Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Na(1)—O(1$^{i}$) | 2.325 (4) | Na(2)—O(4$^{vi}$) | 2.464 (1) |
| Na(1)—O(1$^{ii}$) | 2.863 (3) | Mg—O(1$^{ii}$) | 2.040 (3) |
| Na(1)—O(1$^{iii}$) | 2.740 (4) | Mg—O(1$^{viii}$) | 2.040 (3) |
| Na(1)—O(2$^{ii}$) | 2.782 (4) | Mg—O(2$^{i}$) | 2.117 (3) |
| Na(1)—O(2$^{iv}$) | 2.395 (3) | Mg—O(2$^{vi}$) | 2.117 (3) |
| Na(1)—O(3) | 2.321 (4) | Mg—O(4) | 2.127 (2) |
| Na(1)—O(4) | 2.579 (3) | Mg—O(4$^{ix}$) | 2.127 (2) |
| Na(1)—O(4$^{v}$) | 2.656 (3) | P—O(1) | 1.518 (3) |
| Na(2)—O(2) | 2.477 (1) | P—O(2) | 1.534 (2) |
| Na(2)—O(2$^{vi}$) | 2.477 (1) | P—O(3) | 1.566 (2) |
| Na(2)—O(3$^{ii}$) | 2.537 (2) | P—O(4$^{iv}$) | 1.528 (2) |
| Na(2)—O(3$^{vii}$) | 2.537 (2) | H—O(3) | 1.221 (2) |
| Na(2)—O(4) | 2.464 (1) | | |
| O(1$^{ii}$)—Mg—O(2$^{vi}$) | 88.5 (1) | O(1)—P—O(4$^{iv}$) | 111.0 (3) |
| O(1$^{viii}$)—Mg—O(4$^{ix}$) | 88.8 (1) | O(2)—P—O(3) | 107.6 (3) |
| O(2$^{vi}$)—Mg—O(4) | 85.4 (1) | O(2)—P—O(4$^{iv}$) | 111.2 (1) |
| O(1)—P—O(2) | 110.9 (3) | O(3)—P—O(4$^{iv}$) | 108.4 (3) |
| O(1)—P—O(3) | 107.7 (2) | | |

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

The intensities of the reflections were measured at the X-ray laboratory of Okayama University, Japan. Data collection, cell refinement and data reduction: *AFC/MSC Diffractometer Control Program* (Rigaku Corporation, 1991). Structure solution: *TEXSAN* (Molecular Structure Corporation, 1985). Structure refinement: *RSFLS*4 (Sakurai, 1971). Geometric calculations: *CCPC* (Kawamura & Kawahara, 1980). Molecular graphics: *ORTEP* (Johnson, 1971), *ATOMS* (Dowty, 1992). Preparation of material for archive: *LISTHKL* (Yamakawa & Kawahara, 1994).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Ben Amara, M., Vlasse, M., Olazcuaga, R., Le Flem, G. & Hagenmuller, P. (1983). *Acta Cryst.* C**39**, 936–939.

Ben Amor, M. & Romdhane, S. S. (1992). *J. Alloy. Compd.* **188**, 102–106.

Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* B**32**, 1957–1959.

Corbridge, D. E. C. (1971). *Bull. Soc. Fr. Mineral. Cristallogr.* **94**, 271–299.

Dowty, E. (1992). *ATOMS. A Computer Program for Displaying Atomic Structures.* 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Ghorbel, A., d'Yvoire, F. & Dorémieux-Morin, C. (1974). *Bull. Soc. Chim. Fr.* pp. 1239–1242.

Johnson, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Kawamura, K. & Kawahara, A. (1980). *CCPC. Calculation of Coordination Polyhedra.* Unpublished.

Misaki, S. (1988). Doctoral thesis, The Graduate School of Natural Science and Technology, Okayama Univ.; deposited in the Library of Okayama Univ., Japan.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Morris, M. C. & MacMundy, O. F. (1984). *Natl Bur. Stand. US Monogr.* **21**, 117.

Rigaku Corporation (1991). *AFC/MSC Diffractometer Control System.* Rigaku Corporation, Tokyo, Japan.

Sakurai, T. (1971). Editor. *Universal Crystallographic System.* Crystallographic Society of Japan, Tokyo, Japan.

Takano, T., Tanaka, N. & Kusunoki, M. (1973). *ABSC. Absorption Correction.* Publication of the Institute for Protein Research, Osaka Univ., Japan.

Yamakawa, J. & Kawahara, A. (1994). *LISTHKL. Program for $F_o$ and $F_c$ Tables.* Earth Science Report, Vol. 1, No. 1, Okayama Univ., Japan.

Yamakawa, J., Yamada, T. & Kawahara, A. (1994). *Acta Cryst.* C**50**, 986–988.

