Electronic Supplementary Information

BaBOF₃ : A New Aurivillius-Like Borate Containing Two Types of F

Atoms

Dequan Jiang,^{a,b} Ying Wang,^{*a} Hao Li,^{a,b} Zhihua Yang^a and Shilie Pan^{*a}

^aCAS 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, 40-1 South Beijing Road, Urumqi 830011, China.
 ^bUniversity of the Chinese Academy of Sciences, Beijing 100049, China
 *Corresponding authors, E-mails: wangying@ms.xjb.ac.cn; slpan@ms.xjb.ac.cn

Experimental Section

Reagents NaBF₄ (Tianjin Guangfu Chemical Reagent Co., Ltd., 99.0%), BaF₂ (Tianjin Dengke Chemical Reagent Co., Ltd., 98.0%), B₂O₃ (Aladdin Industrial Co., Ltd., 98.0%), H₃BO₃ (Tianjin Baishi Chemical Reagent Co., Ltd., 99.5%), BaCO₃ (Tianjin Baishi Chemical Reagent Co., Ltd., 99.0%), and HBF₄ solution (Tianjin Damao Chemical Reagent Co., Ltd., \geq 40.0*wt%*), NH₄BF₄ (Aladdin Industrial Co., Ltd., 99.5%) were used as received.

The preparation of $Ba(BF_4)_2$: $BaCO_3$ was placed into a 23ml Teflon, afterwards excess HBF₄ were dropwise added to ensure the complete reaction of $BaCO_3$. Then, the Teflon was heated to $180^{\circ}C$ to evaporate H₂O and HBF₄ gas. The X-ray diffraction pattern of the white residual powder was in good agreement with the calculated one of $Ba(BF_4)_2$.

Crystal growth The single crystals of $BaBOF_3$ were obtained by the high-temperature process in a vacuum system. A mixture of B_2O_3 (0.114g, 69.62 mmol), $NaBF_4$ (0.314g, 2.859 mmol), and BaF_2 (0.072g, 0.411 mmol) was sealed into a tidy quartz tube, and the tube was flame-sealed under 10^{-3} Pa to create a vacuum environment. Then, the tube was placed into a programmable temperature muffle furnace. The tube was gradually heated to 700°C in 12 h, and then held for 10 h. Finally, the tube was cooled slowly to the room temperature. Millimeter-level rod-like crystals were separated mechanically from the tube for structure determination.

Solid-state synthesis The polycrystalline sample of BaBOF₃ was obtained in a closed Teflon autoclave using boric as a flux. Two types of starting reagents were used with the same program, *i.e.*, (i) Ba(BF₄)₂ and H₃BO₃ with the stoichiometric ratio of 1 : 1, (ii) NH₄BF₄, BaF₂, and H₃BO₃ with the stoichiometric ratio of 2 : 2 : 1. Then the starting reagents were sufficiently ground before sealing into the 23ml Teflon autoclave. The autoclave was heated to 220°C and kept for 3 days and cooled to the room temperature at the rate of 2.4°C/h.

Structure determination A single crystal of the title compound with the dimensions of 0.162 mm × 0.108 mm × 0.039 mm was chosen for the crystal structure determination. The structure data were performed by the single-crystal X-ray diffraction on a Bruker SMART APEX II CCD diffractometer at 296(2) K using monochromatic Mo-K α radiation with $\lambda = 0.71073$ Å. The numerical absorption correction was carried out by the SCALE program for area detectors and integrated with the SAINT program.¹ All the calculations were performed with programs from the SHELXTL crystallographic software package.² All the atoms were refined using full matrix least-squares techniques, and final least-squares refinement was on F_o^2 with data having $F_o^2 \ge 2\sigma(F_o^2)$. The structure of the title compound was checked for missing symmetry elements with the program Platon.³ Crystal data and structure refinement information of BaBOF₃ are presented in Table S2. Relevant atomic coordinates, equivalent isotropic displacement parameters, and selected interatomic distances, angles are listed in Tables S3 and S4.

