

Ba₃Y₂B₆O₁₅, a novel cubic borateSangen Zhao,^{a,b} Jiyong Yao,^a Guochun Zhang,^{a*} Peizhen Fu^a and Yicheng Wu^a^aKey Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China, and ^bGraduate University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

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Single crystals of tribarium diyttrium hexaborate, which crystallized in the cubic system, have been obtained by spontaneous crystallization from a high-temperature melt using Li₂O–BaO–B₂O₃ as flux. Its structure is composed of isolated [B₂O₅]^{4−} groups, irregular BaO₉ polyhedra and regular YO₆ polyhedra which occupy alternate sites running along the [111] direction. Irregular BaO₉ polyhedra and regular YO₆ polyhedra construct a three-dimensional framework, which is reinforced by [B₂O₅]^{4−} groups.

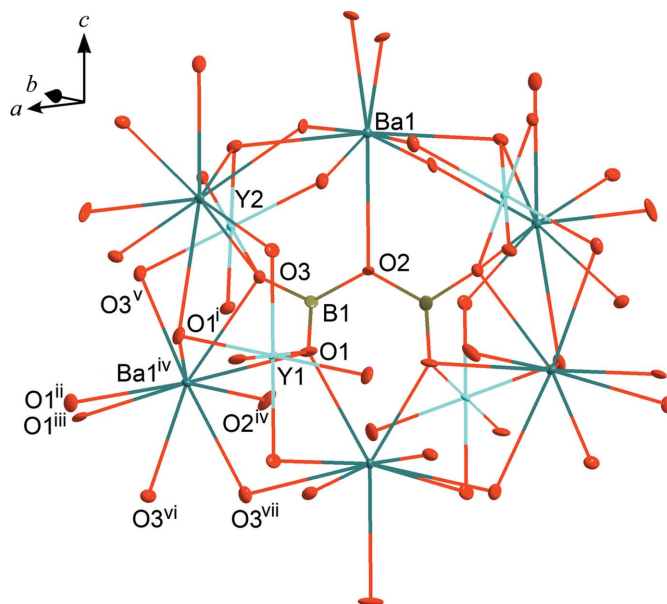
Comment

Rare-earth borates have attracted considerable attention in the past few decades owing to their practical applications as nonlinear optical (NLO) materials (Mills, 1962; Norrestam *et al.*, 1992; Wu *et al.*, 2001; Gravereau *et al.*, 2002) and plasma display panel (PDP) phosphors (Chadeyron *et al.*, 1997). To date, five ternary compounds, BaYB₉O₁₆ (Fu *et al.*, 1987), Ba₃YB₉O₁₈ (Li, Wang *et al.*, 2004), Ba₃Y(BO₃)₃ (α and β phases) (Pan & Wang, 2003; Li, Chen *et al.*, 2004a), Ba₃Y₂(BO₃)₄ (Ma *et al.*, 2005) and BaY₃B₃O₁₀ (Li, Chen *et al.*, 2004b), have been reported in the BaO–Y₂O₃–B₂O₃ system. Herein we describe the crystal structure of a novel borate, Ba₃Y₂B₆O₁₅. It crystallized in the cubic system, which is very rare in borates [about 1.18% of PDF (ICDD, 2011) compounds containing boron and oxygen crystallize in this system, and the figure is even less in borates, according to Wu *et al.* (2005)].

