Syntheses, Structures and Properties of Metal Phosphates $Pb_2Mg(PO_4)_2$, $Pb_4Zn_8(PO_4)_8$ and α-$BaZn_2(PO_4)_2$

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Single Crystal data

Table S1. Atomic coordinates ($\times 10^4$)，equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $Pb_2Mg(PO_4)_2$

Atom	x	y	z	U(eq)[a]	BVS[b, c]
Pb(1)	2610(1)	7327(1)	3155(1)	12(1)	1.958
Pb(2)	-2449(1)	4913(1)	3210(1)	12(1)	1.775
Mg(1)	7779(11)	8631(3)	4761(6)	10(1)	1.977
P(1)	2454(7)	5745(3)	778(5)	7(1)	4.893
P(2)	2589(8)	3362(3)	4087(5)	8(1)	4.836
O(1)	6720(20)	8195(8)	2659(15)	18(3)	1.946
O(2)	-1010(20)	7393(8)	5266(15)	18(3)	1.872
O(3)	4650(20)	6361(8)	1203(14)	16(3)	1.998
O(4)	200(20)	5989(8)	1855(14)	15(3)	1.992
O(5)	-1530(20)	4000(8)	911(15)	18(3)	1.987
O(6)	1100(20)	4187(8)	4294(14)	16(3)	2.022
O(7)	3060(30)	4810(8)	979(15)	19(3)	1.908
O(8)	5130(30)	3476(9)	5023(15)	23(3)	1.850

[a] U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

[b] Bond valences calculated with the program Bond Valence Calculator Version 2.00, C. Hormillosa, S. Healy, T. Stephen, McMaster University, 1993;

[c] Valence sums calculated with the formula: Si = exp[(R0-Ri)/B], where Si = valence of bond “i” and B = 0.37.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $Pb_4Zn_8(PO_4)_8$

Atoms	x	y	z	U(eq)[a]	BVS[b, c]
Pb(1)	2509(1)	6975(1)	1246(1)	11(1)	1.965
Pb(2)	5033(1)	9486(1)	1242(1)	11(1)	1.977
Pb(3)	5347(1)	4813(1)	1260(1)	11(1)	1.938
Pb(4)	2849(1)	2276(1)	1246(1)	12(1)	1.967
Zn(1)	582(1)	7883(1)	-328(1)	9(1)	2.091
Zn(2)	3256(1)	5528(1)	-326(1)	10(1)	2.139
Zn(3)	4234(1)	11968(1)	324(1)	9(1)	2.116
Zn(4)	3339(1)	4653(1)	2168(1)	10(1)	2.002
Zn(5)	3729(1)	9819(1)	2163(1)	10(1)	1.954
Zn(6)	1908(1)	4664(1)	328(1)	10(1)	2.096
Zn(7)	1140(1)	7393(1)	2173(1)	9(1)	1.988
Zn(8)	5912(1)	7059(1)	2158(1)	10(1)	1.909
P(1)	4178(1)	7151(2)	1900(1)	7(1)	4.937
P(2)	1619(1)	4675(2)	1897(1)	7(1)	4.993
P(3)	1991(1)	9917(2)	1907(1)	7(1)	4.878
P(4)	4450(1)	12480(2)	1897(1)	7(1)	4.954
P(5)	6025(1)	7166(2)	612(1)	7(1)	5.063
P(6)	3447(1)	9568(2)	608(1)	7(1)	5.005
P(7)	936(1)	7107(2)	611(1)	7(1)	5.014
P(8)	3513(1)	4653(2)	611(1)	7(1)	4.982
O(1)	1619(2)	10550(4)	2293(1)	12(1)	2.020
O(2)	5519(2)	7383(5)	220(1)	12(1)	2.115
O(3)	4518(2)	10984(4)	1960(1)	13(1)	1.912
O(4)	1994(2)	8400(5)	1957(1)	14(1)	1.877
O(5)	5261(2)	13069(4)	1871(1)	11(1)	1.994
O(6)	3564(2)	10419(5)	217(1)	13(1)	2.117
O(7)	3524(2)	6155(4)	1818(1)	11(1)	1.983
O(8)	3042(2)	5032(5)	977(1)	17(1)	1.931

O(9)	4928(2)	6369(5)	1956(1)	14(1)	1.886
O(10)	3014(2)	4920(5)	219(1)	14(1)	2.121
O(11)	2686(2)	8832(5)	563(1)	18(1)	1.955
O(12)	3661(2)	3158(4)	646(1)	14(1)	2.106
O(13)	1041(2)	7969(4)	221(1)	13(1)	2.114
O(14)	5542(3)	7523(5)	972(1)	18(1)	1.967
O(15)	982(2)	3638(4)	1823(1)	10(1)	1.990
O(16)	4268(2)	5400(4)	571(1)	14(1)	1.930
O(17)	4013(2)	13097(5)	2265(1)	10(1)	2.034
O(18)	4164(2)	8160(5)	1561(1)	16(1)	1.983
O(19)	6761(2)	7952(5)	572(2)	20(1)	1.972
O(20)	181(2)	6340(5)	564(2)	18(1)	1.933
O(21)	2819(2)	10418(4)	1861(1)	11(1)	1.923
O(22)	1421(2)	5536(4)	2279(1)	13(1)	2.068
O(23)	1605(2)	6130(5)	653(1)	14(1)	2.094
O(24)	4110(2)	8588(5)	652(1)	17(1)	2.087
O(25)	6203(3)	5687(5)	656(1)	17(1)	2.086
O(26)	1627(2)	5614(5)	1541(1)	16(1)	2.010
O(27)	2370(2)	3941(5)	1976(1)	14(1)	1.924
O(28)	3507(3)	10490(5)	974(1)	18(1)	1.943
O(29)	996(3)	8002(5)	977(1)	17(1)	1.964
O(30)	4014(2)	12890(5)	1515(1)	15(1)	1.997
O(31)	1520(2)	10420(5)	1544(1)	20(1)	1.917
O(32)	4031(2)	7966(5)	2298(1)	11(1)	2.015

[a] U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

[b] Bond valences calculated with the program Bond Valence Calculator Version 2.00, C. Hormillosa, S. Healy, T. Stephen, McMaster University, 1993;

[c] Valence sums calculated with the formula: Si = exp[(R0-Ri)/B], where Si = valence of bond “i” and B = 0.37.

