Supplementary Information

A Tri-Alkali/Alkaline-Earth Metal Fluorophosphate Deep-Ultraviolet Birefringent Crystal with Coexisting PO_3F and PO_2F_2

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CONTENTS

Synthesis

All chemical reagents including KF, H_3PO_4, $BaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 6H_2O$, and KH_2PO_4 (all 99.0% purity) were obtained from Aladdin Chemical Co. and utilized without further purification. $KBaSr(PO_2F_2)(PO_3F)$ (KBSPF) single crystals were grown through an optimized hydrothermal synthesis protocol using triethylamine (TEA)-H_2O mixed solvent system.

The synthetic procedure involved three main stages: First, a mineralizer solution was prepared by sequential addition of deionized water, KH_2PO_4, and a trace amount of H_2O_2 solution into KF solution, achieving final concentrations of 3 mol/L KF, 0.1 mol/L KH_2PO_4, and 0.1% H_2O_2. Subsequently, stoichiometric quantities of $BaCl_2 \cdot 2H_2O$ (0.3 g, 1.23 mmol) and $SrCl_2 \cdot 6H_2O$ (0.4 g, 1.50 mmol) were accurately weighed and transferred into a 23 mL Teflon-lined autoclave. The reactive mixture was formulated by introducing 2 mL mineralizer solution, 3 mL TEA, and 2 mL H_3PO_4 followed by mechanical stirring to homogenize the slurry.

The sealed reaction vessel underwent hydrothermal treatment at 230°C for 96 hours under autogenous pressure conditions, followed by controlled cooling to ambient temperature at $4°C \cdot h^{-1}$. Subsequent washing cycles with distilled water yielded colorless block crystals of KBSPF with optical transparency.

Single-Crystal Structure Determination.

A high-quality colorless crystal of $KBaSr(PO_2F_2)(PO_3F)$ (KBSPF) was selected using an optical microscope for single-crystal X-ray diffraction (XRD) analysis. The diffraction data were collected by using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 293(2) K on an Rigaku Oxford diffractometer. The collection of the intensity data, cell refinement, and data reduction was carried out with the CrysAlisPro software (version 1.171.41.116a). Using Olex2,[1] the structure was solved with the

SHELXS[2] structure solution program using Direct Methods and refined with the SHELXL[3] refinement package using Least Squares minimisation. Final refinements include anisotropic displacement parameters. Both structures were verified by the ADDSYM algorithm from the program PLATON,[4] and no higher symmetry was found. Details of crystal parameters, data collection, and structure refinement were summarized in Table S1. The atomic coordinates and equivalent isotropic displacement parameters were listed in Table S2. The anisotropic displacement parameters were listed in Table S3. Selected bond lengths and bond angles were presented in Table S4 and Table S5.

Powder X-Ray Diffraction.

Powder X-ray diffraction (PXRD) measurement for the sample of KBSPF was carried out with a Miniflex 600 diffractometer equipped with an incident beam monochromator set of Cu Kα radiation (λ = 1.5418 Å), and the 2θ range of 5-70°, with a scan step width of 0.02° and a scanning rate of 0.15° min^{-1}.

Elemental Analysis and Scanning Electron Microscope Mapping.

The elemental analysis was performed on the Vario MICRO cube Elementar. In addition, the scanning electron microscope (SEM) elemental mapping on the KBSPF single crystal was collected on a field emission SEM (Hitachi SU8010).

Thermal Stability.

The thermal stability was investigated by the differential thermal analysis (DTA) on a simultaneous NETZSCH STA 449C thermal analyzer in an atmosphere of flowing N_2. About 6.935 mg KBSPF powders were placed into an Al_2O_3 crucible, and heated at a rate of 10 K·min^{-1} from room temperature to 723 K (Figure S4). According to the

thermogravimetry - differential thermal analysis (TG-DTA) curves of KBSPF, an endothermic peak appears at 550 K on the DTA curve and corresponds to the mass loss on the TG curve.

FTIR Analysis

The Fourier transform infrared spectroscopy (IR) spectrum of KBSPF was recorded on a Bruker VERTEX 70 infrared spectrometer at room temperature in the wavenumber from 400 to 4000 cm^{-1} .

Birefringence Tests.

The birefringence of KBSPF was characterized by the polarized method under the polarized microscope (Nikon ECLIPSE LV100N POL) equipped with a Berek compensator. The wavelength of the light source was typically white light (such as halogen lamps). The relative error is small enough because of the clear boundary lines of the first-, second- and third-order interference color. In order to improve the accuracy of the birefringence, small and transparent KBSPF crystals were chosen. The tested crystal planes were determined by single-crystal XRD diffraction. The formula for calculating the birefringence is listed below:[5, 6]

$$R = | n_e - n_o | \times d = \Delta n \times d$$

Here, R represents the optical path difference, Δn is the birefringence, and d denotes the thickness of the tested crystal.

Theoretical Calculations.

The first-principles calculations were carried out with the CASTEP software,[7] a plane-wave pseudopotential package[8] on the basis of the density functional theory (DFT).[9] The exchange-correlation energy was described by the generalized gradient

approximation (GGA) scheme of the Perdew-Burke-Ernzerhof (PBE) functional, as implemented in the CASTEP code.[10] Norm-conserving pseudopotentials were employed to simulate the ion-electron interactions for each atomic specie with following valence configurations: O $2s^2$ $2p^4$, F $2s^2$ $2p^5$, P $3s^2$ $3p^3$, Ba $5s^2$ $5p^6$ $6s^2$, Sr $4p^6$ $5s^2$ K $3s^2$ $3p^6$ $4s^1$.[11] A cutoff energy of 900 eV and the Monkhorst-Pack[12] k-point meshes (3×3×1) spacing about 0.05 $Å^{-1}$ in the Brillouin zone were chosen for the calculation.

Solid-State NMR

Solid-state NMR was analyzed on a Bruker Avance 400 III HD spectrometer (magnetic field strength 9.7 T) at resonance frequency of 376.5 MHz for ^{19}F and 162.0 MHz for ^{31}P on a 2.5 mm H/F/X magnetic-angle spinning (MAS) triple resonance probe. For ^{19}F, the total suppression of sidebands (TOSS) sequences was applied to suppress all sidebands arising from the spinning of the outer rotor in ^{19}F MAS NMR experiments at a spinning speed of 34 kHz, with a 3.3 us ^{19}F $\pi/2$ pulse and a recycle delay of 6 s. The F signal of ammonium trifluoroacetate at -72.0 ppm was used as the reference of ^{19}F chemical shift. For ^{31}P, ^{19}F-^{31}P cross-polarization (CP) was performed at a spinning speed of 20 kHz, with a 3.3 us ^{19}F $\pi/2$ pulse, a 4 ms CP pulse, and a recycle delay of 10 s.

