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Ab Initio Structure Determination of New Compound $LiAlB_2O_5$

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A new compound $LiAlB_2O_5$ has been synthesized by solid-state reaction and its structure has been solved *ab initio* from X-ray powder diffraction data. The structure determination was based on direct methods combined with difference-Fourier techniques and the refinement was carried out using the Rietveld method. The final refinement converged with $R_p = 6.95\%$, $R_{wp} = 9.43\%$, $R_{exp} = 3.93\%$. This compound belongs to the monoclinic space group $C2/c$, with lattices parameters $a = 9.9096(1)$ Å, $b = 10.0634(1)$ Å, $c = 9.3552(1)$ Å, and $\beta = 120.0681(3)°$. There are eight molecules per unit cell and 10 atoms in the asymmetric unit. The structure of $LiAlB_2O_5$ exhibits some similarities to that of LiB_3O_5. Structural units found in $LiAlB_2O_5$, $[B_2AlO_7]^{5-}$ anionic groups, can be described as $[B_3O_7]^{5-}$ with the tetra-coordinated B replaced by an Al atom, which may possess higher second-order microscopic susceptibility than $[B_3O_7]^{5-}$. © 2001 Academic Press

Key Words: **$LiAlB_2O_5$; structure determination; X-ray powder diffraction.**

1. INTRODUCTION

Alkali borate crystals with benzene-ring-like $[B_3O_7]^{5-}$ groups have attracted much research interest in recent years. A series of important nonlinear optical materials, such as LiB_3O_5(LBO) (1), CsB_3O_5(CBO) (2), and $CsLiB_6O_{10}$(CLBO) (3) have been discovered in these compounds.

The excellent nonlinear optical property of alkali borate crystals mainly comes from their anionic groups (4). According to the previous work (5), the larger the distortions in oxygen polyhedra or any other anionic groups of a structure and the more inhomogeneous the electron density distribution on the bonds in these groups, the higher the values of the second-order microscopic susceptibility. The charge distribution on the conjugated π orbital of $[B_3O_7]^{5-}$ is asymmetry, so this kind of anionic group has a great second-order microscopic susceptibility.

In order to enhance the second-order microscopic susceptibility, we hope to replace tetra-coordinate B of $[B_3O_7]^{5-}$ groups with other atoms. Al seems a good candidate since it is often tetrahedrally coordinated in compounds and has an outer electronic structure similar to B. Therefore, a new compound $LiAlB_2O_5$ is expected to exist if the tetra-coordinated B in LiB_3O_5 can be replaced by Al. Kim and Hummel (6) reported a compound, $Li_4Al_4B_6O_{17}$, in 1962 (6), but Abdullaev *et al.* denied the existence of this compound and reported a compound $Li_2Al_2B_4O_{10}$ (7). However, no structural information such as unit cell or space group was given for either $Li_4Al_4B_6O_{17}$ or $Li_2Al_2B_4O_{10}$.

In this work, we synthesized the compound of $LiAlB_2O_5$ by solid-state reaction method. Powder X-ray diffraction suggested that the formation of $LiAlB_2O_5$ needs a long time annealing at a certain temperature. The diffraction pattern of $LiAlB_2O_5$ is different from either $Li_2Al_2B_4O_{10}$ reported by Abdullaev *et al.* (7) or $Li_4Al_4B_6O_{17}$ reported by Kim and Hummel (6). Here we report the synthesis and the structure of $LiAlB_2O_5$ determined *ab initio* from X-ray powder diffraction data.

2. EXPERIMENTAL

Polycrystalline $LiAlB_2O_5$ samples were prepared by solid-state reaction from a finely ground and stoichiometric mixture of analytically pure Li_2CO_3, Al_2O_3, and H_3BO_3. The powder was fired at 750°C for 1 or 2 days with an intermediate grinding and its diffraction measurement was performed. The process was repeated until its diffraction pattern had no further changes. A chemical analysis showed that the loss of Li and B was negligible in the course of a solid-state reaction.

