Electronic Supplementary Information (ESI)

$K_6Mo_8PO_{29}OH·H_2O$ and $K_6Mo_5P_2O_{23}·7H_2O$: Strongly distorted $[MoO_6]$ octahedral groups effectively enhance birefringence

Jianlong Huang,[a] Wenhu Wang,[b] Juanjuan Lu,[b] Feng Yu,[a*] and Jian Han[b]*

[a]Key Laboratory for Green Processing of Chemical Engineering of XinjiangBingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China.

[b]Research Center for Crystal Materials; CAS Key Laboratory of Functional Materials and Devices for Special Environmental Conditions; Xinjiang Key Laboratory of Functional Crystal Materials; Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 40-1 South Beijing Road, Urumqi 830011, China.

*Corresponding authors, Emails: yufeng05@mail.ipc.ac.cn; hanjian@ms.xjb.ac.cn.

Table S1 Crystal data and structure refinement for $K_6Mo_8PO_{29}OH \cdot H_2O$ and $K_6Mo_5P_2O_{23} \cdot 7H_2O$.

Empirical formula	$K_6Mo_8PO_{29}OH \cdot H_2O$	$K_6Mo_5P_2O_{23} \cdot 7H_2O$
Formula weight	1532.11	1270.35
Temperature / K	273.2	293
Crystal system	Orthorhombic	Orthorhombic
Space group	*Cmcm*	$P2_12_12_1$
a / Å	8.2244(3)	12.7446(7)
b / Å	22.5016(8)	12.8972(9)
c / Å	15.3928(6)	18.0769(14)
α / °	90	90
β / °	90	90
γ / °	90	90
Z, ρ_{calc} / $Mg \cdot m^{-3}$	4, 3.572	4, 2.840
Volume / $Å^3$	2848.62(18)	2971.3(4)
F (000)	2864	2432
Theta range for data collection (°)	1.810 to 27.506	1.955 to 27.506
Index ranges	-10<=h<=10, -29<=k<=29, -19<=l<=19	-16<=h<=16, -16<=k<=16, -23<=l<=23
Reflections collected / unique	21512 / 1824 [R(int) = 0.0727]	6820 [R(int) = 0.0840]
Completeness (%)	100	99.9
Data / restraints / parameters	1824 / 1 / 127	6820 / 33 / 422
Goodness-of-fit on F^2	1.124	1.026
Final R indices [$I \geq 2\sigma(I)$] [a]	R_1 = 0.0250, wR_2 = 0.0561	R_1 = 0.0332, wR_2 = 0.0741
R indices (all data)[a]	R_1 = 0.0305, wR_2 = 0.0600	R_1 = 0.0378, wR_2 = 0.0787
Largest diff. peak and hole ($e \cdot Å^{-3}$)	1.339 and -0.937	0.883 and -0.583

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

Table S2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3), and bond valence sums (BVS) for $K_6Mo_8PO_{29}OH·H_2O$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U_{eq}	BVS
K(1)	10000	3817(1)	4681(1)	27(1)	1.042
K(2)	5000	6355(1)	7500	38(1)	1.027
K(3)	5000	3650(1)	4896(1)	27(1)	1.255
K(4)	0	3874(1)	7500	36(1)	0.960
Mo(1)	6953(1)	4910(1)	6480(1)	16(1)	6.187
Mo(2)	3061(1)	2619(1)	6416(1)	16(1)	5.998
P(1)	5000	3744(1)	7500	11(1)	4.901
O(1)	8229(4)	4467(1)	5937(2)	29(1)	2.115
O(2)	8202(5)	5077(2)	7500	20(1)	2.044
O(3)	7061(4)	5594(1)	5997(2)	29(1)	2.026
O(4)	5000	5168(2)	7500	17(1)	1.783
O(5)	5000	4599(2)	5997(2)	18(1)	2.222
O(6)	6539(4)	4126(1)	7500	14(1)	1.938
O(7)	5000	3334(2)	6687(2)	13(1)	2.016
O(8)	5000	2423(2)	5785(2)	22(1)	2.145
O(9)	2083(4)	3078(1)	5712(2)	26(1)	1.988
O(10)	2220(5)	2893(2)	7500	17(1)	2.127
O(11)	2084(4)	1949(1)	6344(2)	29(1)	2.018
O(12)	5000	2284(2)	7500	20(1)	1.976
O(13)	10000	3887(3)	2500	78(4)	2.000
H(12)	5000	1933	7500	30	/
H(13)	10910	4132	2500	116	/

Table S3 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3), and bond valence sums (BVS) for $K_6Mo_5P_2O_{23}·7H_2O$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U_{eq}	BVS
K(1)	6279(2)	7030(2)	4824(1)	42(1)	1.04
K(2)	5038(2)	3941(2)	4630(1)	32(1)	1.21
K(3)	5301(2)	5742(1)	6851(1)	32(1)	1.17
K(4)	7470(2)	1414(2)	6671(1)	33(1)	0.85
K(5)	4063(3)	75(2)	5401(2)	67(1)	0.89
K(6)	4(2)	1050(2)	8000(1)	35(1)	1.10
Mo(1)	6147(1)	8565(1)	6729(1)	18(1)	6.02
Mo(2)	4664(1)	2898(1)	6560(1)	18(1)	6.08
Mo(3)	2580(1)	2485(1)	5480(1)	20(1)	6.01
Mo(4)	310(1)	3362(1)	6554(1)	18(1)	6.08
Mo(5)	1243(1)	3627(1)	8291(1)	19(1)	6.07
P(1)	2618(2)	4588(1)	6744(1)	15(1)	5.01
P(2)	2407(2)	1728(1)	7264(1)	17(1)	4.96
O(1)	7750(15)	6308(13)	2374(14)	83(7)	2.0
O(1A)	8250(17)	5899(16)	2989(14)	72(7)	/
O(2)	6062(8)	9180(6)	4757(4)	56(2)	2.0
O(3)	8492(7)	6952(6)	4764(7)	73(3)	2.0
O(4)	6286(6)	5353(6)	3842(5)	49(2)	2.0
O(5)	4275(6)	5824(6)	5291(4)	45(2)	2.0
O(6)	7084(7)	5562(6)	5809(5)	48(2)	2.0
O(7)	-1845(6)	2194(6)	8215(5)	54(2)	2.0
O(8)	5977(5)	9726(4)	6271(3)	29(1)	1.85
O(9)	5342(5)	7723(4)	6263(3)	29(1)	1.96
O(10)	3217(4)	5561(4)	6595(3)	22(1)	1.64

O(11)	4662(4)	3839(4)	7414(3)	20(1)	2.07
O(12)	2567(4)	4357(4)	7590(3)	18(1)	1.97
O(13)	1486(4)	4649(4)	6465(3)	18(1)	1.84
O(14)	5462(5)	3714(5)	6081(3)	30(1)	2.07
O(15)	5484(5)	1954(5)	6889(4)	31(2)	2.06
O(16)	3479(4)	2253(4)	7428(3)	17(1)	1.98
O(17)	3141(4)	3647(4)	6351(3)	18(1)	1.99
O(18)	4029(4)	2177(4)	5755(3)	24(1)	2.09
O(19)	2335(5)	1405(5)	4953(3)	31(1)	1.88
O(20)	1197(4)	2846(4)	5784(3)	20(1)	2.14
O(21)	2394(4)	1415(4)	6453(3)	20(1)	1.73
O(22)	-513(5)	4168(5)	6097(4)	31(2)	2.00
O(23)	-428(4)	2259(4)	6670(4)	27(1)	2.05
O(24)	238(4)	3980(4)	7521(3)	22(1)	2.01
O(25)	1514(4)	2550(4)	7374(3)	17(1)	2.00
O(26)	2222(5)	809(4)	7766(3)	28(1)	1.52
O(27)	2545(5)	3090(4)	8658(3)	24(1)	2.00
O(28)	483(5)	2829(4)	8816(3)	29(1)	2.03
O(29)	1196(5)	4798(4)	8746(3)	28(1)	2.00
O(30)	2812(5)	3418(5)	4825(3)	32(1)	1.99

Table S4 Bond distances [Å] and angles [°] for $K_6Mo_8PO_{29}OH \cdot H_2O$.

