K$_2$ZnMoP$_2$O$_{10}$: A Novel Nonlinear Optical Molybdophosphate with a Strong Second Harmonic Generation Response and Moderate Birefringence

Haonan Liu, Hongping Wu,* Hongwei Yu,* Zhanggui Hu, Jiyang Wang, and Yicheng Wu

Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin 300384, China.
To whom correspondence should be addressed. E-mail: hwyu15@gmail.com (Hongwei Yu).

CONTENTS

Table S1. Crystallographic Data and Structure Refinements for $K_2ZnMoP_2O_{10}$.

Empirical formula	$K_2ZnMoP_2O_{10}$
Fw(g/mol)	461.45
Temperature(K)	295(2)
Radiation, Wavelength	Mo Kα, λ = 0.71073 Å
Crystal size (mm)	0.044 × 0.045 × 0.059
Cryst syst.	Orthorhombic
Space group	$P2_12_12_1$ (No.19)
Unit cell dimensions(Å)	a = 9.418(3)
	b = 9.693(3)
	c = 10.141(2)
Unit cell volume(Å^3)	925.8(4)
Z, D_{calcd}(mg/m^3)	4, 3.311
μ (mm^{-1})	5.230
F(000)	880
Theta range for data collection	2.91 to 25.49°
Limiting indices	$-11 \le h \le 11, -11 \le k \le 11, -12 \le l \le 12$
Reflections collected/unique	7344 /1725
R(int)	0.0669
Coverage of independent reflections	100.0 %
Absorption correction	Numerical Mu From Formula
Max. and min. transmission	0.8670 and 0.7650
Refinement method	Full-matrix least-squares on F^2
Data/restraints/param	1725 / 0 / 145
GOF on F^2	1.056
R indices [I > 2σ (I)]^a	R$_1$ = 0.0364, wR$_2$ = 0.0679
R indices (all data)	R$_1$ = 0.0449, wR$_2$ = 0.0712
Absolute structure parameter	0.06(2)
Largest diff. peak and hole (e Å^{-3})	0.686 and -0.850

^{a} R$_1$ = $\sum$ ||F$_o$| - |F$_c$|| / $\sum$ |F$_o$|, wR$_2$ = {$\sum$ [w(F$_o^2$ - F$_c^2$)^2] / $\sum$ [w(F$_o^2$)^2]}$^{1/2}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $K_2ZnMoP_2O_{10}$.

Atom	x	y	z	U(eq)	BVS
K1	0.3589(3)	0.9896(3)	0.4447(3)	0.0284(7)	1.00
K2	0.8753(3)	0.1804(3)	0.2386(2)	0.0233(6)	1.09
Zn1	0.54453(13)	0.64478(12)	0.40290(11)	0.0134(3)	2.18
Mo1	0.69033(9)	0.16988(9)	0.61643(8)	0.0105(2)	6.15
P1	0.2875(3)	0.6278(3)	0.5733(2)	0.0107(6)	5.07
P2	0.5572(3)	0.3166(3)	0.3506(2)	0.0092(6)	5.03
O1	0.5684(8)	0.2583(8)	0.2111(7)	0.0177(18)	1.90
O2	0.2390(10)	0.5198(8)	0.4757(7)	0.029(2)	2.09
O3	0.2177(8)	0.7638(8)	0.5383(7)	0.0185(18)	2.18
O4	0.2420(7)	0.5799(7)	0.7154(7)	0.0114(16)	1.80
O5	0.6711(8)	0.2365(8)	0.4324(6)	0.0215(19)	2.10
O6	0.4130(7)	0.2920(8)	0.4145(7)	0.0171(18)	1.95
O7	0.5230(8)	0.1084(8)	0.6339(7)	0.0226(19)	2.14
O8	0.6713(8)	0.3306(8)	0.6821(6)	0.0228(18)	2.07
O9	0.6028(8)	0.4665(8)	0.3454(8)	0.027(2)	2.10
O10	0.4479(8)	0.6453(9)	0.5718(6)	0.027(2)	1.85

Table S3. Selected bond distances (Å) and angles (°) for $K_2ZnMoP_2O_{10}$.

