F | $\Delta\rho_{max}$=0.23 eÅ$^{-3}$ |
| R=0.0222 | $\Delta\rho_{min}$=-0.22 eÅ$^{-3}$: |
| wR=0.0583 | Extinction collection: |
| S=1.171 | Empirical (Shelxl 93) |
| 2,296 reflections | Extinction coefficient: |
| 83 parameters | 1.8395 |
| w=1/{$\sigma^2(F_o^2)$+(0.0436P)$^2$ +0.04P} | Atomic scattering factors from International |
| where P=($F_o^2$+2$F_c^2$)/3 | Tables Vol C, Tables 4.2.6.8 and 6.1.1.4 |

The diffraction data were collected on an Enraf-nonius CAD4 diffractometer. The lattice constants were refined by least square method from 25 reflection with 10°<$\theta$<15°. The experimental data are listed in Table 1. This structure was solved by direct method and expanded by Fourier techniques. All atoms were refined anisotropically. All computations were performed using SHELXS 86[4] and SHELXL 93[5] crystallographic softwares.

## 3. Discussion

Atomic parameters and temperature factors from the final refinement are listed in Table 2, and the selective interatomic distances and bond angles are listed in Table 3. The structure is composed of two $B_3O_7$, $B_3O_8$ groups a unit cell respectively. This is shown in Fig. 1. In this structure two kinds of the boron-oxygen bonds exist; $BO_3$ and $BO_4$ polyhedra. The average bond lengths of B1-O and B2-O are 1.370 Å and 1.468 Å respectively. This is the same as that of the

**Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) with e.s.d.'s in parentheses, $B_{eq}=(4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$**

| | x | y | z | Beq |
|---|---|---|---|---|
| O1 | 0.08651(10) | 0.50437(12) | 0.8011(2) | 0.0091(2) |
| O2 | 0.11633(10) | 0.29501(11) | 0.1520(2) | 0.0081(2) |
| O3 | 0.05811(11) | 0.79811(11) | 0.9840(2) | 0.0085(2) |
| O4 | 0.26098(9) | 0.09030(11) | 0.6889(2) | 0.0069(2) |
| O5 | 0.83880(9) | 0.12489(11) | 0.8826(2) | 0.0078(2) |
| B1 | 0.0094(2) | 0.6644(2) | 0.8084(3) | 0.0073(3) |
| B2 | 0.1944(2) | 0.4435(2) | 0.0055(3) | 0.0058(3) |
| B3 | 0.15698(14) | 0.7486(2) | 0.1885(3) | 0.0067(3) |
| Li1 | 0.0875(4) | 0.0669(4) | 0.9538(7) | 0.0204(6) |

**Table 3. Selective bond lengths and bond angles with e.s.d.'s in parentheses**

| | | | |
|---|---|---|---|
| B1-O1 | 1.3470(15) | B1-O2 | 1.361(2) |
| B1-O3 | 1.394(2) | B2-O1 | 1.456(2) |
| B2-O2 | 1.479(2) | B2-O5 | 1.460(2) |
| B2-O4 | 1.480(2) | B3-O4 | 1.3557(14) |
| B3-O5 | 1.361(2) | B3-O3 | 1.385(2) |
| Li1-O2 | 1.977(3) | Li1-O3 | 2.001(3) |
| Li1-O4 | 2.000(4) | Li1-O5 | 2.171(3) |
| | | | |
| O1-B1-O2 | 123.49(12) | O1-B1-O3 | 119.58(12) |
| O2-B1-O3 | 116.93(12) | O1-B2-O5 | 108.58(15) |
| O1-B2-O2 | 108.24(11) | O5-B2-O2 | 109.51(10) |
| O1-B2-O4 | 112.85(12) | O5-B2-O4 | 108.18(10) |
| O2-B2-O4 | 109.4(2) | O4-B3-O5 | 125.02(13) |
| O4-B3-O3 | 122.31(13) | O5-B3-O3 | 112.66(13) |
| O2-Li1-O4 | 100.57(14) | O2-Li1-O3 | 144.7(2) |
| O4-Li1-O3 | 103.19(13) | O2-Li1-O5 | 92.13(12) |
| O4-Li1-O5 | 125.2(2) | O3-Li1-O5 | 95.04(12) |
| O2-Li1-O5 | 90.0(2) | O4-Li1-O5 | 115.4(2) |
| O3-Li1-O5 | 56.24(10) | O5-Li1-O5 | 117.69(13) |