Table S3. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for α-$BaZn_2(PO_4)_2$.

Atom	x	y	z	U(eq)[a]	BVS[b, c]
Ba(1)	10000	0	10000	32(1)	1.804
Zn(1)	6667	3333	13128(4)	24(1)	2.122
P(1)	6667	3333	7306(8)	19(2)	5.086
O(1)	6667	3333	5470(20)	34(5)	2.069
O(2)	5110(30)	220(60)	8090(40)	40(13)	1.987
O(3)	6300(90)	450(80)	7950(50)	19(11)	2.043

[a] U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

[b] Bond valences calculated with the program Bond Valence Calculator Version 2.00, C. Hormillosa, S. Healy, T. Stephen, McMaster University, 1993;

[c] Valence sums calculated with the formula: Si = exp[(R0-Ri)/B], where Si = valence of bond “i” and B = 0.37.

Table S4. Selected bond distances (Å) and angles (deg) for $Pb_2Mg(PO_4)_2$.

Pb(1)-O(8)#1	2.324(13)	O(6)-Pb(2)-O(5)	82.7(4)
Pb(1)-O(3)	2.489(12)	O(6)-Pb(2)-O(4)	93.1(4)
Pb(1)-O(1)	2.601(13)	O(5)-Pb(2)-O(4)	84.9(4)
Pb(1)-O(2)	2.628(14)	O(6)-Pb(2)-O(6)#3	74.3(4)
Pb(1)-O(4)	2.684(12)	O(5)-Pb(2)-O(6)#3	152.7(4)
Pb(1)-O(5)#6	2.787(31)	O(4)-Pb(2)-O(6)#3	81.9(4)
Pb(2)-O(6)	2.381(12)	O(1)-Mg(1)-O(7)#4	88.3(6)
Pb(2)-O(5)	2.466(13)	O(1)-Mg(1)-O(3)#5	108.0(6)
Pb(2)-O(4)	2.473(12)	O(7)#4-Mg(1)-O(3)#5	90.1(6)
Pb(2)-O(6)#3	2.640(12)	O(1)-Mg(1)-O(2)#6	87.4(5)
Mg(1)-O(1)	1.990(14)	O(7)#4-Mg(1)-O(2)#6	172.0(6)
Mg(1)-O(7)#4	1.995(14)	O(3)#5-Mg(1)-O(2)#6	97.6(5)
Mg(1)-O(3)#5	2.061(14)	O(1)-Mg(1)-O(5)#4	96.6(6)
Mg(1)-O(2)#6	2.080(14)	O(7)#4-Mg(1)-O(5)#4	82.8(6)
Mg(1)-O(5)#4	2.146(15)	O(3)#5-Mg(1)-O(5)#4	154.3(6)
Mg(1)-O(4)#7	2.272(13)	O(2)#6-Mg(1)-O(5)#4	91.0(6)
P(1)-O(7)	1.503(13)	O(1)-Mg(1)-O(4)#7	161.8(6)
P(1)-O(4)	1.552(13)	O(7)#4-Mg(1)-O(4)#7	97.6(5)
P(1)-O(3)	1.553(13)	O(3)#5-Mg(1)-O(4)#7	89.3(5)
P(1)-O(5)#8	1.567(13)	O(2)#6-Mg(1)-O(4)#7	84.6(5)
P(2)-O(6)	1.521(13)	O(5)#4-Mg(1)-O(4)#7	67.3(5)
P(2)-O(2)#3	1.546(13)	O(7)-P(1)-O(4)	109.6(7)
P(2)-O(1)#11	1.549(14)	O(7)-P(1)-O(3)	114.4(7)
P(2)-O(8)	1.574(14)	O(4)-P(1)-O(3)	106.8(7)
O(8)#1-Pb(1)-O(3)	83.8(4)	O(7)-P(1)-O(5)#8	114.7(7)
O(8)#1-Pb(1)-O(1)	87.5(4)	O(4)-P(1)-O(5)#8	103.6(7)
O(3)-Pb(1)-O(1)	80.9(4)	O(3)-P(1)-O(5)#8	106.9(7)
O(8)#1-Pb(1)-O(2)	86.8(4)	O(6)-P(2)-O(2)#3	108.8(7)
O(3)-Pb(1)-O(2)	142.7(4)	O(6)-P(2)-O(1)#11	112.0(7)
O(1)-Pb(1)-O(2)	134.6(4)	O(2)#3-P(2)-O(1)#11	109.9(7)

O(8)#1-Pb(1)-O(4)	95.7(4)	O(6)-P(2)-O(8)	106.9(7)
O(3)-Pb(1)-O(4)	57.5(4)	O(2)#3-P(2)-O(8)	111.8(7)
O(1)-Pb(1)-O(4)	137.5(4)	O(1)#11-P(2)-O(8)	107.5(7)
O(2)-Pb(1)-O(4)	87.9(4)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

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

Table S5. Selected bond distances (Å) and angles (deg) for $Pb_4Zn_8(PO_4)_8$.

