

High-temperature behaviour of lithium borates

Part II: High-temperature X-ray diffractometric and dilatometric studies

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Abstract

High-temperature X-Ray diffractometric (HTXRD) and dilatometric studies of lithium borates, namely Li_3BO_3 , $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, $\beta\text{-Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$, $\alpha\text{-LiBO}_2$, $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$, LiB_3O_5 , and $\text{Li}_2\text{B}_8\text{O}_{13}$ have been carried out, which revealed that $\text{Li}_2\text{B}_8\text{O}_{13}$ underwent a solid-phase transition from triclinic to monoclinic at temperatures >543 K in air. The variation in lattice parameters with temperature, unit-cell volume as well as linear coefficient of thermal expansion (α_a , α_b and α_c), volume expansion of the unit cell (α_v) of the compounds as well as bulk thermal expansion coefficients have been determined by HTXRD and dilatometry respectively. © 1998 Elsevier Science B.V.

Keywords: Dilatometry; High-temperature X-ray diffractometry; Lithium borates; Phase transition; Thermal expansion

1. Introduction

In our previous paper [1], we reported on the synthesis, characterization and thermal stability of nine lithium borates, viz. Li_3BO_3 , $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, $\beta\text{-Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$, $\alpha\text{-LiBO}_2$, $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$, LiB_3O_5 , and $\text{Li}_2\text{B}_8\text{O}_{13}$ in air. For these compounds, the data on high-temperature X-ray diffractometric (HTXRD) studies has been reported only for LiB_3O_5 [2]. HTXRD studies on all the lithium borates formed in the $\text{Li}_2\text{O-B}_2\text{O}_3$ system in air were therefore undertaken. In order to further confirm the results obtained by HTXRD, dilatometric studies on the bulk thermal expansion of all the lithium borates in the $298 \leq T \leq 873$ K range in air were also carried out. Except for $\alpha\text{-LiBO}_2$ and $\text{Li}_2\text{B}_4\text{O}_7$, this data is reported

for the first time. The studies in this communication also include identification of the high-temperature phases, lattice and bulk thermal expansion characteristics of these compounds.

2. Experimental

Lithium borates were prepared by heat treatment of quenched melts of the corresponding compositions of Li_2CO_3 and H_3BO_3 in air and were characterized by XRD using $\text{CuK}\alpha$ radiation. High-temperature X-ray powder diffraction studies were carried out using an MRC Model X-86-N3 high temperature diffractometric attachment described elsewhere [3]. A small amount of the sample was ground to ca. $100 \mu\text{m}$ and mounted on a Pt-40% Rh stage-heating element. A Pt/Pt-13%Rh thermocouple spot-welded to the bottom of

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the stage was used for temperature measurement. The temperature was controlled by a MRC Model 1 X-8600-5000-2 proportional temperature controller. A uniform zone was maintained to within ± 5 K over the entire temperature range of investigation. XRD patterns were recorded at different temperatures in the $10 < 2\theta < 60^\circ$ range, using Ni filtered $\text{CuK}\alpha$ radiation. While XRD patterns of the compounds $\alpha\text{-LiBO}_2$, $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$ and LiB_3O_5 were recorded in the 298–1063 K range, for the rest of the compounds, viz. Li_3BO_3 , $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, $\beta\text{-Li}_4\text{B}_2\text{O}_3$, $\text{Li}_6\text{B}_4\text{O}_9$ and $\text{Li}_2\text{B}_8\text{O}_{13}$, the upper limit of temperature was ca. 883 K. The unit-cell parameters were determined by computer program using the least-squares refinement method [4]. The unit-cell volumes were calculated from the cell parameters, and the coefficients of linear and volume thermal expansions were also evaluated.

Bulk thermal expansion measurements were carried out from ambient to 873 K in air at a heating rate of 5 K min^{-1} , using a Model LKB 3185 fused quartz push rod dilatometer. Samples used were in the form of cylindrical pellets sintered at 873 K for 6 h in air with ca. 65% theoretical bulk density.

3. Results and discussions

3.1. Identification of high-temperature phases

The only noticeable changes in room and high-temperature diffraction patterns of the compounds, except $\text{Li}_2\text{B}_8\text{O}_{13}$, were the progressive shifts in peak positions and minor variations in peak intensities. The shifts in peak positions are attributed to the expansion or contraction of the lattice, while the variation in intensities can be attributed to the changes in thermal parameters because of increase in temperature. However, for $\text{Li}_2\text{B}_8\text{O}_{13}$, XRD patterns recorded above 543 K showed some additional features. The diffractograms of the compound obtained in the $10 < 2\theta < 34^\circ$ range at 298, 408, 543, 625 and 677 K are shown in Fig. 1(a–e). The intensities of the peaks at higher angles were very weak and, hence, are not shown. As can be seen from Fig. 1(a–c), no significant changes were observed in the patterns recorded up to 543 K, except the shifts in peak positions and the variations in the intensities, thus compounds which were triclinic at room temperature retained their symmetry up to 543 K in air. The diffractogram obtained at

