Electronic Supplementary Information

$K_2MgMoP_2O_{10}$ and $K_3Mg_2MoP_3O_{14}$: two new molybdophosphates exhibiting different optical anisotropy induced by variable dimensionality of the anion framework

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Table S1. Crystal data and structure refinement for two new compounds.

Empirical formula	$K_2MgMoP_2O_{10}$	$K_3Mg_2MoP_3O_{14}$
Formula weight	420.39	584.52
Temperature (K)	298	298
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pnma*
a / Å	8.7629(18)	16.4088(10)
b / Å	9.7379(16)	15.8303(10)
c / Å	10.6366(19)	5.4483(5)
α / °	90	90
β / °	92.593(9)	90
γ / °	90	90
V / Å^3	906.7(3)	1415.23(18)
Z	4	4
Calculated density (g/cm^3)	3.080	2.743
μ (mm^{-1})	2.828	2.316
F (000)	808	1131
Theta range for data collection	2.837 to 27.544°.	2.482 to 27.525°
Index ranges	$-11 \le h \le 11$	$-20 \le h \le 21$
	$-12 \le k \le 12$	$-20 \le k \le 20$
	$-13 \le l \le 13$	$-7 \le l \le 6$
Reflections collected	13912	10032
Independent reflections	2089 [$R_{(int)}$ = 0.0831]	1684 [$R_{(int)}$ = 0.1215]
Completeness (%)	100.0	99.9
Goodness−of−fit on F^2	1.029	1.074
Final *R* indices [$I > 2\sigma(I)$][a]	R_1 = 0.0327	R_1 = 0.0466
	wR_2 = 0.0620	wR_2 = 0.1053
R indices (all data) [a]	R_1 = 0.0477	R_1 = 0.0710
	wR_2 = 0.0671	wR_2 = 0.1162
largest diff. peak/hole (e·Å^{-3})	0.641 / -0.817	0.783 / -1.301

[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 $F_o^2 > 2\sigma(F_o^2)$

Table S2**.** Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) and bond valence sum (BVS)* calculations for $K_2MgMoP_2O_{10}$ and $K_3Mg_2MoP_3O_{14}$ U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
			$K_2MgMoP_2O_{10}$		
K(1)	-65(1)	6989(1)	6955(1)	22(1)	1.172
K(2)	9551(2)	2868(1)	9008(1)	32(1)	1.060
Mg(1)	3209(2)	5437(2)	8637(1)	10(1)	2.099
Mo(1)	2479(1)	6261(1)	4236(1)	10(1)	6.140
P(1)	7004(1)	5453(1)	8550(1)	10(1)	5.046
P(2)	1643(1)	3775(1)	6138(1)	9(1)	5.120
O(1)	2462(4)	7076(3)	5652(3)	16(1)	2.167
O(2)	4385(4)	6241(4)	4004(3)	20(1)	2.082
O(3)	2330(3)	4380(3)	4918(3)	12(1)	2.117
O(4)	1984(4)	4695(3)	7255(3)	18(1)	2.052
O(5)	-69(4)	3696(3)	5857(3)	19(1)	1.995
O(6)	2330(4)	2361(3)	6313(3)	16(1)	2.011
O(7)	5340(4)	5041(3)	8492(3)	21(1)	1.964
O(8)	7172(4)	6998(3)	8207(3)	16(1)	2.190
O(9)	7920(4)	4679(3)	7573(3)	12(1)	2.085
O(10)	7754(4)	5169(3)	9840(3)	16(1)	1.976
			$K_3Mg_2MoP_3O_{14}$		
K(1)	7105(2)	2500	2611(7)	96(1)	0.724
K(2)	4938(1)	1112(1)	2726(2)	22(1)	1.208
Mg(1)	6590(1)	4382(1)	7230(3)	14(1)	2.252
Mo(1)	8955(1)	2500	6802(1)	16(1)	5.876
P(1)	5715(1)	2500	7248(4)	18(1)	4.992
P(2)	8616(1)	4556(1)	7206(3)	15(1)	5.204
O(1)	4897(3)	2500	5765(11)	21(1)	2.225
O(2)	5436(5)	2500	9925(12)	40(2)	1.672
O(3)	6187(2)	3283(2)	6460(9)	27(1)	2.071
O(4)	8070(3)	2500	8352(12)	27(1)	2.007
O(5)	7734(2)	4329(3)	7083(8)	30(1)	2.001
O(6)	8861(2)	4934(2)	9633(8)	26(1)	2.159
O(7)	8865(2)	5152(2)	5150(8)	25(1)	2.076
O(8)	9142(2)	3740(2)	6902(8)	27(1)	2.164
O(9)	8706(4)	2500	3758(12)	35(2)	2.077

(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 S3. Selected bond distances (Å) and angles (deg) for $K_2MgMoP_2O_{10}$.

