Supporting Information

$A_2Sb_2SO_4F_6$ ($A = NH_4^+$, Na^+): Two Sulfate Fluoride Crystals Exhibiting Enhanced Birefringence Driven by Stereochemically Active Antimony (III)

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EXPERIMENTAL SECTION

Synthesis

(1) Reagents.

$(NH_4)_2SO_4$ (AR, 99 %), Na_2SO_4 (AR, 99 %), and SbF_3 (AR, 99 %) are commercially available and used without further purification.

(2) Single crystal synthesis.

$(NH_4)_2Sb_2SO_4F_6$: $(NH_4)_2SO_4$ (2.515 g) and SbF_3 (7.485 g) with a stoichiometry of 1 : 2.2 were placed in a disposable plastic cup and 20 ml of deionized water was added. Stir thoroughly, filter the undissolved raw materials and evaporate the deionized water at room temperature. After a large number of crystals have precipitated, a small amount of colorless and transparent rod-shaped crystals can be extracted from the block like product, washed with deionized water, and dried, as shown in Figure S1.

$Na_2Sb_2SO_4F_6$: Na_2SO_4 (0.105 g) and SbF_3 (0.395 g) with a stoichiometry of 1 : 3 were placed in a disposable plastic cup and 40 ml of deionized water was added. Stir thoroughly and evaporate the deionized water at room temperature. After the deionized water has completely evaporated, micrometer sized crystals can be extracted from the product under a polarizing microscope.

(3) Synthesis of polycrystalline powder.

$(NH_4)_2Sb_2SO_4F_6$: $(NH_4)_2SO_4$ (0.126 g) and SbF_3 (0.374 g) with a stoichiometry of 1 : 2.2 were placed in a disposable plastic cup and 30 ml of deionized water was added. Stir thoroughly and strain the undissolved raw materials, deionized water was evaporated at room temperature. After the deionized water is completely evaporated, the pure phase of $(NH_4)_2Sb_2SO_4F_6$ is obtained.

$Na_2Sb_2SO_4F_6$: Na_2SO_4 (0.133 g) and SbF_3 (0.367 g) with a stoichiometry of 1 : 2.2 were placed in a disposable plastic cup and 30 ml of deionized water was added. Stir thoroughly and filter the undissolved raw materials. Cover and seal the disposable plastic cup with plastic wrap, and make some small holes in the plastic wrap, and slowly evaporate the deionized water at room temperature. After the deionized water is completely evaporated, the pure phase of $Na_2Sb_2SO_4F_6$ is obtained.

Structural Determination

Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data reduction and integration were performed with the SAINT-Plus program,[1] and absorption corrections were applied using SADABS. The structures were solved and refined with the SHELX program package implemented in Olex. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method.[2] The possible higher symmetry of the structures was checked using the PLATON program,[3] and the CheckCIF reports confirmed the reliability of the refined structures.

Powder X-ray Diffraction

Phase purity was examined by powder X-ray diffraction (XRD) using a Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.5418 Å). The diffraction data were collected over a 2θ range of 5-70° with a step size of 0.02° and a counting time of 1 s per step. The experimental patterns match well with the simulated ones, indicating the good phase purity of the samples.

IR Spectroscopy

Infrared spectra were recorded on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the range of 400-4000 cm^{-1} with a resolution of 1 cm^{-1}. The

samples were dried and ground with KBr in a mass ratio of approximately 1 : 100, followed by pressing into pellets for measurement.

UV−vis−NIR Diffuse Reflectance Spectroscopy

Diffuse reflectance spectra were measured using a Shimadzu SolidSpec-3700 DUV spectrophotometer in the wavelength range of 200-2600 nm to determine the UV cutoff edges of the compounds.

