

Na₂[BeB₂O₅]

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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{O}-\text{B}) = 0.001$ Å; R factor = 0.022; wR factor = 0.059; data-to-parameter ratio = 10.2.

Single crystals of disodium beryllodiborate have been obtained by spontaneous nucleation from a high-temperature melt. Na₂[BeB₂O₅] adopts a new structure type and contains [BeB₂O₇]⁶⁻ rings as building units that are made up from one BeO₄ tetrahedron and two BO₃ triangles. These rings are further condensed and form {[BeB₂O₅]²⁻}_∞ two-dimensional layers extending parallel to the *ab* plane with the Na⁺ cations in a [6 + 1] coordination located between the layers. All atoms except Be and an O atom (both with site symmetry .2) are in general positions.

Related literature

Nonlinear optical (NLO) applications of borate crystals with trigonal BO₃ anions have been discussed by Chen *et al.* (1999). Among this group of compounds, beryllium borates are reported to exhibit the shortest transmission cut-off wavelength (Li, 1989). A review of the geometry of the BO₃ group is given by Zobetz (1982), and a similar configuration of the [BeB₂O₇]⁶⁻ unit is found in LiB₃O₅ (LBO) (Chen *et al.*, 2005), where [B₃O₇]⁵⁻ rings are present.

Experimental

Crystal data

Na ₂ [BeB ₂ O ₅]	$V = 420.30$ (7) Å ³
$M_r = 156.61$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 5.8117$ (5) Å	$\mu = 0.39$ mm ⁻¹
$b = 8.1666$ (7) Å	$T = 293$ (2) K
$c = 8.9830$ (8) Å	$0.12 \times 0.10 \times 0.05$ mm
$\beta = 99.665$ (14)°	

Data collection

Rigaku Mercury CCD diffractometer	Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku, 2000)
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$T_{\min} = 0.866$, $T_{\max} = 0.884$
(expected range = 0.961–0.981)
1621 measured reflections

489 independent reflections
450 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.059$
 $S = 1.17$
489 reflections

48 parameters
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Na—O2 ⁱ	2.3279 (10)	Na—O1	2.8197 (10)
Na—O1 ⁱⁱ	2.3402 (9)	B—O1	1.3529 (15)
Na—O1 ⁱⁱⁱ	2.4203 (10)	B—O2 ⁱⁱ	1.3675 (15)
Na—O3	2.4824 (10)	B—O3 ^v	1.4123 (14)
Na—O2 ^{iv}	2.5473 (9)	Be—O1 ^{vi}	1.6391 (14)
Na—O2	2.6243 (9)	Be—O2 ^{vii}	1.6584 (14)
O1—B—O2 ⁱⁱ	123.15 (11)	O1—Be—O2 ^{vii}	109.86 (4)
O1—B—O3 ^v	120.16 (11)	O1—Be—O2 ^{iv}	111.37 (4)
O2 ⁱⁱ —B—O3 ^v	116.70 (11)	O2 ^{vii} —Be—O2 ^{iv}	107.07 (12)
O1—Be—O1 ^{vi}	107.35 (12)		

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

Data collection: *CrystalClear* (Rigaku, 2000); 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: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2126).

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supplementary materials

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Na₂[BeB₂O₅]

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Comment

Borate crystals containing parallel aligned BO₃ anions are predicted to have large nonlinear optical (NLO) coefficients, moderate birefringence and wide transparency in the UV region. Therefore they are considered to be good candidates for NLO applications (Chen *et al.*, 1999). Based on a theoretical study, 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 studied intensively with the purpose of searching for new NLO materials in the UV region. The title compound, Na₂[BeB₂O₅], (I), was found from the investigation of the pseudo-ternary system Na₂O-BeO-B₂O₃.

A perspective view of the structure of (I) along the *a* direction is shown in Fig.1. The Be atoms are bonded to four O atoms to form slightly distorted BeO₄ tetrahedra (site symmetry. 2). The Be—O bonds can be classified into two groups with different bond lengths of 1.6391 (14) Å for Be—O1 and 1.6584 (14) Å for Be—O2. The O—Be—O angles vary from 107.07 (12) to 111.37 (4)°, indicating a slight distortion from the ideal tetrahedron. The B atoms are coordinated to three O atoms to form planar BO₃ triangles with a mean B—O bond length of 1.378 Å (Table 1) and O—B—O angles ranging from 116.70 (11) to 123.15 (11)°, which is in good agreement with the results of geometric studies for the triangular BO₃ group (Zobetz, 1982). Two BO₃ groups, slightly tilted against each other, share one O3 atom, and each of them also share a different O1 atom with a BeO₄ tetrahedron to form a six-membered [BeB₂O₇]⁶⁻ ring (Fig. 2). These [BeB₂O₇]⁶⁻ rings are further condensed, resulting in a [BeB₂O₅]_∞²⁻ layer parallel to the *ab* plane. Between adjacent [BeB₂O₅]_∞²⁻ layers the Na⁺ cations are located in a [6 + 1] coordination, with one considerably longer Na—O bond of 2.8197 (10) Å (Table 1).

