

LiZnBO₃: 결정구조

張 起 錫

공군사관학교 화학과
(2000. 9. 14 접수)

LiZnBO₃: Crystal Structure

Ki-Seog Chang

Department of Chemistry, Korea Air Force Academy, Cheongwon 363-840, Korea
(Received September 14, 2000)

요 약. LiZnBO₃ 화합물의 결정구조에 대한 실험은 단결정 X-ray 회절 분광법에 의해서 수행되었다. 화합물의 단위포 격자상수는 a=5.0915(9)Å, b=5.059(1)Å, c=6.156(1)Å, V=120.6(1)Å³, α=65.81(1)°, β=65.56(1)°와 γ=59.77(1)° 이고, 공간그룹은 P1̄(Z=2)이다. 화합물의 구조는 704개의 독특한 반사 복사선들에 의해서 결정되었으며, 최종, R값은 0.039이고, wR값은 0.056이다. 이 화합물은 평면삼각형의 BO₃ 그룹과 사각리진 사면체 구조의 LiO₄와 ZnO₄ 그룹으로 구성되어 있으며, Li 원자와 Zn 원자들이 불연속적으로 배열되었다. 변각이 가면서 불연속적으로 배열된 원자의 중심들은 각각 원자들, Li1, Li2, Zn1와 Zn2 격자위치에서 약 50° 이었다.

ABSTRACT. The structure of the lithium zinc borate LiZnBO₃ has been established by single-crystal X-ray diffraction methods. It crystallizes in the triclinic space group P1̄(Z=2), with unit-cell parameters a=5.0915(9)Å, b=5.059(1)Å, c=6.156(1)Å, V=120.6(1)Å³, α=65.81(1)°, β=65.56(1)° and γ=59.77(1)°. The structure was determined from 704 unique reflections and refined to the final residuals R=0.039 and wR=0.056. It is characterized by an association of BO₃ triangles and LiO₄ and ZnO₄ tetrahedra. The Li and Zn atoms are disordered around the average positions between Li1 and Li2 atoms or between Zn1 and Zn2 atoms. The disorder can be described by four half-occupied positions about Li1, Li2, Zn1 and Zn2 atoms.

INTRODUCTION

The phase LiZnBO₃ was first described by Lehmann and Schadow, following a study of the quasibinary system ZnO-LiBO₂.¹ The preparation of LiZnBO₃ has been achieved by heating the corresponding ZnO with excess LiBO₂ at 800°C in the air and extracting the unreacted LiBO₂ by means of CH₃OH. The form was identified as a hexagonal material forming in cell parameters: a=5.10Å, c=8.08Å and Z=3. Later, Bodareva, Simonov, Tismenko and Belov reported an X-ray structural investigation of the LiZnBO₃ crystal obtained by hydrothermal synthesis and the method of least squares in the isotropic approximation to R_{int}=0.067.² This material crystallizes in a centrosymmetric

structure having a monoclinic crystal system in space group C2/c(Z=8) and the sizes of the unit cell constants: a=5.094(1)Å, b=8.806(3)Å, c=10.374(4)Å, V=463.2(3)Å³ and α=91.09(3)°. The monoclinic cell parameters were refined on a RKOP automatic diffractometer.

The X-ray powder patterns of these previous papers mismatched any other phase in our experiments. Furthermore, we describe the phase transition of LiZnBO₃ with DTA analysis (Fig. 1) at chemistry department of Colorado State University.

