

Crystal Structures of New Gallo-Borates $MGa_2B_2O_7$, $M = Sr, Ba$

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Two new gallo-borates, $MGa_2B_2O_7$ ($M = Sr, Ba$), have been synthesized and structurally characterized. The structure of $SrGa_2B_2O_7$ ($Cmcm$, $a = 11.7260(7)$ Å, $b = 8.3745(4)$ Å, $c = 5.7062(3)$ Å, $Z = 4$) has been determined by single-crystal X-ray diffraction ($wR(F^2) = 0.089$ for 732 unique reflections). $BaGa_2B_2O_7$ ($Cmcm$, $a = 11.7434(6)$ Å, $b = 8.7076(4)$ Å, $c = 5.8038(3)$ Å, $Z = 4$) has been shown to be isostructural by *ab initio* structure determination and Rietveld refinement using powder X-ray data ($R_{wp} = 0.119$, $\chi^2 = 2.16$). The $MGa_2B_2O_7$ structure, formulated as $MGa_2(B_2O_5)O_2$, consists of a framework of corner-sharing tetrahedral (GaO_4) chains and pyroborate (B_2O_5) groups with the M atoms filling eight-coordinated framework cavities. It represents a new structure-type for anhydrous borates and, in particular, is structurally distinct from the $MA_2B_2O_7$ ($M = Ca, Sr, Ba$) alumino-borate analogs. © 2000

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Key Words: $SrGa_2B_2O_7$; $BaGa_2B_2O_7$; borates; pyroborates; gallo-borates; structure determination.

INTRODUCTION

Recent research on inorganic borates has focused on the synthesis, crystal growth, and characterization of compounds with potential applications as optical materials, for instance, materials for second harmonic generation or host materials for fluorescence. Besides the well-known binary borates, β - BaB_2O_4 and LiB_3O_5 , a number of ternary borates have recently been structurally characterized, including $Sr_2Be_2B_2O_7$ (1), $K_2Ga_2B_2O_7$ (2), $K_2Al_2B_2O_7$ (3), and $MA_2B_2O_7$ with $M = Ca$ (4), Sr (5), and Ba (6). Rather surprisingly, the detailed structure determinations of the alumino-borates only happened about 30 years after the initial studies of the $CaO-Al_2O_3-B_2O_3$ (7) and $BaO-Al_2O_3-B_2O_3$ (8) systems. Indeed, very few systematic studies of ternary borate systems have been carried out since then. For the purpose of comparison with the alumino-borates, we have undertaken the investigation the $MO-Ga_2O_3-B_2O_3$ ($M = Sr, Ba$) systems by means of solid-state reactions, crystal growth experiments, and hydrothermal reactions. Several new hydrated and anhydrous gallo-borates have been discovered so far, including the

$SrGa_2B_2O_7$ and $BaGa_2B_2O_7$ compounds described here. Interestingly, these compounds are structurally entirely distinct from their alumino-borate analogs.

EXPERIMENTAL

The $SrGa_2B_2O_7$ and $BaGa_2B_2O_7$ compounds were initially synthesized in microcrystalline form from stoichiometric mixtures of reagent-grade boric acid with Sr/Ba carbonates and high-purity gallium oxide. Pellets of 0.5 g each were heated up to 850°C for 2 to 3 days with several intermediate remixings. The progress of the reactions was followed by powder X-ray diffraction with a Guinier-Hägg camera (using $CuK\alpha_1$ radiation and Si as an internal standard). The C-centered orthorhombic unit-cell of the $MGa_2B_2O_7$ compounds was determined by the automatic indexing (9) of the Guinier-Hägg pattern for $BaGa_2B_2O_7$. The same powder pattern was then used for the *ab initio* structure determination (see below).

Single crystals of $SrGa_2B_2O_7$ were obtained during a preliminary Czochralski crystal growth experiment using a melt of composition $SrO-Ga_2O_3-B_2O_3$. Approximately 50 g of powder was contained in a platinum crucible and melted at 980°C in an induction furnace under normal atmosphere. Solidification was initiated on a tungsten wire pulled from the melt at a rate of 0.1 mm/h over a period of 3 days. Although most of the recovered sample was glassy, it contained a number of small platy crystals embedded in the glass. These crystals were identified as $SrGa_2B_2O_7$ by powder X-ray diffraction.

