

## Meta-barium borate, II-BaB<sub>2</sub>O<sub>4</sub>, at 163 and 293 K

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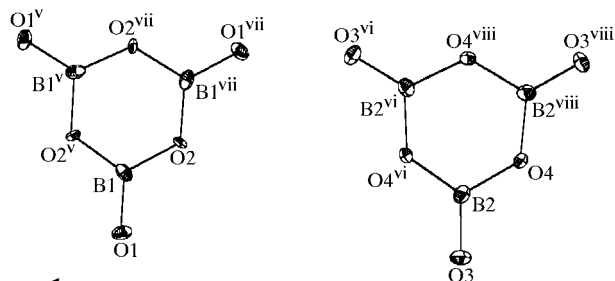
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The single-crystal X-ray diffraction structure analysis of an excellent non-linear optical material, *viz.* II-BaB<sub>2</sub>O<sub>4</sub> or Ba<sub>3</sub>(B<sub>3</sub>O<sub>6</sub>)<sub>2</sub>, has been carried out at 163 and 293 K. The two sets of structural data are compared and indicate a significant shortening of the *c* axial length in the unit cell at 163 K, whereas the *a* and *b* axial lengths essentially do not change.

### Comment

In 1982, the low-temperature form of meta-barium borate, II-BaB<sub>2</sub>O<sub>4</sub> (abbreviated BBO hereinafter), was first reported by us to crystallize in the trigonal crystal system (Lu *et al.*, 1982), instead of in the monoclinic system (space group *C2/c*) as was determined by Hübner's early work (Hübner, 1969). Using matrix transformation, we also demonstrated that the unit-cell parameters of BBO obtained both in our structure analysis and in Hübner's actually reflect the same crystal lattice. However, regrettably, on account of some limitations in our experimental conditions at that time, we were not sufficiently confident to eliminate several relatively weak reflections which violated the systematic extinction by the *c*-glide plane, and thus we assigned the space group of BBO as simply *R3*, although we pointed out that it is, at the same time, very close to *R3c*. In addition, the coordination number of the Ba cation



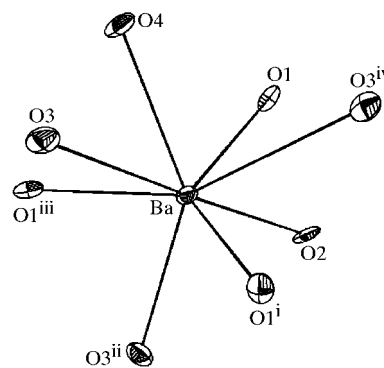
**Figure 1**

Views of the anion groups at 163 K. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (v)  $-x + y, 1 - x, z$ ; (vi)  $-x + y, -x, z$ ; (vii)  $1 - y, 1 + x - y, z$ ; (viii)  $-y, x - y, z$ .]

was erroneously stated as 7, rather than 8 as shown in our present work. Nevertheless, the results of our crystal structure analysis of BBO still provided a reasonable structural foundation for the development of BBO as an excellent UV second-harmonic generation (UV-SHG) material in our institute (Chen *et al.*, 1985). Following our work, some papers on the crystal structure of BBO were published, such as articles reported by Liebertz *et al.* (1983), Fröhlich (1984) and Ito *et al.* (1990). They all showed the space group of BBO to be *R3c*. It is noteworthy that, in the more than 20 years since our first work was published, the optical non-linearity of BBO has been studied extensively (Chen *et al.*, 1989; Xue & Zhang, 1998; Banks *et al.*, 1999), and it has become one of the most common UV-SHG crystals in the field. In a recent review paper, Abrahams (2006) made a suggestion regarding a further measurement of the crystal structure of BBO from the point of view of the prediction of new ferroelectrics. We now respond to this proposal, and in this paper the crystal structures of BBO at 163 and 293 K are reported once again, in the hope that they are helpful for research into the properties of BBO.

Figs. 1–4 show the [B<sub>3</sub>O<sub>6</sub>]<sup>3-</sup> anion group and the coordination environment of the Ba cation at the two different temperatures, *viz.* 163 and 293 K. A view of the packing structure at 163 K is depicted in Fig. 5. It is apparent from a comparison of the main structural parameters at low temperature (163 K) with those at room temperature (293 K) that the equivalent isotropic displacement (*U*<sub>eq</sub>) values of all atoms at 163 K (*U*<sub>eq</sub> = 0.005–0.010 Å<sup>2</sup>) are about half those at 293 K (*U*<sub>eq</sub> = 0.010–0.018 Å<sup>2</sup>). In particular, with the change in temperature from 293 to 163 K, the *c* axial length is noticeably shortened, by about 0.064 Å, while the volume of the unit cell is reduced accordingly by about 9 Å<sup>3</sup> [*c* = 12.721 (4) Å and *V* = 1729.9 (7) Å<sup>3</sup> at 293 K, and *c* = 12.659 (4) Å and *V* = 1721.0 (7) Å<sup>3</sup> at 163 K]. On the other hand, the *a* and *b* axial lengths do not change, approximately within the error range [*a* = *b* = 12.531 (3) Å at 293 K and *a* = *b* = 12.530 (3) Å at 163 K].

