

A new orthoborate, $\text{Sr}_3\text{Ga}_3(\text{BO}_3)_4\text{-O}(\text{OH})$

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The crystal structure of tristrontium trigallium tetraborate oxide hydroxide has been determined by X-ray diffraction using a crystal grown by hydrothermal crystallization of a strontium gallo-borate glass. It represents a new orthoborate structure type built of complex layers formed by BO_3 triangles sharing corners with Ga_2O_7 tetrahedral dimers and GaO_4OH square pyramids. The Sr atoms occupy both inter- and intralayer sites.

Comment

In spite of the ongoing interest in borates as optical materials, a very limited number of ternary borates have been characterized in detail. For instance, the crystal structures of the alumino-borates $\text{MAl}_2\text{B}_2\text{O}_7$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) have only been determined recently (Chang & Keszler, 1998; Lucas *et al.*, 2000; Ye *et al.*, 1998), even though some of the compounds have been known for decades. This has prompted us to undertake the investigation of the analogous gallo-borate systems, which, according to the crystallographic databases,

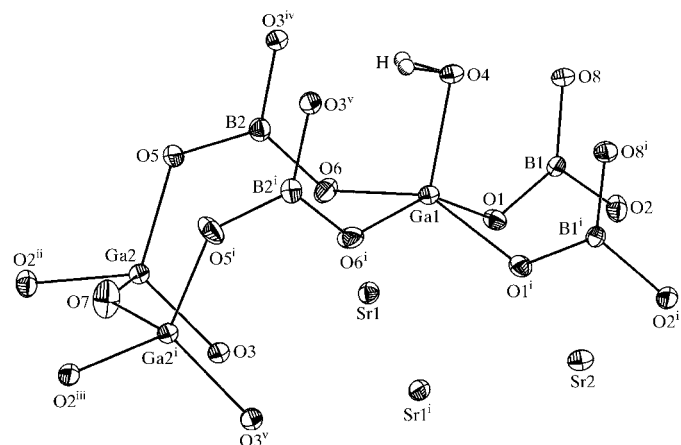


Figure 1

Part of the $\text{Sr}_3\text{Ga}_3\text{B}_4\text{O}_{13}\text{OH}$ structure viewed near the $[010]$ direction. The displacement ellipsoids are drawn at the 50% probability level. The H atom of the O4-H hydroxyl group is disordered over two equivalent positions across the (010) mirror plane. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $x, y, z - 1$; (iii) $x, \frac{1}{2} - y, z - 1$; (iv) $x - 1, y, z$; (v) $x - 1, \frac{1}{2} - y, z$.]

remain completely unexplored. Initial work has led to the characterization of two new gallo-borates, $\text{MGA}_2\text{B}_2\text{O}_7$ ($M = \text{Sr}, \text{Ba}$; Park & Barbier, 2000*a*), and two new borate fluorides, BaMBO_3F_2 ($M = \text{Al}, \text{Ga}$; Park & Barbier, 2000*b*). The present compound, $\text{Sr}_3\text{Ga}_3\text{B}_4\text{O}_{13}\text{OH}$, represents yet another new gallo-borate which has been synthesized under hydrothermal conditions.