Pb(1)-O(26)	2.290(4)	O(18)-Pb(2)-O(15)#1	83.54(14)
Pb(1)-O(8)	2.348(5)	O(14)-Pb(2)-O(15)#1	76.69(15)
Pb(1)-O(23)	2.631(4)	O(18)-Pb(2)-O(24)	75.14(15)
Pb(1)-O(7)	2.692(4)	O(14)-Pb(2)-O(24)	70.24(15)
Pb(2)-O(18)	2.287(4)	O(15)#1-Pb(2)-O(24)	141.30(14)
Pb(2)-O(14)	2.352(4)	O(31)#2-Pb(3)-O(29)#2	86.54(17)
Pb(2)-O(15)#1	2.649(4)	O(31)#2-Pb(3)-O(25)	73.40(16)
Pb(2)-O(24)	2.662(5)	O(29)#2-Pb(3)-O(25)	71.20(15)
Pb(3)-O(31)#2	2.313(5)	O(31)#2-Pb(3)-O(5)#3	85.99(15)
Pb(3)-O(29)#2	2.350(4)	O(29)#2-Pb(3)-O(5)#3	79.94(15)
Pb(3)-O(25)	2.664(4)	O(25)-Pb(3)-O(5)#3	145.14(13)
Pb(3)-O(5)#3	2.683(4)	O(30)#3-Pb(4)-O(28)#3	85.41(17)
Pb(4)-O(30)#3	2.284(4)	O(30)#3-Pb(4)-O(12)	73.39(15)
Pb(4)-O(28)#3	2.324(4)	O(28)#3-Pb(4)-O(12)	72.06(15)
Pb(4)-O(12)	2.610(4)	O(24)#4-Zn(1)-O(16)#4	114.9(2)
Zn(1)-O(24)#4	1.911(5)	O(24)#4-Zn(1)-O(13)	115.8(2)
Zn(1)-O(16)#4	1.928(4)	O(16)#4-Zn(1)-O(13)	106.77(19)
Zn(1)-O(13)	1.969(4)	O(24)#4-Zn(1)-O(2)#4	106.28(19)
Zn(1)-O(2)#4	1.974(4)	O(16)#4-Zn(1)-O(2)#4	109.69(18)
Zn(2)-O(25)#5	1.900(4)	O(13)-Zn(1)-O(2)#4	102.63(17)
Zn(2)-O(11)#4	1.918(4)	O(25)#5-Zn(2)-O(11)#4	114.3(2)
Zn(2)-O(10)	1.956(4)	O(25)#5-Zn(2)-O(10)	116.4(2)
Zn(2)-O(13)#4	1.973(4)	O(11)#4-Zn(2)-O(10)	106.52(18)
Zn(3)-O(12)#6	1.899(4)	O(25)#5-Zn(2)-O(13)#4	106.46(19)
Zn(3)-O(20)#1	1.922(4)	O(11)#4-Zn(2)-O(13)#4	109.64(19)
Zn(3)-O(2)#7	1.968(4)	O(10)-Zn(2)-O(13)#4	102.86(18)
Zn(3)-O(6)	1.976(4)	O(12)#6-Zn(3)-O(20)#1	115.6(2)
Zn(4)-O(27)	1.929(4)	O(12)#6-Zn(3)-O(2)#7	115.32(19)
Zn(4)-O(7)	1.937(4)	O(20)#1-Zn(3)-O(2)#7	106.61(18)
Zn(4)-O(17)#3	1.981(4)	O(12)#6-Zn(3)-O(6)	106.51(18)

Zn(4)-O(1)#8	1.998(4)	O(20)#1-Zn(3)-O(6)	108.23(19)
Zn(5)-O(3)	1.937(4)	O(2)#7-Zn(3)-O(6)	103.74(18)
Zn(5)-O(21)	1.953(4)	O(27)-Zn(4)-O(7)	104.34(19)
Zn(5)-O(32)	1.988(5)	O(27)-Zn(4)-O(17)#3	105.73(19)
Zn(5)-O(22)#9	2.002(5)	O(7)-Zn(4)-O(17)#3	127.62(17)
Zn(6)-O(23)	1.906(4)	O(27)-Zn(4)-O(1)#8	118.62(18)
Zn(6)-O(19)#10	1.923(5)	O(7)-Zn(4)-O(1)#8	100.12(18)
Zn(6)-O(6)#4	1.968(4)	O(17)#3-Zn(4)-O(1)#8	101.66(19)
Zn(6)-O(10)	1.982(4)	O(3)-Zn(5)-O(21)	102.02(18)
Zn(7)-O(5)#10	1.935(4)	O(3)-Zn(5)-O(32)	117.43(17)
Zn(7)-O(4)	1.947(4)	O(21)-Zn(5)-O(32)	127.86(19)
Zn(7)-O(22)	1.964(5)	O(3)-Zn(5)-O(22)#9	101.92(18)
Zn(7)-O(17)#8	2.010(4)	O(21)-Zn(5)-O(22)#9	103.95(18)
Zn(8)-O(15)#1	1.943(4)	O(32)-Zn(5)-O(22)#9	99.89(18)
Zn(8)-O(9)	1.953(4)	O(23)-Zn(6)-O(19)#10	114.8(2)
Zn(8)-O(1)#2	2.001(4)	O(23)-Zn(6)-O(6)#4	115.67(19)
Zn(8)-O(32)#11	2.018(4)	O(19)#10-Zn(6)-O(6)#4	106.8(2)
P(1)-O(18)	1.515(5)	O(23)-Zn(6)-O(10)	106.33(19)
P(1)-O(9)	1.534(4)	O(19)#10-Zn(6)-O(10)	109.3(2)
P(1)-O(7)	1.538(4)	O(6)#4-Zn(6)-O(10)	103.23(17)
P(1)-O(32)	1.574(4)	O(5)#10-Zn(7)-O(4)	103.27(18)
P(2)-O(26)	1.511(5)	O(5)#10-Zn(7)-O(22)	128.21(19)
P(2)-O(27)	1.519(4)	O(4)-Zn(7)-O(22)	111.91(18)
P(2)-O(15)	1.540(4)	O(5)#10-Zn(7)-O(17)#8	103.52(18)
P(2)-O(22)	1.573(5)	O(4)-Zn(7)-O(17)#8	105.70(18)
P(3)-O(31)	1.527(5)	O(22)-Zn(7)-O(17)#8	102.09(19)
P(3)-O(21)	1.536(4)	O(15)#1-Zn(8)-O(9)	99.27(18)
P(3)-O(4)	1.537(5)	O(15)#1-Zn(8)-O(1)#2	134.80(17)
P(3)-O(1)	1.575(4)	O(9)-Zn(8)-O(1)#2	109.67(19)
P(4)-O(30)	1.518(5)	O(15)#1-Zn(8)-O(32)#11	97.70(18)
P(4)-O(3)	1.526(5)	O(9)-Zn(8)-O(32)#11	119.50(17)
P(4)-O(5)	1.535(4)	O(1)#2-Zn(8)-O(32)#11	97.27(19)

