Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Experimental characterization and first principle calculation on linear and nonlinear optical properties of two orthophosphates $A_3Al_2(PO_4)_3$ (A=Rb, K)

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Table S1. Crystal data and structure refinements for $Rb_3Al_2(PO_4)_3$ and $K_3Al_2(PO_4)_3$.

Empirical formula	$Rb_3Al_2(PO_4)_3$	$K_3Al_2(PO_4)_3$
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Cmc*2_1	*Pna*2_1
Formula weight	595.28	456.17
a (Å)	17.145(6)	8.671(3)
b (Å)	8.622(2)	16.906(5)
c (Å)	8.796(3)	8.445(2)
Z, Volume (Å^3)	4, 1300.3(7)	4, 1238.0(6)
ρ_{Calcd} (Mg/m^3)	3.041	2.447
μ(/mm)	11.806	1.689
F(000)	1112	896
R(int)	0.1303	0.0523
Goodness-of-fit on F^2	0.943	1.081
Final R indices [$F_o^2>2\sigma(F_o^2)$][a]	R1 = 0.0497, wR2=0.0776	R1 =0.0387, wR2=0.0691
R indices (all data)[a]	R1 = 0.0725, wR2=0.0878	R1= 0.0489, wR2=0.0766
Absolute structure parameter	0.017(17)	0.31(8)
Largest diff. peak and hole (e·Å^{-3})	1.675 and 1.482	0.513 and 0.524

[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 S2a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for $Rb_3Al_2(PO_4)_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Rb(1)	3848(1)	10462(1)	7384(2)	23(1)
Rb(2)	5000	3551(2)	4468(3)	46(1)
P(1)	5000	7655(5)	5174(4)	15(1)
P(2)	7052(2)	3295(3)	4245(3)	13(1)
Al(1)	6674(2)	6528(4)	5840(3)	14(1)
O(1)	7897(4)	3037(8)	4841(9)	22(2)
O(2)	5000	9392(11)	5219(13)	23(2)
O(3)	6727(4)	4775(10)	4936(13)	36(2)
O(4)	7158(4)	3631(9)	2538(10)	34(2)
O(5)	5000	6988(14)	3616(13)	34(3)
O(6)	6523(4)	1964(9)	4534(9)	29(2)
O(7)	5713(4)	7034(9)	6122(8)	24(2)

Table S2b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_3Al_2(PO_4)_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
K(1)	-437(2)	6423(1)	92(2)	24(1)
K(2)	131(2)	6013(1)	4858(2)	24(1)
K(3)	3252(2)	4910(1)	7097(2)	36(1)
P(1)	6599(2)	7134(1)	3184(2)	13(1)
P(2)	2966(2)	6884(1)	8111(2)	14(1)
P(3)	2394(2)	4971(1)	2395(3)	17(1)
Al(1)	3514(2)	6604(1)	1758(2)	13(1)
Al(2)	6309(2)	6688(1)	6663(2)	14(1)
O(1)	5823(5)	7068(3)	4817(6)	17(1)
O(2)	5307(5)	7044(3)	1937(6)	18(1)
O(3)	7161(5)	8001(3)	3064(6)	18(1)
O(4)	3703(5)	5599(3)	2081(6)	24(1)
O(5)	7860(5)	6550(3)	2912(6)	21(1)
O(6)	2835(5)	6904(3)	9915(6)	25(1)
O(7)	898(5)	5275(3)	1754(7)	28(1)
O(8)	2929(6)	4246(3)	1400(6)	25(1)
O(9)	2369(6)	4764(3)	4119(7)	30(1)
O(10)	1815(6)	6340(3)	7423(7)	34(1)
O(11)	4633(5)	6644(3)	7749(6)	34(2)
O(12)	2749(5)	7740(3)	7548(7)	27(1)

Table S3a. Selected bond distances (Å) and angles (deg) for $Rb_3Al_2(PO_4)_3$.

