Supporting Information

Rational Design of a Series of Non-centrosymmetric Antiperovskite and double Antiperovskite Borate Fluorides

Fuqiang Chen,[a] Hongping Wu,*[a] Zhanggui Hu,[a] Jiyang Wang,[a] Yicheng Wu,[a] and Hongwei Yu*[a]

CONTENTS

Experimental Details.

Reagents.

$BaCO_3$ (Aladdin Chemistry Co., Ltd., 99.9%), $CaCO_3$ (Aladdin Chemistry Co., Ltd., 99.9%), K_2CO_3 (Aladdin Chemistry Co., Ltd., 99.9%), Rb_2CO_3 (Aladdin Chemistry Co., Ltd., 99.9%), Cs_2CO_3 (Aladdin Chemistry Co., Ltd., 99.9%), KF (Aladdin Chemistry Co., Ltd., 99.9%), RbF (Aladdin Chemistry Co., Ltd., 99.9%), CsF (Aladdin Chemistry Co., Ltd., 99.9%) and H_3BO_3 (Aladdin Chemistry Co., Ltd., 99.9%). All materials were used as received.

Syntheses.

The polycrystalline samples of $[(M/Ba)_2Ca]F[B_2O_5]$ (M = K, Rb) and $[CsBaCa]F[B_2O_5]$ were all synthesized via conventional solid-state reactions in open air. Mixtures of MF (M = K, Rb, Cs), $BaCO_3$, $CaCO_3$ and H_3BO_3 in a molar ratio of 1:1:1:2 were relatively transferred to Pt crucibles. The samples were preheated at 300 °C, and kept at this temperature for 24 h to eliminate the water and decompose the carbonates. And then the samples were gradually heated to 700 °C and held at this temperature for 72 h with several intermediate grindings and mixings. The phase purity of the resultant solids was confirmed by powder X-ray diffraction (PXRD), which shows good agreement with the calculated XRD patterns from the single crystal models (Figure S1).

The single crystals of $[(M/Ba)_2Ca]F[B_2O_5]$ (M = K, Rb) and $[CsBaCa]F[B_2O_5]$ were obtained via high-temperature solution method with a mixture of pure polycrystalline samples, $K_2CO_3/Rb_2CO_3/Cs_2CO_3$ and H_3BO_3, with a molar ratio of 1:0.65:4. The mixtures were put into platinum crucibles, which were put in a vertical programmable temperature furnace. To obtain a homogeneous melt, these samples were heated to 780 °C, 750 °C and 720 °C for K-, Rb- and Cs-based compounds, respectively, and held for 12 hours, then they were cooled to 550 °C at a rate of 5 °C/h, subsequently cooled to room temperature by switching off the furnace. During the process of spontaneous crystallization, small single crystals of the title compounds were obtained (yields, about 80%, 85% and 90% based on Ba for $[(K/Ba)_2Ca]F[B_2O_5]$, $[(Rb/Ba)_2Ca]F[B_2O_5]$ and $[CsBaCa]F[B_2O_5]$, respectively,). Several colorless crystals could be obtained from the reaction products for further characterization by single-

crystal X-ray diffraction measurements.

Single crystal X-ray diffraction and Powder XRD Analysis.

The crystals were determined by the single-crystal XRD method. Diffraction data were collected at 298 K on a Bruker SMART APEX II 4K CCD diffractometer equipped with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) and integrated with the SAINT42 program.[1] The direct method of SHElXS-201443 was used to deal with the structure.[2] Finally, the full-matrix least-squares technique was employed to refine all atoms in the structure. The PLATON was used to check the symmetry of the structure, and no higher symmetry was found.[3] The crystallographic data are listed in Table 1. The related crystal data, including selected bond lengths and atomic coordinate equivalent isotropic displacement parameters are listed in Tables S2−S7. Powder XRD measurements for the targeted $[(M/Ba)_2Ca]F[B_2O_5]$ (M=K, Rb) and $[CsBaCa]F[B_2O_5]$ were carried out on a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation at room temperature. The 2θ range is 5−70° with a step size of 0.02° and a fixed counting time of 1 s/step.

Thermal Analysis.

Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were carried out on a NETZSCH STA 449C thermal analysis instrument. With the help of flowing nitrogen atmosphere condition, powder sample (~9 mg) was heated from 25 to 1100 °C at a rate of 5 °C/min.

UV Diffuse-reflectance and Infrared (IR) Spectroscopy.

The UV−vis−NIR diffuse reflectance data for the polycrystalline powders were measured employing the Hitachi UV−vis−NIR spectrophotometer (Japan) at room temperature, and the data were collected in the wavelength range of 190−2500 nm. Infrared spectroscopy was carried out on a Nicolet iS50 Fourier transform infrared (FT-IR) spectrometer to specify and compare the coordination of the B atoms in title compounds. The samples were measured in the range from 400 to 4000 cm^{-1}.

Powder Second-Harmonic Generation Measurements.

The powder SHG measurements for targeted $[(M/Ba)_2Ca]F[B_2O_5]$ (M=K, Rb) and $[CsBaCa]F[B_2O_5]$ were carried out on the basis of the Kurtz−Perry method at room

temperature.[4] A Q-switched Nd:YVO_4 solid-state laser was selected as the source of radiation at λ_ω = 1064 nm, and the radiation was doubled to second harmonics $\lambda_{2\omega}$ = 532 nm. The crystal aggregates were ground and sieved into a series of distinct size ranges: 38−55, 55−88, 88−105, 105−150, and 150−200 μm, which were placed into a light-tight box and irradiated with the laser. The intensities of the frequency-doubled output emitted from the samples were collected by a photomultiplier tube. The commercial NLO crystal KDP was also ground and sieved into the same particle size range for the reference.

Computational Methods.

The band structures, the PDOS of $[(M/Ba)_2Ca]F[B_2O_5]$ (M=K, Rb) and $[CsBaCa]F[B_2O_5]$ were calculated by the CASTEP package based on DFT. The pseudopotential was set as norm-conserving pseudopotential (NCP) and the exchange-correlation energy chosen was the generalized gradient approximation (GGA) parametrized by Perdew-Burke-Ernzerhof (PBE) functional. The orbital electrons of K: $3s^23p^64s^1$, Rb: $4s^24p^65s^1$, Cs: $5s^25p^66s^1$, Ba: $5s^25p^66s^2$, Ca: $3s^23p^64s^2$, B: $2s^22p^1$, and O: $2s^22p^4$, F: $2s^22p^5$ were treated as valence electrons. The plane wave energy cutoff energy was set at 910.0 eV with a grid of Monkhorst-Pack k-point meshes of 4×4×4. Since the PBE usually underestimates the E_g, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional was chosen to provide more accurate E_g values and the related parameter settings are the same as for PBE. For calculating the optical properties, the same Monkhorst-pack grid and plane-wave cutoff energy were used and the dielectric function is defined as $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, in which real part $\epsilon_1(\omega)$, refractive index n(ω) were obtained by the Kramers-Kronig transform. The optical property calculations were scissor corrected (1.8, 0.5, and 1.64 eV for $[(K/Ba)_2Ca]F[B_2O_5]$, $[(Rb/Ba)_2Ca]F[B_2O_5]$, and $[CsBaCa]F[B_2O_5]$, respectively) by the energy gap difference between the PBE and the experimental values.

