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The Ternary System Li_2O–Al_2O_3–B_2O_3: Compounds and Phase Relations

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The ternary system Li_2O–Al_2O_3–B_2O_3 is reinvestigated with solid-state reaction and X-ray powder diffraction technique to clarify some long-standing uncertainties. The phase relations are constructed based on the phase identifications of 51 ternary samples. Six ternary compounds, $Li_2AlB_5O_{10}$, $LiAlB_2O_5$, $Li_3AlB_2O_6$, Li_2AlBO_4, $LiAl_7B_4O_{17}$ and a compound with a composition close to $0.66Li_2O \cdot 0.06Al_2O_3 \cdot 0.28B_2O_3$, are observed or confirmed in this system, and the thermal stability of these ternary compounds is also discussed on the basis of DTA experimental results. © 2002 Elsevier Science (USA)

Key Words: **Li_2O–Al_2O_3–B_2O_3 system; phase relations; compounds; thermal stability.**

1. INTRODUCTION

High polarizability and excellent transparency in ultraviolet region of planar $[BO_3]^{3-}$ imply that borates are attractive candidates in the search for new nonlinear optical materials (1, 2). So a great deal of research interest has been focused on the synthesis and characterization of inorganic borates during the past decades. Many excellent nonlinear optical materials, such as β-BaB_2O_4 (3), LiB_3O_5 (4) and CsB_3O_5 (5), have been found in binary borates. Recently, there has been an extension of the scope of exploring new optical materials to ternary systems. $CsLiB_6O_{10}$ (6), $Sr_2Be_2B_2O_7$ (7) and $K_2Al_2B_2O_7$ (8) are successful examples of these explorations. Moreover, the anisotropy of polarizability of planar $[BO_3]^{3-}$ groups indicates that borates are also potential birefringent materials if their $[BO_3]^{3-}$ groups are in suitable configuration. To further search new nonlinear and birefringent materials, many ternary borate systems have been investigated (9, 10).

Al has an outer electronic structure similar to that of B and is often in tetra-coordination, so it may act like tetrahedrally coordinated B in compounds. If Al can replace tetra-coordinated B then many new borates are expected to exist. In order to synthesize new borates and search for new optical materials, we have studied the system Li_2O–Al_2O_3–B_2O_3.

Many researchers have investigated this system before us. However, they left a lot of uncertainties in their work. Kim and Hummel (11) first reported the ternary phase diagram of this system in 1962. In their studies, only two ternary borates, $Li_4Al_4B_6O_{17}$ and Li_2AlBO_4 were observed. In 1983, Abdullaev *et al.* (12) studied this system in more detail and identified six ternary compounds: $Li_2Al_2B_4O_{10}$, Li_2AlBO_4, $Li_3AlB_2O_6$, $Li_2Al_2B_2O_7$, $Li_2Al_4B_4O_{13}$ and $Li_4Al_2B_4O_{11}$. Among all these compounds, only $Li_3AlB_2O_6$ was structurally characterized (13, 14). No structural information but unindexed X-ray powder diffraction patterns have been presented for other compounds. Recently, Psycharis *et al.* (15) confirmed the existence of Li_2AlBO_4 and solved its structure using an X-ray powder diffraction technique. Another compound $LiAl_7B_4O_{17}$ was reported by Åhman *et al.* (16) in 1997. So it is necessary to reinvestigate this system to clarify these uncertainties or inconsistencies in previous literatures and establish a more reliable diagram. In our recent studies, we have systematically investigated this ternary system. Experimental work was found to be difficult because Li_2O and B_2O_3 are volatile and corrosive. Especially the Li_2O-rich samples can even erode Pt crucibles strongly at temperatures above 650°C. Another difficulty is that the temperature range of stability changes greatly from one compound to another. Some compounds can only be synthesized at very high temperature, and some melt or dissociate at rather low temperatures. In our study, most samples with the content of Li_2O lower than 50% were treated at 700–800°C. Our experiments indicated that the loss of Li_2O and B_2O_3 in reaction is negligible in this temperature range. We also found that the stoichiometric starting materials do not necessarily lead to single phase; even chemical analysis suggests that the compositions of samples really change little in reaction. Sometimes the results of experiments seem to be very confused and hard to interpret. This may explain as to why there are so many uncertainties and inconsistencies in previous reports. In this study we have made

