Supporting Information

Contents

Elements	Atom ratio
O K	61.63
Al K	11.49
P K	26.88

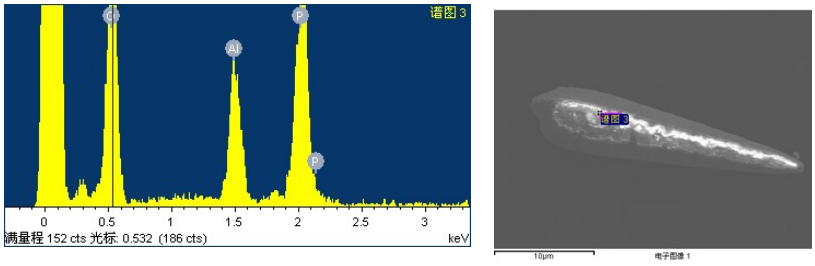


Figure S1: EDX and SEM image of $Al[P_2O_3(OH)_3](H_2O)$.

Elements	Atom ratio
O K	39.71
Al K	5.49
P K	6.60

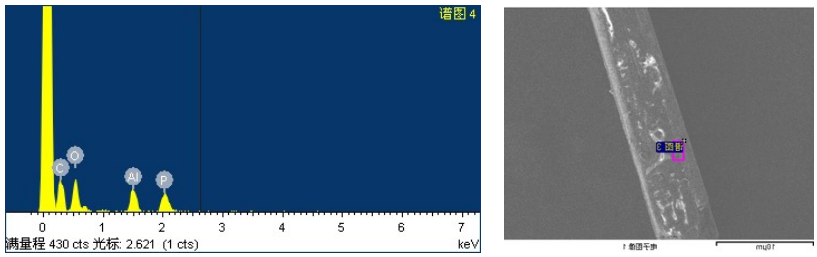


Figure S2: EDX and SEM image of $Al[(HPO_3)(OH)(H_2O)]$.

Elements	Atom ratio
O K	60.84
Ca K	17.45
P K	18.89

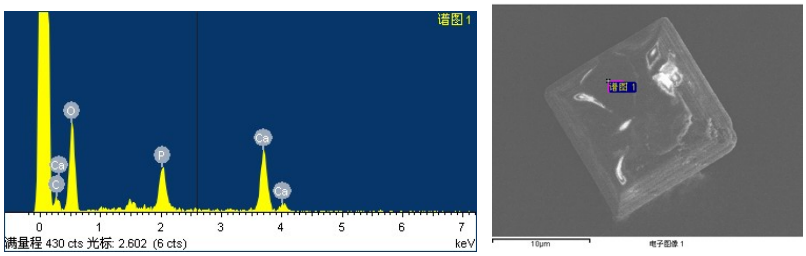


Figure S3: EDX and SEM image of $Ca[HPO_3]$.