Details of the bonding data are presented in Tables 1 and 2. In the B–O B<sub>3</sub>O<sub>6</sub> ring, which is located exactly in the *ab* layer,

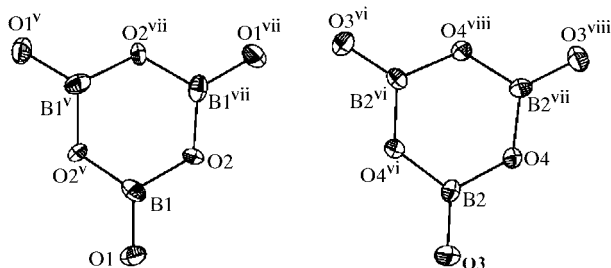


**Figure 2**

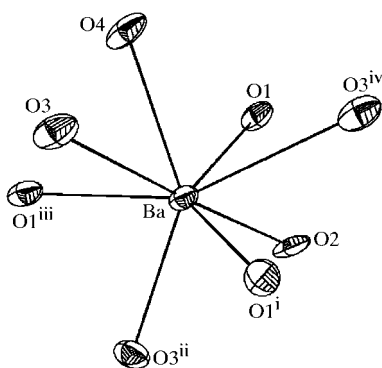
A view of the coordination environment of the Ba cation at 163 K. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (i)  $\frac{1}{3} + x, \frac{2}{3} + x - y, \frac{1}{6} + z$ ; (ii)  $\frac{2}{3} - x + y, \frac{1}{3} + y, z - \frac{1}{6}$ ; (iii)  $\frac{2}{3} - y, \frac{1}{3} - x, z - \frac{1}{6}$ ; (iv)  $\frac{1}{3} - y, \frac{2}{3} - x, z + \frac{1}{6}$ .]

the average intra-ring and extra-ring B—O bond lengths are 1.404 (5) and 1.314 (5) Å, respectively, at 293 K, and 1.404 (5) and 1.316 (5) Å, respectively, at 163 K. This means that the size of the rigid B<sub>3</sub>O<sub>6</sub> group is almost unchanged from room temperature down to low temperature. This may be why no noticeable reduction has been found in the *a* and *b* axial lengths at 163 K. It is interesting to note that the difference between the maximum and minimum intra-ring B—O bond lengths in the structure at 163 K is slightly smaller than the difference at 293 K (1.409 – 1.394 = 0.015 Å at 163 K, and 1.411 – 1.392 = 0.019 Å at 293 K), *i.e.* the B—O bond lengths of the six-membered B<sub>3</sub>O<sub>3</sub> ring are more averaged, indicating the conjugated  $\pi$ -bonding character of this ring at 163 K.

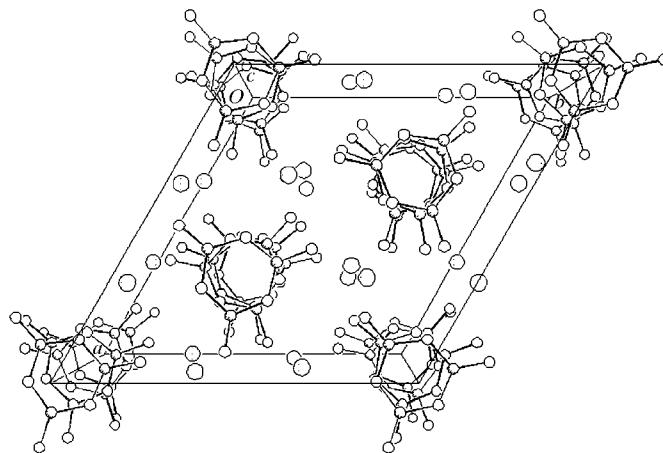
With regard to the coordination environment of the Ba cation, although no change is observed between the room- and low-temperature structures, most of the Ba—O bond lengths are shortened at 163 K, except for two [Ba—O<sup>3</sup> and Ba—O<sup>3</sup><sup>ii</sup>; symmetry code: (ii)  $\frac{2}{3} - x + y, \frac{1}{3} + y, z - \frac{1}{6}$ ], owing to the small displacement parameter of the O atom in the direction of the Ba—O bond. In particular for those linking the B<sub>3</sub>O<sub>6</sub> ring layers to the Ba layers, *i.e.* those located on the two sides of the B<sub>3</sub>O<sub>6</sub> ring layer, for instance, Ba—O<sup>3</sup><sup>iv</sup>, Ba—O<sup>1</sup><sup>i</sup>, Ba—O<sup>1</sup><sup>iii</sup> *etc.* [symmetry codes: (i)  $\frac{1}{3} + x, \frac{2}{3} + x - y, \frac{1}{6} + z$ ; (iii)  $\frac{2}{3} - y, \frac{1}{3} - x, z - \frac{1}{6}$ ; (iv)  $\frac{1}{3} - y, \frac{2}{3} - x, z + \frac{1}{6}$ ], the Ba—O bond lengths are shortened more markedly, with a maximum shortening of