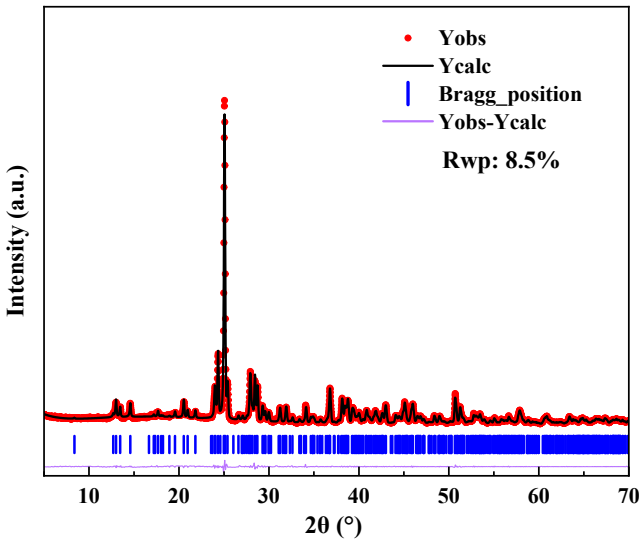

Figure S1. Comparison of the observed (Yobs) and calculated (Ycalc) XRD. Yobs-Ycalc is the difference between experimental and calculated intensities.

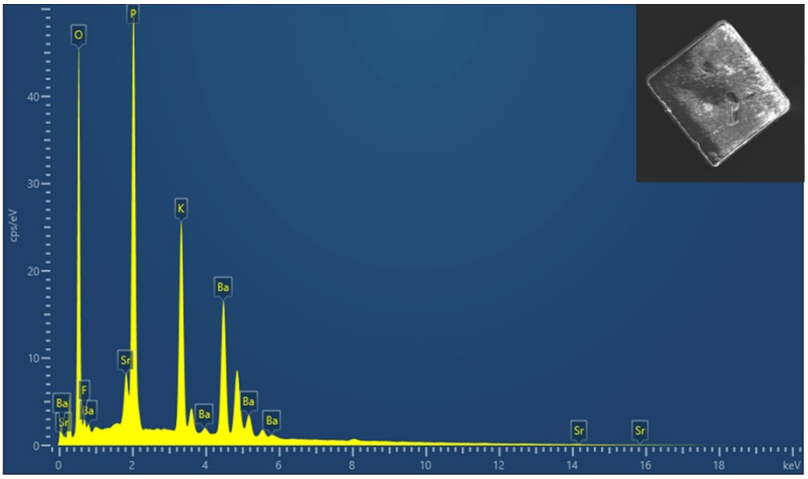

Figure S2. Energy dispersive X-ray (EDX) analysis of KBSPF.

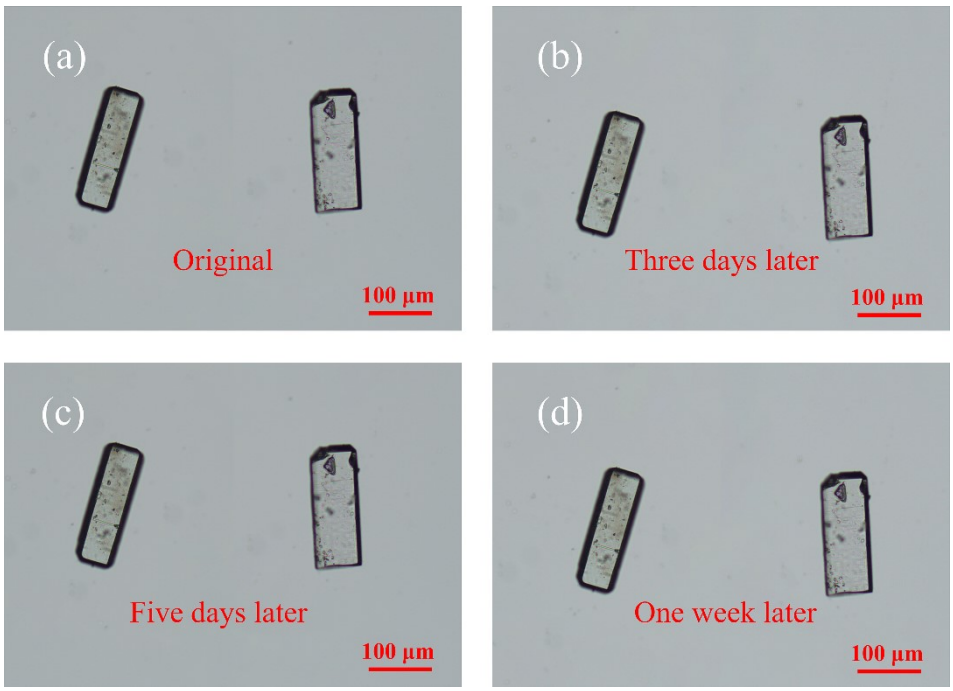

Figure S3. Comparative morphology images of the crystal under polarized light microscopy before and after one week.

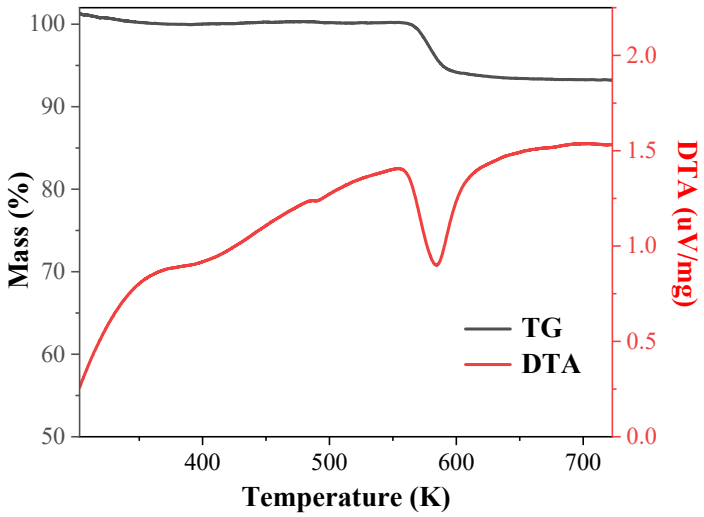

Figure S4. TG and DTA curves of KBSPF.

