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High-temperature behaviour of lithium borates:
Part I: Characterization and thermal stability

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Abstract

Nine compounds, namely Li_3BO_3, α-$Li_4B_2O_5$, β-$Li_4B_2O_5$, $Li_6B_4O_9$, α-$LiBO_2$, $Li_2B_4O_7$, $Li_3B_7O_{12}$, LiB_3O_5 and $Li_2B_8O_{13}$ in the Li_2O–B_2O_3 system have been synthesized and characterized. The unit-cell parameters, density and solubility in water at room temperature of all the compounds are reported. The densities of the compounds were found to be in the 1.90–2.50 g cm^{-3} range, while their solubility in water at room temperature was in the 0.91–8.64$\times 10^{-2}$ g cm^{-3} range. Determination of the thermal stability of the compounds by quenching and differential thermal analysis (DTA) showed that only α-$LiBO_2$ and $Li_2B_4O_7$ retained their original symmetry up to their congruent melting at 1121 and 1188 K, respectively, in air. © 1998 Elsevier Science B.V.

Keywords: Density; DTA; Lattice parameter; Lithium borates; Solubility; Thermal stability

1. Introduction

At ambient pressure, the binary Li_2O–B_2O_3 system is characterized by the formation of nine lithium borate compounds, namely Li_3BO_3, α-$Li_4B_2O_5$, β-$Li_4B_2O_5$, $Li_6B_4O_9$, α-$LiBO_2$, $Li_2B_4O_7$, $Li_3B_7O_{12}$, LiB_3O_5 and $Li_2B_8O_{13}$ [1–3]. There are many reports [4–11] on the applications of $Li_2B_4O_7$ and LiB_3O_5 in surface acoustic wave (SAW) and non-linear optical (NLO) devices, respectively. However, the data on the unit-cell parameters, density, solubility in water, thermal stability and thermal expansion characteristics, etc. of these compounds are incomplete and scantily reported. Therefore, detailed studies on the Li_2O–B_2O_3 system were undertaken. For this purpose, these compounds were prepared, characterized and their high-temperature behaviour was studied by means of X-ray diffractometry, DTA, high-temperature XRD[1] and dilatometry[2].

In this paper (Part I), we report on the synthesis of lithium borates and results obtained on the determination of

1. unit-cell parameters;
2. density;
3. solubility in water at room temperature; and
4. thermal stability by quenching and differential thermal analysis methods.

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[1] To be reported elsewhere.

[2] Same as Footnote 1.

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2. Experimental

Lithium borates were prepared from the starting materials Li_2CO_3 and H_3BO_3, both of G.R. grade. Appropriate quantities of these materials, to give the desired mole percent of Li_2O and B_2O_3, were melted in platinum crucibles at 1223 K for 15 min in a vertical furnace. The completely melted samples were quenched in Hg at room temperature. The quenched products were finely powdered and heated at 823 K for 48 h with intermittent grindings. The samples thus prepared were subsequently heated at different, required temperatures in the 873–1073 K range depending on composition. For the identification of the compounds, powder XRD patterns were recorded from $10<2\theta<70^\circ$, using monochromatic CuK_α radiation on a Philips X-ray diffractometer, Model PW 1729. Cell parameters were accurately determined using a computer program based on the least-squares refinement method. Densities of the compounds were determined pyknometrically using CCl_4 as immersion solvent, and the saturated solution method was used for the determination of their solubility in water at room temperature. Determination of thermal stability by the quenching method involved heating of each compound for 18 h at different temperatures in the 823–1198 K range, air quenching of the heated products, followed by characterization using powder XRD. Differential thermal analysis (DTA) was carried out using an equipment designed and fabricated in this laboratory [12]. The sample size was ca. 80 mg and the heating rate – 10 K min^{-1}. Calcined alumina was used as the reference material.

3. Results and discussion

All the lithium borates reported in the literature have been obtained by heat treatment of the quenched melt of the corresponding compositions of the starting materials and confirmed by comparing their XRD patterns with the reported ones [1,3,13–16]. The time involved and the reaction temperature required for the complete formation of these compounds are given in Table 1.

