Fluoroborophosphates: a family of potential deep ultraviolet NLO materials

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Supporting information

Content

Table S1. Crystal data and structure refinements for $RbBPO_4F$, $CsBPO_4F$ and $(NH_4)_2BPO_4F_2$.

Formula	$RbBPO_4F$	$CsBPO_4F$	$(NH_4)_2BPO_4F_2$
Formula weight	210.25	257.69	179.86
Temperature	293(2) K	293(2) K	293
Wavelength	0.71073	0.71073	1.54178
Space group	$P2_13$	$P2_13$	$P2_1$
a (Å), α (deg.)	7.6147, 90	7.7275, 90	4.5122, 90
b (Å), β (deg.)	7.6147, 90	7.7275, 90	11.5395, 89.957
c (Å), γ (deg.)	7.6147, 90	7.7275, 90	12.7360, 90
Volume ($Å^3$)	441.53(7)	461.44(6)	663.14(8)
Z, Calculated density	4, 3.163 Mg/m^3	4, 3.709 Mg/m^3	4, 1.802 Mg/m^3
Absorption coefficient	11.504 mm^{-1}	8.303 mm^{-1}	3.912 mm^{-1}
F(000)	392	464	368
Theta range for data collection	3.78 to 28.72 deg	3.73 to 28.84 deg	3.47 to 74.53 deg
Limiting indices	-9<=h<=9, -10<=k<=9, -10<=l<=9	-10<=h<=8, -9<=k<=9, -10<=l<=10	-5<=h<=5, -9<=k<=14, -15<=l<=14
Reflections collected/unique	3167 / 369 [R(int) = 0.0814]	3389 / 400 [R(int) = 0.1683]	4078 / 2012 [R(int) = 0.0262]
Completeness to theta	96.2 %	96.8 %	97.2 %
Refinement method	Full-matrix least-squares on F_0^2	Full-matrix least-squares on F_0^2	Full-matrix least-squares on F_0^2
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0609	R1 = 0.0293, wR2 = 0.0662	R1 = 0.0383, wR2 = 0.0992
R indices (all data)[a]	R1 = 0.0297, wR2 = 0.0637	R1 = 0.0325, wR2 = 0.0693	R1 = 0.0386, wR2 = 0.0995
Largest diff. peak and hole	0.395 and -0.701 e.A^{-3}	0.669 and -1.003 e.A^{-3}	0.517 and -0.412 e.A^{-3}

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

Table S2. Selected bond lengths (Å) for RbBPO$_4$F, CsBPO$_4$F and (NH$_4$)$_2$BPO$_4$F$_2$.

RbBPO$_4$F		CsBPO$_4$F		(NH$_4$)$_2$BPO4F$_2$	
Rb(1)-O(2)	3.082(2)	Cs(1)-O(2)	3.136(3)	B(1)-F(1)	1.398(7)
Rb(1)-O(2)#1	3.082(2)	Cs(1)-O(2)#1	3.136(3)	B(1)-O(1)	1.416(7)
Rb(1)-O(2)#2	3.082(2)	Cs(1)-O(2)#2	3.136(3)	B(1)-F(2)	1.434(6)
Rb(1)-O(1)#3	3.152(2)	Cs(1)-F(1)#3	3.263(3)	B(1)-O(4)#1	1.478(6)
Rb(1)-O(1)#4	3.152(2)	Cs(1)-F(1)#4	3.263(3)	B(2)-F(3)	1.395(6)
Rb(1)-O(1)#5	3.152(2)	Cs(1)-F(1)#2	3.263(3)	B(2)-F(4)	1.399(6)
Rb(1)-O(1)#6	3.232(2)	Cs(1)-O(1)#5	3.263(4)	B(2)-O(5)	1.410(7)
Rb(1)-O(1)#7	3.232(2)	Cs(1)-O(1)#6	3.263(4)	B(2)-O(6)#2	1.493(7)
Rb(1)-O(1)#8	3.232(2)	Cs(1)-O(1)#7	3.263(4)	P(1)-O(3)	1.505(3)
Rb(1)-F(1)#9	3.258(2)	Cs(1)-O(1)#8	3.328(4)	P(1)-O(2)	1.511(3)
Rb(1)-F(1)#10	3.258(2)	Cs(1)-O(1)#9	3.328(4)	P(1)-O(1)	1.557(3)
Rb(1)-F(1)	3.258(2)	Cs(1)-O(1)#10	3.328(4)	P(1)-O(4)	1.560(4)
B(1)-F(1)	1.408(7)	B(1)-F(1)	1.408(12)	P(2)-O(7)	1.495(3)
B(1)-O(1)#11	1.460(3)	B(1)-O(1)#10	1.461(5)	P(2)-O(8)	1.497(4)
B(1)-O(1)#12	1.460(3)	B(1)-O(1)#11	1.461(5)	P(2)-O(6)	1.559(4)
B(1)-O(1)	1.460(3)	B(1)-O(1)	1.461(5)	P(2)-O(5)	1.590(4)
P(1)-O(2)	1.484(4)	P(1)-O(2)	1.495(7)		
P(1)-O(1)	1.554(2)	P(1)-O(1)	1.560(3)		
P(1)-O(1)#13	1.554(2)	P(1)-O(1)#12	1.560(3)		
P(1)-O(1)#14	1.554(2)	P(1)-O(1)#13	1.560(3)		

