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Supporting Information

$Na_7(IO_3)(SO_4)_3$: The First Noncentrosymmetric Alkaline-Metal Iodate-Sulfate with Isolated $[IO_3]$ and $[SO_4]$ Units

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Experimental Section

Reagents.

NaCl (99.5%), and Na_2SO_4 (99.0%) were purchased from Tianjin Fuchen Chemical Reagents Factory, and HIO_3 (99.5%) was purchased from Aladdin Chemical Industry Co., Ltd. All of the reagents were used as received without further processing.

Synthesis.

Single crystals of $Na_7(IO_3)(SO_4)_3$ were produced by the hydrothermal method. The powder mixtures were prepared from NaCl (0.1562g, 2.67×10^{-3} mol), HIO_3 (0.7051g, 4.01×10^{-3} mol), Na_2SO_4 (1.1387g, 8.02×10^{-3} mol), and then added 25ml H_2O to dissolve the mixtures forming a stable and clear solution in a beaker. The beaker was put in an ultrasonic instrument to vibrate 60 minutes, and placed in an oven which was set at 50 °C until the solution has evaporated to dryness. Thus, colorless crystals of above compound were obtained (Figure S1).

Powder X-ray Diffraction

The polycrystalline samples of $Na_7(IO_3)(SO_4)_3$ was tested at room temperature by the SmartLab9KW X-ray diffractometer (Cu K_α radiation), and the data were collected in the 2 θ angular range of 10–70° with 0.01° per step and 2 s per step. The purity of polycrystalline samples of $Na_7(IO_3)(SO_4)_3$ was confirmed by powder X-ray diffraction (PXRD) patterns (Figure 1).

Single-Crystal X-ray Diffraction.

The crystal structures of $Na_7(IO_3)(SO_4)_3$ was determined by single-crystal X-ray diffraction, and the data were collected on a Bruker SMART APEX II 4K CCD with Mo−Kα radiation (λ = 0.71073 Å) at 100(2) K. We handled the structure and refined the structure's atomic positions using the SHELXS-97 and a full matrix least-squares technique, respectively.[1–2] We further checked the missing structural symmetry of $Na_7(IO_3)(SO_4)_3$ with PLATON.[3] The crystal data and structure refinement details are given in Table S1 and the atomic coordination, displacement parameters, bond valence calculations, bond lengths for all atoms are listed in Tables S2 and S3.

UV-vis-NIR Diffuse Reflectance Spectroscopy

The UV-Vis-NIR diffuse reflectance spectrum of $Na_7(IO_3)(SO_4)_3$ was measured on a Shimadzu SolidSpec-3700DUV spectrophotometer at room temperature with the spectral range of 200–2500 nm. $BaSO_4$ was used as a reference. Reflectance spectra were converted to absorbance with the Kubelka−Munk function,[4,5] $F(R) = (1 - R)^2/2R = K/S$, where R represents the reflectance, K the absorption, and S the scattering factor.

Infrared Spectroscopy

The infrared spectrum of $Na_7(IO_3)(SO_4)_3$ was tested on a Shimadzu IR Affinity spectrometer at room temperature with a spectral range of 400–4000 cm^{-1}.

Thermal Stability

Thermogravimetric (TG) and differential scanning calorimetry (DSC) of $Na_7(IO_3)(SO_4)_3$ were carried out by a NETZSCH STA 449C thermal analysis instrument. Powder samples (∼10 mg) were heated to 800 °C at a speed of 5 °C/min in flowing nitrogen.

Second-Order NLO Measurements.

The SHG measurement on the powder sample of $Na_7(IO_3)(SO_4)_3$ was measured by using the method of the Kurtz−Perry.[6] Polycrystalline samples of $Na_7(IO_3)(SO_4)_3$ was ground and classified into seven categories according to the different standard sizes, as follows: 25–53, 53–75, 75–106, 106–120, 120–150, 150–180 and 180–212μm, and the KDP was treated as reference material.

