Supplementary Information

Achieving balanced UV SHG response, optical band gap and birefringence in rare earth compounds $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln = Y, Gd, Er, Ho, Dy, Eu)

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Synthesis

The raw materials required for the synthesis of the crystals are I_2O_5, $(NH_3)_2SO_4$, HNO_3(68%), Eu_2O_3, $GdCl_3$, Er_2O_3, Ho_2O_3, $Y(NO_3)_3·6H_2O$, Dy_2O_3, and none of the raw materials used have been re-refined or purified. The synthesis of $Eu(IO_3)(SO_4)·3H_2O$. I_2O_5 (0.5 mmol), $(NH_4)_2SO_4$ (1.5 mmol), Eu_2O_3 (0.5 mmol), HNO_3 (0.2 ml),H_2O (2 ml), The synthesis of $Gd(IO_3)(SO_4)·3H_2O$, I_2O_5 (1 mmol), $(NH_4)_2SO_4$ (1 mmol), $GdCl_3$ (1 mmol) , HNO_3 (0.1 ml), H_2O (2 ml), the synthesis of $Y(IO_3)(SO_4)·3H_2O$, I_2O_5 (1 mmol), $(NH_4)_2SO_4$ (2 mmol), $Y(NO_3)_3·6H_2O$ (2 mmol), HNO_3 (0.1 ml), H_2O (2 ml), the synthesis of $Er(IO_3)(SO_4)·3H_2O$, I_2O_5 (1 mmol), $(NH_4)_2SO_4$ (1.3 mmol), Er_2O_3 (0.5 mmol), HNO_3 (0.2 ml), H_2O (2 ml), the synthesis of $Dy(IO_3)(SO_4)·3H_2O$, I_2O_5 (0.5 mmol), $(NH_4)_2SO_4$ (1 mmol), Dy_2O_3 (0.5 mmol), HNO_3 (0.2 ml), H_2O (2 ml), the synthesis of $Ho(IO_3)(SO_4)·3H_2O$, I_2O_5 (0.5 mmol), $(NH_4)_2SO_4$ (1.5 mmol), Ho_2O_3 (0.5 mmol), HNO_3 (0.2 ml), H_2O (2 ml). The raw materials required for the synthesis of the crystals were poured into 23 mL Teflon-lined autoclaves and stirred to mix them well and uniformly for a complete reaction. After that, sealed and encapsulated, for 90 minutes to 100 °, holding for one day, 90 minutes to 200 °, holding for two days, cooling down to 6 ° every hour, slowly cooling to room temperature, filtration and recovery the product and washed with deionized water, drying to obtain the Colorless cylinder crystals $Gd(IO_3)(SO_4)·3H_2O$, $Eu(IO_3)(SO_4)·3H_2O$, $Y(IO_3)(SO_4)·3H_2O$, $Dy(IO_3)(SO_4)·3H_2O$, light yellow columnar $Ho(IO_3)(SO_4)·3H_2O$ and light pink columnar $Er(IO_3)(SO_4)·3H_2O$, The crystals have the same shape, only different colors. It is worth noting that the solubility of $(NH_4)_2SO_4$ in water is high, $(NH_4)_2SO_4$ needs to be put more in the process of use, but too much $(NH_4)_2SO_4$ will result in smaller crystals of growth, so it should be used wisely.

Properties characterization

Collection of single crystal x-ray diffraction data was tested at room temperature on Bruker APEX II CCD instrument equipped with graphite monochromatic Mo-Kα (λ = 0.71073 Å). The crystal structures were resolved by direct method using the SHELXS-97 software package and refined using SHELXL-2014. The validity of the final results was checked with PLATON, and no recommendations for higher symmetry operations were selected.

Powder X-ray data of the crystals were collected using a PANalytical X'pert3 equipment diffractometer equipped with Cu Kα radiation (λ = 1.541886 Å) in the 2θ range of 10-70°, with

a scanning step of 0.02°, and the crystal cif-files were simulated and compared with the experimental ones by converting the resulting files The pure phase of the crystals was synthesized by comparing the cif file with the experimental one to determine its experimental and theoretical agreement. Elemental determination of the title compounds was carried out using energy-dispersive X-ray spectrometry.

The infrared spectra of the title compounds were tested using Nicolet NEXUS-470 FT-IR spectrometer with KBr backing in the wavelength range of 400-4000 cm^{-1}. The UV−vis−NIR diffuse reflectance spectra were measured on a PerkinElmer Lambda 1050 spectrophotometer in the range of 200-1200 nm. The optical absorption spectra were derived from the diffuse reflectance spectra using the Kubelka-Munk function $\alpha/S = (1 - R)^2/2R$, where α, S, and R are the absorption, scattering, and diffusion coefficients, respectively.

Powder second harmonic generation (SHG) measurements were made by the well-known Kurtz-Perry method. The SHG intensities of the six compounds were measured with a Q-switched 1064 nm Nd: YAG laser at room temperature. Compounds 1-6 and KH_2PO_4 (KDP) samples were screened into different particle sizes (26-48, 48-75, 75-100, 100-150, 150-180, 180-250 and 250-315 μm).

The electronic structure and optical properties of the nonlinear optical crystal $Y(IO_3)(SO_4)\cdot 3H_2O$ is investigated in detail by the density-functional theory (DFT) method. The first-principles plane-wave pseudopotential technique is used to calculate the electronic structure and density of states (DOS) applying the GGA-PBE functional. Monkhorst-Pack k-point sampling was performed using 2 × 2 × 1 at the 830 eV cutoff kinetic-energy to determine the plane wave numbers of the two compounds and to realize the numerical integration in the Brillouin zone. The orbital electrons of I $5s^25p^5$, S $3s^23p^4$, Y $4p^64d^15s^2$, O $2s^22p^4$, and H $1s^1$ are considered valence electrons.

Table S1. Crystallographic data and structure refinement details for $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Er, Ho, Dy, Eu).

