Supporting Information for

Photoconversion Mechanisms and the Origin of Second-Harmonic Generation in Metal Iodates with Wide Transparency, $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu) and $NaLa(IO_3)_4:Ln^{3+}$ (Ln = Sm and Eu)

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Table S1. Selected bond distances for $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

$NaLa(IO_3)_4$				$NaCe(IO_3)_4$			
La(1)−O(1)	2.433(8)	I(1)−O(1)	1.809(8)	Ce(1)−O(1)	2.405(13)	I(1)−O(1)	1.823(11)
La(1)−O(2)	2.403(8)	I(1)−O(2)	1.791(9)	Ce(1)−O(2)	2.391(12)	I(1)−O(2)	1.796(11)
La(1)−O(3)	2.478(8)	I(1)−O(23)	1.825(9)	Ce(1)−O(3)	2.442(12)	I(1)−O(23)	1.833(12)
La(1)−O(5)	2.542(8)	I(2)–O(3)	1.817(8)	Ce(1)−O(5)	2.532(11)	I(2)–O(3)	1.824(12)
La(1)−O(6)	2.483(8)	I(2)–O(4)	1.821(8)	Ce(1)−O(6)	2.488(13)	I(2)–O(4)	1.793(12)
La(1)−O(9)	2.679(8)	I(2)–O(5)	1.819(8)	Ce(1)−O(9)	2.687(12)	I(2)–O(5)	1.823(11)
La(1)−O(20)	2.497(8)	I(3)–O(6)	1.823(8)	Ce(1)−O(20)	2.501(9)	I(3)–O(6)	1.822(12)
La(1)−O(23)	2.497(9)	I(3)–O(7)	1.802(8)	Ce(1)−O(23)	2.490(11)	I(3)–O(7)	1.811(11)
La(2)−O(12)	2.398(8)	I(3)–O(8)	1.798(8)	Ce(2)−O(12)	2.387(12)	I(3)–O(8)	1.791(13)
La(2)−O(13)	2.420(8)	I(4)–O(9)	1.823(8)	Ce(2)−O(13)	2.412(12)	I(4)–O(9)	1.815(12)
La(2)−O(14)	2.492(8)	I(4)–O(10)	1.798(9)	Ce(2)−O(14)	2.497(11)	I(4)–O(10)	1.803(10)
La(2)−O(16)	2.536(8)	I(4)–O(11)	1.789(8)	Ce(2)−O(16)	2.509(11)	I(4)–O(11)	1.790(13)
La(2)−O(17)	2.486(8)	I(5)–O(12)	1.813(9)	Ce(2)−O(17)	2.461(12)	I(5)–O(12)	1.811(11)
La(2)−O(21)	2.549(8)	I(5)–O(13)	1.810(8)	Ce(2)−O(21)	2.536(11)	I(5)–O(13)	1.803(11)
La(2)−O(22)	2.466(8)	I(5)–O(24)	1.823(8)	Ce(2)−O(22)	2.474(10)	I(5)–O(24)	1.832(11)
La(2)−O(24)	2.530(8)	I(6)–O(14)	1.831(8)	Ce(2)−O(24)	2.503(11)	I(6)–O(14)	1.836(11)
		I(6)–O(15)	1.804(8)			I(6)–O(15)	1.809(13)
		I(6)–O(16)	1.806(8)			I(6)–O(16)	1.812(11)
		I(7)–O(17)	1.840(8)			I(7)–O(17)	1.834(12)
		I(7)–O(18)	1.819(8)			I(7)–O(18)	1.777(12)
		I(7)–O(19)	1.786(9)			I(7)–O(19)	1.792(14)
		I(8)–O(20)	1.818(8)			I(8)–O(20)	1.810(10)
		I(8)–O(21)	1.842(8)			I(8)–O(21)	1.822(10)
		I(8)–O(22)	1.826(9)			I(8)–O(22)	1.807(9)

