Electronic Supplementary Information

$BaB_4O_5F_4$ with reversible phase transition featuring unprecedented fundamental building block $[B_{16}O_{21}F_{16}]$ in α and $[B_4O_6F_4]$ in β-phase

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Experimental Section

Synthesis. Crystals of *β*-$BaB_4O_5F_4$ were obtained by spontaneous crystallization in a closed vacuum. A mixture of $Ba(BF_4)_2$, and B_2O_3 at the molar ratio of 1 : 2, was sealed into a silica glass tube (Φ 10 mm × 20 mm), and the tube was flame-sealed under ~ 10^{-3} Pa to create a vacuum environment. Then, the tube was placed in a computer-controlled furnace, heated to 520 °C in 13h, held at this temperature for 16 h and then the temperature was cooled to 50 °C with a rate of 2 °C h^{-1}, finally the transparent crystals of *β*-$BaB_4O_5F_4$ were obtained.

The polycrystalline sample of *β*-$BaB_4O_5F_4$ was obtained by the solid-state reaction with $Ba(BF_4)_2$ and B_2O_3 at the molar ratio of 1 : 2. The mixture was loaded into a fused-silica glass tube, which was then heated to 450 °C and kept at this temperature for several days, finally the polycrystalline sample was obtained, which was confirmed by powder XRD measurement.

Structural Determination. The structure data were performed by the single-crystal X-ray diffraction on a Bruker SMART APEX II CCD diffractometer at 303 and 153 K using monochromatic Mo-Kα radiation (λ = 0.71073 Å). All the calculations were performed with programs from the SHELXTL crystallographic software package.[1] All the atoms were refined using full matrix least-squares techniques, and final least-squares refinement was on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. In *β*-$BaB_4O_5F_4$, it is worth noting that the F(4) atom can be split into two sites, and without splitting treatment, the residual (R) values and equivalent isotropic displacement parameters were also allowed in a reasonable range. In addition, the ratio of Data / Parameter cannot be improved after several crystal data collections, due to the weak collected diffraction points in *α*-$BaB_4O_5F_4$. The structure of the title compound was checked for missing symmetry elements with PLATON.[2] Relevant atomic coordinates, equivalent isotropic displacement parameters, and selected interatomic distances, angles are listed in Tables S1-S4.

Powder XRD. The powder XRD of *β*-$BaB_4O_5F_4$ was confirmed using a Bruker D2 PHASER X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). The 2θ range was 10-70°, the fixed counting time and scan step width were 1 s/step and 0.02 °, respectively.

UV–Vis–NIR Diffuse-reflectance Spectrum. The optical diffuse reflectance spectrum of *β*-$BaB_4O_5F_4$ was measured by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 175-2000 nm at room temperature. The collected reflectance spectrum was transformed into the absorbance spectrum with the Kubelka–Munk function.[3]

IR Spectroscopy. The IR spectrum of *β*-$BaB_4O_5F_4$ was inspected by Shimadzu IR Affinity-1 Fourier transform IR spectrometer over 500 - 4000 cm^{-1} to verify the coordination of the B atoms. During the measurement, the sample was mixed thoroughly and pressed into discs with dried KBr (1 mg of the sample and 100 mg of KBr).

Elemental Spectrum Analysis. Energy dispersive X-ray spectroscopy (EDS) is used to verify the existence of F atoms or O atoms, it is equipped with energy dispersive X-ray spectrometer (BRUKER X-ray flash - SDD - 5010) of the SUPRA 55VP field emission scanning electron microscope, on a clean surface of single crystal.

Measured Refractive Index Difference of *β*-$BaB_4O_5F_4$. The refractive index difference of the block crystal of the *β*-$BaB_4O_5F_4$ was measured by using the cross-polarizing microscope equipped with Berek compensator at the wavelength of 546 nm (Figure S8). According to the optical path difference (R=1300 nm) and the thickness (d=0.0275 mm) of the crystal, the refractive index difference was calculated by the equation of R= Δn × d, where R, Δn and d were retardation, refractive index difference, and thickness, respectively. The refractive index difference of β-$BaB_4O_5F_4$ is measured to be 0.047 at 546 nm. So, the birefringence of β-$BaB_4O_5F_4$ is larger or equal to 0.047 at 546 nm.

Measured NMR of the β-$BaB_4O_5F_4$. The ^{19}F and ^{11}B MAS NMR experiments were performed on a Bruker Avance III 500 WB (11.75 T) spectrometer operating at a frequency of 470.96 and 160.61 MHz for ^{19}F and ^{11}B, respectively. A commercial DVT quadruple resonance H/F/X/Y 2.5 mm CP/MAS probe was used with a spinning frequency of 30.0 kHz. Solid-state ^{19}F MAS NMR spectra were recorded with a single pulse excitation using a 90 degree pulse width of 1.9 us (pi/2) and a recycle delay of 5 s to obtain quantitative results. There is no fluorine background from the H/F/X/Y probehead. ^{19}F chemical shifts were determined using a solid external reference, poly(tetrafluoroethylene) (PTFE). The CF2 groups of PTFE resonate at -122 ppm relative to tetramethylsilane (TMS). ^{11}B MAS NMR spectra was recorded, with a single pulse excitation using a short pulse length (0.32 us) to obtain quantitative results, and a recycle delay of 10 s (the tip angle was pi/12). 11B chemical shifts were referenced using H_3BO_3 1 M in solution as an external reference (19.6 ppm). The presence of B-F bonds was checked employing $^{11}B\{^{19}F\}$-REDOR NMR spectroscopy, which enables the determination of the heteronuclear ^{11}B -^{19}F dipole coupling and hence the evaluation of internuclear distances.

Theoretical Calculation. The influence of the atomic positions and molecular configurations of the structures on the optical properties of α, β-$BaB_4O_5F_4$, were analyzed based on the first-principles density functional theory (DFT) within the CASTEP software package.[4] In the process of analysis, the Perdew-Burke-Ernzerhof (PBE) method in generalized gradient approximation (GGA) was adopted to treat the exchange and correlation effects,[5] and the interactions between the ionic cores and valence electrons were verified with norm-conserving pseudopotential (NCP).[6] The valence electrons distribution was as follows: Ba $5s^2$ $5p^6$ $6s^2$, B $2s^2$ $2p^1$, O $2s^2$ $2p^4$ and F $2s^2$ $2p^5$. The kinetic energy cut-off value was set to 830 eV and the Monkhorst-Pack K-point grid was adjusted to 4×1×3 in the Brillouin zone for α, β-$BaB_4O_5F_4$. The convergence conditions and other parameters used in the calculation were consistent with the default parameters of CASTEP. Besides, the nonlocal exchange functional HSE06 was adopted to calculate bandgaps,

$$E^{HSE}_{xc} = aE^{HF,SR}_{x}(\omega) + (1 - a)E^{PBE,SR}_{x}(\omega) + E^{PBE,LR}_{x}(\omega) + E^{PBE}_{c}(\omega)$$

In HSE06, the parameters are suggested as a=0.25 and ω=0.11 $bohr^{-1}$.