Rb(1)-O(2)	2.894(9)	O(1)#3-Rb(1)-O(1)#6	117.9(2)
Rb(1)-O(6)#1	2.891(8)	O(4)#3-Rb(1)-O(1)#6	74.5(2)
Rb(1)-O(6)#2	2.892(8)	O(5)#4-Rb(1)-O(1)#6	159.7(2)
Rb(1)-O(1)#3	3.002(7)	O(2)#4-Rb(1)-O(1)#6	145.1(2)
Rb(1)-O(4)#3	3.004(8)	O(7)#5-Rb(1)-O(1)#6	48.68(18)
Rb(1)-O(5)#4	3.148(10)	O(6)#5-Rb(2)-O(6)	124.7(3)
Rb(1)-O(2)#4	3.184(9)	O(6)#5-Rb(2)-O(5)	117.04(15)
Rb(1)-O(7)#5	3.245(7)	O(6)-Rb(2)-O(5)	117.04(15)
Rb(1)-O(1)#6	3.469(7)	O(6)#5-Rb(2)-O(3)	168.3(2)
Rb(2)-O(6)#5	2.949(8)	O(6)-Rb(2)-O(3)	47.5(2)
Rb(2)-O(6)	2.949(8)	O(5)-Rb(2)-O(3)	73.10(18)
Rb(2)-O(5)	3.057(12)	O(6)#5-Rb(2)-O(3)#5	47.5(2)
Rb(2)-O(3)	3.170(8)	O(6)-Rb(2)-O(3)#5	168.3(2)
Rb(2)-O(3)#5	3.170(8)	O(5)-Rb(2)-O(3)#5	73.10(18)
Rb(2)-O(7)#7	3.227(8)	O(3)-Rb(2)-O(3)#5	138.2(3)
Rb(2)-O(7)#8	3.227(8)	O(6)#5-Rb(2)-O(7)#7	67.0(2)
P(1)-O(5)	1.487(11)	O(6)-Rb(2)-O(7)#7	106.3(2)
P(1)-O(2)	1.498(10)	O(5)-Rb(2)-O(7)#7	85.9(2)
P(1)-O(7)	1.574(7)	O(3)-Rb(2)-O(7)#7	121.6(2)
P(1)-O(7)#5	1.574(7)	O(3)#5-Rb(2)-O(7)#7	79.4(2)
P(2)-O(6)	1.485(8)	O(6)#5-Rb(2)-O(7)#8	106.3(2)
P(2)-O(3)	1.519(9)	O(6)-Rb(2)-O(7)#8	67.0(2)
P(2)-O(4)	1.540(9)	O(5)-Rb(2)-O(7)#8	85.9(2)
P(2)-O(1)	1.555(8)	O(3)-Rb(2)-O(7)#8	79.4(2)
Al(1)-O(3)	1.710(9)	O(3)#5-Rb(2)-O(7)#8	121.6(2)
Al(1)-O(4)#9	1.715(9)	O(7)#7-Rb(2)-O(7)#8	44.5(3)
Al(1)-O(7)	1.722(8)	O(6)#5-Rb(2)-O(7)#5	94.55(18)
Al(1)-O(1)#10	1.734(8)	O(6)-Rb(2)-O(7)#5	133.5(2)
O(2)-Rb(1)-O(6)#1	110.5(3)	O(5)-Rb(2)-O(7)#5	44.0(2)
O(2)-Rb(1)-O(6)#2	73.9(2)	O(3)-Rb(2)-O(7)#5	89.26(19)
O(6)#1-Rb(1)-O(6)#2	147.4(3)	O(3)#5-Rb(2)-O(7)#5	49.0(2)
O(2)-Rb(1)-O(1)#3	169.1(2)	O(7)#7-Rb(2)-O(7)#5	112.03(18)
O(6)#1-Rb(1)-O(1)#3	73.8(2)	O(7)#8-Rb(2)-O(7)#5	129.48(17)
O(6)#2-Rb(1)-O(1)#3	108.1(2)	O(6)#5-Rb(2)-O(7)	133.5(2)
O(2)-Rb(1)-O(4)#3	140.4(2)	O(6)-Rb(2)-O(7)	94.55(18)
O(6)#1-Rb(1)-O(4)#3	86.9(2)	O(5)-Rb(2)-O(7)	44.0(2)
O(6)#2-Rb(1)-O(4)#3	73.2(2)	O(3)-Rb(2)-O(7)	49.0(2)
O(1)#3-Rb(1)-O(4)#3	48.0(2)	O(3)#5-Rb(2)-O(7)	89.26(19)
O(2)-Rb(1)-O(5)#4	91.2(2)	O(7)#7-Rb(2)-O(7)	129.48(17)
O(6)#1-Rb(1)-O(5)#4	114.7(3)	O(7)#8-Rb(2)-O(7)	112.03(18)
O(6)#2-Rb(1)-O(5)#4	97.1(3)	O(7)#5-Rb(2)-O(7)	40.2(2)
O(1)#3-Rb(1)-O(5)#4	78.0(2)	O(5)-P(1)-O(2)	114.3(7)

