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$Rb_3Y_2(BO_3)_3$ with a noncentrosymmetric structure

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Trirubidium diyttrium triborate contains zigzag chains of corner-sharing $[Y_2O_{10}]$ dimers. The chains are reinforced by one independent BO_3 group and crosslinked by the other two types of BO_3 groups to form a three-dimensional framework. Channels along the [100] direction accommodate the Rb^+ cations.

Comment

Though there are several Li- and Na-containing rare earth borate compounds, including $Li_6Y(BO_3)_3$ (Tu *et al.*, 1989), $LiGd_6O_5(BO_3)_3$ (Chaminade *et al.*, 1999), $Li_3Nd_2(BO_3)_3$ (Abdullaev & Mamedov, 1977), $Li_2Yb_5O_4(BO_3)_3$ (Jubera *et al.*, 2001), $Na_3Nd(BO_3)_2$ (Mascetti *et al.*, 1981), $Na_3La_2(BO_3)_3$ (Zhang *et al.*, 2001), $Na_2Gd_2O(BO_3)_2$ (Corbel & Leblanc, 1999) and $Na_3La_9O_3(BO_3)_8$ (Gravereau *et al.*, 2002), relatively few compounds with late alkali metal elements have been reported. Recently, we have discovered two K-containing rare earth borates, $K_3Y_3(BO_3)_4$ (Gao & Li, 2007*a*) and $K_3Y(BO_3)_2$ (Gao & Li, 2007*b*) in the K_2O–Y_2O_3–B_2O_3 system. We report here the structure of the title compound, which to our knowledge is the first rubidium rare earth borate.

In the structure of $Rb_3Y_2(BO_3)_3$ (Fig. 1), atom Y1 adopts an octahedral coordination with six Y—O bonds in the range 2.169 (6)–2.336 (6) Å (Table 1) and a bond valence sum (BVS) of 3.07 (Brown & Altermatt, 1985). Atom Y2 is coordinated by seven O atoms in a distorted pentagonal bipyramid with five shorter Y—O bonds [ranging from 2.204 (6) to 2.362 (6) Å] and two slightly longer Y—O bonds [2.431 (6) and 2.507 (5) Å], and with a BVS value of 3.12. As shown in Fig. 2(*a*), the basic structural unit of $Rb_3Y_2(BO_3)_3$ is a $[Y_2O_{10}]$ dimer formed by face-sharing of the $Y1O_6$–$Y2O_7$ polyhedra. Such a face-sharing unit can also be found in $Na_2Gd_2O(BO_3)_2$ and $K_3Y_3(BO_3)_4$. The dimers share corners, forming a zigzag chain along the *a* direction, and the chain is reinforced by the $B2O_3$ group, which uses all its three bonds to join neighboring dimers (Fig. 2*a*). Along the *b* and *c* directions, these chains are connected to each other *via* the $B1O_3$ and $B3O_3$ groups, respectively, thereby constructing a three-dimensional framework. Atoms Rb1 and Rb2 are located in the larger channels and atom Rb3 sits in the smaller channels along the *a* direction (Fig. 2*b*). The three Rb atoms are found to coordinate to seven, four and six O atoms (with BVS values of 1.00, 0.67 and 1.19, respectively), if the Rb—O contacts longer than those of Rb to B [Rb$\cdots$B = 3.114 (9)–3.191 (11) Å] are neglected.

The mean O—B—O bond angles for the BO_3 groups are all equal to 120°. The $B3O_3$ group, which connects two $Y1O_6$ octahedra and one $Y2O_7$ pentagonal bipyramid from three different dimers, has a more regular triangular coordination, with a mean B3—O bond length of 1.371 Å [range 1.370 (10)–1.374 (11) Å], whereas the other two BO_3 groups both contain two O atoms from single $Y2O_7$ polyhedra and show a more distorted triangular coordination, with B—O bond lengths ranging from 1.354 (12) to 1.408 (12) Å.

Both $Li_3Nd_2(BO_3)_3$ and $Na_3La_2(BO_3)_3$ are closely related to the title compound in stoichiometry, but they differ in structure. They crystallize in the monoclinic space group $P2_1/n$ and the orthorhombic space group $Amm2$, respectively. In those structures, because of their larger ionic sizes, Nd and La atoms adopt nine-coordinated REO_9 (RE is the rare earth element) polyhedra, which are different from those of the title compound. Similar coordination environments for the Y atoms can be found in $K_3Y_3(BO_3)_4$ and $K_3Y(BO_3)_2$ reported recently by us. In $K_3Y_3(BO_3)_4$, the Y atoms coordinate to seven or eight O atoms and the seven-coordinate YO_7 polyhedron, a pentagonal bipyramid, is similar to $Y2O_7$ in $Rb_3Y_2(BO_3)_3$. In $K_3Y(BO_3)_2$, the Y atoms are coordinated by six O atoms in an octahedron, which is also similar to the $Y1O_6$ polyhedron in $Rb_3Y_2(BO_3)_3$. Considering the Y—O coordination only, it seems that the title compound is in a transition stage between $K_3Y(BO_3)_2$ and $K_3Y_3(BO_3)_4$, which is also inferred by the ratios of alkali metal to rare earth elements in the chemical formula. This observation reiterates our early findings that the rare earth element will coordinate to a smaller number of O atoms when its size is smaller and the alkaline content increases.

