Supporting Information

Cation-Tuned Synthesis of $A_2SO_4 \cdot SbF_3$ ($A=Na^+$, NH_4^+, K^+, Rb^+) Family with Nonlinear Optical Property

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Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $Na_2SO_4 \cdot SbF_3$.

atom	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
Sb(1)	0.5000	0.88927 (3)	0.66366 (2)	0.01225 (9)	3.035
S(1)	0.31660 (5)	1.0000	0.5000	0.01027 (14)	5.937
Na(1)	0.2500	0.72040 (19)	0.2500	0.0206 (3)	1.026
Na(2)	0.38226 (10)	0.5000	0.5000	0.0294 (4)	1.070
F(1)	0.5000	0.6262 (3)	0.6157 (2)	0.0191 (4)	1.149
F(2)	0.59015 (10)	0.8119 (2)	0.78056 (13)	0.0250 (3)	1.011
O(1)	0.37424 (11)	0.8368 (2)	0.52382 (16)	0.0183 (3)	1.882
O(2)	0.26091 (11)	0.9652 (2)	0.39369 (14)	0.0171 (3)	2.066

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $(NH_4)_2SO_4 \cdot SbF_3$.

atom	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
Sb(1)	0.43893 (2)	0.37970 (2)	0.37964 (2)	0.01079 (8)	2.952
S(1)	0.73344 (6)	0.38431 (5)	0.50098 (5)	0.01119 (13)	6.008
F(1)	0.48323 (14)	0.24537 (14)	0.29092 (12)	0.0186 (3)	0.936
F(2)	0.50792 (15)	0.48475 (14)	0.27535 (12)	0.0193 (3)	0.948
F(3)	0.28492 (15)	0.38115 (12)	0.30596 (12)	0.0186 (3)	0.947
O(1)	0.66884 (18)	0.32678 (18)	0.41649 (15)	0.0224 (4)	1.778
O(2)	0.76936 (18)	0.51018 (17)	0.47385 (13)	0.0204 (4)	1.588
O(3)	0.64926 (18)	0.38861 (15)	0.58824 (15)	0.0155 (4)	1.672
O(4)	0.84395 (18)	0.31329 (19)	0.52618 (17)	0.0278 (5)	1.765
N1	0.05682 (19)	0.3629 (2)	0.40778 (19)	0.0140 (4)	
N2	0.7588 (2)	0.13502 (17)	0.28870 (18)	0.0164 (5)	

Table S3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $K_2SO_4 \cdot SbF_3$.

atom	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
Sb(1)	0.47303 (18)	0.55762 (8)	0.47751 (5)	0.0249 (5)	3.093
K(1)	−0.0034 (6)	0.5089 (4)	0.6910 (2)	0.0344 (8)	0.921
K(2)	0.4809 (6)	0.1863 (3)	0.6114 (2)	0.0318 (8)	0.860
S(1)	0.5227 (7)	0.7935 (3)	0.6614 (2)	0.0257 (8)	6.255
F(1)	0.4623 (18)	0.4070 (10)	0.3760 (5)	0.036 (2)	1.018
F(2)	0.2532 (14)	0.4224 (9)	0.5389 (5)	0.0263 (17)	1.283
F(3)	0.7162 (16)	0.4261 (10)	0.5357 (7)	0.035 (2)	1.137
O(1)	0.742 (2)	0.7733 (13)	0.7135 (9)	0.042 (3)	1.984
O(2)	0.573 (3)	0.8777 (13)	0.5742 (9)	0.043 (3)	1.962
O(3)	0.427 (3)	0.6504 (13)	0.6313 (8)	0.048 (3)	2.094
O(4)	0.347 (3)	0.868 (3)	0.7174 (14)	0.082 (6)	1.998

Table S4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $Rb_2SO_4 \cdot SbF_3$.

