

Electronic Supporting Information

Ba₃B₁₀O₁₇F₂·0.1KF: The First Mixed Alkali/Alkaline-Earth Metal Fluorooxoborate with Unprecedented Double-layered B-O/F Anionic Arrangement

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Experimental Section

Reagents. KF (Aladdin Industrial Co., Ltd., 99%), BaF₂ (Aladdin Industrial Co., Ltd., 99%) and B₂O₃ (Aladdin Industrial Co., Ltd., 98%) were used as received from commercial sources without any purification.

Synthesis of Ba₃B₁₀O₁₇F₂·0.1KF. The single crystals of Ba₃B₁₀O₁₇F₂·0.1KF were synthesized by the high-temperature solution reaction with the spontaneous nucleation method. A mixture of KF (0.0581 g, 1 mmol), BaF₂ (1.227 g, 7 mmol) and B₂O₃ (0.696 g, 10 mmol) were put into a platinum crucible, which was placed in the vertical programmable temperature electric furnace. The mixture was gradually heated to 750 °C in 2 h and dwelled at 750 °C for 5 h, then cooled to 400 °C at a rate of 1 °C/h, and after that, powered off the electric furnace. Small single crystals were formed during the process of spontaneous crystallization.

The polycrystalline samples of Ba₃B₁₀O₁₇F₂·0.1KF were obtained by the same way of single crystal preparation. By repeating many times, enough millimeter-level single crystals of Ba₃B₁₀O₁₇F₂·0.1KF were obtained. The single crystals of Ba₃B₁₀O₁₇F₂·0.1KF were ground into powder samples. The purity of the samples was checked by the powder X-ray diffraction (XRD).

Structure Determination. A single crystal was picked up and placed on a glass fiber with epoxy for data collection. The diffraction data of Ba₃B₁₀O₁₇F₂·0.1KF was collected on a Bruker SMART APEX II CCD diffractometer using monochromatic Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K and integrated with the SAINT program.¹ The crystal structure was solved, determined and refined by the SHELXTL^{2,3}

crystallographic software package, respectively. Then the structure was further examined using the Addsym subroutine of PLATON,⁴ and no other higher symmetry could be applied to the models. The details of the crystal parameters, data collection and structure refinement were listed in Table S1. The atomic coordinates, equivalent isotropic displacement parameters and important bond lengths and angles were listed in Tables S2 and S3.

Powder X-ray Diffraction. The powder XRD data were collected using a Bruker D2 PHASER diffractometer equipped with monochromatic Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The pattern was taken in 2θ range from 5 to 70° with a scan step width of 0.02° , and a fixed counting time of 2s per step.

Energy dispersive X-ray (EDX) spectroscopy. Elemental analysis of $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$ was carried on clean single crystal surfaces with the aid of a field emission scanning electron microscope (SEM, SUPRA 55VP) equipped with an EDX spectroscopy (BRUKER x-flash-sdd-5010).

Thermal Behavior Analysis. Thermal gravimetric (TG) and differential scanning calorimetry (DSC) of $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$ were investigated using a NETZSCH STA 449C simultaneous thermal analyzer. The sample and reference Al_2O_3 were placed in the platinum crucible and heated from 50 to 850°C at a rate of $5^\circ\text{C}/\text{min}$ under the flowing of N_2 gas.

Vibrational Spectroscopy and Optical Properties. The IR spectrum was measured on a Shimadzu IRAffinity-1 spectrometer. The sample was mixed thoroughly with dried KBr (6 mg of the sample and 600 mg of KBr), and the spectrum data were collected

in the range from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} .

The UV-Vis-NIR diffuse reflectance data for the polycrystalline powders of the $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$ were collected using a Shimadzu SolidSpec-3700DUV Spectrophotometer with the measurement range extending from 190 to 2600 nm at room temperature.

