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$KPb_2(PO_3)_5$: A Novel Nonlinear Optical Lead Polyphosphate with Short Deep-UV Cutoff Edge

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Table S1. The final coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of non-hydrogen atoms for $KPb_2(PO_3)_5$, $RbPb_2(PO_3)_5$ and $CsPb_2(PO_3)_5$. $\boldsymbol{U_{eq}}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor for each atom in asymmetric unit.

Atom	*x*	*y*	*z*	U_{eq}
		$KPb_2(PO_3)_5$		
K(1)	7187(4)	3593(4)	4056(3)	25(1)
Pb(1)	4052(1)	1400(1)	6867(1)	19(1)
Pb(2)	9004(1)	1713(1)	7688(1)	19(1)
P(1)	751(3)	8561(3)	5202(3)	14(1)
P(2)	5797(4)	6536(4)	6841(3)	16(1)
P(3)	7238(3)	-960(4)	5033(3)	14(1)
P(4)	8133(3)	6453(3)	8872(3)	13(1)
P(5)	10994(3)	4592(4)	5937(3)	13(1)
O(1)	9115(9)	4765(11)	8700(8)	26(2)
O(2)	7080(9)	621(10)	5953(7)	22(2)
O(3)	1070(11)	10193(11)	5988(9)	28(2)
O(4)	7413(10)	7133(12)	7581(8)	19(2)
O(5)	1222(10)	6801(11)	5995(9)	22(2)
O(6)	5685(10)	4488(11)	6755(8)	27(2)
O(7)	4470(9)	7678(11)	7316(8)	23(2)
O(8)	8911(9)	8103(10)	9507(8)	22(2)
O(9)	6537(9)	5884(12)	9578(8)	25(2)
O(10)	6869(12)	-557(11)	3701(9)	27(2)
O(11)	12044(9)	3825(10)	6949(8)	21(2)
O(12)	9293(9)	4087(11)	5973(8)	19(2)
O(13)	1362(12)	8453(11)	3916(9)	35(3)
O(14)	-1074(10)	8133(12)	5048(13)	49(3)
O(15)	6231(10)	-2702(12)	5445(7)	26(2)
		$RbPb_2(PO_3)_5$		
Rb(1)	5296(1)	1440(1)	7789(1)	23(1)
Pb(1)	8461(1)	3586(1)	4950(1)	19(1)
Pb(2)	3593(1)	3307(1)	4093(1)	21(1)
P(1)	6659(4)	-1464(4)	4937(3)	17(1)
P(2)	11535(3)	407(3)	5843(2)	13(1)
P(3)	6773(3)	3589(3)	1569(2)	14(1)
P(4)	5291(3)	-3946(3)	6748(2)	16(1)
P(5)	4440(3)	-1379(3)	2868(2)	15(1)
O(1)	5110(9)	-2107(11)	4155(7)	21(2)
O(2)	7972(8)	-2648(10)	4569(7)	28(2)
O(3)	10408(8)	1122(10)	4904(6)	22(2)
O(4)	11368(11)	-1795(11)	5776(9)	32(2)
O(5)	6496(12)	5193(11)	759(8)	41(2)
O(6)	6043(8)	-880(10)	2215(6)	21(2)
O(7)	13202(7)	946(10)	5736(7)	23(2)
O(8)	6129(13)	3484(11)	2814(9)	50(3)
O(9)	6109(9)	-2081(10)	6296(7)	28(2)
O(10)	3628(8)	-2969(9)	2228(7)	23(2)
O(11)	6767(9)	594(10)	4944(7)	27(2)
O(12)	3494(7)	345(9)	3028(6)	22(2)
O(13)	3573(12)	-3258(14)	6829(14)	72(3)
O(14)	5757(13)	-4264(11)	8030(7)	44(3)
O(15)	5523(8)	-5484(9)	5861(6)	25(2)
		$CsPb_2(PO_3)_5$		
Cs(1)	9460(3)	8549(3)	-260(3)	52(1)

