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# Synthesis and *ab initio* X-ray powder diffraction structure of the new alkali and alkali earth metal borate NaCa($BO_3$)

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A sodium calcium borate, $NaCaBO_3$, has been synthesized by the solid-state reaction method and the structure solved from X-ray powder diffraction data. The compound crystallizes in space group *Pmmn* and has a desired structure type containing isolated planar $BO_3^{3-}$ anions. Mixed occupancy is found to exist in the Ca site, with partial replacement by Na. One Ca/Na mixed atom and one Na atom are at sites with *mm*2 symmetry, and a second Ca/Na mixed atom, an Na atom, two B and two O atoms are on mirror planes.

## Comment

Borate crystals have attracted much attention due to their outstanding linear and non-linear optical properties. A variety of BO atomic groups are considered to be a dominant factor for the physical properties, in particular the optical properties, of borates. Among the various anionic groups, the planar $BO_3^{3-}$ group has attracted our attention, because low absorption and anisotropic polarizability indicate that some borates are likely to be good candidates for future deep-UV non-linear optical and birefringent materials. The title compound was first mentioned by Stoch & Waclawska (1990), but the structure has not been established to date. In the present study, the structure is determined and refined from powder diffraction data, as shown in Fig. 1.

The fundamental building units are the isolated $BO_3^{3-}$ anionic groups distributed parallel to four directions, *viz*. [301], [$\bar{3}$01], [032] and [0$\bar{3}$2], as shown in Figs. 2 and 3. The B—O distances vary from 1.319 (8) to 1.483 (15) Å, with an average value of 1.372 Å, and the O—B—O angle range from 115.82 (8) to 128.31 (7)°, which are rather common in borates.

Both the $Ca^{2+}$ and $Na^+$ cations in $NaCaBO_3$ appear in two crystallographically different environments, as shown in Fig. 4. Mixed occupancy is found to exist in the Ca sites, with partial replacement by 20% Na (denoted *M* in the following text, *i.e.* *M* is 80% Ca and 20% Na). The *M*1 atoms (in the 8*g* position) are coordinated to seven O atoms, forming seven-top decahedra. The *M*2 atoms (in the 2*b* position) are six-coordinated to O atoms, forming $M2O_6$ octahedra. Each $M2O_6$ octahedron shares four edges with four adjacent $M1O_7$ polyhedra, forming an $M_5O_{26}$ repeat unit, which can be seen clearly in Fig. 4. The other two special Wyckoff positions (2*a* and 4*f*) are occupied by Na atoms. The Na3 atoms (in the 2*a* position) show a rather peculiar coordination, with four short distances [2.437 (6) Å] on one side and four very long distances [2.982 (6) Å] on the opposite side directed along the orthorhombic *c* axis. A similar phenomenon is found in some other borates, such as $Na_3Ln(BO_3)_2$ (Ln is La or Nd; 2.301–2.960 Å; Mascetti *et al.*, 1981) and $Na_2B_8O_{13}$ (2.259–2.926 Å; Hyman *et al.*, 1967). It is believed to be the oxygen environment around the Na3 atoms which allows a rather large vibrational movement of this atom along one direction.

