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Electronic Supporting Information

Polar Polymorphism: *α*-, and *β*-$KCsWP_2O_9$ Nonlinear Optical Materials with Strong Second Harmonic Generation Response

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Table 1(a). Crystal data and structure refinements for α-, and β-$KCsWP_2O_9$.

Empirical formula	α-$KCsWP_2O_9$	β-$KCsWP_2O_9$
Formula weight	561.80	561.80
Crystal system	Trigonal	Hexagonal
Space group, Z	$P3_2$, 3	$P6_1$, 6
Unit cell dimensions (Å)	a = 8.501(6)	a = 8.464(11)
	c = 10.940(19)	c = 21.882(19)
Volume (Å^3)	684.82(13)	1357.9(5)
Density (calc) (g/cm^3)	4.087	4.122
θ range for data collection (deg)	1.861-27.488	2.779-27.214
Limiting indices	$11 \leq h \leq 11$, $-11 \leq k \leq 9$, $-14 \leq l \leq 14$	$-10 \leq h \leq 7$, $-9 \leq k \leq 10$, $-27 \leq l \leq 28$
Reflections collected/unique	4234/2061 [R(int) = 0.0316]	8167/1997 [R(int) = 0.0574]
Completeness (%)	99.9	100
Goodness of fit on F_o^2	0.833	0.935
Final R indices [$F_o^2 > 2\delta(F_o^2)$][a]	R_1 = 0.0248, wR_2 = 0.0490	R_1 = 0.0327, wR_2 = 0.0633
R indices (all data)[a]	R_1 = 0.0254, wR_2 = 0.0492	R_1 = 0.0433, wR_2 = 0.0672
Largest diff. peak and hole (e/Å^3)	1.115 and -0.800	0.864 and -1.162
Absolute structure parameter	-0.002(9)	0.025(11)

[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 S1(b). The final Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *α*-, and *β*-$KCsWP_2O_9$, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum for each atom in asymmetric unit.

α-$KCsWP_2O_9$ ($P3_2$)

Atom	x	y	z	U(eq)	BVS
K(1)	781(5)	145(5)	2434(3)	29(1)	1.155
Cs(1)	5210(2)	-32(2)	4000(1)	33(1)	0.907
W(1)	5094(1)	4989(1)	3718(1)	13(1)	6.308
P(1)	-745(5)	-4076(5)	4162(3)	15(1)	5.146
P(2)	855(4)	3653(5)	4288(3)	14(1)	5.132
O(1)	5801(14)	6726(13)	4757(8)	23(2)	2.130
O(2)	4468(16)	3170(14)	4660(9)	30(3)	1.941
O(3)	2609(13)	4553(15)	3504(8)	25(2)	2.079
O(4)	-2391(14)	-4501(17)	3375(9)	30(3)	2.136
O(5)	788(15)	-2228(14)	3941(10)	34(3)	1.908
O(6)	-1248(13)	-4487(13)	5491(8)	19(2)	2.012
O(7)	-150(15)	1692(13)	4151(10)	31(2)	2.148
O(8)	1233(13)	4364(12)	5589(8)	16(2)	1.928
O(9)	-313(14)	4419(15)	3650(10)	20(2)	2.198

β-$KCsWP_2O_9$ ($P6_1$)

Atom	x	y	z	U(eq)	BVS
K(1)	9575(6)	9710(7)	4221(2)	56(2)	1.218
Cs(1)	10122(2)	5082(2)	5030(1)	32(1)	0.963
W(1)	5051(1)	255(1)	4893(1)	18(1)	6.290
P(1)	5881(6)	6903(6)	5144(2)	21(1)	5.135
P(2)	3601(6)	3032(6)	5141(2)	22(1)	5.118
O(1)	7732(16)	7175(18)	5030(6)	44(3)	2.010
O(2)	5531(17)	8226(15)	4761(5)	34(3)	2.124
O(3)	5450(14)	6919(14)	5803(5)	22(2)	2.032
O(4)	4307(17)	5026(13)	4874(7)	29(3)	2.257
O(5)	1610(15)	1997(17)	5052(6)	41(3)	2.088
O(6)	4629(17)	2341(15)	4751(4)	32(3)	2.107
O(7)	4239(13)	3245(13)	5800(5)	20(2)	1.892
O(8)	3237(15)	-884(15)	5382(5)	28(3)	2.032
O(9)	6798(15)	1375(16)	5397(5)	31(3)	2.105

Table S2. Selected bond distances (Å) and angles (deg) for *α*-, and *β*-$KCsWP_2O_9$.

α-$KCsWP_2O_9$ ($P3_2$)