Pb(1)	6301(1)	6416(1)	2575(1)	20(1)
Pb(2)	11172(1)	6692(1)	3432(1)	22(1)
P(1)	13215(7)	9599(8)	1709(5)	16(1)
P(2)	9473(7)	3938(8)	784(6)	17(1)
P(3)	5312(7)	8626(8)	-329(6)	15(1)
P(4)	3123(9)	8549(9)	-2373(7)	21(2)
P(5)	7979(7)	6406(7)	5967(6)	16(1)
O(1)	4330(20)	8840(20)	2636(15)	17(3)
O(2)	9240(20)	5470(20)	1658(15)	23(4)
O(3)	8240(30)	4770(30)	6790(20)	47(6)
O(4)	11257(18)	9680(20)	4484(16)	23(4)
O(5)	6124(18)	7050(20)	309(15)	19(3)
O(6)	3790(20)	8970(30)	338(16)	23(4)
O(7)	3012(19)	10600(20)	-2380(17)	25(4)
O(8)	1788(19)	7320(30)	-1981(19)	32(4)
O(9)	11550(20)	9020(30)	1781(17)	27(4)
O(10)	8550(40)	6520(30)	4700(20)	62(9)
O(11)	4625(18)	7990(20)	-1554(14)	10(3)
O(12)	8710(20)	2110(20)	1273(15)	21(4)
O(13)	8310(30)	8180(30)	6980(30)	48(6)
O(14)	9010(30)	4300(30)	-490(20)	43(6)
O(15)	11140(30)	3310(30)	770(30)	56(7)

Table S2a. Selected bond distances (Å) and bond angles (deg) for $KPb_2(PO_3)_5$.

K(1)-O(12)	2.714(9)	P(1)-O(3)	1.459(9)
K(1)-O(7)#5	2.850(8)	P(1)-O(13)	1.469(9)
K(1)-O(1)#2	2.889(8)	P(1)-O(5)	1.564(8)
K(1)-O(11)#2	2.901(8)	P(1)-O(14)	1.591(10)
K(1)-O(2)	2.932(8)	P(2)-O(6)	1.473(8)
K(1)-O(10)	3.008(9)	P(2)-O(7)	1.490(8)
K(1)-O(8)#2	3.089(8)	P(2)-O(15)#6	1.625(8)
Pb(1)-O(11)#1	2.440(7)	P(2)-O(4)	1.631(8)
Pb(1)-O(8)#2	2.528(8)	P(3)-O(10)	1.471(10)
Pb(1)-O(6)	2.617(8)	P(3)-O(2)	1.502(8)
Pb(1)-O(7)#3	2.731(8)	P(3)-O(14)#7	1.578(9)
Pb(1)-O(2)#4	2.825(7)	P(3)-O(15)	1.580(8)
Pb(1)-O(13)#11	2.911(9)	P(4)-O(1)	1.483(8)
Pb(1)-O(10)#11	2.778(9)	P(4)-O(8)	1.509(8)
Pb(1)-O(10)#9	2.829(9)	P(4)-O(4)	1.569(9)
Pb(2)-O(1)	2.437(8)	P(4)-O(9)	1.614(8)
Pb(2)-O(12)	2.505(8)	P(5)-O(11)	1.491(9)
Pb(2)-O(2)	2.567(8)	P(5)-O(12)	1.495(8)
Pb(2)-O(13)#4	2.620(9)	P(5)-O(5)#8	1.596(9)
Pb(2)-O(3)#8	2.762(9)	P(5)-O(9)#5	1.558(8)
Pb(2)-O(10)#9	2.779(9)		
O(11)#1-Pb(1)-O(8)#2	85.0(3)	O(3)-P(1)-O(13)	120.4(5)
O(11)#1-Pb(1)-O(6)	76.9(3)	O(3)-P(1)-O(14)	112.7(6)
O(8)#2-Pb(1)-O(6)	81.6(3)	O(13)-P(1)-O(14)	104.7(6)
O(11)#1-Pb(1)-O(7)#3	141.1(2)	O(5)-P(1)-O(14)	98.2(5)
O(8)#2-Pb(1)-O(7)#3	108.3(2)	O(7)-P(2)-O(4)	109.4(4)
O(6)-Pb(1)-O(7)#3	139.9(2)	O(12)-K(1)-O(1)#2	129.2(2)
O(1)-Pb(2)-O(12)	73.0(3)	O(7)#5-K(1)-O(1)#2	132.2(3)
O(1)-Pb(2)-O(2)	127.5(3)	O(12)-K(1)-O(11)#2	120.9(3)
O(12)-Pb(2)-O(2)	75.9(2)	O(7)#5-K(1)-O(11)#2	74.1(2)
O(1)-Pb(2)-O(13)#4	81.3(3)	O(1)#2-K(1)-O(11)#2	67.2(2)
O(12)-Pb(2)-O(13)#4	119.1(3)	O(12)-K(1)-O(2)	66.9(2)
O(2)-Pb(2)-O(13)#4	78.4(3)	O(7)#5-K(1)-O(2)	103.9(2)
O(12)-K(1)-O(7)#5	94.4(2)	O(1)#2-K(1)-O(2)	110.3(2)
O(11)#2-K(1)-O(2)	171.9(3)	O(12)-K(1)-O(10)	106.2(3)
O(7)#5-K(1)-O(10)	70.4(2)	O(10)-K(1)-O(8)#2	63.3(2)
O(1)#2-K(1)-O(10)	107.8(2)	O(7)#5-K(1)-O(8)#2	127.0(2)
O(11)#2-K(1)-O(10)	122.1(3)	O(1)#2-K(1)-O(8)#2	50.3(2)