In addition, α-$BaB_4O_5F_4$ crystallizes in the non-centrosymmetry group $P2_1$ (point group 2), which can exhibit SHG behavior. According to the anionic theory,[7] the SHG behavior of NLO borate mainly originates from the $[BO_3]$ groups. However, the almost antiparallel arrangement of $[BO_3]$ group will cancel out the SHG effects. The maximum SHG coefficient d_{22} of α-$BaB_4O_5F_4$, was calculated from electronic wave functions with the length-gauge formalism, which is exactly zero.

Table S1. The atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for α-$BaB_4O_5F_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum (BVS) for each atom in asymmetric unit.

	x	y	z	U(eq)	BVS
Ba(1)	4022(1)	2318(1)	5078(1)	12(1)	2.18
Ba(2)	396(1)	4584(1)	7370(1)	11(1)	2.02
Ba(3)	4627(1)	2305(1)	141(1)	11(1)	2.05
Ba(4)	1000(1)	4632(1)	2410(1)	12(1)	2.03
B(1)	6390(20)	5498(6)	4206(8)	12(2)	3.08
B(2)	3980(20)	477(6)	836(7)	11(2)	3.04
B(3)	10600(20)	1252(7)	1728(8)	14(2)	2.98
B(4)	8777(19)	3784(5)	-13(6)	11(2)	3.02
B(5)	2716(19)	2144(6)	-2195(7)	12(2)	2.87
B(6)	-350(20)	6296(7)	3305(8)	13(2)	3.00
B(7)	6230(20)	3094(5)	7499(6)	11(2)	2.92
B(8)	-436(17)	3770(6)	5106(7)	16(2)	3.01
B(9)	5486(17)	3153(6)	2359(6)	13(2)	2.99
B(10)	2420(19)	2199(6)	2791(7)	13(2)	2.93
B(11)	4560(20)	5665(6)	5826(7)	10(2)	3.07
B(12)	-1320(20)	1443(7)	3287(7)	11(2)	3.04
B(13)	7719(18)	-231(6)	292(8)	14(2)	3.13
B(14)	-5588(19)	5636(6)	797(7)	8(2)	3.06
B(15)	8900(20)	1430(7)	-1676(7)	11(2)	3.02
B(16)	2680(18)	4772(6)	4726(8)	13(2)	3.13
O(1)	639(11)	1968(4)	3490(4)	12(1)	2.12
O(2)	6098(11)	-17(4)	1026(4)	12(1)	2.09
O(3)	12175(11)	599(4)	1503(5)	12(1)	2.12
O(4)	2610(11)	5095(4)	5538(4)	13(1)	2.13
O(5)	4423(11)	4967(4)	4018(4)	14(1)	2.14
O(6)	3790(12)	813(4)	-29(4)	10(1)	2.03
O(7)	7104(11)	1282(4)	-974(4)	10(1)	2.10
O(8)	2488(11)	1850(4)	1914(4)	9(1)	1.91
O(9)	1445(12)	6139(3)	2549(5)	12(1)	2.13
O(10)	2360(11)	1868(4)	6878(4)	9(1)	1.91
O(11)	976(12)	4198(4)	4458(4)	15(1)	1.97
O(12)	4049(12)	2747(4)	3062(5)	17(1)	2.06

O(13)	4671(11)	2616(4)	-1909(4)	13(1)	2.03
O(14)	6429(12)	5851(4)	5049(4)	10(1)	2.04
O(15)	8244(12)	5618(4)	3551(5)	13(1)	2.09
O(16)	1083(11)	1888(4)	-1463(4)	11(1)	2.05
O(17)	-7448(11)	5031(4)	552(4)	15(1)	2.20
O(18)	3236(11)	6326(4)	6041(4)	11(1)	2.11
O(19)	10323(12)	4250(4)	-565(5)	13(1)	1.99
O(20)	8751(12)	1075(4)	2471(5)	14(1)	2.14
F(1)	-3974(10)	5404(3)	1601(4)	13(1)	0.87
F(2)	-3839(10)	5396(3)	6592(3)	13(1)	0.93
F(3)	9013(10)	1471(3)	884(4)	15(1)	0.81
F(4)	8787(10)	1540(3)	5861(3)	16(1)	0.84
F(5)	6071(8)	3682(2)	-373(3)	16(1)	0.93
F(6)	6482(8)	2868(2)	6578(3)	17(1)	1.09
F(7)	9940(8)	3089(2)	53(3)	16(1)	1.06
F(8)	5072(9)	3804(2)	7490(3)	17(1)	1.02
F(9)	-2529(9)	4146(2)	5557(3)	22(1)	0.83
F(10)	3606(8)	3403(2)	1643(3)	22(1)	0.97
F(11)	1442(8)	3541(2)	5857(3)	21(1)	0.95
F(12)	6552(10)	3787(2)	2798(3)	26(1)	0.97
F(13)	-1468(9)	3146(2)	4685(3)	23(1)	1.04
F(14)	7522(9)	2780(2)	1935(3)	22(1)	0.91
F(15)	8932(8)	3199(2)	7890(3)	16(1)	0.89
F(16)	8532(9)	4043(2)	922(3)	16(1)	1.00

Table S2. Selected bond distances (Å) and angles (deg) for α-BaB$_4$O$_5$F$_4$.