The Laser Damage Thresholds Measurements.

The laser damage thresholds (LDTs) of $[(M/Ba)_2Ca]F[B_2O_5]$ (M = K, Rb) and $[CsBaCa]F[B_2O_5]$ were measured using a high-power laser irradiation of 1064 nm

(pulse width τ_p= 8.10 ns) by the single-pulse method. The measurement processes were performed by gradually increasing the laser power until the damaged spot was observed. The measured LDTs for $[(M/Ba)_2Ca]F[B_2O_5]$ (M = K, Rb) and $[CsBaCa]F[B_2O_5]$ are around 2.23, 2.20 and 2.18 GW cm^{-2}, respectively, which are comparable with some commercialized UV NLO crystals, e.g. β-BBO (2.6 GW cm^{-2} at 1064 nm and 10 ns).[5]

Table S1. The atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[(K/Ba)_2Ca]F[B_2O_5]$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the BVS for each atom in the asymmetric unit of $[(K/Ba)_2Ca]F[B_2O_5]$.

Atom	Wyckoff position	x	y	z	U_{eq}	BVS
$K(1)_{0.5}Ba(1)_{0.5}$	4e	0.19294(12)	0.30706(12)	0.0002(14)	0.0326(6)	1.32
Ca1	2b	0.500000	0.500000	0.500000	0.0300(11)	2.32
B1	4e	0.3956(14)	0.1044(14)	0.49(2)	0.020(4)	3.25
O1	2c	0.500000	0.000000	0.620(8)	0.122(17)	2.14
O2	8f	0.4423(18)	0.2447(13)	0.456(16)	0.130(14)	1.90
F1	2a	0.500000	0.500000	0.000000	0.202(17)	1.08

Table S2. The atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[(Rb/Ba)_2Ca]F[B_2O_5]$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the BVS for each atom in the asymmetric unit of $[(Rb/Ba)_2Ca]F[B_2O_5]$.

Atom	Wyckoff position	x	y	z	U_{eq}	BVS
$Rb(1)_{0.5}Ba(1)_{0.5}$	4e	0.69531(8)	0.19531(8)	1.0005(4)	0.0298(5)	1.26
Ca1	2b	0.500000	0.500000	0.500000	0.0183(7)	2.27
B1	4e	0.8968(12)	0.3968(12)	0.469(5)	0.0238(19)	3.01
O1	2c	1.000000	0.500000	0.368(6)	0.071(2)	2.47
O2	8f	0.7553(11)	0.4442(12)	0.569(3)	0.054(3)	2.03
F1	2a	0.500000	0.500000	0.000000	0.095(2)	1.12

Table S3. The atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [CsBaCa]F[B_2O_5]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the BVS for each atom in the asymmetric unit of [CsBaCa]F[B_2O_5].

Atom	Wyckoff position	x	y	z	U_{eq}	BVS
Cs1	4e	0.69833(7)	0.80167(7)	0.50169(12)	0.0189(5)	0.98
Ba1	4e	0.19882(6)	0.69882(6)	-0.00150(10)	0.0126(4)	1.87
Ca1	4d	0.500000	0.500000	0.2455(2)	0.0079(7)	2.12
B1	4e	0.6063(18)	0.1063(18)	0.214(2)	0.014(2)	3.03
B2	4e	0.102(2)	0.398(2)	0.224(2)	0.025(2)	2.97
O1	2c	0.000000	0.500000	0.301(2)	0.039(2)	1.99
O2	2c	0.500000	0.000000	0.138(2)	0.035(2)	1.98
O3	8f	0.5550(10)	0.2456(10)	0.2177(11)	0.023(3)	2.01
O4	8f	0.2441(10)	0.4464(11)	0.2051(11)	0.029(3)	1.99
F1	2a	0.500000	0.500000	0.000000	0.059(2)	0.76
F2	2b	0.500000	0.500000	0.500000	0.0230(17)	0.78

Table S4. Selected lengths (Å) and bond angles (°) for $[(K/Ba)_2Ca]F[B_2O_5]$.