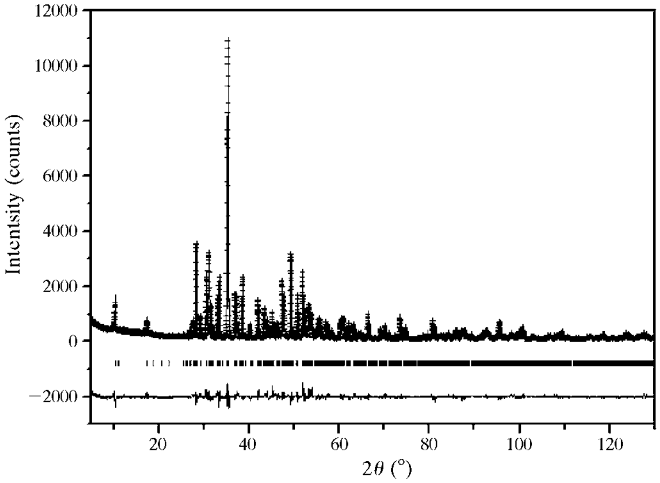

**Figure 1**
The final Rietveld refinement plot for $NaCaBO_3$. Small crosses (+) correspond to experimental values and the continuous line to the calculated pattern. Vertical bars indicate the positions of Bragg peaks. The lower trace depicts the difference between the experimental and calculated intensity values.

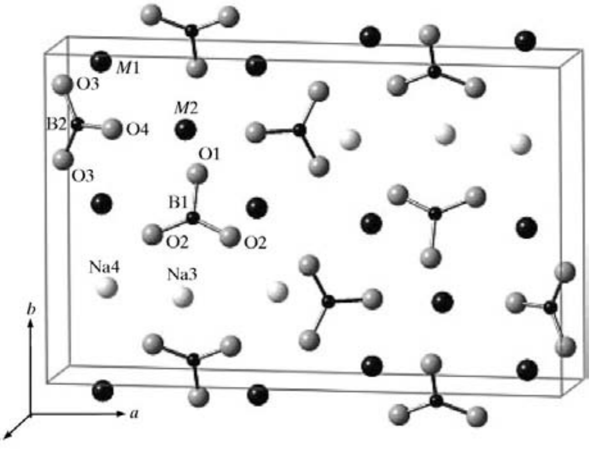

**Figure 2**
The structure of $NaCaBO_3$ viewed along [001]. Large black spheres denote *M* atoms (*M* is 80% Ca and 20% Na), small black spheres B atoms, grey spheres O atoms and white spheres Na atoms.

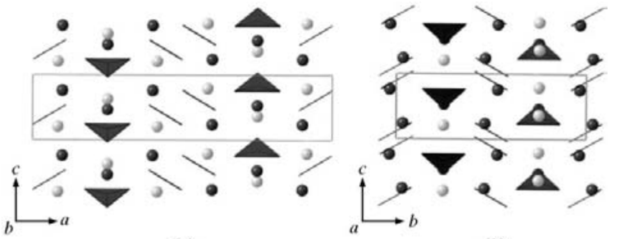

**Figure 3**
The projection of $NaCaBO_3$ viewed along (*a*) [010] and (*b*) [100]. B and O atoms have been omitted for clarity. Black triangles denote $BO_3$ and short black lines the side faces. Black spheres denote *M* atoms (*M* is 80% Ca and 20% Na) and white spheres Na atoms.

The Na and eight-coordinated O atoms form a cuboid, sharing two edges with the adjacent two $Na4O_6$ (in the 4*f* position, six-coordinated) trigonal prisms, forming $Na_3O_{16}$ repeat units. The $M_5O_{26}$ and $Na_3O_{16}$ groups are distributed alternately along the [100] and [010] directions. The $BO_3^{3-}$ groups are located between the two kinds of repeat units, sharing one edge with $Na_3O_{16}$ and two edges with $M_5O_{26}$ groups, forming infinite three-dimensional networks (Fig. 5).