The crystal structure of $\text{Sr}_3\text{Ga}_3\text{B}_4\text{O}_{13}\text{OH}$, or $\text{Sr}_3\text{Ga}_3(\text{BO}_3)_4\text{O}(\text{OH})$, is depicted in Fig. 1 approximately along the $[100]$ direction of the monoclinic unit cell. The structure consists of a stacking of identical complex (010) layers formed by corner-sharing BO_3 triangles, GaO_4 tetrahedra (dimerized into Ga_2O_7 pyrogallate groups) and GaO_4OH square pyramids. The Sr atoms occupy inter- and intralayer sites in eight- and sevenfold coordination, respectively. $\text{Sr}_3\text{Ga}_3(\text{BO}_3)_4\text{-O}(\text{OH})$ represents a new orthoborate structure type (Heller, 1986; Grice *et al.*, 1999), in part as a result of the unusual square-pyramidal coordination of the Ga atoms. Bond-valence calculations (Brese & O'Keeffe, 1991) yield correct valence sums for all atoms (with a maximum deviation from the expected values of 0.13), with the exception of Sr2 which remains slightly underbonded ($\Sigma s = 1.71$ for sevenfold coordination including all bonds up to 3 \AA). There is, however, no indication of a strong anisotropy or of a displacement of the Sr2 atom from the (010) mirror plane. Bond-valence calculations also confirm that the O4 position (bonded to one Ga and two Sr atoms) corresponds to a hydroxyl group ($\Sigma s = 0.94$). The refined H-atom position yields an O4-H bond distance

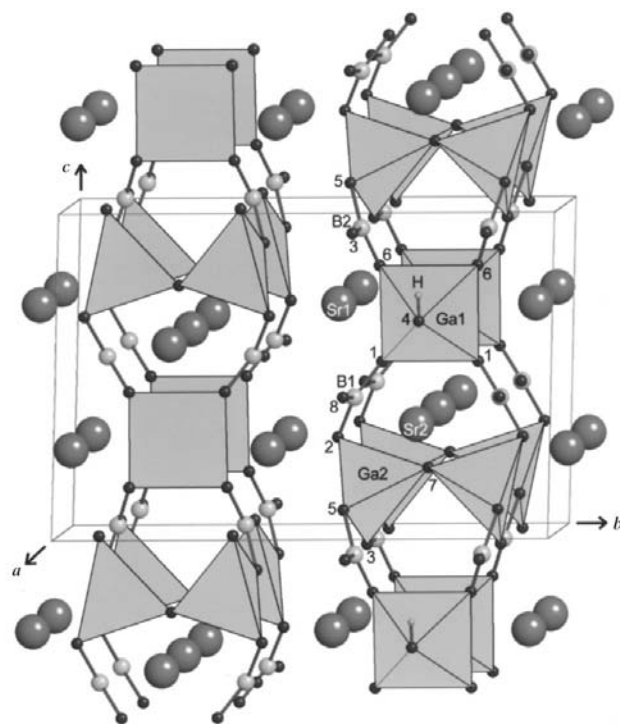


Figure 2

View of the $\text{Sr}_3\text{Ga}_3\text{B}_4\text{O}_{13}\text{OH}$ structure. The small numbers at the corners of the polyhedra refer to the O-atom positions. Only the average position of the H atom of the O4-H hydroxyl group has been drawn in the (010) mirror plane (see Fig. 1).

of 0.77 (8) Å. Finally, the bond-valence sum ($\Sigma s = 2.03$) around the dangling O8 atom of the BIO_3 borate group shows that O8 is a simple O atom (bonded to one B and three Sr atoms).

Experimental

Single crystals of $\text{Sr}_3\text{Ga}_3\text{B}_4\text{O}_{13}\text{OH}$ were recovered from hydrothermal crystallization experiments using a glass of composition $2\text{SrO}\cdot\text{Ga}_2\text{O}_3\cdot\text{B}_2\text{O}_3$. The glass was obtained by melting and cooling a mixture of SrCO_3 , Ga_2O_3 and $\text{B}(\text{OH})_3$ powders in a covered platinum crucible between 1523 and 1173 K. A number of hydrothermal experiments were carried out using 0.25 g of glass sealed with 9 ml of de-ionized water in a 25 ml teflon-lined Parr reactor which was then heated at temperatures between 500 and 550 K for several days. Different initial pH conditions were also used by adding small amounts of concentrated HNO_3 (pH = 2) or $\text{Sr}(\text{OH})_2$ (pH = 10) solutions. Regardless of the temperature and the initial pH, the reaction products always consisted of small (sub-millimeter size) $\text{Sr}_3\text{Ga}_3\text{B}_4\text{O}_{13}\text{OH}$ crystals in a strongly basic solution (final pH = 11–12). The chemical composition of the crystals was determined during the course of the structure determination. However, the presence of hydroxyl groups was also confirmed by laser Raman spectra recorded from several crystals through an optical microscope. The spectra showed a sharp well isolated band at 3521 cm^{-1} , which, by analogy with the Raman spectra of borate minerals (Kloprogge & Frost, 1999), can be associated with an OH stretching mode.