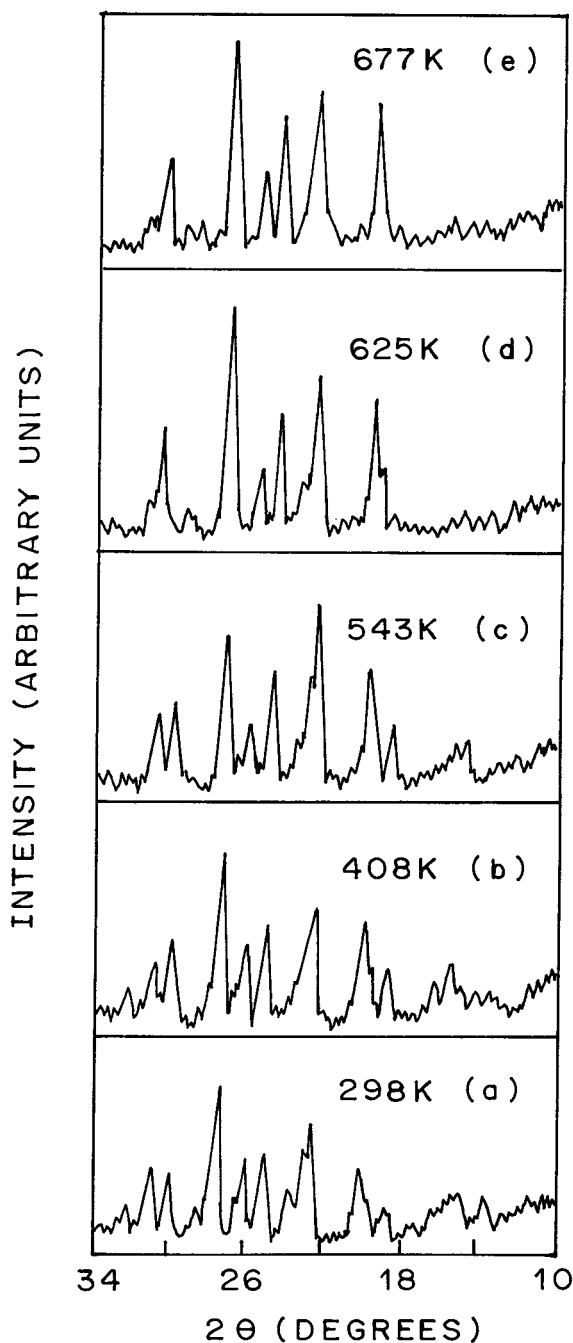


Fig. 1. X-ray powder diffraction patterns of $\text{Li}_2\text{B}_8\text{O}_{13}$ at various temperatures.

625 K (see Fig. 1(d)) showed the absence of peaks at 2θ equal to 14.82° , 15.35° , 16.15° , 18.70° , 23.60° and 32.40° at temperatures < 625 K. This indicated a

possible phase transition from low to one of higher symmetry. However, the observed phase transition was found to be complete only above 625 K. This was evident from the merging of the doublets at $2\theta=19.40^\circ/19.85^\circ$ as well as at $2\theta=22.70^\circ/23.30^\circ$ (see Fig. 1(d)) into singlets at $2\theta=19.80^\circ$ and 22.65° , respectively, occurring only in the pattern obtained at 677 K (Fig. 1(e)). Therefore, it may be concluded that while XRD pattern at 625 K indicated that the sample was biphasic (low- and high-temperature forms of $\text{Li}_2\text{B}_8\text{O}_{13}$ coexisting), the pattern obtained at 677 K corresponding to the high-temperature form of the compound. Here, identification of the high-temperature form of $\text{Li}_2\text{B}_8\text{O}_{13}$ was carried out for the first time. All the observed peaks at 677 K could be indexed to a monoclinic unit cell with $a=4.584(5)$ Å, $b=11.07(2)$ Å, $c=22.44(2)$ Å, $\beta=114.05(06)^\circ$, and $Z=4$. The XRD patterns of the compound recorded at 777 K and 869 K remained essentially the same, except for a few peaks of very low intensities due to LiB_3O_5 , with slight shifts indicating the stability of the high-temperature form of $\text{Li}_2\text{B}_8\text{O}_{13}$ up to ~ 869 K in air.

3.2. The variations of cell parameters and unit-cell volumes with temperature

The variation of cell parameters, i.e. a , b and c of the lithium borates as a function of temperature are plotted in Fig. 2(i–ix). As can be seen (with increase in temperature), the cell parameters, ' a ', ' b ', and ' c ' of all the compounds except LiB_3O_5 and $\text{Li}_2\text{B}_8\text{O}_{13}$ showed an almost linear increase. It was also observed that, with increase in temperature, the rate of increase in cell parameters along different axes of most of the compounds varied considerably from one another. For LiB_3O_5 , the cell parameters ' a ' and ' b ' increased almost linearly with temperature, whereas ' c ' decreased non-linearly up to ca. 977 K and, thereafter, remained almost constant up to 1056 K (Fig. 2(viii)). The cell parameters of LiB_3O_5 at different temperatures were found to be in good agreement with those reported in the literature [2]. The cell parameters of both triclinic and monoclinic forms of $\text{Li}_2\text{B}_8\text{O}_{13}$ showed anomalous behaviour (Fig. 2(ix)). The cell parameters of triclinic $\text{Li}_2\text{B}_8\text{O}_{13}$ decreased negligibly in the 298–543 K range. However, in its high-temperature form, cell parameter ' a ' increased negligibly,

and ' b ' and ' c ' decreased with increasing temperatures, the rate of decrease being much higher along the ' c ' axis.

The calculated cell volumes of the compounds at different temperatures are plotted in Fig. 3(i–ix). As can be seen, the unit cell volumes of all the compounds except $\text{Li}_2\text{B}_8\text{O}_{13}$ increased almost linearly with increase in temperature. The unit-cell volumes of both triclinic and monoclinic forms of $\text{Li}_2\text{B}_8\text{O}_{13}$ were found to decrease in the temperature range of stability of each (see (Fig. 3(ix))).

