Electronic Supplementary Information

$Ba_2B_7O_{12}F$ with Novel FBB [$B_7O_{16}F$] and Deep-ultraviolet Cutoff Edge

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Content

Experimental Section

Reagents BaF_2 (Shanghai Aladdin Reagent Co., Ltd., 98.0%), CsF (Shanghai Aladdin Reagent Co., Ltd., 98.0%), H_3BO_3 (Tianjin Bodi Chemical Co., Ltd., Ltd., 99.5%) were selected to obtain target product.

Crystal Synthesis Single crystal of $Ba_2B_7O_{12}F$ was obtained by high-temperature solution method. Mixtures of BaF_2, CsF and H_3BO_3 in a molar ratio of 1: 2: 9 with total weight of 3.5 g were prepared in a platinum (Pt) crucible, which was put into a programmable temperature furnace. It was preheated to 200 °C within 1 h, and kept at this temperature for 4 h to ensure H_3BO_3 decompose completely. Then, it was heated to 700 °C for 5 h and kept at this temperature for 12 h to ensure the mixtures melt entirely. Then the solution was cooled to 670 °C for 25 minutes and kept at this temperature for 2 h, then cooled to 450 °C at the rate of 1 °C·h^{-1}. Finally, the furnace was turned off and cooled to room temperature. Transparent and colorless $Ba_2B_7O_{12}F$ crystals were obtained.

Solid-State Synthesis The $Ba_2B_7O_{12}F$ polycrystalline was obtained by solid-state reaction techniques. Mixtures of BaF_2 and H_3BO_3 in a molar ratio of 2: 7 with total weight of 6 g were ground thoroughly and put into a corundum crucible. First, the mixtures were heated to 200 °C and kept at this temperature for 24 h to make sure H_3BO_3 decompose into H_2O and B_2O_3 completely. Then, with several intermediate grindings, the pre-sintered mixtures were heated slowly to 700 °C and held at this temperature for 24 h to ensure that the reaction was complete. Finally, the purity of the sample was confirmed by powder XRD.

Single-Crystal X-ray Diffraction The crystal of $Ba_2B_7O_{12}F$ with dimensions 0.098 × 0.085 × 0.068 mm^3 was filtered to determine the structure. The structure was observed by single-crystal X-ray diffraction on an APEX II CCD diffractometer using monochromatic Mo Kα radiation (λ = 0.71073 Å) at 296(2) K and integrated with the SAINT program.[1] The full-matrix least-squares method in the SHELXL-97 systems was used to refine the structures and final least-squares refinement was on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$.[2] The missing symmetry elements of the structures were verified with PLATON.[3] Relevant crystallographic data and structure refinement information are displayed in Table S1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table S2. Interatomic bond lengths and angles are given in Table S3.

Powder X-ray Diffraction PXRD patterns were taken on an automated Bruker D2 X-ray

diffractometer equipped with a Cu Kα radiation source (λ = 1.5418 Å, T = 296 K). The scanning over the range of 2ϑ = 10~70°. The step width of 2ϑ was 0.01 ° and a fixed counting time was 0.5 s/step.

IR Spectrum Infrared spectrum was carried out on a Shimadzu IR Affinity-1 Fourier transform Infrared spectrometer. And the wavelength ranges from 400 to 4000 cm^{-1}. The test was carried out by thoroughly mixing sample and dried KBr (5 mg of the sample and 500 mg of KBr).

UV-Vis-NIR Diffuse Reflectance Spectroscopy The UV-Vis-NIR Diffuse Reflectance spectrum of $Ba_2B_7O_{12}F$ powder sample was measured on the SolidSpec-3700DUV spectrophotometer at room temperature with scanning wavelength over the range of 190 to 2600 nm. The absorption date was obtained by the Kubelka-Munk function: $F(R)=(1-R)^2/2R=K/S$, where R is the reflectance, K is the absorption, and S is the scattering.

The Energy Dispersive X-ray Spectroscope Elemental analysis of $Ba_2B_7O_{12}F$ was performed on a clean single crystal surface 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).

Thermal Analysis The thermogravimetry and differential scanning calorimetry (TG-DSC) for $Ba_2B_7O_{12}F$ was implemented on a NETZSCH STA 449 F3 simultaneous thermal analyzer with over the range of 40 to 1000 °C at a speed of 5 °C·min^{-1} under flowing nitrogen. To further verify the thermal behaviors of $Ba_2B_7O_{12}F$. The pure solid sample was put into a small platinum Pt crucible and heated from room temperature (RT) to 950 °C until it melted transparently. Then it was slowly cooled down to RT. The powder XRD analysis result shown in Figure S5b reveals that the residual is not the initial compound, which suggests that $Ba_2B_7O_{12}F$ is an incongruent melting compound.

Theoretical Calculations Based on the density functional theory (DFT), electronic-structure and optical property calculations were implemented in the CASTEP package.[4] For embodying correlation, core-electron interactions were characterized by norm-conserving pseudopotentials (NCP). Meanwhile the generalized gradient approximation (GGA) of Perdew-Buker-Ernzerhof (PBE) was exerted.[5-7] Then geometry optimization $Ba_2B_7O_{12}F$ in unit cell was performed with a good converged criterion which was fixed to the origin structure. The value of plane-wave basis cutoff energy 850 eV and 3 × 2 × 1 Monkhorst-Pack k-point meshes were carried out in calculation.[8]

Table S1 Crystal data and structure refinement for $Ba_2B_7O_{12}F$.

