Electronic Supplementary Information

Structure Comparision and Optical Properties of $Na_7Mg_{4.5}(P_2O_7)_4$: A Sodium Magnesium Phosphates with Isolated P_2O_7 Units

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CONTENTS

Mg(1)-O(10)#3	2.260(3)	Na(1)-O(9)#7	2.613(3)
Mg(1)-O(10)	2.260(3)	Na(2)-O(6)	2.352(3)
Mg(1)-O(8)#4	2.377(3)	Na(2)-O(14)#8	2.482(4)
Mg(1)-O(8)#5	2.377(3)	Na(2)-O(7)#4	2.500(3)
Mg(2)-O(9)	2.030(3)	Na(2)-O(7)#11	2.527(3)
Mg(2)-O(8)#5	2.077(3)	Na(2)-O(8)#4	2.747(3)
Mg(2)-O(5)#1	2.099(3)	Na(3)-O(3)#8	2.294(3)
Mg(2)-O(10)	2.112(3)	Na(3)-O(4)	2.358(3)
Mg(2)-O(12)#6	2.125(3)	Na(3)-O(5)	2.578(3)
Mg(2)-O(2)	2.156(3)	Na(3)-O(13)	2.693(3)
Mg(3)-O(13)	1.977(3)	Na(3)-O(2)#9	2.805(4)
Mg(3)-O(3)	1.985(3)	Na(3)-O(10)#9	2.820(3)
Mg(3)-O(6)#4	2.010(3)	Na(3)-O(3)	2.855(4)
Mg(3)-O(4)	2.044(3)	Na(3)-O(13)#8	2.967(5)
Mg(3)-O(2)	2.190(3)	Na(4)-O(5)	2.202(5)
Mg(3)-O(7)	2.274(3)	Na(4)-O(10)#2	2.376(5)
Na(1)-O(12)#9	2.249(3)	Na(4)-O(11)#8	2.392(7)
Na(1)-O(14)#10	2.332(4)	Na(4)-O(8)#8	2.486(6)
Na(1)-O(7)	2.416(3)	Na(4)-O(11)#5	2.519(7)
Na(1)-O(4)	2.504(3)	P(1)-O(9)	1.503(3)
Na(1)-O(14)	2.512(4)	P(1)-O(4)	1.510(3)

Table S1. Selected bond lengths (Å) and angles (deg.) for $Na_7Mg_{4.5}(P_2O_7)_4$.

P(1)-O(5)	1.521(3)	P(4)-O(8)	1.512(3)
P(1)-O(1)	1.600(3)	P(4)-O(11)	1.638(3)
P(2)-O(6)	1.500(3)	P(3)-O(7)	1.529(3)
P(2)-O(3)	1.502(3)	P(3)-O(2)	1.530(3)
P(2)-O(10)	1.508(3)	P(3)-O(1)#7	1.589(3)
P(2)-O(11)#8	1.622(3)	P(4)-O(13)	1.498(3)
P(3)-O(12)	1.496(3)	P(4)-O(14)	1.501(13)
O(8)#5-Mg(2)-O(5)#1	88.57(11)	O(8)#5-Mg(2)-O(12)#6	86.72(11)
O(9)-Mg(2)-O(10)	99.75(12)	O(5)#1-Mg(2)-O(12)#6	87.14(11)
O(8)#5-Mg(2)-O(10)	88.00(11)	O(10)-Mg(2)-O(12)#6	168.97(12)
O(5)#1-Mg(2)-O(10)	83.06(11)	O(9)-Mg(2)-O(2)	90.70(11)

