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From Centrosymmetric to Noncentrosymmetric: Effects of Cation on the Crystal Structures and Birefringences of $(NH_4)_{n-2}AE(PO_2F_2)_n$ (AE = Mg, Sr and Ba; n = 2, 3 and 4)

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Structures refinement

Colorless, block-shaped single crystals with suitable dimensions of the title compounds were selected under an optical microscope from the above-mentioned samples for structural characterization. A Bruker SMART APEX II diffractometer equipped with a 4K CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was essential. Data integration and absorption corrections were carried out using Bruker SAINT and the SCALE program,[1]respectively.The structures were determined by direct methods and refined by full-matrix least squares fitted on F^2 using the SHELXTL program package.[2]The structure was solved using Intrinsic Phasing method provide by the ShelXT structure solution program and refined using the ShelXL least-squaresrefinement package. The structure was checked for possible higher symmetry using the ADDSYM algorithm missing symmetry elements.[3] During the refinement section of this series structures, we found that the F(5),F(6),F(11)and F(12) atoms in **2** and F(1),F(2) atoms in **4** should be split (Figure S4). Therefore, judging from the atomic thermal displacement parameters, the F(5),F(6),F(11) and F(12) atoms were set to be disordered with the 33.0° rotation of F(5) and the 29.9° rotation of F(6), and $[P(6)O_2F_2]^-$group is disordered with the 25.7° rotation of F(11) and the 26.8° rotation of F(12), which can help us get relatively better residual (R) values and reasonable equivalent isotropic displacement parameters. The F(1),F(2) atoms in **4** are also split. Furthermore, in **2**, P(3) and P(6) are split, and the P(1) atoms in **4** are also split.

Rietveld refinement

The room temperature powder XRD pattern and related Rietveld refinement results are given.[4]

SHG Assessment of 4

As the $(PO_2F_2)^-$ groups are not in an optimal arrangement in the crystal structure of **4**, the sample was irradiated with a 1064 nm Nd:YAG laser beam, and there was very weak second harmonic generation signal (532 nm, green light). The SHG intensity of $Ba(PO_2F_2)_2$ should be very weak possibly due to the nonpolar space group of the material, and from the view of structure, the arrangement of the PO_2F_2 tetrahedra in the compounds is unfavorable to generate the large SHG effect. In other words, in the structure, the overall alignment patterns of the PO_2F_2 groups are largely non-uniform, therefore, it leads to considerable cancellation for anionic group's contribution.

Solid State Nuclear Magnetic Resonance (NMR)

Crystals ground into a powder were characterized by solid state Nuclear Magnetic

Resonance (NMR), which was carried out with a Bruker Avance III 500 WB (11.75 T) spectrometer operating at a frequency of 470.96 and 202.63 MHz for ^{19}F and ^{31}P, 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 CF_2 groups of PTFE resonate at -122 ppm relative to tetramethylsilane (TMS). ^{31}P MAS NMR spectra was recorded with a 90 degree pulse width of 2.5 us (pi/2) and a recycle delay of 30s. The presence of P-F bonds was checked employing $^{31}P\{^{19}F\}$-REDOR NMR spectroscopy, which enables the determination of the heteronuclear ^{31}P-^{19}F dipole coupling and hence the evaluation of internuclear distances.

More details for the calculation of $Ba(PO_2F_2)_2$ and $NH_4Sr(PO_2F_2)_3$

For the theoretical analysis of $Ba(PO_2F_2)_2$, we chose a virtual structure model with the occupation of F1A being 100 %, F2A being 100 % and P1 being 100 %. For the theoretical analysis of $NH_4Sr(PO_2F_2)_3$, we chose a virtual structure model with the occupations of F5A, F6A, F11, F12, P3A and P6 being 100 %. And then the BFGS[5] geometry optimization was performed for the two structure models. This strategy has been used in the previous work.[6, 7]

Table S1.Crystallographic data for these compounds

Empirical formula	$NH_4Mg(PO_2F_2)_3$	$NH_4Sr(PO_2F_2)_3$	$(NH_4)_2Ba(PO_2F_2)_4$	$Ba(PO_2F_2)_2$
Formula weight	345.26	408.57	577.3	339.28
Temperature (K)	273.15	296.15	273.15	296.15
Wavelength (Å)		0.71073		
Crystal system	Orthorhombic	Triclinic	Monoclinic	Tetragonal
Space group	*Cmcm*	$P\bar{1}$	$P2/n$	$I\bar{4}2d$
a / Å	5.411(4)	7.3703(17)	14.285(4)	10.4935(8)
b / Å	15.201(12)	11.054(3)	5.4715(17)	10.4935(8)
c / Å	12.681(10)	13.645(3)	19.474(6)	26.030(4)
α/°	90	88.861(6)	90	90
β /°	90	87.435(6)	97.607(4)	90
γ/°	90	89.323(5)	90	90
Z, ρ_{calcd} / g·cm^{-3}	4, 2.199	4, 2.444	4, 2.542	16, 3.145
Volume /Å^3	1043.0(14)	1110.3(4)	1508.7(8)	2866.2(6)
Theta range for data collection (°)	3.125 to 27.598	1.494 to 27.497	2.110 to 27.529	2.093 to 27.506
F(000)	680	784	1096	2464
Limiting indices	-7≤h≤7,	-9≤h≤9,	-18≤h≤16,	-13≤h≤10,
	-9≤k≤19,	-14≤k≤14,	-7≤k≤5,	-13≤k≤12,
	-15≤l≤16	-17≤l≤17	-25≤l≤25	-33≤l≤23
Reflections collected / unique	3195 / 695	15491 / 5039	8865 / 3433	8518 / 1658
	[R_{int} = 0.0362]	[R_{int} = 0.0376]	[R_{int} = 0.0271]	[R_{int} = 0.0307]
Completeness (%)	99.30	99.40	99.60	100.00
Goodness-of-fit on F^2	1.122	1.043	1.032	1.044
Final R indices [I>2sigma(I)] [a]	R_1 = 0.0549,	R_1 = 0.0355,	R_1 = 0.0281,	R_1 = 0.0215,
	wR_2 = 0.1450	wR_2 = 0.0808	wR_2 = 0.0690	wR_2 = 0.0498
R indices (all data)[a]	R_1 = 0.0628,	R_1 = 0.0480,	R_1 = 0.0408,	R_1 = 0.0224,
	wR_2 = 0.1513	wR_2 = 0.0863	wR_2 = 0.0744	wR_2 = 0.0503
Extinction coefficient	0.006(2)	0.0019(4)	0.00119(16)	0.00061(5)
Largest diff. peak and hole (e·Å^{-3})	0.632 and -0.662	1.287 and -0.774	0.840 and -0.490	1.007 and -0.601