The room temperature XRD, density and solubility data obtained for all the compounds are summarised in Table 2. The observed values of unit cell parameters, number of molecules per unit cell (Z) and density of the compounds are in good agreement with the known values [3,13–20]. However, the corresponding data for $Li_2B_8O_{13}$ is reported, for the first time herein. All the observed reflections in the XRD pattern of this compound could be indexed on the basis of a triclinic unit cell with parameters a=8.619(5) Å, b=8.756(6) Å, c=7.151(5) Å, α=95.38(0.06)°, β=90.06(0.05)° and Γ=92.32(0.05)°, and Z=2, with calculated density=1.91 g cc^{-1}.

The values of solubility of lithium borates in water at room temperature as determined experimentally (Table 2) are plotted in Fig. 1 as a function of composition (mol% B_2O_3). As can be seen from the figure, the solubility of these compounds decreases with increase in B_2O_3 content up to 70 mol% (corresponding to the compound $Li_3B_7O_{12}$). Beyond this composition, the solubility of the compounds increases with increase in B_2O_3 content. Though it is difficult to rationalize this behaviour at this stage, it appears

Table 1
Synthesis of lithium borates by heat treatment of quickly quenched melts

S. No.	Reactant mixture[a] (composition)	Final heating schedule [b]		Phase present
		temperature/K	time/h	
1.	$3Li_2O : B_2O_3$	873	24	Li_3BO_3
2.	$2Li_2O : B_2O_3$	883	24	α-$Li_4B_2O_5$
3.	$2Li_2O : B_2O_3$	898	24	β-$Li_4B_2O_5$
4.	$3Li_2O : 2B_2O_3$	873	24	$Li_6B_4O_9$
5.	$Li_2O : B_2O_3$	1073	24	α-$LiBO_2$
6.	$Li_2O : 2B_2O_3$	1073	24	$Li_2B_4O_7$
7.	$3Li_2O : 7B_2O_3$	998	120	$Li_3B_7O_{12}$
8.	$Li_2O : 3B_2O_3$	1023	24	LiB_3O_5
9.	$Li_2O : 4B_2O_3$	873	24	$Li_2B_8O_{13}$

[a] Li_2O as Li_2CO_3 and B_2O_3 as H_3BO_3.
[b] The melts were initially heated at 873 K for 48 h in air with intermittent grinding.

Table 2
Room temperature XRD, density and solubility data of lithium borates

S. No.	Compound [a]	Unit-cell parameters/Å			β/°	Z	Density/ (g cc^{-1})		Solubility/ (g (100 ml)$^{-1}$)
		a	b	c			observed	calculated	
1.	Li_3BO_3 (M)	8.323(7)	9.171(6)	3.258(3)	101.65	4	2.13	2.17	8.64
2.	α-$Li_4B_2O_5$ (O)	10.15(1)	17.58(1)	4.729(2)	—	8	1.99	2.04	7.80
3.	β-$Li_4B_2O_5$ (M)	10.21(1)	4.704(4)	8.795(3)	93.69	4	1.98	2.04	7.86
4.	$Li_6B_4O_9$ (M)	9.186(5)	23.42(4)	3.326(1)	92.59	4	2.08	2.13	6.98
5.	α-$LiBO_2$ (M)	5.839(4)	4.352(2)	6.453(6)	115.07	4	2.18	2.22	5.67
6.	$Li_2B_4O_7$ (Te)	9.470(6)	9.470(6)	10.28(1)		8	2.40	2.44	1.31
7.	$Li_3B_7O_{12}$ (Tr)	6.489(8)	7.834(9)	8.505(9)		2	2.29	2.32	0.91
α=92.45°	β=104.61°	Γ=99.38°							
8.	LiB_3O_5 (O)	8.444(2)	7.380(3)	5.142(2)	—	4	2.43	2.48	1.84
9.	$Li_2B_8O_{13}$ (Tr)	8.619(5)	8.757(6)	7.151(5)		2	1.87	1.91	2.82
α=95.38°	β=90.06°	Γ=92.32°							

[a] M, monoclinic; O, orthorhombic; Te, tetragonal; Tr, triclinic.