K(1)-O(1)#5	2.829(3)	K(3)-O(8)	3.080(4)
K(1)-O(1)	2.829(3)	K(4)-O(10)	2.865(4)
K(1)-O(9)#2	2.867(3)	K(4)-O(10)#12	2.865(4)
K(1)-O(9)#3	2.867(3)	K(4)-O(6)#11	2.903(4)
K(1)-O(8)#4	2.881(4)	K(4)-O(6)#13	2.903(4)
K(1)-O(3)#6	2.948(3)	K(4)-O(2)#11	3.084(4)
K(1)-O(3)#7	2.948(3)	K(4)-O(2)#13	3.084(4)
K(1)-O(11)#8	3.349(3)	K(4)-O(1)#11	3.113(3)
K(1)-O(11)#4	3.349(3)	K(4)-O(1)#13	3.113(3)
K(1)-O(13)	3.3603(14)	K(4)-O(1)#14	3.113(3)
K(2)-O(4)	2.672(5)	K(4)-O(1)#2	3.113(3)
K(2)-O(11)#15	2.809(3)	P(1)-O(6)#11	1.530(4)
K(2)-O(11)#16	2.809(3)	P(1)-O(6)	1.530(4)
K(2)-O(11)#17	2.809(3)	P(1)-O(7)	1.554(3)
K(2)-O(11)#18	2.809(3)	P(1)-O(7)#1	1.554(3)
K(2)-O(3)	3.341(3)	Mo(1)-O(1)	1.670(3)
K(2)-O(3)#2	3.341(3)	Mo(1)-O(3)	1.711(3)
K(2)-O(3)#1	3.341(3)	Mo(1)-O(5)	1.9034(19)
K(2)-O(3)#11	3.341(3)	Mo(1)-O(2)	1.913(2)
K(3)-O(5)	2.727(4)	Mo(1)-O(4)	2.3197(13)
K(3)-O(3)#7	2.768(3)	Mo(1)-O(6)	2.386(2)
K(3)-O(3)#9	2.768(3)	Mo(2)-O(9)	1.699(3)
K(3)-O(7)	2.847(3)	Mo(2)-O(11)	1.712(3)
K(3)-O(11)#10	2.898(3)	Mo(2)-O(10)	1.9090(18)
K(3)-O(11)#8	2.898(3)	Mo(2)-O(8)	1.919(2)
K(3)-O(9)	2.998(3)	Mo(2)-O(7)	2.303(2)
K(3)-O(9)#2	2.998(3)	Mo(2)-O(12)	2.4292(16)

O(1)#5-K(1)-O(1)	61.99(13)	O(9)#3-K(1)-O(3)#7	161.23(9)
O(1)#5-K(1)-O(9)#2	103.24(9)	O(8)#4-K(1)-O(3)#7	110.36(8)
O(1)-K(1)-O(9)#2	67.28(9)	O(3)#6-K(1)-O(3)#7	110.17(12)
O(1)#5-K(1)-O(9)#3	67.28(9)	O(1)#5-K(1)-O(11)#8	163.16(9)
O(1)-K(1)-O(9)#3	103.24(9)	O(1)-K(1)-O(11)#8	102.68(8)
O(9)#2-K(1)-O(9)#3	73.38(13)	O(9)#2-K(1)-O(11)#8	62.24(8)
O(1)#5-K(1)-O(8)#4	132.13(9)	O(9)#3-K(1)-O(11)#8	112.96(9)
O(1)-K(1)-O(8)#4	132.13(9)	O(8)#4-K(1)-O(11)#8	51.99(6)
O(9)#2-K(1)-O(8)#4	64.90(8)	O(3)#6-K(1)-O(11)#8	130.72(9)
O(9)#3-K(1)-O(8)#4	64.90(8)	O(3)#7-K(1)-O(11)#8	58.51(8)
O(1)#5-K(1)-O(3)#6	65.60(9)	O(1)#5-K(1)-O(11)#4	102.68(8)
O(1)-K(1)-O(3)#6	115.56(10)	O(1)-K(1)-O(11)#4	163.16(9)
O(9)#2-K(1)-O(3)#6	161.23(9)	O(9)#2-K(1)-O(11)#4	112.96(9)
O(9)#3-K(1)-O(3)#6	88.10(8)	O(9)#3-K(1)-O(11)#4	62.24(8)
O(8)#4-K(1)-O(3)#6	110.36(8)	O(8)#4-K(1)-O(11)#4	51.99(6)
O(1)#5-K(1)-O(3)#7	115.56(10)	O(3)#6-K(1)-O(11)#4	58.51(8)
O(1)-K(1)-O(3)#7	65.60(9)	O(3)#7-K(1)-O(11)#4	130.72(9)
O(9)#2-K(1)-O(3)#7	88.10(8)	O(11)#8-K(1)-O(11)#4	91.49(11)
O(1)#5-K(1)-O(13)	131.20(11)	O(3)#2-K(2)-O(3)#1	118.29(11)
O(1)-K(1)-O(13)	131.20(11)	O(4)-K(2)-O(3)#11	59.14(6)
O(9)#2-K(1)-O(13)	125.46(10)	O(11)#15-K(2)-O(3)#11	96.60(8)
O(9)#3-K(1)-O(13)	125.46(10)	O(11)#16-K(2)-O(3)#11	111.91(9)
O(8)#4-K(1)-O(13)	78.29(14)	O(11)#17-K(2)-O(3)#11	59.73(8)
O(3)#6-K(1)-O(13)	68.01(8)	O(11)#18-K(2)-O(3)#11	172.88(9)
O(3)#7-K(1)-O(13)	68.01(8)	O(3)-K(2)-O(3)#11	118.29(11)
O(11)#8-K(1)-O(13)	63.48(9)	O(3)#2-K(2)-O(3)#11	87.66(11)
O(11)#4-K(1)-O(13)	63.48(9)	O(3)#1-K(2)-O(3)#11	60.97(11)

