Supporting Information

Syntheses, structures and characterization of noncentrosymmetric $MZnPO_4$(M= K, NH_4)

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å2 ×103) for $KZnPO_4$. Ueq is defined as one-third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)	BVS
Zn(1)	-6737(2)	-8415(3)	-1936(3)	11.9(7)	2.225
Zn(2)	-6666.67	-3333.33	-688(3)	5.7(9)	2.011
K(1)	-10000	-10000	1091(9)	18.6(17)	0.819
K(2)	-5223(5)	-4804(5)	-3754(6)	10.2(8)	1.170
P(1)	-6666.67	-3333.33	-6717(11)	6.5(16)	5.665
P(2)	-8309(9)	-6727(5)	-793(7)	16.1(12)	4.799
O(1)	-7199(19)	-5278(17)	-1370(18)	15(2)	2.124
O(2)	-8324(18)	-8038(17)	-1600(20)	20(2)	1.991
O(3)	-3333.33	-6666.67	-3470(30)	25(4)	1.914
O(4)	-5142(18)	-3012(19)	-6020(20)	16(3)	1.911
O(5)	-7760(17)	-6792(18)	877(19)	21(3)	2.040
O(6)	-9700(19)	-6868(19)	-800(20)	29(3)	2.441

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å2 ×103) for NH_4ZnPO_4. Ueq is defined as one-third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)	BVS
N(1)	10320(60)	5100(60)	7590(80)	3(10)	5.001
N(2)	10000	10000	7610(40)	-32(7)	5.211
Zn(1)	8350(7)	6742(5)	9509(9)	15(3)	2.075
Zn(2)	6667	3333.01	5766(8)	3(3)	2.158
P(1)	8304(19)	6728(17)	5670(30)	22(5)	4.896
P(2)	6667	3333.01	9760(40)	12(5)	4.971
O(1)	10220(70)	8160(90)	9810(100)	110(40)	1.752
O(2)	7770(70)	6780(70)	7340(60)	36(17)	1.747
O(3)	6930(90)	7100(90)	10670(70)	80(20)	1.728
O(4)	7810(80)	4940(80)	10220(60)	56(17)	1.737
O(5)	7160(50)	5240(40)	4980(50)	19(9)	1.735
O(6)	6667	3333.01	7700(200)	70(40)	1.939

Table S3. Selected bond distances (Å) and angles (degrees) for $KZnPO_4$.

