

Structure of Lithium Heptaborate, $\text{Li}_3\text{B}_7\text{O}_{12}$

BY JIANG AIDONG,* LEI SHIRONG, HUANG QINGZHEN, CHEN TIANBIN AND KE DEMING

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002 Fujian, People's Republic of China

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Abstract. $M_r = 288.49$, triclinic, $P\bar{1}$, $a = 6.487$ (1), $b = 7.840$ (1), $c = 8.510$ (2) Å, $\alpha = 92.11$ (2), $\beta = 104.85$ (2), $\gamma = 99.47$ (1)°, $V = 411.2$ Å³, $Z = 2$, $D_x = 2.33$, $D_m = 2.32$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 2.02$ cm⁻¹, $F(000) = 280$, $T = 296$ K, $R = 0.061$ for 3264 unique reflections. The structure contains a network of B_3O_7 , B_3O_8 and BO_3 units with Li^+ cations located in the interstices.

Introduction. The excellent nonlinear optical (NLO) properties of β -BaB₂O₄ (BBO) are restricted to wavelengths above 200 nm (Chen *et al.*, 1989) because (1) the ultraviolet absorption edge of the planar B_3O_6 group present in BBO is at a longer wavelength than that of non-planar groups such as BO_4 and (2) all z components of the second harmonic generation coefficients of the crystal are very small or even zero owing to the symmetry and shape of the B_3O_6 group. Chen, Wu & Li (1985) suggested that if one or two boron atoms in the B_3O_6 ring were changed from trigonal to tetrahedral coordination, thus forming B_3O_7 or B_3O_8 groups, these deficiencies would be overcome. The NLO properties of LiB_3O_5 , which contains B_3O_7 groups, accord with this suggestion. LiB_3O_5 is part of the pseudobinary 1:3 Li_2O – B_2O_3 system which also contains two other compounds, $2\text{Li}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, in the B_2O_3 -rich region (Sastry & Hummel, 1958). The structures of the latter two compounds are unknown but they may involve anionic groups responsible for NLO effects. During attempts to grow crystals of these substances we obtained a new compound, $3\text{Li}_2\text{O} \cdot 7\text{B}_2\text{O}_3$, previously incorrectly described as $2\text{Li}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ (Sastry & Hummel, 1958). The structure of this new compound is reported here.

Experimental. The single crystals were successfully grown with an MoO_3 -based flux system after attempts to use B_2O_3 as a self flux were unsuccessful. Analytically pure Li_2CO_3 , H_3BO_3 and MoO_3 were weighed at the appropriate ratio, mixed thoroughly and then heated in a platinum crucible at 1113 K for 12 h. The melt was cooled slowly to 1023 K over a

period of one week and then annealed to room temperature. The X-ray powder diffraction pattern of the compound thus obtained is the same as that of $2\text{Li}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, reported by Sastry & Hummel (1958). However, from the crystal density, measured by flotation in a $\text{CH}_3\text{I}/\text{CH}_2\text{I}_2$ mixture, and the unit-cell parameters we concluded that the correct composition was $3\text{Li}_2\text{O} \cdot 7\text{B}_2\text{O}_3$ rather than $2\text{Li}_2\text{O} \cdot 5\text{B}_2\text{O}_3$. The percentage compositions corresponding to these formulae are sufficiently similar that distinguishing between them by chemical analysis is very difficult.

A crystal with dimensions $0.72 \times 0.58 \times 0.35$ mm was used for the X-ray analysis. Enraf–Nonius CAD-4 diffractometer, 25 reflections with $21 < \theta < 21.5^\circ$ for refinement of lattice parameters; ω – 2θ scan technique in the range $1 < \theta < 35^\circ$ ($-10 < h < 10$, $-12 < k < 12$, $0 < l < 13$), scan speed from 2 to 7° min^{-1} , scan width $(0.5 + 0.35 \tan \theta)^\circ$, 3810 measured reflections, 3613 unique reflections. Three standard reflections were measured during data collection, and no decay in intensity was detected. The data were corrected for Lorentz–polarization effects and empirically for absorption; max. and min. absorption corrections were 1.0146 and 0.9866 respectively. 3264 independent reflections with $I > 3\sigma(I)$ were considered observed and used in the structure analysis. The structure was solved by direct methods using *MULTAN* (Main *et al.*, 1982) and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all atoms (200 variables). Final $R = 0.061$, $wR = 0.085$ and $S = 0.82$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/[\sigma(F_o)^2 + (0.03F_o)^2 + 1]$, $(\Delta/\sigma)_{\text{max}} = 0.26$. Maximum and minimum heights in final difference Fourier synthesis were $+0.86$ and $-0.87 \text{ e } \text{Å}^{-3}$, respectively. Secondary-extinction correction was applied [$F_{\text{corr}} = F_c/(1 + X \cdot \text{FSQ})$ where X was refined to a final value of 5.77×10^{-5} and FSQ was F_c^2 multiplied by the L_p factor]. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a VAX 785 computer using *SDP* (Frenz, 1978).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1;