Empirical formula	$Ba_2B_7O_{12}F$
Formula weight	561.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	*a* = 9.328(3) Å
	b = 10.910(3) Å, *β* = 100.136(4)°
	c = 18.817(6) Å
Volume	1885.1(10) Å^3
Z, Calculated density	8, 3.956 Mg/m^3
Absorption coefficient	8.397 mm^{-1}
F(000)	2016
Crystal size	0.098 × 0.085 × 0.068 mm^3
Theta range for data collection	2.199 to 27.516°
Limiting indices	$-12 \le h \le 9$, $-13 \le k \le 14$, $-24 \le l \le 24$
Reflections collected / unique	5729 / 2166 [R_{int} = 0.0357]
Completeness to theta = 27.516°	99.90%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2166 / 24 / 201
Goodness-of-fit on F^2	1.015
Final *R* indices [I>2sigma(I)][a]	R_1 = 0.0255, wR_2 = 0.0507
R indices (all data)[a]	R_1 = 0.0321, wR_2 = 0.0531
Extinction coefficient	0.00068(4)
Largest diff. peak and hole	1.093 and -1.058 e·Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2 Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) and bond valence sums (BVS) for $Ba_2B_7O_{12}F$.

	x	y	z	U(eq)	BVS
Ba(1)	0	5358(1)	2500	10(1)	2.03
Ba(2)	-97(1)	12126(1)	256(1)	9(1)	2.103
Ba(3)	0	9880(1)	2500	12(1)	1.981
B(1)	2152(6)	5327(5)	4359(3)	7(1)	3.026
B(2)	1446(6)	7524(5)	3806(3)	6(1)	2.991
B(3)	-1863(6)	9618(4)	706(3)	3(1)	3.017
B(4)	600(6)	4993(5)	785(3)	6(1)	3.071
B(5)	2489(6)	3720(5)	3446(3)	5(1)	3.026
B(6)	-2664(6)	7429(5)	2326(3)	6(1)	3.08
B(7)	-2569(6)	11462(5)	1409(3)	8(1)	3.058
O(1)	-1504(3)	10677(3)	1166(2)	7(1)	2.122
O(2)	-2442(4)	12724(3)	1115(2)	9(1)	1.953
O(3)	2591(4)	8609(3)	2290(2)	11(1)	2.121
O(4)	1457(4)	7371(3)	3077(2)	8(1)	2.161
O(5)	904(4)	6091(3)	1114(2)	12(1)	1.998
O(6)	2548(4)	4903(3)	3671(2)	8(1)	1.938
O(7)	817(4)	4645(3)	4442(2)	8(1)	1.929
O(8)	1954(3)	6677(3)	4315(2)	7(1)	2.052
O(9)	838(3)	8593(3)	4009(2)	7(1)	2.044
O(10)	3309(3)	5074(3)	4963(2)	5(1)	2.012
O(11)	-3338(3)	9156(3)	734(2)	7(1)	2.021
O(12)	-2619(4)	6413(3)	2809(2)	9(1)	2.151
F(1)	963(3)	12398(3)	1830(2)	16(1)	0.875

Table S3 Bond lengths [Å] and angles [°] for $Ba_2B_7O_{12}F$.

