Electronic Supplementary Information

Four Noncentrosymmetric Molybdophosphates Discovered by Chemical Substitution Strategy

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Experimental Section

Compound Synthesis.

Reagents: Na_2CO_3 (99.9 %), K_2CO_3 (99.0 %), Rb_2CO_3 (99.0 %), Cs_2CO_3 (99.0 %), MoO_3 (99.0 %), $NH_4H_2PO_4$ (99.0 %) from Aladdin Chemical Industry Co., Ltd. were used as received from commercial sources without any further purification.

The single crystals of $A_xB_{4-x}Mo_5P_2O_{22}$ (A = Na, K, B = Rb, Cs) were obtained through spontaneous crystallization. The stoichiometric reagents of $(A/B)_2CO_3$, (A = Na, K, B = Rb, Cs), MoO_3, and $NH_4H_2PO_4$ were mixed thoroughly and placed in platinum crucibles, which were further placed in vertical, programmable temperature furnaces. The mixtures were heated to 780 ℃, held at this temperature for 12 h, and then slowly cooled down to 400 ℃ at a rate of 3 ℃·h^{-1}, followed by rapid cooling to room temperature. The crystals were separated mechanically from the crucible, and polycrystalline powder was obtained by grinding single crystals from spontaneous crystallization for performance characterization.

Single Crystal X-ray Diffraction.

Selected high−quality single crystals with a suitable size were used for structural characterization. The selected single crystals were stuck to a glass fiber separately to collect the crystal structure data by a Bruker D8 Venture diffractometer with Mo target (Kα radiation, wavelength λ = 0.71073 Å) at room temperature. The program SAINT was utilized to perform data integration, cell refinement, and absorption corrections. The structure models were solved under the direct method and refined through the full matrix least−squares fitting on F^2 with OLEX2 and SHELXTL programs.[1-2] The structural validity of them was confirmed by the ADDSYM algorithm from PLATON.[3] Table S6 shows the crystal data and structure refinements. The atomic coordinates, equivalent isotropic displacement parameters, and BVS calculations are given in Table S1. Selected bond lengths and angles are listed in Tables S2−5.

Powder X-ray Diffraction.

Powder X−ray diffraction (XRD) data of polycrystalline materials were obtained via a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation (λ = 0.71073 Å) at room temperature. The 2θ range, step size, and fixed counting time were adjusted to 10−70°, step size 0.02°, and 1 s/step, respectively. No impurities were observed, and the experimental powder XRD profiles are in good agreement with the calculated ones derived from the single−crystal data (Figure S2).

Thermal Analysis.

Thermal gravimetric (TG) and differential scanning calorimetry (DSC) were carried out on a NETZSCH STA 449C instrument at a temperature range of 50−650 ℃ with a heating rate of 5 ℃·min^{-1} in an atmosphere of flowing N_2.

Optical Spectroscopy.

The IR performance of $A_xB_{4-x}Mo_5P_2O_{22}$ (A = Na, K, B = Rb, Cs) in the wavelength region 400−4000 cm^{-1} was inspected via a Shimadzu IR Affinity−1 spectrometer at room temperature. The powder sample (nearly 5 mg) was mixed well with about 500 mg of dried KBr (99.9% purity) and compressed into thin cylindrical plates. Meanwhile, the UV diffuse reflectance data of the four compounds were collected with a Shimadzu SolidSpec−3700DUV spectrophotometer at room temperature; the measurement was carried out within the wavelength region 245−2500 nm. By using the Kubelka−Munk function[4] collected UV reflectance spectrum data was translated into absorbance data.

Powder SHG Measurement.

This measurement was operated according to the Kurtz−Perry method using a Q−switched Nd: YVO_4 solid−state laser at 1064 nm.[5] The polycrystalline samples underwent grinding and sieving, resulting in the classification of particles into specific size ranges as follows: 38−55, 55−88, 88−105, 105−150, 150−200, and 200−250 μm. KDP samples were used as the reference.

Theoretical Calculations.

The optical properties and electronic structures were investigated by utilizing CASTEP based on density functional theory, a plane−wave pseudopotential total energy package.[6-7] The generalized gradient approximation (GGA) with the Perdew−Burke−Ernzerhof exchange−correlation functional was opted for all the calculations,[8-9] with the energy cutoffs 750 eV. Norm−conserving pseudopotentials were used, and valence electrons were established by considering the following orbital electrons: O $2s^2 2p^4$, Na $3s^1$, P $3s^2 3p^3$, K $4s^1$, Rb $5s^1$, Cs $6s^1$.[10] In the Brillouin zone corresponding to the primitive cell, the k−point separation for $K_4Mo_5P_2O_{22}$, $KCs_3Mo_5P_2O_{22}$, and $NaRb_3Mo_5P_2O_{22}$ were set as 0.02, 0.04, and 0.04 $Å^{-1}$ respectively. The value of the scissor operator was set as the difference between the experimental band gap and the band gap calculated by the GGA method for the calculation of optical properties. The refractive indices were determined from the real part of the dielectric constant, which was obtained by a Kramers−Kronig transformation of the calculated imaginary part of the dielectric function.

Table S1. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3), and bond valence sum (BVS) calculations for $K_4Mo_5P_2O_{22}$, $K_2Rb_2Mo_5P_2O_{22}$, $KCs_3Mo_5P_2O_{22}$, and $NaRb_3Mo_5P_2O_{22}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U($_{eq}$)	BVS
		$K_4Mo_5P_2O_{22}$			
K(1)	5406(3)	7400(1)	3972(1)	42(1)	0.992
K(2)	475(4)	5000	5000	47(1)	0.723
K(3)	10000	4228(1)	7500	31(1)	1.292
Mo(1)	5000	7447(1)	7500	16(1)	6.119
Mo(2)	5753(1)	6441(1)	5900(1)	20(1)	6.107
Mo(3)	5021(1)	4759(1)	6410(1)	19(1)	6.033
P(1)	7812(3)	5947(1)	7680(1)	16(1)	5.060
O(1)	6753(9)	7996(3)	7924(3)	27(1)	2.161
O(2)	6669(8)	7157(3)	6631(3)	20(1)	2.074
O(3)	4062(10)	6916(3)	5350(3)	32(1)	2.090
O(4)	7998(10)	6424(3)	5374(4)	39(1)	1.903
O(5)	6689(8)	6538(2)	8098(3)	17(1)	2.021
O(6)	10000	6294(3)	7500	26(2)	2.157
O(7)	6844(8)	5766(2)	6887(3)	19(1)	1.949
O(8)	8078(8)	5316(2)	8176(3)	19(1)	1.965
O(9)	7410(9)	4460(3)	6145(3)	30(1)	1.974
O(10)	4691(8)	5529(2)	5709(3)	24(1)	2.041
O(11)	5000	4543(3)	7500	21(1)	2.123
O(12)	3364(9)	4151(3)	6047(3)	29(1)	1.929
		$K_2Rb_2Mo_5P_2O_{22}$			
K(1)	0	5790(1)	2500	30(1)	1.28
K(2)|0.5 (S.O.F.)	4630(2)	2640(1)	6017(1)	34(1)	1.24
Rb(1)	-446(3)	5000	5000	47(1)	0.83
Rb(2)|0.5 (S.O.F.)	4630(2)	2640(1)	6017(1)	34(1)	1.24
Mo(1)	4999(1)	5264(1)	3573(1)	19(1)	6.06
Mo(2)	4285(1)	3580(1)	4078(1)	20(1)	6.14
Mo(3)	5000	2574(1)	2500	17(1)	6.23
P(1)	2185(3)	4076(1)	2332(1)	16(1)	4.99
O(1)	6647(12)	5873(4)	3928(5)	30(2)	1.97
O(2)	2644(12)	5571(4)	3832(5)	30(2)	2.00
O(3)	5000	5481(4)	2500	21(2)	2.10
O(4)	5320(11)	4497(3)	4261(4)	24(2)	2.06
O(5)	3159(10)	4260(3)	3113(4)	20(1)	1.91

O(6)	1953(10)	4710(3)	1840(4)	21(2)	1.96
O(7)	0	3729(4)	2500	25(2)	2.13
O(8)	3309(9)	3485(3)	1925(4)	18(1)	2.01
O(9)	3261(11)	2022(3)	2100(4)	27(2)	2.26
O(10)	3395(10)	2864(4)	3366(4)	22(2)	2.13
O(11)	5994(13)	3111(4)	4617(4)	35(2)	2.14
O(12)	2099(13)	3581(4)	4607(5)	38(2)	2.03
		$KCs_3Mo_5P_2O_{22}$			
K(1)	0	836(3)	7500	37(1)	1.19
Cs(1)	4657(3)	5000	5000	41(1)	0.81
Cs(2)	4724(2)	2330(1)	5995(1)	40(1)	1.35
Mo(1)	0	2630(1)	7500	21(1)	6.35
Mo(2)	60(3)	5300(1)	6466(1)	23(1)	6.16
Mo(3)	625(2)	3634(1)	9035(1)	24(1)	6.15
P(1)	2824(6)	4119(2)	7359(3)	19(1)	5.12
O(1)	2720(30)	3624(8)	9575(8)	38(4)	2.11
O(2)	-1120(30)	3203(7)	9555(8)	39(4)	2.18
O(3)	1492(19)	2914(6)	8364(8)	25(3)	2.16
O(4)	1730(20)	2079(6)	7156(8)	29(3)	2.31
O(5)	5000	3780(8)	7500	28(4)	2.12
O(6)	1700(19)	3548(6)	6965(7)	19(2)	2.02
O(7)	3040(20)	4753(6)	6896(8)	24(3)	1.92
O(8)	0	5497(8)	7500	29(4)	2.19
O(9)	-1890(20)	4303(6)	6891(7)	25(3)	1.93
O(10)	360(20)	4556(6)	5788(7)	31(3)	2.05
O(11)	1690(20)	5888(7)	6119(9)	33(3)	2.12
O(12)	-2220(20)	5640(7)	6203(8)	31(3)	1.99
		$NaRb_3Mo_5P_2O_{22}$			
Na(1)	10000	5751(3)	2500	36(2)	0.75
Rb(1)	5387(2)	2645(1)	6019(1)	36(1)	1.22
Rb(2)	10458(4)	5000	5000	55(1)	0.80
Mo(1)	5679(2)	3572(1)	4055(1)	26(1)	6.22
Mo(2)	4975(2)	5306(1)	3555(1)	27(1)	6.25
Mo(3)	5000	2522(1)	2500	26(1)	6.16
P(1)	7826(5)	4087(2)	2342(2)	22(1)	5.06
O(1)	3274(16)	1948(5)	2880(6)	36(3)	2.15
O(2)	6559(14)	2831(5)	3368(5)	27(2)	2.12
O(3)	6709(13)	3487(5)	1941(5)	24(2)	2.03
O(4)	3979(16)	3108(5)	4584(5)	35(3)	2.21
O(5)	7870(17)	3602(6)	4576(6)	39(3)	2.00
O(6)	4598(15)	4514(4)	4219(5)	33(2)	2.10
O(7)	7310(16)	5604(6)	3806(6)	38(3)	2.02
O(8)	3335(17)	5919(5)	3911(6)	38(3)	2.04

O(9)	10000	3726(6)	2500	27(3)	2.13
O(10)	6870(15)	4269(5)	3111(5)	24(2)	1.93
O(11)	8101(14)	4753(5)	1874(5)	28(2)	1.85
O(12)	5000	5520(6)	2500	29(3)	2.07

(BVS)*： The bond valence sums were calculated using the formula $V_i = \sum S_{ij} = \sum \exp[(r_0 - r_{ij}) / B]$, where S_{ij} is the bond valence associated with bond length r_{ij}, and r_0 and B (usually 0.37) are empirically determined parameters.