Cs(1)-O(1)#3	3.150(10)	K(1)-O(7)#4	2.617(11)
Cs(1)-O(1)#1	3.158(9)	W(1)-O(1)	1.717(10)
Cs(1)-O(2)	3.170(10)	W(1)-O(2)	1.707(10)
Cs(1)-O(2)#1	3.189(10)	W(1)-O(3)	1.968(9)
Cs(1)-O(4)#2	3.677(10)	W(1)-O(4)#7	1.994(10)
Cs(1)-O(5)	3.256(11)	W(1)-O(6)#4	2.151(9)
Cs(1)-O(6)#4	3.726(10)	W(1)-O(8)#8	2.142(9)
Cs(1)-O(7)#5	3.458(11)	P(1)-O(4)	1.524(10)
Cs(1)-O(8)#1	3.415(9)	P(1)-O(5)	1.476(11)
Cs(1)-O(9)#6	3.321(11)	P(1)-O(6)	1.507(10)
K(1)-O(1)#1	2.911(10)	P(1)-O(9)#3	1.598(11)
K(1)-O(5)	2.608(11)	P(2)-O(3)	1.550(10)
K(1)-O(5)#4	2.908(12)	P(2)-O(7)	1.452(10)
K(1)-O(6)#4	2.942(10)	P(2)-O(8)	1.517(9)
K(1)-O(7)	2.632(11)	P(2)-O(9)	1.596(12)
O(1)#3-Cs(1)-O(1)#1	108.4(3)	O(2)-Cs(1)-O(5)	80.1(3)
O(1)#3-Cs(1)-O(2)#1	108.8(3)	O(2)#1-Cs(1)-O(5)	110.8(3)
O(1)#1-Cs(1)-O(2)#1	49.3(2)	O(2)-Cs(1)-O(6)#4	45.9(2)
O(1)#3-Cs(1)-O(2)	151.5(2)	O(2)#1-Cs(1)-O(6)#4	56.1(2)
O(1)#1-Cs(1)-O(2)	96.1(2)	O(2)-Cs(1)-O(7)#5	107.4(3)
O(1)#3-Cs(1)-O(4)#2	87.3(3)	O(2)#1-Cs(1)-O(7)#5	72.2(3)
O(1)#1-Cs(1)-O(4)#2	162.9(2)	O(2)-Cs(1)-O(8)#1	158.9(2)
O(1)#1-Cs(1)-O(5)	62.1(3)	O(2)#1-Cs(1)-O(8)#1	64.4(2)
O(1)#3-Cs(1)-O(5)	98.5(3)	O(2)#1-Cs(1)-O(9)#6	157.0(3)
O(1)#3-Cs(1)-O(6)#4	162.5(2)	O(2)-Cs(1)-O(9)#6	67.3(3)
O(1)#1-Cs(1)-O(6)#4	55.7(2)	O(4)#2-Cs(1)-O(6)#4	107.7(2)
O(1)#3-Cs(1)-O(7)#5	73.2(2)	O(5)-Cs(1)-O(4)#2	123.5(3)
O(1)#1-Cs(1)-O(7)#5	119.4(3)	O(5)-Cs(1)-O(6)#4	81.0(2)
O(1)#1-Cs(1)-O(8)#1	63.9(2)	O(5)-Cs(1)-O(7)#5	171.6(2)
O(1)#3-Cs(1)-O(8)#1	49.2(2)	O(5)-Cs(1)-O(8)#1	94.8(3)
O(1)#1-Cs(1)-O(9)#6	145.7(3)	O(5)-Cs(1)-O(9)#6	85.0(3)
O(1)#3-Cs(1)-O(9)#6	84.2(3)	O(7)#5-Cs(1)-O(4)#2	57.8(3)
O(2)-Cs(1)-O(2)#1	98.1(3)	O(7)#5-Cs(1)-O(6)#4	106.8(2)
O(2)-Cs(1)-O(4)#2	70.7(3)	O(8)#1-Cs(1)-O(4)#2	127.4(2)
O(2)#1-Cs(1)-O(4)#2	120.2(2)	O(8)#1-Cs(1)-O(6)#4	113.23(19)
O(8)#1-Cs(1)-O(7)#5	79.3(2)	O(2)-W(1)-O(1)	101.3(4)
O(9)#6-Cs(1)-O(4)#2	39.4(3)	O(2)-W(1)-O(3)	94.7(5)
O(9)#6-Cs(1)-O(6)#4	113.1(2)	O(2)-W(1)-O(4)#7	97.2(5)
O(9)#6-Cs(1)-O(7)#5	94.5(3)	O(2)-W(1)-O(6)#4	89.7(4)
O(9)#6-Cs(1)-O(8)#1	133.0(2)	O(2)-W(1)-O(8)#8	168.6(4)
O(1)#1-K(1)-O(6)#4	67.6(3)	O(3)-W(1)-O(4)#7	162.3(3)

O(5)-K(1)-O(1)#1	73.4(3)	O(3)-W(1)-O(6)#4	84.9(4)
O(5)#4-K(1)-O(1)#1	86.2(3)	O(3)-W(1)-O(8)#8	82.1(4)
O(5)-K(1)-O(5)#4	156.9(2)	O(4)#7-W(1)-O(6)#4	82.0(4)
O(5)-K(1)-O(6)#4	109.9(3)	O(4)#7-W(1)-O(8)#8	83.7(4)
O(5)#4-K(1)-O(6)#4	50.5(3)	O(8)#8-W(1)-O(6)#4	79.1(3)
O(5)-K(1)-O(7)#4	103.9(4)	O(4)-P(1)-O(9)#3	99.4(6)
O(5)-K(1)-O(7)	93.0(4)	O(5)-P(1)-O(4)	112.2(7)
O(7)#4-K(1)-O(1)#1	91.0(3)	O(5)-P(1)-O(6)	113.7(6)
O(7)-K(1)-O(1)#1	151.1(3)	O(5)-P(1)-O(9)#3	111.1(6)
O(7)-K(1)-O(5)#4	100.2(4)	O(6)-P(1)-O(4)	111.7(6)
O(7)#4-K(1)-O(5)#4	86.8(3)	O(6)-P(1)-O(9)#3	107.7(6)
O(7)#4-K(1)-O(6)#4	131.6(3)	O(3)-P(2)-O(9)	101.4(6)
O(7)-K(1)-O(6)#4	94.7(3)	O(7)-P(2)-O(3)	112.2(6)
O(7)#4-K(1)-O(7)	117.37(15)	O(7)-P(2)-O(8)	116.1(6)
O(1)-W(1)-O(3)	97.0(5)	O(7)-P(2)-O(9)	107.1(6)
O(1)-W(1)-O(4)#7	93.5(5)	O(8)-P(2)-O(3)	111.3(6)
O(1)-W(1)-O(6)#4	168.6(4)	O(8)-P(2)-O(9)	107.4(5)
O(1)-W(1)-O(8)#8	90.0(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x-y,z-1/3 #2 -x+y+1,-x,z+1/3 #3 x,y-1,z #4 -y,x-y,z-1/3
#5 x+1,y,z #6 -x+y,-x,z+1/3 #7 x+1,y+1,z #8 -y+1,x-y+1,z-1/3
#9 -x+y+1,-x+1,z+1/3 #10 x,y+1,z #11 -y,x-y-1,z-1/3 #12 x-1,y,z
#13 x-1,y-1,z #14 -x+y,-x+1,z+1/3