[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 ($Å^2\times 10^3$) and BVS for **1**. U_{eq} is defined as one-third of the trace of the orthogonalizedU_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Mg(1)	5000	0	0	19(1)	2.28
N(1)	5000	1589(5)	2500	38(1)	-
P(1)	0	1359(1)	353(1)	24(1)	5.27
P(2)	5000	-843(1)	2500	30(1)	5.46
O(1)	2357(5)	920(2)	395(3)	57(1)	1.91
O(2)	5000	-364(4)	1538(4)	74(2)	2.10
F(1)	0	2036(3)	-537(3)	77(1)	1.03
F(2)	0	2019(3)	1266(3)	70(1)	1.02
F(3)	2869(8)	-1503(3)	2500	77(1)	1.03

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2\times 10^3$) for **2**. U_{eq} is defined as one-third of the trace of the orthogonalizedU_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Sr(1)	-2407(1)	9527(1)	928(1)	16(1)	2.11
Sr(2)	-2258(1)	4489(1)	4115(1)	16(1)	2.13
N(1)	-592(5)	8010(3)	3879(3)	30(1)	-
N(2)	-66(5)	7075(4)	-1230(3)	32(1)	-
P(1)	-4478(1)	2866(1)	6233(1)	24(1)	5.00
P(2)	-7326(1)	3661(1)	3838(1)	23(1)	5.03
P(3)	-1283(2)	6235(1)	1702(1)	38(1)	5.25
P(4)	-2113(2)	11215(1)	3383(1)	24(1)	5.08
P(5)	-7557(1)	9837(1)	1589(1)	22(1)	5.05
P(6)	-4680(2)	12567(1)	470(1)	28(1)	5.00
O(1)	-6252(4)	3396(3)	5997(2)	28(1)	1.77
O(2)	-2839(4)	3075(3)	5602(2)	29(1)	1.79
O(3)	-8846(4)	4180(3)	4444(2)	26(1)	1.97
O(4)	-5505(4)	4144(3)	3883(2)	32(1)	1.94
O(5)	-1013(5)	5457(3)	2539(3)	52(1)	1.96
O(6)	-1531(5)	7535(3)	1762(2)	40(1)	1.88
O(7)	-8972(4)	10054(3)	870(2)	25(1)	1.96
O(8)	-5698(4)	9555(3)	1258(2)	32(1)	1.96
O(9)	-1832(4)	10310(3)	2627(2)	33(1)	1.85
O(10)	-1627(4)	12490(3)	3221(2)	32(1)	1.79
O(11)	-6469(4)	12089(3)	256(2)	27(1)	1.76
O(12)	-3113(4)	11785(3)	671(2)	34(1)	1.80
F(1)	-4718(4)	1493(2)	6371(3)	54(1)	1.01
F(2)	-4063(4)	3185(3)	7286(2)	56(1)	1.02
F(3)	-7315(4)	2285(2)	4031(2)	47(1)	1.00
F(4)	-7878(4)	3669(3)	2770(2)	48(1)	1.02
F(5)	-3202(11)	5764(6)	1346(6)	62(3)	0.82
F(5A)	-2291(15)	5667(8)	902(8)	72(4)	1.11
F(6)	-328(14)	5846(7)	797(6)	59(3)	1.22
F(6A)	587(14)	6053(7)	1050(6)	62(3)	0.87
F(7)	-1108(6)	10744(3)	4291(2)	66(1)	0.97

F(8)	-4031(5)	11141(3)	3822(3)	71(1)	1.07
F(9)	-8235(4)	8863(3)	2323(2)	50(1)	1.03
F(10)	-7578(4)	10916(3)	2280(2)	51(1)	1.01
F(11)	-4912(8)	13629(7)	1101(7)	47(2)	1.20
F(12)	-4028(8)	13277(7)	-524(6)	47(2)	0.82
F(12A)	-4115(9)	13664(8)	-99(8)	45(3)	1.02

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2\times 10^3$) for **3**. U_{eq} is defined as one-third of the trace of the orthogonalizedU_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Ba(1)	6096(1)	7500(1)	5377(1)	19(1)	2.04
N(1)	7500	7432(8)	7500	33(1)	-
N(2)	8885(2)	7779(5)	4719(2)	24(1)	-
N(3)	2500	12587(10)	7500	91(3)	-
P(1)	4371(1)	7024(2)	8478(1)	35(1)	5.31
P(2)	3438(1)	7192(2)	5862(1)	23(1)	4.98
P(3)	8026(1)	2487(2)	6009(1)	24(1)	5.02
P(4)	5463(1)	12215(2)	6536(1)	21(1)	4.97
O(1)	4630(3)	7921(6)	9178(2)	61(1)	1.57
O(2)	3899(3)	4709(7)	8376(2)	83(1)	1.62
O(3)	2972(2)	4988(5)	5556(1)	34(1)	1.81
O(4)	4177(2)	8424(5)	5532(1)	28(1)	1.92
O(5)	5208(2)	13354(5)	5846(1)	28(1)	1.90
O(6)	7620(2)	10459(5)	5572(1)	31(1)	1.82
O(7)	6052(2)	10013(4)	6604(1)	30(1)	1.78
O(8)	7487(2)	4678(5)	6138(1)	34(1)	1.76
F(1)	5240(2)	6998(6)	8105(2)	75(1)	1.06
F(2)	3814(2)	8957(6)	8045(2)	84(1)	1.06
F(3)	2691(2)	9130(4)	5992(1)	39(1)	0.97
F(4)	3812(2)	6669(4)	6624(1)	43(1)	1.00
F(5)	4565(2)	11764(4)	6869(1)	38(1)	1.01
F(6)	5913(2)	14188(4)	7036(1)	39(1)	1.00
F(7)	8456(2)	1447(5)	6712(1)	54(1)	1.02
F(8)	8944(2)	3275(5)	5736(2)	54(1)	1.00

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for **4**. U_{eq} is defined as one-third of the trace of the orthogonalizedU_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Ba(1)	5607(1)	2600(1)	2113(1)	20(1)	2.05
P(1)	7128(2)	5749(2)	2705(1)	40(1)	5.36
P(2)	5226(2)	1767(2)	3559(1)	22(1)	4.98
F(1A)	7843(13)	5500(14)	3172(4)	63(5)	1.26
F(1B)	6980(20)	5314(19)	3292(6)	81(7)	0.84
F(2A)	8358(9)	5800(10)	2343(4)	66(3)	0.85
F(2B)	8482(16)	5790(19)	2820(8)	70(7)	1.26
F(3)	5256(5)	3214(4)	3610(2)	46(1)	1.04
F(4)	6245(4)	1435(5)	3969(2)	37(1)	1.09
O(1)	6464(8)	4725(7)	2476(3)	62(2)	1.85
O(2)	6607(5)	7044(5)	2689(2)	34(1)	1.78
O(3)	5734(5)	1380(5)	3058(2)	28(1)	1.68
O(4)	3980(5)	1278(5)	3733(2)	30(1)	1.66

Table S6. Selected bond distances (Å) and angles (deg)for **1**.