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*Acta Cryst.* (1995). C**51**, 2222–2224

# Caesium Lithium Borate: a New Nonlinear Optical Crystal

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## Abstract

The structure of the title compound, $CsLiB_6O_{10}$, comprises eight-coordinate Cs atoms and four-coordinate Li atoms, and an anion network of chains formed from $B_3O_7$ groups. The Cs and Li atoms occupy alternate sites in the channel along the *c* axis.

## Comment

Borate crystals are of interest for the generation of coherent UV light because of their superior nonlinear optical properties. Various nonlinear optical borate crystals [$\beta$-$BaB_2O_4$ (BBO) (Chen, Wu, Jiang & You, 1985), $LiB_3O_5$ (LBO) (Chen *et al.*, 1989) and $CsB_3O_5$ (CBO) (Wu *et al.*, 1993)] have been found to date. Recently, we discovered a new borate crystal, $CsLiB_6O_{10}$ (CLBO) (Sasaki *et al.*, 1995; Mori, Kuroda, Nakajima, Sasaki & Nakai, 1995), which has a different space group ($I\bar{4}2d$) compared with LBO ($Pna2_1$) and CBO ($P2_12_12_1$). CLBO, LBO and CBO contain the same basic unit in the borate network. It consists of a six-membered ring in which two of the B atoms are threefold coordinated and the third B atom is fourfold coordinated by O atoms. The borate network of CLBO surrounds eight-coordinate Cs atoms and four-coordinate Li atoms.

The title compound can be grown from stoichiometric melt and also from solution. Large high quality crystals can be obtained more readily than those of LBO, CBO and BBO. A superlarge CLBO crystal with dimensions of 13 × 12 × 10 cm was grown in 12 days by means of the top-seeded Kyropoulos method (Sasaki *et al.*, 1995).

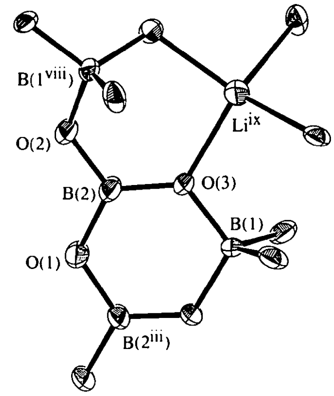

Fig. 1. Perspective view showing the coordination geometry of the Li atoms in the borate anion framework. Symmetry codes: (iii) $x, \frac{1}{2} - y, \frac{1}{4} - z$; (viii) $1 - y, x, -z$; (ix) $\frac{1}{2} + x, \frac{1}{2} + y, z - \frac{1}{2}$.

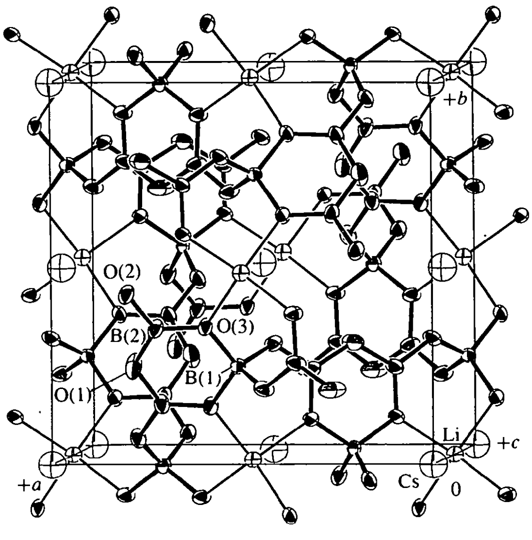

Fig. 2. Molecular packing in the crystal showing the three-dimensional framework built up from triborate groups.

## Experimental

Crystals of the title compound were grown by the top-seeded Kyropoulos technique in a platinum crucible by using a vertical cylindrical electric furnace. Starting materials were prepared from a mixture of $Cs_2CO_3$, $Li_2CO_3$ and $B_2O_3$ powders. Crystal growth was carried out at 1121 K under an air ambient. The chemical formula of the obtained compound was determined by using inductively coupled plasma spectrochemical analysis.