Theoretical Calculation Details. The first-principles method was performed to calculate the electronic structures of $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$ using density functional calculations in the CASTEP package.⁵ To achieve more accurate values of band gaps, we also adopted the nonlocal exchange functional HSE06 in Pwmat, a widely used hybrid functional with a relatively high efficiency.⁶⁻⁸ The valence electrons of $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$ were calculated as: Ba $5s^25p^66s^2$, B $2S^22P^1$, O $2s^22p^4$, F $2s^22P^5$, respectively. The Brillouin zones were set as $3 \times 2 \times 2$ with a separation of Monkhorst-Pack k-point sampling of $0.05 \text{ \AA}^{-1}$. For the aim of energy convergence, the plane-wave cut-off energy was 940 eV. On the basis of the scissor-corrected electron band structures, the imaginary part of the dielectric function is calculated. Consequently, the real part of the dielectric functions was obtained by the Kramers-Kronig transform, and the refractive indices were determined.^{9,10}

Table S1. Crystal data and structure refinement for Ba₃B₁₀O₁₇F₂·0.1KF

Empirical formula	Ba ₃ B ₁₀ O ₁₇ F ₂ ·0.1KF	
Formula weight	835.06	
Crystal system	Triclinic	
Space group, Z	$P\bar{1}$, 2	
Unit cell dimensions	$a=6.6187(3)\text{\AA}$	$\alpha=108.909(4)^\circ$
	$b=11.2123(6)\text{\AA}$	$\beta=94.499(4)^\circ$
	$c=11.3236(6)\text{\AA}$	$\gamma=90.543(4)^\circ$
Volume ($\text{\AA}^3$)	791.99(7)	
Calculated density (Mg/m ³)	3.502	
Absorption coefficient (/mm)	7.517	
F(000)	749.0	
The range for data collection	1.92 to 27.50°	
R(int)	0.0377	
Completeness	99.4%	
Data / restraints / parameters	3626 / 12 / 304	
Goodness-of-fit on F^2	1.028	
Final R indices [$F_o^2 > 2\sigma(F_o^2)$] ^a	$R_1 = 0.0291$	
	$wR_2 = 0.0490$	
	$R_1 = 0.0391$	
R indices (all data) ^a	$wR_2 = 0.0520$	
	1.50 and -0.85	
Largest diff. peak and hole (e·Å ⁻³)	1.50 and -0.85	

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Bond valence sum of all atoms for $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$.

Atoms	Wyck	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$	BVS
K1	1g	10000	5000	5000	25(2)	1.16
Ba1	2i	13372.3(4)	8758.5(3)	5890.4(3)	11.16(8)	2.20
Ba2	2i	12583.2(4)	1653.5(3)	9754.6(3)	11.46(8)	2.03
Ba3	2i	8797.8(5)	4442.4(3)	8154.6(3)	13.07(8)	2.39
B1	2i	13451(8)	6065(6)	7730(5)	9.5(12)	3.03
B2	2i	10080(8)	6961(6)	7523(5)	11.7(12)	3.05
B3	2i	6405(8)	6710(5)	6709(5)	8.5(12)	3.01
B4	2i	8743(8)	7679(6)	5760(5)	10.3(12)	3.06
B5	2i	7943(8)	8188(5)	3804(5)	7.9(12)	3.02
B6	2i	6083(9)	6272(6)	2435(5)	12.4(13)	3.07
B7	2i	4454(8)	8343(6)	2916(5)	8.5(12)	3.09
B8	2i	2549(9)	8087(6)	-719(5)	9.6(12)	3.02
B9	2i	3126(8)	9629(6)	1529(5)	8.5(12)	3.07
B10	2i	836(9)	8948(6)	2814(5)	10.5(12)	3.07
O1	2i	11303(4)	5898(3)	7426(3)	7.9(7)	2.24
O2	2i	7923(5)	6570(3)	7535(3)	10.8(8)	2.13
O3	2i	10298(5)	7508(3)	6517(3)	13.5(8)	2.28
O4	2i	4418(5)	6429(3)	6746(3)	12.9(8)	1.87
O5	2i	9154(5)	8354(3)	4993(3)	10.9(8)	1.99
O6	2i	7876(5)	6827(3)	3061(3)	11.0(8)	1.98
O7	2i	6798(5)	7217(3)	5778(3)	11.2(8)	2.12
O8	2i	5599(5)	5031(3)	2060(3)	12.2(8)	2.01
O9	2i	5899(4)	8661(3)	4011(3)	7.8(7)	2.04
O10	2i	4606(5)	7016(3)	2147(3)	16.4(8)	2.07
O11	2i	2380(5)	8457(3)	3362(3)	12.1(8)	2.07
O12	2i	4750(5)	9171(3)	2176(3)	9.3(7)	2.06
O13	2i	1134(5)	9404(3)	1859(3)	12.0(8)	2.02
O14	2i	-1112(5)	8934(3)	3108(3)	10.3(7)	2.03
O15	2i	3226(5)	9213(3)	183(3)	11.1(8)	2.10
O16	2i	3911(5)	7159(3)	-1072(3)	9.7(7)	2.00
O17	2i	634(5)	8000(3)	-1267(3)	12.9(8)	2.01
F1	2i	3571(4)	10986(3)	1902(2)	16.3(7)	0.91
F2	2i	10988(5)	3721(3)	9738(3)	22.3(7)	1.07
F3	2i	12340(70)	6230(50)	4290(40)	50(13)	0.95