Symmetry codes for the generated atoms:

For RbBPO$_4$F: #1 x+1/2, -y+3/2, -z; #2 -x+3/2, -y+2, z-1/2; #3 -y+1, z+1/2, -x+1/2;
#4 z+1/2, -x+3/2, -y; #5 -x+3/2, -y+1, z-1/2; #6 y+1/2, -z+3/2, -x+1; #7 -x+2, y+1/2, -z+1/2;
#8 -z+3/2, -x+2, y-1/2; #9 -x+2, y+1/2, -z-1/2; #10 x-1/2, -y+3/2, -z; #11 -z+1, x-1/2, -y+1/2;
#12 y+1/2, -z+1/2, -x+1; #13 -y+3/2, -z+1, x-1/2; #14 z+1/2, -x+3/2, -y+1.
For CsBPO$_4$F: #1 -x+1, y+1/2, -z+1/2; #2 -x+3/2, -y, z+1/2; #3 x, y, z+1; #4 x-1/2, -y+1/2, -z; #5 y, z, x; #6 -x+1, y-1/2, -z+1/2; #7 z+1/2, -x+1/2, -y+1; #8 z+1, x, y; #9 x+1/2, -y+1/2, -z; #10 -y+1, z+1/2, -x+1/2; #11 -z+1/2, -x+1, y-1/2; #12 z+1/2, -x+1/2, -y; #13 -y+1/2, -z, x-1/2.
For (NH$_4$)$_2$BPO$_4$F$_2$: #1 x-1, y, z; #2 x+1, y, z.

Table S3. Hydrogen bond lengths [Å] for $(NH_4)_2BPO_4F_2$.

N(1)…O(3)	2.801(6)	N(1) …F(2)#2	2.912(6)
N(1) …O(3)#1	2.808(7)	N(2) …O(2)#2	2.839(6)
N(1) …O(8)#1	2.818(5)	N(2) …F(4)#3	2.887(5)
N(2) …O(4)#4	2.895(6)	N(4) …O(7)	2.764(6)
N(2) …F(1)	2.923(7)	N(4) …O(7)#1	2.778(6)
N(3) …O(8)#1	2.854(6)	N(4) …F(2)#2	2.855(5)
N(3) …O(2)	2.889(5)	N(4) …O(6)#6	2.866(6)
N(3) …F(3)#5	2.988(5)		

Symmetry codes for the generated atoms:

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

Table S4. The calculated SHG tensors of $RbBPO_4F$, $CsBPO_4F$ and $(NH_4)_2BPO_4F_2$.