The first-principles Calculations

The electronic structure of $Na_7(IO_3)(SO_4)_3$ was performed by a plane-wave pseudopotential method implemented in the total energy code CASTEP package.[7–8] We selected Perdew−Burke−Ernzerhof (PBE) in the generalized gradient approximation (GGA) for the exchange and correlation functional, and used norm-conserving pseudopotential to describe the relationship between the ionic cores and the electrons.[9–10] The valence-electron configurations, Na $2s^22p^63s^1$, I $4d^{10}5s^25p^2$, S $3s^23p^4$, O $2s^22^4$, were considered in the computation. In the basis sets, the numbers of plane waves were

decided by cutoff energy of 830 eV. We used Monkhorst-Pack *k*-point sampling, 4 × 2 × 1, to carry on numerical integration of the Brillouin zone for $Na_7(IO_3)(SO_4)_3$.

Based on the electron band structure of the scissor-corrected, we calculated the imaginary part of the dielectric function according to the electron transition from the valence bands (VB) to the conduction band (CB). Consequently, through the Kramers-Kronig transform,[11] we obtained the real part of the dielectric function and ascertained the calculated refractive index.

The Birefringence Experiment

The birefringence of $Na_7(IO_3)(SO_4)_3$ was measured by a Nikon Eclipse polarizing microscope E200MV POL equipped with a visible light filter. According to crystal optics, the retardation is proportional to birefringence and thickness of crystal. The specific formula is $R = \Delta n \times d$, where R, Δn and d represent retardation, birefringence and thickness of crystal, respectively.

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Table S1. The reported compounds containing IO_3 and SO_4 units.

Chemical formula	Units	Space group	Bands gap(eV)	Birefringence (@1064nm)	SHG
$Nb_2O_3(IO_3)_2(SO_4)$	IO_3, SO_4	$P2_1$	3.25	0.22	6.0×KDP
$AgBi(IO_3)_2(SO_4)$	IO_3, SO_4	$P1$	3.40	/	3.9×KDP
$Bi_2O(IO_3)_2(SO_4)$	IO_3, SO_4	$P2_1/n$	2.40	/	/
$Eu(IO_3)(SO_4)$	IO_3, SO_4	$P2_1/c$	/	/	/
$Dy(IO_3)(SO_4)(H_2O)$	IO_3, SO_4	$P2_12_12_1$	/	/	/
$K_2H(IO_3)(SO_4)$	IO_3, SO_4	$P2_1/n$	/	/	/
$Na_9(IO_3)(SO_4)_4$	IO_3, SO_4	$P2_1/a$	/	/	/
$K_{7.2}Na_{8.8}Mg_{10}(IO_3)_{12}(SO_4)_{12}(H_2O)_{12}$	IO_3, SO_4	$P\bar{3}c1$	/	/	/
$Na_7(IO_3)(SO_4)_3$ (This work)	IO_3, SO_4	$P2_12_12_1$	4.83	0.075	0.5×KDP

Table S2. Crystal data and structure refinement for $Na_7(IO_3)(SO_4)_3$.

Empirical formula	$Na_7(IO_3)(SO_4)_3$
Formula weight	624.01
Temperature	100(2) K
Crystal system	Orthorhombic
space group	$P2_12_12_1$
Unit cell dimensions	a = 6.839(3) Å
	b = 10.851(5) Å
	c = 18.519(8) Å
Z, Volume /Å^3	4, 1374.2(11)
Density (g/cm^3)	3.016
Absorption coefficient /mm^{-1}	3.093
Reflections collected	28116
Completeness to	99.90%
Goodness-of-fit on F^2	1.119
Final R indices [F_o^2>2s(F_o^2)][a]	R_1 = 0.0500,
	wR_2 = 0.0899
R indices (all data)	R_1 = 0.0751,
	wR_2 = 0.1008
Absolute structure parameter	0.47(7)
Largest diff. peak and hole (e·Å^3)	1.940 and -1.140