Mg(1)-O(1)	2.062(3)	P(2)-F(3)#3	1.528(4)
Mg(1)-O(1)#1	2.062(3)	O(1)#4-P(1)-O(1)	124.6(3)
Mg(1)-O(1)#2	2.062(3)	O(1)#4-P(1)-F(1)	109.82(15)
Mg(1)-O(1)#3	2.062(3)	O(1)-P(1)-F(1)	109.82(15)
Mg(1)-O(2)#1	2.027(5)	O(1)#4-P(1)-F(2)	106.03(16)
Mg(1)-O(2)	2.027(5)	O(1)-P(1)-F(2)	106.03(16)
P(1)-O(1)#4	1.440(3)	F(1)-P(1)-F(2)	96.7(3)
P(1)-O(1)	1.440(3)	O(2)#5-P(2)-O(2)	118.3(5)
P(1)-F(1)	1.528(4)	O(2)#5-P(2)-F(3)	109.66(16)
P(1)-F(2)	1.532(4)	O(2)#5-P(2)-F(3)#3	109.66(16)
P(2)-O(2)#5	1.421(4)	O(2)-P(2)-F(3)	109.66(16)
P(2)-O(2)	1.421(4)	O(2)-P(2)-F(3)#3	109.66(16)
P(2)-F(3)	1.528(4)	F(3)-P(2)-F(3)#3	98.0(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z	#2 -x+1,y,z	#3 x,-y,-z
#4 -x,y,z	#5 x,y,-z+1/2	

Table S7. Selected bond distances (Å) and angles (deg)for **2**.

Sr(1)-O(6)	2.548(3)	P(4)-O(9)	1.457(3)
Sr(1)-O(7)#1	2.647(3)	P(4)-O(10)	1.468(3)
Sr(1)-O(7)#3	2.603(3)	P(4)-F(7)	1.550(3)
Sr(1)-O(8)	2.447(3)	P(4)-F(8)	1.513(3)
Sr(1)-O(9)	2.546(3)	P(5)-O(7)	1.478(3)
Sr(1)-O(11)#1	2.599(3)	P(5)-O(8)	1.455(3)
Sr(1)-O(12)	2.564(3)	P(5)-F(9)	1.528(3)
Sr(2)-O(1)#4	2.576(3)	P(5)-F(10)	1.535(3)
Sr(2)-O(2)	2.561(3)	P(6)-O(11)	1.470(3)
Sr(2)-O(3)#3	2.592(3)	P(6)-O(12)	1.467(3)
Sr(2)-O(3)#4	2.642(3)	P(6)-F(11)	1.474(6)
Sr(2)-O(4)	2.463(3)	P(6)-F(12)	1.611(7)
Sr(2)-O(5)	2.523(3)	O(1)-P(1)-F(1)	107.83(18)
Sr(2)-O(10)#6	2.572(3)	O(1)-P(1)-F(2)	108.98(18)
N(1)-H(1BC)	0.941(18)	O(2)-P(1)-O(1)	121.81(17)
N(1)-H(1AA)	0.937(18)	O(2)-P(1)-F(1)	108.20(17)
N(1)-H(1BD)	0.944(18)	O(2)-P(1)-F(2)	108.49(19)
N(1)-H(1AB)	0.967(18)	F(2)-P(1)-F(1)	99.2(2)
N(2)-H(2A)	0.941(18)	O(3)-P(2)-F(3)	107.34(17)
N(2)-H(2B)	0.948(18)	O(3)-P(2)-F(4)	108.15(16)
N(2)-H(2C)	0.944(18)	O(5)-P(3)-F(6)	114.5(3)
N(2)-H(2D)	0.953(18)	O(6)-P(3)-F(5)	104.1(3)
P(1)-O(1)	1.473(3)	O(6)-P(3)-F(6)	113.8(3)
P(1)-O(2)	1.469(3)	F(6)-P(3)-F(5)	92.1(6)
P(1)-F(1)	1.537(3)	O(9)-P(4)-O(10)	122.59(19)
P(1)-F(2)	1.531(3)	O(9)-P(4)-F(7)	106.69(18)
P(2)-O(3)	1.479(3)	O(9)-P(4)-F(8)	109.9(2)
P(2)-O(4)	1.455(3)	O(10)-P(4)-F(7)	107.44(19)
P(2)-F(3)	1.538(3)	O(10)-P(4)-F(8)	109.41(18)
P(2)-F(4)	1.530(3)	F(8)-P(4)-F(7)	97.9(2)
P(3)-O(5)	1.435(3)	O(7)-P(5)-F(9)	108.22(16)
P(3)-O(6)	1.450(3)	O(7)-P(5)-F(10)	108.00(17)
P(3)-F(5)	1.612(7)	O(8)-P(5)-O(7)	120.37(18)
P(3)-F(6)	1.464(7)	O(8)-P(5)-F(9)	109.46(17)

O(8)-P(5)-F(10)	109.86(18)	O(12)-P(6)-O(11)	122.86(18)
F(9)-P(5)-F(10)	98.77(19)	O(12)-P(6)-F(11)	115.3(3)
O(11)-P(6)-F(11)	109.6(3)	O(12)-P(6)-F(12)	102.9(3)
O(11)-P(6)-F(12)	104.3(3)	F(11)-P(6)-F(12)	97.6(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1,-y+2,-z	#3 x+1,y,z	#4 -x-1,-y+1,-z+1
#6 x,y-1,z		

Table S8. Selected bond distances (Å) and angles (deg)for **3**.