The conformation of the [BeB₂O₇]⁶⁻ rings is similar to that of the [B₃O₇]⁵⁻ units in LiB₃O₅ (LBO) (Chen *et al.*, 2005), with the BO₄ tetrahedron replaced by a BeO₄ tetrahedron. From the study of LBO, it is known that the [B₃O₇]⁵⁻ group can yield large NLO effects and short UV transmission cut-offs, but the spatial arrangement of the helical [B₃O₅]_∞ chains along the *c* axis is unfavorable for the generation of a large birefringence. Therefore, compounds with a [BeB₂O₅]_∞ layer structure may be good candidates for deep UV NLO applications. Unfortunately, in the case of (I), the direction of the [BeB₂O₇]⁶⁻ groups in the two adjacent layers are completely opposite, and thus their contributions to the NLO effect are eliminated.

Experimental

Single crystals of compound (I) were grown using a Na₄B₂O₅ flux. The composition of the mixture for crystal growth was 2:1:3 of Na₂CO₃ (Hongguang Materials, 99.8%), BeO (Shuikoushan Materials, 99.8%), and H₃BO₃ (Jinghua Materials, 95%). This mixture was heated in a Pt crucible to 1073 K, held at this temperature for several hours, and then cooled at a rate of 3 K h⁻¹ from 1073 to 873 K. The remaining solidified flux attached to the crystals was readily dissolved in water. Crystals with an average size of 0.5 mm and mostly block-shaped habit were obtained.

Figures

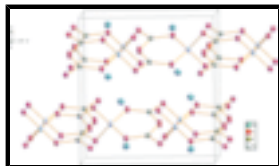


Fig. 1. The structure of (I) in a projection approximately along the *a* axis with anisotropic displacement ellipsoids drawn at the 60% probability level. Na—O bonds were omitted for clarity.

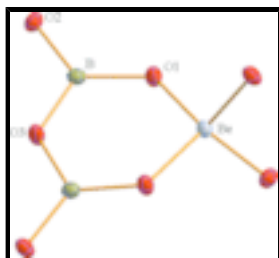


Fig. 2. $[\text{BeB}_2\text{O}_7]^{(6-)}$ building unit in compound (I).

disodium beryllodiborate

Crystal data

$\text{Na}_2[\text{BeB}_2\text{O}_5]$

$M_r = 156.61$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 5.8117\ (5)\ \text{\AA}$

$b = 8.1666\ (7)\ \text{\AA}$

$c = 8.9830\ (8)\ \text{\AA}$

$\beta = 99.665\ (14)^\circ$

$V = 420.30\ (7)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 304$

$D_x = 2.475\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 616 reflections

$\theta = 2.3\text{--}27.5^\circ$

$\mu = 0.39\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Prism, colourless

$0.12 \times 0.10 \times 0.05\ \text{mm}$

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: Sealed Tube

Monochromator: Graphite Monochromator

Detector resolution: $14.6306\ \text{pixels mm}^{-1}$

$T = 293.1500\ \text{K}$

CCD_Profile_fitting scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2000)

