This article can be cited before page numbers have been issued, to do this please use: M. Gai, Y. Wang, T. Tong, L. Wang, Z. Yang, X. Zhou and S. Pan, *Chem. Commun.*, 2020, DOI: 10.1039/C9CC06532F.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
COMMUNICATION

Ba(B$_2$OF$_3$(OH)$_2$)$_2$ with well-ordered OH/F anions constructing a unique B$_2$OF$_3$(OH)$_3$ dimer

Minliang Gai,a,b Tinghao Tong,a Ling Wang,a Zhihua Yang,a,† Xin Zhou,a and Shilie Pan*a

In minerals and artificial crystals, the OH and F groups often co-exist and have a high probability of disordered structure. The OH/F position cannot be determined accurately in the crystal structure only with the direct X-ray diffraction method because of the poor contrast between O and F and the weak diffractivity of hydrogen atom. In this work, a new fluorooxoborate Ba[B$_2$O$_5$(OH)$_2$]$_2$, with a size of up to 12 × 4 × 3 mm$^3$, has been synthesized successfully by a facile hydrothermal reaction. The BOF$_3$ units with well-ordered OH/F positions are observed for the first time in alkali/alkaline earth metal fluorooxoborates. Owing to the selective fluorination of BO$_4$ Ba[B$_2$O$_5$(OH)$_2$]$_2$ exhibits a large birefringence which can be used as a DUV birefringent material. This work will guide the study of structural chemistry of oxyfluorides.

In this contribution, we reported a new fluorooxoborate compound, Ba[B$_2$O$_5$(OH)$_2$]$_2$ (BBOFH), containing a unique B$_2$OF$_3$(OH)$_3$ dimer. More than twenty-nine fluoro-oxoborates have been reported up to now, and there are 16 kinds of oxyfluorides FBBs and anionic frameworks of fluorooxoborate crystals reported (Figure S5). Although most of these fluoro-oxoborates also have a regular arrangement of F, the title compound is more specific in that both OH and F coexist simultaneously, and are well-ordered on the tetrahedral and triangular ligands, respectively, which is relatively rare. The BOF$_3$ unit was also discovered for the first time in alkali/alkaline earth metal fluorooxoborates to the best of our knowledge. The method of determining the position of OH and F was systematically discussed.

The BBOFH crystal with a size of up to 12 × 4 × 3 mm$^3$ was grown by the facile hydrothermal growth method. The BBOFH crystal data were obtained at 153 K. BBOFH crystallizes in centrosymmetric space group $P2_1/m$ (No. 12) of monoclinic system with the unit cell parameters of $a=6.803(3)\,\AA$, $b=7.008(2)\,\AA$, $c=9.588(3)\,\AA$, $\beta=92.960(4)^\circ$, and $Z=2$. The unbiased F$_o$–F$_c$ difference electron density maps (model without hydrogen) obtained from single-crystal data were given in Figures 1a, 1b and 1c. The positive difference peaks clearly indicate the possible

---

a) CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 401 South Beijing Road, Urumqi 830011, China. E-mail address: sjpan@ms.xjb.ac.cn (Shilie Pan)
b) Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.
c) Key Laboratory of Magnetic Resonance in Biological Systems, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, National Center for Magnetic Resonance in Wuhan, Wuhan Institute of Physics and Mathematics, CAS, Wuhan 430071, China.
† These authors contributed equally to this work.
* Electronic Supplementary Information (ESI) available: [synthesis, crystallographic studies, characterization, computational descriptions]. See DOI: 10.1039/s0x0000000x

DOI: 10.1039/C9CC06532F
positions of hydrogen atoms around the O1 and O2 atoms, while no difference peaks were found near the F atoms, which provide primary evidence for the F–F and O–H bonds. The assignment of the O and F atoms was also verified by bond valence calculation (BVS) (Table S2), which shows that the valences of Ba (2.089), O (1.873-2.087), F (0.964-1.068) and B (3.029-3.132) are reasonable.

