$M^IM^{II}P_3O_9$ (M^I = Rb, M^{II} = Cd, Mg, Ca; M^I = Cs, M^{II} = Pb, Sr; M^I = K, M^{II} =Mg): Cation Substitution Application in Cyclophosphate Family and Nonlinear Optical Properties

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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 $RbCdP_3O_9$, $KMgP_3O_9$, $CsPbP_3O_9$, $CsSrP_3O_9$, $RbMgP_3O_9$, and $RbCaP_3O_9$. ***U*eq** is defined as one-third of the trace of the orthogonalized Uij tensor, and the Bond Valence Sum for each atom in asymmetric unit.

Atom	*x*	*y*	*z*	*Ueq*	BVS
			$RbCdP_3O_9$		
Rb(1)	3333	6667	0	26(1)	1.26
Cd(1)	0	0	0	13(1)	2.29
P(1)	7206(2)	6049(2)	7500	11(1)	5.15
O(1)	7351(5)	7205(5)	8742(2)	3	2.06
O(2)	8963(6)	5192(6)	7500	24(1)	2.10
			$KMgP_3O_9$		
K(1)	9667	3333	0	20(1)	1.21
Mg(1)	3333	6667	0	11(1)	2.17
P(1)	598(2)	7767(1)	2500	8(1)	5.08
O(1)	784(3)	6723(3)	1204(2)	17(1)	2.00
O(2)	2390(5)	503(4)	2500	16(1)	2.15
			$CsPbP_3O_9$		
Cs(1)	7022(1)	5842(1)	1241(1)	23(1)	1.15
Pb(1)	5420(1)	7344(1)	6398(1)	14(1)	1.80
P(1)	2989(3)	6444(2)	3163(3)	14(1)	4.86
P(2)	7527(3)	8634(2)	9509(3)	15(1)	4.94
P(3)	6489(2)	311(2)	1608(3)	13(1)	4.98
O(1)	3476(6)	6643(4)	1205(10)	17(1)	2.16
O(2)	2288(9)	7379(5)	3896(10)	30(2)	1.84
O(3)	4847(6)	590(4)	1443(13)	26(1)	1.81
O(4)	7062(8)	9790(5)	9884(8)	19(2)	2.19
O(5)	8627(7)	8677(6)	8063(9)	25(2)	1.94
O(6)	6160(8)	7969(6)	9385(9)	31(2)	1.85
O(7)	7573(8)	1135(5)	2105(9)	32(2)	1.94
O(8)	6643(8)	9392(5)	2925(8)	16(1)	2.19
O(9)	4328(8)	6000(6)	4059(8)	26(2)	1.87
			$CsSrP_3O_9$		
Cs(1)	6111(1)	2500	5827(1)	30(1)	0.83
Sr(1)	4830(1)	2500	2724(1)	15(1)	2.38
P(1)	2559(1)	592(2)	6484(1)	18(1)	5.08
P(2)	2124(2)	2500	4640(1)	20(1)	5.07
O(1)	2988(4)	2500	6811(3)	20(1)	2.22
O(2)	3790(3)	9607(4)	6322(2)	29(1)	2.05
O(3)	1095(4)	2500	3848(3)	32(1)	1.97
O(4)	1852(3)	913(4)	5401(2)	22(1)	2.09
O(5)	1567(3)	9952(4)	7215(2)	33(1)	2.00

O(6)	3539(4)	2500	4356(3)	32(1)	1.94
			$RbMgP_3O_9$		
Rb(1)	1008(1)	2500	4141(1)	19(1)	1.19
Mg(1)	9898(2)	2500	7153(1)	9(1)	2.20
P(1)	7068(1)	2500	5501(1)	9(1)	4.99
P(2)	7431(1)	423(1)	3492(1)	9(1)	5.03
O(1)	7811(4)	2500	3087(3)	12(1)	2.22
O(2)	6022(4)	2500	6414(3)	16(1)	1.93
O(3)	8811(3)	9456(3)	3651(2)	15(1)	2.09
O(4)	6349(3)	9664(3)	2731(2)	16(1)	2.00
O(5)	8630(4)	2500	5716(3)	16(1)	2.01
O(6)	6707(3)	782(3)	4687(2)	12(1)	2.10
			$RbCaP_3O_9$		
Rb(1)	4018(1)	2500	4168(1)	30(1)	0.86
Ca(1)	5168(1)	2500	7200(1)	12(1)	2.35
P(1)	7959(2)	2500	5394(1)	16(1)	5.12
P(2)	7492(1)	534(2)	3498(1)	14(1)	5.11
O(1)	2037(5)	2500	1834(4)	17(1)	2.22
O(2)	8994(6)	2500	6231(4)	29(1)	2.01
O(3)	8269(3)	866(5)	4605(3)	18(1)	2.10
O(4)	8489(4)	9895(6)	2711(3)	28(1)	2.02
O(5)	6209(4)	9547(6)	3700(3)	25(1)	2.05
O(6)	6480(5)	2500	5642(4)	28(2)	1.99

Table S2a. Selected bond distances (Å) and bond angles (deg) for $RbCdP_3O_9$.

Rb(1)-O(1)#1	2.884(3)	Rb(1)-O(2)	3.662(4)
Rb(1)-O(1)#2	2.884(3)	Cd(1)-O(1)	2.261(2)
Rb(1)-O(1)#3	2.884(3)	Cd(1)-O(1)#8	2.261(2)
Rb(1)-O(1)#4	2.884(3)	Cd(1)-O(1)#9	2.261(2)
Rb(1)-O(1)#5	2.884(3)	Cd(1)-O(1)#10	2.261(2)
Rb(1)-O(1)	2.884(3)	Cd(1)-O(1)#2	2.261(2)
Rb(1)-O(2)	3.662(4)	Cd(1)-O(1)#11	2.261(2)
Rb(1)-O(2)	3.662(4)	P(1)-O(1)	1.467(2)
Rb(1)-O(2)	3.662(4)	P(1)-O(1)#14	1.467(2)
Rb(1)-O(2)	3.662(4)	P(1)-O(2)	1.579(4)
Rb(1)-O(2)	3.662(4)	P(1)-O(2)#15	1.601(4)
O(1)#1-Rb(1)-O(1)#2	167.31(11)	O(1)-Cd(1)-O(1)#10	91.09(10)
O(1)#1-Rb(1)-O(1)#3	101.79(6)	O(1)#8-Cd(1)-O(1)#10	85.85(16)
O(1)#2-Rb(1)-O(1)#3	88.75(12)	O(1)#9-Cd(1)-O(1)#10	92.13(13)
O(1)#1-Rb(1)-O(1)#4	88.75(12)	O(1)-Cd(1)-O(1)#2	92.13(13)
O(1)#2-Rb(1)-O(1)#4	101.79(6)	O(1)#8-Cd(1)-O(1)#2	91.09(10)
O(1)#3-Rb(1)-O(1)#4	68.76(9)	O(1)#9-Cd(1)-O(1)#2	91.09(10)
O(1)#1-Rb(1)-O(1)#5	68.76(9)	O(1)#10-Cd(1)-O(1)#2	175.60(15)
O(1)#2-Rb(1)-O(1)#5	101.79(6)	O(1)-Cd(1)-O(1)#11	91.09(10)
O(1)#3-Rb(1)-O(1)#5	167.31(11)	O(1)#8-Cd(1)-O(1)#11	92.13(13)
O(1)#4-Rb(1)-O(1)#5	101.79(6)	O(1)#9-Cd(1)-O(1)#11	175.60(15)
O(1)#1-Rb(1)-O(1)	101.79(6)	O(1)#10-Cd(1)-O(1)#11	91.09(10)
O(1)#2-Rb(1)-O(1)	68.76(9)	O(1)#2-Cd(1)-O(1)#11	85.85(15)
O(1)#3-Rb(1)-O(1)	101.79(6)	O(1)-P(1)-O(1)#14	118.9(3)
O(1)#4-Rb(1)-O(1)	167.31(11)	O(1)-P(1)-O(2)	109.93(14)
O(1)#5-Rb(1)-O(1)	88.75(12)	O(1)#14-P(1)-O(2)	109.93(14)
O(1)-Cd(1)-O(1)#8	175.60(15)	O(1)-P(1)-O(2)#15	106.55(13)
O(1)-Cd(1)-O(1)#9	85.85(16)	O(1)#14-P(1)-O(2)#15	106.55(13)
O(1)#8-Cd(1)-O(1)#9	91.09(10)	O(2)-P(1)-O(2)#15	103.8(3)