STRUCTURE DETERMINATIONS

The structure of $BaGa_2B_2O_7$ was determined *ab initio* using powder X-ray data recorded with a Guinier-Hägg camera and the EXPO software package (10, 11). The $Cmcm$ space group suggested by the indexing of the powder pattern proved to be the only one leading to a structure solution. The alternative noncentrosymmetric $Cmc2_1$ space group was subsequently rejected during the structure determination of $SrGa_2B_2O_7$ by single-crystal X-ray diffraction

TABLE 1
Details of the Structure Refinements

SrGa ₂ B ₂ O ₇		BaGa ₂ B ₂ O ₇	
Sample	Single crystal	Sample	Powder
Wavelength	MoK α	Wavelength	CuK α
Absorption coeff.	9.02 mm ⁻¹	2 θ Range	11.00–89.75°
2 θ Max	72.36°	Step size	0.04°
Index ranges	– 19 < h < 18 – 13 < k < 10 – 7 < l < 9	Excluded region ^a	1 4.10–15.30°
Unique reflections	732	R_{wp} ^b	0.119
Absorption corr.	SADABS	R_{exp}	0.081
Transmission min, max	0.0736, 0.1721	χ^2	2.16
R_{int}	0.080	R_{Bragg}	0.044
Refined parameters	39	Reflections	145
Goodness-of-fit	1.045	Refined parameters	30
$R [F > 4\sigma(F)]$	0.037		
wR(F ²)	0.089		
Difference map	–1.25, + 2.29 e Å ⁻³		

^aCorresponds to a weak (400 counts) unidentified impurity peak.

^bAgreement indices are defined as follows:

$R_{wp} = [\sum w_i(Y_{io} - Y_{id})^2 / \sum w_i Y_{io}^2]^{1/2}$; $R_{exp} = [(N - P) / \sum w_i Y_{io}^2]^{1/2}$, N = number of data points, P = number of parameters; $\chi^2 = (R_{wp}/R_{exp})^2$; $R_{Bragg} = \sum |I_{ko} - I_{kc}| / \sum I_{ko}$.

(see below). The *ab initio* structure solution for BaGa₂B₂O₇ yielded atomic positions for the Ba, Ga, and O1-4 atoms. The B position was then determined by calculating Fourier difference maps. Finally, the Rietveld refinement of the BaGa₂B₂O₇ structure was carried out with the FULLPROF software package (12), using powder X-ray data collected with a Nicolet-I2 diffractometer. The details of the refinement are listed in Table 1 and the plots of the observed and calculated profiles are shown in Fig. 1. The crystal data are given in Table 2, and the atomic coordinates and selected bond distances are listed in Tables 3a and 4, respectively. Although the Rietveld refinement of the BaGa₂B₂O₇ structure is of average quality (in particular, the quality of the powder X-ray data did not allow the refinement of the displacement B parameters), the resulting structural details are nevertheless in good agreement with the SrGa₂B₂O₇ structure determined by single-crystal X-ray diffraction. The Ba and Sr compounds are clearly isostructural.

The single-crystal X-ray data for SrGa₂B₂O₇ were collected with a Siemens P4 diffractometer equipped with a MoK α rotating-anode X-ray source and a SMART-1K area detector. The raw intensity data were processed with the SAINT software (13) and an empirical absorption