atom	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
Sb1	0.69104 (5)	0.27084 (9)	0.77280 (3)	0.02192 (14)	3.083
Rb1	1.06604 (7)	0.26613 (15)	0.63374 (5)	0.02486 (18)	1.174
Rb2	0.73735 (7)	0.75502 (15)	0.56096 (4)	0.02600 (17)	1.149
S1	0.4547 (2)	0.2177 (4)	0.59576 (12)	0.0226 (4)	5.977
F1	0.8199 (6)	0.0341 (7)	0.7170 (4)	0.0271 (13)	1.065
F2	0.8408 (5)	0.2853 (8)	0.8720 (3)	0.0259 (10)	1.127
F3	0.8222 (6)	0.4825 (8)	0.7116 (3)	0.0240 (12)	1.243
O1	0.3764 (7)	0.1658 (10)	0.6833 (4)	0.0296 (14)	1.914
O2	0.4671 (7)	0.0082 (10)	0.5403 (4)	0.0293 (14)	2.108
O3	0.3795 (8)	0.3999 (11)	0.5458 (5)	0.0426 (17)	1.860
O4	0.6024 (6)	0.3029 (10)	0.6211 (4)	0.0297 (14)	1.950

Table S5. Bond lengths [Å] and angles [°] for $Na_2SO_4 \cdot SbF_3$.

Sb(1)-F(1)	1.9613(19)	F(2)-Sb(1)-O(1)	154.48(7)
Sb(1)-F(2)	1.9632(14)	O(1)#1-Sb(1)-O(1)	100.25(8)
Sb(1)-F(2)#1	1.9632(14)	O(2)-S(1)-O(1)	110.27(10)
Sb(1)-O(1)#1	2.4859(17)	O(2)#2-S(1)-O(1)	109.26(9)
Sb(1)-O(1)	2.4860(17)	O(1)-S(1)-O(1)#2	107.89(14)
S(1)-O(2)	1.4704(16)	O(2)#5-Na(1)-F(2)#9	103.33(6)
S(1)-O(2)#2	1.4704(16)	O(2)#7-Na(1)-F(2)#9	84.61(6)
S(1)-O(1)	1.4855(17)	F(1)-Na(2)-F(1)#11	82.61(9)
S(1)-O(1)#2	1.4855(17)	F(1)-Na(2)-O(1)#12	118.31(7)
Na(1)-O(2)	2.3763(19)	F(1)-Na(2)-O(1)	66.48(6)
Na(1)-O(2)#5	2.3763(19)	O(1)#12-Na(2)-O(1)	174.27(11)
Na(1)-O(2)#6	2.4317(19)	F(1)-Na(2)-O(2)#7	161.98(6)
Na(1)-O(2)#7	2.4317(19)	O(1)-Na(2)-O(2)#7	96.17(7)
Na(1)-F(2)#8	2.4594(15)	F(1)-Na(2)-O(2)#3	111.30(5)
Na(1)-F(2)#9	2.4594(15)	O(2)#7-Na(2)-O(2)#3	57.98(8)
Na(2)-F(1)	2.3776(19)	F(1)-Na(2)-F(2)#13	66.75(6)
Na(2)-F(1)#11	2.3776(18)	F(1)#11-Na(2)-F(2)#13	99.85(7)
Na(2)-O(1)#12	2.4344(17)	O(1)-Na(2)-F(2)#13	112.99(5)
Na(2)-O(1)	2.4344(17)	O(2)#3-Na(2)-F(2)#13	76.62(5)
Na(2)-O(2)#7	2.483(2)	F(1)#11-Na(2)-F(2)#9	66.75(6)
Na(2)-O(2)#3	2.483(2)	O(1)#12-Na(2)-F(2)#9	112.99(5)
Na(2)-Na(1)#14	3.7673(10)	O(2)#7-Na(2)-F(2)#9	76.62(5)
F(1)-Na(2)#11	2.3776(18)	F(2)#13-Na(2)-F(2)#9	162.88(9)
F(2)-Na(1)#15	2.4594(15)	Sb(1)-F(1)-Na(2)	120.84(6)
F(2)-Na(2)#15	2.8112(16)	Na(2)#11-F(1)-Na(2)	97.39(9)
O(2)-Na(1)#4	2.4318(19)	Sb(1)-F(2)-Na(2)#15	122.53(8)
O(2)-Na(2)#3	2.483(2)	S(1)-O(1)-Na(2)	142.49(11)
F(1)-Sb(1)-F(2)	84.61(7)	S(1)-O(1)-Sb(1)	116.28(9)
F(2)-Sb(1)-F(2)#1	88.31(9)	Na(2)-O(1)-Sb(1)	100.35(7)
F(2)-Sb(1)-O(1)#1	80.40(6)	S(1)-O(2)-Na(2)#3	96.08(8)
F(1)-Sb(1)-O(1)	71.67(6)	Na(1)-O(2)-Na(2)#3	109.32(7)

Symmetry transformations used to generate equivalent atoms:

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

#4 x,y+1/2,-z+1/2 #5 -x+1/2,y+0,-z+1/2 #6 x,y-1/2,-z+1/2

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

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

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

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

Table S6. Bond lengths [Å] and angles [°] for $(NH_4)_2SO_4 \cdot SbF_3$.