K(1)-O(1)	2.667(3)	Mg(1)-O(4)	1.921(3)
K(1)-O(2)#3	2.837(3)	Mg(1)-O(6)#4	1.933(3)
K(1)-O(3)#2	3.054(3)	Mg(1)-O(7)	1.919(4)
K(1)-O(4)	2.875(3)	Mg(1)-O(10)#9	1.952(3)
K(1)-O(5)	3.413(4)	Mo(1)-O(1)	1.704(3)
K(1)-O(5)#2	3.072(3)	Mo(1)-O(2)	1.699(3)
K(1)-O(6)#4	2.978(3)	Mo(1)-O(3)	1.977(3)
K(1)-O(7)#4	3.018(3)	Mo(1)-O(5)#2	2.110(3)
K(1)-O(8)#1	2.815(3)	Mo(1)-O(8)#10	2.029(3)
K(1)-O(9)#1	2.952(3)	Mo(1)-O(9)#11	2.145(3)
K(2)-O(1)#5	2.737(4)	P(1)-O(7)	1.511(3)
K(2)-O(2)#5	2.771(3)	P(1)-O(8)	1.558(3)
K(2)-O(3)#7	3.112(3)	P(1)-O(9)	1.539(3)
K(2)-O(4)#6	3.398(4)	P(1)-O(10)	1.519(3)
K(2)-O(6)#7	3.206(3)	P(2)-O(3)	1.570(3)
K(2)-O(8)#5	2.868(3)	P(2)-O(4)	1.508(3)
K(2)-O(9)	2.699(3)	P(2)-O(5)	1.518(3)
K(2)-O(10)	2.899(3)	P(2)-O(6)	1.511(3)
K(2)-O(10)#8	3.236(4)		
O(1)-K(1)-O(2)#3	123.63(10)	O(2)#5-K(2)-O(10)#8	80.45(9)
O(1)-K(1)-O(3)#2	101.86(9)	O(3)#7-K(2)-O(4)#6	162.86(8)
O(1)-K(1)-O(4)	63.45(10)	O(3)#7-K(2)-O(6)#7	45.86(8)
O(1)-K(1)-O(5)	80.80(9)	O(3)#7-K(2)-O(10)#8	138.90(8)
O(1)-K(1)-O(5)#2	55.37(9)	O(6)#7-K(2)-O(4)#6	150.87(8)
O(1)-K(1)-O(6)#4	69.71(10)	O(6)#7-K(2)-O(10)#8	102.08(8)
O(1)-K(1)-O(7)#4	87.07(9)	O(8)#5-K(2)-O(3)#7	74.60(9)
O(1)-K(1)-O(8)#1	176.32(10)	O(8)#5-K(2)-O(4)#6	91.38(9)
O(1)-K(1)-O(9)#1	131.24(9)	O(8)#5-K(2)-O(6)#7	107.01(10)
O(2)#3-K(1)-O(3)#2	129.67(10)	O(8)#5-K(2)-O(10)	101.89(10)
O(2)#3-K(1)-O(4)	120.91(10)	O(8)#5-K(2)-O(10)#8	146.47(9)
O(2)#3-K(1)-O(5)	146.74(9)	O(9)-K(2)-O(1)#5	137.51(11)
O(2)#3-K(1)-O(5)#2	153.54(10)	O(9)-K(2)-O(2)#5	163.10(10)
O(2)#3-K(1)-O(6)#4	67.11(9)	O(9)-K(2)-O(3)#7	108.25(10)
O(2)#3-K(1)-O(7)#4	60.50(9)	O(9)-K(2)-O(4)#6	71.15(9)
O(2)#3-K(1)-O(9)#1	99.66(9)	O(9)-K(2)-O(6)#7	98.85(9)
O(3)#2-K(1)-O(5)	51.40(8)	O(9)-K(2)-O(8)#5	58.87(9)
O(3)#2-K(1)-O(5)#2	47.35(8)	O(9)-K(2)-O(10)	52.18(8)
O(4)-K(1)-O(3)#2	96.76(9)	O(9)-K(2)-O(10)#8	100.76(9)
O(4)-K(1)-O(5)	45.49(8)	O(10)-K(2)-O(3)#7	95.33(9)
O(4)-K(1)-O(5)#2	83.58(9)	O(10)#8-K(2)-O(4)#6	55.46(8)
O(4)-K(1)-O(6)#4	62.90(9)	O(10)-K(2)-O(4)#6	97.22(9)
O(4)-K(1)-O(7)#4	145.85(10)	O(10)-K(2)-O(6)#7	57.56(8)
O(4)-K(1)-O(9)#1	76.12(9)	O(10)-K(2)-O(10)#8	79.92(10)