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

Table S3. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for $Na_7(IO_3)(SO_4)_3$. Ueq is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	BVS
Na(1)	4840(10)	2208(5)	9917(4)	8(2)	1.26
Na(2)	10022(7)	148(6)	7354(3)	11(1)	1.24
Na(3)	7605(11)	2752(6)	6698(4)	16(2)	1.09
Na(4)	5052(7)	5214(5)	7423(3)	14(1)	1.08
Na(5)	5155(11)	2795(6)	5064(4)	11(2)	1.25
Na(6)	-2701(7)	5252(5)	9081(3)	13(1)	1.17
Na(7)	2410(9)	2538(5)	8339(3)	7(1)	1.07
I(1)	9286(1)	5028(1)	5771(1)	8(1)	5.24
S(1)	7470(7)	2488(4)	8350(2)	7(1)	5.93
S(2)	2459(4)	5003(4)	9142(2)	8(1)	6.08
S(3)	2618(7)	2765(4)	6642(2)	8(1)	6.00
O(1)	917(15)	3487(9)	6899(5)	12(2)	1.88
O(2)	4037(14)	5826(8)	9357(5)	11(2)	1.96
O(3)	7483(17)	3772(9)	8086(5)	12(2)	2.04
O(4)	579(14)	5657(8)	9204(5)	13(2)	1.98
O(5)	9111(14)	2331(8)	8864(5)	9(2)	1.92
O(6)	8012(13)	5397(8)	6594(5)	8(2)	2.26
O(7)	4437(15)	3415(9)	6833(5)	14(2)	2.05
O(8)	7743(14)	1633(8)	7733(5)	10(2)	2.14
O(9)	5592(15)	2208(9)	8702(5)	12(2)	2.02
O(10)	2495(13)	2612(8)	5861(5)	7(2)	2.13
O(11)	2489(15)	3887(8)	9582(5)	10(2)	2.01
O(12)	2625(17)	1541(9)	7001(5)	11(2)	2.11
O(13)	8070(14)	3608(9)	5557(5)	12(2)	2.38
O(14)	2757(14)	4659(8)	8373(5)	12(2)	2.09
O(15)	8057(14)	6037(9)	5153(5)	8(2)	2.31

Table S4. Bond lengths [Å] and angles [deg.] for $Na_7(IO_3)(SO_4)_3$.