Symmetry transformations used to generate equivalent atoms:

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

#6 x,y+1,z #7 x+1,y-1,z #8 x+1,y,z #9 x-1/2,-y+1,z+1/2 #10 x-1,y+1,z

Table S2b. Selected bond distances (Å) and bond angles (deg) for $RbPb_2(PO_3)_5$.

Rb(1)-O(3)#2	2.929(7)	Pb(2)-O(5)#6	2.778(9)
Rb(1)-O(12)#3	3.025(7)	P(1)-O(2)	1.468(8)
Rb(1)-O(15)#4	3.039(7)	P(1)-O(11)	1.478(7)
Rb(1)-O(9)	3.080(8)	P(1)-O(9)	1.609(8)
Rb(1)-O(14)#4	3.114(8)	P(1)-O(1)	1.625(7)
Rb(1)-O(10)#3	3.121(7)	P(2)-O(3)	1.477(8)
Rb(1)-O(4)#2	3.344(10)	P(2)-O(7)	1.483(7)
Rb(1)-O(11)	3.392(7)	P(2)-O(6)#3	1.583(7)
Pb(1)-O(3)	2.428(7)	P(2)-O(4)	1.586(8)
Pb(1)-O(10)#3	2.498(7)	P(3)-O(8)	1.463(8)
Pb(1)-O(11)	2.587(7)	P(3)-O(5)	1.461(8)
Pb(1)-O(2)#4	2.761(7)	P(3)-O(13)#7	1.578(11)
Pb(1)-O(5)#6	2.860(9)	P(3)-O(4)#6	1.579(8)
Pb(1)-O(14)#12	2.920(9)	P(4)-O(14)	1.450(9)
Pb(1)-O(15)#11	2.794(7)	P(4)-O(15)	1.475(7)
Pb(1)-O(8)#7	3.020(1)	P(4)-O(13)	1.553(10)
Pb(2)-O(12)	2.414(7)	P(4)-O(9)	1.589(7)
Pb(2)-O(7)#1	2.477(7)	P(5)-O(12)	1.489(7)
Pb(2)-O(8)	2.594(9)	P(5)-O(10)	1.497(7)
Pb(2)-O(15)#4	2.646(7)	P(5)-O(1)	1.580(8)
Pb(2)-O(14)#6	2.750(10)	P(5)-O(6)	1.593(7)
O(3)#2-Rb(1)-O(12)#3	69.61(19)	O(3)-Pb(1)-O(10)#3	82.2(2)
O(3)#2-Rb(1)-O(15)#4	170.5(2)	O(3)-Pb(1)-O(11)	77.4(2)
O(12)#3-Rb(1)-O(15)#4	107.26(19)	O(10)#3-Pb(1)-O(11)	83.0(2)
O(3)#2-Rb(1)-O(9)	83.63(19)	O(3)-Pb(1)-O(2)#4	144.1(2)
O(12)#3-Rb(1)-O(9)	59.07(19)	O(10)#3-Pb(1)-O(2)#4	109.0(2)
O(15)#4-Rb(1)-O(9)	102.65(18)	O(11)-Pb(1)-O(2)#4	136.6(2)
O(3)#2-Rb(1)-O(14)#4	123.5(2)	O(12)-Pb(2)-O(7)#1	74.7(2)
O(12)#3-Rb(1)-O(14)#4	107.4(2)	O(12)-Pb(2)-O(8)	79.2(2)
O(15)#4-Rb(1)-O(14)#4	47.97(19)	O(7)#1-Pb(2)-O(8)	122.6(3)
O(9)-Rb(1)-O(14)#4	145.5(2)	O(12)-Pb(2)-O(15)#4	130.3(2)
O(3)#2-Rb(1)-O(10)#3	110.73(19)	O(7)#1-Pb(2)-O(15)#4	78.4(2)
O(12)#3-Rb(1)-O(10)#3	48.59(18)	O(8)-Pb(2)-O(15)#4	81.4(3)
O(15)#4-Rb(1)-O(10)#3	62.81(19)	O(12)-Pb(2)-O(14)#6	89.9(2)
O(9)-Rb(1)-O(10)#3	88.34(19)	O(7)#1-Pb(2)-O(14)#6	109.8(2)
O(14)#4-Rb(1)-O(10)#3	63.6(2)	O(8)-Pb(2)-O(14)#6	120.4(3)
O(3)#2-Rb(1)-O(4)#2	45.0(2)	O(15)#4-Pb(2)-O(14)#6	138.8(2)
O(12)#3-Rb(1)-O(4)#2	73.6(2)	O(10)#3-Rb(1)-O(4)#2	85.7(2)