Powder X-ray diffraction The X-ray diffraction pattern was performed at room temperature on a Bruker D2 PHASER diffractometer equipped with an incident beam monochromator with Cu-K α radiation with λ = 1.5418 Å. The pattern was taken in the 2 ϑ range from 10° to 70°, with a scan step width of 0.02°, and a fixed counting time of 1 s/step.

The UV-VIS diffuse reflectance spectrum The diffuse reflectance spectrum of powder sample was obtained at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. Data was collected in the wavelength range of 200–800nm.

The Energy dispersive X-ray spectroscope Elemental analysis was carried on clean single crystal surfaces with the aid of a field emission scanning electron microscope (SEM, SUPRA 55VP)

equipped with an energy dispersive X-ray spectroscope (BRUKER x-flash-sdd-5010).

Calculation details The electronic structures of BaBOF₃ were calculated by the first-principles method. We implemented density functional calculations (DFT) by the CASTEP package⁴ within the Gradient Generalized Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)⁵⁻⁷ on the experimentally refined structure. The valence electrons of the elements in BaBOF₃ were calculated as follows: Ba $5s^25p^66s^2$, B $2s^22p^1$, O $2s^22p^4$, and F $2s^22p^5$, respectively. The Monkhorst-Pack⁸ *k*-points within the Brillouin zone were chosen as $3 \times 1 \times 3$. The plane-wave cut-off energy is 940 eV. Our test shows that these parameters make good convergence in the present studies.

compounds		ERII	anionic groups
compoditas	[BOF] groups	FDU	anome groups
LiB ₆ O ₉ F ⁹	[BO ₃ F] ⁴⁻ , [BO ₃] ³⁻	[B ₆ O ₁₁ F] ⁵⁻	$[B_6O_9F]^-$ layer
$Li_2B_6O_9F_2^{10}$	[BO ₂ F ₂] ³⁻ , [BO ₃] ³⁻ , [BO ₄] ⁵⁻	$[B_6O_{11}F_2]^{6-1}$	$[B_6O_9F_2]^{2-}$ network
$Li_2B_3O_4F_3^{11}$	[BO ₂ F ₂] ³⁻ , [BO ₃ F] ⁴⁻ , [BO ₃] ³⁻	[B ₃ O ₅ F ₃] ⁴⁻	$[B_3O_4F_3]^{2-}$ chain
$Na_2B_6O_9F_2^{12}$	[BO ₃ F] ⁴⁻ , [BO ₃] ³⁻	$[B_6O_{11}F_2]^{6-1}$	$[B_6O_9F_2]^{2-}$ layer
$Na_{3}B_{3}O_{3}F_{6}^{13}$	[BO ₂ F ₂] ³⁻	[B ₃ O ₃ F ₆] ³⁻	[B ₃ O ₃ F ₆] ^{3−} cluster
$K_3B_3O_3F_6^{14}$	[BO ₂ F ₂] ³⁻	[B ₃ O ₃ F ₆] ³⁻	[B ₃ O ₃ F ₆] ^{3−} cluster
$NH_4B_4O_6F^{15}$	[BO ₃] ³⁻ , [BO ₃ F] ⁴⁻	[B ₄ O ₈ F] ⁵⁻	$[B_4O_6F]^-$ layer
$RbB_4O_6F^{16}$	[BO ₃] ³⁻ , [BO ₃ F] ⁴⁻	[B ₄ O ₈ F] ⁵⁻	$[B_4O_6F]^-$ layer
CsB ₄ O ₆ F ¹⁷	[BO ₃] ³⁻ , [BO ₃ F] ⁴⁻	[B ₄ O ₈ F] ⁵⁻	[B₄O ₆ F] ⁻ layer
$CsKB_8O_{12}F_2^{16}$	[BO ₃] ³⁻ , [BO ₃ F] ⁴⁻	[B ₄ O ₈ F] ⁵⁻	[B₄O ₆ F] ⁻ layer
$CsRbB_8O_{12F_2^{16}}$	[BO ₃] ³⁻ , [BO ₃ F] ⁴⁻	[B ₄ O ₈ F] ⁵⁻	[B₄O ₆ F]⁻ layer
$Li_2Na_{0.9}K_{0.1}B_5O_8F_2^{18}$	[BO ₃ F] ⁴⁻ , [BO ₃] ³⁻ , [BO ₄] ⁵⁻	[B ₅ O ₁₀ F ₂] ⁷⁻	$[B_5O_8F_2]^{3-}$ layer
$BaB_4O_6F_2{}^{19}$	[BO ₃] ³⁻ , [BO ₃ F] ⁴⁻	$[B_4O_8F_2]^{6-1}$	$[B_4O_6F_2]^{2-}$ layer
BaBOF ₃ ²⁰	[BOF ₃] ²⁻	[BOF ₃] ²⁻	[BOF ₃] ²⁻ cluster
BiB ₂ O ₄ F ²¹	[BO ₃ F] ⁴⁻ , [BO ₄] ⁵⁻	$[B_2O_6F]^{7-1}$	$[B_2O_4F]^{3-}$ chain