3.3. The coefficients of average linear and volume thermal expansion

The average coefficients of linear thermal expansion calculated along the ' a ', ' b ' and ' c ' axes of the compounds in different temperature ranges are listed in Table 1. The average coefficients of linear thermal expansion along ' a ', ' b ', and ' c ' axes of all the lithium borates, except LiB_3O_5 and $\text{Li}_2\text{B}_8\text{O}_{13}$, are positive. For LiB_3O_5 , the coefficients along ' a ' and ' b ' axes were positive, whereas it was negative along the ' c ' axis. In the case of $\text{Li}_2\text{B}_8\text{O}_{13}$, except for the average coefficient of the linear thermal expansion along the ' a ' axis of the monoclinic form, all the other coefficients were negative for both, the triclinic and monoclinic forms. The coefficients of volume thermal expansion $\Delta V/V_{298} \times \Delta T$ in the $298 \leq T \leq 873$ K range for the lithium borate compounds are shown in Table 2. It can be seen from this table that, in the $298 \leq T \leq 873$ K range, the average coefficients of volume expansion of Li_3BO_3 , $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, $\beta\text{-Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$ and $\alpha\text{-LiBO}_2$, are in the region of $(47\text{--}74) \times 10^{-6} \text{ K}^{-1}$, whereas those of $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$ and LiB_3O_5 were very nearly the same region, i.e. of the order of $(30\text{--}34) \times 10^{-6} \text{ K}^{-1}$. However, the coefficient of volume expansion of $\text{Li}_2\text{B}_8\text{O}_{13}$ showed a sudden decrease (Table 2).

A close analysis of the coefficients of linear expansion along each crystallographic axes (α_a , α_b and α_c) and of average volume thermal expansion (α_v) of $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$, LiB_3O_5 and $\text{Li}_2\text{B}_8\text{O}_{13}$ reveals that the low values of α_v of these compounds are particularly due to low α_c of the respective compounds (Table 1). This shows that the interatomic bonding along the c -axis of these compounds is much stronger than that along either a - or b -axis. The variation in