Table S2. Selected bond lengths (Å) and angles (°) for $KCs_3Mo_5P_2O_{22}$.

K(1)-O(4)	2.742(13)	Cs(2)-O(6)	3.546(13)
K(1)-O(4)#3	2.742(13)	Cs(2)-O(11)#4	3.099(15)
K(1)-O(7)#1	2.694(14)	Cs(2)-O(12)#4	3.548(15)
K(1)-O(7)#2	2.694(14)	Mo(1)-O(3)	1.910(13)
K(1)-O(8)#1	3.352(3)	Mo(1)-O(3)#3	1.910(13)
K(1)-O(8)#4	3.352(3)	Mo(1)-O(4)	1.679(14)
K(1)-O(11)#1	3.289(16)	Mo(1)-O(4)#3	1.679(14)
K(1)-O(11)#2	3.289(16)	Mo(1)-O(6)	2.313(12)
K(1)-O(12)#4	2.973(15)	Mo(1)-O(6)#3	2.313(12)
K(1)-O(12)#5	2.973(15)	Mo(2)-O(7)	2.360(13)
Cs(1)-O(1)#9	3.274(16)	Mo(2)-O(8)	1.887(3)
Cs(1)-O(1)#10	3.274(16)	Mo(2)-O(9)	2.447(13)
Cs(1)-O(7)	3.581(14)	Mo(2)-O(10)	1.899(12)
Cs(1)-O(7)#8	3.581(14)	Mo(2)-O(11)	1.687(14)
Cs(1)-O(10)	3.269(14)	Mo(2)-O(12)	1.707(14)
Cs(1)-O(10)#8	3.269(14)	Mo(3)-O(1)	1.680(15)
Cs(1)-O(11)	3.282(15)	Mo(3)-O(2)	1.698(15)
Cs(1)-O(11)#8	3.282(15)	Mo(3)-O(3)	1.929(14)
Cs(1)-O(12)#6	3.221(14)	Mo(3)-O(6)#3	2.356(11)
Cs(1)-O(12)#7	3.221(14)	Mo(3)-O(9)#3	2.264(14)
Cs(2)-O(1)#10	3.194(16)	Mo(3)-O(10)#3	1.935(11)
Cs(2)-O(1)#11	3.530(16)	P(1)-O(5)	1.595(8)
Cs(2)-O(2)#3	3.074(16)	P(1)-O(6)	1.508(12)
Cs(2)-O(2)#11	2.923(15)	P(1)-O(7)	1.493(13)
Cs(2)-O(3)#10	2.964(12)	P(1)-O(9)#3	1.516(14)
Cs(2)-O(4)	2.901(15)		
O(7)#1-K(1)-O(7)#2	77.1(6)	O(7)-Cs(1)-O(7)#8	145.6(4)
O(7)#1-K(1)-O(4)#3	125.6(4)	O(4)-Cs(2)-O(2)#11	141.5(4)
O(7)#2-K(1)-O(4)#3	142.9(4)	O(4)-Cs(2)-O(3)#10	111.0(4)
O(7)#1-K(1)-O(4)	142.9(4)	O(2)#11-Cs(2)-O(3)#10	102.3(4)
O(7)#2-K(1)-O(4)	125.6(4)	O(4)-Cs(2)-O(2)#3	78.4(4)
O(4)#3-K(1)-O(4)	56.2(6)	O(2)#11-Cs(2)-O(2)#3	99.0(3)
O(7)#1-K(1)-O(12)#4	83.1(4)	O(3)#10-Cs(2)-O(2)#3	123.9(4)
O(7)#2-K(1)-O(12)#4	85.4(4)	O(4)-Cs(2)-O(11)#4	94.6(4)
O(4)#3-K(1)-O(12)#4	122.8(4)	O(2)#11-Cs(2)-O(11)#4	67.0(4)
O(4)-K(1)-O(12)#4	71.6(4)	O(3)#10-Cs(2)-O(11)#4	88.2(4)
O(7)#1-K(1)-O(12)#5	85.4(4)	O(2)#3-Cs(2)-O(11)#4	147.6(4)
O(7)#2-K(1)-O(12)#5	83.1(4)	O(4)-Cs(2)-O(1)#10	135.9(4)
O(4)#3-K(1)-O(12)#5	71.6(4)	O(2)#11-Cs(2)-O(1)#10	80.4(4)
O(4)-K(1)-O(12)#5	122.8(4)	O(3)#10-Cs(2)-O(1)#10	51.7(4)
O(12)#4-K(1)-O(12)#5	165.3(6)	O(2)#3-Cs(2)-O(1)#10	82.4(4)
O(7)#1-K(1)-O(11)#2	129.8(4)	O(11)#4-Cs(2)-O(1)#10	121.1(4)
O(7)#2-K(1)-O(11)#2	53.7(4)	O(4)-Cs(2)-O(1)#11	96.7(4)

O(4)#3-K(1)-O(11)#2	94.5(4)	O(2)#11-Cs(2)-O(1)#11	47.4(4)
O(4)-K(1)-O(11)#2	82.4(4)	O(3)#10-Cs(2)-O(1)#11	149.4(4)
O(12)#4-K(1)-O(11)#2	100.5(4)	O(2)#3-Cs(2)-O(1)#11	73.2(4)
O(12)#5-K(1)-O(11)#2	79.9(4)	O(11)#4-Cs(2)-O(1)#11	76.4(4)
O(7)#1-K(1)-O(11)#1	53.7(4)	O(1)#10-Cs(2)-O(1)#11	115.1(2)
O(7)#2-K(1)-O(11)#1	129.8(4)	O(4)-Cs(2)-O(6)	51.9(3)
O(4)#3-K(1)-O(11)#1	82.4(4)	O(2)#11-Cs(2)-O(6)	147.5(4)
O(4)-K(1)-O(11)#1	94.5(4)	O(3)#10-Cs(2)-O(6)	91.5(3)
O(12)#4-K(1)-O(11)#1	79.9(4)	O(2)#3-Cs(2)-O(6)	49.8(3)
O(12)#5-K(1)-O(11)#1	100.5(4)	O(11)#4-Cs(2)-O(6)	143.6(3)
O(11)#2-K(1)-O(11)#1	176.5(5)	O(1)#10-Cs(2)-O(6)	85.7(3)
O(7)#1-K(1)-O(8)#1	51.6(4)	O(1)#11-Cs(2)-O(6)	116.6(3)
O(7)#2-K(1)-O(8)#1	108.3(4)	O(4)-Cs(2)-O(12)#4	61.6(3)
O(4)#3-K(1)-O(8)#1	76.5(4)	O(2)#11-Cs(2)-O(12)#4	82.9(4)
O(4)-K(1)-O(8)#1	125.4(4)	O(3)#10-Cs(2)-O(12)#4	128.1(3)
O(12)#4-K(1)-O(8)#1	125.2(3)	O(2)#3-Cs(2)-O(12)#4	105.5(4)
O(12)#5-K(1)-O(8)#1	51.2(3)	O(11)#4-Cs(2)-O(12)#4	45.9(3)
O(11)#2-K(1)-O(8)#1	130.8(3)	O(1)#10-Cs(2)-O(12)#4	162.5(4)
O(11)#1-K(1)-O(8)#1	50.1(3)	O(1)#11-Cs(2)-O(12)#4	54.8(3)
O(7)#1-K(1)-O(8)#4	108.3(4)	O(6)-Cs(2)-O(12)#4	111.5(3)
O(7)#2-K(1)-O(8)#4	51.6(4)	O(4)-Mo(1)-O(4)#3	100.6(9)
O(4)#3-K(1)-O(8)#4	125.4(4)	O(4)-Mo(1)-O(3)	97.6(6)
O(4)-K(1)-O(8)#4	76.5(4)	O(4)#3-Mo(1)-O(3)	103.6(6)
O(12)#4-K(1)-O(8)#4	51.2(3)	O(4)-Mo(1)-O(3)#3	103.6(6)
O(12)#5-K(1)-O(8)#4	125.2(3)	O(4)#3-Mo(1)-O(3)#3	97.6(6)
O(11)#2-K(1)-O(8)#4	50.1(3)	O(3)-Mo(1)-O(3)#3	146.5(7)
O(11)#1-K(1)-O(8)#4	130.8(3)	O(4)-Mo(1)-O(6)	90.9(5)
O(8)#1-K(1)-O(8)#4	157.3(5)	O(4)#3-Mo(1)-O(6)	166.2(6)
O(12)#6-Cs(1)-O(12)#7	100.9(5)	O(3)-Mo(1)-O(6)	82.1(5)
O(12)#6-Cs(1)-O(10)	111.4(3)	O(3)#3-Mo(1)-O(6)	72.0(5)
O(12)#7-Cs(1)-O(10)	137.3(3)	O(4)-Mo(1)-O(6)#3	166.2(6)
O(12)#6-Cs(1)-O(10)#8	137.3(3)	O(4)#3-Mo(1)-O(6)#3	90.9(5)
O(12)#7-Cs(1)-O(10)#8	111.4(3)	O(3)-Mo(1)-O(6)#3	72.0(5)
O(10)-Cs(1)-O(10)#8	60.7(5)	O(3)#3-Mo(1)-O(6)#3	82.1(5)
O(12)#6-Cs(1)-O(1)#9	60.2(4)	O(6)-Mo(1)-O(6)#3	78.9(6)
O(12)#7-Cs(1)-O(1)#9	80.0(4)	O(11)-Mo(2)-O(12)	101.3(8)
O(10)-Cs(1)-O(1)#9	140.4(3)	O(11)-Mo(2)-O(8)	103.6(6)
O(10)#8-Cs(1)-O(1)#9	98.0(4)	O(12)-Mo(2)-O(8)	99.9(5)
O(12)#6-Cs(1)-O(1)#10	80.0(4)	O(11)-Mo(2)-O(10)	102.4(6)
O(12)#7-Cs(1)-O(1)#10	60.2(4)	O(12)-Mo(2)-O(10)	102.2(7)
O(10)-Cs(1)-O(1)#10	98.0(4)	O(8)-Mo(2)-O(10)	141.5(6)
O(10)#8-Cs(1)-O(1)#10	140.4(3)	O(11)-Mo(2)-O(7)	84.0(6)
O(1)#9-Cs(1)-O(1)#10	116.4(6)	O(12)-Mo(2)-O(7)	174.6(6)
O(12)#6-Cs(1)-O(11)#8	171.0(3)	O(8)-Mo(2)-O(7)	77.9(4)