Ba(1)-O(3)$^{\#1}$	2.749(3)	O(1)-P(1)-F(1)	109.3(2)
Ba(1)-O(4)$^{\#2}$	2.841(3)	O(1)-P(1)-F(2)	109.71(19)
Ba(1)-O(4)	2.844(3)	O(2)-P(1)-O(1)	118.9(2)
Ba(1)-O(5)$^{\#3}$	2.811(3)	O(2)-P(1)-F(1)	109.0(2)
Ba(1)-O(5)$^{\#2}$	2.861(2)	O(2)-P(1)-F(2)	109.7(2)
Ba(1)-O(6)	2.699(2)	F(2)-P(1)-F(1)	98.3(2)
Ba(1)-O(7)	2.766(3)	O(3)-P(2)-O(4)	120.91(16)
Ba(1)-O(8)	2.784(2)	O(3)-P(2)-F(3)	110.12(15)
P(1)-O(1)	1.451(3)	O(3)-P(2)-F(4)	108.72(15)
P(1)-O(2)	1.436(4)	O(4)-P(2)-F(3)	107.90(15)
P(1)-F(1)	1.519(3)	O(4)-P(2)-F(4)	109.26(15)
P(1)-F(2)	1.512(3)	F(4)-P(2)-F(3)	97.35(14)
P(2)-O(3)	1.465(3)	O(6)$^{\#3}$-P(3)-F(7)	108.48(15)
P(2)-O(4)	1.469(3)	O(6)$^{\#3}$-P(3)-F(8)	107.53(15)
P(2)-F(3)	1.549(2)	O(8)-P(3)-O(6)$^{\#3}$	122.77(16)
P(2)-F(4)	1.537(2)	O(8)-P(3)-F(7)	107.91(16)
P(3)-O(6)$^{\#3}$	1.470(3)	O(8)-P(3)-F(8)	108.73(16)
P(3)-O(8)	1.465(3)	F(7)-P(3)-F(8)	98.80(17)
P(3)-F(7)	1.534(2)	O(5)-P(4)-F(5)	109.37(15)
P(3)-F(8)	1.540(3)	O(5)-P(4)-F(6)	108.13(14)
P(4)-O(5)	1.481(3)	O(7)-P(4)-F(5)	109.35(15)
P(4)-O(7)	1.465(2)	O(7)-P(4)-F(6)	109.45(14)
P(4)-F(5)	1.533(3)	F(5)-P(4)-F(6)	98.50(14)
P(4)-F(6)	1.537(2)		

Symmetry transformations used to generate equivalent atoms:

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

Table S9. Selected bond distances (Å) and angles (deg)for **4**.

Ba(1)-F(4)$^{\#2}$	2.977(5)	F(1A)-P(1)-F(1B)	36.8(6)
Ba(1)-O(1)	2.584(7)	F(1A)-P(1)-F(2A)	94.7(6)
Ba(1)-O(2)$^{\#3}$	2.725(5)	F(1A)-P(1)-O(2)	112.5(6)
Ba(1)-O(2)$^{\#4}$	2.790(5)	F(2A)-P(1)-F(1B)	130.4(9)
Ba(1)-O(3)$^{\#5}$	2.894(5)	F(2B)-P(1)-F(1A)	47.8(10)
Ba(1)-O(3)	2.778(5)	O(1)-P(1)-F(1A)	118.1(7)
Ba(1)-O(4)$^{\#6}$	2.799(5)	O(1)-P(1)-F(1B)	97.9(8)
Ba(1)-O(4)$^{\#1}$	2.844(5)	O(1)-P(1)-F(2A)	100.1(5)
P(1)-F(1A)	1.453(10)	O(1)-P(1)-F(2B)	126.3(9)
P(1)-F(1B)	1.602(15)	O(1)-P(1)-O(2)	120.7(4)
P(1)-F(2A)	1.599(9)	O(2)-P(1)-F(1B)	104.8(8)
P(1)-F(2B)	1.452(16)	O(2)-P(1)-F(2A)	104.7(5)
P(1)-O(1)	1.413(7)	F(3)-P(2)-F(4)	98.6(3)
P(1)-O(2)	1.466(6)	O(3)-P(2)-F(3)	110.2(3)
P(2)-F(3)	1.525(5)	O(3)-P(2)-F(4)	107.4(3)
P(2)-F(4)	1.551(5)	O(3)-P(2)-O(4)	119.9(3)
P(2)-O(3)	1.466(5)	O(4)-P(2)-F(3)	109.8(3)
P(2)-O(4)	1.476(5)	O(4)-P(2)-F(4)	108.8(3)

Symmetry transformations used to generate equivalent atoms:

#1 y+1/2,-x+1/2,-z+1/2	#2 -y+1/2,-x+1,z-1/4	#3 -y+3/2,x-1/2,-z+1/2
#4 -x+1,-y+1,z	#5 -y+1/2,x-1/2,-z+1/2	#6 y+1/2,x,z-1/4

Table S10. Hydrogen coordinates and isotropic displacement parameters for **1**.

Atom	x	y	z	U(eq)
H(1A)	3570(70)	1950(30)	2500	46
H(1B)	40	1300(30)	3170(30)	46

Table S11. Hydrogen coordinates and isotropic displacement parameters for **2**.

Atom	x	y	z	U(eq)
H(1BC)	10540(30)	7640(40)	3980(30)	37
H(1AA)	9300(60)	8350(40)	3259(17)	37
H(1BD)	8410(40)	7490(30)	4030(30)	37
H(1AB)	9260(60)	8610(30)	4380(20)	37
H(2A)	8810(30)	7380(40)	9030(30)	37
H(2B)	10900(40)	7420(30)	9110(30)	37
H(2C)	10090(60)	7270(40)	8102(14)	37
H(2D)	9970(60)	6223(17)	8860(30)	37

Table S12. Hydrogen coordinates and isotropic displacement parameters for **3**.

Atom	x	y	z	U(eq)
H(1A)	7640(30)	6350(70)	7169(18)	65
H(2A)	9000(20)	9260(30)	4492(16)	65
H(1B)	7010(30)	8520(70)	7320(20)	65
H(3A)	2889(18)	11570(40)	7256(15)	65
H(2B)	8385(18)	8010(60)	4988(16)	65
H(3B)	2108(18)	13580(40)	7175(12)	65
H(2C)	8770(20)	6450(40)	4419(14)	65
H(2D)	9449(16)	7540(60)	5034(16)	65

Table S13. Hydrogen bonds for **1**. D, donor; H, hydrogen; A, acceptor.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...F(2)	0.947(19)	2.49(3)	3.193(3)	131(2)
N(1)-H(1A)...F(2)#6	0.947(19)	2.49(3)	3.193(3)	131(2)
N(1)-H(1B)...O(1)#7	0.954(19)	2.388(19)	3.195(4)	142.2(10)
N(1)-H(1B)...O(1)#5	0.954(19)	2.388(19)	3.195(4)	142.2(10)

Symmetry transformations used to generate equivalent atoms:

#5 x,y,-z+1/2	#6 -x,y,-z+1/2	#7 -x+1,y,-z+1/2

Table S14. Hydrogen bonds for **2**. D, donor; H, hydrogen; A, acceptor.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1BC...O2$^{\#1}$	0.941(18)	1.96(2)	2.897(5)	170(5)
N1-H1AA...O6	0.937(18)	2.37(5)	3.056(5)	130(5)
N1-H1AA...O9	0.937(18)	2.45(5)	3.183(5)	135(5)
N1-H1AA...F9$^{\#2}$	0.937(18)	2.23(5)	2.837(5)	122(5)
N1-H1BD...O1$^{\#3}$	0.944(18)	1.88(2)	2.809(5)	166(4)
N1-H1BD...F3$^{\#3}$	0.944(18)	2.75(5)	3.193(5)	110(3)
N1-H1AB...F7$^{\#4}$	0.967(18)	2.43(5)	3.188(5)	135(5)
N1-H1AB...F7	0.967(18)	2.36(5)	3.101(5)	133(5)
N2-H2A...O11$^{\#5}$	0.941(18)	2.04(2)	2.971(5)	171(5)
N2-H2A...F10$^{\#5}$	0.941(18)	2.73(5)	3.163(5)	109(4)
N2-H2B...O12$^{\#6}$	0.948(18)	1.91(2)	2.815(5)	160(4)
N2-H2C...O10$^{\#6}$	0.944(18)	2.09(3)	2.972(5)	154(5)
N2-H2C...F4$^{\#7}$	0.944(18)	2.32(5)	2.787(5)	110(4)
N2-H2D...F6	0.953(18)	2.68(6)	3.056(9)	104(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,1-y,1-z	#21+x,+y,+z	#3-1-x,1-y,1-z
#4 -x,2-y,1-z	#5 -1-x,2-y,-z	#6 -x,2-y,-z
#7 -1-x,1-y,-z		

Table S14. Hydrogen bonds for **3**. D, donor; H, hydrogen; A, acceptor.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2A...O1[#1]	0.945(10)	1.930(14)	2.841(4)	161(3)
N1-H1B...O7	0.950(19)	1.99(3)	2.892(3)	157(4)
N3-H3A...F2	0.955(13)	2.37(3)	2.840(5)	110(2)
N3-H3B...O2[#2]	0.955(13)	1.788(13)	2.711(4)	162(3)
N2-H2D...O1[#3]	0.954(10)	1.897(15)	2.813(4)	160(3)
N2-H2D...F6	0.953(18)	2.68(6)	3.056(9)	104(4)

Symmetry transformations used to generate equivalent atoms:

#1 1/2+x,2-y,-1/2+z	#21/2-x,1+y,3/2-z	#33/2-x,+y,3/2-z

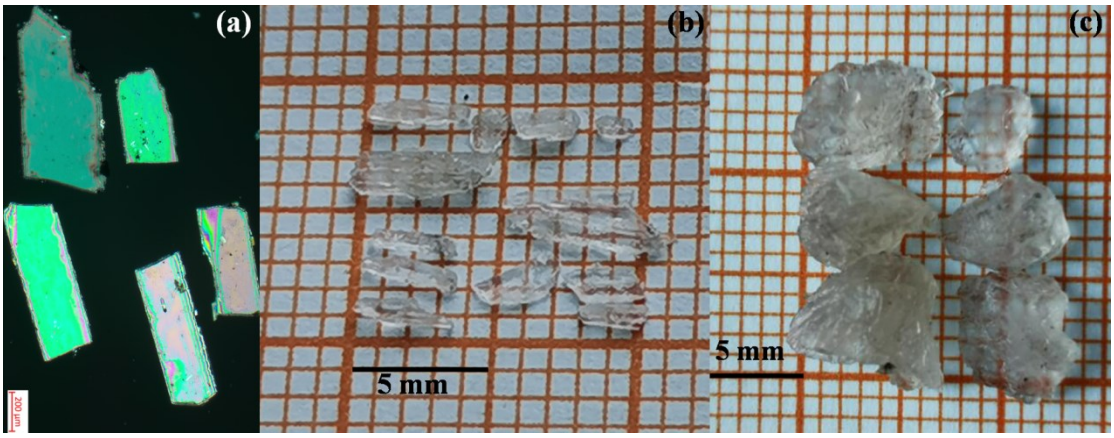

Figure S1. Crystal photograph of (a) **1**, (b) **2** and (c) **3**crystals, respectively.

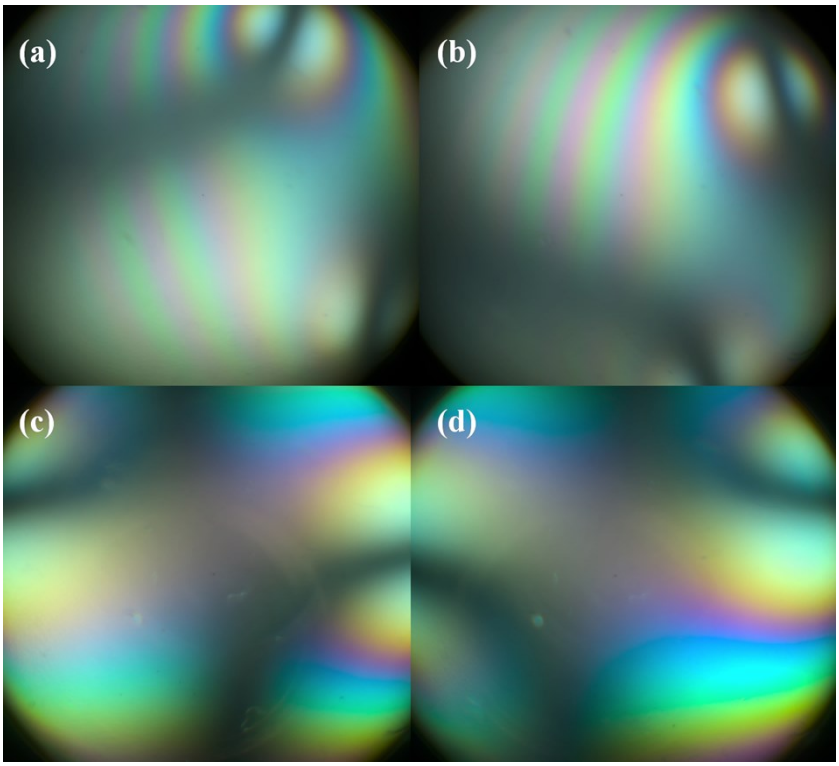

Figure S2. The conoscopic interference patterns of (a, b) **2** and (c, d) **3** crystals.