Ba(1)-O(4)#1	2.707(3)	O(1)-Ba(2)-O(2)	48.36(8)
Ba(1)-O(4)	2.707(3)	O(10)#6-Ba(2)-O(2)	83.21(9)
Ba(1)-O(12)	2.852(3)	O(10)#7-Ba(2)-O(2)	137.98(8)
Ba(1)-O(12)#1	2.852(3)	O(7)#8-Ba(2)-O(2)	58.41(8)
Ba(1)-O(3)#2	2.922(3)	O(8)#7-Ba(2)-O(2)	132.22(9)
Ba(1)-O(3)#3	2.922(3)	F(1)-Ba(2)-O(2)	65.70(9)
Ba(1)-O(6)#1	2.985(3)	O(9)#4-Ba(2)-O(8)#4	46.94(8)
Ba(1)-O(6)	2.985(3)	O(11)#5-Ba(2)-O(8)#4	57.89(8)
Ba(1)-O(5)#1	2.988(3)	O(1)-Ba(2)-O(8)#4	168.30(9)
Ba(1)-O(5)	2.988(3)	O(10)#6-Ba(2)-O(8)#4	126.87(8)
Ba(2)-O(9)#4	2.758(3)	O(10)#7-Ba(2)-O(8)#4	79.31(8)
Ba(2)-O(11)#5	2.808(3)	O(7)#8-Ba(2)-O(8)#4	84.29(8)
Ba(2)-O(1)	2.818(3)	O(8)#7-Ba(2)-O(8)#4	62.84(10)
Ba(2)-O(10)#6	2.826(3)	F(1)-Ba(2)-O(8)#4	113.31(8)
Ba(2)-O(10)#7	2.864(3)	O(2)-Ba(2)-O(8)#4	142.32(8)
Ba(2)-O(7)#8	2.908(3)	O(9)#4-Ba(2)-O(2)#9	67.07(9)
Ba(2)-O(8)#7	2.941(3)	O(11)#5-Ba(2)-O(2)#9	121.53(8)
Ba(2)-F(1)	2.966(3)	O(1)-Ba(2)-O(2)#9	100.19(9)
Ba(2)-O(2)	3.012(3)	O(10)#6-Ba(2)-O(2)#9	66.46(8)
Ba(2)-O(8)#4	3.114(3)	O(10)#7-Ba(2)-O(2)#9	106.38(8)
Ba(2)-O(2)#9	3.142(3)	O(7)#8-Ba(2)-O(2)#9	87.16(8)
Ba(2)-O(5)#10	3.212(3)	O(8)#7-Ba(2)-O(2)#9	141.51(8)
Ba(3)-O(12)#5	2.760(3)	F(1)-Ba(2)-O(2)#9	151.82(9)
Ba(3)-O(12)#11	2.760(3)	O(2)-Ba(2)-O(2)#9	86.26(9)
Ba(3)-O(1)#1	2.791(3)	O(8)#4-Ba(2)-O(2)#9	86.79(8)
Ba(3)-O(1)	2.791(3)	O(9)#4-Ba(2)-O(5)#10	63.47(8)
Ba(3)-O(3)	2.873(3)	O(11)#5-Ba(2)-O(5)#10	79.67(9)
Ba(3)-O(3)#1	2.873(3)	O(1)-Ba(2)-O(5)#10	139.35(9)
Ba(3)-O(9)	3.140(3)	O(10)#6-Ba(2)-O(5)#10	108.44(8)
Ba(3)-O(9)#1	3.140(3)	O(10)#7-Ba(2)-O(5)#10	114.70(8)
Ba(3)-O(4)	3.162(3)	O(7)#8-Ba(2)-O(5)#10	63.57(8)
Ba(3)-O(4)#1	3.162(3)	O(8)#7-Ba(2)-O(5)#10	113.75(8)
Ba(3)-F(1)	3.216(3)	F(1)-Ba(2)-O(5)#10	136.94(8)
Ba(3)-F(1)#1	3.216(3)	O(2)-Ba(2)-O(5)#10	102.11(9)
B(1)-O(10)	1.449(6)	O(8)#4-Ba(2)-O(5)#10	50.95(8)
B(1)-O(6)	1.481(6)	O(2)#9-Ba(2)-O(5)#10	43.50(8)
B(1)-O(7)	1.483(6)	O(12)#5-Ba(3)-O(12)#11	105.35(13)
B(1)-O(8)	1.485(6)	O(12)#5-Ba(3)-O(1)#1	50.44(9)
B(2)-O(8)	1.356(6)	O(12)#11-Ba(3)-O(1)#1	105.02(9)
B(2)-O(9)	1.379(6)	O(12)#5-Ba(3)-O(1)	105.02(9)
B(2)-O(4)	1.383(6)	O(12)#11-Ba(3)-O(1)	50.44(9)
B(3)-O(1)	1.447(6)	O(1)#1-Ba(3)-O(1)	143.69(12)
B(3)-O(10)#6	1.473(6)	O(12)#5-Ba(3)-O(3)	69.90(9)