Distances (Å)			
K1-O7	2.719(8)	Zn1-O1#6	1.918(7)
K1-O8#7	2.795(8)	Zn1-O3#9	1.950(7)
K1-O9#4	2.973(8)	Zn1-O10	1.939(7)
K1-O9#7	3.244(8)	Mo1-O7	1.694(7)
K1-O3#1	2.731(8)	Mo1-O5	1.983(6)
K1-O1#4	2.828(8)	Mo1-O2#8	2.113(7)
K1-O6	2.991(8)	Mo1-O8	1.704(7)
K1-O5#7	3.425(8)	Mo1-O4#5	2.018(7)
K2-O7#8	2.793(8)	Mo1-O6#8	2.152(7)
K2-O4#8	2.857(7)	P1-O2	1.512(7)
K2-O8#8	2.903(8)	P1-O10	1.520(7)
K2-O1	3.000(8)	P2-O9	1.516(8)
K2-O7#2	3.144(8)	P2-O1	1.528(7)
K2-O5	2.802(7)	P1-O3	1.516(7)
K2-O2#4	2.882(8)	P1-O4	1.574(7)
K2-O10#3	2.914(8)	P2-O6	1.524(7)
K2-O3#4	3.051(8)	P2-O5	1.563(7)
Zn1-O9	1.904(8)		

Angles (°)

O7-K1-O3#1	111.8(2)	O5-K2-O8#13	118.2(2)
O3#1-K1-O8#11	110.6(2)	O2#7-K2-O8#13	123.2(2)
O3#1-K1-O1#7	71.1(2)	O5-K2-O10#5	133.4(3)
O7-K1-O9#7	131.4(2)	O2#7-K2-O10#5	95.1(2)
O8#11-K1-O9#7	70.6(2)	O7#13-K2-O1	109.8(2)
O7-K1-O6	63.9(2)	O4#13-K2-O1	79.3(2)
O8#11-K1-O6	56.6(2)	O8#13-K2-O1	163.8(2)
O9#7-K1-O6	87.2(2)	O7#13-K2-O3#7	112.0(2)
O3#1-K1-O9#11	61.0(2)	O4#13-K2-O3#7	104.9(2)
O1#7-K1-O9#11	130.6(2)	O8#13-K2-O3#7	122.7(2)
O6-K1-O9#11	93.8(2)	O1-K2-O3#7	64.59(19)
O3#1-K1-O5#11	104.1(2)	O5-K2-O7#3	128.2(2)
O1#7-K1-O5#11	160.6(2)	O2#7-K2-O7#3	51.5(2)
O6-K1-O5#11	50.62(18)	O10#5-K2-O7#3	98.4(2)
O7-K1-O8#11	114.8(2)	O3#7-K2-O7#3	90.7(2)
O7-K1-O1#7	126.3(2)	O9-Zn1-O1#9	119.7(3)
O8#11-K1-O1#7	113.0(2)	O1#9-Zn1-O10	105.7(3)
O3#1-K1-O9#7	110.0(2)	O1#9-Zn1-O3#14	112.8(3)
O1#7-K1-O9#7	50.0(2)	O9-Zn1-O10	114.1(3)
O3#1-K1-O6	154.7(2)	O9-Zn1-O3#14	105.4(3)
O1#7-K1-O6	132.7(2)	O10-Zn1-O3#14	97.0(3)
O7-K1-O9#11	84.5(2)	O7-Mo1-O8	100.5(4)
O8#11-K1-O9#11	75.5(2)	O8-Mo1-O5	93.5(3)
O9#7-K1-O9#11	138.52(17)	O8-Mo1-O4#8	95.6(3)
O7-K1-O5#11	73.1(2)	O7-Mo1-O2#13	86.7(4)
O8#11-K1-O5#11	50.03(18)	O5-Mo1-O2#13	83.5(3)
O9#7-K1-O5#11	118.8(2)	O7-Mo1-O6#13	169.1(3)
O9#11-K1-O5#11	43.61(18)	O5-Mo1-O6#13	84.0(3)
O7#13-K2-O5	82.8(2)	O2#13-Mo1-O6#13	82.7(3)
O5-K2-O4#13	75.8(2)	O7-Mo1-O5	97.3(3)
O5-K2-O2#7	112.2(2)	O7-Mo1-O4#8	93.1(3)
O7#13-K2-O8#13	54.6(2)	O5-Mo1-O4#8	164.7(3)
O4#13-K2-O8#13	110.1(2)	O8-Mo1-O2#13	172.5(4)
O7#13-K2-O10#5	63.8(2)	O4#8-Mo1-O2#13	85.9(3)
O4#13-K2-O10#5	149.1(2)	O8-Mo1-O6#13	90.1(3)
O8#13-K2-O10#5	68.5(2)	O4#8-Mo1-O6#13	83.7(3)
O5-K2-O1	49.87(19)	O2-P1-O10	111.8(5)
O2#7-K2-O1	72.9(2)	O2-P1-O4	108.3(4)
O10#5-K2-O1	110.5(2)	O10-P1-O4	108.2(4)
O5-K2-O3#7	113.4(2)	O9-P2-O6	114.7(4)
O2#7-K2-O3#7	48.84(19)	O6-P2-O1	113.4(4)
O10#5-K2-O3#7	58.4(2)	O6-P2-O5	108.0(4)
O7#13-K2-O7#3	131.11(12)	O2-P1-O3	108.5(4)