O(12)#7-Cs(1)-O(11)#8	76.6(3)	O(10)-Mo(2)-O(7)	77.1(5)
O(10)-Cs(1)-O(11)#8	67.1(4)	O(11)-Mo(2)-O(9)	170.2(6)
O(10)#8-Cs(1)-O(11)#8	50.6(3)	O(12)-Mo(2)-O(9)	86.0(6)
O(1)#9-Cs(1)-O(11)#8	127.0(4)	O(8)-Mo(2)-O(9)	81.2(5)
O(1)#10-Cs(1)-O(11)#8	91.4(3)	O(10)-Mo(2)-O(9)	69.4(5)
O(12)#6-Cs(1)-O(11)	76.6(3)	O(7)-Mo(2)-O(9)	88.7(5)
O(12)#7-Cs(1)-O(11)	171.0(3)	O(1)-Mo(3)-O(2)	103.5(8)
O(10)-Cs(1)-O(11)	50.6(3)	O(1)-Mo(3)-O(3)	96.1(6)
O(10)#8-Cs(1)-O(11)	67.1(4)	O(2)-Mo(3)-O(3)	100.4(7)
O(1)#9-Cs(1)-O(11)	91.4(3)	O(1)-Mo(3)-O(10)#3	101.0(7)
O(1)#10-Cs(1)-O(11)	127.0(4)	O(2)-Mo(3)-O(10)#3	98.1(7)
O(11)#8-Cs(1)-O(11)	107.2(5)	O(3)-Mo(3)-O(10)#3	151.0(5)
O(12)#6-Cs(1)-O(7)	67.0(3)	O(1)-Mo(3)-O(9)#3	97.1(6)
O(12)#7-Cs(1)-O(7)	140.1(3)	O(2)-Mo(3)-O(9)#3	158.8(7)
O(10)-Cs(1)-O(7)	45.7(3)	O(3)-Mo(3)-O(9)#3	81.7(5)
O(10)#8-Cs(1)-O(7)	100.8(3)	O(10)#3-Mo(3)-O(9)#3	73.1(5)
O(1)#9-Cs(1)-O(7)	119.0(3)	O(1)-Mo(3)-O(6)#3	164.9(7)
O(1)#10-Cs(1)-O(7)	80.0(3)	O(2)-Mo(3)-O(6)#3	86.6(6)
O(11)#8-Cs(1)-O(7)	109.3(4)	O(3)-Mo(3)-O(6)#3	70.7(5)
O(11)-Cs(1)-O(7)	47.1(3)	O(10)#3-Mo(3)-O(6)#3	88.4(5)
O(12)#6-Cs(1)-O(7)#8	140.1(3)	O(9)#3-Mo(3)-O(6)#3	74.1(5)
O(12)#7-Cs(1)-O(7)#8	67.0(3)	O(7)-P(1)-O(6)	113.4(8)
O(10)-Cs(1)-O(7)#8	100.8(3)	O(7)-P(1)-O(9)#3	109.5(7)
O(10)#8-Cs(1)-O(7)#8	45.7(3)	O(6)-P(1)-O(9)#3	112.9(7)
O(1)#9-Cs(1)-O(7)#8	80.0(3)	O(7)-P(1)-O(5)	110.0(7)
O(1)#10-Cs(1)-O(7)#8	119.0(3)	O(6)-P(1)-O(5)	102.0(7)
O(11)#8-Cs(1)-O(7)#8	47.1(3)	O(9)#3-P(1)-O(5)	108.7(6)
O(11)-Cs(1)-O(7)#8	109.3(4)		

Symmetry transformations used to generate equivalent atoms:

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

Table S3. Selected bond lengths (Å) and angles (°) for $K_4Mo_5P_2O_{22}$.

K(1)-O(1)#2	2.665(6)	K(3)-O(12)#8	3.291(6)
K(1)-O(2)#1	2.752(5)	K(3)-O(12)#12	3.291(6)
K(1)-O(3)	2.667(6)	Mo(1)-O(1)	1.706(5)
K(1)-O(3)#3	2.933(7)	Mo(1)-O(1)#8	1.706(5)
K(1)-O(4)#1	2.960(6)	Mo(1)-O(2)	1.911(5)
K(1)-O(5)#2	3.144(5)	Mo(1)-O(2)#8	1.911(5)
K(1)-O(12)#4	3.259(6)	Mo(1)-O(5)	2.297(5)
K(2)-O(4)#5	3.233(7)	Mo(1)-O(5)#8	2.296(5)
K(2)-O(4)#6	3.233(7)	Mo(2)-O(2)	1.948(5)
K(2)-O(8)#7	3.296(5)	Mo(2)-O(3)	1.703(6)
K(2)-O(8)#8	3.296(5)	Mo(2)-O(4)	1.700(6)
K(2)-O(9)#5	2.961(6)	Mo(2)-O(5)#8	2.328(5)
K(2)-O(9)#6	2.961(6)	Mo(2)-O(7)	2.236(5)
K(2)-O(10)	3.141(5)	Mo(2)-O(10)	1.911(5)
K(2)-O(10)#4	3.141(5)	Mo(3)-O(7)	2.406(5)
K(2)-O(12)	3.050(6)	Mo(3)-O(8)#8	2.373(5)
K(2)-O(12)#4	3.050(6)	Mo(3)-O(9)	1.703(6)
K(3)-O(1)#9	2.722(5)	Mo(3)-O(10)	1.912(5)
K(3)-O(1)#11	2.722(5)	Mo(3)-O(11)	1.9010(15)
K(3)-O(8)	2.691(5)	Mo(3)-O(12)	1.699(5)
K(3)-O(8)#10	2.691(5)	P(1)-O(5)	1.523(5)
K(3)-O(9)	2.881(6)	P(1)-O(6)	1.589(3)
K(3)-O(9)#10	2.881(6)	P(1)-O(7)	1.526(5)
K(3)-O(11)	3.2771(12)	P(1)-O(8)	1.488(5)
K(3)-O(11)#12	3.2771(12)		
O(1)#2-K(1)-O(2)#1	116.08(18)	O(8)-K(3)-O(1)#11	126.86(17)
O(1)#2-K(1)-O(3)	135.34(19)	O(8)#10-K(3)-O(1)#9	126.86(16)
O(1)#2-K(1)-O(3)#3	80.78(17)	O(8)#10-K(3)-O(1)#11	139.01(15)
O(1)#2-K(1)-O(4)#1	146.0(2)	O(8)#10-K(3)-O(8)	77.8(2)
O(1)#2-K(1)-O(5)#2	57.36(14)	O(8)-K(3)-O(9)	87.42(15)
O(1)#2-K(1)-O(12)#4	90.53(16)	O(8)-K(3)-O(9)#10	78.66(16)
O(2)#1-K(1)-O(3)#3	135.22(17)	O(8)#10-K(3)-O(9)	78.66(16)
O(2)#1-K(1)-O(4)#1	56.29(16)	O(8)#10-K(3)-O(9)#10	87.42(15)
O(2)#1-K(1)-O(5)#2	98.21(15)	O(8)-K(3)-O(11)	53.42(14)
O(2)#1-K(1)-O(12)#4	85.81(16)	O(8)-K(3)-O(11)#12	107.95(15)
O(3)-K(1)-O(2)#1	98.74(19)	O(8)#10-K(3)-O(11)	107.95(15)
O(3)-K(1)-O(3)#3	94.08(14)	O(8)#10-K(3)-O(11)#12	53.42(14)
O(3)-K(1)-O(4)#1	76.47(19)	O(8)-K(3)-O(12)#8	53.91(13)
O(3)#3-K(1)-O(4)#1	86.00(18)	O(8)-K(3)-O(12)#12	131.24(16)
O(3)-K(1)-O(5)#2	146.68(17)	O(8)#10-K(3)-O(12)#8	131.24(15)
O(3)#3-K(1)-O(5)#2	54.34(14)	O(8)#10-K(3)-O(12)#12	53.91(13)
O(3)-K(1)-O(12)#4	63.81(16)	O(9)-K(3)-O(9)#10	162.1(2)
O(3)#3-K(1)-O(12)#4	137.55(16)	O(9)-K(3)-O(11)	53.29(12)