Formula	$ErH_6IO_{10}S$	$YH_6IO_{10}S$	$HoH_6IO_{10}S$	$DyH_6IO_{10}S$	$GdH_6IO_{10}S$	$EuH_6IO_{10}S$
F.W.	492.27	413.92	489.94	487.51	482.26	476.97
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)
a (Å)	6.6822(2)	6.6961(5)	6.7098(2)	6.7142(5)	6.7498(4)	6.7813(5)
b (Å)	8.7719(2)	8.7941(8)	8.8093(3)	8.8166(7)	8.8689(6)	8.915(2)
c (Å)	13.6104(4)	13.6473(11)	13.6558(5)	13.6666(11)	13.7695(7)	13.810(3)
α	90	90	90	90	90	90
β	90	90	90	90	90	90
γ	90	90	90	90	90	90
V (Å^3)	797.78(4)	803.64(1)	807.18(5)	809.01(1)	824.29(9)	834.9(3)
Z	4	4	4	4	4	4
ρ_{calc} [g/cm^{-3}]	4.099	3.421	4.032	4.003	3.886	3.795
μ (mm^{-1})	14.686	11.394	13.921	13.345	12.079	11.494
2θ range [°]	5.53 to 55.06 (0.77 Å)	5.51 to 55.08 (0.77 Å)	5.50 to 55.12 (0.77 Å)	5.50 to 55.12 (0.77 Å)	5.46 to 55.15 (0.77 Å)	5.44 to 55.10 (0.77 Å)
Limiting indices	$-8 \le h \le 8$, $-11 \le k \le$	$-8 \le h \le 8$, $-6 \le k \le$	$-8 \le h \le 8$, $-11 \le k \le$	$-8 \le h \le 8$, $-11 \le k \le$	$-8 \le h \le 8$, $-11 \le k \le$	$-8 \le h \le 8$, $-9 \le k \le$

	11, −12 ≤ l ≤ 17	11, −16 ≤ l ≤ 17	10, −17 ≤ l ≤ 16	10, −17 ≤ l ≤ 17	9, −17 ≤ l ≤ 16	11, −17 ≤ l ≤ 15
Reflections collected	3701	4129	4365	3988	4091	4523
Independent reflections	1798 R_{int} = 0.0209 R_{sigma} = 0.0303	1818 R_{int} = 0.0174 R_{sigma} = 0.0242	1842 R_{int} = 0.0218 R_{sigma} = 0.0264	1836 R_{int} = 0.0213 R_{sigma} = 0.0289	1774 R_{int} = 0.0171 R_{sigma} = 0.0231	1905 R_{int} = 0.0195 R_{sigma} = 0.0252
GOF on F^2	1.003	1.050	1.039	1.034	1.006	1.036
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0184 wR_2 = 0.0488	R_1 = 0.0182 wR_2 = 0.0476	R_1 = 0.0165 wR_2 = 0.0404	R_1 = 0.0229 wR_2 = 0.0595	R_1 = 0.0147 wR_2 = 0.0375	R_1 = 0.0181 wR_2 = 0.0446
Final R indexes [all data]	R_1 = 0.0185 wR_2 = 0.0489	R_1 = 0.0186 wR_2 = 0.0478	R_1 = 0.0167 wR_2 = 0.0405	R_1 = 0.0230 wR_2 = 0.0595	R_1 = 0.0148 wR_2 = 0.0376	R_1 = 0.0182 wR_2 = 0.0447
Flack X parameter	0.322(16)	0.590(8)	0.383(14)	0.64(2)	0.276(15)	0.67(2)

[a] $R_1 = \Sigma\left|\left|F_o\right| - \left|F_c\right|\right| / \Sigma\left|F_o\right|, wR_2 = \left[\Sigma w\left(F_o^2 - F_c^2\right)^2 / \Sigma w\left(F_o^2\right)^2\right]^{1/2}$

Table S2. Atomic coordinates and BVS for $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Er, Ho, Dy, Eu).

Atomic coordinates and BVS for $Y(IO_3)(SO_4)\cdot 3H_2O$.

Atom	*x*	*y*	*z*	U_{eq}	BVS
Y1	0.24019(7)	0.63665(6)	0.31367(4)	0.00518(12)	3.337(14)
I1	0.04341(5)	0.48315(4)	0.07190(2)	0.00610(10)	5.268(34)
S1	0.24379(19)	0.00238(17)	0.68339(8)	0.0061(2)	6.095(35)
O1	0.0017(6)	0.2927(5)	0.1127(3)	0.0145(9)	-2.454(23)
O2	0.0848(5)	0.0636(5)	0.2378(3)	0.0096(8)	-1.989(18)
O3	0.7003(6)	0.0594(5)	0.0310(3)	0.0145(9)	-2.282(25)
O4	0.2277(6)	0.1645(5)	0.7081(3)	0.0145(9)	-2.020(20)
O5	0.2294(6)	0.0137(5)	0.0786(3)	0.0146(8)	-1.986(24)
O6	0.2488(6)	0.5384(5)	0.1497(3)	0.0118(8)	-2.070(23)
O7	0.4350(6)	0.0789(5)	0.2178(3)	0.0143(9)	-2.012(18)
O8	0.4468(8)	0.2245(5)	0.4693(4)	0.0221(10)	-1.722(63)
O9	0.5833(7)	0.3433(6)	0.1027(3)	0.0184(10)	-1.797(39)
O10	0.2185(7)	0.3647(5)	0.3262(3)	0.0187(10)	-1.834(58)
H1	0.399(9)	0.158(6)	0.508(4)	0.028	
H2	0.548(7)	0.189(7)	0.440(5)	0.028	
H3	0.574(9)	0.342(9)	0.0408(11)	0.028	
H4	0.474(6)	0.373(8)	0.128(4)	0.028	
H5	0.199(11)	0.308(6)	0.276(3)	0.028	
H6	0.295(9)	0.319(6)	0.366(4)	0.028	

