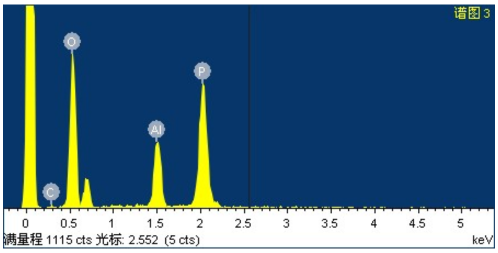
Supporting Information

$Li_3[Al(PO_4)_2(H_2O)_{1.5}]$ and $Na[AlP_2O_7]$ from 2D Layered Polar to 3D Centrosymmetric Framework Structures

Contents

Elements	Atom ratio
O K	61.73
Al K	13.25
P K	26.02



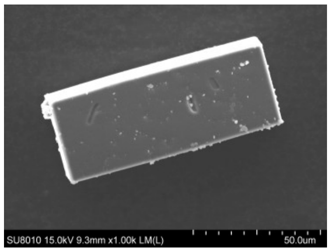
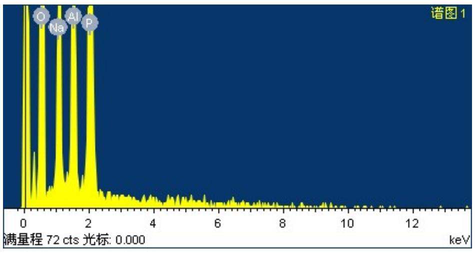


Figure S1: EDX and SEM image of $Li_3[Al(PO_4)_2(H_2O)_{1.5}]$.

Elements	Atom ratio
O K	62.01
Na K	9.77
Al K	9.58
P K	18.64



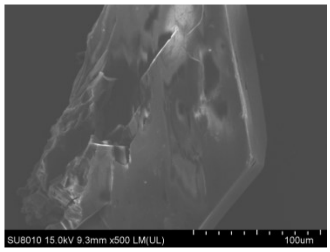
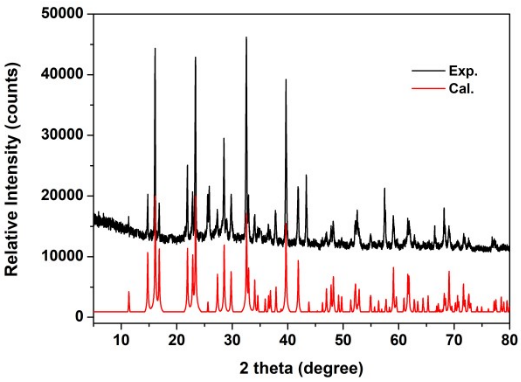


Figure S2: EDX and SEM image of $Na[AlP_2O_7]$.



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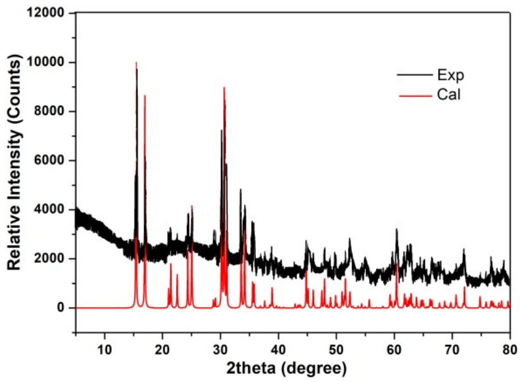
(a)



(b)

Figure S3: Experimental (black) and simulated (red) PXRD of $Li_3[Al(PO_4)_2(H_2O)_{1.5}]$ (a) and $Na[AlP_2O_7]$ (b).

Table S1. Important Bond Lengths (angstroms) and Important Bond angles (degrees) for $Li_3[Al(PO_4)_2(H_2O)_{1.5}]$ and $Na[AlP_2O_7]$.

