Supporting Information

Synergistic effect of $^2[V_2P_2O_{14}]_\infty$ layers and hydrogen bonds inducing large birefringence in $M(VO)_2(PO_4)_2 \cdot 4H_2O$ (M = Ca, Sr, Ba) system

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Table S1 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1-3**.

Atom	x	y	z	U(eq)
		$Ca(VO)_2(PO_4)_2·4H_2O$		
V(1)	2892(2)	11014(2)	4365(2)	4(1)
V(2)	-1432(2)	6101(2)	2536(2)	4(1)
P(1)	3215(3)	6101(3)	3499(3)	4(1)
P(2)	8204(3)	11091(3)	3364(3)	4(1)
Ca(1)	-1814(3)	13041(2)	8115(2)	8(1)
O(1)	5844(9)	10786(8)	4854(9)	6(1)
O(2)	8939(9)	9222(8)	1994(9)	6(1)
O(3)	2867(8)	4079(8)	5000(8)	5(1)
O(4)	5606(8)	6421(9)	2112(9)	7(1)
O(5)	8414(9)	13057(8)	1777(8)	7(1)
O(6)	9631(9)	11342(9)	4884(9)	6(1)
O(7)	2482(9)	7883(8)	5004(9)	6(1)
O(8)	1855(9)	5991(9)	1900(9)	6(1)
O(9)	1619(9)	11026(9)	8146(9)	6(1)
O(10)	-2043(9)	5672(9)	5083(9)	6(1)
O(11)	3614(9)	11134(9)	1840(9)	7(1)
O(12)	-5518(9)	14150(8)	8483(8)	6(1)
O(13)	-3407(9)	9458(8)	8521(9)	10(1)
O(14)	-530(9)	6450(8)	-1257(8)	8(1)
		$Sr(VO)_2(PO_4)_2·4H_2O$		
Sr(1)	2396(1)	8094(1)	3843(1)	7(1)
V(1)	3592(1)	8928(1)	865(1)	5(1)
V(2)	-1146(1)	8878(1)	1766(1)	4(1)
P(1)	1234(2)	8573(2)	6313(2)	4(1)
P(2)	1233(2)	6430(2)	1290(2)	5(1)
O(1)	2419(5)	7692(5)	7098(4)	6(1)
O(2)	1975(5)	9511(5)	5540(4)	5(1)
O(3)	426(5)	9538(5)	7022(4)	6(1)
O(4)	144(5)	7537(5)	5593(4)	7(1)
O(5)	2353(5)	5413(5)	2002(4)	6(1)
O(6)	-33(5)	5557(5)	590(4)	6(1)
O(7)	2025(5)	7309(5)	504(4)	6(1)
O(8)	615(5)	7464(5)	2064(4)	6(1)
O(9)	-1508(5)	8736(5)	499(4)	10(1)
O(10)	3758(5)	8879(5)	2135(4)	7(1)
O(11)	1237(5)	5407(5)	3806(4)	9(1)
O(12)	4925(5)	6889(5)	3821(5)	10(1)
O(13)	3343(5)	10861(5)	3971(4)	8(1)
O(14)	-512(5)	8967(5)	3621(4)	6(1)

$Ba(VO)_2(PO_4)_2 \cdot 4H_2O$				
Ba(1)	6464(2)	7496(1)	9110(2)	12(1)
V(1)	2540(2)	9558(1)	6849(2)	6(1)
V(2)	8677(2)	5445(1)	5150(2)	6(1)
P(1)	7574(3)	10001(2)	6851(3)	5(1)
P(2)	8645(3)	4966(2)	177(3)	6(1)
O(1)	6780(11)	4201(5)	32(10)	10(1)
O(2)	8427(15)	7286(7)	5187(15)	17(2)
O(3)	10599(10)	4275(5)	323(12)	10(1)
O(4)	7763(11)	10701(5)	4923(10)	8(1)
O(5)	8742(13)	5682(6)	-1748(11)	9(2)
O(6)	2510(20)	7671(8)	7161(19)	11(2)
O(7)	5630(12)	9283(6)	6726(13)	10(2)
O(8)	8451(12)	5707(5)	2049(11)	11(1)
O(9)	9458(11)	9252(5)	7062(11)	10(1)
O(10)	7440(11)	10755(5)	8729(10)	10(1)
O(11)	2495(15)	10804(7)	6739(13)	15(2)
O(12)	8812(14)	4198(7)	5098(14)	15(2)
O(13)	10460(20)	7493(12)	10780(20)	17(3)
O(14)	4891(16)	7559(8)	13061(15)	17(2)

Table S2 Hydrogen coordinates and equivalent isotropic displacement parameters of each atom for **1**-**3**.

Atom	x	y	z	U(eq)
		$Ca(VO)_2(PO_4)_2·4H_2O$		
H(9B)	2138	12112	8458	10
H(9A)	1472	9860	8936	10
H(12B)	-4804	14575	7182	9
H(12A)	-6316	15153	9216	9
H(13A)	-3992	9322	7476	15
H(13B)	-4485	9315	9655	15
H(14A)	-1150	7485	-1732	12
H(14B)	840	6670	-1859	12
		$Sr(VO)_2(PO_4)_2·4H_2O$		
H(11A)	1804	5185	3361	14
H(11B)	1518	4981	4403	14
H(12A)	5652	7040	4335	16
H(12B)	5319	6968	3267	16
H(13A)	4183	10962	3761	12
H(13B)	2689	11479	3633	12
H(14A)	-1033	8335	3915	9
H(14B)	-581	9836	3866	9
		$Ba(VO)_2(PO_4)_2·4H_2O$		
H(2A)	9605	7593	5115	25
H(2B)	7722	7537	4175	25
H(6A)	1495	7680	8100	16
H(6B)	2967	7051	6892	16
H(13A)	10471	7956	11775	26
H(13B)	10473	6880	11292	26
H(14A)	4536	6945	13424	25
H(14B)	3915	8014	13119	25

Table S3 Selected bond distances (Å) and angles (deg.) of **1-3**.

