Electronic Supplementary Information

Two-Stage Evolution from Phosphate to Sulfate of New KTP-type family Members as UV Nonlinear Optical Materials through Chemical Cosubstitution-Oriented Design

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Table of contents

Section S1. Materials and Methods

Synthesis. All of the starting reagents were analytical grade and used without further purification process, $(NH_4)_3PO_4·3H_2O$(AR 99%), $(NH_4)_2SO_4$ (AR 99%), SbF_3 (AR 99%). The single crystals of $NH_4SbFPO_4·H_2O$ and $NH_4SbF_2SO_4$ were synthesized by hydrothermal method. The constituent are as follows: $(NH_4)_3PO_4·3H_2O$ (0.203 g, 1 mmol), SbF_3 (0.358 g, 2 mmol) and 0.6 mL H_2O for $NH_4SbFPO_4·H_2O$, and $(NH_4)_2SO_4$ (0.132 g, 1 mmol), SbF_3 (0.356 g, 2 mmol) and 1 mL H_2SO_4 (4 mol/L) for $NH_4SbF_2SO_4$, respectively. The reactants were sealed in a 23 mL Teflon autoclave and then were put into the oven. The oven temperature held at 180 °C for 4 days, and then cooled down to the ambient temperature with the rate of 5°C/h. Transparent colorless crystals were achieved with 60-70% yield (based on Sb).

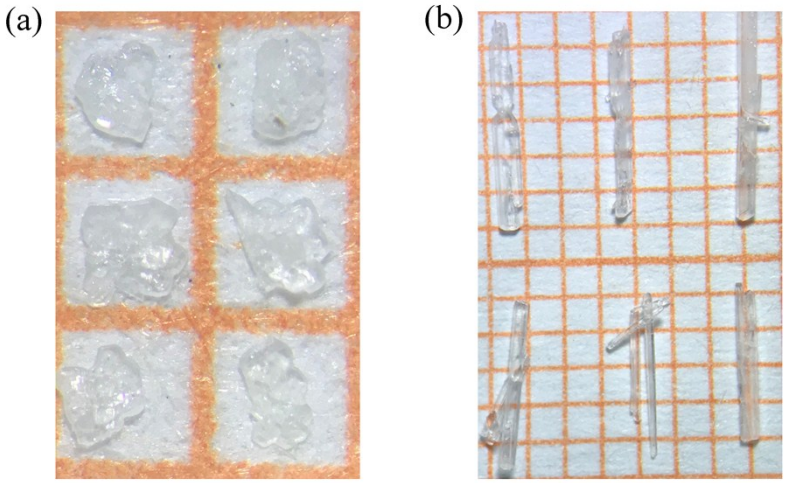

Fig. S1. The crystal photographs of (a) $NH_4SbFPO_4·H_2O$ and (b) $NH_4SbF_2SO_4$.

Instrumentations. Data collections for single crystals of the compounds were performed on a Bruker D8 Venture diffractometer and equipped with a graphite monochromatic Mo-*K*α radiation (λ = 0.71073 Å) at 150(2) K. The crystal structures were solved by direct methods and refined by a full-matrix least-squares on F^2 with SHELX-2014[1] and Olex2. The structures were checked by PLATON,[2] and no higher symmetries were found. Crystallographic data and structural refinements information are summarized in Table 1. Atomic coordinates and isotropic displacement parameters, and selected bond lengths are listed in Table S1-S4. Powder X-ray diffraction patterns of the compounds were measured at room temperature by a Smart lab powder X-ray diffractometer using Cu Kα radiation (λ=1.540598 Å) in the 2θ range of 5-70° with a step width of 0.08° and a fixed counting time of 0.2 s/step. The IR data were recorded with a Vertex 70 Fourier transform infrared (FT-IR) spectrometer in the range of 4000-400 cm^{-1}.

Thermogravimetric analysis (TGA) were measured on a DISCOVERYTGA thermal analyzer and sample powders were heated under N_2 gas atmosphere from room temperature to 800 °C at a rate of 10 °C /min. UV/vis diffuse reflectance data for compounds were recorded with a Shimadzu UV-2600 spectrophotometer at room temperature in the wavelength range 200-800 nm with the resolution of 1 nm for the UV/vis range. The power frequency-doubling signal of $NH_4SbF_2SO_4$ was measured by the Kurtz and Perry method at room temperature with 1064nm Q-switch Nd:YAG laser on powdered samples.[3] All of the samples were ground and divided into the following six distinct particle size: 25-45, 45-58, 58-75, 75-106, 106-150 and 150-212 μm, respectively. Sieved powders of KDP (KH_2PO_4) were used as reference. To better understand the electronic structures of $NH_4SbFPO_4{\cdot}H_2O$ and $NH_4SbF_2SO_4$, their structures were optimized and band structures and density of states (DOS)/ partial DOS (PDOS) were then calculated by employing the density functional theory (DFT) in the CASTEP suite of program.[4] In all calculations, the Perdew-Burke-Ernzerhof (PBE) functional with generalized gradient approximation (GGA) was adopted.[5] The kinetic energy cutoff of 850 eV and 300.0 eV were chosen for $NH_4SbFPO_4{\cdot}H_2O$ and $NH_4SbF_2SO_4$, respectively, and the *k*-point sampling in the Brilliouin zone were used to be 5×5×5 for $NH_4SbFPO_4{\cdot}H_2O$ and 3×3×6 for $NH_4SbF_2SO_4$. Ultrasoft pseudopotentials (USP) were employed for all the valence electrons.[6]