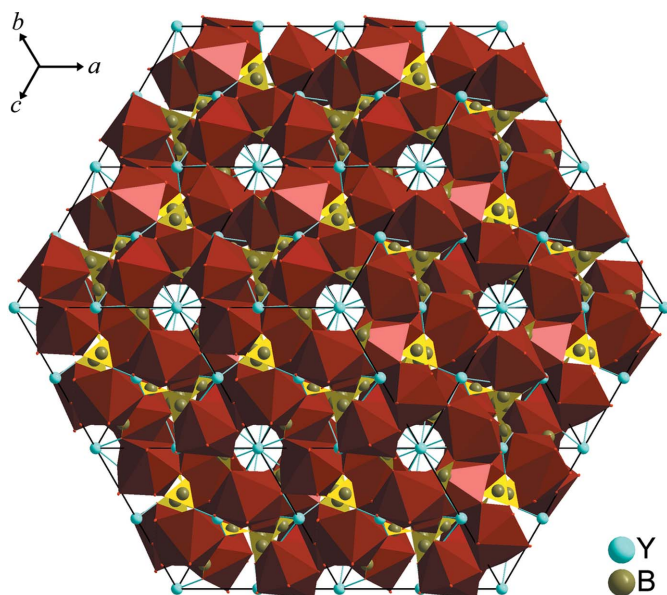
The fundamental building unit of Ba₃Y₂B₆O₁₅ is an isolated [B₂O₅]^{4−} group, which is formed by two identical BO₃ triangles sharing the bridging O2 atom. Each [B₂O₅]^{4−} anionic group connects to six Ba atoms and four Y atoms *via* O atoms (Fig. 1). The B–O bond lengths range from 1.356 (4) to 1.406 (4) Å and the mean O–B–O bond angles are equal to 120 (3)°, which indicates that they are almost planar. These values are normal for the [B₂O₅]^{4−} group. The Ba atoms are coordinated by nine O atoms in irregular polyhedra, with

Ba–O bond lengths ranging from 2.732 (3) to 3.018 (3) Å. These values compare well with those of Ba–O bond lengths of the nine-coordinate Ba²⁺ ion in Ba₃YB₉O₁₈. The Y atoms appear in two crystallographically different environments. Both Y1 and Y2 atoms are octahedrally coordinated by borate O atoms, forming regular YO₆ octahedra running right along the [111] direction alternately (Fig. 2). The YO₆ octahedra are isolated from each other by the intervening BaO₉ polyhedra and pyroborate groups. The Y1–O1 and Y2–O3 bond distances [2.271 (3) and 2.250 (3) Å, respectively] are consistent with the sum of crystal radii (Brown & Altermatt, 1985). Irregular BaO₉ polyhedra and regular YO₆ polyhedra are interconnected to each other, constructing a three-dimensional framework which is reinforced by [B₂O₅]^{4−} groups.

The structure of the title compound is closely related to that of Al₄B₆O₁₅ (Ju *et al.*, 2004), which could be described with pseudo-cubic symmetry. The fundamental building unit of Al₄B₆O₁₅ is the [B₂O₅]^{4−} group. Within the [B₂O₅]^{4−} group, the B–O–B angle (119.8°) is almost equal to that of Ba₃Y₂B₆O₁₅ [122.0 (4)°], but the interplanar angle (16.9°) between the two terminal BO₂ planes is much smaller than that of Ba₃Y₂B₆O₁₅ [59.0 (3)°]. According to Thompson *et al.* (1991), the terminal BO₂ planes pivot about the torsion angles to afford deviations from coplanarity that range from 0 to 76.8°, while the central B–O–B angle ranges from 111.8 to 180°. The O···O repulsive interactions can be relieved by torsional motions which produce nonzero interplanar angles between the two terminal BO₂ planes. Because of the small interplanar angle, the O···O repulsive interactions could not be relieved efficiently, which might be one of the reasons why the compound Al₄B₆O₁₅ is difficult to synthesize. Because of

**Figure 1**

The coordination environment of the [B₂O₅]^{4−} group. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (i) $-z + \frac{1}{2}, x + \frac{1}{2}, y$; (ii) $z, x + \frac{1}{2}, -y$; (iii) $-y + \frac{1}{2}, z, -x$; (iv) z, x, y ; (v) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-y + \frac{1}{2}, z, -x$; (vii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]


Figure 2

A projection of the structure of $\text{Ba}_3\text{Y}_2\text{B}_6\text{O}_{15}$. BaO_9 polyhedra and YO_6 polyhedra construct a three-dimensional framework, which is reinforced by $[\text{B}_2\text{O}_5]^{4-}$ groups. Atoms Y1 and Y2 occupy alternate sites running along the $[111]$ direction.