β-$KCsWP_2O_9$ ($P6_1$)

W(1)-O(2)#3	1.974(11)	Cs(1)-O(9)#7	3.137(11)
W(1)-O(3)#4	2.162(10)	K(1)-O(1)#9	2.691(14)
W(1)-O(6)	1.993(10)	K(1)-O(1)	2.612(13)
W(1)-O(7)#4	2.146(10)	K(1)-O(2)	3.224(13)
W(1)-O(8)	1.718(11)	K(1)-O(3)#9	3.264(12)
W(1)-O(9)	1.704(10)	K(1)-O(5)#8	2.585(13)
Cs(1)-O(1)	3.289(12)	K(1)-O(5)#7	2.589(13)
Cs(1)-O(3)#4	3.497(10)	K(1)-O(8)#7	3.260(12)
Cs(1)-O(4)#5	3.583(13)	P(1)-O(1)	1.486(12)
Cs(1)-O(4)#6	3.376(15)	P(1)-O(2)	1.541(11)
Cs(1)-O(5)#5	3.420(13)	P(1)-O(3)	1.490(11)
Cs(1)-O(6)#6	3.665(10)	P(1)-O(4)	1.591(12)
Cs(1)-O(7)#7	3.618(10)	P(2)-O(4)	1.594(11)
Cs(1)-O(8)#8	3.195(11)	P(2)-O(5)	1.473(12)
Cs(1)-O(8)#7	3.166(11)	P(2)-O(6)	1.529(11)
Cs(1)-O(9)	3.095(11)	P(2)-O(7)	1.518(11)
O(2)#3-W(1)-O(3)#4	83.2(4)	O(4)#6-Cs(1)-O(5)#5	87.7(3)