As shown in Figures 1f, 1g and 1h, the fundamental building block (FBB) of BBOFH is the \( B_2O(F)\) group, which is composed of the BO(OH)\(_2\) triangle and the BOF\(_x\) tetrahedron through sharing the bridge O3 atom, and the B\(_2O(F)\) groups are linked with each other by hydrogen bonding to form a 1D \([B_2O(F)OH]_n\) short chain. The parallel \([B_2O(F)OH]_n\) chains extend along the b and c axes with the Ba1 cations located between each two adjacent chains. In general, as the ratio of F:O increases, there is a higher possibility for the anionic framework in fluorooxoborates to be low-dimensional.

Figure 1. The unbiased \( F_2\)–F, difference electron density maps of BBOFH (a, b, c). The most positive difference peaks (red) indicate the possible hydrogen atom positions.

Crystal structures of BBOFH (d, e, f, g, h). The B-F and O-H bonds in BBOFH exist (Figure 1k). The crystal structure of BBOFH clearly demonstrates that tetrahedrally coordinated B nuclei with B-F bonds in BBOFH exist (Figure 1k). The crystal structure of BBOFH has two unique H sites, the H1, H2 atoms are coordinated with the O1 and O2 atoms, respectively. The \( ^1H\) MAS NMR spectrum shows two resonances at \( \delta = 4.3 \) and 7.6 ppm (Figure 1l), which are assigned to the H signals in the BO(OH)\(_2\) groups with two different O–H distances. This further confirms the existence of the hydroxyl groups in BBOFH.

The ordering of F and OH can be understood by using the bond valence model. The mean bond valences of the B-O and B-F bonds in BBOFH are 0.75 and 1, respectively. According to the Pauling’s second crystal rule (PSCR), a stable ionic structure is arranged to preserve local electroneutrality, so that the sum of the strengths of the electrostatic bond to an anion equal to the charge on that anion. When hydroxyl competes with F to have a relatively stable phase, compared to the BO\(_3\) units, the BO\(_3\) species are prone to connect with the F atoms with high electronegativity to reduce the bond valence of B-O bonds. Thus, the reduced partial negative charge at the respective terminal oxygen and/or fluorine atoms in fourfold coordination of the B atoms commonly acts as pinning sites for the cations. Herein, the \([BO_3F_4]^2-\) (\(x = 1, 2,3\)) groups should be more stable than the virtual \([BO_3F_5]^2-\) (\(x = 1, 2\)) groups in metal fluorooxoborates containing both the BO\(_3\) and BO\(_2\)F\(_x\) groups. As the introduction of F will preferentially modify the BO\(_3\) groups to form \([BO_3F_n]^2-x\) (\(x = 1, 2,3\)), Li\(_2\)BO\(_3\)F\(_x\) and \([BO_2F_2]^2-\) (\(A = NH_4\), Na, Rb, Cs, K/Cs, Rb/Cs) series are all typical examples. The formation of the free electron accepting ability of the Ba atom, most of the F atoms with strong electronegativity are tended to connect with Ba in the B\(_2O(F)OH\)\(_2\) groups. This may act as a scissor to “break” the layers of the B-O framework, and further produce 1D short chains of \([B_2O(F)OH]_n\). Therefore, if the hydroxyl groups in the BO(OH)\(_2\) triangles are partially or completely replaced by the F atoms, the B-O will most likely connect with eleven or more fluorine atoms, and the virtual \([BO_3F_2OHF]_n^2-X\) (\(x = 1, 2\)) groups will not link with each other by hydrogen bonding to form a 1D chain (Figure S2). This may lead to an unstable structure. Moreover, the phonon dispersion curves obtained by the first-principles calculations confirm that BBOFH has no negative frequencies and is dynamically stable, while the artificial \("Ba[B_2O(F)OHF]_SF\) (\(x = 1, 2\)) structures with mutual substitution of OH and F are not stable (Figure S11). Thus, \([BO_3F_4]^2-\) and the artificial \([BO_3F_5]^2-\) (\(x = 1, 2\)) groups co-exist in BBOFH will be difficult to achieve.