O(4)#3-Rb(1)-O(5)#4	114.1(2)	O(5)-P(1)-O(7)	110.9(4)
O(2)-Rb(1)-O(2)#4	96.01(8)	O(2)-P(1)-O(7)	109.0(4)
O(6)#1-Rb(1)-O(2)#4	69.7(2)	O(5)-P(1)-O(7)#5	110.9(4)
O(6)#2-Rb(1)-O(2)#4	142.9(2)	O(2)-P(1)-O(7)#5	109.0(4)
O(1)#3-Rb(1)-O(2)#4	75.9(2)	O(7)-P(1)-O(7)#5	102.0(6)
O(4)#3-Rb(1)-O(2)#4	123.5(2)	O(6)-P(2)-O(3)	110.9(5)
O(5)#4-Rb(1)-O(2)#4	46.6(3)	O(6)-P(2)-O(4)	112.6(5)
O(2)-Rb(1)-O(7)#5	47.7(2)	O(3)-P(2)-O(4)	106.0(5)
O(6)#1-Rb(1)-O(7)#5	67.4(2)	O(6)-P(2)-O(1)	113.6(5)
O(6)#2-Rb(1)-O(7)#5	99.4(2)	O(3)-P(2)-O(1)	109.1(4)
O(1)#3-Rb(1)-O(7)#5	139.90(19)	O(4)-P(2)-O(1)	104.2(4)
O(4)#3-Rb(1)-O(7)#5	118.4(2)	O(3)-Al(1)-O(4)#9	108.0(5)
O(5)#4-Rb(1)-O(7)#5	127.5(2)	O(3)-Al(1)-O(7)	110.0(4)
O(2)#4-Rb(1)-O(7)#5	99.2(2)	O(4)#9-Al(1)-O(7)	111.0(4)
O(2)-Rb(1)-O(1)#6	72.8(2)	O(3)-Al(1)-O(1)#10	113.9(5)
O(6)#1-Rb(1)-O(1)#6	83.23(18)	O(4)#9-Al(1)-O(1)#10	107.2(4)
O(6)#2-Rb(1)-O(1)#6	66.9(2)	O(7)-Al(1)-O(1)#10	106.8(4)

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

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

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

#8 x,-y+1,z-1/2 #9 x,-y+1,z+1/2 #10 -x+3/2,y+1/2,z

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

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

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

Table S3b. Selected bond distances (Å) and angles (deg) for $K_3Al_2(PO_4)_3$.