the different bond lengths of $\text{Al}-\text{O}$, $\text{Y}-\text{O}$ and $\text{Ba}-\text{O}$, their coordination environments are different. Each AlO_6 octahedron shares three independent edges with adjacent AlO_6 octahedra, while each YO_6 octahedron shares six interconnected edges with adjacent BaO_9 polyhedra. Each BaO_9 polyhedron connects to four BaO_9 polyhedra and four YO_6 octahedra by sharing edges.

Bond-valence sums (BVS; Brown & Altermatt, 1985) were calculated for the Ba, Y1, Y2 and B atoms as 2.0, 3.0, 3.2 and 3.0, respectively. All these values are close to expected values.

Experimental

Single crystals of $\text{Ba}_3\text{Y}_2\text{B}_6\text{O}_{15}$ were grown from an $\text{Li}_2\text{O}-\text{BaO}-\text{B}_2\text{O}_3$ flux system by spontaneous crystallization. Mixtures of analytically pure BaCO_3 , Y_2O_3 and H_3BO_3 in stoichiometric proportions were sintered at 773 K for 24 h, and then sintered at 1123 K for 72 h with several intermediate grindings. Prepared $\text{Ba}_3\text{Y}_2\text{B}_6\text{O}_{15}$ polycrystalline samples (54.090 g) and analytically pure Li_2CO_3 (2.220 g), BaCO_3 (23.730 g), H_3BO_3 (18.750 g) were melted in a 40×40 mm Pt crucible at 1373 K for 5 h to ensure homogeneity, cooled to 1273 K at a rate of 2 K h^{-1} , and finally cooled to room temperature at a rate of 50 K h^{-1} . A clear colourless crystal was physically separated from the melt for analysis.

Crystal data

$\text{Ba}_3\text{Y}_2\text{B}_6\text{O}_{15}$	$Z = 8$
$M_r = 894.70$	Mo $K\alpha$ radiation
Cubic, $Ia\bar{3}$	$\mu = 16.05 \text{ mm}^{-1}$
$a = 14.253(6) \text{ \AA}$	$T = 153 \text{ K}$
$V = 2895(2) \text{ \AA}^3$	$0.22 \times 0.20 \times 0.17 \text{ mm}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

$\text{Ba1}-\text{O1}^i$	3.018 (3)	$\text{Y2}-\text{O3}$	2.250 (3)
$\text{Ba1}-\text{O2}$	2.971 (4)	$\text{B1}-\text{O1}$	1.360 (4)
$\text{Ba1}-\text{O3}^{ii}$	2.732 (3)	$\text{B1}-\text{O2}$	1.406 (4)
$\text{Ba1}-\text{O3}^{iii}$	2.862 (3)	$\text{B1}-\text{O3}$	1.356 (4)
$\text{Y1}-\text{O1}$	2.271 (3)		
$\text{O3}-\text{B1}-\text{O1}$	122.5 (3)	$\text{O1}-\text{B1}-\text{O2}$	121.2 (3)
$\text{O3}-\text{B1}-\text{O2}$	116.3 (3)	$\text{B1}^{iv}-\text{O2}-\text{B1}$	122.0 (4)

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

Data collection

Rigaku AFC10 diffractometer	12264 measured reflections
Absorption correction: multi-scan (<i>ABSCOR</i> ; Higashi, 1995)	712 independent reflections
$T_{\min} = 0.635$, $T_{\max} = 1.000$	704 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	43 parameters
$wR(F^2) = 0.047$	$\Delta\rho_{\max} = 0.81 \text{ e \AA}^{-3}$
$S = 1.09$	$\Delta\rho_{\min} = -0.62 \text{ e \AA}^{-3}$
712 reflections	

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); 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: OV3004). Services for accessing these data are described at the back of the journal.

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