Symmetry transformations used to generate equivalent atoms:

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

#5 -y+1,-x+1,-z+2 #6 -x+y,-x+1,-z+3/2 #7 -x+y,y,z+1/2 #8 -y+2,-x+2,-z+2

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

#14 x,y,-z+3/2 #15 -y+1,x-y,z #16 -x+y+1,-x+1,-z+3/2

Table S2b. Selected bond distances (Å) and bond angles (deg) for $KMgP_3O_9$.

K(1)-O(1)#1	2.7752(18)	Mg(1)-O(1)	2.0693(16)
K(1)-O(1)	2.7752(18)	Mg(1)-O(1)#2	2.0693(16)
K(1)-O(1)#2	2.7752(18)	Mg(1)-O(1)#11	2.0693(16)
K(1)-O(1)#3	2.7752(18)	Mg(1)-O(1)#12	2.0693(16)
K(1)-O(1)#4	2.7752(18)	P(1)-O(2)	1.589(3)
K(1)-O(1)#5	2.7752(18)	P(1)-O(2)#16	1.592(3)
Mg(1)-O(1)#9	2.0693(16)	P(1)-O(1)	1.4762(16)
Mg(1)-O(1)#10	2.0693(16)	P(1)-O(1)#15	1.4762(16)
O(1)#1-K(1)-O(1)	162.74(7)	O(1)#9-Mg(1)-O(1)#10	90.45(10)
O(1)#1-K(1)-O(1)#2	103.30(4)	O(1)#9-Mg(1)-O(1)	87.91(10)
O(1)-K(1)-O(1)#2	63.92(6)	O(1)#10-Mg(1)-O(1)	90.83(7)
O(1)#1-K(1)-O(1)#3	63.92(6)	O(1)#9-Mg(1)-O(1)#2	90.83(7)
O(1)-K(1)-O(1)#3	103.30(4)	O(1)#10-Mg(1)-O(1)#2	178.22(11)
O(1)#2-K(1)-O(1)#3	91.40(7)	O(1)-Mg(1)-O(1)#2	90.45(10)
O(1)#1-K(1)-O(1)#4	91.40(7)	O(1)#9-Mg(1)-O(1)#11	90.83(7)
O(1)-K(1)-O(1)#4	103.30(4)	O(1)#10-Mg(1)-O(1)#11	87.91(10)
O(1)#2-K(1)-O(1)#4	162.74(7)	O(1)-Mg(1)-O(1)#11	178.22(11)
O(1)#3-K(1)-O(1)#4	103.30(4)	O(1)#2-Mg(1)-O(1)#11	90.83(6)
O(1)#1-K(1)-O(1)#5	103.30(4)	O(1)#9-Mg(1)-O(1)#12	178.22(11)
O(1)-K(1)-O(1)#5	91.40(7)	O(1)#10-Mg(1)-O(1)#12	90.83(7)
O(1)#2-K(1)-O(1)#5	103.30(4)	O(1)-Mg(1)-O(1)#12	90.83(7)
O(1)#3-K(1)-O(1)#5	162.74(7)	O(1)#2-Mg(1)-O(1)#12	87.91(10)
O(1)#4-K(1)-O(1)#5	63.92(6)	O(1)#11-Mg(1)-O(1)#12	90.45(10)
O(1)-P(1)-O(1)#15	118.18(15)	O(1)-P(1)-O(2)#16	107.07(8)
O(1)-P(1)-O(2)	110.02(9)	O(1)#15-P(1)-O(2)#16	107.07(8)
O(1)#15-P(1)-O(2)	110.02(9)	O(2)-P(1)-O(2)#16	103.37(18)

Symmetry transformations used to generate equivalent atoms:

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

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

#9 -y+1, -x+1, -z #10 -x+y, -x+1, z #11 -x+y, y, -z #12 -y+1, x-y+1, z #13 x+1, y+1, z

#14 x+1, y, z #15 x, y, -z+1/2 #16 -x+y-1, -x+1, z #17 -y+1, x-y+2, z

Table S2c. Selected bond distances (Å) and bond angles (deg) for $CsPbP_3O_9$.