Atom–Atom	**Length [Å]**	$O2^{\#4}$–Ba1–$F1^{\#6}$	57.7(3)
Ba1–$O1^{\#1}$	2.87(2)	$F1^{\#5}$–Ba1–$F1^{\#6}$	154.20(3)
Ba1–$O2^{\#2}$	2.886(16)	$O1^{\#1}$–Ba1–$B1^{\#3}$	175.2(7)
Ba1–$O2^{\#3}$	2.886(16)	$O2^{\#2}$–Ba1–$B1^{\#3}$	86.3(4)
Ba1–O2	2.896(16)	$O2^{\#3}$–Ba1–$B1^{\#3}$	86.3(4)
Ba1–$O2^{\#4}$	2.896(16)	O2–Ba1–$B1^{\#3}$	83.0(5)
Ba1–$O2^{\#6}$	3.321(16)	$O2^{\#4}$–Ba1–$B1^{\#3}$	83.0(5)
Ba1–$O2^{\#1}$	3.321(16)	$F1^{\#5}$–Ba1–$B1^{\#3}$	80.02(6)
Ba1–$O2^{\#7}$	3.325(16)	$F1^{\#6}$–Ba1–$B1^{\#3}$	80.02(6)
Ba1–$O2^{\#5}$	3.325(16)	$O1^{\#1}$–Ba1–$O2^{\#6}$	43.7(4)
Ba1–$F1^{\#5}$	3.1656(5)	$O2^{\#2}$–Ba1–$O2^{\#6}$	87.0(4)
Ba1–$F1^{\#6}$	3.1656(5)	$O2^{\#3}$–Ba1–$O2^{\#6}$	132.1(5)
Ca1–$O2^{\#1}$	2.318(14)	O2–Ba1–$O2^{\#6}$	90.10(9)
Ca1–$O2^{\#9}$	2.318(14)	$O2^{\#4}$–Ba1–$O2^{\#6}$	63.9(4)
Ca1–$O2^{\#10}$	2.318(14)	$F1^{\#5}$–Ba1–$O2^{\#6}$	129.0(3)
Ca1–O2	2.318(14)	$F1^{\#6}$–Ba1–$O2^{\#6}$	62.4(2)
Ca1–$F1^{\#5}$	2.1420(5)	$B1^{\#3}$–Ba1–$O2^{\#6}$	139.0(3)
Ca1–F1	2.1420(5)	$O1^{\#1}$–Ba1–$O2^{\#1}$	43.7(4)
$B1^{\#8}$–O1	1.360(19)	$O2^{\#2}$–Ba1–$O2^{\#1}$	132.1(5)
$B1^{\#1}$–O1	1.360(19)	$O2^{\#3}$–Ba1–$O2^{\#1}$	87.0(4)
$B1^{\#1}$–O1	1.347(18)	O2–Ba1–$O2^{\#1}$	63.9(4)
Atom–Atom–Atom	**Angle [°]**	$O2^{\#4}$–Ba1–$O2^{\#1}$	90.10(9)
$O1^{\#1}$–Ba1–$O2^{\#2}$	90.1(5)	$F1^{\#5}$–Ba1–$O2^{\#1}$	62.4(2)
$O1^{\#1}$–Ba1–$O2^{\#3}$	90.1(5)	$F1^{\#6}$–Ba1–$O2^{\#1}$	129.0(3)
$O2^{\#2}$–Ba1–$O2^{\#3}$	80.3(6)	$B1^{\#3}$–Ba1–$O2^{\#1}$	139.0(3)
$O1^{\#1}$–Ba1–O2	101.4(6)	$O2^{\#6}$–Ba1–$O2^{\#1}$	68.2(5)
$O2^{\#2}$–Ba1–O2	160.09(9)	$O1^{\#1}$–Ba1–$O2^{\#7}$	153.5(4)
$O2^{\#3}$–Ba1–O2	115.6(5)	$O2^{\#2}$–Ba1–$O2^{\#7}$	63.9(4)
$O1^{\#1}$–Ba1–$O2^{\#4}$	101.4(6)	$O2^{\#3}$–Ba1–$O2^{\#7}$	90.19(10)
$O2^{\#2}$–Ba1–$O2^{\#4}$	115.6(5)	O2–Ba1–$O2^{\#7}$	102.4(4)
$O2^{\#3}$–Ba1–$O2^{\#4}$	160.09(8)	$O2^{\#4}$–Ba1–$O2^{\#7}$	86.8(4)
O2–Ba1–$O2^{\#4}$	46.5(6)	$F1^{\#5}$–Ba1–$O2^{\#7}$	101.9(2)
$O1^{\#1}$–Ba1–$F1^{\#5}$	100.63(9)	$F1^{\#6}$–Ba1–$O2^{\#7}$	62.3(3)
$O2^{\#2}$–Ba1–$F1^{\#5}$	136.4(3)	$B1^{\#3}$–Ba1–$O2^{\#7}$	23.7(3)
$O2^{\#3}$–Ba1–$F1^{\#5}$	57.8(3)	$O2^{\#6}$–Ba1–$O2^{\#7}$	124.7(4)
O2–Ba1–$F1^{\#5}$	57.7(3)	$O2^{\#1}$–Ba1–$O2^{\#7}$	162.70(7)
$O2^{\#4}$–Ba1–$F1^{\#5}$	103.6(3)	$O1^{\#1}$–Ba1–$O2^{\#5}$	153.5(4)
$O1^{\#1}$–Ba1–$F1^{\#6}$	100.63(9)	$O2^{\#2}$–Ba1–$O2^{\#5}$	90.19(10)
$O2^{\#2}$–Ba1–$F1^{\#6}$	57.8(3)	$O2^{\#3}$–Ba1–$O2^{\#5}$	63.9(4)
$O2^{\#3}$–Ba1–$F1^{\#6}$	136.4(3)	O2–Ba1–$O2^{\#5}$	86.8(4)
O2–Ba1–$F1^{\#6}$	103.6(3)	$O2^{\#4}$–Ba1–$O2^{\#5}$	102.4(4)
$F1^{\#5}$–Ba1–$O2^{\#5}$	62.3(3)	F1–Ca1–$O2^{\#1}$	82.2(4)

F1$^{\#6}$–Ba1–O2$^{\#5}$	101.9(2)	F1$^{\#5}$–Ca1–O2$^{\#10}$	97.8(4)
B1$^{\#3}$–Ba1–O2$^{\#5}$	23.7(3)	F1–Ca1–O2$^{\#10}$	82.2(4)
O2$^{\#6}$–Ba1–O2$^{\#5}$	162.70(7)	O2$^{\#1}$–Ca1–O2$^{\#10}$	164.5(8)
O2$^{\#1}$–Ba1–O2$^{\#5}$	124.7(4)	F1$^{\#5}$–Ca1–O2$^{\#11}$	82.2(4)
O2$^{\#7}$–Ba1–O2$^{\#5}$	40.2(5)	F1–Ca1–O2$^{\#11}$	97.8(4)
B1$^{\#8}$–O1–B1$^{\#1}$	146(3)	O2$^{\#1}$–Ca1–O2$^{\#11}$	91.05(11)
B1$^{\#8}$–O1–Ba1$^{\#9}$	99.6(8)	O2$^{\#10}$–Ca1–O2$^{\#11}$	91.05(11)
B1$^{\#1}$–O1–Ba1$^{\#9}$	99.6(8)	F1$^{\#5}$–Ca1–O2	82.2(4)
B1$^{\#8}$–O1–Ba1$^{\#10}$	99.6(8)	F1–Ca1–O2	97.8(4)
B1$^{\#1}$–O1–Ba1$^{\#10}$	99.6(8)	O2$^{\#1}$–Ca1–O2	91.05(11)
Ba1$^{\#9}$–O1–Ba1$^{\#10}$	111.7(12)	O2$^{\#10}$–Ca1–O2	91.05(11)
F1$^{\#5}$–Ca1–F1	180.0	O2$^{\#11}$–Ca1–O2	164.5(8)
F1$^{\#5}$–Ca1–O2$^{\#1}$	97.8(4)		

Symmetry transformations used to generate equivalent atoms:

#1: +Y, 1-X, 1-Z; #2: -0.5+X, 0.5-Y, -Z; #3: +Y, 1-X, -Z; #4: 0.5-Y, 0.5-X, +Z; #5: 0.5-X, -0.5+Y, -Z; #6: -0.5+X, 0.5-Y, 1-Z; #7: 0.5-Y, 0.5-X, -1+Z; #8: +X, +Y, -1+Z; #9: 1-X, -Y, +Z; #10: 1-Y, +X, 1-Z; #11: +Y, -X, 1-Z; #12: +X, +Y, 1+Z; #13: 1-X, 1-Y, +Z; #14: 1-X, 1-Y, 1+Z; #15: +Y, -X, -Z; #16: 1-Y, +X, -Z;

Table S5. Selected lengths (Å) and bond angles (°) for $[(Rb/Ba)_2Ca]F[B_2O_5]$.