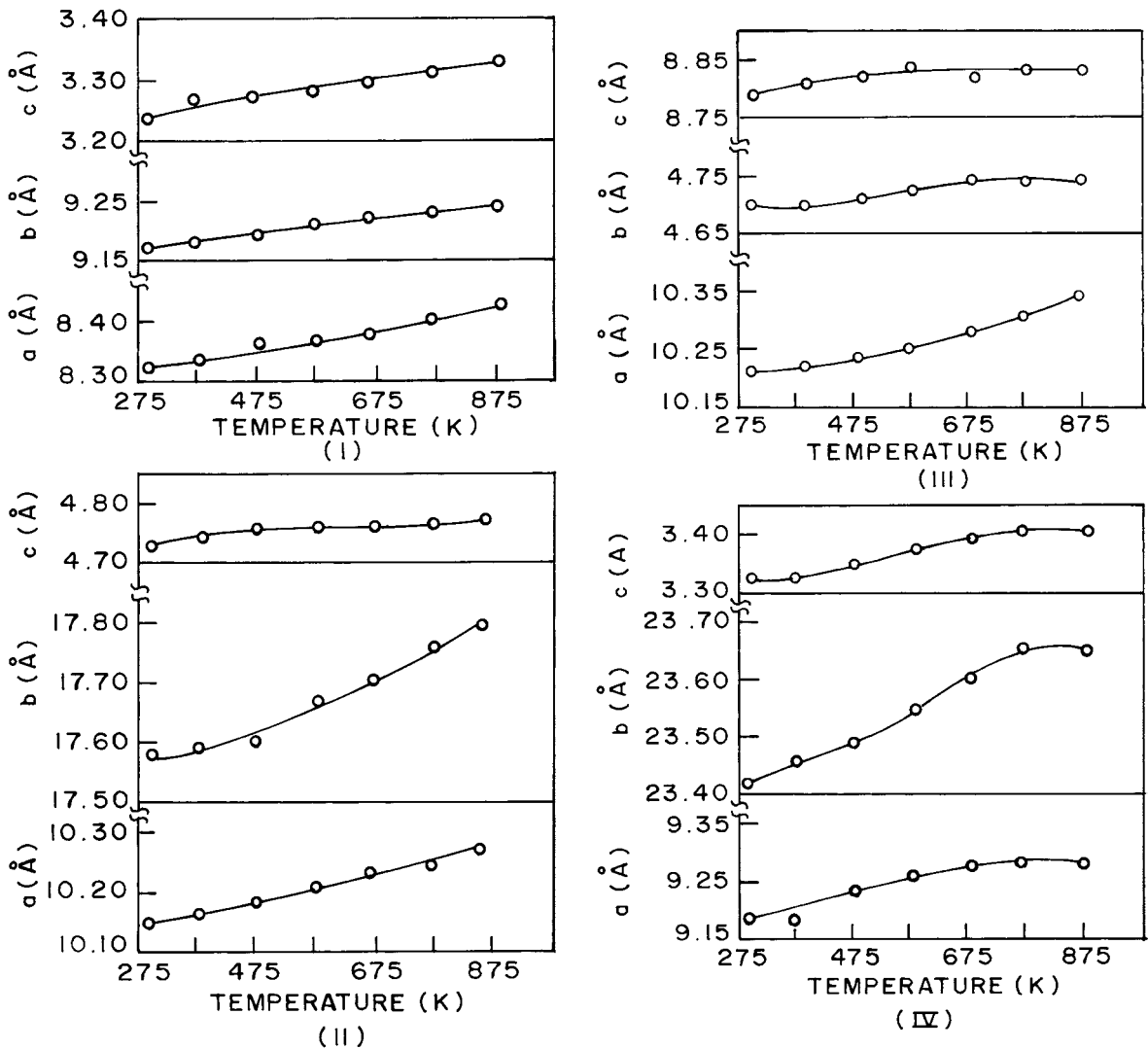


Fig. 2. Variation of cell parameters with temperature for (i) Li_3BO_3 , (ii) $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, (iii) $\beta\text{-Li}_4\text{B}_2\text{O}_5$, (iv) $\text{Li}_6\text{B}_4\text{O}_9$, (v) $\alpha\text{-LiBO}_2$, (vi) $\text{Li}_2\text{B}_4\text{O}_7$, (vii) $\text{Li}_3\text{B}_7\text{O}_{12}$, (viii) LiB_3O_5 and (ix) $\text{Li}_2\text{B}_8\text{O}_{13}$.

expansion along each crystallographic axis with temperature will also depend on the amount of distortion or twisting of the borate structural groups which are different in different lithium borates [2,5–13]. Lin et al. [2] observed that the negative expansion of LiB_3O_5 along the c -axis with temperature could be due to the directional changes and the decrease in bond angle of the triborate groups which spirals along the c -axis. The negative value of α_v obtained for the compound $\text{Li}_2\text{B}_8\text{O}_{13}$ was attributed to the anomalous thermal

expansion behaviour along the three crystallographic axes.

3.4. Bulk thermal expansion studies

Dilatometric measurements on lithium borates Li_3BO_3 , $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, $\beta\text{-Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$, $\alpha\text{-LiBO}_2$, $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$ and LiB_3O_5 showed that, with the corresponding increase in temperature, the rate of expansion of the compounds varied from one to another.

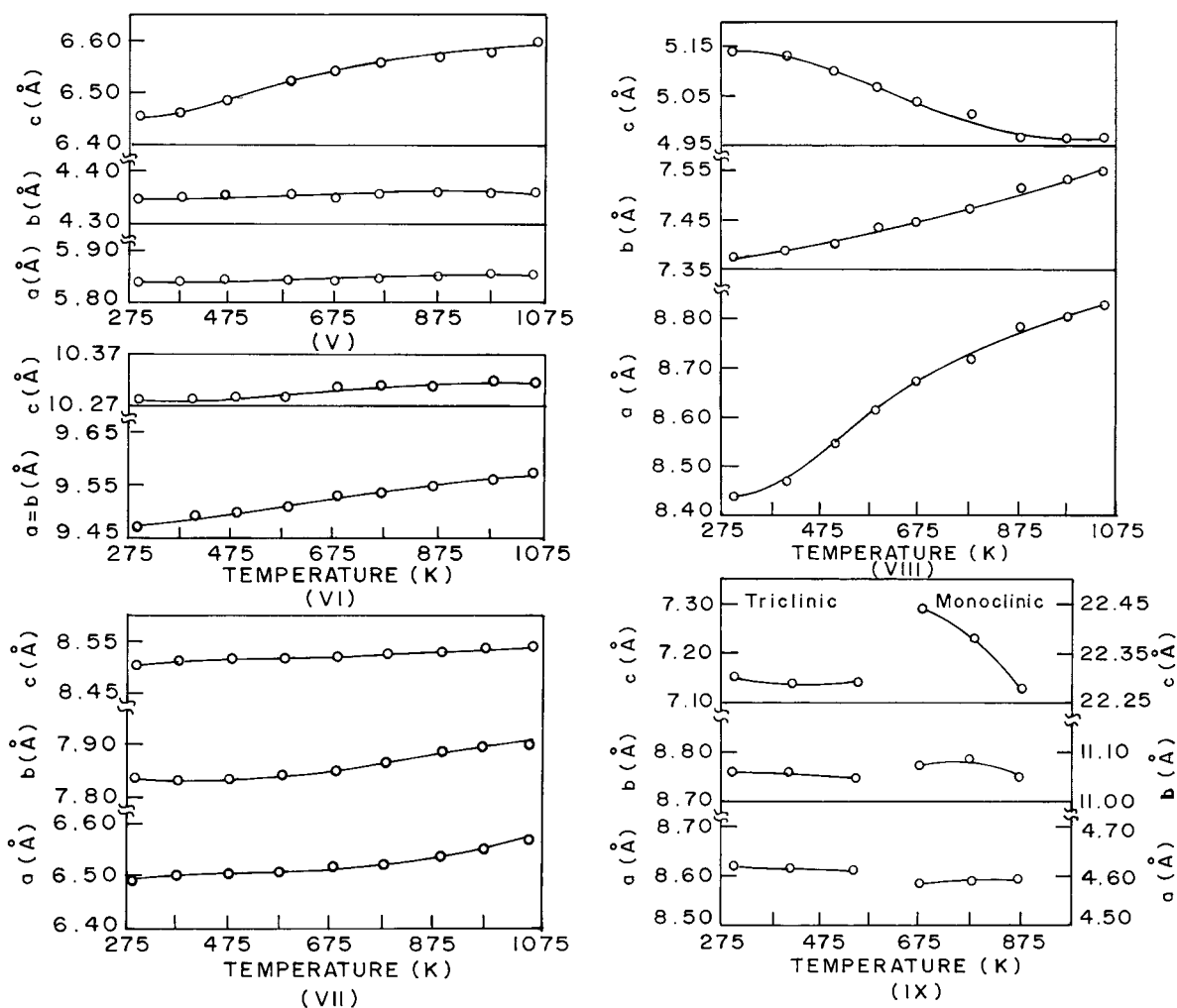


Fig. 2. (Continued)