Elements	Atom ratio
O K	61.89
Al K	9.92
P K	20.29

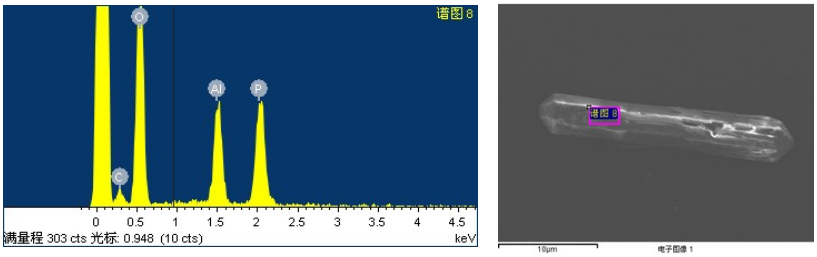
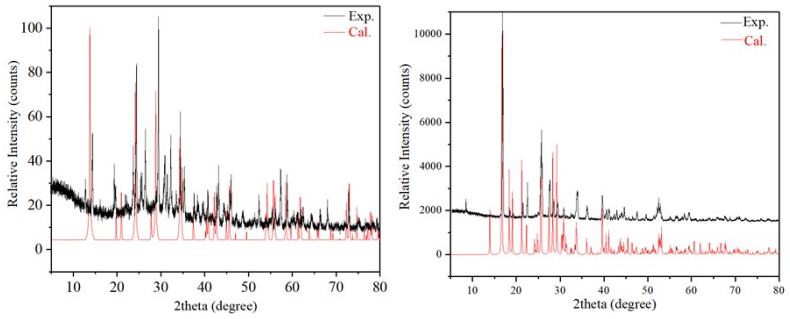
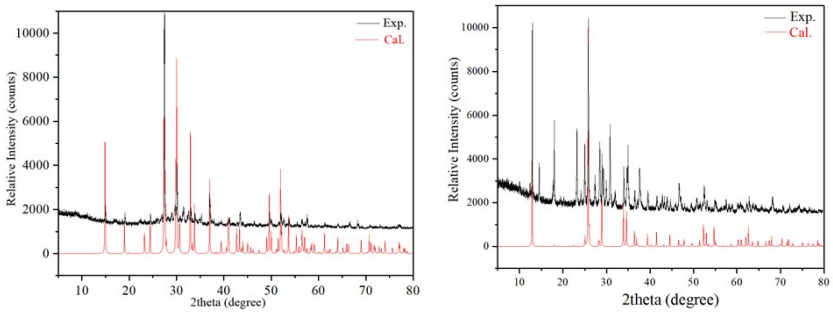


Figure S4: EDX and SEM image of $Al_3P_6O_{19.5}$.





(c) (d)

Figure S5: Experimental (black) and simulated (red) **PXRD** of $Al[P_2O_3(OH)_3](H_2O)$ (a), $Al[(HPO_3)(OH)(H_2O)]$ (b), $Ca[HPO_3]$ (c) and $Al_3P_6O_{19.5}$ (d).

Table S1. Important Bond Lengths (angstroms) and Important Bond Angles (degrees) for $Al[P_2O_3(OH)_3](H_2O)$, $Al[(HPO_3)(OH)](H_2O)$, $Ca[HPO_3]$ and $Al_4P_6O_{21}$.