O4#13-K2-O7#3	53.30(19)	O3-P1-O10	109.4(5)
O8#13-K2-O7#3	76.6(2)	O3-P1-O4	110.7(4)
O1-K2-O7#3	119.1(2)	O9-P2-O1	107.7(4)
O7#13-K2-O4#13	142.3(2)	O9-P2-O5	107.5(5)
O7#13-K2-O2#7	158.6(2)	O1-P2-O5	105.0(4)
O4#13-K2-O2#7	58.8(2)		

Table S4. Experimental and calculated refractive indices for $K_2ZnMoP_2O_{10}$.

$\lambda/\mu m$	$n_x (n_a)$		$n_y (n_b)$		$n_z (n_c)$		n_z- n_x
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
0.4502	1.6613	1.6613	1.6763	1.6767	1.7147	1.7144	0.0534
0.532	1.6482	1.6479	1.6620	1.6613	1.6955	1.6951	0.0473
0.6365	1.6389	1.6386	1.6511	1.6511	1.6863	1.683	0.0474
0.8293	1.6298	1.6301	1.6420	1.6420	1.6713	1.6715	0.0415
1.0626	1.6254	1.6252	1.6369	1.6368	1.6653	1.6651	0.0399

Table S5. The dipole moments in ZnO_4, MoO_6 and PO_4 polyhedra in the unit cell of $K_2ZnMoP_2O_{10}$.

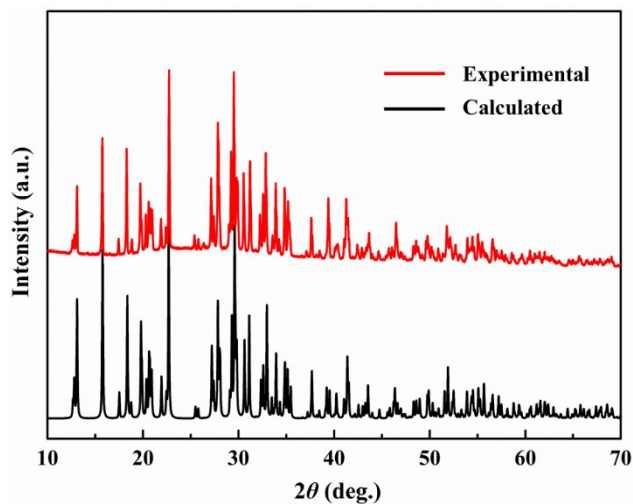|	$Zn(1)O_4$	$Mo(1)O_6$	$P(1)O_4$	$P(2)O_4$
local dipole moments	2.35	0.94	0.42	3.00
flexible dipole moments	0.135	0.142	0.135	0.134