$Ca(VO)_2(PO_4)_2 \cdot 4H_2O$			
V(1)-O(1)	1.992(5)	Ca(1)-O(13)	2.452(5)
V(1)-O(3)#1	2.016(5)	Ca(1)-O(14)#6	2.415(5)
V(1)-O(6)#2	2.007(6)	P(1)-O(3)	1.535(5)
V(1)-O(7)	2.000(6)	P(1)-O(4)	1.529(6)
V(1)-O(9)	2.378(6)	P(1)-O(7)	1.538(6)
V(1)-O(11)	1.584(6)	P(1)-O(8)	1.545(6)
V(2)-O(2)#2	1.987(6)	P(2)-O(1)	1.535(6)
V(2)-O(4)#2	1.984(5)	P(2)-O(2)	1.530(6)
V(2)-O(5)#4	2.037(5)	P(2)-O(5)	1.546(5)
V(2)-O(8)	2.004(5)	P(2)-O(6)	1.545(6)
V(2)-O(10)	1.606(6)	O(9)-H(9B)	0.827
V(2)-O(14)	2.382(5)	O(9)-H(9A)	0.8613
Ca(1)-O(3)#1	3.116(6)	O(12)-H(12B)	0.866
Ca(1)-O(5)#5	2.452(6)	O(12)-H(12A)	0.8916
Ca(1)-O(6)#2	2.388(6)	O(13)-H(13A)	0.8789
Ca(1)-O(9)	2.526(6)	O(13)-H(13B)	0.8513
Ca(1)-O(10)#1	2.541(6)	O(14)-H(14A)	0.85
Ca(1)-O(12)	2.399(6)		
O(1)-V(1)-O(3)#1	88.7(2)	O(13)-Ca(1)-O(9)	82.18(18)
O(1)-V(1)-O(6)#2	161.5(2)	O(13)-Ca(1)-O(10)#1	121.38(19)
O(1)-V(1)-O(7)	88.8(2)	O(14)#6-Ca(1)-O(3)#1	70.03(16)
O(1)-V(1)-O(9)	83.5(2)	O(14)#6-Ca(1)-O(5)#5	69.28(18)
O(3)#1-V(1)-O(9)	74.2(2)	O(14)#6-Ca(1)-O(9)	97.06(19)
O(6)#2-V(1)-O(3)#1	84.6(2)	O(14)#6-Ca(1)-O(10)#1	71.78(18)
O(6)#2-V(1)-O(9)	78.1(2)	O(14)#6-Ca(1)-O(13)	164.65(19)
O(7)-V(1)-O(3)#1	157.1(2)	O(3)-P(1)-O(7)	104.2(3)
O(7)-V(1)-O(6)#2	90.7(2)	O(3)-P(1)-O(8)	110.8(3)
O(7)-V(1)-O(9)	82.8(2)	O(4)-P(1)-O(3)	112.6(3)
O(11)-V(1)-O(1)	99.6(3)	O(4)-P(1)-O(7)	111.9(3)
O(11)-V(1)-O(3)#1	103.0(3)	O(4)-P(1)-O(8)	104.9(3)
O(11)-V(1)-O(6)#2	98.7(3)	O(7)-P(1)-O(8)	112.6(3)
O(11)-V(1)-O(7)	99.9(3)	O(1)-P(2)-O(5)	111.5(3)
O(11)-V(1)-O(9)	175.9(2)	O(1)-P(2)-O(6)	104.3(3)
O(2)#2-V(2)-O(5)#4	156.4(2)	O(2)-P(2)-O(1)	112.4(3)
O(2)#2-V(2)-O(8)	87.1(2)	O(2)-P(2)-O(5)	105.8(3)
O(2)#2-V(2)-O(14)	79.4(2)	O(2)-P(2)-O(6)	111.4(3)
O(4)#2-V(2)-O(2)#2	87.3(2)	O(6)-P(2)-O(5)	111.5(3)
O(4)#2-V(2)-O(5)#4	86.5(2)	P(2)-O(1)-V(1)	132.8(3)
O(4)#2-V(2)-O(8)	160.7(2)	P(2)-O(2)-V(2)#7	134.3(3)
O(4)#2-V(2)-O(14)	78.6(2)	V(1)#8-O(3)-Ca(1)#8	85.58(18)
O(5)#4-V(2)-O(14)	77.1(2)	P(1)-O(3)-V(1)#8	130.5(3)
O(8)-V(2)-O(5)#4	91.3(2)	P(1)-O(3)-Ca(1)#8	118.8(3)

O(8)-V(2)-O(14)	82.2(2)	P(1)-O(4)-V(2)#7	136.3(4)
O(10)-V(2)-O(2)#2	105.0(3)	V(2)#9-O(5)-Ca(1)#10	109.4(2)
O(10)-V(2)-O(4)#2	101.6(3)	P(2)-O(5)-V(2)#9	124.6(3)
O(10)-V(2)-O(5)#4	98.5(2)	P(2)-O(5)-Ca(1)#10	125.6(3)
O(10)-V(2)-O(8)	97.7(3)	V(1)#7-O(6)-Ca(1)#7	108.7(2)
O(10)-V(2)-O(14)	175.6(2)	P(2)-O(6)-V(1)#7	129.8(3)
O(5)#5-Ca(1)-O(3)#1	108.21(17)	P(2)-O(6)-Ca(1)#7	120.2(3)
O(5)#5-Ca(1)-O(9)	74.60(18)	P(1)-O(7)-V(1)	129.3(3)
O(5)#5-Ca(1)-O(10)#1	138.82(19)	P(1)-O(8)-V(2)	127.3(3)
O(5)#5-Ca(1)-O(13)	95.90(19)	V(1)-O(9)-Ca(1)	93.65(19)
O(6)#2-Ca(1)-O(3)#1	57.14(16)	V(1)-O(9)-H(9B)	106.6
O(6)#2-Ca(1)-O(5)#5	142.1(2)	V(1)-O(9)-H(9A)	120.4
O(6)#2-Ca(1)-O(9)	68.77(19)	Ca(1)-O(9)-H(9B)	88.7
O(6)#2-Ca(1)-O(10)#1	73.17(19)	Ca(1)-O(9)-H(9A)	118.2
O(6)#2-Ca(1)-O(12)	110.81(19)	H(9B)-O(9)-H(9A)	121.7
O(6)#2-Ca(1)-O(13)	70.28(19)	V(2)-O(10)-Ca(1)#8	144.8(3)
O(6)#2-Ca(1)-O(14)#6	123.9(2)	Ca(1)-O(12)-H(12B)	75.9
O(9)-Ca(1)-O(3)#1	55.25(16)	Ca(1)-O(12)-H(12A)	131.6
O(9)-Ca(1)-O(10)#1	123.61(18)	H(12B)-O(12)-H(12A)	113.7
O(10)#1-Ca(1)-O(3)#1	69.46(16)	Ca(1)-O(13)-H(13A)	108.2
O(12)-Ca(1)-O(3)#1	137.23(16)	Ca(1)-O(13)-H(13B)	109.6
O(12)-Ca(1)-O(5)#5	102.33(18)	H(13A)-O(13)-H(13B)	105
O(12)-Ca(1)-O(9)	165.92(17)	V(2)-O(14)-Ca(1)#3	99.9(2)
O(12)-Ca(1)-O(10)#1	67.82(17)	V(2)-O(14)-H(14A)	113.5
O(12)-Ca(1)-O(13)	84.51(18)	V(2)-O(14)-H(14B)	112.9
O(12)-Ca(1)-O(14)#6	94.55(18)	Ca(1)#3-O(14)-H(14A)	113.5
O(13)-Ca(1)-O(3)#1	120.38(17)	Ca(1)#3-O(14)-H(14B)	112.9
$Sr(VO)_2(PO_4)_2 \cdot 4H_2O$			
Sr(1)-O(2)	2.601(5)	V(2)-O(9)	1.599(6)
Sr(1)-O(6)#2	3.154(5)	V(2)-O(14)	2.337(5)
Sr(1)-O(8)	2.597(5)	P(1)-O(1)	1.544(5)
Sr(1)-O(9)#2	2.721(5)	P(1)-O(2)	1.540(5)
Sr(1)-O(10)	2.781(6)	P(1)-O(3)	1.530(5)
Sr(1)-O(11)	2.628(4)	P(1)-O(4)	1.533(5)
Sr(1)-O(12)	2.527(5)	P(2)-O(5)	1.533(5)
Sr(1)-O(13)	2.625(4)	P(2)-O(6)	1.532(5)
Sr(1)-O(14)	2.699(4)	P(2)-O(7)	1.550(6)
V(1)-O(2)#3	2.011(4)	P(2)-O(8)	1.533(5)
V(1)-O(4)#4	1.996(5)	O(11)-H(11A)	0.8539
V(1)-O(6)#5	1.990(5)	O(11)-H(11B)	0.8501
V(1)-O(7)	2.021(5)	O(12)-H(12A)	0.8502
V(1)-O(10)	1.603(6)	O(12)-H(12B)	0.8503
V(1)-O(13)#3	2.398(6)	O(13)-H(13A)	0.8522
V(2)-O(1)#6	2.010(5)	O(13)-H(13B)	0.8664

