Supporting Information

Synthesis and Characterization of a New Aluminophosphate with $[Al_3P_6O_{24}]^{9-}$ Three-dimensional Framework

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Experimental Details

Polycrystalline samples of $K_6Na_3Al_3P_6O_{24}$ were synthesized via solid-state reactions of the stoichiometric starting components (0.02mol) of $NaNO_3$ (99.0%), KNO_3 (99.0%), $Al(NO_3)_3 \cdot 9H_2O$ (99.0%) and $NH_4H_2PO_4$ (99.5%). The sample was placed in an alumina crucible and heated to 620 °C slowly in air, held for 2 d with several intermediate grindings and mixings. Purity was confirmed by powder XRD. The single crystals were grown by spontaneous crystallization from the melt of polycrystalline samples (5g). The reaction was completed in a platinum crucible under air by applying the following temperature program: heating up to 950 °C, holding at this temperature for 24 h, and then cooling slowly down to 800 °C (2 °C/h) before rapid cooling to RT. Powder XRD data were collected on a Bruker D2 PHASER diffractometer using Cu Kα radiation (λ = 1.5418 Å) with a step size of 0.02° and a fixed counting time of 1s/step. IR spectrum was obtained via a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in a range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The sample was mixed thoroughly with dried KBr (5 mg of the sample, 500 mg of KBr). The UV-Vis-NIR optical diffuse reflectance spectrum was measured with a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range 250-2600 nm. The reflectance spectrum was converted to absorbance with the Kubelka–Munk function.[1] Thermal analysis was carried out on NETZSCH STA 449C instrument from 50 to 1000 °C, with a heating rate of 5 °C /min in an atmosphere of flowing N_2.

Reference

1 (a) P. Kubelka, F. Z. Munk, *Technol. Phys.* **1931**, *12*, 593; (b) J. Tauc, *Mater. Res. Bull.* 1970, **5**, 721.

Structure Determination

Single crystal XRD data were collected at room temperature on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The reduction of data was carried out with the Bruker Suite software package.[1] A face-indexed absorption correction was performed with the SADABS program and integrated with the SAINT program.[2] The structure was solved with SHELXS-97 by direct methods.[3] During the refinement, two oxygen atoms, O(5) and O(6)) behave strongly anisotropically, and each of them may be split into two partial-occupied sites (O(5A)-O(5B) and O(6A)-O(6B), respectively). To formulate the disorder, "PART" instruction and two additional free variables were used. Final least-squares refinement was on F_o^2 with data having $F_o^2 \geq 2\sigma (F_o^2)$. The structure was checked for missing symmetry elements with PLATON.[4]

Reference

1 Bruker Suite, Bruker AXS Inc., Madison, USA, 2008.

2 Bruker SMART, and SADABS, version 2.05, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.

3 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2010, **64**, 112-122.

4 A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7-13.

Table S1. Crystallographic Data and Structure Refinement for $K_6Na_3Al_3P_6O_{24}$.

Empirical formula	$K_6Na_3Al_3P_6O_{24}$
Formula weight	954.33
crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 19.9204(16) Å b = 9.6139(8) Å β = 98.934(4)° c = 13.2845(11) Å
Volume	2513.3(4) $Å^3$
Z, Calculated density	4, 2.522 g/cm^3
Absorption coefficient	1.683 mm^{-1}
F(000)	1872
Crystal size	0.22 × 0.14 × 0.09 mm^3
Theta range for data collection	1.03 to 24.99°
Limiting indices	$-23 \le h \le 23$, $-11 \le k \le 11$, $-15 \le l \le 15$
Reflections collected / unique	39102 / 4430 [R(int) = 0.0341]
Completeness to theta = 24.99	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.8605 and 0.7084
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4430 / 12 / 399
Goodness-of-fit on F^2	1.047
Final R indices $[F_o^2 > 2\sigma(F_o^2)]^a$	R1 = 0.0370, wR2 = 0.1033
R indices (all data) ^{a}	R1 = 0.0431, wR2 = 0.1076
Largest diff. peak and hole	0.817 and -1.495 $e \cdot Å^{-3}$