Cs(1)-O(4)#3	3.284(7)	Pb(1)-O(3)#7	2.724(6)
Cs(1)-O(7)#4	3.302(7)	Pb(1)-O(9)	2.724(7)
Cs(1)-O(8)#4	3.436(7)	P(1)-O(9)	1.480(7)
Cs(1)-O(1)#1	3.537(6)	P(1)-O(2)	1.488(8)
Cs(1)-O(3)#1	3.096(6)	P(1)-O(8)#9	1.615(8)
Cs(1)-O(2)#1	3.144(8)	P(1)-O(1)	1.622(8)
Cs(1)-O(9)#2	3.192(7)	P(2)-O(6)	1.477(7)
Cs(1)-O(9)	3.233(7)	P(2)-O(5)	1.489(7)
Cs(1)-O(5)#3	3.235(7)	P(2)-O(4)	1.599(8)
Cs(1)-O(6)	3.241(7)	P(2)-O(1)#1	1.612(7)
Cs(1)-O(1)	3.255(5)	P(3)-O(3)	1.478(5)
Pb(1)-O(7)#3	2.423(7)	P(3)-O(7)	1.487(7)
Pb(1)-O(5)#5	2.439(7)	P(3)-O(8)	1.597(7)
Pb(1)-O(6)#6	2.575(7)	P(3)-O(4)	1.601(7)
Pb(1)-O(2)#1	2.579(7)		
O(3)#1-Cs-O(2)#1	111.0(2)	O(7)#3-Pb(1)-O(2)#1	79.4(2)
O(3)#1-Cs-O(9)#2	81.85(18)	O(5)#5-Pb(1)-O(2)#1	152.9(2)
O(2)#1-Cs-O(9)#2	161.57(17)	O(6)#6-Pb(1)-O(2)#1	119.8(3)
O(3)#1-Cs-O(9)	125.3(2)	O(7)#3-Pb(1)-O(3)#7	135.3(2)
O(2)#1-Cs-O(9)	63.16(18)	O(5)#5-Pb(1)-O(3)#7	119.1(2)
O(9)#2-Cs-O(9)	98.79(10)	O(6)#6-Pb(1)-O(3)#7	72.1(3)
O(3)#1-Cs-O(5)#3	65.25(17)	O(2)#1-Pb(1)-O(3)#7	85.6(2)
O(2)#1-Cs-O(5)#3	111.75(19)	O(7)#3-Pb(1)-O(9)	88.9(2)
O(9)#2-Cs-O(5)#3	60.58(17)	O(5)#5-Pb(1)-O(9)	77.6(2)
O(9)-Cs-O(5)#3	68.0(2)	O(6)#6-Pb(1)-O(9)	155.8(2)
O(3)#1-Cs-O(6)	136.89(19)	O(2)#1-Pb(1)-O(9)	78.0(2)
O(2)#1-Cs-O(6)	71.2(2)	O(3)#7-Pb(1)-O(9)	128.7(2)
O(9)#2-Cs-O(6)	108.98(18)	O(9)-P(1)-O(2)	117.5(5)
O(9)-Cs-O(6)	95.03(19)	O(9)-P(1)-O(8)#9	110.8(4)
O(5)#3-Cs-O(6)	156.59(17)	O(2)-P(1)-O(8)#9	108.1(4)
O(3)#1-Cs-O(1)	161.22(14)	O(9)-P(1)-O(1)	108.2(4)
O(2)#1-Cs-O(1)	80.53(19)	O(2)-P(1)-O(1)	110.1(4)
O(9)#2-Cs-O(1)	83.83(17)	O(6)-P(2)-O(5)	119.2(4)
O(9)-Cs-O(1)	45.60(18)	O(6)-P(2)-O(4)	111.8(4)
O(5)#3-Cs-O(1)	97.06(16)	O(5)-P(2)-O(4)	105.5(4)
O(6)-Cs-O(1)	59.93(17)	O(6)-P(2)-O(1)#1	109.4(4)
O(3)#1-Cs-O(4)#3	60.5(2)	O(5)-P(2)-O(1)#1	108.4(4)
O(2)#1-Cs-O(4)#3	73.33(18)	O(3)-P(3)-O(7)	117.0(4)
O(9)#2-Cs-O(4)#3	103.96(17)	O(3)-P(3)-O(8)	109.0(4)
O(9)-Cs-O(4)#3	66.54(17)	O(7)-P(3)-O(8)	109.0(4)

O(7)#3-Pb(1)-O(5)#5	88.6(3)	O(3)-P(3)-O(4)	109.3(5)
O(7)#3-Pb(1)-O(6)#6	79.6(2)	O(7)-P(3)-O(4)	109.7(4)
O(5)#5-Pb(1)-O(6)#6	80.9(2)		

Symmetry transformations used to generate equivalent atoms:

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

#5 x-1/2,-y+3/2,z+1 #6 x,y,z+1 #7 -x+1,-y+2,z+1/2 #8 -x+1,-y+1,z+1/2

#9 x-1/2,-y+3/2,z #10 -x+3/2,y+1/2,z-1/2 #11 -x+3/2,y+1/2,z+1/2 #12 -x+1,-y+2,z-1/2

#13 x+1/2,-y+3/2,z-1 #14 x,y,z-1

Table S2d. Selected bond distances (Å) and bond angles (deg) for $CsSrP_3O_9$.

Cs(1)-O(6)	3.226(4)	Sr(1)-O(5)#8	2.456(3)
Cs(1)-O(2)#1	3.237(3)	Sr(1)-O(2)#2	2.478(3)
Cs(1)-O(2)#2	3.237(3)	Sr(1)-O(2)#1	2.478(3)
Cs(1)-O(5)#3	3.253(3)	Sr(1)-O(6)	2.491(4)
Cs(1)-O(5)#4	3.253(3)	P(1)-O(5)	1.467(3)
Cs(1)-O(2)	3.306(3)	P(1)-O(2)	1.474(3)
Cs(1)-O(2)#5	3.306(3)	P(1)-O(1)	1.5971(18)
Cs(1)-O(1)	3.403(4)	P(1)-O(4)	1.597(3)
Cs(1)-O(1)#4	3.609(4)	P(2)-O(3)	1.462(4)
Cs(1)-O(4)#1	3.710(3)	P(2)-O(6)	1.476(4)
Cs(1)-O(4)#2	3.710(3)	P(2)-O(4)#5	1.602(3)
Sr(1)-O(3)#6	2.410(4)	P(2)-O(4)	1.602(3)
Sr(1)-O(5)#7	2.456(3)		
O(6)-Cs(1)-O(2)#1	60.87(8)	O(3)#6-Sr(1)-O(5)#7	94.38(10)
O(6)-Cs(1)-O(2)#2	60.87(8)	O(3)#6-Sr(1)-O(5)#8	94.38(10)
O(2)#1-Cs(1)-O(2)#2	60.53(11)	O(5)#7-Sr(1)-O(5)#8	101.25(16)
O(6)-Cs(1)-O(5)#3	125.29(7)	O(3)#6-Sr(1)-O(2)#2	97.24(11)
O(2)#1-Cs(1)-O(5)#3	167.59(8)	O(5)#7-Sr(1)-O(2)#2	165.15(10)
O(2)#2-Cs(1)-O(5)#3	111.43(8)	O(5)#8-Sr(1)-O(2)#2	87.08(11)
O(6)-Cs(1)-O(5)#4	125.29(7)	O(3)#6-Sr(1)-O(2)#1	97.24(11)
O(2)#1-Cs(1)-O(5)#4	111.43(8)	O(5)#7-Sr(1)-O(2)#1	87.08(11)
O(2)#2-Cs(1)-O(5)#4	167.59(8)	O(5)#8-Sr(1)-O(2)#1	165.15(10)
O(5)#3-Cs(1)-O(5)#4	74.66(11)	O(2)#2-Sr(1)-O(2)#1	82.32(15)
O(6)-Cs(1)-O(2)	62.88(7)	O(3)#6-Sr(1)-O(6)	179.53(15)
O(2)#1-Cs(1)-O(2)	81.28(8)	O(5)#7-Sr(1)-O(6)	85.92(9)
O(2)#2-Cs(1)-O(2)	122.10(4)	O(5)#8-Sr(1)-O(6)	85.92(9)
O(5)#3-Cs(1)-O(2)	111.04(8)	O(2)#2-Sr(1)-O(6)	82.41(10)
O(5)#4-Cs(1)-O(2)	62.43(7)	O(2)#1-Sr(1)-O(6)	82.41(10)
O(6)-Cs(1)-O(2)#5	62.88(7)	O(5)-P(1)-O(2)	119.6(2)
O(2)#1-Cs(1)-O(2)#5	122.10(4)	O(5)-P(1)-O(1)	109.0(2)
O(2)#2-Cs(1)-O(2)#5	81.28(8)	O(2)-P(1)-O(1)	106.7(2)
O(5)#3-Cs(1)-O(2)#5	62.43(7)	O(5)-P(1)-O(4)	108.55(17)
O(5)#4-Cs(1)-O(2)#5	111.04(8)	O(2)-P(1)-O(4)	109.36(16)
O(2)-Cs(1)-O(2)#5	85.32(10)	O(1)-P(1)-O(4)	102.25(17)
O(6)-Cs(1)-O(1)	58.42(9)	O(3)-P(2)-O(6)	120.8(3)
O(2)#1-Cs(1)-O(1)	110.67(8)	O(3)-P(2)-O(4)#5	108.28(16)
O(2)#2-Cs(1)-O(1)	110.67(7)	O(6)-P(2)-O(4)#5	108.64(15)
O(5)#3-Cs(1)-O(1)	80.63(7)	O(3)-P(2)-O(4)	108.28(16)
O(5)#4-Cs(1)-O(1)	80.63(7)	O(6)-P(2)-O(4)	108.64(15)
O(2)-Cs(1)-O(1)	43.09(5)	O(4)#5-P(2)-O(4)	100.2(2)

