Supporting Information

$Na_2SnSO_4F_2$: An Ultraviolet Transparent Sulfate Crystal with Large Birefringence Driven by Stereochemically Active Tin(II)

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EXPERIMENTAL SECTION

Synthesis

Reagents. Na_2SO_4 (AR, 99 %) and SnF_2 (AR, 99 %) are commercially available and used without further purification.

Synthesis of $Na_2SnSO_4F_2$. Using hydrothermal method, Na_2SO_4 (0.475 g) and SnF_2 (0.525 g) with a stoichiometric ratio of 1:1 were placed in 2 mL of deionized water. After thorough stirring at room temperature, the mixture was sealed in a 23 mL PTFE autoclave. Raise the temperature from room temperature to 220 ℃ using 240 minutes and hold for 3 days, then cooled down to 190 ℃ after 1800 minutes, cooled down to 150 ℃ through 1590 minutes, cooled down to 120 ℃ after 700 minutes, cooled down to 90 ℃ after 510 minutes, and finally cooled down to room temperature after 480 minutes. After the experiment, the product was washed with deionized water to obtain colorless and transparent rod-shaped crystals (Figures S1a, S1b).

Structural Determination.

Crystal data for $Na_2SnSO_4F_2$ were collected using a Bruker SMART APEX II CCD

diffractometer under Mo Kα radiation (λ = 0.71073 Å). The SAINT-Plus and SADABS programs were used for the collection and integration of diffraction data, as well as for the indexing of reflections or digital absorption corrections, respectively. Crystal structure data were parsed and refined using the SHELX and Olex software packages, and atomic coordinates and anisotropic displacement parameters were refined using full-matrix least squares.[1] The PLATON program is used to verify that the crystal structure has no higher symmetric space group.[2] Validation report for CheckCIF confirms that the structure of $Na_2SnSO_4F_2$ is reasonable.

Powder X-ray Diffraction

The purity of $Na_2SnSO_4F_2$ was confirmed by powder X-ray diffraction (XRD). The powder XRD patterns of $Na_2SnSO_4F_2$ were carried out using a Bruker D2 PHASER X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). The 2θ range was 5-70°, the fixed counting time and scan step width were 1 s/step and 0.02 °, respectively. The diffraction patterns are in good agreement with the calculated ones (Figure 3b).

IR Spectroscopy

The infrared spectroscopy testing instrument is Shimadzu IR Affinity-1 Fourier transform IR spectrometer with a wavenumber range of 400-4000 cm^{-1} and a minimum resolution of 1 cm^{-1}. The sample needs to be dried in advance, and then mixed evenly with potassium bromide KBr at a ratio of 1:100 by grinding, and pressed into a fixed specification disc for testing[3].

UV−vis−NIR Diffuse Reflectance Spectroscopy

The UV cutoff edge was obtained by diffuse reflectance test of solid powder. The instrument is Shimadzu SolidSpec-3700 DUV spectrophotometer, and the test wavelength range is 200-2600 nm.

Theoretical Calculations

The electronic structure and optical properties of $Na_2SnSO_4F_2$ were calculated using the CASTEP software package.[4] The breaking energy by the plane wave interception is 850 eV, and the grid density at point k is set to 5×6×2. In the pseudopotential selection, the valence electron composition of $Na_2SnSO_4F_2$ is: Na-$2p^6$ $3s^1$, Sn-$5s^2$ $5p^2$, S-$3s^2$ $3p^4$, O-$2s^2$ $2p^4$, F-$2s^2$ $2p^5$. The real part of the dielectric function was determined

by using the Kramers-Kronig transformation[5], and thus obtained the refractive index n and the birefringence Δn of $Na_2SnSO_4F_2$.