$NaSm(IO_3)_4$				$NaEu(IO_3)_4$			
Sm(1)−O(1)	2.35(2)	I(1)−O(1)	1.81(2)	Eu(1)−O(1)	2.374(12)	I(1)−O(1)	1.804(13)
Sm(1)−O(2)	2.33(2)	I(1)–O(2)	1.80(2)	Eu(1)−O(2)	2.324(13)	I(1)−O(2)	1.814(14)
Sm(1)−O(3)	2.38(2)	I(1)−O(23)	1.81(2)	Eu(1)−O(3)	2.380(14)	I(1)−O(23)	1.828(13)
Sm(1)−O(5)	2.49(2)	I(2)–O(3)	1.84(2)	Eu(1)−O(5)	2.476(14)	I(2)–O(3)	1.821(15)
Sm(1)−O(6)	2.47(2)	I(2)–O(4)	1.81(2)	Eu(1)−O(6)	2.402(13)	I(2)–O(4)	1.783(12)
Sm(1)−O(9)	2.61(2)	I(2)–O(5)	1.84(2)	Eu(1)−O(9)	2.627(15)	I(2)–O(5)	1.812(14)
Sm(1)−O(20)	2.401(17)	I(3)–O(6)	1.79(2)	Eu(1)−O(20)	2.450(13)	I(3)–O(6)	1.847(14)
Sm(1)−O(23)	2.43(2)	I(3)–O(7)	1.82(2)	Eu(1)−O(23)	2.424(13)	I(3)–O(7)	1.806(15)
Sm(2)−O(12)	2.33(2)	I(3)–O(8)	1.80(2)	Eu(2)−O(12)	2.334(11)	I(3)–O(8)	1.812(14)
Sm(2)−O(13)	2.367(18)	I(4)–O(9)	1.811(19)	Eu(2)−O(13)	2.329(13)	I(4)–O(9)	1.807(12)
Sm(2)−O(14)	2.45(2)	I(4)–O(10)	1.812(19)	Eu(2)−O(14)	2.429(12)	I(4)–O(10)	1.825(13)
Sm(2)−O(16)	2.47(2)	I(4)–O(11)	1.81(2)	Eu(2)−O(16)	2.455(13)	I(4)–O(11)	1.801(14)
Sm(2)−O(17)	2.42(2)	I(5)–O(12)	1.81(2)	Eu(2)−O(17)	2.446(14)	I(5)–O(12)	1.799(12)
Sm(2)−O(21)	2.50(2)	I(5)–O(13)	1.781(19)	Eu(2)−O(21)	2.432(12)	I(5)–O(13)	1.822(14)
Sm(2)−O(22)	2.427(17)	I(5)–O(24)	1.84(2)	Eu(2)−O(22)	2.403(13)	I(5)–O(24)	1.828(12)
Sm(2)−O(24)	2.447(19)	I(6)–O(14)	1.82(2)	Eu(2)−O(24)	2.437(12)	I(6)–O(14)	1.811(12)
		I(6)–O(15)	1.79(2)			I(6)–O(15)	1.832(13)
		I(6)–O(16)	1.78(2)			I(6)–O(16)	1.820(12)
		I(7)–O(17)	1.84(2)			I(7)–O(17)	1.806(15)
		I(7)–O(18)	1.78(2)			I(7)–O(18)	1.775(15)
		I(7)–O(19)	1.80(2)			I(7)–O(19)	1.803(14)
		I(8)–O(20)	1.86(2)			I(8)–O(20)	1.818(14)
		I(8)–O(21)	1.822(18)			I(8)–O(21)	1.841(12)
		I(8)–O(22)	1.812(17)			I(8)–O(22)	1.810(13)

Table S2. Crystallographic information for $NaLa_{1-x}Sm_x(IO_3)_4$ (x = 0-0.9) solid solutions

Formula	$NaLa(IO_3)_4$	$NaLa_{0.95}Sm_{0.05}(IO_3)_4$	$NaLa_{0.94}Sm_{0.06}(IO_3)_4$	$NaLa_{0.93}Sm_{0.07}(IO_3)_4$
FW (g mol^{-1})	861.51	862.08	862.19	862.31
Space group	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)
a (Å)	31.769(2)	31.759(7)	31.754(8)	31.7424(15)
b (Å)	5.7007(4)	5.6981(12)	5.6976(14)	5.6944(3)
c (Å)	12.9508(9)	12.940(3)	12.937(3)	12.9288(6)
β (°)	90.6558(15)	90.6714(12)	90.6752(16)	90.6929(7)
V ($Å^3$)	2345.3(5)	2341.6(14)	2340.4(17)	2336.7(3)
Z	8	8	8	8
2θ range (°)	10-110	15-70	15-70	15-110
R_p	4.28	9.69	10.31	4.41
R_{wp}	5.55	12.91	13.67	5.73
R_{exp}	3.98	11.45	11.41	4.10
χ^2	1.988	1.326	1.497	2.006
Goodness of fit	1.41	1.15	1.22	1.42