Ba(1)-F(6)	2.606(4)	B(3)-O(20)	1.442(13)
Ba(1)-F(13)#1	2.749(4)	B(3)-O(8)#1	1.460(13)
Ba(1)-O(14)#2	2.749(7)	B(3)-F(3)	1.457(11)
Ba(1)-O(18)#2	2.797(7)	B(3)-O(3)	1.477(13)
Ba(1)-O(1)	2.810(6)	B(4)-O(19)	1.402(11)
Ba(1)-O(10)	2.820(6)	B(4)-F(5)	1.403(10)
Ba(1)-F(11)	2.843(4)	B(4)-F(7)	1.416(11)
Ba(1)-F(4)	2.912(5)	B(4)-F(16)	1.416(10)
Ba(1)-O(12)	2.958(6)	B(5)-O(13)	1.345(11)
Ba(1)-F(13)	3.111(5)	B(5)-O(16)	1.406(12)
Ba(1)-F(4)#3	3.154(6)	B(5)-O(10)#6	1.412(11)
Ba(2)-F(8)	2.693(4)	B(6)-O(9)	1.429(13)
Ba(2)-F(2)	2.751(5)	B(6)-F(4)#4	1.451(11)
Ba(2)-F(15)#3	2.784(4)	B(6)-O(10)#7	1.464(13)
Ba(2)-O(3)#4	2.795(7)	B(6)-O(15)#3	1.484(13)
Ba(2)-O(20)#4	2.821(7)	B(7)-F(6)	1.376(9)
Ba(2)-O(2)#4	2.884(6)	B(7)-F(15)	1.418(10)
Ba(2)-F(11)	2.945(4)	B(7)-F(8)	1.437(11)
Ba(2)-F(8)#3	2.972(4)	B(7)-O(13)#8	1.451(11)
Ba(2)-O(19)#5	2.984(6)	B(8)-F(13)	1.393(12)
Ba(2)-O(4)	2.990(6)	B(8)-F(9)	1.404(10)
Ba(2)-F(9)	2.997(5)	B(8)-O(11)	1.408(12)
Ba(3)-F(7)#3	2.701(4)	B(8)-F(11)	1.439(10)
Ba(3)-F(5)	2.766(4)	B(9)-F(14)	1.363(10)
Ba(3)-O(7)	2.773(7)	B(9)-F(10)	1.417(9)
Ba(3)-F(3)	2.809(5)	B(9)-F(12)	1.424(11)
Ba(3)-O(6)	2.823(7)	B(9)-O(12)	1.446(11)
Ba(3)-O(8)	2.871(6)	B(10)-O(12)	1.340(12)
Ba(3)-O(16)	2.903(6)	B(10)-O(8)	1.401(11)
Ba(3)-O(13)	2.954(6)	B(10)-O(1)	1.401(11)
Ba(3)-F(7)	2.967(4)	B(11)-F(2)#1	1.403(11)
Ba(3)-F(14)	2.989(5)	B(11)-O(18)	1.428(13)
Ba(3)-F(10)	3.001(4)	B(11)-O(4)	1.472(12)
Ba(4)-F(16)#3	2.624(4)	B(11)-O(14)	1.486(11)
Ba(4)-F(12)#3	2.741(4)	B(12)-O(20)#3	1.344(12)
Ba(4)-O(15)#3	2.813(7)	B(12)-O(18)#9	1.368(12)

Ba(4)-O(9)	2.827(7)	B(12)-O(1)	1.387(12)
Ba(4)-O(5)	2.837(6)	B(13)-O(17)#10	1.291(12)
Ba(4)-F(10)	2.849(4)	B(13)-O(2)	1.380(11)
Ba(4)-O(17)#1	2.854(6)	B(13)-O(19)#11	1.401(11)
Ba(4)-F(1)	3.001(5)	B(14)-F(1)	1.424(10)
Ba(4)-O(11)	3.004(6)	B(14)-O(7)#12	1.438(13)
Ba(4)-F(1)#1	3.082(5)	B(14)-O(6)#12	1.453(11)
Ba(4)-F(12)	3.150(5)	B(14)-O(17)	1.478(12)
B(1)-O(15)	1.329(13)	B(15)-O(9)#13	1.353(12)
B(1)-O(14)	1.361(12)	B(15)-O(7)	1.370(12)
B(1)-O(5)	1.395(12)	B(15)-O(16)#1	1.385(12)
B(2)-O(3)#3	1.327(13)	B(16)-O(4)	1.297(13)
B(2)-O(6)	1.374(12)	B(16)-O(5)	1.379(12)
B(2)-O(2)	1.397(12)	B(16)-O(11)	1.396(11)

O(15)-B(1)-O(14)	122.6(9)	F(6)-B(7)-F(15)	107.4(7)
O(15)-B(1)-O(5)	117.5(9)	F(6)-B(7)-F(8)	108.8(7)
O(3)#3-B(2)-O(6)	121.7(9)	F(15)-B(7)-F(8)	103.4(7)
O(3)#3-B(2)-O(2)	118.4(9)	F(6)-B(7)-O(13)#8	114.8(8)
O(6)-B(2)-O(2)	119.9(9)	F(15)-B(7)-O(13)#8	110.6(7)
O(20)-B(3)-O(8)#1	116.5(8)	F(8)-B(7)-O(13)#8	111.1(7)
O(20)-B(3)-F(3)	109.5(7)	F(13)-B(8)-F(9)	110.9(7)
O(8)#1-B(3)-F(3)	104.1(8)	F(13)-B(8)-O(11)	111.9(8)
O(20)-B(3)-O(3)	107.8(8)	F(9)-B(8)-O(11)	112.7(9)
O(8)#1-B(3)-O(3)	110.2(8)	F(13)-B(8)-F(11)	106.0(8)
F(3)-B(3)-O(3)	108.5(8)	F(9)-B(8)-F(11)	105.2(7)
O(19)-B(4)-F(5)	113.1(7)	O(11)-B(8)-F(11)	109.7(6)
O(19)-B(4)-F(7)	112.7(7)	F(14)-B(9)-F(10)	108.2(6)
F(5)-B(4)-F(7)	105.4(7)	F(14)-B(9)-F(12)	111.0(6)
O(19)-B(4)-F(16)	111.7(8)	F(10)-B(9)-F(12)	104.6(8)
F(5)-B(4)-F(16)	106.1(7)	F(14)-B(9)-O(12)	114.0(9)
F(7)-B(4)-F(16)	107.3(7)	F(10)-B(9)-O(12)	110.5(6)
O(13)-B(5)-O(16)	114.2(7)	F(12)-B(9)-O(12)	108.2(6)
O(13)-B(5)-O(10)#6	125.4(9)	O(12)-B(10)-O(8)	125.2(8)
O(16)-B(5)-O(10)#6	120.2(7)	O(12)-B(10)-O(1)	113.8(8)
O(9)-B(6)-F(4)#4	111.0(7)	O(8)-B(10)-O(1)	120.9(8)
O(9)-B(6)-O(10)#7	115.8(8)	F(2)#1-B(11)-O(18)	112.7(8)
F(4)#4-B(6)-O(10)#7	103.9(8)	F(2)#1-B(11)-O(4)	106.7(7)
O(9)-B(6)-O(15)#3	107.3(9)	O(18)-B(11)-O(4)	113.1(8)
F(4)#4-B(6)-O(15)#3	108.0(8)	F(2)#1-B(11)-O(14)	108.6(7)
O(10)#7-B(6)-O(15)#3	110.7(8)	O(18)-B(11)-O(14)	104.2(8)
O(20)#3-B(12)-O(18)#9	123.5(10)	O(4)-B(11)-O(14)	111.5(7)