Theoretical Calculations

Electronic structure and optical properties were calculated using the CASTEP package based on density functional theory.[4] The plane-wave cutoff energy was set to 850 eV, and the Brillouin zone was sampled with a *k*-point mesh of 3×6×2. The valence electron composition of $(NH_4)_2Sb_2SO_4F_6$ and $Na_2Sb_2SO_4F_6$ are H-1s^1, N-2$s^2$2p^3, Sb-5$s^2$5p^3, S-3$s^2$3p^4, O-2$s^2$2p^4, F-2$s^2$2p^5 and Na-2$p^6$3s^1, Sb-5$s^2$5p^3, S-3$s^2$3p^4, O-2$s^2$2p^4, F-2$s^2$2p^5. The real part of the dielectric function was obtained via the Kramers–Kronig transformation and obtained the birefringence of $(NH_4)_2Sb_2SO_4F_6$ and $Na_2Sb_2SO_4F_6$.[5]

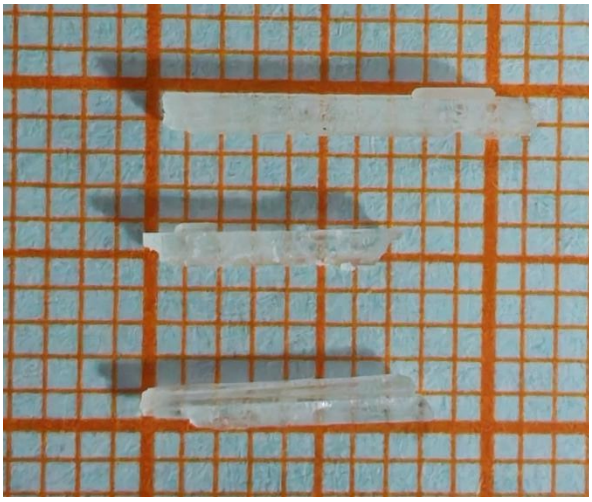

Figure S1. Crystal photograph of $(NH_4)_2Sb_2SO_4F_6$.

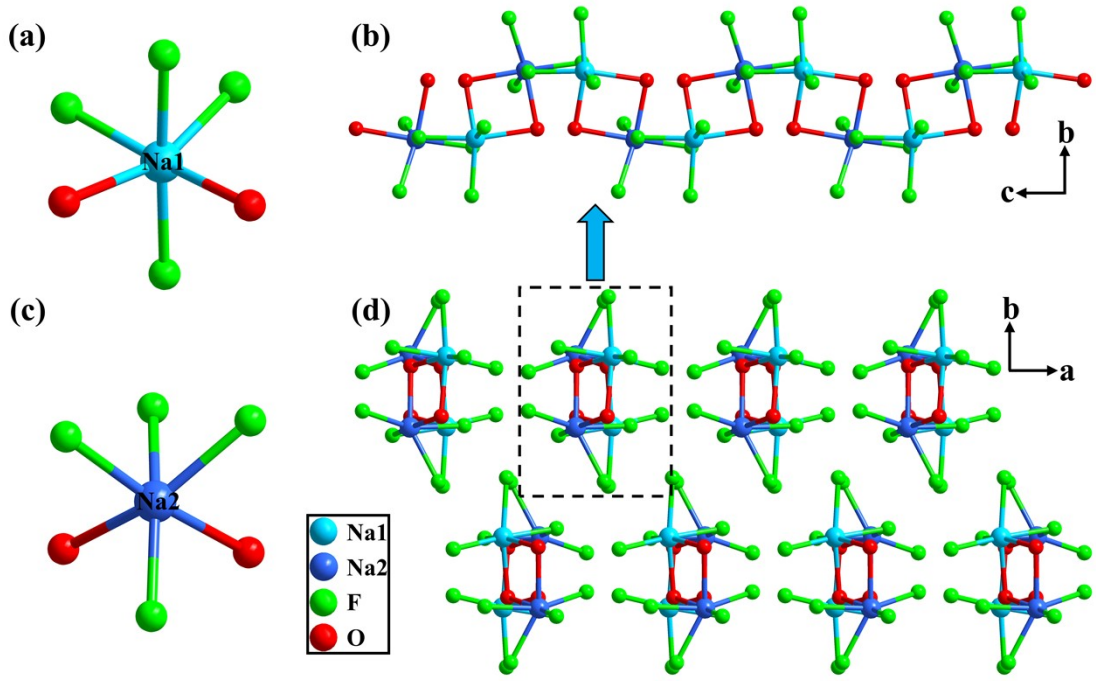

Figure S2 (a) The [$Na1O_2F_4$] polyhedron. (b) The one-dimensional chain displayed along the *a*-axis direction. (c) The [$Na2O_2F_4$] polyhedron. (d) The one-dimensional chain displayed along the *c*-axis direction.