Formula	$NaLa_{0.92}Sm_{0.08}(IO_3)_4$	$NaLa_{0.91}Sm_{0.09}(IO_3)_4$	$NaLa_{0.90}Sm_{0.10}(IO_3)_4$	$NaLa_{0.89}Sm_{0.11}(IO_3)_4$
FW (g mol^{-1})	862.42	862.54	862.65	862.77
Space group	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)
a (Å)	31.741(7)	31.740(9)	31.732(2)	31.724(10)
b (Å)	5.6944(13)	5.6941(15)	5.6919(4)	5.6893(18)
c (Å)	12.929(3)	12.928(4)	12.9223(9)	12.917(4)
β (°)	90.6839(16)	90.6910(17)	90.6960(10)	90.6964(1)
V ($Å^3$)	2336.7(16)	2336.4(19)	2333.8(5)	2331(2)
Z	8	8	8	8
2θ range (°)	15-70	15-70	15-110	15-70
R_p	9.30	9.41	4.50	9.17
R_{wp}	12.36	12.46	6.17	12.43
R_{exp}	11.63	11.83	4.10	11.55
χ^2	1.178	1.158	2.313	1.208
Goodness of fit	1.09	1.08	1.52	1.10

Formula	$NaLa_{0.88}Sm_{0.12}(IO_3)_4$	$NaLa_{0.87}Sm_{0.13}(IO_3)_4$	$NaLa_{0.80}Sm_{0.20}(IO_3)_4$	$NaLa_{0.70}Sm_{0.30}(IO_3)_4$
FW (g mol^{-1})	862.88	863.00	863.80	864.94
Space group	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)
a (Å)	31.718(13)	31.715(10)	31.703(11)	31.6610(24)
b (Å)	5.689(2)	5.6875(18)	5.6835(20)	5.6737(4)
c (Å)	12.915(5)	12.910(4)	12.898(5)	12.8674(10)
β (°)	90.698(2)	90.7115(18)	90.735(2)	90.7653(10)
V ($Å^3$)	2330(3)	2329(2)	2324(3)	2311.2(5)
Z	8	8	8	8
2θ range (°)	15-70	15-70	15-70	15-110
R_p	10.02	8.89	9.03	4.03
R_{wp}	13.50	11.82	11.90	5.18
R_{exp}	12.12	11.18	11.44	4.00
χ^2	1.293	1.166	1.128	1.710
Goodness of fit	1.14	1.08	1.06	1.31

Formula	$NaLa_{0.60}Sm_{0.40}(IO_3)_4$	$NaLa_{0.50}Sm_{0.50}(IO_3)_4$	$NaLa_{0.30}Sm_{0.70}(IO_3)_4$	$NaLa_{0.10}Sm_{0.90}(IO_3)_4$	$Sm(IO_3)_3$:La
FW (g mol^{-1})	866.09	867.23	869.52	871.81	> 675.07[a]
Space group	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)	$P2_1/a$ (No. 14)
a (Å)	31.637(16)	31.583(3)	31.529(3)	31.465(5)	31.67(9)
b (Å)	5.665(3)	5.6546(6)	5.6417(6)	5.6239(10)	8.72(6)
c (Å)	12.844(6)	12.8100(13)	12.7663(14)	12.718(2)	7.29(5)
β (°)	90.804(3)	90.8387(14)	90.8932(12)	90.945(2)	99.94(5)
V ($Å^3$)	2302(3)	2287.5(7)	2270.6(7)	2250.4(12)	855(17)
Z	8	8	8	8	4
2θ range (°)	15-70	15-110	15-110	15-110	
R	9.08	3.80	4.67	4.78	
R_{wp}	11.87	4.87	6.01	6.27	
R_{exp}	10.94	3.95	3.75	3.73	
χ^2	1.229	1.556	2.633	2.633	
Goodness of fit	1.11	1.25	1.62	1.70	

[a] FW of $Sm(IO_3)_3$.

Table S3. Atomic ratios for $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu) determined by EDX analyses.

