Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Constructing Ultraviolet Nonlinear Optical Crystals with Large second harmony generation and short absorption edge by using polar tetrahedral S_2O_3 group

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Table of Contents

Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å² × 10^3) for $(NH_4)_2S_2O_3$

Atom	x	y	z	U(eq)
S(1)	2070(1)	5013(2)	7283(1)	10(1)
S(2)	1595(1)	6829(2)	8981(1)	14(1)
O(1)	3467(3)	4352(6)	7556(4)	13(1)
O(2)	1934(4)	6156(7)	5832(4)	18(1)
O(3)	1197(3)	3175(6)	7217(4)	14(1)
N(1)	1446(4)	4989(8)	2769(5)	13(1)
N(2)	5000	6317(11)	10000	14(1)
N(3)	5000	4980(20)	5000	57(3)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Selected bond lengths (Å) and angles (degrees) for $(NH_4)_2S_2O_3$

S(1)-S(2)	1.9751(17)	O(2)-S(1)-S(2)	109.32(18)
S(1)-O(1)	1.486(3)	O(2)-S(1)-O(1)	108.8(2)
S(1)-O(2)	1.465(4)	O(2)-S(1)-O(3)	110.4(2)
S(1)-O(3)	1.485(4)	O(3)-S(1)-S(2)	109.56(16)
O(1)-S(1)-S(2)	109.10(16)	O(3)-S(1)-O(1)	109.6(2)

Symmetry transformations used to generate equivalent atoms

Table S3. Anisotropic displacement parameters (Å² × 10^3) for $(NH_4)_2S_2O_3$

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2hka^* b^* U12]$

	U11	U22	U33	U23	U13	U12
S(1)	8(1)	8(1)	12(1)	0(1)	0(1)	-2(1)
S(2)	12(1)	14(1)	15(1)	-2(1)	2(1)	2(1)
O(1)	6(2)	14(2)	18(2)	-4(2)	1(1)	-1(1)
O(2)	28(2)	16(2)	10(2)	2(2)	-4(2)	0(2)
O(3)	9(2)	8(2)	26(2)	-2(2)	-1(2)	-3(2)
N(1)	12(2)	9(2)	17(2)	0(2)	0(2)	-2(2)
N(2)	9(3)	16(4)	15(3)	0	-4(2)	0
N(3)	73(7)	47(6)	58(6)	0	53(6)	0

Table S4. Direction and magnitude for the dipole moments of the S_2O_3 and NH_4 groups in $(NH_4)_2S_2O_3$.

Species	Direction			Magnitude
	x/a	y/b	z/c	Debye
$^{i}S_2O_3$	3.56	-8.36	-10.21	13.67
$^{ii}S_2O_3$	3.56	-8.36	-10.21	13.67
$^{iii}S_2O_3$	-3.56	-8.36	10.21	13.67
$^{iv}S_2O_3$	-3.56	-8.36	10.21	13.67
$^{i}NH_4$	0.11	-0.22	-0.07	0.26
$^{ii}NH_4$	0.11	-0.22	-0.07	0.26
$^{iii}NH_4$	-0.18	-0.19	0.10	0.28
$^{iv}NH_4$	-0.18	-0.19	0.10	0.28
$^{v}NH_4$	0.08	-0.09	-0.004	0.13
$^{vi}NH_4$	0.08	-0.09	-0.004	0.13
$^{vii}NH_4$	-0.11	-0.22	0.10	0.27
$^{viii}NH_4$	-0.11	-0.22	0.10	0.27
All S_2O_3	0	-33.44	0	33.44
All NH_4	-0.2	-1.44	0.25	1.48
unit cell	-0.2	-34.88	0.25	34.88