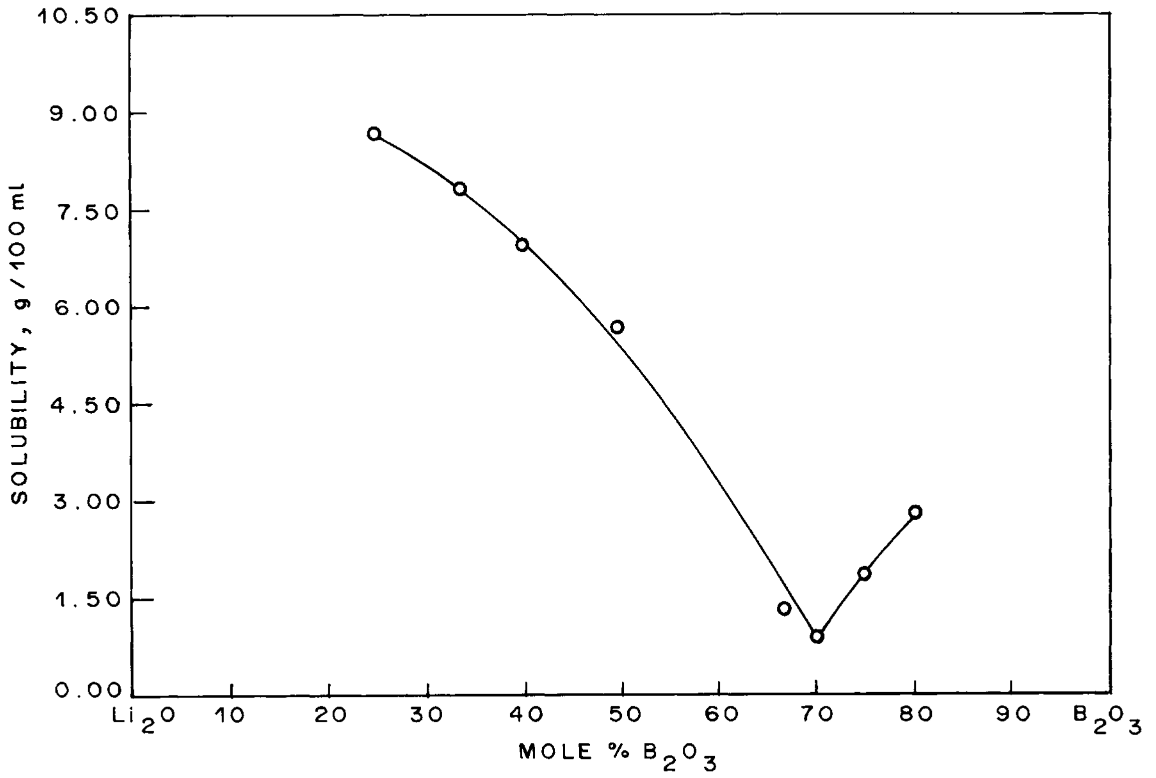

Fig. 1. Solubility of lithium borates as a function of composition (mol% B_2O_3).

that the factor contributing to solubility might be their lattice energy. It appears from this data that among the lithium borates, $Li_3B_7O_{12}$ has the highest lattice energy, and, on either side of this composition, the lattice energy of the compounds decreases.

