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The new pentaborate $Na_3SrB_5O_{10}$

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Sodium strontium pentaborate, $Na_3SrB_5O_{10}$, maintains the same, previously unobserved, structure type at 200, 250 and 293 K. The fundamental building units are anionic $[B_5O_{10}]^{5-}$ groups distorted from *mm*2 point symmetry. The Sr atoms are eightfold coordinated by O atoms, forming trigonal dodecahedra. The Na atoms appear in three crystallographically different environments. The present single-crystal results correct a previous report in which a monoclinic cell was deduced for this compound on the basis of powder diffraction data. The structure of the title compound is discussed in the crystalochemical context of other borates with the same formula type. Although the unit cell of the present compound is similar to that determined in a previous study of the analogous Ca-containing compound, this study demonstrates that the structures of the two are different. These novel alkali–alkaline earth borates are considered as potential host materials for optical applications (fluorescence materials or phosphors).

Comment

Inorganic borates have long been a focus of research due to their variety of structure types, transparency over a wide range of wavelengths, high laser-damage tolerance and high optical quality. Studies of alkali metal and alkaline earth metal borates have produced a large family of compounds with outstanding physical properties (Becker, 1998; Chen *et al.*, 1999), such as β-BaB_2O_4 (Chen *et al.*, 1985), LiB_3O_5 (Chen *et al.*, 1989), $Sr_2Be_2B_2O_7$ (Chen *et al.*, 1995) and $K_2Al_2B_2O_7$ (Hu *et al.*, 1999). Recently, photoluminescence has also been observed in many rare earth ion-doped alkaline earth metal borates (Pei & Su, 1993; Schaffers & Keszler, 1994; Diaz & Keszler, 1996, 1997). Some have been developed into useful phosphors, such as UV-emitting Eu^{2+}-doped SrB_4O_7 in lamps for medical applications and skin tanning (Pei & Su, 1993). Because it has a similar radius and identical valence to Sr^{2+} and Ba^{2+}, it is easy to substitute Eu^{2+} for Sr^{2+} and Ba^{2+} in crystals, giving photoluminescent doped systems. These properties depend on the crystal structures of the borates, which have a variety of $[B_nO_m]$ polyhedral groups. The richness of their crystal chemistry and optical properties led us to explore more borates in the system M_2O–$M'O$–B_2O_3 (M is an alkali metal and M' is an alkaline earth metal) to search for new functional materials. Four ternary compounds, $NaSrBO_3$ (Wu *et al.*, 2006), $NaSr_4(BO_3)_3$ (Wu *et al.*, 2005), $NaSrB_5O_9$ (Wu, Zhang, Chen *et al.*, 2007) and the title compound, $Na_3SrB_5O_{10}$, were found while investigating subsolidus phase relations in the system Na_2O–SrO–B_2O_3. The space group of $Na_3SrB_5O_{10}$ was at first thought to be *C*2 based on the indexing of a powder pattern (Wu, Zhang, Chen *et al.*, 2007). In the present study, we have employed single-crystal X-ray diffraction at various temperatures to determine and refine the structure of the title compound.

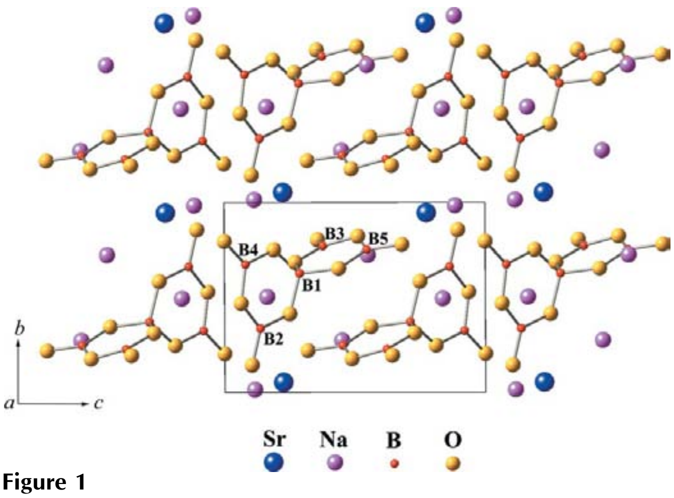

Figure 1
Projection of the structure of $Na_3SrB_5O_{10}$, viewed along [100].