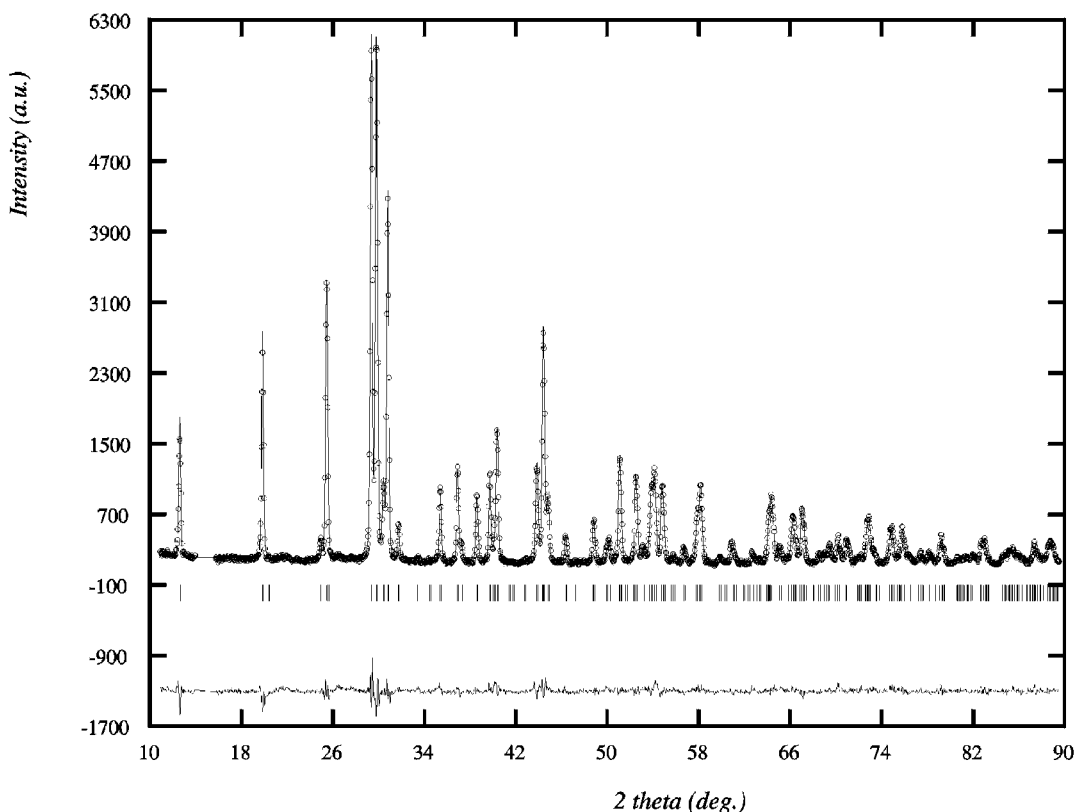


FIG. 1. Observed (circles) and calculated (full line) profiles for the Rietveld refinement of the BaGa₂B₂O₇ structure by powder X-ray diffraction. The difference between the observed and calculated profiles is plotted at the bottom. The vertical bars indicate the positions of Bragg reflections. A weak (400 counts maximum) impurity peak at $2\theta = 14.7^\circ$ has been excluded from the Rietveld refinement.

TABLE 2
Crystal Data for $MGa_2B_2O_7$

Compound	SrGa ₂ B ₂ O ₇	BaGa ₂ B ₂ O ₇
Space group	<i>Cmcm</i>	<i>Cmcm</i>
Unit cell (Å)		
<i>a</i>	11.7260(7)	11.7434(6)
<i>b</i>	8.3745(4)	8.7076(4)
<i>c</i>	5.7062(3)	5.8038(3)
Volume (Å ³)	560.35	593.48
<i>Z</i>	4	4
Calc. density (g cm ⁻³)	4.275	4.684

correction was applied using the SADABS program (14). The structure was then solved and refined anisotropically with the SHELXS (15) and SHELXL (16) softwares. The refinement details and the crystal data are listed in Tables 1 and 2, respectively. The final atomic coordinates and isotropic displacement parameters are given in Table 3b, and the anisotropic displacement parameters are given in Table 3c. Selected bond distances and their associated bond valences are listed in Table 4.

DESCRIPTION OF THE $MGa_2B_2O_7$ STRUCTURES
($M = \text{Sr, Ba}$)

The structure of SrGa₂B₂O₇ is depicted in Fig. 2. It consists of a framework of corner-sharing GaO₄ tetrahedra (forming [001] chains) and BO₃ triangles (forming B₂O₅ pyroborate groups), with eight-coordinated Sr atoms occupying the framework cavities. It represents a new structure type for anhydrous borates (17) and, in particular, it is structurally distinct from the alumino-borates MA₁B₂O₇ ($M = \text{Ca, Sr, Ba}$) (cf. next section). The $MGa_2B_2O_7$ structure shows some similarities with the MA₁O₇ and MGa_4O_7 ($M = \text{Ca, Sr}$) structures (18–21). The latter crystallize with monoclinic (*C2/c*) unit cells (e.g., $a = 13.46$, $b = 9.19$, $c = 5.69$ Å, $\beta = 105.8^\circ$ for SrGa₄O₇ (21)) which are similar to the orthorhombic (*Cmcm*) unit cells of the gallo-borates (cf. Table 2). Although the tetraaluminates and gallates are based on tetrahedral coordination only, they contain [001] tetrahedral chains and M^{2+} sites similar to those in the gallo-borates.