Symmetry transformations used to generate equivalent atoms:

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

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

#9 -x+1,-y+1,-z+1 #10 x-1/2,y,-z+3/2 #11 x-1/2,y,-z+1/2 #12 -x+1/2,-y,z+1/2

Table S2e. Selected bond distances (Å) and bond angles (deg) for $RbMgP_3O_9$.

Rb(1)-O(5)	2.913(4)	Mg(1)-O(2)#8	2.013(4)
Rb(1)-O(3)#1	3.001(3)	Mg(1)-O(4)#9	2.060(3)
Rb(1)-O(3)#2	3.001(3)	Mg(1)-O(4)#10	2.060(3)
Rb(1)-O(4)#3	3.046(3)	Mg(1)-O(3)#2	2.085(3)
Rb(1)-O(4)#4	3.046(3)	Mg(1)-O(3)#1	2.085(3)
Rb(1)-O(3)	3.052(3)	P(1)-O(2)	1.467(4)
Rb(1)-O(3)#5	3.052(3)	P(1)-O(6)	1.608(2)
Rb(1)-O(1)#3	3.157(4)	P(1)-O(6)#5	1.608(2)
Rb(1)-O(1)	3.240(4)	P(1)-O(5)	1.481(4)
Rb(1)-O(6)#1	3.473(3)	P(2)-O(4)	1.466(3)
Rb(1)-O(6)#2	3.473(3)	P(2)-O(3)	1.475(3)
Rb(1)-O(5)#2	3.6062(17)	P(2)-O(6)	1.605(2)
Mg(1)-O(5)	2.091(4)	P(2)-O(1)	1.6067(16)
O(5)-Rb(1)-O(3)#1	58.06(8)	O(3)#1-Rb(1)-O(1)	113.35(7)
O(5)-Rb(1)-O(3)#2	58.06(8)	O(3)#2-Rb(1)-O(1)	113.35(7)
O(3)#1-Rb(1)-O(3)#2	55.73(10)	O(4)#3-Rb(1)-O(1)	78.97(6)
O(5)-Rb(1)-O(4)#3	123.87(6)	O(2)#8-Mg(1)-O(4)#9	90.43(11)
O(3)#1-Rb(1)-O(4)#3	163.02(7)	O(2)#8-Mg(1)-O(4)#10	90.43(11)
O(3)#2-Rb(1)-O(4)#3	109.40(7)	O(4)#9-Mg(1)-O(4)#10	97.81(16)
O(5)-Rb(1)-O(4)#4	123.87(6)	O(2)#8-Mg(1)-O(3)#2	95.38(12)
O(3)#1-Rb(1)-O(4)#4	109.40(7)	O(4)#9-Mg(1)-O(3)#2	88.55(11)
O(3)#2-Rb(1)-O(4)#4	163.02(7)	O(4)#10-Mg(1)-O(3)#2	171.36(12)
O(4)#3-Rb(1)-O(4)#4	83.80(10)	O(2)#8-Mg(1)-O(3)#1	95.38(12)
O(5)-Rb(1)-O(3)	67.27(7)	O(4)#9-Mg(1)-O(3)#1	171.36(12)
O(3)#1-Rb(1)-O(3)	122.83(4)	O(4)#10-Mg(1)-O(3)#1	88.55(11)
O(3)#2-Rb(1)-O(3)	82.73(7)	O(3)#2-Mg(1)-O(3)#1	84.55(16)
O(4)#3-Rb(1)-O(3)	56.66(7)	O(2)#8-Mg(1)-O(5)	176.95(17)
O(4)#4-Rb(1)-O(3)	113.96(7)	O(4)#9-Mg(1)-O(5)	87.57(11)
O(5)-Rb(1)-O(3)#5	67.27(7)	O(4)#10-Mg(1)-O(5)	87.57(11)
O(3)#1-Rb(1)-O(3)#5	82.73(7)	O(3)#2-Mg(1)-O(5)	86.87(11)
O(3)#2-Rb(1)-O(3)#5	122.83(4)	O(3)#1-Mg(1)-O(5)	86.87(11)
O(4)#3-Rb(1)-O(3)#5	113.96(7)	O(2)-P(1)-O(5)	121.7(2)
O(4)#4-Rb(1)-O(3)#5	56.66(7)	O(2)-P(1)-O(6)	108.32(13)
O(3)-Rb(1)-O(3)#5	91.37(10)	O(5)-P(1)-O(6)	108.16(13)
O(5)-Rb(1)-O(1)#3	162.61(9)	O(2)-P(1)-O(6)#5	108.32(13)
O(3)#1-Rb(1)-O(1)#3	135.77(7)	O(5)-P(1)-O(6)#5	108.16(13)
O(3)#2-Rb(1)-O(1)#3	135.77(7)	O(6)-P(1)-O(6)#5	100.09(18)
O(4)#3-Rb(1)-O(1)#3	47.21(5)	O(4)-P(2)-O(3)	120.49(15)
O(4)#4-Rb(1)-O(1)#3	47.21(5)	O(4)-P(2)-O(6)	109.01(15)
O(3)-Rb(1)-O(1)#3	101.24(7)	O(3)-P(2)-O(6)	109.10(14)

O(3)#5-Rb(1)-O(1)#3	101.24(7)	O(4)-P(2)-O(1)	107.92(17)
O(5)-Rb(1)-O(1)	63.39(9)	O(3)-P(2)-O(1)	106.42(17)

Symmetry transformations used to generate equivalent atoms:

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

#5 x, -y+1/2, z #6 -x+2, -y+1, -z+1 #7 x-1/2, y, -z+1/2 #8 x+1/2, y, -z+3/2

#9 -x+3/2, -y, z+1/2 #10 -x+3/2, y+1/2, z+1/2 #11 x-1/2, y, -z+3/2 #12 -x+3/2, -y, z-1/2

Table S2f. Selected bond distances (Å) and bond angles (deg) for $RbCaP_3O_9$.