Symmetry transformations used to generate equivalent atoms:

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

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

Table S2c. Selected bond distances (Å) and bond angles (deg) for $CsPb_2(PO_3)_5$.

Cs(1)-O(1)#2	2.947(16)	Pb(2)-O(14)#11	2.768(2)
Cs(1)-O(4)#3	3.026(17)	P(1)-O(1)#1	1.478(17)
Cs(1)-O(2)	3.039(17)	P(1)-O(9)	1.488(18)
Cs(1)-O(14)	3.08(2)	P(1)-O(13)#2	1.62(3)
Cs(1)-O(12)#4	3.117(17)	P(1)-O(6)#1	1.635(19)
Cs(1)-O(5)	3.118(17)	P(2)-O(14)	1.45(2)
Cs(1)-O(13)#5	3.14(3)	P(2)-O(2)	1.462(17)
Cs(1)-O(7)#6	3.428(19)	P(2)-O(15)	1.50(3)
Pb(1)-O(1)	2.421(16)	P(2)-O(12)	1.559(16)
Pb(1)-O(5)	2.497(16)	P(3)-O(4)#3	1.472(16)
Pb(1)-O(7)#6	2.591(17)	P(3)-O(5)	1.491(16)
Pb(1)-O(8)#7	2.749(19)	P(3)-O(11)	1.513(17)
Pb(1)-O(3)#8	2.867(2)	P(3)-O(6)	1.516(18)
Pb(1)-O(14)#11	2.936(2)	P(4)-O(7)	1.472(18)
Pb(1)-O(10)#10	2.976(2)	P(4)-O(8)	1.51(2)
Pb(1)-O(2)#5	2.798(2)	P(4)-O(11)	1.600(16)
Pb(2)-O(4)	2.428(16)	P(4)-O(12)#12	1.627(18)
Pb(2)-O(9)	2.468(19)	P(5)-O(10)	1.46(2)
Pb(2)-O(10)	2.65(3)	P(5)-O(3)	1.49(2)
Pb(2)-O(2)	2.661(16)	P(5)-O(15)#8	1.59(3)
Pb(2)-O(3)#10	2.73(2)	P(5)-O(13)	1.70(3)
O(1)#2-Cs(1)-O(4)#3	69.0(5)	O(1)-Pb(1)-O(7)#6	78.3(5)
O(1)#2-Cs(1)-O(2)	170.7(4)	O(5)-Pb(1)-O(7)#6	83.9(6)
O(4)#3-Cs(1)-O(2)	107.6(5)	O(1)-Pb(1)-O(8)#7	142.9(5)
O(1)#2-Cs(1)-O(14)	124.2(5)	O(5)-Pb(1)-O(8)#7	110.8(6)
O(4)#3-Cs(1)-O(14)	107.1(5)	O(7)#6-Pb(1)-O(8)#7	135.8(5)
O(2)-Cs(1)-O(14)	47.7(5)	O(4)-Pb(2)-O(9)	75.0(6)
O(1)#2-Cs(1)-O(12)#4	83.5(4)	O(4)-Pb(2)-O(10)	79.4(6)
O(4)#3-Cs(1)-O(12)#4	60.8(4)	O(9)-Pb(2)-O(10)	121.8(8)
O(2)-Cs(1)-O(12)#4	102.5(4)	O(4)-Pb(2)-O(2)	130.1(5)
O(14)-Cs(1)-O(12)#4	145.7(5)	O(9)-Pb(2)-O(2)	77.6(6)
O(1)#2-Cs(1)-O(5)	110.4(4)	O(10)-Pb(2)-O(2)	80.8(8)
O(4)#3-Cs(1)-O(5)	48.2(4)	O(4)-Pb(2)-O(3)#10	128.9(6)
O(2)-Cs(1)-O(5)	63.1(4)	O(9)-Pb(2)-O(3)#10	72.3(7)
O(14)-Cs(1)-O(5)	63.9(5)	O(10)-Pb(2)-O(3)#10	151.6(7)
O(12)#4-Cs(1)-O(5)	88.9(4)	O(2)-Pb(2)-O(3)#10	78.8(6)
O(1)#2-Cs(1)-O(13)#5	46.5(6)	O(12)#4-Cs(1)-O(13)#5	120.8(6)