Atomic coordinates and BVS for $Gd(IO_3)(SO_4)\cdot 3H_2O$

Atom	*x*	*y*	*z*	U_{eq}	BVS
Gd1	0.23929(4)	0.63695(3)	0.31393(2)	0.00766(9)	3.375(14)
I1	0.04453(5)	0.48336(4)	0.07258(2)	0.00910(10)	5.283(37)
S1	0.24448(19)	0.00220(16)	0.68320(8)	0.0090(2)	6.087(36)
O1	0.0051(6)	0.2944(5)	0.1136(3)	0.0185(10)	-2.212(22)

O2	0.0852(6)	0.0597(5)	0.2386(3)	0.0147(9)	-1.980(19)
O3	0.6977(7)	0.0578(5)	0.0300(3)	0.0169(10)	-2.447(23)
O4	0.2221(7)	0.1624(5)	0.7076(3)	0.0204(9)	-2.170(22)
O5	0.2254(7)	0.0143(5)	0.0789(3)	0.0211(9)	-1.567(18)
O6	0.2495(7)	0.5387(5)	0.1488(3)	0.0162(8)	-2.413(26)
O7	0.4309(6)	0.0813(5)	0.2153(3)	0.0209(10)	-2.210(21)
O8	0.4462(7)	0.2244(5)	0.4706(4)	0.0249(10)	-1.718(51)
O9	0.5852(7)	0.3471(6)	0.0995(3)	0.0229(10)	-1.787(59)
O10	0.2231(7)	0.3603(5)	0.3250(3)	0.0205(10)	-1.840(51)
H1	0.549(6)	0.277(6)	0.482(5)	0.031	
H2	0.478(9)	0.138(4)	0.450(5)	0.031	
H3	0.496(8)	0.407(6)	0.119(5)	0.031	
H4	0.591(10)	0.270(5)	0.136(4)	0.031	
H5	0.232(11)	0.316(6)	0.271(2)	0.031	
H6	0.293(9)	0.317(7)	0.367(3)	0.031	

Atomic coordinates and BVS for $Er(IO_3)(SO_4)\cdot 3H_2O$

Atom	***x***	***y***	***z***	U_{eq}	**BVS**
Er1	0.23996(4)	0.63654(4)	0.31370(2)	0.00376(12)	3.122(18)
I1	0.04328(7)	0.48315(5)	0.07195(3)	0.00488(13)	5.341(50)
S1	0.2435(3)	0.0022(2)	0.68328(12)	0.0053(3)	6.077(51)
O1	0.0012(9)	0.2921(7)	0.1128(5)	0.0143(13)	-2.178(31)
O2	0.0841(8)	0.0639(7)	0.2383(4)	0.0098(12)	-1.933(26)
O3	0.6987(9)	0.0596(7)	0.0310(4)	0.0111(13)	-2.292(29)
O4	0.2275(9)	0.1644(7)	0.7076(4)	0.0132(12)	-2.220(31)
O5	0.2303(10)	0.0147(6)	0.0777(4)	0.0123(11)	-1.801(30)
O6	0.2480(10)	0.5377(7)	0.1500(4)	0.0111(11)	-2.450(38)
O7	0.4354(10)	0.0782(7)	0.2181(5)	0.0152(13)	-1.996(30)
O8	0.4480(11)	0.2239(7)	0.4692(5)	0.0195(14)	-1.722(86)

O9	0.5822(10)	0.3424(8)	0.1027(5)	0.0177(14)	-1.771(78)
O10	0.2188(10)	0.3648(7)	0.3258(4)	0.0151(12)	-1.810(76)
H1	0.401(14)	0.147(6)	0.499(7)	0.023	
H2	0.545(11)	0.197(10)	0.433(6)	0.023	
H3	0.626(13)	0.306(12)	0.157(4)	0.023	
H4	0.470(9)	0.385(12)	0.113(6)	0.023	
H5	0.204(17)	0.318(9)	0.271(3)	0.023	
H6	0.289(14)	0.311(9)	0.365(5)	0.023	

Atomic coordinates and BVS for $Ho(IO_3)(SO_4)\cdot 3H_2O$

Atom	***x***	***y***	***z***	U_{eq}	**BVS**
Ho1	0.23980(4)	0.63659(3)	0.31368(2)	0.00672(10)	3.328(15)
I1	0.04352(6)	0.48320(4)	0.07207(3)	0.00803(11)	5.278(40)
S1	0.2435(2)	0.00234(18)	0.68317(9)	0.0079(3)	6.003(39)
O1	0.0026(7)	0.2929(6)	0.1129(4)	0.0175(11)	-2.325(27)
O2	0.0840(7)	0.0631(5)	0.2383(4)	0.0129(10)	-1.800(20)
O3	0.7005(7)	0.0594(5)	0.0306(3)	0.0130(10)	-2.531(26)
O4	0.2264(8)	0.1644(5)	0.7075(3)	0.0176(10)	-2.009(20)
O5	0.2297(8)	0.0148(5)	0.0778(3)	0.0174(10)	-1.933(28)
O6	0.2482(8)	0.5380(6)	0.1497(3)	0.0152(9)	-2.224(27)
O7	0.4348(7)	0.0789(6)	0.2177(4)	0.0168(11)	-2.315(29)
O8	0.4467(10)	0.2248(6)	0.4697(4)	0.0237(12)	-1.679(62)
O9	0.5843(9)	0.3442(7)	0.1028(4)	0.0218(12)	-1.797(77)
O10	0.2196(8)	0.3635(6)	0.3259(4)	0.0176(10)	-1.837(67)
H5	0.223(15)	0.323(9)	0.382(3)	0.05(3)	
H6	0.290(12)	0.313(8)	0.286(4)	0.03(3)	
H1	0.568(6)	0.217(11)	0.453(9)	0.08(5)	
H3	0.582(13)	0.351(10)	0.0408(12)	0.03(2)	
H4	0.508(16)	0.273(10)	0.121(6)	0.09(6)	

H2	0.396(13)	0.137(5)	0.477(8)	0.05(3)	