Table S3. Selected bond lengths (Å) and angles (deg.) for Ba₃B₁₀O₁₇F₂·0.1KF.

K1-O1	2.669(3)	B1-O1	1.432(6)
K1-O1#4	2.669(3)	B1-O4#1	1.489(6)
K1-O3	2.776(4)	B1-O8#4	1.464(7)
K1-O3#4	2.776(4)	B1-O16#8	1.512(6)
K1-F3	2.41(5)	B2-O1	1.426(7)
K1-F3#4	2.41(5)	B2-O2	1.492(6)
Ba1-O3	2.725(3)	B2-O3	1.473(6)
Ba1-O4#1	3.132(3)	B2-O17#8	1.499(7)
Ba1-O5	2.875(3)	B3-O2	1.363(6)
Ba1-O7#1	2.850(3)	B3-O4	1.356(6)
Ba1-O9#1	2.784(3)	B3-O7	1.391(6)
Ba1-O9#2	2.893(3)	B4-O3	1.343(6)
Ba1-O11#1	2.796(3)	B4-O5	1.364(6)
Ba1-O12#2	2.820(3)	B4-O7	1.387(6)
Ba1-O14#3	2.942(3)	B5-O5	1.467(6)
Ba1-F1#2	3.026(3)	B5-O6	1.484(6)
Ba1-F3	2.87(5)	B5-O9	1.466(6)
Ba2-O2#5	3.116(3)	B5-O14#1	1.485(6)
Ba2-O12#4	2.842(3)	B6-O6	1.366(7)
Ba2-O13#6	2.938(3)	B6-O8	1.345(7)
Ba2-O14#6	3.162(3)	B6-O10	1.378(7)
Ba2-O15#4	2.951(3)	B7-O9	1.449(6)
Ba2-O15#7	2.959(3)	B7-O10	1.469(7)
Ba2-O16#4	2.738(3)	B7-O11	1.492(6)
Ba2-O17#6	2.788(3)	B7-O12	1.459(6)
Ba2-F1#7	2.800(3)	B8-O15	1.386(6)
Ba2-F2	2.561(3)	B8-O16	1.364(7)
Ba3-O1	2.670(3)	B8-O17	1.356(6)
Ba3-O2	2.751(3)	B9-O12	1.444(6)
Ba3-O6#4	2.834(3)	B9-O13	1.440(6)
Ba3-O8#6	2.982(3)	B9-O15	1.449(6)
Ba3-O10#6	2.705(3)	B9-F1	1.461(6)
Ba3-O11#6	3.202(4)	B10-O11	1.366(7)
Ba3-F2	2.554(3)	B10-O13	1.362(6)
Ba3-F2#5	2.591(3)	B10-O14	1.358(6)
Ba3-F3#4	2.67(4)		
O1-B1-O4#1	109.9(4)	O1-B2-O2	108.4(4)
O1-B1-O8#4	113.6(4)	O1-B2-O3	113.5(4)
O1-B1-O16#8	109.8(4)	O1-B2-O17#8	110.8(4)
O4#1-B1-O16#8	105.5(4)	O2-B2-O17#8	107.0(4)
O8#4-B1-O4#1	111.2(4)	O3-B2-O2	110.6(4)
O8#4-B1-O16#8	106.3(4)	O3-B2-O17#8	106.3(4)

