

Lithium potassium borate and lithium rubidium borate: new non-linear optical crystals

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The title compounds, LiKB_4O_7 and LiRbB_4O_7 , are newly developed non-linear optical crystals containing two kinds of anionic groups, namely $(\text{B}_3\text{O}_8)^{7-}$ and $(\text{B}_5\text{O}_{10})^{5-}$. The $(\text{B}_3\text{O}_8)^{7-}$ groups form infinite spiral chains parallel to the [100] direction, which are interconnected by sharing O atoms with $(\text{B}_5\text{O}_{10})^{5-}$ groups.

Comment

Since the discovery of $\beta\text{-BaB}_2\text{O}_4$ (BBO) (Chen *et al.*, 1985), various non-centrosymmetric borate crystals, *e.g.* LiB_3O_5 (LBO; Chen *et al.*, 1989), CsB_3O_5 (CBO; Wu *et al.*, 1993), $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (SBBO; Chen *et al.*, 1995) and $\text{CsLiB}_6\text{O}_{10}$ (CLBO; Sasaki, Koroda *et al.*, 1995), have been synthesized and intensively studied because of their excellent non-linear optical (NLO) properties, such as frequency conversion of laser light into the ultraviolet region. The title compounds, LiKB_4O_7 and LiRbB_4O_7 , are isomorphous and newly developed NLO crystals denoted LKB4 and LRB4, respectively. They have sufficient mechanical strength, good chemical stability and wide transparent range down to a wavelength of 190 nm. Both single crystals exhibit frequency-doubling for an incident pumping light ($\lambda = 720\text{--}780$ nm) from a Ti:Al₂O₃ pulsed-laser.

The B atoms in LKB4 and LRB4 are either trigonally or tetrahedrally coordinated by O atoms. All BO_3^{3-} trigonal groups are almost perfectly planar, with a mean B—O bond length of 1.368 (4) Å, and O—B—O bond angles ranging from 115.2 (4) to 125.2 (5)°. Tetrahedral groups, BO_4^{5-} , are slightly distorted from the ideal tetrahedron. The B—O distances lie between 1.437 (6) and 1.488 (6) Å, and the O—B—O angles

are in the range 105.74 (12)–112.4 (4)°. LBO (Radaev *et al.*, 1992) and CLBO (Sasaki, Mori *et al.*, 1995) also contain both BO_3^{3-} and BO_4^{5-} groups with similar bond lengths and angles. Chen *et al.* (1990) classified the known NLO borate crystals by their coordinated anionic groups and succeeded in predicting second-order NLO susceptibilities. According to their classification, framework structures of LKB4 and LRB4 contain two kinds of anionic groups, $(\text{B}_3\text{O}_8)^{7-}$ and $(\text{B}_5\text{O}_{10})^{5-}$, in the unit cells. The $(\text{B}_3\text{O}_8)^{7-}$ anionic group is a six-membered ring consisting of one BO_3^{3-} and two BO_4^{5-} groups, while the $(\text{B}_5\text{O}_{10})^{5-}$ group is composed of two six-membered rings joined by sharing a tetrahedrally coordinated B atom, *i.e.* a double six-membered ring. As an example, the crystal structure of LKB4 is shown in Fig. 1. The $(\text{B}_3\text{O}_8)^{7-}$ six-membered rings form infinite spiral chains parallel to the [100] direction through the O2 bridging atoms. The adjacent $(\text{B}_3\text{O}_8)^{7-}$ chains

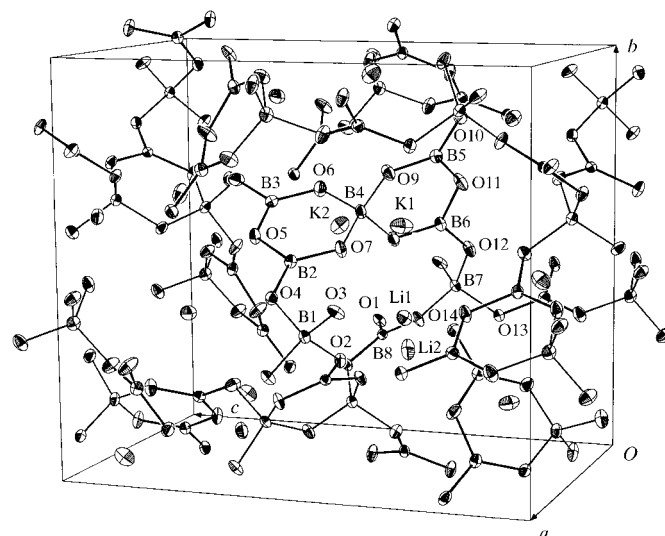


Figure 1

The molecular packing in LiKB_4O_7 showing the three-dimensional borate framework structure. Thick and thin solid lines represent B—O bonds in BO_3 triangles and in BO_4 tetrahedra, respectively. Displacement ellipsoids are shown at the 50% probability level.