X-ray diffraction measurements were performed using an automated Rigaku D/Max-2400 diffractometer working in the step scanning mode and equipped with a graphite monochromator. More details on the X-ray diffraction experiment can be found in Table 1.

3. RESULTS AND DISCUSSION

The X-ray diffraction of $LiAlB_2O_5$ synthesized in the present study is very different from that of $Li_2Al_2B_4O_{10}$

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TABLE 1
Experimental Details

Diffractometer	Rigaku D/Max 2400
Radiation type	Cu$K\alpha$
Wavelength (Å)	1.5418
Profile Range (°2θ)	10–135
Step size (°2θ)	0.02
Step scan time (s)	1
No. of observations (N)	6251
No. of contributing reflections	1450 ($K\alpha1 + K\alpha2$)
No. of structure parameters (P_1)	40
No. of profile parameters (p_2)	17
R_p (%)	6.95
R_{wp} (%)	9.43
R_{exp} (%)	3.93
S	2.39

Note. $R_p = \sum|y_{io} - y_{ic}|/y_{io}$, $R_{wp} = \sum[w_i(y_{io} - y_{ic})^2/w_i y_{io}^2]^{1/2}$, $R_{exp} = \sum(N - P_1 - P_2)/[w_i y_{io}^2]^{1/2}$, $S = \sum[w_i(y_{io} - y_{ic})^2]^{1/2}/(N - P_1 - P_2)$.

reported by Abdullaev *et al.* (7). We also found that the diffraction data of $Li_2Al_2B_4O_{10}$ cannot be indexed with the Dicvol program (8).

All peaks of $LiAlB_2O_5$ synthesized in this work can be indexed based on a monoclinic cell with lattice parameters $a = 9.902$ Å, $b = 10.053$ Å, $c = 9.348$ Å, $\beta = 120.052°$. The systematic absence of hkl with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$ suggests that the possible space groups are Cc or $C2/c$.

The symmetry information, the unit cell dimensions, and the data were then input to Fullprof program (9) to decompose the pattern. Total 733 values of $|F_{obs}|$ were extracted. The agreement indices corresponding to Cc and $C2/c$ converged to the values $R_{wp} = 12.7\%$, $R_{exp} = 5.39\%$ and $R_{wp} = 12.6\%$, $R_{exp} = 5.39\%$, respectively. Because the latter possesses a higher symmetry, the space group $C2/c$ is tested firstly.

The density of the samples was measured to be 2.39 g/cm^3. According to this result and the symmetry information, it is determined that there are eight $LiAlB_2O_5$ molecules in one unit cell.

Direct methods were applied with Shelxs-86 program (10) to $|F_{obs}|$ obtained by using the program Fullprof program (9). The list of interatomic distances showed that 5 of the 12 peaks listed in the E-map were likely to correspond to the correct positions of atoms. The strongest one of the five peaks was assigned to Al, the weakest B(1) and the remaining O(1)–O(3) according to the interatomic distances. The other atoms were located by using difference Fourier synthesis with Shelxl-93 (11) and approximate $|F_{obs}|$ values derived by the pattern decomposition method. In this

TABLE 2
Crystallographic Data

Chemical formula	$LiAlB_2O_5$
Cell setting	Monoclinic
Space group	$C\,2/c$
a (Å)	9.9096(1)
b (Å)	10.0634(1)
c (Å)	9.3552(1)
β (°)	120.0681(3)
V (Å^3)	807.39(1)
Z	8
D_m (g cm^{-3})	2.39
D_x (g cm^{-3})	2.229