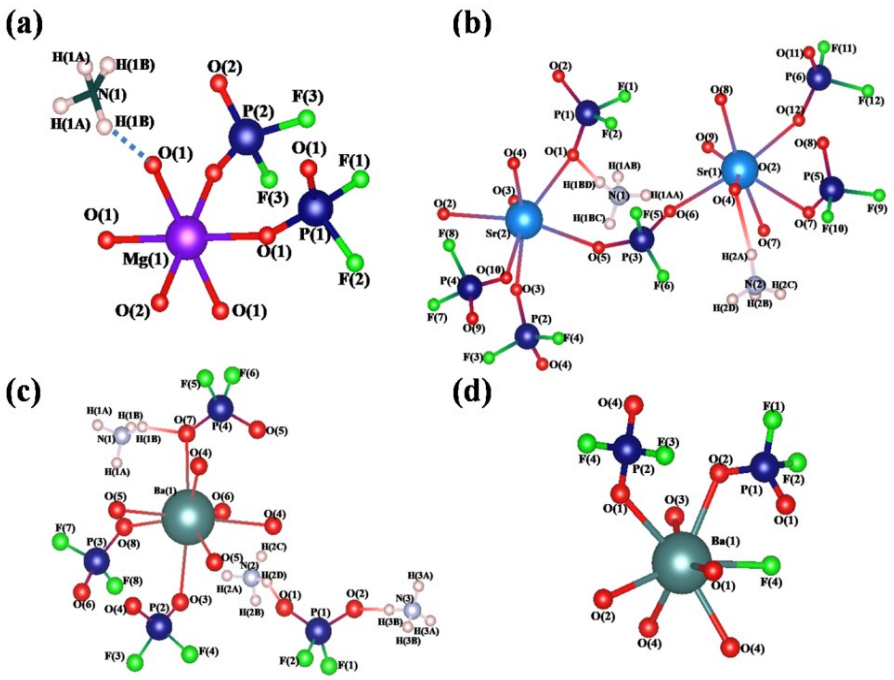

Figure S3. The asymmetric units of (a) **1** (b)**2** (c) **3** and (d)**4.**

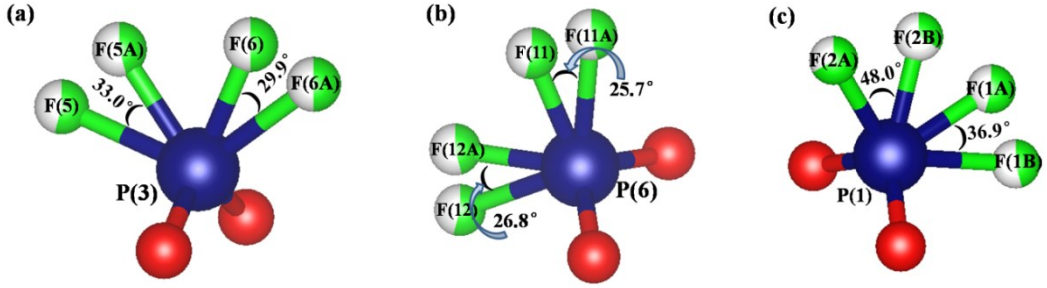

Figure S4. The $[PO_2F_2]^-$ units of (a, b) P(3) and P(6) in **2** and(c)P(1) in **4.**

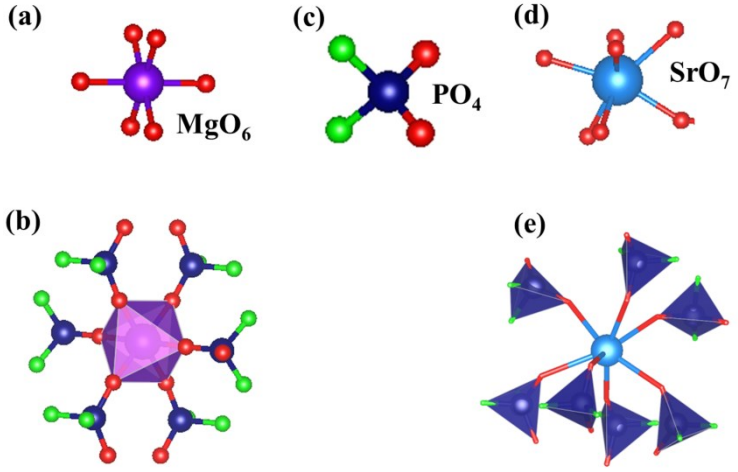

Figure S5. (a) MgO_6 octahedron; (b) $[MgP_6O_{12}F_{12}]^{6-}$ cluster; (c) $(PO_2F_2)^-$ tetrahedron in four compounds; (d) Seven-fold coordination of Sr; (e) $[SrP_7O_{14}F_{14}]^{5-}$ cluster.

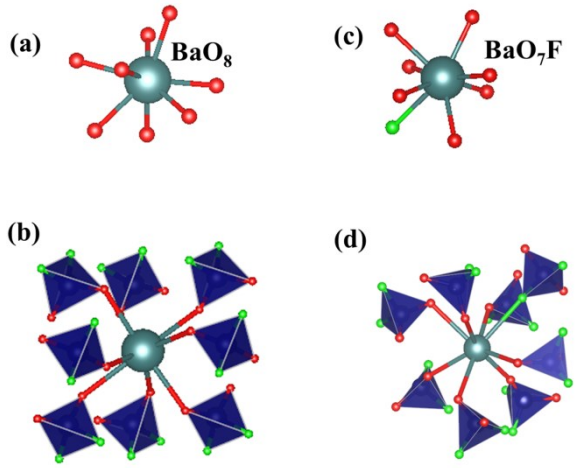

Figure S6. Structures of **3** and **4**. (a) BaO_8 polyhedron; (b) $[BaP_8O_{16}F_{16}]^{6-}$ cluster in **3**; (c) BaO_7F polyhedron; (d) The $[BaP_8O_{16}F_{16}]^{6-}$ cluster in **4**.

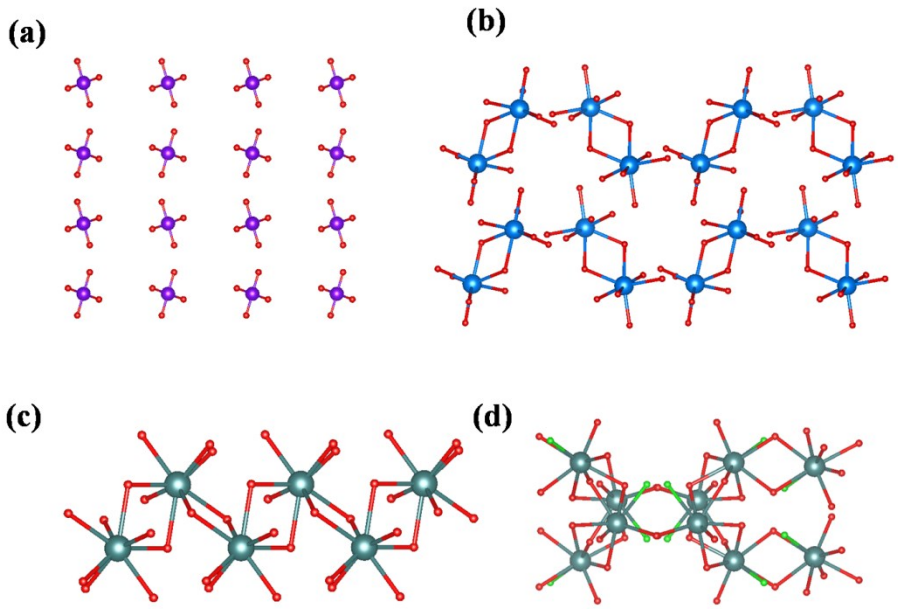

Figure S7. The different cations connectionsof the four compounds. (a) the 0D Mg-Ooctahedra; (b) the 0D Sr-O dimmers; (c) the 1D Ba-O chain; (d) the 3D Ba-O-F framework of **4**.