Table 3
Phase analysis of air-quenched products of lithium borates heated at various temperatures for 18 h

S. No.	Compound	T_1 [a]/K	T_2 [b]/K	Phases identified at T_2	Temperature limit of stability
1.	Li_3BO_3	923	963	Li_2O[c]	$923\leq T\leq 963$
2.	α-$Li_4B_2O_5$	853	893	β-$Li_4B_2O_5$	$853\leq T\leq 893$
3.	β-$Li_4B_2O_5$	873	915	Li_3BO_3, $Li_6B_4O_9$	$873\leq T\leq 915$
4	$Li_6B_4O_9$	908	948	α-$LiBO_2$	$908\leq T\leq 948$
5	α-$LiBO_2$	1085	1123	glassy [d]	$1085\leq T\leq 1123$
6	Li_2B_4O7	1155	1198	glassy [d]	$1155\leq T\leq 1198$
7	$Li_3B_7O_{12}$	1108	1148	$Li_2B_4O_7$	$1108\leq T\leq 1148$
8	LiB_3O_5	1083	1123	$Li_3B_7O_{12}$	$1083\leq T\leq 1123$
9	$Li_2B_8O_{13}$	885	923	LiB_3O_5	$885\leq T\leq 923$

[a] Temperature up to which the original phase is retained.
[b] Temperature at, and above, which the original phase is not retained.
[c] Inferred by the presence of LiOH and Li_2CO_3.
[d] Few very weak lines of the original phase observed.

The results of XRD analysis of the air-quenched products obtained after heat treatment of lithium borates at different temperatures (Table 3) revealed that only α-$LiBO_2$ and $Li_2B_4O_7$ retained their original symmetry up to the liquidus temperatures in air. The other compounds are found to retain original symmetry only up to a certain temperature and, thereafter, either to transform to a different symmetry or decompose or melt incongruently before the respective liquidus temperature. The compound α-$Li_4B_2O_5$ transformed at $\approx$893 K to β-$Li_4B_2O_5$ which, in turn, decomposed to Li_3BO_3 and $Li_6B_4O_9$ at $\approx$915 K in air. Likewise, Li_3BO_3, $Li_6B_4O_9$, $Li_3B_7O_{12}$, LiB_3O_5 and $Li_2B_8O_{13}$ melted incongruently at certain temperatures in the range of $898\leq T\leq 1148$ K in air. This is evident from the absence of these compounds in the air-quenched products obtained after their heating at 963, 948, 1148, 1123 and 923 K, respectively, in air (Table 3).

The present data on the thermal stability of lithium borates, except α-$Li_4B_2O_5$, β-$Li_4B_2O_5$ and LiB_3O_5 are found to be in fair agreement with those reported in the literature [1–3]. According to Sastry et al. [1,2], although these three compounds could be quenched to room temperature from the upper stability temperature range, by subsequent heating at temperatures below their lower limits of stability, α-$Li_4B_2O_5$ decomposed to Li_3BO_3 and $Li_6B_4O_9$, whereas β-$Li_4B_2O_5$ reverted to its low-temperature form and LiB_3O_5 decomposed to $Li_2B_4O_7$ and $Li_2B_8O_{13}$ in air. However, the present data for α-$Li_4B_2O_5$, β-$Li_4B_2O_5$ and LiB_3O_5 suggest that once the compounds are formed by the proper heat treatment, their subsequent heating at lower temperatures does not bring about either dissociation or reversion. This is in agreement with the observations of Zhao et al. [19] and Lin et al. [20] for LiB_3O_5. Likewise, the temperature range of stabilty of $Li_3B_7O_{12}$ (70 mol% B_2O_3) is in agreement with that of Jiang et al. [3] who contradicted the findings of Sastry et al. [1] for their reported compound $Li_4B_{10}O_{17}$ (71.42 mol% B_2O_3).