B(3)-O(11)	1.476(6)	O(12)#11-Ba(3)-O(3)	158.25(9)
B(3)-O(9)#1	1.508(6)	O(1)#1-Ba(3)-O(3)	88.41(9)
B(4)-O(5)	1.356(6)	O(1)-Ba(3)-O(3)	109.18(9)
B(4)-O(11)#12	1.363(6)	O(12)#5-Ba(3)-O(3)#1	158.25(9)
B(4)-O(7)#1	1.369(6)	O(12)#11-Ba(3)-O(3)#1	69.90(9)
B(5)-O(6)	1.356(6)	O(1)#1-Ba(3)-O(3)#1	109.17(9)
B(5)-O(2)#13	1.370(6)	O(1)-Ba(3)-O(3)#1	88.41(9)
B(5)-O(3)#3	1.380(6)	O(3)-Ba(3)-O(3)#1	122.29(12)
B(6)-O(12)	1.429(6)	O(12)#5-Ba(3)-O(9)	91.00(8)
B(6)-F(1)#2	1.447(6)	O(12)#11-Ba(3)-O(9)	121.65(8)
B(6)-O(4)#1	1.465(6)	O(1)#1-Ba(3)-O(9)	47.17(8)
B(6)-O(3)#1	1.472(6)	O(1)-Ba(3)-O(9)	163.42(9)
B(7)-O(1)	1.446(6)	O(3)-Ba(3)-O(9)	80.03(8)
B(7)-O(12)#11	1.452(6)	O(3)#1-Ba(3)-O(9)	75.02(9)
B(7)-O(5)#14	1.490(6)	O(12)#5-Ba(3)-O(9)#1	121.65(8)
B(7)-O(2)	1.496(6)	O(12)#11-Ba(3)-O(9)#1	91.00(8)
O(4)#1-Ba(1)-O(4)	71.59(14)	O(1)#1-Ba(3)-O(9)#1	163.42(9)
O(4)#1-Ba(1)-O(12)	50.71(9)	O(1)-Ba(3)-O(9)#1	47.17(8)
O(4)-Ba(1)-O(12)	88.75(10)	O(3)-Ba(3)-O(9)#1	75.02(9)
O(4)#1-Ba(1)-O(12)#1	88.75(10)	O(3)#1-Ba(3)-O(9)#1	80.03(8)
O(4)-Ba(1)-O(12)#1	50.71(9)	O(9)-Ba(3)-O(9)#1	126.89(11)
O(12)-Ba(1)-O(12)#1	132.37(12)	O(12)#5-Ba(3)-O(4)	99.86(9)
O(4)#1-Ba(1)-O(3)#2	98.95(10)	O(12)#11-Ba(3)-O(4)	151.46(9)
O(4)-Ba(1)-O(3)#2	154.68(9)	O(1)#1-Ba(3)-O(4)	80.97(9)
O(12)-Ba(1)-O(3)#2	67.98(9)	O(1)-Ba(3)-O(4)	134.13(8)
O(12)#1-Ba(1)-O(3)#2	154.47(8)	O(3)-Ba(3)-O(4)	46.25(8)
O(4)#1-Ba(1)-O(3)#3	154.68(9)	O(3)#1-Ba(3)-O(4)	81.72(9)
O(4)-Ba(1)-O(3)#3	98.95(10)	O(9)-Ba(3)-O(4)	43.85(8)
O(12)-Ba(1)-O(3)#3	154.47(8)	O(9)#1-Ba(3)-O(4)	86.97(8)
O(12)#1-Ba(1)-O(3)#3	67.98(9)	O(12)#5-Ba(3)-O(4)#1	151.46(9)
O(3)#2-Ba(1)-O(3)#3	98.44(13)	O(12)#11-Ba(3)-O(4)#1	99.86(9)
O(4)#1-Ba(1)-O(6)#1	63.92(9)	O(1)#1-Ba(3)-O(4)#1	134.13(8)
O(4)-Ba(1)-O(6)#1	135.20(9)	O(1)-Ba(3)-O(4)#1	80.97(9)
O(12)-Ba(1)-O(6)#1	67.55(9)	O(3)-Ba(3)-O(4)#1	81.72(9)
O(12)#1-Ba(1)-O(6)#1	121.08(8)	O(3)#1-Ba(3)-O(4)#1	46.25(8)
O(3)#2-Ba(1)-O(6)#1	45.39(8)	O(9)-Ba(3)-O(4)#1	86.97(8)
O(3)#3-Ba(1)-O(6)#1	119.00(9)	O(9)#1-Ba(3)-O(4)#1	43.85(8)
O(4)#1-Ba(1)-O(6)	135.20(9)	O(4)-Ba(3)-O(4)#1	60.10(12)
O(4)-Ba(1)-O(6)	63.92(9)	O(12)#5-Ba(3)-F(1)	45.16(8)
O(12)-Ba(1)-O(6)	121.08(8)	O(12)#11-Ba(3)-F(1)	70.69(9)
O(12)#1-Ba(1)-O(6)	67.55(9)	O(1)#1-Ba(3)-F(1)	87.47(8)
O(3)#2-Ba(1)-O(6)	119.00(9)	O(1)-Ba(3)-F(1)	60.78(8)
O(3)#3-Ba(1)-O(6)	45.39(8)	O(3)-Ba(3)-F(1)	93.36(8)
O(6)#1-Ba(1)-O(6)	160.84(12)	O(3)#1-Ba(3)-F(1)	139.98(8)