I(1)-O(15)	1.793(9)	O(1)#7-Na(2)-O(14)#7	86.8(4)
I(1)-O(13)	1.796(10)	O(6)#12-Na(2)-O(14)#7	159.2(4)
I(1)-O(6)	1.800(9)	O(8)-Na(2)-O(3)#12	174.9(4)
S(1)-O(9)	1.472(11)	O(1)#7-Na(2)-O(3)#12	85.3(4)
S(1)-O(3)	1.477(11)	O(6)#12-Na(2)-O(3)#12	87.0(4)
S(1)-O(5)	1.482(10)	O(14)#7-Na(2)-O(3)#12	103.6(4)
S(1)-O(8)	1.483(10)	O(8)-Na(2)-O(12) #6	98.0(4)
S(2)-O(2)	1.456(10)	O(1)#7-Na(2)-O(12)#6	146.4(4)
S(2)-O(11)	1.460(10)	O(6)#12-Na(2)-O(12)#6	74.6(4)
S(2)-O(4)	1.473(10)	O(14)#7-Na(2)-O(12)#6	124.8(4)
S(2)-O(14)	1.487(9)	O(3)#12-Na(2)-O(12)#6	77.0(3)
S(3)-O(10)	1.458(10)	O(8)-Na(2)-O(4)#7	94.1(3)
S(3)-O(7)	1.474(11)	O(1)#7-Na(2)-O(4)#7	132.4(4)
S(3)-O(1)	1.481(11)	O(6)#12-Na(2)-O(4)#7	148.5(4)
S(3)-O(12)	1.486(11)	O(14)#7-Na(2)-O(4)#7	51.9(3)
Na(1)-O(9)	2.308(12)	O(3)#12-Na(2)-O(4)#7	83.4(3)
Na(1)-O(11)#9	2.357(12)	O(12)#6-Na(2)-O(4)#7	74.0(3)
Na(1)-O(15)#7	2.358(12)	O(8)-Na(3)-O(7)	96.6(4)
Na(1)-O(5)#10	2.366(11)	O(8)-Na(3)-O(13)	166.6(5)
Na(1)-O(15)#11	2.426(11)	O(7)-Na(3)-O(13)	95.9(4)
Na(1)-O(11)	2.508(11)	O(8)-Na(3)-O(1)#6	90.4(4)
Na(2)-O(8)	2.349(11)	O(7)-Na(3)-O(1)#6	139.5(4)
Na(2)-O(1)#7	2.361(11)	O(13)-Na(3)-O(1)#6	83.2(4)
Na(2)-O(6)#12	2.383(10)	O(8)-Na(3)-O(3)	55.8(3)
Na(2)-O(14)#7	2.388(10)	O(7)-Na(3)-O(3)	75.4(4)
Na(2)-O(3)#12	2.409(12)	O(13)-Na(3)-O(3)	132.8(4)
Na(2)-O(12)#6	2.425(12)	O(1)#6-Na(3)-O(3)	76.0(4)
Na(2)-O(4)#7	2.966(11)	O(8)-Na(3)-O(6)	125.7(4)
Na(3)-O(8)	2.271(11)	O(7)-Na(3)-O(6)	77.7(4)
Na(3)-O(7)	2.297(13)	O(13)-Na(3)-O(6)	62.0(3)
Na(3)-O(13)	2.331(12)	O(1)#6-Na(3)-O(6)	66.1(3)
Na(3)-O(1)#6	2.430(13)	O(3)-Na(3)-O(6)	70.8(3)
Na(3)-O(3)	2.799(12)	O(7)-Na(4)-O(12)#2	148.4(5)
Na(3)-O(6)	2.890(11)	O(7)-Na(4)-O(14)	90.9(4)
Na(4)-O(7)	2.276(11)	O(12)#2-Na(4)-O(14)	104.8(4)
Na(4)-O(12)#2	2.394(12)	O(7)-Na(4)-O(8) #2	109.6(4)
Na(4)-O(14)	2.433(10)	O(12)#2-Na(4)-O(8)#2	101.0(4)
Na(4)-O(8)#2	2.471(11)	O(14)-Na(4)-O(8)#2	74.9(3)
Na(4)-O(6)	2.548(10)	O(7)-Na(4)-O(6)	85.7(4)
Na(4)-O(3)	2.592(12)	O(12)#2-Na(4)-O(6)	72.2(4)
Na(5)-O(10)	2.351(11)	O(14)-Na(4)-O(6)	165.3(4)
Na(5)-O(13)	2.363(12)	O(8)#2-Na(4)-O(6)	119.7(4)
Na(5)-O(4)#1	2.368(12)	O(7)-Na(4)-O(3)	80.1(4)

