

$\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$ Judith L. Kissick<sup>a\*</sup> and Douglas A. Keszler<sup>b</sup><sup>a</sup>Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, England, and <sup>b</sup>Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331, USA

Correspondence e-mail:

j.l.kissick@reading.ac.uk

## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{O}-\text{B}) = 0.005 \text{ \AA}$ 

R factor = 0.030

wR factor = 0.075

Data-to-parameter ratio = 19.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Rubidium aluminium borate,  $\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$ , is characterized by an association of  $\text{AlO}_4$  tetrahedra and  $\text{BO}_3$  triangles which form a complete three-dimensional aluminium borate framework.  $\text{Rb}^+$  cations occupy eight- and nine-coordinate positions within the three-dimensional channel system created by the framework.

Received 15 August 2002

Accepted 30 August 2002

Online 6 September 2002

## Comment

The phase  $\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$  is a new phase first described here, following a study of the system  $M_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ , where  $M = \text{Na}, \text{K}, \text{Rb}$ .  $\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$  crystallizes in the monoclinic space group  $P2_1/c$  and is characterized by a three-dimensional framework built from corner-sharing  $\text{AlO}_4$  tetrahedra and  $\text{BO}_3$  triangles surrounding a three-dimensional channel system in which the Rb atoms are located. Two crystallographically distinct Al atoms and two distinct B atoms are present in distorted tetrahedral  $\text{AlO}_4$  and trigonal-planar  $\text{BO}_3$  groups (Fig. 1). Each  $\text{AlO}_4$  group is connected to three  $\text{BO}_3$  groups and one  $\text{AlO}_4$  group to form an  $\text{Al}_2\text{O}_7$  unit in which the  $\text{Al}-\text{O}-\text{Al}$  bond angle is  $146.9 (2)^\circ$ .

The structure can be considered to be built up from ten-membered  $\text{Al}_6\text{B}_4\text{O}_{10}$  rings, generated from corner-sharing  $\text{AlO}_4$  and  $\text{BO}_3$  polyhedra. The rings are linked in herring-bone fashion to form sheets in the  $bc$  plane (Fig. 2). Adjacent sheets are connected in a staggered formation through four-membered  $\text{Al}_2\text{B}_2\text{O}_4$  rings and eight-membered  $\text{Al}_4\text{B}_4\text{O}_8$  rings perpendicular to the  $b$  and  $c$  axes, respectively. Both crystallographically distinct Rb atoms have site symmetry 1. Rb1 is eight-coordinate within a coordination sphere of  $3.5 \text{ \AA}$  and has a calculated bond valence of  $+1.01 (1)$ . Rb2 is nine-coordinate within a  $3.5 \text{ \AA}$  coordination sphere and has a calculated bond

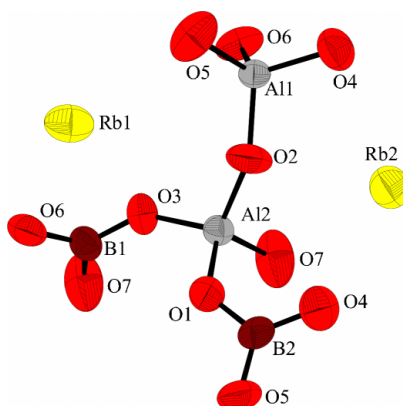
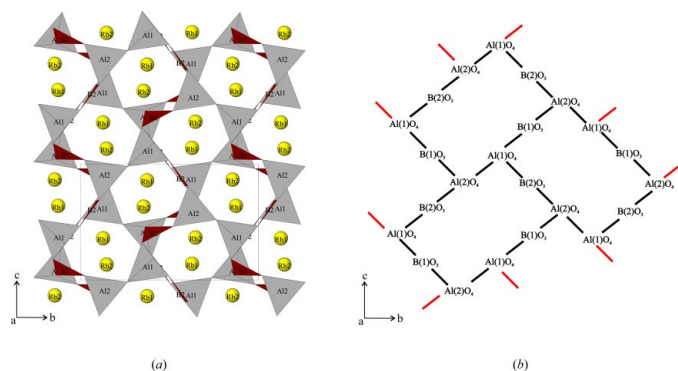


Figure 1

The local coordination of atoms in  $\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$  (50% probability ellipsoids).