Compounds	$NaLa(IO_3)_4$	$NaCe(IO_3)_4$	$NaSm(IO_3)_4$	$NaEu(IO_3)_4$
Ln	1.0	1.0	1.0	1.0
Na	1.2	1.1	0.9	0.8
I	3.8	4.0	3.9	4.1
O	11.5	11.1	11.4	11.2

Table S4. Bond-valence sum calculations for $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

	$NaLa(IO_3)_4$	$NaCe(IO_3)_4$	$NaSm(IO_3)_4$	$NaEu(IO_3)_4$
Na(1)	0.93	0.93	0.94	1.02
Na(2)	0.90	0.89	1.00	0.97
Ln(1)	3.35	3.26	3.22	3.13
Ln(2)	3.47	3.38	3.24	3.29
I(1)	5.08 (5.54)[a]	4.96 (5.39)[a]	5.05 (5.50)[a]	4.98 (5.44)[a]
I(2)	4.93 (5.37)[a]	5.02 (5.42)[a]	4.82 (5.22)[a]	5.12 (5.54)[a]
I(3)	5.09 (5.33)[a]	5.08 (5.30)[a]	5.11 (5.37)[a]	4.90 (5.15)[a]
I(4)	5.16 (5.33)[a]	5.15 (5.32)[a]	5.06 (5.29)[a]	5.04 (5.25)[a]
I(5)	4.98 (5.45)[a]	4.99 (5.47)[a]	5.04 (5.54)[a]	4.97 (5.51)[a]
I(6)	5.01 (5.49)[a]	4.94 (5.41)[a]	5.23 (5.72)[a]	4.91 (5.41)[a]
I(7)	4.99 (5.22)[a]	5.19 (5.42)[a]	5.12 (5.37)[a]	5.27 (5.53)[a]
I(8)	4.81 (5.21)[a]	5.01 (5.46)[a]	4.79 (5.29)[a]	4.88 (5.39)[a]

[a] also consideration of I···O interaction with the bond length of 2.48-3.16 Å.

Table S5. Calculated dipole moments for LnO_8 and IO_3 polyhedra for $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

Compounds	$NaLa(IO_3)_4$	$NaCe(IO_3)_4$	$NaSm(IO_3)_4$	$NaEu(IO_3)_4$
$Ln(1)O_8$	1.60	1.86	1.88	1.82
$Ln(2)O_8$	0.94	0.94	0.97	1.08
$I(1)O_3$	17.0	16.6	16.3	16.7
$I(2)O_3$	14.4	14.6	13.6	15.2
$I(3)O_3$	14.7	14.6	15.4	14.0
$I(4)O_3$	15.0	15.1	14.8	15.1
$I(5)O_3$	16.5	16.5	16.9	16.5
$I(6)O_3$	15.2	15.3	16.8	15.1
$I(7)O_3$	14.2	15.3	14.6	16.2
$I(8)O_3$	15.5	16.3	14.8	15.9

Table S6. Net direction of dipole moments for IO_3 polyhedra in $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