Na(5)-O(13)#13	2.381(12)	O(12)#2-Na(4)-O(3)	74.1(3)
Na(5)-O(10) #4	2.386(11)	O(14)-Na(4)-O(3)	85.5(4)
Na(5)-O(2)#7	2.453(11)	O(8)#2-Na(4)-O(3)	158.1(4)
Na(6)-O(4)	2.297(11)	O(6)-Na(4)-O(3)	79.8(3)
Na(6)-O(2)#14	2.372(11)	O(10)-Na(5)-O(13)	116.2(4)
Na(6)-O(15)#15	2.441(11)	O(10-Na(5)-O(4)#1	108.5(4)
Na(6)-O(12)#16	2.445(11)	O(13)-Na(5)-O(4)#1	100.0(4)
Na(6)-O(3)#14	2.448(11)	O(10)-Na(5)-O(13)#13	77.6(4)
Na(6)-O(10)#16	2.567(10)	O(13)-Na(5)-O(13)#13	158.4(4)
Na(6)-O(13)#15	3.010(11)	O(4)#1-Na(5)-O(13)#13	90.1(4)
Na(7)-O(9)	2.306(12)	O(10)-Na(5)-O(10)#4	162.6(3)
Na(7)-O(14)	2.314(10)	O(13)-Na(5)-O(10)#4	77.3(4)
Na(7)-O(6)#7	2.344(10)	O(4)#1-Na(5)-O(10)#4	77.9(4)
Na(7)-O(5)#14	2.467(12)	O(13)#13-Na(5)-O(10)#4	86.4(4)
Na(7)-O(12)	2.706(12)	O(10)-Na(5)-O(2)#7	80.0(4)
Na(7)-O(11)	2.729(11)	O(13)-Na(5)-O(2)#7	88.1(4)
O(15)-I(1)-O(13)	99.5(5)	O(4)#1-Na(5)-O(2)#7	163.5(4)
O(15)-I(1)-O(6)	100.2(4)	O(13)#13-Na(5)-O(2)#7	77.8(4)
O(13)-I(1)-O(6)	98.8(4)	O(10)#4-Na(5)-O(2)#7	90.1(4)
O(9)-S(1)-O(3)	110.3(7)	O(4)-Na(6)-O(2)#14	147.9(4)
O(9)-S(1)-O(5)	110.6(6)	O(4)-Na(6)-O(15)#15	97.3(4)
O(3)-S(1)-O(5)	108.4(6)	O(2)#14-Na(6)-O(15)#15	83.2(4)
O(9)-S(1)-O(8)	108.8(6)	O(4)-Na(6)-O(12)#16	87.2(4)
O(3)-S(1)-O(8)	109.6(6)	O(2)#14-Na(6)-O(12)#16	92.7(4)
O(5)-S(1)-O(8)	109.1(6)	O(15)#15-Na(6)-O(12)#16	175.5(4)
O(2)-S(2)-O(11)	110.2(6)	O(4)-Na(6)-O(3)#14	98.6(4)
O(2)-S(2)-O(4)	109.3(6)	O(2)#14-Na(6)-O(3)#14	112.5(4)
O(11)-S(2)-O(4)	111.6(6)	O(15)#15-Na(6)-O(3)#14	104.0(4)
O(2)-S(2)-O(14)	108.4(5)	O(12)#16-Na(6)-O(3)#14	75.9(3)
O(11)-S(2)-O(14)	108.9(6)	O(4)-Na(6)-O(10)#16	75.6(3)
O(4)-S(2)-O(14)	108.4(6)	O(2)#14-Na(6)-O(10) #16	77.3(3)
O(10)-S(3)-O(7)	110.0(6)	O(15)#15-Na(6)-O(10)#16	122.9(4)
O(10)-S(3)-O(1)	109.5(6)	O(12)#16-Na(6)-O(10)#16	57.5(3)
O(7)-S(3)-O(1)	109.4(6)	O(3)#14-Na(6)-O(10)#16	133.1(4)
O(10)-S(3)-O(12)	110.1(6)	O(4)-Na(6)-O(2)#15	85.0(3)
O(7)-S(3)-O(12)	108.5(6)	O(2)#14-Na(6)-O(2)#15	67.5(3)
O(1)-S(3)-O(12)	109.3(6)	O(15)#15-Na(6)-O(2)#15	59.2(3)
O(9)-Na(1)-O(11)#9	102.3(4)	O(12)#16-Na(6)-O(2)#15	120.7(4)
O(9)-Na(1)-O(15)#7	97.7(4)	O(3)#14-Na(6)-O(2)#15	163.2(4)
O(11)#9-Na(1)-O(15)#7	113.3(4)	O(10)#16-Na(6)-O(2)#15	63.7(3)
O(9)-Na(1)-O(5)#10	167.8(5)	O(9)-Na(7)-O(14)	92.8(4)
O(11)#9-Na(1)-O(5)#10	83.8(4)	O(9)-Na(7)-O(6)#7	87.0(4)
O(15)#7-Na(1)-O(5)#10	89.4(4)	O(14)-Na(7)-O(6)#7	175.2(4)
O(9)-Na(1)-O(15)#11	92.5(4)	O(9)-Na(7)-O(5)#14	137.2(4)