O(5)#2-K(1)-O(5)	57.47(10)	O(4)-Mg(1)-O(6)#4	104.86(15)
O(6)#4-K(1)-O(3)#2	159.65(9)	O(4)-Mg(1)-O(7)	112.01(16)
O(6)#4-K(1)-O(5)	108.31(8)	O(4)-Mg(1)-O(10)#9	105.86(15)
O(6)#4-K(1)-O(5)#2	124.29(9)	O(6)#4-Mg(1)-O(10)#9	98.90(14)
O(6)#4-K(1)-O(7)#4	91.94(9)	O(7)-Mg(1)-O(6)#4	115.91(15)
O(7)#4-K(1)-O(3)#2	106.40(9)	O(7)-Mg(1)-O(10)#9	117.69(16)
O(7)#4-K(1)-O(5)	150.77(9)	O(1)-Mo(1)-O(3)	95.95(13)
O(7)#4-K(1)-O(5)#2	93.83(9)	O(1)-Mo(1)-O(5)#2	89.06(14)
O(8)#1-K(1)-O(2)#3	56.99(9)	O(1)-Mo(1)-O(8)#10	94.69(13)
O(8)#1-K(1)-O(3)#2	76.26(9)	O(1)-Mo(1)-O(9)#11	169.91(14)
O(8)#1-K(1)-O(4)	119.74(10)	O(2)-Mo(1)-O(1)	100.48(16)
O(8)#1-K(1)-O(5)	100.21(9)	O(2)-Mo(1)-O(3)	97.14(15)
O(8)#1-K(1)-O(5)#2	122.20(10)	O(2)-Mo(1)-O(5)#2	168.96(13)
O(8)#1-K(1)-O(6)#4	113.10(10)	O(2)-Mo(1)-O(8)#10	92.21(15)
O(8)#1-K(1)-O(7)#4	90.42(9)	O(2)-Mo(1)-O(9)#11	89.21(13)
O(8)#1-K(1)-O(9)#1	50.30(8)	O(3)-Mo(1)-O(5)#2	87.30(13)
O(9)#1-K(1)-O(3)#2	55.61(8)	O(3)-Mo(1)-O(8)#10	164.32(13)
O(9)#1-K(1)-O(5)	50.86(8)	O(3)-Mo(1)-O(9)#11	85.57(11)
O(9)#1-K(1)-O(5)#2	95.80(9)	O(5)#2-Mo(1)-O(9)#11	81.03(12)
O(9)#1-K(1)-O(6)#4	115.31(9)	O(8)#10-Mo(1)-O(5)#2	81.38(13)
O(9)#1-K(1)-O(7)#4	137.85(10)	O(8)#10-Mo(1)-O(9)#11	81.99(11)
O(1)#5-K(2)-O(2)#5	56.71(9)	O(7)-P(1)-O(8)	110.36(19)
O(1)#5-K(2)-O(3)#7	111.62(9)	O(7)-P(1)-O(9)	112.02(18)
O(1)#5-K(2)-O(4)#6	66.41(9)	O(7)-P(1)-O(10)	111.48(19)
O(1)#5-K(2)-O(6)#7	119.30(9)	O(9)-P(1)-O(8)	104.85(17)
O(1)#5-K(2)-O(8)#5	119.34(10)	O(10)-P(1)-O(8)	110.25(18)
O(1)#5-K(2)-O(10)	134.96(10)	O(10)-P(1)-O(9)	107.65(17)
O(1)#5-K(2)-O(10)#8	55.90(9)	O(4)-P(2)-O(3)	111.00(18)
O(2)#5-K(2)-O(3)#7	63.51(9)	O(4)-P(2)-O(5)	110.14(19)
O(2)#5-K(2)-O(4)#6	121.35(10)	O(4)-P(2)-O(6)	112.38(18)
O(2)#5-K(2)-O(6)#7	64.63(9)	O(5)-P(2)-O(3)	105.59(17)
O(2)#5-K(2)-O(8)#5	127.21(10)	O(6)-P(2)-O(3)	106.15(17)
O(2)#5-K(2)-O(10)	112.19(10)	O(6)-P(2)-O(5)	111.30(19)

