A new rubidium beryllium borate, RbBe$_4$(BO$_3$)$_3$

Xiao-Hong Wen,‡ R.-K. Li* and C.-T. Chen

Beijing Centre for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Correspondence e-mail: rkli@cl.cryo.ac.cn

Single crystals of a new rubidium beryllium borate, RbBe$_4$(BO$_3$)$_3$, have been obtained by spontaneous nucleation from a high-temperature melt. This new orthorhombic (*Pnma*) structure type contains [Be$_2$BO$_4$]$^-$ rings, made of two BeO$_4$ tetrahedra and one BO$_3$ triangle, which constitute the basic structural units. The *m* plane runs through the B and one of the O atoms and intersects the ring. These rings form chains in the *a* direction, which are connected in the *b* and *c* directions to form zeolite-type cages in which the Rb$^+$ cations are located, at sites of *m* symmetry.

Comment

Since the discovery of β-BaB$_2$O$_4$ (BBO) as a non-linear optical (NLO) material about 20 years ago (Chen *et al.*, 1985), several borate NLO crystals have been developed which can sustain high laser damage (Chen *et al.*, 1989; Wu *et al.*, 1993; Mori *et al.*, 1995). Based on a theoretical study, one of the present authors has proposed that beryllium borates possess the largest energy gap among all alkaline and alkaline earth borates, and hence the shortest transmission cut-off wavelength (Li, 1989). Therefore, beryllium borates are good candidates for NLO applications in the ultraviolet (UV) region. In reality, two families of crystals, *viz*. ABe$_2$BO$_3$F$_2$ (A = Na, K, Rb and Cs) (Baydina *et al.*, 1975; Mei *et al.*, 1994, 1995) and M_2Be$_2$B$_2$O$_7$ (M = Sr and Ba) (Chen *et al.*, 1995; Qi & Chen, 2001), have been found to crystallize in non-centrosymmetric space groups and to possess NLO properties. Among these, KBBF (KBe$_2$BO$_3$F$_2$) has proved to be the best material for deep-UV (DUV) applications and is the only material that can generate coherent light down to 170 nm by direct second-harmonic generation (Lu *et al.*, 2001). Apart from these two families of compounds, partially because of the high toxicity of the Be compounds used as starting materials during preparation, relatively few synthetic beryllium borate compounds are known, which include MBe$_2$B$_2$O$_6$ (M = Sr and

Ba) (Schaffers & Keszler, 1990, 1994), CaBeB$_2$O$_5$ (Schaffers & Keszler, 1993) and Li$_{14}$Be$_5$B(BO$_3$)$_9$ (Luce *et al.*, 1994). In this paper, we describe the crystal structure of a new rubidium beryllium borate, RbBe$_4$(BO$_3$)$_3$.

A perspective view of the RbBe$_4$(BO$_3$)$_3$ structure along the *a* direction is shown in Fig. 1. In the structure, both B atoms are coordinated to three O atoms to form planar BO$_3$ groups, with a mean B—O bond length of 1.372 Å and O—B—O bond angles ranging from 115.9 (2) to 123.7 (2)°. The two Be atoms are bonded to four O atoms and the BeO$_4$ tetrahedra are distorted, with Be—O bond lengths ranging from 1.585 (3) to 1.666 (3) Å and O—Be—O angles from 95.5 (2) to 116.3 (2)°. All O atoms except O3 are threefold coordinated, as is typical for dense borate compounds (Parthé, 2004). Except for atom O3, the B—O bond lengths are close to their average value of 1.372 Å. The B2—O3 bond involving the two-coordinated O3 atom is the shortest [1.339 (3) Å] and is significantly shorter than the mean B—O length of 1.365 Å in the BO$_3$ groups of most borate compounds (Wells, 1984). The same observation applies to the Be1—O3 bond. Even shorter B—O bonds have been found in other rubidium borate compounds, such as RbLi$_2$Ga$_2$(BO$_3$)$_3$ (Kissick *et al.*, 2000) and LiRbB$_4$O$_7$ (Ono *et al.*, 2000). The short B2—O3 and Be1—O3 bonds reflect not only strong Be1—O3 and B2—O3 bonding, but also under-bonding between atoms Rb and O3. The small O5—Be2—O5 angle [95.5 (2)°] corresponds to edge-sharing between two very distorted Be2O$_4$ tetrahedra.