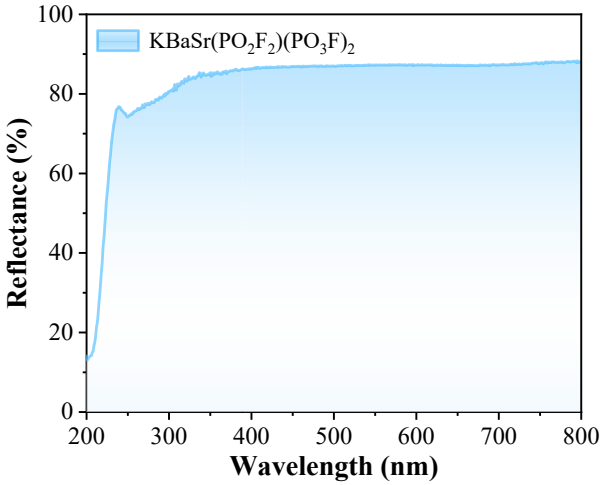

Figure S5. The UV-Vis-NIR diffuse reflectance spectrum of KBSPF.

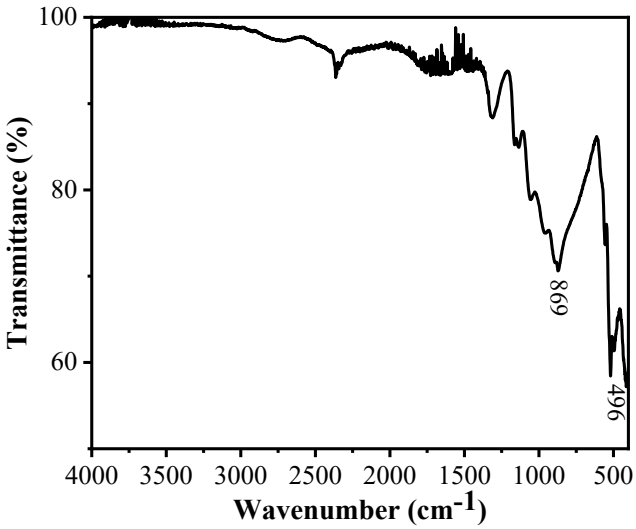

Figure S6. FTIR of KBSPF.

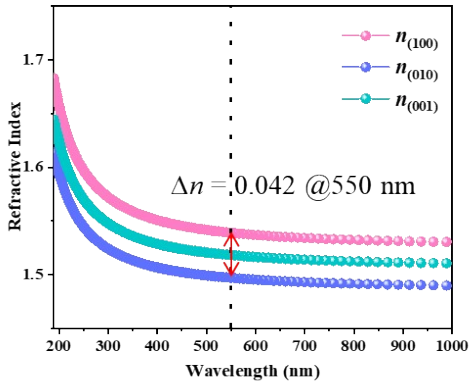

Figure S7. The calculated refractive index of KBSPF.

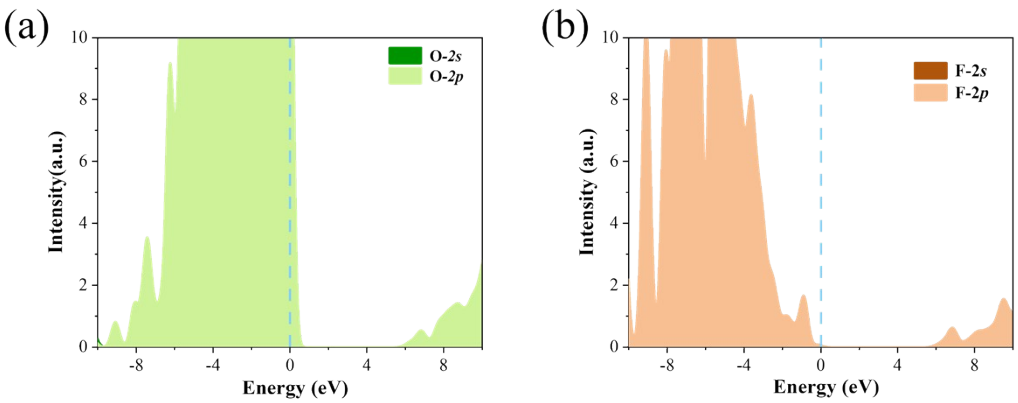

Figure S8. The PDOS of the O (a) and F (b).

Table S1. Crystallographic data and structural refinement for KBSPF.

Empirical formula	$KBaSr(PO_2F_2)(PO_3F)_2$
Formula weight	560.97
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.06380(10)
b/Å	7.43060(10)
c/Å	21.3633(3)
α/°	90
β/°	93.3860(10)
γ/°	90
Volume/Å^3	1119.37(3)
Z	4
ρ(g/cm^3)	3.329
μ/mm^{-1}	9.147
F(000)	1032.0
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.82 to 61.502
Index ranges	$-10 \le h \le 9$, $-10 \le k \le 10$, $-30 \le l \le 30$
Reflections collected	47769
Independent reflections	3179 [R_{int} = 0.0396, R_{sigma} = 0.0178]
Data/restraints/parameters	3179/0/164
Goodness-of-fit on F^2	1.053
Final R indexes ($I \ge 2\sigma(I)$)[a]	R_1 = 0.0236, wR_2 = 0.0564
Final R indexes (all data)[a]	R_1 = 0.0260, wR_2 = 0.0575
Largest diff. peak/hole (e Å^{-3})	0.89/-0.96

[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 ($Å^2 \times 10^3$) for KBSPF.