O(2)#3-W(1)-O(6)	162.6(4)	O(4)#6-Cs(1)-O(6)#6	40.2(2)
O(2)#3-W(1)-O(7)#4	82.2(4)	O(4)#5-Cs(1)-O(6)#6	61.8(3)
O(6)-W(1)-O(3)#4	82.6(4)	O(4)#5-Cs(1)-O(7)#7	71.8(2)
O(6)-W(1)-O(7)#4	85.2(4)	O(4)#6-Cs(1)-O(7)#7	134.1(3)
O(7)#4-W(1)-O(3)#4	79.2(4)	O(5)#5-Cs(1)-O(3)#4	76.2(3)
O(8)-W(1)-O(2)#3	96.8(5)	O(5)#5-Cs(1)-O(4)#5	41.2(2)
O(8)-W(1)-O(3)#4	168.5(5)	O(5)#5-Cs(1)-O(6)#6	60.9(3)
O(8)-W(1)-O(6)	95.1(5)	O(5)#5-Cs(1)-O(7)#7	109.2(3)
O(8)-W(1)-O(7)#4	89.4(4)	O(7)#7-Cs(1)-O(6)#6	111.8(2)
O(9)-W(1)-O(2)#3	94.5(5)	O(8)#7-Cs(1)-O(1)	65.3(3)
O(9)-W(1)-O(3)#4	90.4(4)	O(8)#8-Cs(1)-O(1)	79.9(3)
O(9)-W(1)-O(6)	95.7(5)	O(8)#8-Cs(1)-O(3)#4	159.1(2)
O(9)-W(1)-O(7)#4	169.3(5)	O(8)#7-Cs(1)-O(3)#4	60.4(3)
O(9)-W(1)-O(8)	101.1(5)	O(8)#8-Cs(1)-O(4)#5	75.2(3)
O(1)-Cs(1)-O(3)#4	93.1(3)	O(8)#8-Cs(1)-O(4)#6	87.3(3)
O(1)-Cs(1)-O(4)#6	88.7(3)	O(8)#7-Cs(1)-O(4)#6	151.4(3)
O(1)-Cs(1)-O(4)#5	152.3(3)	O(8)#7-Cs(1)-O(4)#5	106.8(3)
O(1)-Cs(1)-O(5)#5	166.4(3)	O(8)#8-Cs(1)-O(5)#5	113.0(3)
O(1)-Cs(1)-O(6)#6	122.1(3)	O(8)#7-Cs(1)-O(5)#5	114.6(3)
O(1)-Cs(1)-O(7)#7	82.5(3)	O(8)#7-Cs(1)-O(6)#6	167.6(3)
O(3)#4-Cs(1)-O(4)#5	105.9(3)	O(8)#8-Cs(1)-O(6)#6	73.9(3)
O(3)#4-Cs(1)-O(6)#6	125.5(3)	O(8)#8-Cs(1)-O(7)#7	46.8(3)
O(3)#4-Cs(1)-O(7)#7	113.0(3)	O(8)#7-Cs(1)-O(7)#7	57.5(3)
O(4)#6-Cs(1)-O(3)#4	112.4(3)	O(8)#7-Cs(1)-O(8)#8	99.1(4)
O(4)#6-Cs(1)-O(4)#5	101.8(3)	O(9)-Cs(1)-O(1)	93.1(3)
O(9)#7-Cs(1)-O(1)	114.5(3)	O(2)-K(1)-O(8)#7	99.3(3)
O(9)#7-Cs(1)-O(3)#4	62.7(3)	O(5)#7-K(1)-O(1)	137.9(4)
O(9)-Cs(1)-O(3)#4	49.0(2)	O(5)#8-K(1)-O(1)	92.2(4)
O(9)-Cs(1)-O(4)#5	114.5(3)	O(5)#8-K(1)-O(1)#9	138.2(4)
O(9)#7-Cs(1)-O(4)#5	60.5(3)	O(5)#7-K(1)-O(1)#9	90.4(4)
O(9)-Cs(1)-O(4)#6	63.4(3)	O(5)#8-K(1)-O(2)	102.3(4)
O(9)#7-Cs(1)-O(4)#6	156.0(3)	O(5)#7-K(1)-O(2)	156.1(4)
O(9)-Cs(1)-O(5)#5	73.6(3)	O(5)#7-K(1)-O(3)#9	120.6(4)
O(9)#7-Cs(1)-O(5)#5	68.3(3)	O(5)#8-K(1)-O(3)#9	92.9(4)
O(9)#7-Cs(1)-O(6)#6	121.0(3)	O(5)#8-K(1)-O(5)#7	100.0(3)
O(9)-Cs(1)-O(6)#6	85.8(3)	O(5)#7-K(1)-O(8)#7	70.6(4)
O(9)-Cs(1)-O(7)#7	161.5(2)	O(5)#8-K(1)-O(8)#7	133.4(4)
O(9)#7-Cs(1)-O(7)#7	59.5(3)	O(8)#7-K(1)-O(3)#9	131.9(3)
O(9)-Cs(1)-O(8)#7	104.3(3)	O(1)-P(1)-O(2)	111.5(7)
O(9)#7-Cs(1)-O(8)#7	49.6(3)	O(1)-P(1)-O(3)	113.9(7)
O(9)-Cs(1)-O(8)#8	150.1(3)	O(1)-P(1)-O(4)	112.6(7)
O(9)#7-Cs(1)-O(8)#8	102.1(3)	O(2)-P(1)-O(4)	98.9(6)
O(9)-Cs(1)-O(9)#7	107.2(4)	O(3)-P(1)-O(2)	112.5(6)
O(1)-K(1)-O(1)#9	106.7(3)	O(3)-P(1)-O(4)	106.4(7)

O(1)#9-K(1)-O(2)	67.3(3)	O(5)-P(2)-O(4)	107.0(7)
O(1)-K(1)-O(2)	49.4(3)	O(5)-P(2)-O(6)	113.5(7)
O(1)#9-K(1)-O(3)#9	48.4(3)	O(5)-P(2)-O(7)	115.5(7)
O(1)-K(1)-O(3)#9	98.5(3)	O(6)-P(2)-O(4)	102.5(7)
O(1)#9-K(1)-O(8)#7	88.3(3)	O(7)-P(2)-O(4)	107.5(7)
O(1)-K(1)-O(8)#7	71.8(4)	O(7)-P(2)-O(6)	109.8(6)
O(2)-K(1)-O(3)#9	50.1(3)		

Symmetry transformations used to generate equivalent atoms:

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

Figure S1. The photographs of powder samples of α-, and β-$KCsWP_2O_9$.

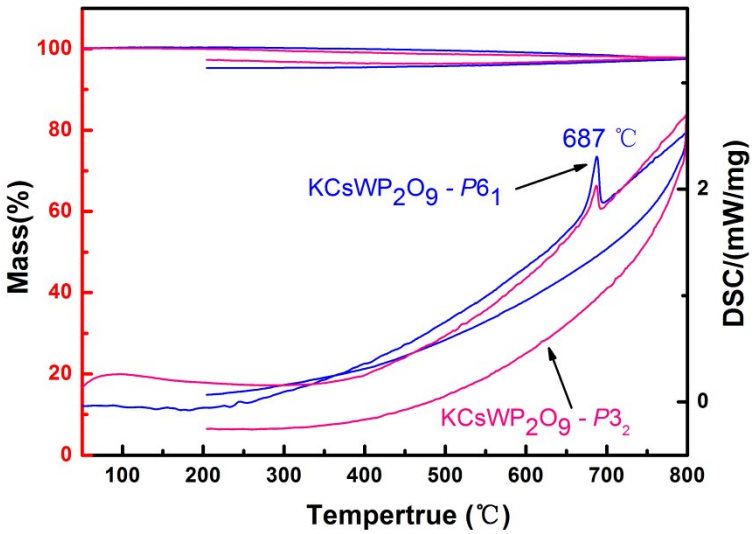

Figure S2. The TG-DSC curves of polycrystalline e samples of α-, and β-$KCsWP_2O_9$.