Some known compounds, *viz*. $LiMBO_3$ (*M* is Mg, Ca, Sr or Ba; Norrestam, 1989; Wu *et al.*, 2004; Cheng *et al.*, 2001; Schlaeger & Hoppe, 1993), have the same formula type as the title compound and contain isolated planar $BO_3$ groups. However, their structures are all different from this new synthesized ternary borate. The fundamental building units, *viz*. $BO_3^{3-}$ groups, are distributed along two different directions in the four lithium borates. They are almost parallel to each other in $LiMgBO_3$ and are perpendicular to each other in $LiCaBO_3$ Moreover, the cations of $NaCaBO_3$ have more complex coordination than the other four compounds, and mixed occupancy is found in the Ca sites. The Mg atoms are five-coordinated by O atoms to form roughly trigonal–bipyramidal coordination polyhedra. The Ca atoms are coordinated by seven O atoms, forming monocapped distorted trigonal prisms, and share edges with each other, which is similar to the coordination of Sr atoms in $LiSrBO_3$. The Ba atoms are nine-coordinated, forming a monocapped distorted square antiprism. The Li atoms in the four compounds are all five-coordinated, forming different distorted trigonal bipyramids. No mixed occupancy is found in the four lithium borates. The similar radii of the $Na^+$ and $Ca^{2+}$ cations, and the large difference between the radii of Li and other alkali earth metal cations, might be one of the reasons why mixed occupancy is only found in $NaCaBO_3$.

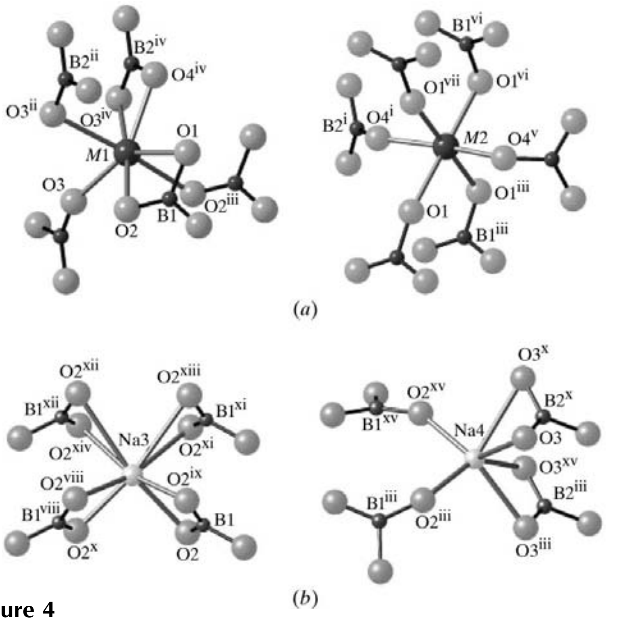

**Figure 4**
The coordination surroundings of (*a*) *M* atoms (*M* is 80% Ca and 20% Na) and (*b*) Na atoms with O atoms. Large black spheres denote *M* atoms, small black spheres B atoms, grey spheres O atoms and white spheres Na atoms. [Symmetry codes: (i) $1-x, y-\frac{1}{2}, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $x, y, 1+z$; (iv) $1-x, 1-y, 1-z$; (v) $\frac{1}{2}+x, 1-y, 1-z$; (vi) $\frac{3}{2}-x, \frac{1}{2}-y, 1+z$; (vii) $\frac{3}{2}-x, \frac{1}{2}-y, z$; (viii) $\frac{3}{2}-x, \frac{3}{2}-y, z$; (ix) $\frac{3}{2}-x, y, z$; (x) $x, \frac{3}{2}-y, z$; (xi) $x, y, z-1$; (xii) $\frac{3}{2}-x, \frac{3}{2}-y, z-1$; (xiii) $\frac{3}{2}-x, y, z-1$; (xiv) $x, \frac{3}{2}-y, z-1$; (xv) $x, \frac{3}{2}-y, 1+z$.]

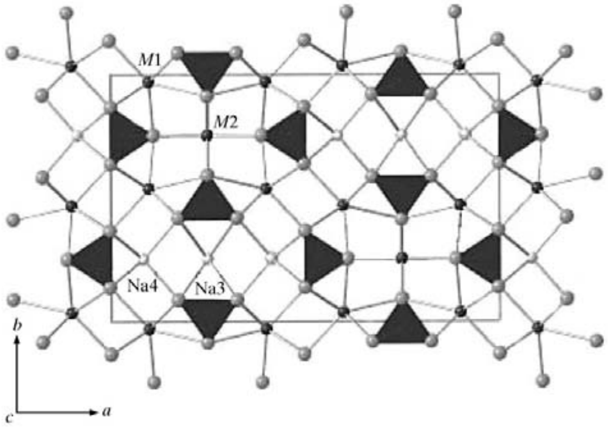

**Figure 5**
The network of $NaCaBO_3$ projected along [001]. Black triangles denote $BO_3$, black spheres *M* atoms (*M* is 80% Ca and 20% Na), grey spheres O atoms and white spheres Na atoms.