DTA curves recorded for lithium borates in the temperature range up to 1293 K in air during heating and cooling are given in Figs. 2–5. As can be seen in Fig. 2(a), the DTA scan of Li_3BO_3 showed two endotherms, one at 935 K and the other at 978 K during heating, which can be attributed to its incongruent melting to Li_2O and its liquidus, respectively. DTA scan of α-$Li_4B_2O_5$ (Fig. 2(b)) showed two endotherms while heating. The endotherm at 892 K corresponds to the phase transition to the monoclinic form (β-$Li_4B_2O_5$). The endotherm at 930 K as well as that observed for β-$Li_4B_2O_5$ at 933 K during its heating (Fig. 3(a)) can be attributed to the decomposition of β-$Li_4B_2O_5$ to Li_3BO_3 and $Li_6B_4O_9$, and probably simultaneous melting of the phases thus formed. The air-quenched products obtained after heating of β-$Li_4B_2O_5$ at 915 K showed the presence of Li_3BO_3 and $Li_6B_4O_9$ (Table 3). The absence of any other endotherm above 933 K for β-$Li_4B_2O_5$ (either obtained by the phase transition of α-$Li_4B_2O_5$ or

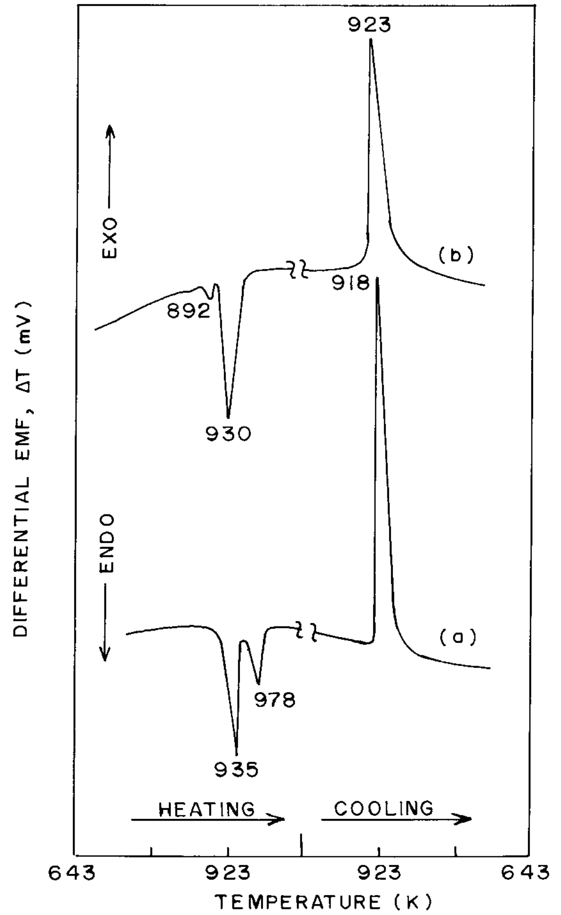

Fig. 2. DTA curves of (a) Li_3BO_3 and (b) α-$Li_4B_2O_5$.

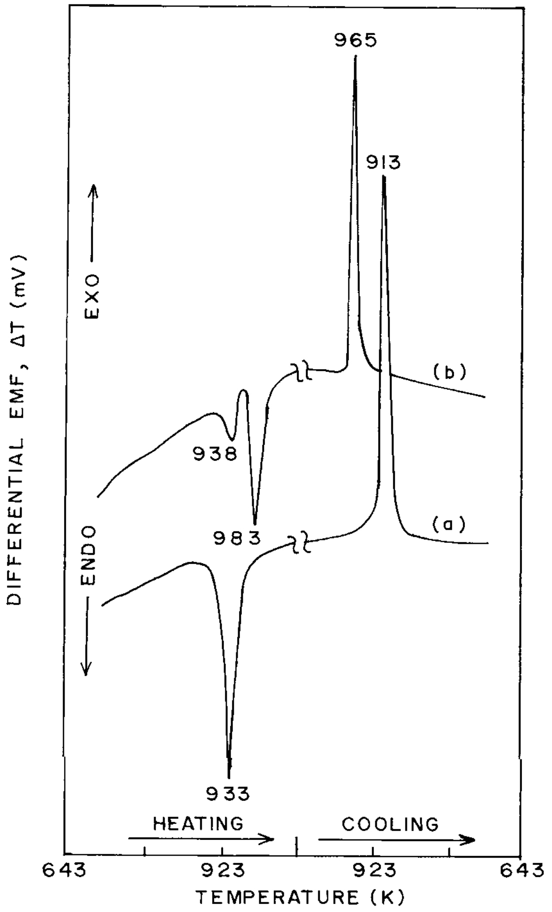

Fig. 3. DTA curves of (a) β-$Li_4B_2O_5$ and (b) $Li_6B_4O_9$.