Atom–Atom	**Length [Å]**	$O2^{\#4}$–Ba1–O2	47.3(4)
Ba1–$O1^{\#1}$	2.899(14)	$O1^{\#1}$–Ba1–$F1^{\#5}$	100.27(6)
Ba1–$O2^{\#2}$	2.915(11)	$O2^{\#2}$–Ba1–$F1^{\#5}$	57.8(2)
Ba1–$O2^{\#3}$	2.915(11)	$O2^{\#3}$–Ba1–$F1^{\#5}$	135.8(2)
Ba1–$O2^{\#4}$	2.918(11)	$O2^{\#4}$–Ba1–$F1^{\#5}$	57.8(2)
Ba1–O2	2.918(11)	O2–Ba1–$F1^{\#5}$	104.6(2)
Ba1–$O2^{\#7}$	3.326(11)	$O1^{\#1}$–Ba1–$F1^{\#6}$	100.27(6)
Ba1–$O2^{\#6}$	3.326(11)	$O2^{\#2}$–Ba1–$F1^{\#6}$	135.8(2)
Ba1–$O2^{\#5}$	3.329(11)	$O2^{\#3}$–Ba1–$F1^{\#6}$	57.8(2)
Ba1–$O2^{\#1}$	3.329(11)	$O2^{\#4}$–Ba1–$F1^{\#6}$	104.6(2)
Ba1–$F1^{\#5}$	3.1745(2)	O2–Ba1–$F1^{\#6}$	57.8(2)
Ba1–$F1^{\#6}$	3.1745(2)	$F1^{\#5}$–Ba1–$F1^{\#6}$	155.32(3)
Ca1–O2	2.311(10)	F1–Ca1–$O2^{\#1}$	82.6(3)
Ca1–$O2^{\#1}$	2.311(10)	O2–Ca1–$O2^{\#1}$	90.95(8)
Ca1–$O2^{\#9}$	2.311(10)	$F1^{\#6}$–Ca1–$O2^{\#10}$	97.4(3)
Ca1–$O2^{\#10}$	2.311(10)	F1–Ca1–$O2^{\#10}$	82.6(3)
Ca1–$F1^{\#6}$	2.15865(15)	O2–Ca1–$O2^{\#10}$	90.95(8)
Ca1–F1	2.15865(15)	$O2^{\#1}$–Ca1–$O2^{\#10}$	165.2(6)
B1–O1	1.352(17)	$F1^{\#6}$–Ca1–$O2^{\#11}$	82.6(3)
B1–O2	1.378(14)	F1–Ca1–$O2^{\#11}$	97.4(3)
B1–O2	1.378(14)	O2–Ca1–$O2^{\#11}$	165.2(6)
Atom–Atom–Atom	**Angle [°]**	$O2^{\#1}$–Ca1–$O2^{\#11}$	90.95(8)
$O1^{\#1}$–Ba1–$O2^{\#7}$	152.4(3)	$O2^{\#10}$–Ca1–$O2^{\#11}$	90.95(8)
$O2^{\#2}$–Ba1–$O2^{\#7}$	63.3(3)	$O2^{\#4}$–Ba1–$O2^{\#6}$	103.6(3)
$O2^{\#3}$–Ba1–$O2^{\#7}$	90.10(7)	$F1^{\#6}$–Ba1–$O2^{\#6}$	62.18(18)
$O2^{\#4}$–Ba1–$O2^{\#7}$	87.2(3)	$O2^{\#7}$–Ba1–$O2^{\#6}$	41.2(4)
O2–Ba1–$O2^{\#7}$	103.6(3)	$O1^{\#1}$–Ba1–$O2^{\#5}$	44.0(3)
$F1^{\#5}$–Ba1–$O2^{\#7}$	62.18(18)	$O2^{\#2}$–Ba1–$O2^{\#5}$	87.2(3)
$F1^{\#6}$–Ba1–$O2^{\#7}$	102.80(18)	$O2^{\#3}$–Ba1–$O2^{\#5}$	131.9(4)
$O1^{\#1}$–Ba1–$O2^{\#6}$	152.4(3)	$O2^{\#4}$–Ba1–$O2^{\#5}$	63.3(3)
$O2^{\#2}$–Ba1–$O2^{\#6}$	90.10(7)	O2–Ba1–$O2^{\#5}$	90.00(6)
$O2^{\#3}$–Ba1–$O2^{\#6}$	63.3(3)	$F1^{\#5}$–Ba1–$O2^{\#5}$	62.15(18)
$O1^{\#1}$–Ba1–$O2^{\#2}$	89.5(4)	$F1^{\#6}$–Ba1–$O2^{\#5}$	128.83(19)
$O1^{\#1}$–Ba1–$O2^{\#3}$	89.5(4)	$O2^{\#7}$–Ba1–$O2^{\#5}$	124.3(3)
$O2^{\#2}$–Ba1–$O2^{\#3}$	79.5(4)	$O2^{\#6}$–Ba1–$O2^{\#5}$	163.42(5)
$O1^{\#1}$–Ba1–$O2^{\#4}$	101.4(5)	$F1^{\#5}$–Ba1–$O2^{\#6}$	102.80(18)
$O2^{\#2}$–Ba1–$O2^{\#4}$	115.6(4)	O2–Ba1–$O2^{\#6}$	87.2(3)
$O2^{\#3}$–Ba1–$O2^{\#4}$	161.06(6)	$O1^{\#1}$–Ba1–$O2^{\#1}$	44.0(3)
$O1^{\#1}$–Ba1–O2	101.4(5)	$O2^{\#2}$–Ba1–$O2^{\#1}$	131.9(4)
$O2^{\#2}$–Ba1–O2	161.06(6)	$O2^{\#3}$–Ba1–$O2^{\#1}$	87.2(3)
$O2^{\#3}$–Ba1–O2	115.6(4)	$O2^{\#4}$–Ba1–$O2^{\#1}$	90.00(6)
O2–Ba1–$O2^{\#1}$	63.3(3)	$O2^{\#5}$–Ba1–$O2^{\#1}$	68.1(4)

F1$^{\#5}$–Ba1–O2$^{\#1}$	128.83(19)	O1–B1–O2$^{\#4}$	120.1(7)
F1$^{\#6}$–Ba1–O2$^{\#1}$	62.15(18)	O1–B1–O2	120.1(7)
O2$^{\#7}$–Ba1–O2$^{\#1}$	163.42(5)	O2$^{\#4}$–B1–O2	116.5(15)
O2$^{\#6}$–Ba1–O2$^{\#1}$	124.3(3)		

Symmetry transformations used to generate equivalent atoms:

#1: +Y, 1-X, 1-Z; #2: 1.5-X, -0.5+Y, 2-Z; #3: +Y, 1-X, 2-Z; #4: 0.5+Y, -0.5+X, +Z; #5: 1.5-X, -0.5+Y, 1-Z;

#6: +X, +Y, 1+Z; #7: 0.5+Y, -0.5+X, 1+Z; #8: 2-X, 1-Y, +Z; #9: 1+Y, 1-X, 1-Z; #10: 1-Y, +X, 1-Z;

#11: 1-X, 1-Y, +Z; #12: 1-Y, +X, 2-Z; #13: +X, +Y, -1+Z; #14: 1-X, 1-Y, -1+Z;

Table S6. Selected lengths (Å) and bond angles (°) for [CsBaCa]F[B_2O_5].