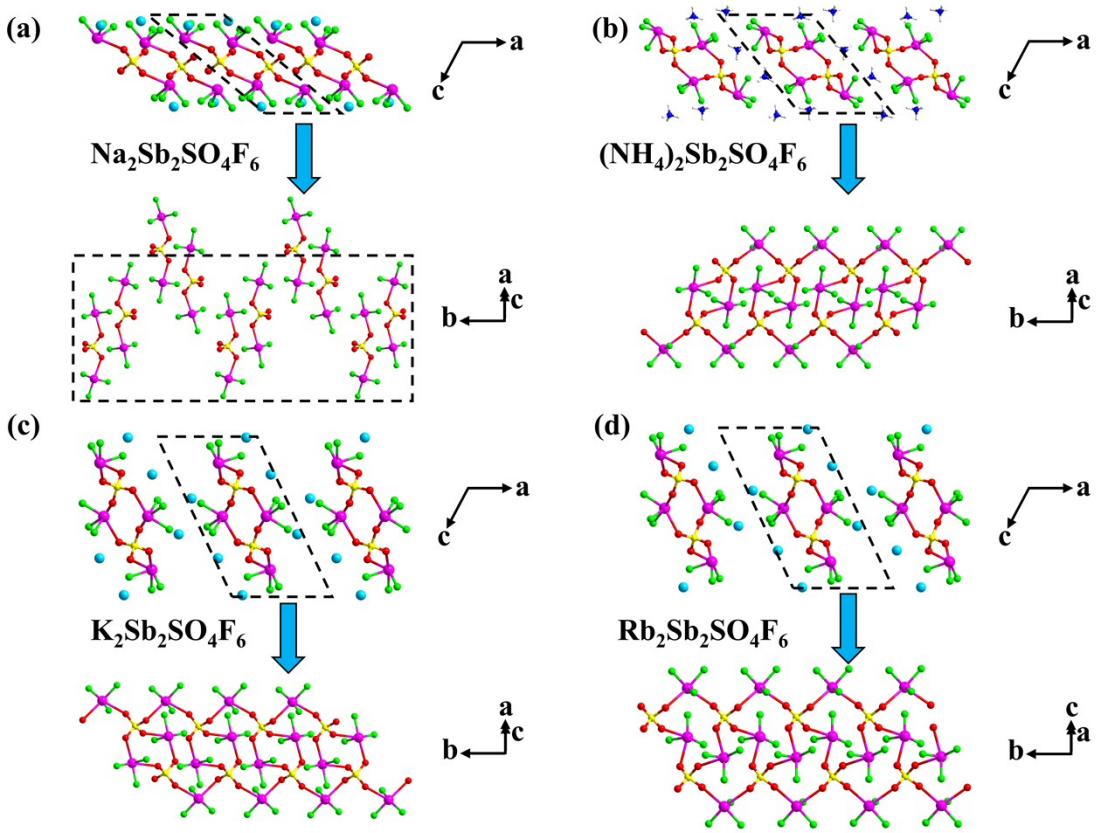

Figure S3 (a) The structure of $Na_2Sb_2SO_4F_6$. (b) The structure of $(NH_4)_2Sb_2SO_4F_6$. (c) The structure of $K_2Sb_2SO_4F_6$. (d) The structure of $Rb_2Sb_2SO_4F_6$.

