# Crystal Structures of the New Borate Fluorides Ba*M*BO$_3$F$_2$ (*M* = Ga, Al)

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Two new borate fluorides, Ba*M*BO$_3$F$_2$ (*M* = Ga, Al), have been synthesized by hydrothermal and solid-state reactions. The structure of BaGaBO$_3$F$_2$ has been determined by single-crystal X-ray diffraction ($P6_3/m$, $a = 4.907(2)$ Å, $c = 9.620(5)$ Å, $Z = 2$, w$R(F^2) = 0.039$ for 334 unique reflections). BaAlBO$_3$F$_2$ has been confirmed to be isostructural by Rietveld refinement of powder X-ray data ($a = 4.882(1)$ Å, $c = 9.398(1)$ Å, $Z = 2$, $R_{wp} = 0.222$, $\chi^2 = 2.59$). The Ba*M*BO$_3$F$_2$ structure-type is built of (001) layers of corner-sharing $MO_3F_2$ triangular bipyramids and BO$_3$ triangles, with the Ba atoms filling 12-coordinated interlayer sites.  © 2000 Academic press

**Key Words:** BaGaBO$_3$F$_2$; BaAlBO$_3$F$_2$; borate fluorides.

## INTRODUCTION

As part of our research on the synthesis and structural characterization of new ternary borates (1), hydrothermal experiments yielded single crystals of a new compound identified as BaGaBO$_3$F$_2$. Its crystal structure is described here, together with that of the Al analog, BaAlBO$_3$F$_2$, synthesized by solid-state reaction under anhydrous conditions. These two compounds represent new members of the family of fluoride borates which, from a survey of the inorganic databases (2, 3), is so far limited to a handful of well-characterized compounds. These include $M_5(BO_3)_3F$ with $M$ = Mg, Ca (4, 5), Ba$_5$(B$_2$O$_5$)$_2$F$_2$ (6), BaCaBO$_3$F (7), Mg$_3$BO$_3$F$_3$ (8), Mg$_2$BO$_3$F (9), Be$_2$BO$_3$F (10), Al$_6$(BO$_3$)$_5$F$_3$ (11), $Ln_3$(BO$_3$)$_2$F$_3$ ($Ln$ = Sm, Eu, Gd) (12) and $M$Be$_2$BO$_3$F$_2$ ($M$ = Na, K, Rb, Cs) (13–15). The latter compounds are noncentrosymmetric and, for $M$ = Na and K, have been shown to possess interesting nonlinear optical properties (14, 15). They also display structural similarities with the Ba*M*BO$_3$F$_2$ ($M$ = Ga, Al) compounds that are described here.

## EXPERIMENTAL

Single crystals of the BaGaBO$_3$F$_2$ compound were recovered from exploratory hydrothermal syntheses in the BaO–Ga$_2$O$_3$–B$_2$O$_3$ system. The starting material consisted of a glass obtained by melting a powder mixture (3 g

BaGa$_2$B$_2$O$_7$ + 1.2 g B$_2$O$_3$ + 1.2 g NaF) at 1050°C in a covered platinum crucible. The finely ground glass (1.5 g) was then recrystallized in 10 cm$^3$ of deionized water contained in a 25-cm$^3$ Teflon-lined Parr hydrothermal bomb heated at 200°C for 7 days. The recrystallization products consisted of small doubly terminated hexagonal prisms of BaGaBO$_3$F$_2$ together with an unidentified microcrystalline phase. The presence of fluorine in the crystals, which was initially inferred from the structure determination (cf. below), was later confirmed by qualitative electron microprobe analysis. On the other hand, laser Raman spectra recorded on several single crystals were consistent with the absence of hydroxyl groups as shown by the absence of a characteristic O–H band in the 3300–3600 cm$^{-1}$ region.

To confirm the stability and the anhydrous nature of the BaGaBO$_3$F$_2$ compound, its synthesis was attempted by direct solid-state reaction in the BaF$_2$–Ga$_2$O$_3$–B$_2$O$_3$ system. First, calcite-type GaBO$_3$ was synthesized by heating stoichiometric quantities of Ga$_2$O$_3$ (99.99% pure) and H$_3$BO$_3$ (99.9% pure) powders at 800°C (16). Then, a 0.5-g pellet containing a 1:1 molar mixture of BaF$_2$ (99.5% pure) and GaBO$_3$ powders was fired at 800°C, in a platinum boat, under flowing argon for three 1-h periods with intermediate remixings. The inert atmosphere was found to be necessary to prevent the transformation of BaF$_2$ into BaO and the formation of BaGa$_2$B$_2$O$_7$ (1). The final reaction products identified by powder X-ray diffraction consisted of well-crystallized BaGaBO$_3$F$_2$ and unreacted, possibly partially oxidized, grey-colored BaF$_2$.