O(4)#1-K(1)-O(5)#2	89.60(17)	O(9)-K(3)-O(11)#12	122.71(13)
O(4)#1-K(1)-O(12)#4	119.45(19)	O(9)#10-K(3)-O(11)	122.71(13)
O(5)#2-K(1)-O(12)#4	146.09(14)	O(9)#10-K(3)-O(11)#12	53.29(12)
O(4)#5-K(2)-O(4)#6	120.8(2)	O(9)-K(3)-O(12)#8	103.12(15)
O(4)#5-K(2)-O(8)#7	78.33(14)	O(9)-K(3)-O(12)#12	77.71(15)
O(4)#5-K(2)-O(8)#8	118.77(14)	O(9)#10-K(3)-O(12)#8	77.71(15)
O(4)#6-K(2)-O(8)#7	118.77(14)	O(9)#10-K(3)-O(12)#12	103.12(15)
O(4)#6-K(2)-O(8)#8	78.33(14)	O(11)#12-K(3)-O(11)	158.7(2)
O(8)#8-K(2)-O(8)#7	147.2(2)	O(11)#12-K(3)-O(12)#8	130.96(10)
O(9)#5-K(2)-O(4)#5	80.70(16)	O(11)#12-K(3)-O(12)#12	50.30(10)
O(9)#5-K(2)-O(4)#6	60.23(16)	O(12)#8-K(3)-O(12)#12	174.8(2)
O(9)#6-K(2)-O(4)#5	60.23(16)	O(1)-Mo(1)-O(1)#8	103.6(3)
O(9)#6-K(2)-O(4)#6	80.70(16)	O(1)-Mo(1)-O(2)#8	103.1(2)
O(9)#5-K(2)-O(8)#7	68.54(15)	O(1)#8-Mo(1)-O(2)	103.1(2)
O(9)#5-K(2)-O(8)#8	137.98(15)	O(1)#8-Mo(1)-O(2)#8	97.8(2)
O(9)#6-K(2)-O(8)#7	137.98(15)	O(1)-Mo(1)-O(2)	97.8(2)
O(9)#6-K(2)-O(8)#8	68.54(15)	O(1)-Mo(1)-O(5)	88.3(2)
O(9)#5-K(2)-O(9)#6	96.4(2)	O(1)-Mo(1)-O(5)#8	166.4(2)
O(9)#5-K(2)-O(10)	135.70(14)	O(1)#8-Mo(1)-O(5)	166.4(2)
O(9)#5-K(2)-O(10)#4	115.93(15)	O(1)#8-Mo(1)-O(5)#8	88.3(2)
O(9)#6-K(2)-O(10)	115.93(15)	O(2)-Mo(1)-O(2)#8	146.0(3)
O(9)#6-K(2)-O(10)#4	135.70(14)	O(2)-Mo(1)-O(5)	81.56(19)
O(9)#5-K(2)-O(12)	168.11(14)	O(2)-Mo(1)-O(5)#8	72.6(2)
O(9)#5-K(2)-O(12)#4	80.50(16)	O(2)#8-Mo(1)-O(5)	72.65(19)
O(9)#6-K(2)-O(12)	80.50(16)	O(2)#8-Mo(1)-O(5)#8	81.56(19)
O(9)#6-K(2)-O(12)#4	168.11(14)	O(5)#8-Mo(1)-O(5)	80.8(2)
O(10)-K(2)-O(4)#5	140.95(15)	O(2)-Mo(2)-O(5)#8	71.31(19)
O(10)-K(2)-O(4)#6	94.41(15)	O(2)-Mo(2)-O(7)	80.53(19)
O(10)#4-K(2)-O(4)#5	94.41(15)	O(3)-Mo(2)-O(2)	99.5(2)
O(10)#4-K(2)-O(4)#6	140.95(15)	O(3)-Mo(2)-O(5)#8	85.8(2)
O(10)-K(2)-O(8)#7	100.19(14)	O(3)-Mo(2)-O(7)	157.8(2)
O(10)-K(2)-O(8)#8	48.25(13)	O(3)-Mo(2)-O(10)	99.9(2)
O(10)#4-K(2)-O(8)#7	48.25(13)	O(4)-Mo(2)-O(2)	95.3(3)
O(10)#4-K(2)-O(8)#8	100.19(14)	O(4)-Mo(2)-O(3)	105.4(3)
O(10)#4-K(2)-O(10)	60.31(19)	O(4)-Mo(2)-O(5)#8	164.1(3)
O(12)-K(2)-O(4)#5	87.85(14)	O(4)-Mo(2)-O(7)	96.7(3)
O(12)-K(2)-O(4)#6	129.79(16)	O(4)-Mo(2)-O(10)	101.4(3)
O(12)#4-K(2)-O(4)#5	129.79(16)	O(7)-Mo(2)-O(5)#8	73.07(18)
O(12)#4-K(2)-O(4)#6	87.84(14)	O(10)-Mo(2)-O(2)	150.0(2)
O(12)-K(2)-O(8)#7	106.15(15)	O(10)-Mo(2)-O(5)#8	87.5(2)
O(12)-K(2)-O(8)#8	51.46(13)	O(10)-Mo(2)-O(7)	72.95(19)
O(12)#4-K(2)-O(8)#7	51.46(13)	O(8)#8-Mo(3)-O(7)	86.93(17)
O(12)#4-K(2)-O(8)#8	106.14(15)	O(9)-Mo(3)-O(7)	85.4(2)
O(12)-K(2)-O(10)	54.65(14)	O(9)-Mo(3)-O(8)#8	172.3(2)

O(12)-K(2)-O(10)#4	61.53(14)	O(9)-Mo(3)-O(10)	101.3(3)
O(12)#4-K(2)-O(10)	61.53(14)	O(9)-Mo(3)-O(11)	101.0(2)
O(12)#4-K(2)-O(10)#4	54.65(14)	O(10)-Mo(3)-O(7)	68.98(19)
O(12)-K(2)-O(12)#4	104.8(2)	O(10)-Mo(3)-O(8)#8	75.0(2)
O(1)#11-K(3)-O(1)#9	59.0(2)	O(11)-Mo(3)-O(7)	81.4(2)
O(1)#9-K(3)-O(9)	125.99(17)	O(11)-Mo(3)-O(8)#8	78.65(15)
O(1)#9-K(3)-O(9)#10	71.50(16)	O(11)-Mo(3)-O(10)	140.9(2)
O(1)#11-K(3)-O(9)	71.50(16)	O(12)-Mo(3)-O(7)	169.5(2)
O(1)#11-K(3)-O(9)#10	125.99(17)	O(12)-Mo(3)-O(8)#8	83.7(2)
O(1)#9-K(3)-O(11)	124.66(16)	O(12)-Mo(3)-O(9)	103.8(3)
O(1)#9-K(3)-O(11)#12	75.71(15)	O(12)-Mo(3)-O(10)	103.7(2)
O(1)#11-K(3)-O(11)	75.71(15)	O(12)-Mo(3)-O(11)	101.5(2)
O(1)#11-K(3)-O(11)#12	124.66(16)	O(5)-P(1)-O(6)	101.4(3)
O(1)#9-K(3)-O(12)#8	91.99(16)	O(5)-P(1)-O(7)	112.9(3)
O(1)#9-K(3)-O(12)#12	83.50(16)	O(7)-P(1)-O(6)	106.7(2)
O(1)#11-K(3)-O(12)#8	83.50(16)	O(8)-P(1)-O(5)	113.5(3)
O(1)#11-K(3)-O(12)#12	91.99(16)	O(8)-P(1)-O(6)	110.5(3)
O(8)-K(3)-O(1)#9	139.01(15)	O(8)-P(1)-O(7)	111.3(3)

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Selected bond lengths (Å) and angles (°) for $K_2Rb_2Mo_5P_2O_{22}$.

K(1)-O(3)	3.2985(16)	Rb(2)-O(1)#2	3.146(8)
K(1)-O(3)#8	3.2985(16)	Rb(2)-O(12)#4	3.040(8)
K(1)-O(6)	2.687(7)	Rb(2)-O(12)	3.454(9)
K(1)-O(6)#10	2.687(7)	Mo(1)-O(3)	1.904(2)
K(1)-O(9)#13	2.712(7)	Mo(1)-O(4)	1.907(6)
K(1)-O(9)#14	2.712(7)	Mo(1)-O(5)	2.405(7)
K(1)-O(2)#10	2.906(8)	Mo(1)-O(6)#3	2.357(7)
K(1)-O(2)	2.906(8)	Mo(1)-O(2)	1.698(7)
K(1)-O(1)#3	3.297(8)	Mo(1)-O(1)	1.700(7)
K(1)-O(1)#8	3.297(8)	Mo(2)-O(4)	1.913(6)
K(2)-O(11)	2.735(8)	Mo(2)-O(5)	2.245(7)
Rb(1)-O(4)#8	3.182(7)	Mo(2)-O(10)	1.936(7)
Rb(1)-O(4)#9	3.182(7)	Mo(2)-O(8)#3	2.343(6)
Rb(1)-O(6)#10	3.380(7)	Mo(2)-O(11)	1.708(8)
Rb(1)-O(6)#11	3.380(7)	Mo(2)-O(12)	1.689(8)
Rb(1)-O(2)#2	3.052(8)	Mo(3)-O(10)#3	1.908(7)
Rb(1)-O(2)	3.052(8)	Mo(3)-O(10)	1.908(7)
Rb(1)-O(1)#8	3.134(8)	Mo(3)-O(8)#3	2.295(7)
Rb(1)-O(1)#9	3.134(8)	Mo(3)-O(8)	2.295(7)
Rb(1)-O(12)	3.261(8)	Mo(3)-O(9)	1.696(7)
Rb(1)-O(12)#2	3.261(8)	Mo(3)-O(9)#3	1.696(7)
Rb(2)-O(10)#4	2.837(7)	P(1)-O(5)	1.534(7)
Rb(2)-O(8)#12	3.285(6)	P(1)-O(8)	1.522(7)
Rb(2)-O(11)#7	2.975(9)	P(1)-O(6)	1.495(7)
Rb(2)-O(11)	2.735(8)	P(1)-O(7)	1.594(4)
Rb(2)-O(9)#12	2.732(7)		
O(1)#8-K(1)-O(3)	131.12(14)	O(4)#8-Rb(1)-O(6)#11	100.36(17)
O(1)#8-K(1)-O(3)#8	50.18(13)	O(4)#9-Rb(1)-O(6)#10	100.36(17)
O(1)#3-K(1)-O(3)	50.18(13)	O(4)#9-Rb(1)-O(6)#11	47.21(17)
O(1)#3-K(1)-O(3)#8	131.12(14)	O(4)#8-Rb(1)-O(6)#10	47.21(17)
O(1)#8-K(1)-O(1)#3	174.5(3)	O(4)#8-Rb(1)-O(12)	95.68(19)
O(2)#10-K(1)-O(3)#8	52.63(14)	O(4)#9-Rb(1)-O(12)#2	95.68(19)
O(2)-K(1)-O(3)#8	123.68(16)	O(4)#8-Rb(1)-O(12)#2	140.86(18)
O(2)#10-K(1)-O(3)	123.68(16)	O(4)#9-Rb(1)-O(12)	140.86(18)
O(2)-K(1)-O(3)	52.63(14)	O(6)#10-Rb(1)-O(6)#11	146.4(2)
O(2)#10-K(1)-O(2)	163.3(3)	O(12)-Rb(1)-O(6)#11	118.75(19)
O(2)#10-K(1)-O(1)#8	102.28(19)	O(12)#2-Rb(1)-O(6)#10	118.75(19)
O(2)-K(1)-O(1)#3	102.29(19)	O(12)#2-Rb(1)-O(6)#11	79.17(19)
O(2)-K(1)-O(1)#8	78.53(19)	O(12)-Rb(1)-O(6)#10	79.17(19)
O(2)#10-K(1)-O(1)#3	78.53(19)	O(12)-Rb(1)-O(12)#2	119.2(3)
O(3)-K(1)-O(3)#8	159.2(3)	O(1)#2-Rb(2)-O(8)#12	145.66(18)
O(6)-K(1)-O(3)	52.90(19)	O(1)#2-Rb(2)-O(12)	75.1(2)
O(6)#10-K(1)-O(3)#8	52.90(19)	O(8)#12-Rb(2)-O(12)	114.02(18)

