Supporting Information

In Situ Hydrothermal Synthesis of Polar Second-Order Nonlinear Optical Selenate $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$

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Theoretical Calculations

Table S1. Selected bond distances (Å) and angles (deg) for $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum for each atom in asymmetric unit.

Table S3. Hydrogen-bonding interactions for $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Figure S1. Experimental and simulated powder X-ray diffraction patterns of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Figure S2. Coordination environments of the Na atoms in $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Figure S3. IR spectrum of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Figure S4. Thermogravimetric analyses of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$ under a N_2 atmosphere.

Figure S5. Calculated refractive index and phase-matching ability in $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Figure S6. Energy dispersive spectroscopy result of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Theoretical Calculations: The bandgap calculated by standard DFT is inconsistent with the experimental data due to the discontinuity in the exchange-correlation functional, so a scissor operator[S1] was used to shift the conduction band upward to agree with the measured value. Based on the scissor-operator-corrected electronic band structure, the imaginary part of the dielectric function from the electronic transition between the valence band (VB) and the conduction band (CB) can be calculated. The real part of the dielectric function, i.e., the refractive indices, can be determined by a Kramers-Kronig transform.[S2] The anisotropic SHG coefficients were calculated by the program developed by our group.[S3,S4] In the SHG-weighted electronic cloud calculations, the probability densities of all occupied (valence) or unoccupied (conduction) states projected onto the real space are multiplied by a weighting factor that is related to the contribution to the SHG efficiency by the virtual electron (VE) and virtual hole (VH) processes.[S5] This ensures that the quantum states irrelevant to SHG are not shown in the occupied or unoccupied "SHG-densities", while the orbitals vital to SHG are intuitively highlighted in the real space.

Table S1. Selected bond distances (Å) and angles (deg) for $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

Se(1)-O(2)	1.595(9)	Se(1)-O(4)	1.597(12)
Se(1)-O(1)	1.612(11)	Se(1)-O(3)	1.675(11)
Se(2)-O(5)	1.608(11)	Se(2)-O(6)	1.618(8)
Se(2)-O(7)	1.623(10)	Se(2)-O(8)	1.717(11)
Se(3)-O(9)	1.601(10)	Se(3)-O(10)	1.643(10)
Se(3)-O(11)	1.635(8)	Se(3)-O(12)	1.685(9)
Se(4)-O(15)	1.599(10)	Se(4)-O(14)	1.607(10)
Se(4)-O(16)	1.663(10)	Se(4)-O(13)	1.667(9)
Na(1)-O(1)	2.410(12)	Na(1)-O(8)	2.475(13)
Na(1)-O(11)	2.443(10)	Na(1)-O(10)#2	2.399(12)
Na(1)-O(12)#8	2.403(11)	Na(1)-O(14)#5	2.465(12)
Na(2)-O(2)	2.601(10)	Na(2)-O(5)	2.389(13)
Na(2)-O(15)	2.383(12)	Na(2)-O(9)#2	2.342(11)
Na(2)-O(6)#2	2.378(12)	Na(2)-O(7)#8	2.465(12)
Na(3)-O(1)	2.391(14)	Na(3)-O(6)	2.418(11)
Na(3)-O(11)	2.447(10)	Na(3)-O(2)#1	2.341(12)
Na(3)-O(4)#7	2.513(13)	Na(3)-O(13)#1	2.337(12)
Na(4)-O(3)	2.532(13)	Na(4)-O(15)	2.455(12)
Na(4)-O(5)	2.372(12)	Na(4)-O(14)#1	2.433(12)
Na(4)-O(16)#7	2.444(11)	Na(4)-O(10)#6	2.466(12)
Na(5)-O(1)	2.843(12)	Na(5)-O(4)	2.455(11)
Na(5)-O(1W)	2.497(9)	Na(5)-O(2W)	2.344(11)
Na(5)-O(1W)#7	2.413(8)	Na(5)-O(2W)#3	2.546(12)
Na(5)-O(4)#7	2.709(11)		
O(2)-Se(1)-O(4)	109.5(5)	O(2)-Se(1)-O(1)	110.4(5)
O(4)-Se(1)-O(1)	113.3(6)	O(2)-Se(1)-O(3)	111.2(6)
O(4)-Se(1)-O(3)	107.0(5)	O(1)-Se(1)-O(3)	105.4(6)
O(5)-Se(2)-O(6)	111.6(5)	O(5)-Se(2)-O(7)	111.8(6)
O(6)-Se(2)-O(7)	118.5(5)	O(5)-Se(2)-O(8)	102.2(6)
O(6)-Se(2)-O(8)	103.6(5)	O(7)-Se(2)-O(8)	107.4(6)
O(9)-Se(3)-O(11)	113.9(5)	O(9)-Se(3)-O(10)	112.0(5)
O(11)-Se(3)-O(10)	110.3(5)	O(9)-Se(3)-O(12)	103.1(5)
O(11)-Se(3)-O(12)	104.7(4)	O(10)-Se(3)-O(12)	112.4(5)
O(15)-Se(4)-O(14)	112.3(5)	O(15)-Se(4)-O(13)	113.8(6)
O(14)-Se(4)-O(13)	108.0(6)	O(15)-Se(4)-O(16)	112.6(5)
O(14)-Se(4)-O(16)	106.8(5)	O(13)-Se(4)-O(16)	102.6(5)