O(4)#1-Ba(1)-O(5)#1	86.22(9)	O(9)-Ba(3)-F(1)	133.96(8)
O(4)-Ba(1)-O(5)#1	68.37(9)	O(9)#1-Ba(3)-F(1)	93.99(7)
O(12)-Ba(1)-O(5)#1	47.96(9)	O(4)-Ba(3)-F(1)	137.85(8)
O(12)#1-Ba(1)-O(5)#1	116.96(9)	O(4)#1-Ba(3)-F(1)	137.52(8)
O(3)#2-Ba(1)-O(5)#1	87.96(9)	O(12)#5-Ba(3)-F(1)#1	70.69(9)
O(3)#3-Ba(1)-O(5)#1	112.68(8)	O(12)#11-Ba(3)-F(1)#1	45.16(8)
O(6)#1-Ba(1)-O(5)#1	112.24(9)	O(1)#1-Ba(3)-F(1)#1	60.78(8)
O(6)-Ba(1)-O(5)#1	73.18(9)	O(1)-Ba(3)-F(1)#1	87.47(8)
O(4)#1-Ba(1)-O(5)	68.37(9)	O(3)-Ba(3)-F(1)#1	139.98(8)
O(4)-Ba(1)-O(5)	86.22(9)	O(3)#1-Ba(3)-F(1)#1	93.36(8)
O(12)-Ba(1)-O(5)	116.96(9)	O(9)-Ba(3)-F(1)#1	93.99(7)
O(12)#1-Ba(1)-O(5)	47.96(9)	O(9)#1-Ba(3)-F(1)#1	133.96(8)
O(3)#2-Ba(1)-O(5)	112.68(8)	O(4)-Ba(3)-F(1)#1	137.52(8)
O(3)#3-Ba(1)-O(5)	87.96(9)	O(4)#1-Ba(3)-F(1)#1	137.85(8)
O(6)#1-Ba(1)-O(5)	73.18(9)	F(1)-Ba(3)-F(1)#1	62.65(11)
O(6)-Ba(1)-O(5)	112.24(9)	O(10)-B(1)-O(6)	111.1(4)
O(5)#1-Ba(1)-O(5)	148.92(12)	O(10)-B(1)-O(7)	110.2(4)
O(9)#4-Ba(2)-O(11)#5	104.03(9)	O(6)-B(1)-O(7)	106.2(4)
O(9)#4-Ba(2)-O(1)	127.46(9)	O(10)-B(1)-O(8)	107.5(4)
O(11)#5-Ba(2)-O(1)	123.81(9)	O(6)-B(1)-O(8)	108.0(4)
O(9)#4-Ba(2)-O(10)#6	80.01(9)	O(7)-B(1)-O(8)	113.9(4)
O(11)#5-Ba(2)-O(10)#6	171.89(9)	O(8)-B(2)-O(9)	119.4(4)
O(1)-Ba(2)-O(10)#6	49.97(9)	O(8)-B(2)-O(4)	123.7(4)
O(9)#4-Ba(2)-O(10)#7	51.39(8)	O(9)-B(2)-O(4)	116.9(4)
O(11)#5-Ba(2)-O(10)#7	109.92(9)	O(1)-B(3)-O(10)#6	109.5(4)
O(1)-Ba(2)-O(10)#7	89.66(9)	O(1)-B(3)-O(11)	111.7(4)
O(10)#6-Ba(2)-O(10)#7	66.91(11)	O(10)#6-B(3)-O(11)	111.7(4)
O(9)#4-Ba(2)-O(7)#8	123.58(8)	O(1)-B(3)-O(9)#1	108.3(4)
O(11)#5-Ba(2)-O(7)#8	48.25(9)	O(10)#6-B(3)-O(9)#1	109.8(4)
O(1)-Ba(2)-O(7)#8	105.28(9)	O(11)-B(3)-O(9)#1	105.7(3)
O(10)#6-Ba(2)-O(7)#8	135.14(9)	O(5)-B(4)-O(11)#12	121.9(5)
O(10)#7-Ba(2)-O(7)#8	157.95(9)	O(5)-B(4)-O(7)#1	120.1(4)
O(9)#4-Ba(2)-O(8)#7	74.75(9)	O(11)#12-B(4)-O(7)#1	117.7(4)
O(11)#5-Ba(2)-O(8)#7	63.00(9)	O(6)-B(5)-O(2)#13	124.8(4)
O(1)-Ba(2)-O(8)#7	106.75(9)	O(6)-B(5)-O(3)#3	112.9(4)
O(10)#6-Ba(2)-O(8)#7	112.14(9)	O(2)#13-B(5)-O(3)#3	122.2(4)
O(10)#7-Ba(2)-O(8)#7	48.08(9)	O(12)-B(6)-F(1)#2	108.4(4)
O(7)#8-Ba(2)-O(8)#7	110.93(9)	O(12)-B(6)-O(4)#1	110.9(4)
O(9)#4-Ba(2)-F(1)	141.11(9)	F(1)#2-B(6)-O(4)#1	109.8(4)
O(11)#5-Ba(2)-F(1)	61.87(8)	O(12)-B(6)-O(3)#1	111.8(4)
O(1)-Ba(2)-F(1)	63.83(8)	F(1)#2-B(6)-O(3)#1	107.2(4)
O(10)#6-Ba(2)-F(1)	110.57(8)	O(4)#1-B(6)-O(3)#1	108.6(4)
O(10)#7-Ba(2)-F(1)	97.00(8)	O(1)-B(7)-O(12)#11	109.4(4)
O(7)#8-Ba(2)-F(1)	76.04(8)	O(1)-B(7)-O(5)#14	112.8(4)

O(8)#7-Ba(2)-F(1)	66.56(8)	O(12)#11-B(7)-O(5)#14	107.7(4)
O(9)#4-Ba(2)-O(2)	152.47(9)	O(1)-B(7)-O(2)	109.0(4)
O(11)#5-Ba(2)-O(2)	95.50(9)	O(12)#11-B(7)-O(2)	113.8(4)
		O(5)#14-B(7)-O(2)	104.2(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2	#2 x-1/2,y-1/2,z	#3 -x+1/2,y-1/2,-z+1/2
#4 x,-y+2,z-1/2	#5 x+1/2,y+1/2,z	#6 x-1/2,-y+3/2,z-1/2
#7 -x+1/2,y+1/2,-z+1/2	#8 -x,y+1,-z+1/2	#9 -x-1/2,-y+5/2,-z
#10 -x,-y+2,-z	#11 -x-1/2,y+1/2,-z+1/2	#12 x+1/2,y-1/2,z
#13 -x,y-1,-z+1/2	#14 x-1/2,y+1/2,z	#15 x,-y+2,z+1/2
#16 x,y-1,z	#17 x+1/2,-y+3/2,z+1/2	#18 -x-1/2,y-1/2,-z+1/2

Table S4 The summary of published fluorooxoborates.