**Figure 2**

(a) View of  $\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$  along [100], showing the 10-membered  $\text{Al}_6\text{B}_4\text{O}_{10}$  rings and the Rb atoms in the channels, and (b) schematic diagram showing the herring-bone arrangement of the 10-membered rings in the  $bc$  plane. Yellow spheres = Rb atoms, grey tetrahedra =  $\text{AlO}_4$ , and brown triangles =  $\text{BO}_3$  (ATOMS; Shape Software, 2002).

valence of +0.88 (1). Bond valences consistent with expected integral values are computed for each of the remaining atoms in the structure (Bresle & O'Keeffe, 1991).

The structure of the material  $M_2\text{Al}_2\text{B}_2\text{O}_7$  depends on the nature of the  $M$  cation. Na, K and Rb analogues assume three different structures, even when synthesized under identical conditions. Both the Na and K analogues of  $M_2\text{Al}_2\text{B}_2\text{O}_7$  crystallize in trigonal space groups [ $P\bar{3}1c$ ,  $a = 4.8087$  (6),  $c = 15.2734$  (6) Å and  $Z = 2$  (Chang, 1998; He *et al.*, 2001);  $P321$ ,  $a = 8.5657$  (9),  $c = 8.463$  (2) Å and  $Z = 3$  (Hu *et al.*, 1998)]. Their structures are characterized by six-membered  $\text{Al}_3\text{B}_3\text{O}_6$  rings, built from  $\text{AlO}_4$  tetrahedra and  $\text{BO}_3$  triangles, that are linked together to form nearly planar sheets in the  $ab$  plane. In the Na analogue, these sheets are connected in pairs through linear Al—O—Al bonds to form layers, which are linked through Na atoms to form a three-dimensional structure. In the K analogue, a three-dimensional Al—B—O framework is generated by Al—O—Al bonds between adjacent sheets and the K atoms are located in the space between these sheets.

We have found that up to 2.5% of the Rb atoms in  $\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$  can be replaced by either Na or K and the three-dimensional monoclinic structure is retained with essentially unchanged cell dimensions. Substitution of greater amounts of either Na or K causes the material to assume a structure more closely related to that of  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ .

## Experimental

Single crystals of  $\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$  were grown in a covered Pt crucible by melting a mixture of 42.0 wt%  $\text{Rb}_2\text{CO}_3$  (99.8%, Alfa), 18.6 wt%  $\text{Al}_2\text{O}_3$  (99.997%, Alfa), 13.3 wt%  $\text{B}_2\text{O}_3$  (99.98%, Alfa) and 26.1 wt%  $\text{LiBO}_2$  (99.995%, Alfa), which acts as a flux to ensure congruent melting. The melt was heated at 1373 K for 16 h to ensure homogeneity, it was then cooled to room temperature at a rate of  $0.07 \text{ K min}^{-1}$ . Numerous crystals formed in the crucible and a clear colourless block was physically separated from the matrix for analysis.

## Crystal data

$\text{Rb}_2\text{Al}_2\text{B}_2\text{O}_7$   
 $M_r = 358.52$   
 Monoclinic,  $P2_1/c$   
 $a = 8.901$  (2) Å  
 $b = 7.539$  (1) Å  
 $c = 11.905$  (2) Å  
 $\beta = 103.97$  (1)°  
 $V = 775.3$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 3.072 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 21 reflections  
 $\theta = 15\text{--}20^\circ$   
 $\mu = 12.85 \text{ mm}^{-1}$   
 $T = 293$  (2) K  
 Block, colourless  
 $0.20 \times 0.15 \times 0.10 \text{ mm}$

## Data collection

Rigaku AFC-6R diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.113$ ,  $T_{\max} = 0.277$   
 4763 measured reflections  
 2281 independent reflections  
 1541 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$   
 $\theta_{\text{max}} = 30.1^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -10 \rightarrow 10$   
 $l = -16 \rightarrow 16$   
 3 standard reflections  
 every 400 reflections  
 intensity decay: 0.6%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.075$   
 $S = 1.01$   
 2281 reflections  
 119 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 0.6214P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0097 (5)

**Table 1**

Selected geometric parameters (Å, °).