$T_{\min} = 0.866$, $T_{\max} = 0.884$

1621 measured reflections

489 independent reflections

450 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 4.4^\circ$

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 10$

$l = -10 \rightarrow 11$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.2765P]$
$wR(F^2) = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{\max} < 0.001$
489 reflections	$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
48 parameters	$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Na	-0.01389 (8)	0.30641 (6)	0.42612 (6)	0.0142 (2)
O1	-0.34432 (14)	0.32884 (10)	0.15850 (10)	0.0113 (2)
O2	0.16865 (14)	0.58926 (10)	0.37065 (10)	0.0108 (2)
O3	0	0.07376 (14)	0.25	0.0140 (3)
B	-0.3344 (2)	0.49318 (16)	0.17748 (15)	0.0087 (3)
Be	-0.5	0.2100 (2)	0.25	0.0087 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.0145 (3)	0.0145 (3)	0.0150 (3)	-0.00079 (18)	0.0065 (2)	-0.00110 (18)
O1	0.0127 (4)	0.0078 (4)	0.0154 (4)	-0.0005 (3)	0.0082 (3)	-0.0002 (3)
O2	0.0109 (4)	0.0099 (4)	0.0124 (4)	0.0028 (3)	0.0046 (3)	0.0008 (3)
O3	0.0135 (6)	0.0073 (6)	0.0243 (7)	0	0.0120 (5)	0
B	0.0074 (6)	0.0097 (6)	0.0087 (6)	0.0003 (4)	0.0008 (5)	0.0010 (5)
Be	0.0090 (9)	0.0064 (9)	0.0115 (10)	0	0.0043 (8)	0

Geometric parameters (\AA , $^\circ$)

Na—O2 ⁱ	2.3279 (10)	O2—Na ⁱ	2.3279 (10)
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supplementary materials

Na—O1 ⁱⁱ	2.3402 (9)	O2—Na ^{viii}	2.5473 (9)
Na—O1 ⁱⁱⁱ	2.4203 (10)	O3—B ^v	1.4123 (14)
Na—O3	2.4824 (10)	O3—B ^{ix}	1.4123 (14)
Na—O2 ^{iv}	2.5473 (9)	O3—Na ⁱⁱ	2.4824 (10)
Na—O2	2.6243 (9)	B—O1	1.3529 (15)
Na—B ^v	2.8128 (14)	B—O2 ⁱⁱ	1.3675 (15)
Na—B ⁱⁱ	2.8145 (14)	B—O3 ^x	1.4123 (14)
Na—O1	2.8197 (10)	B—Na ^{xi}	2.8128 (14)
Na—Be ^{vi}	2.9000 (6)	B—Na ⁱⁱ	2.8145 (14)
Na—B	3.0639 (13)	Be—O1 ^{xii}	1.6391 (14)
Na—Be	3.0991 (7)	Be—O2 ^v	1.6584 (14)
O1—Be	1.6391 (14)	Be—O2 ^{iv}	1.6584 (14)
O1—Na ⁱⁱ	2.3402 (9)	Be—Na ^{vi}	2.9000 (6)
O1—Na ^{vii}	2.4203 (10)	Be—Na ^{vii}	2.9000 (6)
O2—B ⁱⁱ	1.3675 (15)	Be—Na ^{xii}	3.0991 (7)
O2—Be ^{viii}	1.6584 (14)		
O2 ⁱ —Na—O1 ⁱⁱ	135.07 (4)	Be—O1—Na	83.58 (4)
O2 ⁱ —Na—O1 ⁱⁱⁱ	69.25 (3)	Na ⁱⁱ —O1—Na	75.89 (3)
O1 ⁱⁱ —Na—O1 ⁱⁱⁱ	93.45 (3)	Na ^{vii} —O1—Na	145.70 (4)
O2 ⁱ —Na—O3	146.94 (3)	B ⁱⁱ —O2—Be ^{viii}	120.32 (8)
O1 ⁱⁱ —Na—O3	74.16 (3)	B ⁱⁱ —O2—Na ⁱ	147.49 (8)
O1 ⁱⁱⁱ —Na—O3	98.53 (3)	Be ^{viii} —O2—Na ⁱ	91.79 (4)
O2 ⁱ —Na—O2 ^{iv}	92.62 (3)	B ⁱⁱ —O2—Na ^{viii}	86.32 (7)
O1 ⁱⁱ —Na—O2 ^{iv}	130.21 (3)	Be ^{viii} —O2—Na ^{viii}	92.48 (6)
O1 ⁱⁱⁱ —Na—O2 ^{iv}	91.58 (3)	Na ⁱ —O2—Na ^{viii}	87.38 (3)
O3—Na—O2 ^{iv}	56.11 (2)	B ⁱⁱ —O2—Na	83.32 (7)
O2 ⁱ —Na—O2	92.78 (3)	Be ^{viii} —O2—Na	115.71 (6)
O1 ⁱⁱ —Na—O2	57.28 (3)	Na ⁱ —O2—Na	87.22 (3)
O1 ⁱⁱⁱ —Na—O2	116.52 (3)	Na ^{viii} —O2—Na	151.43 (4)
O3—Na—O2	119.69 (3)	B ^v —O3—B ^{ix}	124.46 (14)
O2 ^{iv} —Na—O2	151.43 (4)	B ^v —O3—Na	88.00 (6)
O2 ⁱ —Na—O1	110.32 (3)	B ^{ix} —O3—Na	138.43 (6)
O1 ⁱⁱ —Na—O1	103.51 (3)	B ^v —O3—Na ⁱⁱ	138.43 (6)
O1 ⁱⁱⁱ —Na—O1	152.30 (3)	B ^{ix} —O3—Na ⁱⁱ	88.00 (6)
O3—Na—O1	66.22 (2)	Na—O3—Na ⁱⁱ	80.12 (4)
O2 ^{iv} —Na—O1	60.74 (3)	O1—B—O2 ⁱⁱ	123.15 (11)
O2—Na—O1	91.15 (3)	O1—B—O3 ^x	120.16 (11)
B—O1—Be	122.68 (10)	O2 ⁱⁱ —B—O3 ^x	116.70 (11)
B—O1—Na ⁱⁱ	95.57 (7)	O1—Be—O1 ^{xii}	107.35 (12)
Be—O1—Na ⁱⁱ	135.44 (7)	O1—Be—O2 ^v	109.86 (4)
B—O1—Na ^{vii}	124.34 (7)	O1 ^{xii} —Be—O2 ^v	111.37 (4)