However, all of them exhibited an almost linear relation between expansion and temperature over the range of investigation. A representative curve of % linear thermal expansion with temperature for $\text{Li}_2\text{B}_4\text{O}_7$ is shown in Fig. 4. In the case of $\text{Li}_2\text{B}_8\text{O}_{13}$, a negative thermal expansion was observed throughout the temperature range of investigation, see Fig. 5. The change in slope at ca. 550 K is due to a phase transition from triclinic to monoclinic form, as also observed by HTXRD.

The dilatometric linear thermal expansion of the compounds with respect to temperature could be expressed by a least-squares fit of the data, valid over the 298–873 K range in air.

For Li_3BO_3

$$\begin{aligned} \% \text{Linear expansion} &= 2.55 \times 10^{-4}(T - 298) \\ &+ 8.80 \times 10^{-6}(T - 298)^2 \\ &- 1.10 \times 10^{-8}(T - 298)^3 \end{aligned} \quad (1)$$

For $\alpha\text{-Li}^4\text{B}^2\text{O}^5$

$$\begin{aligned} \% \text{Expansion} &= 7.32 \times 10^{-4}(T - 298) \\ &+ 5.98 \times 10^{-6}(T - 298)^2 \\ &- 7.92 \times 10^{-9}(T - 298)^3 \end{aligned} \quad (2)$$

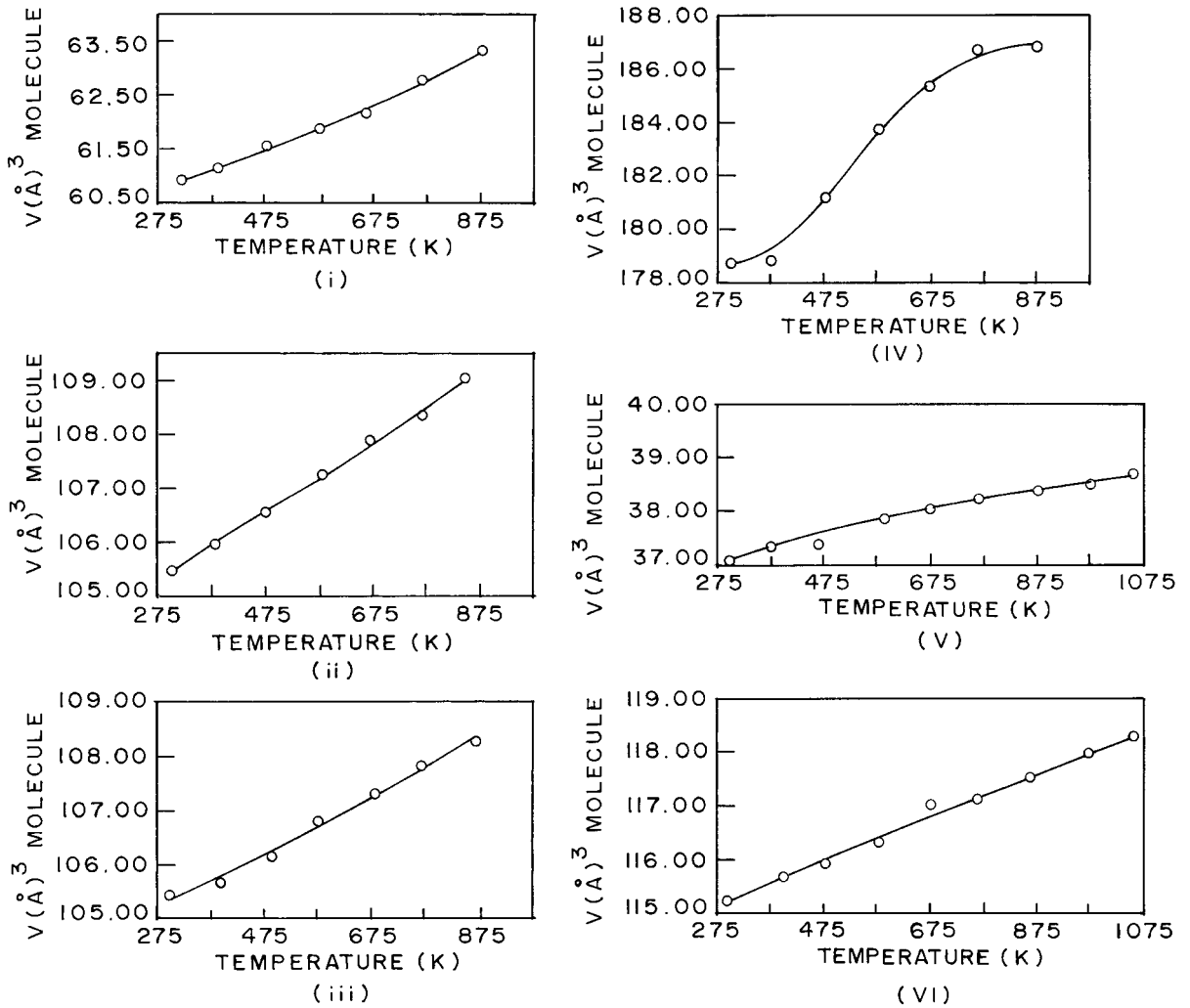


Fig. 3. Variation of unit-cell volume with temperature for (i) Li_3BO_3 , (ii) $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, (iii) $\beta\text{-Li}_4\text{B}_2\text{O}_5$, (iv) $\text{Li}_6\text{B}_4\text{O}_9$, (v) $\alpha\text{-LiBO}_2$, (vi) $\text{Li}_2\text{B}_4\text{O}_7$, (vii) $\text{Li}_3\text{B}_7\text{O}_{12}$, (viii) LiB_3O_5 , and (ix) $\text{Li}_2\text{B}_8\text{O}_{13}$.