Sb1—F3	1.9419 (16)	O(4)-S(1)-O(1)	109.97(13)
Sb1—F1	1.9456 (15)	O(4)-S(1)-O(2)	109.36(12)
Sb1—F2	1.9539 (15)	O(1)-S(1)-O(2)	109.60(12)
S1—O4	1.468 (2)	O(4)-S(1)-O(3)	109.94(12)
S1—O1	1.470 (2)	O(1)-S(1)-O(3)	108.83(11)
S1—O2	1.4728 (18)	O(2)-S(1)-O(3)	109.12(11)
S1—O3	1.483 (2)	H2A—N2—H2B	108.7
N2—H2A	0.8342	H2A—N2—H2C	102.7
N2—H2B	0.8322	H2B—N2—H2C	111.3
N2—H2C	0.8997	H2A—N2—H2D	114.5
N2—H2D	0.8985	H2B—N2—H2D	106.5
N1—H1B	0.8150	H2C—N2—H2D	113.1
N1—H1A	0.8626	H1B—N1—H1A	106.3
N1—H1C	0.9029	H1B—N1—H1C	109.9
N1—H1D	0.8704	H1A—N1—H1C	111.9
F(3)-Sb(1)-F(1)	84.86(6)	H1B—N1—H1D	120.3
F(3)-Sb(1)-F(2)	87.95(7)	H1A—N1—H1D	98.0
F(1)-Sb(1)-F(2)	84.96(7)	H1C—N1—H1D	109.8

Table S7. Bond lengths [Å] and angles [°] for $K_2SO_4 \cdot SbF_3$.

Sb(1)-F(2)	1.946(8)	F(1)-Sb(1)-F(3)	84.8(4)
Sb(1)-F(1)	1.989(8)	F(2)-Sb(1)-O(3)	75.0(4)
Sb(1)-F(3)	1.992(9)	F(1)-Sb(1)-O(3)	156.2(4)
Sb(1)-O(3)	2.355(12)	F(3)-Sb(1)-O(3)	84.6(5)
Sb(1)-O(2)#1	2.434(14)	F(2)-Sb(1)-O(2)#1	72.8(4)
K(1)-O(4)#5	2.653(16)	F(1)-Sb(1)-O(2)#1	85.4(4)
K(1)-F(2)	2.712(8)	F(3)-Sb(1)-O(2)#1	154.3(4)
K(1)-F(1)#6	2.745(8)	O(3)-Sb(1)-O(2)#1	95.3(5)
K(1)-F(3)#7	2.810(10)	O(4)-S(1)-O(1)	111.2(10)
K(1)-O(1)#7	2.812(13)	O(4)-S(1)-O(3)	108.9(12)
K(1)-O(3)	2.863(14)	O(1)-S(1)-O(3)	110.2(8)
K(2)-F(2)	2.701(9)	O(4)-S(1)-O(2)	110.5(11)
K(2)-F(3)	2.765(10)	O(1)-S(1)-O(2)	109.4(7)
K(2)-F(1)#3	2.835(11)	O(3)-S(1)-O(2)	106.5(7)
K(2)-O(1)#8	2.894(13)	Sb(1)-F(1)-K(1)#4	120.0(4)
K(2)-O(2)#10	2.899(12)	Sb(1)-F(1)-K(2)#2	100.9(4)
S(1)-O(4)	1.436(16)	Sb(1)-F(1)-K(2)#3	96.9(4)
S(1)-O(1)	1.448(12)	Sb(1)-F(2)-K(2)	111.9(3)
S(1)-O(3)	1.470(12)	Sb(1)-F(2)-K(1)	120.6(4)
S(1)-O(2)	1.482(12)	Sb(1)-F(2)-K(2)#2	103.1(3)
F(1)-K(1)#4	2.745(8)	Sb(1)-F(3)-K(2)#3	106.0(4)
F(1)-K(2)#2	2.835(11)	Sb(1)-F(3)-K(2)	107.9(4)
F(2)-K(2)#2	2.803(9)	K(2)#3-F(3)-K(2)	105.0(3)
F(3)-K(2)#3	2.758(10)	Sb(1)-F(3)-K(1)#13	123.2(4)
F(3)-K(1)#13	2.810(10)	S(1)-O(1)-K(1)#13	118.8(7)
O(1)-K(1)#13	2.812(13)	S(1)-O(1)-K(2)#11	96.1(6)
O(1)-K(2)#11	2.894(13)	K(1)#13-O(1)-K(2)#11	94.8(3)
O(2)-Sb(1)#14	2.434(14)	S(1)-O(1)-K(1)#11	124.7(7)
O(2)-K(2)#12	2.899(12)	K(1)#13-O(1)-K(1)#11	115.1(4)
O(4)-K(1)#9	2.653(16)	K(2)#11-O(1)-K(1)#11	91.0(4)
F(2)-Sb(1)-F(1)	82.6(4)	S(1)-O(2)-Sb(1)#14	123.4(7)
F(2)-Sb(1)-F(3)	82.5(4)	S(1)-O(2)-K(2)#12	108.3(7)
F(1)-Sb(1)-F(3)	84.8(4)	Sb(1)#14-O(2)-K(2)#12	89.1(4)
F(2)-Sb(1)-O(3)	75.0(4)	S(1)-O(3)-Sb(1)	123.1(7)
F(3)-Sb(1)-O(3)	84.6(5)	Sb(1)-O(3)-K(1)	101.9(4)
F(2)-Sb(1)-O(2)#1	72.8(4)	S(1)-O(4)-K(1)#9	175.7(13)