Atom–Atom	**Length [Å]**	O1$^{\#13}$–Cs1–O3$^{\#7}$	92.7(3)
Cs1–O3$^{\#7}$	3.329(10)	F2$^{\#15}$–Cs1–O3$^{\#7}$	103.86(16)
Cs1–O3$^{\#5}$	3.380(9)	F2–Cs1–O3$^{\#7}$	62.39(16)
Cs1–O3$^{\#14}$	3.380(9)	O3$^{\#15}$–Cs1–O3$^{\#7}$	42.1(3)
Cs1–O3$^{\#13}$	3.329(10)	O1$^{\#13}$–Cs1–O3$^{\#5}$	96.1(3)
Cs1–O4$^{\#15}$	3.429(10)	F2$^{\#15}$–Cs1–O3$^{\#5}$	128.34(16)
Cs1–O4$^{\#11}$	3.429(10)	F2–Cs1–O3$^{\#5}$	61.82(15)
Cs1–O4$^{\#5}$	3.444(10)	O3$^{\#15}$–Cs1–O3$^{\#5}$	164.28(4)
Cs1–O4$^{\#14}$	3.444(10)	O3$^{\#7}$–Cs1–O3$^{\#5}$	124.2(3)
Cs1–O1	3.028(11)	O1$^{\#13}$–Cs1–O3$^{\#16}$	96.1(3)
Cs1–F2$^{\#13}$	3.2012(2)	F2$^{\#15}$–Cs1–O3$^{\#16}$	61.82(15)
Cs1–F2	3.2012(2)	F2–Cs1–O3$^{\#16}$	128.34(16)
Ba1–O2$^{\#1}$	2.765(8)	O3$^{\#15}$–Cs1–O3$^{\#16}$	124.2(3)
Ba1–O4$^{\#2}$	2.875(10)	O3$^{\#7}$–Cs1–O3$^{\#16}$	164.28(4)
Ba1–O4$^{\#1}$	2.875(10)	O3$^{\#5}$–Cs1–O3$^{\#16}$	67.8(3)
Ba1–O4$^{\#3}$	2.907(10)	O1$^{\#13}$–Cs1–O4$^{\#17}$	42.5(2)
Ba1–O4	2.907(10)	F2$^{\#15}$–Cs1–O4$^{\#17}$	63.04(15)
Ba1–O3$^{\#4}$	2.949(9)	F2–Cs1–O4$^{\#17}$	127.79(16)
Ba1–O3$^{\#5}$	2.949(9)	O3$^{\#15}$–Cs1–O4$^{\#17}$	57.7(2)
Ba1–O3$^{\#2}$	2.972(10)	O3$^{\#7}$–Cs1–O4$^{\#17}$	81.7(3)
Ba1–O3$^{\#1}$	2.972(9)	O3$^{\#5}$–Cs1–O4$^{\#17}$	135.38(18)
Ba1–F1	3.1999(6)	O3$^{\#16}$–Cs1–O4$^{\#17}$	96.0(2)
Ba1–F1	3.1999(6)	O1$^{\#13}$–Cs1–O4$^{\#13}$	42.5(2)
Ca1–O3	2.320(9)	F2$^{\#15}$–Cs1–O4$^{\#13}$	127.79(16)
Ca1–O3$^{\#5}$	2.320(9)	F2–Cs1–O4$^{\#13}$	63.04(15)
Ca1–O4$^{\#5}$	2.345(9)	O3$^{\#15}$–Cs1–O4$^{\#13}$	81.7(3)
Ca1–O4	2.345(9)	O3$^{\#7}$–Cs1–O4$^{\#13}$	57.7(2)
Ca1–F1	2.1522(18)	O3$^{\#5}$–Cs1–O4$^{\#13}$	96.0(2)
Ca1–F1	2.1522(18)	O3$^{\#16}$–Cs1–O4$^{\#13}$	135.38(18)
B1–O2	1.49(2)	O4$^{\#17}$–Cs1–O4$^{\#13}$	66.0(3)
B1–O3$^{\#10}$	1.317(11)	O1$^{\#13}$–Cs1–O4$^{\#5}$	152.6(3)
B1–O3	1.317(11)	F2$^{\#15}$–Cs1–O4$^{\#5}$	102.93(16)
B2–O1	1.45(3)	F2–Cs1–O4$^{\#5}$	62.88(16)
B2–O4	1.343(14)	O3$^{\#15}$–Cs1–O4$^{\#5}$	111.43(19)
B2–O4	1.343(14)	O3$^{\#7}$–Cs1–O4$^{\#5}$	96.7(2)
Atom–Atom–Atom	**Angle [°]**	O3$^{\#5}$–Cs1–O4$^{\#5}$	57.5(2)
O1$^{\#13}$–Cs1–F2$^{\#15}$	99.72(4)	O3$^{\#16}$–Cs1–O4$^{\#5}$	81.4(3)
O1$^{\#13}$–Cs1–F2	99.72(4)	O4$^{\#17}$–Cs1–O4$^{\#5}$	164.66(4)
F2$^{\#15}$–Cs1–F2	156.64(3)	O4$^{\#13}$–Cs1–O4$^{\#5}$	125.9(3)
O1$^{\#13}$–Cs1–O3$^{\#15}$	92.7(3)	O1$^{\#13}$–Cs1–O4$^{\#16}$	152.6(2)
F2$^{\#15}$–Cs1–O3$^{\#15}$	62.39(16)	F2$^{\#15}$–Cs1–O4$^{\#16}$	62.88(16)
F2–Cs1–O3$^{\#15}$	103.86(16)	O4$^{\#2}$–Ba1–O3$^{\#1}$	99.1(3)