Table S1. The investigation of anionic groups of the reported fluoroxoborates.

Empirical formula	BaBOF ₃	
Formula weight	221.15	
Temperature	296(2) K	
Crystal system	Monoclinic	
Space group, Z	<i>P2₁/c</i> (No.14), 4	
	<i>a</i> = 4.6196(19) Å	
Unit cell dimensions	<i>b</i> = 15.186(6) Å	
	<i>c</i> = 4.4257(18) Å	
	<i>b</i> = 92.045(4) °	
Volume	310.3(2) Å ³	
Absorption coefficient	12.690 mm ⁻¹	
F(000)	384	
Crystal size	0.162 mm × 0.108 mm × 0.039 mm	
The range for data collection	2.68 - 27.55 °	
R(int)	0.0313	
Completeness	98.3 %	
Data / restraints / parameters	701 / 0 / 55	
GOF on <i>F</i> ²	0.997	
Final R indices $[F_o^2 > 2\sigma(F_o^2)]^a$	$R_1 = 0.0264$	
	$wR_2 = 0.0608$	
<i>R</i> indices (all data) ^{<i>a</i>}	$R_1 = 0.0352$	
	$wR_2 = 0.0657$	
Largest diff peak and hole	1.670 and -1.034 e∙Å ⁻³	

Table S2. Crystal data and structure refinement for BaBOF₃.

 ${}^{a}R_{1} = \mathbf{\Sigma} ||F_{o}| - |F_{c}||/\mathbf{\Sigma}|F_{o}| \text{ and } wR_{2} = [\mathbf{\Sigma}w(F_{o}{}^{2} - F_{c}{}^{2})^{2}/\mathbf{\Sigma}wF_{o}{}^{4}]^{1/2} \text{ for } F_{o}{}^{2} > 2\sigma (F_{o}{}^{2}).$

Atoms	x/a	y/b	z/c	U _{eq}
Ba1	2641(1)	9071(1)	2425(1)	10(1)
B1	7793(15)	7088(5)	1884(15)	13(2)
01	7042(9)	7819(3)	3720(9)	14(1)
F1	901(8)	8060(3)	-2727(8)	20(1)
F2	6550(9)	6289(3)	2837(8)	21(1)
F3	2359(7)	10037(3)	-2585(6)	14(1)

Table S3. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for BaBOF₃. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Ba1-F3	2.658(3)	B1-F2	1.413(8)
Ba1-F3 ^{#1}	2.659(3)	B1-O1	1.426(8)
Ba1-F3 ^{#2}	2.676(4)	B1-O1 ^{#4}	1.438(8)
Ba1-F3 ^{#3}	2.681(4)	B1-F1 ^{#8}	1.457(7)
Ba1-F1 ^{#1}	2.780(4)	F2-B1-O1	112.9(5)
Ba1-F2 ^{#4}	2.818(4)	F2-B1-O1 ^{#4}	106.8(5)
Ba1-O1	2.827(4)	O1-B1-O1 ^{#4}	115.0(5)
Ba1-F1	2.841(4)	F2-B1-F1 ^{#8}	104.0(5)
Ba1-F2 ^{#5}	2.998(4)	O1-B1-F1 ^{#8}	108.1(5)
Ba1-O1 ^{#6}	3.277(5)	O1 ^{#4} -B1-F1 ^{#8}	109.4(5)

Table S4. Bond lengths (Å) and angles (deg.) for $BaBOF_3$.