EXPERIMENTAL

A powdered sample of LiZnBO₃ was prepared by

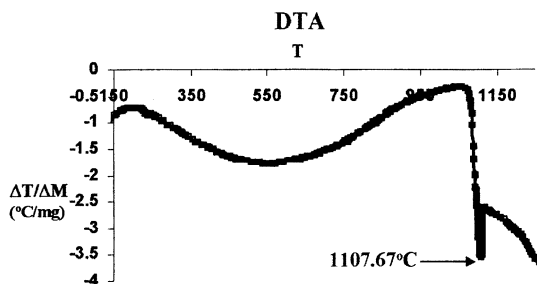


Fig. 1. DTA analysis of LiZnBO_3 .

heating a stoichiometric mixture of the reagents ZnO (Alfa, 99.99%) and LiBO_2 (Alfa, 99.997%). The mixture was heated in a Pt crucible at 893 K for 1 h, cooled, ground at room temperature, and again heated in a Pt crucible at 1273 K for 12 h. The X-ray powder diffraction patterns are shown in Fig. 2. The X-ray powder diffraction pattern (Fig. 1a) of the product, obtained with a Phillips diffractometer, matched that generated with the computer program LAZY-PULVERIX³ and the results of the single-crystal X-ray study (*vide infra*) (Fig. 1b). The crystals were grown in a Pt crucible from a melt containing 1ZnO and 1.1LiBO₂. The melt was cooled at 4 K/h from 1370 to 800 K, and then 5 K/min to room temperature. Then, the 0.1LiBO₂ was washed with a weak acidic solution. A clear, colorless crystal was physically separated from the matrix for X-ray measurements.

The colorless block crystal, having approximate dimensions of 0.420×0.350×0.280 mm, was mounted on a glass fiber and analyzed on a Rigaku AFC6R X-ray diffractometer. Unit-cell parameters were derived from least-squares refinement with the setting angles of 2θ automatically centered reflections in the range 30.42<2θ<35.60°. Intensity data were collected at room temperature by using the ω-scan technique with a rate=16°(ω)/min and peak widths = 1.50 - 0.30 tan θ. The lattice parameters and Laue symmetry $\bar{1}$ correspond to the triclinic system. The intensity data were collected over the range of indices -7<h<7, -7<k<7, -8<l<8 to 2θ_{max}=60°. From the 777 measured, a total of 550 reflections were observed [$I_{\text{obs}} > 3\sigma(I^2)$]. The intensities of three standard reflections varied by an average of 3% during the data collection.

The structure was solved and refined by using programs from the TEXSAN crystallographic software

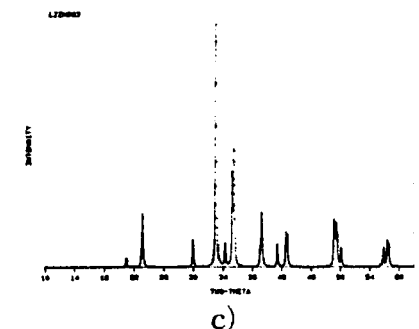
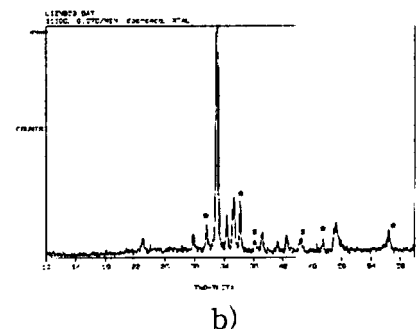
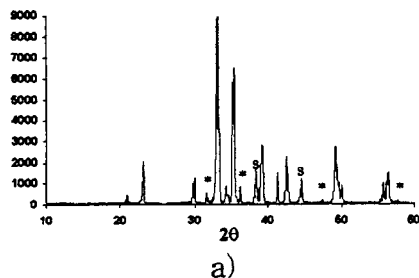


Fig. 2. (a) Powder X-ray diffraction trace of LiZnBO_3 synthesised at 700 °C: *—ZnO, s—Sample holder. (b) Powder X-ray diffraction trace of LiZnBO_3 synthesised at above melting point, 1110 °C: *—ZnO, s—Sample holder. (c) Powder X-ray diffraction trace generated with the computer program LAZY-PULVERIX³ and the results of the single-crystal data.