$Li_3[Al(PO_4)_2(H_2O)_{1.5}]$		$Na[AlP_2O_7]$	
Al(1)-O(2)	1.790(8)	P(1)-O(3)	1.505(4)
Al(1)-O(3)	1.819(7)	P(1)-O(1)	1.516(4)
Al(1)-O(1)#1	1.874(9)	P(1)-O(2)	1.521(3)
Al(1)-O(5)#2	1.889(8)	P(1)-O(4)	1.525(13)
Al(1)-O(4)	1.901(10)	Al(1)-O(3)#1	1.880(4)
Al(1)-O(7)#3	1.896(8)	Al(1)-O(3)#2	1.880(4)
P(1A)-O(6)	1.504(12)	Al(1)-O(2)#3	1.893(4)
P(1A)-O(4)	1.519(7)	Al(1)-O(2)#4	1.893(4)
P(1A)-O(7)	1.545(11)	Al(1)-O(1)	1.913(4)
P(1A)-O(9)	1.603(16)	Al(1)-O(1)#5	1.913(4)
P(1A)-O(11)	2.25(7)	Na(1)-O(2)	2.250(4)
P(1B)-O(11)	1.48(7)	Na(1)-O(2)#8	2.250(4)
P(1B)-O(4)	1.487(8)	Na(1)-O(1)#9	2.535(4)
P(1B)-O(6)	1.482(13)	Na(1)-O(1)#6	2.535(4)
P(1B)-O(7)	1.574(11)	Na(1)-O(4)#10	2.796(13)
Li(1)-O(1)	2.15(4)	Na(1)-O(4)#11	2.796(13)
Li(3)-O(2)	1.96(2)	O(1)-Na(1)#6	2.535(4)
Li(4)-O(2)	2.02(5)	O(4)-Na(1)#13	2.796(13)
Li(1)-O(2)	2.19(3)		
Li(3)#4-O(2)	2.237(19)	O(3)-P(1)-O(1)	113.9(2)
Li(2)-O(3)	1.868(17)	O(3)-P(1)-O(2)	107.5(2)
Li(1)#1-O(3)	1.91(3)	O(1)-P(1)-O(2)	112.2(2)
Li(5)-O(3)	1.96(4)	O(3)-P(1)-O(4)	99.1(6)
Li(2)#3-O(3)	2.277(17)	O(1)-P(1)-O(4)	109.6(5)
Li(1)-O(4)	2.17(4)	O(2)-P(1)-O(4)	113.9(5)
Li(4)#4-O(4)	2.61(5)	O(3)#1-Al(1)-O(3)#2	89.9(3)
Li(4)#5-O(5)	1.92(6)	O(3)#1-Al(1)-O(2)#3	179.0(2)
Li(3)#5-O(5)	2.16(3)	O(3)#2-Al(1)-O(2)#3	89.1(2)
Li(5)#5-O(6)	1.85(5)	O(3)#1-Al(1)-O(2)#4	89.1(2)
Li(2)#5-O(6)	2.10(3)	O(3)#2-Al(1)-O(2)#4	179.0(2)
Li(1)#6-O(6)	2.15(3)	O(2)#3-Al(1)-O(2)#4	91.8(2)
Li(2)-O(7)	1.87(3)	O(3)#1-Al(1)-O(1)	89.74(18)
Li(5)-O(7)	2.21(6)	O(3)#2-Al(1)-O(1)	93.28(18)
Li(3)-O(8)	1.84(3)	O(2)#3-Al(1)-O(1)	90.37(16)
Li(1)#9-O(8)	2.07(3)	O(2)#4-Al(1)-O(1)	86.66(15)
Li(4)-O(8)	2.19(7)	O(3)#1-Al(1)-O(1)#5	93.28(18)
Li(4)#6-O(9)	1.93(6)	O(3)#2-Al(1)-O(1)#5	89.74(18)
Li(4)#4-O(9)	2.00(5)	O(2)#3-Al(1)-O(1)#5	86.66(15)
Li(5)#7-O(10)	1.97(4)	O(2)#4-Al(1)-O(1)#5	90.37(16)
Li(5)#8-O(10)	2.02(3)	O(1)-Al(1)-O(1)#5	175.7(2)
Li(3)-O(12)	2.66(6)		
Li(2)#6-OW1	2.02(2)		
Li(2)#12-OW1	2.02(2)		
Li(2)#3-OW1	2.02(2)		
Li(2)-OW1	2.02(2)		
Li(3)#13-OW2	2.00(3)		
Li(3)#9-OW2	2.00(3)		
Li(3)#4-OW2	2.00(3)		
Li(3)-OW2	2.00(3)		
O(2)-Al(1)-O(3)	178.5(4)		
O(2)-Al(1)-O(1)#1	94.7(3)		
O(3)-Al(1)-O(1)#1	86.6(4)		
O(2)-Al(1)-O(5)#2	87.8(4)		
O(3)-Al(1)-O(5)#2	91.4(4)		
O(1)#1-Al(1)-O(5)#2	90.0(4)		
O(2)-Al(1)-O(4)	86.0(4)		
O(3)-Al(1)-O(4)	92.7(3)		