Atom	x	y	z	U(eq)
Ba(1)	10507.3(2)	8118.2(2)	4171.2(2)	5.90(6)
K(1)	6538.0(10)	6880.3(9)	5838.5(3)	9.32(13)
P(2)	5515.6(11)	8148.2(11)	4130.6(4)	5.46(15)
P(3)	8635.8(11)	13106.3(10)	4208.6(4)	5.30(15)
F(2)	4253(3)	9486(3)	4480.4(10)	17.8(4)
F(3)	9711(3)	11541(3)	4503.3(11)	19.7(5)
F(4)	9813(3)	14580(3)	3945.1(11)	18.9(4)
O(4)	6919(3)	7219(3)	4593.6(11)	8.2(4)
O(5)	4123(3)	6765(3)	3806.1(10)	7.7(4)
O(6)	6611(3)	9132(3)	3636.6(11)	9.0(4)
O(7)	7374(3)	13907(3)	4731.7(11)	9.2(4)
O(8)	7209(3)	12428(3)	3661.1(11)	9.4(4)
Sr(1)	6061.4(4)	-791.6(4)	2360.6(2)	8.36(8)
P(1)	4066.6(11)	4171.0(11)	2448.8(4)	7.18(15)
F(1)	5274(3)	2769(3)	2156.3(11)	23.4(5)
O(1)	2902(4)	5153(3)	1891.7(12)	16.4(5)
O(2)	5319(3)	5653(3)	2782.2(11)	8.8(4)
O(3)	2685(3)	3423(3)	2902.6(11)	10.4(4)

Table S3. Anisotropic displacement parameters ($Å^2$) for KBSPF.

Atom	U11	U22	U33	U23	U13	U12
Ba(1)	5.97(9)	5.19(9)	6.57(9)	-0.05(6)	0.73(6)	-0.25(6)
K(1)	8.1(3)	11.5(3)	8.4(3)	1.5(2)	0.5(2)	1.0(2)
P(2)	4.8(3)	5.4(3)	6.2(3)	-1.1(3)	0.6(3)	-0.6(3)
P(3)	5.4(3)	4.7(3)	5.8(3)	0.8(3)	0.1(3)	0.2(3)
F(2)	18.1(10)	17.9(11)	17.4(10)	-2.1(9)	0.8(8)	1.0(9)
F(3)	21.5(11)	16.2(10)	21.0(11)	1.9(9)	-0.8(9)	2.6(9)
F(4)	19.5(11)	16.1(10)	21.3(11)	0.3(9)	2.6(9)	-1.3(9)
O(4)	6.9(10)	8.1(10)	9.5(10)	-1.1(8)	-0.6(8)	1.8(8)
O(5)	6.9(10)	8.4(10)	7.8(10)	-2.8(8)	0.2(8)	-2.0(8)
O(6)	12.2(11)	7.6(10)	7.8(10)	-1.3(8)	4.8(8)	-2.4(9)
O(7)	11.2(11)	6.8(10)	10.2(11)	0.3(8)	5.6(8)	0.5(8)
O(8)	9.9(10)	9.4(10)	8.4(10)	2.1(8)	-4.5(8)	-2.1(9)
Sr(1)	8.61(14)	8.84(14)	7.51(14)	0.45(10)	-0.4(1)	-0.81(11)
P(1)	8.9(4)	6.2(3)	6.4(3)	-2.1(3)	0.0(3)	-0.7(3)
F(1)	23.5(12)	24.3(12)	22.7(12)	-5.7(10)	3.6(9)	0.2(10)
O(1)	24.3(13)	13.3(12)	10.2(11)	0.0(9)	-9.7(10)	1.3(10)
O(2)	8.6(10)	8.0(10)	9.6(10)	-3.3(8)	-1.0(8)	-2.1(8)
O(3)	9.0(10)	12.2(11)	10.4(11)	-3.4(9)	3.6(8)	-3.1(9)

Table S4. Selected bond distances (Å) for KBSPF.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ba(1)	P(2)	3.5220(8)	P(2)	F(2)	1.556(2)
Ba(1)	P(2)[1]	3.5440(8)	P(2)	O(4)	1.524(2)
Ba(1)	F(2)[1]	2.875(2)	P(2)	O(5)	1.557(2)
Ba(1)	F(3)	2.708(2)	P(2)	O(6)	1.531(2)
Ba(1)	F(3)[2]	2.856(2)	P(3)	F(3)	1.507(2)
Ba(1)	F(4)[3]	2.713(2)	P(3)	F(4)	1.504(2)
Ba(1)	O(4)	2.821(2)	P(3)	O(7)	1.586(2)
Ba(1)	O(5)[1]	2.894(2)	P(3)	O(8)	1.581(2)
Ba(1)	O(6)	3.013(2)	P(3)	Sr(1)[8]	3.4698(8)
Ba(1)	O(7)[2]	3.096(2)	F(4)	Sr(1)[8]	2.835(2)
Ba(1)	F(1)[4]	2.869(2)	O(6)	Sr(1)[9]	2.731(2)
Ba(1)	O(1)[4]	3.001(3)	O(8)	Sr(1)[8]	2.885(2)
K(1)	P(3)[2]	3.4166(10)	Sr(1)	Sr(1)[4]	4.2598(3)
K(1)	P(3)[5]	3.6501(10)	Sr(1)	P(1)[10]	3.6691(9)
K(1)	F(2)[5]	2.832(2)	Sr(1)	P(1)[11]	3.4416(9)
K(1)	F(3)[2]	3.026(2)	Sr(1)	F(1)	2.733(3)
K(1)	F(4)[2]	2.810(2)	Sr(1)	F(1)[11]	2.932(2)
K(1)	O(4)	2.700(2)	Sr(1)	O(2)[11]	2.806(2)
K(1)	O(5)[6]	2.859(2)	Sr(1)	O(2)[3]	2.850(2)
K(1)	O(7)[5]	3.011(2)	Sr(1)	O(3)[10]	2.736(2)
K(1)	O(7)[3]	3.315(2)	P(1)	F(1)	1.505(2)
K(1)	O(8)[5]	2.958(2)	P(1)	O(1)	1.584(3)
K(1)	O(1)[7]	3.255(3)	P(1)	O(2)	1.558(2)
K(1)	O(3)[6]	2.722(2)	P(1)	O(3)	1.521(2)

[1]1+X,+Y,+Z;[2]2-X,2-Y,1-Z;[3]+X,-1+Y,+Z;[4]3/2-X,1/2+Y,1/2-Z;[5]1-X,2-Y,1-Z;[6]1-X,1-Y,1-Z;[7]1/2+X,3/2-Y,1/2+Z;[8]3/2-X,3/2+Y,1/2-Z;[9]+X,1+Y,+Z;[10]1/2-X,-1/2+Y,1/2-Z;[11]3/2-X,-