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Selected bond lengths (Å) and angles (deg.) for $K_3Mg_2MoP_3O_{14}$.

K(1)-O(2)#2	3.105(8)	Mg(1)-O(5)	1.880(4)
K(1)-O(3)	2.865(5)	Mg(1)-O(6)#7	1.929(4)
K(1)-O(3)#1	2.865(5)	Mg(1)-O(7)#8	1.906(4)
K(1)-O(4)#2	2.809(7)	Mo(1)-O(1)#9	2.035(5)
K(1)-O(9)	2.700(7)	Mo(1)-O(4)	1.679(6)
K(2)-O(1)	2.752(4)	Mo(1)-O(8)	1.987(4)
K(2)-O(2)#2	2.797(4)	Mo(1)-O(8)#1	1.987(4)
K(2)-O(3)#1	3.042(5)	Mo(1)-O(9)	1.708(6)
K(2)-O(6)#3	2.906(4)	P(1)-O(1)	1.567(5)
K(2)-O(6)#4	2.816(4)	P(1)-O(2)	1.529(6)
K(2)-O(7)#3	2.853(4)	P(1)-O(3)	1.523(4)
K(2)-O(7)#5	3.092(4)	P(1)-O(3)#1	1.523(4)
K(2)-O(8)#4	3.213(5)	P(2)-O(5)	1.493(4)
K(2)-O(8)#5	2.849(5)	P(2)-O(6)	1.506(4)
K(2)-O(9)#6	3.093(5)	P(2)-O(7)	1.520(4)
Mg(1)-O(3)	1.909(4)	P(2)-O(8)	1.562(4)
O(3)-K(1)-O(2)#2	83.16(15)	O(7)#3-K(2)-O(6)#3	50.72(11)
O(3)#1-K(1)-O(2)#2	83.16(15)	O(7)#3-K(2)-O(7)#5	78.35(12)
O(3)-K(1)-O(3)#1	51.28(16)	O(7)#3-K(2)-O(8)#4	140.07(11)
O(4)#2-K(1)-O(2)#2	96.2(2)	O(7)#5-K(2)-O(8)#4	106.12(11)
O(4)#2-K(1)-O(3)	154.32(8)	O(7)#3-K(2)-O(9)#6	134.41(15)
O(4)#2-K(1)-O(3)#1	154.32(8)	O(7)#5-K(2)-O(9)#6	87.42(12)
O(9)-K(1)-O(2)#2	165.3(2)	O(8)#5-K(2)-O(3)#1	150.99(11)
O(9)-K(1)-O(3)	110.02(19)	O(8)#5-K(2)-O(6)#3	132.85(12)
O(9)-K(1)-O(3)#1	110.02(19)	O(8)#5-K(2)-O(7)#3	85.64(12)
O(9)-K(1)-O(4)#2	69.1(2)	O(8)#5-K(2)-O(7)#5	48.99(10)
O(1)-K(2)-O(2)#2	73.04(14)	O(8)#5-K(2)-O(8)#4	127.88(14)
O(1)-K(2)-O(3)#1	50.43(12)	O(8)#5-K(2)-O(9)#6	53.89(14)
O(1)-K(2)-O(6)#3	108.31(14)	O(9)#6-K(2)-O(8)#4	85.45(14)
O(1)-K(2)-O(6)#4	98.42(13)	O(3)-Mg(1)-O(6)#7	102.6(2)
O(1)-K(2)-O(7)#3	137.58(14)	O(5)-Mg(1)-O(3)	107.23(19)
O(1)-K(2)-O(7)#5	143.86(13)	O(5)-Mg(1)-O(6)#7	112.2(2)
O(1)-K(2)-O(8)#4	51.95(12)	O(5)-Mg(1)-O(7)#8	116.4(2)
O(1)-K(2)-O(8)#5	117.09(13)	O(7)#8-Mg(1)-O(3)	113.6(2)
O(1)-K(2)-O(9)#6	64.79(15)	O(7)#8-Mg(1)-O(6)#7	104.16(19)
O(2)#2-K(2)-O(3)#1	85.45(17)	O(4)-Mo(1)-O(1)#9	109.2(3)
O(2)#2-K(2)-O(6)#3	120.07(17)	O(4)-Mo(1)-O(8)	96.89(11)
O(2)#2-K(2)-O(6)#4	157.47(18)	O(4)-Mo(1)-O(8)#1	96.89(11)
O(2)#2-K(2)-O(7)#3	87.06(14)	O(4)-Mo(1)-O(9)	106.3(3)
O(2)#2-K(2)-O(7)#5	113.47(16)	O(8)-Mo(1)-O(1)#9	82.23(12)
O(2)#2-K(2)-O(8)#4	123.93(13)	O(8)#1-Mo(1)-O(1)#9	82.23(12)
O(2)#2-K(2)-O(8)#5	65.56(16)	O(8)-Mo(1)-O(8)#1	161.9(2)
O(2)#2-K(2)-O(9)#6	59.36(17)	O(9)-Mo(1)-O(1)#9	144.5(3)