Atomic coordinates and BVS for $Dy(IO_3)(SO_4)\cdot 3H_2O$

Atom	***x***	***y***	***z***	U_{eq}	**BVS**
Dy1	0.23949(5)	0.63672(4)	0.31371(2)	0.00638(12)	3.081(21)
I1	0.04400(8)	0.48297(6)	0.07228(4)	0.00813(14)	5.319(55)
S1	0.2443(3)	0.0028(3)	0.68258(13)	0.0086(4)	6.006(58)
O1	0.0036(10)	0.2927(8)	0.1127(5)	0.0158(14)	-2.173(35)
O2	0.0838(12)	0.0621(9)	0.2385(6)	0.024	-1.767(33)
O3	0.6989(10)	0.0600(8)	0.0305(4)	0.0125(14)	-2.429(35)
O4	0.2249(11)	0.1643(7)	0.7076(5)	0.0177(14)	-2.145(32)
O5	0.2298(11)	0.0159(8)	0.0781(4)	0.0167(13)	-1.825(33)
O6	0.2486(11)	0.5380(8)	0.1494(4)	0.0148(13)	-2.236(36)
O7	0.4352(11)	0.0788(8)	0.2170(5)	0.0166(13)	-2.250(38)
O8	0.4460(13)	0.2241(9)	0.4696(6)	0.0234(16)	-1.666(95)
O9	0.5843(13)	0.3438(10)	0.1018(5)	0.0236(17)	-1.770(66)
O10	0.2197(12)	0.3621(8)	0.3264(5)	0.0198(15)	-1.796(80)
H1	0.376(13)	0.153(8)	0.494(9)	0.030	
H2	0.549(10)	0.187(10)	0.442(8)	0.030	
H3	0.61(2)	0.435(4)	0.117(7)	0.030	
H4	0.56(2)	0.292(9)	0.153(4)	0.030	
H5	0.297(15)	0.302(11)	0.296(6)	0.030	
H6	0.222(18)	0.343(13)	0.3873(19)	0.030	

Atomic coordinates and BVS for $Eu(IO_3)(SO_4)\cdot 3H_2O$

Atom	***x***	***y***	***z***	U_{eq}	**BVS**
Eu1	0.23892(4)	0.63727(4)	0.31405(2)	0.00648(9)	3.352(18)
I1	0.04511(6)	0.48322(5)	0.07289(3)	0.00870(11)	5.262(44)
S1	0.2455(2)	0.00176(19)	0.68235(11)	0.0087(3)	5.998(46)

O1	0.0063(8)	0.2958(6)	0.1141(4)	0.0173(12)	-2.222(27)
O2	0.0848(7)	0.0597(6)	0.2384(4)	0.0125(11)	-1.975(23)
O3	0.6975(8)	0.0572(6)	0.0301(4)	0.0158(12)	-2.287(27)
O4	0.2216(9)	0.1623(6)	0.7071(4)	0.0198(12)	-2.115(26)
O5	0.2252(9)	0.0137(6)	0.0787(4)	0.0204(11)	-1.809(29)
O6	0.2488(8)	0.5390(6)	0.1491(3)	0.0162(10)	-2.418(30)
O7	0.4300(8)	0.0822(7)	0.2145(4)	0.0199(13)	-2.157(28)
O8	0.4462(10)	0.2257(7)	0.4712(5)	0.0256(13)	-1.722(78)
O9	0.5879(9)	0.3480(8)	0.0996(4)	0.0233(13)	-1.786(76)
O10	0.2238(9)	0.3603(6)	0.3257(4)	0.0217(12)	-1.830(72)
H1	0.553(8)	0.192(9)	0.448(6)	0.032	
H2	0.392(11)	0.161(7)	0.507(6)	0.032	
H3	0.505(11)	0.412(7)	0.121(6)	0.032	
H4	0.591(14)	0.274(7)	0.138(5)	0.032	
H5	0.284(13)	0.314(8)	0.370(4)	0.032	
H6	0.210(15)	0.304(7)	0.277(4)	0.032	

Table S3. Bond lengths and angles for $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Er, Ho, Dy, Eu).

Bond lengths and angles of $Y(IO_3)(SO_4)\cdot 3H_2O$

Atom–Atom	Length [Å]	Atom–Atom	Length [Å]
Y1–O3$^{\#1}$	2.262(4)	I1–O1	1.787(4)
Y1–O7$^{\#1}$	2.274(4)	I1–O3$^{\#4}$	1.793(4)
Y1–O4$^{\#2}$	2.276(4)	I1–O6	1.804(4)
Y1–O1$^{\#3}$	2.348(4)	S1–O5$^{\#5}$	1.449(4)
Y1–O2$^{\#3}$	2.376(4)	S1–O4	1.469(4)
Y1–O6	2.399(4)	S1–O7$^{\#5}$	1.471(4)
Y1–O10	2.402(5)	S1–O2$^{\#5}$	1.485(4)
Y1–O9$^{\#1}$	2.450(4)		

Symmetry transformations used to generate equivalent atoms:

#1: 1-X, 0.5+Y, 0.5-Z; #2: 0.5-X, 1-Y, -0.5+Z; #3: -X, 0.5+Y, 0.5-Z; #4: -0.5+X, 0.5-Y, -Z; #5: 0.5-X, -Y, 0.5+Z.

Bond lengths and angles of $Gd(IO_3)(SO_4)\cdot 3H_2O$

Atom–Atom	Length [Å]	Atom–Atom	Length [Å]
Gd1–O3$^{\#1}$	2.300(4)	S1–O5$^{\#5}$	1.458(4)
Gd1–O7$^{\#1}$	2.316(4)	S1–O7$^{\#5}$	1.465(4)
Gd1–O4$^{\#2}$	2.319(4)	S1–O4	1.468(4)
Gd1–O1$^{\#3}$	2.381(4)	S1–O2$^{\#5}$	1.485(4)
Gd1–O2$^{\#3}$	2.407(4)	I1–O1	1.788(4)
Gd1–O6	2.436(4)	I1–O6	1.804(4)
Gd1–O10	2.461(4)	I1–O3$^{\#4}$	1.788(4)
Gd1–O9$^{\#1}$	2.510(5)		

Symmetry transformations used to generate equivalent atoms:

#1: 1-X, 0.5+Y, 0.5-Z; #2: 0.5-X, 1-Y, -0.5+Z; #3: -X, 0.5+Y, 0.5-Z; #4: -0.5+X, 0.5-Y, -Z; #5: 0.5-X, -Y, 0.5+Z.