O(9)-Mg(2)-O(12)#6	89.96(12)	O(8)#5-Mg(2)-O(2)	176.31(11)
O(9)-Mg(2)-O(8)#5	90.39(11)	O(5)#1-Mg(2)-O(2)	90.51(11)
O(9)-Mg(2)-O(5)#1	176.97(12)	O(10)-Mg(2)-O(2)	88.34(10)
O(10)#3-Mg(1)-O(10)	180.00(14)	O(12)#6-Mg(2)-O(2)	96.81(10)
O(10)#3-Mg(1)-O(8)#4	77.71(9)	O(13)-Mg(3)-O(3)	92.02(13)
O(10)-Mg(1)-O(8)#4	102.29(9)	O(13)-Mg(3)-O(6)#4	92.54(12)
O(10)#3-Mg(1)-O(8)#5	102.29(9)	O(3)-Mg(3)-O(6)#4	96.25(12)
O(10)-Mg(1)-O(8)#5	77.71(9)	O(13)-Mg(3)-O(4)	85.44(12)
O(8)#4-Mg(1)-O(8)#5	180.00(13)	O(3)-Mg(3)-O(4)	91.14(12)
O(3)-Mg(3)-O(2)	102.38(11)	O(6)#4-Mg(3)-O(4)	172.40(12)
O(6)#4-Mg(3)-O(2)	91.01(11)	O(13)-Mg(3)-O(2)	164.71(13)
O(4)-Mg(3)-O(2)	89.10(10)	O(6)-Na(2)-O(7)#4	74.43(10)
O(13)-Mg(3)-O(7)	98.09(12)	O(14)#8-Na(2)-O(7)#4	99.18(12)
O(3)-Mg(3)-O(7)	169.45(11)	O(6)-Na(2)-O(7)#11	160.73(13)
O(6)#4-Mg(3)-O(7)	86.32(10)	O(14)#8-Na(2)-O(7)#11	84.90(11)
O(4)-Mg(3)-O(7)	86.71(11)	O(7)#4-Na(2)-O(7)#11	94.38(10)
O(2)-Mg(3)-O(7)	67.29(10)	O(6)-Na(2)-O(8)#4	85.01(10)
O(12)#9-Na(1)-O(14)#10	96.77(11)	O(14)#8-Na(2)-O(8)#4	150.48(12)
O(12)#9-Na(1)-O(7)	159.28(11)	O(7)#4-Na(2)-O(8)#4	102.36(10)
O(14)#10-Na(1)-O(7)	90.78(11)	O(7)#11-Na(2)-O(8)#4	113.08(10)
O(12)#9-Na(1)-O(4)	96.02(10)	O(3)#8-Na(3)-O(4)	136.96(13)
O(14)#10-Na(1)-O(4)	164.36(12)	O(3)#8-Na(3)-O(5)	161.74(13)
O(7)-Na(1)-O(4)	74.20(9)	O(3)#8-Na(3)-O(13)	71.97(10)
O(12)#9-Na(1)-O(14)	99.62(11)	O(4)-Na(3)-O(13)	64.99(10)
O(14)#10-Na(1)-O(14)	81.05(12)	O(5)-Na(3)-O(13)	126.04(11)
O(7)-Na(1)-O(14)	100.60(11)	O(3)#8-Na(3)-O(2)#9	111.80(13)
O(4)-Na(1)-O(14)	105.62(11)	O(4)-Na(3)-O(2)#9	82.88(11)
O(12)#9-Na(1)-O(9)#7	73.95(10)	O(5)-Na(3)-O(2)#9	68.17(9)
O(14)#10-Na(1)-O(9)#7	75.37(11)	O(13)-Na(3)-O(2)#9	107.93(13)
O(7)-Na(1)-O(9)#7	89.47(10)	O(3)#8-Na(3)-O(10)#9	100.88(11)
O(4)-Na(1)-O(9)#7	99.66(10)	O(4)-Na(3)-O(10)#9	121.40(10)
O(14)-Na(1)-O(9)#7	154.47(12)	O(5)-Na(3)-O(10)#9	62.10(8)
O(6)-Na(2)-O(14)#8	81.58(12)	O(13)-Na(3)-O(10)#9	166.89(13)
O(2)#9-Na(3)-O(10)#9	63.85(9)	O(11)#8-Na(4)-O(11)#5	97.4(3)
O(3)#8-Na(3)-O(3)	93.31(11)	O(8)#8-Na(4)-O(11)#5	118.9(2)