P(4)-O(17)	1.573(4)	O(18)-P(1)-O(9)	115.8(2)
P(5)-O(14)	1.512(4)	O(18)-P(1)-O(7)	107.8(3)
P(5)-O(19)	1.514(4)	O(9)-P(1)-O(7)	108.2(3)
P(5)-O(25)	1.529(5)	O(18)-P(1)-O(32)	105.5(3)
P(5)-O(2)	1.568(4)	O(9)-P(1)-O(32)	108.6(3)
P(6)-O(11)	1.522(4)	O(7)-P(1)-O(32)	110.9(2)
P(6)-O(24)	1.523(5)	O(26)-P(2)-O(27)	114.6(3)
P(6)-O(28)	1.526(5)	O(26)-P(2)-O(15)	108.5(3)
P(6)-O(6)	1.566(4)	O(27)-P(2)-O(15)	108.1(3)
P(7)-O(29)	1.511(5)	O(26)-P(2)-O(22)	106.5(3)
P(7)-O(20)	1.528(4)	O(27)-P(2)-O(22)	109.4(3)
P(7)-O(23)	1.529(4)	O(15)-P(2)-O(22)	109.5(2)
P(7)-O(13)	1.569(5)	O(31)-P(3)-O(21)	107.6(3)
P(8)-O(8)	1.522(4)	O(31)-P(3)-O(4)	114.5(3)
P(8)-O(16)	1.524(4)	O(21)-P(3)-O(4)	109.7(2)
P(8)-O(12)	1.533(5)	O(31)-P(3)-O(1)	106.1(3)
P(8)-O(10)	1.568(4)	O(21)-P(3)-O(1)	110.4(3)
O(1)-Zn(4)#9	1.998(4)	O(4)-P(3)-O(1)	108.4(2)
O(1)-Zn(8)#12	2.001(4)	O(30)-P(4)-O(3)	114.7(3)
O(2)-Zn(3)#7	1.968(4)	O(30)-P(4)-O(5)	107.0(3)
O(2)-Zn(1)#4	1.974(4)	O(3)-P(4)-O(5)	108.7(2)
O(5)-Zn(7)#1	1.935(4)	O(30)-P(4)-O(17)	107.1(3)
O(5)-Pb(3)#6	2.683(4)	O(3)-P(4)-O(17)	108.9(2)
O(6)-Zn(6)#4	1.968(4)	O(5)-P(4)-O(17)	110.4(2)
O(11)-Zn(2)#4	1.917(4)	O(14)-P(5)-O(19)	115.3(3)
O(12)-Zn(3)#3	1.899(4)	O(14)-P(5)-O(25)	105.8(3)
O(13)-Zn(2)#4	1.973(4)	O(19)-P(5)-O(25)	110.4(3)
O(15)-Zn(8)#10	1.943(4)	O(14)-P(5)-O(2)	107.7(2)
O(15)-Pb(2)#10	2.649(4)	O(19)-P(5)-O(2)	108.5(3)
O(16)-Zn(1)#4	1.928(4)	O(25)-P(5)-O(2)	108.9(3)
O(17)-Zn(4)#6	1.981(4)	O(11)-P(6)-O(24)	110.5(3)
O(17)-Zn(7)#9	2.010(4)	O(11)-P(6)-O(28)	114.8(3)