Bond lengths and angles of $Er(IO_3)(SO_4)\cdot.3H_2O$

Atom–Atom	Length [Å]	Atom–Atom	Length [Å]
Er1–O3$^{\#1}$	2.256(5)	S1–O7$^{\#5}$	1.466(6)
Er1–O7$^{\#1}$	2.271(6)	S1–O2$^{\#5}$	1.491(6)
Er1–O4$^{\#2}$	2.276(6)	S1–O5$^{\#5}$	1.456(5)
Er1–O1$^{\#3}$	2.337(6)	S1–O4	1.465(6)
Er1–O2$^{\#3}$	2.366(6)	I1–O3$^{\#4}$	1.784(6)
Er1–O6	2.391(5)	I1–O1	1.788(6)
Er1–O10	2.393(6)	I1–O6	1.797(6)
Er1–O9$^{\#1}$	2.443(6)		

Symmetry transformations used to generate equivalent atoms:

#1: 1-X, 0.5+Y, 0.5-Z; #2: 0.5-X, 1-Y, -0.5+Z; #3: -X, 0.5+Y, 0.5-Z; #4: -0.5+X, 0.5-Y, -Z; #5: 0.5-X, -Y, 0.5+Z.

Bond lengths and angles of $Ho(IO_3)(SO_4)\cdot3H_2O$

Atom–Atom	Length [Å]	Atom–Atom	Length [Å]
Ho1–O3$^{\#1}$	2.268(4)	S1–O7$^{\#5}$	1.471(5)
Ho1–O7$^{\#1}$	2.282(5)	S1–O2$^{\#5}$	1.496(5)
Ho1–O4$^{\#2}$	2.286(5)	S1–O5$^{\#5}$	1.458(4)
Ho1–O1$^{\#3}$	2.355(5)	S1–O4	1.470(5)
Ho1–O2$^{\#3}$	2.375(5)	I1–O1	1.788(5)
Ho1–O6	2.402(4)	I1–O6	1.801(5)
Ho1–O10	2.415(5)	I1–O3$^{\#4}$	1.794(5)
Ho1–O9$^{\#1}$	2.458(6)		

Symmetry transformations used to generate equivalent atoms:

#1: 1-X, 0.5+Y, 0.5-Z; #2: 0.5-X, 1-Y, -0.5+Z; #3: -X, 0.5+Y, 0.5-Z; #4: -0.5+X, 0.5-Y, -Z; #5: 0.5-X, -Y, 0.5+Z.

Bond lengths and angles of $Dy(IO_3)(SO_4)\cdot 3H_2O$

Atom–Atom	Length [Å]	Atom–Atom	Length [Å]
Dy1–O3$^{\#1}$	2.272(6)	S1–O7$^{\#5}$	1.481(7)
Dy1–O7$^{\#1}$	2.282(7)	S1–O2$^{\#5}$	1.497(8)
Dy1–O4$^{\#2}$	2.289(6)	S1–O5$^{\#5}$	1.448(6)
Dy1–O1$^{\#3}$	2.359(6)	S1–O4	1.469(6)
Dy1–O2$^{\#3}$	2.378(8)	I1–O1	1.787(7)
Dy1–O6	2.409(6)	I1–O3$^{\#4}$	1.789(6)
Dy1–O10	2.431(7)	I1–O6	1.798(7)
Dy1–O9$^{\#1}$	2.463(8)		

Symmetry transformations used to generate equivalent atoms:

#1: 1-X, 0.5+Y, 0.5-Z; #2: 0.5-X, 1-Y, -0.5+Z; #3: -X, 0.5+Y, 0.5-Z; #4: -0.5+X, 0.5-Y, -Z; #5: 0.5-X, -Y, 0.5+Z.

Bond lengths and angles of $Eu(IO_3)(SO_4)\cdot 3H_2O$

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Eu1–O3$^{\#1}$	2.308(5)	S1–O4	1.481(5)
Eu1–O7$^{\#1}$	2.332(5)	S1–O2$^{\#5}$	1.491(5)
Eu1–O4$^{\#2}$	2.333(5)	S1–O5$^{\#5}$	1.452(5)
Eu1–O1$^{\#3}$	2.397(5)	S1–O7$^{\#5}$	1.475(5)
Eu1–O2$^{\#3}$	2.413(5)	I1–O1	1.785(5)
Eu1–O6	2.442(5)	I1–O3$^{\#4}$	1.794(5)
Eu1–O10	2.476(6)	I1–O6	1.806(5)
Eu1–O9$^{\#1}$	2.516(6)		

Symmetry transformations used to generate equivalent atoms:

#1: 1-X, 0.5+Y, 0.5-Z; #2: 0.5-X, 1-Y, -0.5+Z; #3: -X, 0.5+Y, 0.5-Z; #4: -0.5+X, 0.5-Y, -Z; #5: 0.5-X, -Y, 0.5+Z.

Table S4. Calculation of dipole moments for IO_3, SO_4 and LnO_8 polyhedra in $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Eu).