O(4)-Na(3)-O(3)	66.21(10)	O(9)-P(1)-O(4	114.72(16)
O(5)-Na(3)-O(3)	93.67(10)	O(9)-P(1)-O(5)	112.14(16)
O(13)-Na(3)-O(3)	61.73(10)	O(4)-P(1)-O(5)	112.20(15)
O(2)#9-Na(3)-O(3)	149.01(10)	O(9)-P(1)-O(1)	107.12(15)
O(10)#9-Na(3)-O(3)	130.69(13)	O(4)-P(1)-O(1)	103.60(14)
O(3)#8-Na(3)-O(13)#8	64.12(10)	O(5)-P(1)-O(1)	106.17(14)
O(4)-Na(3)-O(13)#8	124.09(13)	O(6)-P(2)-O(3)	112.07(15)
O(5)-Na(3)-O(13)#8	105.18(12)	O(6)-P(2)-O(10)	114.02(16)
O(13)-Na(3)-O(13)#8	102.28(11)	O(3)-P(2)-O(10)	112.67(15)
O(2)#9-Na(3)-O(13)#8	146.38(11)	O(6)-P(2)-O(11)#8	104.60(15)
O(10)#9-Na(3)-O(13)#8	83.64(10)	O(3)-P(2)-O(11)#8	108.06(15)
O(3)-Na(3)-O(13)#	60.80(9)	O(10)-P(2)-O(11)#8	104.62(14)
O(5)-Na(4)-O(10)#2	133.3(3)	O(12)-P(3)-O(7)	113.40(15)
O(5)-Na(4)-O(11)#8	117.5(2)	O(12)-P(3)-O(2)	116.33(15)
O(10)#2-Na(4)-O(11)#8	109.2(2)	O(7)-P(3)-O(2)	107.94(14)
O(5)-Na(4)-O(8)#8	129.9(3)	O(12)-P(3)-O(1)#7	107.27(14)
O(10)#2-Na(4)-O(8)#8	3.49(18)	O(7)-P(3)-O(1)#7	106.96(15)
O(11)#8-Na(4)-O(8)#8	60.94(14)	O(2)-P(3)-O(1)#7	104.16(14)
O(5)-Na(4)-O(11)#5	11.1(2)	O(13)-P(4)-O(14)	113.0(2)
O(10)#2-Na(4)-O(11)#5	60.74(14)	O(14)-P(4)-O(8)	114.83(17)
O(14)-P(4)-O(8)	114.83(17)	O(14)-P(4)-O(11)	107.53(17)
O(13)-P(4)-O(11)	104.52(15)	O(8)-P(4)-O(11)	103.53(14)

Note: Symmetry transformations used to generate equivalent atoms:

#1 -x, y-1/2, -z; #2 -x, -y+1, -z; #3 x-1, y, z; #4 x-1/2, y, -z-1/2; #5 -x+1/2, y-1/2 ,z-1/2; #6 -x+1/2, -y+1, z-1/2; #7 -x+1, -y+1, -z; #8 -x+1, y-1/2, -z; #9 -x+1/2, -y+1, z+1/2; #10 x+1/2, y, -z+1/2; #11 x+1, y, z; #12 x, -y+3/2, z; #13 x-1/2, y, -z+1/2; #14 x, -y+1/2, z; #15 x-1, -y+1/2, z; #16 x+1/2, y, -z-1/2

Table S2. Existing barium phosphates, space group, cation/ phosphorus ratio and P-O groups.

	compounds	space group	cation/ phosphorus ratio	P-O groups
1	$KBa_2(PO_3)_5$ [1]	*Pc*	0.6	$[PO_3]_n$ chain
2	$NaBa(PO_3)_3$ [2]	$P2_12_12_1$	0.67	P_3O_9 ring
3	$Rb_2Ba_3(P2O_7)_2$ [3]	$P2_12_12_1$	1.25	P_2O_7
4	$Cs_2BaP_2O_7$ [4]	$P2_1/n$	1.5	P_2O_7
5	$LiCsBaP_2O_7$ [4]	$P2_1/c$	1.5	P_2O_7
6	$KBaPO_4$ [5]	*Pnma*	2	PO_4