1/2+Y,1/2-

Table S5. Selected bond angles (°) for KBSPF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P(2)	Ba(1)	P(2)1	177.10(3)	F(3)	P(3)	Sr(1)^{9}	121.84(10)
F(2)^{1}	Ba(1)	P(2)	155.50(5)	F(4)	P(3)	Ba(1)^{2}	118.63(9)
F(2)^{1}	Ba(1)	P(2)1	25.42(4)	F(4)	P(3)	K(1)^{2}	54.00(9)
F(2)^{1}	Ba(1)	O(5)1	50.94(6)	F(4)	P(3)	K(1)^{5}	124.23(10)
F(2)^{1}	Ba(1)	O(6)	143.76(6)	F(4)	P(3)	F(3)	116.24(14)
F(2)^{1}	Ba(1)	O(7)2	66.46(6)	F(4)	P(3)	O(7)	109.69(13)
F(2)^{1}	Ba(1)	O(1)3	67.37(7)	F(4)	P(3)	O(8)	107.31(13)
F(3)	Ba(1)	P(2)	77.14(5)	F(4)	P(3)	Sr(1)^{9}	53.10(9)
F(3)	Ba(1)	P(2)1	102.92(5)	O(7)	P(3)	Ba(1)^{2}	59.08(9)
F(3)^{2}	Ba(1)	P(2)1	97.83(5)	O(7)	P(3)	K(1)^{5}	54.19(9)
F(3)^{2}	Ba(1)	P(2)	84.91(5)	O(7)	P(3)	K(1)^{2}	128.54(10)
F(3)^{2}	Ba(1)	F(2)1	81.01(6)	O(7)	P(3)	Sr(1)^{9}	131.43(9)
F(3)	Ba(1)	F(2)1	79.07(7)	O(8)	P(3)	Ba(1)^{2}	134.06(9)
F(3)	Ba(1)	F(3)2	68.46(8)	O(8)	P(3)	K(1)^{5}	52.19(9)
F(3)	Ba(1)	F(4)4	156.73(7)	O(8)	P(3)	K(1)^{2}	124.94(10)
F(3)	Ba(1)	O(4)	86.23(7)	O(8)	P(3)	O(7)	106.32(13)
F(3)	Ba(1)	O(5)^{1}	126.65(7)	O(8)	P(3)	Sr(1)^{9}	55.48(9)
F(3)^{2}	Ba(1)	O(5)^{1}	113.46(6)	Sr(1)^{9}	P(3)	Ba(1)^{2}	166.74(3)
F(3)	Ba(1)	O(6)	70.44(7)	Sr(1)^{9}	P(3)	K(1)^{5}	95.25(2)
F(3)^{2}	Ba(1)	O(6)	104.60(6)	K(1)^{5}	F(2)	Ba(1)^{8}	96.66(7)
F(3)	Ba(1)	O(7)^{2}	110.90(6)	P(2)	F(2)	Ba(1)^{8}	102.10(10)
F(3)^{2}	Ba(1)	O(7)^{2}	49.04(6)	P(2)	F(2)	K(1)^{5}	127.16(12)
F(3)	Ba(1)	F(1)^{3}	108.24(7)	Ba(1)	F(3)	Ba(1)^{2}	111.54(8)
F(3)^{2}	Ba(1)	F(1)^{3}	165.84(7)	Ba(1)	F(3)	K(1)^{2}	95.88(7)

F(3)^{2}	Ba(1)	O(1)^{3}	138.60(7)	Ba(1)^{2}	F(3)	K(1)^{2}	107.71(7)
F(3)	Ba(1)	O(1)^{3}	79.51(7)	P(3)	F(3)	Ba(1)	136.30(13)
F(4)^{4}	Ba(1)	P(2)^{1}	99.90(5)	P(3)	F(3)	Ba(1)^{2}	106.88(11)
F(4)^{4}	Ba(1)	P(2)	80.30(5)	P(3)	F(3)	K(1)^{2}	91.54(11)
F(4)^{4}	Ba(1)	F(2)^{1}	122.54(7)	Ba(1)^{10}	F(4)	K(1)^{2}	100.98(7)
F(4)^{4}	Ba(1)	F(3)^{2}	104.05(7)	Ba(1)^{10}	F(4)	Sr(1)^{9}	107.23(8)
F(4)^{4}	Ba(1)	O(4)	70.78(7)	K(1)^{2}	F(4)	Sr(1)^{9}	105.59(7)
F(4)^{4}	Ba(1)	O(5)^{1}	76.61(6)	P(3)	F(4)	Ba(1)^{10}	137.47(13)
F(4)^{4}	Ba(1)	O(6)	91.34(7)	P(3)	F(4)	K(1)^{2}	100.34(11)
F(4)^{4}	Ba(1)	O(7)^{2}	74.81(6)	P(3)	F(4)	Sr(1)^{9}	101.79(11)
F(4)^{4}	Ba(1)	F(1)^{3}	73.39(7)	K(1)	O(4)	Ba(1)	118.73(8)
F(4)^{4}	Ba(1)	O(1)^{3}	115.17(7)	P(2)	O(4)	Ba(1)	104.31(11)
O(4)	Ba(1)	P(2)	24.79(5)	P(2)	O(4)	K(1)	125.64(12)
O(4)	Ba(1)	P(2)^{1}	157.90(5)	K(1)6	O(5)	Ba(1)^{8}	95.56(7)
O(4)	Ba(1)	F(2)^{1}	147.41(6)	P(2)	O(5)	Ba(1)^{8}	101.26(10)
O(4)	Ba(1)	F(3)^{2}	66.53(7)	P(2)	O(5)	K(1)^{6}	128.02(12)
O(4)	Ba(1)	O(5)^{1}	145.88(6)	P(2)	O(6)	Ba(1)	96.14(11)
O(4)	Ba(1)	O(6)	50.39(6)	P(2)	O(6)	Sr(1)^{10}	130.55(13)
O(4)	Ba(1)	O(7)^{2}	92.64(6)	Sr(1)^{10}	O(6)	Ba(1)	117.15(8)
O(4)	Ba(1)	F(1)^{3}	99.84(7)	Ba(1)^{2}	O(7)	K(1)^{10}	83.25(6)
O(4)	Ba(1)	O(1)^{3}	138.17(7)	K(1)^{5}	O(7)	Ba(1)^{2}	127.09(8)
O(5)^{1}	Ba(1)	P(2)	153.33(5)	K(1)^{5}	O(7)	K(1)^{10}	102.72(7)
O(5)^{1}	Ba(1)	P(2)^{1}	25.52(5)	P(3)	O(7)	Ba(1)^{2}	94.85(10)
O(5)^{1}	Ba(1)	O(6)	141.78(6)	P(3)	O(7)	K(1)^{5}	100.52(11)
O(5)^{1}	Ba(1)	O(7)^{2}	68.92(6)	P(3)	O(7)	K(1)^{10}	152.12(13)
O(5)^{1}	Ba(1)	O(1)^{3}	66.13(7)	P(3)	O(8)	K(1)^{5}	102.83(11)
O(6)	Ba(1)	P(2)^{1}	151.65(5)	P(3)	O(8)	Sr(1)^{9}	97.69(10)
O(6)	Ba(1)	P(2)	25.60(4)	Sr(1)^{9}	O(8)	K(1)^{5}	128.44(8)
O(6)	Ba(1)	O(7)^{2}	143.00(6)	P(3)^{11}	Sr(1)	Sr(1)^{3}	106.549(17)