K(1)-O(7)	2.660(5)	O(10)-K(2)-O(5)#2	144.77(17)
K(1)-O(9)#1	2.741(5)	O(10)-K(2)-O(7)#6	82.72(17)
K(1)-O(5)#2	2.811(5)	O(5)#2-K(2)-O(7)#6	111.59(15)
K(1)-O(6)#3	2.955(5)	O(10)-K(2)-O(3)#5	88.43(17)
K(1)-O(10)#3	2.985(6)	O(5)#2-K(2)-O(3)#5	86.06(14)
K(1)-O(12)#4	3.015(5)	O(7)#6-K(2)-O(3)#5	159.57(14)
K(1)-O(2)#5	3.093(5)	O(10)-K(2)-O(9)	87.69(16)
K(1)-O(6)#4	3.204(5)	O(5)#2-K(2)-O(9)	126.17(17)
K(2)-O(10)	2.669(6)	O(7)#6-K(2)-O(9)	77.07(14)
K(2)-O(5)#2	2.721(5)	O(3)#5-K(2)-O(9)	84.23(14)
K(2)-O(7)#6	2.847(5)	O(10)-K(2)-O(7)	132.73(16)
K(2)-O(3)#5	2.858(5)	O(5)#2-K(2)-O(7)	76.69(14)
K(2)-O(9)	2.935(6)	O(7)#6-K(2)-O(7)	104.15(8)
K(2)-O(7)	2.978(6)	O(3)#5-K(2)-O(7)	68.91(14)
K(2)-O(8)#6	2.988(5)	O(9)-K(2)-O(7)	50.49(14)
K(2)-O(1)#5	3.298(5)	O(10)-K(2)-O(8)#6	99.35(16)
K(3)-O(9)	2.641(6)	O(5)#2-K(2)-O(8)#6	70.68(14)
K(3)-O(10)	2.734(6)	O(7)#6-K(2)-O(8)#6	50.55(12)
K(3)-O(5)#7	2.737(5)	O(3)#5-K(2)-O(8)#6	149.69(13)
K(3)-O(4)#7	2.777(5)	O(9)-K(2)-O(8)#6	125.06(14)
K(3)-O(11)	3.215(6)	O(7)-K(2)-O(8)#6	121.36(14)
P(1)-O(5)	1.491(4)	O(10)-K(2)-O(1)#5	72.89(14)
P(1)-O(1)	1.538(5)	O(5)#2-K(2)-O(1)#5	78.31(13)
P(1)-O(2)	1.545(5)	O(7)#6-K(2)-O(1)#5	144.62(15)
P(1)-O(3)	1.548(4)	O(3)#5-K(2)-O(1)#5	46.30(12)
P(2)-O(10)	1.477(5)	O(9)-K(2)-O(1)#5	125.79(14)
P(2)-O(6)	1.529(6)	O(7)-K(2)-O(1)#5	111.22(14)
P(2)-O(11)	1.532(5)	O(8)#6-K(2)-O(1)#5	108.07(13)
P(2)-O(12)	1.535(5)	O(9)-K(3)-O(10)	92.62(17)
P(3)-O(7)	1.496(5)	O(9)-K(3)-O(5)#7	93.07(16)
P(3)-O(9)	1.498(6)	O(10)-K(3)-O(5)#7	127.69(17)
P(3)-O(8)	1.558(5)	O(9)-K(3)-O(4)#7	104.02(18)
P(3)-O(4)	1.576(5)	O(10)-K(3)-O(4)#7	135.04(16)
Al(1)-O(4)	1.730(5)	O(5)#7-K(3)-O(4)#7	93.29(14)
Al(1)-O(2)	1.730(5)	O(9)-K(3)-O(11)	110.85(15)
Al(1)-O(6)#3	1.739(6)	O(10)-K(3)-O(11)	49.15(14)
Al(1)-O(3)#5	1.743(5)	O(5)#7-K(3)-O(11)	155.57(16)
Al(2)-O(11)	1.720(5)	O(4)#7-K(3)-O(11)	85.92(13)
Al(2)-O(8)#7	1.725(5)	O(5)-P(1)-O(1)	114.3(3)
Al(2)-O(1)	1.738(5)	O(5)-P(1)-O(2)	111.2(3)
Al(2)-O(12)#8	1.747(5)	O(1)-P(1)-O(2)	106.6(3)
O(7)-K(1)-O(9)#1	83.68(16)	O(5)-P(1)-O(3)	112.7(3)