Compounds	Anionic groups	Direction of Dipole moments			Dipole moments (Debye)	Approximate direction
		x	*y*	*z*		
NaLa(IO3)4	I(1)O3	16.497	-4.029	0.694	17.0	[1 -1 0]
	I(2)O3	13.069	4.802	3.807	14.4	[1 3 0]
	I(3)O3	1.450	14.623	1.035	14.7	[0 1 0]
	I(4)O3	13.365	2.178	-6.535	15.0	[1 1 -1]
	I(5)O3	-16.113	3.457	0.019	16.5	[-1 1 0]
	I(6)O3	-13.142	-6.986	-3.198	15.2	[-1 -3 -1]
	I(7)O3	-0.668	-14.203	-0.595	14.2	[0 -1 0]
	I(8)O3	0.104	-2.726	-15.284	15.5	[0 -1 -2]
	La(1)O8	1.158	0.314	-1.066	1.60	[1 2 -3]
	La(2)O8	-0.807	0.456	-0.169	0.94	[-1 3 -1]
	Total	**14.914**	**-2.114**	**-21.292**	26.1	[1 -1 -4]
NaCe(IO3)4	I(1)O3	16.224	-3.650	0.786	16.6	[1 -1 0]
	I(2)O3	12.808	5.366	4.410	14.6	[1 3 0]
	I(3)O3	1.521	14.495	0.517	14.6	[0 1 0]
	I(4)O3	13.391	2.458	-6.549	15.1	[1 1 -1]
	I(5)O3	-16.164	3.246	0.275	16.5	[-1 1 0]
	I(6)O3	-13.283	-6.790	-3.506	15.3	[-1 -3 -1]
	I(7)O3	-0.626	-15.179	-1.612	15.3	[0 -1 0]
	I(8)O3	0.430	-2.489	-16.074	16.3	[0 -1 -2]
	Ce(1)O8	1.382	0.719	-1.041	1.87	[1 2 -3]
	Ce(2)O8	-0.821	0.444	0.201	0.95	[-1 3 -1]
	Total	**14.861**	**-1.378**	**-22.593**	27.1	[1 -1 -4]
NaSm(IO3)4	I(1)O3	15.899	-3.551	0.619	16.3	[1 -1 0]
	I(2)O3	11.674	5.539	4.174	13.6	[1 3 0]
	I(3)O3	2.256	15.197	0.703	15.4	[0 1 0]
	I(4)O3	12.835	2.234	-7.064	14.8	[1 1 -1]
	I(5)O3	-16.573	3.023	1.052	16.9	[-1 1 0]
	I(6)O3	-14.387	-7.678	-4.185	16.8	[-1 -3 -1]
	I(7)O3	-1.251	-14.446	-1.875	14.6	[0 -1 0]
	I(8)O3	0.971	-2.360	-14.574	14.8	[0 -1 -3]
	Sm(1)O8	1.214	0.699	-1.254	1.88	[1 2 -3]
	Sm(2)O8	-0.808	0.463	0.052	0.93	[-1 3 -1]
	Total	**11.829**	**-0.880**	**-22.353**	25.3	[1 -0-5]
NaEu(IO3)4	I(1)O3	16.346	-3.251	0.135	16.7	[1 -1 0]
	I(2)O3	13.122	5.982	4.871	15.2	[1 3 0]
	I(3)O3	0.761	13.919	0.762	14.0	[0 1 0]
	I(4)O3	13.132	2.741	-6.842	15.1	[1 1 -1]
	I(5)O3	-16.095	3.413	-0.246	16.5	[-1 1 0]
	I(6)O3	-13.462	-5.941	-3.402	15.1	[-1 -3 -1]
	I(7)O3	-1.731	-15.851	-2.691	16.2	[0 -1 0]
	I(8)O3	0.709	-2.828	-15.605	15.9	[0 -1 -2]
	Eu(1)O8	0.608	0.809	-1.528	1.83	[1 2 -3]
	Eu(2)O8	-0.951	0.437	-0.279	1.08	[-1 3 -1]
	Total	**12.439**	**-0.570**	**-24.824**	27.8	[1 -0-5]

Table S7. Fitted values of decay curves for $NaLa_{0.93}Sm_{0.07}(IO_3)_4$ and $NaEu(IO_3)_4$

	$NaLa_{0.93}Sm_{0.07}(IO_3)_4$		$NaLa_{0.93}Sm_{0.07}(IO_3)_4$		$NaEu(IO_3)_4$	
Model	Inokuti and Hirayama		Second-order exponential		First-order exponential	
Equation	$I(t) = I_0 + A\exp\left[-\frac{t}{\tau_0} - a\left(\frac{t}{\tau_0}\right)^{3/s}\right]$		$I(t) = B + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$		$I(t) = I_0 + A\exp(-t/\tau_0)$	
Constants	I_0	10678.984	B	9850.890	I_0	2057
	A	23732.016	A_1	14180.536	A	57938
	a	0.472	A_2	10379.575		
Lifetime (μs)	τ_0	59.9	τ_1	17.5	τ_0	716
			τ_2	95.7		
			$\tau_{avg}{}^{a}$	80.1		