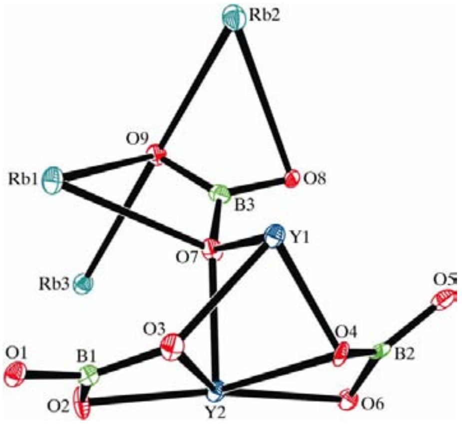

Figure 1
The asymmetric unit of $Rb_3Y_2(BO_3)_3$. Displacement ellipsoids are drawn at the 50% probability level.

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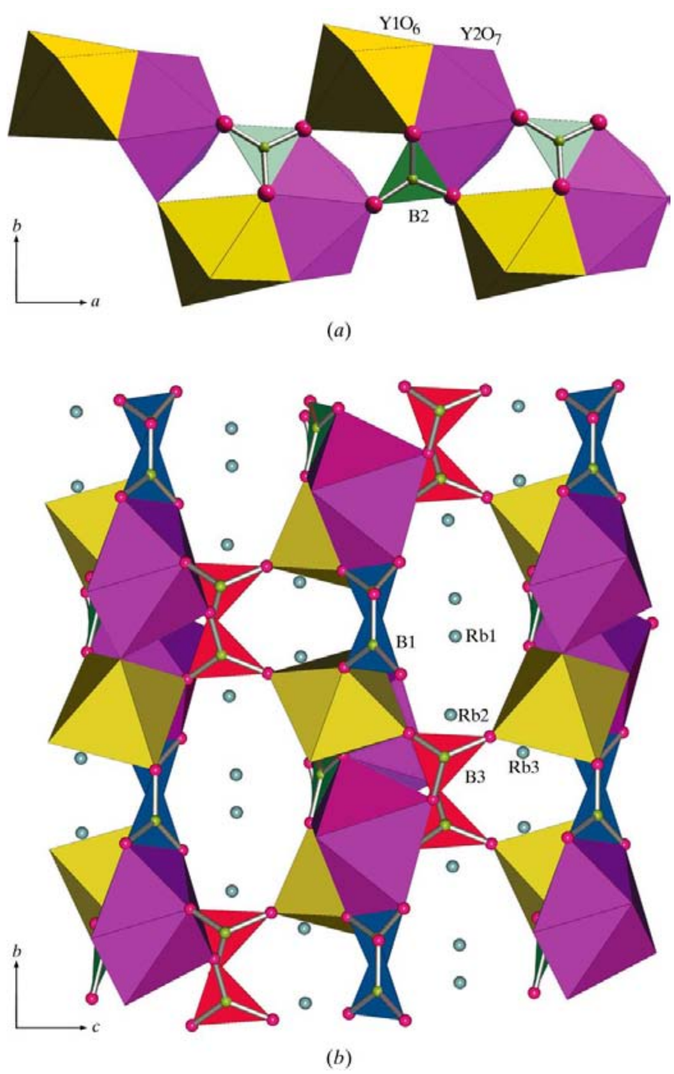

Figure 2
(*a*) A polyhedral representation of the zigzag-like chains of $Rb_3Y_2(BO_3)_3$. (*b*) A polyhedral representation of the structure of $Rb_3Y_2(BO_3)_3$, viewed along the *a* direction.

Although the title compound has a noncentrosymmetric structure, second harmonic generation (SHG) tests performed on crushed crystals using Kurtz methods (Kurtz & Perry, 1968) with a 1064 nm laser source failed to show an observable second-harmonic signal at 532 nm. Theoretical calculations based on a group approximation (Chen *et al.*, 1989, 1990) show that the SHG coefficients are $d_{31} = -0.08$ pm V^{-1}, $d_{32} = -0.17$ pm V^{-1} and $d_{33} = 0.25$ pm V^{-1}, and only the $B3O_3$ group makes a significant contribution (95% to d_{33} and 58% to d_{32}). Both the $B1O_3$ and the $B2O_3$ groups are arranged in such a way that their contributions to the SHG coefficients are cancelled out by equivalent groups oriented in the opposite directions.