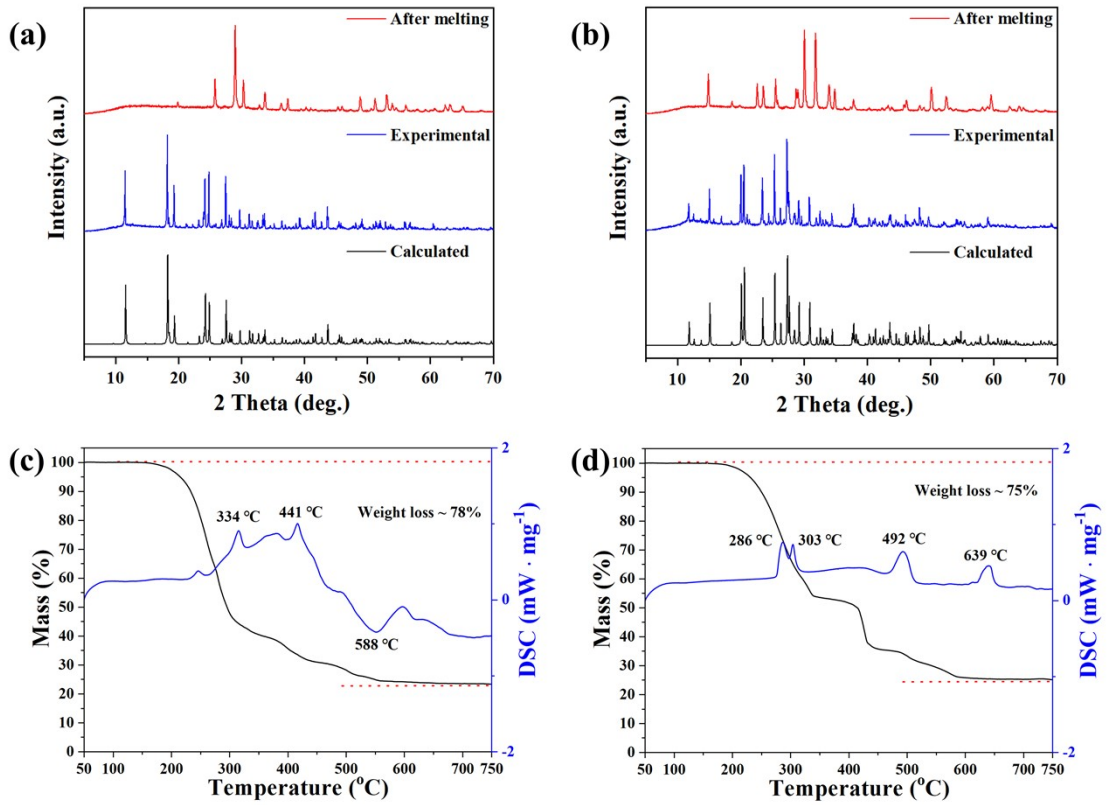

Figure S4 (a, b) X-ray powder diffraction patterns of $(NH_4)_2Sb_2SO_4F_6$ and $Na_2Sb_2SO_4F_6$. (c, d) TG-DSC curves of $(NH_4)_2Sb_2SO_4F_6$ and $Na_2Sb_2SO_4F_6$.

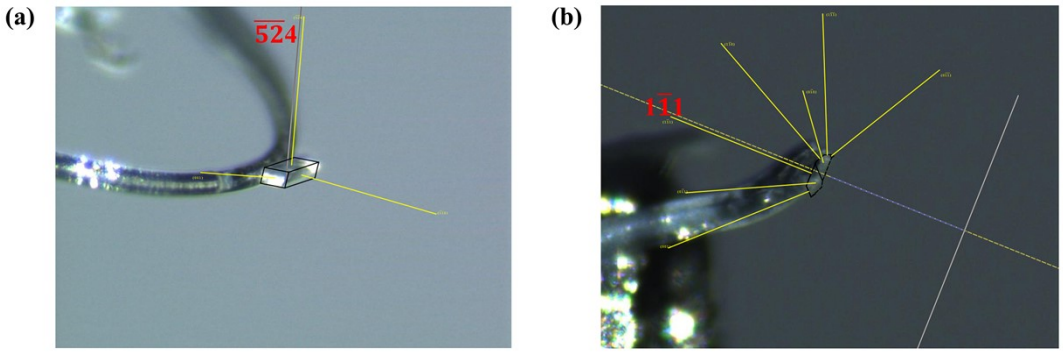

Figure S5 (a) The specific crystal orientations of $(NH_4)_2Sb_2SO_4F_6$. (b) The specific crystal orientations of $Na_2Sb_2SO_4F_6$.