O(6)#10-K(1)-O(3)	108.9(2)	O(9)#12-Rb(2)-O(10)#4	114.5(2)
O(6)-K(1)-O(3)#8	108.9(2)	O(9)#12-Rb(2)-O(8)#12	55.21(18)
O(6)#10-K(1)-O(6)	78.8(3)	O(9)#12-Rb(2)-O(11)	138.8(2)
O(6)-K(1)-O(9)#13	139.6(2)	O(9)#12-Rb(2)-O(11)#7	79.9(2)
O(6)#10-K(1)-O(9)#14	139.6(2)	O(9)#12-Rb(2)-O(1)#2	92.8(2)
O(6)#10-K(1)-O(9)#13	125.9(2)	O(9)#12-Rb(2)-O(12)	92.0(2)
O(6)-K(1)-O(9)#14	125.9(2)	O(9)#12-Rb(2)-O(12)#4	142.2(2)
O(6)-K(1)-O(2)	87.0(2)	O(10)#4-Rb(2)-O(8)#12	95.44(18)
O(6)#10-K(1)-O(2)#10	87.0(2)	O(10)#4-Rb(2)-O(11)#7	131.0(2)
O(6)-K(1)-O(2)#10	80.1(2)	O(10)#4-Rb(2)-O(1)#2	86.6(2)
O(6)#10-K(1)-O(2)	80.1(2)	O(10)#4-Rb(2)-O(12)	148.7(2)
O(6)-K(1)-O(1)#8	131.8(2)	O(10)#4-Rb(2)-O(12)#4	54.3(2)
O(6)#10-K(1)-O(1)#8	53.64(19)	O(11)-Rb(2)-O(10)#4	99.7(2)
O(6)-K(1)-O(1)#3	53.64(19)	O(11)#7-Rb(2)-O(8)#12	52.91(19)
O(6)#10-K(1)-O(1)#3	131.8(2)	O(11)-Rb(2)-O(8)#12	146.1(2)
O(9)#13-K(1)-O(3)#8	75.4(2)	O(11)-Rb(2)-O(11)#7	95.15(18)
O(9)#13-K(1)-O(3)	124.5(2)	O(11)-Rb(2)-O(1)#2	65.9(2)
O(9)#14-K(1)-O(3)	75.4(2)	O(11)#7-Rb(2)-O(1)#2	141.4(2)
O(9)#14-K(1)-O(3)#8	124.5(2)	O(11)-Rb(2)-O(12)	49.8(2)
O(9)#14-K(1)-O(9)#13	58.4(3)	O(11)#7-Rb(2)-O(12)	67.4(2)
O(9)#13-K(1)-O(2)	125.1(2)	O(11)-Rb(2)-O(12)#4	76.7(2)
O(9)#14-K(1)-O(2)#10	125.1(2)	O(11)#7-Rb(2)-O(12)#4	85.0(2)
O(9)#13-K(1)-O(2)#10	71.2(2)	O(12)#4-Rb(2)-O(8)#12	88.2(2)
O(9)#14-K(1)-O(2)	71.2(2)	O(12)#4-Rb(2)-O(1)#2	119.5(2)
O(9)#14-K(1)-O(1)#8	92.4(2)	O(12)#4-Rb(2)-O(12)	113.78(15)
O(9)#13-K(1)-O(1)#3	92.4(2)	O(1)-Mo(1)-O(3)	101.7(3)
O(9)#14-K(1)-O(1)#3	82.8(2)	O(1)-Mo(1)-O(4)	103.8(3)
O(9)#13-K(1)-O(1)#8	82.8(2)	O(1)-Mo(1)-O(5)	169.8(3)
O(10)#4-K(2)-O(8)#12	95.44(18)	O(1)-Mo(1)-O(6)#3	83.8(3)
O(10)#4-K(2)-O(11)#7	131.0(2)	O(2)-Mo(1)-O(1)	103.4(4)
O(10)#4-K(2)-O(1)#2	86.6(2)	O(2)-Mo(1)-O(3)	100.5(3)
O(10)#4-K(2)-O(12)#4	54.3(2)	O(2)-Mo(1)-O(4)	101.6(3)
O(11)-K(2)-O(10)#4	99.7(2)	O(2)-Mo(1)-O(5)	85.4(3)
O(11)#7-K(2)-O(8)#12	52.91(19)	O(2)-Mo(1)-O(6)#3	172.7(3)
O(11)-K(2)-O(8)#12	146.1(2)	O(3)-Mo(1)-O(4)	141.1(3)
O(11)-K(2)-O(11)#7	95.15(18)	O(3)-Mo(1)-O(5)	81.5(3)
O(11)#7-K(2)-O(1)#2	141.4(2)	O(3)-Mo(1)-O(6)#3	78.6(2)
O(11)-K(2)-O(1)#2	65.9(2)	O(4)-Mo(1)-O(5)	68.9(2)
O(11)-K(2)-O(12)#4	76.7(2)	O(4)-Mo(1)-O(6)#3	75.5(3)
O(11)#7-K(2)-O(12)#4	85.0(2)	O(4)-Mo(2)-O(5)	72.6(3)
O(9)#12-K(2)-O(10)#4	114.5(2)	O(4)-Mo(2)-O(10)	149.9(3)
O(9)#12-K(2)-O(8)#12	55.21(18)	O(4)-Mo(2)-O(8)#3	87.7(3)
O(9)#12-K(2)-O(11)	138.8(2)	O(5)-Mo(2)-O(8)#3	73.1(2)
O(9)#12-K(2)-O(11)#7	79.9(2)	O(10)-Mo(2)-O(5)	81.0(3)

O(9)#12-K(2)-O(1)#2	92.8(2)	O(10)-Mo(2)-O(8)#3	70.8(3)
O(9)#12-K(2)-O(12)#4	142.2(2)	O(11)-Mo(2)-O(4)	99.7(3)
O(1)#9-Rb(1)-O(4)#9	53.46(17)	O(11)-Mo(2)-O(5)	157.9(3)
O(1)#8-Rb(1)-O(4)#8	53.46(17)	O(11)-Mo(2)-O(10)	99.6(3)
O(1)#8-Rb(1)-O(4)#9	63.63(19)	O(11)-Mo(2)-O(8)#3	86.1(3)
O(1)#9-Rb(1)-O(4)#8	63.63(19)	O(12)-Mo(2)-O(4)	101.8(3)
O(1)#9-Rb(1)-O(6)#11	49.86(18)	O(12)-Mo(2)-O(5)	97.5(3)
O(1)#9-Rb(1)-O(6)#10	107.24(19)	O(12)-Mo(2)-O(10)	95.5(3)
O(1)#8-Rb(1)-O(6)#11	107.24(19)	O(12)-Mo(2)-O(8)#3	164.2(3)
O(1)#8-Rb(1)-O(6)#10	49.86(18)	O(12)-Mo(2)-O(11)	104.4(4)
O(1)#9-Rb(1)-O(1)#8	106.0(3)	O(6)#3-Mo(1)-O(5)	87.4(2)
O(1)#8-Rb(1)-O(12)#2	88.88(19)	O(8)-Mo(3)-O(8)#3	80.4(3)
O(1)#9-Rb(1)-O(12)	88.88(19)	O(9)-Mo(3)-O(8)	89.0(3)
O(1)#9-Rb(1)-O(12)#2	129.0(2)	O(9)#3-Mo(3)-O(8)	166.6(3)
O(1)#8-Rb(1)-O(12)	129.0(2)	O(9)#3-Mo(3)-O(8)#3	89.0(3)
O(2)-Rb(1)-O(4)#9	136.44(18)	O(9)-Mo(3)-O(8)#3	166.6(3)
O(2)#2-Rb(1)-O(4)#8	136.44(18)	O(9)#3-Mo(3)-O(9)	102.6(5)
O(2)#2-Rb(1)-O(4)#9	114.21(19)	O(9)-Mo(3)-O(10)	98.1(3)
O(2)-Rb(1)-O(4)#8	114.21(19)	O(9)-Mo(3)-O(10)#3	103.0(3)
O(2)-Rb(1)-O(6)#11	139.07(18)	O(9)#3-Mo(3)-O(10)	103.0(3)
O(2)#2-Rb(1)-O(6)#10	139.07(18)	O(9)#3-Mo(3)-O(10)#3	98.1(3)
O(2)-Rb(1)-O(6)#10	67.95(19)	O(10)-Mo(3)-O(8)	81.7(3)
O(2)#2-Rb(1)-O(6)#11	67.95(19)	O(10)#3-Mo(3)-O(8)	72.4(3)
O(2)-Rb(1)-O(2)#2	97.8(3)	O(10)-Mo(3)-O(8)#3	72.4(3)
O(2)#2-Rb(1)-O(1)#9	79.1(2)	O(10)#3-Mo(3)-O(10)	146.0(4)
O(2)#2-Rb(1)-O(1)#8	168.69(18)	O(10)#3-Mo(3)-O(8)#3	81.7(3)
O(2)-Rb(1)-O(1)#8	79.1(2)	O(5)-P(1)-O(7)	107.6(3)
O(2)-Rb(1)-O(1)#9	168.69(18)	O(8)-P(1)-O(5)	112.5(4)
O(2)-Rb(1)-O(12)#2	60.3(2)	O(8)-P(1)-O(7)	101.5(4)
O(2)#2-Rb(1)-O(12)#2	80.2(2)	O(6)-P(1)-O(5)	110.8(4)
O(2)#2-Rb(1)-O(12)	60.3(2)	O(6)-P(1)-O(8)	113.2(4)
O(2)-Rb(1)-O(12)	80.2(2)	O(6)-P(1)-O(7)	110.8(4)
O(4)#8-Rb(1)-O(4)#9	60.6(2)		

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Selected bond lengths (Å) and angles (°) for $NaRb_3Mo_5P_2O_{22}$.