O(7)^{2}	Ba(1)	P(2)	117.41(4)	P(3)^{11}	Sr(1)	P(1)^{12}	102.890(19)
O(7)^{2}	Ba(1)	P(2)^{1}	65.35(4)	F(4)^{11}	Sr(1)	P(3)^{11}	25.11(5)
F(1)^{3}	Ba(1)	P(2)^{1}	96.33(5)	F(4)^{11}	Sr(1)	O(8)^{11}	51.50(6)
F(1)^{3}	Ba(1)	P(2)	80.94(5)	F(4)^{11}	Sr(1)	Sr(1)^{3}	97.31(5)
F(1)^{3}	Ba(1)	F(2)^{1}	112.32(7)	F(4)^{11}	Sr(1)	P(1)^{12}	87.18(5)
F(1)^{3}	Ba(1)	O(5)^{1}	79.83(7)	F(4)^{11}	Sr(1)	P(1)^{13}	105.99(5)
F(1)^{3}	Ba(1)	O(6)	61.96(6)	F(4)^{11}	Sr(1)	F(1)^{13}	121.23(7)
F(1)^{3}	Ba(1)	O(7)^{2}	139.52(7)	F(4)^{11}	Sr(1)	O(2)^{4}	111.58(7)
F(1)^{3}	Ba(1)	O(1)^{3}	49.92(7)	O(6)^{4}	Sr(1)	P(3)^{11}	161.11(5)
O(1)^{3}	Ba(1)	P(2)	113.40(5)	O(6)^{4}	Sr(1)	F(4)^{11}	173.74(7)
O(1)^{3}	Ba(1)	P(2)^{1}	63.86(5)	O(6)^{4}	Sr(1)	O(8)^{11}	134.76(7)
O(1)^{3}	Ba(1)	O(6)	87.80(7)	O(6)^{4}	Sr(1)	Sr(1)^{3}	80.79(5)
O(1)^{3}	Ba(1)	O(7)^{2}	129.19(7)	O(6)^{4}	Sr(1)	P(1)^{13}	78.43(5)
P(3)^{2}	K(1)	P(3)^{5}	176.72(3)	O(6)^{4}	Sr(1)	P(1)^{12}	88.40(5)
F(2)^{5}	K(1)	P(3)^{2}	99.97(5)	O(6)^{4}	Sr(1)	F(1)	101.24(7)
F(2)^{5}	K(1)	P(3)^{5}	78.92(5)	O(6)^{4}	Sr(1)	F(1)^{13}	64.57(7)
F(2)^{5}	K(1)	F(3)^{2}	74.66(6)	O(6)^{4}	Sr(1)	O(2)^{13}	92.28(7)
F(2)^{5}	K(1)	O(5)^{6}	159.09(7)	O(6)^{4}	Sr(1)	O(2)^{4}	71.54(7)
F(2)^{5}	K(1)	O(7)^{4}	120.32(6)	O(6)^{4}	Sr(1)	O(3)^{12}	106.23(7)
F(2)^{5}	K(1)	O(7)^{5}	85.67(7)	O(8)^{11}	Sr(1)	P(3)^{11}	26.83(5)
F(2)^{5}	K(1)	O(8)^{5}	75.71(7)	O(8)^{11}	Sr(1)	Sr(1)^{3}	106.62(5)
F(2)^{5}	K(1)	O(1)^{7}	64.33(6)	O(8)^{11}	Sr(1)	P(1)^{13}	67.71(5)
F(3)^{2}	K(1)	P(3)^{2}	26.15(4)	O(8)^{11}	Sr(1)	P(1)^{12}	123.05(5)
F(3)^{2}	K(1)	P(3)^{5}	151.85(5)	O(8)^{11}	Sr(1)	F(1)^{13}	72.21(7)
F(3)^{2}	K(1)	O(7)^{4}	83.73(6)	P(1)^{13}	Sr(1)	P(3)^{11}	89.67(2)
F(3)^{2}	K(1)	O(1)^{7}	71.13(7)	P(1)^{12}	Sr(1)	Sr(1)^{3}	117.200(15)
F(4)^{2}	K(1)	P(3)^{5}	155.91(5)	P(1)^{13}	Sr(1)	Sr(1)^{3}	61.641(16)
F(4)^{2}	K(1)	P(3)^{2}	25.66(5)	P(1)^{13}	Sr(1)	P(1)^{12}	166.82(3)
F(4)^{2}	K(1)	F(2)^{5}	125.01(7)	F(1)	Sr(1)	P(3)^{11}	95.62(5)