No.	Compounds	Space Group	FBB	No.	Compounds	Space Group	FBB
1	$BaBOF_3$[9]	$P2_1/c$	BO_2F_2	23	$CsKB_8O_{12}F_2$[10]	$P321$	B_4O_8F
2	$SnB_2O_3F_2$[11]	$P31m$	$B_2O_5F_2$	24	$CsRbB_8O_{12}F_2$[10]	$P\bar{6}2c$	B_4O_8F
3	$PbB_2O_3F_2$[12]	$P31m$	$B_2O_5F_2$	25	$SrB_4O_6F_2$[13]	$P\bar{1}$	$B_4O_8F_2$
4	$BaB_2O_3F_2$[14]	$P2_1$	B_2O_6F	26	$CaB_4O_6F_2$[13]	$P\bar{1}$	$B_4O_8F_2$
5	BiB_2O_4F[15, 16]	$P32$	B_2O_6F	27	$BaB_4O_6F_2$[17]	$P2_1/c$	$B_4O_8F_2$
6	$Ba[B_2OF_3(OH)_2]_2$[18]	$C2/m$	$B_2OF_3(OH)_2$	28	$KNiB_4O_6F_3$[19]	$P2_1/c$	$B_4O_9F_3$
7	$Cs_{1.29}Rb1.71B_3O_3F_6$[20]	$P2_1/c$	$B_3O_3F_6$	29	$CaB_5O_7F_3$[21]	$Cmc2_1$	$B_5O_9F_3$
8	$Na_{0.76}Rb_{2.24}B_3O_3F_6$[20]	$P2_1/c$	$B_3O_3F_6$	30	$PbB_5O_7F_3$[22]	$Cmc2_1$	$B_5O_9F_3$
9	$K_{2.64}Cs_{0.36}B_3O_3F_6$[20]	$P2_1/c$	$B_3O_3F_6$	31	$SrB_5O_7F_3$[23]	$Cmc2_1$	$B_5O_9F_3$
10	$K_{1.66}Rb_{1.34}B_3O_3F_6$[20]	$P2_1/c$	$B_3O_3F_6$	32	PbB_5O_8F[24]	$Pbca$	$B_5O_{10}F$
11	$K_{0.42}Rb_{2.58}B_3O_3F_6$[25]	$Pbcn$	$B_3O_3F_6$	33	$BaB_5O_8F{\cdot}xH_2O$[26]	$Pbca$	$B_5O_{10}F$
12	$KCs_2B_3O_3F_6$[20]	$P2_1/c$	$B_3O_3F_6$	34	$Li_2Na_{0.9}K_{0.1}B_5O_8F_2$[27]	$Pbcn$	$B_5O_{10}F_2$
13	$K_2RbB_3O_3F_6$[20]	$Pbcn$	$B_3O_3F_6$	35	LiB_6O_9F[28]	$Pna2_1$	$B_6O_{11}F$
14	$Rb_3B_3O_3F_6$[20]	$P2_1/c$	$B_3O_3F_6$	36	$Li_2B_6O_9F_2$[29]	Cc	$B_6O_{11}F_2$
15	$Na_3B_3O_3F_6$[30]	$C2/c$	$B_3O_3F_6$	37	$Na_2B_6O_9F_2$[31]	$P2_1/c$	$B_6O_{11}F_2$
16	$K_3B_3O_3F_6$[32]	$P2_1/c$	$B_3O_3F_6$	38	$NaRbB_6O_9F_2$[33]	$P2_1/c$	$B_6O_{11}F_2$
17	$Li_2B_3O_4F_3$[34]	$P2_12_12_1$	$B_3O_5F_3$	39	$K_3B_6O_9F_3$[35]	$P21/c$	$B_6O_{11}F_3$
18	NaB_4O_6F[36]	$C2$	B_4O_8F	40	$Na_3B_7O_{11}F_2$[37]	$Pnma$	$B_7O_{13}F_2$
19	$NH_4B_4O_6F$[38]	$Pna2_1$	B_4O_8F	41	$K_{10}B_{13}O_{15}F_{19}$[39]	$R3m$	$B_{10}O_{12}F_{13}$
20	CsB_4O_6F[40]	$Pna2_1$	B_4O_8F	42	$Rb_{10}B_{13}O_{15}F_{19}$[39]	$R3m$	$B_{10}O_{12}F_{13}$
21	$BaB_8O_{12}F_2$[41]	$R3c$	B_4O_8F	43	$Ba_3B_{10}O_{17}F_2{\cdot}0.1KF$[42]	$P\bar{1}$	$B_{10}O_{21}F$
22	RbB_4O_6F[10]	$Pna2_1$	B_4O_8F				