O(4)-K(2)-O(11)#15	118.42(7)	O(3)#7-K(3)-O(8)	140.51(7)
O(4)-K(2)-O(11)#16	118.42(7)	O(3)#9-K(3)-O(8)	140.51(7)
O(11)#15-K(2)-O(11)#16	123.15(14)	O(7)-K(3)-O(8)	49.19(10)
O(4)-K(2)-O(11)#17	118.42(7)	O(11)#10-K(3)-O(8)	82.87(9)
O(11)#15-K(2)-O(11)#17	75.20(14)	O(11)#8-K(3)-O(8)	82.87(9)
O(11)#16-K(2)-O(11)#17	78.60(12)	O(9)-K(3)-O(8)	55.23(6)
O(4)-K(2)-O(11)#18	118.42(7)	O(9)#2-K(3)-O(8)	55.23(6)
O(11)#15-K(2)-O(11)#18	78.60(12)	O(9)-K(3)-O(9)#2	106.33(11)
O(11)#16-K(2)-O(11)#18	75.20(14)	O(5)-K(3)-O(8)	115.22(11)
O(11)#17-K(2)-O(11)#18	123.15(14)	O(5)-K(3)-O(3)#7	80.01(9)
O(4)-K(2)-O(3)	59.15(6)	O(5)-K(3)-O(3)#9	80.01(9)
O(11)#15-K(2)-O(3)	111.91(9)	O(3)#7-K(3)-O(3)#9	75.52(13)
O(11)#16-K(2)-O(3)	96.60(8)	O(5)-K(3)-O(7)	66.03(10)
O(11)#17-K(2)-O(3)	172.88(9)	O(3)#7-K(3)-O(7)	129.37(8)
O(11)#18-K(2)-O(3)	59.73(8)	O(3)#9-K(3)-O(7)	129.37(8)
O(4)-K(2)-O(3)#2	59.14(6)	O(5)-K(3)-O(11)#10	140.69(7)
O(11)#15-K(2)-O(3)#2	172.88(9)	O(3)#7-K(3)-O(11)#10	108.74(10)
O(11)#16-K(2)-O(3)#2	59.73(8)	O(3)#9-K(3)-O(11)#10	66.23(9)
O(11)#17-K(2)-O(3)#2	111.91(9)	O(7)-K(3)-O(11)#10	121.46(8)
O(11)#18-K(2)-O(3)#2	96.60(8)	O(5)-K(3)-O(11)#8	140.69(7)
O(3)-K(2)-O(3)#2	60.97(11)	O(3)#7-K(3)-O(11)#8	66.23(9)
O(4)-K(2)-O(3)#1	59.14(6)	O(3)#9-K(3)-O(11)#8	108.74(10)
O(11)#15-K(2)-O(3)#1	59.73(8)	O(7)-K(3)-O(11)#8	121.46(8)
O(11)#16-K(2)-O(3)#1	172.88(9)	O(11)#10-K(3)-O(11)#8	72.52(13)
O(11)#17-K(2)-O(3)#1	96.60(8)	O(5)-K(3)-O(9)	94.35(8)
O(11)#18-K(2)-O(3)#1	111.91(9)	O(3)#7-K(3)-O(9)	164.14(9)
O(3)-K(2)-O(3)#1	87.66(11)	O(3)#9-K(3)-O(9)	88.96(8)

O(7)-K(3)-O(9)	59.16(6)	O(6)#13-K(4)-O(2)#11	107.40(11)
O(11)#10-K(3)-O(9)	66.61(8)	O(10)-K(4)-O(2)#13	169.06(11)
O(11)#8-K(3)-O(9)	123.35(9)	O(10)#12-K(4)-O(2)#13	111.76(10)
O(5)-K(3)-O(9)#2	94.35(8)	O(6)#11-K(4)-O(2)#13	107.40(11)
O(3)#7-K(3)-O(9)#2	88.96(8)	O(6)#13-K(4)-O(2)#13	50.10(10)
O(3)#9-K(3)-O(9)#2	164.14(9)	O(2)#11-K(4)-O(2)#13	57.30(14)
O(7)-K(3)-O(9)#2	59.16(6)	O(10)-K(4)-O(1)#11	91.84(8)
O(11)#10-K(3)-O(9)#2	123.35(9)	O(10)#12-K(4)-O(1)#11	128.95(6)
O(11)#8-K(3)-O(9)#2	66.61(8)	O(6)#11-K(4)-O(1)#11	57.13(6)
O(10)-K(4)-O(10)#12	79.19(16)	O(6)#13-K(4)-O(1)#11	112.05(7)
O(10)-K(4)-O(6)#11	61.65(10)	O(2)#11-K(4)-O(1)#11	53.08(6)
O(10)#12-K(4)-O(6)#11	140.84(12)	O(2)#13-K(4)-O(1)#11	81.27(8)
O(10)-K(4)-O(6)#13	140.84(12)	O(10)-K(4)-O(1)#13	128.95(6)
O(10)#12-K(4)-O(6)#13	61.65(10)	O(10)#12-K(4)-O(1)#13	91.84(8)
O(6)#11-K(4)-O(6)#13	157.51(15)	O(6)#11-K(4)-O(1)#13	112.05(7)
O(10)-K(4)-O(2)#11	111.76(10)	O(6)#13-K(4)-O(1)#13	57.13(6)
O(10)#12-K(4)-O(2)#11	169.06(11)	O(2)#11-K(4)-O(1)#13	81.27(8)
O(6)#11-K(4)-O(2)#11	50.10(10)	O(2)#13-K(4)-O(1)#13	53.08(6)
O(10)-K(4)-O(1)#2	91.84(8)	O(1)#11-K(4)-O(1)#13	129.22(13)
O(10)#12-K(4)-O(1)#2	128.95(6)	O(10)-K(4)-O(1)#14	128.95(6)
O(6)#11-K(4)-O(1)#2	57.13(6)	O(10)#12-K(4)-O(1)#14	91.84(8)
O(6)#13-K(4)-O(1)#2	112.05(7)	O(6)#11-K(4)-O(1)#14	112.05(7)
O(2)#11-K(4)-O(1)#2	53.08(6)	O(6)#13-K(4)-O(1)#14	57.13(6)
O(2)#13-K(4)-O(1)#2	81.27(8)	O(2)#11-K(4)-O(1)#14	81.27(8)
O(1)#11-K(4)-O(1)#2	101.20(11)	O(2)#13-K(4)-O(1)#14	53.08(6)
O(1)#13-K(4)-O(1)#2	55.81(11)	O(1)#11-K(4)-O(1)#14	55.81(11)
O(1)#14-K(4)-O(1)#2	129.22(13)	O(1)#13-K(4)-O(1)#14	101.20(11)

O(6)#11-P(1)-O(6)	111.6(3)	O(5)-Mo(1)-O(6)	82.23(13)
O(6)#11-P(1)-O(7)	109.48(9)	O(2)-Mo(1)-O(6)	71.47(12)
O(6)-P(1)-O(7)	109.48(9)	O(4)-Mo(1)-O(6)	68.94(13)
O(6)#11-P(1)-O(7)#1	109.48(9)	O(9)-Mo(2)-O(11)	105.79(15)
O(6)-P(1)-O(7)#1	109.48(9)	O(9)-Mo(2)-O(10)	100.95(14)
O(7)-P(1)-O(7)#1	107.2(3)	O(11)-Mo(2)-O(10)	99.82(15)
O(1)-Mo(1)-O(3)	106.62(15)	O(9)-Mo(2)-O(8)	102.16(15)
O(1)-Mo(1)-O(5)	96.63(14)	O(11)-Mo(2)-O(8)	98.91(15)
O(3)-Mo(1)-O(5)	101.77(16)	O(10)-Mo(2)-O(8)	144.87(14)
O(1)-Mo(1)-O(2)	100.98(15)	O(9)-Mo(2)-O(7)	91.10(13)
O(3)-Mo(1)-O(2)	98.77(15)	O(11)-Mo(2)-O(7)	162.09(13)
O(5)-Mo(1)-O(2)	147.77(14)	O(10)-Mo(2)-O(7)	82.33(13)
O(1)-Mo(1)-O(4)	157.28(16)	O(8)-Mo(2)-O(7)	71.15(12)
O(3)-Mo(1)-O(4)	96.04(16)	O(9)-Mo(2)-O(12)	159.70(15)
O(5)-Mo(1)-O(4)	76.81(10)	O(11)-Mo(2)-O(12)	94.50(15)
O(2)-Mo(1)-O(4)	76.56(10)	O(10)-Mo(2)-O(12)	74.77(11)
O(1)-Mo(1)-O(6)	88.74(13)	O(8)-Mo(2)-O(12)	74.36(10)
O(3)-Mo(1)-O(6)	163.38(12)	O(7)-Mo(2)-O(12)	68.75(13)