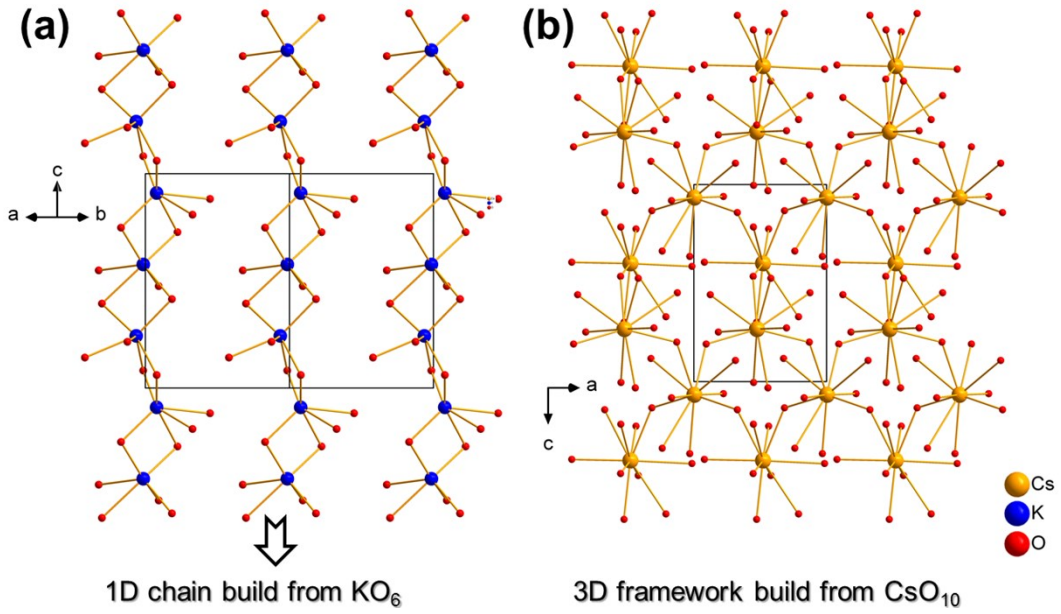

Figure S3. Cation coordination environments of K, and Cs atoms in α-$KCsWP_2O_9$.

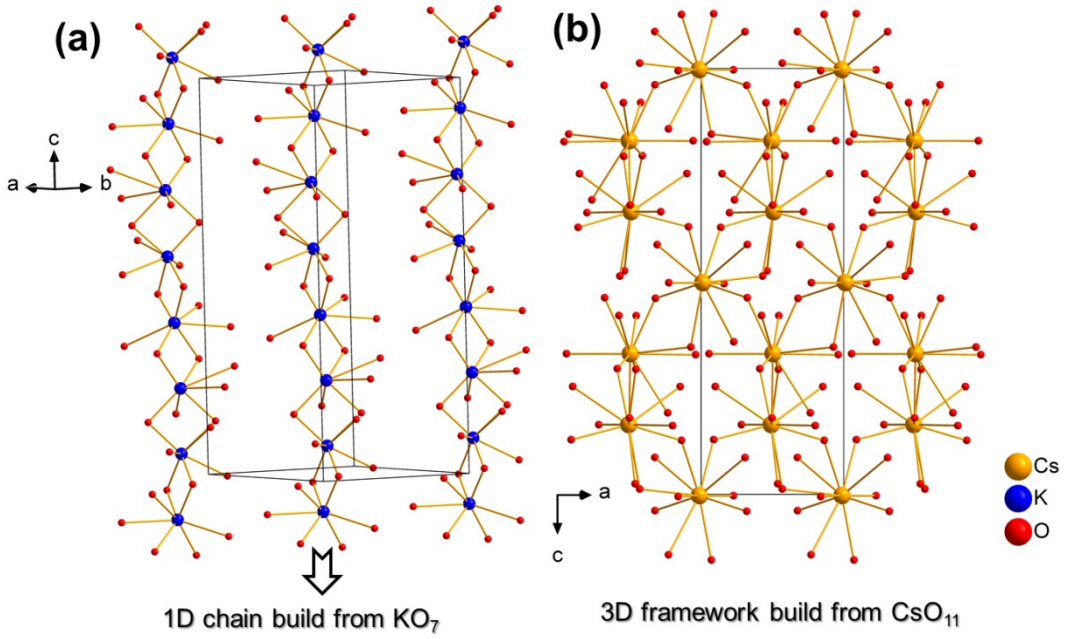

Figure S4. Cation coordination environments of K, and Cs atoms in *β*-$KCsWP_2O_9$.