Symmetry codes: #1 x, y, z-1; #2 x, y, z+1; #3 x, -y, z+1/2; #4 x, -y+1, z-1/2; #5 x+1/2, -y+1/2, z-1/2; #6 x-1/2, -y+1/2, z+1/2; #7 x, -y, z-1/2; #8 x, -y+1, z+1/2; #9 x+1/2, -y+1/2, z+1/2; #10 x-1/2, -y+1/2, z-1/2.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum for each atom in asymmetric unit.

Atom	x	y	z	U_{eq}(Å^2)	BVS
Se(1)	-2071(1)	1110(1)	-3183(2)	16(1)	6.31
Se(2)	-3202(1)	3889(1)	-6777(2)	15(1)	5.95
Se(3)	-1112(1)	3719(1)	-9565(2)	9(1)	6.00
Se(4)	-4162(1)	1284(1)	-406(2)	11(1)	6.07
O(1)	-1664(7)	1772(8)	-4592(16)	24(3)	2.05
O(2)	-2142(5)	1762(7)	-1315(13)	24(2)	2.11
O(3)	-2917(6)	817(8)	-4531(18)	33(3)	1.40
O(4)	-1655(6)	55(9)	-2508(14)	26(3)	2.11
O(5)	-3602(7)	3250(8)	-5329(16)	22(3)	2.05
O(6)	-3020(5)	3176(6)	-8499(12)	20(2)	1.91
O(7)	-3610(6)	4983(8)	-7353(14)	24(2)	1.79
O(8)	-2335(6)	4133(9)	-5343(16)	24(2)	1.43
O(9)	-1915(5)	4042(7)	-10833(14)	13(2)	1.96
O(10)	-569(6)	3228(9)	-10916(15)	20(2)	1.85
O(11)	-1155(5)	2954(7)	-7753(12)	12(2)	1.86
O(12)	-772(5)	4825(7)	-8503(12)	16(2)	1.49
O(13)	-3353(6)	940(8)	1033(16)	26(3)	1.82
O(14)	-4690(6)	1747(8)	939(14)	16(2)	1.95
O(15)	-4069(6)	2047(8)	-2114(15)	27(3)	2.09
O(16)	-4533(5)	164(7)	-1240(12)	16(2)	1.59
O(1W)	-187(4)	1157(5)	-1119(12)	37(2)	0.34
O(2W)	-79(7)	1076(7)	-6408(19)	78(3)	0.34
Na(1)	-1055(4)	3417(5)	-4344(10)	21(1)	1.13
Na(2)	-3090(4)	3274(4)	-1908(11)	18(1)	1.14
Na(3)	-2181(4)	1723(4)	-8012(11)	21(1)	1.19
Na(4)	-4199(4)	1630(5)	-5571(10)	22(1)	1.05
Na(5)	-604(3)	151(3)	-4173(7)	47(1)	1.03