Table S1. Crystal data and structure refinement details for $(NH_4)_2Sb_2SO_4F_6$ and $Na_2Sb_2SO_4F_6$.

Empirical formula	$(NH_4)_2Sb_2SO_4F_6$	$Na_2Sb_2SO_4F_6$
Formula weight	489.64	499.54
Crystal system	Monoclinic	Monoclinic
Space group, Z	$P2_1/c$, 4	$P2_1/c$, 4
a / Å	9.9968(14)	6.9733(4)
b / Å	5.7135(7)	14.0305(10)
c / Å	18.886(3)	9.5562(7)
β / °	103.718(5)	112.392(2)
V / Å^3	1048.0(2)	864.47(10)
Calculated density (g/cm^3)	3.103	3.838
Absorption coefficient (mm^{-1})	5.441	6.683
F (000)	904	904
2θ range (°)	2.097 - 27.500	2.724 - 27.501
Limiting indices	$-12 \le h \le 12$ $-7 \le k \le 7$ $-24 \le l \le 24$	$-9 \le h \le 9$ $-18 \le k \le 18$ $-12 \le l \le 12$
Reflections collected	35766	30072
Independent reflections (R_{int})	2404 (0.0584)	1984 (0.0793)
Completeness (%)	99.7	99.9
Goodness-of-fit on F^2	1.039	1.076
Data/restraints/parameters	2403 / 1 / 95	1984 / 0 / 136
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0186$ $wR_2 = 0.0453$	$R_1 = 0.0188$ $wR_2 = 0.0411$
R indices (all data)[a]	$R_1 = 0.0219$ $wR_2 = 0.0471$	$R_1 = 0.0254$ $wR_2 = 0.0434$
Largest diff. peak / hole (e·Å^{-3})	0.505 / -0.778	0.632 / -0.785

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2=[w(F_o^2 - F_c^2)^2/wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Selected bond lengths (Å) and angles (deg) for $(NH_4)_2Sb_2SO_4F_6$.

Sb(1)-O(1)	2.4185	Sb(2)-F(4)	1.9472
Sb(1)-O(2)#1	2.6044	Sb(2)-F(5)	1.9539
Sb(1)-F(1)	1.9582	Sb(2)-F(6)	1.9165
Sb(1)-F(2)	1.9796	S(1)-O(1)	1.4761
Sb(1)-F(3)	1.9124	S(1)-O(2)	1.4581
Sb(2)-O(3)#2	2.5938	S(1)-O(3)	1.4574
Sb(2)-O(4)#3	2.5793	S(1)-O(4)	1.454
O(1)-Sb(1)-O(2)#1	114.8	F(4)-Sb(2)-F(5)	84.6
F(1)-Sb(1)-O(1)	76.1	F(5)-Sb(2)-O(3)#2	83.8
F(1)-Sb(1)-O(2)#1	158.3	F(5)-Sb(2)-O(4)#3	154.6
F(1)-Sb(1)-F(2)	81.9	F(6)-Sb(2)-O(3)#2	80.9
F(2)-Sb(1)-O(1)	153.1	F(6)-Sb(2)-O(4)#3	72.7
F(2)-Sb(1)-O(2)#1	81.7	F(6)-Sb(2)-F(4)	87.5
F(3)-Sb(1)-O(1)	80.4	F(6)-Sb(2)-F(5)	85.7
F(3)-Sb(1)-O(2)#1	76.1	O(2)-S(1)-O(1)	108.6
F(3)-Sb(1)-F(1)	88	O(3)-S(1)-O(1)	109.9
F(3)-Sb(1)-F(2)	83.5	O(3)-S(1)-O(2)	107.3
O(4)#3-Sb(2)-O(3)#2	105.2	O(4)-S(1)-O(1)	109.1
F(4)-Sb(2)-O(3)#2	164.2	O(4)-S(1)-O(2)	112
F(4)-Sb(2)-O(4)#3	81.4	O(4)-S(1)-O(3)	109.9

Symmetry codes: #1 -x+1,-y,-z+1; #2 -x,-y+1,-z+1; #3 -x,-y,-z+1.