O2-B3-O7	121.1(4)	O9-B7-O12	111.1(4)
O4-B3-O2	124.3(4)	O10-B7-O11	106.1(4)
O4-B3-O7	114.5(4)	O12-B7-O10	110.5(4)
O3-B4-O5	116.9(4)	O12-B7-O11	110.9(4)
O3-B4-O7	121.6(4)	O16-B8-O15	117.6(5)
O5-B4-O7	121.5(5)	O17-B8-O15	118.6(5)
O5-B5-O6	107.8(4)	O17-B8-O16	123.6(5)
O5-B5-O14#1	110.0(4)	O12-B9-O15	113.0(4)
O6-B5-O14#1	110.0(4)	O12-B9-F1	104.1(4)
O9-B5-O5	111.5(4)	O13-B9-O12	114.1(4)
O9-B5-O6	111.4(4)	O13-B9-O15	111.7(4)
O9-B5-O14#1	106.1(4)	O13-B9-F1	109.7(4)
O6-B6-O10	119.2(5)	O15-B9-F1	103.3(4)
O8-B6-O6	125.5(5)	O13-B10-O11	121.5(4)
O8-B6-O10	115.3(5)	O14-B10-O11	123.0(5)
O9-B7-O10	110.6(4)	O14-B10-O13	115.4(5)
O9-B7-O11	107.6(4)		
Symmetry transformations used to generate equivalent atoms:			
#1 +X,+Y,+Z	#2 2-X,2-Y,1-Z	#3 1-X,2-Y,1-Z	#4 2-X,1-Y,1-Z
#5 2-X,1-Y,2-Z	#6 1-X,1-Y,1-Z	#7 1+X,-1+Y,1+Z	#8 1+X,+Y,1+Z

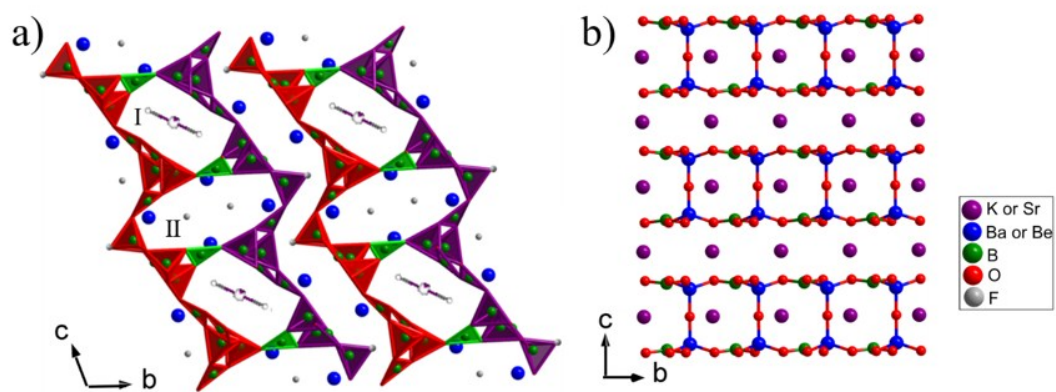


Figure S1. The crystal structures of $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$ and $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$.