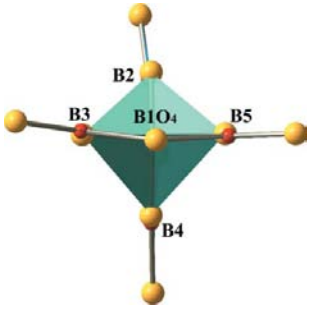

Figure 2
The anionic $[B_5O_{10}]^{5-}$ group of the title compound.

The single-crystal study at 200 K showed that crystalline $Na_3SrB_5O_{10}$ is in fact triclinic. As illustrated in Fig. 1, the fundamental building unit of $Na_3SrB_5O_{10}$ is the $[B_5O_{10}]^{5-}$ group, which is composed of four $[BO_3]$ triangles (Δ) (labelled B2, B3, B4 and B5) and one $[BO_4]$ tetrahedron (T) (labelled B1). In the $[B_5O_{10}]$ group, one T(B1) in the middle is connected to Δ(B2)+Δ(B4) and Δ(B3)+Δ(B5) on two sides, forming two $[B_3O_3]$ six-membered rings approximately perpendicular to each other. A constraint to planarity for the six-membered rings was tried during structure refinement but led to a significant increase of the *R* value, which means that the distortion from local *mm*2 point symmetry for the ideal $[B_5O_{10}]$ group is real. The four terminal O atoms lie near the

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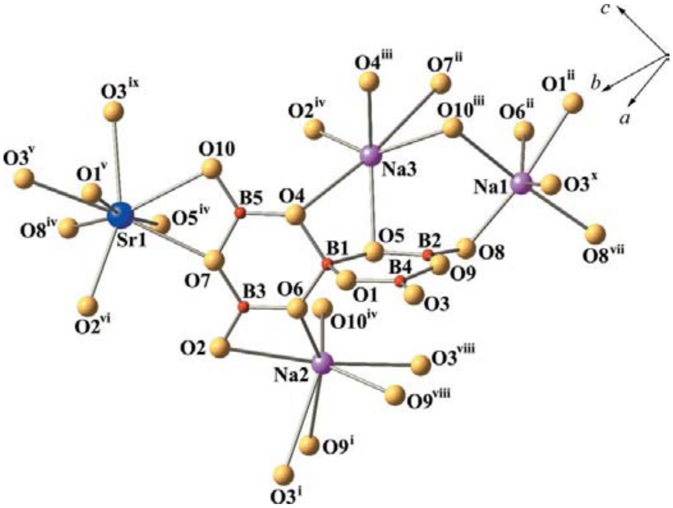

Figure 3
A view of the $[B_5O_{10}]^{5-}$ group and the adjacent Na and Sr coordination. [Symmetry codes: (i) $x + 1, y, z$; (ii) $x, y - 1, z$; (iii) $-x, 1 - y, 1 - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $-x, 2 - y, 1 - z$; (vi) $1 - x, 2 - y, 1 - z$; (vii) $1 - x, -y, -z$; (viii) $1 - x, 1 - y, -z$; (ix) $x, y, z + 1$; (x) $-x, 1 - y, -z$.]

planes of their respective six-membered rings, but with small deviations which lead to a dihedral angle of 9.43 (14)° between $\Delta(B2)$ and $\Delta(B4)$, and of 11.72 (13)° between $\Delta(B3)$ and $\Delta(B5)$ (Fig. 2). The $[B_5O_{10}]^{5-}$ groups are not directly linked to each other but connected *via* SrO_8 and NaO_n (n = 6 or 7) polyhedra (Fig. 3), forming a complex three-dimensional array.