A similar procedure was also used to synthesize the analogous BaAlBO$_3$F$_2$ compound. In this case, the reactants consisted of BaF$_2$ with a 50% molar excess of a prereacted powder with a nominal composition of AlBO$_3$ to ensure complete reaction of the BaF$_2$ powder. The crystalline products were identified as BaAlBO$_3$F$_2$ plus a small amount of an unidentified, probably borate-rich phase (see below).

### Structure Determinations

The single-crystal data for BaGaBO$_3$F$_2$ were collected with a Siemens P4 diffractometer equipped with a Mo*K*α

**TABLE 1**
**Details of the Refinements of the Ba$M$BO$_3$F$_2$ Structures**

|  | BaGaBO$_3$F$_2$ |  | BaAlBO$_3$F$_2$ |
|---|---|---|---|
| Sample | Single crystal | Sample | Powder |
|  | 0.15 × 0.04 × |  |  |
|  | 0.03 mm$^3$ |  |  |
| Wavelength | Mo$K\alpha$ | Wavelength | Cu$K\alpha$ |
| Absorption coeff. | 16.37 mm$^{-1}$ | $2\theta$ range | 16.0°–88.0° |
| $2\theta$ max | 72.53° | Step size, count time | 0.03°, 3 s |
| Index ranges | $-8 < h < 6$ | Excluded regions$^a$ | 67.7°–69.1° |
|  | $-7 < k < 8$ |  | 76.4°–77.8° |
|  | $-15 < l < 12$ | $R_{wp}$ | 0.222 |
| Unique reflections | 334 | $R_e$ | 0.138 |
| $T_{min}$, $T_{max}$ | 0.2604, 0.4520 | $\chi^2$ | 2.59 |
| $R_{int}$ | 0.030 | $R$ (Bragg) | 0.091 |
| Refined parameters | 18 | Reflections | 82 |
| Goodness-of-fit | 1.179 | Refined parameters | 18 |
| w$R(F^2)$ | 0.039 |  |  |
| Difference map | $-0.78$, $+1.24$ |  |  |
| (e Å$^{-3}$) |  |  |  |
| Twinning | (110) plane |  |  |
| Vol% of twins | 66(1)/34(1) |  |  |

$^a$ Corresponding to an unidentified impurity due to an excess of aluminum borate (see text).

rotating anode X-ray source and a Smart-1K area detector. The raw intensity data were processed with the SAINT software (17) and an empirical absorption correction was applied using the SADABS program (18). The structure was then solved and refined fully anisotropically with the SHELXS (19) and SHELXL (20) programs. The refinement details and the crystal data for BaGaBO$_3$F$_2$ are listed in Tables 1 and 2, respectively. Twinning of the crystal on the (110) plane was detected during the course of the structure refinement. The final atomic coordinates and isotropic displacement parameters are given in Table 3a, and the anisotropic displacement parameters in Table 3b. Selected bond distances and their associated bond valences are in Table 4.

The structure of the BaAlBO$_3$F$_2$ compound was refined by the Rietveld method using powder X-ray data collected with a Nicolet I2 diffractometer. The refinement was carried

**TABLE 2**
**Crystal Data for the Ba$M$BO$_3$F$_2$ Compounds**

|  | Compound | |
|---|---|---|
|  | BaGaO$_3$F$_2$ | BaAlBO$_3$F$_2$ |
| Space group | $P6_3/m$ | $P6_3/m$ |
| Unit cell |  |  |
| $a$ (Å) | 4.907(2) | 4.882(1) |
| $c$ (Å) | 9.620(5) | 9.398(1) |
| Volume (Å$^3$) | 200.6(2) | 194.0(1) |
| $Z$ | 2 | 2 |
| Calc. density (g cm$^{-3}$) | 5.03 | 4.47 |

**TABLE 3a**
**Atomic Coordinates and Isotropic Displacement Parameters for BaGaBO$_3$F$_2$**

|  | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Ba | 0 | 0 | 0 | 0.0099(1) |
| Ga | $\frac{1}{3}$ | $\frac{2}{3}$ | $\frac{1}{4}$ | 0.0073(1) |
| B | $\frac{2}{3}$ | $\frac{1}{3}$ | $\frac{1}{4}$ | 0.0121(9) |
| F | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.0457(2) | 0.0151(4) |
| O | 0.3775(6) | 0.3114(6) | $\frac{1}{4}$ | 0.0123(4) |