V(2)-O(3)#3	1.993(4)	O(14)-H(14A)	0.8652
V(2)-O(5)#7	1.992(5)	O(14)-H(14B)	0.8471
V(2)-O(8)	2.014(4)		
O(2)-Sr(1)-O(6)#2	54.59(12)	O(5)#7-V(2)-O(1)#6	88.57(19)
O(2)-Sr(1)-O(9)#2	74.62(15)	O(5)#7-V(2)-O(3)#3	87.77(18)
O(2)-Sr(1)-O(10)	132.97(14)	O(5)#7-V(2)-O(8)	160.2(2)
O(2)-Sr(1)-O(11)	110.35(16)	O(5)#7-V(2)-O(14)	82.57(18)
O(2)-Sr(1)-O(13)	65.08(15)	O(8)-V(2)-O(14)	77.90(19)
O(2)-Sr(1)-O(14)	70.13(14)	O(9)-V(2)-O(1)#6	97.8(2)
O(8)-Sr(1)-O(2)	132.57(14)	O(9)-V(2)-O(3)#3	103.4(2)
O(8)-Sr(1)-O(6)#2	164.11(15)	O(9)-V(2)-O(5)#7	100.9(2)
O(8)-Sr(1)-O(9)#2	128.97(14)	O(9)-V(2)-O(8)	98.7(2)
O(8)-Sr(1)-O(10)	70.02(15)	O(9)-V(2)-O(14)	176.5(2)
O(8)-Sr(1)-O(11)	66.64(15)	O(2)-P(1)-O(1)	111.7(3)
O(8)-Sr(1)-O(13)	113.80(15)	O(3)-P(1)-O(1)	104.6(3)
O(8)-Sr(1)-O(14)	62.46(15)	O(3)-P(1)-O(2)	112.1(2)
O(9)#2-Sr(1)-O(6)#2	64.23(13)	O(3)-P(1)-O(4)	112.3(3)
O(9)#2-Sr(1)-O(10)	127.91(16)	O(4)-P(1)-O(1)	111.7(3)
O(10)-Sr(1)-O(6)#2	94.98(14)	O(4)-P(1)-O(2)	104.6(3)
O(11)-Sr(1)-O(6)#2	127.18(14)	O(5)-P(2)-O(7)	111.0(3)
O(11)-Sr(1)-O(9)#2	62.95(15)	O(5)-P(2)-O(8)	104.8(3)
O(11)-Sr(1)-O(10)	116.68(15)	O(6)-P(2)-O(5)	112.4(2)
O(11)-Sr(1)-O(14)	83.74(13)	O(6)-P(2)-O(7)	105.2(3)
O(12)-Sr(1)-O(2)	119.13(16)	O(6)-P(2)-O(8)	111.7(3)
O(12)-Sr(1)-O(6)#2	67.97(14)	O(8)-P(2)-O(7)	111.9(3)
O(12)-Sr(1)-O(8)	108.19(16)	P(1)-O(1)-V(2)#2	128.2(3)
O(12)-Sr(1)-O(9)#2	63.15(17)	V(1)#1-O(2)-Sr(1)	107.8(2)
O(12)-Sr(1)-O(10)	64.79(16)	P(1)-O(2)-Sr(1)	114.3(2)
O(12)-Sr(1)-O(11)	87.79(15)	P(1)-O(2)-V(1)#1	129.1(3)
O(12)-Sr(1)-O(13)	97.10(15)	P(1)-O(3)-V(2)#1	135.0(3)
O(12)-Sr(1)-O(14)	169.37(15)	P(1)-O(4)-V(1)#8	133.5(3)
O(13)-Sr(1)-O(6)#2	53.33(13)	P(2)-O(5)-V(2)#9	135.6(3)
O(13)-Sr(1)-O(9)#2	117.14(15)	V(1)#10-O(6)-Sr(1)#6	90.42(15)
O(13)-Sr(1)-O(10)	67.93(15)	P(2)-O(6)-Sr(1)#6	126.2(2)
O(13)-Sr(1)-O(11)	174.52(16)	P(2)-O(6)-V(1)#10	134.0(3)
O(13)-Sr(1)-O(14)	91.67(13)	P(2)-O(7)-V(1)	127.0(3)
O(14)-Sr(1)-O(6)#2	122.45(13)	V(2)-O(8)-Sr(1)	111.6(2)
O(14)-Sr(1)-O(9)#2	117.79(15)	P(2)-O(8)-Sr(1)	117.3(2)
O(14)-Sr(1)-O(10)	113.63(15)	P(2)-O(8)-V(2)	128.7(3)
O(2)#3-V(1)-O(7)	90.32(18)	V(2)-O(9)-Sr(1)#6	144.6(3)
O(2)#3-V(1)-O(13)#3	78.68(18)	V(1)-O(10)-Sr(1)	145.9(3)
O(4)#4-V(1)-O(2)#3	158.1(2)	Sr(1)-O(11)-H(11A)	86.7
O(4)#4-V(1)-O(7)	88.12(19)	Sr(1)-O(11)-H(11B)	110.2
O(4)#4-V(1)-O(13)#3	79.44(19)	H(11A)-O(11)-H(11B)	112.1