**Figure 3**  
Views of the anion groups at 293 K. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (v)  $-x + y, 1 - x, z$ ; (vi)  $-x + y, -x, z$ ; (vii)  $1 - y, 1 + x - y, z$ ; (viii)  $-y, x - y, z$ .]



**Figure 4**  
A view of the coordination environment of the Ba cation at 293 K. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (i)  $\frac{1}{3} + x, \frac{2}{3} + x - y, \frac{1}{6} + z$ ; (ii)  $\frac{2}{3} - x + y, \frac{1}{3} + y, z - \frac{1}{6}$ ; (iii)  $\frac{2}{3} - y, \frac{1}{3} - x, z - \frac{1}{6}$ ; (iv)  $\frac{1}{3} - y, \frac{2}{3} - x, z + \frac{1}{6}$ .]



**Figure 5**  
A view of the packing of the structure measured at 163 K.

0.023 Å (3.049 – 3.026 = 0.023 Å for Ba—O<sup>3</sup><sup>iv</sup>). Therefore, it is reasonable to believe that it is the variation of the Ba—O bond lengths that results in the shrinkage of the *c* axial length mentioned above. Incidentally, on account of the unusually small atomic displacement parameters of some O atoms in the B<sub>3</sub>O<sub>6</sub> ring (*e.g.* O<sup>2</sup> and O<sup>3</sup>) along the lines of B—O and Ba—O at 163 K, a prolate displacement ellipsoid may be observed.

If a comparison is made between the unit-cell parameters measured by Ito and Fröhlich with our present values at 293 K, the result are as follows. Ito:  $a = b = 12.5316$  (3) Å and  $c = 12.7285$  (9) Å; Fröhlich:  $a = b = 12.519$  Å and  $c = 12.723$  Å; this work:  $a = b = 12.531$  (3) Å and  $c = 12.721$  (4) Å. It can be seen that the values obtained by us are quite close to those of Ito, whereas there is a large difference from those found by Fröhlich, especially for the *a* and *b* axes (difference of about 0.012 Å). Considering the description by Abrahams of the comparison of the r.m.s. thermal displacement  $\Delta\epsilon$  for these three data sets, "It is notable that no atom in a unit cell with  $R3c$  symmetry, derived from Lu *et al.*'s (1982) determination, ... has  $\Delta\epsilon \geq 1.1$  Å with respect to  $R3c$ , as is the case with the more accurate coordinates of Ito *et al.* (1990)", it can be said that the very close agreement in unit-cell parameters between Ito's work and ours is consistent with Abrahams's assessment.

## Experimental

Transparent crystals of the title compound were obtained using the TSSG (top seeded solution growth) method in a BaB<sub>2</sub>O<sub>4</sub>–Na<sub>2</sub>B<sub>2</sub>O<sub>4</sub> flux system and were provided by the laboratory of Professor Jian Zhuang and Mr Wen-Rong Zeng.

### BBO at 293 K

#### Crystal data

Ba<sub>3</sub>(B<sub>3</sub>O<sub>6</sub>)<sub>2</sub>  
 $M_r = 668.85$   
 Trigonal,  $R3c$   
 $a = 12.531$  (3) Å  
 $c = 12.721$  (4) Å  
 $V = 1729.9$  (7) Å<sup>3</sup>  
 $Z = 6$

$D_x = 3.852$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 10.19$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, colourless  
 $0.16 \times 0.14 \times 0.11$  mm

## Data collection

Rigaku Saturn70 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Jacobson, 1998)  
 $T_{\min} = 0.213$ ,  $T_{\max} = 0.326$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.013$   
 $wR(F^2) = 0.030$   
 $S = 1.06$   
 628 reflections  
 64 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0142P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983),  
 with 197 Friedel pairs  
 Flack parameter: 0.02 (3)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for BBO at 293 K.