F(4)^{2}	K(1)	F(3)^{2}	51.80(6)	F(1)^{13}	Sr(1)	P(3)^{11}	98.65(5)
F(4)^{2}	K(1)	O(5)^{6}	75.70(7)	F(1)	Sr(1)	F(4)^{11}	73.64(7)
F(4)^{2}	K(1)	O(7)^{4}	70.10(6)	F(1)	Sr(1)	O(8)^{11}	114.49(7)
F(4)^{2}	K(1)	O(7)^{5}	143.40(7)	F(1)^{13}	Sr(1)	Sr(1)^{3}	82.23(5)
F(4)^{2}	K(1)	O(8)^{5}	147.10(7)	F(1)	Sr(1)	Sr(1)^{3}	43.03(5)
F(4)^{2}	K(1)	O(1)^{7}	85.21(7)	F(1)	Sr(1)	P(1)^{13}	102.68(5)
O(4)	K(1)	P(3)^{5}	97.49(5)	F(1)^{13}	Sr(1)	P(1)^{12}	144.61(5)
O(4)	K(1)	P(3)^{2}	79.23(5)	F(1)	Sr(1)	P(1)^{12}	80.33(5)
O(4)	K(1)	F(2)^{5}	72.78(7)	F(1)^{13}	Sr(1)	P(1)^{13}	25.76(5)
O(4)	K(1)	F(3)^{2}	65.59(7)	F(1)	Sr(1)	F(1)^{13}	125.20(7)
O(4)	K(1)	F(4)^{2}	93.11(7)	F(1)	Sr(1)	O(2)^{13}	77.92(7)
O(4)	K(1)	O(5)^{6}	112.15(7)	F(1)	Sr(1)	O(2)^{4}	155.27(7)
O(4)	K(1)	O(7)^{4}	47.72(6)	F(1)	Sr(1)	O(3)^{12}	89.33(7)
O(4)	K(1)	O(7)^{5}	76.23(7)	O(2)^{4}	Sr(1)	P(3)^{11}	96.29(5)
O(4)	K(1)	O(8)^{5}	118.88(7)	O(2)^{13}	Sr(1)	P(3)^{11}	82.92(5)
O(4)	K(1)	O(1)^{7}	125.10(7)	O(2)^{13}	Sr(1)	F(4)^{11}	90.16(7)
O(4)	K(1)	O(3)^{6}	162.67(7)	O(2)^{4}	Sr(1)	O(8)^{11}	84.72(7)
O(5)^{6}	K(1)	P(3)^{5}	80.27(5)	O(2)^{13}	Sr(1)	O(8)^{11}	70.36(7)
O(5)^{6}	K(1)	P(3)^{2}	100.92(5)	O(2)^{13}	Sr(1)	Sr(1)^{3}	41.53(5)
O(5)^{6}	K(1)	F(3)^{2}	126.18(7)	O(2)^{4}	Sr(1)	Sr(1)^{3}	149.26(5)
O(5)^{6}	K(1)	O(7)^{5}	76.29(7)	O(2)^{4}	Sr(1)	P(1)^{12}	75.92(5)
O(5)^{6}	K(1)	O(7)^{4}	66.21(6)	O(2)^{13}	Sr(1)	P(1)^{13}	26.47(5)
O(5)^{6}	K(1)	O(8)^{5}	84.55(7)	O(2)^{4}	Sr(1)	P(1)^{13}	98.99(5)
O(5)^{6}	K(1)	O(1)^{7}	120.30(7)	O(2)^{13}	Sr(1)	P(1)^{12}	157.94(5)
O(7)^{5}	K(1)	P(3)^{2}	151.91(5)	O(2)^{4}	Sr(1)	F(1)^{13}	74.07(7)
O(7)^{5}	K(1)	P(3)^{5}	25.28(4)	O(2)^{13}	Sr(1)	F(1)^{13}	52.16(7)
O(7)^{4}	K(1)	P(3)^{2}	76.16(5)	O(2)^{13}	Sr(1)	O(2)^{4}	125.08(6)
O(7)^{4}	K(1)	P(3)^{5}	101.68(5)	O(3)^{12}	Sr(1)	P(3)^{11}	82.25(5)
O(7)^{5}	K(1)	F(3)^{2}	140.66(7)	O(3)^{12}	Sr(1)	F(4)^{11}	70.52(7)

O(7)^{5}	K(1)	O(7)^{4}	77.28(7)	O(3)^{12}	Sr(1)	O(8)^{11}	101.21(7)
O(7)^{5}	K(1)	O(1)^{7}	129.68(7)	O(3)^{12}	Sr(1)	Sr(1)^{3}	131.49(5)
O(8)^{5}	K(1)	P(3)^{5}	24.97(5)	O(3)^{12}	Sr(1)	P(1)^{13}	166.17(5)
O(8)^{5}	K(1)	P(3)^{2}	157.83(5)	O(3)^{12}	Sr(1)	P(1)^{12}	21.85(5)
O(8)^{5}	K(1)	F(3)^{2}	146.60(7)	O(3)^{12}	Sr(1)	F(1)^{13}	144.88(7)
O(8)^{5}	K(1)	O(7)^{4}	125.07(7)	O(3)^{12}	Sr(1)	O(2)^{13}	159.35(7)
O(8)^{5}	K(1)	O(7)^{5}	50.23(6)	O(3)^{12}	Sr(1)	O(2)^{4}	70.95(7)
O(8)^{5}	K(1)	O(1)^{7}	82.37(7)	Ba(1)^{13}	P(1)	K(1)^{6}	155.42(3)
O(1)^{7}	K(1)	P(3)^{2}	76.30(5)	Ba(1)^{13}	P(1)	Sr(1)^{14}	104.42(2)
O(1)^{7}	K(1)	P(3)^{5}	105.80(5)	Sr(1)^{3}	P(1)	Ba(1)^{13}	88.601(19)
O(1)^{7}	K(1)	O(7)^{4}	152.45(7)	Sr(1)^{3}	P(1)	K(1)^{6}	93.23(2)
O(3)^{6}	K(1)	P(3)^{2}	83.45(5)	Sr(1)^{14}	P(1)	K(1)^{6}	74.104(19)
O(3)^{6}	K(1)	P(3)^{5}	99.83(5)	Sr(1)^{3}	P(1)	Sr(1)^{14}	166.82(3)
O(3)^{6}	K(1)	F(2)^{5}	110.01(7)	F(1)	P(1)	Ba(1)^{13}	50.59(10)
O(3)^{6}	K(1)	F(3)^{2}	98.17(7)	F(1)	P(1)	K(1)^{6}	110.91(10)
O(3)^{6}	K(1)	F(4)^{2}	71.09(7)	F(1)	P(1)	Sr(1)^{14}	129.68(10)
O(3)^{6}	K(1)	O(5)^{6}	71.68(7)	F(1)	P(1)	Sr(1)^{3}	57.84(10)
O(3)^{6}	K(1)	O(7)^{5}	120.69(7)	F(1)	P(1)	O(1)	106.78(14)
O(3)^{6}	K(1)	O(7)^{4}	127.98(7)	F(1)	P(1)	O(2)	111.00(14)
O(3)^{6}	K(1)	O(8)^{5}	77.88(7)	F(1)	P(1)	O(3)	114.36(14)
O(3)^{6}	K(1)	O(1)^{7}	48.63(7)	O(1)	P(1)	Ba(1)^{13}	56.20(10)
Ba(1)	P(2)	Ba(1)^{8}	177.10(3)	O(1)	P(1)	K(1)^{6}	137.48(11)
Ba(1)	P(2)	K(1)	80.874(19)	O(1)	P(1)	Sr(1)^{14}	66.91(11)
Ba(1)^{8}	P(2)	K(1)	96.22(2)	O(1)	P(1)	Sr(1)^{3}	123.80(11)
F(2)	P(2)	Ba(1)	126.42(9)	O(2)	P(1)	Ba(1)^{13}	121.24(9)
F(2)	P(2)	Ba(1)^{8}	52.48(9)	O(2)	P(1)	K(1)^{6}	78.32(9)
F(2)	P(2)	K(1)	77.22(9)	O(2)	P(1)	Sr(1)^{3}	53.36(9)
F(2)	P(2)	O(5)	105.70(13)	O(2)	P(1)	Sr(1)^{14}	118.79(9)
O(4)	P(2)	Ba(1)	50.90(9)	O(2)	P(1)	O(1)	105.88(14)