Symmetry transformations used to generate equivalent atoms:

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

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

#10 x+1/2,-y+1,z-1/2 #11 x,y-1,z #12 x-1/2,-y+1,z-1/2 #13 x-1,y,z #14 x,y,z+1

Table S3. Detailed contributions from the RbO_{10}, PbO_n polyhedra and PO_4 tetrahedra as well as the total polarization of the whole unit cell in the $RbBa_2(PO_3)_5$ compound.

Species		Dipole moment			
		x	*y*	*z*	Magnitude
$Rb(1)O_{10}$		-7.126	-4.589	-0.215	8.366
$Ba(1)O_8$		8.786	2.639	-13.419	20.273
$Ba(2)O_8$		0.247	-9.887	-6.087	11.685
$P(1)O_4$		4.199	4.157	2.303	5.308
$P(2)O_4$		-0.273	4.366	-0.024	4.374
$P(3)O_4$		-5.930	2.937	-3.486	5.496
$P(4)O_4$		2.329	0.900	-2.276	4.244
$P(5)O_4$		-2.951	-2.013	-2.813	3.215
Unit cell	ΣRbO_{10}	-14.253	0	-0.429	**13.990**
	ΣBaO_8	18.065	0.004	-39.012	**52.207**
Z=2	ΣPO_4	-5.250	0.003	-12.588	**10.185**
	Total polarization	**-1.438**	**0.006**	**-52.028**	**51.145**