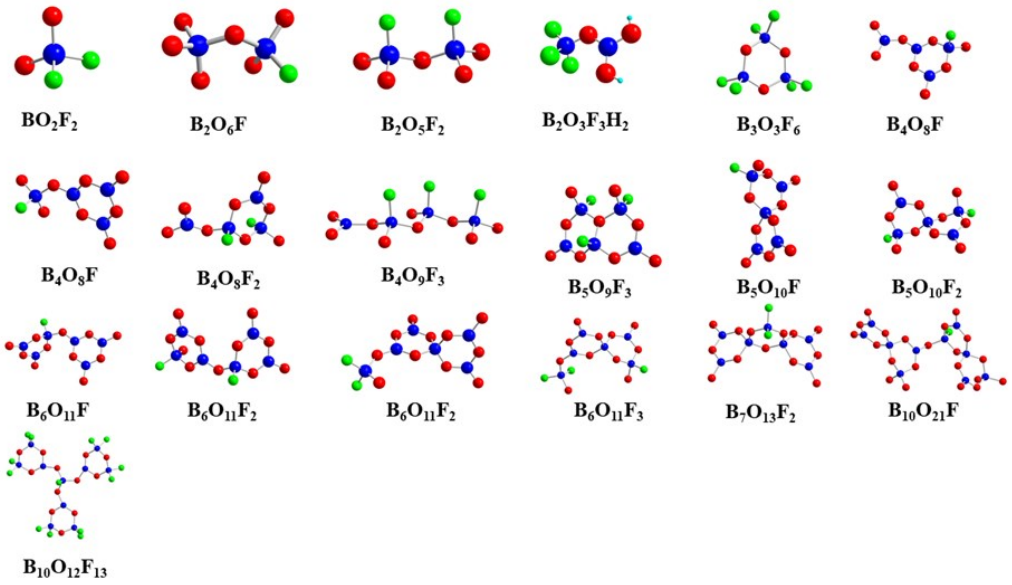

Figure S1. The different types of FBBs in published fluorooxoborates.

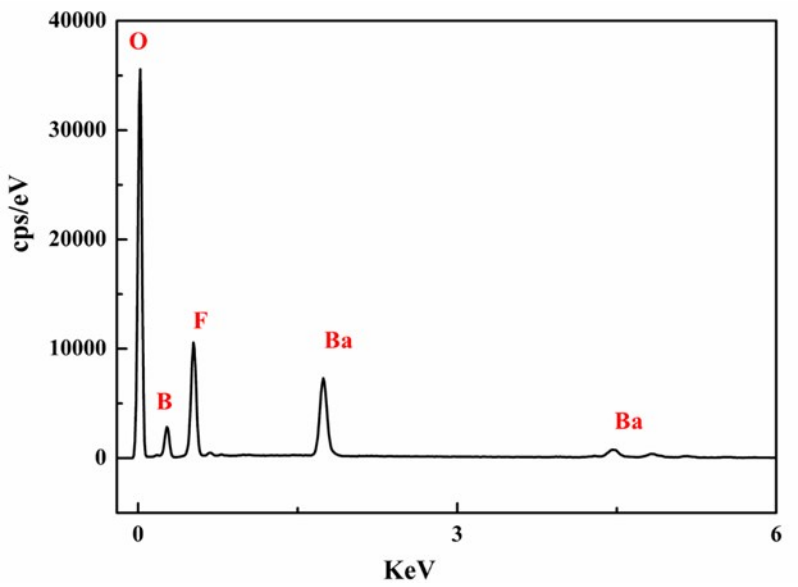

Figure S2. The energy dispersive X-ray spectrum for $Ba_2B_7O_{12}F$.

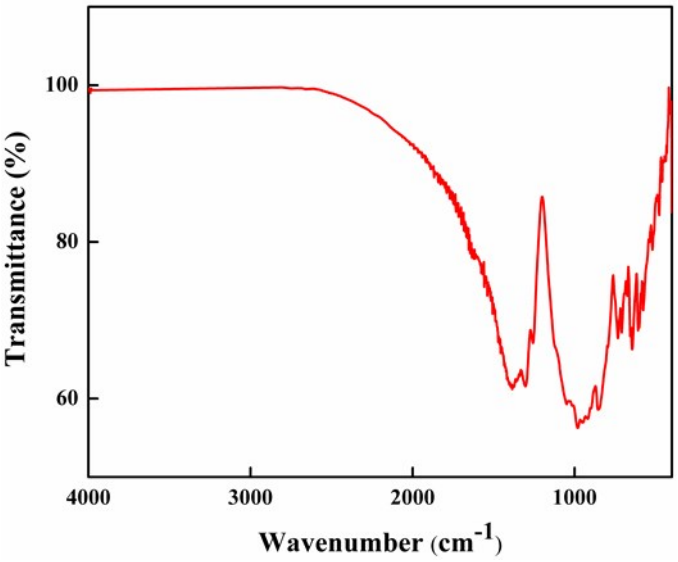

Figure S3. The infrared spectrum of $Ba_2B_7O_{12}F$.

Assignment of the absorption bands observed in the IR spectrum for $Ba_2B_7O_{12}F$.