Experimental

A mixture of analytically pure Rb_2CO_3 (3.80 g, 0.0165 mol), Y_2O_3 (0.60 g, 0.00266 mol) and H_3BO_3 (1.20 g, 0.01941 mol) was transferred to an Au crucible. The sample was melted at 1200 K for one day, cooled to 950 K at a rate of 5 K h^{-1}, and finally cooled to room temperature in the furnace with the power off. Colorless crystals were recovered by washing the contents of the crucible with hot water.

Crystal data

$Rb_3Y_2(BO_3)_3$
$M_r = 610.66$
Orthorhombic, $Pna2_1$
$a = 8.6811$ (4) Å
$b = 9.5627$ (4) Å
$c = 12.1914$ (6) Å
$V = 1012.07$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 25.77$ mm^{-1}
$T = 113$ (2) K
0.24 × 0.21 × 0.20 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: numerical (*NUMABS*; Rigaku, 2005)
$T_{\rm min} = 0.063$, $T_{\rm max} = 0.079$
12567 measured reflections
2602 independent reflections
2338 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.113$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.079$
$S = 1.00$
2602 reflections
155 parameters
7 restraints
$\Delta\rho_{\rm max} = 1.47$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.14$ e Å^{-3}
Absolute structure: Flack (1983), 1238 Friedel pairs
Flack parameter: 0.013 (15)

Table 1
Selected geometric parameters (Å, °).

Rb1—O2^{i}	2.849 (5)	Y1—O7	2.292 (6)
Rb1—O1^{i}	2.904 (6)	Y1—O3	2.323 (6)
Rb1—O7	2.970 (6)	Y1—O4	2.336 (6)
Rb1—O9	2.999 (6)	Y2—O5^{vi}	2.204 (6)
Rb1—O5^{ii}	3.023 (6)	Y2—O8^{vi}	2.221 (5)
Rb1—O4^{ii}	3.116 (6)	Y2—O2	2.264 (5)
Rb1—O6^{iii}	3.119 (7)	Y2—O7	2.335 (5)
Rb2—O2^{iv}	2.807 (5)	Y2—O4	2.362 (6)
Rb2—O8^{v}	2.857 (5)	Y2—O3	2.431 (6)
Rb2—O9	3.043 (6)	Y2—O6	2.507 (5)
Rb2—O4^{ii}	3.069 (6)	O1—B1	1.404 (12)
Rb3—O5^{iii}	2.706 (6)	O2—B1	1.354 (12)
Rb3—O8^{vi}	2.790 (5)	O3—B1	1.408 (12)
Rb3—O3^{vii}	2.805 (6)	O4—B2	1.384 (12)
Rb3—O1^{vii}	2.904 (6)	O5—B2	1.371 (12)
Rb3—O9	3.030 (6)	O6—B2	1.397 (12)
Rb3—O9^{vi}	3.048 (6)	O7—B3	1.374 (11)
Y1—O9^{viii}	2.169 (6)	O8—B3	1.370 (10)
Y1—O1^{i}	2.220 (6)	O9—B3	1.370 (12)
Y1—O6^{v}	2.290 (6)		
O2—B1—O1	122.5 (9)	O4—B2—O6	115.8 (9)
O2—B1—O3	116.7 (8)	O8—B3—O9	120.6 (8)
O1—B1—O3	120.8 (9)	O8—B3—O7	119.1 (9)
O5—B2—O4	120.0 (9)	O9—B3—O7	120.3 (8)
O5—B2—O6	124.1 (9)		

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

Direct phase determination showed the positions of five heavy atoms, which were assigned to three Y and two Rb atoms. Subsequent difference Fourier syntheses revealed the positions of the O atoms. Taking into account the distances of heavy atoms to oxygen, the heavy atoms were assigned as three Rb and two Y atoms. The final difference electron-density map shows a highest peak located 0.14 Å from atom Rb3 and a deepest hole located 0.78 Å from atom Y2. The final result was tested using *PLATON* (Spek, 2003), and no additional symmetry was found. The centrosymmetric space group *Pnma* was also proposed by *XPREP* (Sheldrick, 1997); however, structure solution could not proceed further after the Y and Rb atoms were found.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Balls & Sticks* (Sung & Ozawa, 2004); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3116). Services for accessing these data are described at the back of the journal.

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