The Sr atoms are eightfold coordinated by O atoms, forming polyhedra with 12 faces. These form edge-sharing pairs, as shown in Fig. 4. Each SrO_8 polyhedron connects to five $[B_5O_{10}]^{5-}$ groups through three edges and two vertices.

The Na atoms appear in three crystallographically different environments (Fig. 5). Atom Na1 is sixfold coordinated by O atoms at distances of 2.246 (2)–2.7220 (18) Å with a bond-valence sum (Brown & Altermatt, 1985) of 1.181, forming a distorted octahedron that shares one edge and four vertices with five adjacent $[B_5O_{10}]^{5-}$ groups. Two of these distorted octahedra share one edge with each other. Atom Na2 has close contacts from six O atoms at distances in the range 2.3210 (16)–2.705 (2) Å, and is weakly bonded to one additional O-atom neighbour at a distance of 3.024 (2) Å. A bond-valence calculation gives sums of 0.968 and 1.005 for atom Na2 when six and seven bonds are taken into account, respectively, which means the long Na—O distance also participates in the coordination scheme, forming a distorted polyhedron with nine faces. Two of the $[Na2O_7]$ polyhedra share a common face, and each shares three edges and one vertex with four neighbouring $[B_5O_{10}]^{5-}$ groups. Atom Na3 is coordinated by five O atoms at distances in the range 2.248 (2)–2.705 (2) Å and by one further O atom at a distance of 3.151 (2) Å. The five shortest bonds give a bond-valence sum of 0.917 for atom Na3, but this increases to 0.943 when the sixth bond is taken into account, indicating that the distorted octahedron is the coordination polyhedron. Two of the $[Na3O_6]$ polyhedra share a common edge, and each shares two edges and two vertices with four $[B_5O_{10}]^{5-}$ groups.

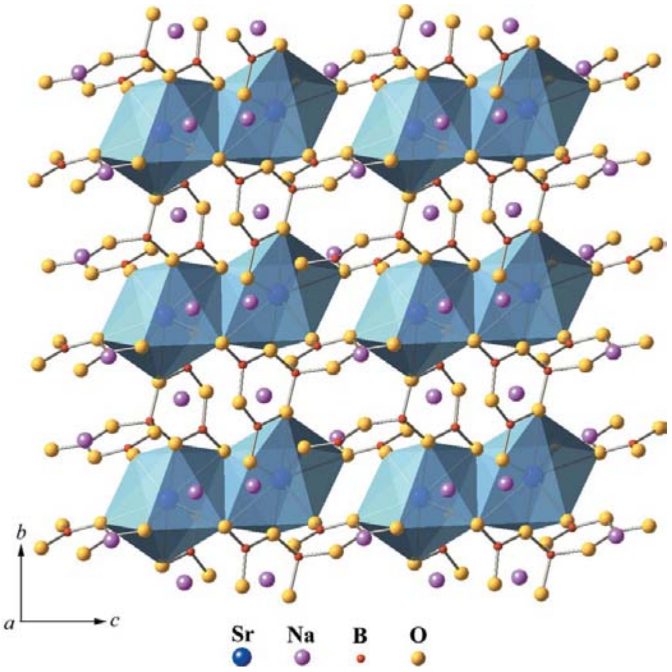

Figure 4
The SrO_8 coordination polyhedra.