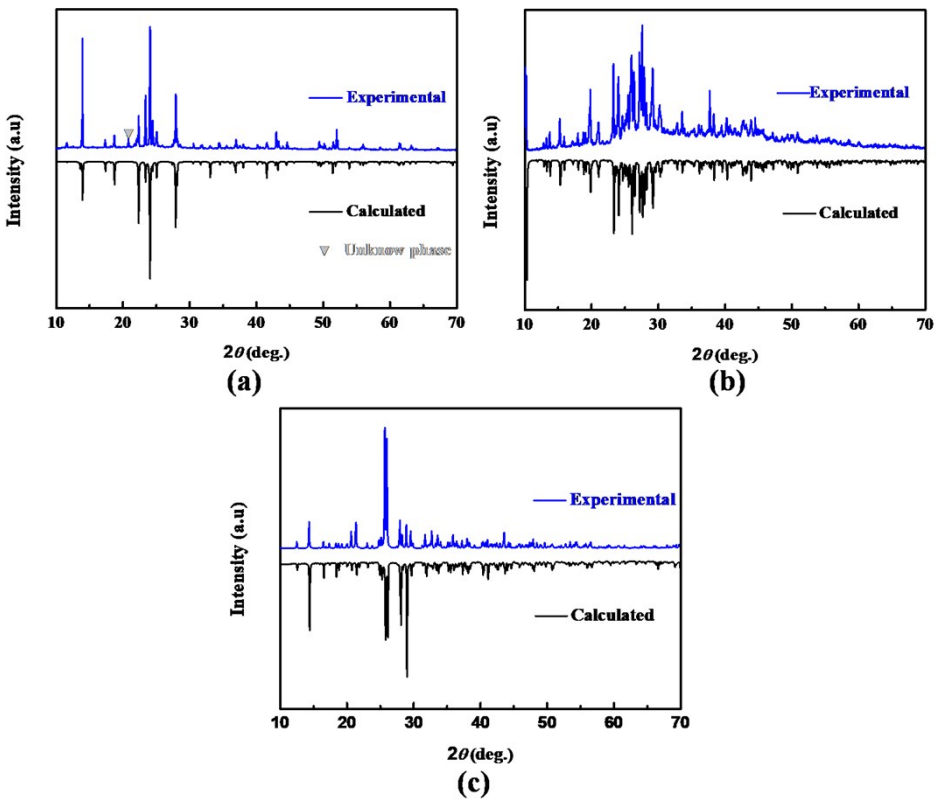

Figure S8. Calculated and experimental powder X-ray diffraction patterns for **1**, **2** and **3**.

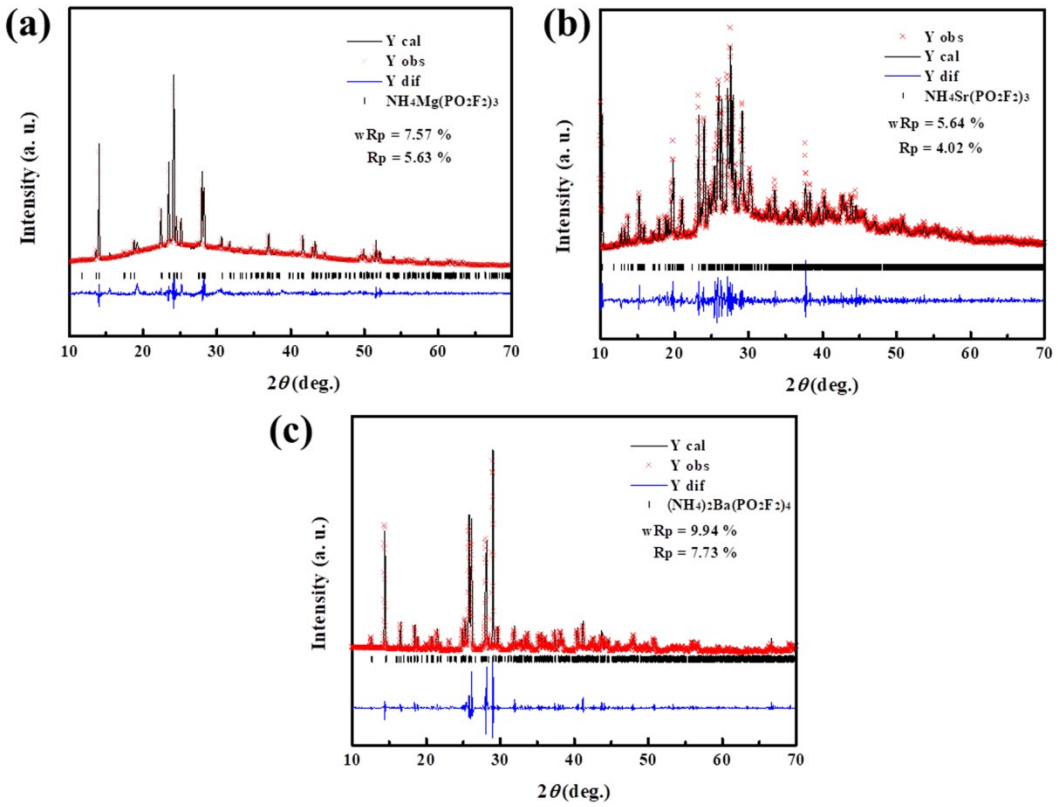

Figure S9. Rietveld refinement of three compounds powder polycrystalline. The observed and calculated XRD patterns as well as the difference profile are in red, black and blue, respectively. The vertical lines indicate the possible Bragg reflection positions of **1**, **2** and **3** (black) compounds.