O(19)-Zn(6)#1	1.923(5)	O(24)-P(6)-O(28)	106.2(3)
O(20)-Zn(3)#10	1.922(4)	O(11)-P(6)-O(6)	108.3(3)
O(22)-Zn(5)#8	2.002(5)	O(24)-P(6)-O(6)	108.9(3)
O(24)-Zn(1)#4	1.911(5)	O(28)-P(6)-O(6)	108.1(3)
O(25)-Zn(2)#5	1.900(4)	O(29)-P(7)-O(20)	115.4(3)
O(28)-Pb(4)#6	2.324(4)	O(29)-P(7)-O(23)	105.7(3)
O(29)-Pb(3)#12	2.350(4)	O(20)-P(7)-O(23)	109.6(3)
O(30)-Pb(4)#6	2.284(4)	O(29)-P(7)-O(13)	108.6(3)
O(31)-Pb(3)#12	2.313(5)	O(20)-P(7)-O(13)	108.1(2)
O(32)-Zn(8)#11	2.018(4)	O(23)-P(7)-O(13)	109.3(2)
O(26)-Pb(1)-O(8)	86.24(17)	O(8)-P(8)-O(16)	115.0(3)
O(26)-Pb(1)-O(23)	74.12(15)	O(8)-P(8)-O(12)	106.2(3)
O(8)-Pb(1)-O(23)	71.57(14)	O(16)-P(8)-O(12)	110.4(2)
O(26)-Pb(1)-O(7)	87.34(14)	O(8)-P(8)-O(10)	108.3(2)
O(8)-Pb(1)-O(7)	75.56(14)	O(16)-P(8)-O(10)	108.1(2)
O(23)-Pb(1)-O(7)	142.98(14)	O(12)-P(8)-O(10)	108.8(3)
O(18)-Pb(2)-O(14)	86.61(17)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

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

Table S6. Selected bond distances (Å) and angles (deg) for α-$BaZn_2(PO_4)_2$.

Ba(1)-O(3)#1	2.66(6)	O(3)#6-Ba(1)-O(3)#11	180.000(8)
Ba(1)-O(3)#2	2.66(6)	O(3)#7-Ba(1)-O(3)#11	85.6(11)
Ba(1)-O(3)#3	2.66(6)	O(3)-Ba(1)-O(3)#11	102.7(15)
Ba(1)-O(3)#4	2.66(6)	O(3)#8-Ba(1)-O(3)#11	54.5(16)
Ba(1)-O(3)#5	2.66(6)	O(3)#9-Ba(1)-O(3)#11	37.7(14)
Ba(1)-O(3)#6	2.66(6)	O(3)#10-Ba(1)-O(3)#11	85.6(11)
Ba(1)-O(3)#7	2.66(6)	O(1)#12-Zn(1)-O(2)#13	121.0(10)
Ba(1)-O(3)	2.66(6)	O(1)#12-Zn(1)-O(2)#3	121.0(10)
Ba(1)-O(3)#8	2.66(6)	O(2)#13-Zn(1)-O(2)#3	95.8(13)
Ba(1)-O(3)#9	2.66(6)	O(1)#12-Zn(1)-O(2)#14	121.0(10)
Ba(1)-O(3)#10	2.66(6)	O(2)#13-Zn(1)-O(2)#14	95.8(14)
Ba(1)-O(3)#11	2.66(6)	O(2)#3-Zn(1)-O(2)#14	95.8(14)
Zn(1)-O(1)#12	1.884(17)	O(1)#12-Zn(1)-O(3)#6	115.4(11)
Zn(1)-O(2)#13	1.90(3)	O(2)#13-Zn(1)-O(3)#6	17.0(12)
Zn(1)-O(2)#3	1.90(3)	O(2)#3-Zn(1)-O(3)#6	86.4(13)
Zn(1)-O(2)#14	1.90(3)	O(2)#14-Zn(1)-O(3)#6	110.9(12)
Zn(1)-O(3)#6	2.03(3)	O(1)#12-Zn(1)-O(3)#13	115.4(12)
Zn(1)-O(3)#13	2.03(3)	O(2)#13-Zn(1)-O(3)#13	17.0(12)
Zn(1)-O(3)#3	2.03(3)	O(2)#3-Zn(1)-O(3)#13	110.9(11)
Zn(1)-O(3)#15	2.03(3)	O(2)#14-Zn(1)-O(3)#13	86.4(13)
Zn(1)-O(3)#16	2.03(3)	O(3)#6-Zn(1)-O(3)#13	33(3)
Zn(1)-O(3)#14	2.03(3)	O(1)#12-Zn(1)-O(3)#3	115.4(11)
P(1)-O(1)	1.479(17)	O(2)#13-Zn(1)-O(3)#3	86.4(13)
P(1)-O(3)#10	1.53(5)	O(2)#3-Zn(1)-O(3)#3	17.0(12)
P(1)-O(3)#18	1.53(5)	O(2)#14-Zn(1)-O(3)#3	110.9(12)
P(1)-O(3)#19	1.53(5)	O(3)#6-Zn(1)-O(3)#3	74(3)
P(1)-O(3)#20	1.53(5)	O(3)#13-Zn(1)-O(3)#3	103.0(14)
P(1)-O(3)	1.53(5)	O(1)#12-Zn(1)-O(3)#15	115.4(12)
P(1)-O(3)#21	1.53(5)	O(2)#13-Zn(1)-O(3)#15	110.9(12)
P(1)-O(2)#18	1.56(3)	O(2)#3-Zn(1)-O(3)#15	17.0(12)
P(1)-O(2)	1.56(3)	O(2)#14-Zn(1)-O(3)#15	86.4(13)