The centrosymmetric *Cmcm* space group of the $MGa_2B_2O_7$ structure constrains the B₂O₅ groups to be perfectly planar, with the B, O1, O2, and O3 atoms positioned on the mirror planes perpendicular to the *c* axis (cf. Table 3b and Fig. 2). However, the displacement of the bridging O1 atom is strongly anisotropic, with a large value of the U_{33} parameter (cf. Table 3c) suggesting local deviations from centrosymmetry. Attempts to refine the SrGa₂B₂O₇ structure in the noncentrosymmetric *Cmc2₁* space group led to poor convergence without any significant

TABLE 3a
Atomic Coordinates and Isotropic Displacement Parameters for BaGa₂B₂O₇

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²) ^a
Ba	0.5	0.3045(3)	0.25	0.3
Ga	0.2076(2)	0.0819(4)	0.25	0.3
B	0.3951(6)	0.8899(9)	0.25	0.5
O1	0.5	0.8214(15)	0.25	0.5
O2	0.1993(7)	0.2969(14)	0.25	0.5
O3	0.3709(8)	0.0439(9)	0.25	0.5
O4	0.1370(8)	0.0	0.0	0.5

^aThe *B* parameters were kept constant during the Rietveld refinement.

TABLE 3b
Atomic Coordinates and Isotropic Displacement Parameters for SrGa₂B₂O₇

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Sr	0.5	0.31565(6)	0.25	0.0131(2)
Ga	0.20901(5)	0.08470(5)	0.25	0.0107(2)
B	0.3909(5)	0.9027(6)	0.25	0.0128(8)
O1	0.5	0.8382(6)	0.25	0.0181(9)
O2	0.1992(3)	0.3041(4)	0.25	0.0154(6)
O3	0.3692(4)	0.0654(4)	0.25	0.0124(6)
O4	0.1303(3)	0.0	0.0	0.0124(5)

TABLE 3c
Anisotropic Displacement Parameters for SrGa₂B₂O₇

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	0.0103(3)	0.0117(3)	0.0173(3)	0.000	0.000	0.000
Ga	0.0069(3)	0.0125(3)	0.0128(3)	0.000	0.000	– 0.0002 8(15)
B	0.004(2)	0.014(2)	0.020(2)	0.000	0.000	– 0.0017 (15)
O1	0.001(2)	0.016(2)	0.037(3)	0.000	0.000	0.000
O2	0.009(2)	0.0140(13)	0.0238(15)	0.000	0.000	0.0012(11)
O3	0.0074(15)	0.0122(11)	0.0178(13)	0.000	0.000	0.0002(10)
O4	0.0050(13)	0.0187(12)	0.0135(11)	–0.0002(10)	0.000	0.000

improvement in the agreement factors, and it was therefore concluded that the structure is best described as centrosymmetric. A small distortion is present in the borate triangles due to a slightly shorter B–O2 bond (1.34 Å vs 1.38 Å; cf. Table 4). This distortion can be understood by considering the bonding topology of the SrGa₂B₂O₇ structure in which the O2 atom is two-coordinated only (1 Ga + 1 B), whereas the O1 and O3 atoms are four (2 Sr + 2 B)- and three (1 Sr + 1 Ga + 1 B)-coordinated, respectively (cf. Fig. 2). Consequently, the bonds to O2 are expected to be stronger

TABLE 4
Selected Bond Distances (l), Bond Valences (s), and Bond Angles ($^\circ$) in $MGa_2B_2O_7$