Symmetry transformations used to generate equivalent atoms:

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

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

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

#11 -x+1,y,-z+3/2 #12 -x,y,-z+3/2 #13 x-1,y,z

#14 x-1,y,-z+3/2 #15 x+1/2,y+1/2,-z+3/2 #16 -x+1/2,y+1/2,z

#17 -x+1/2,y+1/2,-z+3/2 #18 x+1/2,y+1/2,z #19 -x+1,-y+1,z+1/2

#20 x-1/2,y-1/2,z #21 x,y,-z+1/2

Table S5 Bond distances [Å] and angles [°] for $K_6Mo_5P_2O_{23}\cdot 7H_2O$.

K(1)-O(27)#5	3.412(6)	K(4)-O(29)#3	2.793(6)
K(1)-O(9)	2.998(7)	K(4)-O(12)#3	2.971(5)
K(1)-O(28)#11	2.897(6)	K(4)-O(8)#7	2.979(7)
K(1)-O(2)	2.789(8)	K(4)-O(23)#6	2.892(6)
K(1)-O(3)	2.825(9)	K(4)-O(30)#8	2.747(6)
K(1)-O(4)	2.798(8)	K(4)-O(15)	2.654(6)
K(1)-O(5)	3.107(8)	K(4)-O(7)#6	3.094(10)
K(1)-O(6)	2.794(8)	K(4)-O(1)#9	3.21(2)
K(1)-O(7)#11	3.159(10)	K(5)-O(21)	3.336(6)
K(2)-O(29)#11	2.769(6)	K(5)-O(8)#7	2.937(7)
K(2)-O(18)	3.311(6)	K(5)-O(18)	2.787(6)
K(2)-O(23)#8	2.876(6)	K(5)-O(22)#8	2.928(7)
K(2)-O(14)	2.694(6)	K(5)-O(19)	2.907(7)
K(2)-O(20)#8	2.839(6)	K(5)-O(2)#7	3.029(10)
K(2)-O(19)#8	3.057(6)	K(5)-O(3)#2	2.730(9)
K(2)-O(30)	2.936(6)	K(5)-O(1A)#2	3.34(3)
K(2)-O(4)	2.806(9)	K(6)-O(25)	2.954(6)
K(2)-O(5)	2.876(8)	K(6)-O(26)	2.875(6)
K(3)-O(11)	2.778(6)	K(6)-O(13)#10	2.795(6)
K(3)-O(10)	2.706(6)	K(6)-O(24)#10	2.847(6)
K(3)-O(26)#5	3.234(6)	K(6)-O(23)	2.917(7)
K(3)-O(16)#5	2.814(5)	K(6)-O(28)	2.796(6)
K(3)-O(9)	2.769(6)	K(6)-O(22)#10	2.996(7)
K(3)-O(14)	2.970(6)	K(6)-O(7)	2.808(8)
K(3)-O(15)#5	2.938(7)	Mo(1)-O(11)#5	1.895(6)
K(3)-O(5)	3.110(8)	Mo(1)-O(12)#5	2.291(5)
K(3)-O(6)	2.961(10)	Mo(1)-O(27)#5	1.908(6)

Mo(1)-O(8)	1.725(6)	Mo(4)-O(23)	1.719(5)
Mo(1)-O(16)#5	2.327(5)	Mo(4)-O(20)	1.913(5)
Mo(1)-O(9)	1.715(6)	Mo(4)-O(22)	1.693(6)
Mo(2)-O(11)	1.964(5)	Mo(5)-O(29)	1.721(5)
Mo(2)-O(17)	2.201(5)	Mo(5)-O(12)	2.310(5)
Mo(2)-O(16)	2.330(5)	Mo(5)-O(27)	1.917(6)
Mo(2)-O(18)	1.908(5)	Mo(5)-O(25)	2.189(5)
Mo(2)-O(14)	1.701(6)	Mo(5)-O(24)	1.945(6)
Mo(2)-O(15)	1.712(6)	Mo(5)-O(28)	1.703(6)
Mo(3)-O(17)	2.288(5)	P(1)-O(12)	1.558(5)
Mo(3)-O(21)	2.248(5)	P(1)-O(10)	1.494(5)
Mo(3)-O(18)	1.953(6)	P(1)-O(17)	1.557(5)
Mo(3)-O(20)	1.904(5)	P(1)-O(13)	1.530(5)
Mo(3)-O(19)	1.716(6)	P(2)-O(25)	1.569(5)
Mo(3)-O(30)	1.714(6)	P(2)-O(21)	1.522(5)
Mo(4)-O(25)	2.376(5)	P(2)-O(26)	1.510(6)
Mo(4)-O(13)	2.243(5)	P(2)-O(16)	1.554(5)
Mo(4)-O(24)	1.923(6)		
O(6)-K(1)-O(27)#5	66.27(18)	O(3)-K(1)-O(7)#11	75.4(3)
O(6)-K(1)-O(9)	78.2(2)	O(4)-K(1)-O(27)#5	144.9(2)
O(6)-K(1)-O(28)#11	136.7(2)	O(4)-K(1)-O(9)	141.5(2)
O(6)-K(1)-O(3)	68.5(3)	O(4)-K(1)-O(28)#11	69.7(2)
O(6)-K(1)-O(4)	83.1(2)	O(4)-K(1)-O(3)	86.8(3)
O(6)-K(1)-O(5)	77.9(2)	O(4)-K(1)-O(5)	77.8(2)
O(6)-K(1)-O(7)#11	135.8(3)	O(4)-K(1)-O(7)#11	70.1(2)
O(7)#11-K(1)-O(27)#5	120.85(18)	O(5)-K(1)-O(27)#5	110.06(19)
O(9)-K(1)-O(27)#5	50.05(16)	O(5)-K(1)-O(7)#11	126.6(2)