P(1)-O(2)#20	1.56(3)	O(3)#6-Zn(1)-O(3)#15	103.0(14)
O(1)-Zn(1)#23	1.884(17)	O(3)#13-Zn(1)-O(3)#15	124.4(19)
O(2)-Zn(1)#13	1.90(3)	O(3)#3-Zn(1)-O(3)#15	33(3)
O(2)-Ba(1)#17	3.066(16)	O(1)#12-Zn(1)-O(3)#16	115.4(11)
O(3)-Zn(1)#13	2.03(3)	O(2)#13-Zn(1)-O(3)#16	86.4(13)
O(3)#1-Ba(1)-O(3)#2	54.5(16)	O(2)#3-Zn(1)-O(3)#16	110.9(12)
O(3)#1-Ba(1)-O(3)#3	85.6(11)	O(2)#14-Zn(1)-O(3)#16	17.0(12)
O(3)#2-Ba(1)-O(3)#3	37.7(14)	O(3)#6-Zn(1)-O(3)#16	103.0(14)
O(3)#1-Ba(1)-O(3)#4	85.6(11)	O(3)#13-Zn(1)-O(3)#16	74(3)
O(3)#2-Ba(1)-O(3)#4	102.7(15)	O(3)#3-Zn(1)-O(3)#16	124.4(19)
O(3)#3-Ba(1)-O(3)#4	85.6(11)	O(3)#15-Zn(1)-O(3)#16	103.0(14)
O(3)#1-Ba(1)-O(3)#5	37.7(14)	O(1)#12-Zn(1)-O(3)#14	115.4(11)
O(3)#2-Ba(1)-O(3)#5	85.6(11)	O(2)#13-Zn(1)-O(3)#14	110.9(12)
O(3)#3-Ba(1)-O(3)#5	102.7(15)	O(2)#3-Zn(1)-O(3)#14	86.4(13)
O(3)#4-Ba(1)-O(3)#5	54.5(16)	O(2)#14-Zn(1)-O(3)#14	17.0(12)
O(3)#1-Ba(1)-O(3)#6	102.7(15)	O(3)#6-Zn(1)-O(3)#14	124.4(19)
O(3)#2-Ba(1)-O(3)#6	85.6(11)	O(3)#13-Zn(1)-O(3)#14	103.0(13)
O(3)#3-Ba(1)-O(3)#6	54.5(16)	O(3)#3-Zn(1)-O(3)#14	103.0(14)
O(3)#4-Ba(1)-O(3)#6	37.7(14)	O(3)#15-Zn(1)-O(3)#14	74(3)
O(3)#5-Ba(1)-O(3)#6	85.6(11)	O(3)#16-Zn(1)-O(3)#14	33(3)
O(3)#1-Ba(1)-O(3)#7	125.5(16)	O(1)-P(1)-O(3)#10	109.8(14)
O(3)#2-Ba(1)-O(3)#7	180.000(5)	O(1)-P(1)-O(3)#18	109.8(14)
O(3)#3-Ba(1)-O(3)#7	142.3(14)	O(3)#10-P(1)-O(3)#18	44(3)
O(3)#4-Ba(1)-O(3)#7	77.3(15)	O(1)-P(1)-O(3)#19	109.8(14)
O(3)#5-Ba(1)-O(3)#7	94.4(11)	O(3)#10-P(1)-O(3)#19	109.1(14)
O(3)#6-Ba(1)-O(3)#7	94.4(11)	O(3)#18-P(1)-O(3)#19	68(3)
O(3)#1-Ba(1)-O(3)	180.000(7)	O(1)-P(1)-O(3)#20	109.8(14)
O(3)#2-Ba(1)-O(3)	125.5(16)	O(3)#10-P(1)-O(3)#20	138(3)
O(3)#3-Ba(1)-O(3)	94.4(11)	O(3)#18-P(1)-O(3)#20	109.1(14)
O(3)#4-Ba(1)-O(3)	94.4(11)	O(3)#19-P(1)-O(3)#20	44(3)
O(3)#5-Ba(1)-O(3)	142.3(15)	O(1)-P(1)-O(3)	109.8(14)
O(3)#6-Ba(1)-O(3)	77.3(15)	O(3)#10-P(1)-O(3)	68(3)