Compound	Polar unit	Local dipole moment (D)
$Y(IO_3)(SO_4)\cdot 3H_2O$	IO_3	27.8823
	SO_4	1.1702
	YO_8	4.3600
$Gd(IO_3)(SO_4)\cdot 3H_2O$	IO_3	27.8973
	SO_4	1.1840
	GdO_8	3.6735
$Eu(IO_3)(SO_4)\cdot 3H_2O$	IO_3	27.7063
	SO_4	1.2442
	EuO_8	4.7849

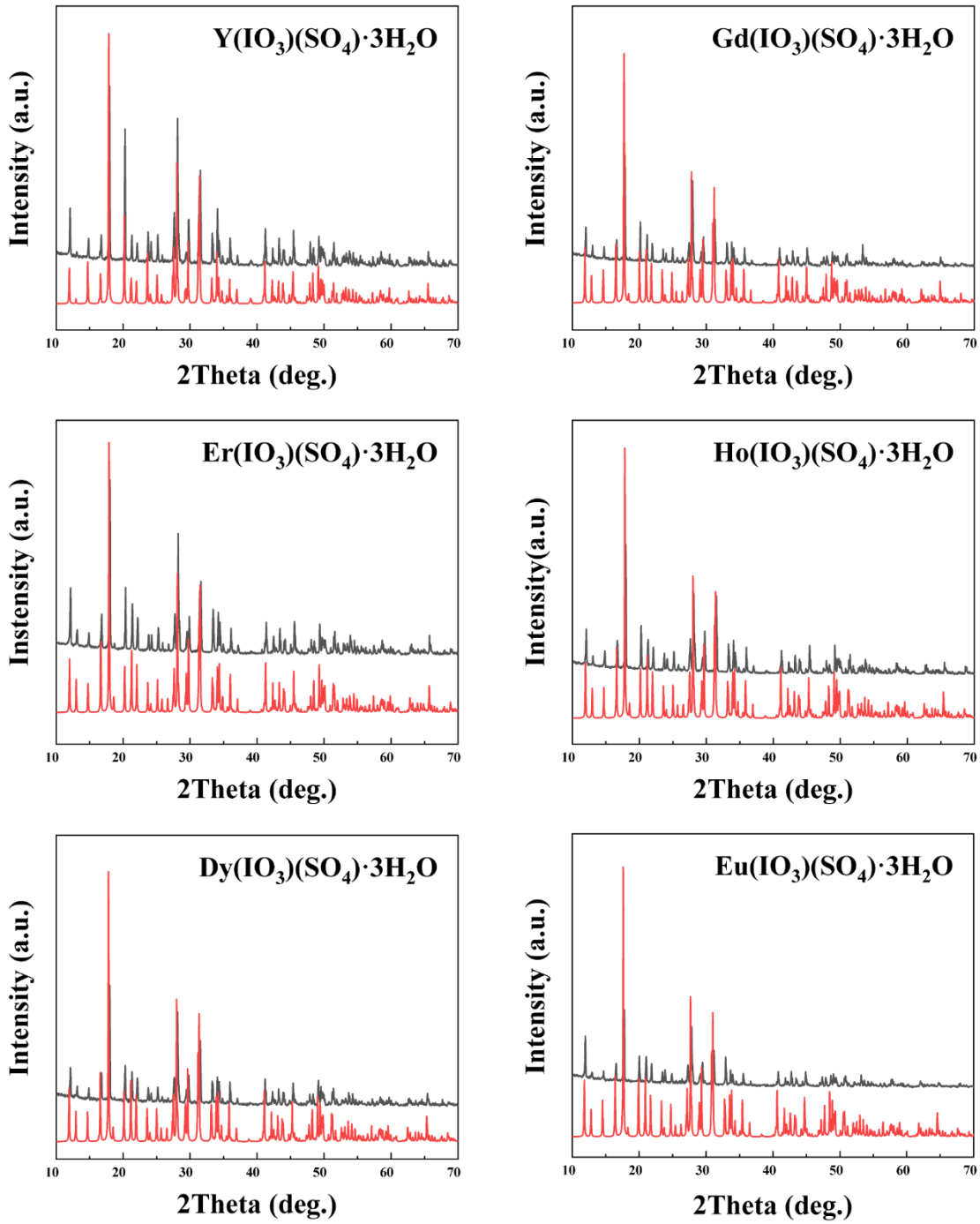
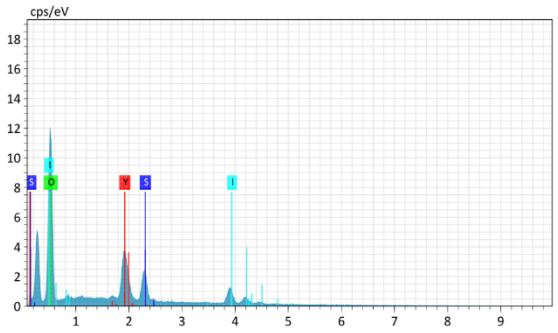
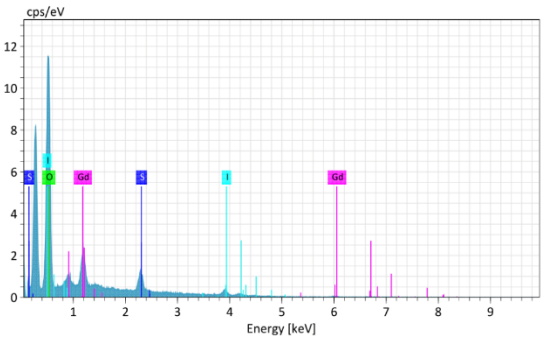
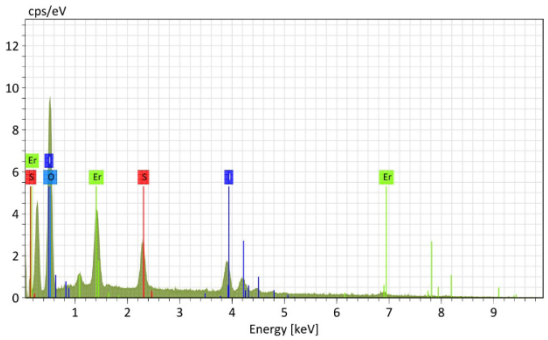


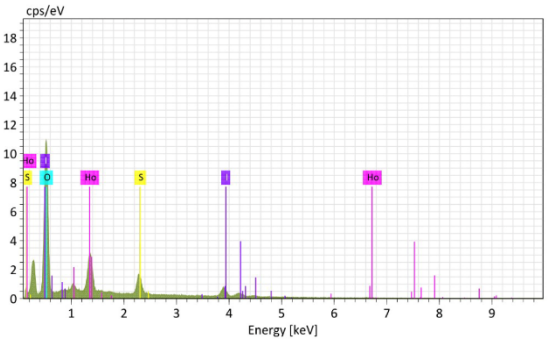
Figure S1. Experimental and simulated powder X-ray diffraction (PXRD) patterns for $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Er, Ho, Dy, Eu).