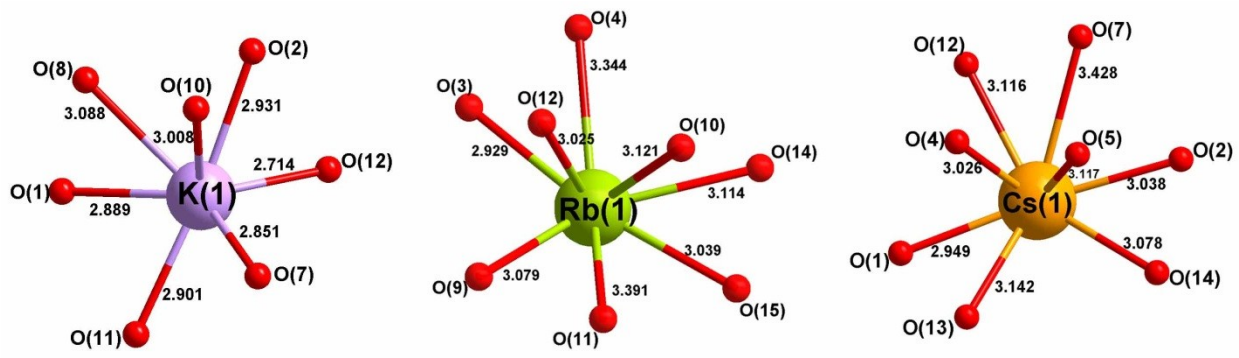


Figure S1 The coordination environment of the A (K, Rb, Cs) atoms

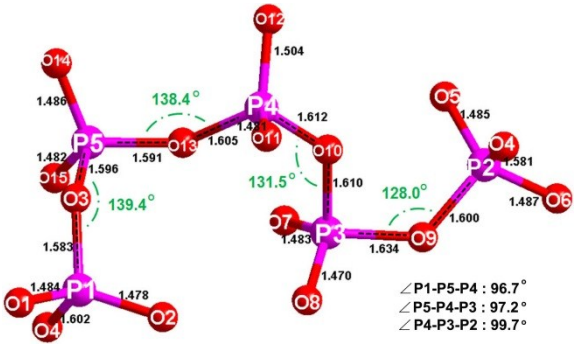


Figure S2 The bond lengths and angles of the repeat unit in the structure of $RbBa_2(PO_3)_5$

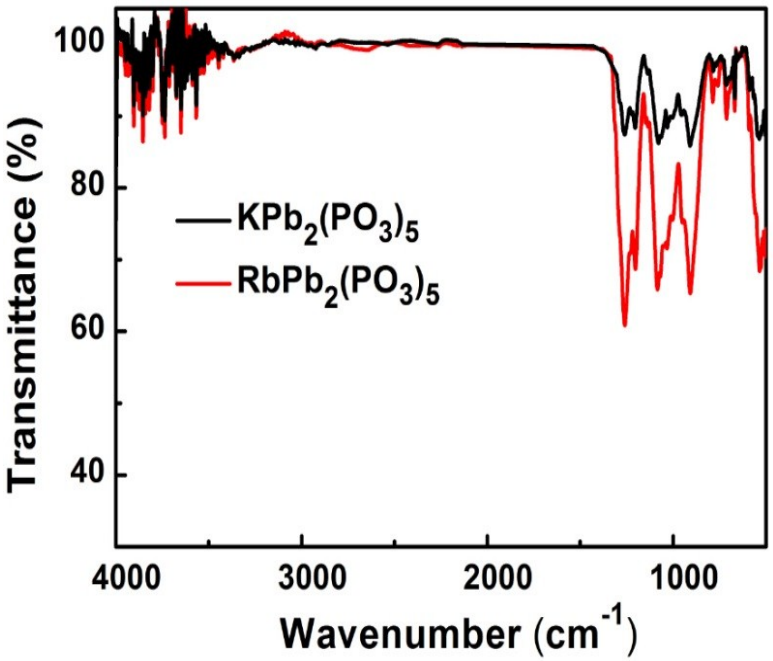


Figure S3 The IR spectra of $KPb_2(PO_3)_5$ and $RbPb_2(PO_3)_5$

Calculations Detail

The exchange-correlation functional and pseudo potential chosen were generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional and norm-conserving pseudo potential (NCP). The energy cut-off of the plane wave basis set was 830 eV for $RbBa_2(PO_3)_5$ and the Brillouin zone comprised 4×3×2 with a separation of Monkhorst-Pack k-point sampling of 0.04 /Å. The optimized valence electronic configurations for NCP are: Rb: $4s^24p^65s^1$, Ba: $5s^25p^66s^2$, P: $3s^23p^3$, O: $2s^22p^4$.