Be—O1—Na ^{vii}	89.03 (5)	O1—Be—O2 ^{iv}	111.37 (4)
Na ⁱⁱ —O1—Na ^{vii}	86.55 (3)	O1 ^{xii} —Be—O2 ^{iv}	109.86 (4)
B—O1—Na	87.04 (7)	O2 ^v —Be—O2 ^{iv}	107.07 (12)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, y, -z+1/2$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $x-1/2, y-1/2, z$; (v) $-x-1/2, y-1/2, -z+1/2$; (vi) $-x-1/2, -y+1/2, -z+1$; (vii) $x-1/2, -y+1/2, z-1/2$; (viii) $x+1/2, y+1/2, z$; (ix) $x+1/2, y-1/2, z$; (x) $x-1/2, y+1/2, z$; (xi) $-x-1/2, y+1/2, -z+1/2$; (xii) $-x-1, y, -z+1/2$.

Fig. 1

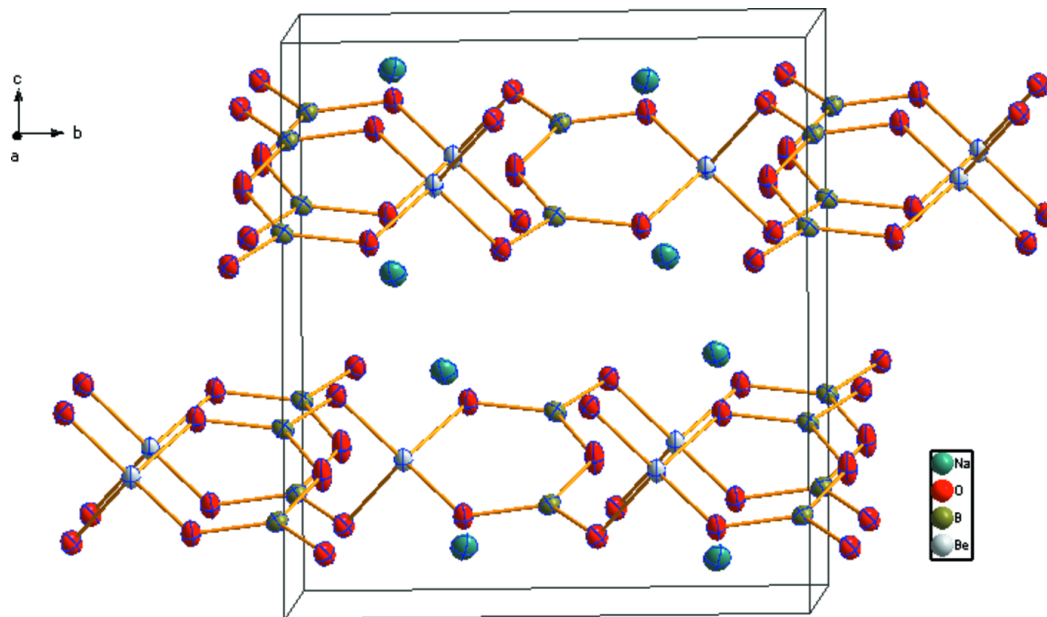


Fig. 2