O(20)#3-B(12)-O(1)	120.1(8)	F(1)-B(14)-O(17)	105.6(7)
O(18)#9-B(12)-O(1)	116.4(9)	O(7)#12-B(14)-O(17)	111.7(7)
O(17)#10-B(13)-O(2)	122.8(8)	O(6)#12-B(14)-O(17)	112.0(7)
O(17)#10-B(13)-O(19)#11	124.3(9)	O(9)#13-B(15)-O(7)	121.2(9)
O(2)-B(13)-O(19)#11	113.0(9)	O(9)#13-B(15)-O(16)#1	121.0(8)
F(1)-B(14)-O(7)#12	112.8(8)	O(7)-B(15)-O(16)#1	117.8(9)
F(1)-B(14)-O(6)#12	109.7(7)	O(4)-B(16)-O(5)	123.6(8)
O(7)#12-B(14)-O(6)#12	105.2(8)	O(4)-B(16)-O(11)	124.2(8)
F(6)-Ba(1)-O(14)#2	118.60(15)	O(5)-B(16)-O(11)	112.2(9)
F(13)#1-Ba(1)-O(14)#2	127.46(15)	O(14)#2-Ba(1)-F(11)	142.14(15)
F(8)-Ba(2)-O(4)	84.36(15)	O(17)#1-Ba(4)-F(12)	92.32(15)
F(3)-Ba(3)-O(13)	116.40(15)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1, y, z #2 -x+1, y-1/2, -z+1 #3 x-1, y, z

#4 -x+1, y+1/2, -z+1 #5 x-1, y, z+1 #6 x, y, z-1

#7 -x, y+1/2, -z+1 #8 x, y, z+1 #9 -x, y-1/2, -z+1

#10 -x, y-1/2, -z #11 -x+2, y-1/2, -z

#12 -x, y+1/2, -z #13 -x+1, y-1/2, -z

#14 -x+1, y+1/2, -z #15 -x+2, y+1/2, -z

#16 x+1, y, z-1

Table S3. The atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for *β*-$BaB_4O_5F_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum (BVS) for each atom in asymmetric unit.

	x	y	z	U(eq)	BVS
Ba(1)	2135(1)	1176(1)	7499(1)	13(1)	2.15
B(1)	1482(6)	2954(1)	8961(4)	11(1)	3.06
B(2)	3162(6)	2827(2)	5754(4)	12(1)	3.04
B(3)	3522(7)	322(2)	12407(4)	16(1)	3.13
B(4)	211(6)	1308(1)	2959(4)	13(1)	3.01
O(1)	32(4)	1591(1)	11216(3)	15(1)	1.99
O(2)	4670(4)	2188(1)	5313(3)	14(1)	2.10
O(3)	1341(4)	2639(1)	7262(3)	13(1)	2.08
O(4)	2064(4)	808(1)	3541(3)	17(1)	2.07
O(5)	-1488(4)	1546(1)	4368(2)	14(1)	2.09
F(1)	6537(4)	1943(1)	9159(2)	20(1)	1.14
F(2)	3774(4)	-227(1)	6950(4)	44(1)	0.90
F(3)	-2389(4)	360(1)	7508(3)	48(1)	0.95
F(4)	3552(7)	531(1)	10585(3)	81(1)	1.06

Table S4. Selected bond distances (Å) and angles (deg) for β-$BaB_4O_5F_4$.

Ba(1)-F(4)	2.591(5)	B(1)-O(5)#3	1.385(6)
Ba(1)-F(3)	2.680(4)	B(2)-F(1)#4	1.432(6)
Ba(1)-O(2)	2.782(4)	B(2)-O(2)	1.454(6)
Ba(1)-F(1)	2.806(3)	B(2)-O(3)	1.455(6)
Ba(1)-O(3)	2.808(4)	B(2)-O(1)#5	1.458(6)
Ba(1)-F(2)	2.810(4)	B(3)-F(4)	1.364(8)
Ba(1)-O(5)	2.881(4)	B(3)-F(2)#6	1.383(7)
Ba(1)-O(4)	2.908(4)	B(3)-F(3)#7	1.408(7)
Ba(1)-O(1)	2.976(4)	B(3)-O(4)#8	1.429(7)
Ba(1)-F(3)#1	3.066(5)	B(4)-O(1)#9	1.354(7)
Ba(1)-F(1)#2	3.303(6)	B(4)-O(4)	1.360(7)
B(1)-O(3)	1.353(6)	B(4)-O(5)	1.400(6)
B(1)-O(2)#2	1.356(6)		

F(4)-Ba(1)-F(3)	85.97(18)	O(5)-Ba(1)-F(3)#1	128.88(12)
F(4)-Ba(1)-O(2)	133.25(15)	O(4)-Ba(1)-F(3)#1	82.11(12)
F(3)-Ba(1)-O(2)	140.69(14)	O(1)-Ba(1)-F(3)#1	116.93(12)
F(4)-Ba(1)-F(1)	72.63(15)	O(3)-B(1)-O(2)#2	122.4(5)
F(3)-Ba(1)-F(1)	155.00(13)	O(3)-B(1)-O(5)#3	120.5(4)
O(2)-Ba(1)-F(1)	62.41(10)	O(2)#2-B(1)-O(5)#3	117.1(4)
F(4)-Ba(1)-O(3)	123.16(14)	F(1)#4-B(2)-O(2)	110.5(4)
F(3)-Ba(1)-O(3)	117.51(12)	F(1)#4-B(2)-O(3)	109.4(4)
O(2)-Ba(1)-O(3)	49.06(10)	O(2)-B(2)-O(3)	105.8(4)
F(1)-Ba(1)-O(3)	67.20(10)	F(1)#4-B(2)-O(1)#5	105.5(4)
F(4)-Ba(1)-F(2)	66.73(16)	O(2)-B(2)-O(1)#5	111.8(4)
F(3)-Ba(1)-F(2)	71.74(13)	O(3)-B(2)-O(1)#5	113.8(4)
O(2)-Ba(1)-F(2)	116.41(13)	F(4)-B(3)-F(2)#6	107.5(5)
F(1)-Ba(1)-F(2)	109.70(11)	F(4)-B(3)-F(3)#7	110.1(5)
O(3)-Ba(1)-F(2)	165.34(13)	F(2)#6-B(3)-F(3)#7	103.3(5)
F(4)-Ba(1)-O(5)	156.30(15)	F(4)-B(3)-O(4)#8	112.1(5)
F(3)-Ba(1)-O(5)	70.51(14)	F(2)#6-B(3)-O(4)#8	112.0(5)
O(2)-Ba(1)-O(5)	70.42(11)	F(3)#7-B(3)-O(4)#8	111.5(5)
F(1)-Ba(1)-O(5)	129.31(10)	O(1)#9-B(4)-O(4)	125.8(5)
O(3)-Ba(1)-O(5)	68.47(10)	O(1)#9-B(4)-O(5)	120.5(5)
F(2)-Ba(1)-O(5)	106.88(12)	O(4)-B(4)-O(5)	113.6(5)
F(4)-Ba(1)-O(4)	134.95(14)	F(3)-Ba(1)-O(1)	81.30(12)
F(3)-Ba(1)-O(4)	83.02(13)	O(2)-Ba(1)-O(1)	119.04(10)
O(2)-Ba(1)-O(4)	67.29(11)	F(1)-Ba(1)-O(1)	76.34(10)
F(1)-Ba(1)-O(4)	121.27(10)	O(3)-Ba(1)-O(1)	75.06(10)
O(3)-Ba(1)-O(4)	100.48(10)	F(2)-Ba(1)-O(1)	118.80(13)
F(2)-Ba(1)-O(4)	68.32(13)	O(5)-Ba(1)-O(1)	114.11(10)
O(5)-Ba(1)-O(4)	47.03(10)	O(4)-Ba(1)-O(1)	159.18(10)
F(4)-Ba(1)-O(1)	57.29(13)	F(4)-Ba(1)-F(3)#1	63.28(16)