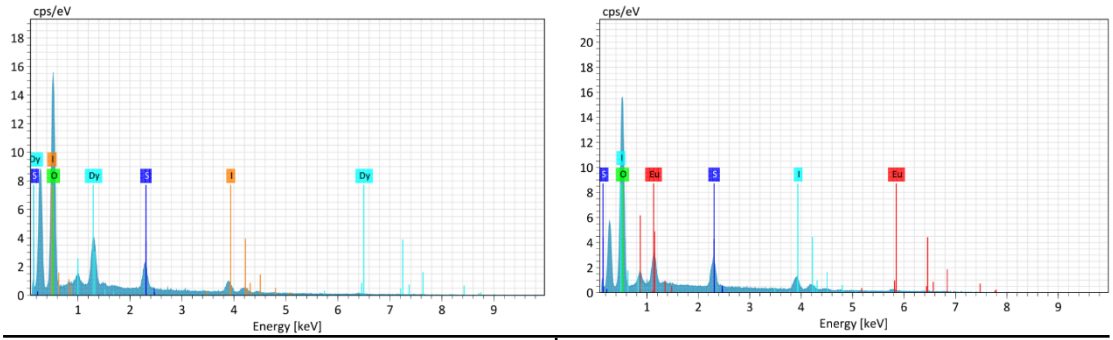


$Y(IO_3)(SO_4)\cdot 3H_2O$			$Gd(IO_3)(SO_4)\cdot 3H_2O$		
Elements	AN	Atoms[%]	Elements	AN	Atoms[%]
I	53	8.56	I	53	19.59
S	16	9.38	S	16	18.81
Y	39	10.07	Gd	64	20.89
O	8	72.00	O	8	39.71





$Er(IO_3)(SO_4)\cdot 3H_2O$			$Ho(IO_3)(SO_4)\cdot 3H_2O$		
Elements	AN	Atoms[%]	Elements	AN	Atoms[%]
I	53	11.15	I	53	8.56
S	16	12.67	S	16	10.36
Er	68	10.70	Ho	67	8.83
O	8	65.48	O	8	72.25



$Dy(IO_3)(SO_4)\cdot 3H_2O$			$Eu(IO_3)(SO_4)\cdot 3H_2O$		
Elements	AN	Atoms[%]	Elements	AN	Atoms[%]
I	53	9.06	I	53	12.83
S	16	9.60	S	16	13.60
Dy	66	8	Eu	63	11.35
O	8	73.34	O	8	62.21

Figure S2. The EDS quantitative analysis for $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Er, Ho, Dy, Eu).

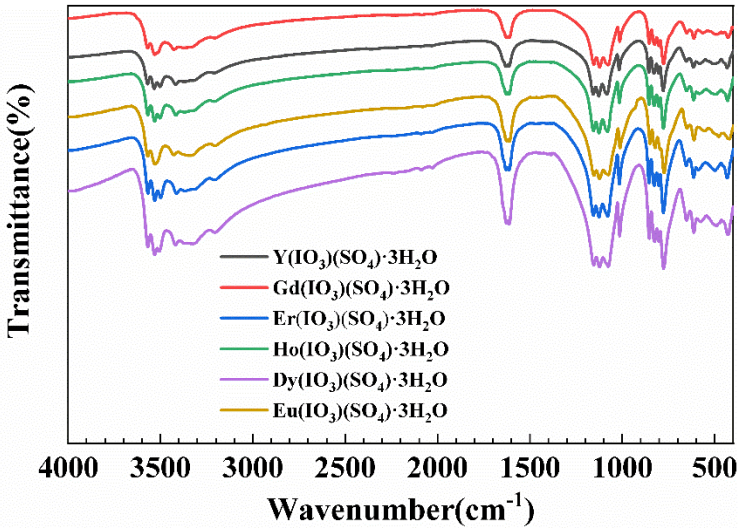


Figure S3. Infrared spectroscopy for $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Er, Ho, Dy, Eu).