In the RbBe$_4$(BO$_3$)$_3$ structure, two BeO$_4$ tetrahedra share one common O atom, and each of them also shares a different O atom with a BO$_3$ group, to form a six-membered [Be$_2$BO$_{2\times3/3}$O$_{3/3}$O$_{2/2}$]$^-$ ring (hereinafter referred to as [Be$_2$BO$_4$]$^-$) (Fig. 2). These rings are repeated in the *a* direction to form a zigzag chain. The basic structural unit,
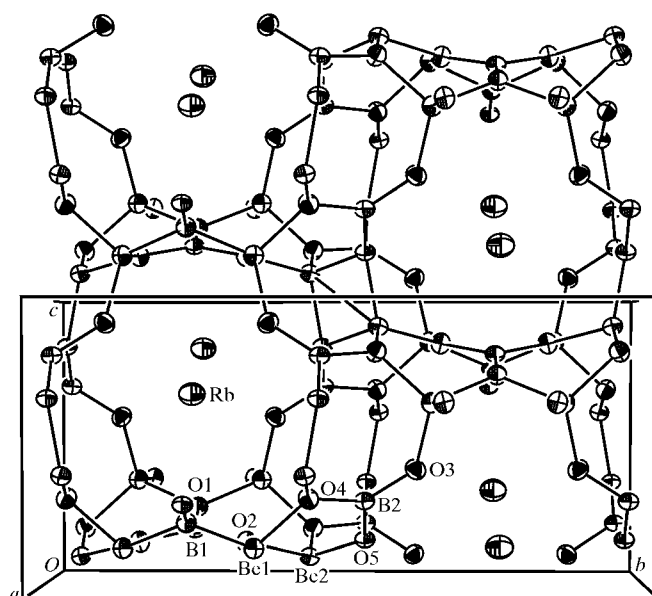
Figure 1
The crystal structure of RbBe$_4$(BO$_3$)$_3$, viewed along the *a* axis.

‡ Also at Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China.

DOI: 10.1107/S0108270106003131

inorganic compounds
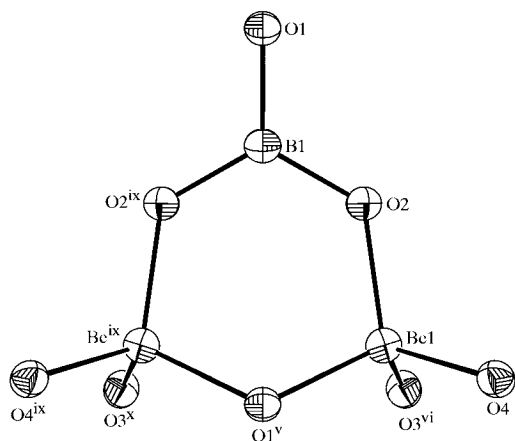
Figure 2
The $[Be_2BO_4]^-$ unit in $RbBe_4(BO_3)_3$. [Symmetry codes: (v) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (vi) $\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$; (ix) $x, \frac{1}{2}-y, z$; (x) $\frac{3}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}+z$.]

$[Be_2BO_4]^-$, is similar to the $[Be_2BO_3F_2]^-$ unit in $KBe_2BO_3F_2$. However, the $[Be_2BO_3F_2]^-$ rings in KBBF are coplanar, with the Be—F bonds alternating up and down, whereas in the title compound both Be—O bonds point in the same direction and bend the $[Be_2BO_4]^-$ unit into a zigzag chain. From the study of KBBF and $Sr_2Be_2B_2O_7$, it is known that the $[Be_2BO_4]^-$ unit can yield large NLO effects and short UV transmission cut-offs. If the $[Be_2BO_4]_\infty$ chain can be arranged favourably, the resulting structure may be a good candidate for DUV NLO applications. Unfortunately, in the case of $RbBe_4(BO_3)_3$, adjacent chains of $[Be_2BO_4]^-$ rings in the b direction point in exactly opposite directions and, therefore, their contributions to the NLO effect cancel out.