For $\beta\text{-Li}_4\text{B}_2\text{O}_5$

$$\begin{aligned} \% \text{Expansion} = & 3.97 \times 10^{-4}(T - 298) + 4.72 \\ & \times 10^{-6}(T - 298)^2 - 5.29 \times 10^{-9}(T - 298)^3 \end{aligned} \quad (3)$$

For $\text{Li}_6\text{B}_4\text{O}_9$

$$\begin{aligned} \% \text{Expansion} = & -2.49 \times 10^{-4}(T - 298) \\ & + 6.17 \times 10^{-6}(T - 298)^2 - 4.34 \\ & \times 10^{-9}(T - 298)^3 \end{aligned} \quad (4)$$

For $\alpha\text{-LiBO}_2$

$$\begin{aligned} \% \text{Expansion} = & 3.06 \times 10^{-4}(T - 298) \\ & + 4.03 \times 10^{-6}(T - 298)^2 - 3.50 \\ & \times 10^{-9}(T - 298)^3 \end{aligned} \quad (5)$$

For $\text{Li}_2\text{B}_4\text{O}_7$

$$\begin{aligned} \% \text{Expansion} = & 1.09 \times 10^{-4}(T - 298) \\ & + 4.48 \times 10^{-6}(T - 298)^2 - 4.69 \\ & \times 10^{-9}(T - 298)^3 \end{aligned} \quad (6)$$

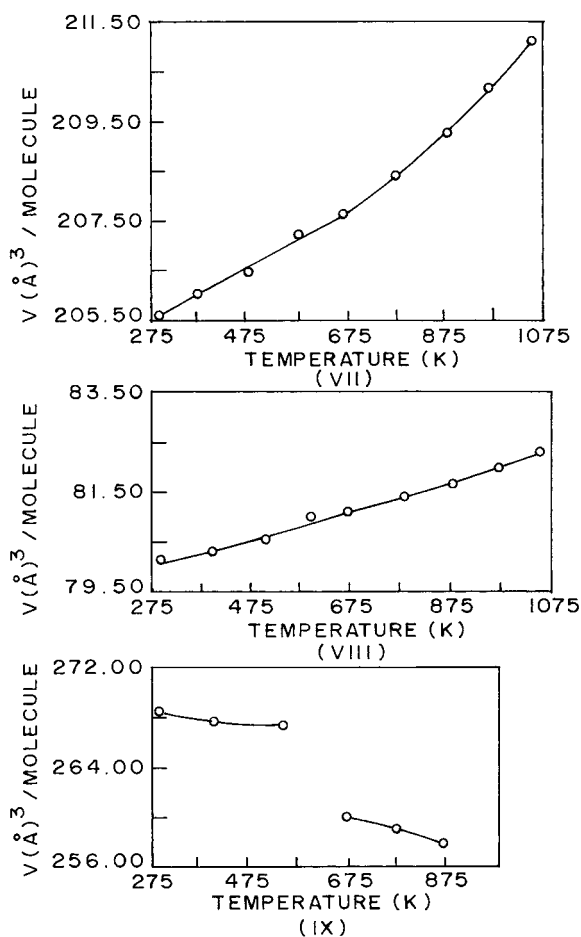


Fig. 3. (Continued)

Table 2

Coefficients of the average volume thermal expansion ($\alpha_v \times 10^6 \text{ K}^{-1}$) of the lithium borate compounds in the $298 \leq T \leq 873 \text{ K}$ range in air

S. No.	Compound	$(\alpha_v \pm 2.00) \times 10^6 / (\text{K}^{-1})$
1	Li_3BO_3	64.86
2	$\alpha\text{-Li}_4\text{B}_2\text{O}_5$	58.59
3	$\beta\text{-Li}_4\text{B}_2\text{O}_5$	46.86
4	$\text{Li}_6\text{B}_4\text{O}_9$	73.84
5	$\alpha\text{-LiBO}_2$	55.26
6	$\text{Li}_2\text{B}_4\text{O}_7$	34.39
7	$\text{Li}_3\text{B}_7\text{O}_{12}$	29.83
8	LiB_3O_5	32.32
9	$\text{Li}_2\text{B}_8\text{O}_{13}$	-67.06

For $\text{Li}_3\text{B}_7\text{O}_{12}$

$$\begin{aligned} \% \text{Expansion} = & -2.13 \times 10^{-4}(T - 298) + 4.08 \\ & \times 10^{-6}(T - 298)^2 - 3.74 \times 10^{-9}(T - 298)^3 \end{aligned} \quad (7)$$

For LiB_3O_5

$$\begin{aligned} \% \text{Expansion} = & 3.92 \times 10^{-4}(T - 298) + 2.19 \\ & \times 10^{-6}(T - 298)^2 - 1.31 \times 10^{-9}(T - 298)^3 \end{aligned} \quad (8)$$

For $\text{Li}_2\text{B}_8\text{O}_{13}$

$$\begin{aligned} \% \text{Expansion} = & -3.79 \times 10^{-3}(T - 298) \\ & + 6.81 \times 10^{-6}(T - 298)^2 - 5.21 \\ & \times 10^{-9}(T - 298)^3 \end{aligned} \quad (9)$$

(where T is measured in K).