To check the thermal stability of BBOFH, thermogrammetric and differential scanning calorimetry (TG-DSC) were performed (Figure S6). There are three obvious endothermic peaks around 282, 697 and 803 °C on the TG curve for BBOFH. It should be noticed that there is almost 13.8 % mass loss at around 282 °C, which may be assigned to the part of removal of the BF\(_3\) gas and the dehydration of the hydroxyls. The ultraviolet-visible-near-infrared transmittance spectrum of BBOFH was collected on the ground crystals (Figure S4). We can see that the wide optical transmission spectrum (180–1200 nm) range can be obtained in BBOFH. The first-principles calculations were performed by employing the CASTEP package. BBOFH owns an indirect band gap of 8.35 eV (HSE06) using the PWmat code (Figure S10a), which is comparable to that of the landmark deep-ultraviolet

[References]

Please do not adjust margins
material KBe₂BO₂F₃ (KBBF) (8.43 eV).\(^{21}\) The total and partial densities of states (DOS and PDOS) of BBOFH are shown in Figure S10b. There are three energy parts from -9 to 9 eV, which show that the top of VB and the bottom of CB are mainly occupied by O-2p, B-2p and F-2p orbitals, revealing that the optical properties of BBOFH are mainly determined by the BOF₃, BO₃ groups and d orbitals of the Ba atoms. The calculated birefringence of BBOFH is about 0.109 at 200 nm and 0.086 at 1064 nm, respectively (Figure S9). Considering the birefringence of α-Be₂O₃ (0.120@1064 nm),\(^{22}\) KBBF (0.080@1064 nm)\(^{21}\) and the absorption edge of BBOFH lower than 180 nm, BBOFH may have potential applications in the deep-UV region. To better understand the origin of the birefringence in BBOFH, we investigated the material using response electron distribution anisotropy (REDA) approximation method.\(^{23}\) Based on the REDA analysis, the origin of birefringence in BBOFH is mainly attributed to the synergic effect of BOF₃ (16.2 %) and BO₃ (83.8 %) groups. It indicates that the well-ordered OH/F group with regular arrangement makes a significant contribution for the large birefringence.

In summary, a new centimetre-scale fluorooxoborate crystal BBOFH with unique BOF₃₃ (KBBF) (8.43 eV).\(^{21}\) The total and partial densities of states (DOS and PDOS) of BBOFH are shown in Figure S10b. There are three energy parts from -9 to 9 eV, which show that the top of VB and the bottom of CB are mainly occupied by O-2p, B-2p and F-2p orbitals, revealing that the optical properties of BBOFH are mainly determined by the BOF₃, BO₃ groups and d orbitals of the Ba atoms. The calculated birefringence of BBOFH is about 0.109 at 200 nm and 0.086 at 1064 nm, respectively (Figure S9). Considering the birefringence of α-Be₂O₃ (0.120@1064 nm),\(^{22}\) KBBF (0.080@1064 nm)\(^{21}\) and the absorption edge of BBOFH lower than 180 nm, BBOFH may have potential applications in the deep-UV region. To better understand the origin of the birefringence in BBOFH, we investigated the material using response electron distribution anisotropy (REDA) approximation method.\(^{23}\) Based on the REDA analysis, the origin of birefringence in BBOFH is mainly attributed to the synergic effect of BOF₃ (16.2 %) and BO₃ (83.8 %) groups. It indicates that the well-ordered OH/F group with regular arrangement makes a significant contribution for the large birefringence.

