Supporting Information

Structure, optical and luminescent properties of anhydrous samarium iodate $Sm_3(IO_3)_9(HIO_3)_4$

Ruixin Guo,[a,b] Changcheng Tang,[a,c] Mingjun Xia,[a] Lijuan Liu,[*,a] and Xiaoyang Wang[*,a]

a Beijing Centre for Crystal Research and Development, Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

b University of Chinese Academy of Sciences, Beijing 100190, P.R. China

c College of Mechanical and Electrical Engineerng, WuYi University, Nanping, Fujian 354300, China.

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Structure Determination. A transparent yellow crystal was selected, and was glued to the glass wire with epoxy resin. Afterwards, placed it on the Bruker APEX II single crystal X-ray diffraction instrument with λ=1.5418 A (Mo Kα) for data collection. The preliminary structure was analyzed by using ShelXS-97 software, and the F_2 was refined by using ShelXL-97 program. All atoms except hydrogen atoms were refined with anisotropic displacement parameters. The relevant crystallographic data are listed in **Table 1** and **Table S1-S4**.

Powder X-ray Diffraction (PXRD). A large number of crystals were ground into power. Then the powder was analyzed with a Bruker D8 X-ray diffractometer (Cu Kα radiation; λ = 0.71073 Å), step width 0.02°, scanning rate 0.1°. The experimental XRD pattern was well-suited to the calculated one (**Figure 1**).

Thermal Analysis. Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) were measured by NETZCH STA 2500. The samples were heated to 1200℃ with the test conditions: N_2 atmosphere, heating rate 10℃/ min, cooling rate 10℃/ min.

UV-Vis Diffuse Reflectance Spectroscopy. Perkin-elmer Lambda 900UV-Vis-NIR spectrometer was used to measure the optical transmission curve of $Sm_3(IO_3)_9(HIO_3)_4$, and the test range was 200~2000nm.

Infrared Spectroscopy. The crystals were ground into powder and mixed with KBr, then these substances were pressed into sheets. The Excalibur 3100 Fourier transform infrared spectrometer (FTIR) was used to record infrared spectra in the range of 400−4000cm^{-1}.

SHG Measurements. The powder frequency-doubling effects were performed by the Kurtz−Perry method, and the pumping light was a 1064 nm Q-switched Nd: YAG solid-state laser. Crystals of $Sm_3(IO_3)_9(HIO_3)_4$ were ground and the size range were 20−41 μm. Sieved KDP samples with the corresponding size was used as the reference.

Luminescence Spectroscopy. The excitation spectrum, emission spectrum and fluorescence lifetime decay curve of Sm3(IO3)9(HIO3)4 crystal were measured by an Edinburgh Instruments FLS920 spectrophotometer. The 410 nm radiations was emitted by xenon lamp laser.