$Al[P_2O_3(OH)_3](H_2O)$		$Al[(HPO_3)(OH)(H_2O)]$	
P(1)-O(2)#1	1.514(5)	P(1)-O(8)	1.51(2)
P(1)-O(2)#2	1.514(5)	P(1)-O(1)	1.55(2)
P(1)-O(2)	1.514(5)	P(1)-O(9)	1.56(2)
P(2)-O(1)	1.535(5)	P(2)-O(10)	1.50(2)
P(2)-O(1)#3	1.535(5)	P(2)-O(7)	1.52(3)
P(2)-O(1)#4	1.535(5)	P(2)-O(3)	1.54(3)
Al(1)-O(2)#5	1.896(6)	Al(l)-O(4)#1	1.77(2)
Al(1)-O(2)#6	1.896(6)	Al(l)-O(4)	1.77(2)
Al(1)-O(2)#7	1.896(6)	Al(l)-O(3)	1.82(2)
Al(1)-O(1)#4	1.901(5)	Al(1)-O(3)#1	1.82(2)
Al(1)-O(1)#8	1.901(5)	Al(1)-O(6)#1	1.92(2)
Al(1)-O(1)#9	1.901(5)	Al(1)-O(6)	1.92(2)
O(1)-Al(1)#10	1.904(5)	Al(2)-O(2)	1.794(18)
O(2)-Al(1)#11	1.896(6)	Al(2)-O(2)#2	1.794(18)
		Al(2)-O(9)	1.82(2)
O(2)#1-P(1)-O(2)#2	113.0(2)	Al(2)-O(9)#2	1.82(2)
O(2)#1-P(1)-O(2)	113.0(2)	Al(2)-O(5)	1.91(3)
O(2)#2-P(1)-O(2)	113.0(2)	Al(2)-O(5)#2	1.91(3)
O(1)-P(2)-O(1)#3	110.5(2)	Al(3)-O(2)#3	1.825(18)
O(1)-P(2)-O(1)#4	110.5(2)	Al(3)-O(2)	1.825(18)
O(1)#3-P(2)-O(1)#4	110.5(2)	Al(3)-O(7)	1.85(3)
O(2)#5-Al(1)-O(2)#6	88.9(3)	Al(3)-O(7)#3	1.85(3)
O(2)#5-Al(1)-O(2)#7	88.9(3)	Al(3)-O(1)#3	1.85(2)
O(2)#6-Al(1)-O(2)#7	88.9(3)	Al(3)-O(1)	1.85(2)
O(2)#5-Al(1)-O(1)#4	91.15(15)	Al(4)-O(10)#4	1.80(3)
O(2)#6-Al(1)-O(1)#4	91.15(15)	Al(4)-O(10)#5	1.80(3)
O(2)#7-Al(1)-O(1)#4	179.9(3)	Al(4)-O(4)#5	1.83(2)
O(2)#5-Al(1)-O(1)#8	179.9(3)	Al(4)-O(4)#4	1.83(2)
O(2)#6-Al(1)-O(1)#8	91.15(15)	Al(4)-O(8)#6	1.86(2)
O(2)#7-Al(1)-O(1)#8	91.15(15)	Al(4)-O(8)	1.86(2)
O(1)#4-Al(1)-O(1)#8	88.8(2)	O(4)-Al(4)#7	1.83(2)
O(2)#5-Al(1)-O(1)#9	91.15(15)	O(10)-Al(4)#7	1.80(3)
O(2)#6-Al(1)-O(1)#9	179.9(3)		
O(2)#7-Al(1)-O(1)#9	91.15(15)	O(8)-P(1)-O(1)	112.8(12)
O(1)#4-Al(1)-O(1)#9	88.8(2)	O(8)-P(1)-O(9)	112.4(15)
O(1)#8-Al(1)-O(1)#9	88.8(2)	O(1)-P(1)-O(9)	110.1(12)
		O(10)-P(2)-O(7)	110.7(14)
		O(10)-P(2)-O(3)	108.8(15)
		O(7)-P(2)-O(3)	109.4(15)
		O(4)#1-Al(1)-O(4)	180.0

