

KBa₇Mg₂B₁₄O₂₈F₅, a new borate with an unusual heptaborate group and double perovskite unit

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A new borate, potassium barium magnesium borate fluoride, KBa₇Mg₂B₁₄O₂₈F₅, with a nominal 7:1 composition of BaB₂O₄ to KMg₂F₅, has been found during the growth of BaMgBO₃F crystals with a KF flux. It crystallized in the space group *C2/c* and is composed of isolated heptaborate [B₇O₁₄]⁷⁻ groups and double perovskite [Mg₂O₆F₅]¹³⁻ units.

Comment

Borate crystals have found a wide range of applications as laser hosts, phosphors and nonlinear optical (NLO) materials. Owing to the relatively large electron affinity difference between boron and oxygen, borate crystals often show a wide transparency range and a high resistance to laser or other radiation damage. Studies of borate systems have led to the discovery of many new crystals possessing nonlinear optical properties, among which the low-temperature form LT-BaB₂O₄ (BBO; Chen *et al.*, 1985) and LiB₃O₅ (LBO; Chen *et al.*, 1989) are important industrial materials. Recently, fluoroborates have become a prime focus of our laboratory (Chen *et al.*, 2006) because of their transmission cut-off at the

deep ultraviolet (DUV) range ($\lambda < 200$ nm). For example, KB₂BO₃F (KBBF; Chen *et al.*, 1996) and RbBe₂BO₃F (RBBF; Chen *et al.*, 2009) were found to be the only NLO crystals capable of generating a laser output below 200 nm by direct second-harmonic generation (SHG). In an attempt to grow crystals of a recently found noncentrosymmetric fluoroborate, BaMgBO₃F, with a KF flux, a single crystal of the title compound, KBa₇Mg₂B₁₄O₂₈F₅, (I), was obtained.

Fig. 1 illustrates the unit-cell contents of (I). A notable feature in the structure of (I) is the [B₇O₁₄]⁷⁻ group (Fig. 2), which is composed of a combination of two B₃O₇ rings and one B₃O₈ ring. According to the scheme proposed by Christ & Clark (1977), the [B₇O₁₄]⁷⁻ group can be classified as 7:[5 Δ + 2 Γ]. It is worth noting that all the terminal B–O bonds [1.318 (5)–1.352 (5) Å, average 1.331 (11) Å] in [B₇O₁₄]⁷⁻ are significantly shorter than those within the rings [average 1.393 (11) Å for BO₃ and 1.473 (19) Å for BO₄]. The systematic variations of the B–O bond lengths within the rings ($B^T-O^T = 1.453$ Å and $B^T-O^\Delta = 1.479$ Å; $B^\Delta-O^\Delta = 1.407$ Å and $B^\Delta-O^T = 1.385$ Å) are also in good agreement with the scheme proposed by Filatov & Bubnova (2000). Though the B–O bond lengths display large variations [1.318 (5)–1.490 (4) Å], a bond valence sum (BVS) calculation (Brown & Altermatt, 1985) for B gives values ranging from 2.962 to 3.043 (average 3.012), in good agreement with the ideal B valence. According to a recent survey of borate structure types (Touboul *et al.*, 2003), such heptaborate groups have not been reported previously in any anhydrous borates. Only very recently, similar heptaborate groups with terminal hydroxy groups (OH) were found in two hydrated alkaline borates (Liu & Li, 2006; Liu *et al.*, 2006) and some organic templated hydrated borates (Schubert & Knobler, 2009).

Another distinctive feature of the structure is the double perovskite unit [Mg₂O₆F₅]¹³⁻. The six O atoms in the unit come from six [B₇O₁₄]⁷⁻ groups. By sharing these O atoms, [B₇O₁₄]⁷⁻ groups connect [Mg₂O₆F₅]¹³⁻ to form a three-dimensional net with Ba atoms (partially K) occupying the voids. In the double perovskite units, two MgO₃F₃ octahedra share a common atom F1 and are related by a twofold rotation axis through F1. Along the axial direction of the double perovskite unit, Mg–F bonds show alternating short [1.968 (2) Å],

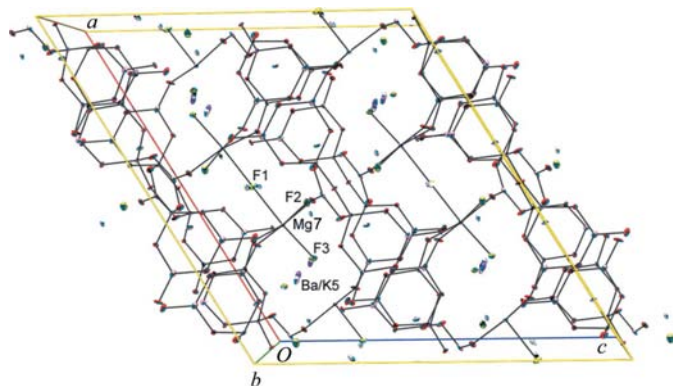


Figure 1

The unit-cell contents of KBa₇Mg₂B₁₄O₂₈F₅. Displacement ellipsoids are drawn at the 50% probability level.