O(6)#5-V(1)-O(2)#3	84.29(18)	Sr(1)-O(12)-H(12A)	119.5
O(6)#5-V(1)-O(4)#4	88.7(2)	Sr(1)-O(12)-H(12B)	119.1
O(6)#5-V(1)-O(7)	157.0(2)	H(12A)-O(12)-H(12B)	104.5
O(6)#5-V(1)-O(13)#3	73.18(18)	Sr(1)-O(13)-H(13A)	112.2
O(7)-V(1)-O(13)#3	83.82(19)	Sr(1)-O(13)-H(13B)	113.1
O(10)-V(1)-O(2)#3	99.2(2)	V(1)#1-O(13)-Sr(1)	96.20(17)
O(10)-V(1)-O(4)#4	102.6(2)	V(1)#1-O(13)-H(13A)	112.6
O(10)-V(1)-O(6)#5	104.6(2)	V(1)#1-O(13)-H(13B)	112.6
O(10)-V(1)-O(7)	98.3(2)	H(13A)-O(13)-H(13B)	109.7
O(10)-V(1)-O(13)#3	177.0(2)	Sr(1)-O(14)-H(14A)	110.8
O(1)#6-V(2)-O(8)	91.81(19)	Sr(1)-O(14)-H(14B)	111.3
O(1)#6-V(2)-O(14)	81.90(19)	V(2)-O(14)-Sr(1)	98.69(17)
O(3)#3-V(2)-O(1)#6	158.7(2)	V(2)-O(14)-H(14A)	111.4
O(3)#3-V(2)-O(8)	84.73(18)	V(2)-O(14)-H(14B)	112.7
O(3)#3-V(2)-O(14)	76.87(19)	H(14A)-O(14)-H(14B)	111.3
$Ba(VO)_2(PO_4)_2 \cdot 4H_2O$			
Ba(1)-O(2)	2.819(10)	V(2)-O(5)#1	2.005(7)
Ba(1)-O(5)#1	2.793(7)	V(2)-O(8)	2.014(7)
Ba(1)-O(6)	2.820(13)	V(2)-O(12)	1.598(9)
Ba(1)-O(7)	2.795(8)	P(1)-O(4)	1.528(7)
Ba(1)-O(8)#1	3.218(7)	P(1)-O(7)	1.546(8)
Ba(1)-O(9)	3.228(7)	P(1)-O(9)	1.544(7)
Ba(1)-O(11)#2	2.823(9)	P(1)-O(10)	1.541(7)
Ba(1)-O(12)#3	2.822(9)	P(2)-O(1)	1.543(7)
Ba(1)-O(13)	2.766(13)	P(2)-O(3)	1.532(7)
Ba(1)-O(14)	2.721(10)	P(2)-O(5)	1.535(7)
V(1)-O(4)#4	1.996(7)	P(2)-O(8)	1.532(7)
V(1)-O(6)	2.422(10)	O(2)-H(2A)	0.85
V(1)-O(7)	2.007(8)	O(2)-H(2B)	0.8499
V(1)-O(9)#5	2.012(7)	O(6)-H(6A)	0.8854
V(1)-O(10)#6	2.034(7)	O(6)-H(6B)	0.862
V(1)-O(11)	1.594(9)	O(13)-H(13A)	0.8687
V(2)-O(1)#7	2.035(7)	O(13)-H(13B)	0.8499
V(2)-O(2)	2.359(9)	O(14)-H(14A)	0.8499
V(2)-O(3)#3	2.001(7)	O(14)-H(14B)	0.8528
O(2)-Ba(1)-O(6)	90.9(3)	O(3)#3-V(2)-O(2)	75.8(3)
O(2)-Ba(1)-O(8)#1	106.0(2)	O(3)#3-V(2)-O(5)#1	86.3(3)
O(2)-Ba(1)-O(9)	56.0(2)	O(3)#3-V(2)-O(8)	87.5(3)
O(2)-Ba(1)-O(11)#2	119.9(3)	O(5)#1-V(2)-O(1)#7	89.2(3)
O(2)-Ba(1)-O(12)#3	113.2(3)	O(5)#1-V(2)-O(2)	80.8(3)
O(5)#1-Ba(1)-O(2)	60.8(2)	O(5)#1-V(2)-O(8)	161.5(3)
O(5)#1-Ba(1)-O(6)	116.4(3)	O(8)-V(2)-O(1)#7	89.6(3)
O(5)#1-Ba(1)-O(7)	132.1(2)	O(8)-V(2)-O(2)	80.7(3)
O(5)#1-Ba(1)-O(8)#1	47.11(19)	O(12)-V(2)-O(1)#7	99.7(4)

O(5)#1-Ba(1)-O(9)	100.9(2)	O(12)-V(2)-O(2)	179.0(4)
O(5)#1-Ba(1)-O(11)#2	129.4(3)	O(12)-V(2)-O(3)#3	103.5(4)
O(5)#1-Ba(1)-O(12)#3	73.7(2)	O(12)-V(2)-O(5)#1	99.8(4)
O(6)-Ba(1)-O(8)#1	131.7(3)	O(12)-V(2)-O(8)	98.6(4)
O(6)-Ba(1)-O(9)	107.2(3)	O(4)-P(1)-O(7)	111.8(4)
O(6)-Ba(1)-O(11)#2	114.1(3)	O(4)-P(1)-O(9)	111.7(4)
O(6)-Ba(1)-O(12)#3	67.8(3)	O(4)-P(1)-O(10)	105.4(4)
O(7)-Ba(1)-O(2)	71.2(3)	O(9)-P(1)-O(7)	105.1(4)
O(7)-Ba(1)-O(6)	61.7(3)	O(10)-P(1)-O(7)	111.4(4)
O(7)-Ba(1)-O(8)#1	166.6(2)	O(10)-P(1)-O(9)	111.4(4)
O(7)-Ba(1)-O(9)	47.40(19)	O(3)-P(2)-O(1)	105.5(4)
O(7)-Ba(1)-O(11)#2	74.9(2)	O(3)-P(2)-O(5)	111.0(4)
O(7)-Ba(1)-O(12)#3	129.5(3)	O(3)-P(2)-O(8)	112.2(4)
O(8)#1-Ba(1)-O(9)	119.84(19)	O(5)-P(2)-O(1)	111.3(4)
O(11)#2-Ba(1)-O(8)#1	96.3(2)	O(8)-P(2)-O(1)	112.0(4)
O(11)#2-Ba(1)-O(9)	64.4(2)	O(8)-P(2)-O(5)	105.0(4)
O(12)#3-Ba(1)-O(8)#1	63.9(2)	P(2)-O(1)-V(2)#9	127.5(4)
O(12)#3-Ba(1)-O(9)	168.8(2)	Ba(1)-O(2)-H(2A)	113.6
O(12)#3-Ba(1)-O(11)#2	126.6(3)	Ba(1)-O(2)-H(2B)	113.8
O(13)-Ba(1)-O(2)	86.0(3)	V(2)-O(2)-Ba(1)	97.7(3)
O(13)-Ba(1)-O(5)#1	66.0(4)	V(2)-O(2)-H(2A)	113.7
O(13)-Ba(1)-O(6)	174.3(4)	V(2)-O(2)-H(2B)	113.9
O(13)-Ba(1)-O(7)	112.7(3)	H(2A)-O(2)-H(2B)	104.5
O(13)-Ba(1)-O(8)#1	54.0(3)	P(2)-O(3)-V(2)#10	133.9(4)
O(13)-Ba(1)-O(9)	67.0(3)	P(1)-O(4)-V(1)#11	133.6(4)
O(13)-Ba(1)-O(11)#2	63.8(4)	V(2)#8-O(5)-Ba(1)#8	108.1(3)
O(13)-Ba(1)-O(12)#3	117.8(4)	P(2)-O(5)-Ba(1)#8	108.4(4)
O(14)-Ba(1)-O(2)	173.8(3)	P(2)-O(5)-V(2)#8	134.5(4)
O(14)-Ba(1)-O(5)#1	113.6(3)	Ba(1)-O(6)-H(6A)	111.1
O(14)-Ba(1)-O(6)	94.3(3)	Ba(1)-O(6)-H(6B)	73.4
O(14)-Ba(1)-O(7)	114.3(3)	V(1)-O(6)-Ba(1)	96.2(4)
O(14)-Ba(1)-O(8)#1	68.0(2)	V(1)-O(6)-H(6A)	92.7
O(14)-Ba(1)-O(9)	125.2(2)	V(1)-O(6)-H(6B)	153.9
O(14)-Ba(1)-O(11)#2	60.8(3)	H(6A)-O(6)-H(6B)	113.3
O(14)-Ba(1)-O(12)#3	65.9(3)	V(1)-O(7)-Ba(1)	107.9(3)
O(14)-Ba(1)-O(13)	89.2(4)	P(1)-O(7)-Ba(1)	107.8(4)
O(4)#4-V(1)-O(6)	75.7(3)	P(1)-O(7)-V(1)	133.1(5)
O(4)#4-V(1)-O(7)	86.7(3)	V(2)-O(8)-Ba(1)#8	136.0(3)
O(4)#4-V(1)-O(9)#5	88.2(3)	P(2)-O(8)-Ba(1)#8	91.0(3)
O(4)#4-V(1)-O(10)#6	158.9(3)	P(2)-O(8)-V(2)	131.3(4)
O(7)-V(1)-O(6)	80.5(4)	V(1)#12-O(9)-Ba(1)	138.0(3)
O(7)-V(1)-O(9)#5	158.6(3)	P(1)-O(9)-Ba(1)	90.3(3)
O(7)-V(1)-O(10)#6	87.4(3)	P(1)-O(9)-V(1)#12	129.5(4)