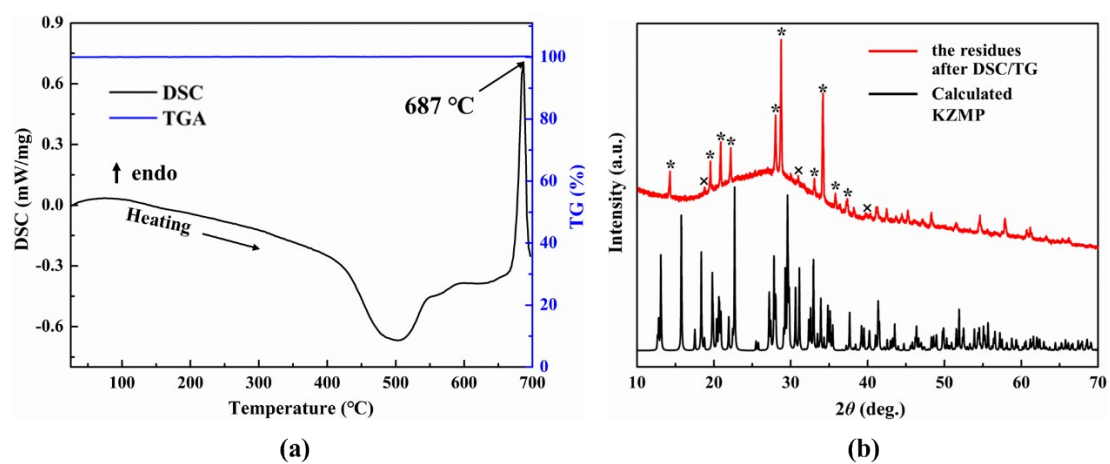**Figure S1**. Calculated and experimental PXRD patterns for $K_2ZnMoP_2O_{10}$.

Figure S2. (a) TG/DSC patterns of $K_2ZnMoP_2O_{10}$. (b) The PXRD patterns of residues after TG/DSC of $K_2ZnMoP_2O_{10}$ (* = $KZnPO_4$, × = other unkown phase).
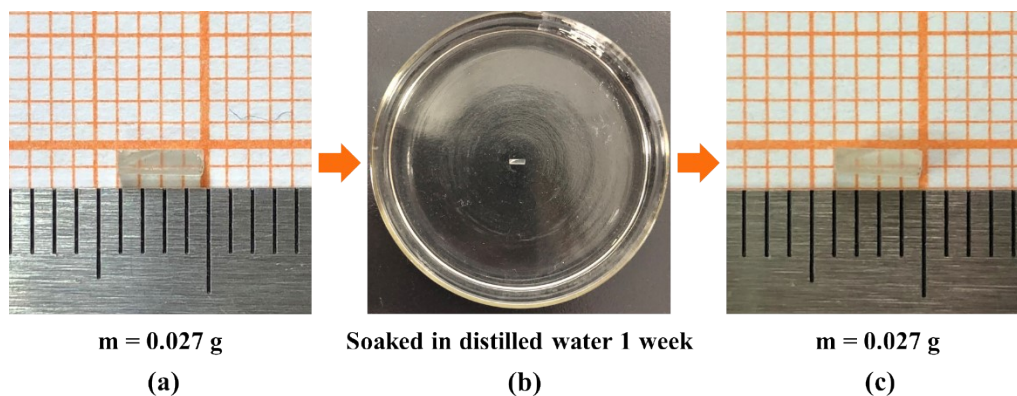

Figure S3. The moisture-stable analysis for $K_2ZnMoP_2O_{10}$: the $K_2ZnMoP_2O_{10}$ crystal was soaked in the water for one week: (a) before soaking, (b) submerged sample, and(c) after soaking in water.
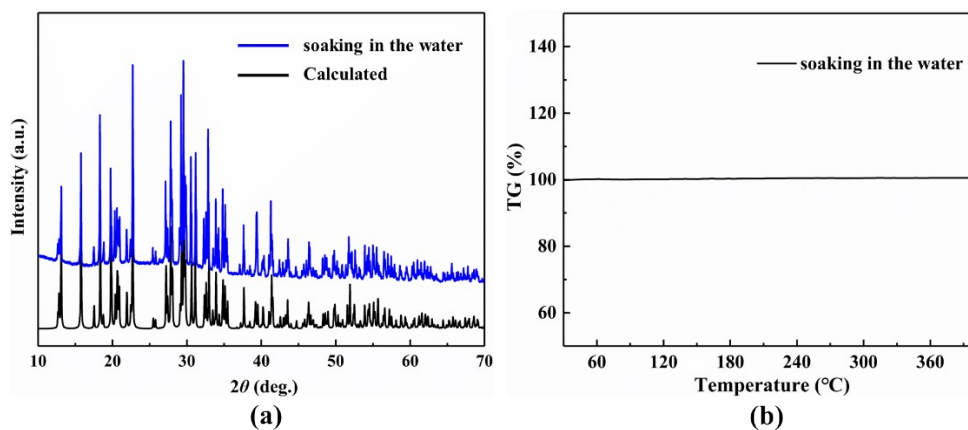
Figure S4. The PXRD (a) and TG (b) patterns of residues after moisture-stable analysis for $K_2ZnMoP_2O_{10}$.