package⁴ on a μ -VAX-II computer. The space group P1 and $\bar{1}$ has been chosen on the basis of the Laue symmetry -1. The space group $\bar{1}$ has been selected only on the basis of the distribution of intensities and the successful solution and refinement of the structure. The efficiency of the second-harmonic generation from a selection of small crystals of LiZnBO_3 was not measured by the frequency conversion measurement, the method of Kurtz and Perry.⁵ The centrosymmetric crystal, the space group

Table 1. Crystallographic data for LiZnBO₃

Chemical formula	LiZnBO ₃
Formula weight, u	131.13
Crystal dimensions(mm)	0.420 0.350 · 0.280
Crystal system	triclinic
Space group	P $\bar{1}$ (No.2)
a	5.0915(9)Å
b	5.059(1)Å
c	6.156(1)Å
α	65.81(1) $^\circ$
β	65.56(1) $^\circ$
γ	59.77(1) $^\circ$
V	120.6(1)Å ³
Z	2
ρ_{calc} , gcm ⁻³	3.612
F ₀₀₀	124
Radiation	Mo K α (λ =0.71069Å) graphite monochromated
Temperature, K	296
Scan type	ω -2 θ
Scan rate, $^\circ$ in ω	16
$\sin \theta_{\text{max}}$, λ	1.50
Linear absorption coeff, cm ⁻¹	101.5
Transmission factors	0.81-1.09
Secondary extinction coefficient	0.21056 · 10 ⁻⁴
Total no. measured data	777
no. observations	
$F_o^2 \geq 3\sigma(F_o^2)$	550
R(F_o) ^a	0.039
R _w (F_o) ^b	0.056
p factor	0.03
Goodness of fit	2.28
Maximum shift/error in final cycle	0.01

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]}{2}$$

P $\bar{1}$, was expected by this experiment (Fundamental IR radiation, 1064 nm light, was generated with a Q-switched

Table 2. Positional parameters for LiZnBO₃

Atom	x	y	z
Zn1	0.7466(2)	0.0678(3)	0.8030(3)
Zn2	0.1179(3)	0.4330(3)	0.6952(3)
O1	0.7075(6)	0.5022(7)	0.6941(5)
O2	0.4039(6)	-0.0020(7)	0.8044(5)
O3	0.1539(7)	0.7501(8)	0.7468(8)
B1	0.577(1)	0.250(1)	0.254(1)
Li1	0.048(2)	0.401(2)	0.810(2)
Li2	0.761(3) \bar{y}	0.102(2)	0.684(2)

Molelectron MY-34 Nd³⁺: YAG laser, filtered and passed through the sample mounted on a silica glass plate. The second harmonic was directed onto a photomultiplier tube through a dichroic mirror and monitored with a Tektronix 2467B oscilloscope). The atom Zn was located by using the direct methods program SHELXS⁶. Following the analysis, the remaining atoms were placed on different electron density maps. After a full-matrix, least-squares refinement of the model with isotropic displacement coefficients on each atom, an absorption correction was applied by using the program DIFABS⁷ (transmission factors = 0.81-1.09); the data was then averaged ($R_{\text{int}} = 0.038$) final refinement with 274 averaged reflections and anisotropic displacement coefficients on each atom resulted in the residuals $R = 0.039$ and $wR = 0.056$. The largest peak in the final difference electron-density map corresponds to 2.1 σ of the Zn atom. Relevant crystallographic data and atomic parameters are listed in Table 1 and 2, respectively; anisotropic displacement coefficients are summarized in Table 3.

Results and Discussion

Fig. 1 shows the differential thermal analysis (DTA) of the title compound LiZnBO₃. One peak can be observed