O(9)#5-V(1)-O(6)	78.1(4)	P(1)-O(10)-V(1)#2	129.6(4)
O(9)#5-V(1)-O(10)#6	90.0(3)	V(1)-O(11)-Ba(1)#6	143.1(5)
O(10)#6-V(1)-O(6)	83.3(3)	V(2)-O(12)-Ba(1)#10	143.4(5)
O(11)-V(1)-O(4)#4	102.2(4)	Ba(1)-O(13)-H(13A)	106.5
O(11)-V(1)-O(6)	177.4(4)	Ba(1)-O(13)-H(13B)	98.9
O(11)-V(1)-O(7)	101.0(4)	H(13A)-O(13)-H(13B)	110.2
O(11)-V(1)-O(9)#5	100.4(4)	Ba(1)-O(14)-H(14A)	109
O(11)-V(1)-O(10)#6	98.8(4)	Ba(1)-O(14)-H(14B)	109.4
O(1)#7-V(2)-O(2)	81.0(3)	H(14A)-O(14)-H(14B)	115
O(3)#3-V(2)-O(1)#7	156.8(3)		

Symmetry transformations used to generate equivalent atoms:

$Ca(VO)_2(PO_4)_2 \cdot 4H_2O$

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

5 x-1, y, z+1 # 6 x, y+1, z+1 # 7 x+1, y, z # 8 x, y-1, z

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

$Sr(VO)_2(PO_4)_2 \cdot 4H_2O$

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

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

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

$Ba(VO)_2(PO_4)_2 \cdot 4H_2O$

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

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

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

Table S4 Hydrogen-bond interactions of **1-3**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
$Ca(VO)_2(PO_4)_2·4H_2O$				
O(9)-H(9B)...O(12)#7	0.83	1.97	2.751(7)	156.1
O(9)-H(9A)...O(2)#5	0.86	2.19	2.770(7)	124.7
O(12)-H(12B)...O(10)#1	0.87	1.98	2.758(8)	149.4
O(12)-H(12A)...O(8)#11	0.89	1.92	2.717(8)	148
O(13)-H(13A)...O(1)#2	0.88	1.93	2.665(8)	140.7
O(13)-H(13B)...O(11)#5	0.85	2.02	2.718(8)	138.9
O(14)-H(14A)...O(13)#12	0.85	1.88	2.663(7)	152.7
O(14)-H(14B)...O(7)#12	0.85	2.11	2.732(8)	129.7
$Sr(VO)_2(PO_4)_2·4H_2O$				
O(11)-H(11A)...O(5)	0.85	1.9	2.676(8)	150.4
O(11)-H(11B)...O(6)#11	0.85	2.29	2.863(7)	124.8
O(12)-H(12A)...O(7)#2	0.85	1.85	2.692(7)	168.9
O(12)-H(12B)...O(3)#4	0.85	2.1	2.740(8)	131.2
O(13)-H(13A)...O(11)#5	0.85	1.91	2.683(6)	150.9
O(13)-H(13B)...O(1)#3	0.87	2.07	2.720(7)	131
O(14)-H(14B)...O(12)#7	0.85	1.9	2.661(6)	148
$Ba(VO)_2(PO_4)_2·4H_2O$				
O(2)-H(2A)...O(6)#12	0.85	2.27	2.936(15)	135.3
O(2)-H(2B)...O(14)#8	0.85	1.94	2.655(10)	140.8
O(6)-H(6A)...O(13)#5	0.89	1.85	2.669(10)	152.6
O(6)-H(6B)...O(1)#3	0.86	2.13	2.792(12)	133
O(13)-H(13B)...O(8)#1	0.85	2.04	2.744(16)	140.1
O(14)-H(14A)...O(3)#13	0.85	2.09	2.791(13)	139.7
O(14)-H(14B)...O(10)#4	0.85	1.88	2.698(12)	161.4

Symmetry transformations used to generate equivalent atoms:

$Ca(VO)_2(PO_4)_2 \cdot 4H_2O$

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

5 x-1, y, z+1 #6 x, y+1, z+1 # 7 x+1, y, z # 8 x, y-1, z

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

$Sr(VO)_2(PO_4)_2 \cdot 4H_2O$

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

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

9 x+1/2, y-1/2, z # 10 x-1/2, y-1/2, z # 11 x, -y+1, z+1/2

$Ba(VO)_2(PO_4)_2 \cdot 4H_2O$

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

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

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

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

Table S5 Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**-**3**.

Atom	U11	U22	U33	U23	U13	U12
$Ca(VO)_2(PO_4)_2 \cdot 4H_2O$						
V(1)	4(1)	4(1)	4(1)	-1(1)	-1(1)	1(1)
V(2)	5(1)	3(1)	4(1)	0(1)	-2(1)	0(1)
Ca(1)	10(1)	7(1)	8(1)	-2(1)	-5(1)	2(1)
P(1)	4(1)	3(1)	4(1)	1(1)	-1(1)	0(1)
P(2)	4(1)	3(1)	4(1)	-1(1)	-1(1)	0(1)
O(1)	6(3)	8(3)	6(2)	0(2)	-3(2)	1(2)
O(2)	10(3)	3(2)	5(3)	1(2)	1(2)	0(2)
O(3)	6(3)	4(2)	6(3)	-1(2)	-4(2)	3(2)
O(4)	3(3)	8(3)	8(3)	1(2)	-1(2)	-1(2)
O(5)	10(3)	4(2)	4(3)	2(2)	0(2)	2(2)
O(6)	4(2)	7(2)	7(2)	-4(2)	0(2)	3(2)
O(7)	11(3)	3(2)	4(2)	-2(2)	0(2)	1(2)
O(8)	4(3)	8(2)	5(2)	0(2)	-2(2)	0(2)
O(9)	7(2)	6(2)	5(2)	0(1)	-1(1)	-3(1)
O(10)	6(3)	6(3)	6(3)	0(2)	-2(2)	1(2)
O(11)	10(3)	6(2)	8(3)	-1(2)	-6(2)	3(2)
O(12)	9(3)	5(2)	4(2)	0(2)	-1(2)	-1(2)
O(13)	12(3)	7(2)	8(2)	1(2)	1(2)	4(2)
O(14)	7(3)	8(2)	9(3)	-2(2)	-2(2)	5(2)
$Sr(VO)_2(PO_4)_2 \cdot 4H_2O$						
Sr(1)	7(1)	6(1)	8(1)	-1(1)	1(1)	0(1)
V(1)	5(1)	3(1)	5(1)	0(1)	1(1)	1(1)
V(2)	4(1)	3(1)	5(1)	0(1)	1(1)	1(1)
P(1)	4(1)	4(1)	5(1)	1(1)	0(1)	0(1)
P(2)	5(1)	3(1)	6(1)	0(1)	2(1)	-1(1)
O(1)	7(2)	4(2)	7(2)	-1(2)	0(2)	2(2)
O(2)	7(2)	3(2)	6(2)	-1(2)	1(2)	-3(2)
O(3)	5(2)	6(2)	8(3)	2(2)	2(2)	2(2)
O(4)	7(2)	5(2)	9(3)	-1(2)	0(2)	-3(2)
O(5)	6(2)	5(2)	8(3)	0(2)	3(2)	1(2)
O(6)	5(2)	7(2)	7(3)	-1(2)	2(2)	-4(2)
O(7)	7(2)	3(2)	8(3)	-1(2)	1(2)	-2(2)
O(8)	5(2)	4(2)	8(2)	-1(2)	1(2)	0(2)
O(9)	8(2)	9(2)	12(3)	0(2)	2(2)	0(2)
O(10)	8(2)	8(2)	6(3)	-2(2)	0(2)	-1(2)
O(11)	9(2)	11(2)	8(3)	3(2)	2(2)	1(2)
O(12)	10(2)	11(3)	9(3)	0(2)	1(2)	1(2)
O(13)	4(2)	7(2)	13(3)	1(2)	3(2)	3(2)
O(14)	9(2)	3(2)	7(2)	-2(2)	2(2)	0(2)
$Ba(VO)_2(PO_4)_2 \cdot 4H_2O$						
Ba(1)	13(1)	11(1)	12(1)	0(1)	1(1)	2(1)
V(1)	5(1)	7(1)	5(1)	1(1)	0(1)	1(1)