O(7)-K(1)-O(5)#2	80.62(16)	O(1)-P(1)-O(3)	105.3(3)
O(9)#1-K(1)-O(5)#2	89.35(15)	O(2)-P(1)-O(3)	106.1(3)
O(7)-K(1)-O(6)#3	79.03(15)	O(10)-P(2)-O(6)	110.9(3)
O(9)#1-K(1)-O(6)#3	140.67(16)	O(10)-P(2)-O(11)	113.2(3)
O(5)#2-K(1)-O(6)#3	121.74(15)	O(6)-P(2)-O(11)	105.9(3)
O(7)-K(1)-O(10)#3	94.57(16)	O(10)-P(2)-O(12)	112.5(3)
O(9)#1-K(1)-O(10)#3	97.99(16)	O(6)-P(2)-O(12)	106.2(3)
O(5)#2-K(1)-O(10)#3	170.77(15)	O(11)-P(2)-O(12)	107.6(3)
O(6)#3-K(1)-O(10)#3	49.24(14)	O(7)-P(3)-O(9)	114.8(4)
O(7)-K(1)-O(12)#4	160.98(16)	O(7)-P(3)-O(8)	109.5(3)
O(9)#1-K(1)-O(12)#4	79.12(15)	O(9)-P(3)-O(8)	110.1(3)
O(5)#2-K(1)-O(12)#4	107.08(15)	O(7)-P(3)-O(4)	109.4(3)
O(6)#3-K(1)-O(12)#4	109.62(15)	O(9)-P(3)-O(4)	109.3(3)
O(10)#3-K(1)-O(12)#4	79.94(15)	O(8)-P(3)-O(4)	103.0(3)
O(7)-K(1)-O(2)#5	104.76(15)	O(4)-Al(1)-O(2)	108.8(2)
O(9)#1-K(1)-O(2)#5	153.17(15)	O(4)-Al(1)-O(6)#3	117.4(3)
O(5)#2-K(1)-O(2)#5	67.57(13)	O(2)-Al(1)-O(6)#3	104.9(3)
O(6)#3-K(1)-O(2)#5	66.07(13)	O(4)-Al(1)-O(3)#5	109.9(2)
O(10)#3-K(1)-O(2)#5	106.48(14)	O(2)-Al(1)-O(3)#5	112.6(2)
O(12)#4-K(1)-O(2)#5	94.27(14)	O(6)#3-Al(1)-O(3)#5	103.1(3)
O(7)-K(1)-O(6)#4	150.67(17)	O(11)-Al(2)-O(8)#7	110.6(3)
O(9)#1-K(1)-O(6)#4	110.27(15)	O(11)-Al(2)-O(1)	106.8(2)
O(5)#2-K(1)-O(6)#4	74.11(13)	O(8)#7-Al(2)-O(1)	108.4(3)
O(6)#3-K(1)-O(6)#4	101.75(9)	O(11)-Al(2)-O(12)#8	113.6(3)
O(10)#3-K(1)-O(6)#4	108.20(15)	O(8)#7-Al(2)-O(12)#8	106.7(3)
O(12)#4-K(1)-O(6)#4	46.26(14)	O(1)-Al(2)-O(12)#8	110.6(3)
O(2)#5-K(1)-O(6)#4	51.76(12)		

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

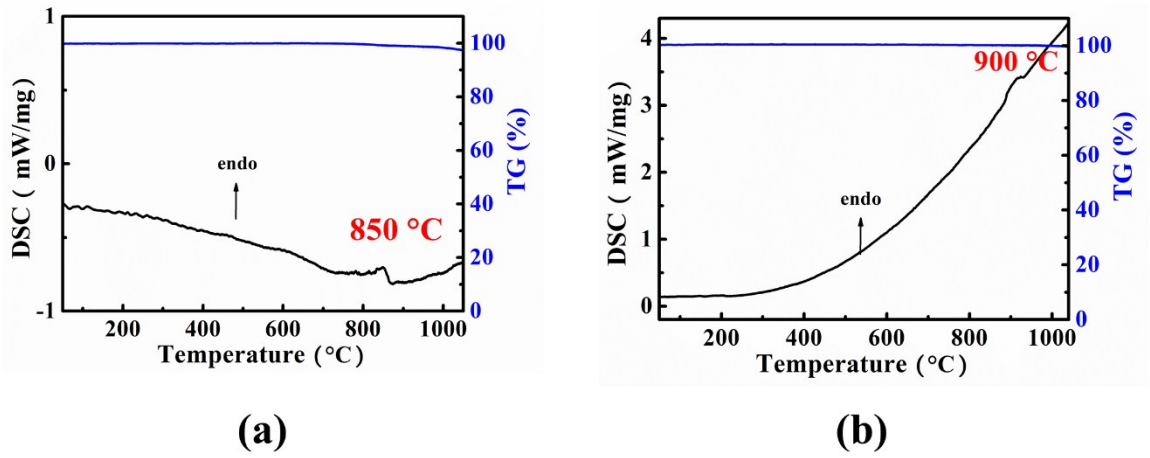

Fig. S1. TG-DSC curves of (a) $Rb_3Al_2(PO_4)_3$ and (b) $K_3Al_2(PO_4)_3$.