O(9)-K(1)-O(5)	65.6(2)	O(23)#8-K(2)-O(19)#8	108.70(16)
O(9)-K(1)-O(7)#11	142.66(19)	O(23)#8-K(2)-O(30)	77.01(18)
O(28)#11-K(1)-O(27)#5	145.16(17)	O(14)-K(2)-O(29)#11	137.7(2)
O(28)#11-K(1)-O(9)	102.60(19)	O(14)-K(2)-O(18)	53.49(16)
O(28)#11-K(1)-O(5)	64.2(2)	O(14)-K(2)-O(23)#8	141.11(19)
O(28)#11-K(1)-O(7)#11	65.06(19)	O(14)-K(2)-O(20)#8	93.63(18)
O(2)-K(1)-O(27)#5	71.3(2)	O(14)-K(2)-O(19)#8	63.35(17)
O(2)-K(1)-O(9)	72.6(2)	O(14)-K(2)-O(30)	92.97(18)
O(2)-K(1)-O(28)#11	80.4(2)	O(14)-K(2)-O(4)	116.8(2)
O(2)-K(1)-O(3)	97.6(3)	O(14)-K(2)-O(5)	75.8(2)
O(2)-K(1)-O(4)	137.9(3)	O(20)#8-K(2)-O(18)	78.80(15)
O(2)-K(1)-O(5)	115.3(3)	O(20)#8-K(2)-O(23)#8	56.99(16)
O(2)-K(1)-O(6)	137.5(3)	O(20)#8-K(2)-O(19)#8	56.46(16)
O(2)-K(1)-O(7)#11	70.6(2)	O(20)#8-K(2)-O(30)	110.36(18)
O(3)-K(1)-O(27)#5	66.8(3)	O(20)#8-K(2)-O(5)	166.2(2)
O(3)-K(1)-O(9)	116.2(3)	O(19)#8-K(2)-O(18)	96.87(17)
O(3)-K(1)-O(28)#11	138.8(3)	O(30)-K(2)-O(18)	52.66(16)
O(3)-K(1)-O(5)	144.4(2)	O(30)-K(2)-O(19)#8	149.53(18)
O(5)-K(2)-O(30)	79.5(2)	O(4)-K(2)-O(18)	167.8(2)
O(4)-K(2)-O(23)#8	93.0(2)	O(29)#11-K(2)-O(18)	122.50(17)
O(4)-K(2)-O(20)#8	95.62(19)	O(29)#11-K(2)-O(23)#8	74.19(17)
O(4)-K(2)-O(19)#8	71.1(2)	O(29)#11-K(2)-O(20)#8	128.37(19)
O(4)-K(2)-O(30)	139.3(2)	O(29)#11-K(2)-O(19)#8	140.56(19)
O(4)-K(2)-O(5)	81.7(2)	O(29)#11-K(2)-O(30)	69.87(18)
O(5)-K(2)-O(18)	101.15(18)	O(29)#11-K(2)-O(4)	69.4(2)
O(5)-K(2)-O(23)#8	136.4(2)	O(29)#11-K(2)-O(5)	63.4(2)
O(5)-K(2)-O(19)#8	110.2(2)	O(23)#8-K(2)-O(18)	92.98(16)

O(11)-K(3)-O(26)#5	103.37(16)	O(6)-K(3)-O(5)	75.4(2)
O(11)-K(3)-O(16)#5	127.16(18)	O(15)#5-K(3)-O(5)	122.8(2)
O(11)-K(3)-O(14)	54.16(16)	O(9)-K(3)-O(15)#5	79.24(18)
O(11)-K(3)-O(15)#5	94.95(17)	O(9)-K(3)-O(5)	68.16(19)
O(11)-K(3)-O(5)	103.84(19)	O(9)-K(3)-O(6)	79.2(2)
O(11)-K(3)-O(6)	112.9(2)	O(14)-K(3)-O(26)#5	93.22(16)
O(10)-K(3)-O(11)	72.50(16)	O(14)-K(3)-O(5)	68.53(19)
O(10)-K(3)-O(26)#5	175.80(17)	O(15)#5-K(3)-O(26)#5	98.76(17)
O(10)-K(3)-O(16)#5	132.94(17)	O(15)#5-K(3)-O(14)	148.84(18)
O(10)-K(3)-O(9)	91.85(18)	O(15)-K(4)-O(8)#7	67.60(18)
O(10)-K(3)-O(14)	84.96(17)	O(15)-K(4)-O(23)#6	141.65(18)
O(10)-K(3)-O(15)#5	81.03(18)	O(15)-K(4)-O(30)#8	106.1(2)
O(10)-K(3)-O(5)	55.62(19)	O(15)-K(4)-O(7)#6	92.8(2)
O(10)-K(3)-O(6)	129.6(2)	O(15)-K(4)-O(1)#9	67.5(4)
O(16)#5-K(3)-O(26)#5	48.90(15)	O(7)#6-K(4)-O(1)#9	50.9(4)
O(16)#5-K(3)-O(14)	142.09(18)	O(29)#3-K(4)-O(12)#3	57.64(16)
O(16)#5-K(3)-O(15)#5	57.35(16)	O(29)#3-K(4)-O(8)#7	77.19(17)
O(16)#5-K(3)-O(5)	128.95(19)	O(29)#3-K(4)-O(23)#6	73.59(17)
O(16)#5-K(3)-O(6)	85.67(19)	O(29)#3-K(4)-O(7)#6	108.3(2)
O(9)-K(3)-O(11)	164.06(19)	O(29)#3-K(4)-O(1)#9	147.3(4)
O(9)-K(3)-O(26)#5	92.23(17)	O(12)#3-K(4)-O(8)#7	56.43(16)
O(9)-K(3)-O(16)#5	61.83(17)	O(12)#3-K(4)-O(7)#6	83.61(18)
O(9)-K(3)-O(14)	129.13(19)	O(12)#3-K(4)-O(1)#9	129.5(4)
O(15)#5-K(3)-O(6)	142.8(2)	O(8)#7-K(4)-O(7)#6	129.5(2)
O(5)-K(3)-O(26)#5	127.13(19)	O(8)#7-K(4)-O(1)#9	135.1(4)
O(6)-K(3)-O(26)#5	52.32(18)	O(23)#6-K(4)-O(12)#3	110.56(17)
O(6)-K(3)-O(14)	65.14(19)	O(23)#6-K(4)-O(8)#7	150.08(18)

O(23)#6-K(4)-O(7)#6	67.41(19)	O(8)#7-K(5)-O(21)	107.68(18)
O(23)#6-K(4)-O(1)#9	74.7(4)	O(8)#7-K(5)-O(2)#7	56.6(2)
O(30)#8-K(4)-O(29)#3	72.34(18)	O(8)#7-K(5)-O(1A)#2	74.5(3)
O(30)#8-K(4)-O(12)#3	121.06(18)	O(18)-K(5)-O(21)	49.82(15)
O(30)#8-K(4)-O(8)#7	85.44(19)	O(18)-K(5)-O(8)#7	92.22(18)
O(30)#8-K(4)-O(23)#6	79.80(19)	O(18)-K(5)-O(22)#8	83.73(19)
O(30)#8-K(4)-O(7)#6	144.8(2)	O(18)-K(5)-O(19)	58.51(17)
O(30)#8-K(4)-O(1)#9	109.4(4)	O(18)-K(5)-O(2)#7	118.2(2)
O(15)-K(4)-O(29)#3	144.7(2)	O(18)-K(5)-O(1A)#2	99.3(3)
O(15)-K(4)-O(12)#3	98.76(18)	O(22)#8-K(5)-O(21)	118.13(17)
O(1A)#2-K(5)-O(21)	60.0(3)	O(22)#8-K(5)-O(8)#7	113.2(2)
O(22)#8-K(5)-O(2)#7	67.5(2)	O(25)-K(6)-O(22)#10	126.74(17)
O(22)#8-K(5)-O(1A)#2	171.8(4)	O(26)-K(6)-O(25)	51.26(15)
O(19)-K(5)-O(21)	50.92(16)	O(26)-K(6)-O(23)	97.03(17)
O(19)-K(5)-O(8)#7	150.29(19)	O(26)-K(6)-O(22)#10	77.27(17)
O(19)-K(5)-O(22)#8	71.65(18)	O(13)#10-K(6)-O(25)	177.32(17)
O(19)-K(5)-O(2)#7	139.0(2)	O(13)#10-K(6)-O(26)	130.49(17)
O(19)-K(5)-O(1A)#2	103.3(3)	O(13)#10-K(6)-O(24)#10	55.58(16)
O(2)#7-K(5)-O(21)	162.3(2)	O(13)#10-K(6)-O(23)	120.18(17)
O(2)#7-K(5)-O(1A)#2	117.0(3)	O(13)#10-K(6)-O(28)	119.73(18)
O(3)#2-K(5)-O(21)	112.9(3)	O(13)#10-K(6)-O(22)#10	55.58(16)
O(3)#2-K(5)-O(8)#7	97.7(3)	O(13)#10-K(6)-O(7)	73.82(19)
O(3)#2-K(5)-O(18)	162.3(3)	O(24)#10-K(6)-O(25)	123.96(17)
O(3)#2-K(5)-O(22)#8	105.5(3)	O(24)#10-K(6)-O(26)	87.52(17)
O(3)#2-K(5)-O(19)	109.5(2)	O(24)#10-K(6)-O(23)	102.04(17)
O(3)#2-K(5)-O(2)#7	79.5(3)	O(24)#10-K(6)-O(22)#10	56.24(17)
O(3)#2-K(5)-O(1A)#2	69.6(4)	O(23)-K(6)-O(25)	57.15(15)