Rb(1)-O(6)	3.021(5)	Ca(1)-O(6)	2.325(5)
Rb(1)-O(5)#1	3.083(4)	Ca(1)-O(5)#2	2.331(4)
Rb(1)-O(5)#2	3.083(4)	Ca(1)-O(5)#1	2.331(4)
Rb(1)-O(4)#3	3.099(4)	P(1)-O(2)	1.451(5)
Rb(1)-O(4)#4	3.099(4)	P(1)-O(6)	1.472(5)
Rb(1)-O(5)#5	3.134(4)	P(1)-O(3)	1.604(4)
Rb(1)-O(5)	3.134(4)	P(1)-O(3)#5	1.604(4)
Rb(1)-O(1)#6	3.193(5)	P(2)-O(4)	1.462(4)
Rb(1)-O(1)	3.492(5)	P(2)-O(5)	1.474(4)
Ca(1)-O(2)#7	2.267(5)	P(2)-O(3)	1.595(4)
Ca(1)-O(4)#8	2.315(4)	P(2)-O(1)#6	1.598(2)
Ca(1)-O(4)#9	2.315(4)		
O(6)-Rb(1)-O(5)#1	62.01(10)	O(2)#7-Ca(1)-O(6)	177.0(2)
O(6)-Rb(1)-O(5)#2	62.01(10)	O(4)#8-Ca(1)-O(6)	85.46(14)
O(5)#1-Rb(1)-O(5)#2	59.96(16)	O(4)#9-Ca(1)-O(6)	85.46(13)
O(6)-Rb(1)-O(4)#3	126.34(9)	O(2)#7-Ca(1)-O(5)#2	97.28(15)
O(5)#1-Rb(1)-O(4)#3	163.20(11)	O(4)#8-Ca(1)-O(5)#2	166.32(15)
O(5)#2-Rb(1)-O(4)#3	108.98(11)	O(4)#9-Ca(1)-O(5)#2	86.69(15)
O(6)-Rb(1)-O(4)#4	126.34(9)	O(6)-Ca(1)-O(5)#2	84.96(14)
O(5)#1-Rb(1)-O(4)#4	108.98(11)	O(2)#7-Ca(1)-O(5)#1	97.28(15)
O(5)#2-Rb(1)-O(4)#4	163.20(11)	O(4)#8-Ca(1)-O(5)#1	86.69(15)
O(6)-Rb(1)-O(5)#5	64.79(9)	O(6)-Ca(1)-O(5)#1	84.96(14)
O(5)#1-Rb(1)-O(5)#5	81.66(11)	O(5)#2-Ca(1)-O(5)#1	82.8(2)
O(5)#2-Rb(1)-O(5)#5	124.30(6)	O(2)-P(1)-O(6)	121.8(3)
O(4)#3-Rb(1)-O(5)#5	114.86(10)	O(2)-P(1)-O(3)	108.2(2)
O(4)#4-Rb(1)-O(5)#5	61.55(10)	O(6)-P(1)-O(3)	108.25(19)
O(6)-Rb(1)-O(5)	64.79(9)	O(2)-P(1)-O(3)#5	108.2(2)
O(5)#1-Rb(1)-O(5)	124.30(6)	O(6)-P(1)-O(3)#5	108.25(19)
O(5)#2-Rb(1)-O(5)	81.66(11)	O(3)-P(1)-O(3)#5	100.1(3)
O(4)#3-Rb(1)-O(5)	61.55(10)	O(4)-P(2)-O(5)	120.8(2)
O(4)#4-Rb(1)-O(5)	114.86(10)	O(4)-P(2)-O(3)	108.6(2)
O(5)#5-Rb(1)-O(5)	90.31(14)	O(5)-P(2)-O(3)	109.4(2)
O(6)-Rb(1)-O(1)#6	60.59(13)	O(4)-P(2)-O(1)#6	108.3(3)
O(5)#1-Rb(1)-O(1)#6	113.82(11)	O(5)-P(2)-O(1)#6	106.1(3)
O(5)#2-Rb(1)-O(1)#6	113.82(11)	O(3)-P(2)-O(1)#6	102.2(2)

Symmetry transformations used to generate equivalent atoms:

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

#5 x,-y+1/2,z #6 x+1/2,y,-z+1/2 #7 x-1/2,y,-z+3/2 #8 -x+3/2,y+1/2,z+1/2

#9 -x+3/2,-y,z+1/2 #10 -x+1,-y+1,-z+1 #11 x+1/2,y,-z+3/2 #12 -x+3/2,-y,z-1/2

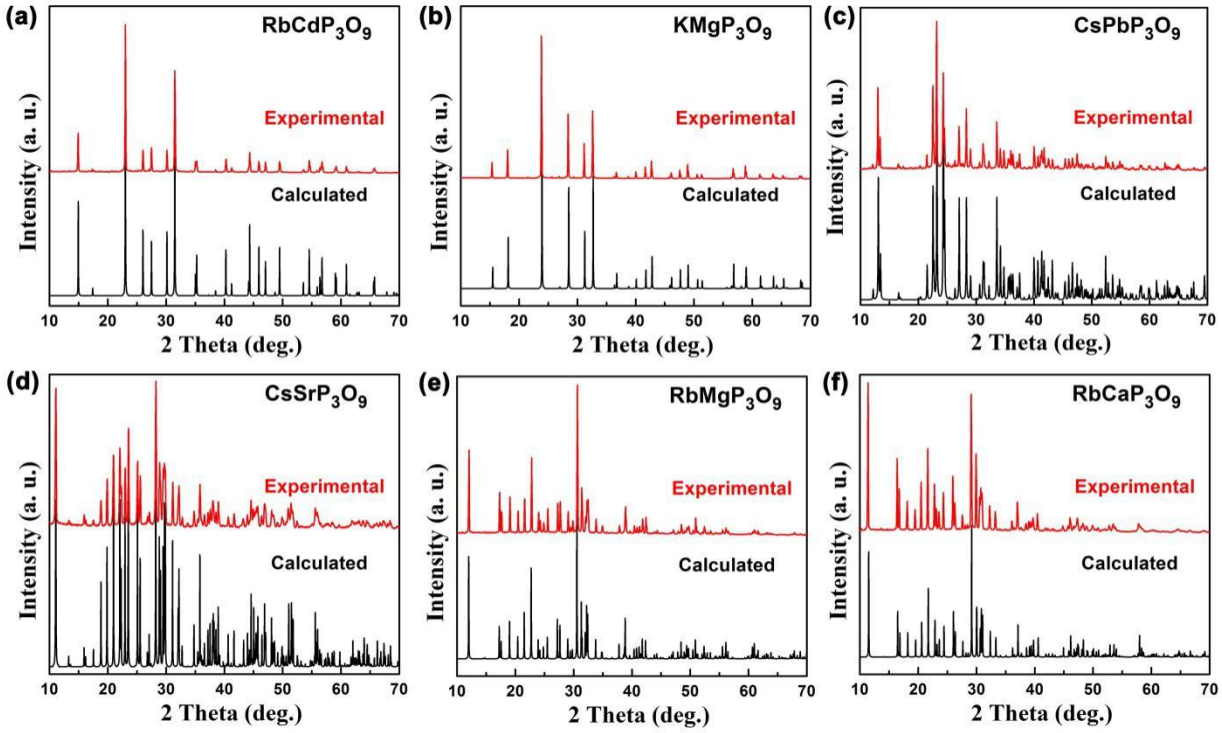

Figure S1. Experimental and calculated powder X-ray diffraction patterns of (a) $RbCdP_3O_9$, (b) $KMgP_3O_9$, (c) $CsPbP_3O_9$, (d) $CsSrP_3O_9$, (e) $RbMgP_3O_9$ and (f) $RbCaP_3O_9$

Table S3. The anhydrous compounds of M^I-M^{II}-P-O (M^I: alkaline metals, M^{II}: alkaline-earth metals) system, space group, M/P ratio and P-O framework configuration

Compounds	Space group	M/P ratio	P-O Framework	Compounds	Space group	M/P ratio	P-O Framework
$LiMgPO_4$	*Pnma* (62)	2.00	Isolate $[PO_4]$	$Na_3Mg_3(PO_4)_3$	$P2_12_12_1$ (19)	2.00	Isolate $[PO_4]$
$LiCaPO_4$	*P*31*c* (159)	2.00	Isolate $[PO_4]$	$KMgPO_4$	$P2_1/c$ (14)	2.00	Isolate $[PO_4]$
$NaCaPO_4$	$P\bar{3}m1$ (164)	2.00	Isolate $[PO_4]$	$KSrPO_4$	*Pnma* (62)	2.00	Isolate $[PO_4]$
$NaCaPO_4$	$Pna2_1$ (33)	2.00	Isolate $[PO_4]$	$KBaPO_4$	*Pmcn* (62)	2.00	Isolate $[PO_4]$
$KCaPO_4$	$P\bar{3}m1$ (164)	2.00	-	$KBaPO_4$	*Pnma* (62)	2.00	Isolate $[PO_4]$
$CsMgPO_4$	*Pnma* (62)	2.00	Isolate $[PO_4]$	$RbMgPO_4$	$Pna2_1$ (33)	2.00	Isolate $[PO_4]$
$NaBaPO_4$	*C*2/*m* (12)	2.00	Isolate $[PO_4]$	$RbMgPO_4$	*Pnma* (62)	2.00	Isolate $[PO_4]$
$NaBaPO_4$	$P\bar{3}m1$ (164)	2.00	Isolate $[PO_4]$	$RbBaPO_4$	*Pnma* (62)	2.00	Isolate $[PO_4]$
$Na_2Mg_5(PO_4)_4$	$P\bar{1}$ (2)	1.75	Isolate $[PO_4]$	$Na_4Mg_3(PO_4)_2(P_2O_7)$	$Pna2_1$ (33)	1.75	Isolate $[P_2O_7]$ $[PO_4]$
$KMg_4(PO_4)_3$	*Pnnm* (58)	1.67	Isolate $[PO_4]$	$NaMg_4(PO_4)_3$	*Pnma* (62)	1.67	Isolate $[PO_4]$
$Li_{1.05}Ca_{9.95}(PO_4)_7$	*R*3*c* (161)	1.57	Isolate $[PO_4]$	$CsCa_{10}(PO_4)_7$	*R*3*c* (161)	1.57	Isolate $[PO_4]$
$KCa_{10}(PO_4)_7$	*R*3*c* (161)	1.57	Isolate $[PO_4]$	$NaCa_{10}(PO_4)_7$	*R*3*c* (161)	1.57	Isolate $[PO_4]$
$Li_2BaP_2O_7$	*A*2/*a* (15)	1.50	Isolate $[P_2O_7]$	$Li_2BaP_2O_7$	*C*2/*c* (15)	1.50	Isolate $[P_2O_7]$
$Na_2CaP_2O_7$	$P\bar{1}$ (2)	1.50	Isolate $[P_2O_7]$	$Rb_2SrP_2O_7$	*C*2/*c* (15)	1.50	Isolate $[P_2O_7]$
$Cs_2CaP_2O_7$	*C*2/*m* (12)	1.50	Isolate $[P_2O_7]$	$K_2SrP_2O_7$	$P2_1/c$ (14)	1.50	Isolate $[P_2O_7]$
$Cs_2SrP_2O_7$	*C*2/*c* (15)	1.50	Isolate $[P_2O_7]$	$Na_{3.64}Mg_{2.18}(P_2O_7)_2$	$P\bar{1}$ (2)	1.46	Isolate $[P_2O_7]$
$Na_7Mg_{4.5}(P_2O_7)_4$	$P\bar{1}$ (2)	1.44	Isolate $[P_2O_7]$	$K_4Mg_4(P_2O_7)_3$	*Pc* (7)	1.33	Isolate $[P_2O_7]$
$Rb_4Mg_4(P_2O_7)_3$	*Amm*2 (38)	1.33	Isolate $[P_2O_7]$	$LiMg_3(PO_4)P_2O_7$	*Pnma* (62)	1.33	Isolate $[P_2O_7][PO_4]$
$Cs_2Ba_3(P_2O_7)_2$	$P2_12_12_1$ (19)	1.25	Isolate $[P_2O_7]$	$Rb_2Ba_3(P_2O_7)_2$	$P2_12_12_1$ (19)	1.25	Isolate $[P_2O_7]$
$K_2Ba_3(P_2O_7)_2$	$Pmn2_1$ (31)	1.25	Isolate $[P_2O_7]$	$Na_3Sr_7(P_3)_3O$	$P6_3/mcm$ (193)	1.11	-
$CsBaP_2O_7$	$P2_1/n$ (14)	1.00	Isolate $[P_2O_7]$	$KMg_6(P_2O_7)_2(P_3O_{10})$	$P2_1/m$ (11)	1.00	Isolate $[P_2O_7][P_3O_{10}]$
$Na_3Mg_2P_5O_{16}$	*P*2/*a* (13)	1.00	1D Chain	$K_2CaP_2O_7$	$P2_1/n$ (14)	1.00	Isolate $[P_2O_7]$
$Cs_4Ba(PO_3)_6$	*P*31*c* (159)	0.83	1D Chain	$Na_4Ca(P_3O_9)_2$	*C*2/*c* (15)	0.83	Isolate $[P_3O_9]$
$Na_2SrP_4O_{12}$	*P*4/*nbm* (125)	0.75	Isolate $[P_4O_{12}]$	$K_2Sr(PO_3)_4$	$I\bar{6}$ (82)	0.75	Isolate $[P_4O_{12}]$
$Na_2Ca(PO_3)_4$	*P*4/*nbm* (125)	0.75	Isolate $[P_4O_{12}]$	$Li_3Ba_2(PO_3)_7$	$P2_1/a$ (14)	0.71	1D Chain
$RbBa_2(PO_3)_5$	*Pc* (7)	0.60	1D Chain	$Rb_3Sr_2P_7O_{21}$	$P2_1/n$ (14)	0.71	1D Chain
$KBa_2(PO_3)_5$	*Pc* (7)	0.60	1D Chain	$Cs_3Sr_2P_7O_{21}$	*C*2/*c* (15)	0.71	1D Chain and $[P_4O_{12}]$