Table 3. Anisotropic displacement coefficients for LiZnBO₃

ATOM	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Zn1	0.0132(6)	0.0150(6)	0.030(1)	-0.0054(4)	-0.0051(6)	-0.0077(6)
Zn2	0.0174(7)	0.0156(7)	0.029(1)	-0.0039(5)	-0.0115(7)	-0.0080(7)
O1	0.010(1)	0.010(1)	0.010(2)	-0.003(1)	-0.004(1)	-0.001(1)
O2	0.015(1)	0.012(1)	0.009(2)	-0.007(1)	-0.004(1)	-0.002(1)
O3	0.013(2)	0.024(2)	0.061(3)	-0.003(1)	-0.015(2)	-0.021(2)
B	0.010(2)	0.010(2)	0.012(2)	-0.003(2)	-0.005(2)	-0.002(2)
Li1	-0.013(4)	-0.009(4)	-0.015(5)	0.002(3)	0.007(4)	0.008(4)
Li2	0.021(7)	0.007(6)	-0.024(4)	-0.009(5)	-0.010(5)	0.008(4)

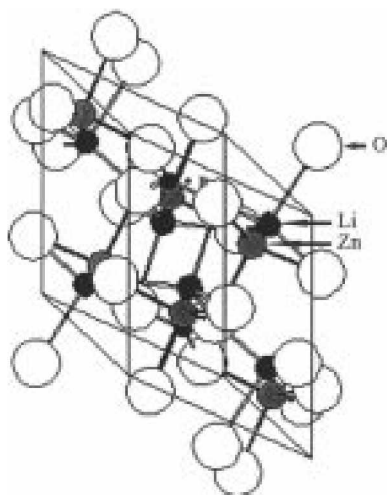


Fig. 3. Crystal structure of LiZnBO_3 .

in the DTA analysis, the peak at 1107.67°C is ascribed to the thermal decomposition in the phase transition as an endothermic peak. The compound LiZnBO_3 has a single phase below the melting point, 1107.67°C .

The structure (Fig. 3) of the title compound LiZnBO_3 contains layers of Planar BO_3 groups that are linked through Zn and Li atoms in LiO_4 and ZnO_4 distorted tetrahedra. Selected interatomic distances and angles are

listed in Table 4: The Zn atom is surrounded by four oxygen atoms at the vertices of a distorted tetrahedra - no site symmetry 1. The Zn-O distances, $1.945(3)\text{\AA}$ in Zn1-O1 distance, $2.044(3)\text{\AA}$ in Zn1-O2 distance, $1.873(3)\text{\AA}$ in Zn1-O3 distance, $2.034(4)\text{\AA}$ in Zn2-O1 distance, $1.946(3)\text{\AA}$ in Zn2-O2 distance and $1.863(3)\text{\AA}$ in Zn2-O3 distance, are normal, and the O-Zn-O angles in the ZnO_4 tetra, $92.6(1)^\circ$ - $118.4(2)^\circ$, are consistent with a tetrahedron. The distorted tetrahedral LiO_4 group exhibits no point-group symmetry with six Li-O distances of $1.90(1)\text{\AA}$ in Li1-O1 distance, $1.93(1)\text{\AA}$ in Li1-O2 distance, two $1.95(1)\text{\AA}$ in Li1-O3 distances, $1.92(1)\text{\AA}$ in Li2-O1 distance, $1.91(1)\text{\AA}$ in Li2-O2 distance and two $1.95(1)\text{\AA}$ in Li2-O3 distances. These lengths are reflected in the angles O-Li-O's, $94.8(5)^\circ$ - $119.8(6)^\circ$. The B-O distances, $1.374(5)\text{\AA}$ in B1-O1 distance, $1.391(5)\text{\AA}$ in B1-O2 distance and $1.366(1)\text{\AA}$ in B1-O3 distance, and the O-B-O angles, $120.6(4)^\circ$ in O1-B1-O2 angle, $120.2(4)^\circ$ in O1-B1-O3 angle and $119.3(3)^\circ$ in O2-B1-O3 angle, in the distorted trigonal BO_3 group is normal.

The Zn-Li interatomic distances, are $0.66(1)\text{\AA}$ in the Zn1-Li2 distance and $0.64(1)\text{\AA}$ in the Zn2-Li1 distance. Then, around 2 electrons are shown at the Li atom site listed with temperature factors β_{eq} of Table 5. During the structural refinement, it became apparent that the Li and

Table 4. Selected interatomic distances(\AA) and angles($^\circ$) for LiZnBO_3 .