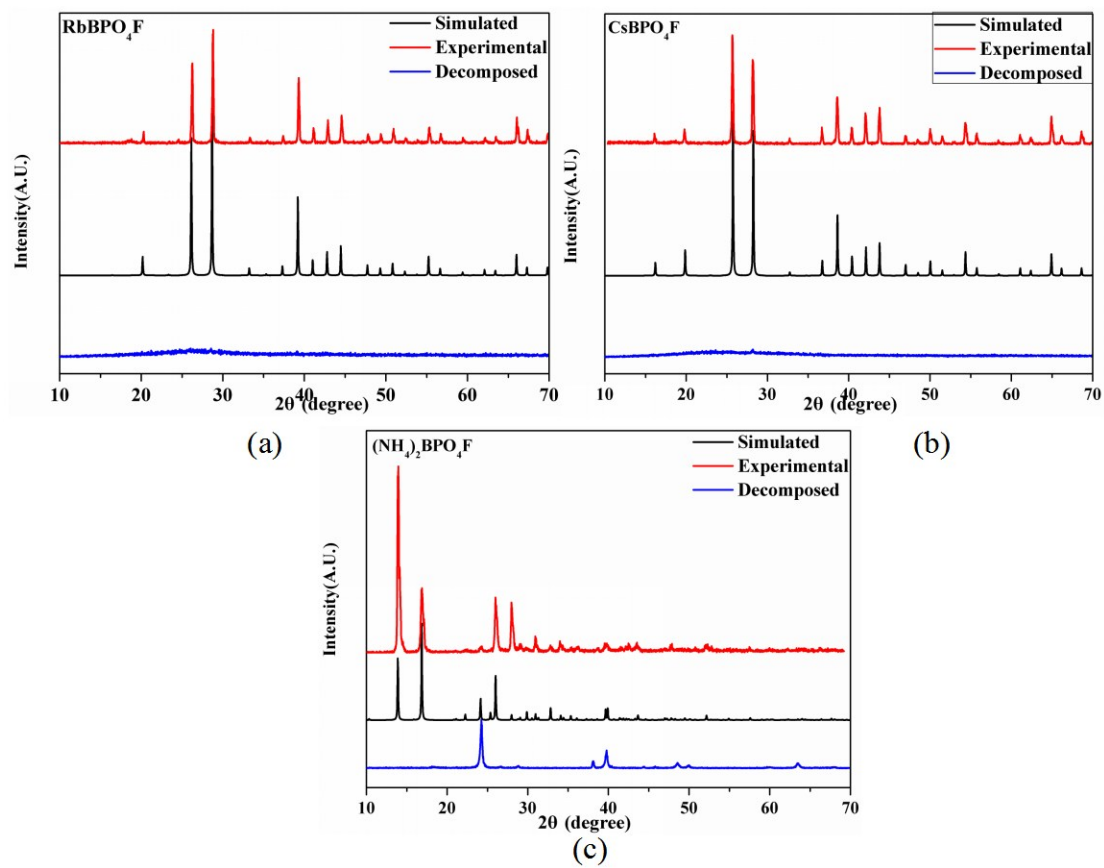|	$RbBPO_4F$	$CsBPO_4F$	$(NH_4)_2BPO_4F_2$
calculated SHG coefficient tensors (× 10^{-9} esu)	$d_{14}=d_{25}=d_{36}=1.24$	$d_{14}=d_{25}=d_{36}=1.75$	$d_{14}=d_{25}=d_{36}=1.10$ $d_{16}=d_{21}=0.55$ $d_{22}=2.10$ $d_{23}=d_{34}=1.57$