		O(4)#1-Al(1)-O(3)	89.7(11)
		O(4)-Al(1)-O(3)	90.3(11)
		O(4)#1-Al(1)-O(3)#1	90.3(11)
		O(4)-Al(1)-O(3)#1	89.7(11)
		O(3)-Al(1)-O(3)#1	180.0
		O(4)#1-Al(1)-O(6)#1	92.0(11)
		O(4)-Al(1)-O(6)#1	88.0(11)
		O(3)-Al(1)-O(6)#1	91.7(13)
		O(3)#1-Al(1)-O(6)#1	88.3(13)
		O(4)#1-Al(1)-O(6)	88.0(11)
		O(4)-Al(1)-O(6)	92.0(11)
		O(3)-Al(1)-O(6)	88.3(13)
		O(3)#1-Al(1)-O(6)	91.7(13)
		O(6)#1-Al(1)-O(6)	180.0
		O(2)-Al(2)-O(2)#2	180.0(10)
		O(2)-Al(2)-O(9)	91.0(10)
		O(2)#2 -Al(2)-O(9)	89.0(10)
		O(2) -Al(2)-O(9)#2	89.0(10)
		O(2) #2-Al(2)-O(9)#2	91.0(10)
		O(9)-Al(2)-O(9)#2	180.0
		O(2)-Al(2)-O(5)	90.0(10)
		O(2)#2-Al(2)-O(5)	90.0(10)
		O(9)-Al(2)-O(5)	89.0(12)
		O(9)#2-Al(2)-O(5)	91.0(12)
		O(2)-Al(2)-O(5)#2	90.0(10)
		O(2)#2-Al(2)-O(5)#2	90.0(10)
		O(9)-Al(2)-O(5)#2	91.0(12)
		O(9)#2-Al(2)-O(5)#2	89.0(12)
		O(5)-Al(2)-O(5)	180.0
		O(2)#3-Al(3)-O(2)	180.0
		O(2)#3-Al(3)-O(7)	87.9(11)
		O(2)-Al(3)-O(7)	92.1(11)
		O(2)#3-Al(3)-O(7)#3	92.1(11)
		O(2)-Al(3)-O(7)#3	87.9(11)
		O(7)-Al(3)-O(7)#3	180.0
		O(2)#3-Al(3)-O(1)#3	92.7(9)
		O(2)-Al(3)-O(1)#3	87.3(9)
		O(7)-Al(3)-O(1)#3	90.3(10)
		O(7)#3-Al(3)-O(1)#3	89.7(10)
		O(2)#3-Al(3)-O(1)	87.3(9)
		O(2)-Al(3)-O(1)	92.7(9)
		O(7)-Al(3)-O(1)	89.7(10)
		O(7)#3-Al(3)-O(1)	90.3(10)
		O(1)#3-Al(3)-O(1)	180.0
		O(10)#4-Al(4)-O(10)#5	180.0(19)
		O(10)#4-Al(4)-O(4)#5	93.1(10)
		O(10)#5-Al(4)-O(4)#5	86.9(10)
		O(10)#4-Al(4)-O(4)#4	86.9(10)
		O(10)#5-Al(4)-O(4)#4	93.1(10)
		O(4)#5-Al(4)-O(4)#4	180.0
		O(10)#4-Al(4)-O(8)#6	93.6(13)
		O(10)#5-Al(4)-O(8)#6	86.4(13)
		O(4)#5-Al(4)-O(8)#6	92.2(11)
		O(4)#4-Al(4)-O(8)#6	87.8(11)
		O(10)#4-Al(4)-O(8)	86.4(13)
		O(10)#5-Al(4)-O(8)	93.6(13)
		O(4)#5-Al(4)-O(8)	87.8(11)
		O(4)#4-Al(4)-O(8)	92.2(11)
		O(8)#6-Al(4)-O(8)	180.0
$Ca[HPO_3]$		$Al_3P_6O_{19.5}$	
Ca(1)- O(1)	2.298(2)	P(1)-O(3)	1.342(2)
Ca(1)- O(3)	2.373(2)	P(1)-O(1)#1	1.515(2)
Ca(1)- O(3)#1	2.404(2)	P(1)-O(1)#2	1.515(2)