Na(1)-O(1)#2	2.587(11)	Rb(2)-O(11)#11	3.453(10)
Na(1)-O(1)#4	2.587(11)	Mo(1)-O(2)	1.921(10)
Na(1)-O(7)	2.902(11)	Mo(1)-O(3)#12	2.347(9)
Na(1)-O(7)#3	2.902(11)	Mo(1)-O(4)	1.686(10)
Na(1)-O(11)	2.490(10)	Mo(1)-O(5)	1.699(10)
Na(1)-O(11)#3	2.490(10)	Mo(1)-O(6)	1.912(8)
Rb(1)-O(1)#7	2.804(10)	Mo(1)-O(10)	2.244(9)
Rb(1)-O(2)#5	2.861(9)	Mo(2)-O(6)	1.898(9)
Rb(1)-O(3)#8	3.264(9)	Mo(2)-O(7)	1.681(10)
Rb(1)-O(4)	2.818(10)	Mo(2)-O(8)	1.686(10)
Rb(1)-O(4)#7	2.929(11)	Mo(2)-O(10)	2.423(9)
Rb(1)-O(5)	3.497(11)	Mo(2)-O(11)#12	2.378(9)
Rb(1)-O(5)#5	3.031(11)	Mo(2)-O(12)	1.894(3)
Rb(1)-O(7)#6	3.509(11)	Mo(3)-O(1)	1.689(10)
Rb(1)-O(8)#6	2.994(10)	Mo(3)-O(1)#12	1.689(10)
Rb(2)-O(5)	3.191(11)	Mo(3)-O(2)	1.921(9)
Rb(2)-O(5)#6	3.191(10)	Mo(3)-O(2)#12	1.921(9)
Rb(2)-O(6)#9	3.163(10)	Mo(3)-O(3)#12	2.333(9)
Rb(2)-O(6)#10	3.163(10)	Mo(3)-O(3)	2.333(9)
Rb(2)-O(7)	3.143(11)	P(1)-O(3)	1.509(9)
Rb(2)-O(7)#6	3.144(11)	P(1)-O(9)	1.595(6)
Rb(2)-O(8)#9	3.180(11)	P(1)-O(10)	1.526(9)
Rb(2)-O(8)#10	3.180(11)	P(1)-O(11)	1.500(10)
Rb(2)-O(11)#3	3.453(10)		
O(1)#4-Na(1)-O(1)#2	60.8(5)	O(7)-Rb(2)-O(6)#9	138.2(2)
O(1)#2-Na(1)-O(7)	67.3(3)	O(7)#6-Rb(2)-O(6)#9	111.8(3)
O(1)#4-Na(1)-O(7)	123.3(3)	O(7)-Rb(2)-O(6)#10	111.8(3)
O(1)#2-Na(1)-O(7)#3	123.3(3)	O(7)-Rb(2)-O(7)#6	98.4(4)
O(1)#4-Na(1)-O(7)#3	67.3(3)	O(7)#6-Rb(2)-O(8)#9	78.0(3)
O(7)-Na(1)-O(7)#3	169.2(5)	O(7)#6-Rb(2)-O(8)#10	168.4(2)
O(11)-Na(1)-O(1)#4	138.3(3)	O(7)-Rb(2)-O(8)#9	168.4(2)
O(11)#3-Na(1)-O(1)#2	138.3(3)	O(7)-Rb(2)-O(8)#10	78.0(3)
O(11)-Na(1)-O(1)#2	122.7(3)	O(7)-Rb(2)-O(11)#11	140.0(2)
O(11)#3-Na(1)-O(1)#4	122.7(3)	O(7)#6-Rb(2)-O(11)#3	140.0(2)
O(11)#3-Na(1)-O(7)#3	88.7(3)	O(7)#6-Rb(2)-O(11)#11	65.8(3)
O(11)-Na(1)-O(7)#3	83.2(3)	O(7)-Rb(2)-O(11)#3	65.8(3)
O(11)-Na(1)-O(7)	88.7(3)	O(8)#9-Rb(2)-O(5)	90.8(2)
O(11)#3-Na(1)-O(7)	83.2(3)	O(8)#10-Rb(2)-O(5)#6	90.8(2)
O(11)-Na(1)-O(11)#3	83.5(5)	O(8)#9-Rb(2)-O(5)#6	127.7(3)
O(1)#7-Rb(1)-O(2)#5	114.3(3)	O(8)#10-Rb(2)-O(5)	127.7(3)
O(1)#7-Rb(1)-O(3)#8	56.1(3)	O(8)#9-Rb(2)-O(8)#10	107.6(4)
O(1)#7-Rb(1)-O(4)	138.9(3)	O(8)#10-Rb(2)-O(11)#3	48.5(2)
O(1)#7-Rb(1)-O(4)#7	80.8(3)	O(8)#9-Rb(2)-O(11)#11	48.5(2)

O(1)#7-Rb(1)-O(5)	92.9(3)	O(8)#9-Rb(2)-O(11)#3	109.9(3)
O(1)#7-Rb(1)-O(5)#5	144.0(3)	O(8)#10-Rb(2)-O(11)#11	109.9(3)
O(1)#7-Rb(1)-O(7)#6	56.5(3)	O(11)#11-Rb(2)-O(11)#3	148.4(3)
O(1)#7-Rb(1)-O(8)#6	91.8(3)	O(2)-Mo(1)-O(3)#12	71.5(3)
O(2)#5-Rb(1)-O(3)#8	96.9(2)	O(2)-Mo(1)-O(10)	81.3(3)
O(2)#5-Rb(1)-O(4)#7	133.4(3)	O(4)-Mo(1)-O(2)	100.0(4)
O(2)#5-Rb(1)-O(5)#5	54.5(3)	O(4)-Mo(1)-O(3)#12	86.5(4)
O(2)#5-Rb(1)-O(5)	146.6(3)	O(4)-Mo(1)-O(5)	105.9(5)
O(2)#5-Rb(1)-O(7)#6	124.6(3)	O(4)-Mo(1)-O(6)	98.3(5)
O(2)#5-Rb(1)-O(8)#6	82.6(3)	O(4)-Mo(1)-O(10)	158.7(4)
O(3)#8-Rb(1)-O(5)	114.8(2)	O(5)-Mo(1)-O(2)	96.3(4)
O(3)#8-Rb(1)-O(7)#6	110.5(2)	O(5)-Mo(1)-O(3)#12	164.2(4)
O(4)-Rb(1)-O(2)#5	98.4(3)	O(5)-Mo(1)-O(6)	101.5(4)
O(4)-Rb(1)-O(3)#8	146.1(3)	O(5)-Mo(1)-O(10)	95.0(4)
O(4)#7-Rb(1)-O(3)#8	53.5(2)	O(6)-Mo(1)-O(2)	149.8(4)
O(4)-Rb(1)-O(4)#7	94.8(2)	O(6)-Mo(1)-O(3)#12	85.9(4)
O(4)-Rb(1)-O(5)	49.2(3)	O(6)-Mo(1)-O(10)	73.0(4)
O(4)-Rb(1)-O(5)#5	75.5(3)	O(10)-Mo(1)-O(3)#12	73.7(3)
O(4)#7-Rb(1)-O(5)#5	86.7(3)	O(6)-Mo(2)-O(10)	69.1(3)
O(4)#7-Rb(1)-O(5)	67.1(3)	O(6)-Mo(2)-O(11)#12	75.4(4)
O(4)#7-Rb(1)-O(7)#6	101.0(3)	O(7)-Mo(2)-O(6)	102.3(5)
O(4)-Rb(1)-O(7)#6	84.8(3)	O(7)-Mo(2)-O(8)	104.7(5)
O(4)-Rb(1)-O(8)#6	67.5(3)	O(7)-Mo(2)-O(10)	83.4(4)
O(4)#7-Rb(1)-O(8)#6	143.1(3)	O(7)-Mo(2)-O(11)#12	172.4(4)
O(5)#5-Rb(1)-O(3)#8	89.5(3)	O(7)-Mo(2)-O(12)	100.4(4)
O(5)#5-Rb(1)-O(5)	113.09(17)	O(8)-Mo(2)-O(6)	102.5(5)
O(5)#5-Rb(1)-O(7)#6	159.5(3)	O(8)-Mo(2)-O(10)	169.7(4)
O(5)-Rb(1)-O(7)#6	54.8(2)	O(8)-Mo(2)-O(11)#12	82.8(4)
O(8)#6-Rb(1)-O(3)#8	144.7(3)	O(8)-Mo(2)-O(12)	103.1(4)
O(8)#6-Rb(1)-O(5)#5	117.1(3)	O(11)#12-Mo(2)-O(10)	89.1(3)
O(8)#6-Rb(1)-O(5)	77.4(3)	O(12)-Mo(2)-O(6)	140.0(4)
O(8)#6-Rb(1)-O(7)#6	47.6(3)	O(12)-Mo(2)-O(10)	81.3(3)
O(5)-Rb(2)-O(5)#6	116.1(4)	O(12)-Mo(2)-O(11)#12	77.8(3)
O(5)-Rb(2)-O(11)#3	79.2(2)	O(1)#12-Mo(3)-O(1)	101.6(7)
O(5)#6-Rb(2)-O(11)#3	118.4(2)	O(1)-Mo(3)-O(2)#12	98.6(4)
O(5)-Rb(2)-O(11)#11	118.4(2)	O(1)#12-Mo(3)-O(2)#12	103.3(4)
O(5)#6-Rb(2)-O(11)#11	79.2(2)	O(1)#12-Mo(3)-O(2)	98.6(4)
O(6)#9-Rb(2)-O(5)#6	96.7(3)	O(1)-Mo(3)-O(2)	103.3(4)
O(6)#10-Rb(2)-O(5)#6	141.9(2)	O(1)-Mo(3)-O(3)	166.5(4)
O(6)#10-Rb(2)-O(5)	96.7(3)	O(1)#12-Mo(3)-O(3)	90.1(4)
O(6)#9-Rb(2)-O(5)	141.9(2)	O(1)#12-Mo(3)-O(3)#12	166.5(4)
O(6)#9-Rb(2)-O(6)#10	62.6(3)	O(1)-Mo(3)-O(3)#12	90.1(4)
O(6)#10-Rb(2)-O(8)#9	66.5(3)	O(2)#12-Mo(3)-O(2)	145.1(5)
O(6)#10-Rb(2)-O(8)#10	52.3(2)	O(2)#12-Mo(3)-O(3)#12	81.3(3)

O(6)#9-Rb(2)-O(8)#9	52.3(2)	O(2)-Mo(3)-O(3)#12	71.8(3)
O(6)#9-Rb(2)-O(8)#10	66.5(3)	O(2)#12-Mo(3)-O(3)	71.8(3)
O(6)#9-Rb(2)-O(11)#11	46.8(2)	O(2)-Mo(3)-O(3)	81.3(3)
O(6)#9-Rb(2)-O(11)#3	102.6(2)	O(3)#12-Mo(3)-O(3)	79.1(5)
O(6)#10-Rb(2)-O(11)#11	102.6(2)	O(3)-P(1)-O(9)	101.5(5)
O(6)#10-Rb(2)-O(11)#3	46.8(2)	O(3)-P(1)-O(10)	112.4(5)
O(7)-Rb(2)-O(5)#6	61.2(3)	O(10)-P(1)-O(9)	107.7(4)
O(7)#6-Rb(2)-O(5)	61.2(3)	O(11)-P(1)-O(3)	114.5(5)
O(7)-Rb(2)-O(5)	77.9(3)	O(11)-P(1)-O(9)	109.8(5)
O(7)#6-Rb(2)-O(5)#6	77.9(3)	O(11)-P(1)-O(10)	110.5(6)
O(7)#6-Rb(2)-O(6)#10	138.2(2)		

Symmetry transformations used to generate equivalent atoms:

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

Table S6. Dipole moments (debye) of MoO_6, and PO_4 polyhedra in $K_4Mo_5P_2O_{22}$, $KCs_3Mo_5P_2O_{22}$, $Rb_4Mo_5P_2O_{22}$ and $Cs_4Mo_5P_2O_{22}$.