Table S1. Crystal Data and Structure Refinements for $NH_4SbFPO_4·H_2O$ and $NH_4SbF_2SO_4$.

Formula	**$NH_4SbFPO_4·H_2O$**	**$NH_4SbF_2SO_4$**
Formula weight	271.78	273.85
Crystal system	Triclinic	Orthorhombic
Space group	*P*-1	$Pna2_1$
***a* (Å)**	6.5374(4)	9.5730 (7)
***b* (Å)**	6.5425(5)	11.5948 (7)
***c* (Å)**	8.3743(6)	5.1311 (4)
***V* (Å^3)**	306.95(4)	569.54 (7)
***α* (°)**	68.272 (3)	90
***β* (°)**	68.966 (3)	90
***γ* (°)**	89.938 (4)	90
Z	2	2
D_{calcd}(g·cm^{-3})	2.941	3.194
Temperature (K)	150 (2)	150 (2)
***λ* (Å)**	0.71073	0.71073
***F*(000)**	256	512
***μ* (mm^{-1})**	4.735	5.202
GOF on F^2	0.973	1.005
R_1,wR_2 ($I>2\sigma(I)$)[a]	0.0344/0.0910	0.0223/0.0537
R_1,wR_2 (all data)	0.0396/0.0948	0.0261/0.0554

$R_1(F) = \sum||F_o|-|F_c||/\sum|F_o|$. $wR_2(F_o^2) = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $NH_4SbFPO_4 \cdot H_2O$.

atom	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
Sb1	0.27454 (5)	0.77565 (5)	0.44372 (4)	0.01015 (14)	3.194
P1	0.2497 (2)	0.25022 (19)	0.4996 (2)	0.0100 (2)	4.739
F1	0.3973 (5)	0.9030 (5)	0.1748 (4)	0.0144 (6)	0.922
O1	0.3710 (6)	0.2490 (6)	0.6277 (5)	0.0133 (7)	1.720
O2	0.3679 (6)	0.1300 (6)	0.3727 (5)	0.0126 (7)	1.736
O3	0.2485 (6)	0.4912 (5)	0.3742 (5)	0.0121 (7)	1.781
O4	0.0104 (6)	0.1310 (6)	0.6258 (5)	0.0140 (7)	1.774
O5	0.1482 (8)	0.2278 (8)	0.9962 (7)	0.0293 (10)	2.028
N1	0.7194 (8)	0.3482 (9)	0.0132 (7)	0.0179 (9)	

Table S3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $NH_4SbF_2SO_4$.

atom	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
Sb1	0.16783 (4)	0.58335 (3)	0.17349 (17)	0.02151 (15)	2.928
S1	0.21412 (18)	0.36668 (15)	0.7173 (4)	0.0238 (4)	5.951
F1	0.3690 (4)	0.5735 (3)	0.1498 (18)	0.0272 (11)	0.915
F2	0.1719 (4)	0.6512 (4)	−0.1692 (9)	0.0264 (11)	0.930
N1	0.5089 (6)	0.3456 (5)	1.194 (2)	0.0259 (13)	
O1	0.3067 (6)	0.4448 (5)	0.5810 (13)	0.0276 (12)	1.684
O2	0.0952 (5)	0.3316 (4)	0.5590 (12)	0.0283 (12)	1.692
O3	0.2965 (6)	0.2631 (5)	0.8061 (13)	0.0310 (13)	1.886
O4	0.1608 (6)	0.4194 (5)	0.9655 (14)	0.0291 (14)	1.961

Table S4. Selected Bond lengths (Å) and angles (deg) for $NH_4SbFPO_4 \cdot H_2O$.