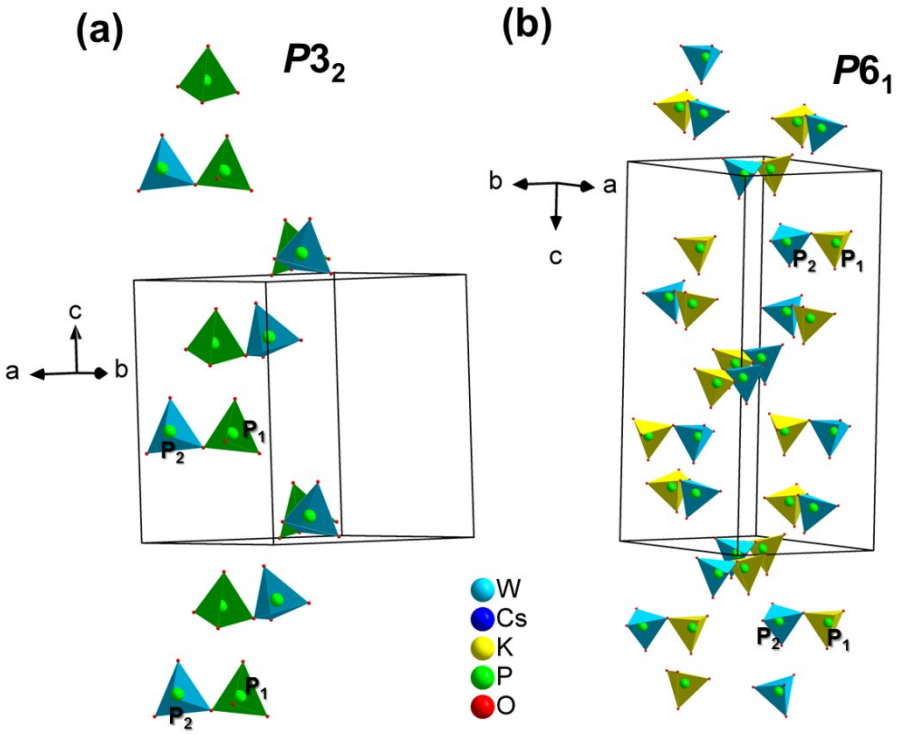

Figure S5. Spatial arrangement patterns of the PO_4 tetrahedra in α-, and β-$KCsWP_2O_9$.

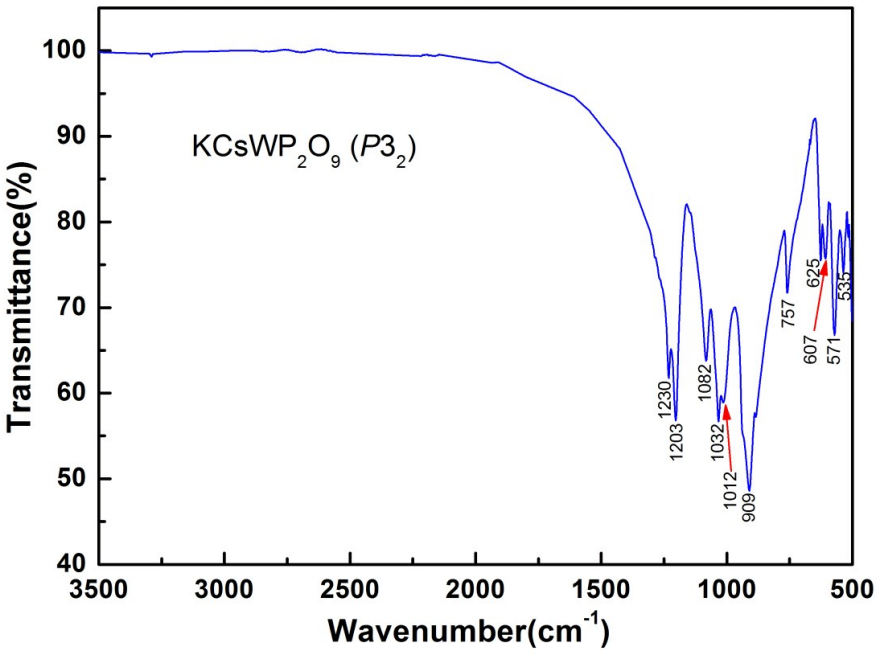

Figure S6. The IR spectrum of α-$KCsWP_2O_9$.

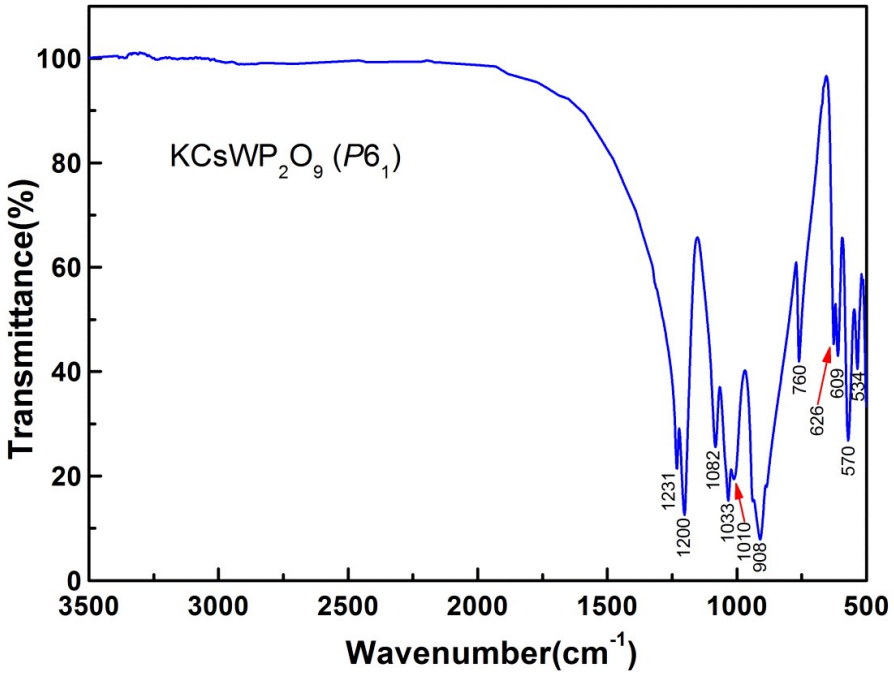

Figure S7. The IR spectrum of β-$KCsWP_2O_9$.