## Experimental

Analytically pure $NaCO_3$, $CaCO_3$ and $H_3BO_3$ were mixed in a 1:1:1 ratio, thoroughly ground and then fired at 923 K to decompose the carbonate and eliminate water. The sintering temperature was then raised from 973 to 1073 K in steps of 50 K, each temperature being held for 24 h with intermediate grindings. No further changes were found from the diffraction patterns during the course of the reaction. The title compound was obtained as a white powder.

*Crystal data*

$NaCa(BO_3)$
$M_r = 487.52$
Orthorhombic, *Pmmn*
$a = 16.0933$ (2) Å
$b = 10.2100$ (1) Å
$c = 3.49811$ (4) Å
$V = 574.78$ (2) Å$^3$
$Z = 2$

$D_x = 2.817$ Mg m$^{-3}$
Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation
$T = 295$ K
Specimen shape: flat sheet
15 × 35 × 1 mm
Specimen prepared at 1073 K
Particle morphology: plate-like, white

*Data collection*

Rigaku RINT2400 diffractometer
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode

$T = 295$ K
$2\theta_{min} = 5$, $2\theta_{max} = 135°$
Increment in $2\theta = 0.02°$

Acta Cryst. (2005). C61, i32–i34 L. Wu et al. • NaCa(BO3) i33

*Refinement*

Refinement on $I_{\mathrm{net}}$
$R_p = 0.089$
$R_{\mathrm{wp}} = 0.119$
$R_{\mathrm{exp}} = 0.058$
$S = 2.06$
$2\theta_{\mathrm{min}} = 5$, $2\theta_{\mathrm{max}} = 135°$
Increment in $2\theta = 0.02°$
Wavelength of incident radiation:
1.540562 and 1.544390 Å
Excluded region(s): none

Profile function: pseudo-Voigt
1170 reflections
51 parameters
$w = 1/Y_i$
$(\Delta/\sigma)_{\mathrm{max}} = 0.01$
Preferred orientation correction:
$I_{\mathrm{corr}} = I_{\mathrm{obs}}[G_2 + (1 - G_2) - \exp(G_1 a^2)]$, axis (001) (Toraya, 1986)

**Table 1**
Selected geometric parameters (Å, °).

*M* is 80% Ca and 20% Na.