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many improvements and clarified some long-standing uncertainties. A completely new ternary compound $Li_2Al B_5O_{10}$ was identified and structurally characterized. The existence of $Li_2Al_2B_4O_{10}$ was confirmed and its structure was determined ab initio from X-ray powder diffraction data. It is interesting to point out that its powder diffraction pattern is quite different from previous reports. The existence of $Li_3AlB_2O_6$ was confirmed but its structure was found to be different from the one reported by Abdullaev *et al.* (13, 14) and so is its powder diffraction pattern. $LiAl_7B_4O_{17}$, which did not occur in previous phase diagrams (11, 12), could be easily synthesized by solid-state reaction. Another ternary compound with composition close to $0.66Li_2O \cdot 0.06Al_2O_3 \cdot 0.28B_2O_3$ was observed but its structure was still unknown. Since the exact formula of this compound is still unknown, we named it X-phase. In this paper, the partial phase relations in the system Li_2O–Al_2O_3–B_2O_3 are presented and crystallographic data of the ternary compounds are summarized. The thermal stability of these ternary compounds is also reported here.

2. EXPERIMENTAL

A series of samples of different compositions in the system Li_2O–Al_2O_3–B_2O_3 were prepared by solid-state reaction using analytical pure Li_2CO_3, Al_2O_3 and H_3BO_3 as starting materials. The starting materials were thoroughly mixed, ground in an agate mortar and then sintered for about 2 days in an electrical furnace. Most samples with the content of Li_2O lower than 50% were calcined at temperatures between 700°C and 800°C, depending on the sample composition. The products of the Li_2O-rich samples are found to be very sensitive to the reaction temperature. In this study, all the Li_2O-rich ($Li_2O\% \geq 50\%$) samples were treated at 620°C. Products of solid-state reaction were analyzed by X-ray powder diffraction with a Rigaku D/Max-2400 diffractometer. The above process was repeated until no further changes could be observed in the powder diffraction patterns.

A CP-G differential thermal instrument was employed to perform DTA experiments with a heating rate of 10°C/min.

Chemical analysis was performed using inductivity coupled plasma-atomic emission spectrometry (ICP-AES) technique.

3. RESULTS AND DISCUSSION

3.1. Binary Systems

According to the phase diagrams reported by Sastry *et al.* (17, 18), there are eight binary compounds with molar ratios Li_2O: B_2O_3 of 3:1, 2:1, 3:2, 1:1, 1:2, 2:5, 1:3 and 1:4 in the binary system Li_2O–B_2O_3. For one of them, $2Li_2O \cdot 5B_2O_3$, it was found by Jiang *et al.* (19) in 1990 that the true composition is $3Li_2O \cdot 7B_2O_3$. In our experiments, only six compounds, $3Li_2O \cdot B_2O_3$, $2Li_2O \cdot B_2O_3$, $3Li_2O \cdot 2B_2O_3$, $Li_2O \cdot B_2O_3$, $Li_2O \cdot 2B_2O_3$ and $Li_2O \cdot 3B_2O_3$, were observed. $Li_2O \cdot 4B_2O_3$ and $3Li_2O \cdot 7B_2O_3$ were not obtained. This result is in agreement with Sastry et al.'s reports (17, 18) about thermal stability of these two compounds. They found that $2Li_2O \cdot 5B_2O_3$ ($3Li_2O \cdot 7B_2O_3$) decomposes when the temperature is lower than 696 ± 4°C while $Li_2O \cdot 4B_2O_3$ is stable only when the temperature is lower than 635 ± 10°C. Since samples related with these two compounds were heated between 700–800°C in our experiments, they could not be observed.

In the phase diagrams reported by Kim *et al.* (11) and Abdullaev *et al.* (12), there exist two binary compounds in the system Al_2O_3–B_2O_3: $9Al_2O_3 \cdot 2B_2O_3$ and $2Al_2O_3 \cdot B_2O_3$. However, structure analysis performed by Garsche *et al.* (20) indicates that the formula of $9Al_2O_3 \cdot 2B_2O_3$ should be $5Al_2O_3 \cdot B_2O_3$. But the authors of the same paper also pointed out that the substitution of B atoms for less than 2% Al atoms will result in a formula of $9Al_2O_3 \cdot 2B_2O_3$. In our study, the existence of $5Al_2O_3 \cdot B_2O_3$ was confirmed and its diffraction pattern was found to be consistent with ICDD PDF 77-0395. The compound $Al_2O_3 \cdot B_2O_3$, which was synthesized previously under hydrothermal conditions (21), has never been observed in the present study. The results about the sample $2Al_2O_3 \cdot B_2O_3$ were puzzling. After a prolonged heating at about 880°C, the reflections of this sample are still extraordinarily wide. The pure phase of $2Al_2O_3 \cdot B_2O_3$ has never been obtained though many reflections of the diffraction pattern are close to those reported in ICDD PDF 29-0010. When this sample was fired at higher temperature (1000°C), only reflections of $5Al_2O_3 \cdot B_2O_3$ could be observed in its diffraction pattern.