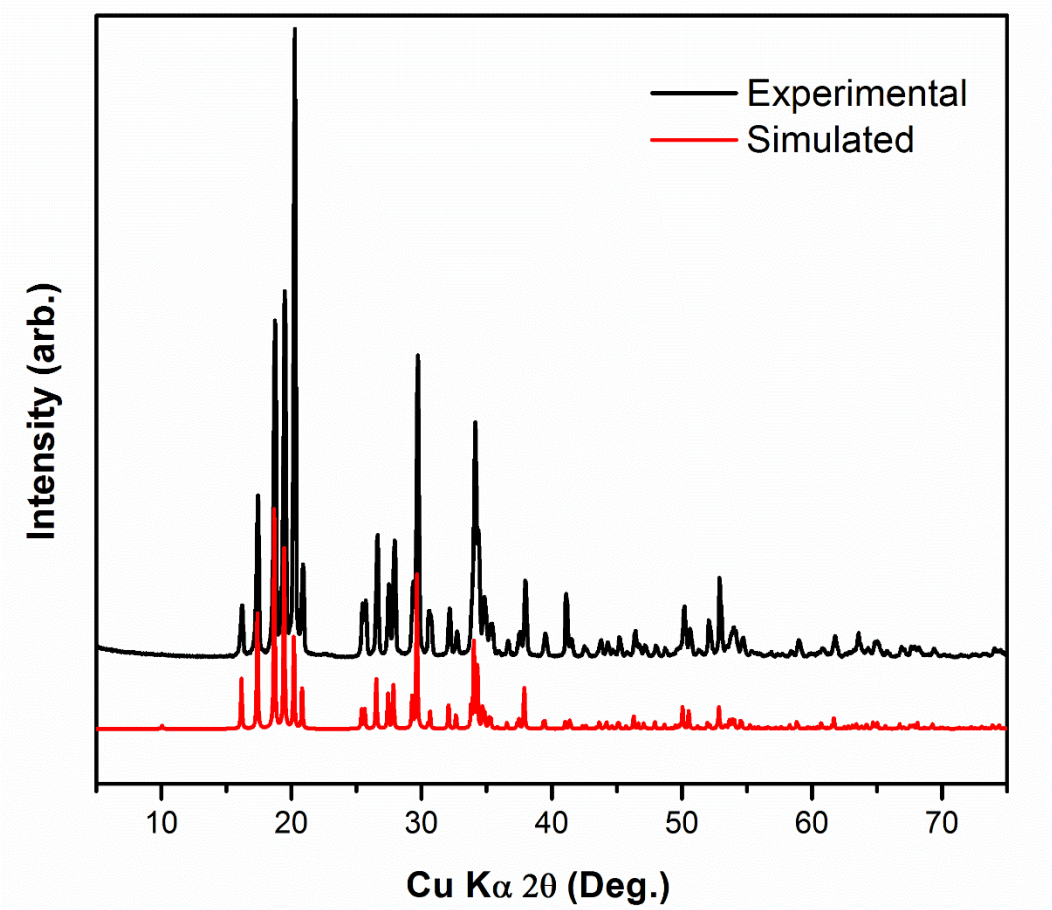

Figure S1. Simulated and experimental powder X-ray diffraction patterns of $(NH_4)_2S_2O_3$

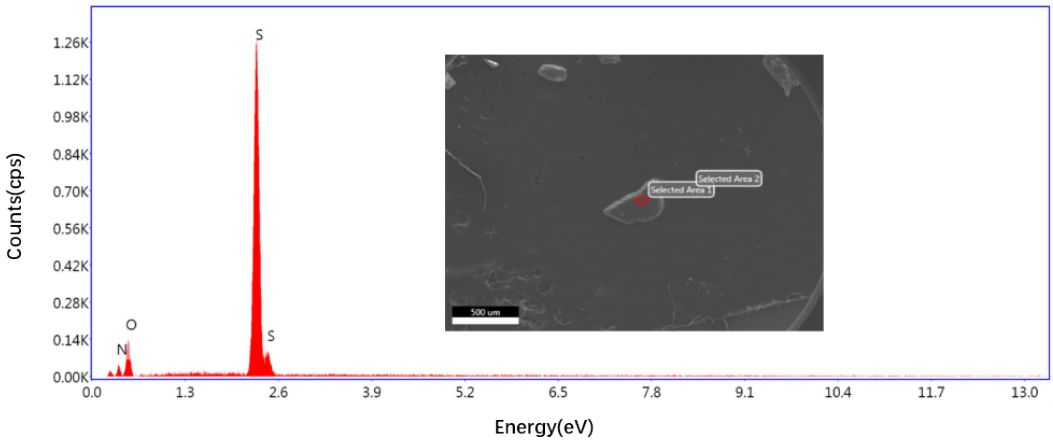

Figure S2. EDS analysis for $(NH_4)_2S_2O_3$. The inset is the SEM image of the tested crystal. Scale bar, 500 μm.