[a] $\tau_{avg} = (A_1\tau_1^2+A_2\tau_2^2)/(A_1\tau_1+A_2\tau_2)$

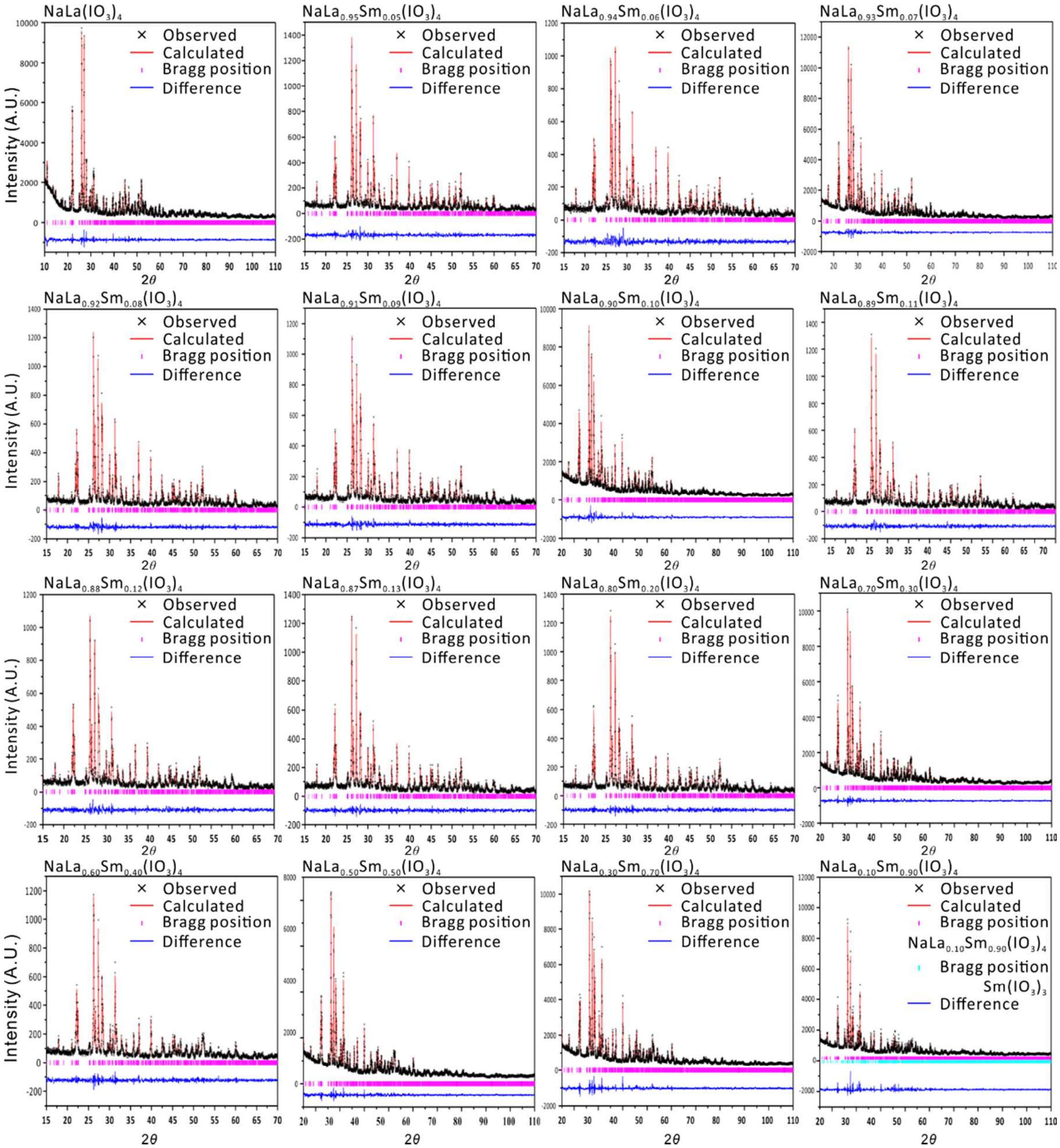

Figure S1. Rietveld plots for $NaLa(IO_3)_4$ and Sm^{3+}-doped solid solutions (observed, black cross; calculated, red line; Bragg positions, magenta or cyan bar; difference, blue line).