**TABLE 3b**
**Anistropic Displacement Parameters for BaGaBO$_3$F$_2$**

| Ba | 0.00980(11) | 0.00980(11) | 0.01001(14) | 0.000 | 0.000 | 0.00490(6) |
|---|---|---|---|---|---|---|
| Ga | 0.00575(14) | 0.00575(14) | 0.0105(2) | 0.000 | 0.000 | 0.00287(7) |
| B | 0.0111(13) | 0.0111(13) | 0.014(2) | 0.000 | 0.000 | 0.0056(6) |
| F | 0.0162(6) | 0.0162(6) | 0.0130(9) | 0.000 | 0.000 | 0.0081(3) |
| O | 0.0065(10) | 0.0072(10) | 0.0231(12) | 0.000 | 0.000 | 0.0031(8) |

**TABLE 3c**
**Atomic Coordinates and Isotropic Displacement Parameters for BaAlBO$_3$F$_2$**

|  | $x$ | $y$ | $z$ | $B$ (Å$^2$)$^a$ |
|---|---|---|---|---|
| Ba | 0 | 0 | 0 | 0.2 |
| Al | $\frac{1}{3}$ | $\frac{2}{3}$ | $\frac{1}{4}$ | 0.2 |
| B | $\frac{2}{3}$ | $\frac{1}{3}$ | $\frac{1}{4}$ | 0.5 |
| F | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.053(1) | 0.5 |
| O | 0.381(3) | 0.319(4) | $\frac{1}{4}$ | 0.5 |

$^a$ Not refined during the Rietveld refinement.

out with the FULLPROF program (21) using the atomic parameters of the BaGaBO$_3$F$_2$ structure as a starting model. A total of 18 parameters were refined including 5 structural parameters (two cell parameters plus three

**TABLE 4**
**Selected Bond Distances ($l$ in Å) and Bond Valences ($s$)$^a$ in Ba$M$BO$_3$F$_2$**

|  | $M$ = Ga | | $M$ = Al | |
|---|---|---|---|---|
|  | $l$ | $s$ | $l$ | $s$ |
| Ba–F (× 6) | 2.867(2) | 0.160 | 2.862(2) | 0.163 |
| Ba–O (× 6) | 2.953(2) | 0.167 | 2.92(1) | 0.182 |
|  |  | $\sum s = 1.96$ |  | $\sum s = 2.07$ |
| $M$–O (× 3) | 1.861(3) | 0.702 | 1.82(2) | 0.633 |
| $M$–F (× 2) | 1.965(2) | 0.393 | 1.85(1) | 0.439 |
|  |  | $\sum s = 2.89$ |  | $\sum s = 2.78$ |
| B–O (× 3) | 1.368(3) | 1.008 | 1.36(2) | 1.030 |
|  |  | $\sum s = 3.02$ |  | $\sum s = 3.09$ |

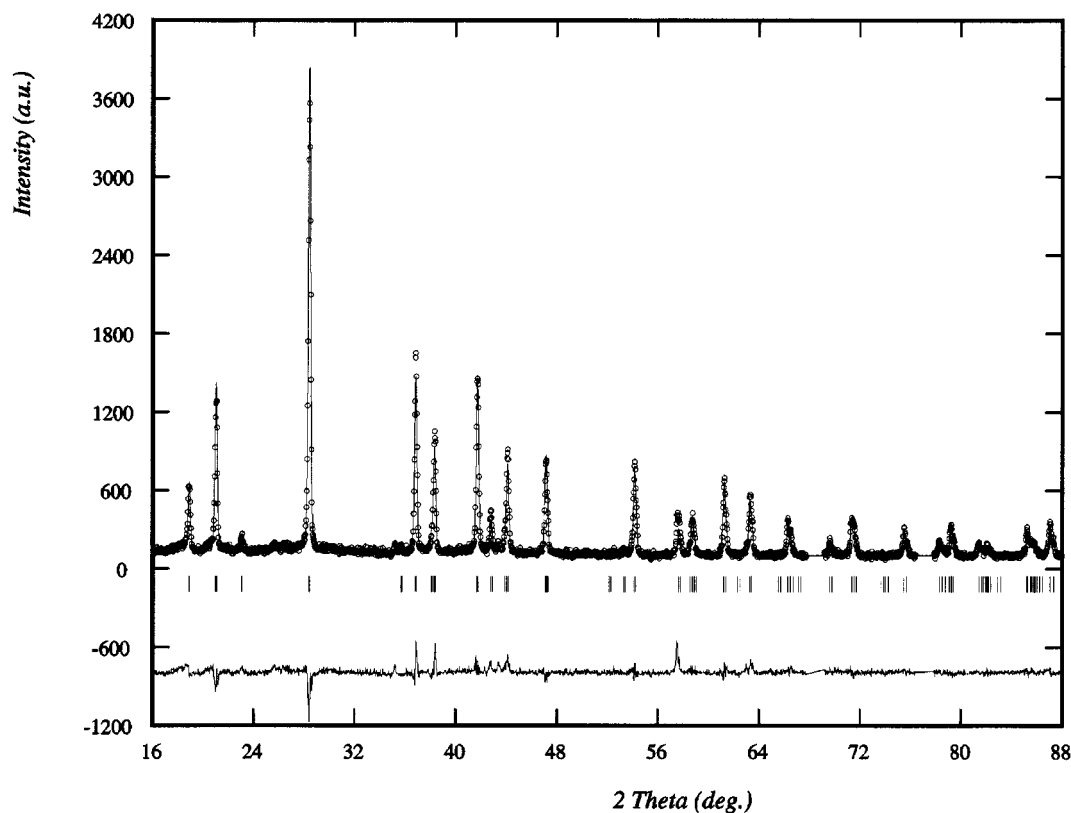$^a$ Bond valences calculated with the parameters of Brese and O'Keeffe (22).