Ba—O1 <sup>i</sup>	2.638 (3)	Ba—O3 <sup>iv</sup>	3.049 (4)
Ba—O3 <sup>iii</sup>	2.699 (3)	B1—O1	1.317 (6)
Ba—O4	2.758 (3)	B1—O2 <sup>v</sup>	1.392 (6)
Ba—O2	2.769 (3)	B1—O2	1.409 (5)
Ba—O3	2.819 (3)	B2—O3	1.310 (6)
Ba—O1 <sup>iii</sup>	2.821 (3)	B2—O4	1.403 (6)
Ba—O1	2.906 (3)	B2—O4 <sup>vi</sup>	1.411 (6)
O1—B1—O2 <sup>v</sup>	123.5 (4)	O3—B2—O4 <sup>vi</sup>	123.9 (4)
O1—B1—O2	120.2 (5)	O4—B2—O4 <sup>vi</sup>	114.9 (4)
O2 <sup>v</sup> —B1—O2	116.2 (4)	B1 <sup>viii</sup> —O2—B1	123.8 (4)
O3—B2—O4	121.2 (4)	B2—O4—B2 <sup>viii</sup>	125.0 (4)

Symmetry codes: (i)  $x + \frac{1}{3}, x - y + \frac{2}{3}, z + \frac{1}{6}$ ; (ii)  $-x + y + \frac{2}{3}, y + \frac{1}{3}, z - \frac{1}{6}$ ; (iii)  $-y + \frac{2}{3}, -x + \frac{1}{3}, z - \frac{1}{6}$ ; (iv)  $-y + \frac{1}{3}, -x + \frac{2}{3}, z + \frac{1}{6}$ ; (v)  $-x + y, -x + 1, z$ ; (vi)  $-x + y, -x, z$ ; (vii)  $-y + 1, x - y + 1, z$ ; (viii)  $-y, x - y, z$ .

## BBO at 163 K

## Crystal data

Ba<sub>3</sub>(B<sub>3</sub>O<sub>6</sub>)<sub>2</sub>  
 $M_r = 668.85$   
 Trigonal,  $R3c$   
 $a = 12.530 (3) \text{ \AA}$   
 $c = 12.657 (4) \text{ \AA}$   
 $V = 1721.0 (7) \text{ \AA}^3$   
 $Z = 6$

$D_x = 3.872 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 10.24 \text{ mm}^{-1}$   
 $T = 163 (2) \text{ K}$   
 Block, colourless  
 $0.16 \times 0.14 \times 0.11 \text{ mm}$

## Data collection

Rigaku Saturn70 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Jacobson, 1998)  
 $T_{\min} = 0.212$ ,  $T_{\max} = 0.324$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.011$   
 $wR(F^2) = 0.027$   
 $S = 1.08$   
 625 reflections  
 64 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0095P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983),  
 with 198 Friedel pairs  
 Flack parameter: 0.05 (3)

Table 2

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for BBO at 163 K.

Ba—O1 <sup>i</sup>	2.630 (3)	Ba—O3 <sup>iv</sup>	3.026 (3)
Ba—O3 <sup>iii</sup>	2.701 (3)	B1—O1	1.318 (5)
Ba—O4	2.752 (3)	B1—O2 <sup>v</sup>	1.394 (5)
Ba—O2	2.765 (3)	B1—O2	1.409 (5)
Ba—O1 <sup>iii</sup>	2.813 (3)	B2—O3	1.315 (5)
Ba—O3	2.821 (3)	B2—O4	1.402 (6)
Ba—O1	2.900 (3)	B2—O4 <sup>vi</sup>	1.409 (6)
O1—B1—O2 <sup>v</sup>	123.9 (4)	O3—B2—O4 <sup>vi</sup>	123.9 (4)
O1—B1—O2	119.9 (4)	O4—B2—O4 <sup>vi</sup>	115.1 (4)
O2 <sup>v</sup> —B1—O2	116.0 (4)	B1 <sup>viii</sup> —O2—B1	123.9 (4)
O3—B2—O4	120.9 (4)	B2—O4—B2 <sup>viii</sup>	124.8 (4)

Symmetry codes: (i)  $x + \frac{1}{3}, x - y + \frac{2}{3}, z + \frac{1}{6}$ ; (ii)  $-x + y + \frac{2}{3}, y + \frac{1}{3}, z - \frac{1}{6}$ ; (iii)  $-y + \frac{2}{3}, -x + \frac{1}{3}, z - \frac{1}{6}$ ; (iv)  $-y + \frac{1}{3}, -x + \frac{2}{3}, z + \frac{1}{6}$ ; (v)  $-x + y, -x + 1, z$ ; (vi)  $-x + y, -x, z$ ; (vii)  $-y + 1, x - y + 1, z$ ; (viii)  $-y, x - y, z$ .

For both compounds, data collection: *CrystalClear* (Rigaku/MS, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3008). Services for accessing these data are described at the back of the journal.

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