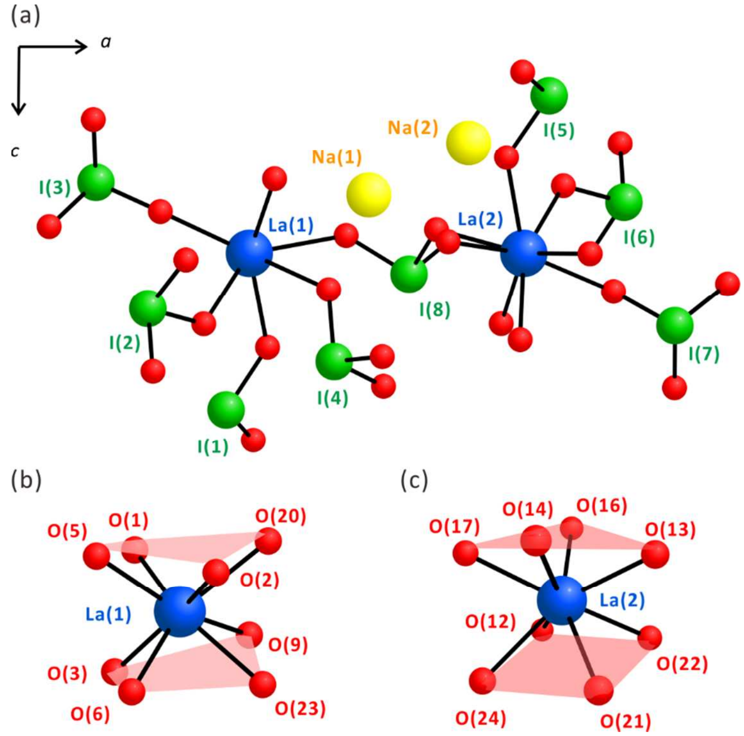

Figure S2. Ball-and-stick representations of (a) an asymmetric unit, (b) La(1)O_8, and (c) La(2)O_8 polyhedra in $NaLa(IO_3)_4$.

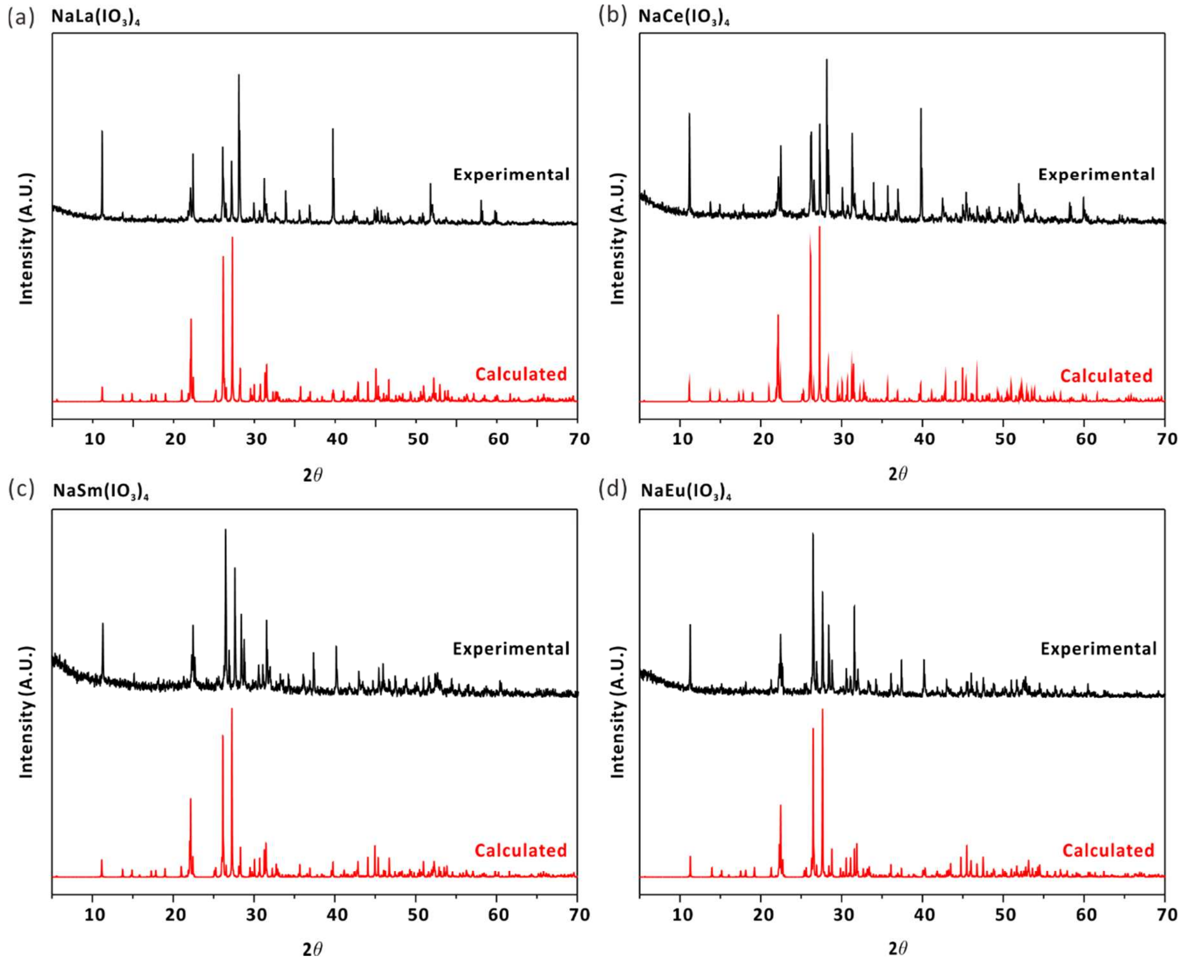

Figure S3. PXRD patterns for $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