Table S3. Assignment of observed absorption bands for α-, and β-$KCsWP_2O_9$ in the IR spectra.

Peaks (cm^{-1})		Assignment
$P3_2$	$P6_1$	
1230, 1205	1231, 1200	Asymmetric stretching vibrations of O-P-O
1082, 1032, 1032	1082, 1033, 1010	Symmetric stretching vibrations of O-P-O
909	908	Asymmetric vibrations of P-O-P
757	760	Symmetric vibrations of P-O-P
625, 607, 571, 535	626, 609, 570, 534	Bending vibration of O-P-O

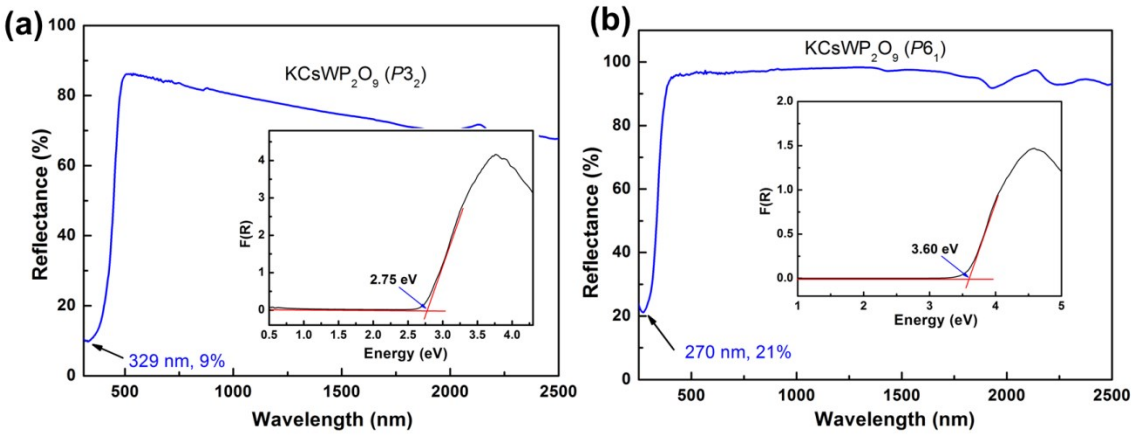

Figure S8. UV−Vis−NIR diffuse reflectance spectra of α-, and β-$KCsWP_2O_9$.

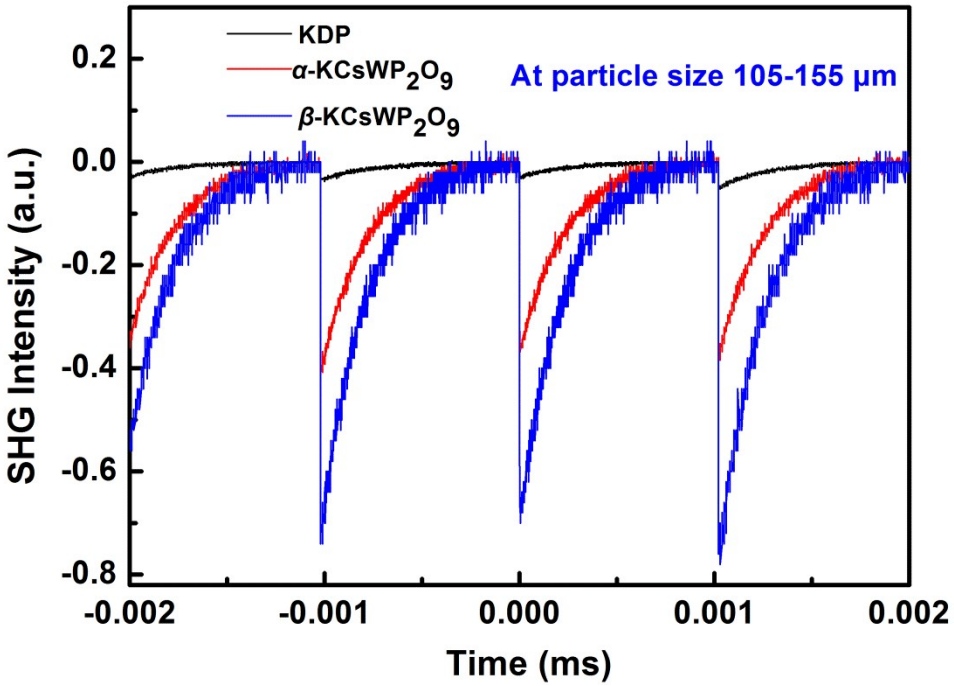

Figure S9. Oscilloscope traces of the SHG signals for the powders (105-155 μm) for KDP and *α*-, and *β*-$KCsWP_2O_9$ (at 1064 nm Q-switched Nd:YAG laser).