The $[Be_2BO_4]_\infty$ chains in $RbBe_4(BO_3)_3$ are connected by O—Be2—O—Be2—O and O—B2—O bonds in the b direction, and by O—Be1—O—B2—O bonds in the c direction, to build three-dimensional zeolite-like cages 6 Å in diameter and tunnels of 5 and 4 Å along the a and b axes, respectively (Fig. 1). The Rb^+ cations are located at the centres of the cages and are coordinated by ten O atoms with a bond valence sum (BVS; Brown & Altermatt, 1985) of 0.94. The BVS value for Rb and O3 (-1.94) show that they are slightly underbonded and may indicate a possible mobilization of the Rb^+ cations in the tunnels at elevated temperature.

Experimental

Single crystals of $RbBe_4(BO_3)_3$ were obtained from a melt in a tightly covered Pt crucible with initial materials of BeF_2 (0.14 mol), BeO (0.14 mol), Rb_2CO_3 (0.187 mol), NaF (0.3 mol) and B_2O_3 (0.4 mol). The melt was cooled slowly from 988 to 853 K at a rate of 3 K d^{-1} and then to room temperature at a rate of 20 K h^{-1}. Block-shaped crystals of dimensions up to $8 \times 4 \times 4$ mm were obtained after treating the contents of the crucible in hot dilute hydrochloric acid to remove the excess flux. The title compound and its Cs analogue can also be synthesized by solid-state reaction, with the determined composition of $RbBe_4(BO_3)_3$.

Crystal data

$RbBe_4(BO_3)_3$	Mo $K\alpha$ radiation
$M_r = 297.94$	Cell parameters from 44
Orthorhombic, $Pnma$	reflections
$a = 8.496\ (4)$ Å	$\theta = 5.7$–$15.9°$
$b = 13.274\ (6)$ Å	$\mu = 7.01$ mm^{-1}
$c = 6.292\ (4)$ Å	$T = 295\ (2)$ K
$V = 709.7\ (6)$ Å^3	Block, colourless
$Z = 4$	$0.4 \times 0.4 \times 0.2$ mm
$D_x = 2.789$ Mg m^{-3}	

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.043$
ω scans	$\theta_{max} = 32.5°$
Absorption correction: empirical	$h = -12 \rightarrow 12$
(using intensity measurements)	$k = -20 \rightarrow 20$
via ψ scan (North *et al.*, 1968)	$l = -9 \rightarrow 9$
$T_{min} = 0.088$, $T_{max} = 0.246$	3 standard reflections
2586 measured reflections	every 97 reflections
1324 independent reflections	intensity decay: none
1156 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$\Delta\rho_{max} = 2.01$ e Å^{-3}
$wR(F^2) = 0.112$	$\Delta\rho_{min} = -1.46$ e Å^{-3}
$S = 1.06$	Extinction correction: *SHELXL97*
1324 reflections	(Sheldrick, 1997)
83 parameters	Extinction coefficient: 0.083 (6)
$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2$	
$+ 0.2245P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Rb—O3^i	2.9954 (18)	B2—O4	1.397 (3)
Rb—O3^{ii}	2.9974 (18)	Be1—O3^{vi}	1.585 (3)
Rb—O5^{iii}	3.187 (2)	Be1—O4	1.647 (3)
Rb—O2^{iv}	3.271 (2)	Be1—O1^v	1.662 (3)
Rb—O1^v	3.345 (3)	Be1—O2	1.667 (3)
Rb—O1	3.454 (3)	Be2—O4^{vii}	1.592 (3)
B1—O2	1.367 (2)	Be2—O2	1.616 (3)
B1—O1	1.369 (4)	Be2—O5	1.632 (3)
B2—O3	1.339 (3)	Be2—O5^{viii}	1.649 (3)
B2—O5	1.394 (3)		
O2—B1—O2^{ix}	119.0 (3)	O4—Be1—O2	106.95 (17)
O2—B1—O1	120.48 (13)	O1^v—Be1—O2	105.07 (17)
O3—B2—O5	120.43 (19)	O4^{vii}—Be2—O2	112.63 (17)
O3—B2—O4	123.68 (19)	O4^{vii}—Be2—O5	116.26 (17)
O5—B2—O4	115.87 (18)	O2—Be2—O5	107.93 (16)
O3^{vi}—Be1—O4	111.92 (18)	O4^{vii}—Be2—O5^{viii}	113.20 (17)
O3^{vi}—Be1—O1^v	110.95 (18)	O2—Be2—O5^{viii}	110.03 (16)
O4—Be1—O1^v	107.20 (18)	O5—Be2—O5^{viii}	95.48 (15)
O3^{vi}—Be1—O2	114.28 (18)		