the original one) and the presence of a large endotherm at ca. 930 K indicate that the temperature of decomposition and melting of the decomposition products are close to each other and the endotherms corresponding to these events seem to have manifested into large single peaks (Fig. 2(b) and Fig. 3(a)). The endotherms at 938 and 983 K in the DTA scan of $Li_6B_4O_9$ during heating (Fig. 3(b)) can be attributed to its incongruent melting to α-$LiBO_2$ and its liquidus, respectively. The α-$LiBO_2$ and $Li_2B_4O_7$ exhibited an endotherm at 1121 and 1188 K, respectively, (Fig. 4(a and b)) which correspond to their congruent melting in air. DTA scan of $Li_3B_7O_{12}$ (Fig. 5(a)) showed a broad endotherm at 1185 K while heating. The temperature range of stability of the compound as determined by the quenching method revealed that the compound melted incongruently to $Li_2B_4O_7$ at $1108 \leq T \leq 1148$ K in air (Table 3). Only a very broad peak exhibited by the compound indicates that the endotherms corresponding to the incongruent melting and liquidus merged into a single peak. The observed peak temperature is in agreement with the reported [3] liquidus temperature of the compound. Contrary to the behaviour of $Li_3B_7O_{12}$, DTA scan of LiB_3O_5 gave three overlapping, but distinct and small, endotherms at 1118, 1153 and 1180 K while heating (Fig. 5(b)). The first endotherm at 1118 K is attributed to the incongruent melting of the compound to $Li_3B_7O_{12}$ while those at 1153 and 118 K are ascribed to the incongruent melting of $Li_3B_7O_{12}$ to $Li_2B_4O_7$ and liquidus, respectively. $Li_2B_8O_{13}$ showed only an endotherm at 1103 K while heating, which

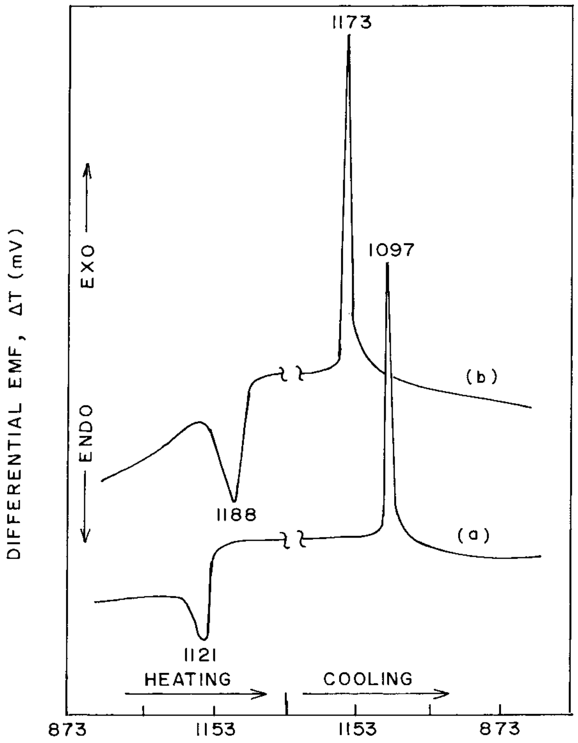

Fig. 4. DTA curves of (a) α-$LiBO_2$ and (b) $Li_2B_4O_7$.