Zn(1)-O(1)^{1}	1.937(16)	P(1)-K(1)^{3}	3.721(8)
Zn(1)-O(1)^{2}	1.937(16)	P(1)-K(2)	3.721(6)
Zn(1)-O(1)	1.937(16)	P(1)-O(4)	1.38(2)
Zn(1)-O(2)^{3}	1.88(3)	P(2)-O(2)^{9}	1.50(3)
Zn(1) -K(1)^{4}	3.778(5)	P(2)-O(5)^{2}	1.566(17)
Zn(1)-K(1)^{5}	3.778(5)	P(2)-O(5)^{1}	1.566(17)
Zn(1)- K(1)^{3}	3.778(5)	P(2)-O(5)	1.566(17)
Zn(1)-K(1)^{1}	3.712(6)	P(2)-K(1)^{1}	3.647(8)
Zn(1)-K(1)^{2}	3.712(6)	P(2)-K(1)^{11}	3.819(6)
Zn(1)-K(1)	3.712(6)	P(2)-K(1)^{12}	3.819(6)
Zn(2)-O(5)^{5}	1.935(18)	P(2)-K(1)^{9}	3.819(6)
Zn(2)- O(3)^{6}	1.958(16)	P(2)-K(1)	3.647(8)
Zn(2)- O(6)	1.910(17)	O(1)-K(1)^{2}	3.647(8)
Zn(2)-K(1)^{7}	3.920(5)	O(1)-K(1)^{5}	3.286(19)
Zn(2)- K(1)^{5}	3.995(6)	O(1)-K(1)	2.699(16)
Zn(2)- K(1)	3.634(6)	O(2)-K(1)^{8}	3.410(4)
Zn(2)- K(1)^{8}	3.573(5)	O(1)-K(1)^{13}	3.410(4)
Zn(2)- K(2)^{9}	3.402(4)	O(1)-K(1)	3.410(4)
Zn(2)- K(2)	3.920(6)	O(5)-K(1)^{2}	3.366(18)
Zn(2)-O(4)^{10}	2.044(17)	O(5)-K(1)	2.670(19)
P(1)-O(1)	1.486(16)	O(5)-K(1)^{12}	3.398(19)
P(1)-O(3)	1.548(18)	O(6)-K(2)^{9}	2.741(17)
P(1)-O(6)	1.533(17)	O(6)-K(2)	2.993(17)
P(1)-K(1)	3.786(9)	K(1)-O(4)^{6}	2.80(2)
P(1)-K(1)^{5}	3.647(9)	K(1)-O(4)^{2}	3.300(19)
O(1)^{1}-Zn(1)-O(1)^{2}	111.2(4)	O(1)^{12}-K(1)-O(5)^{1}	101.9(5)
O(1)^{1}-Zn(1)-O(1)	111.2(4)	O(1)^{12}-K(1)-O(4)^{2}	104.6(4)
O(1)^{2}-Zn(1)-O(1)	111.2(4)	O(1)-K(1)-O(4)^{2}	74.9(5)
O(2)^{5}-Zn(1)-O(1)	107.7(5)	O(1)-K(1)-O(4)^{6}	103.2(5)
O(2)^{5}-Zn(1)-O(1)^{1}	107.7(5)	O(5)-K(5)-O(1)^{2}	115.9(5)
O(2)^{5}-Zn(1)-O(1)^{2}	107.7(5)	O(5)-K(5)-O(1)^{12}	74.1(5)
O(6)-Zn(2)-O(3)^{6}	108.6(7)	O(5)-K(5)-O(2)	128.8(6)
O(6)-Zn(2)-O(4)^{10}	109.6(7)	O(5)^{4}-K(5)-O(2)	43.7(5)
O(5)^{4}-Zn(2)-O(3)^{6}	118.8(8)	O(5)^{1}-K(5)-O(2)	137.7(5)
O(5)^{4}-Zn(2)-O(4)^{10}	102.2(8)	O(5)-K(5)-O(5)^{4}	138.5(5)
O(1)-K(1)-O(1)^{12}	169.8(3)	O(5)^{1}-K(5)-O(5)^{4}	138.5(5)
O(1)- K(1)-O(2)	115.3(6)	O(5)-K(5)-O(5)^{1}	47.8(6)
O(1)^{12}-K(1)-O(2)	54.8(5)	O(5)^{1}-K(5)-O(4)^{2}	109.8(5)
O(1)-K(1)-O(5)^{4}	71.8(5)	O(5)^{1}-K(5)-O(4)^{6}	87.8(6)

O(1)^{12}-K(1)-O(5)^{4}	98.4(4)	O(4)^{6}-K(1)-O(1)^{12}	74.0(5)
O(6)^{16}-K(2)-O(6)^{17}	108.8(4)	O(6)^{5}-K(2)-O(6)^{17}	108.8(4)
O(6)^{8}-K(2)-O(6)^{16}	74.7(6)	O(4)^{6}-K(1)-O(4)^{2}	161.5(4)
O(6)^{17}-K(2)-O(6)	67.5(5)	O(1) -P(1)-O(3)	102.5(10)
O(6)^{16}-K(2)-O(6)^{10}	67.5(5)	O(1) -P(1)-O(6)	112.9(11)
O(6)^{5}-K(2)-O(6)^{10}	175.4(5)	O(6)-P(1)-O(3)	102.3(9)
O(6)^{5}-K(2)-O(6)^{16}	74.7(6)	O(4)-P(1)-O(1)	113.9(11)
O(6)^{8}-K(2)-O(6)^{5}	74.7(6)	O(4)-P(1)-O(3)	112.7(12)
O(6)^{8}-K(2)-O(6)^{17}	175.4(5)	O(4)-P(1)-O(6)	111.5(10)
O(6)^{8}-K(2)-O(6)	108.8(4)	O(5)^{9}-P(2)-O(5)^{2}	111.4(8)
O(6)^{10}-K(2)-O(6)	67.5(5)	O(5)^{9}-P(2)-O(5)	111.3(8)
O(6)^{8}-K(2)-O(6)^{10}	108.8(4)	O(5)^{9}-P(2)-O(5)^{1}	111.4(8)
O(6)^{16}-K(2)-O(6)	175.4(5)	O(5)^{1}-P(2)-O(5) ^{1}	107.5(9)
O(6)^{5}-K(2)-O(6)	108.8(4)	O(5)^{2}-P(2)-O(5)	107.5(9)
O(6)^{16}-K(2)-O(6)^{10}	108.8(4)	O(5)^{2}-P(2)-O(5) ^{1}	107.5(9)