O(3)#1-K(2)-O(7)#5	157.86(11)	O(9)-Mo(1)-O(8)	93.64(14)
O(3)#1-K(2)-O(8)#4	68.99(11)	O(9)-Mo(1)-O(8)#1	93.64(14)
O(3)#1-K(2)-O(9)#6	113.05(12)	O(2)-P(1)-O(1)	103.6(4)
O(6)#3-K(2)-O(3)#1	60.41(11)	O(3)-P(1)-O(1)	106.8(2)
O(6)#4-K(2)-O(3)#1	105.42(12)	O(3)#1-P(1)-O(1)	106.8(2)
O(6)#4-K(2)-O(6)#3	82.27(12)	O(3)−P(1)-O(2)	114.9(2)
O(6)#3-K(2)-O(7)#5	98.74(11)	O(3)#1-P(1)-O(2)	114.9(2)
O(6)#4-K(2)-O(7)#3	111.73(11)	O(3)#1-P(1)-O(3)	109.0(3)
O(6)#4-K(2)-O(7)#5	61.40(11)	O(5)-P(2)-O(6)	113.1(2)
O(6)#3-K(2)-O(8)#4	89.82(11)	O(5)-P(2)-O(7)	112.1(2)
O(6)#4-K(2)-O(8)#4	47.37(10)	O(5)-P(2)-O(8)	109.4(2)
O(6)#4-K(2)-O(8)#5	102.31(12)	O(6)-P(2)-O(7)	109.2(2)
O(6)#3-K(2)-O(9)#6	173.10(14)	O(6)-P(2)-O(8)	105.9(2)
O(6)#4-K(2)-O(9)#6	98.11(13)	O(7)-P(2)-O(8)	106.7(2)
O(7)#3-K(2)-O(3)#1	91.88(12)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z	#2 x,y,z-1	#3 -x+3/2,y-1/2,z-1/2
#4 x-1/2,-y+1/2,-z+3/2	#5 x-1/2,-y+1/2,-z+1/2	#6 x-1/2,y,-z+1/2
#7 -x+3/2,-y+1,z-1/2	#8 -x+3/2,-y+1,z+1/2	#9 x+1/2,y,-z+3/2
#10 x,y,z+1	#11 x,-y+1/2,z+1	#12 -x+1,y+1/2,-z+1
#13 x+1/2,-y+1/2,-z+3/2	#14 x+1/2,y,-z+1/2	#15 x+1/2,-y+1/2,-z+1/2
#16 x-1/2,y,-z+3/2	#17 -x+3/2,y+1/2,z+1/2	

Table S5. The polarization anisotropy of $K_2MgMoP_2O_{10}$ and $K_3Mg_2MoP_3O_{14}$.