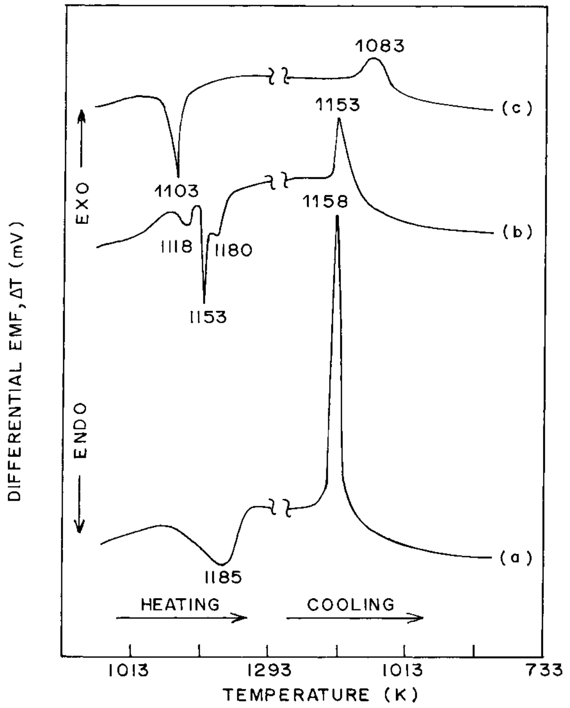

Fig. 5. DTA curves of (a) $Li_3B_7O_{12}$, (b) LiB_3O_5 and (c) $Li_2B_8O_{13}$.

Table 4
DTA data of lithium borates

S. No.	Compound	During heating		Reaction [a]	During cooling [b]	
		peak temp./K	ΔH/(cal g^{-1})		peak temp./K	ΔH/(cal g^{-1})
1	Li_3BO_3	935	64.7	I.M.		
		978	22.6	L	918	122.5
2	α-$Li_4B_2O_5$	892	9.3	P.T.		
		930	96.0	D-L	923	113.2
3	β-$Li_4B_2O_5$	933	140.8	D-L	913	151.2
4	$Li_6B_4O_9$	938	26.6	I.M.		
		983	85.1	L	965	91.0
5	α-$LiBO_2$	1121	107.4	C.M.	1097	133.7
6	$Li_2B_4O_7$	1188	94.5	C.M.	1173	124.5
7	$Li_3B_7O_{12}$	1185	156.1	I.M.-L	1158	173.4
8	LiB_3O_5	1118	8.3	I.M.		
		1153	34.7	I.M.		
		1180	22.5	L	1153	46.4
9	$Li_2B_8O_{13}$	1103	61.4	L	1083	35.6

[a] I.M., Incongruent melting; L, liquidus; P.T., phase transition;D-L, decomposition followed by liquidus; C.M., congruent melting; and I.M.-L, incongruent melting followed by liquidus.

[b] Freezing temperature.

corresponds to its liquidus (Fig. 5(c)). However, the DTA curve did not show any endotherm due to the incongruent melting of the compound to LiB_3O_5 at $885 \leq T \leq 923$ K as observed by XRD analysis (Table 3), probably due to very slow incongruent melting spread over a large temperature range as also revealed by the high-temperature XRD data reported elsewhere [21]. DTA curves of lithium borates obtained during cooling are also shown in Figs. 2–5 along with the respective heating curves. All the compounds showed an exotherm each during cooling which is ascribed to freezing the melts while cooling. The peak temperatures of both endothermic and exothermic processes of all the compounds as well as the values of heat of reaction (ΔH) associated with each event are given in Table 4. The ΔH values were obtained by comparing the area under DTA peaks of melting as well as phase transition of standard substances (NaCl and Na_2CO_3) in air.

4. Conclusion

From the foregoing, it may be concluded that among all the lithium borates, the solubility of Li_3BO_3 is highest (8.64 g/100 ml) and that of $Li_3B_7O_{12}$ is lowest (0.91 g/100 ml). Their thermal behaviour indicates that except for the congruently melting α-$LiBO_2$ and $Li_2B_4O_7$, the rest of the compounds undergo either phase transition, decomposition or incongruent melting below their liquidus temperatures in air.

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