V(2)	6(1)	6(1)	4(1)	0(1)	1(1)	1(1)
P(1)	4(1)	7(1)	5(1)	0(1)	-1(1)	-1(1)
P(2)	6(1)	6(1)	4(1)	0(1)	1(1)	0(1)
O(1)	8(3)	9(3)	15(4)	-2(3)	1(3)	0(2)
O(2)	13(4)	22(5)	15(4)	5(3)	-6(3)	1(3)
O(3)	9(4)	10(3)	10(4)	1(3)	0(3)	-1(2)
O(4)	10(4)	7(3)	8(3)	3(2)	0(3)	-1(3)
O(5)	17(4)	8(3)	3(3)	0(3)	2(3)	3(3)
O(6)	16(5)	5(4)	11(4)	1(3)	6(3)	-2(3)
O(7)	4(4)	13(4)	14(5)	4(3)	0(3)	-3(3)
O(8)	14(4)	11(3)	7(3)	2(3)	0(3)	1(3)
O(9)	10(4)	11(3)	10(4)	1(3)	-3(3)	0(3)
O(10)	15(4)	8(3)	7(3)	2(2)	3(3)	-2(3)
O(11)	18(5)	10(4)	17(5)	1(3)	1(4)	4(3)
O(12)	13(5)	15(4)	17(4)	1(3)	-1(4)	-1(3)
O(13)	19(5)	8(4)	25(6)	-1(3)	-2(4)	-3(3)
O(14)	26(5)	8(4)	16(4)	0(4)	-2(3)	-1(4)

Table S6 The calculated bond valence values of **1-3**.

$Ca(VO)_2(PO_4)_2·4H_2O$					
Atom	Ca(1)	V(1)	V (2)	P (1)	P (2)
	1.9463	4.1188	4.0435	4.7979	4.7690
Atom	O (1)	O (2)	O (3)	O (4)	O (5)
	1.7750	1.7991	1.7840	1.8071	1.9440
Atom	O (6)	O (7)	O (8)	O (9)	O (10)
	2.0404	1.7531	1.7247	1.8159	1.8298
Atom	O(11)	O(12)	O(13)	O(14)	
	1.7169	1.5660	1.5753	1.8070	
$Sr(VO)_2(PO_4)_2·4H_2O$					
Atom	Sr(1)	V(1)	V (2)	P (1)	P (2)
	2.0136	4.057	4.1096	4.7978	4.7950
Atom	O (1)	O (2)	O (3)	O (4)	O (5)
	1.7189	2.0130	1.7898	1.7754	1.7815
Atom	O (6)	O (7)	O (8)	O (9)	O (10)
	1.8487	1.6841	2.0226	1.8447	1.7976
Atom	O(11)	O(12)	O(13)	O(14)	
	1.5486	1.6407	1.7468	1.6900	
$Ba(VO)_2(PO_4)_2·4H_2O$					
Atom	Ba(1)	V(1)	V (2)	P (1)	P (2)
	2.2194	3.9935	3.9966	4.7561	4.8172
Atom	O (1)	O (2)	O (3)	O (4)	O (5)
	1.6867	1.7637	1.7711	1.7886	2.0121
Atom	O (6)	O (7)	O (8)	O (9)	O (10)
	1.7741	1.9746	1.8351	1.7965	1.6931
Atom	O(11)	O(12)	O(13)	O(14)	
	1.9022	1.8906	1.5877	1.6027	

Table S7 Crystal data and structure refinement parameters for **1-3.**

Empirical formula	$Ca(VO_2(PO_4)_2 \cdot 4H_2O$	$Sr(VO_2(PO_4)_2 \cdot 4H_2O$	$Ba(VO_2(PO_4)_2 \cdot 4H_2O$
Formula weight	435.965	483.50	533.22
Crystal system,	Triclinic,	Monoclinic,	Monoclinic
Space group	*P*1	*C*c	*P*c
a(Å)	6.3369(5)	9.0039(3)	6.3867(8)
b(Å)	6.3410(5)	8.9895(3)	12.7855(16)
c(Å)	6.5675(6)	12.7798(5)	6.3889(8)
Unit cell dimensions	$\alpha = 85.84°$ $\beta = 73.14°$ $\gamma = 89.9°$	$\beta = 110.4°$	$\beta = 90.165°$
Volume [Å^3],*Z*	251.84(4), 1	1017.39(6), 4	521.70(11), 2
ρ_{calcd} (Mg/m^3)	2.875	3.157	3.394
μ [mm^{-1}]	2.768	7.423	5.877
F(000)	216	936	504
Crystal size [mm^3]	0.15 × 0.14 × 0.10	0.15 × 0.12 × 0.11	0.07 × 0.05 × 0.02
Theta range for data collection [°]	3.229 to 29.561	3.229 to 29.514	3.187 to 27.385
Limiting indices	-8≤ h≤ 8, -8≤ k≤ 8, -8≤ l≤ 8	-11≤ h≤ 11, -11≤ k≤ 10, -15≤ l≤ 16	-8≤ h≤ 7, -11≤ k≤ 16, -8≤ l≤ 8
Reflections collected / unique	10713/ 2444 [R_{int} = 0.0436]	4090/ 2053 [R_{int} = 0.0323]	3164/ 2123 [R_{int} = 0.0187]
Completeness [%]	98.9 %	99.9 %	99.5 %
Data / restraints / parameters	2444 /9 /172	2053/ 28 / 173	2123 / 8 / 193
Goodness-of-fit on F_o^2	1.075	1.032	1.047
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0393, wR_2 = 0.1027	R_1 = 0.0295, wR_2 = 0.0656	R_1 = 0.0249, wR_2 = 0.0530
R indices (all data) [a]	R_1 = 0.0406, wR_2 = 0.1040	R_1 = 0.0303, wR_2 = 0.0651	R_1 = 0.0306, wR_2 = 0.0557
Absolutestructure parameter	0.038(17)	0.456 (11)	0.23(4)
Extinction coefficient	0.011(5)	0.00824(19)	0.0068(8)
Largest diff. peak and hole [e·Å^{-3}]	1.434 and -0.798	0.640 and -0.749	0.506 and -0.502

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ *and* $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ *for* $F_o^2 > 2\sigma(F_o^2)$

Figure S1 Experimental and calculated XRD patterns of (a) **1**; (b) **2** and (c) **3**.