$Li_2O \cdot 2B_2O_3$ compound. $LiB_3O_5$ consisted of Li and $(B_3O_7)^{5-}$ anionic group which has two 3 fold bonding and two 4 fold bonding. And the lithium ion is surrounded by four close oxygen atoms in the range from 1.977 Å to 2.171 Å. This anionic groups are filled with network structure which has screw axis structure along with c axis. The anisotropic thermal parameters are shown in Table 4. From the data, we are able to know that the thermal parameter of Li atom which is light element is two times larger than that of B and O atoms.

The molecular configurations of borate anionic group are shown in Fig. 2.[7] Most of borate compound mainly consists of $(B_3O_7)^{5-}$ and $(B_3O_8)^{7-}$ groups. $LiB_3O_5$ has only $B_3O_7$ anionic group in the unit cell. This makes $LiB_3O_5$ very high non-linear optic coefficient. Chen *et al.* reported that $(BO_3)^{3-}$ and $(B_3O_6)^{3-}$ groups has small non-linear optic coefficient to perpendicular direction be-

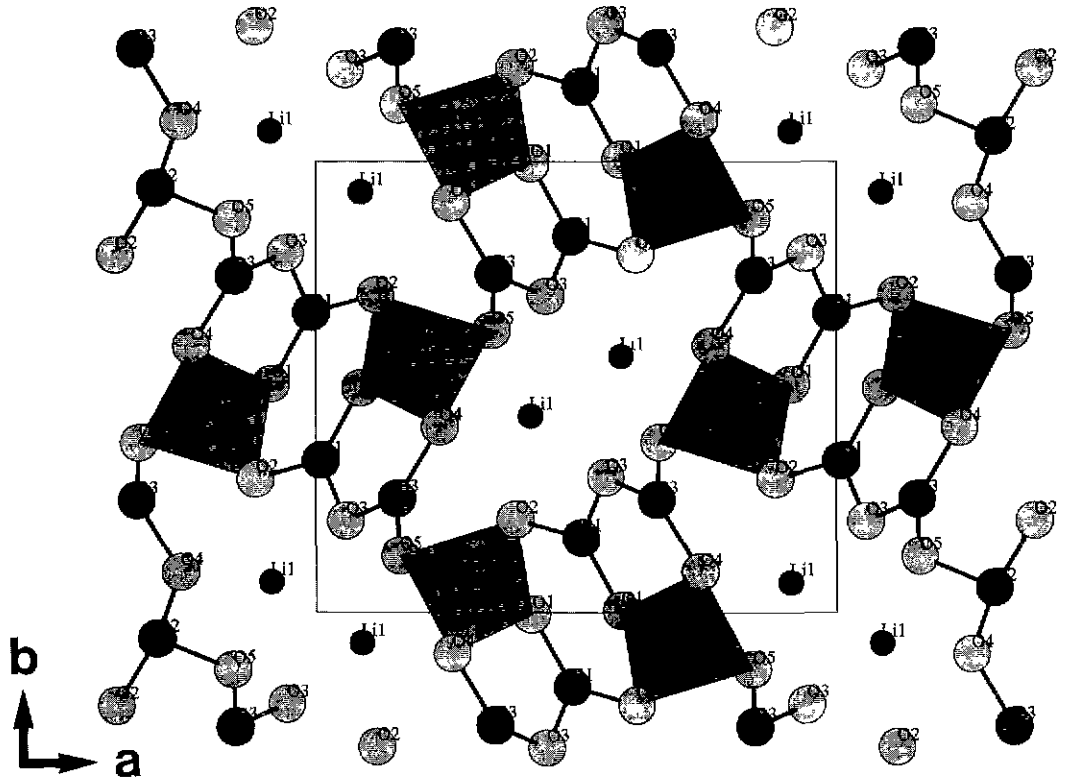


**Fig. 1. A projection of the crystal structure of $LiB_3O_5$ onto the (001) plane.**

**Table 4. Anisotropic temperature factors ($Å^2$) with e.s.d.'s in parentheses**

| | U11 | U22 | U33 | U12 | U23 | U13 |
|---|---|---|---|---|---|---|
| O1 | 0.0125(4) | 0.0081(4) | 0.0068(5) | -0.0016(3) | -0.0038(4) | 0.0019(3) |
| O2 | 0.0107(4) | 0.0066(4) | 0.0069(4) | 0.0000(4) | 0.0033(3) | 0.0000(3) |
| O3 | 0.0124(4) | 0.0063(4) | 0.0068(5) | -0.0005(4) | -0.0039(3) | 0.0013(3) |
| O4 | 0.0095(4) | 0.0058(4) | 0.0054(4) | -0.0023(4) | 0.0012(3) | -0.0009(3) |
| O5 | 0.0078(4) | 0.0076(4) | 0.0080(4) | 0.0039(3) | 0.0015(4) | 0.0000(3) |