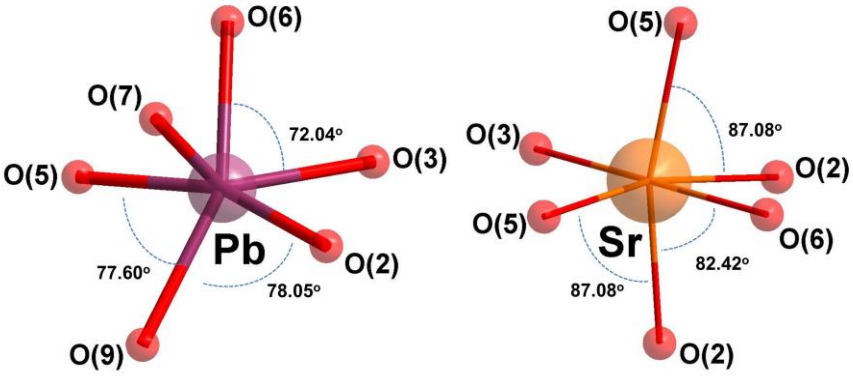

Figure S2 Polarization of PbO_6 octahedra and SrO_6 octahedra

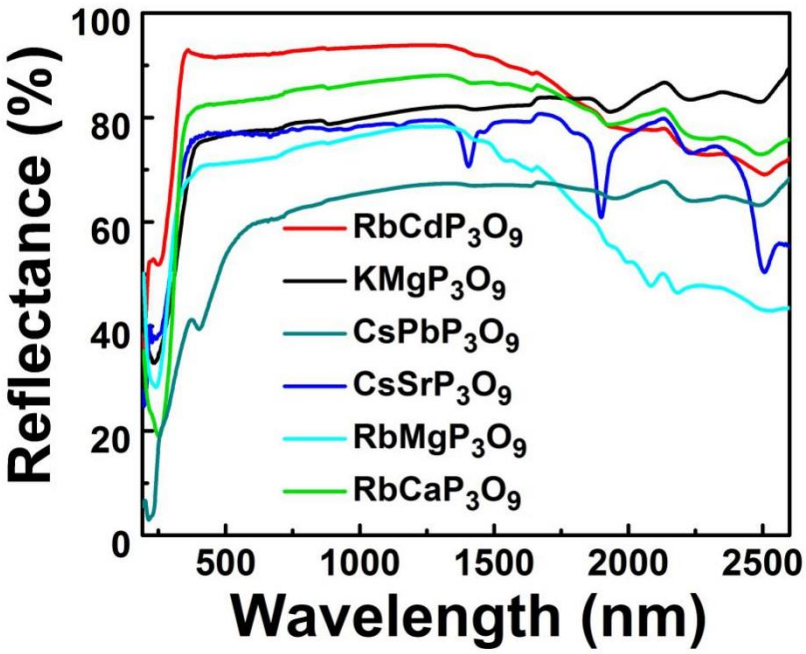

Figure S3. UV−Vis−NIR diffuse reflectance spectra of six compounds

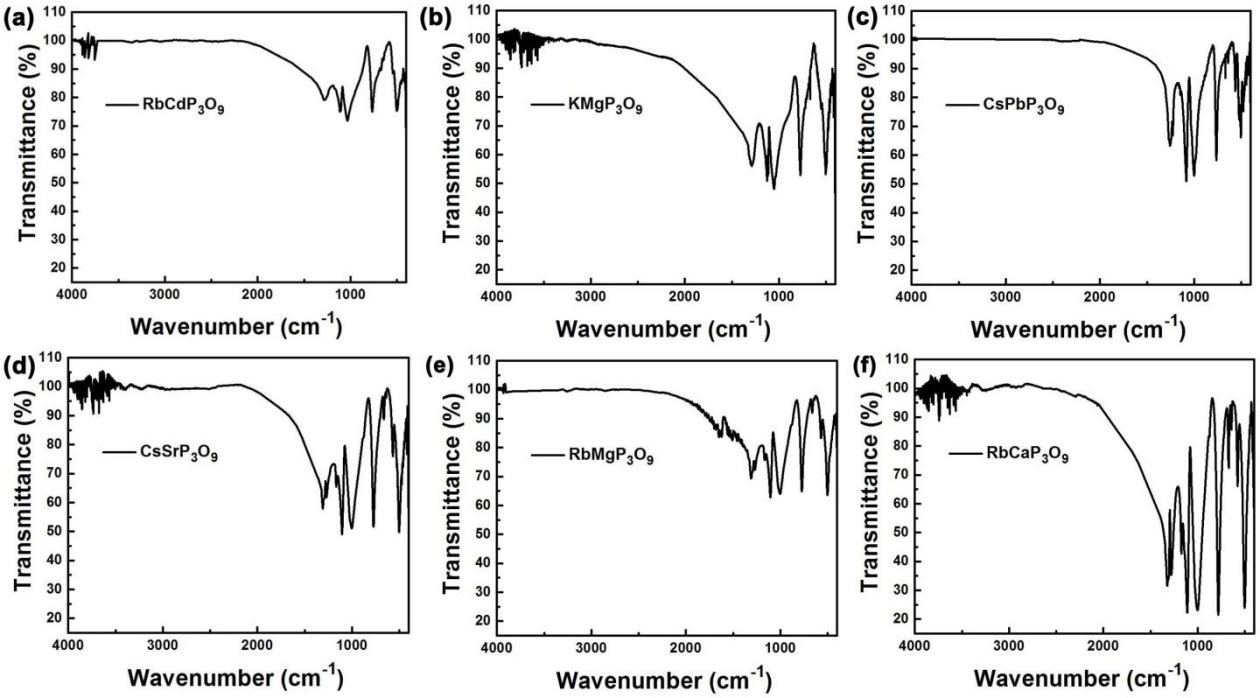

Figure S4. IR spectra of six compounds

Table S4. Assignment of the absorption bands observed in the IR spectra for $RbCdP_3O_9$, $KMgP_3O_9$, $CsSrP_3O_9$, $RbMgP_3O_9$, and $RbCaP_3O_9$.