O(3)#7-Ba(1)-O(3)	54.5(16)	O(3)#18-P(1)-O(3)	109.1(14)
O(3)#1-Ba(1)-O(3)#8	94.4(11)	O(3)#19-P(1)-O(3)	138(3)
O(3)#2-Ba(1)-O(3)#8	142.3(14)	O(3)#20-P(1)-O(3)	109.1(14)
O(3)#3-Ba(1)-O(3)#8	180.000(7)	O(1)-P(1)-O(3)#21	109.8(14)
O(3)#4-Ba(1)-O(3)#8	94.4(11)	O(3)#10-P(1)-O(3)#21	109.1(14)
O(3)#5-Ba(1)-O(3)#8	77.3(15)	O(3)#18-P(1)-O(3)#21	138(3)
O(3)#6-Ba(1)-O(3)#8	125.5(16)	O(3)#19-P(1)-O(3)#21	109.1(14)
O(3)#7-Ba(1)-O(3)#8	37.7(14)	O(3)#20-P(1)-O(3)#21	68(3)
O(3)-Ba(1)-O(3)#8	85.6(11)	O(3)-P(1)-O(3)#21	44(3)
O(3)#1-Ba(1)-O(3)#9	94.4(11)	O(1)-P(1)-O(2)#18	113.8(11)
O(3)#2-Ba(1)-O(3)#9	77.3(15)	O(3)#10-P(1)-O(2)#18	22.0(15)
O(3)#3-Ba(1)-O(3)#9	94.4(11)	O(3)#18-P(1)-O(2)#18	22.0(15)
O(3)#4-Ba(1)-O(3)#9	180.0(18)	O(3)#19-P(1)-O(2)#18	87.8(15)
O(3)#5-Ba(1)-O(3)#9	125.5(16)	O(3)#20-P(1)-O(2)#18	123.6(14)
O(3)#6-Ba(1)-O(3)#9	142.3(14)	O(3)-P(1)-O(2)#18	87.8(15)
O(3)#7-Ba(1)-O(3)#9	102.7(15)	O(3)#21-P(1)-O(2)#18	123.6(14)
O(3)-Ba(1)-O(3)#9	85.6(11)	O(1)-P(1)-O(2)	113.8(11)
O(3)#8-Ba(1)-O(3)#9	85.6(11)	O(3)#10-P(1)-O(2)	87.8(15)
O(3)#1-Ba(1)-O(3)#10	142.3(15)	O(3)#18-P(1)-O(2)	123.6(14)
O(3)#2-Ba(1)-O(3)#10	94.4(11)	O(3)#19-P(1)-O(2)	123.6(14)
O(3)#3-Ba(1)-O(3)#10	77.3(15)	O(3)#20-P(1)-O(2)	87.8(15)
O(3)#4-Ba(1)-O(3)#10	125.5(16)	O(3)-P(1)-O(2)	22.0(15)
O(3)#5-Ba(1)-O(3)#10	180.000(9)	O(3)#21-P(1)-O(2)	22.0(15)
O(3)#6-Ba(1)-O(3)#10	94.4(11)	O(2)#18-P(1)-O(2)	104.8(13)
O(3)#7-Ba(1)-O(3)#10	85.6(11)	O(1)-P(1)-O(2)#20	113.8(11)
O(3)-Ba(1)-O(3)#10	37.7(14)	O(3)#10-P(1)-O(2)#20	123.6(14)
O(3)#8-Ba(1)-O(3)#10	102.7(15)	O(3)#18-P(1)-O(2)#20	87.8(15)
O(3)#9-Ba(1)-O(3)#10	54.5(16)	O(3)#19-P(1)-O(2)#20	22.0(15)
O(3)#1-Ba(1)-O(3)#11	77.3(15)	O(3)#20-P(1)-O(2)#20	22.0(15)
O(3)#2-Ba(1)-O(3)#11	94.4(11)	O(3)-P(1)-O(2)#20	123.6(14)
O(3)#3-Ba(1)-O(3)#11	125.5(16)	O(3)#21-P(1)-O(2)#20	87.8(14)
O(3)#4-Ba(1)-O(3)#11	142.3(14)	O(2)#18-P(1)-O(2)#20	104.8(13)

O(3)#5-Ba(1)-O(3)#11	94.4(11)	O(2)-P(1)-O(2)#20	104.8(13)

Symmetry transformations used to generate equivalent atoms:

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

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

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

#8 -y+1,x-y-1,z #9 -x+y+2,-x+1,z

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

#13 -x+1,-y,-z+2 #14 x-y,x,-z+2 #15 y+1,x,-z+2

#16 -x+1,-x+y+1,-z+2 #17 x-1,y,z

#18 -y+1,x-y,z #19 x,x-y,z #20 -x+y+1,-x+1,z

#21 -x+y+1,y,z #22 x,y+1,z #23 x,y,z-1

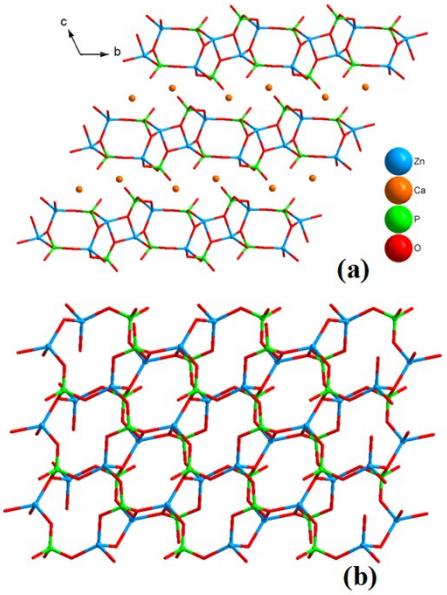

Figure S1. (a) Crystal structure of $CaZn_2(PO_4)_2$. (b) The $[Zn_2P_2O_8]_\infty$ layer.

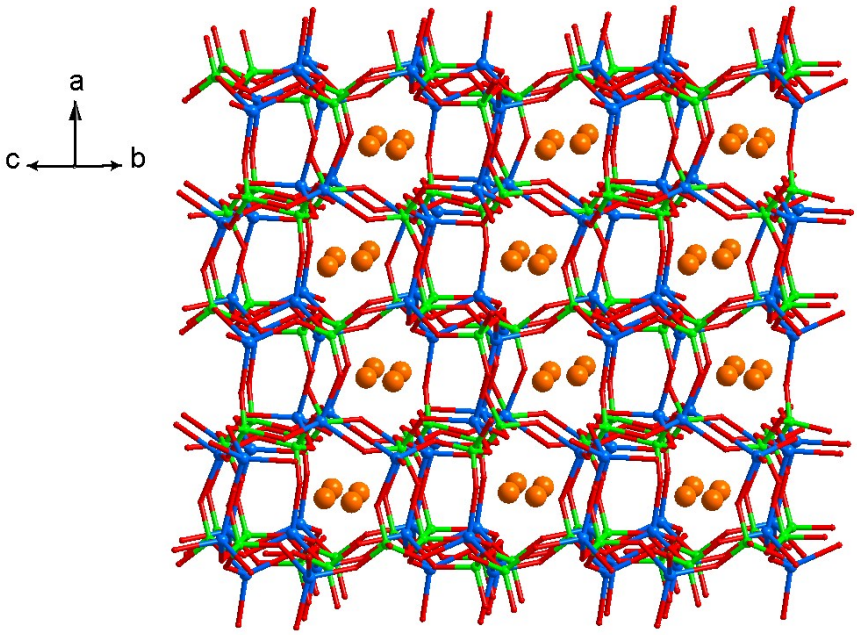

Figure S2. Crystal structure of β-$BaZn_2(PO_4)_2$ and $SrZn_2(PO_4)_2$, Ba or Sr atoms are represented by orange, Zn, P and O atoms re represented by light blue, bright green and red, respectively.