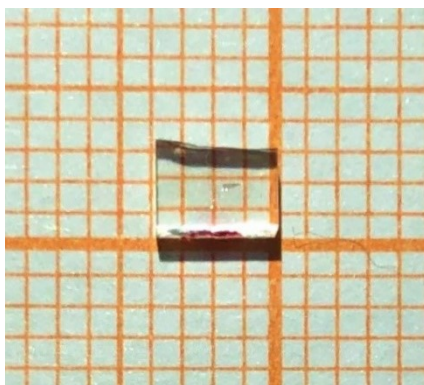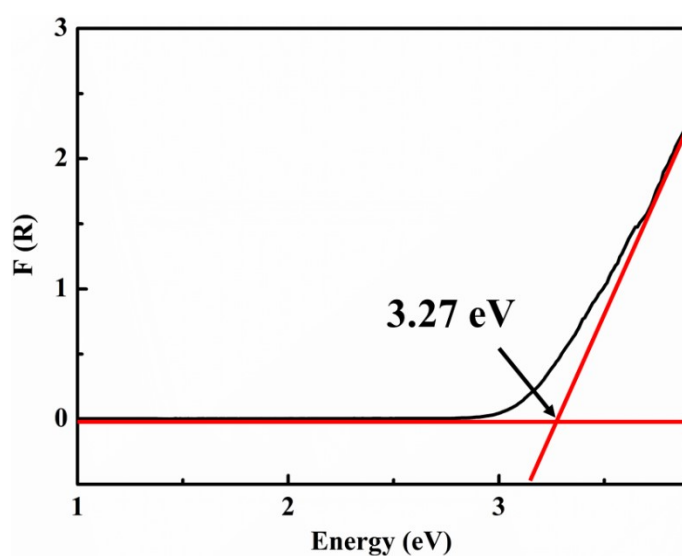**Figure S5**. Photograph of a [001]-faced wafer cut from the crystal.

Figure S6. Band gap for $K_2ZnMoP_2O_{10}$ of 3.27 eV.

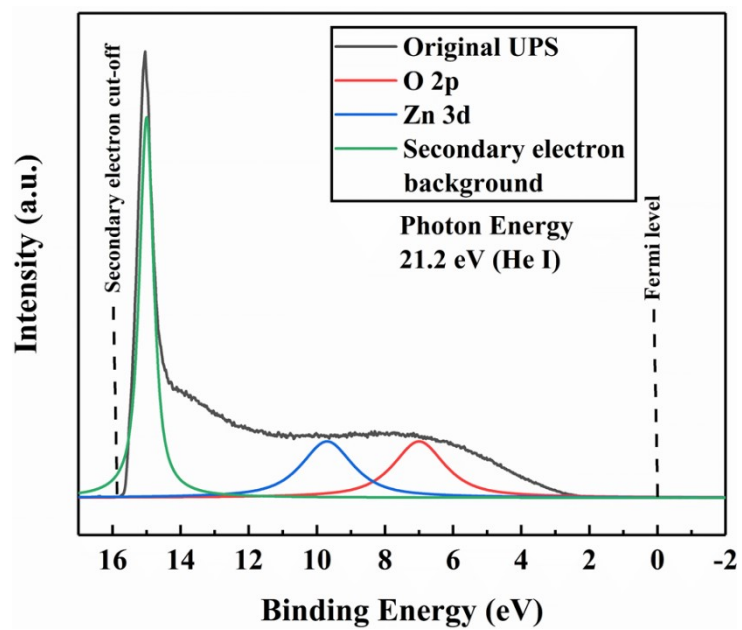**Figure S7.** UPS spectrum of a $K_2ZnMoP_2O_{10}$.