Table 1

The coefficients of the average linear thermal expansion along 'a', 'b' and 'c' axes ($\alpha_i \times 10^6 \text{ K}^{-1}$) of the lithium borate compounds in various temperature ranges in air

S. No.	Compound	Temperature range/K	$(\alpha_a \pm 0.50) \times 10^6 / (\text{K}^{-1})$	$(\alpha_b \pm 0.50) \times 10^6 / (\text{K}^{-1})$	$(\alpha_c \pm 0.50) \times 10^6 / (\text{K}^{-1})$
1	Li_3BO_3	298–883	19.92	12.30	33.58
2	$\alpha\text{-Li}_4\text{B}_2\text{O}_5$	298–863	21.30	21.52	15.24
3	$\beta\text{-Li}_4\text{B}_2\text{O}_5$	298–863	22.53	15.05	7.65
4	$\text{Li}_6\text{B}_4\text{O}_9$	298–877	17.67	16.96	39.98
5	$\alpha\text{-LiBO}_2$	298–878	3.24	1.98	31.26
		298–1063	3.36	2.70	30.99
6	$\text{Li}_2\text{B}_4\text{O}_7$	298–863	14.76	14.76	4.65
		298–1061	14.80	14.80	3.827
7	$\text{Li}_3\text{B}_7\text{O}_{12}$	298–885	13.91	13.05	5.41
		298–1060	17.39	11.56	5.71
8	LiB_3O_5	298–885	65.77	29.08	-62.51
		298–1056	57.96	28.42	-47.72
9	$\text{Li}_2\text{B}_8\text{O}_{13}$	298–543	-3.79	-5.59	-5.14
		677–869	7.95	-9.41	-37.13

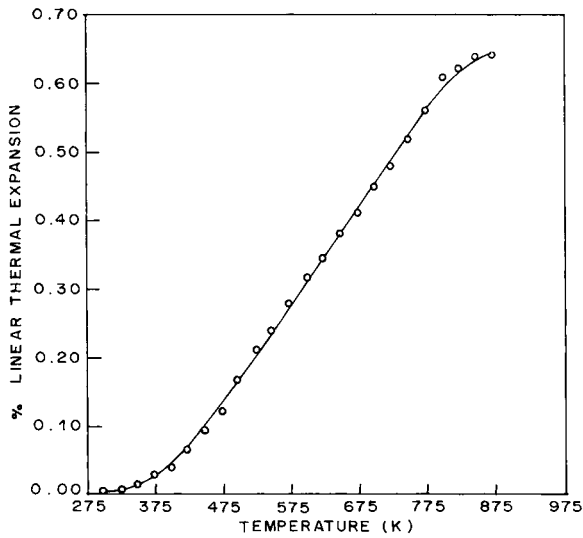


Fig. 4. Percent linear expansion of $\text{Li}_2\text{B}_4\text{O}_7$ as a function of temperature.

The temperature dependence of coefficients of linear thermal expansion (α_1) of lithium borates derived from Eqs. (1)–(9) is represented by Eqs. (10)–(18).

1. Li_3BO_3

$$\alpha_1 = 2.55 \times 10^{-6} + 8.80 \times 10^{-8}(T - 298) - 1.10 \times 10^{-10}(T - 298)^2 \quad (10)$$

2. $\alpha\text{-Li}_4\text{B}_2\text{O}_5$

$$\alpha_1 = 7.32 \times 10^{-6} + 5.98 \times 10^{-8}(T - 298) - 7.92 \times 10^{-11}(T - 298)^2 \quad (11)$$

3. $\beta\text{-Li}_4\text{B}_2\text{O}_5$

$$\alpha_1 = 3.97 \times 10^{-6} + 4.72 \times 10^{-8}(T - 298) - 5.29 \times 10^{-11}(T - 298)^2 \quad (12)$$

4. $\text{Li}_6\text{B}_4\text{O}_9$

$$\alpha_1 = -2.49 \times 10^{-6} + 6.17 \times 10^{-8}(T - 298) - 4.34 \times 10^{-11}(T - 298)^2 \quad (13)$$

5. $\alpha\text{-LiBO}_2$

$$\alpha_1 = 3.06 \times 10^{-6} + 4.03 \times 10^{-8}(T - 298) - 3.50 \times 10^{-11}(T - 298)^2 \quad (14)$$

6. $\text{Li}_2\text{B}_4\text{O}_7$

$$\alpha_1 = 1.09 \times 10^{-6} + 4.48 \times 10^{-8}(T - 298) - 4.69 \times 10^{-11}(T - 298)^2 \quad (15)$$

7. $\text{Li}_3\text{B}_7\text{O}_{12}$

$$\alpha_1 = -2.13 \times 10^{-6} + 4.08 \times 10^{-8}(T - 298) - 3.74 \times 10^{-11}(T - 298)^2 \quad (16)$$

8. LiB_3O_5

$$\alpha_1 = 3.92 \times 10^{-6} + 2.19 \times 10^{-8}(T - 298) - 1.31 \times 10^{-11}(T - 298)^2 \quad (17)$$