| | | | |
|---|---|---|---|
| *M*1—O3 | 2.348 (5) | Na3—O2 | 2.982 (6) |
| *M*1—O4 | 2.365 (3) | Na3—O2$^{\mathrm{xi}}$ | 2.982 (6) |
| *M*1—O2 | 2.445 (5) | Na3—O2$^{\mathrm{xii}}$ | 2.982 (6) |
| *M*1—O3$^{\mathrm{i}}$ | 2.501 (6) | Na3—O2$^{\mathrm{xiii}}$ | 2.982 (6) |
| *M*1—O2$^{\mathrm{ii}}$ | 2.506 (5) | Na3—B1$^{\mathrm{viii}}$ | 2.702 (13) |
| *M*1—O1 | 2.599 (3) | Na3—B1$^{\mathrm{ii}}$ | 2.702 (13) |
| *M*1—O3$^{\mathrm{iii}}$ | 2.631 (6) | Na3—B1 | 2.895 (13) |
| *M*1—B2$^{\mathrm{iv}}$ | 2.903 (8) | Na3—B1$^{\mathrm{xii}}$ | 2.895 (13) |
| *M*1—B1 | 2.913 (7) | Na4—O2$^{\mathrm{v}}$ | 2.248 (5) |
| *M*1—B2$^{\mathrm{v}}$ | 3.142 (8) | Na4—O2$^{\mathrm{i}}$ | 2.248 (5) |
| *M*2—O4 | 2.241 (7) | Na4—O3$^{\mathrm{v}}$ | 2.374 (6) |
| *M*2—O4$^{\mathrm{vi}}$ | 2.241 (7) | Na4—O3$^{\mathrm{i}}$ | 2.374 (6) |
| *M*2—O1$^{\mathrm{ii}}$ | 2.385 (8) | Na4—O3$^{\mathrm{iii}}$ | 2.657 (7) |
| *M*2—O1$^{\mathrm{vii}}$ | 2.385 (8) | Na4—O3$^{\mathrm{iv}}$ | 2.657 (7) |
| *M*2—O1$^{\mathrm{vi}}$ | 2.392 (8) | Na4—B2$^{\mathrm{iv}}$ | 2.476 (12) |
| *M*2—O1 | 2.392 (8) | Na4—B2$^{\mathrm{v}}$ | 2.611 (12) |
| *M*2—B1$^{\mathrm{ii}}$ | 3.098 (12) | B1—O1 | 1.483 (15) |
| *M*2—B1$^{\mathrm{vii}}$ | 3.098 (12) | B1—O2 | 1.319 (8) |
| Na3—O2$^{\mathrm{viii}}$ | 2.437 (6) | B1—O2$^{\mathrm{xiii}}$ | 1.319 (8) |
| Na3—O2$^{\mathrm{ix}}$ | 2.437 (6) | B2—O3 | 1.321 (7) |
| Na3—O2$^{\mathrm{ii}}$ | 2.437 (6) | B2—O3$^{\mathrm{xi}}$ | 1.321 (7) |
| Na3—O2$^{\mathrm{x}}$ | 2.437 (6) | B2—O4$^{\mathrm{xiv}}$ | 1.470 (14) |
| | | | |
| O2—B1—O2$^{\mathrm{xiii}}$ | 127.79 (8) | O3$^{\mathrm{xi}}$—B2—O3 | 128.32 (7) |
| O2—B1—O1 | 116.09 (8) | O3$^{\mathrm{xi}}$—B2—O4$^{\mathrm{xiv}}$ | 115.82 (9) |
| O2$^{\mathrm{xiii}}$—B1—O1 | 116.09 (8) | O3—B2—O4$^{\mathrm{xiv}}$ | 115.82 (9) |

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

The powder pattern was indexed based on an orthorhombic cell. Systematic extinctions are consistent with space group *Pmmn*. The *FULLPROF* program (Rodriguez-Carvajal, 2003) was applied to the pattern and a total of 397 independent $|F_{\mathrm{obs}}|$ were extracted. A satisfactory preliminary structure was obtained by applying direct methods (*SHELXL97*; Sheldrick, 1997) to these extracted $|F_{\mathrm{obs}}|$. The $BO_3^{3-}$ group and $Ca^{2+}$ and $Na^{+}$ cations were discerned according to the interatomic distances and angles in the electron-density map. The structure was refined by the Reitveld method.

Data collection: *RINT2400* (Rigaku, 1993); cell refinement: *HIGHSCORE* (Philips, 2002); data reduction: *HIGHSCORE*; program(s) used to solve structure: *SHEXLS97* (Sheldrick, 1997); program(s) used to refine structure: *FULLPROF* (Rodriguez-Carvajal, 2003); molecular graphics: *BALLS & STICKS* (Kang & Ozawa, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1043). Services for accessing these data are described at the back of the journal.

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i34 L. Wu *et al.* • NaCa($BO_3$) *Acta Cryst.* (2005). C**61**, i32–i34