^{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 and Equivalent Isotropic Displacement Parameters For $K_6Na_3Al_3P_6O_{24}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

atom	Wyck.	S.O.F.	*x/a*	*y/b*	*z/c*	U_{eq}
Na(1)	4*e*	1	0.26906(7)	0.55797(15)	0.35713(11)	0.024(1)
Na(2)	4*e*	1	0.42086(7)	0.96744(15)	0.18782(11)	0.023(1)
Na(3)	4*e*	1	0.06685(7)	0.43333(15)	0.31870(11)	0.023(1)
K(1)	4*e*	1	0.05460(5)	0.16634(10)	0.08008(7)	0.032(1)
K(2	4*e*	1	0.20005(5)	0.18444(9)	0.40232(7)	0.031(1)
K(3)	4*e*	1	0.28702(4)	0.66646(9)	0.08147(7)	0.030(1)
K(4)	4*e*	1	0.44934(5)	0.81613(9)	-0.09782(7)	0.031(1)
K(5)	4*e*	1	0.13566(5)	0.81379(10)	0.27746(7)	0.030(1)
K(6)	4*e*	1	0.39566(6)	0.34089(14)	0.24559(9)	0.053(1)
Al(1)	4*e*	1	0.40312(5)	0.43237(11)	-0.04789(8)	0.016(1)
Al(2)	4*e*	1	0.24234(5)	0.07465(10)	0.11809(8)	0.016(1)
Al(3)	4*e*	1	0.10240(5)	0.56523(11)	0.05686(8)	0.015(1)
P(1)	4*e*	1	0.03304(4)	0.06753(9)	0.35518(7)	0.015(1)
P(2)	4*e*	1	0.35613(5)	0.15033(10)	-0.00432(8)	0.023(1)
P(3)	4*e*	1	0.20751(5)	0.37795(9)	0.18467(7)	0.016(1)
P(4)	4*e*	1	0.45866(5)	0.61859(10)	0.12810(7)	0.019(1)
P(5)	4*e*	1	0.14315(5)	0.86253(10)	0.00763(7)	0.019(1)
P(6)	4*e*	1	0.30381(5)	0.90378(10)	0.30507(7)	0.020(1)
O(1)	4*e*	1	-0.04376(13)	0.0437(3)	0.3609(2)	0.032(1)
O(2)	4*e*	1	0.07052(14)	-0.0437(3)	0.42915(19)	0.026(1)
O(3)	4*e*	1	0.04320(13)	0.0281(3)	0.24934(19)	0.025(1)
O(4)	4*e*	1	0.05575(15)	0.2106(3)	0.3906(2)	0.033(1)
O(5A)	4*e*	0.88	0.17321(18)	0.4090(5)	0.2759(3)	0.030(2)
O(6A)	4*e*	0.81	0.2095(2)	0.2192(4)	0.1738(6)	0.037(2)
O(5B)	4*e*	0.12	0.1571(16)	0.338(4)	0.250(3)	0.036(9)
O(6B)	4*e*	0.19	0.2089(9)	0.2333(19)	0.118(3)	0.031(6)
O(7)	4*e*	1	0.28140(13)	0.1154(3)	0.0138(2)	0.032(1)
O(8)	4*e*	1	0.37682(16)	0.0431(3)	-0.0749(3)	0.048(1)
O(9)	4*e*	1	0.34690(12)	0.2932(3)	-0.0605(2)	0.022(1)
O(10)	4*e*	1	0.40293(15)	0.1666(3)	0.0947(2)	0.044(1)
O(11)	4*e*	1	0.16462(14)	0.4383(3)	0.0864(2)	0.035(1)
O(12)	4*e*	1	0.27734(14)	0.4374(3)	0.1963(2)	0.036(1)
O(13)	4*e*	1	0.30316(17)	0.7514(3)	0.2843(2)	0.041(1)
O(14)	4*e*	1	0.13480(14)	0.7322(3)	0.0765(2)	0.029(1)
O(15)	4*e*	1	0.07619(15)	0.9071(3)	-0.0485(3)	0.045(1)
O(16)	4*e*	1	0.16901(14)	0.9772(3)	0.0872(2)	0.032(1)
O(17)	4*e*	1	0.25123(14)	0.9558(3)	0.3641(2)	0.034(1)
O(18)	4*e*	1	0.19662(17)	0.8300(3)	-0.0549(3)	0.043(1)
O(19)	4*e*	1	0.30033(15)	0.9825(4)	0.2014(2)	0.048(1)