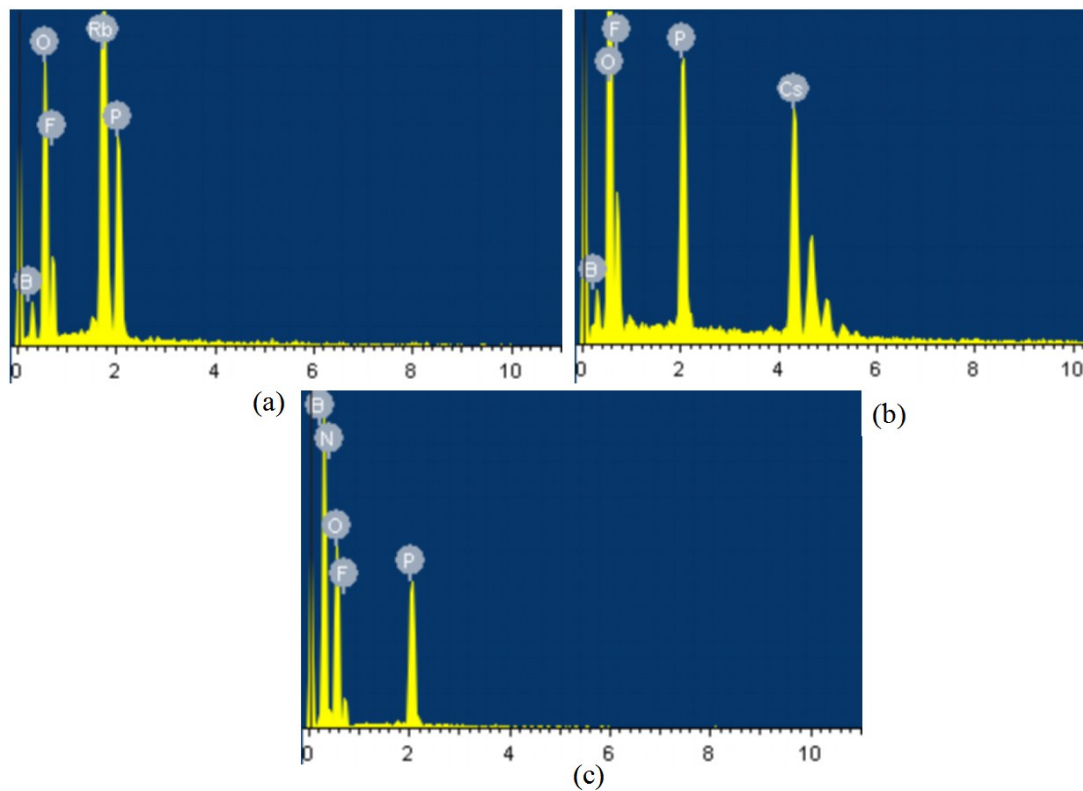**Figure S1.** Powder X-ray diffraction patterns of RbBPO$_4$F, CsBPO$_4$F and (NH$_4$)$_2$BPO$_4$F$_2$.

Figure S2. The Energy dispersive X-ray spectroscopy of RbBPO$_4$F, CsBPO$_4$F and (NH$_4$)$_2$BPO$_4$F$_2$.
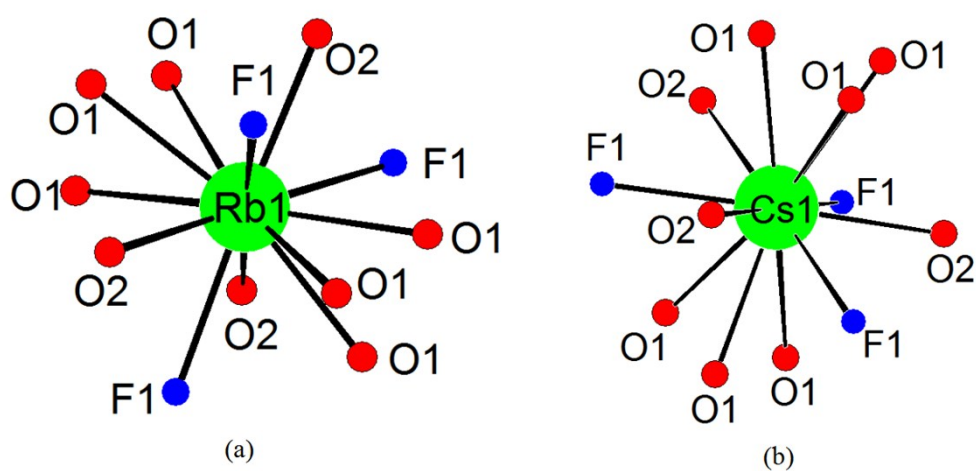