Sb1—F1	1.930 (3)	P1—O2	1.540 (4)
Sb1—O4^{i}	2.167 (4)	P1—O4	1.542 (4)
Sb1—O3	2.169 (3)	P1—O1	1.544 (4)
Sb1—O2^{ii}	2.196 (3)	O1—Sb1^{iii}	2.198 (3)
Sb1—O1^{iii}	2.198 (4)	O2—Sb1^{iv}	2.196 (3)
P1—O3	1.539 (3)	O4—Sb1^{i}	2.167 (3)
F1—Sb1—O4^{i}	76.53 (14)	O3—P1—O2	108.0 (2)
F1—Sb1—O3	76.68 (13)	O3—P1—O4	110.3 (2)
O4^{i}—Sb1—O3	87.35 (13)	O2—P1—O4	110.4 (2)
F1—Sb1—O2^{ii}	76.61 (13)	O3—P1—O1	110.1 (2)
O4^{i}—Sb1—O2^{ii}	86.90 (13)	O2—P1—O1	110.6 (2)
O3—Sb1—O2^{ii}	153.29 (14)	O4—P1—O1	107.5 (2)
F1—Sb1—O1^{iii}	76.66 (13)	P1—O1—Sb1^{iii}	123.2 (2)
O4^{i}—Sb1—O1^{iii}	153.19 (15)	P1—O2—Sb1^{iv}	123.3 (2)
O3—Sb1—O1^{iii}	87.02 (13)	P1—O3—Sb1	124.1 (2)
O2^{ii}—Sb1—O1^{iii}	86.46 (13)	P1—O4—Sb1^{i}	123.6 (2)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, y+1, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y-1, z$.

Table S5. Selected Bond lengths (Å) and angles (deg) for $NH_4SbF_2SO_4$.

Sb1—F2	1.927 (5)	S1—O3	1.507 (6)
Sb1—F1	1.933 (4)	N1—H1	0.96 (6)
Sb1—O4^{i}	2.181 (6)	N1—H2	0.83 (12)
Sb1—O3^{ii}	2.219 (6)	N1—H3	0.92 (11)
S1—O1	1.447 (6)	N1—H4	0.82 (12)
S1—O2	1.456 (6)	O3—Sb1^{iii}	2.219 (6)
S1—O4	1.502 (7)	O4—Sb1^{iv}	2.181 (6)
F2—Sb1—F1	87.0 (3)	O2—S1—O3	110.8 (3)
F2—Sb1—O4^{i}	84.8 (2)	O4—S1—O3	104.2 (4)
F1—Sb1—O4^{i}	87.0 (2)	H1—N1—H2	109 (10)
F2—Sb1—O3^{ii}	83.9 (2)	H1—N1—H3	115 (8)
F1—Sb1—O3^{ii}	85.5 (2)	H2—N1—H3	94 (10)
O4i—Sb1—O3^{ii}	166.8 (2)	H1—N1—H4	112 (7)
O1—S1—O2	112.6 (4)	H2—N1—H4	116 (8)
O1—S1—O4	111.3 (3)	H3—N1—H4	109 (10)
O2—S1—O4	108.7 (3)	S1—O3—Sb1^{iii}	137.4 (4)
O1—S1—O3	108.9 (3)	S1—O4—Sb1^{iv}	139.4 (4)

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1/2, y+1/2, z-1/2$; (iii) $-x+1/2, y-1/2, z+1/2$; (iv) $x, y, z+1$.

Table S6. Calculation of dipole moment for SO_4, SbO_2F_2 polyhedra and net dipole moment for a unit cell in $NH_4SbF_2SO_4$ (D = Debyes).

$NH_4SbF_2SO_4$				
Polar unit (a unit cell)	Dipole moment (D)			
	x-component	*y*-component	*z*-component	total magnitude
SO_4	0.275653	-0.77781	-2.05917	2.218371
	-0.27565	-0.77781	-2.05917	2.218371
	0.275653	0.77781	-2.05917	2.218371
	-0.27565	0.77781	-2.05917	2.218371
	Ux	*Uy*	*Uz*	*Ut*
	1.69E-14	3.38E-14	-8.2367	8.236695
SbO_2F_2	-12.5688	4.27437	12.89603	18.50816
	12.56837	4.27381	12.89628	18.50793
	-12.5712	-4.2766	12.89641	18.5106
	12.57122	-4.2766	12.89641	18.5106
	Ux	*Uy*	*Uz*	*Ut*
	-0.0004	-0.00502	51.58511	51.58511
Net dipole moment	-4.00E-04	-5.02E-03	43.34841	43.34841
Cell Volume	569.54 (7) $Å^3$			