Table S3. Hydrogen-bonding interactions for $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

D—H···A	*d*(D—H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O1—H1WA···O2W	0.8300	2.5300	3.2800	151.00
O1W—H1WB···O10	0.8300	2.0400	2.8085	155.00
O3—H3···Se4	0.8200	2.8500	3.5345	142.00
O3—H3···O13	0.8200	1.6800	2.4921	170.00
O2W—H2WA···O11	0.8500	2.3100	3.1616	176.00
O2W—H2WB···O15	0.8800	2.5500	3.1725	128.00
O8—H8···Se3	0.8200	2.8600	3.5568	143.00
O8—H8···O9	0.8200	1.7700	2.5522	158.00
O12—H12A···Se4	0.8500	2.7600	3.5717	161.00
O12—H12A···O16	0.8500	1.6400	2.4732	164.00

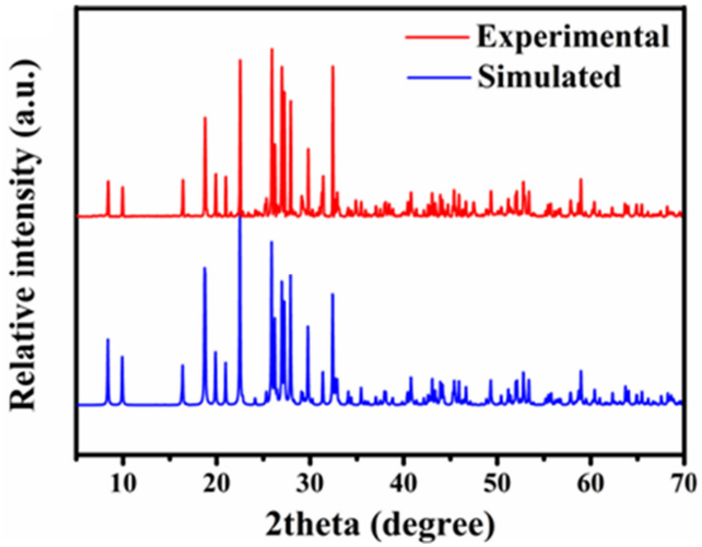

Figure S1. Experimental and simulated powder X-ray diffraction patterns of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