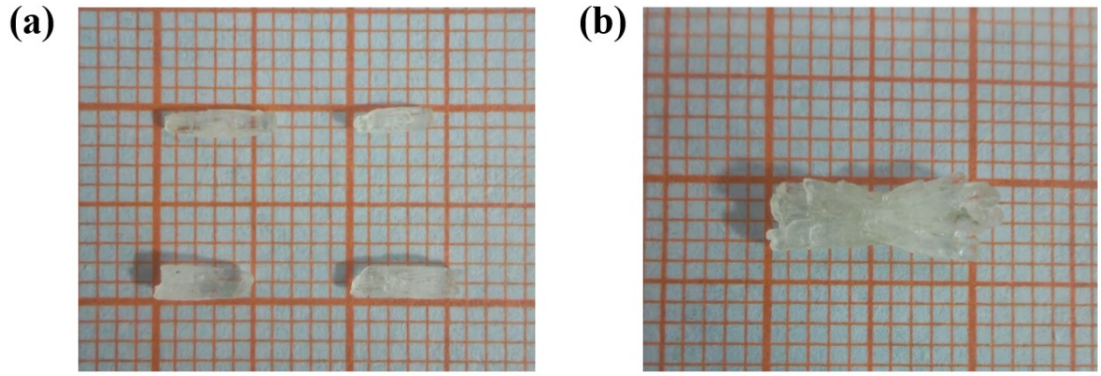

Figure S1. (a) Crystals of $Na_2SnSO_4F_2$ (b) Polycrystalline $Na_2SnSO_4F_2$

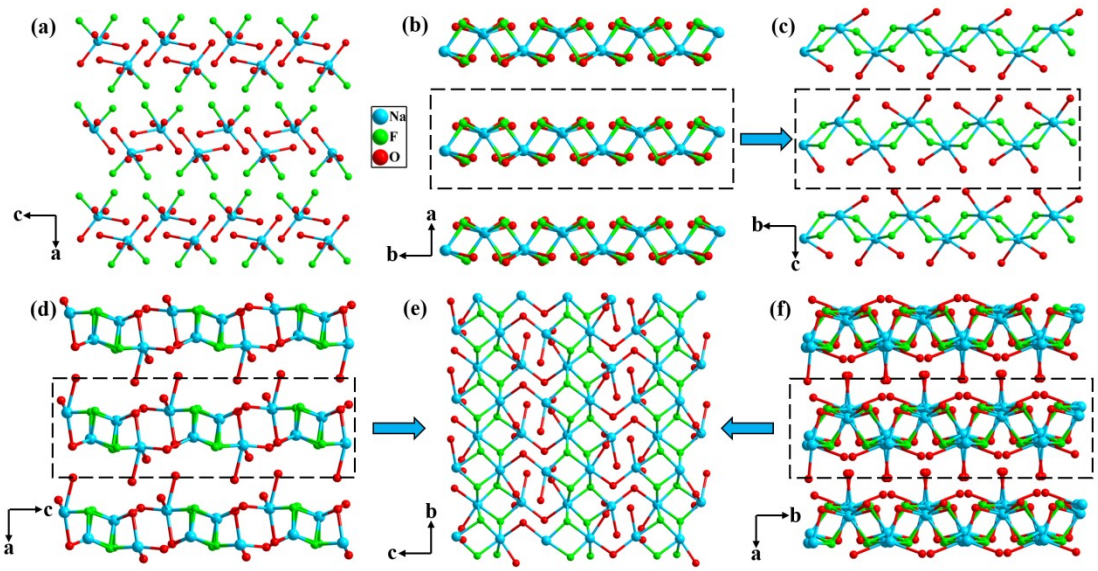

Figure S2. (a) Zero dimensional [NaO_4F_2]. (b, c) One-dimensional chains formed by [NaO_2F_4] are viewed along the *c* and *a* axes. (d, e, f) Two-dimensional layers formed by [NaO_4F_2] and [NaO_2F_4] are viewed along the *b*, *a* and *c* axes.

Table S1. Crystal Data and Structure Refinement Details for $Na_2SnSO_4F_2$.

Empirical formula	$Na_2SnSO_4F_2$
Formula weight	298.73
Crystal system	Monoclinic
Space group	$P2_1/c$ (No.14)
Unit cell dimensions	a = 7.0381 Å, α = 90° b = 5.5378(12) Å, β = 92.650(9)° c = 14.505(3) Å, γ = 90°
Volume	564.7(2) Å^3
Z, Calculated density	4, 3.514 Mg/m^3
Absorption coefficient	5.034 mm^{-1}
F(000)	552
Theta range for data collection	2.812 to 27.520°
Limiting indices	$-9 \le h \le 9$, $-7 \le k \le 7$, $-18 \le l \le 18$
Reflections collected / unique	18036 / 1307 [R(int) = 0.0684]
Completeness to theta = 27.485°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1307 / 0 / 91
Goodness-of-fit on F^2	1.061
Final R indices [I > 2sigma(I)][a]	R_1 = 0.0202, wR_2 = 0.0495
R indices (all data)[a]	R_1 = 0.0249, wR_2 = 0.0520
Largest diff. peak and hole	0.869 and -0.654 e·Å^{-3}