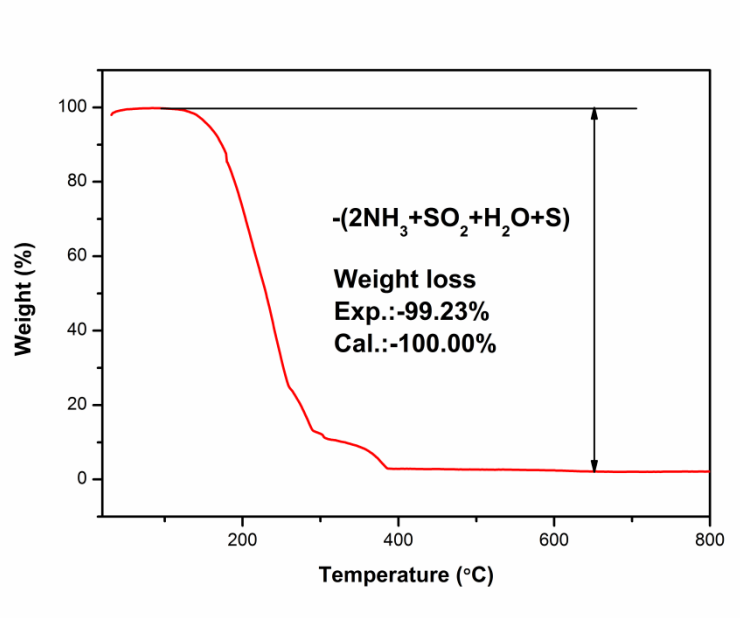

Figure S3. Thermogravimetric-mass curve of $(NH_4)_2S_2O_3$.

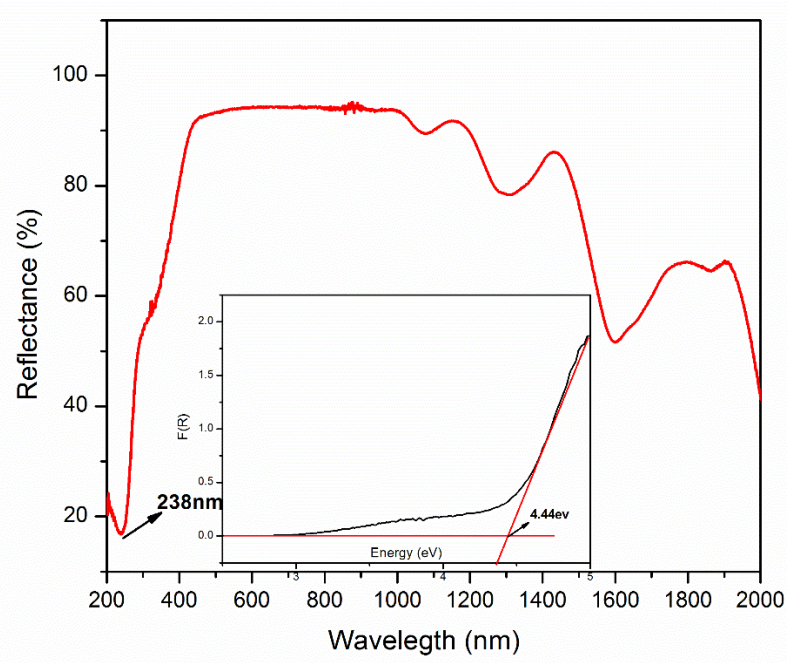

Figure S4. UV-Vis-NIR diffuse reflectance spectra of $(NH_4)_2S_2O_3$.