Table S3. Selected bond lengths (Å) and angles (deg) for $Na_2Sb_2SO_4F_6$.

Na(1)-O(3)#2	2.563	Sb(1)-O(2)#4	2.431
Na(1)-O(4)	2.385	Sb(1)-F(1)	1.967
Na(1)-F(1)	2.283	Sb(1)-F(2)	1.905
Na(1)-F(2)#3	2.325	Sb(1)-F(3)	1.953
Na(1)-F(5)#1	2.316	Sb(2)-O(1)#2	2.441
Na(1)-F(6)	2.308	Sb(2)-F(4)	1.915
Na(2)-O(3)#5	2.433	Sb(2)-F(5)	1.965
Na(2)-O(4)#4	2.489	Sb(2)-F(6)	1.950
Na(2)-F(1)#5	2.326	S(1)-O(1)	1.496
Na(2)-F(3)	2.313	S(1)-O(2)	1.498
Na(2)-F(4)#6	2.390	S(1)-O(3)	1.465
Na(2)-F(5)	2.302	S(1)-O(4)	1.461
O(4)-Na(1)-O(3)#2	89.57	F(1)#5-Na(2)-F(4)#6	69.87
F(1)-Na(1)-O(3)#2	162.80	F(3)-Na(2)-F(1)#5	160.15
F(1)-Na(1)-O(4)	78.92	F(3)-Na(2)-F(4)#6	123.29
F(2)#3-Na(1)-O(3)#2	101.08	F(5)-Na(2)-F(1)#5	82.52
F(2)#3-Na(1)-O(4)	160.84	F(5)-Na(2)-F(3)	108.22
F(5)#1-Na(1)-O(3)#2	84.00	F(5)-Na(2)-F(4)#6	97.36
F(5)#1-Na(1)-O(4)	89.28	F(1)-Sb(1)-O(2)#4	153.42
F(6)-Na(1)-O(3)#2	89.59	F(2)-Sb(1)-O(2)#4	76.30
F(6)-Na(1)-O(4)	88.73	F(2)-Sb(1)-F(1)	85.66
F(1)-Na(1)-F(2)#3	86.86	F(2)-Sb(1)-F(3)	89.76
F(1)-Na(1)-F(5)#1	83.13	F(3)-Sb(1)-O(2)#4	77.68
F(1)-Na(1)-F(6)	102.75	F(3)-Sb(1)-F(1)	82.96
F(5)#1-Na(1)-F(2)#3	76.20	F(4)-Sb(2)-O(1)#2	74.78
F(6)-Na(1)-F(2)#3	107.06	F(4)-Sb(2)-F(5)	85.02
F(6)-Na(1)-F(5)#1	173.30	F(4)-Sb(2)-F(6)	88.19
O(3)#5-Na(2)-O(4)#4	90.23	F(5)-Sb(2)-O(1)#2	153.47
F(1)#5-Na(2)-O(3)#5	82.38	F(6)-Sb(2)-O(1)#2	78.51

F(1)#5-Na(2)-O(4)#4	84.94	F(6)-Sb(2)-F(5)	83.92
F(3)-Na(2)-O(3)#5	81.75	O(1)-S(1)-O(2)	106.37
F(3)-Na(2)-O(4)#4	83.27	O(3)-S(1)-O(1)	109.14
F(4)#6-Na(2)-O(3)#5	151.18	O(3)-S(1)-O(2)	109.27
F(4)#6-Na(2)-O(4)#4	79.99	O(4)-S(1)-O(1)	109.46
F(5)-Na(2)-O(3)#5	86.26	O(4)-S(1)-O(2)	109.09
F(5)-Na(2)-O(4)#4	167.32	O(4)-S(1)-O(3)	113.28

Symmetry codes: #1 x-1, y, z; #2 x, -y+3/2, z-1/2; #3 -x+1, -y+1, -z+1; #4 x+1, -y+3/2, z+1/2; #5 x+1, y, z; #6 -x+2, -y+1, -z+1.