9. $\text{Li}_2\text{B}_8\text{O}_{13}$

$$\alpha_1 = -3.79 \times 10^{-5} + 6.81 \times 10^{-8}(T - 298) - 5.21 \times 10^{-11}(T - 298)^2 \quad (18)$$

The coefficients of linear thermal expansion $\Delta L/L_{298} \times \Delta T$, in the 298–873 K range, for these lithium borates are shown in Table 3. It can be seen that the thermal expansion behaviour of lithium borate compounds can be divided into two groups, i.e. those compounds with composition up to 50 mol% B_2O_3 and those of composition >50 mol% B_2O_3 . The coefficient of average linear thermal expansion (α_1) of Li_3BO_3 , $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, $\beta\text{-Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$ and $\alpha\text{-LiBO}_2$ are found to be higher than those of the latter, i.e. $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$, and LiB_3O_5 . Thus, the first group of lithium borates (<50 mol% B_2O_3) has got α_1 in the range of (14–19) $\times 10^{-6} \text{ K}^{-1}$, whereas those

Table 3

Coefficients of the linear thermal expansion ($\alpha_1 \times 10^6 \text{ K}^{-1}$) and average volume thermal expansion ($\alpha_v \times 10^6 \text{ K}^{-1}$) of lithium borate compounds in the temperature range $298 \leq T \leq 873 \text{ K}$ in air

S. No.	Compound	$\alpha_1 \times 10^6 \text{ K}^{-1}$	$\alpha_v \times 10^6 \text{ K}^{-1}$
1	Li_3BO_3	16.78	64.86
2	$\alpha\text{-Li}_4\text{B}_2\text{O}_5$	15.50	58.59
3	$\beta\text{-Li}_4\text{B}_2\text{O}_5$	13.62	46.86
4	$\text{Li}_6\text{B}_4\text{O}_9$	18.64	73.84
5	$\alpha\text{-LiBO}_2$	14.70	55.26
6	$\text{Li}_2\text{B}_4\text{O}_7$	11.34	34.39
7	$\text{Li}_3\text{B}_7\text{O}_{12}$	9.00	29.83
8	LiB_3O_5	12.00	32.32
9	$\text{Li}_2\text{B}_8\text{O}_{13}$	-16.00	-67.06

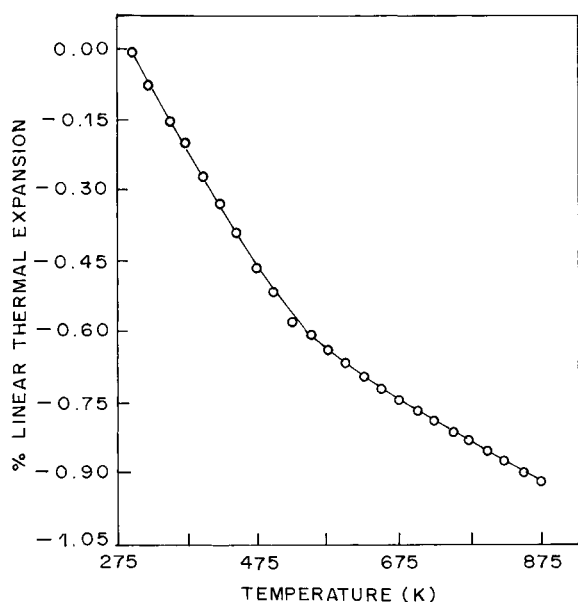


Fig. 5. Percent linear expansion of $\text{Li}_2\text{B}_8\text{O}_{13}$ as a function of temperature.

belonging to the other group (>50 mol% B_2O_3) are of the order of $(9\text{--}12)\times 10^{-6} \text{ K}^{-1}$. This data is in agreement with that obtained by HTXRD also (Table 3).

The coefficient of linear thermal expansion of $\text{Li}_2\text{B}_8\text{O}_{13}$, however, shows a sudden decrease ($\alpha_1 = -16 \times 10^{-6} \text{ K}^{-1}$). Negative thermal expansions, although unusual, are not a new phenomenon and have been known for several oxides [14,15]. Recently, negative thermal expansion have also been reported in $\text{ZrP}_{2-x}\text{V}_x\text{O}_7$, ZrW_2O_8 and HfW_2O_8 [16,17]. In fact, ZrW_2O_8 showed a negative thermal expansion from 0.3 to 1050 K, as confirmed by dilatometry and neutron diffraction. This unusual behaviour was explained as being due to the bending of the nominally linear M–O–M (M=P, V and W) links in these compounds. Other common features of these compounds, showing negative thermal expansion, are that their structures should be open with a low-density framework. It should be noted that the lithium borates also have a framework structure consisting of B–O–B bonds. Of the nine compounds, formed in the

$\text{Li}_2\text{O}\text{--}\text{B}_2\text{O}_3$ system, only $\text{Li}_2\text{B}_8\text{O}_{13}$ might be fulfilling all the structural features required to show a negative thermal expansion.

4. Conclusion

The results reveal that the behaviour of the coefficients of linear and volume expansions of lithium borates as obtained by the HTXRD and dilatometric techniques, respectively, are in good agreement with each other. All other compounds in the $\text{Li}_2\text{O}\text{--}\text{B}_2\text{O}_3$ system, besides $\text{Li}_2\text{B}_8\text{O}_{13}$, show the usual thermal expansion behaviour. Further structural investigations of this compound throughout the temperature range are in progress and will be reported subsequently.

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