F(3)-Ba(1)-F(3)#1	114.40(15)	O(3)-Ba(1)-F(3)#1	127.97(11)
O(2)-Ba(1)-F(3)#1	87.34(12)	F(2)-Ba(1)-F(3)#1	43.47(11)
F(1)-Ba(1)-F(3)#1	67.60(10)		

Symmetry transformations used to generate equivalent atoms:
#1 x+1, y, z #2 x-1/2, -y+1/2, z+1/2
#3 x+1/2, -y+1/2, z+1/2 #4 x-1/2, -y+1/2, z-1/2
#5 x+1/2, -y+1/2, z-1/2 #6 -x+1, -y, -z+2
#7 -x, -y, -z+2 #8 x, y, z+1
#9 x, y, z-1 #10 x-1, y, z

Table S5. Crystallographic data for $P2_1$ and $P2_1/c$ for α, β-$BaB_4O_5F_4$.

Empirical formula	α-$BaB_4O_5F_4$	β-$BaB_4O_5F_4$
Formula weight	336.58	
Temperature	153 K	303 K
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 4.84(6)Å	a = 4.83(5)Å
	b = 18.6(5)Å β=91.93(4)°	b=18.98(6)Å β=122.83(5)°
	c = 14.12(3) Å	c = 8.48(6) Å
Volume	1276.18(8) $Å^3$	654.57(4) $Å^3$
Z, calculated density	8, 3.503g/cm^3	4, 3.415g/cm^3
Absorption coefficient	6.297mm^{-1}	6.138 mm^{-1}
F(000)	1216	608
Theta range for data collection	2.183 to 27.548°	2.145 to 27.507°
Limiting indices	-6≤h≤6, -24≤k≤24, -18≤l≤18	-6≤h≤6, --24≤k≤24, -9≤l≤9
Reflections collected / unique	21588/5826 [R(int) = 0.0451]	10872/1510 [R(int) = 0.0426]
Completeness to theta	99.70%	100%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.744 and 0.278	0.6927 and 0.4190
Goodness-of-fit on F_o^2	1.019	1.08
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0206, wR_2 = 0.0497	R_1 = 0.0169, wR_2 = 0.0394
R indices (all data)[a]	R_1 = 0.0234, wR_2 = 0.0505	R_1 = 0.0185, wR_2 = 0.0399
Largest diff. peak and hole	0.613 and -0.986 e.$Å^{-3}$	0.720 and -0.722 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 $F_o^2 > 2\sigma(F_o^2)$

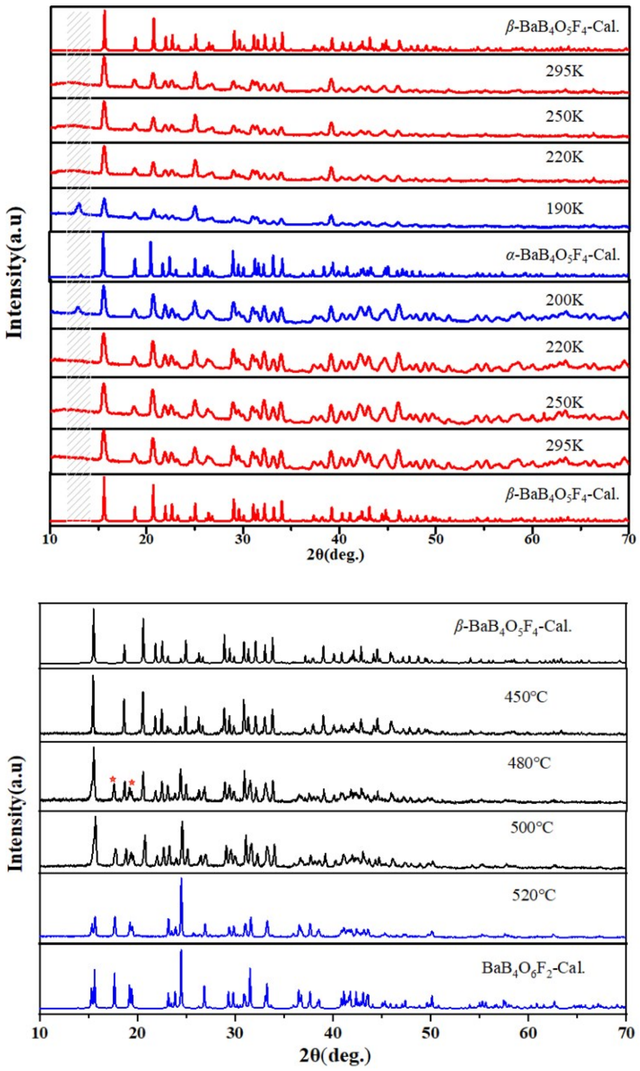

Figure S1. The phase transition process from β-BaB$_4$O$_5$F$_4$ to α -BaB$_4$O$_5$F$_4$ and the XRD patterns comparison at different temperatures. The polycrystalline sample was obtained at 450 ℃. And when the temperature was increased to 480 ℃, BaB$_4$O$_6$F$_2$ appeared. Finally, the sample is completely BaB$_4$O$_6$F$_2$ at 520 ℃.