Ca(1)- O(2)#2	2.414(2)	P(1)-O(2)	1.538(4)
Ca(1)- O(2)	2.429(2)	Al(1)-O(1)#3	1.824(4)
Ca(1)- O(1)#3	2.502(2)	Al(1)-O(1)#4	1.821(2)
Ca(1)- O(3)#4	2.704(3)	Al(1)-O(1)#5	1.821(2)
P(1)- O(1)#8	1.515(2)	Al(1)-O(2)#6	1.981(2)
P(1)- O(2)#9	1.517(2)	Al(1)-O(2)	1.981(2)
P(1)- O(3)	1.541(2)	Al(1)-O(2)#7	1.983(9)
O(1)- P(1)#11	1.515(2)		
O(2)- P(1)#6	1.517(2)		
		O(3)-P(1)-O(1)#1	108.2(8)
O(1)- Ca(1)- O(3)	149.66(9)	O(3)-P(1)-O(1)#2	108.2(8)
O(1)- Ca(1)- O(3)#1	111.98(9)	O(1)#1-P(1)-O(1)#2	114.06(17)
O(3)- Ca(1)- O(3)#1	95.99(6)	O(3)-P(1)-O(2)	103.9(16)
O(1)- Ca(1)- O(2)#2	81.32(9)	O(1)#1-P(1)-O(2)	110.99(10)
O(3)- Ca(1)- O(2)#2	74.64(8)	O(1)#2-P(1)-O(2)	110.99(10)
O(3)#1- Ca(1)- O(2)#2	161.39(9)	O(1)#3-Al(1)-O(1)#4	97.99(10)
O(1)- Ca(1)- O(2)	87.26(9)	O(1)#3-Al(1)-O(1)#5	97.99(10)
O(3)- Ca(1)- O(2)	89.60(9)	O(1)#4-Al(1)-O(1)#5	97.99(10)
O(3)#1- Ca(1)- O(2)	73.81(8)	O(1)#3-Al(1)-O(2)#6	92.02(10)
O(2)#2- Ca(1)- O(2)	121.27(9)	O(1)#4-Al(1)-O(2)#6	164.88(11)
O(1)- Ca(1)- O(1)#3	122.34(7)	O(1)#5-Al(1)-O(2)#6	91.78(10)
O(3)- Ca(1)- O(1)#3	73.19(8)	O(1)#3-Al(1)-O(2)	91.78(10)
O(3)#1- Ca(1)- O(1)#3	78.71(8)	O(1)#4-Al(1)-O(2)	92.02(10)
O(2)#2- Ca(1)- O(1)#3	83.15(9)	O(1)#5-Al(1)-O(2)	164.88(11)
O(2)- Ca(1)- O(1)#3	145.75(9)	O(2)#6-Al(1)-O(2)	76.29(10)
O(1)- Ca(1)- O(3)#4	70.57(8)	O(1)#3-Al(1)-O(2)#7	164.88(11)
O(3)#1- Ca(1)- O(3)#4	129.65(7)	O(1)#4-Al(1)-O(2)#7	91.78(10)
O(3)#1- Ca(1)- O(3)#4	77.22(9)	O(1)#5-Al(1)-O(2)#7	92.02(10)
O(2)#2- Ca(1)- O(3)#4	96.19(8)	O(2)#6-Al(1)-O(2)#7	76.29(10)
O(2)- Ca(1)- O(3)#4	133.19(8)	O(2)-Al(1)-O(2)#7	76.29(10)
O(1)#3- Ca(1)- O(3)#4	56.50(7)		
O(1)#8- P(1)-O(2)#9	115.69(15)		
O(1)#8- P(1)-O(3)	107.91(14)		
O(2)#9- P(1)-O(3)	114.31(15)		

$Al[P_2O_3(OH)_3](H_2O)$. Symmetry transformations used to generate equivalent atoms:
#1 -y+1, x-y, z; #2 -x+y+1, -x+1, z; #3 -y+1, x-y-1, z; #4 -x+y+2, -x+1, z; #5 -y+2, x-y, z; #6 -x+y+1, -x, z ; #7 x+1, y-1, z; #8 x, y-1, z; #9 -y+2, x-y-1, z; #10 x, y+1, z;#11 x-1, y+1, z;
$Al[(HPO_3)(OH)](H_2O)$. Symmetry transformations used to generate equivalent atoms:
#1 -x, -y, -z+3; #2 -x, -y+1, -z+2; #3 -x+1, -y+1, -z+2; #4 -x+1, -y, -z+2; #5 x, y, z-1; #6 -x+1, -y, -z+1; #7 x, y, z+1;
$Ca[HPO_3]$. Symmetry transformations used to generate equivalent atoms:
#1 y+1/2, -x+3/2, z+1/4; #2 -y+3/2, x-1/2, z-1/4; #3 x+1/2, -y+1/2, -z+1/4; #4 x-1/2, -y+1/2, -z+1/4; #5 y, x-1, -z;#6 x-1/2, -y+3/2, -z+1/4; #7 -y+1, -x+1, -z+1/2; #8 x+1, y, z; #9 x+1/2, -y+3/2, -z+1/4; #10 y+1, x, -z; #11 x-1, y, z;
$Al_4P_6O_{21}$. Symmetry transformations used to generate equivalent atoms:
#1 -y+1, x-y+1, -z+1/2; #2 -y+1, x-y+1, z; #3 y, -x+y, -z; #4 x-y+1, x, -z; #5 -x+1, -y+1, -z; #6 -x+y+1, -x+1, z; #7 -y+1, x-y, z; #8 x, y, -z+1/2; #9 -x+y, -x+1, z.