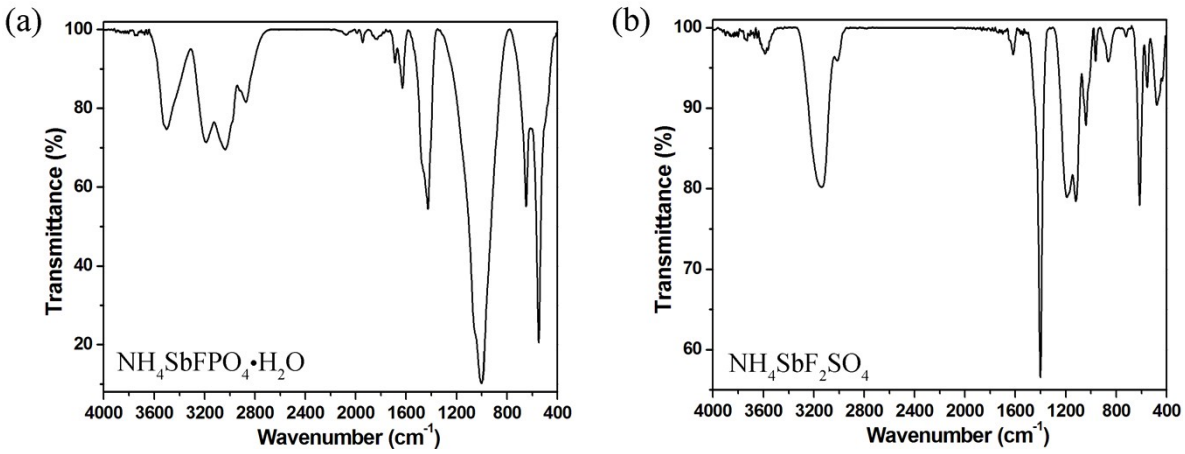

Fig. S2. The IR spectra of (a) $NH_4SbFPO_4 \cdot H_2O$ and (b) $NH_4SbF_2SO_4$.

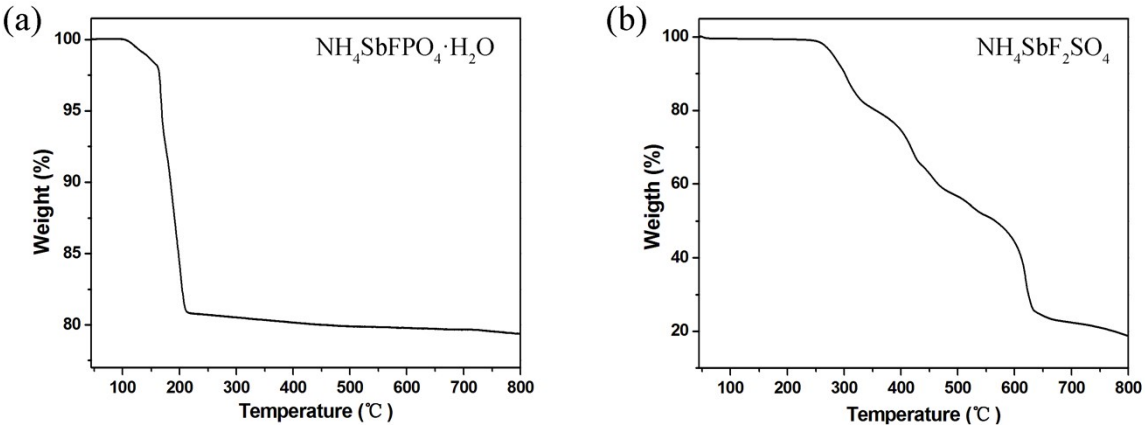

Fig. S3. TGA curves of (a) $NH_4SbFPO_4 \cdot H_2O$ and (b) $NH_4SbF_2SO_4$ under N_2 atmosphere.

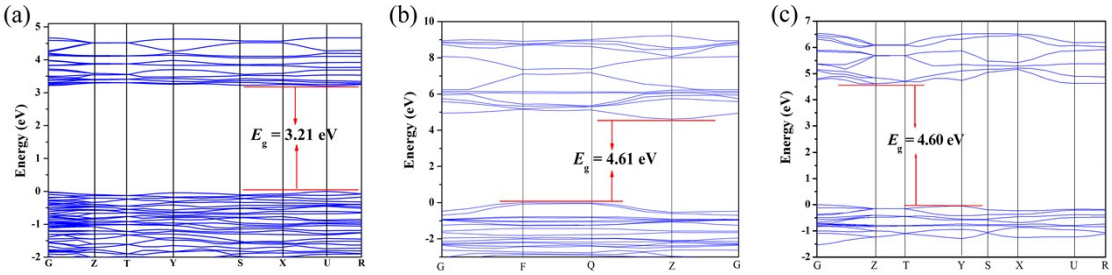

Fig. S4. Calculated band structures of $KTiOPO_4$ (a), $NH_4SbFPO_4 \cdot H_2O$ (b) and $NH_4SbF_2SO_4$ (c).

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