O(20)	4*e*	1	0.37731(13)	0.9442(3)	0.3583(2)	0.028(1)
O21	4*e*	1	0.42291(17)	0.7570(3)	0.1212(3)	0.053(1)
O22	4*e*	1	0.51858(13)	0.6312(3)	0.0652(2)	0.026(1)
O23	4*e*	1	0.48177(15)	0.5629(4)	0.2315(2)	0.051(1)
O24	4*e*	1	0.40852(13)	0.5107(3)	0.0701(2)	0.028(1)

Table S3. Selected Bond Distances (Å) for $K_6Na_3Al_3P_6O_{24}$.

Na(1)-O(13)	2.250(3)	K(5)-O(18)$^{\#1}$	2.740(3)
Na(1)-O(18)$^{\#1}$	2.266(3)	K(5)-O(3)$^{\#4}$	2.750(3)
Na(1)-O(8)$^{\#2}$	2.401(4)	K(5)-O(17)	2.769(3)
Na(1)-O(12)	2.459(3)	K(5)-O(14)	2.780(3)
Na(1)-O(5A)	2.494(5)	K(5)-O(2)$^{\#4}$	2.904(3)
Na(1)-O(7)$^{\#2}$	2.648(3)	K(5)-O(16)	3.133(3)
mean	2.420	K(5)-O(13)	3.377(4)
Na(2)-O(21)	2.211(3)	mean	2.922
Na(2)-O(23)$^{\#3}$	2.260(3)	K(6)-O(12)	2.523(3)
Na(2)-O(10)$^{\#4}$	2.277(3)	K(6)-O(10)	2.634(4)
Na(2)-O(19)	2.440(3)	K(6)-O(8)$^{\#2}$	2.711(4)
Na(2)-O(20)	2.557(3)	K(6)-O(23)	2.763(4)
mean	2.349	K(6)-O(24)	2.890(3)
		K(6)-O(9)$^{\#2}$	3.165(3)
Na(3)-O(5A)	2.289(3)	mean	2.781
Na(3)-O(15)$^{\#1}$	2.323(3)	Al(1)-O(22)$^{\#10}$	1.723(3)
Na(3)-O(5B)	2.330(3)	Al(1)-O(24)	1.727(3)
Na(3)-O(4)	2.369(3)	Al(1)-O(9)	1.736(3)
Na(3)-O(3)$^{\#5}$	2.416(3)	Al(1)-O(20)$^{\#9}$	1.740(3)
Na(3)-O(1)$^{\#5}$	2.586(3)	mean	1.732
mean	2.386	Al(2)-O(6B)	1.665(2)
		Al(2)-O(19)$^{\#8}$	1.717(3)
K(1)-O(3)	2.652(3)	Al(2)-O(16)$^{\#8}$	1.730(3)
K(1)-O(15)$^{\#6}$	2.669(3)	Al(2)-O(7)	1.735(3)
K(1)-O(4)$^{\#7}$	2.785(3)	Al(2)-O(6A)	1.749(4)
K(1)-O(16)$^{\#8}$	2.906(3)	mean	1.719
K(1)-O(15)$^{\#8}$	3.089(4)	Al(3)-O(2)$^{\#7}$	1.729(3)
K(1)-O(6B)	3.103(2)	Al(3)-O(1)$^{\#5}$	1.731(3)
K(1)-O(6A)	3.183(5)	Al(3)-O(14)	1.735(3)
K(1)-O(5B)	3.250(4)	Al(3)-O(11)	1.740(3)
K(1)-O(11)	3.404(3)	mean	1.734
mean	3.004	P(1)-O(3)	1.500(3)
		P(1)-O(4)	1.500(3)
K(2)-O(17)$^{\#8}$	2.508(3)	P(1)-O(1)	1.561(3)
K(2)-O(5B)	2.540(3)	P(1)-O(2)	1.562(3)
K(2)-O(5A)	2.736(4)	mean	1.531
K(2)-O(7)$^{\#2}$	2.789(3)	P(2)-O(8)	1.494(3)
K(2)-O(4)	2.865(3)	P(2)-O(10)	1.497(3)
K(2)-O(9)$^{\#2}$	2.898(3)	P(2)-O(9)	1.560(3)
K(2)-O(11)$^{\#2}$	2.900(3)	P(2)-O(7)	1.581(3)
K(2)-O(6B)$^{\#2}$	2.960(3)	mean	1.533
K(2)-O(6A)	3.088(9)	P(3)-O(5B)	1.470(3)
mean	2.809	P(3)-O(12)	1.490(3)