Symmetry transformations used to generate equivalent atoms:

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

#4 -x+1/2,-y+1,z-1/2 #5 -x,y-1/2,-z+3/2 #6 -x+1/2,-y+1,z+1/2

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

#10 x,y-1,z #11 -x+1,y+1/2,-z+3/2 #12 x,y+1,z

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

Table S8. Bond lengths [Å] and angles [°] for $Rb_2SO_4 \cdot SbF_3$.

Sb(1)-F(3)	1.939(5)	F(1)-Sb(1)-O(4)	83.3(2)
Sb(1)-F(1)	1.987(5)	F(2)-Sb(1)-O(4)	155.52(19)
Sb(1)-F(2)	2.001(4)	F(3)-Sb(1)-O(1)#1	72.1(2)
Sb(1)-O(4)	2.355(5)	F(1)-Sb(1)-O(1)#1	154.1(2)
Sb(1)-O(1)#1	2.447(6)	F(2)-Sb(1)-O(1)#1	87.21(19)
Rb(1)-F(3)	2.818(6)	O(4)-Sb(1)-O(1)#1	94.6(2)
Rb(1)-F(1)#2	2.861(6)	O(3)-S(1)-O(2)	111.3(4)
Rb(1)-F(2)#3	2.907(5)	O(3)-S(1)-O(1)	109.6(4)
Rb(1)-O(3)#7	3.266(8)	O(2)-S(1)-O(1)	109.9(3)
Rb(1)-O(3)#6	3.268(8)	O(3)-S(1)-O(4)	108.8(4)
Rb(2)-F(3)	2.803(5)	O(2)-S(1)-O(4)	109.6(4)
Rb(2)-F(2)#8	2.842(4)	O(1)-S(1)-O(4)	107.6(3)
Rb(2)-O(3)#9	2.845(6)	Rb(2)#4-F(2)-Rb(1)#2	100.46(13)
Rb(2)-F(1)#10	2.880(5)	Sb(1)-F(2)-Rb(1)#3	97.64(16)
Rb(2)-O(2)#10	2.916(6)	Rb(2)#4-F(2)-Rb(1)#3	91.02(12)
Rb(2)-O(4)	3.022(6)	Rb(1)#2-F(2)-Rb(1)#3	146.47(15)
Rb(2)-O(4)#10	3.510(6)	Sb(1)-F(3)-Rb(2)	122.3(2)
S(1)-O(3)	1.455(6)	Sb(1)-F(3)-Rb(1)	114.1(2)
S(1)-O(2)	1.456(6)	Rb(2)-F(3)-Rb(1)	99.32(17)
S(1)-O(1)	1.492(6)	Sb(1)-F(3)-Rb(1)#2	102.8(2)
S(1)-O(4)	1.501(6)	Rb(2)-F(3)-Rb(1)#2	112.17(15)
F(3)-Sb(1)-F(1)	82.49(16)	Rb(1)-F(3)-Rb(1)#2	105.49(18)
F(3)-Sb(1)-F(2)	82.4(2)	S(1)-O(1)-Sb(1)#14	122.2(3)
F(1)-Sb(1)-F(2)	84.5(2)	S(1)-O(4)-Sb(1)	121.4(3)
F(3)-Sb(1)-O(4)	75.1(2)	Sb(1)-O(4)-Rb(2)	101.10(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+3/2 #2 -x+2,y+1/2,-z+3/2 #3 -x+2,y-1/2,-z+3/2
#4 -x+3/2,-y+1,z+1/2 #5 x,y-1,z #6 x+1/2,-y+1/2,-z+1
#7 x+1,y,z #8 -x+3/2,-y+1,z-1/2 #9 x+1/2,-y+3/2,-z+1
#10 x,y+1,z #11 x-1/2,-y+3/2,-z+1 #12 x-1/2,-y+1/2,-z+1
#13 x-1,y,z #14 -x+1,y-1/2,-z+3/2