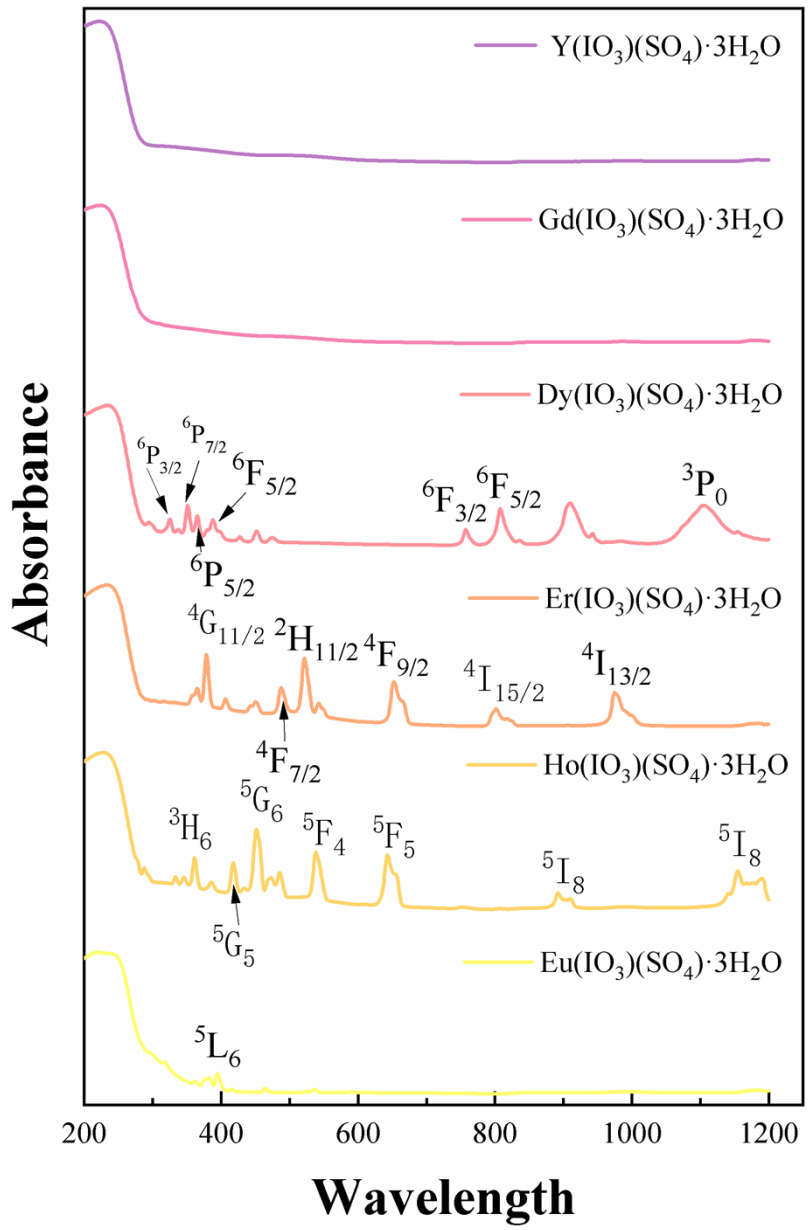


Figure S4. UV−vis−NIR diffuse reflectance spectra for $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Y, Gd, Er, Ho, Dy, Eu).

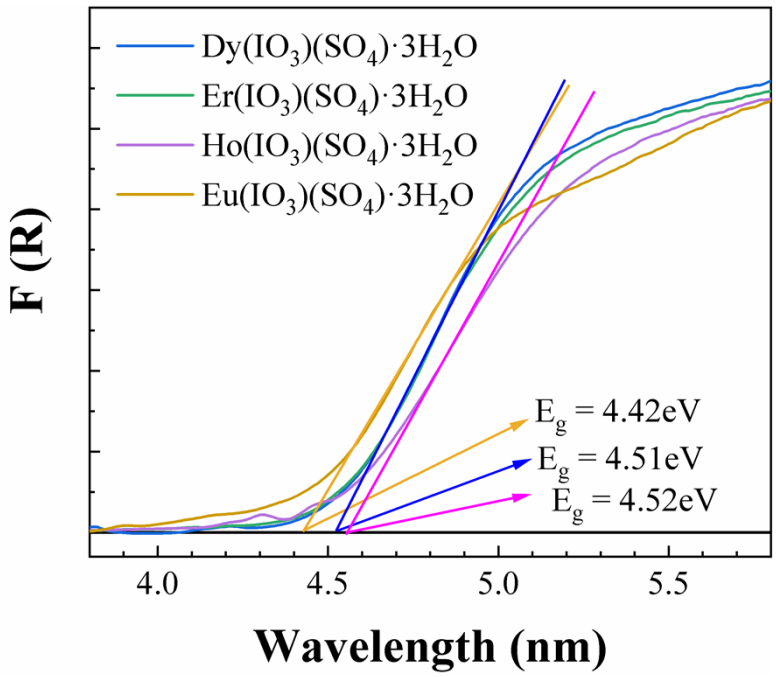


Figure S5. Optical bandgap of $Ln(IO_3)(SO_4)\cdot 3H_2O$ (Ln= Er, Ho, Dy, Eu).

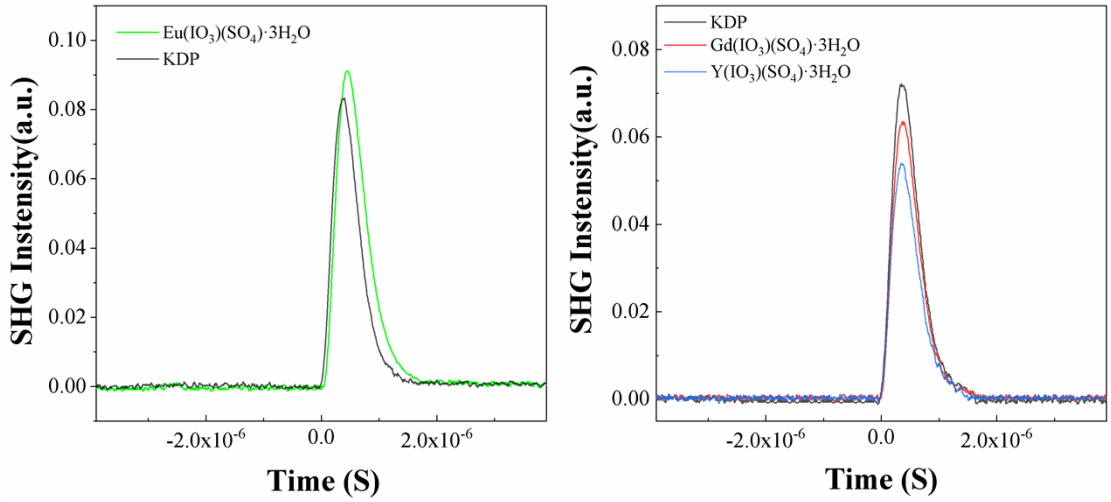


Figure S6. SHG intensity for $Gd(IO_3)(SO_4)\cdot 3H_2O$, $Y(IO_3)(SO_4)\cdot 3H_2O$, and $Eu(IO_3)(SO_4)\cdot 3H_2O$ samples were grounded and sieved into the 100-150 μm (a), 200-250 μm (b) particle size, KDP as a reference with the laser at 1064 nm wavelength;