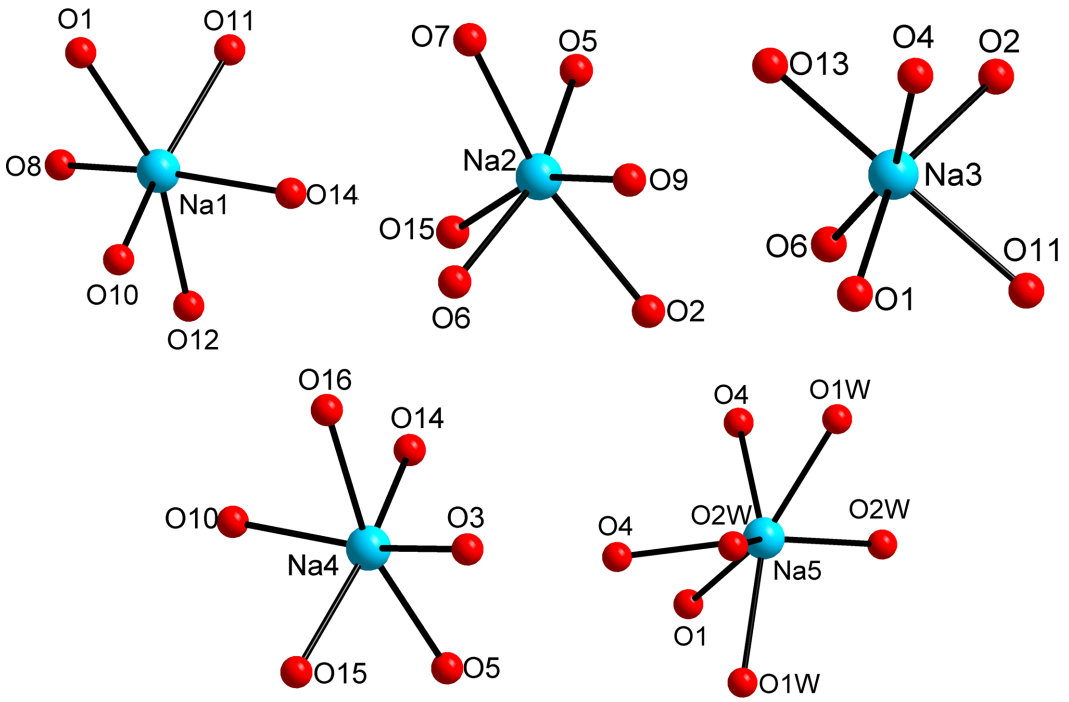

Figure S2. Coordination environments of the Na atoms in $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

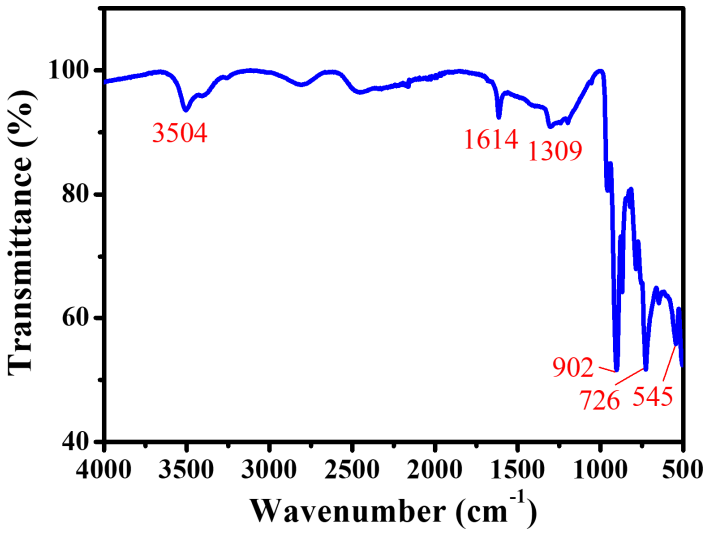

Figure S3. IR spectrum of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

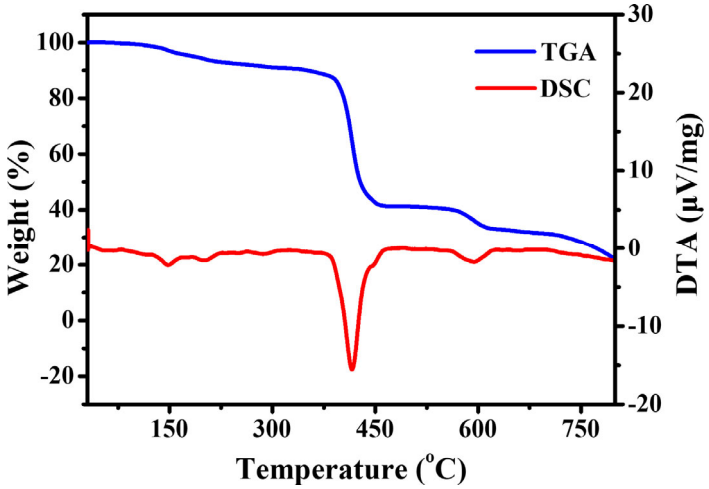

Figure S4. Thermogravimetric analyses of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$ under a N_2 atmosphere.