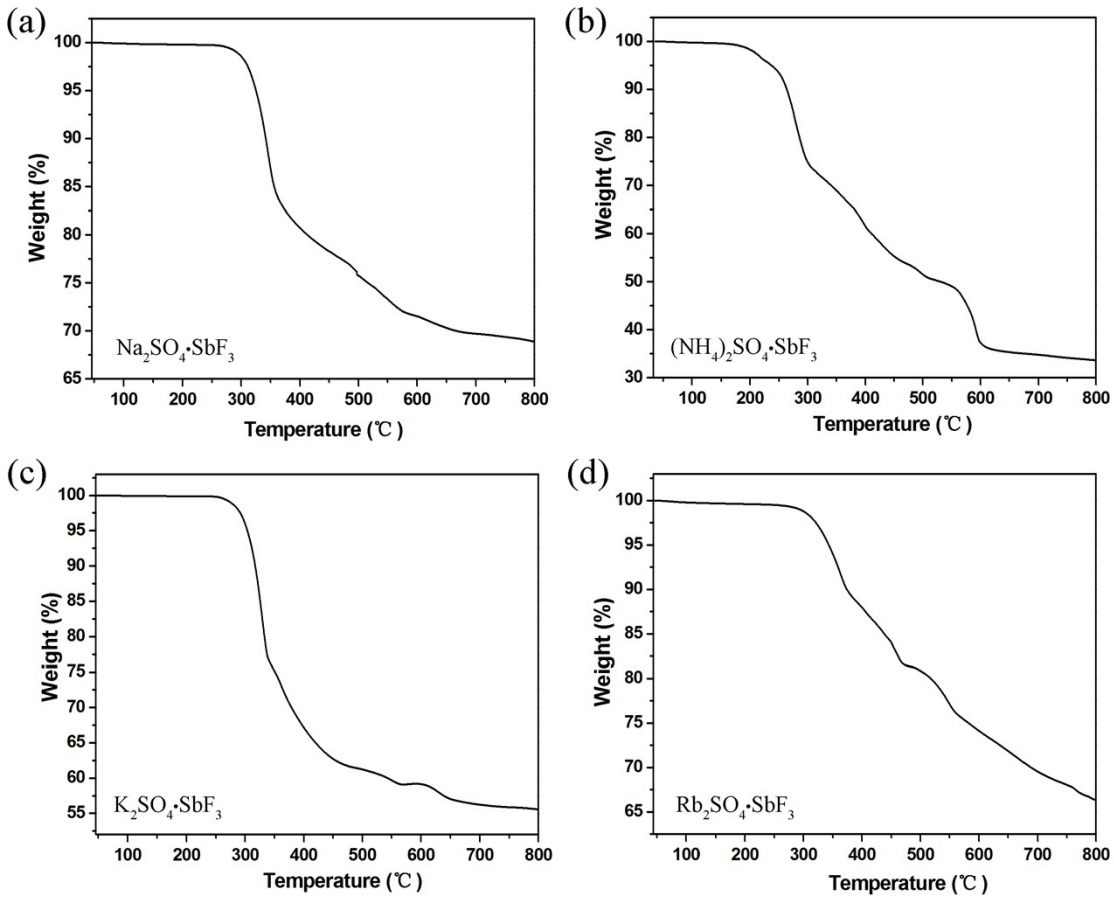

Figure S1. TGA curves of compounds $A_2SO_4 \cdot SbF_3$ ($A=Na^+$, NH_4^+, K^+, Rb^+) under N_2 atmosphere.