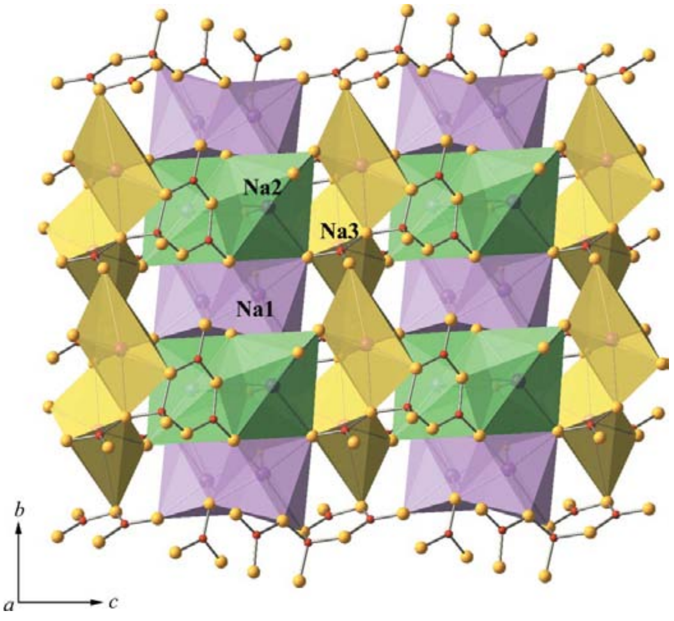

Figure 5
The $Na1O_6$, $Na2O_7$ and $Na3O_6$ coordination polyhedra.

To date, four pentaborates have been described, namely $Na_3MgB_5O_{10}$ (Chen, Li, Zuo *et al.*, 2007), $Na_3CaB_5O_{10}$ (Fayos *et al.*, 1985; Chen, Li, Zuo *et al.*, 2007), $Na_3SrB_5O_{10}$ (this work) and $Na_3ZnB_5O_{10}$ (Chen, Li, Chang *et al.*, 2007). The structure of $Na_3CaB_5O_{10}$ was first reported by Fayos *et al.* (1985). A recent study found that it had a superstructure (Chen, Li, Zuo *et al.*, 2007) with a cell volume twice that reported previously. The present Sr-containing structure has a cell similar to that of the previously reported Ca-containing structure.

$Na_3MgB_5O_{10}$ crystallizes in the orthorhombic space group *Pbca*, and $Na_3ZnB_5O_{10}$ crystallizes in the monoclinic space group $P2_1/n$. The fundamental building unit of the calcium and strontium pentaborates is the isolated polyanionic $[B_5O_{10}]^{5-}$ group, but none of the six-membered rings with terminal O atoms is rigorously planar; they are distorted and only approximately perpendicular to each other. The dihedral angles formed by the six-membered rings are 88.41 (6) and 88.02 (7)/89.63 (7)° for $Na_3SrB_5O_{10}$ and $Na_3CaB_5O_{10}$, respectively. In contrast with the Sr- and Ca-containing borates, in which the $[B_5O_{10}]^{5-}$ groups exist as discrete residues, the $[B_5O_{10}]^{5-}$ groups in the Mg- and Zn-containing compounds are bridged by $[MgO_4]$ or $[ZnO_4]$, and form infinite two-dimensional $[MgB_5O_{10}]^{3-}$ and $[ZnB_5O_{10}]^{3-}$ layers, respectively. Another difference between the Mg-, Ca-, Sr- and Zn-containing compounds relates to the coordination polyhedra of the divalent cations. Both Mg and Zn atoms are four-coordinate. The $[SrO_8]$ coordination polyhedron connects five adjacent $[B_5O_{10}]$ groups by sharing three edges and two vertices with $[BO_3]$, while the $[CaO_6]$ octahedron shares one edge with $[BO_4]$ and four vertices with $[BO_3]$ to bridge five $[B_5O_{10}]$ groups. The coordination environment of Ca in $Na_3CaB_5O_{10}$ is similar to that of atom Na1 in the title compound, as the sites analogous to those occupied by Ca in $Na_3CaB_5O_{10}$ are occupied by atom Na1 in $Na_3SrB_5O_{10}$. Because of the different valences of the alkali metal (Na1) and alkaline earth metal (Ca) cations, the M—O distances are different, in such a way as to reduce the bond valence of the position occupied by Na^+ and improve the bond valence for Sr^{2+}, which is accompanied by a small change in the orientation of the $[B_5O_{10}]$ groups. Some changes are also observed in the environments of the O atoms. A similar situation has been found in $NaMgBO_3$ (Wu, Zhang, Kong *et al.*, 2007) and $NaSrBO_3$, in which the alkali metal and alkaline earth metal atoms exchange positions. As for the Na atoms, they appear in three crystallographically distinct environments in every one of the four borates. In the magnesium pentaborate, all of them are seven-coordinate, but with different coordination polyhedra. In the calcium pentaborate, they are seven-, six- and five-coordinate (Chen, Li, Zuo *et al.*, 2007); in the strontium pentaborate, they are six-, seven- and six-coordinate and, as mentioned above, give the correct bond valences, even with two unusually long distances to the surrounding O atoms; and in the Zn pentaborate, they are eight-, seven- and six-coordinate. It is likely that the different combinations of Mg—O, Ca—O, Sr—O, Zn—O and Na—O bonds cause the six-membered rings to show different degrees of distortion in the different structures.