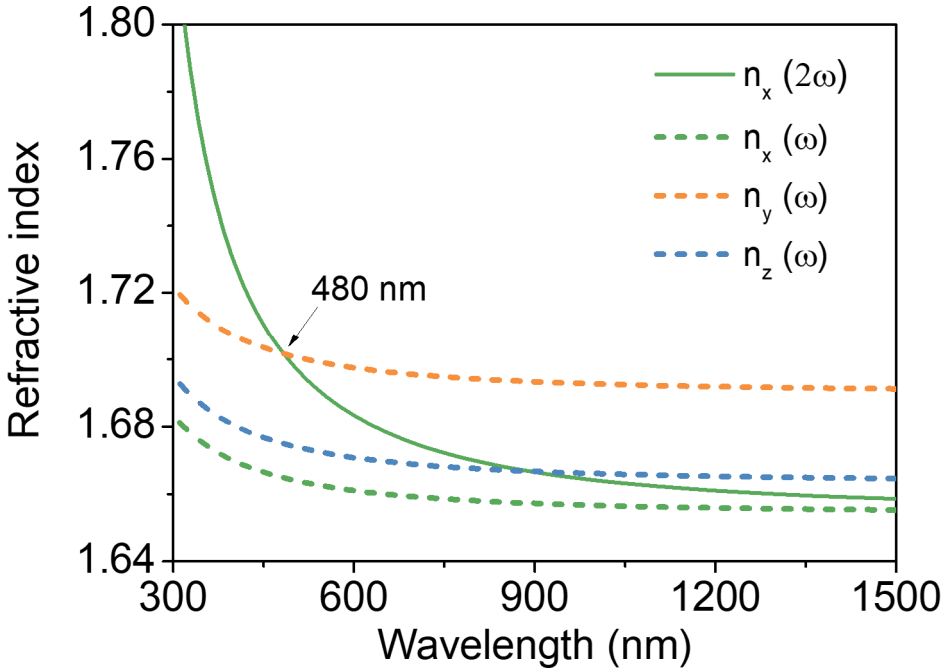

Figure S5. Calculated refractive index and phase-matching ability in $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

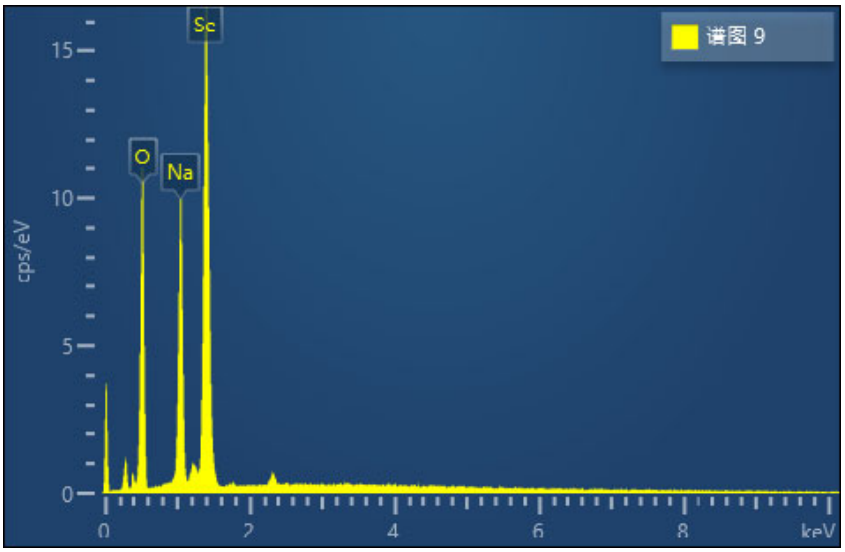

Figure S6. Energy dispersive spectroscopy result of $Na_5(SeO_4)(HSeO_4)_3(H_2O)_2$.

References

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