O3$^{\#15}$–Cs1–O4$^{\#16}$	96.7(2)	F2–Cs1–O4$^{\#16}$	102.93(16)
O3$^{\#7}$–Cs1–O4$^{\#16}$	111.43(19)	O4$^{\#1}$–Ba1–O3$^{\#1}$	68.3(2)
O3$^{\#5}$–Cs1–O4$^{\#16}$	81.4(3)	O4$^{\#3}$–Ba1–O3$^{\#1}$	127.6(2)
O3$^{\#16}$–Cs1–O4$^{\#16}$	57.5(2)	O4–Ba1–O3$^{\#1}$	78.2(2)
O4$^{\#17}$–Cs1–O4$^{\#16}$	125.9(3)	O3$^{\#4}$–Ba1–O3$^{\#1}$	162.31(5)
O4$^{\#13}$–Cs1–O4$^{\#16}$	164.66(4)	O3$^{\#5}$–Ba1–O3$^{\#1}$	116.0(3)
O4$^{\#5}$–Cs1–O4$^{\#16}$	40.6(3)	O3$^{\#2}$–Ba1–O3$^{\#1}$	78.7(3)
O2$^{\#1}$–Ba1–O4$^{\#2}$	109.3(3)	O4$^{\#2}$–Ba1–F1	106.05(19)
O2$^{\#1}$–Ba1–O4$^{\#1}$	109.3(3)	O4$^{\#1}$–Ba1–F1	57.46(19)
O4$^{\#2}$–Ba1–O4$^{\#1}$	49.1(4)	O4$^{\#3}$–Ba1–F1	135.73(19)
O2$^{\#1}$–Ba1–O4$^{\#3}$	82.3(3)	O4–Ba1–F1	57.18(18)
O4$^{\#2}$–Ba1–O4$^{\#3}$	114.6(3)	O3$^{\#4}$–Ba1–F1	105.40(18)
O4$^{\#1}$–Ba1–O4$^{\#3}$	161.92(4)	O3$^{\#5}$–Ba1–F1	58.11(18)
O2$^{\#1}$–Ba1–O4	82.3(3)	O3$^{\#2}$–Ba1–F1	135.37(18)
O4$^{\#2}$–Ba1–O4	161.92(5)	O3$^{\#1}$–Ba1–F1	57.91(17)
O4$^{\#1}$–Ba1–O4	114.6(3)	F1–Ca1–F2	180.0
O4$^{\#3}$–Ba1–O4	79.9(4)	F1–Ca1–O3	84.0(2)
O2$^{\#1}$–Ba1–O3$^{\#4}$	149.3(3)	F2–Ca1–O3	96.0(2)
O4$^{\#2}$–Ba1–O3$^{\#4}$	79.1(2)	F1–Ca1–O3$^{\#5}$	84.0(2)
O4$^{\#1}$–Ba1–O3$^{\#4}$	98.5(2)	F2–Ca1–O3$^{\#5}$	96.0(2)
O4$^{\#3}$–Ba1–O3$^{\#4}$	67.7(2)	O3–Ca1–O3$^{\#5}$	167.9(5)
O4–Ba1–O3$^{\#4}$	98.1(3)	F1–Ca1–O4$^{\#5}$	81.3(2)
O2$^{\#1}$–Ba1–O3$^{\#5}$	149.3(3)	F2–Ca1–O4$^{\#5}$	98.7(2)
O4$^{\#2}$–Ba1–O3$^{\#5}$	98.5(2)	O3–Ca1–O4$^{\#5}$	88.7(4)
O4$^{\#1}$–Ba1–O3$^{\#5}$	79.1(2)	O3$^{\#5}$–Ca1–O4$^{\#5}$	89.5(4)
O4$^{\#3}$–Ba1–O3$^{\#5}$	98.1(3)	F1–Ca1–O4	81.3(2)
O4–Ba1–O3$^{\#5}$	67.7(2)	F2–Ca1–O4	98.7(2)
O3$^{\#4}$–Ba1–O3$^{\#5}$	47.8(4)	O3–Ca1–O4	89.5(4)
O2$^{\#1}$–Ba1–O3$^{\#2}$	48.0(2)	O3$^{\#5}$–Ca1–O4	88.7(4)
O4$^{\#2}$–Ba1–O3$^{\#2}$	68.3(2)	O4$^{\#5}$–Ca1–O4	162.6(5)
O4$^{\#1}$–Ba1–O3$^{\#2}$	99.1(3)	O3–B1–O2	112.8(10)
O4$^{\#3}$–Ba1–O3$^{\#2}$	78.2(2)	O3$^{\#12}$–B1–O3	130(2)
O4–Ba1–O3$^{\#2}$	127.6(2)	O3$^{\#12}$–B1–O2	112.8(10)
O3$^{\#4}$–Ba1–O3$^{\#2}$	116.0(3)	O4–B2–O4$^{\#18}$	126(2)
O3$^{\#5}$–Ba1–O3$^{\#2}$	162.31(5)	O4–B2–O1	116.4(11)
O2$^{\#1}$–Ba1–O3$^{\#1}$	48.0(2)	O4$^{\#18}$–B2–O1	116.4(11)

Symmetry transformations used to generate equivalent atoms:

#1: +Y, 1-X, -Z; #2: 0.5-X, 0.5+Y, -Z; #3: -0.5+Y, 0.5+X, +Z; #4: 0.5-Y, 1.5-X, +Z; #5: 1-X, 1-Y, +Z; #6: -X, 1-Y, +Z; #7: 1-Y, +X, 1-Z; #8: -1+Y, 1-X, 1-Z; #9: 1-X, -Y, +Z; #10: +Y, -X, -Z; #11: 1-Y, +X, -Z; #12: 0.5+Y, -0.5+X, +Z; #13: +Y, 1-X, 1-Z; #14: +X, -1+Y, +Z; #15: 1.5-X, 0.5+Y, 1-Z; #16: 0.5+Y, 0.5+X, +Z; #17: 0.5+X, 1.5-Y, 1-Z; #18: 0.5-Y, 0.5-X, +Z;

Table S7. The important bond distances.

Compounds	B-O (the bridging O)	M-O(1) (M=Rb, Cs)	Ba-O(2)
$[(Rb/Ba)_2Ca]F[B_2O_5]$	1.352(15) Å	2.898(15) Å	2.898(15) Å
$[CsBaCa]F[B_2O_5]$	1.45(2) Å - 1.49(19) Å	3.029(11) Å	2.765(80) Å

Table S8. The dipole moments of the $[B_2O_5]^{4-}$ groups in a unit cell $[(M/Ba)_2Ca]F[B_2O_5]$ (M = K, Rb) and $[CsBaCa]F[B_2O_5]$.

Compounds	$[B_2O_5]^{4-}$ groups	Dipole moment			
		X-axis	Y-axis	Z-axis	Total
$[(K/Ba)_2Ca]F[B_2O_5]$	1	0.0043	0.0043	10.9051	0
	2	-0.0043	-0.0043	-10.9051	
	3	0.0043	0.0043	10.9051	
	4	-0.0043	-0.0043	-10.9051	
$[(Rb/Ba)_2Ca]F[B_2O_5]$	1	0.0020	0.0020	9.0402	0
	2	-0.0020	-0.0020	-9.0402	
	3	0.0020	0.0020	9.0402	
	4	-0.0020	-0.0020	-9.0402	
$[CsBaCa]F[B_2O_5]$	1	0.0046	-0.0046	12.3098	0
	2	-0.0046	0.0046	-12.3098	
	3	0.0046	-0.0046	12.3098	
	4	-0.0046	0.0046	-12.3098	
	5	-0.0022	-0.0022	-6.7646	
	6	0.0022	0.0022	6.7646	
	7	-0.0022	-0.0022	-6.7646	
	8	0.0022	0.0022	6.7646	

Table S9. The number density of $[B_2O_5]^{4-}$ groups and the empirical "flexibility index" F of these three structures.