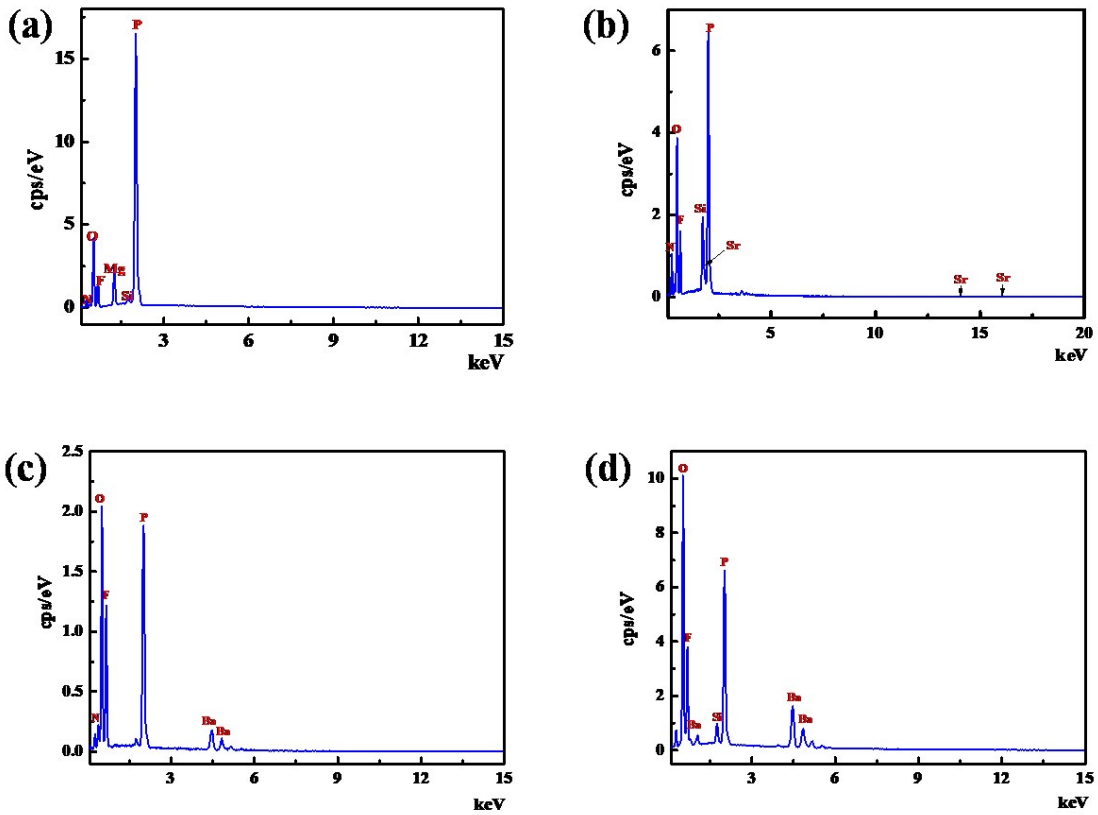

Figure S10. The energy dispersive X-ray spectroscopy of the as-synthesized **1**, **2**, **3** and **4**.

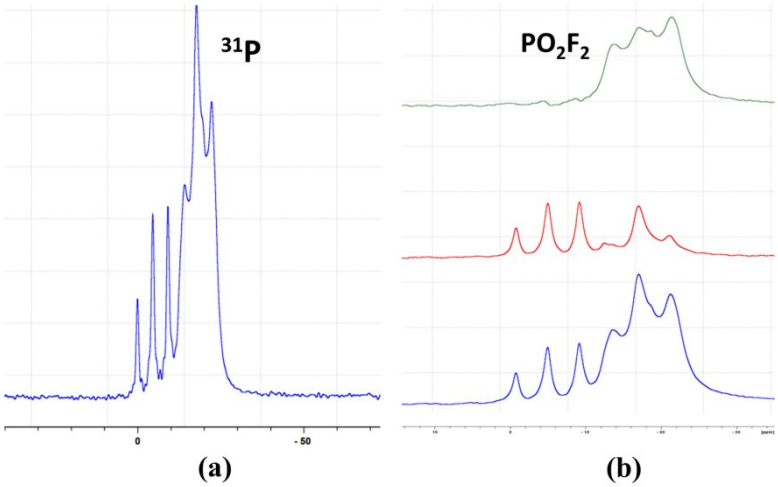

Figure S11. (a) ^{31}P, (b) ^{31}P-^{19}F-REDOR MAS NMR spectra of **3**. Asterisks denote spinning sidebands.

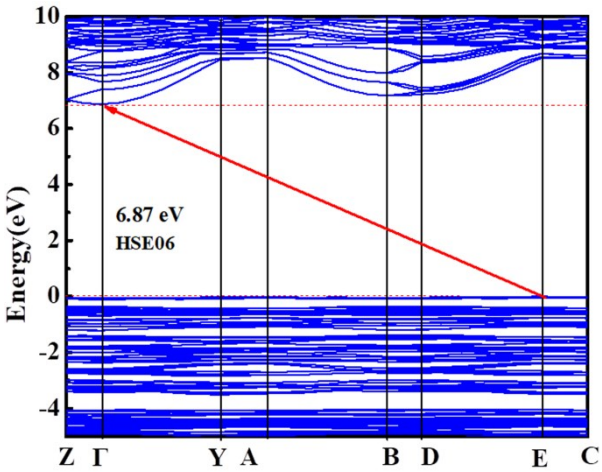

Figure S12. The band structures of **3** calculated by HSE06 hybrid functional.

References

1. *SAINT Plus Version 7.60A*,Bruker Analytical X-ray Instruments Inc., Madison, WI, 2000.
2. G. M. Sheldrick, Crystal Structure Refinement with SHELXL., *Acta Crystallogr. A*, 2015, **71**, 3−8.
3. A. L. Spek, Single-Crystal Structure Validation with the Program PLATON, *J. Appl. Crystallogr.*, 2003, **36**, 7−13.
4. B. H. Toby; R. B. Von Dreele, GSAS-II: The Genesis of A Modern Open-source All Purpose Crystallography Software Package. *J. Appl. Crystallogr.* 2013, **46**, 544-549.
5. T. H. Fischer, J. Almlof, General Methods for Geometry and Wave Function Optimization, *J. Phys. Chem.* 1992, **96**, 9768-9774.
6. L. Bellaiche, D. Vanderbilt, Virtual Crystal Approximation Revisited: Application to Dielectric and Piezoelectric Properties of Perovskites, *Phys. Rev. B* 2000, **61**, 7877-7882.
7. M. L. Zhou, Y. Yang, Y. W. Guo, Z. S. Lin, J. Y. Yao, Y. C. Wu, C. T. Chen, Hg-Based Infrared Nonlinear Optical Material $KHg_4Ga_5Se_{12}$ Exhibits Good Phase-Matchability and Exceptional Second Harmonic Generation Response, *Chem. Mater.* 2017, **29**, 7993-8002.