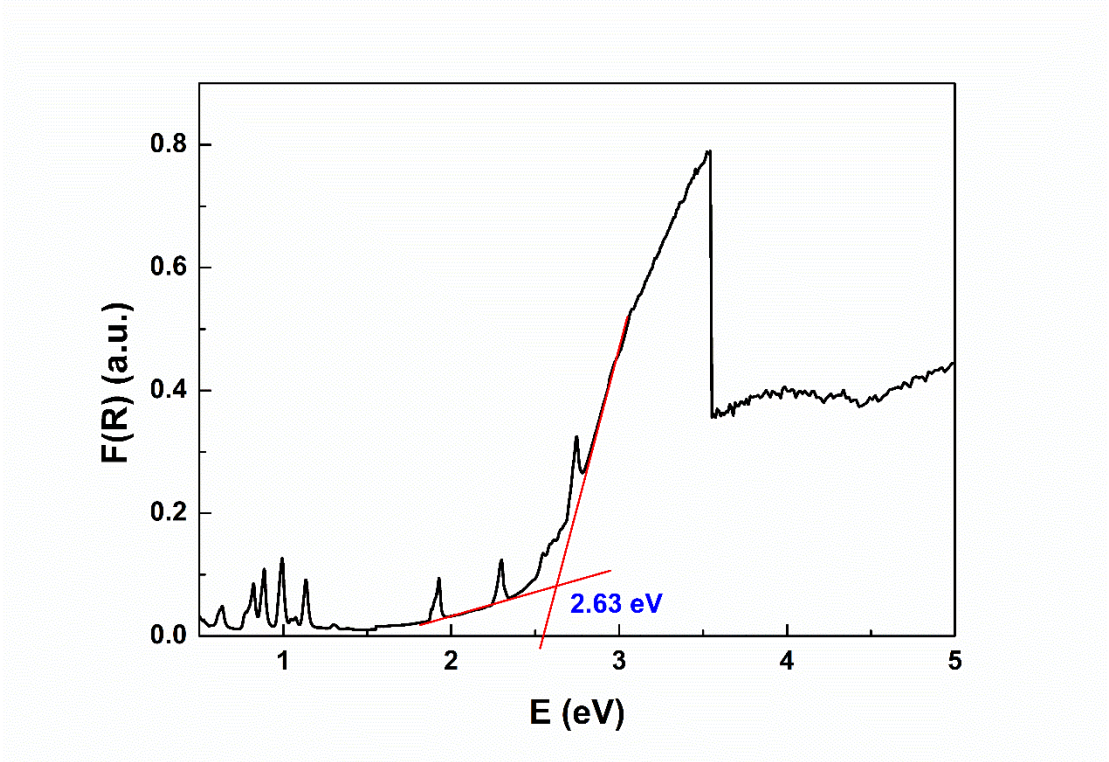

Figure S1 UV−vis−NIR diffuse-reflectance spectrum of $Sm_3(IO_3)_9(HIO_3)_4$.

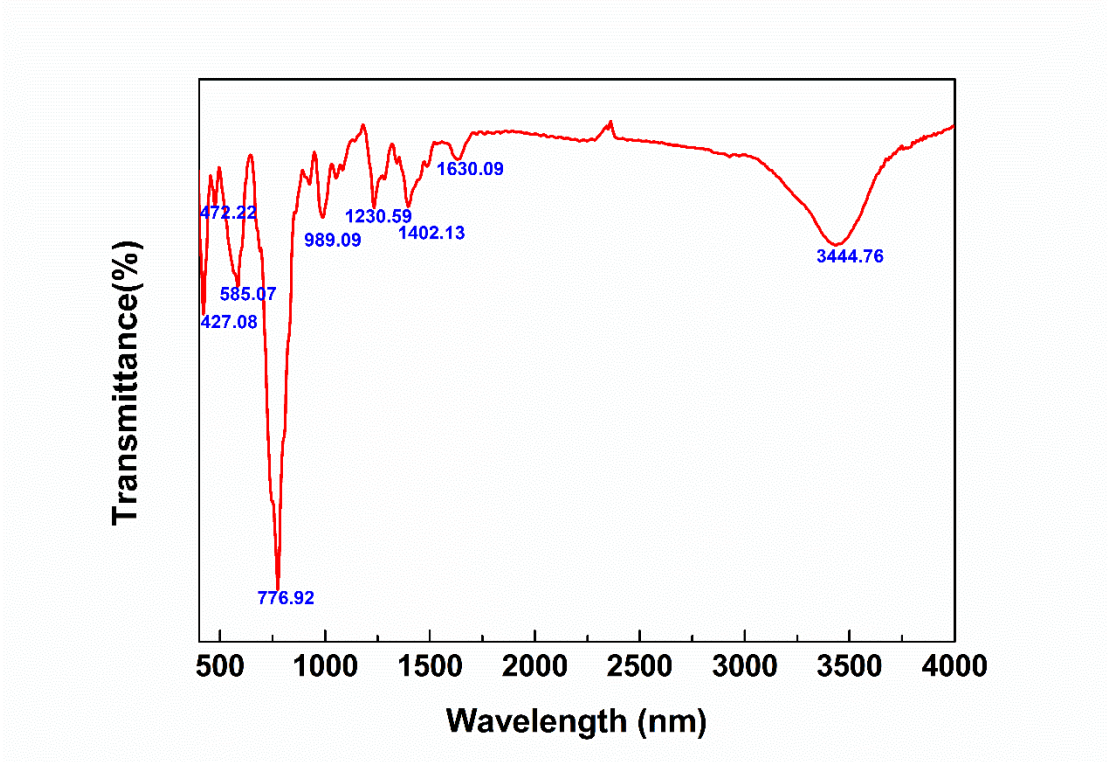

Figure S2 The IR spectra of $Sm_3(IO_3)_9(HIO_3)_4$.