K(3)-O(12)	2.702(3)	P(3)-O(5A)	1.511(3)
K(3)-O(13)	2.786(3)	P(3)-O(6A)	1.534(3)
K(3)-O(21)	2.814(3)	P(3)-O(11)	1.557(3)
K(3)-O(18)	2.825(4)	P(3)-O(6B)	1.605(2)
K(3)-O(24)	2.870(3)	mean	1.535
K(3)-O(14)	3.088(3)	P(4)-O(23)	1.480(3)
K(3)-O(17)#9	3.096(3)	P(4)-O(21)	1.506(3)
K(3)-O(11)	3.288(3)	P(4)-O(24)	1.558(3)
K(3)-O(19)	3.422(4)	P(4)-O(22)	1.565(3)
mean	2.988	mean	1.527
K(4)-O(8)$^{\#4}$	2.660(3)	P(5)-O(18)	1.482(3)
K(4)-O(23)$^{\#9}$	2.714(3)	P(5)-O(15)	1.487(3)
K(4)-O(20)$^{\#9}$	2.899(3)	P(5)-O(16)	1.559(3)
K(4)-O(10)$^{\#10}$	2.941(3)	P(5)-O(14)	1.576(3)
K(4)-O(22)	2.971(3)	mean	1.526
K(4)-O(21)	3.089(4)	P(6)-O(17)	1.489(3)
K(4)-O(13)$^{\#9}$	3.152(4)	P(6)-O(13)	1.490(3)
mean	2.918	P(6)-O(19)	1.563(3)
		P(6)-O(20)	1.573(3)
		mean	1.529

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ x,-y+3/2,z+1/2; $^{\#2}$ x,-y+1/2,z+1/2; $^{\#3}$ -x+1,y+1/2,-z+1/2; $^{\#4}$ x,y+1,z; $^{\#5}$ -x,y+1/2,-z+1/2; $^{\#6}$ -x,-y+1,-z; $^{\#7}$ x,-y+1/2,z-1/2; $^{\#8}$ x,y-1,z; $^{\#9}$ x,-y+3/2,z-1/2; $^{\#10}$ -x+1,-y+1,-z