**FIG. 1.** Observed (circles) and calculated (full line) profiles for the Rietveld refinement of the $BaAlBO_3F_2$ 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. Two weak (400 counts maximum) impurity peaks have been excluded from the Rietveld refinement.

atomic coordinates), 12 profile parameters, and 1 parameter for a (001) preferred orientation, as expected from the layer character of the hexagonal structure (see below). The details of the Rietveld refinement are listed in Table 1, and the plots of the observed and calculated profiles are shown in Fig. 1. Due to the excess of aluminum borate used in the synthesis of $BaAlBO_2F_2$ (cf. above), a small amount of an unidentified phase (or phases) was present in the sample giving rise to several extra weak reflections (with a maximum of 400 counts for the strongest reflection). Where possible, these reflections were excluded from the Rietveld refinement (cf. Fig. 1 and Table 1). The crystal data, atomic parameters, and bond distances for $BaAlBO_3F_2$ are given in Tables 2, 3c, and 4, respectively. Despite the average quality of the structure refinement (note that, in particular, the B parameters were not refined), the structural parameters for the $BaAlBO_3F_2$ compound are in very good agreement with those for the Ga analog, confirming that the two compounds are isostructural.

*Description of the $BaMBO_3F_2$ Structure (M = Ga, Al)*

The hexagonal $BaGaBO_3F_2$ structure is depicted in Fig. 2. It consists of (001) layers of corner-sharing $GaO_3F_2$

trigonal bipyramids and $BO_3$ triangles, with Ba atoms occupying 12-coordinated interlayer sites.

The ordering of the F and O atoms on the axial and equatorial positions of the $GaO_3F_2$ bipyramids is consistent with bond-valence arguments. The O atoms bridge the Ga and B positions and are in fourfold coordination ($OGaBBa_2$) with the expected bond-valence sum ($\sum s = 2.04$; cf. Table 4). The terminal F atoms are also four-coordinated ($FGaBa_3$) with an adequate bond-valence sum of 0.87. Comparison of the $BaGaBO_3F_2$ and $BaAlBO_3F_2$ unit-cell parameters (Table 2) shows that the volume reduction in the Al compound is the result of a contraction along the $c$ axis. As seen in Table 4, this contraction arises from the shorter Al–F axial bonds in the $AlO_3F_2$ trigonal bipyramids.