* To whom correspondence should be addressed.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O1	0.4104 (2)	0.3898 (2)	0.3137 (2)	0.79 (2)
O2	0.3280 (2)	0.6576 (2)	0.2118 (2)	0.47 (2)
O3	0.5607 (2)	0.8011 (2)	0.0695 (2)	0.43 (2)
O4	0.6845 (2)	0.5850 (2)	0.2421 (2)	0.43 (2)
O5	0.2618 (2)	0.0565 (2)	0.1079 (2)	0.35 (2)
O6	0.0601 (2)	0.2390 (2)	0.4741 (2)	0.50 (2)
O7	0.2252 (2)	0.0281 (2)	0.3687 (2)	0.39 (2)
O8	0.7294 (2)	0.2960 (2)	0.3100 (2)	0.44 (2)
O9	-0.0501 (2)	-0.1365 (2)	0.1449 (2)	0.39 (2)
O10	-0.0359 (2)	0.1705 (2)	0.1825 (2)	0.44 (2)
O11	0.0661 (2)	0.4675 (2)	0.2920 (2)	0.58 (2)
O12	0.6394 (2)	0.8627 (2)	0.3576 (2)	0.46 (2)
B1	0.2676 (3)	0.5033 (3)	0.2718 (3)	0.40 (3)
B2	0.0938 (3)	0.0360 (3)	0.2021 (2)	0.29 (3)
B3	0.6156 (3)	0.4269 (3)	0.2872 (3)	0.35 (3)
B4	-0.0424 (3)	0.2906 (3)	0.3136 (2)	0.28 (3)
B5	0.5586 (3)	0.7245 (3)	0.2230 (2)	0.32 (3)
B6	0.2149 (3)	0.1378 (3)	0.4942 (2)	0.33 (3)
B7	0.2491 (3)	0.1319 (3)	-0.0365 (2)	0.29 (3)
Li1	-0.0119 (6)	0.6948 (5)	0.3146 (5)	0.73 (6)
Li2	0.5178 (7)	0.0756 (6)	0.3062 (6)	0.99 (7)
Li3	0.2145 (8)	0.7977 (6)	0.0292 (6)	1.31 (8)

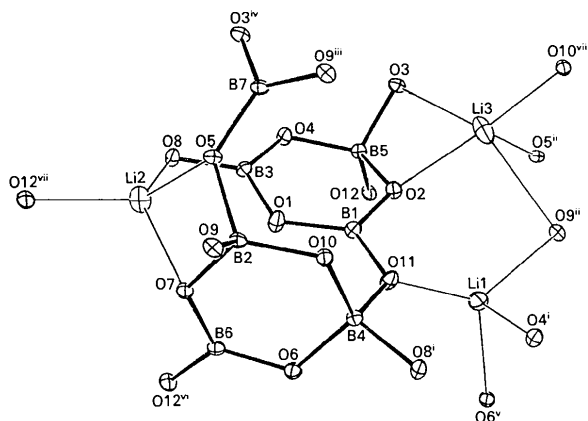


Fig. 1. Atom-numbering scheme.

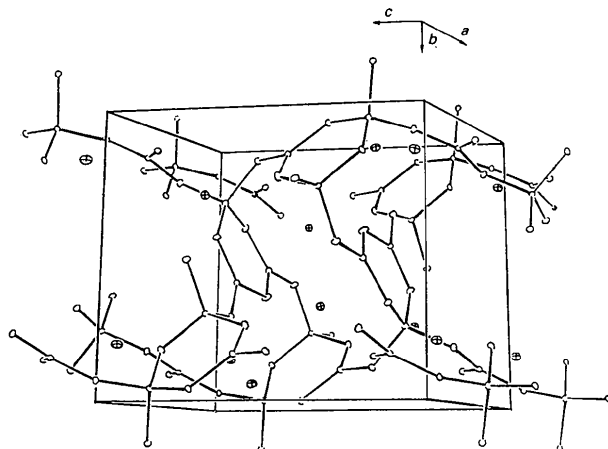


Fig. 2. A view of the packing.