Figure S1. The P_2O_7 unions in $Na_7Mg_{4.5}(P_2O_7)_4$

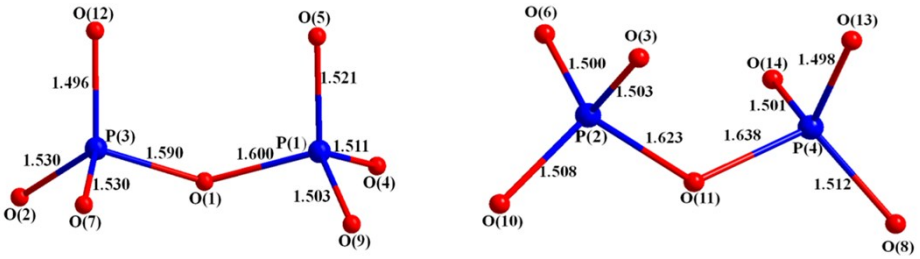


Figure S2. Coordination environment of the Na atoms in $Na_7Mg_{4.5}(P_2O_7)_4$

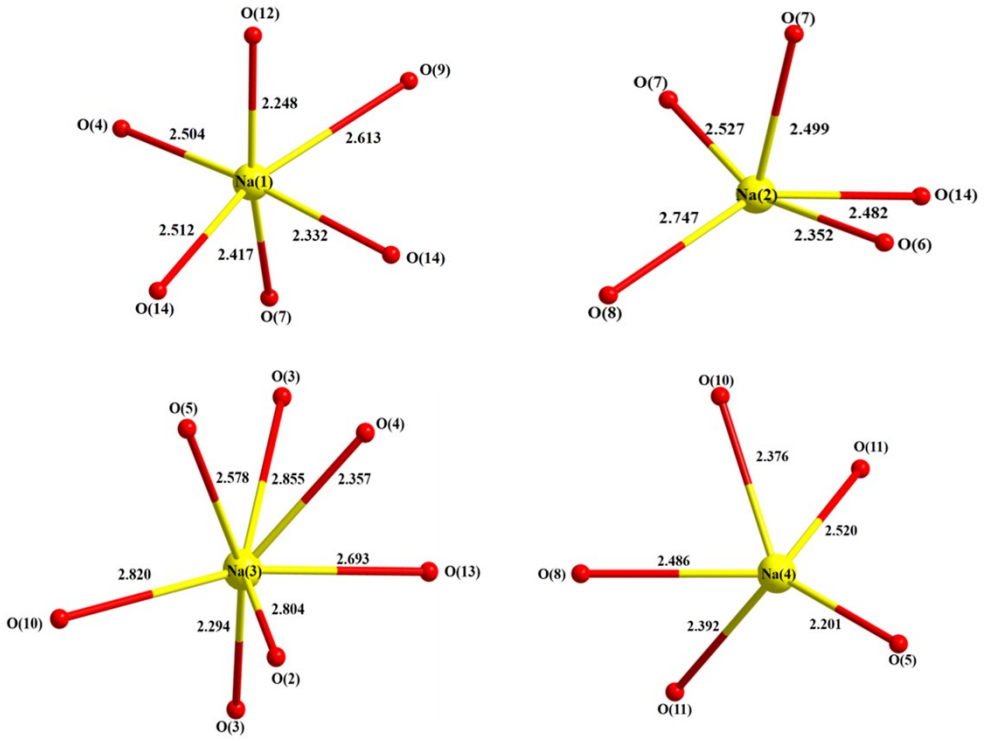


Figure S3. Coordination environment of the Mg atoms in $Na_7Mg_{4.5}(P_2O_7)_4$

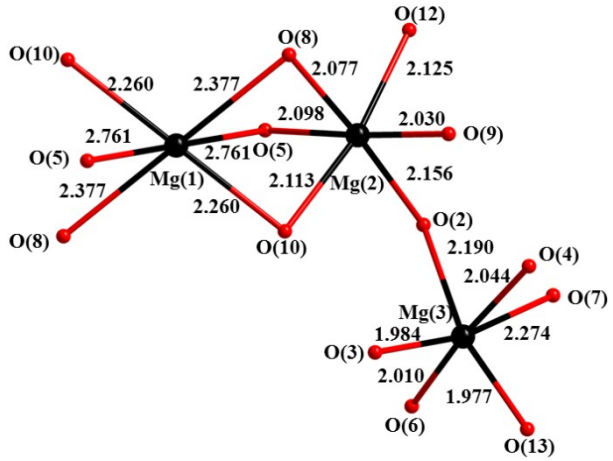


Figure S4. The asymmetric unit and selected symmetry-equivalent atoms in