[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. Atomic coordinates and equivalent isotropic displacement parameters for $Na_2SnSO_4F_2$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	Wyck.	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
Na1	e	1798(2)	2204(2)	4308(1)	27(1)	1.0
Na2	e	876(2)	12550(2)	1875(1)	21(1)	1.0
Sn1	e	4069(1)	7344(1)	3264(1)	19(1)	1.9
S1	e	2868(1)	7256(1)	5584(1)	15(1)	6.2
O1	e	1586(4)	8948(4)	5986(2)	50(1)	1.9
O2	e	4737(4)	7314(4)	6057(2)	48(1)	1.7
O3	e	2083(3)	4814(3)	5591(1)	29(1)	1.9
O4	e	3046(5)	8044(4)	4617(2)	47(1)	2.1
F1	e	1929(2)	9798(3)	2955(1)	22(1)	1.1
F2	e	1818(2)	5000(3)	3146(1)	24(1)	1.2

Table S3. Selected bond lengths (Å) and angles (deg) for $Na_2SnSO_4F_2$.

Sn1-F1	2.0624	F1-Na2-F2^{i}	77.13
Sn1-F2	2.0491	F1-Na2-F2^{iii}	81.07
Sn1-O4	2.1562	F1^{iii}-Na2-F2^{i}	79.70
S1-O3	1.4612	F1^{iii}-Na2-F2^{iii}	68.99
S1-O4	1.4812	F1-Na2-O3^{iv}	92.95
S1-O2	1.4553	F1^{iii}-Na2-O3^{iv}	132.90
S1-O1	1.4422	F1^{iii}-Na2-O1^{v}	79.94
Na2-F1	2.2847	F1-Na2-O1^{v}	147.19
Na2-F1^{iii}	2.3562	F2^{i}-Na2-F2^{iii}	123.37
Na2-F2^{iii}	2.3632	F2^{iii}-Na2-O3^{iv}	88.69
Na2-F2^{i}	2.3592	F2^{i}-Na2-O3^{iv}	143.44
Na2-O3^{iv}	2.4592	F2^{iii}-Na2-O1^{v}	131.63
Na2-O1^{v}	2.3942	F2^{i}-Na2-O1^{v}	84.10
Na1-F1^{vi}	2.3782	O1^{v}-Na2-O3^{iv}	86.29
Na1-F2	2.2902	F1^{vi}-Na1-O4^{vi}	66.69
Na1-O3	2.3582	F1^{vi}-Na1-O2^{vii}	79.15
Na1-O4^{vi}	2.4993	F1^{vi}-Na1-O1^{ii}	77.74
Na1-O2^{vii}	2.5343	F2-Na1-F1^{vi}	76.66
Na1-O1^{ii}	2.4833	F2-Na1-O3	99.42
F1-Sn1-O4	78.92	F2-Na1-O4^{vi}	137.83
F2-Sn1-F1	81.10	F2-Na1-O2^{vii}	74.68
F2-Sn1-O4	84.29	F2-Na1-O1^{ii}	94.92
O3-S1-O4	109.16	O3-Na1-F1^{vi}	171.93
O2-S1-O3	110.54	O3-Na1-O4^{vi}	114.05
O2-S1-O4	109.02	O3-Na1-O2^{vii}	93.05
O1-S1-O3	110.79	O3-Na1-O1^{ii}	109.82
O1-S1-O4	105.85	O4^{vi}-Na1-O2^{vii}	78.50
O1-S1-O2	111.34	O1^{ii}-Na1-O4^{vi}	96.91

F1-Na2-F1^{iii}	121.84	O1^{ii}-Na1-O2^{vii}	156.32

Symmetry codes: (i)x,y+1,z;(ii)-x,-y+1,-z+1; (iii)-x,y+1/2,-z+1/2; (iv)x,-y+3/2,z-1/2; (v)x,-y+5/2,z-1/2;(vi)x,y-1,z; (vii)-x+1,-y+1,-z+1.

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