In the binary system Li_2O–Al_2O_3, only the tetragonal γ-$LiAlO_2$ was obtained and its diffraction pattern is in good agreement with the previously reported data (ICDD PDF 38-1464). $LiAl_5O_8$ (11,12), $Li_2Al_4O_7$ (12) and Li_5AlO_4 (12) reported in previous diagrams were not synthesized under our experimental conditions. Both samples $Li_2O \cdot 5Al_2O_3$ and $Li_2O \cdot 2Al_2O_3$ treated at 750°C consist of γ-$LiAlO_2$ and Al_2O_3. The sample $5Li_2O \cdot Al_2O_3$ heated at 620°C is composed of $LiAlO_2$ and Li_2CO_3. It is interesting to point out that $LiAlO_2$ obtained in this sample belongs to rhombohedral system.

3.2. Ternary System

In the ternary system, six ternary compounds were identified. Fig. 1 shows the phase diagram constructed from XRD data of 51 ternary specimens (Table 1). The results in the binary systems were not included in Table 1. Phase relations in the two shadowed regions are still not so clear because experimental results obtained there are

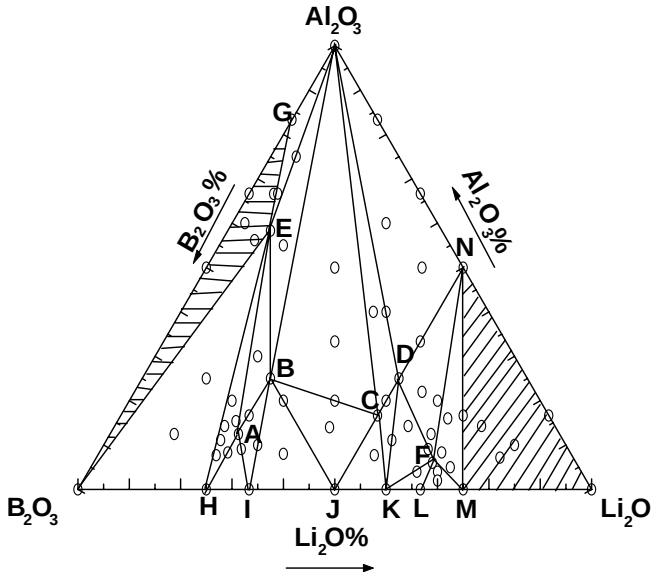

FIG. 1. Subsolidus phase relations in the system Li_2O_3–Al_2O_3–B_2O_3. (A) $Li_2AlB_5O_{10}$, (B) $LiAlB_2O_5$; (C) $Li_3AlB_2O_6$; (D) Li_2AlBO_4; (E) $LiAl_7B_4O_{17}$; (F) $0.66Li_2O \cdot 0.06Al_2O_3 \cdot 0.28B_2O_3$; (G) Al_5BO_9; (H) LiB_3O_5; (I) $Li_2B_4O_7$; (J) $LiBO_2$; (K) $Li_6B_4O_9$; (L) $Li_4B_2O_5$; (M) Li_3BO_3; (N) $LiAlO_2$.

puzzling and difficult to interpret. The compounds $Li_2Al_2B_2O_7$, $Li_4Al_2B_4O_{11}$ and $Li_2Al_4B_4O_{13}$ reported by Abdullaev *et al.* (12) could not be synthesized in our experiments even by different methods and at different sintering temperatures. Detailed discussions on ternary compounds observed in this study are presented as follows.