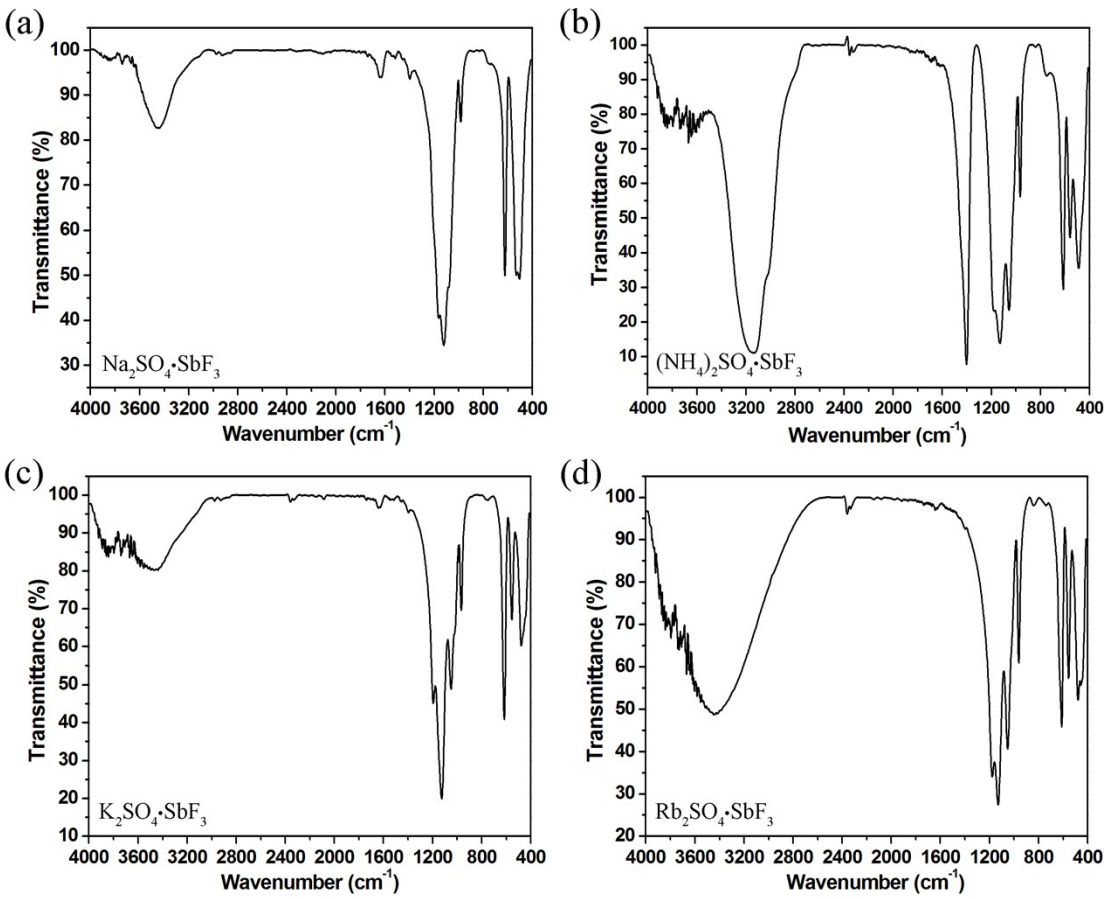

Figure S2. The IR spectra of compounds $A_2SO_4 \cdot SbF_3$ ($A=Na^+$, NH_4^+, K^+, Rb^+).