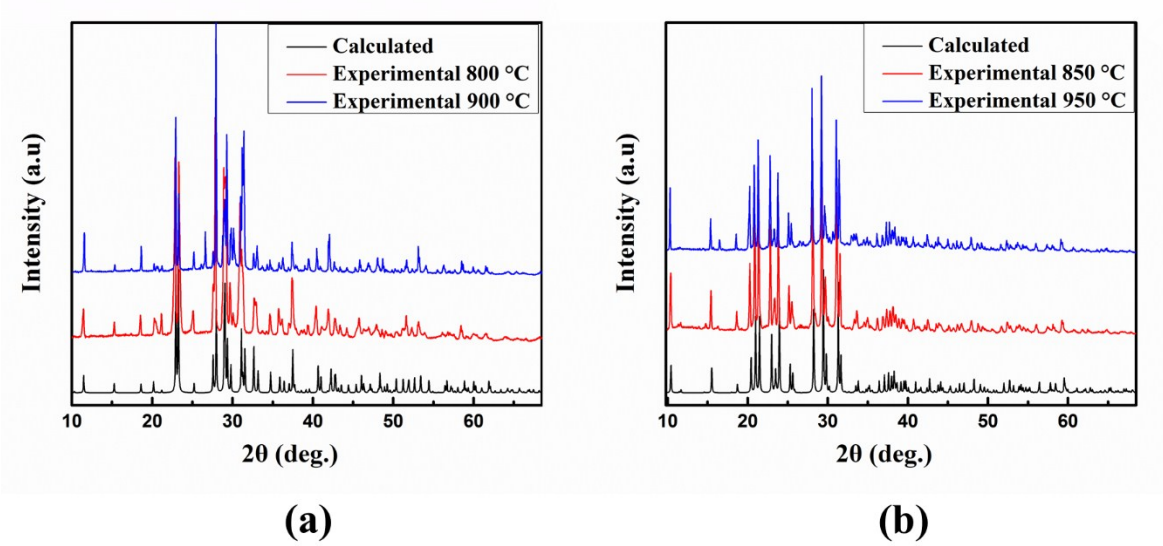

Fig. S2. Experimental and calculated XRD patterns of (a) $Rb_3Al_2(PO_4)_3$ and (b) $K_3Al_2(PO_4)_3$.

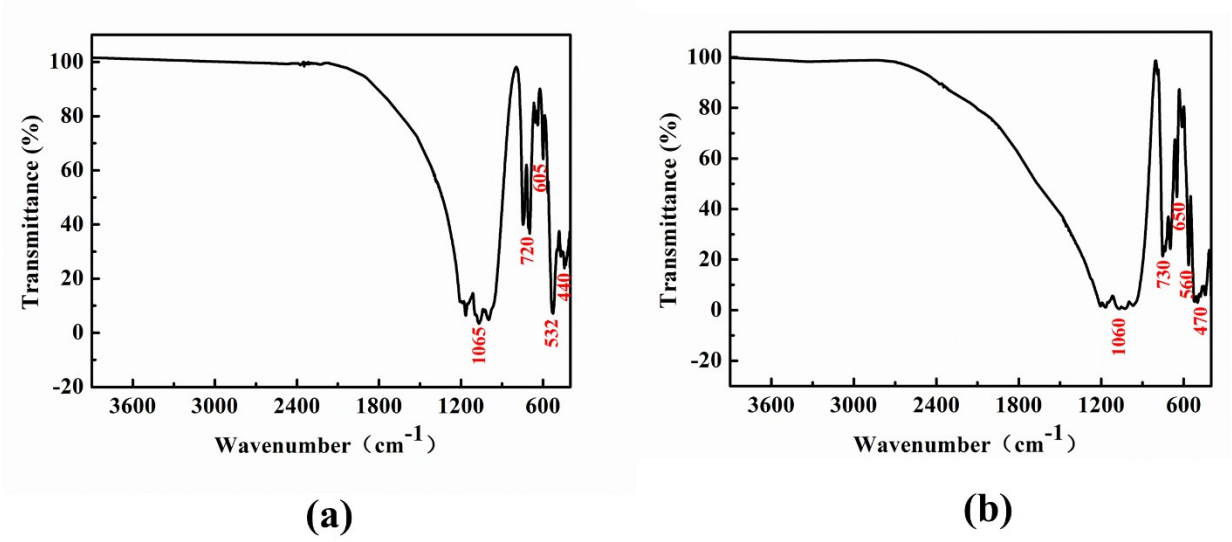

Fig. S3. IR spectra of (a) $Rb_3Al_2(PO_4)_3$ and (b) $K_3Al_2(PO_4)_3$.