O(1)#1-Al(1)-O(4)	179.2(5)		
O(5)#2-Al(1)-O(4)	89.5(4)		
O(2)-Al(1)-O(7)#3	92.7(4)		
O(3)-Al(1)-O(7)#3	88.1(4)		
O(1)#1-Al(1)-O(7)#3	89.3(4)		
O(5)#2-Al(1)-O(7)#3	179.2(7)		
O(4)-Al(1)-O(7)#3	91.2(4)		
O(6)-P(1A)-O(4)	113.3(6)		
O(6)-P(1A)-O(7)	114.9(4)		
O(4)-P(1A)-O(7)	110.5(7)		
O(6)-P(1A)-O(9)	106.9(13)		
O(4)-P(1A)-O(9)	104.2(7)		
O(7)-P(1A)-O(9)	106.2(11)		
O(6)-P(1A)-O(11)	77.8(19)		
O(4)-P(1A)-O(11)	79(3)		
O(7)-P(1A)-O(11)	66(2)		
O(9)-P(1A)-O(11)	172(2)		
O(11)-P(1B)-O(4)	112(5)		
O(11)-P(1B)-O(6)	110(3)		
O(4)-P(1B)-O(6)	116.5(9)		
O(11)-P(1B)-O(7)	90(3)		
O(4)-P(1B)-O(7)	110.6(8)		
O(6)-P(1B)-O(7)	114.5(5)		
O(8)-P(2A)-O(1)	112.6(6)		
O(8)-P(2A)-O(5)	114.1(4)		
O(1)-P(2A)-O(5)	111.2(6)		
O(8)-P(2A)-O(10)	109.3(9)		
O(1)-P(2A)-O(10)	103.4(6)		
O(5)-P(2A)-O(10)	105.5(9)		
O(8)-P(2A)-O(12)	64(2)		
O(1)-P(2A)-O(12)	80(4)		
O(5)-P(2A)-O(12)	78(2)		
O(10)-P(2A)-O(12)	173(2)		
O(12)-P(2B)-O(1)	116(6)		
O(12)-P(2B)-O(8)	89(3)		
O(1)-P(2B)-O(8)	112.9(7)		
O(12)-P(2B)-O(5)	111(4)		
O(1)-P(2B)-O(5)	112.9(7)		
O(8)-P(2B)-O(5)	113.0(4)		

$Li_3[Al(PO_4)_2(H_2O)_{1.5}]$. Symmetry transformations used to generate equivalent atoms: #1 x, y, z-1; #2 -y+1, x, z-1; #3 -y+1, x-1, z; #4 -y+1, x, z; #5 x, y, z+1; #6 y+1, -x+1, z; #7 y, -x+1, z+1; #8 -y+1, x-1, z+1; #9 y, -x+1, z; #10 -x+2, -y+1, z; #11 -x+1, -y, z; #12 -x+2, -y, z; #13 -x+1, -y+1, z.

$Na[AlP_2O_7]$. Symmetry transformations used to generate equivalent atoms: #1-x, -y, -z+1; #2x, -y, z-1/2; #3 -x+1/2, -y+1/2, -z+1; #4 x-1/2, -y+1/2, z-1/2; #5-x, y, -z+1/2; #6-x, y, -z+3/2; #7 x, y, z-1; #8-x+1/2, -y+1/2, -z+2; #9 x+1/2, -y+1/2, z+1/2; #10 x, -y, z+1/2; #11 -x+1/2, y+1/2, -z+3/2; #12 x, y, z+1; #13 -x+1/2, y-1/2, -z+3/2.