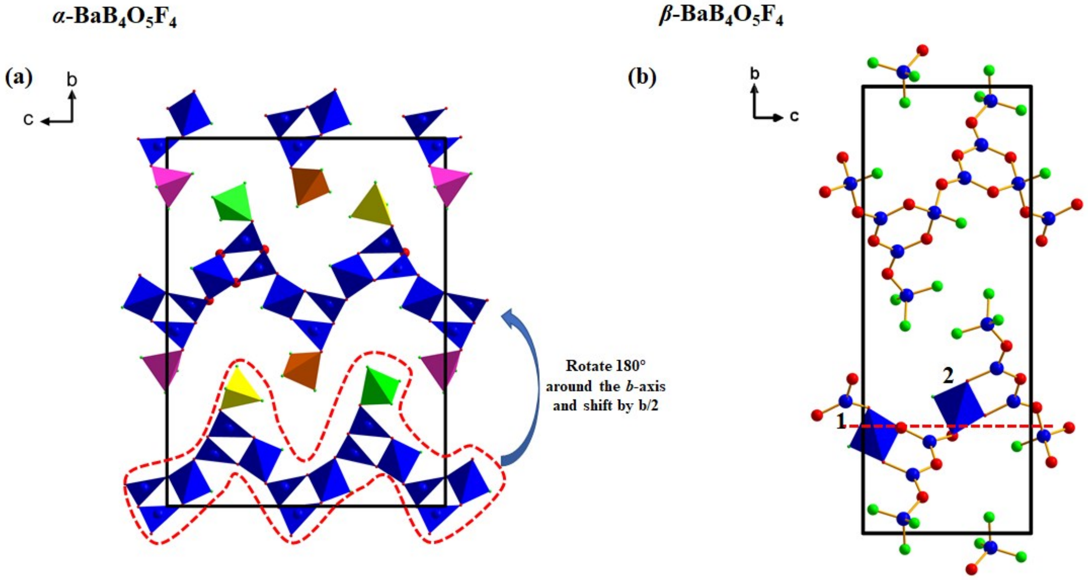

Figure S2. The unit cell of *α, β*-$BaB_4O_5F_4$, [100] projection of the symmetry elements of space groups $P2_1$ and $P2_1/c$.

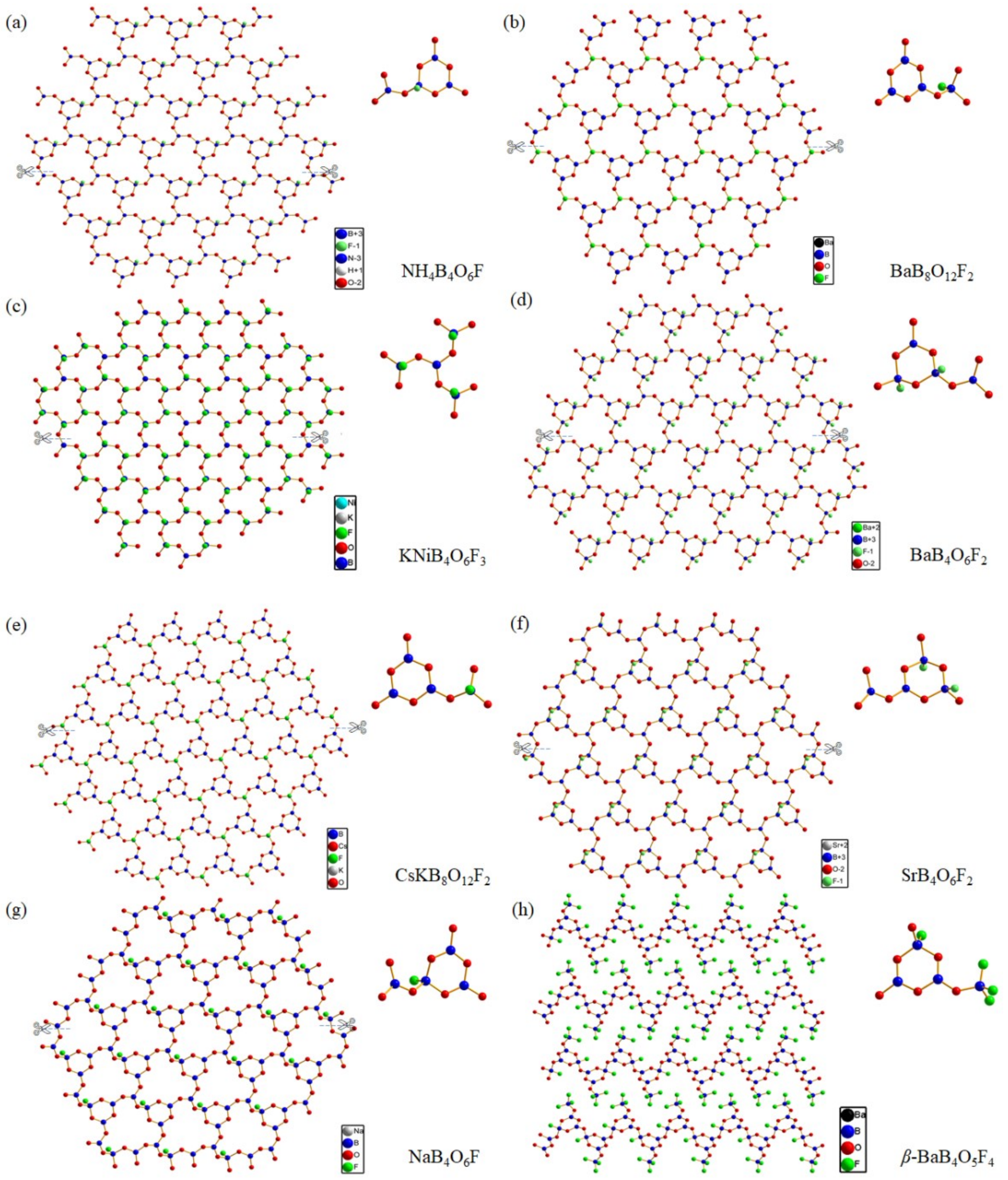

Figure S3. The different fundamental building blocks in the recent reported fluorooxoborates with four B atoms in the molecular formula compared with the title compound.