Table 2. Selected bond distances (Å) and angles (°), with e.s.d.'s in parentheses

B1—O1	1.379 (3)	B6—O7	1.369 (3)
B1—O2	1.367 (3)	B6—O12 ^{vi}	1.369 (3)
B1—O11	1.347 (3)	B7—O3 ^{iv}	1.361 (3)
B2—O5	1.502 (3)	B7—O5	1.372 (3)
B2—O7	1.464 (3)	B7—O9 ⁱⁱⁱ	1.388 (3)
B2—O9	1.497 (3)	Li1—O4 ⁱ	1.944 (5)
B2—O10	1.443 (3)	Li1—O6 ^v	1.968 (5)
B3—O1	1.392 (3)	Li1—O9 ⁱⁱ	1.990 (5)
B3—O4	1.351 (3)	Li1—O11	1.947 (5)
B3—O8	1.351 (3)	Li2—O5	2.023 (5)
B4—O6	1.461 (3)	Li2—O7	2.079 (5)
B4—O8 ⁱ	1.480 (3)	Li2—O8	2.016 (6)
B4—O10	1.447 (3)	Li2—O12 ^{vii}	1.977 (6)
B4—O11	1.489 (3)	Li3—O2	1.992 (5)
B5—O2	1.478 (3)	Li3—O3	2.180 (6)
B5—O3	1.460 (3)	Li3—O5 ⁱⁱ	2.061 (5)
B5—O4	1.460 (3)	Li3—O9 ⁱⁱⁱ	2.302 (6)
B5—O12	1.474 (3)	Li3—O10 ^{viii}	1.925 (5)
B6—O6	1.362 (3)		
O1—B1—O2	121.0 (2)	O7—B6—O12 ^{vi}	117.7 (2)
O1—B1—O11	121.1 (3)	O3 ^{iv} —B7—O5	117.2 (2)
O2—B1—O11	117.9 (2)	O3 ^{iv} —B7—O9 ⁱⁱⁱ	121.8 (2)
O5—B2—O7	102.1 (2)	O5—B7—O9 ⁱⁱⁱ	121.2 (2)
O5—B2—O9	107.4 (2)	O4 ⁱⁱ —Li1—O6 ^v	88.4 (3)
O5—B2—O10	113.8 (2)	O4 ⁱⁱ —Li1—O9 ⁱⁱ	92.2 (3)
O7—B2—O9	108.8 (2)	O4 ⁱⁱ —Li1—O11	88.7 (3)
O7—B2—O10	114.9 (2)	O6 ^v —Li1—O9 ⁱⁱ	117.4 (2)
O9—B2—O10	109.5 (2)	O6 ^v —Li1—O11	116.2 (2)
O1—B3—O4	119.3 (2)	O9 ⁱⁱ —Li1—O11	126.4 (2)
O1—B3—O8	115.0 (2)	O5—Li2—O7	68.4 (2)
O4—B3—O8	125.7 (2)	O5—Li2—O8	109.6 (2)
O6—B4—O8 ⁱ	106.8 (2)	O5—Li2—O12 ^{vii}	116.9 (3)
O6—B4—O10	112.3 (2)	O7—Li2—O8	132.1 (3)
O6—B4—O11	109.8 (2)	O7—Li2—O12 ^{vii}	103.7 (2)
O8 ⁱ —B4—O10	109.7 (2)	O8—Li2—O12 ^{vii}	117.2 (2)
O8 ⁱ —B4—O11	108.7 (2)	O2—Li3—O3	68.2 (2)
O10—B4—O11	109.5 (2)	O2—Li3—O5 ⁱⁱ	111.4 (2)
O2—B5—O3	105.7 (2)	O2—Li3—O9 ⁱⁱⁱ	92.1 (2)
O2—B5—O4	111.2 (2)	O2—Li3—O10 ^{viii}	154.1 (4)
O2—B5—O12	108.0 (2)	O3—Li3—O5 ⁱⁱ	92.8 (2)
O3—B5—O4	109.7 (2)	O3—Li3—O9 ⁱⁱⁱ	145.0 (3)
O3—B5—O12	108.8 (2)	O3—Li3—O10 ^{viii}	121.0 (4)
O4—B5—O12	113.2 (2)	O5 ⁱⁱ —Li3—O9 ⁱⁱⁱ	67.0 (2)
O6—B6—O7	121.1 (2)	O5 ⁱⁱ —Li3—O10 ^{viii}	93.1 (2)
O6—B6—O12 ^{vi}	121.1 (2)	O9 ⁱⁱⁱ —Li3—O10 ^{viii}	89.5 (2)