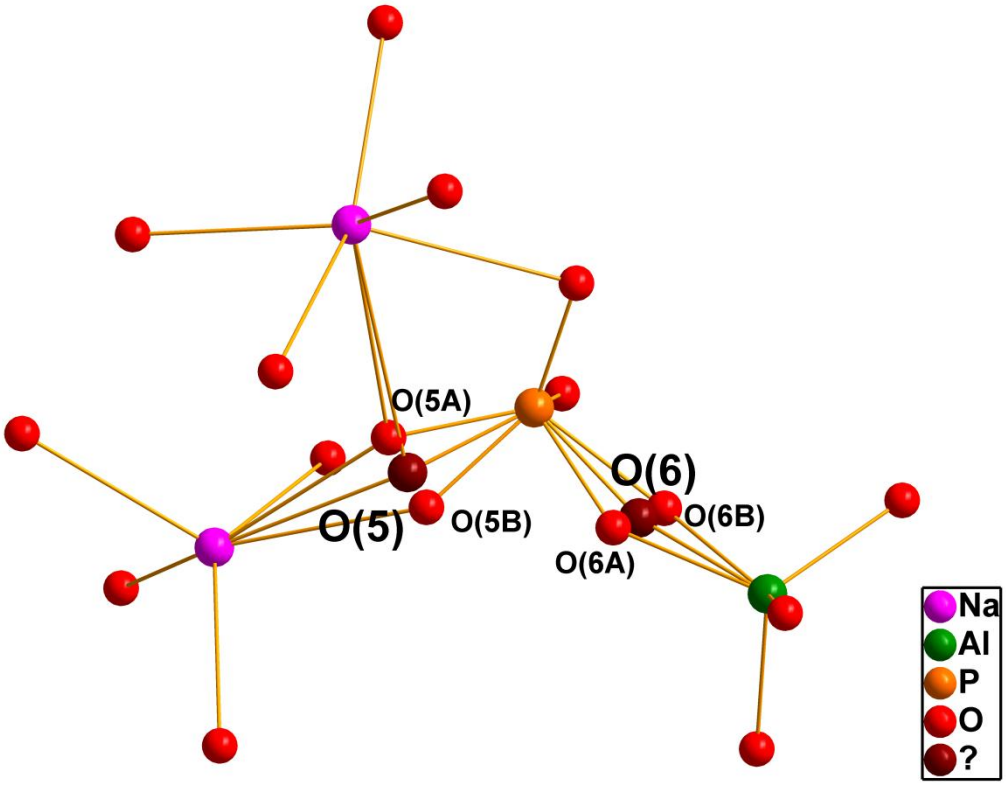

Figure S1. The simplification for the disorder oxygen atoms in $K_6Na_3Al_3P_6O_{24}$ (The dark red atoms stand for the pseudo-atoms, and their position are determined by the average positions between the disorder oxygen atoms).

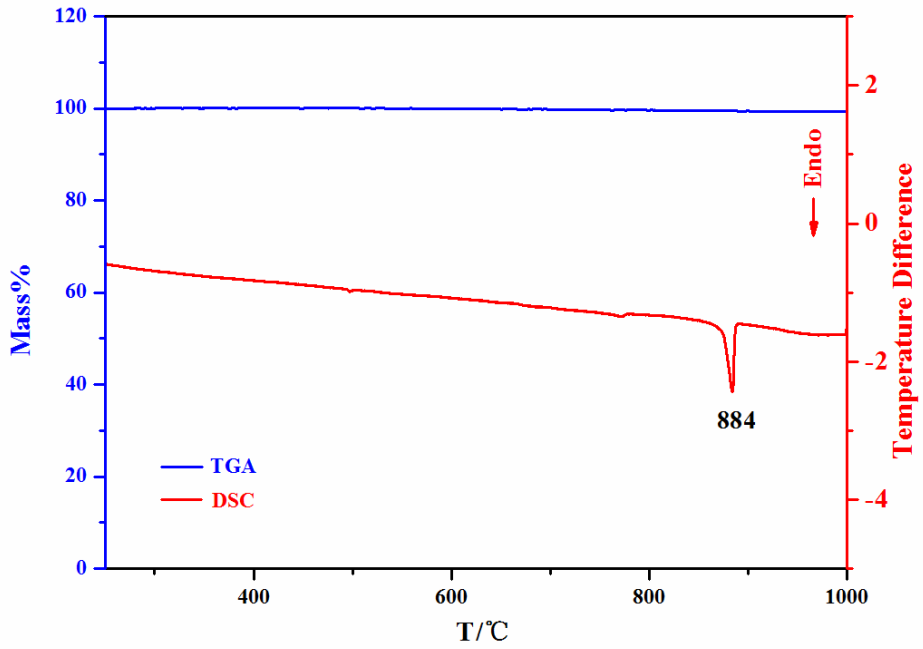

Figure S2. TGA and DSC curves for $K_6Na_3Al_3P_6O_{24}$.