These borates form stable doped systems, without a reducing atmosphere, when the divalent cations are replaced by rare earth ions (Pei & Su, 1993) such as Eu^{2+}. It is known that Eu^{2+}-doped borates will show various emissions when the dopant is placed in different O-atom environments (Diaz & Keszler, 1997). Considering the different environments of the divalent cations and the O atoms in the four pentaborates, it is reasonable to expect photoluminescence with different emissions for these systems when doped with Eu^{2+}.

Experimental

Polycrystalline samples were prepared by solid-state reactions conducted by sintering at high temperature. Mixtures of analytical purity Na_2CO_3, $SrCO_3$ and H_3BO_3 were heated to 873 K to decompose the carbonate and eliminate water, and then elevated to the sintering temperature of 1073 K for 72 h. Between sintering steps, the samples were cooled and ground. The pure powder sample was compacted, then placed in a Pt crucible and fired at 1123 K for 48 h. It was then cooled to 553 K and taken out of the furnace. Small transparent single crystals could be selected from the compacted sample.

Crystal data

$Na_3SrB_5O_{10}$
$M_r = 370.64$
Triclinic, $P\overline{1}$
$a = 7.277$ (2) Å
$b = 7.601$ (2) Å
$c = 9.728$ (2) Å
$\alpha = 81.062$ (16)°
$\beta = 70.538$ (15)°
$\gamma = 61.636$ (15)°
$V = 446.43$ (19) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 6.23$ mm^{-1}
$T = 200$ (1) K
0.1 × 0.1 × 0.02 mm

Data collection

Stoe IPDSII diffractometer
Absorption correction: numerical *via* equivalents (*X-SHAPE* and *X-RED*; Stoe & Cie, 1996)
$T_{min} = 0.335$, $T_{max} = 0.511$
11007 measured reflections
2049 independent reflections
1595 reflections with $I > 2\sigma(I)$
$R_{int} = 0.136$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.089$
$S = 1.08$
2049 reflections
172 parameters
4 restraints
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}

The unit cell was first determined from a powder pattern using *DICVOL91* (Boultif & Louër, 1991) by the successive dichotomy method with Si as the internal standard. This gave a monoclinic unit cell with $a = 7.290$ (1) Å, $b = 13.442$ (2) Å, $c = 9.792$ (1) Å and $\beta = 109.60$ (1)° [ICDD (2005) PDF 56-0146]. Based on the systematic absences, the possible space groups were deduced to be *C*2, *Cm* or *C*2/*m* (Wu, Zhang, Chen *et al.*, 2007). The present single-crystal study at 200 K showed that the actual unit cell is triclinic, with cell constants similar to those of the reduced cell of the previously reported structure of $Na_3CaB_5O_{10}$ (Fayos *et al.*, 1985). The structure was solved by direct methods and refined by full-matrix least-squares techniques, with anisotropic displacement parameters for all atoms. Calculated radial distribution functions (*PLATON*; Spek, 2003) indicated that the title compound and the analogous Ca compound are not isomorphous. The structure was also investigated at different temperatures (250 and 293 K; data available in the archived CIF), with very similar results and no indication of a possible phase transition in this temperature interval.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Balls&Sticks* (Version 1.42; Ozawa & Kang, 2004); software used to prepare material for publication: *WinGX* (Version 1.64; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3144). Services for accessing these data are described at the back of the journal.

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