Compounds	Numbers	Unit cell volume (Å^3)	Number density (Å^{-3})	*F*
$[(K/Ba)_2Ca]F[B_2O_5]$	2	326.32(1)	0.00612	0.096
$[(Rb/Ba)_2Ca]F[B_2O_5]$	2	332.15(3)	0.00602	0.093
$[CsBaCa]F[B_2O_5]$	4	689.26(7)	0.00580	0.092

Figure S1. Powder X-ray diffraction (PXRD) patterns of $[(M/Ba)_2Ca]F[B_2O_5]$ (M = K, Rb) and $[CsBaCa]F[B_2O_5]$ (b). The enlarged version of b in the 2θ region from 8 to 12° is shown in a to prove the difference in PXRD between $[(M/Ba)_2Ca]F[B_2O_5]$ (M = K, Rb) and $[CsBaCa]F[B_2O_5]$.

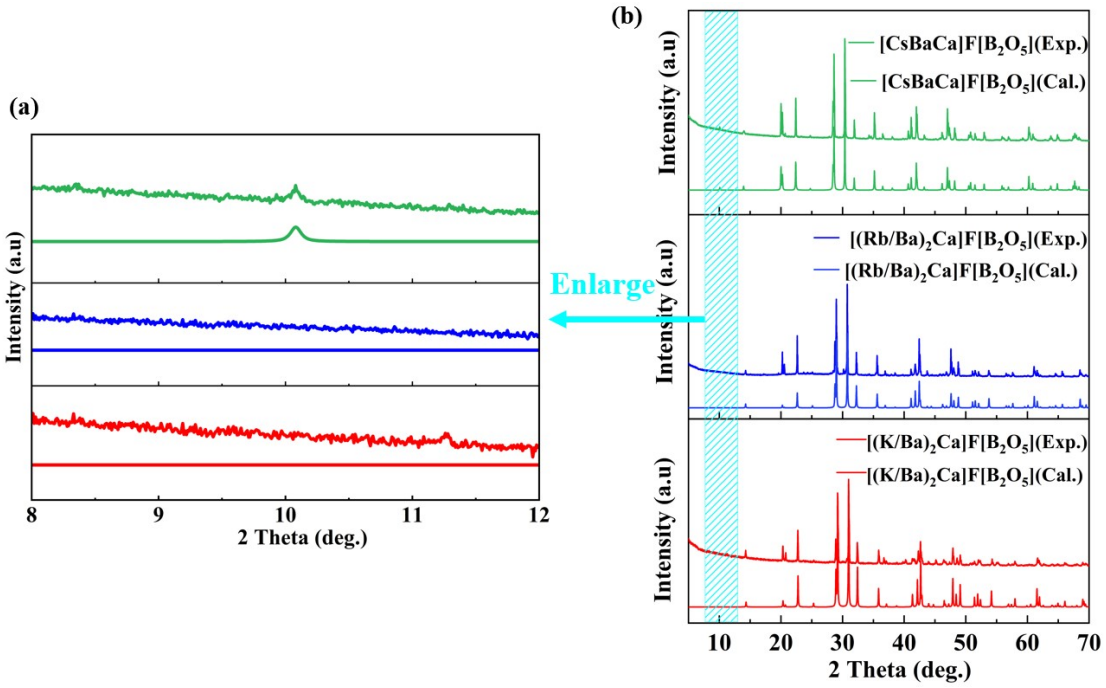


Figure S2. The TG-DSC curves of $[(K/Ba)_2Ca]F[B_2O_5]$ (a), $[(Rb/Ba)_2Ca]F[B_2O_5]$ (b), and CsBaCa]$F[B_2O_5]$ (c); experimental powder XRD patterns of $[(K/Ba)_2Ca]F[B_2O_5]$ (d), $[(Rb/Ba)_2Ca]F[B_2O_5]$ (e), and CsBaCa]$F[B_2O_5]$ (f).

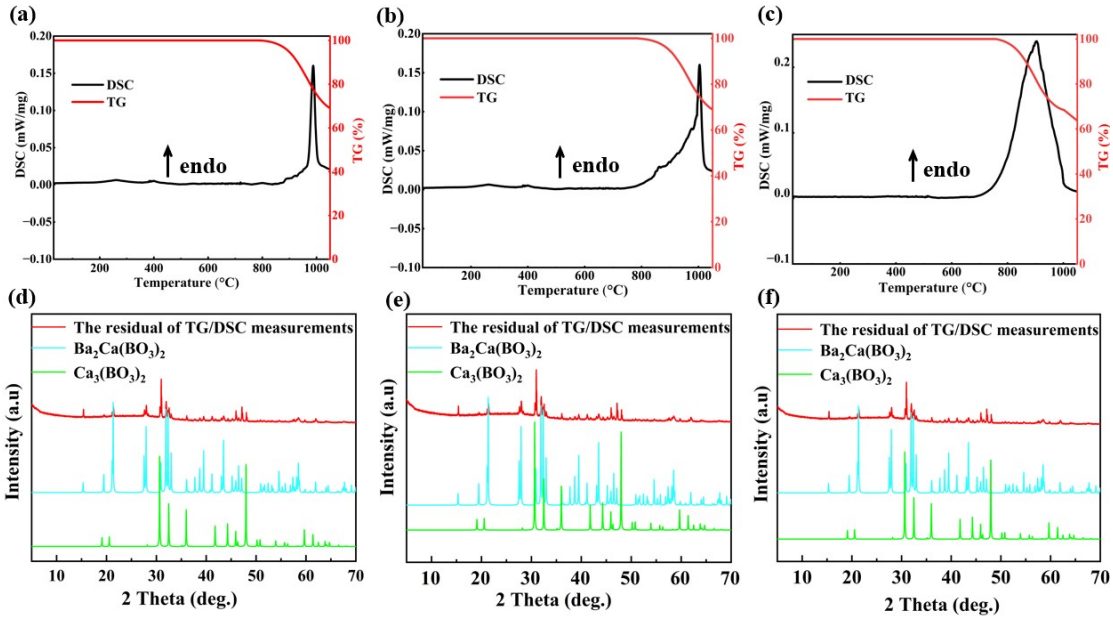


Figure S3. The octahedral rotation angles φ along *c*-axis for $[(Rb/Ba)_2Ca]F[B_2O_5]$ (a), and $[CsBaCa]F[B_2O_5]$ (b).