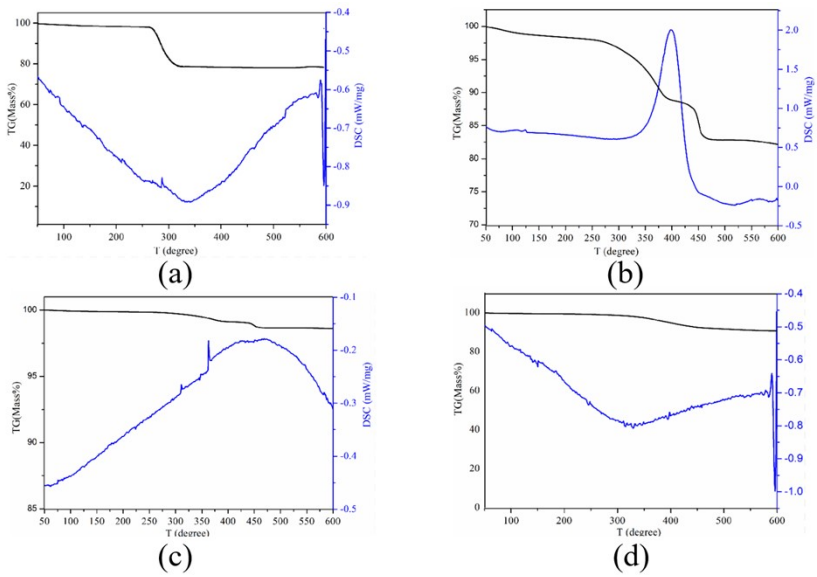


Figure S6: TG-DSC curves of $Al[P_2O_3(OH)_3](H_2O)$ (a), $Al[(HPO_3)(OH)(H_2O)]$ (b), $Ca[HPO_3]$ (c) and $Al_3P_6O_{19.5}$ (d).