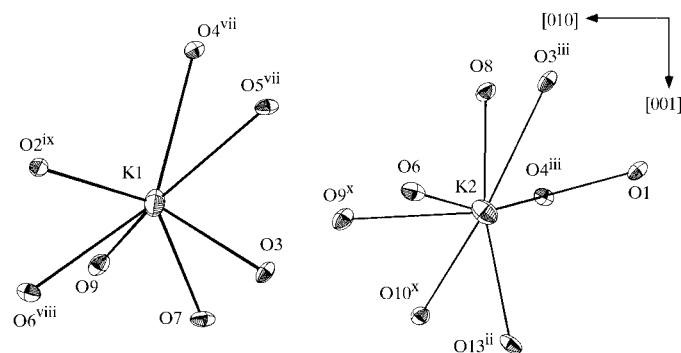


Figure 2

Oxygen coordination around potassium cations in LiKB_4O_7 . Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (ii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $x - 1, y, z$; (vii) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (viii) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; (ix) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (x) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$.]

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are interconnected by sharing O4, O12 and O13 atoms with the $(B_5O_{10})^{5-}$ double six-membered rings. The O10 atom is bonded to the trigonally coordinated B5 atom in the $(B_5O_{10})^{5-}$ group, but is not shared by the other anionic group. The distances between the B5 and O10 atoms, 1.318 (2) Å in LKB4 and 1.303 (7) Å in LRB4, are appreciably short relative to the mean boron–oxygen bond length in the BO_3^{3-} trigonal groups. Similar non-bridging O atoms with comparable bond lengths have been found in $Na_2O \cdot 2B_2O_3$ (Krogh-Moe, 1974a) and $LiBa_2B_5O_{10}$ (Huang *et al.*, 1992).

In the present study, the coordination sphere of each cation was limited to the first gap in cation–oxygen bond lengths ranked in increasing order. The coordination sphere of Li1 contains four O atoms, O1, O8, O10 and O14, which form a distorted tetrahedron. There is a good correspondence between the Li1–O distances in LKB4 and LRB4. Lithium cations in LBO (Radaev *et al.*, 1992) and CLBO (Sasaki, Mori *et al.*, 1995) also occupy such tetrahedral sites. But, another lithium cation, Li2, is situated in a highly distorted LiO_6 octahedron. On the other hand, potassium and rubidium cations do not have a well defined coordination sphere. The cation–oxygen distances are rather widely distributed, as reported in other borate compounds (Krogh-Moe, 1972a,b, 1974a,b,c,d). The potassium cations in $K_2O \cdot 2B_2O_3$ (Krogh-Moe, 1972b) and $5K_2O \cdot 19B_2O_3$ (Krogh-Moe, 1974d) take a coordination number from six to eight within the limit of 3.20 Å. In this range, the K1 and K2 cations in LKB4 are coordinated by seven and eight O atoms, respectively (Fig. 2). The Rb2 cation in LRB4 has eight oxygen neighbours in the range 2.840 (4)–3.423 (4) Å, while for the Rb1 cation, nine oxygen neighbours are found in the same range.

Experimental

Single crystals of $LiKB_4O_7$ and $LiRbB_4O_7$ were grown by the Czochralski technique from a congruent melt in air. Starting materials were prepared by a conventional solid-state reaction at 953 K. Large single crystals (*ca* 15 × 20 mm) with high optical quality were obtained.

Compound LKB4

Crystal data

| | |
|----------------------------------|---|
| $LiKB_4O_7$ | D_m measured by the Archimedes method |
| $M_r = 201.28$ | |
| Orthorhombic, $P2_12_12_1$ | Mo $K\alpha$ radiation |
| $a = 8.4915$ (12) Å | Cell parameters from 24 reflections |
| $b = 11.1454$ (13) Å | $\theta = 12.44$ – 16.48° |
| $c = 12.6558$ (13) Å | $\mu = 0.872$ mm ⁻¹ |
| $V = 1197.8$ (3) Å ³ | $T = 293$ K |
| $Z = 8$ | Sphere, colourless |
| $D_x = 2.233$ Mg m ⁻³ | 0.160 mm (radius) |
| $D_m = 2.19$ Mg m ⁻³ | |

Data collection

| | |
|------------------------------|--------------------------|
| Rigaku AFC-5R diffractometer | $h = -11 \rightarrow 11$ |
| ω - 2θ scans | $k = -15 \rightarrow 15$ |
| 13 549 measured reflections | $l = -17 \rightarrow 17$ |
| 3487 independent reflections | 3 standard reflections |
| $R_{int} = 0.033$ | every 150 reflections |
| $\theta_{max} = 30^\circ$ | intensity decay: 4% |

Table 1
Selected bond lengths (Å) for LKB4.