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

The positions of the Rb atom and some of the O atoms were found in the first round of direct-phase determination. The remaining O, B and Be atoms were located in the subsequent difference Fourier syntheses. The atomic and anisotropic displacement parameters of all atoms were subjected to least-squares refinement. The final difference electron-density map shows a highest peak of 2.01 e Å^{-3} located 0.64 Å from Rb and a deepest hole of -1.46 e Å^{-3} located 1.11 Å from Rb.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Version 1.08; Farrugia, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Baydina, I. A., Bakakin, V. V., Bacanova, L. P., Pal'chik, N. A., Podberezskaya, N. V. & Solov'eva, L. P. (1975). *Zh. Struk. Khim.* **16**, 1050–1053.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Bruker (1997). *XSCANS* (Version 2.2) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, C. T., Wang, Y. B., Wu, B. C., Wu, K. C., Zeng, W. R. & Yu, L. H. (1995). *Nature*, **373**, 322–324.

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

Chen, C. T., Wu, B. C., Jiang, A. D. & You, G. M. (1985). *Sci. Sin. Sect. B*, **28**, 235–243.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Kissick, J. L. & Keszler, D. A. (2000). *Acta Cryst.* C**56**, 631–632.

Li, R. K. (1989). *J. Non-Cryst. Solids*, **111**, 199–204.

Lu, J. H., Wang, G. L., Xu, Z. Y., Chen, C. T., Wang, J. Y., Zhang, C. Q. & Liu, Y. G. (2001). *Opt. Commun.* **200**, 415–418.

Luce, J. L., Schaffers, K. I. & Keszler, D. A. (1994). *Inorg. Chem.* **33**, 2453–2455.

Mei, L., Huang, X., Wang, Y., Wu, Q., Wu, B. & Chen, C. (1995). *Z. Kristallogr.* **210**, 93–95.

Mei, L. F., Wang, Y. B. & Chen, C. T. (1994). *Mater. Res. Bull.* **29**, 81–87.

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

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Ono, Y., Nakaya, M., Kajitani, T., Sugawara, T., Watanabe, N., Shiraishi, H. & Komatsu, R. (2000). *Acta Cryst.* C**56**, 1413–1415.

Parthé, E. (2004). *J. Alloys Compd,* **367**, 126–131.

Qi, H. & Chen, C. T. (2001). *Inorg. Chem. Commun.* **4**, 565–567.

Schaffers, K. I. & Keszler, D. A. (1990). *J. Solid State Chem.* **85**, 270–274.

Schaffers, K. I. & Keszler, D. A. (1993). *Acta Cryst.* C**49**, 647–650.

Schaffers, K. I. & Keszler, D. A. (1994). *Inorg. Chem.* **33**, 1201–1204.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Wells, A. F. (1984). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.

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