In summary, a new centimetre-scale fluorooxoborate crystal BBOFH with unique BOF₃₃ (KBBF) (8.43 eV).\(^{21}\) The total and partial densities of states (DOS and PDOS) of BBOFH are shown in Figure S10b. There are three energy parts from -9 to 9 eV, which show that the top of VB and the bottom of CB are mainly occupied by O-2p, B-2p and F-2p orbitals, revealing that the optical properties of BBOFH are mainly determined by the BOF₃, BO₃ groups and d orbitals of the Ba atoms. The calculated birefringence of BBOFH is about 0.109 at 200 nm and 0.086 at 1064 nm, respectively (Figure S9). Considering the birefringence of α-Be₂O₃ (0.120@1064 nm),\(^{22}\) KBBF (0.080@1064 nm)\(^{21}\) and the absorption edge of BBOFH lower than 180 nm, BBOFH may have potential applications in the deep-UV region. To better understand the origin of the birefringence in BBOFH, we investigated the material using response electron distribution anisotropy (REDA) approximation method.\(^{23}\) Based on the REDA analysis, the origin of birefringence in BBOFH is mainly attributed to the synergic effect of BOF₃ (16.2 %) and BO₃ (83.8 %) groups. It indicates that the well-ordered OH/F group with regular arrangement makes a significant contribution for the large birefringence.

In summary, a new centimetre-scale fluorooxoborate crystal BBOFH with unique BOF₃₃ (KBBF) (8.43 eV).\(^{21}\) The total and partial densities of states (DOS and PDOS) of BBOFH are shown in Figure S10b. There are three energy parts from -9 to 9 eV, which show that the top of VB and the bottom of CB are mainly occupied by O-2p, B-2p and F-2p orbitals, revealing that the optical properties of BBOFH are mainly determined by the BOF₃, BO₃ groups and d orbitals of the Ba atoms. The calculated birefringence of BBOFH is about 0.109 at 200 nm and 0.086 at 1064 nm, respectively (Figure S9). Considering the birefringence of α-Be₂O₃ (0.120@1064 nm),\(^{22}\) KBBF (0.080@1064 nm)\(^{21}\) and the absorption edge of BBOFH lower than 180 nm, BBOFH may have potential applications in the deep-UV region. To better understand the origin of the birefringence in BBOFH, we investigated the material using response electron distribution anisotropy (REDA) approximation method.\(^{23}\) Based on the REDA analysis, the origin of birefringence in BBOFH is mainly attributed to the synergic effect of BOF₃ (16.2 %) and BO₃ (83.8 %) groups. It indicates that the well-ordered OH/F group with regular arrangement makes a significant contribution for the large birefringence.

In summary, a new centimetre-scale fluorooxoborate crystal BBOFH with unique BOF₃₃ (KBBF) (8.43 eV).\(^{21}\) The total and partial densities of states (DOS and PDOS) of BBOFH are shown in Figure S10b. There are three energy parts from -9 to 9 eV, which show that the top of VB and the bottom of CB are mainly occupied by O-2p, B-2p and F-2p orbitals, revealing that the optical properties of BBOFH are mainly determined by the BOF₃, BO₃ groups and d orbitals of the Ba atoms. The calculated birefringence of BBOFH is about 0.109 at 200 nm and 0.086 at 1064 nm, respectively (Figure S9). Considering the birefringence of α-Be₂O₃ (0.120@1064 nm),\(^{22}\) KBBF (0.080@1064 nm)\(^{21}\) and the absorption edge of BBOFH lower than 180 nm, BBOFH may have potential applications in the deep-UV region. To better understand the origin of the birefringence in BBOFH, we investigated the material using response electron distribution anisotropy (REDA) approximation method.\(^{23}\) Based on the REDA analysis, the origin of birefringence in BBOFH is mainly attributed to the synergic effect of BOF₃ (16.2 %) and BO₃ (83.8 %) groups. It indicates that the well-ordered OH/F group with regular arrangement makes a significant contribution for the large birefringence.


A new centimetre-scale fluorooxoborate crystal Ba(B₂OF₃(OH)₂), with well-ordered OH/F units and a new dimer containing BOF₃ units, has been fabricated.