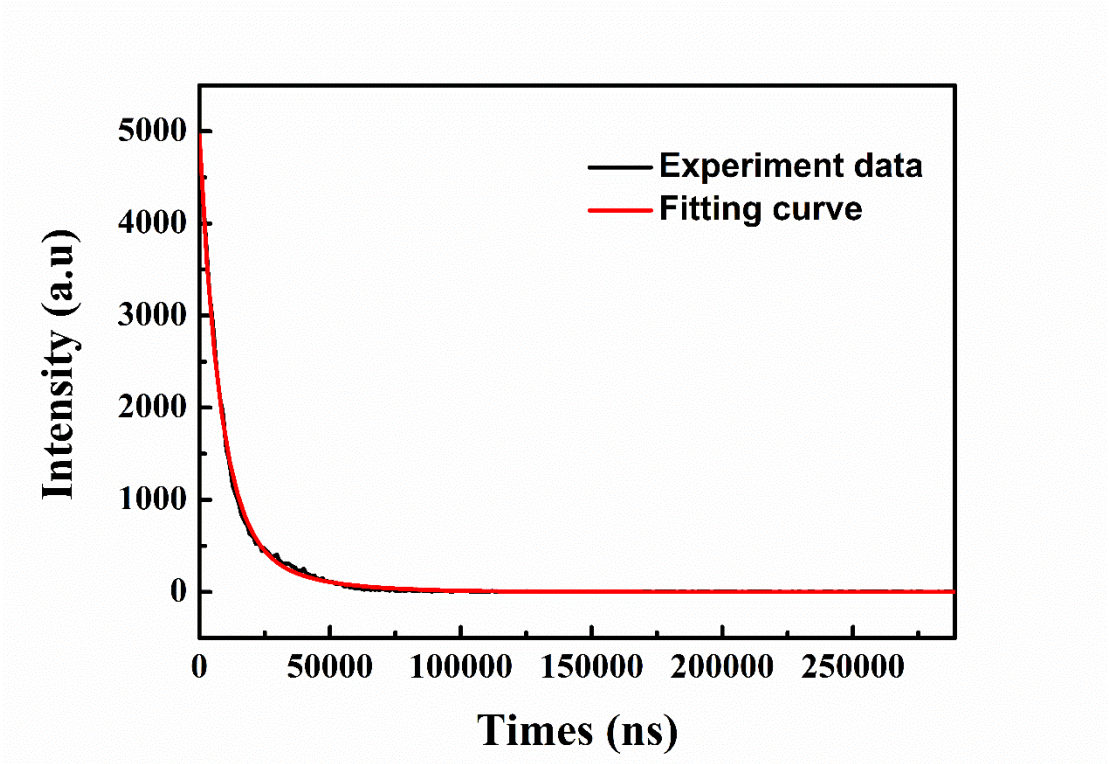

Figure S3 Fluorescence lifetime decay curve of the $^{6}H_{5/2}$-$^{6}H_{7/2}$ luminescence of $Sm_3(IO_3)_9(HIO_3)_4$ crystal under 466 nm excitation.

Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $Sm_3(IO_3)_9(HIO_3)_4$.

$Sm_3(IO_3)_9(HIO_3)_4$					
Atom	x	y	z	U(eq)	Occ. (<1)
Sm1	0.16732 (4)	0.20401 (3)	0.88482 (5)	0.00986 (18)	
I1	−0.03819 (5)	0.13979 (5)	0.93962 (7)	0.0178 (2)	
I2	0.14349 (4)	0.25781 (5)	0.62680 (6)	0.0120 (2)	
I3	0.30483 (4)	0.30270 (4)	1.09182 (7)	0.0126 (2)	
I4	0.16395 (5)	0.38140 (4)	0.86500 (6)	0.0117 (2)	
I5A	0.3333	0.6667	0.95122 (17)	0.0275 (5)	0.862 (5)
I5B	0.3333	0.6667	1.0181 (12)	0.0275 (5)	0.138 (5)
O1	−0.0166 (7)	0.1674 (6)	1.0690 (9)	0.028 (3)	
O2	0.1768 (6)	0.4323 (6)	0.9777 (8)	0.020 (2)	
O3	−0.0971 (6)	0.0457 (6)	0.9668 (8)	0.022 (2)	
O4	0.2549 (6)	0.4251 (6)	0.8284 (10)	0.025 (2)	
O5	0.3511 (7)	0.3965 (7)	1.0750 (11)	0.034 (3)	
O6	0.0593 (5)	0.2071 (6)	0.5624 (8)	0.017 (2)	
O7	0.1585 (7)	0.3049 (6)	0.9253 (8)	0.022 (2)	
O8	0.2798 (5)	0.2744 (6)	0.9617 (8)	0.019 (2)	
O9	0.3811 (5)	0.2904 (5)	1.0900 (7)	0.0132 (18)	
O10	0.1086 (6)	0.1987 (7)	0.7333 (9)	0.032 (3)	
O11	0.0389 (6)	0.1348 (7)	0.9045 (10)	0.034 (3)	
O12	0.1327 (6)	0.3308 (7)	0.6694 (10)	0.031 (3)	
O13	0.2861 (9)	0.5832 (9)	0.8857 (15)	0.051 (4)	

Table S2. Anisotropic displacement parameters (Å^2) for $Sm_3(IO_3)_9(HIO_3)_4$.