$Na_7Mg_{4.5}(P_2O_7)_4$

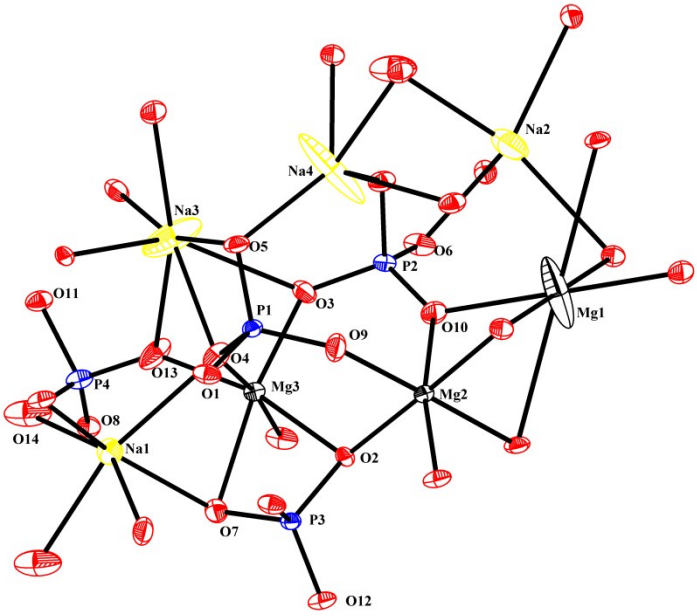


Figure S5. 3D network constructed with the MgO_6 unions

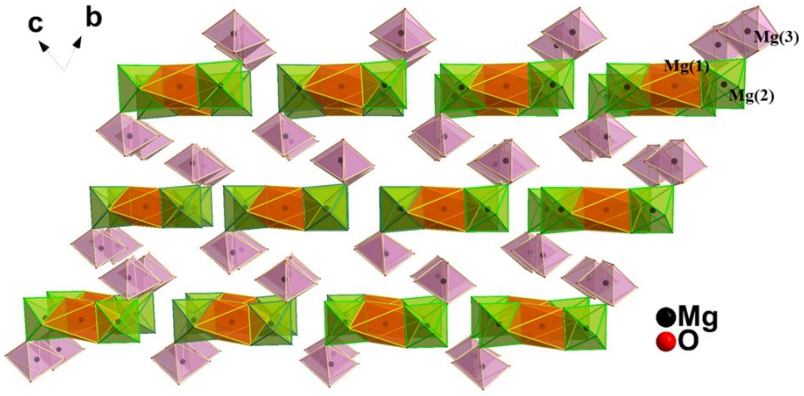


Figure S6. IR spectrum of $Na_7Mg_{4.5}(P_2O_7)_4$

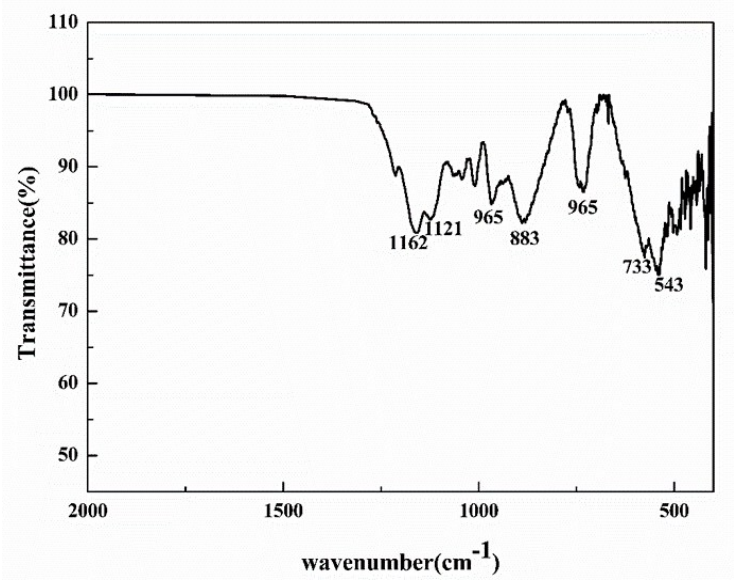
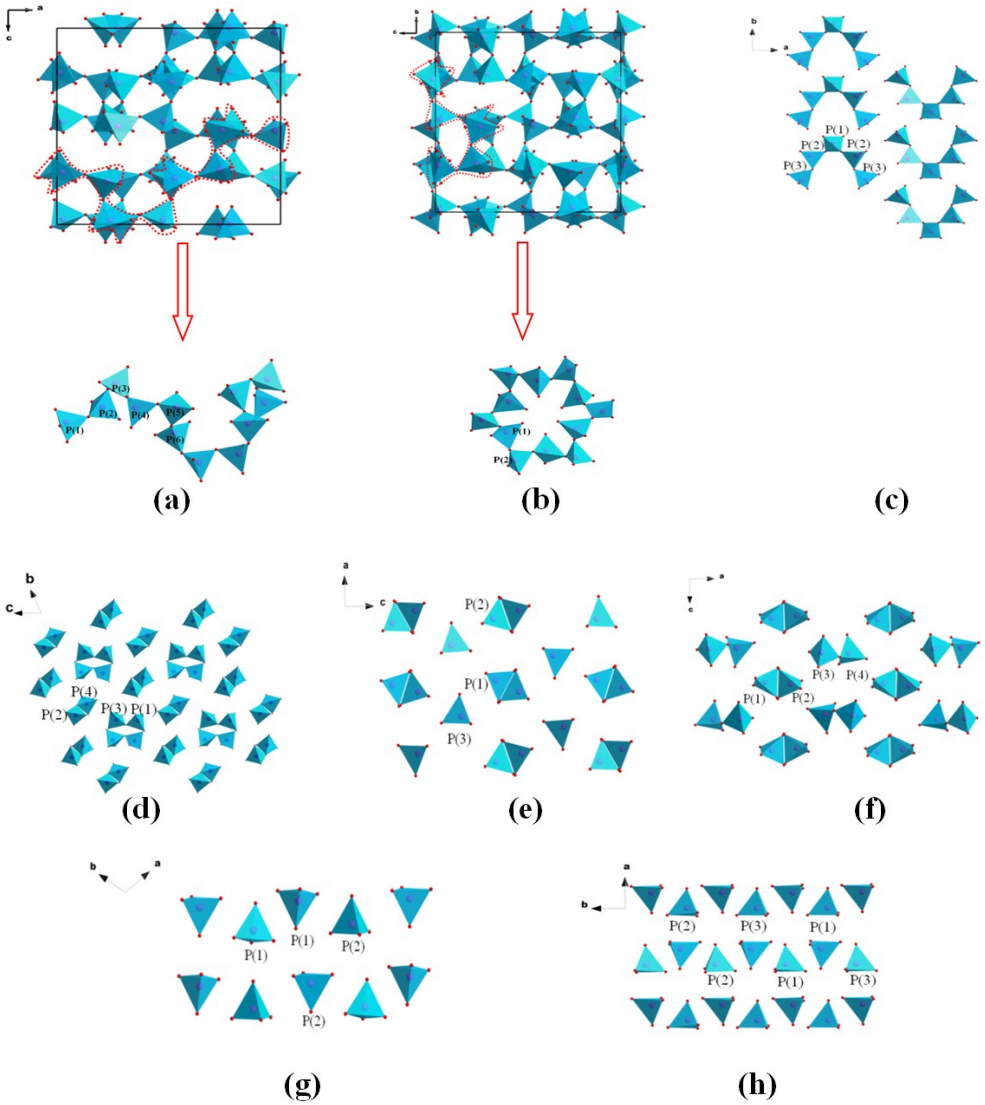


Figure S7. The alignments of the P-O groups in different sodium magnesium phosphates: (a) $[PO_3]_n$ chain in $NaMg(PO_3)_3$ (Ⅰ); (b) isolated $P_{12}O_{36}$ ring in $NaMg(PO_3)_3$ (Ⅱ); (c) isolated P_5O_{16} in $Na_3Mg_2P_5O_{16}$; (d) isolated P_2O_7 in $Na_7Mg_{4.5}(P_2O_7)_4$ and $Na_{3.64}Mg_{2.18}(P_2O_7)_2$; (f) isolated PO_4 and P_2O_7 in $Na_4Mg_3(PO_4)_2(P_2O_7)$; (e) (g) (h) isolated PO_4 in $NaMg_4(PO_4)_3$,$Na_3Mg_3(PO_4)_3$,$Na_2Mg_5(PO_4)_4$.



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