	$K_4Mo_5P_2O_{22}$	$KCs_3Mo_5P_2O_{22}$	$Rb_4Mo_5P_2O_{22}$	$Cs_4Mo_5P_2O_{22}$
$Mo(1)O_6$	2.40	2.05	6.71	6.50
$Mo(2)O_6$	3.17	2.61	6.19	7.04
$Mo(3)O_6$	4.89	2.85	6.07	7.23
$P(1)O_4$	2.90	2.19	2.89	2.67
$[Mo_5P_2O_{23}]^{6-}$ ring	3.11	2.63	8.96	8.37

Figure S1. TG-DSC curves of (a) $K_4Mo_5P_2O_{22}$, (b) $K_2Rb_2Mo_5P_2O_{22}$, (c) $KCs_3Mo_5P_2O_{22}$, and (d) $NaRb_3Mo_5P_2O_{22}$.

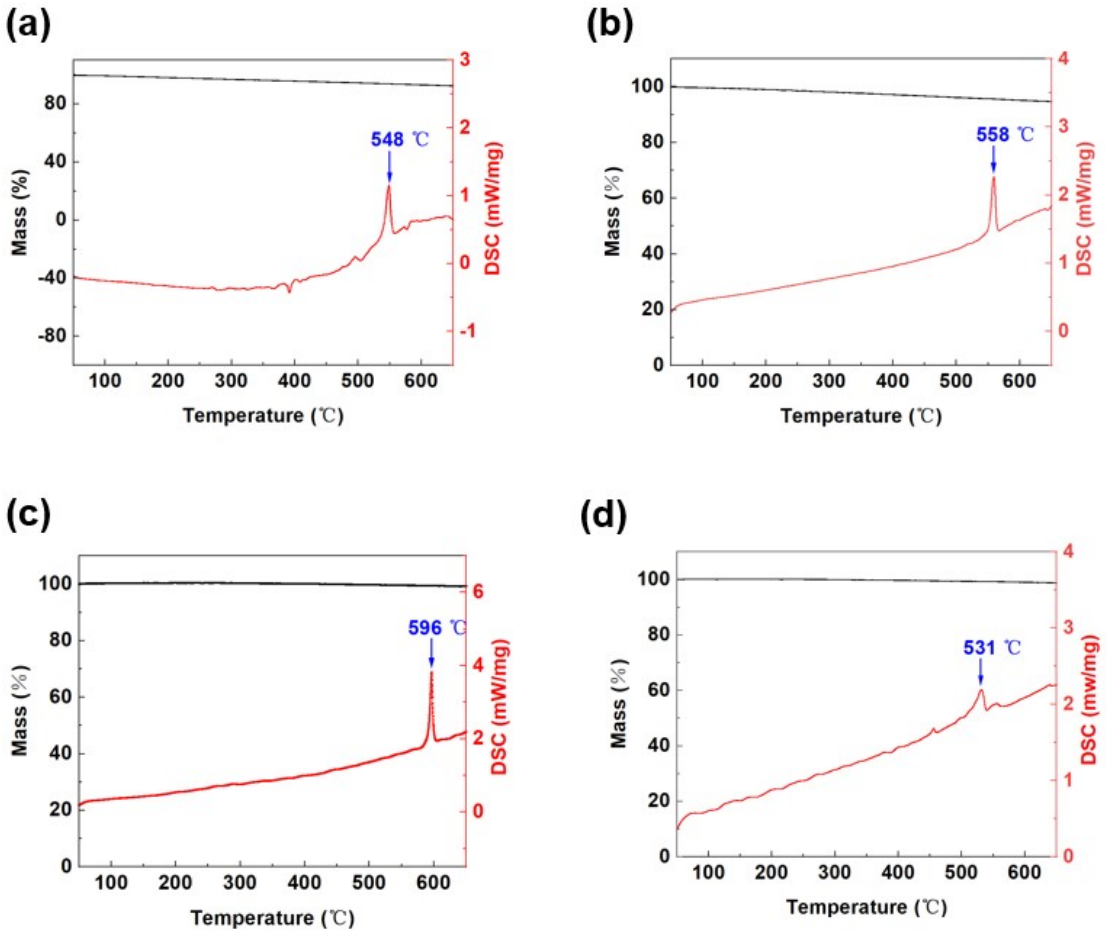


Figure S2. Calculated, experimental and after melting PXRD patterns for (a) $K_4Mo_5P_2O_{22}$, (b) $K_2Rb_2Mo_5P_2O_{22}$, (c) $KCs_3Mo_5P_2O_{22}$, and (d) $NaRb_3Mo_5P_2O_{22}$, (e) calculated PXRD comparison of $K_4Mo_5P_2O_{22}$ with $Cs_4Mo_5P_2O_{22}$ and $Rb_4Mo_5P_2O_{22}$.

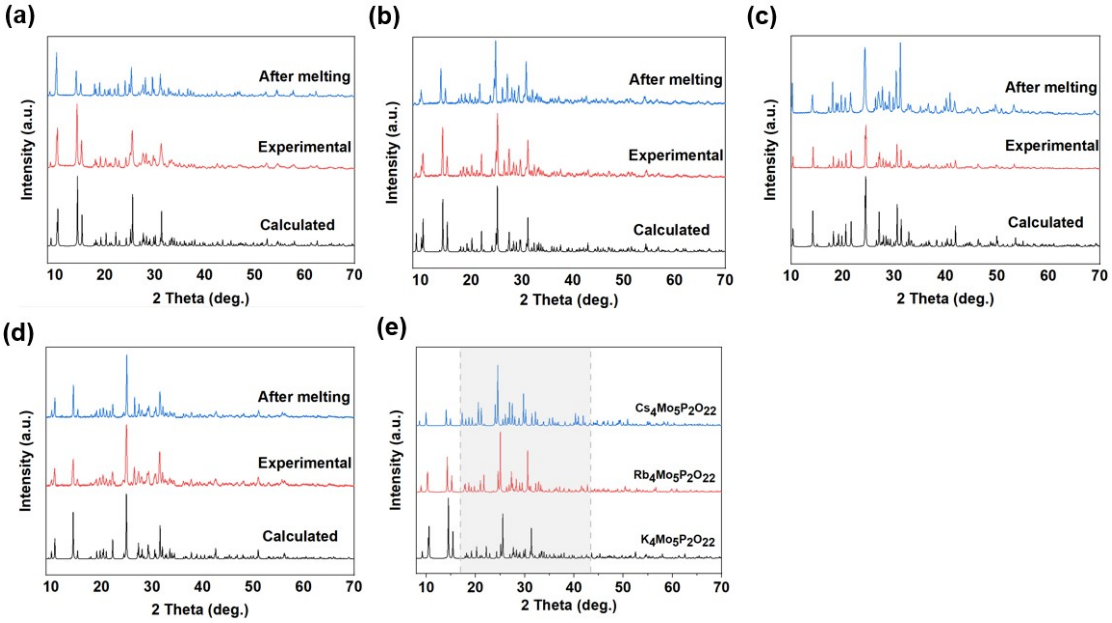


Figure S3. IR data for (a) $K_4Mo_5P_2O_{22}$, (b) $K_2Rb_2Mo_5P_2O_{22}$, (c) $KCs_3Mo_5P_2O_{22}$, and (d) $NaRb_3Mo_5P_2O_{22}$.

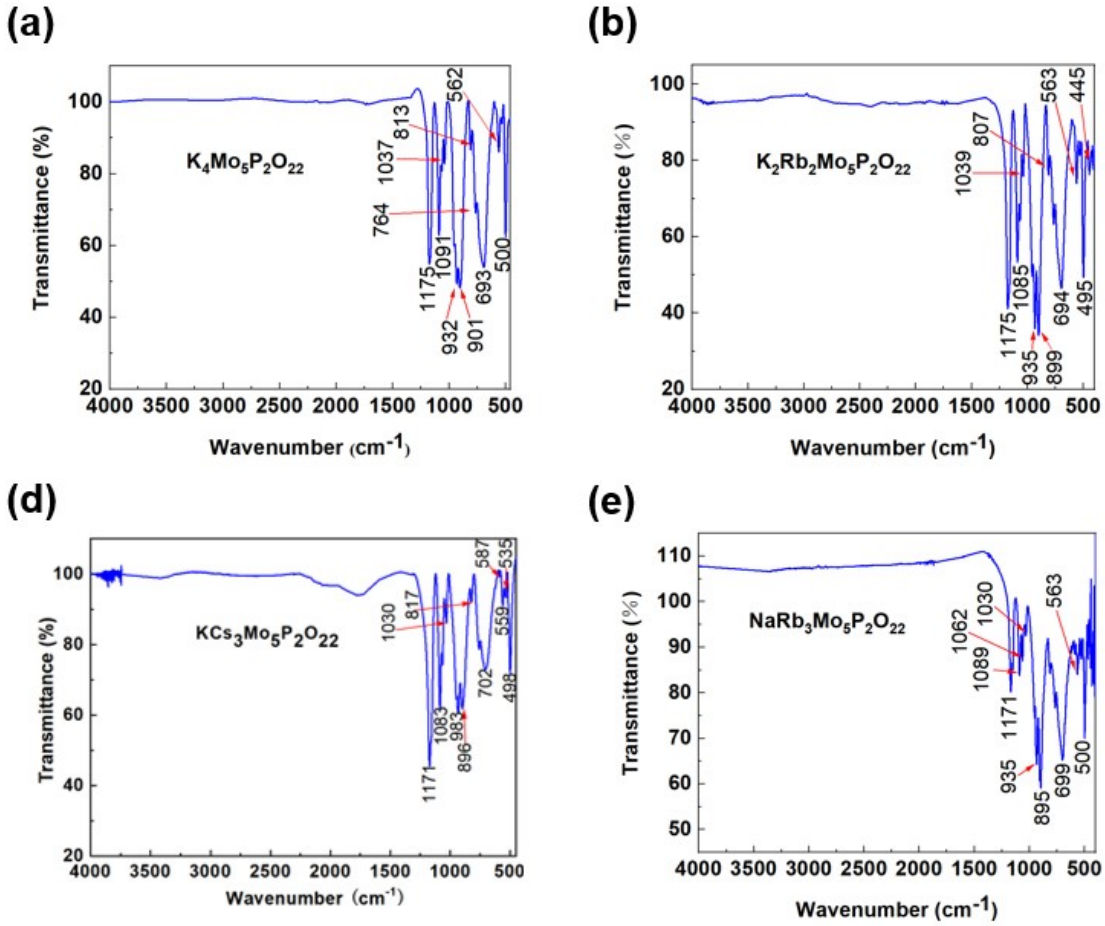


Figure S4. UV−Vis−NIR diffuse−reflectance spectra of (a) $K_4Mo_5P_2O_{22}$, (b) $K_2Rb_2Mo_5P_2O_{22}$, (c) $KCs_3Mo_5P_2O_{22}$, and (d) $NaRb_3Mo_5P_2O_{22}$.