Rb1—O6	2.808 (2)	Rb2—O4 <sup>viii</sup>	3.455 (3)
Rb1—O1 <sup>i</sup>	2.946 (3)	Al1—O2	1.716 (3)
Rb1—O3	2.968 (3)	Al1—O6 <sup>v</sup>	1.746 (3)
Rb1—O3 <sup>ii</sup>	3.048 (3)	Al1—O4 <sup>ix</sup>	1.749 (3)
Rb1—O1	3.056 (3)	Al1—O5 <sup>i</sup>	1.762 (3)
Rb1—O5	3.105 (3)	Al2—O2	1.725 (3)
Rb1—O5 <sup>i</sup>	3.126 (3)	Al2—O3	1.747 (3)
Rb1—O7 <sup>iii</sup>	3.403 (3)	Al2—O7 <sup>x</sup>	1.755 (3)
Rb2—O7 <sup>iv</sup>	2.924 (3)	Al2—O1 <sup>x</sup>	1.764 (3)
Rb2—O2 <sup>v</sup>	3.009 (3)	O3—B1	1.360 (5)
Rb2—O2 <sup>vi</sup>	3.014 (3)	O6—B1	1.380 (5)
Rb2—O6	3.043 (3)	O7—B1 <sup>ii</sup>	1.359 (5)
Rb2—O4 <sup>vii</sup>	3.086 (3)	O1—B2 <sup>i</sup>	1.370 (5)
Rb2—O4	3.200 (3)	O4—B2	1.366 (5)
Rb2—O1 <sup>i</sup>	3.297 (3)	O5—B2	1.360 (5)
Rb2—O7 <sup>v</sup>	3.405 (3)		
O2—Al1—O6 <sup>v</sup>	112.30 (13)	O3—Al2—O1 <sup>x</sup>	108.52 (13)
O2—Al1—O4 <sup>ix</sup>	109.32 (14)	O7 <sup>x</sup> —Al2—O1 <sup>x</sup>	107.89 (14)
O6 <sup>v</sup> —Al1—O4 <sup>ix</sup>	105.08 (14)	O7 <sup>v</sup> —B1—O3	122.8 (4)
O2—Al1—O5 <sup>i</sup>	111.00 (15)	O7 <sup>v</sup> —B1—O6	118.6 (3)
O6 <sup>v</sup> —Al1—O5 <sup>i</sup>	105.17 (14)	O3—B1—O6	118.5 (3)
O4 <sup>ix</sup> —Al1—O5 <sup>i</sup>	113.82 (14)	O5—B2—O4	123.0 (4)
O2—Al2—O3	109.87 (14)	O5—B2—O1 <sup>i</sup>	116.9 (3)
O2—Al2—O7 <sup>x</sup>	109.16 (15)	O4—B2—O1 <sup>i</sup>	120.0 (3)
O3—Al2—O7 <sup>x</sup>	109.03 (14)	Al1—O2—Al2	146.85 (18)
O2—Al2—O1 <sup>x</sup>	112.30 (13)		

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

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the Solid State Chemistry Program of the National Science Foundation. JLK would like to thank Dr A. M. Chippindale for helpful discussion about this work.

## References

- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Chang, K.-S. (1998). PhD dissertation, Oregon State University, USA.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- He, M., Chen, X. L., Zhou, T., Hu, B. Q., Xu, Y. P. & Xu, T. (2001). *J. Alloys Compds.* **327**, 210–214.
- Hu, Z. G., Higashiyama, T., Yoshimura, M., Yap, Y. K., Mori, Y. & Sasaki, T. (1998). *Jpn. J. Appl. Phys. Part 2 Lett.* **32**, L1093–1094.
- Molecular Structure Corporation (1997). *TEXSAN for Windows*. Version 1.0. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1999). *MSC/AFC Diffractometer Control Software*. MSC, 9009 New Trails Drive, The Woodlands, TX 77381 USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Shape Software (1998). *ATOMS*. Shape Software, 521 Hidden Valley Rd, Kingsport, TN 37663, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.