Symmetry code: (i) $x - 1, y, z$; (ii) $x, 1 + y, z$; (iii) $-x, -y, -z$; (iv) $1 - x, 1 - y, -z$; (v) $-x, 1 - y, 1 - z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $x, y - 1, z$; (viii) $-x, 1 - y, -z$.

main bond lengths and angles are given in Table 2. An ORTEP (Johnson, 1976) drawing of the molecule is shown in Fig. 1 together with the numbering scheme. The molecular packing is shown in Fig. 2.*

The structure consists of B_3O_7 , B_3O_8 and BO_3 groups which connect by sharing oxygen atoms to form a three-dimensional network. The Li1 and Li2 atoms are each surrounded by four oxygens to form somewhat distorted tetrahedra; the Li3 atom is coordinated by five oxygen atoms but the Li3—O9ⁱⁱⁱ

* Lists of structure factors and anisotropic thermal parameters, and two figures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53022 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distance of 2.302 (6) Å is much longer than all the other Li—O distances [1.925 (5) – 2.180 (6) Å] in the structure.

Structure analysis indicates that the composition of the compound proposed by us is correct. Differential thermal analysis (DTA), heating at a rate of 10 K min⁻¹, shows two endothermal peaks at 1125 (5) (peritectic reaction) and 1179 (5) K (melting point) in good agreement with Sastry & Hummel (1958).^{*} They also reported decomposition at 969 (4) K which is not observed in our experiment. The X-ray diffraction pattern of a powder specimen which was sintered at 903 K for 25 days shows that the compound remains stable below 969 (4) K in contradiction with the results of Sastry & Hummel (1958). The transmission spectrum of 3Li₂O·7B₂O₃ in the wavelength range 190–900 indicates that the B₃O₇ or B₃O₈ groups confer better ultraviolet transparency than that displayed by crystals containing planar B₃O₆ groups, such as BBO.^{*}

^{*} See deposition footnote.

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Structure of (La_xCa_{1-x})Ba₂Cu₂(Al_yCu_{1-y})O_{6.78} with $x = 0.52$ and $y = 0.64$

BY M. HARTWEG AND B. NICK

Daimler-Benz AG, Forschungszentrum Ulm, Abteilung FUP/MS, Postfach 800230, D-7000 Stuttgart 80, Federal Republic of Germany

AND L. WALZ*

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

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Abstract. La_{0.515}(5)Ca_{0.485}(5)Ba₂Cu_{2.36}(1)Al_{0.64}(1)O_{6.78}(3), $M_r = 641.34$, tetragonal, $P4/mmm$, $a = 3.908$ (1), $c = 11.647$ (3) Å, $V = 177.88$ Å³, $Z = 1$, $D_x = 5.987$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 21.0$ mm⁻¹, $F(000) = 282.1$, $T = 296$ K, $R = 0.030$ for 240 unique reflections. The compound crystallizes in a variant of the YBa₂Cu₃O_{7-x} structure with La and Ca atoms on the Y sites and partial substitution of the Cu chain atoms by Al atoms. The Al content is higher than that previously observed in YBa₂Cu₃O_{7-x} single crystals.

Introduction. During our investigations on high- T_c superconductors it was attempted to reproduce the

synthesis of a YBa₂Cu₃O_{7-x} variant described by Carim, de Jong & de Leeuw (1988) and by Peng, Klavins, Shelton, Radousky, Hahn, Bernardez & Costantino (1989). The model concerning the mixed occupation of the three metal ions La, Ba and Ca on the Y and Ba sites given by these authors is inconsistent with the results presented here and with chemical expectations. While substitution of La by Ca has been widely studied (Nguyen, Er-Rakho, Michel, Choynet & Raveau, 1980), Ca atoms on the Ba positions are less probable. In order to clarify these inconsistencies, single-crystal investigations were carried out.

Experimental. Since no information about the crucible materials is given in the literature cited above, crystal growth experiments were performed in

* Present address: Daimler-Benz AG, Forschungszentrum Ulm, Abteilung FUP/MS, Postfach 800230, D-7000 Stuttgart 80, Federal Republic of Germany.