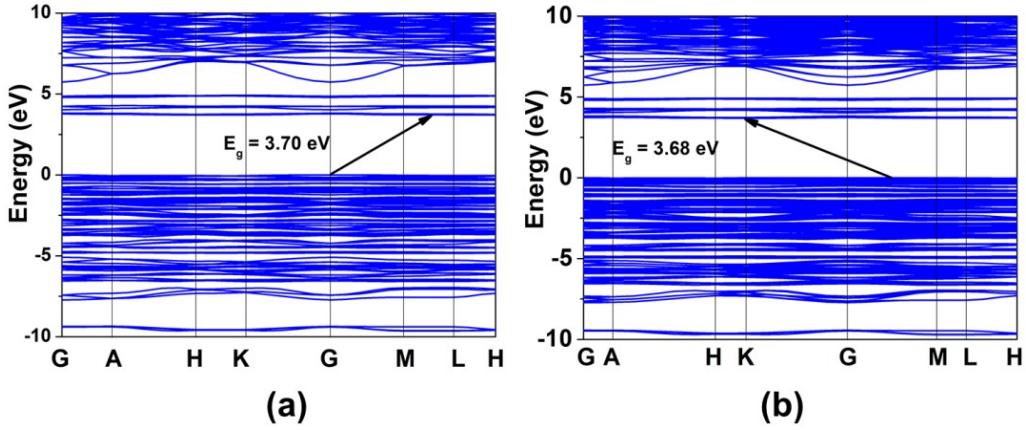

Figure S10. Calculated electronic band structures of α-, and β-$KCsWP_2O_9$.

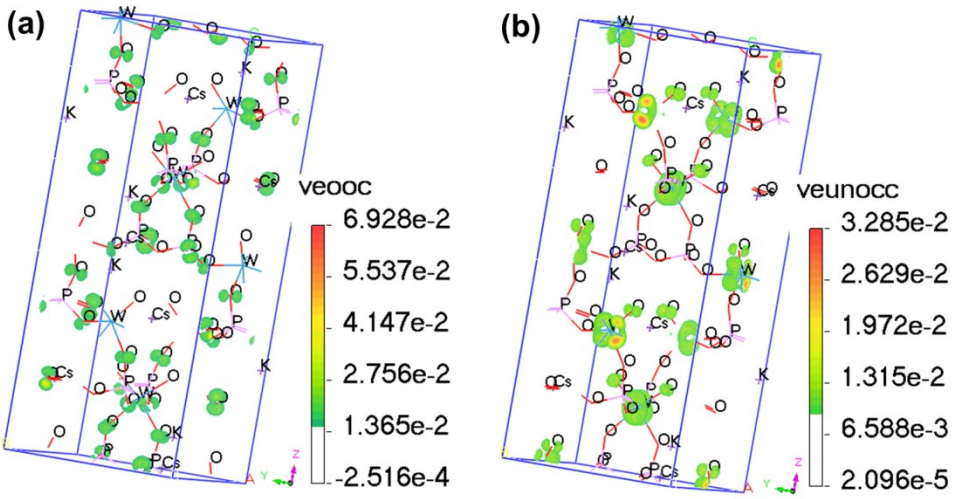

Figure S11. The SHG density maps of the VE occupied (a) and VE unoccupied orbitals (b) of *β*-$KCsWP_2O_9$.

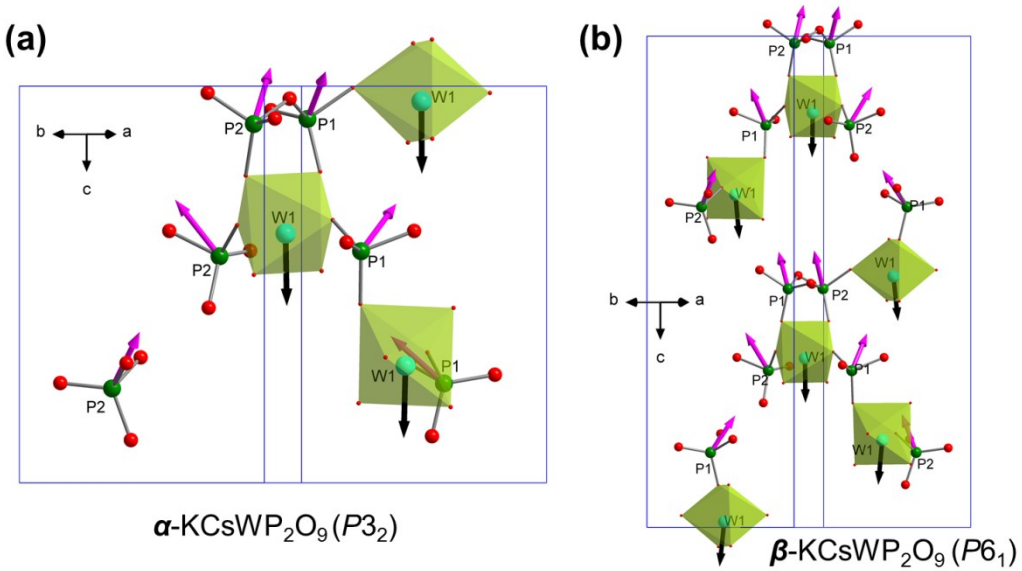

Figure S12. Dipole moment directions of the PO_4 and WO_6 polyhedra in $KCsWP_2O_9$, viewed along (111) direction. (The arrows represent the approximate directions of the dipole moments).