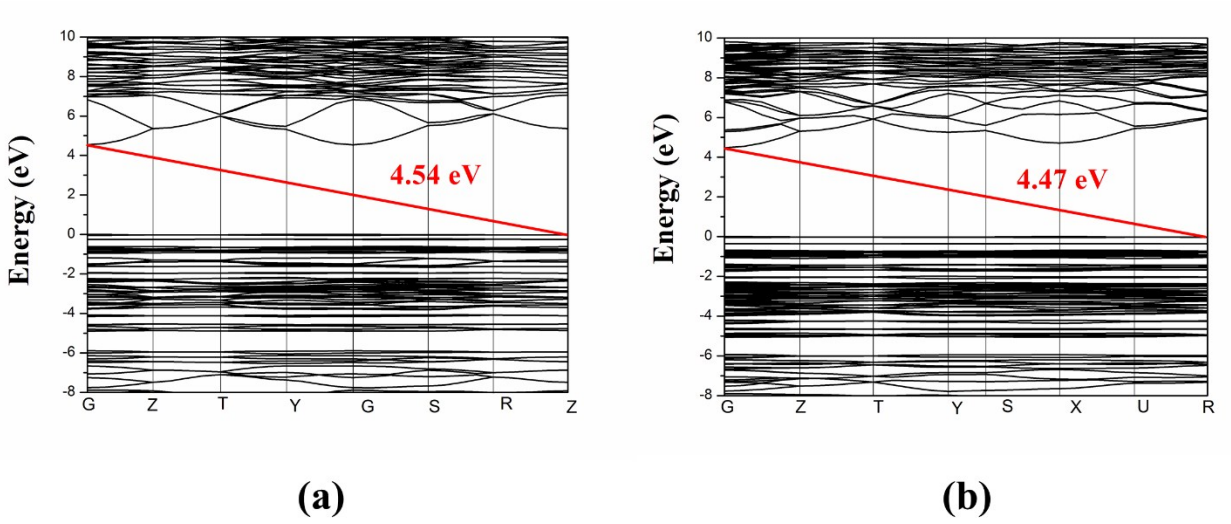

Fig. S4. Band structures of (a) $Rb_3Al_2(PO_4)_3$ and (b) $K_3Al_2(PO_4)_3$.