Symmetry transformations used to generate equivalent atoms:

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

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

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

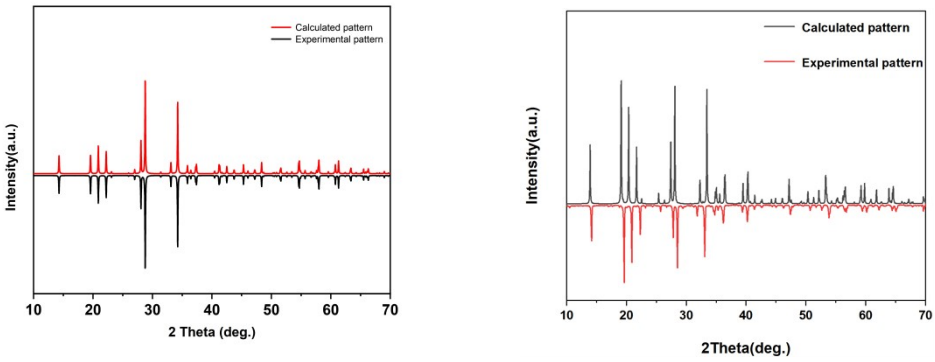
#8 x,-y-1/2,z+1/2 #9 x,y+1,z #10 -x,y+1/2,-z+3/2

#11 x,-y+1/2,z+1/2

Table S4. Selected bond distances (Å) and angles (degrees) for NH_4ZnPO_4.

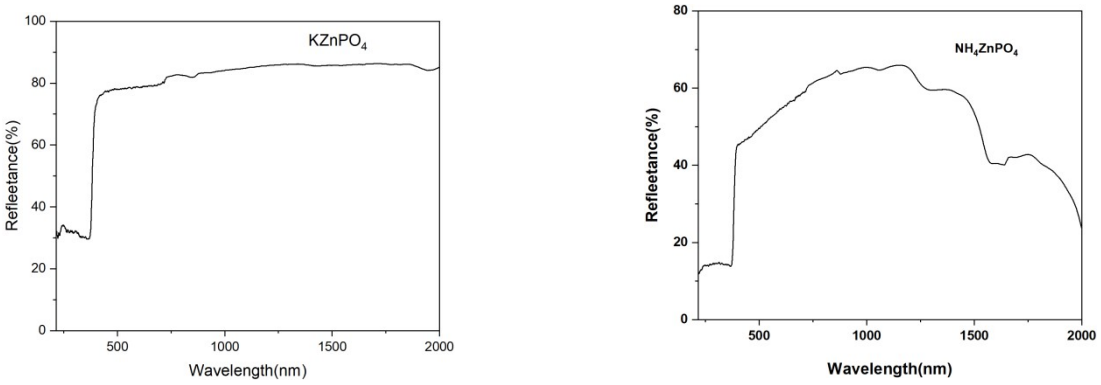
Zn(1)-O(1)	1.9406(9)	P(1)-O(3)	1.5423(9)
Zn(1)-O(2)	1.9493(8)	P(2)-O(6)	1.5081(13)
Zn(1)-O(3)	1.9577(9)	P(2)-O(4)	1.5465(8)
Zn(1)-O(4)	1.9398(8)	N(1)-H(1)	0.83(3)
Zn(2)-O(5)	1.9455(8)	N(1)-H(2)	0.84(3)
Zn(2)-O(6)	1.8953(12)	N(1)-H(3)	0.864(17)
P(1)-O(2)	1.5398(8)	N(1)-H(4)	0.89(2)
P(1)-O(5)	1.5452(8)	N(2)-H(5)	0.94(3)
P(1)-O(3)	1.5423(12)	N(2)-H(6)	0.85(2)
O(1)-Zn(1)-O(2)	106.26(3)	O(1)-P(1)-O(5)	109.29(5)
O(1)-Zn(1)-O(3)	112.19(3)	O(1)-P(1)-O(3)	108.40(4)
O(1)-Zn(1)-O(4)	113.90(3)	O(4)-P(2)-O(6)	111.10(3)
O(2)-Zn(1)-O(3)	105.70(3)	O(4)-P(2)-O(4)	107.79(5)
O(2)-Zn(1)-O(4)	115.82(3)	H(1)-N(1)-H(2)	114(3)
O(3)-Zn(1)-O(4)	102.78(3)	H(1)-N(1)-H(3)	109.3(18)
O(5)-Zn(2)-O(6)	108.92(2)	H(1)-N(1)-H(4)	112(2)
O(5)-Zn(2)-O(5)	110.02(4)	H(2)-N(1)-H(3)	103.0(18)
O(2)-P(1)-O(5)	109.40(4)	H(2)-N(1)-H(4)	109(2)
O(2)-P(1)-O(3)	109.71(4)	H(3)-N(1)-H(4)	109.0(19)
O(1)-P(1)-O(2)	109.75(4)	H(5)-N(2)-H(6)	113.8(13)
O(3)-P(1)-O(5)	110.26(4)		