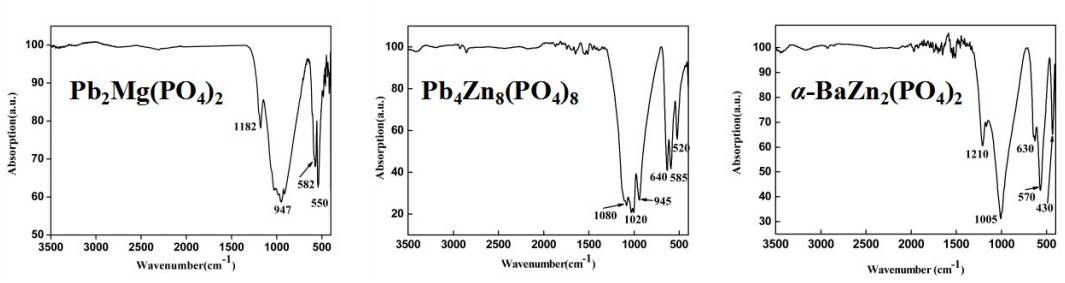

Figure S3. IR Spectroscopy of $Pb_2Mg(PO_4)_2$, $Pb_4Zn_8(PO_4)_8$ and α-$BaZn_2(PO_4)_2$.

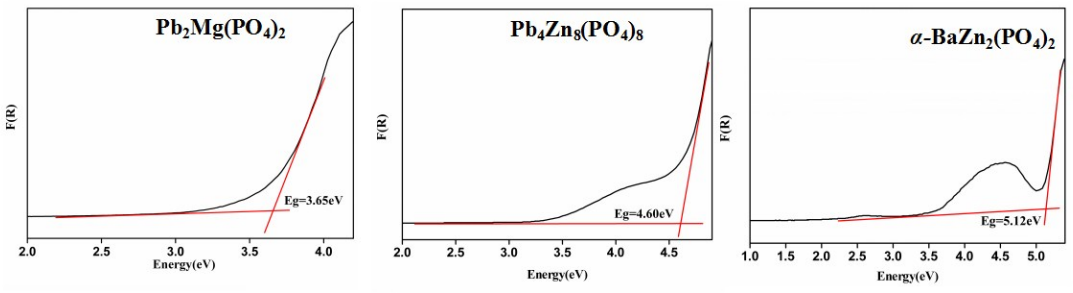

Figure S4. Absorption spectra for $Pb_2Mg(PO_4)_2$, $Pb_4Zn_8(PO_4)_8$ and α-$BaZn_2(PO_4)_2$.

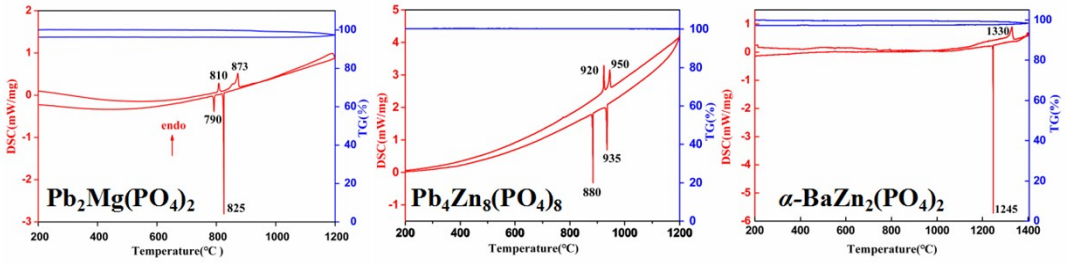

Figure S5. TGA and DSC curves of $Pb_2Mg(PO_4)_2$, $Pb_4Zn_8(PO_4)_8$ and α-$BaZn_2(PO_4)_2$. (TGA curves are represented by blue lines, and DSC curves are represented by red lines.)

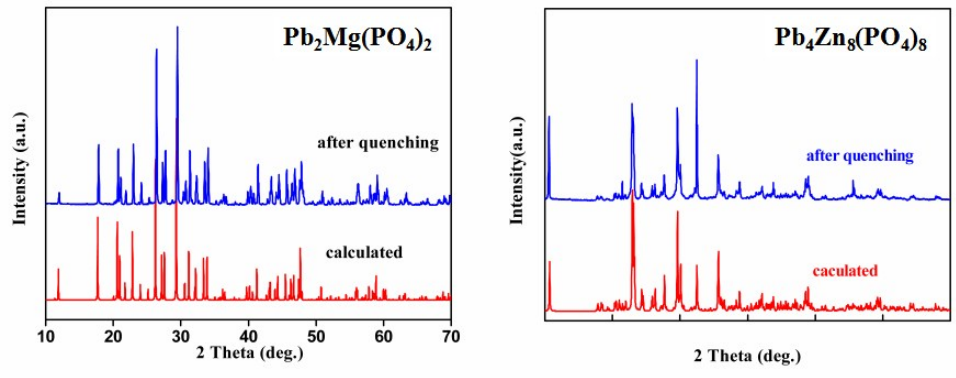

Figure S6. The XRD patterns of $Pb_2Mg(PO_4)_2$ and $Pb_4Zn_8(PO_4)_8$ samples after quenching.