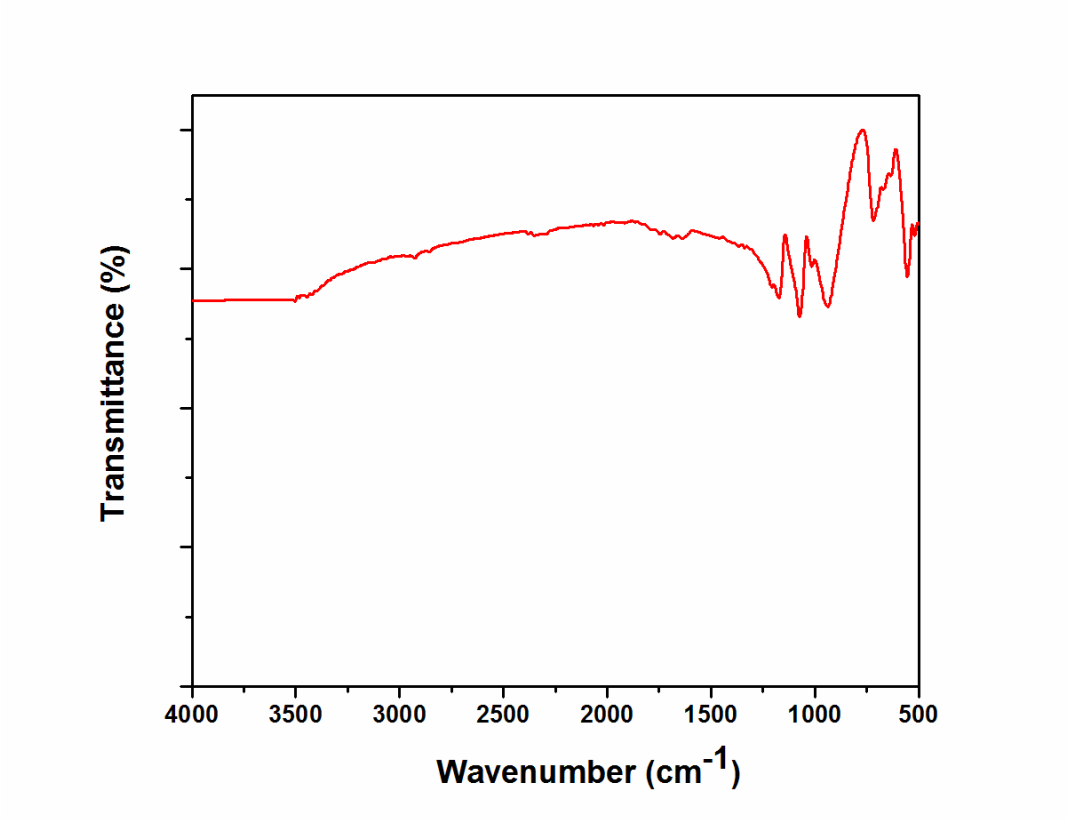

Figure S3. IR Spectroscopy of as-synthesized $K_6Na_3Al_3P_6O_{24}$.