3.2.1. $Li_2AlB_5O_{10}$. $Li_2AlB_5O_{10}$ is a new compound found by us. The products of the stoichiometric starting materials consist of mainly $Li_2AlB_5O_{10}$ and a small amount of $Li_2B_4O_7$ as well as $LiAlB_2O_5$. When about 20% surplus H_3BO_3 was added into the starting materials, we obtained the X-ray pure $Li_2AlB_5O_{10}$. However, chemical analysis indicated that the atomic ratio of Al:B in the product is about 1:5.85, which is close to the original ratio in the starting materials. The formula and structure were determined by single crystal analysis. This compound crystallizes in a monoclinic unit cell with a space group $P2_1/c$. Its lattice parameters are $a = 7.0402(4)$ Å, $b = 14.9404(8)$ Å, $c = 7.0433(4)$ Å and $\beta = 90.7020(10)^\circ$. The detailed description of this structure has been published elsewhere (22). The unique configuration of planar B–O rings in this structure suggests that this compound might be an excellent birefringent material. Attempts to grow a large crystal of this compound are under way. Thermal analysis and powder diffraction indicate that this compound melts congruently at about 793°C (Fig. 2).

3.2.2. $LiAlB_2O_5$. Kim and Hummel (11) reported a compound $Li_4Al_4B_6O_{17}$ in 1962, but Abdullaev *et al.* (12) denied the existence of this compound and reported a compound $Li_2Al_2B_4O_{10}$. 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 our research, we

TABLE 1
List of Phase Identifications for Various Specimens in the System Li_2O–Al_2O_3–B_2O_3

No.	Li_2O (at%)	Al_2O_3 (at%)	B_2O_3 (at%)	Phase identification
1	70	5	25	X-phase + Li_3BO_3
2	69	2	29	X-phase + Li_3BO_3 + $Li_4B_2O_5$
3	68	4	28	X-phase + Li_3BO_3
4	66.7	8.3	25	X-phase + Li_3BO_3 + $LiAlO_2$
5	66	6	0.28	X-phase + $Li_4B_2O_5$ (trace)
6	66.7	16.6	16.7	Li_3BO_3 + $LiAlO_2$
7	64	16	20	$LiAlO_2$ + X-phase
8	64	4	32	X-phase + $Li_6B_4O_9$
9	63.6	9.1	27.3	X-phase + Li_2AlBO_4
10	62.5	12.5	25	X-phase + Li_2AlBO_4 + $LiAlO_2$
11	60	20	20	$LiAlO_2$ + X-phase
12	56	22	22	Li_2AlBO_4 + X-phase + $LiAlO_2$
13	57.1	14.3	28.6	Li_2AlBO_4 + X-phase + $Li_6B_4O_9$
14	55.6	11.1	33.3	Li_2AlBO_4 + $Li_6B_4O_9$
15	53.8	7.7	38.5	$LiBO_2$ + $Li_3AlB_2O_6$ + $Li_6B_4O_9$
16	50	16.7	33.3	$Li_3AlB_2O_6$
17	50	25	25	Li_2AlBO_4 + γ-$LiAlO_2$
18	50	33.3	16.7	Li_2AlBO_4 + γ-$LiAlO_2$
19	50	20	30	$Li_3AlB_2O_6$ + Li_2AlBO_4
20	42	50	8	Li_2AlBO_4 + γ-$LiAlO_2$ + Al_2O_3
21	42	14	44	$Li_3AlB_2O_6$ + $LiBO_2$ + $LiAlB_2O_5$
22	40	40	20	Li_2AlBO_4 + Al_2O_3
23	40	20	40	$Li_3AlB_2O_6$ + $LiAlB_2O_5$
24	37.5	40	22.5	Li_2AlBO_4 + Al_2O_3
25	36	8	56	$Li_2B_4O_7$ + $LiBO_2$ + $LiAlB_2O_5$
26	33.3	33.3	33.4	$Li_3AlB_2O_6$ + $LiAlB_2O_5$ + Al_2O_3
27	30	60	10	Li_2AlBO_4 + $LiAlO_2$ + Al_2O_3
28	30	20	50	$LiAlB_2O_5$ + $LiBO_2$
29	30	10	60	$Li_2B_4O_7$ + $LiAlB_2O_5$
30	27.3	9.1	63.6	$Li_2AlB_5O_{10}$ + $Li_2B_4O_7$
31	26.7	6.6	66.7	$Li_2AlB_5O_{10}$ + LiB_3O_5 + $Li_2B_4O_7$
32	25	50	25	$LiAlB_2O_5$ + Al_2O_3 + $Li_3AlB_2O_6$
33	25	25	50	$LiAlB_2O_5$
34	25	12.5	62.5	$Li_2AlB_5O_{10}$ + $Li_2B_4O_7$ + $LiAlB_2O_5$
35	25	16.7	58.3	$Li_2AlB_5O_{10}$ + $LiAlB_2O_5$
36	25	8.3	66.7	$Li_2AlB_5O_{10}$ + LiB_3O_5
37	23.1	7.7	69.2	$Li_2AlB_5O_{10}$ + LiB_3O_5 + $LiAl_7B_4O_{17}$
38	23.1	15.4	61.5	$Li_2AlB_5O_{10}$ + LiB_3O_5 + $LiAl_7B_4O_{17}$
39	22.2	11.1	66.7	$Li_2AlB_5O_{10}$ + LiB_3O_5 + $LiAl_7B_4O_{17}$
40	21.4	14.3	64.3	$Li_2AlB_5O_{10}$ + LiB_3O_5 + $LiAl_7B_4O_{17}$
41	20	20	60	$Li_2AlB_5O_{10}$ + LiB_3O_5 + $LiAl_7B_4O_{17}$
42	20	30	50	$LiAl_7B_4O_{17}$ + $LiAlB_2O_5$ + $Li_2AlB_5O_{10}$
43	12.5	55	32.5	$LiAl_7B_4O_{17}$ + $LiAlB_2O_5$ + Al_2O_3
44	12.5	12.5	75	$LiAl_7B_4O_{17}$ + LiB_3O_5 + amorphous phase
45	12.5	25	62.5	$LiAl_7B_4O_{17}$ + LiB_3O_5 + amorphous phase
46	8.3	58.3	33.4	$LiAl_7B_4O_{17}$
47	6.3	56.2	37.5	$LiAl_7B_4O_{17}$
48	5.6	66.6	27.8	$LiAl_7B_4O_{17}$ + Al_5BO_9
49	5	75	20	$LiAl_7B_4O_{17}$ + Al_2O_3
50	4.8	66.6	28.6	$LiAl_7B_4O_{17}$ + Al_5BO_9
51	2.5	60	37.5	$LiAl_7B_4O_{17}$