TABLE 3
Positional, Thermal, and Occupancy Parameters for $LiAlB_2O_5$

Atom	Site	x	y	z	B (Å^2)
Li (1)	4e	0.0000	0.378(1)	0.2500	2.6(3)
Li (2)	4e	0.0000	0.159(2)	−0.2500	3.2(3)
Al	8f	0.1948(2)	0.1523(2)	0.1510(2)	1.18(4)
B(1)	8f	−0.0662(7)	0.3266(7)	−0.0308(8)	1.5(1)
B(2)	8f	0.2341(8)	−0.0050(6)	0.4071(8)	1.4(1)
O(1)	8f	0.0582(4)	0.2754(3)	0.1104(4)	1.63(8)
O(2)	8f	−0.1232(3)	0.2944(3)	−0.1897(3)	0.98(8)
O(3)	8f	−0.1386(4)	0.4271(3)	0.0238(4)	1.76(8)
O(4)	8f	0.1581(4)	0.0184(3)	0.2428(4)	1.64(8)
O(5)	8f	0.1846(3)	0.1071(3)	−0.0311(4)	1.19(8)

TABLE 4
Selected Interatomic Distances (Å) and Angles (°)

Bond lengths (Å)		Angles (°)	
Li(1)–O(1)$_{1,3}$:	1.963 (8)		
Li(1)–O(3)$_{1,3}$:	1.923 (5)		
Li(2)–O(2)$_{1,3}$:	2.09 (1)		
Li(2)–O(4)$_{5,7}$:	2.40 (1)		
Li(2)–O(5)$_{1,3}$:	2.014 (6)		
Al–O(1)$_1$:	1.731 (4)	O(1)$_1$–Al–O(2)$_6$:	109.0 (4)
Al–O(2)$_6$:	1.752 (3)	O(1)$_1$–Al–O(4)$_1$:	109.3 (4)
Al–O(4)$_1$:	1.732 (4)	O(1)$_1$–Al–O(5)$_1$:	108.7 (4)
Al–O(5)$_1$:	1.717 (4)	O(2)$_6$–Al–O(4)$_1$:	101.5 (3)
		O(2)$_6$–Al–O(5)$_1$:	116.7 (4)
		O(4)$_1$–Al–O(5)$_1$:	111.3 (4)
B(1)–O(1)$_1$:	1.378 (8)	O(1)$_1$–B(1)–O(2)$_1$:	131 (1)
B(1)–O(2)$_1$:	1.339 (7)	O(1)$_1$–B(1)–O(3)$_1$:	106.4 (7)
B(1)–O(3)$_1$:	1.472 (8)	O(2)$_1$–B(1)–O(3)$_1$:	122.9 (9)
B(2)–O(3)$_6$:	1.421 (8)	O(3)$_6$–B(2)–O(4)$_1$:	123.5 (9)
B(2)–O(4)$_1$:	1.351 (7)	O(3)$_6$–B(2)–O(5)$_5$:	116.9 (8)
B(2)–O(5)$_5$:	1.384 (8)	O(4)$_1$–B(2)–O(5)$_5$:	119.5 (9)

Note. Symmetry codes: (1) x, y, z; (2) $x + 0.5, y + 0.5, z$; (3) $-x, y, -z + 0.5$; (4) $-x + 0.5, y + 0.5, -z + 0.5$; (5) $x, -y, z + 0.5$; (6) $x + 0.5, -y + 0.5, z + 0.5$; (7) $-x, -y, -z$; (8) $-x + 0.5, -y + 0.5, -z$.