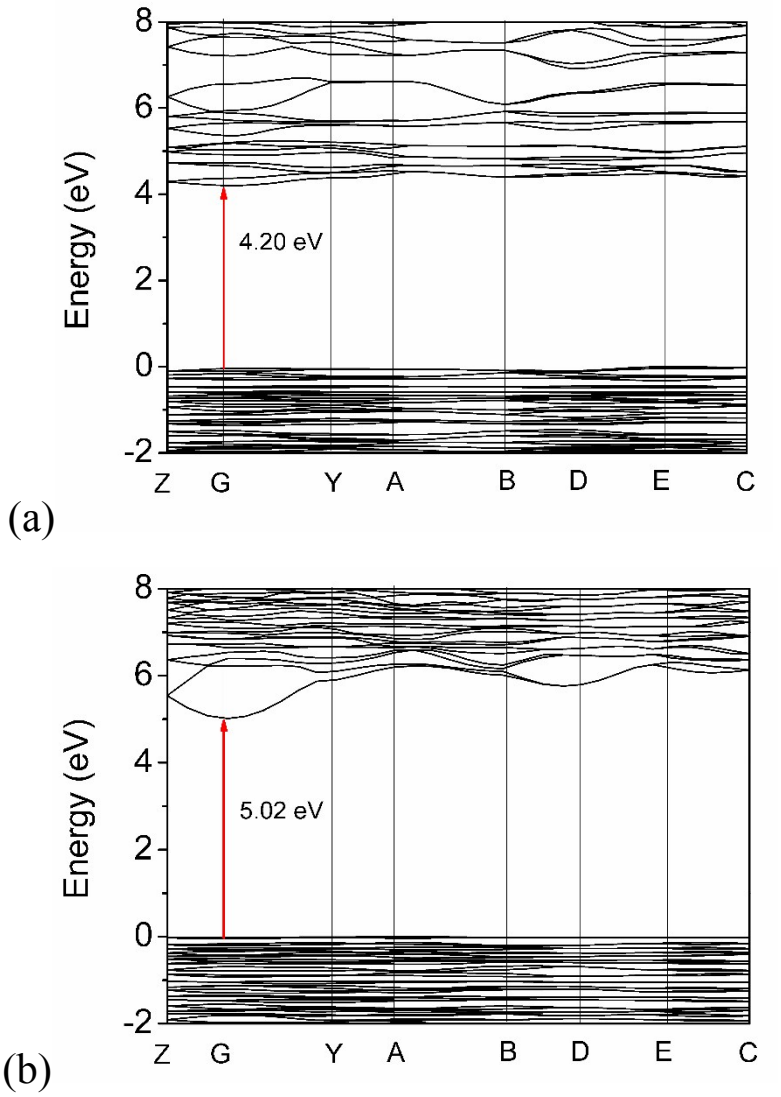


Figure S4 The band structures of (a) $KPb_2(PO_3)_5$ and (b) $RbBa_2(PO_3)_5$

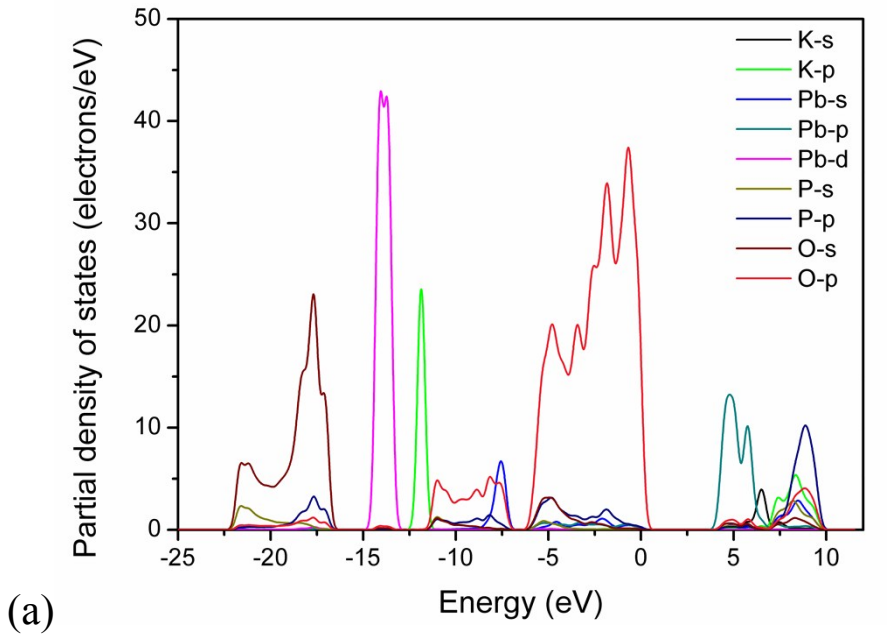
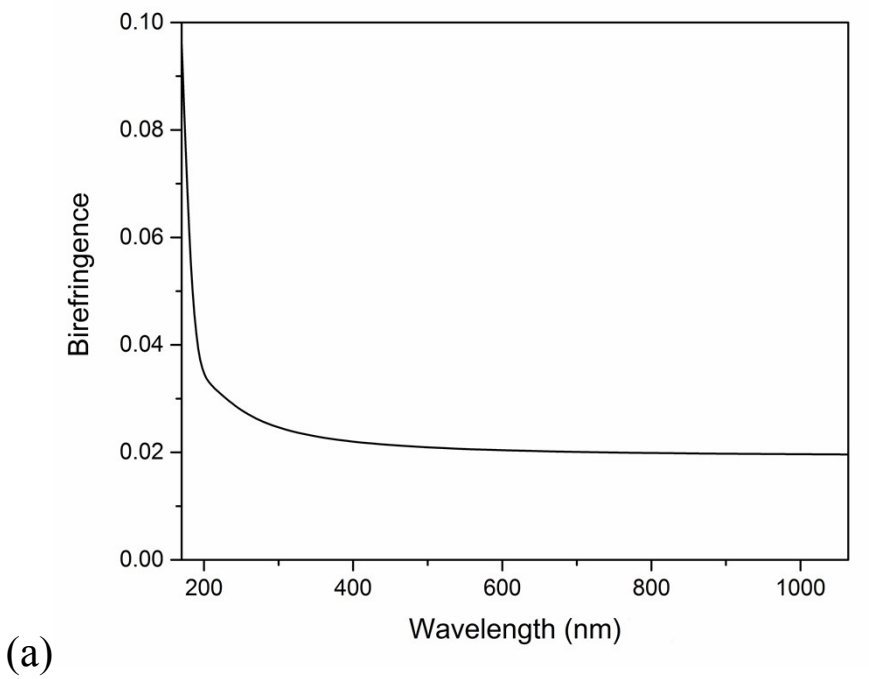
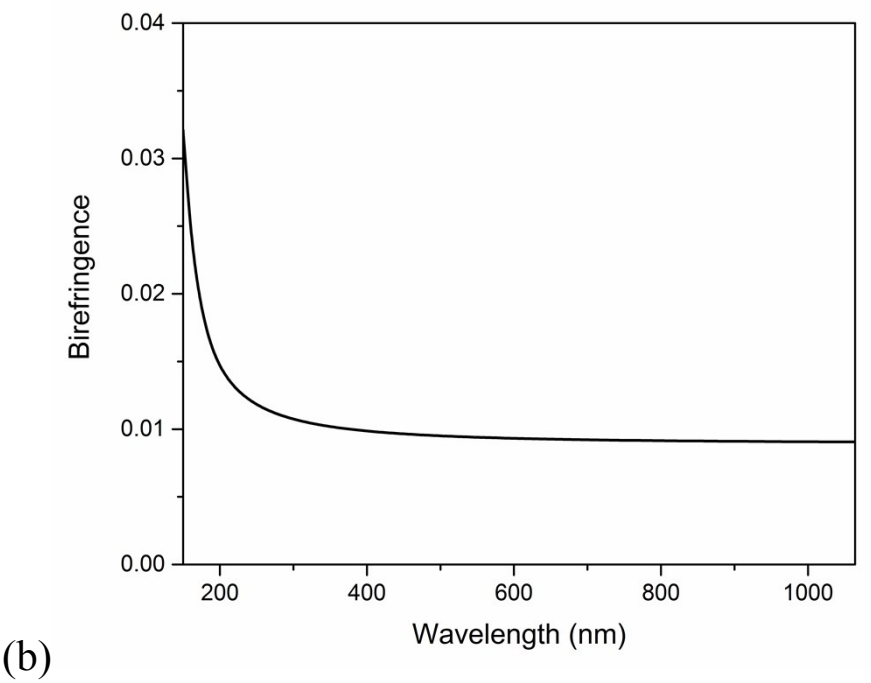


Figure S5 PDOS of (a) $KPb_2(PO_3)_5$ and (b) $RbBa_2(PO_3)_5$



(a)



(b)

Figure S6 Birefringences of (a) $KPb_2(PO_3)_5$ and (b) $RbBa_2(PO_3)_5$

Birefringence Measurement

The rough birefringence of $KPb_2(PO_3)_5$ at 589.3 nm was tested using a GR-5 Gem Refractormeter (Wuhan Zhongdixueyuan Gem Instrument Ltd., China). Drip a drop of contact liquid on the prism surface of refractometer, and put the natural growth surface of $KPb_2(PO_3)_5$ on the prism. The refractive index can be read through eyepiece. The measuring wavelength is 589.3 nm, the range of refractive index is 1.35-1.85 and the accuracy is ±0.002. It birefringence Δn is about 0.030 at 589.3 nm(n_1 = 1.590, n_2 = 1.620, recorded using refractometer at 589.3 nm).