*Crystal data*

$CsLiB_6O_{10}$
$M_r = 364.7$
Tetragonal
$I\bar{4}2d$
$a = 10.494\,(1)$ Å
$c = 8.939\,(2)$ Å
$V = 984.4$ Å$^3$
$Z = 4$
$D_x = 2.461$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 23.5$–$24.0°$
$\mu = 3.798$ mm$^{-1}$
$T = 298$ K
Sphere
0.31 mm (radius)
Colourless

*Data collection*

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from $\Delta F$ (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.876$, $T_{\max} = 1.00$
2520 measured reflections
2463 independent reflections
1260 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.017$
$\theta_{\max} = 40°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 16$
4 standard reflections monitored every 150 reflections intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.023$
$wR = 0.035$
$S = 2.37$
722 reflections
43 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 1.23$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.33$ e Å$^{-3}$
Extinction correction: secondary
Extinction coefficient: $5.625 \times 10^{-6}$
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| Cs | 0 | 0 | 0 | 2.396 (4) |
| O(1) | 0.7982 (3) | 1/4 | 1/8 | 1.94 (5) |
| O(2) | 0.8022 (1) | 0.4434 (1) | −0.0059 (2) | 1.12 (2) |
| O(3) | 0.6029 (1) | 0.3557 (2) | 0.0698 (2) | 1.09 (2) |
| B(1) | 0.5242 (3) | 1/4 | 1/8 | 0.81 (4) |
| B(2) | 0.7325 (2) | 0.3508 (2) | 0.0602 (3) | 0.99 (3) |
| Li | 0 | 0 | 1/2 | 1.32 (6) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| B(1)—O(2$^{i}$) | 1.467 (2) | B(1)—O(3) | 1.469 (2) |
| B(2)—O(1) | 1.389 (2) | B(2)—O(2) | 1.352 (3) |
| B(2)—O(3) | 1.363 (3) | Li—O(3$^{iv}$) | 1.962 (2) |
| O(2$^{i}$)—B(1)—O(2$^{ii}$) | 109.4 (2) | O(3$^{iv}$)—Li—O(3$^{vi}$) | 95.81 (3) |
| O(2$^{i}$)—B(1)—O(3) | 106.67 (8) | O(3$^{iv}$)—Li—O(3$^{vii}$) | 95.81 (3) |
| O(2$^{i}$)—B(1)—O(3$^{iii}$) | 111.30 (9) | O(3$^{v}$)—Li—O(3$^{vi}$) | 95.81 (3) |
| O(2$^{ii}$)—B(1)—O(3) | 111.30 (9) | O(3$^{v}$)—Li—O(3$^{vii}$) | 95.81 (3) |
| O(2$^{ii}$)—B(1)—O(3$^{iii}$) | 106.67 (8) | O(3$^{vi}$)—Li—O(3$^{vii}$) | 142.9 (1) |
| O(3)—B(1)—O(3$^{iii}$) | 111.5 (2) | B(2)—O(1)—B(2$^{iii}$) | 120.5 (3) |
| O(2)—B(2)—O(3) | 122.7 (2) | B(2)—O(2)—B(1$^{viii}$) | 122.0 (2) |

| | | | |
|---|---|---|---|
| O(2)—B(2)—O(1) | 117.4 (2) | B(2)—O(3)—B(1) | 123.6 (2) |
| O(3)—B(2)—O(1) | 119.8 (2) | B(2)—O(3)—$Li^{ix}$ | 123.9 (1) |
| $O(3^{iv})$—Li—$O(3^{v})$ | 142.9 (1) | B(1)—O(3)—$Li^{ix}$ | 112.4 (1) |

Symmetry codes: (i) $y, x-\frac{1}{2}, \frac{1}{4}+z$; (ii) $y, 1-x, -z$; (iii) $x, \frac{1}{2}-y, \frac{1}{4}-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}+z$; (vi) $y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$; (vii) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{1}{2}-z$; (viii) $1-y, x, -z$; (ix) $\frac{1}{2}+x, \frac{1}{2}+y, z-\frac{1}{2}$.

The structure was solved by heavy-atom Patterson methods (Beurskens *et al.*, 1992) and expanded by Fourier techniques (Beurskens *et al.*, 1992). All atoms were refined anisotropically. All computations were performed using *TEXSAN* crystallographic software (Molecular Structure Corporation, 1992).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.

Chen, C. T., Wu, B. C., Jiang, A. D. & You, G. M. (1985). *Sci. Sin.* B**28**, 235–240.

Chen, C. T., Wu, Y. C., Jiang, A. D., Wu, B. C., You, G. M., Li, R. K. & Jin, S. J. (1989). *J. Opt. Soc. Am.* B**6**, 616–621.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, The Woodlands, TX 77381, USA.

Mori, Y., Kuroda, I., Nakajima, S., Sasaki, T. & Nakai, S. (1995). *Jpn. J. Appl. Phys.* **34**, L296–L298.

Sasaki, T., Kuroda, I., Nakajima, S., Yamaguchi, K., Watanabe, S., Mori, Y. & Nakai, S. (1995). *Proc. Adv. Solid-State Lasers Conf.* Memphis, Tennessee, USA.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Wu, Y. C., Sasaki, T., Nakai, S., Yokotani, A., Tang, H. & Chen, C. T. (1993). *Appl. Phys. Lett.* **62**, 2614–2615.