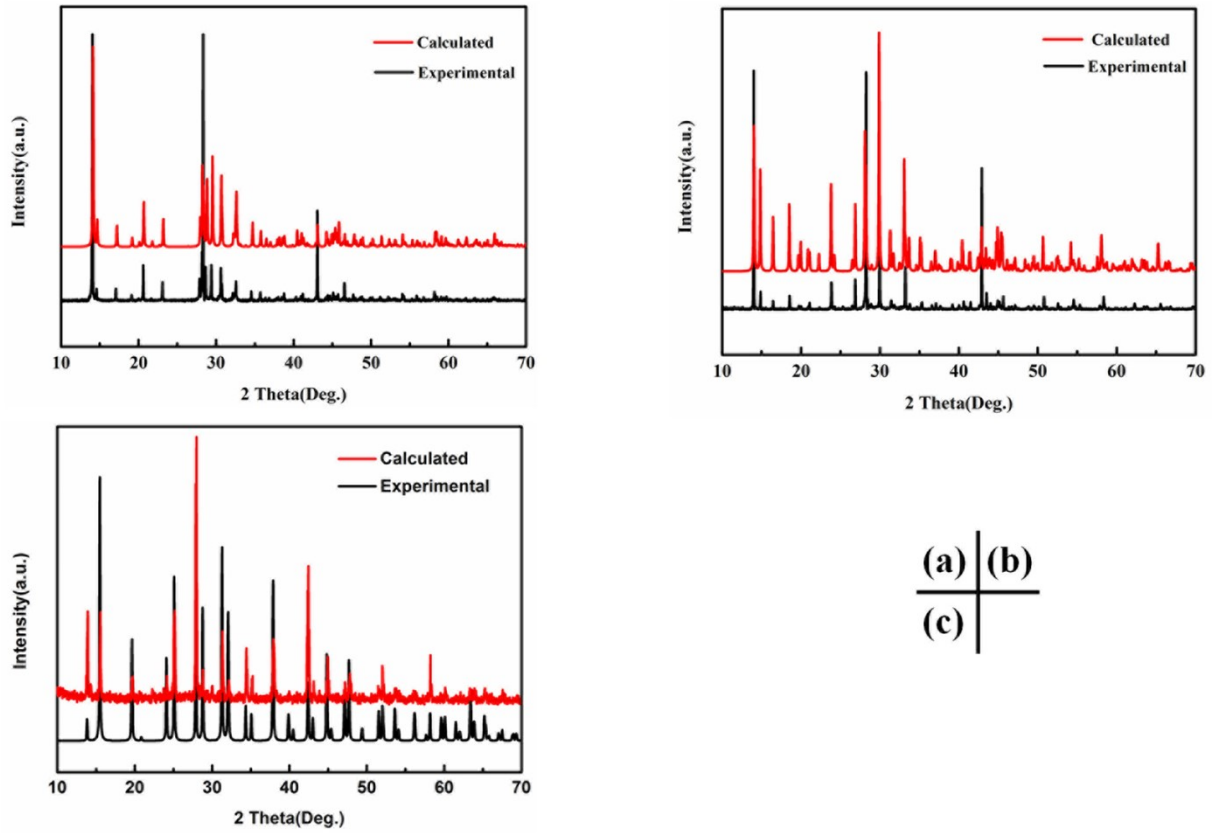


Figure S2 Coordination environment of the M (Ca, Sr, Ba) atom in **1**-**3**.

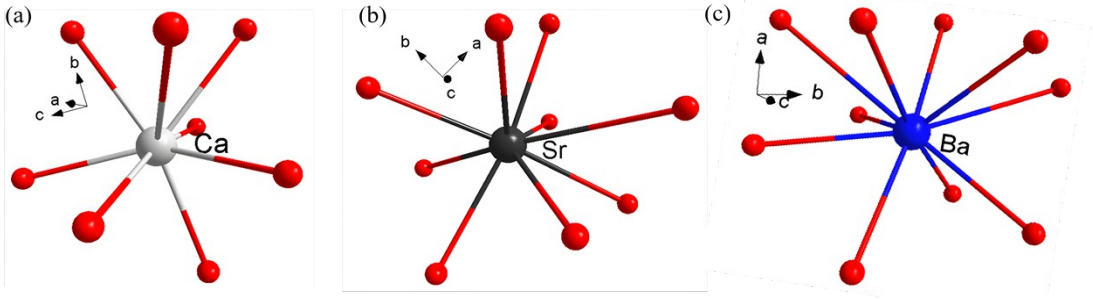
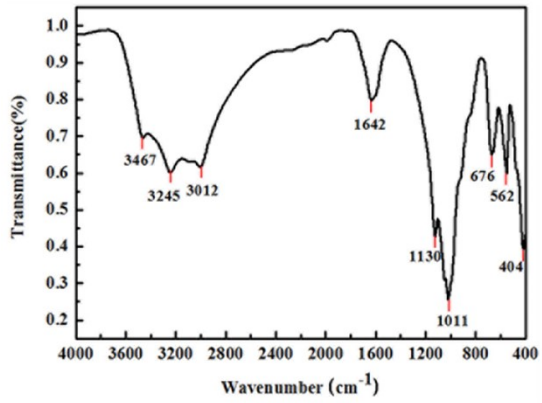
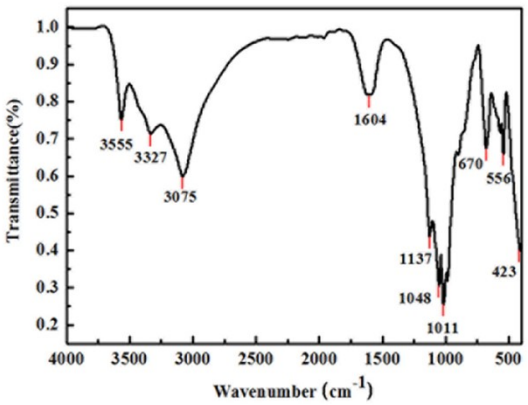


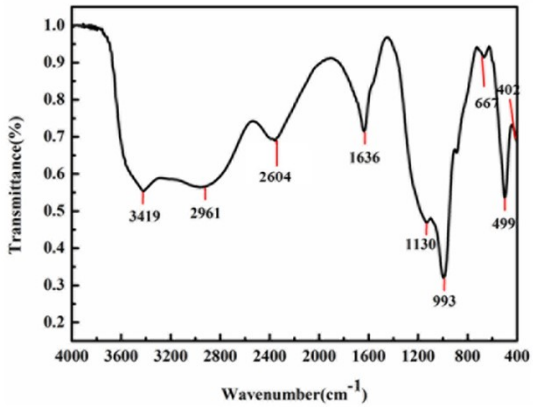
Figure S3 The arrangement of (a) Ca^{2+} cations; (b) Sr^{2+} cations and (c) Ba^{2+} cations.

Sr^{2+}

Figure S4 The IR spectra of (a) **1**; (b) **2** and (c) **3**.