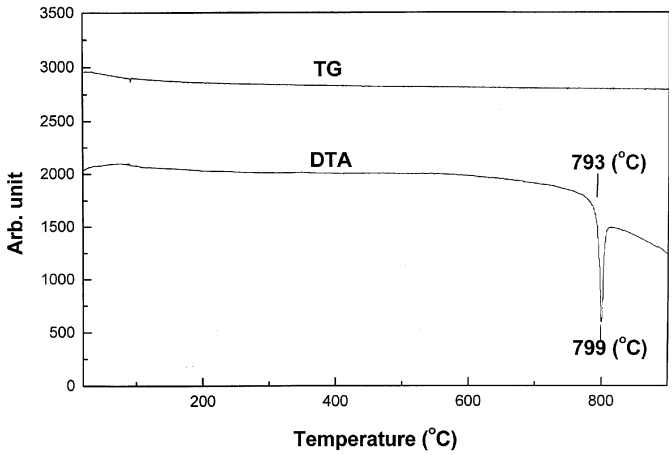

FIG. 2. Thermal gravity (upper) and differential thermal analysis (bottom) curves of $Li_2AlB_5O_{10}$.

synthesized a compound $LiAlB_2O_5$, and determined its structure from X-ray powder diffraction data. Although the chemical compositions of this compound and $Li_2Al_2B_4O_{10}$ reported by Abdullaev*et al.* (12) are identical, their powder diffraction patterns are completely different. The powder diffraction data and indexed results of our compound are presented in Table 2. This compound was found to crystallize in a monoclinic unit cell with a space group $C2/c$. The detailed structure data of this compound have been published in one of our previous papers (23). The most important characteristic of this structure is that AlO_4 tetrahedra connect with two BO_3 triangles to form a new type of anionic group $[AlB_2O_7]^{5-}$, which can be described as a $[B_3O_7]^{5-}$ group with the tetra-coordinated B replaced by an Al atom. We also performed DTA experiments and found that this compound melts congruently around 824°C (Fig. 3).