$Sm_3(IO_3)_9(HIO_3)_4$						
Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sm1	0.0102 (3)	0.0102 (3)	0.0110 (3)	0.0064 (3)	0.0021 (2)	0.0014 (2)
I1	0.0133 (4)	0.0124 (4)	0.0207 (4)	0.0013 (3)	−0.0046 (3)	0.0031 (3)
I2	0.0097 (4)	0.0145 (4)	0.0121 (4)	0.0063 (3)	−0.0017 (3)	−0.0028 (3)
I3	0.0096 (4)	0.0113 (4)	0.0176 (4)	0.0058 (3)	0.0010 (3)	−0.0002 (3)
I4	0.0127 (4)	0.0107 (4)	0.0139 (4)	0.0075 (3)	0.0000 (3)	−0.0018 (3)
I5A	0.0259 (7)	0.0259 (7)	0.0306 (12)	0.0129 (3)	0.000	0.000
I5B	0.0259 (7)	0.0259 (7)	0.0306 (12)	0.0129 (3)	0.000	0.000
O1	0.031 (7)	0.026 (6)	0.026 (6)	0.014 (5)	−0.008 (5)	−0.010 (5)
O2	0.021 (4)	0.026 (4)	0.015 (4)	0.014 (3)	−0.005 (3)	−0.007 (3)
O3	0.016 (5)	0.018 (5)	0.019 (5)	0.000 (4)	−0.009 (4)	0.000 (4)
O4	0.015 (5)	0.017 (5)	0.043 (7)	0.007 (4)	0.003 (5)	0.002 (5)
O5	0.023 (6)	0.020 (6)	0.053 (9)	0.007 (5)	0.001 (6)	−0.006 (6)
O6	0.013 (5)	0.017 (5)	0.017 (5)	0.004 (4)	−0.005 (4)	−0.003 (4)
O7	0.031 (6)	0.023 (5)	0.019 (5)	0.018 (5)	0.003 (4)	−0.001 (4)
O8	0.011 (5)	0.030 (6)	0.014 (5)	0.009 (5)	−0.003 (4)	−0.002 (4)
O9	0.011 (3)	0.017 (4)	0.014 (3)	0.009 (3)	0.000 (3)	−0.002 (3)
O10	0.014 (5)	0.046 (8)	0.019 (5)	0.002 (5)	−0.001 (4)	0.013 (5)
O11	0.017 (5)	0.044 (8)	0.037 (7)	0.012 (5)	0.006 (5)	−0.003 (6)
O12	0.022 (6)	0.036 (7)	0.041 (7)	0.020 (6)	−0.016 (5)	−0.028 (6)
O13	0.040 (8)	0.042 (8)	0.070 (10)	0.020 (7)	−0.010 (8)	−0.022 (8)

Table S3. Selected bond lengths (Å) for $Sm_3(IO_3)_9(HIO_3)_4$.

$Sm_3(IO_3)_9(HIO_3)_4$			
Sm1−O10	2.355 (11)	I3−O8	1.821 (10)
Sm1−O7	2.370 (11)	I4−O4	1.790 (11)
Sm1−O8	2.383 (10)	I4−O2	1.799 (11)
Sm1−O3^{i}	2.384 (10)	I4−O7	1.805 (11)
Sm1−O2^{ii}	2.390 (11)	I5A−I5B	0.886 (15)
Sm1−O6^{iii}	2.399 (10)	I5A−O13^{v}	1.809 (15)
Sm1−O9^{iv}	2.417 (10)	I5A−O13	1.809 (15)
Sm1−O11	2.449 (12)	I5A−O13^{vi}	1.809 (15)
I1−O1 1.800 (12) z	1.375 (3)	I5B−O13^{v}	2.365 (19)
I1−O11	1.805 (12)	I5B−O13	2.365 (19)
I1−O3	1.837 (11)	I5B−O13^{vi}	2.365 (19)
I2−O10	1.805 (11)	O2−Sm1^{vii}	2.390 (11)
I2−O12	1.817 (12)	O3−Sm1^{viii}	2.384 (10)
I2−O6	1.819 (10)	O6−Sm1^{ix}	2.399 (10)
I3−O5	1.792 (13)	O9−Sm1^{x}	2.417 (10)
I3−O9	1.818 (10)		