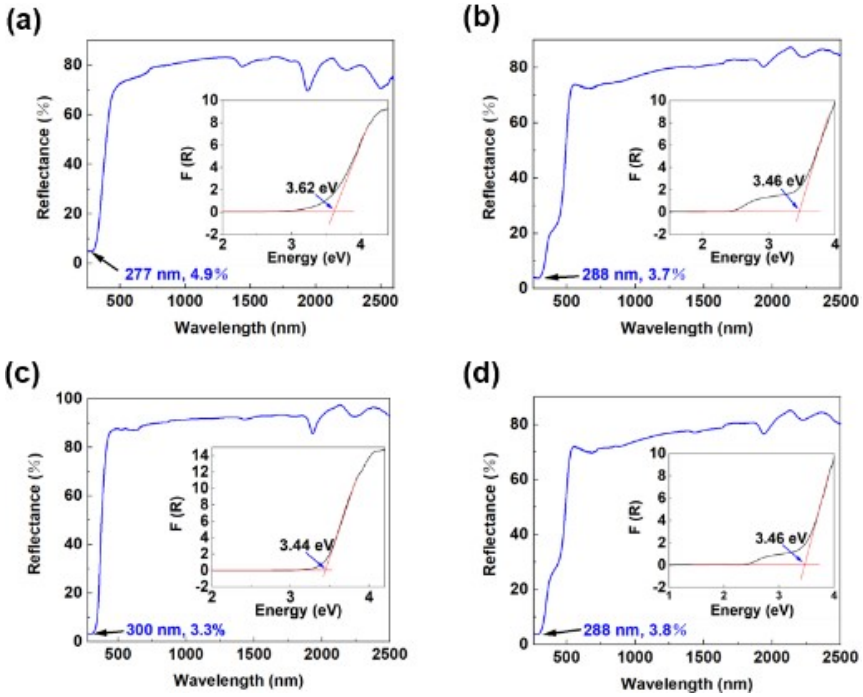


Figure S5. Oscilloscope traces of the SHG signals for the powders for KDP, $K_4Mo_5P_2O_{22}$ (a), and (b) $KCs_3Mo_5P_2O_{22}$ (at 1064 nm Q-switched Nd: YAG laser).

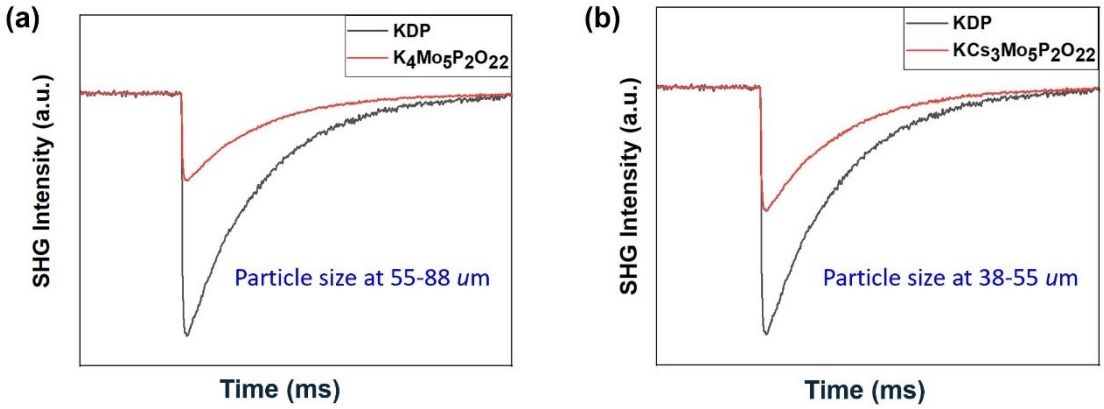
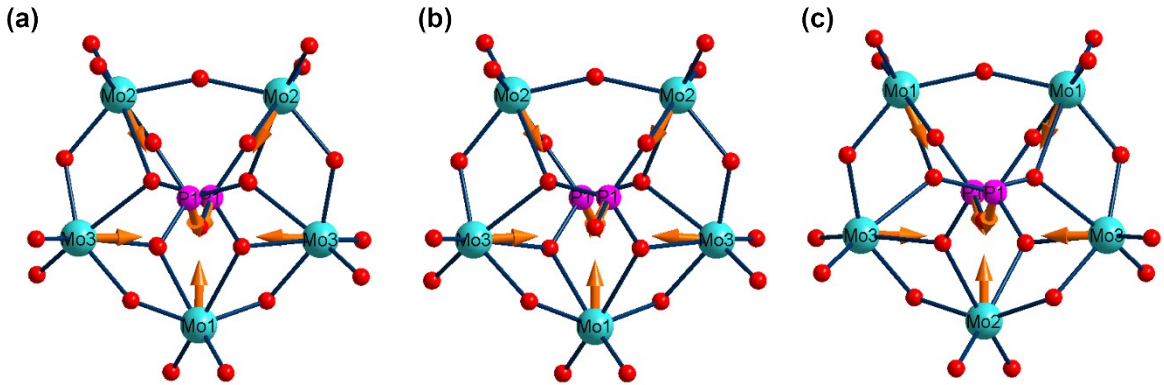


Figure S6. Dipole moment directions of the PO_4 and MoO_6 polyhedra in $KCs_3Mo_5P_2O_{22}$, $K_4Mo_5P_2O_{22}$,



and $Cs_4Mo_5P_2O_{22}$. (The arrows represent the approximate directions of the dipole moments).

Figure S7. The SHG density maps of the VE occupied (left) and VE unoccupied orbitals (right) of $K_4Mo_5P_2O_{22}$ (a-b), $NaRb_3Mo_5P_2O_{22}$ (c-d).

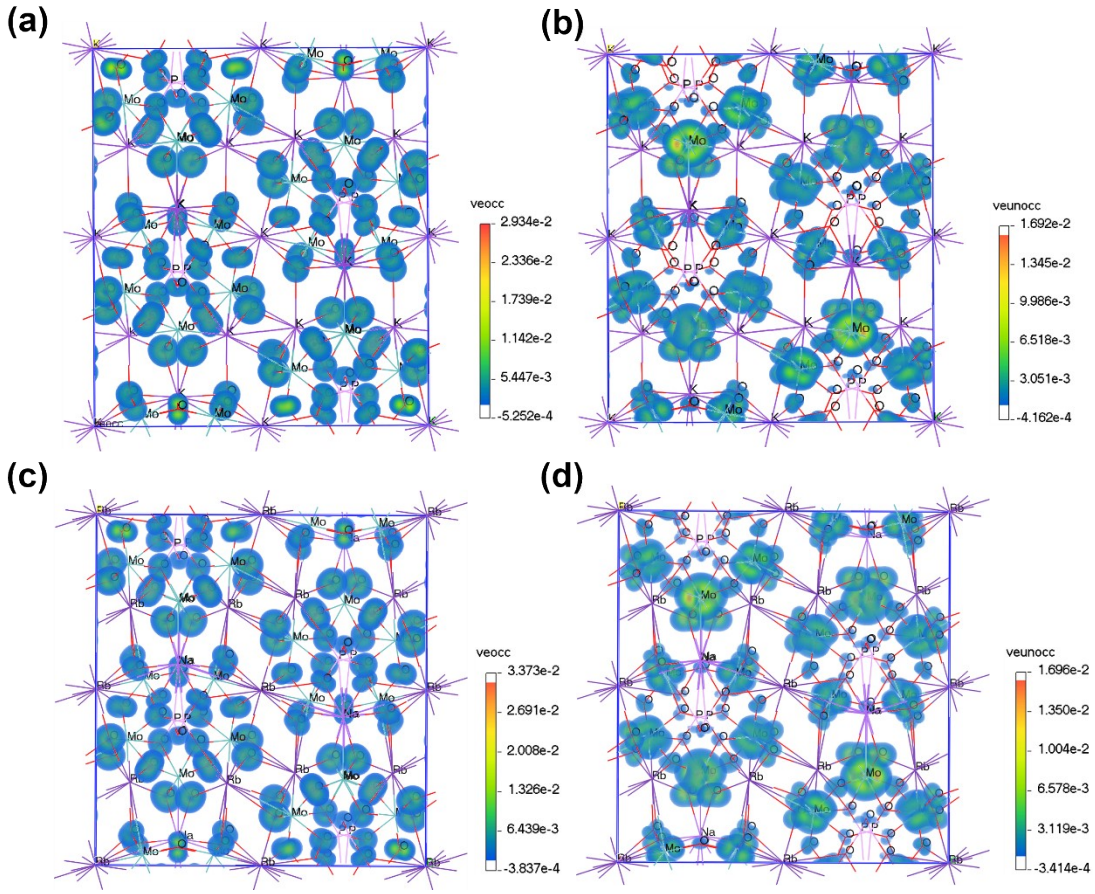
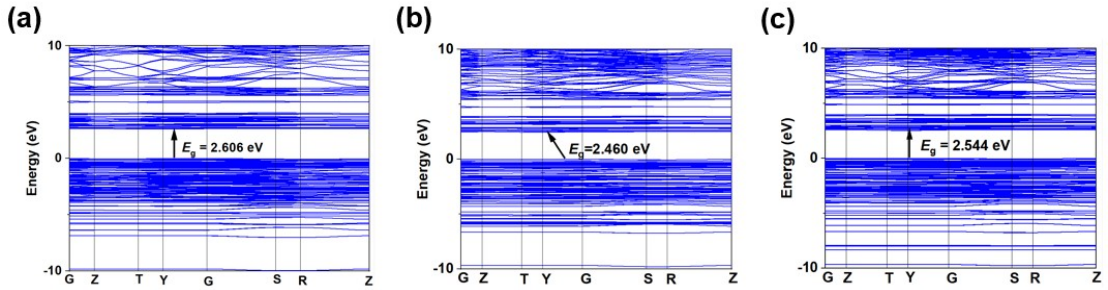


Figure 8. Calculated band structures of the GGA method, (a) $K_4Mo_5P_2O_{22}$, (b) $KCs_3Mo_5P_2O_{22}$ and (c) $NaRb_3Mo_5P_2O_{22}$.


(a)
(b)
(c)
Energy (eV)
10
0
-10
G Z T Y G S R Z
E_g = 2.606 eV
E_g=2.460 eV
E_g = 2.544 eV

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