O(23)-K(6)-O(22)#10	157.35(18)	O(11)-Mo(2)-O(17)	82.1(2)
O(28)-K(6)-O(25)	61.45(16)	O(11)-Mo(2)-O(16)	72.0(2)
O(28)-K(6)-O(26)	87.24(18)	O(17)-Mo(2)-O(16)	72.58(18)
O(28)-K(6)-O(24)#10	165.38(19)	O(18)-Mo(2)-O(11)	154.3(2)
O(28)-K(6)-O(23)	92.14(17)	O(18)-Mo(2)-O(17)	73.1(2)
O(28)-K(6)-O(22)#10	109.24(18)	O(18)-Mo(2)-O(16)	93.7(2)
O(28)-K(6)-O(7)	71.2(2)	O(14)-Mo(2)-O(11)	91.1(3)
O(7)-K(6)-O(25)	104.78(19)	O(14)-Mo(2)-O(17)	99.7(3)
O(7)-K(6)-O(26)	154.5(2)	O(14)-Mo(2)-O(16)	162.0(2)
O(7)-K(6)-O(24)#10	116.6(2)	O(14)-Mo(2)-O(18)	99.6(3)
O(7)-K(6)-O(23)	71.0(2)	O(14)-Mo(2)-O(15)	104.6(3)
O(7)-K(6)-O(22)#10	122.1(2)	O(15)-Mo(2)-O(11)	99.7(3)
O(11)#5-Mo(1)-O(12)#5	82.3(2)	O(15)-Mo(2)-O(17)	155.6(3)
O(11)#5-Mo(1)-O(27)#5	146.7(2)	O(15)-Mo(2)-O(16)	84.7(2)
O(11)#5-Mo(1)-O(16)#5	73.2(2)	O(15)-Mo(2)-O(18)	100.2(3)
O(12)#5-Mo(1)-O(16)#5	79.96(18)	O(21)-Mo(3)-O(17)	84.06(18)
O(27)#5-Mo(1)-O(12)#5	73.5(2)	O(18)-Mo(3)-O(17)	70.3(2)
O(9)-Mo(1)-O(16)#5	89.1(2)	O(18)-Mo(3)-O(21)	77.1(2)
O(27)#5-Mo(1)-O(16)#5	80.1(2)	O(20)-Mo(3)-O(17)	86.0(2)
O(8)-Mo(1)-O(11)#5	99.3(3)	O(20)-Mo(3)-O(21)	80.0(2)
O(8)-Mo(1)-O(12)#5	87.7(2)	O(20)-Mo(3)-O(18)	148.4(2)
O(8)-Mo(1)-O(27)#5	102.3(3)	O(19)-Mo(3)-O(17)	166.0(2)
O(8)-Mo(1)-O(16)#5	166.3(2)	O(19)-Mo(3)-O(21)	85.2(3)
O(9)-Mo(1)-O(11)#5	101.2(3)	O(19)-Mo(3)-O(18)	98.5(3)
O(9)-Mo(1)-O(12)#5	167.1(2)	O(19)-Mo(3)-O(20)	101.0(3)
O(9)-Mo(1)-O(27)#5	98.0(3)	O(30)-Mo(3)-O(17)	87.8(2)
O(9)-Mo(1)-O(8)	103.8(3)	O(30)-Mo(3)-O(21)	171.7(2)

O(30)-Mo(3)-O(18)	98.9(3)	O(27)-Mo(5)-O(25)	84.1(2)
O(30)-Mo(3)-O(20)	100.8(3)	O(27)-Mo(5)-O(24)	154.5(2)
O(30)-Mo(3)-O(19)	102.6(3)	O(25)-Mo(5)-O(12)	74.25(18)
O(20)-Mo(4)-O(24)	146.5(2)	O(28)-Mo(5)-O(29)	104.1(3)
O(22)-Mo(4)-O(25)	167.2(3)	O(24)-Mo(5)-O(12)	89.6(2)
O(22)-Mo(4)-O(13)	85.6(2)	O(24)-Mo(5)-O(25)	73.2(2)
O(22)-Mo(4)-O(24)	99.2(3)	O(28)-Mo(5)-O(12)	165.4(2)
O(22)-Mo(4)-O(23)	103.2(3)	O(28)-Mo(5)-O(27)	94.6(3)
O(22)-Mo(4)-O(20)	103.0(3)	O(28)-Mo(5)-O(25)	97.4(2)
O(13)-Mo(4)-O(25)	86.55(18)	O(28)-Mo(5)-O(24)	99.5(3)
O(24)-Mo(4)-O(25)	69.3(2)	O(10)-P(1)-O(12)	111.0(3)
O(24)-Mo(4)-O(13)	77.9(2)	O(10)-P(1)-O(17)	110.7(3)
O(23)-Mo(4)-O(25)	85.0(2)	O(10)-P(1)-O(13)	112.3(3)
O(23)-Mo(4)-O(13)	171.0(2)	O(17)-P(1)-O(12)	108.5(3)
O(23)-Mo(4)-O(24)	101.9(3)	O(13)-P(1)-O(12)	107.2(3)
O(23)-Mo(4)-O(20)	97.2(3)	O(13)-P(1)-O(17)	107.0(3)
O(20)-Mo(4)-O(25)	85.4(2)	O(21)-P(2)-O(25)	107.1(3)
O(20)-Mo(4)-O(13)	79.0(2)	O(21)-P(2)-O(16)	107.9(3)
O(29)-Mo(5)-O(12)	86.0(2)	O(26)-P(2)-O(25)	110.0(3)
O(29)-Mo(5)-O(27)	100.4(3)	O(26)-P(2)-O(21)	111.7(3)
O(29)-Mo(5)-O(25)	157.5(3)	O(26)-P(2)-O(16)	111.4(3)
O(29)-Mo(5)-O(24)	96.6(3)	O(16)-P(2)-O(25)	108.6(3)
O(27)-Mo(5)-O(12)	72.9(2)		

Symmetry transformations used to generate equivalent atoms:

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

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

#7 x,y-1,z #8 x+1/2,-y+1/2,-z+1 #9 -x+3/2,-y+1,z+1/2

#10 -x,y-1/2,-z+3/2 #11 -x+1/2,-y+1,z-1/2 #12 -x+1/2,-y,z-1/2

#13 -x+1/2,-y+1,z+1/2 #14 x-1,y,z #15 -x+3/2,-y+1,z-1/2

Table S6 Hydrogen bonds for $K_6Mo_8PO_{29}OH \cdot H_2O$.(D, donor; H, hydrogen; A, acceptor.)