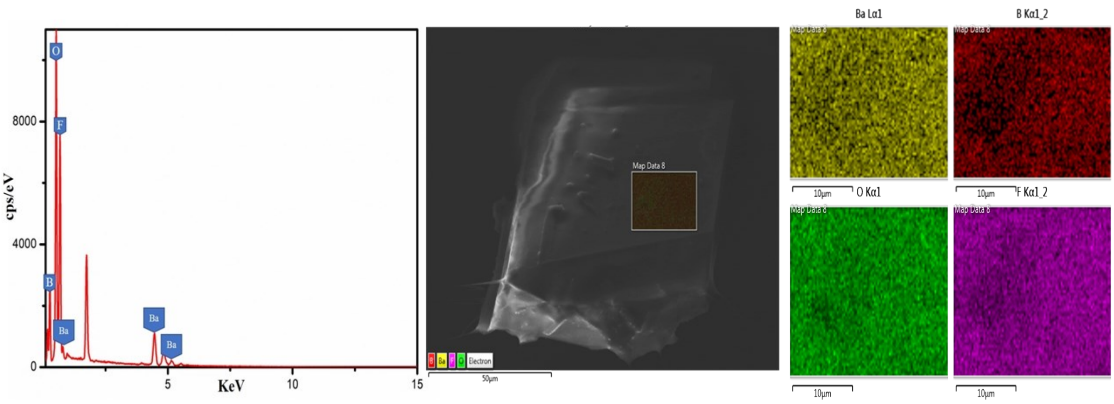

Figure S4. Energy dispersive X-ray spectroscopy was performed to verify the absence or presence of the F and O atoms.

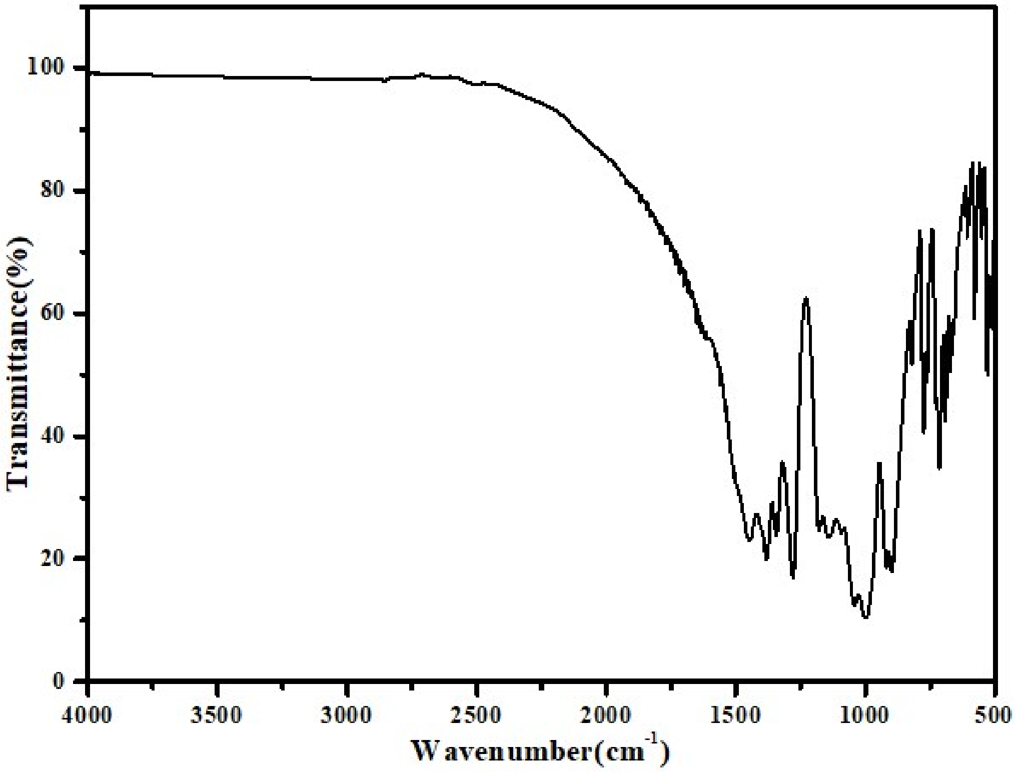

Figure S5. The IR spectrum for *β*-$BaB_4O_5F_4$.[8]

Mode description	IR (cm^{-1}) for *β*-$BaB_4O_5F_4$
Asymmetric stretching vibration of [BO_3] groups	1446 and 1381
Symmetric stretching vibration of [BO_3] groups	1346 and 821
Out-of-plane bending of [BO_3] groups	715
Bending of in plane bending of [BO_3] groups	578 and 530
Asymmetric stretching vibration of B-F bond	1178,1039 and 993
Symmetric stretching vibration of B-F bond	894 and 773

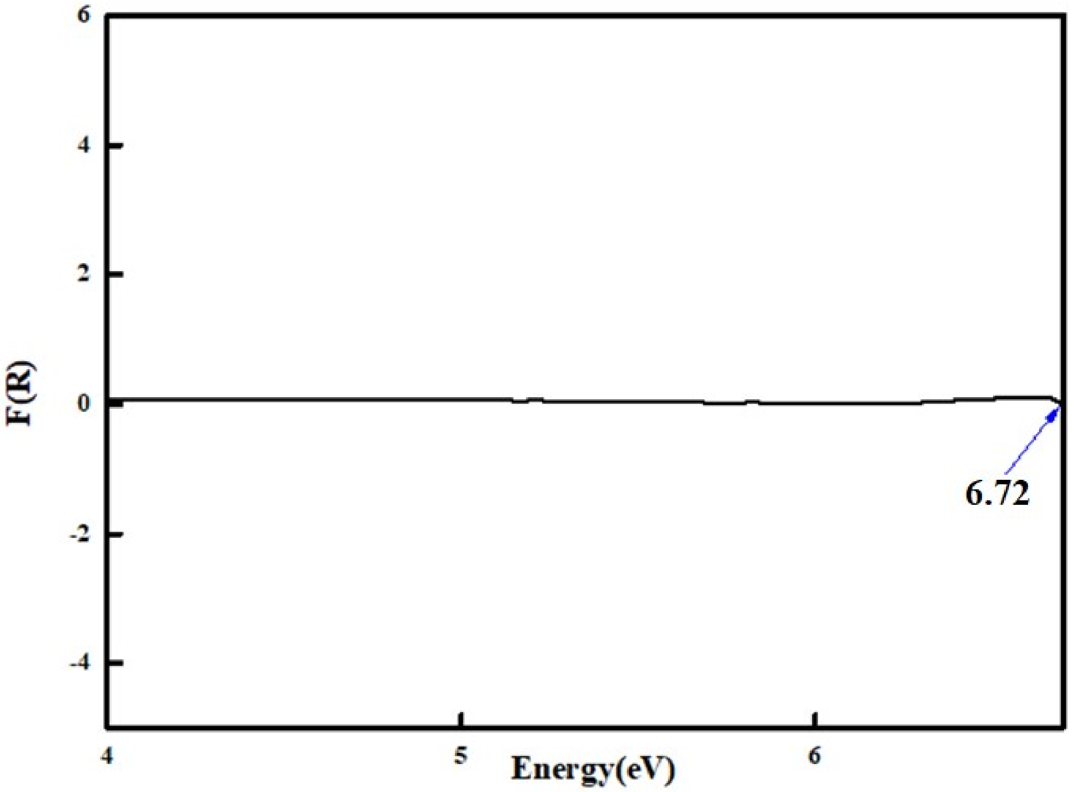

Figure S6. The experimental band gap of *β*-$BaB_4O_5F_4$.