O(11)#9-Na(1)-O(15)#11	82.5(4)	O(14)-Na(7)-O(5)#14	100.0(4)
O(15)#7-Na(1)-O(15)#11	158.6(4)	O(6)#7-Na(7)-O(5)#14	77.1(3)
O(5)#10-Na(1)-O(15)#11	77.7(4)	O(9)-Na(7)-O(12)	98.8(4)
O(9)-Na(1)-O(11)	84.4(4)	O(14)-Na(7)-O(12)	114.6(4)
O(11)#9-Na(1)-O(11)	163.0(4)	O(6)#7-Na(7)-O(12)	70.1(3)
O(15)#7-Na(1)-O(11)	80.7(4)	O(5)#14-Na(7)-O(12)	112.0(4)
O(5)#10-Na(1)-O(11)	87.0(4)	O(9)-Na(7)-O(11)	79.5(4)
O(15)#11-Na(1)-O(11)	81.6(4)	O(14)-Na(7)-O(11)	56.0(3)
O(8)-Na(2)-O(1)#7	99.7(4)	O(6)#7-Na(7)-O(11)	119.3(4)
O(8)-Na(2)-O(6)#12	93.0(4)	O(5)#14-Na(7)-O(11)	74.6(3)
O(1)#7-Na(2)-O(6)#12	76.2(3)	O(12)-Na(7)-O(11)	170.2(4)
O(8)-Na(2)-O(14)#7	78.1(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z-1/2 #2 -x+1,y+1/2,-z+3/2 #3 -x+3/2,-y+1,z-1/2 #4 x+1/2,-y+1/2,-z+1 #5 -x+2,y+1/2,-z+3/2 #6 x+1,y,z #7 -x+1,y-1/2,-z+3/2 #8 -x,y-1/2,-z+3/2 #9 x+1/2,-y+1/2,-z+2 #10 x-1/2,-y+1/2,-z+2 #11 -x+3/2,-y+1,z+1/2 #12 -x+2,y-1/2,-z+3/2 #13 x-1/2,-y+1/2,-z+1 #14 x-1,y,z #15 -x+1/2,-y+1,z+1/2 #16 -x,y+1/2,-z+3/2

Table S5. Flexibility index F of the anionic group of $Na_7(IO_3)(SO_4)_3$.

	R_a(I–O) (Å)	Exp[(R_0-R_a)/B]	$(\sqrt{C_a}+\sqrt{C_b})^2/R_a^2$	F
IO3	2.003	1.748	8.046	0.217
S(1)O4	1.624	1.483	10.983	0.135
S(2)O4	1.624	1.520	11.122	0.137
S(3)O4	1.624	1.499	11.043	0.136

Figure S1. Experimental and calculated PXRD patterns of $Na_7(IO_3)(SO_4)_3$.

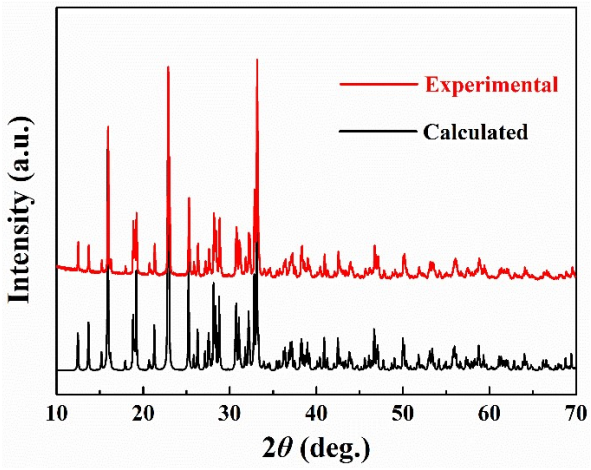

Figure S2. TG and DSC curves of $Na_7(IO_3)(SO_4)_3$.

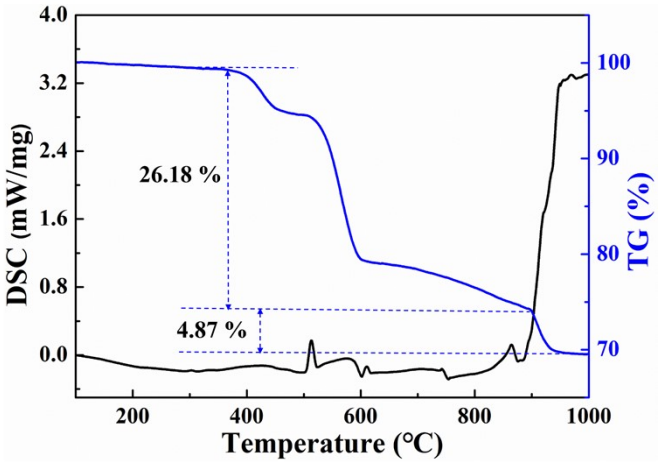

Figure S3. The residual PXRD patterns of the $Na_7(IO_3)(SO_4)_3$.