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
O(12)-H(12)...O(13)#1	0.79	1.85	2.634(8)	180.0
O(13)-H(13)...O(2)#2	0.93	1.93	2.761(7)	148.7

#1 3/2-X,1/2-Y,1/2+Z; #2 2-X,1-Y,-1/2+Z

Table S7 Hydrogen bonds for $K_6Mo_5P_2O_{23}\cdot 7H_2O$.(D, donor; H, hydrogen; A, acceptor.)

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
O(2)-H(2B)...O(13)#16	0.84	1.95	2.730(9)	154.9
O(4)-H(4B)...O(21)#8	0.94	1.90	2.734(9)	146.5
O(5)-H(5A)...O(29)#11	0.84	2.22	2.967(10)	148.3
O(5)-H(5B)...O(10)	0.84	1.91	2.737(10)	168.0
O(6)-H(6B)...O(26)#5	0.837(14)	1.93(3)	2.742(10)	164(9)
O(7)-H(7A)...O(1)#13	0.839(14)	1.95(5)	2.715(18)	151(10)
O(7)-H(7B)...O(10)#10	0.844(14)	1.96(4)	2.759(9)	158(10)
O(1)-H(1B)...O(26)#8	0.85	2.20	2.824(17)	130.3
O(1A)-H(1AA)...O(11)#15	0.85	2.07	2.876(18)	158.3
O(1A)-H(1AB)...O(26)#8	0.85	2.06	2.903(19)	173.7

Symmetry transformations used to generate equivalent atoms:

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

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

#7 x,y-1,z #8 x+1/2,-y+1/2,-z+1 #9 -x+3/2,-y+1,z+1/2

#10 -x,y-1/2,-z+3/2 #11 -x+1/2,-y+1,z-1/2 #12 -x+1/2,-y,z-1/2

#13 -x+1/2,-y+1,z+1/2 #14 x-1,y,z #15 -x+3/2,-y+1,z-1/2

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

Figure S1 Experimental and theoretical powder XRD patterns for $K_6Mo_8PO_{29}OH \cdot H_2O$ (a) and $K_6Mo_5P_2O_{23} \cdot 7H_2O$ (b).

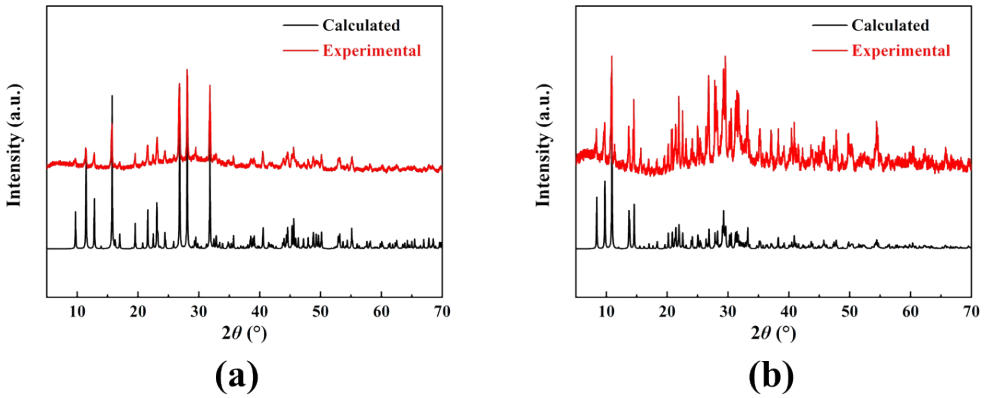

Figure S2 The cationic coordination environment of $K_6Mo_8PO_{29}OH·H_2O$ (a) and $K_6Mo_5P_2O_{23}·7H_2O$ (b).

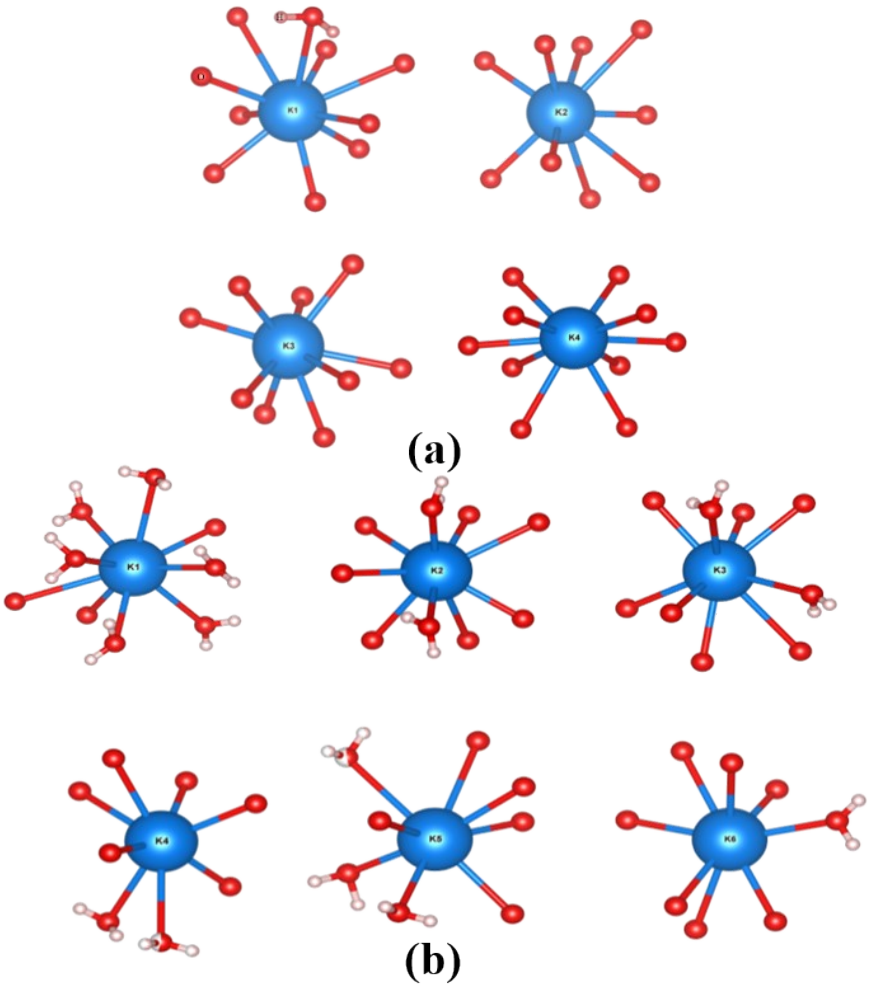

Figure S3 TG-DSC curves for $K_6Mo_5P_2O_{23}\cdot 7H_2O$.