Assignment	ν_{as} (O-P-O)	ν_s (O-P-O)	ν_{as} (P-O-P) and ν_s (P-O-P)	ν_s (P-O-P)	δ_{as} (O-P-O)	δ_s (O-P-O)
$RbCdP_3O_9$	1275	1107, 1026		758		505
$KMgP_3O_9$	1288	1125, 1048		767, 667		500
$CsPbP_3O_9$	1252	1085	999	758, 663, 629	563	500, 477
$CsSrP_3O_9$	1306, 1266,	1166, 1103, 1003		776, 663	568	501
$RbMgP_3O_9$	1306, 1266	1162, 1103, 1003		767, 658	572	500
$RbCaP_3O_9$	1275, 1169	1112	994	776, 667, 636	572	495

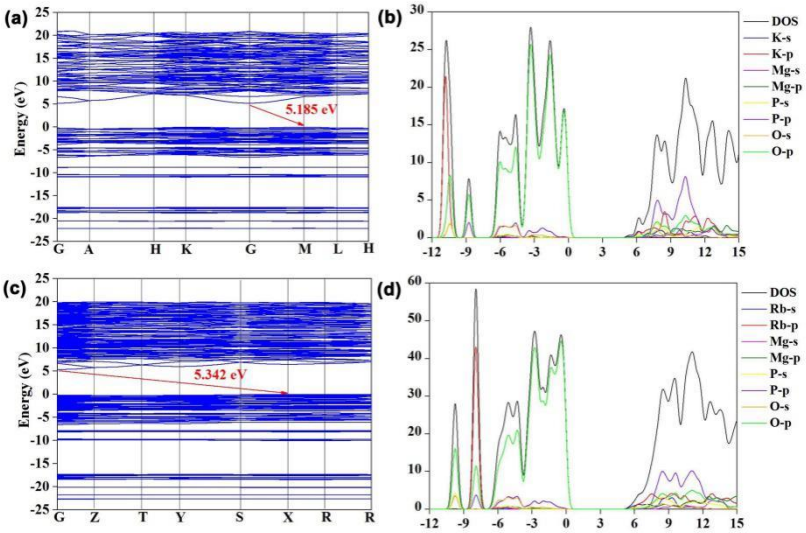

Figure S5. Calculated band structures, the total and partial densities of states of (a) & (b) $KMgP_3O_9$; (c) & (d) $RbMgP_3O_9$

The SHG intensity of $KMgP_3O_9$ is indeed slightly larger than that of $RbCdP_3O_9$ or $CsPbP_3O_9$ in our experimental condition. $KMgP_3O_9$ and $RbCdP_3O_9$ are isostructural and crystallize in space group $P\bar{6}c2$. Compared with $KMgP_3O_9$, the d^{10} transition metal cation Cd in $RbCdP_3O_9$ has almost no contribution to SHG intensity. However, $CsPbP_3O_9$ crystallizes in $Pna2_1$ which is different from that of $KMgP_3O_9$. The stereochemistry activity of the lead atom in the structure of $CsPbP_3O_9$ is weak. In addition, it is hard to avoid a little moisture absorption of $RbCdP_3O_9$ and $CsPbP_3O_9$ compounds, which may influence their SHG intensity.

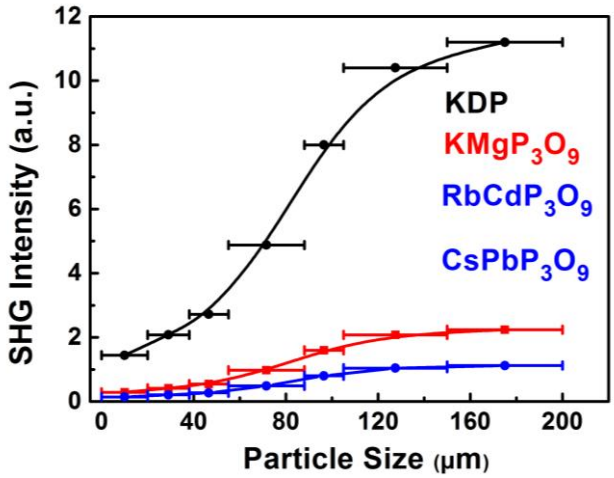

Figure S6. SHG properties of $KMgP_3O_9$, $RbCdP_3O_9$ and $CsPbP_3O_9$ with commercial KDP as a reference.

Table S5 Detailed contributions from the $KO_6/RbO_{11}/Cs_{11}$, $CdO_6/MgO_6/PbO_6$ and PO_4 tetrahedra as well as the total polarization of the whole unit cell.

$RbCdP_3O_9$		Dipole moment			
		x	*y*	*z*	Magnitude (Debye)
RbO_{12}		0.001	-0.001	0	**0.001**
CdO_6		0	0	0	**0**
PO_4		-2.327	-4.566	0	**3.950**
Unit cell Z=2	ΣRbO_{12}	-0.001	-0.001	0	**0.001**
	ΣCdO_6	0	0	0	**0**
	ΣPO_4	-4.653	-9.131	0	**7.900**
	Total polarization	**-4.561**	**4.560**	**0**	**7.899**
$KMgP_3O_9$		Dipole moment			
		x	*y*	*z*	Magnitude (Debye)
KO_6		0	0	0	**0**
MgO_6		-0.005	-0.003	0	**0.004**
PO_4		-2.185	2.185	0	**3.784**
Unit cell Z=2	ΣKO_6	0	0	0	**0**
	ΣMgO_6	-0.009	-0.006	0	**0.008**
	ΣPO_4	-4.370	4.370	0	**7.569**
	Total polarization	-4.379	4.364	0	**7.572**
$CsPbP_3O_9$		Dipole moment			
		x	*y*	*z*	Magnitude (Debye)
CsO_{11}		1.987	-1.121	0.421	**2.320**
PbO_6		-3.265	-3.726	2.758	**5.694**
PO_4		0.974	-3.424	-0.361	**3.578**
Unit cell Z=4	ΣCsO_{11}	0	0	1.683	**1.683**
	ΣPbO_6	0	0	11.032	**11.032**
	ΣPO_4	0	0	-2.470	**2.470**
	Total polarization	0	0	10.246	**10.246**