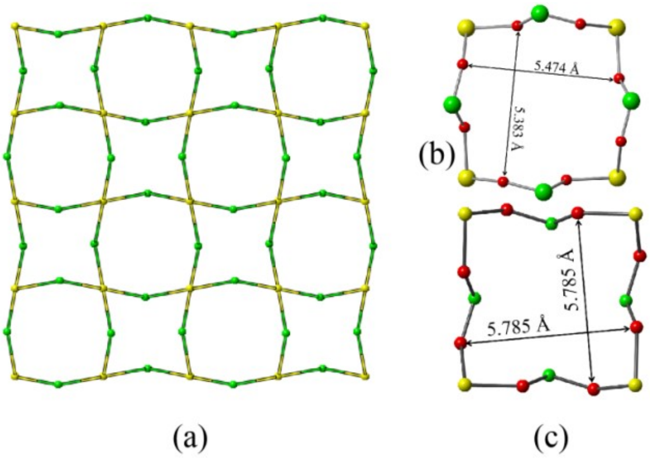


Figure S4: (a) The simplified cationic 2D Layer of $Li_3[Al(PO_4)_2(H_2O)_{1.5}]$ along the *c*-axis (a); two 8-MRs along the *c*-axis with a size of ~5.474 Å × 5.383 Å (b), and ~5.785 Å × 5.785 Å (c). Al nodes, P nodes and O atoms are shown as yellow, green and red, respectively.

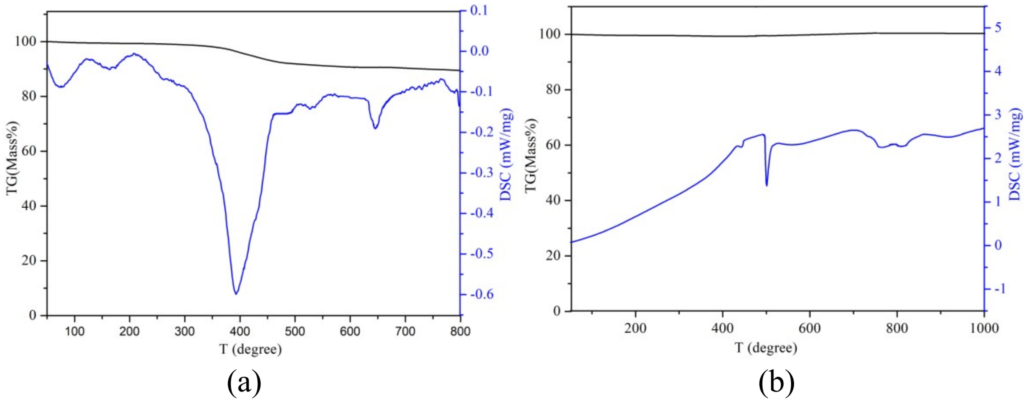


Figure S5: TG-DSC curves of $Li_3[Al(PO_4)_2(H_2O)_{1.5}]$ (a) and $Na[AlP_2O_7]$ (b).

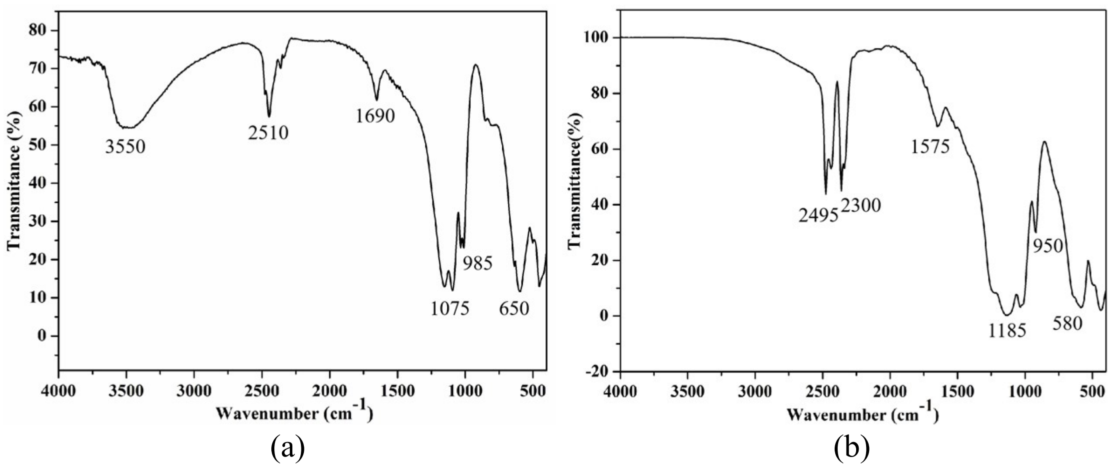


Figure S6: IR spectra of $Li_3[Al(PO_4)_2(H_2O)_{1.5}]$ (a) and $Na[AlP_2O_7]$ (b).