| B1 | 0.0100(5) | 0.0072(5) | 0.0047(5) | 0.0001(5) | -0.0006(5) | -0.0002(4) |
| B2 | 0.0078(5) | 0.0057(5) | 0.0039(5) | -0.0009(4) | 0.0010(5) | 0.0002(4) |
| B3 | 0.0076(5) | 0.0073(5) | 0.0053(5) | -0.0006(5) | -0.0005(5) | -0.0004(4) |
| Li1 | 0.0281(13) | 0.0123(9) | 0.0208(14) | -0.0037(12) | 0.0100(12) | -0.0038(9) |

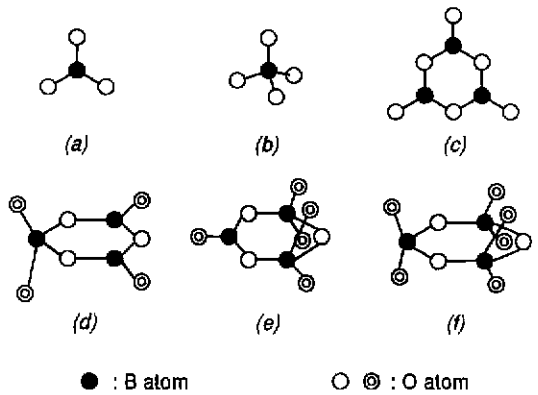


**Fig. 2. The molecular configurations of borate anionic groups; (a) $(BO_3)^{3-}$, (b) $(BO_4)^{5-}$, (c) $(B_3O_6)^{3-}$, (d) $(B_3O_7)^{5-}$, (e) $(B_3O_8)^{2-}$ and (f) $(B_3O_9)^{9-}$.**

cause of its plane shape of anionic bond, however, $(B_3O_7)^{5-}$ has large non-linear optic coefficient. Table 5 shows the number of $B_3O_7$ and $B_3O_8$ groups a unit cell, crystal data and interatomic bond lengths. As the ratio of Li to B of lithium borate systems increases, so the number of $B_3O_7$/$B_3O_8$ unit decreases. The average bond lengths of $LiB_3O_5$ is also slightly larger than that of other lithium botate compounds.

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**Table 5. Comparison of interatomic bond distances, crystal parameters and the number of $B_3O_7$, $B_3O_8$ bonds a unit cell**

| | $Li_2B_4O_7$[2] | $Li_3B_7O_{12}$[6] | $LiB_3O_5$ |
|---|---|---|---|
| B-O bond lengths [Å] | 1.37~1.42<br>1.43~1.47 | 1.333<br>1.412 | 1.347~1.394<br>1.456~1.480 |
| Space group | $I4_1cd$ | P-1 | $Pna2_1$ |
| Cell parameter | a=9.47 Å<br>c=10.26 Å | a=6.500(3) Å, $\alpha$=92.07(2)°<br>b=7.839(2) Å, $\beta$=104.97(2)°<br>c=8.512(1) Å, $\gamma$=99.35(3)° | a=8.431(1) Å<br>b=7.364(1) Å<br>c=5.109(1) Å |
| The number of $B_3O_7$/$B_3O_8$ unit | 0/4 | 2/2 | 4/0 |

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