Symmetry codes: Symmetry codes: (i) −x+y, −x, z; (ii) −y+2/3, −x+1/3, z−1/6; (iii) −x+y, y, z+1/2; (iv) −x+y+1/3, −x+2/3, z−1/3; (v) −x+y, −x+1, z; (vi) −y+1, x−y+1, z;
(vii) −y+1/3, −x+2/3, z+1/6; (viii) −y, x−y, z; (ix) −x+y, y, z−1/2; (x) −y+2/3, x−y+1/3, z+1/3

Table S4. Selected bond angles (degree) for $Sm_3(IO_3)_9(HIO_3)_4$.

O10−Sm1−O7	86.7 (5)	O10−I2−O12	101.1 (7)
O10−Sm1−O8	139.3 (4)	O10−I2−O6	89.6 (5)
O7−Sm1−O8	80.8 (4)	O12−I2−O6	98.4 (5)
O10−Sm1−O3^{i}	119.4 (4)	O5−I3−O9	97.6 (5)
O7−Sm1−O3^{i}	136.6 (4)	O5−I3−O8	100.0 (6)
O8−Sm1−O3^{i}	95.3 (4)	O9−I3−O8	94.5 (5)
O10−Sm1−O2^{ii}	93.9 (5)	O4−I4−O2	96.1 (5)
O7−Sm1−O2^{ii}	148.3 (4)	O4−I4−O7	99.0 (6)
O8−Sm1−O2^{ii}	78.2 (4)	O2−I4−O7	97.1 (5)
O3^{i}−Sm1−O2^{ii}	69.3 (4)	I5B−I5A−O13^{v}	118.7 (7)
O10−Sm1−O6^{iii}	137.5 (4)	I5B−I5A−O13	118.7 (7)
O7−Sm1−O6^{iii}	69.7 (4)	O13^{v}−I5A−O13	98.9 (8)
O8−Sm1−O6^{iii}	72.7 (4)	I5B−I5A−O13^{vi}	118.7 (7)
O3^{i}−Sm1−O6^{iii}	67.9 (4)	O13^{v}−I5A−O13^{vi}	98.9 (8)
O2^{ii}−Sm1−O6^{iii}	124.8 (4)	O13−I5A−O13^{vi}	98.9 (8)
O10−Sm1−O9^{iv}	65.8 (3)	I5A−I5B−O13^{v}	42.1 (6)
O7−Sm1−O9^{iv}	79.3 (4)	I5A−I5B−O13	42.1 (6)
O8−Sm1−O9^{iv}	73.8 (3)	O13^{v}−I5B−O13	71.0 (9)
O3^{i}−Sm1−O9^{iv}	141.3 (4)	I5A−5B−O13^{vi}	42.1 (6)
O2^{ii}−Sm1−O9^{iv}	72.2 (3)	O13^{v}−I5B−O13^{vi}	71.0 (9)
O6^{iii}−Sm1−O9^{iv}	137.2 (3)	O13−I5B−O13^{vi}	71.0 (9)
O10−Sm1−O11	68.4 (4)	I4−O2−Sm1^{vii}	137.6 (6)
O7−Sm1−O11	87.1 (4)	I1−O3−Sm1^{viii}	129.2 (5)
O8−Sm1−O11	148.1 (4)	I2−O6−Sm1^{ix}	127.5 (5)
O3^{i}−Sm1−O11	73.7 (4)	I4−O7−Sm1	139.9 (6)
O2^{ii}−Sm1−O11	122.6 (4)	I3−O8−Sm1	131.5 (5)
O6^{iii}−Sm1−O11	75.4 (4)	I3−O9−Sm1^{x}	133.5 (5)
O9^{iv}−Sm1−O11	132.7 (4)	I2−O10−Sm1	127.4 (6)
O1−I1−O11	99.8 (6)	I1−O11−Sm1	143.9 (7)
O1−I1−O3	96.2 (5)	I5A−O13−I5B	19.2 (3)
O11−I1−O3	97.8 (6)		