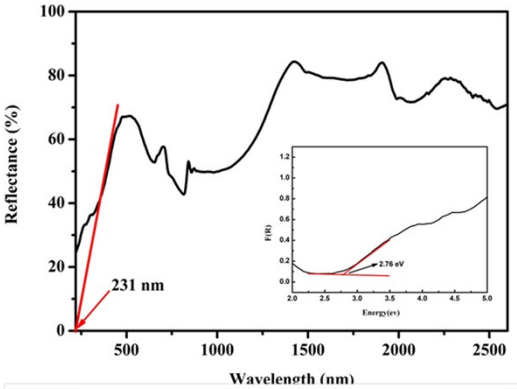


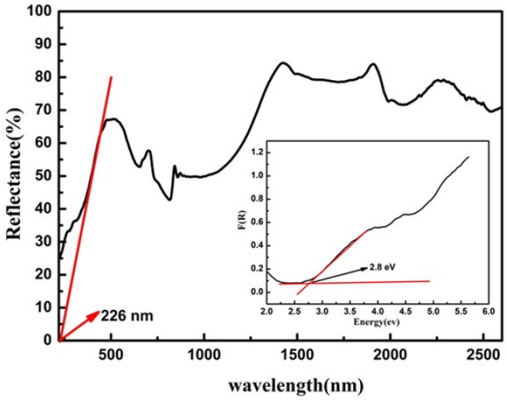


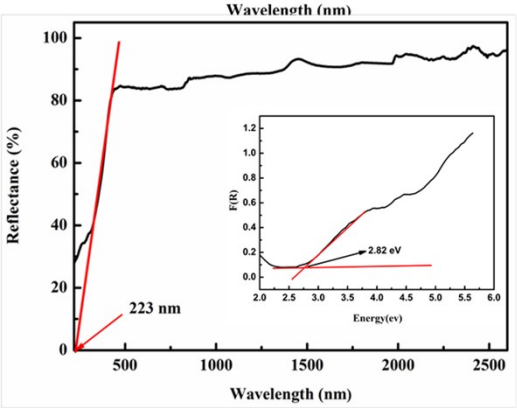
(a) (b)

(c)

Figure S5 The UV-*vis*-NIR diffuse reflectance spectra of (a) **1**; (b) **2** and (c) **3**.







(a) (b)
(c)

Figure S6 Antiparallel arrangement of VO_6 groups and PO_4 tetrahedra in the $^2[V_2P_2O_{14}]_\infty$ layer. (A layer in **1** and **2**, B and C layers in **3**)

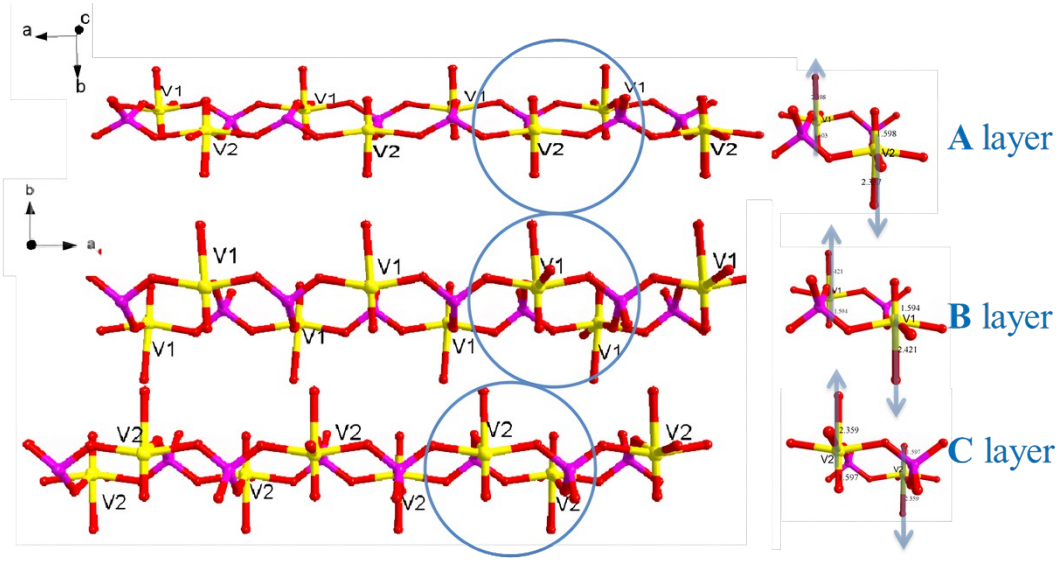


Figure S7 Band structures of (a) **1**; (b) **2** and (c) **3**.

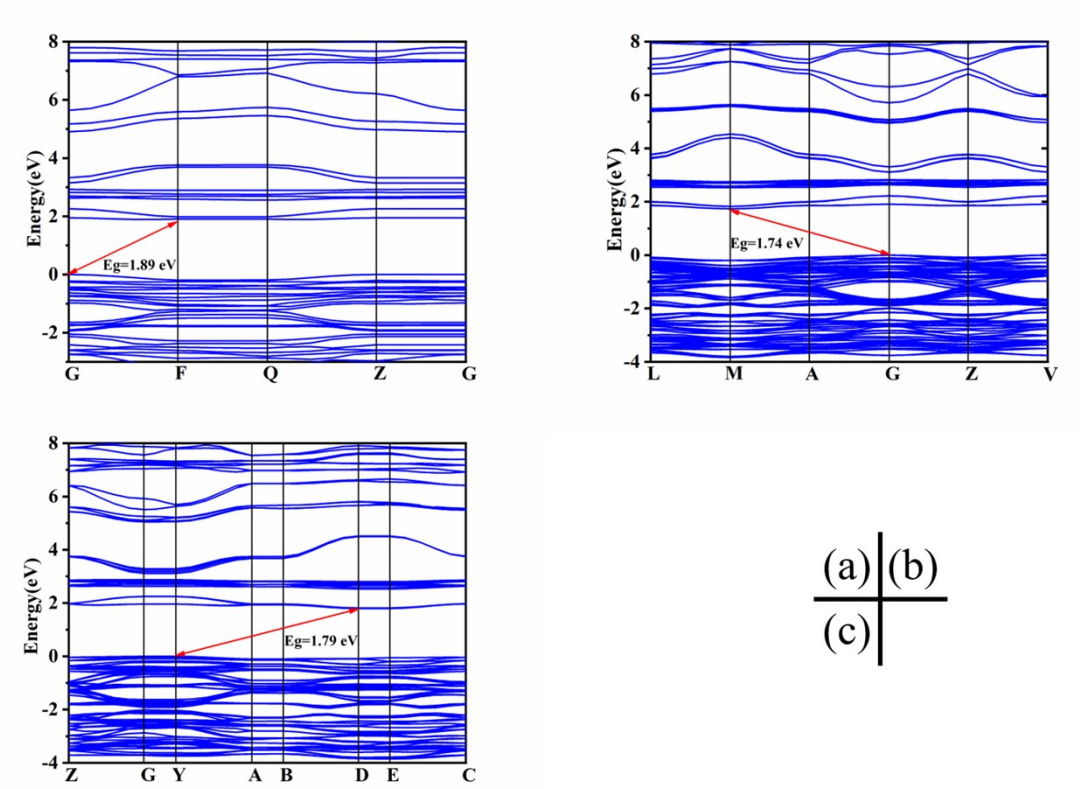


Figure S8 Electron localization function diagrams of (a) **1**; (b) **2** and (c) **3**.