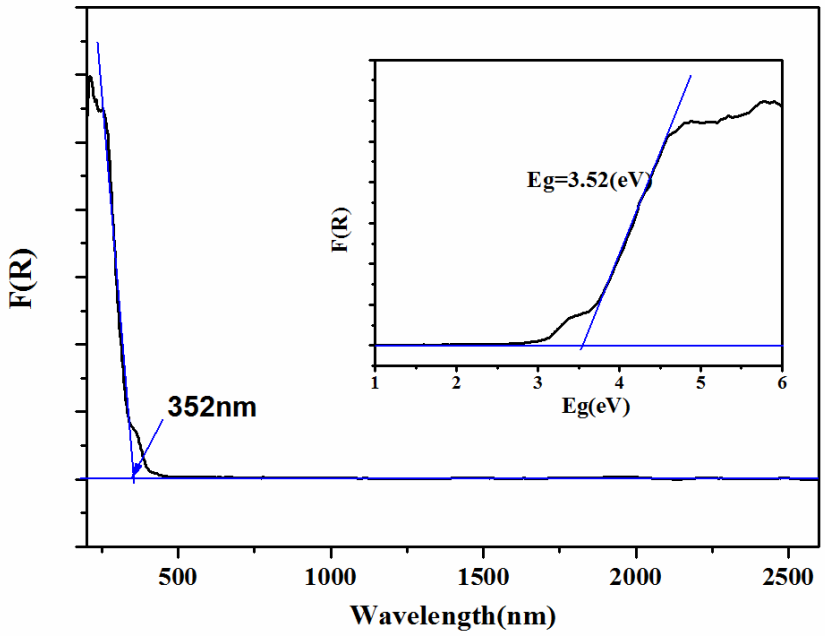

Figure S4. UV-Vis-NIR diffuse-reflectance spectroscopy of $K_6Na_3Al_3P_6O_{24}$.

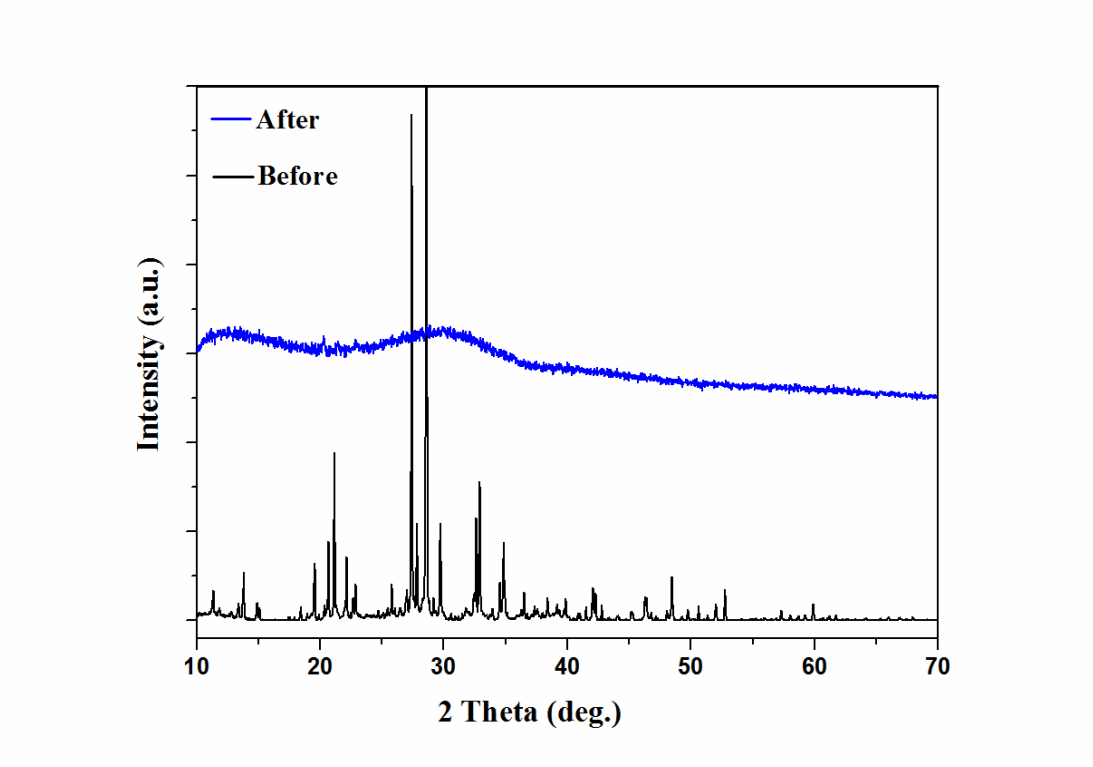

Figure S5. The powder XRD patterns of $K_6Na_3Al_3P_6O_{24}$ before and after ion-exchange experiment (in 1M $NaNO_3$ solution for inllustration).