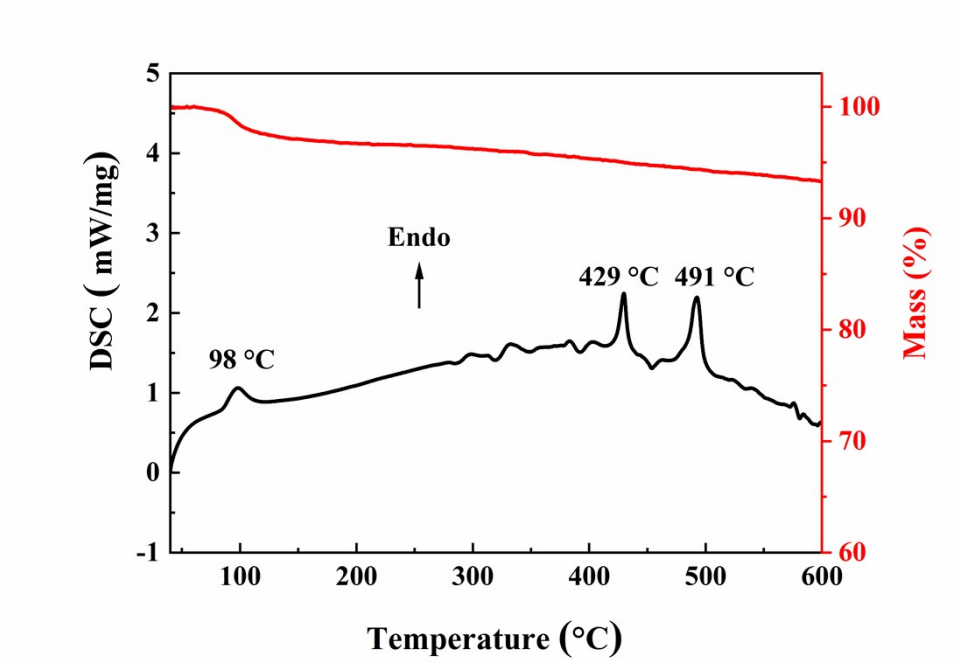

Figure S4 Density of states for $K_6Mo_8PO_{29}OH \cdot H_2O$ (a) and $K_6Mo_5P_2O_{23} \cdot 7H_2O$ (b).

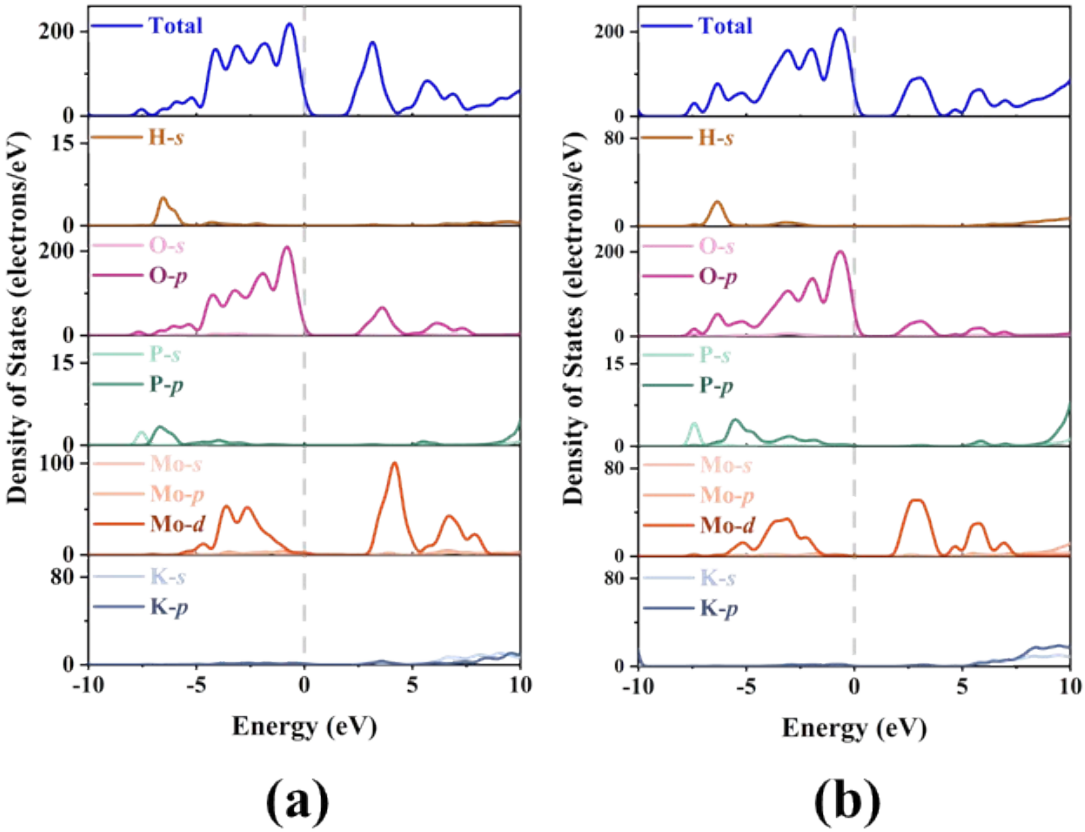

Figure S5 The calculated birefringence of K_3PO_4.

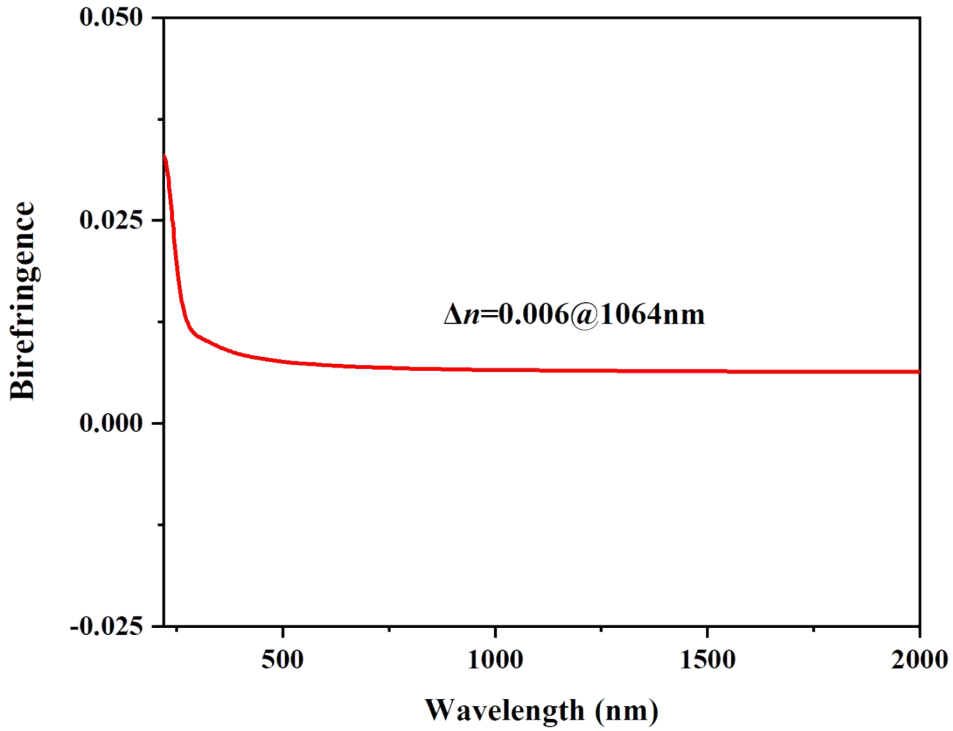

Figure S6 SHG density of the virtual electron (VE) occupied, unoccupied and virtual hole (VH) occupied, unoccupied states for $K_6Mo_5P_2O_{23}\cdot 7H_2O$.