Crystal data

$\text{Sr}_3\text{Ga}_3(\text{BO}_3)_4\text{O}(\text{OH})$	$D_x = 4.198\text{ Mg m}^{-3}$
$M_r = 740.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 15160 reflections
$a = 4.9084(2)\text{ Å}$	$\theta = 2.33\text{--}36.37^\circ$
$b = 13.6795(7)\text{ Å}$	$\mu = 20.449\text{ mm}^{-1}$
$c = 9.0482(4)\text{ Å}$	$T = 299(2)\text{ K}$
$\beta = 105.4140(10)^\circ$	Prism, colourless
$V = 585.68(5)\text{ Å}^3$	$0.09 \times 0.08 \times 0.05\text{ mm}$
$Z = 2$	

Data collection

Siemens SMART 1K CCD area-detector and Siemens P4 diffractometer	2838 independent reflections
Area-detector scans	2232 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.161$, $T_{\text{max}} = 0.360$	$\theta_{\text{max}} = 36.37^\circ$
15160 measured reflections	$h = -8 \rightarrow 8$
	$k = -18 \rightarrow 22$
	$l = -15 \rightarrow 14$

Refinement

Refinement on F^2	Only positional coordinates of the H atom refined
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.119$	$(\Delta/\sigma)_{\text{max}} = 0.040$
2835 reflections	$\Delta\rho_{\text{max}} = 1.00\text{ e Å}^{-3}$
117 parameters	$\Delta\rho_{\text{min}} = -1.85\text{ e Å}^{-3}$

The coordinates of the H atom were determined from the position of maximum electron density (1.15 e Å^{-3}) in the Fourier maps. Initially, the H atom was located in the (010) mirror plane which,

Table 1
Selected bond lengths (Å).

Sr1—O8 ⁱ	2.522 (2)	Ga1—O6	1.944 (2)
Sr1—O2 ⁱⁱ	2.559 (2)	Ga1—O1	1.953 (2)
Sr1—O6	2.572 (3)	Ga2—O7	1.816 (2)
Sr1—O3	2.625 (2)	Ga2—O3	1.824 (2)
Sr1—O1	2.649 (2)	Ga2—O5	1.844 (3)
Sr1—O5 ⁱⁱⁱ	2.681 (2)	Ga2—O2 ^{vi}	1.856 (2)
Sr1—O4 ⁱ	2.8118 (10)	B1—O8	1.354 (4)
Sr2—O8 ⁱ	2.529 (2)	B1—O1	1.383 (4)
Sr2—O1	2.550 (2)	B1—O2	1.417 (4)
Sr2—O7 ^{iv}	2.741 (4)	B2—O6	1.353 (4)
Sr2—O4 ⁱ	2.868 (4)	B2—O3 ^{vii}	1.388 (4)
Sr2—O7 ^v	2.930 (5)	B2—O5	1.391 (4)
Ga1—O4	1.885 (4)		

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

however, led to a short O4—H bond distance of 0.72 Å. That distance increased to 0.77 (8) Å when the H atom was displaced from the mirror plane [$y = 0.235(7)$] and disordered over two equivalent positions. The H-atom coordinates were refined with a fixed U_{iso} parameter (0.02 Å^2).

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL93 (Sheldrick, 1993); molecular graphics: XTALDRAW (Bartelmehs & Downs, 1997); software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1297). Services for accessing these data are described at the back of the journal.

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