	$K_2MgMoP_2O_{10}$	$K_3Mg_2MoP_3O_{14}$
$P(1)O_4$	2.181933635	1.239185939
$P(2)O_4$	0.928486315	1.33783995
MoO_6/MoO_5	27.00898028	3.701073885

Fig. S1. The PXRD patterns of (a) $K_2MgMoP_2O_{10}$, (b) $K_3Mg_2MoP_3O_{14}$

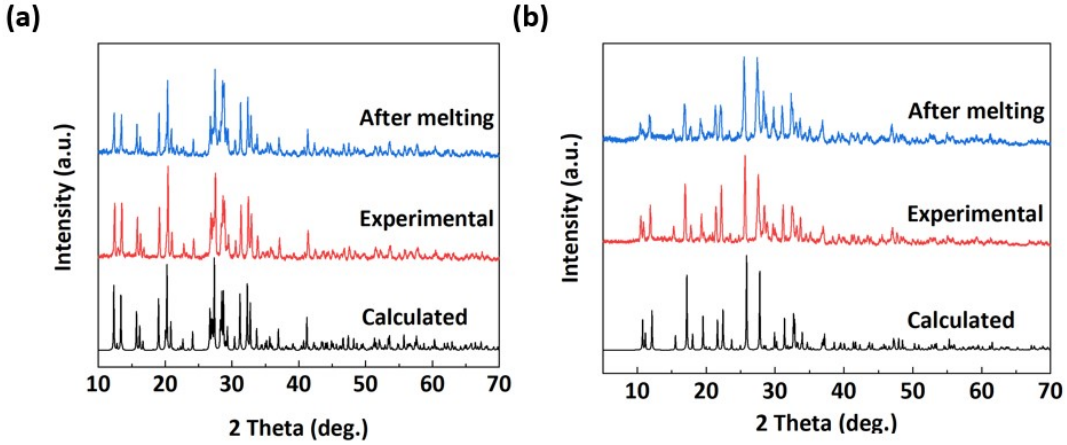

Fig. S2. The IR spectra of (a) $K_2MgMoP_2O_{10}$, (b) $K_3Mg_2MoP_3O_{14}$.

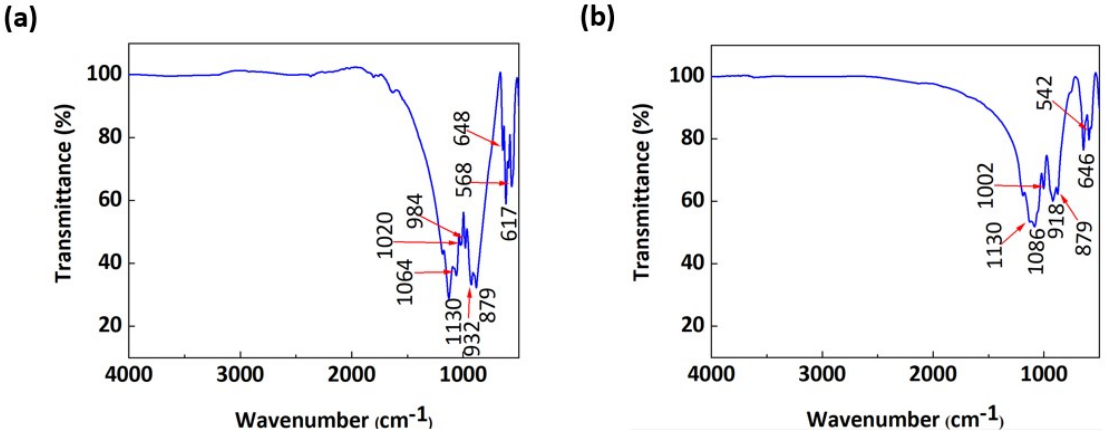

Fig. S3. TG and DSC data for (a) $K_2MgMoP_2O_{10}$, (b) $K_3Mg_2MoP_3O_{14}$.