Table S4. Atomic coordinates and equivalent isotropic displacement parameters for $(NH_4)_2Sb_2SO_4F_6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*Z*	U_{eq} (Å^2)	BVS
Sb(1)	5028	2818	5917	27	3.1
Sb(2)	-557	2484	6626	25	3.1
S(1)	2554	2288	4364	24	6.2
O(1)	2860	3593	5058	40	1.8
O(2)	3809	1124	4284	59	1.7
O(3)	2145	3917	3756	52	1.8
O(4)	1449	634	4362	60	1.8
F(1)	4142	5165	6409	36	0.9
F(2)	6198	2423	6914	42	0.8
F(3)	3905	504	6226	38	1.0
F(4)	1011	361	6849	42	0.9
F(5)	753	4813	7137	45	0.9
F(6)	40	3394	5773	42	1.0

Table S5. Atomic coordinates and equivalent isotropic displacement parameters for $Na_2Sb_2SO_4F_6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*Z*	U_{eq} (Å^2)	BVS
Na(1)	3278	6532	3451	26	1.1
Na(2)	11108	6506	6147	25	1.0
Sb(1)	6930	6142	7684	17	3.0
Sb(2)	7404	6048	1895	18	3.0
S(1)	2102	8768	4767	17	6.0
O(1)	3744	9396	5834	28	1.7
O(2)	498	9418	3710	24	1.7
O(3)	1163	8201	5627	28	1.8
O(4)	2998	8188	3899	26	1.9
F(1)	4376	6557	6028	25	1.2
F(2)	6934	5116	6381	30	1.2
F(3)	8250	6958	6655	27	1.0
F(4)	7173	4990	3088	31	1.1
F(5)	10062	6288	3576	28	1.2
F(6)	6278	6857	3057	26	1.1

Table S6. The two compounds in this work and Sb^{3+} containing sulfates with reported birefringence.

Compound	Space group	Birefringence	Cutoff edge	Bandgap
$(NH_4)_2Sb_2SO_4F_6$	***P*2$_1$/*c***	**0.055@1064 nm**	**236 nm**	**4.74 eV**
$Na_2Sb_2SO_4F_6$	***P*2$_1$/*c***	**0.100@1064 nm**	**218 nm**	**4.73 eV**
$NH_4Sb(SO_4)_2$	$P2_12_12_1$	0.150@546 nm	280 nm	4.43 eV
$NH_4SbSO_4F_2$	$Pna2_1$	0.138@1064 nm	265 nm	4.67 eV
$NH_4SbSO_4Cl_2$	$P2_12_12_1$	0.09@1064 nm	-	4.54 eV
$K_2SbSO_4F_3$	$P2_12_12_1$	0.080@1064 nm	279 nm	4.44 eV
$K_4Sb(SO_4)_3Cl$	$P6_1$	0.066@546 nm	-	4.12 eV
$RbSb(SO_4)_2$	$P2_1/n$	0.187@546 nm	281 nm	-
$RbSbSO_4F_2$	$Pna2_1$	0.100@1064 nm	-	4.75 eV
$RbSbSO_4Cl_2$	$P2_12_12_1$	0.110@1064 nm	-	3.48 eV
$Rb_2SbSO_4F_3$	$P2_12_12_1$	0.090@1064 nm	298 nm	4.15 eV
$Rb_2Sb_2SO_4F_6$	$P2_1$	0.110@1064 nm	264 nm	4.69 eV
$CsSb(SO_4)_2$	$P2_12_12_1$	0.189@546 nm	278 nm	4.68 eV
$CsSbSO_4F_2$	$Pna2_1$	0.112@1064 nm	240 nm	4.76 eV

Table S7. The density of Sb^{3+} cations in a unit cell.

Compound	n (Sb)	V (Å^3)	ρ (Sb) (Å^{-3})	Birefringence
$(NH_4)_2Sb_2SO_4F_6$	8	1,078.71	0.0074	0.055@1064 nm
$Na_2Sb_2SO_4F_6$	8	934.97	0.0086	0.100@1064 nm

n: The number of Sb^{3+} cations in a unit cell.

V: The cell volume.

ρ: The density of Sb^{3+} cations in a unit cell, $\rho = n / V$.

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