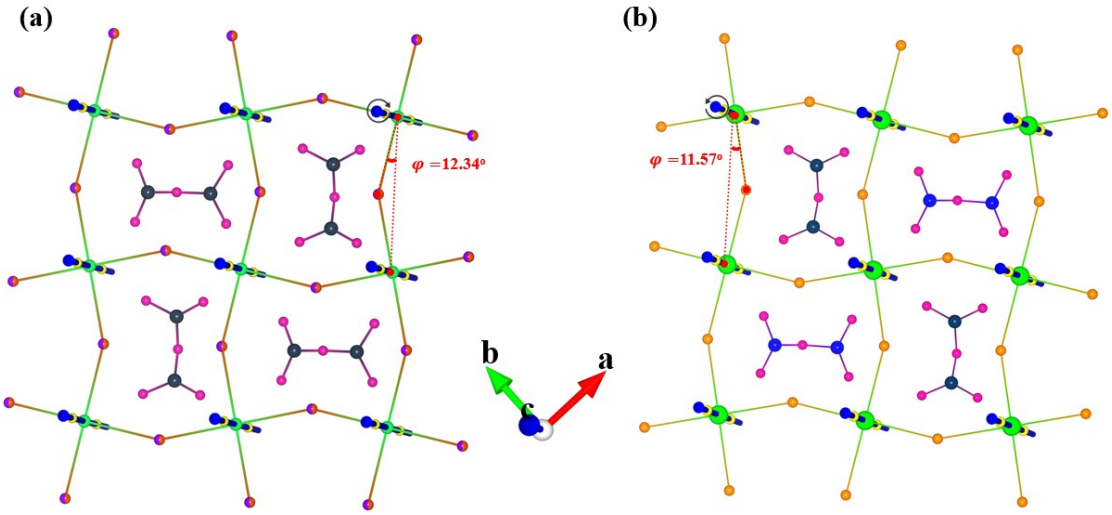


Figure S4. The experimental birefringence for $[(K/Ba)_2Ca]F[B_2O_5]$ (a), $[(Rb/Ba)_2Ca]F[B_2O_5]$ (b), and $[CsBaCa]F[B_2O_5]$ (c).

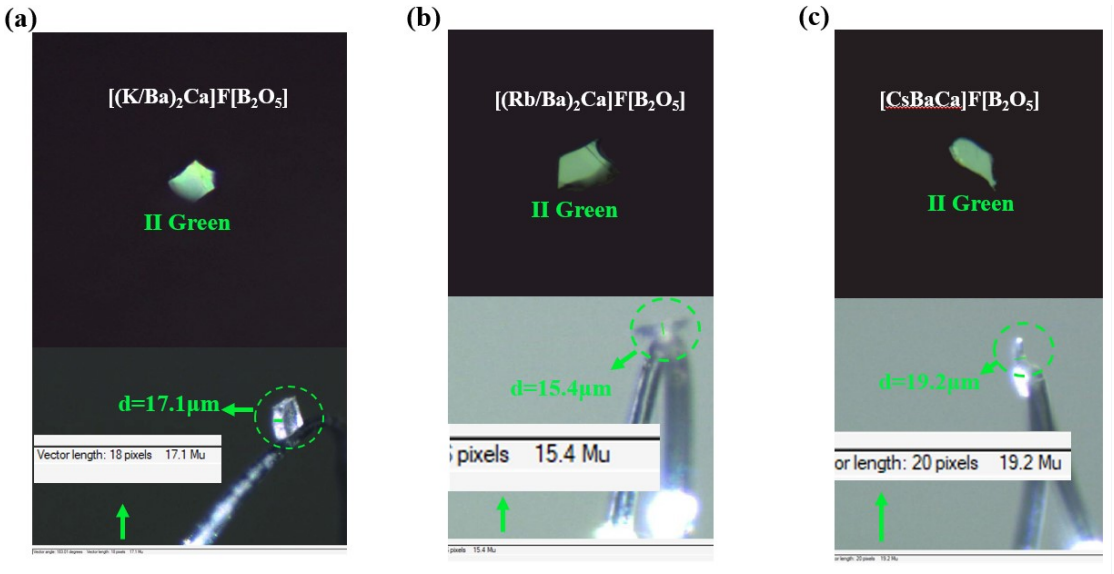
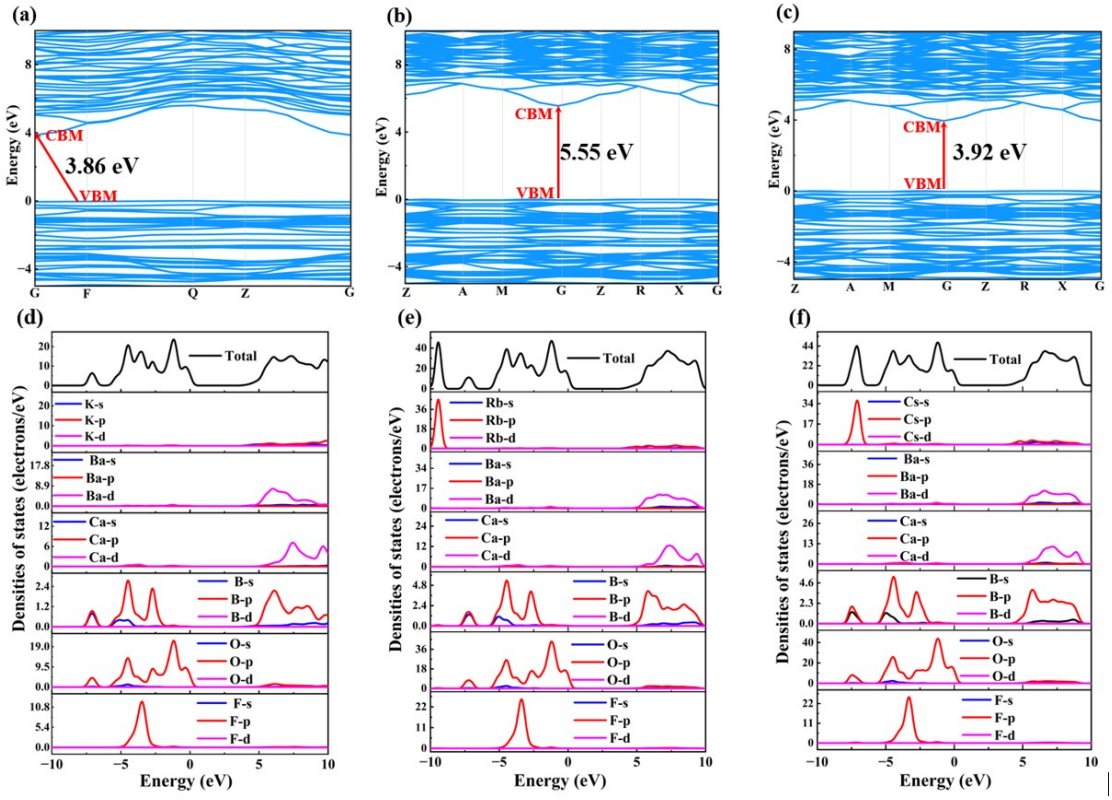


Figure S5. Band structures and density of states (DOS) diagrams of (a, d) $[(K/Ba)_2Ca]F[B_2O_5]$, (b, e) $[(Rb/Ba)_2Ca]F[B_2O_5]$, (c, f) $[CsBaCa]F[B_2O_5]$.



References.

1 G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Adv.*, 2015, **71**, 3-8.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. A.*, 2008, **64**, 112-122.

3 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.

4 S. K. Kurtz and T. T. Perry, *J. Appl. Phys*., 1968, **39**, 3798-3813.

5 H. Kouta, *Appl. Opt.* 1999, **38**, 545.