$SrGa_2B_2O_7$		$BaGa_2B_2O_7$	
l (Å)	s^a	l (Å)	s
$M-O1$ 3.130(2) × 2	0.065 × 2	3.10(1) × 2	0.112 × 2
$M-O3$ 2.597(3) × 2	0.274 × 2	2.73(1) × 2	0.304 × 2
$M-O4$ 2.598(2) × 4	0.273 × 4	2.75(1) × 4	0.288 × 4
	Σs 1.77		Σs 1.98
$Ga-O2$ 1.841(3)	0.741	1.87(1)	0.685
$Ga-O3$ 1.885(4)	0.658	1.95(1)	0.552
$Ga-O4$ 1.841(2) × 2	0.741 × 2	1.82(1) × 2	0.784
	Σs 2.88		Σs 2.80
$B-O1$ 1.389(6)	0.952	1.37(1) ^b	1.014
$B-O2$ 1.341(6)	1.084	1.37(1) ^b	1.014
$B-O3$ 1.386(5)	0.960	1.37(1) ^b	1.014
	Σs 2.99		Σs 3.04
$O1-B-O2$	119.1(4)		
$O1-B-O3$	123.5(5)		
$O2-B-O3$	117.4(5)		
$O2-Ga-O4$	110.7(1)		
$O2-Ga-O4$	110.7(1)		
$O4-Ga-O4$	101.5(1)		
$O2-Ga-O3$	98.5(2)		
$O4-Ga-O3$	117.8(1)		
$O4-Ga-O3$	117.8(1)		
$B-O1-B$	134.2(5)		

^aCalculated using the parameters of Brese and O'Keeffe (22).

^bA soft constraint was imposed on the B–O distances during the Rietveld refinement of $BaGa_2B_2O_7$.

and shorter in order to satisfy the bond-valence sum around O2 ($\Sigma s = 1.82$; cf. Table 4).

The eightfold coordination (or 6 + 2, a bicapped trigonal prism) of the Sr atoms leads to a somewhat low bond-valence sum of 1.77 (cf. Table 4), suggesting that the Sr–O bonds are stretched as a result of the large cavity size imposed by the $Ga_2B_2O_7$ framework. This interpretation is supported by the better bond-valence sum (1.98) achieved around the Ba atoms in the $BaGa_2B_2O_7$ structure, indicating a better match between the cavity size and the larger Ba atom. In addition, attempts to synthesize an analogous $CaGa_2B_2O_7$ compound have been unsuccessful, suggesting that Ca atoms are too small to be accommodated in this particular gallo-borate framework.

COMPARISON OF THE $MGa_2B_2O_7$ AND $MAl_2B_2O_7$ STRUCTURES

The rhombohedral $MAl_2B_2O_7$ structure is illustrated in Fig. 3 for the case of the Ba compound (6). In spite of their identical compositions, the alkaline-earth alumino-borates are structurally entirely distinct from the gallo-borates. The former are orthoborates formulated as $MAl_2(BO_3)_2O$ (4–6), whereas the latter are pyroborates formulated as $MGa_2(B_2O_5)O_2$ (cf. Fig. 2). Furthermore, the alumino-borates crystallize with a layer structure, whereas the gallo-borates adopt a framework structure. The double layers made up of corner-sharing AlO_4 tetrahedra and BO_3 triangles in the $MAl_2B_2O_7$ structures are also found in the hexagonal $Sr_2Be_2B_2O_7$ structure (1).

The difference in structural topology between the alumino- and the gallo-borates is accompanied by a large