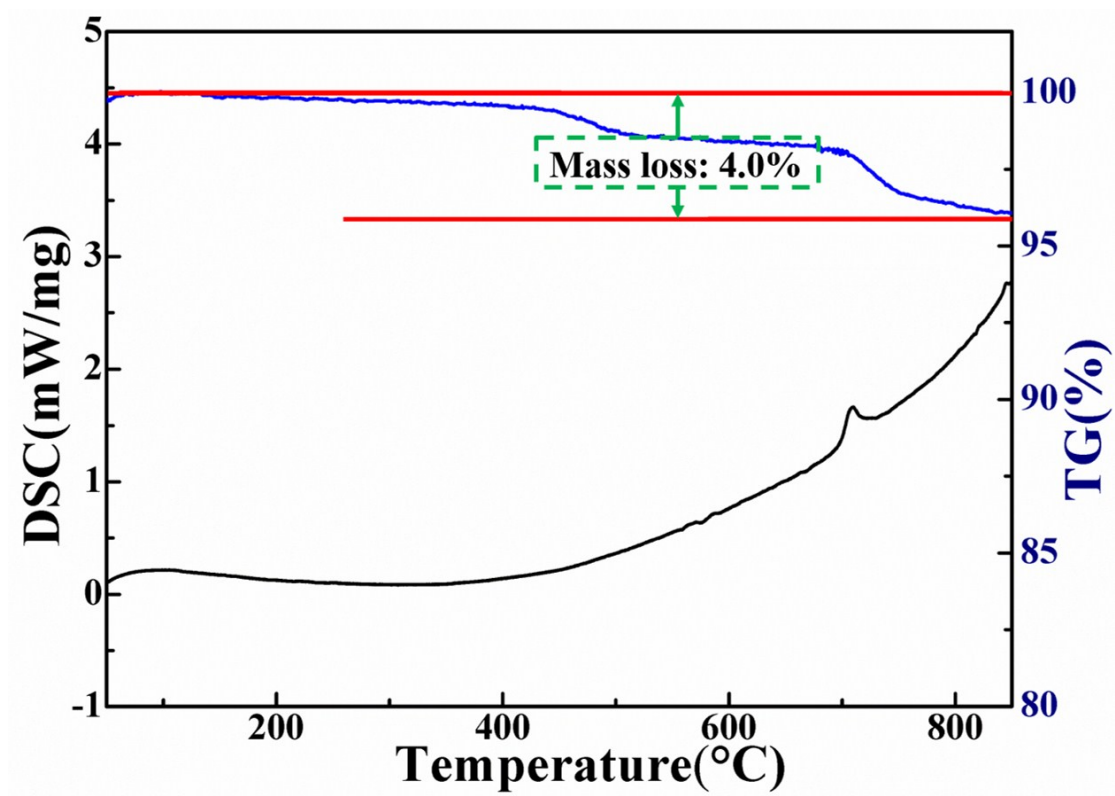


Figure S2. The TG-DSC curves of $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$.

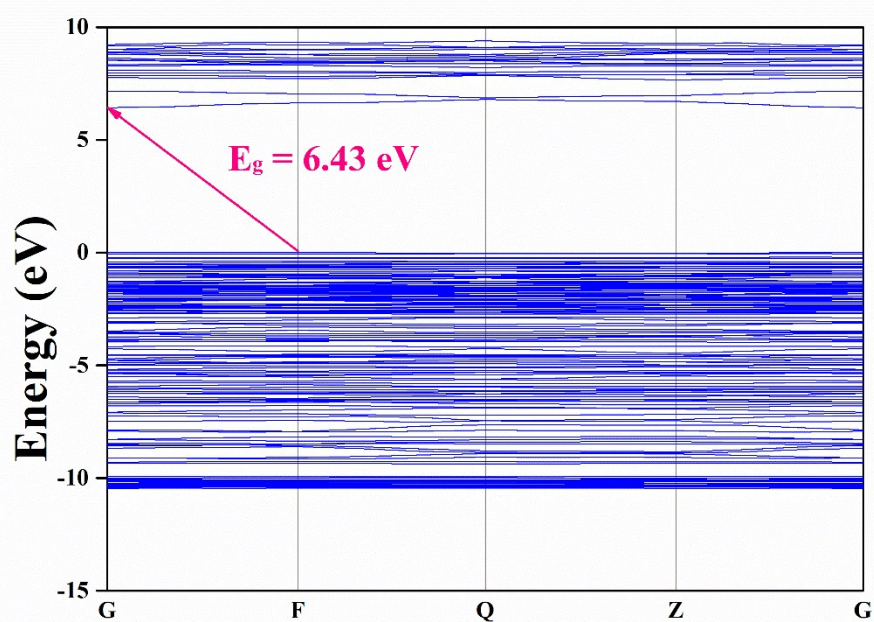


Figure S3. Electron band structure of $\text{Ba}_3\text{B}_{10}\text{O}_{17}\text{F}_2 \cdot 0.1\text{KF}$. The arrow indicates the indirect bandgap.

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