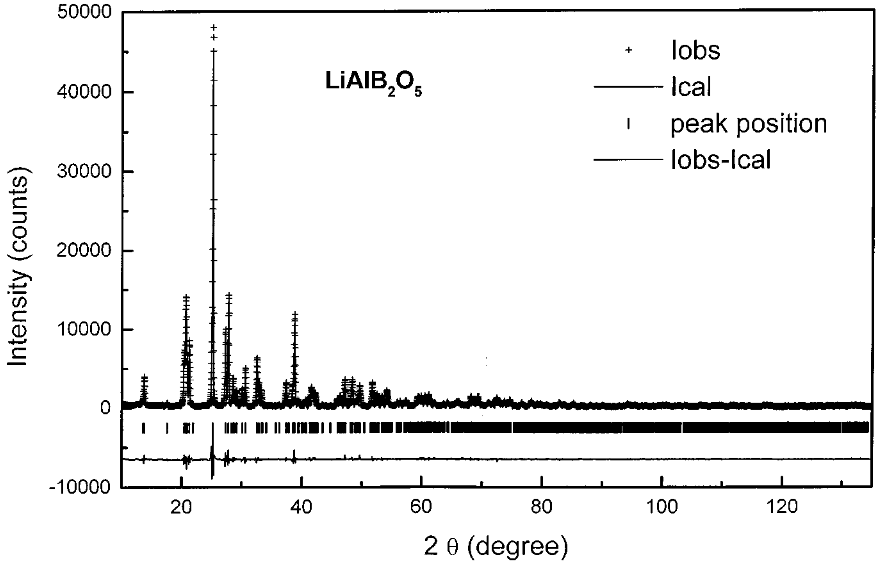

FIG. 1. The final XRD patterns of $LiAlB_2O_5$ refined by Rietveld method. The continuous line corresponds to the calculated spectrum, vertical bars indicate the positions of Bragg peaks. The bottom trace depicts the difference between the experimental and the calculated intensity values.

course, once an atom was located, it would be used for the next run of difference-Fourier synthesis.

Rough structure obtained by using direct methods and difference-Fourier synthesis was input to the DBW9411 program (12) to be refined with the Rietveld method. All atoms were refined isotropically. The refinement is very stable. In the final cycles of refinement, the shifts in all parameters were less than their esds. The space group *Cc* was also tested to refine the approximate structure, but the final atom positions changed little. Therefore, the structure of $LiAlB_2O_5$ is centrosymmetric or very near centrosymmetric.

Crystallographic details are summarized in Table 2. The final positional parameters are listed in Table 3. A list of selected bond lengths and angles is given in Table 4. Final refinement results are presented in Fig. 1.

To provide a check on the consistency of the structure solution, the bond valences *S* have been calculated according to the Brown and Altermatt parameters (13) and are listed in Table 5. It can be seen that the bond valence sum of each cation is in fairly good agreement with the formal oxidization state.

TABLE 5
Li–O, Al–O and B–O Bond Valences in $LiAlB_2O_5$

	O (1)	O (2)	O (3)	O (4)	O (5)	$\sum S$
Li (1)	0.261		0.290			1.10
Li (2)		0.186		0.08	0.227	0.99
Al	0.805	0.762		0.804	0.837	3.21
B (1)	0.982	1.093	0.762			2.84
B (2)			0.875	1.056	0.966	2.90

The projection structure of the compound $LiAlB_2O_5$ was shown in Fig. 2a. For comparison, a projection of LBO along b axis was also shown in Fig. 2b. To give some complete structural units, the part shown in Fig. 2 is not a unit cell. For clarity, a separate structural unit of LiB_3O_5 and $LiAlB_2O_5$ was illustrated in Figs. 3a and 3b, respectively. From Fig. 3 we can see that the structural unit of $LiAlB_2O_5$, $[B_2AlO_7]^{5-}$, is rather similar to that of LBO, $[B_3O_7]^{5-}$. It can be described as $[B_3O_7]^{5-}$ with the tetra-coordinated B substituted with an Al atom. Both $LiAlB_2O_5$ and LBO can be characterized as networks formed by $[B_2AlO_7]^{5-}$ or $[B_3O_7]^{5-}$ rings and the way in which the structural units connect with each other is similar. Every $[B_2AlO_7]^{5-}$ or $[B_3O_7]^{5-}$ ring connects with four adjacent rings via bridging-oxygen atoms, but the configuration of four adjacent rings of $[B_2AlO_7]^{5-}$ group in $LiAlB_2O_5$ is much different from that of $[B_3O_7]^{5-}$ in LBO.

Al has been introduced successfully into benzene-ring-like $[B_3O_7]^{5-}$ groups, but the properties of the Al atom are much different from those of B. The bond length of Al–O is more than 1.7 Å while that of B–O is less than 1.5 Å, so the distribution of electron density on the $[B_2AlO_7]^{5-}$ ring will be more inhomogeneous than that on the $[B_3O_7]^{5-}$ ring. According to the previous work (5), this will lead to a higher second-order microscopic susceptibility. Further work in the measurement of the properties is under way.