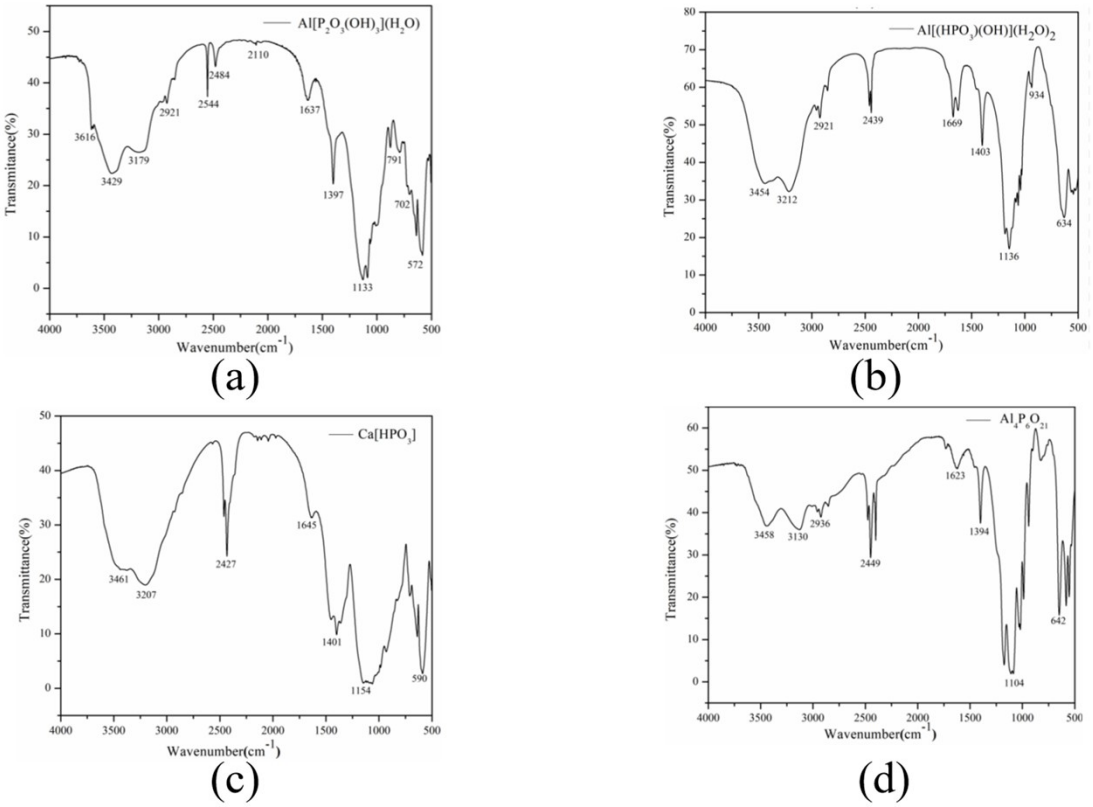


Figure S7: IR spectra of $Al[P_2O_3(OH)_3](H_2O)$ (a), $Al[(HPO_3)(OH)(H_2O)]$ (b), $Ca[HPO_3]$ (c) and $Al_3P_6O_{19.5}$ (d).

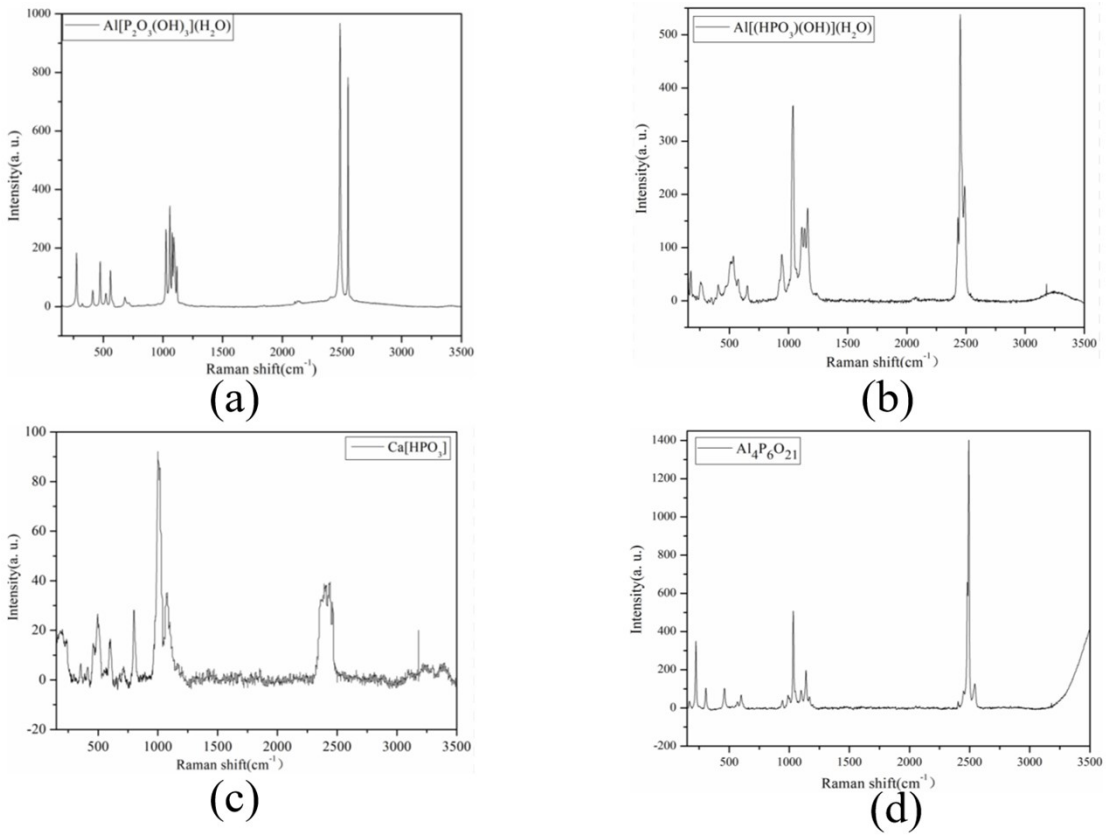


Figure S8: Raman spectra of $Al[P_2O_3(OH)_3](H_2O)$ (a), $Al[(HPO_3)(OH)(H_2O)]$ (b), $Ca[HPO_3]$ (c) and $Al_3P_6O_{19.5}$ (d).