3.3.3. $Li_3AlB_2O_6$. In 1974, Abdullaev *et al.* (13) reported the compound $Li_3AlB_2O_6$ firstly and solved its structure. In 1982, they further refined this structure (14). According to their report, this compound crystallizes in a triclinic unit cell with lattice parameters $a=6.131(2)$ Å, $b=4.819(1)$ Å, $c=8.227(3)$ Å, $\alpha=90.3(0)°$, $\beta=117.0(0)°$ and $\gamma=89.9(0)°$. In our investigation, we obtained a different structure for this compound but never observed the modification reported by Abdullaev *et al.* (13,14). The lattice parameters of our structure are $a=4.876(8)$ Å, $b=6.191(16)$ Å, $c=7.910(20)$ Å, $\alpha=74.46(18)°$, $\beta=89.44(17)°$ and $\gamma=89.52(18)°$. In addition, we also found that our unit cell could not be transformed into the one determined by Abdullaev *et al.* This compound was found to dissociate to Li_2AlBO_4 and $LiBO_2$ at about 792°C. The detailed results of the study on this compound will be reported in a separate paper (24).

TABLE 2
List of Indexes, *d*-Values and Diffraction Intensities of $LiAlB_2O_5$

h	k	l	d_{obs}	d_{cal}	I/I_0
−1	1	1	6.43	6.42	8
0	2	0	5.037	5.034	2
1	1	1	4.338	4.341	16
−2	0	0	4.286	4.294	31
−2	0	2	4.169	4.166	18
−2	2	1	3.531	3.532	100
−2	2	0	3.2661	3.2666	22
−2	2	2	3.2104	3.2096	30
1	3	0	3.126	3.126	9
−3	1	1	3.100	3.101	4
−3	1	2	3.0647	3.0645	5
1	1	2	2.9726	2.9723	5
−1	1	3	2.920	2.919	11
1	3	1	2.7521	2.7523	14
−1	3	2	2.728	2.726	7
2	2	1	2.6939	2.6943	5
0	4	1	2.404	2.403	8
0	2	3	2.380	2.379	1
−3	3	1	2.336	2.338	6
−3	3	2	2.322	2.322	28
3	1	1	2.290	2.292	2
−3	1	4	2.221	2.220	2
−1	1	4	2.1830	2.1839	3
2	2	2	2.1703	2.1704	6
−3	3	3	2.1392	2.1397	4
2	4	1	1.9755	1.9758	3
−1	5	1	1.9573	1.9571	4
−4	2	4	1.9257	1.9249	9
1	3	3	1.8808	1.8807	9
−1	3	4	1.860	1.861	2
−1	5	2	1.8491	1.8493	3
−3	1	5	1.8353	1.8352	7

Note. $a=9.920(4)$ Å, $b=10.067(2)$ Å, $c=9.359(1)$ Å and $\beta=120.05(2)°$, $Z=8$ and space group $C2/c$.

3.3.4. Li_2AlBO_4. Kim and Hummel (11) reported a compound Li_2AlBO_4 in 1962 and Abdullaev *et al.* (12) confirmed its existence in 1983. Recently, Psycharis *et al.* (15) solved its structure by an X-ray powder diffraction technique. This compound crystallizes in a monoclinic unit cell. In this study, we found that starting materials in stoichiometric proportions always led to a mixture of Li_2AlBO_4 and a small quantity of γ-$LiAlO_2$, and the quantity of γ-$LiAlO_2$ increases with the temperature of treatment. When the product obtained at a higher temperature is annealed at a lower temperature for a long time, the content of γ-$LiAlO_2$ decreases again. So we speculate that surplus B_2O_3 did not evaporate when the sample was treated at a higher temperature. Moreover, chemical analysis also indicated that the loss of Li_2O and B_2O_3 is negligible during the process of solid-state reaction. However, when 10% surplus H_3BO_3 was added into the starting materials, only reflections of Li_2AlBO_4 could be observed in the powder pattern of the product and the