Figure S3. The coordination environments around Rb$^+$ and Cs$^+$ in RbBPO$_4$F and CsBPO$_4$F.
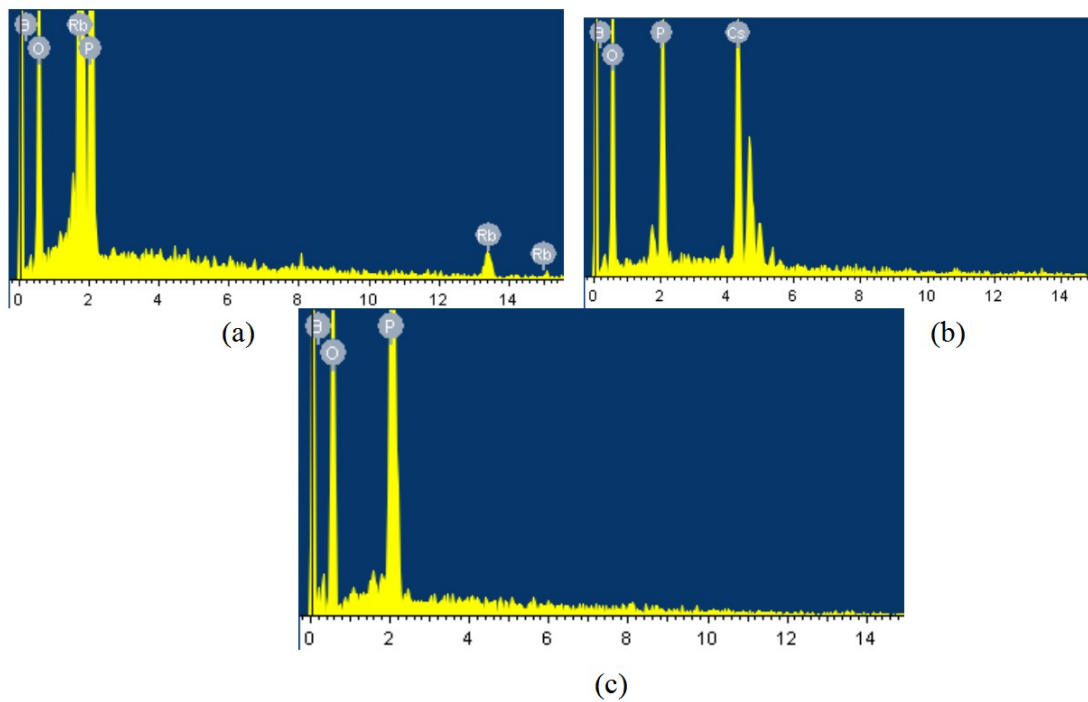
Figure S4. The Energy dispersive X-ray spectroscopy of the thermal decomposition residuals for $RbBPO_4F$, $CsBPO_4F$ and $(NH_4)_2BPO_4F_2$.
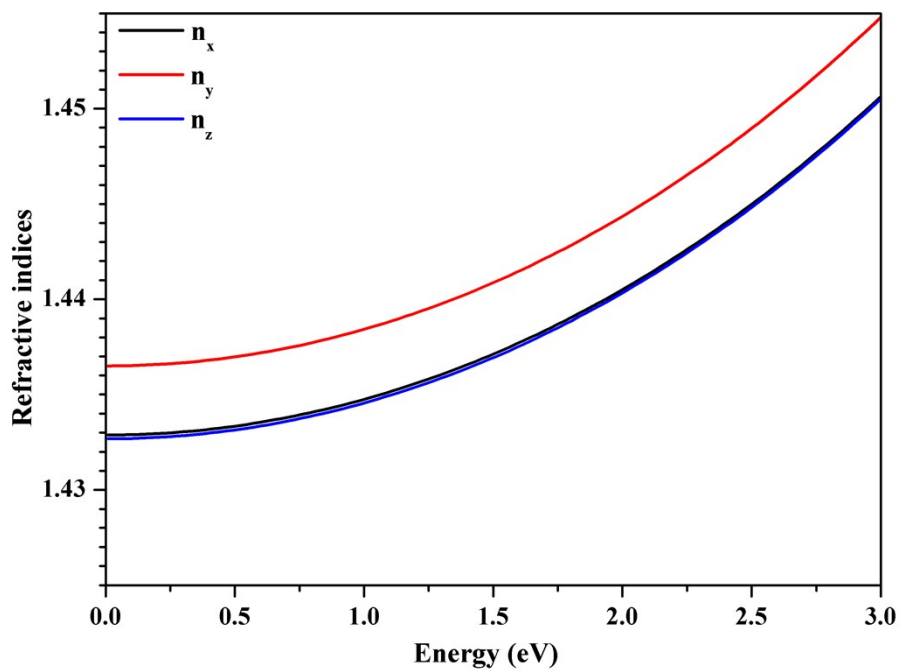

Figure S5. The calculated refractive indices of $(NH_4)_2BPO_4F_2$.