The $BaMBO_3F_2$ structure represents a new structure-type among borates (23) and among the few known borate fluorides (cf. Introduction). However, it shows some similarities with the $MBe_2BO_3F_2$ compounds ($M$ = alkali) that crystallize with a layer structure-type with monoclinic ($M$ = Na) (13, 14) or hexagonal ($M$ = K) (15) symmetry. As illustrated in Fig. 3, the (001) layers in the $KBe_2BO_3F_2$ structure are made up of corner-sharing $BO_3$ triangles and $BeO_3F$ tetrahedra. Like in the $BaMBO_3F_2$ structure, the
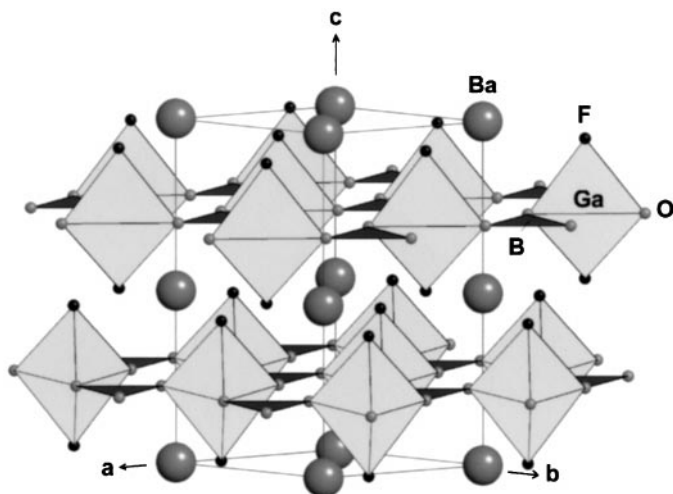
**FIG. 2.** View of the BaGaBO$_3$F$_2$ structure approximately along the [110] direction of the hexagonal unit cell. The structure consists of (001) layers of corner-sharing GaO$_3$F$_2$ trigonal bipyramids (light grey) and BO$_3$ borate groups (dark grey). The Ba atoms (large circles) occupy inter layer sites. The F atoms (small, dark grey circles) and the O atoms (small, light-grey circles) are fully ordered on terminal and bridging positions, respectively.



**FIG. 3.** View of the KBe$_2$BO$_3$F$_2$ structure approximately perpendicular to the [110] direction of the hexagonal unit cell 5. The structure consists of (001) layers of corner-sharing BeO$_3$F tetrahedra and BO$_3$ triangles, with the K atoms (large circles) in between the layers. Like in BaGaBO$_3$F$_2$, the F atoms (small, light-grey circles) and the O atoms (small, dark-grey circles) are fully ordered on terminal and bridging positions, respectively.

O and F atoms occupy bridging and terminal positions, respectively, in the BeO$_3$F tetrahedra. The layer stacking in KBe$_2$BO$_3$F$_2$ results in a 6-fold coordination of the K atoms by fluorine only, with a significant underbonding (K–F = 2.755 Å, $\sum s = 0.76$) that is associated with the easy (001) cleavage of the crystals (15). The absence of K–O bonds is a result of the 3-fold coordination of the O atoms for which the bond-valence requirements are formally met by two O–Be bonds ($s = 1/2 \times 2$) and one O–B bond ($s = 1$) within the layers (cf. Fig. 3). By comparison, the layer stacking in Ba$M$BO$_3$F$_2$ yields a 12-fold coordination of the Ba atoms by 6 fluorine and 6 oxygen atoms, with an adequate bond-valence sum ($\sum s \approx 2.0$, cf. Table 4). In this case, the 2-fold coordination of the O atoms within the layers, with one O–Ga bond ($s = 3/4$) and one O–B bond ($s = 1$) (cf. Fig. 2), is insufficient to achieve a proper bond-valence sum and two additional O–Ba bonds are required.

Work is now in progress to investigate the formation of solid solutions based on the Ba$M$BO$_3$F$_2$ structure, by substitution of Sr or Pb on the Ba site, and/or of other trivalent cations on the 5-coordinated $M$ site. As well, the formation of new rare-earth-based compounds such as $RE$$M'$BO$_3$F$_2$ ($RE$ = large trivalent rare-earth ion, $M'$ = divalent ion) is being investigated. Finally, it could be of interest to study the luminescent properties resulting from Eu$^{2+}$-doping in the Ba$M$BO$_3$F$_2$-type compounds in which the fluorescent ions would be in a mixed (O, F) coordination environment.
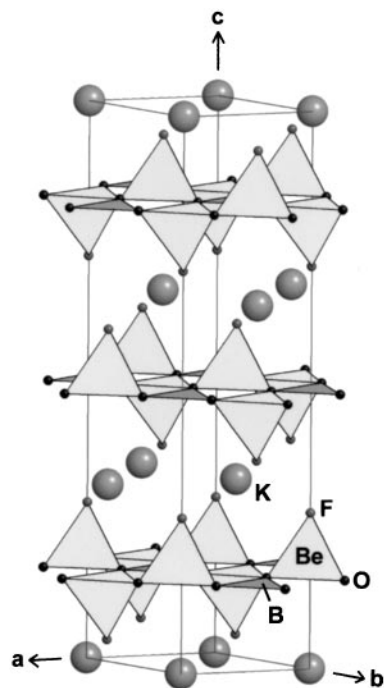
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