| | | | |
|-----------------------|-------------|-----------------------|-------------|
| B1–O1 ⁱ | 1.4759 (19) | B8–O14 | 1.3695 (19) |
| B1–O2 | 1.4734 (19) | Li1–O1 ^v | 2.004 (3) |
| B1–O3 | 1.4426 (19) | Li1–O8 | 2.176 (3) |
| B1–O4 | 1.4822 (19) | Li1–O10 ^{vi} | 1.872 (3) |
| B2–O4 | 1.3497 (19) | Li1–O14 | 2.007 (3) |
| B2–O5 | 1.4057 (19) | Li2–O2 | 1.891 (3) |
| B2–O7 | 1.3507 (19) | Li2–O3 | 2.454 (3) |
| B3–O5 | 1.391 (2) | Li2–O5 ^{vii} | 2.247 (3) |
| B3–O6 | 1.348 (2) | Li2–O10 ^{vi} | 2.043 (3) |
| B3–O13 ⁱⁱⁱ | 1.357 (2) | Li2–O11 ^{vi} | 2.062 (3) |
| B4–O6 | 1.482 (2) | Li2–O13 ⁱ | 2.420 (3) |
| B4–O7 | 1.468 (2) | K1–O3 | 2.7685 (11) |
| B4–O8 | 1.480 (2) | K1–O4 ^{vii} | 3.1937 (12) |
| B4–O9 | 1.457 (2) | K1–O5 ^{vii} | 2.7859 (12) |
| B5–O9 | 1.375 (2) | K1–O6 ^{viii} | 3.1150 (12) |
| B5–O10 | 1.318 (2) | K1–O7 | 2.7707 (12) |
| B5–O11 | 1.426 (2) | K1–O9 | 2.8102 (13) |
| B6–O8 | 1.3643 (19) | K1–O13 ^{ix} | 2.6427 (13) |
| B6–O11 | 1.388 (2) | K2–O1 | 3.1740 (13) |
| B6–O12 | 1.350 (2) | K2–O3 ⁱⁱⁱ | 3.1231 (13) |
| B7–O3 ⁱⁱⁱ | 1.4385 (19) | K2–O4 ⁱⁱⁱ | 2.8464 (12) |
| B7–O12 | 1.4751 (19) | K2–O6 | 2.9117 (14) |
| B7–O13 | 1.486 (2) | K2–O8 | 2.9609 (12) |
| B7–O14 | 1.4828 (19) | K2–O9 ^x | 2.8221 (13) |
| B8–O1 | 1.3616 (19) | K2–O10 ^x | 2.7162 (12) |
| B8–O2 ^{iv} | 1.3653 (19) | K2–O12 ⁱⁱ | 3.0010 (12) |

Symmetry codes: (i) $1+x, y, z$; (ii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (iii) $x-1, y, z$; (iv) $x-\frac{3}{2}, \frac{3}{2}-y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vi) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vii) $\frac{3}{2}-x, 1-y, z-\frac{1}{2}$; (viii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (ix) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (x) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$.

Refinement

| | |
|---|---|
| Refinement on F^2 | $(\Delta/\sigma)_{max} = 0.001$ |
| $R[F^2 > 2\sigma(F^2)] = 0.024$ | $\Delta\rho_{max} = 0.19$ e Å ⁻³ |
| $wR(F^2) = 0.055$ | $\Delta\rho_{min} = -0.27$ e Å ⁻³ |
| $S = 1.123$ | Extinction correction: SHELXL97 (Sheldrick, 1997) |
| 3342 reflections | Extinction coefficient: 0.0345 (14) |
| 236 parameters | Absolute structure: Flack (1983) |
| $w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 0.2677P]$ | Flack parameter = 0.01 (3) |
| where $P = (F_o^2 + 2F_c^2)/3$ | |

Compound LRB4

Crystal data

| | |
|----------------------------------|---|
| $LiRbB_4O_7$ | D_m measured by the Archimedes method |
| $M_r = 247.65$ | |
| Orthorhombic, $P2_12_12_1$ | Mo $K\alpha$ radiation |
| $a = 8.6257$ (12) Å | Cell parameters from 24 reflections |
| $b = 11.2576$ (13) Å | $\theta = 12.28$ – 16.27° |
| $c = 12.8531$ (15) Å | $\mu = 7.920$ mm ⁻¹ |
| $V = 1248.1$ (3) Å ³ | $T = 293$ K |
| $Z = 8$ | Sphere, colourless |
| $D_x = 2.637$ Mg m ⁻³ | 0.155 mm (radius) |
| $D_m = 2.63$ Mg m ⁻³ | |