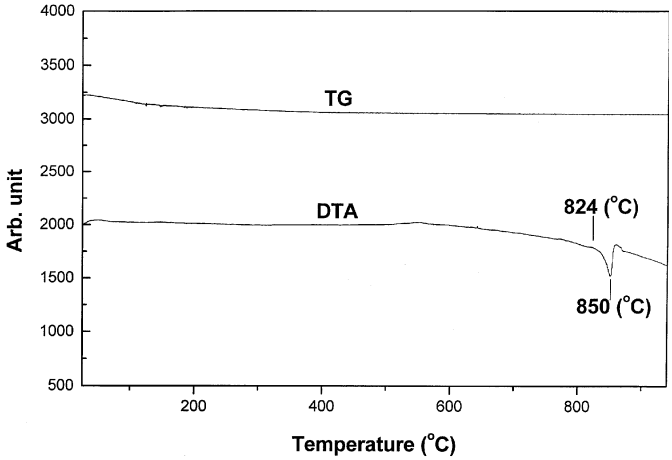

FIG. 3. Thermal gravity (upper) and differential thermal analysis (bottom) curves of $LiAlB_2O_5$.

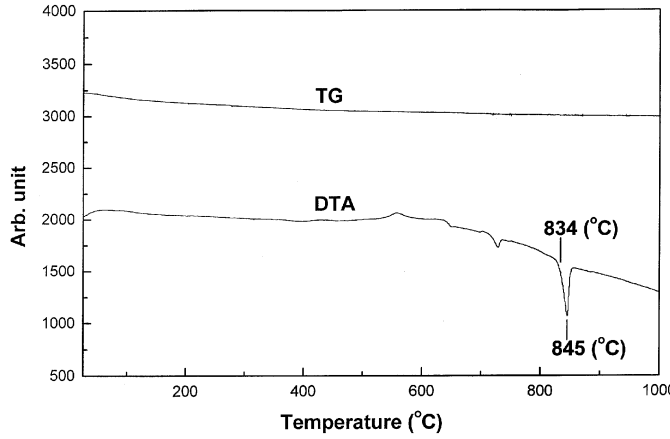

FIG. 4. Thermal gravity (upper) and differential thermal analysis (bottom) curves of Li_2AlBO_4. Peaks in the DTA curve under 800°C might be caused by the surplus B_2O_3.

pattern agreed very well with calculated pattern of the structure reported by Psycharis *et al.* (15). What role the surplus B_2O_3 has played in the reaction is not clear. Since the indexed powder pattern has not been reported so for, we present it in Table 3. Using DTA technique, we found Li_2AlBO_4 samples with surplus B_2O_3 as impurity melts incongruently around 845°C (Fig. 4).

TABLE 3
List of Indexes, *d*-Values and Diffraction Intensities of Li_2AlBO_4

h	*k*	*l*	d_{obs}	d_{cal}	I/I_0
−1	0	0	6.231	6.235	48
0	1	1	4.542	4.542	26
−1	0	2	4.173	4.169	2
−1	1	0	3.934	3.933	2
1	0	2	3.766	3.771	22
1	1	1	3.597	3.595	10
−1	1	2	3.2194	3.2196	100
1	1	2	3.0260	3.0254	9
0	1	3	2.8300	2.8294	9
−2	0	2	2.793	2.792	58
−2	1	0	2.6557	2.6555	5
2	0	2	2.548	2.549	7
0	2	0	2.533	2.534	15
1	1	3	2.499	2.498	54
0	2	1	2.459	2.460	4
−1	2	1	2.3075	2.3077	2
1	2	1	2.2701	2.2694	8
−1	2	2	2.1658	2.1655	2
0	2	3	2.0343	2.0341	8
2	1	3	2.0129	2.0122	5
−1	2	3	1.968	1.969	2
−2	1	4	1.9271	1.9277	2
2	2	1	1.9083	1.9086	6
2	0	4	1.8852	1.8854	4
−2	2	2	1.8765	1.8764	7
−3	1	2	1.8591	1.8587	12

Note. $a = 6.268(2)$ Å, $b = 5.0686(8)$ Å, $c = 10.284(3)$ Å and $\beta = 95.85(1)^\circ$, $Z = 4$ and space group $P2_1/c$.

3.3.5. $LiAl_7B_4O_{17}$. In 1997, Åhman *et al.* (16) first found the compound $LiAl_7B_4O_{17}$ and solved its structure with single-crystal analysis technique. This compound crystallizes in a tetragonal unit cell with lattice parameters $a = 10.5454(7)$ and $c = 5.6246(4)$ Å (16). We confirmed their report and investigated the thermal stability of this compound. When this compound was heated at 1100°C for about 1 day, only reflections of Al_5BO_9 appeared in the powder diffraction pattern of the product. Referring to the results of DTA experiments, we propose that it dissociates to Al_5BO_9 and a liquid phase at about 1039°C (Fig. 5).