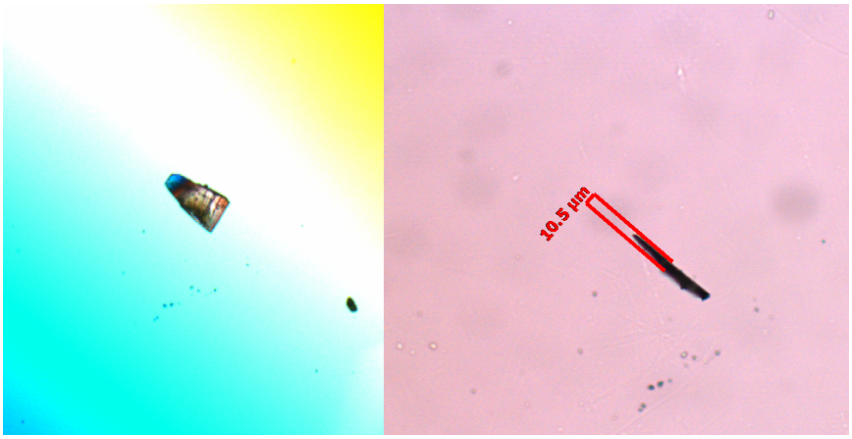

Figure S5. Photograph of $(NH_4)_2S_2O_3$ crystal for the measurement of birefringence.

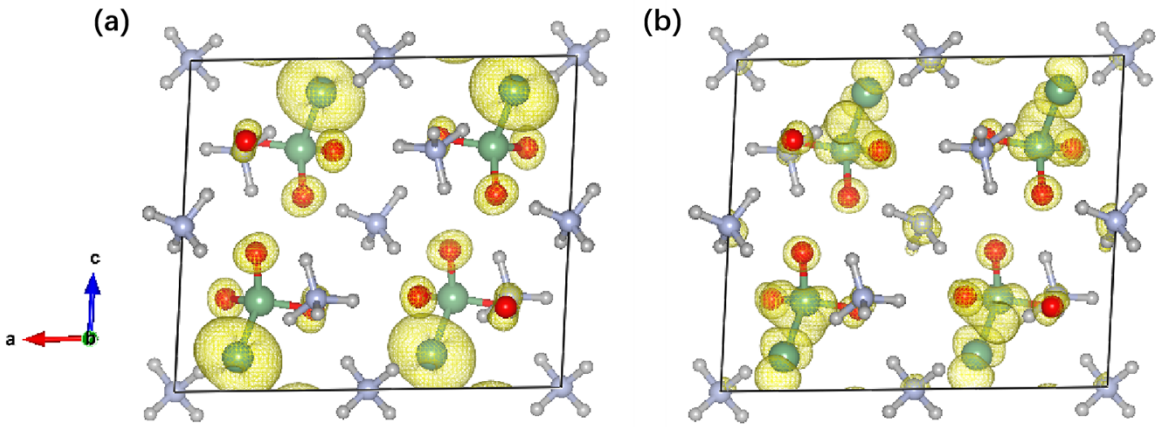

Figure S6. SHG-weighted densities for occupied (a) and unoccupied (b) electronic states for $(NH_4)_2S_2O_3$.

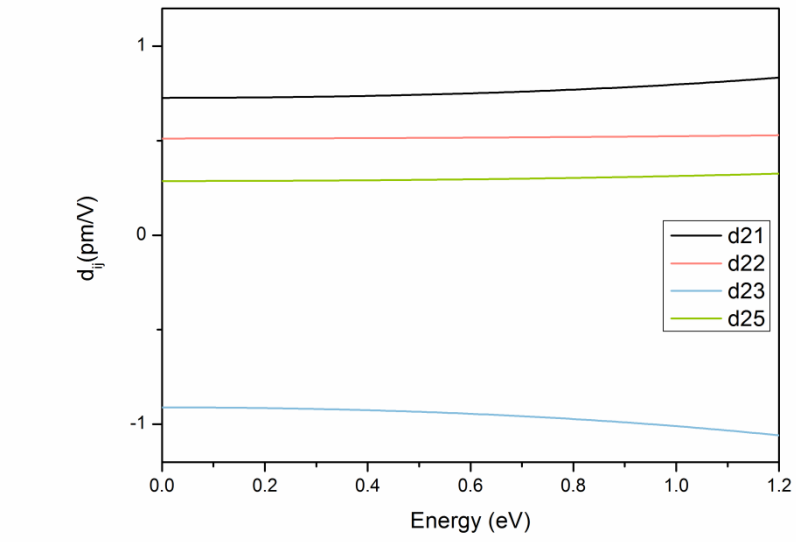

Figure S7. The four calculated independent NLO tensors of $(NH_4)_2S_2O_3$.