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z+1	#2 -x+1, -y+2, -z	#3 -x, -y+2, -z
#4 x, -γ+3/2, z-1/2	#5 x, -y+3/2, z+1/2	#6 x-1, y, z
#7 -x+1, -y+2, -z+1	#8 x+1, -y+3/2, z+1/2	#9 x+1, y, z
#10 x-1, -y+3/2, z-1/2	#11 x, y, z-1	



Figure S1. The coordination environments of the Ba^{2+} cation in $BaBOF_3$.





Figure S3. (a) The SEM image and (b) the Energy dispersive X-ray spectrum (EDX) for BaBOF₃. The EDX spectrum was performed to verify the absence or presence of the F and O atoms.



(a)



(b)

Figure S4. Experimental and calculated powder X-ray diffraction patterns of the title compound. The peaks of BaF_2 were marked by red triangles.



Figure S5. The UV-VIS diffuse reflectance spectrum of BaBOF₃.



Figure S6. (a) Calculated band structures of $BaBOF_3$, (b) the total and partial density of states of $BaBOF_3$.



References

- 1. SAINT, version 7.60A, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2008.
- 2. G. M. Sheldrick, Acta Cryst. A, 2008, 64, 112.
- 3. A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.
- 4. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, Z. *Kristallogr.*, 2005, **220**, 567.
- 5. L. Kleinman and D. M. Bylander, Phys. Rev. Lett., 1982, 48, 1425.
- 6. A. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B*, 1990, **41**, 1227.
- 7. J. S. Lin, A. Qteish, M. C. Payne and V. Heine, Phys. Rev. B, 1993, 47, 4174.
- 8. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.
- 9. G. Cakmak, J. Nuss and M. Jansen, Z. Anorg. Allg. Chem., 2009, 635, 631.
- 10. T. Pilz and M. Jansen, Z. Anorg. Allg. Chem., 2011, 637, 1.
- 11. T. Pilz, H. Nuss and M. Jansen, J. Solid State Chem., 2012, 186, 104.
- 12. G. Q. Shi, F. F. Zhang, B. B. Zhang, D. W. Hou, X. L. Chen, Z. H. Yang and S. L. Pan, *Inorg. Chem.*, 2017, **56**, 344.
- 13. G. Cakmak, T. Pilz and M. Jansen, Z. Anorg. Allg. Chem., 2012, 638, 1411.
- 14. H. P. Wu, H. W. Yu, Q. Bian, Z. H. Yang, S. J. Han and S. L. Pan, Inorg. Chem., 2014, 53, 12686.
- 15. G. Q. Shi, Y. Wang, F. F. Zhang, B. B. Zhang, Z. H. Yang, X. L. Hou, S. L. Pan and K. R. Poeppelmeier, *J. Am. Chem. Soc.*, 2017, **139**, 10645.
- 16. Y. Wang, B. B. Zhang, Z. H. Yang and S. L. Pan, *Angew. Chem. Int. Ed.*, 2017, DOI: 10.1002/anie.201712168.
- 17. X. F. Wang, Y. Wang, B. B. Zhang, F. F. Zhang, Z. H. Yang and S. L. Pan, *Angew. Chem. Int. Ed.*, 2017, **56**, 14119.
- 18. S. J. Han, Y. Wang, B. B. Zhang, Z. H. Yang and S. L. Pan, *Inorg. Chem.*, 2018, **57**, 873.
- 19. S. G. Jantz, F. Pielnhofer, L. van Wüllen, R. Weihrich, M. J. Schäfer and H. A. Höppe, *Chem. Eur. J.*, 2018, **24**, 443.
- 20. D. M. Chackraburtty, Acta Cryst., 1957, 10, 199.
- 21. R. H. Cong, Y. Wang, L. Kang, Z. Y. Zhou, Z. S. Lin and T. Yang, *Inorg. Chem. Front.*, 2015, **2**, 170.