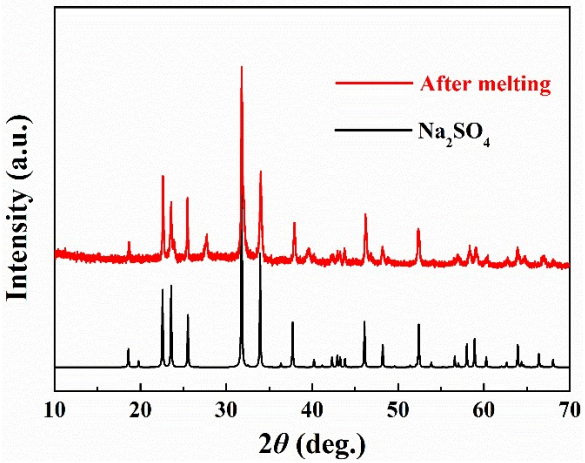

Figure S4. Two types of coordination environments of Na^+ cations.

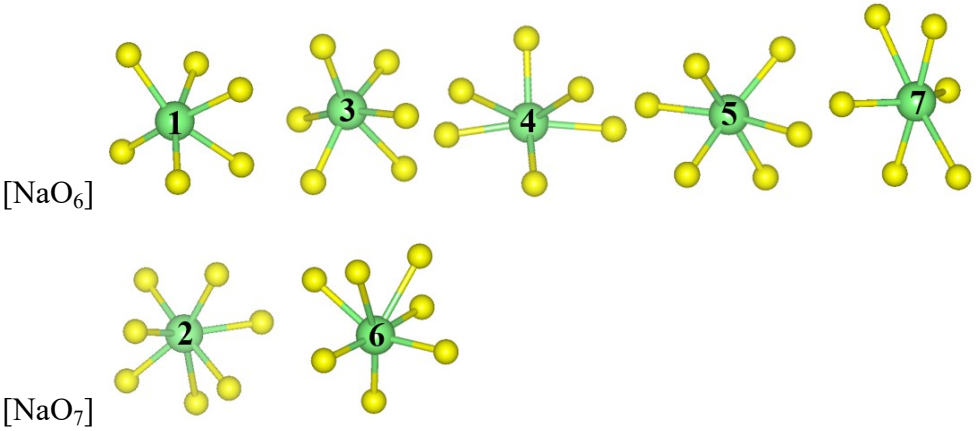

Figure S5. The photo of crystal size for measuring birefringence.

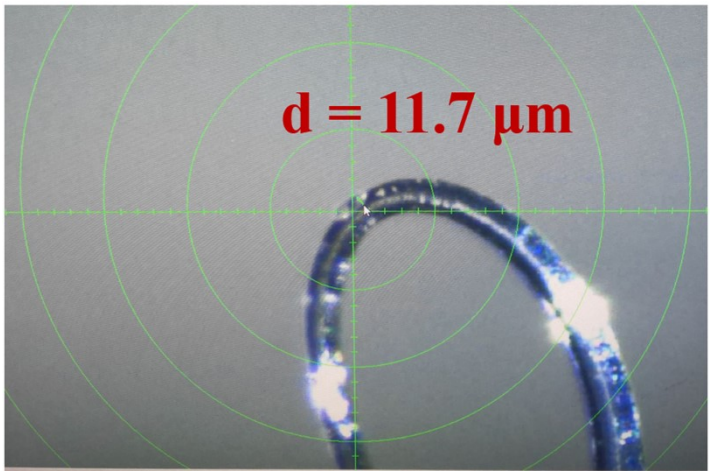

Figure S6. Illustration for the covalent groups along the optical principal axis.