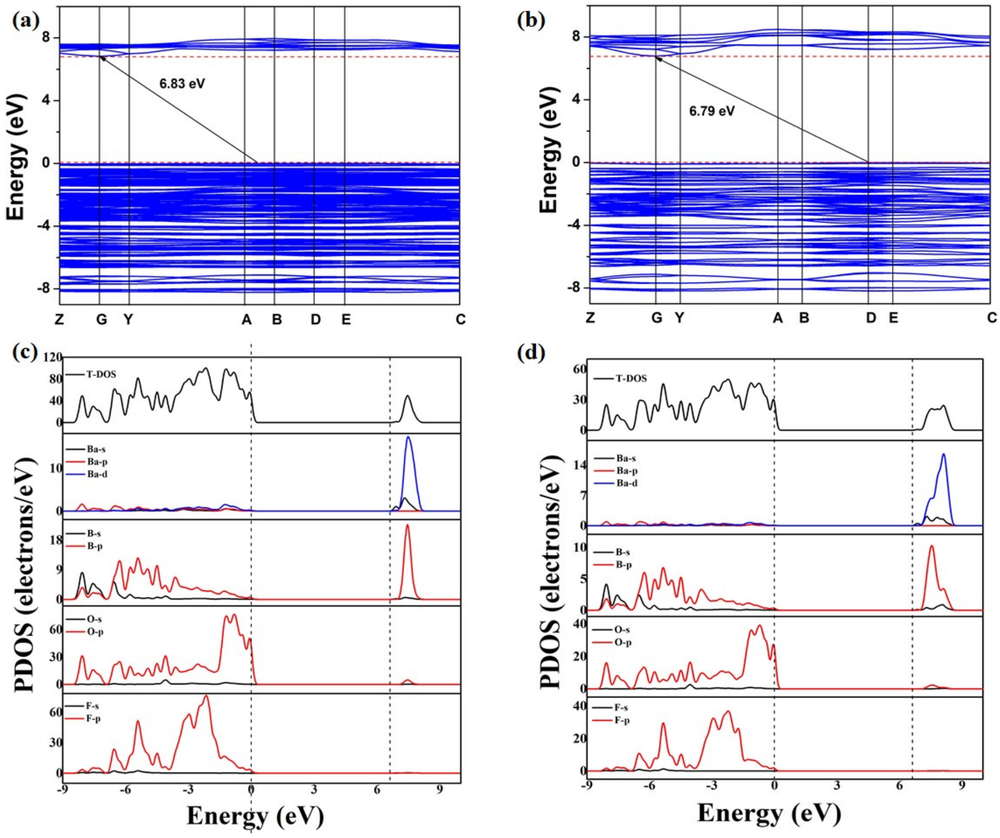

Figure S7. (a), (b) The electronic band gap of *α*, *β*-$BaB_4O_5F_4$ calculated with GGA. (c), (d) The partial density of states (PDOS) of *α*, *β*-$BaB_4O_5F_4$.

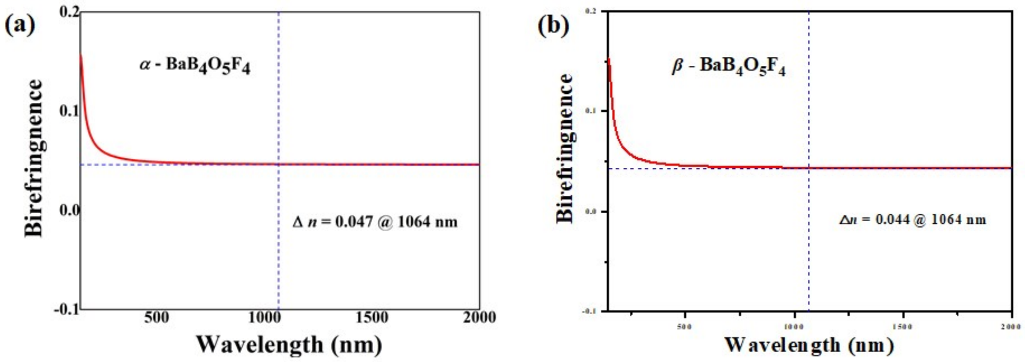

Figure S8. The calculated birefringence of $BaB_4O_5F_4$. It is noteworthy that the birefringence value of $BaB_4O_5F_4$ is comparable to those of recent reported fluorooxoborates, such as $Li_2B_3O_4F_3$ (Δn=0.05 at 1064 nm)[9]; LiB_6O_9F (Δn=0.04 at 1064 nm)[10]; and $A_{10}B_{13}O_{15}F_{19}$ (A=K, Rb) (Δn=0.03 at 1064 nm)[11].

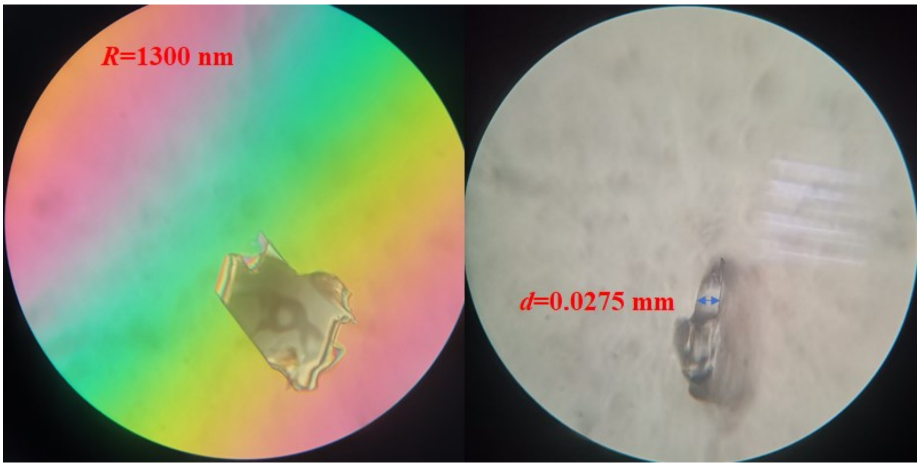

Figure S9. The photograph of β-$BaB_4O_5F_4$ crystal for the birefringence determination. The refractive index difference of β-$BaB_4O_5F_4$ is measured by using the cross-polarizing microscope equipped with Berek to be 0.047 at 546 nm. So, the birefringence of β-$BaB_4O_5F_4$ is larger or equal to 0.047 at 546 nm.

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