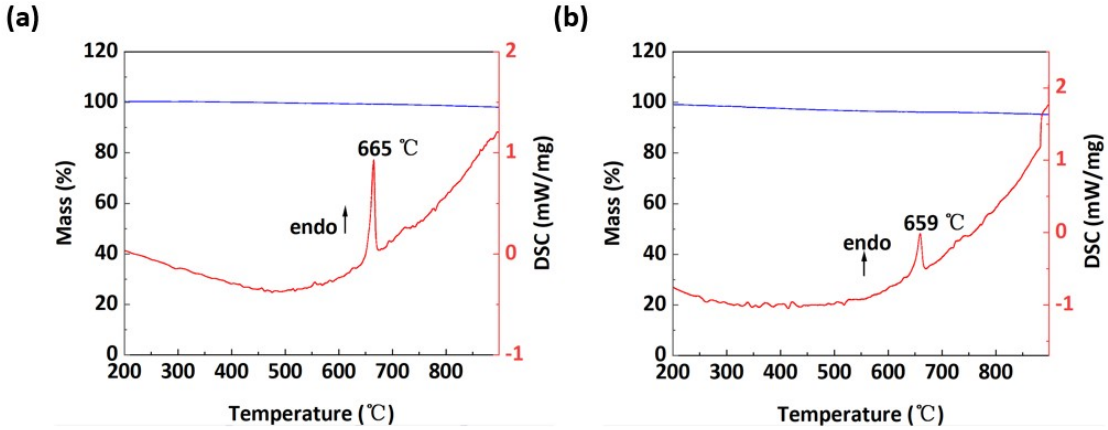

Fig. S4. Calculated band structures of the GGA method, (a) $K_2MgMoP_2O_{10}$, (b) $K_3Mg_2MoP_3O_{14}$.

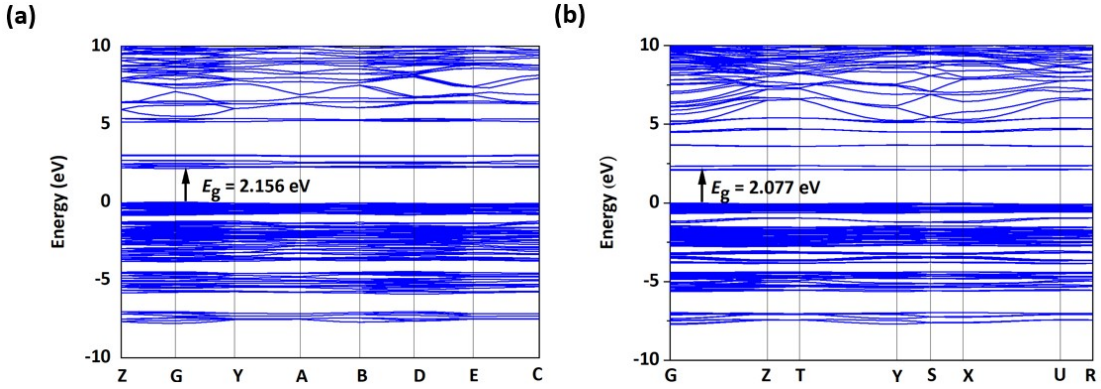

Fig. S5. (a) Original view of the crystal; (b,c) Extinction views of the crystal by negative and positive rotational compensators; (d) View of the crystal thickness; and (e) Orientation of the $K_2MgMoP_2O_{10}$ crystal determined by X−ray single−crystal diffraction

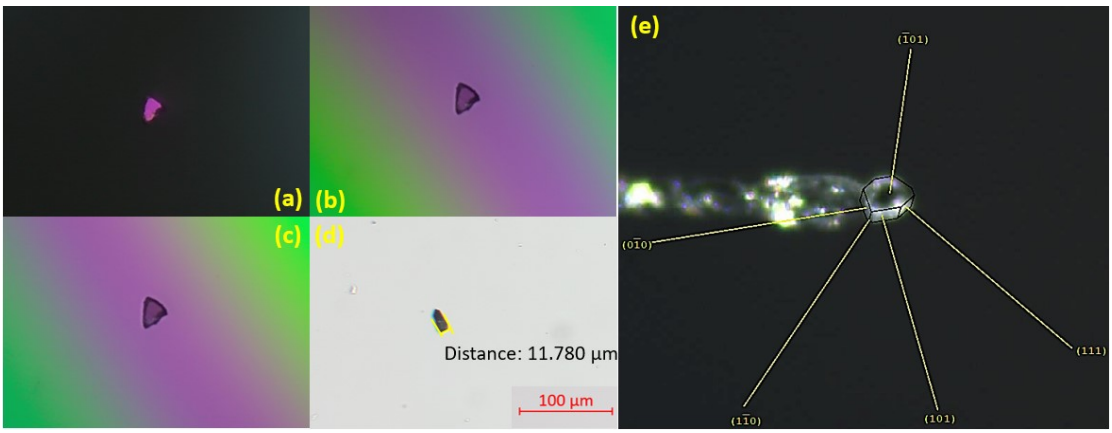

Fig. S6. REDA index (ζ) is used to analyze the contribution of $K_2MgMoP_2O_{10}$ birefringence.