Mode description	**IR (cm^{-1}) for $Ba_2B_7O_{12}F$**
asymmetric stretching vibration of [BO_3] groups	1385 and 1265
asymmetric stretching vibration of [BO_4] groups	1041
asymmetric stretching vibration of [BO_3F] groups	994
symmetric extension of [BO_3] groups	977
symmetric stretching vibration of [BO_4] groups	849
symmetric stretching vibration of [BO_3F] groups	761
out-of-plane bending of [BO_3] groups	642 and 610
bending of in-plane bending of [BO_3] groups	522

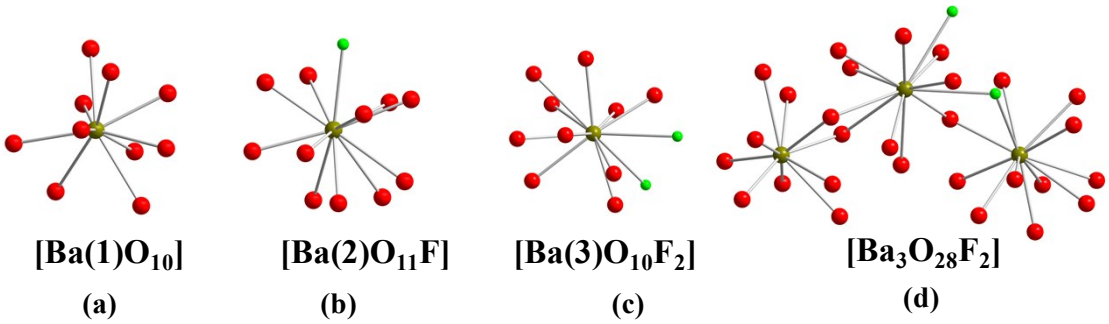

Figure S4. The coordination environments of the Ba^{2+} cations in $Ba_2B_7O_{12}F$.

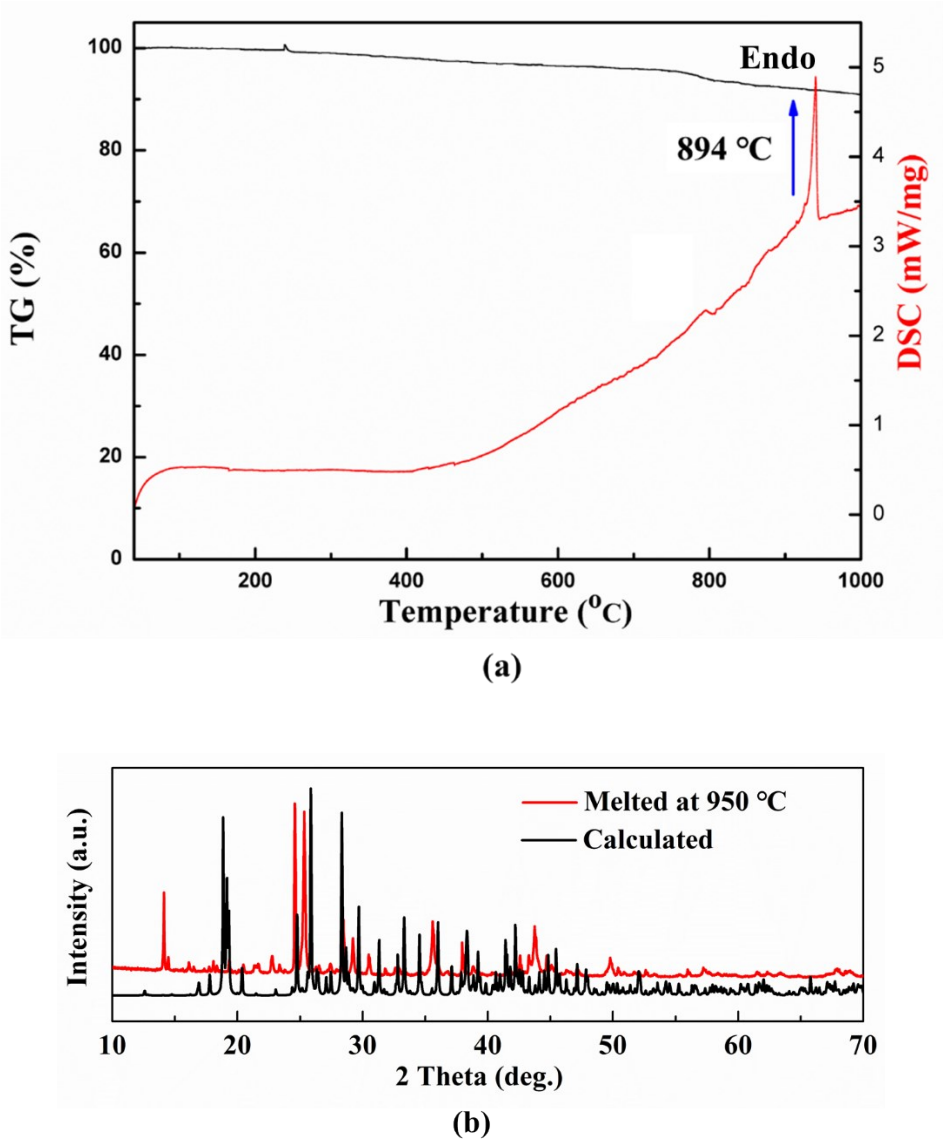

Figure S5. TG-DSC curves of $Ba_2B_7O_{12}F$ (a), and the XRD patterns of the melted residual (b).

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