3.3.6. X-phase. When we heated the starting materials with the composition of $0.66Li_2CO_3 \cdot 0.06Al_2O_3 \cdot 0.28 \times 2H_3BO_3$ at 620°C, a new ternary compound was

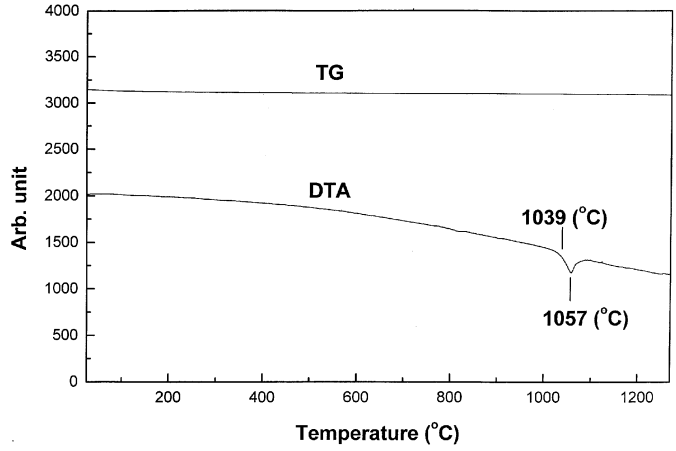

FIG. 5. Thermal gravity (upper) and differential thermal analysis (bottom) curves of $LiAl_7B_4O_{17}$.

TABLE 4
List of Indexes, *d*-Values and Diffraction Intensities of X-Phase

h	*k*	*l*	d_{obs}	d_{cal}	I/I_0
0	0	3	5.86	5.85	4
1	0	1	4.141	4.135	6
1	0	2	3.831	3.829	2
1	0	3	3.445	3.440	1
1	0	4	3.057	3.053	22
0	0	6	2.925	2.923	100
1	0	5	2.709	2.706	8
1	1	0	2.459	2.456	9
1	1	3	2.267	2.265	1
2	0	1	2.1118	2.1118	6
2	0	2	2.0674	2.0674	1
1	1	6	1.881	1.880	2
1	1	8	1.6359	1.6355	1
2	0	7	1.6221	1.6216	7
2	1	1	1.6014	1.6014	2
2	1	2	1.5814	1.5817	3
2	0	8	1.5271	1.5266	2
2	1	4	1.5099	1.5098	1
1	0	11	1.4930	1.4928	1
0	0	12	1.4612	1.4613	1
2	0	9	1.4369	1.4369	1
1	1	10	1.4264	1.4273	1
3	0	0	1.4179	1.4182	2
2	0	10	1.3530	1.3531	2
2	0	11	1.2757	1.2757	2

Note. $a = 4.9129(7)$ Å, $c = 17.536(4)$ Å.

obtained. Chemical analysis indicated that the molar ratio of Li_2O: Al_2O_3: B_2O_3 in the product is 1:0.09:0.42, which is almost the same as the original ratio in the starting materials. However, its exact formula is still unknown. So we named it X-phase. The powder pattern can be indexed based on a hexagonal unit cell with high figures of merit $M(25) = 26$ (25) and $F(25) = 20(0.0193, 67)$ (26). The indexed powder diffraction data are given in Table 4. The structure determination is under way.

4. CONCLUSIONS

In this work, a partial phase diagram in the system Li_2O–Al_2O_3–B_2O_3 is reported. Totally, six ternary compounds, $Li_2AlB_5O_{10}$, $LiAlB_2O_5$, $Li_3AlB_2O_6$, Li_2AlBO_4, $LiAl_7B_4O_{17}$ and X-phase, were identified. All the compounds except for X-phase have been structurally characterized so far. The compounds $Li_2Al_2B_2O_7$, $Li_4Al_2B_4O_{11}$ and $Li_2Al_4B_4O_{13}$ reported by Abdullaev *et al.* were not observed in our experiments. Phase relations in some regions are still not very clear because of the difficulties in experimental work. It is important to emphasize again that the phase relations in the Li-rich part presented here are obtained at a certain temperature (620°C) since the experimental results in this part seem to be sensitive to the temperature.

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