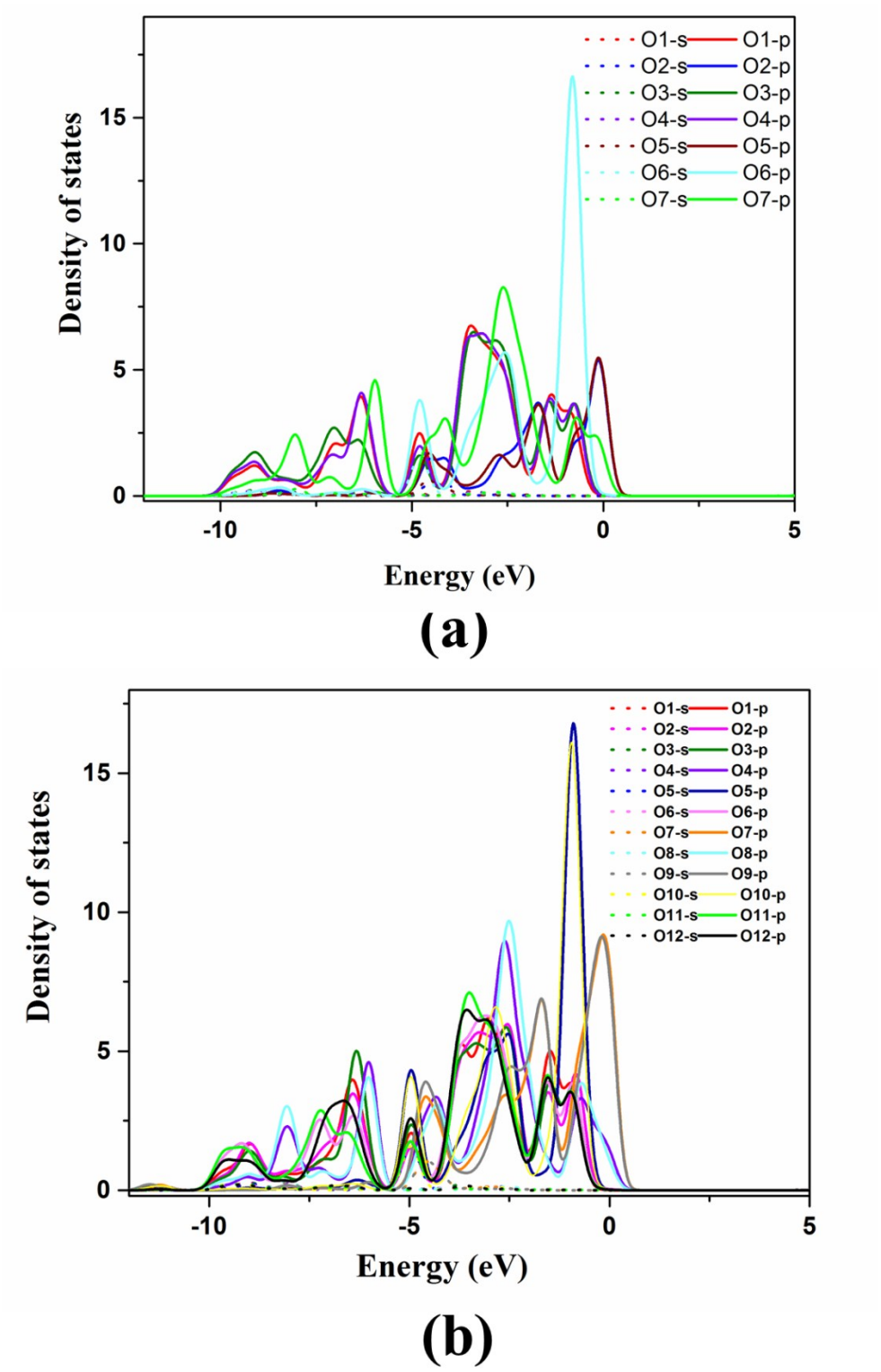

Fig. S5. The detailed PDOSs of the O atoms in (a) $Rb_3Al_2(PO_4)_3$ and (b) $K_3Al_2(PO_4)_3$.

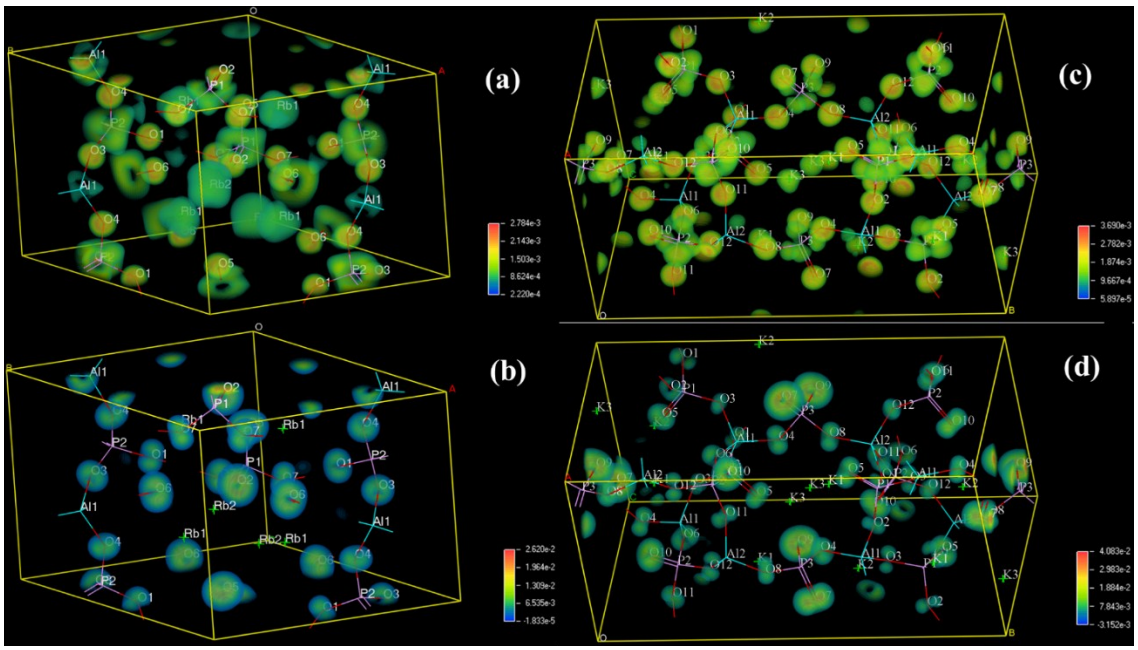

Fig. S6. SHG density of VE processes of (a) unoccupied states and (b) occupied states for $Rb_3Al_2(PO_4)_3$; (c) unoccupied states and (d) occupied states for $K_3Al_2(PO_4)_3$.