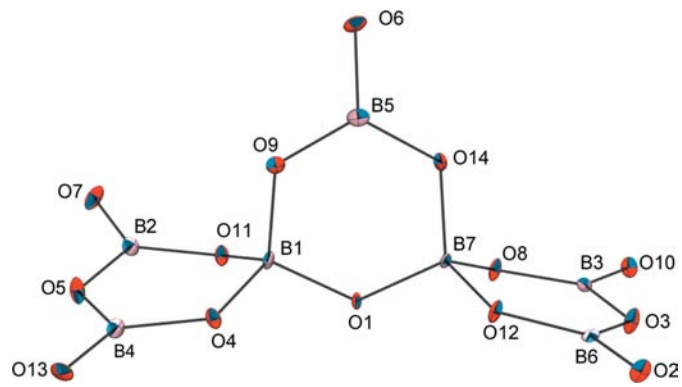


Figure 2

The heptaborate [B₇O₁₄]⁷⁻ group. Displacement ellipsoids are drawn at the 50% probability level.

long [2.0867 (12) Å], long [2.0867 (12) Å] and short [1.968 (2) Å] bond lengths. In contrast, the equatorial Mg–F and Mg–O bond lengths show little variation [2.038 (3)–2.058 (3) Å].

Among the five cations, attention should be paid to the Ba5/K5 site. BVS calculations of Ba²⁺ showed that this site has significant valence deficiency (1.742) compared with the other Ba sites (1.913–2.386), indicating a strong tendency to host a lower-valent cation such as K⁺, which is consistent with our refinement. Close inspection shows that the Ba5 site is located at a crossing of two large voids running along the *a* and *c* directions, leaving room for the split Ba/K position to optimize both Ba and K coordination.

A preliminary study has shown that the sodium analogue of the title compound can also be grown in a similar manner from an NaF flux. The structure reveals that it has a more disordered Ba/Na site with a larger Ba–Na separation than that of Ba–K in the title compound. It will be interesting to see whether other common perovskite units (*e.g.* BaTi₂O₅ or KNi₂F₅, *etc.*) can also be included in the structure of the present compound.

Experimental

The title crystal was obtained from the following analytically pure starting chemicals: MgF₂ (55.8 g), BaCO₃ (177.6 g), H₃BO₃ (111.24 g), BaF₂ (31.6 g) and KF·2H₂O (42.3 g). The mixture of the starting materials was placed in a platinum crucible, heated to 1163 K and stirred for 24 h until the mixture became a clear and homogeneous melt. A Pt wire was dipped into the melt and rotated at a speed of 15 rotations per minute. A column-shaped KBa₇Mg₂B₁₄O₂₈F₅ crystal crystallized on the Pt wire when the melt was cooled to between 1143 and 1133 K at a rate of 0.3–0.5 K d⁻¹. The crystal growth was ended by raising the Pt wire and followed by cooling the furnace to room temperature within 10 h.

Crystal data

KBa ₇ Mg ₂ B ₁₄ O ₂₈ F ₅	<i>V</i> = 2943.3 (9) Å ³
<i>M_r</i> = 1743.44	<i>Z</i> = 4
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 16.638 (3) Å	<i>μ</i> = 9.54 mm ⁻¹
<i>b</i> = 13.609 (2) Å	<i>T</i> = 93 K
<i>c</i> = 15.214 (3) Å	0.24 × 0.23 × 0.20 mm
<i>β</i> = 121.309 (2)°	

Data collection

Rigaku AFC10 diffractometer	11738 measured reflections
Absorption correction: numerical	3301 independent reflections
(<i>CrystalClear</i> ; Rigaku, 2002)	2980 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.121, <i>T</i> _{max} = 0.148	<i>R</i> _{int} = 0.029

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.021	267 parameters
<i>wR</i> (<i>F</i> ²) = 0.041	Δ <i>ρ</i> _{max} = 1.43 e Å ⁻³
<i>S</i> = 1.08	Δ <i>ρ</i> _{min} = -1.06 e Å ⁻³
3301 reflections	

Based on the $|E^2 - 1|$ (1.013) and powder SHG tests, the centrosymmetric space group *C*2/*c* was adopted for the structure solution. Five Ba atoms were originally found by direct methods (*SHELXL97*), with one of them, Ba5, having unusually large displacement parameters. K and Ba atoms were allowed to co-occupy the Ba5 site and all the remaining atoms were found by subsequent difference Fourier synthesis. Refinement with anisotropic displacement parameters resulted in some of the atoms having nonpositive definite anisotropic displacement parameters (ADPs). Close inspection showed that the displacement parameter of the statistically occupied Ba5/K5 site was still large. Therefore, K and Ba were allowed to occupy split sites with constrained ADPs. The refinement proceeded smoothly and led to a 0.3 Å separation between K and Ba and a K-to-Ba occupation ratio of 0.39:0.61. In order to maintain charge balance, we let the rest of the K atom distribute statistically over the other Ba sites. The final difference electron-density map showed a highest peak of 1.43 e Å⁻³ located 0.74 Å from Ba5 and a deepest hole of -1.06 e Å⁻³ located 0.55 Å from Ba5.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3043). Services for accessing these data are described at the back of the journal.

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