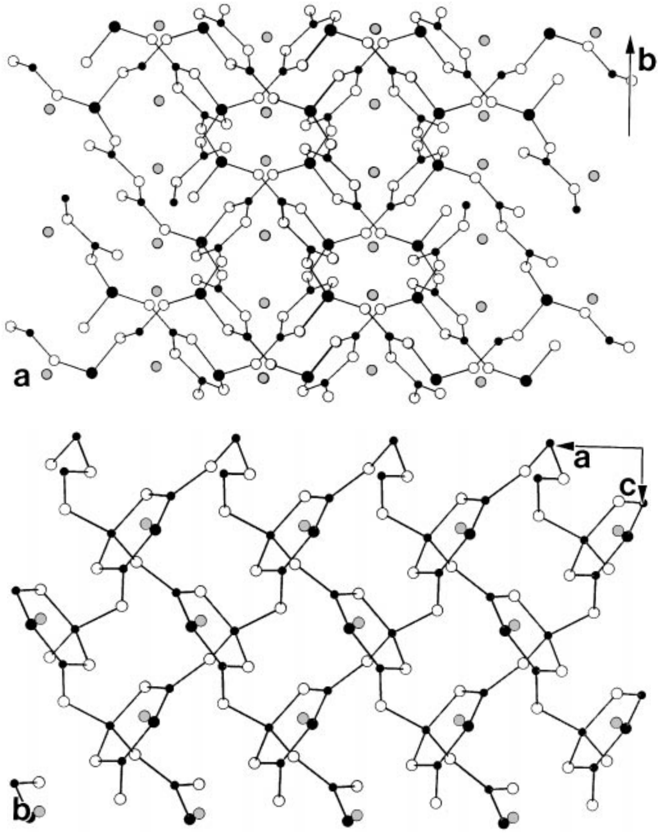

FIG. 2. The projection of $LiAlB_2O_5$ along [101] (a) and LiB_3O_5 along [010] (b). White circles indicate O atoms, gray ones Li atoms, big black ones Al atoms, and small black ones B.

4. CONCLUSIONS

In this work we synthesized the compound of $LiAlB_2O_5$ by solid state reaction and determined its structure directly from X-ray powder diffraction data.

$LiAlB_2O_5$ exhibits structural similarities to LBO. Its structural unit, $[B_2AlO_7]^{5-}$, can be characterized as $[B_3O_7]^{5-}$ group with the tetra-coordinated B replaced by an Al atom. According to the previous work (5), it is reasonable to think that $[B_2AlO_7]^{5-}$ will possess a higher second-order microscopic susceptibility than $[B_3O_7]^{5-}$ group. It gives a strong hint for researcher exploring new nonlinear optical materials.

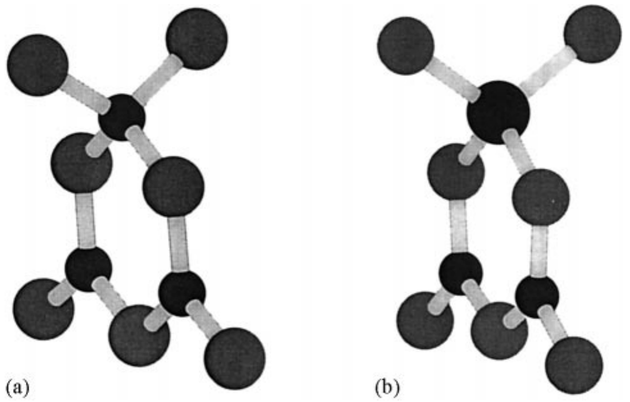

FIG. 3. The structural unit of LiB_3O_5 (a) and $LiAlB_2O_5$ (b). Big black circles represent oxygen atoms and small black ones B. Note the four-coordinated big black circle in (b) is Al atom.

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