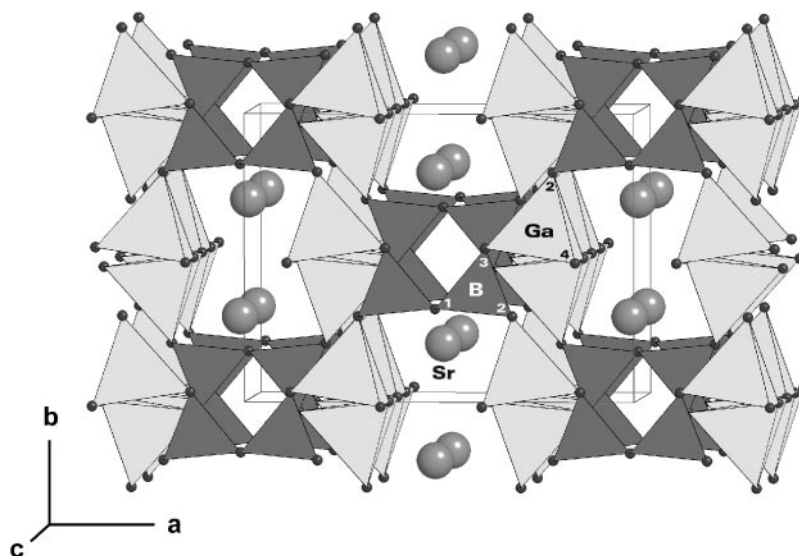


FIG. 2. View of the $SrGa_2B_2O_7$ structure approximately along the c axis of the orthorhombic unit cell. The structure consists of [001] chains of corner-sharing GaO_4 tetrahedra (light gray) joined by planar B_2O_5 pyroborate groups (dark gray). The Sr atoms (large circles) occupy the framework cavities. The numbers in the BO_3 and GaO_4 polyhedra refer to the oxygen positions.

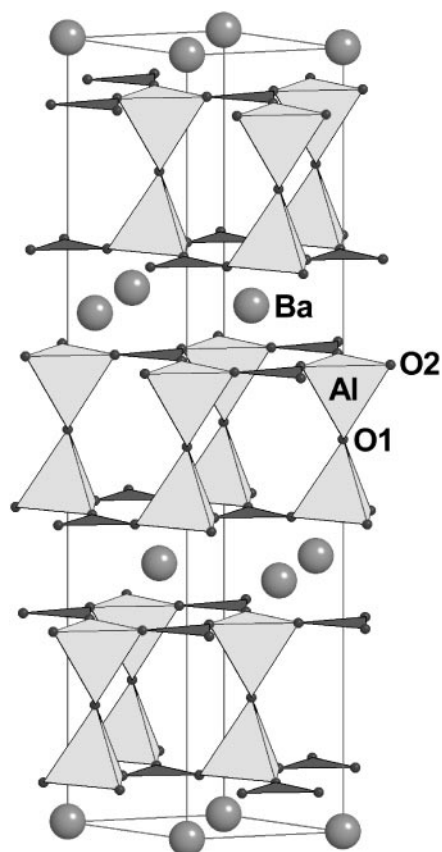


FIG. 3. View of the $BaAl_2B_2O_7$ structure approximately perpendicular to the c axis of the hexagonal unit cell. The structure consists of [001] double layers of corner-sharing AlO_4 tetrahedra and BO_3 triangles, with the Ba atoms in between the layers.

difference in the packing densities of the two structure types. The $MGa_2B_2O_7$ compounds are much more densely packed with, for instance, an increase of 15% in the volume per oxygen atom between $SrGa_2B_2O_7$ and $SrAl_2B_2O_7$ (Table 5). The lower packing density of the alumino-borates is observed in spite of the shorter $\langle Al-O \rangle$ bonds and, as seen in Fig. 3, arises from the fully expanded geometry of the $Al_2B_2O_7$ double layers with linear $Al-O1-Al$ linkages (although strongly anisotropic displacements of the two-coordinated O1 atoms in all the $MAl_2B_2O_7$ structures suggest

local deviations from the linear bonding geometry). The formation of a different structure-type for the gallo-borates might be explained by the instability of similar $O_3Ga-O-GaO_3$ linear linkages, with twofold coordination of the bridging oxygen. The relative packing densities also suggest that the denser $MGa_2B_2O_7$ structure type might represent a high-pressure and/or low-temperature form for the alumino-borates. Work is now in progress to investigate the phase relations in the pseudobinary $MGa_2B_2O_7-MAl_2B_2O_7$ systems and the possible formation of $M(Ga, Al)_2B_2O_7$ solid solutions.

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TABLE 5
Packing Density in Various $MX_2B_2O_7$ Structures

Compound	Volume per oxygen atom (\AA^3)	Reference
$SrGa_2B_2O_7$	20.0	This work
$BaGa_2B_2O_7$	21.2	This work
$CaAl_2B_2O_7$	22.2	4
$SrAl_2B_2O_7$	23.6	5
$BaAl_2B_2O_7$	25.1	6