Interatomic distances(\AA)		Interatomic angles($^\circ$)	
Zn1-O1	1.945(3)	O1-Zn1-O2	99.9(1), 117.1(1)
Zn1-O2(2)	2.044(3)	O1-Zn1-O3	117.4(2)
Zn1-O3	1.873(3)	O2-Zn1-O2	92.6(1)
		O2-Zn1-O3	103.1(2), 118.1(2)
Zn2-O1(2)	2.034(4)	O1-Zn2-O1	92.6(1)
Zn2-O2	1.946(3)	O1-Zn2-O2	100.1(1), 117.3(1)
Zn2-O3	1.863(3)	O1-Zn2-O3	103.4(2), 118.4(2)
		O2-Zn2-O3	117.5(2)
B1-O1	1.374(5)	O1-B1-O2	120.6(4)
B1-O2	1.391(5)	O1-B1-O3	120.2(4)
B1-O3	1.366(1)	O2-B1-O3	119.3(3)
Li1-O1	1.90(1)	O1-Li1-O2	119.8(6)
Li1-O2	1.93(1)	O1-Li1-O3	116.0(6)
Li1-O3(2)	1.95(1)	O2-Li1-O3	114.2(5)
Li2-O1	1.92(1)	O1-Li2-O2	119.0(8)
Li2-O2	1.91(1)	O1-Li2-O3	94.8(5), 114.1(6)
Li2-O3(2)	1.95(1)	O2-Li2-O3	104.0(5), 114.8(6)
		O3-Li2-O3	106.5(7)

Table 5. Atomic temperature factor β_{eq}^* and occupation for Zn and Li atoms of LiZnBO₃

Atom	β_{eq}^*	Occupation
Zn1	1.4(1)	0.460
Zn2	1.5(1)	0.475
Li1	-0.4(8)	0.550
Li2	0.1(9)	0.580

$$*\beta_{eq} = 8 \frac{\pi^2}{3} \sum \sum U_{ij} a_i^* a_j^* a_i a_j$$

Zn atom positions could possibly be disordered. The structure Li and Zn polyhedra consists of zig-zag bands of alternating Li and Zn polyhedra. This disorder could be accounted for by allowing the Li and Zn atoms to occupy two positions around the initial average positions, respectively (Table 5). A super structure was considered in this crystal system. We could not see any evidence in the single-crystal X-ray experimental data. Therefore, the title compound should be disordered around the average positions between Zn and Li atoms.

Acknowledgments. This work was financially supported by the Aerospace Research Institute at the Korean Air Force Academy. KSC thanks Prof. Douglas A.

Keszler for the X-ray diffraction experiment, Dr. Anthony Diaz at Washington State University for assistance with the SHG measurement and Prof. Peter K. Dorhout for the DTA and XRD experiment, respectively.

REFERENCES

1. Lehmann, Von H. V.; Schadow, H. *Z. Anorg. Chem.* **1966**, *348*, 42.
2. Bondareva, O. S.; Simonov, M. A.; Egorov-Tismenko, Yu. K.; Belov, N. V. *Sov. Phys. Crystallogr.* **1982**, *27*, 102.
3. Yvon, K.; Jeitschko, W.; Parthe F. *J. Appl. Cryst.* **1977**, *73*, 10.
4. TEXSAN, *Structure Analysis Package*. Molecular Structure Corp.; MSC 3200A, Research Forest Drive, The Woodlands, TX 77381.
5. Krutz, S. W.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.
6. Sheldrick, G. M. In *Crystallographic Computing 3*, Sheldrick, G. M., Krhger, Goddard, C., Eds.; Oxford Univ. Press: Oxford, U. K., 1985; p 175.
7. Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
8. Buludov, N. T.; Karaev, Z. Sh.; Abdullaev, G. K. *Russ. J. Inorg. Chem.(Engl. Transl.)* **1985**, *30*, 868.