Data collection

| | |
|--|---------------------------|
| Rigaku AFC-5R diffractometer | $R_{int} = 0.092$ |
| ω - 2θ scans | $\theta_{max} = 30^\circ$ |
| Absorption correction: sphere | $h = -12 \rightarrow 12$ |
| (<i>International Tables for X-ray Crystallography</i> , Vol. II, Table 5.3.6B) | $k = -15 \rightarrow 15$ |
| $T_{min} = 0.184, T_{max} = 0.255$ | $l = -18 \rightarrow 18$ |
| 13091 measured reflections | 3 standard reflections |
| 3597 independent reflections | every 150 reflections |
| | intensity decay: 2% |

Table 2
Selected bond lengths (Å) for LRB4.

| | | | |
|----------------------|-----------|------------------------|------------|
| B1—O1 ⁱ | 1.468 (6) | Li1—O1 ^v | 2.021 (10) |
| B1—O2 | 1.468 (6) | Li1—O8 | 2.193 (10) |
| B1—O3 | 1.440 (6) | Li1—O10 ^{vi} | 1.885 (9) |
| B1—O4 | 1.484 (6) | Li1—O14 | 2.114 (10) |
| B2—O4 | 1.364 (6) | Li2—O2 | 1.915 (10) |
| B2—O5 | 1.402 (6) | Li2—O3 | 2.198 (10) |
| B2—O7 | 1.343 (6) | Li2—O5 ^{vii} | 2.433 (10) |
| B3—O5 | 1.391 (7) | Li2—O10 ^{vi} | 2.035 (10) |
| B3—O6 | 1.349 (7) | Li2—O11 ^{vi} | 2.086 (10) |
| B3—O13 ⁱⁱ | 1.340 (7) | Li2—O13 ⁱ | 2.585 (11) |
| B4—O6 | 1.468 (7) | Rb1—O3 | 2.874 (3) |
| B4—O7 | 1.478 (7) | Rb1—O4 ^{vii} | 3.175 (3) |
| B4—O8 | 1.472 (7) | Rb1—O5 ^{vii} | 2.864 (3) |
| B4—O9 | 1.466 (7) | Rb1—O6 ^{viii} | 3.312 (4) |
| B5—O9 | 1.379 (7) | Rb1—O7 | 2.886 (3) |
| B5—O10 | 1.303 (7) | Rb1—O9 | 2.883 (4) |
| B5—O11 | 1.433 (6) | Rb1—O12 ⁱ | 3.262 (4) |
| B6—O8 | 1.367 (6) | Rb1—O13 ^{ix} | 2.712 (4) |
| B6—O11 | 1.398 (6) | Rb1—O14 ^{ix} | 3.345 (4) |
| B6—O12 | 1.345 (7) | Rb2—O1 | 3.236 (4) |
| B7—O3 ⁱⁱⁱ | 1.437 (6) | Rb2—O3 ⁱⁱⁱ | 3.423 (4) |
| B7—O12 | 1.462 (6) | Rb2—O4 ⁱⁱⁱ | 2.942 (3) |
| B7—O13 | 1.478 (7) | Rb2—O6 | 2.953 (4) |
| B7—O14 | 1.488 (6) | Rb2—O8 | 3.041 (4) |
| B8—O1 | 1.369 (7) | Rb2—O9 ^x | 2.961 (4) |
| B8—O2 ^{iv} | 1.367 (6) | Rb2—O10 ^x | 2.840 (4) |
| B8—O14 | 1.366 (6) | Rb2—O12 ⁱⁱ | 3.251 (4) |

Symmetry codes: (i) $1+x, y, z$; (ii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (iii) $x-1, y, z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vi) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vii) $\frac{3}{2}-x, 1-y, z-\frac{1}{2}$; (viii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (ix) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (x) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$.

Refinement

| | |
|---|--|
| Refinement on F^2 | $(\Delta/\sigma)_{\max} = 0.001$ |
| $R[F^2 > 2\sigma(F^2)] = 0.050$ | $\Delta\rho_{\max} = 0.98 \text{ e } \text{Å}^{-3}$ |
| $wR(F^2) = 0.075$ | $\Delta\rho_{\min} = -0.65 \text{ e } \text{Å}^{-3}$ |
| $S = 1.198$ | Extinction correction: <i>SHELXL97</i> |
| 3090 reflections | (Sheldrick, 1997) |
| 236 parameters | Extinction coefficient: 0.0237 (8) |
| $w = 1/[\sigma^2(F_o^2) + (0.0140P)^2]$ | Absolute structure: Flack (1983) |
| where $P = (F_o^2 + 2F_c^2)/3$ | Flack parameter = 0.002 (11) |

The absolute structure determination was carried out using the Flack x parameter (Flack, 1983) implemented in the least-squares program. The number of observed Friedel pairs is 911 for LKB4 and 828 for LRB4.

Data collection: Rigaku AFC-5R software; cell refinement: Rigaku AFC-5R software; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1301). Services for accessing these data are described at the back of the journal.

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