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z+1/2 #2 -x+2,y+1/2,-z+3/2
#3 -x+2,y-1/2,-z+3/2 #4 -x+1,-y,-z+2
#5 -x+2,-y,-z+2 #6 x,y+1,z #7 x,-y-1/2,z-1/2
#8 x,-y+1/2,z-1/2 #9 x,-y-1/2,z+1/2
#10 -x+2,-y,-z+1 #11 x,y-1,z



(a) (b)

Figure S1. Powder XRD patterns of (a) $KZnPO_4$ and (b) NH_4ZnPO_4.



(a) (b)

Figure S2. UV-vis-NIR diffuse reflectance spectra of (a) $KZnPO_4$ and (b) NH_4ZnPO_4.

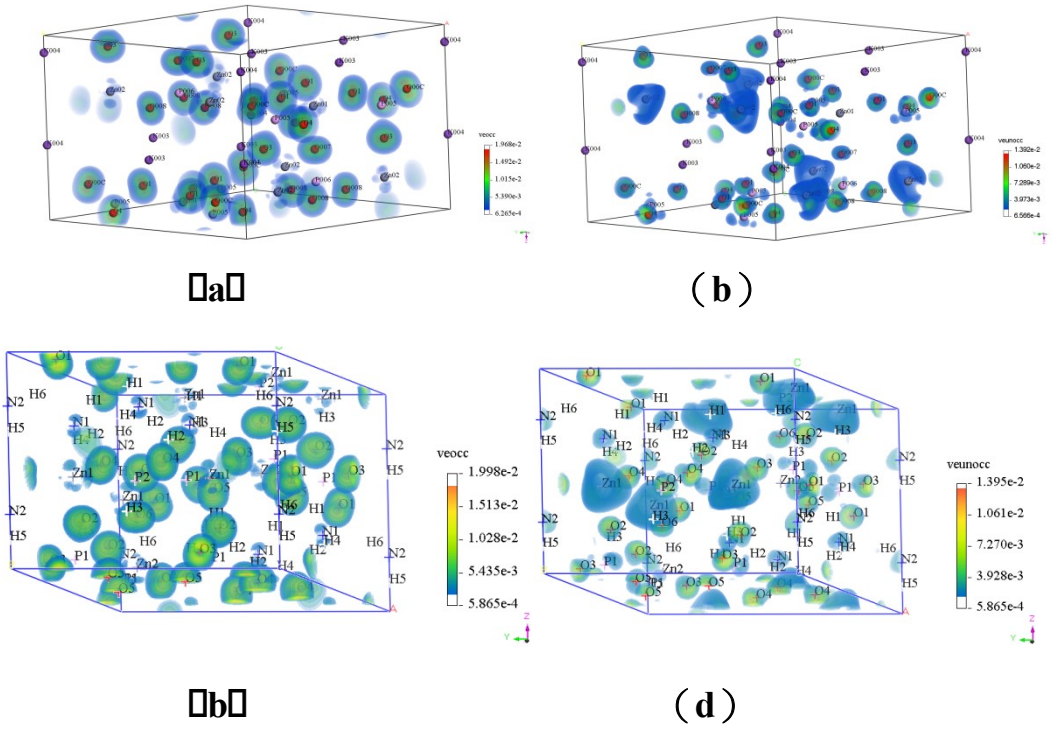


Figure S3. Virtual electron (VE) (a) occupied, and virtual electron (VE) (b)unoccupied orbitals of $KZnPO_4$;Virtual electron (VE) (c) occupied, and virtual electron (VE) (d)unoccupied orbitals of NH_4ZnPO_4.