O(4)	P(2)	Ba(1)[8]	126.38(9)	O(3)	P(1)	Ba(1)[13]	129.09(10)
O(4)	P(2)	K(1)	35.32(9)	O(3)	P(1)	K(1)[6]	36.50(9)
O(4)	P(2)	F(2)	110.31(13)	O(3)	P(1)	Sr(1)[3]	127.04(10)
O(4)	P(2)	O(5)	111.07(13)	O(3)	P(1)	Sr(1)[14]	42.01(10)
O(4)	P(2)	O(6)	109.16(14)	O(3)	P(1)	O(1)	108.84(15)
O(5)	P(2)	Ba(1)[8]	53.22(9)	O(3)	P(1)	O(2)	109.58(13)
O(5)	P(2)	Ba(1)	127.74(9)	Ba(1)[13]	F(1)	Sr(1)[3]	115.42(8)
O(5)	P(2)	K(1)	110.09(9)	Sr(1)	F(1)	Ba(1)[13]	105.71(8)
O(6)	P(2)	Ba(1)	58.26(9)	Sr(1)	F(1)	Sr(1)[3]	97.45(8)
O(6)	P(2)	Ba(1)[8]	124.46(10)	P(1)	F(1)	Ba(1)[13]	105.50(12)
O(6)	P(2)	K(1)	134.90(10)	P(1)	F(1)	Sr(1)[3]	96.41(11)
O(6)	P(2)	F(2)	110.70(13)	P(1)	F(1)	Sr(1)	135.94(14)
O(6)	P(2)	O(5)	109.89(13)	Ba(1)[13]	O(1)	K(1)[15]	85.81(6)
Ba(1)[2]	P(3)	K(1)[5]	97.97(2)	P(1)	O(1)	Ba(1)[13]	97.79(12)
K(1)[2]	P(3)	Ba(1)[2]	85.27(2)	P(1)	O(1)	K(1)[15]	161.92(14)
K(1)[2]	P(3)	K(1)[5]	176.72(3)	Sr(1)[3]	O(2)	Sr(1)[10]	97.73(7)
K(1)[2]	P(3)	Sr(1)[9]	81.51(2)	P(1)	O(2)	Sr(1)[3]	100.17(11)
F(3)	P(3)	Ba(1)[2]	49.48(9)	P(1)	O(2)	Sr(1)[10]	128.36(12)
F(3)	P(3)	K(1)[2]	62.30(9)	K(1)[6]	O(3)	Sr(1)[14]	110.91(8)
F(3)	P(3)	K(1)[5]	119.53(10)	P(1)	O(3)	K(1)[6]	124.09(13)
F(3)	P(3)	O(7)	106.60(13)	P(1)	O(3)	Sr(1)[14]	116.14(13)
F(3)	P(3)	O(8)	110.28(13)				

[1]1+X,+Y,+Z;[2]2-X,2-Y,1-Z;[3]3/2-X,1/2+Y,1/2-Z;[4]+X,-1+Y,+Z;[5]1-X,2-Y,1-Z;[6]1-X,1-Y,1-Z;[7]1/2+X,3/2-Y,1/2+Z;[8]-1+X,+Y,+Z;[9]3/2-X,3/2+Y,1/2-Z;[10]+X,1+Y,+Z;[11]3/2-X,-3/2+Y,1/2-Z;[12]1/2-X,-1/2+Y,1/2-Z;[13]3/2-X,-1/2+Y,1/2-Z;[14]1/2-X,1/2+Y,1/2-Z;[15]-1/2+X,3/2-Y,-1/2+Z

Table S6. Comparison of the birefringence of KBSPF with many famous phosphates and fluorophosphate optical crystals.

Compound	Birefringence	Ref.
$Rb_2Ba_3(P_2O_7)_2$	0.002	15
$Na_4Be_2PO_4F_5$	0.003	28
$RbNaMgP_2O_7$	0.034	16
BPO_4	0.005	29
Cs_2LiPO_4	0.006	30
$(NH_4)_3Sc_3(PO_4)(PO_3F)F_5$	0.008	26
$KLa(PO_3)_4$	0.0082	14
$K_4Mg_4(P_2O_7)_3$	0.108	31
$Ba(PO_2F_2)_2$	0.011	22
β-$CsBa_2(PO_3)_5$	0.015	32
$K_2SrP_4O_{12}$	0.016	33
$Ba_2NaClP_2O_7$	0.017	40
$(NH_4)La(PO_2F_2)$	0.017	20
Cs_2PO_3F	0.017	21
$K_2Sr_4(PO_3)_{10}$	0.017	23
Rb_2PO_3F	0.018	21
$KLa(PO_2F_2)$	0.019	20
K_2PO_3F	0.020	21
$NaK_3(PO_3F)_2$	0.022	35
$(NH_4)_2Ba(PO_2F_2)_4$	0.025	22
$KBe[PO_3(OH)]F$	0.025	28
$K_3Sc_3(PO_4)(PO_3F)F_5$	0.026	25
Na_2PO_3F	0.028	21
$K_X(NH_4)_{2-X}PO_3F$ (x= 0-0.3)	0.030	41
$(NH_4)_2PO_3F$	0.035	39
KH_2PO_4	0.034	37
$Ba_3ZnB_5O_{10}PO_4$	0.035	38
$[C(NH_2)_3]_2PO_3F$	0.039	39
$Na_{1.5}Rb_{0.5}PO_3F\cdot H_2O$	0.040	36
This Work	**0.042**	**-**

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