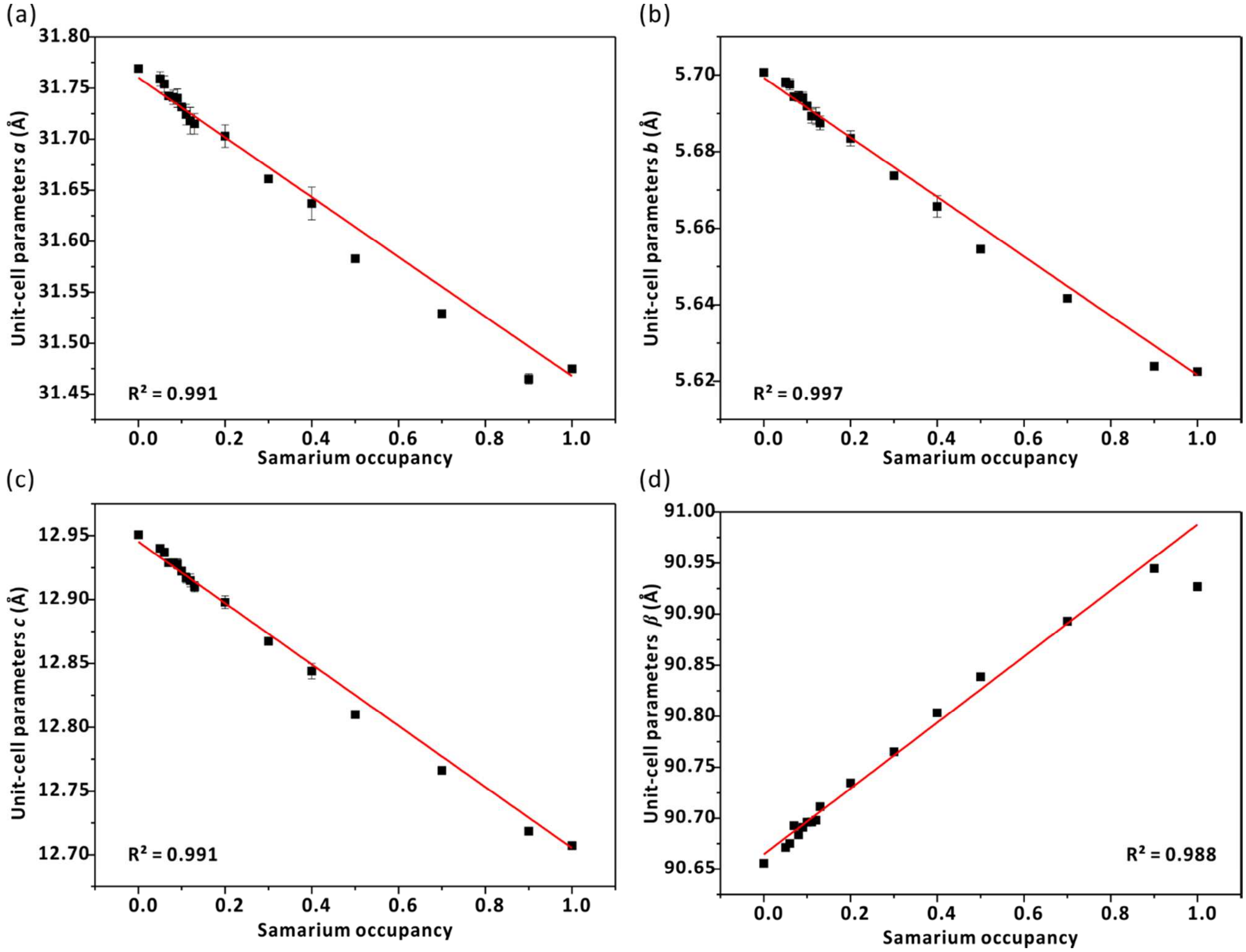

Figure S4. Variation of the unit cell parameters (a) *a*, (b) *b*, (c) *c*, and (d) *β* as a function of the samarium contents for $NaLa_{1-x}Sm_x(IO_3)_4$.

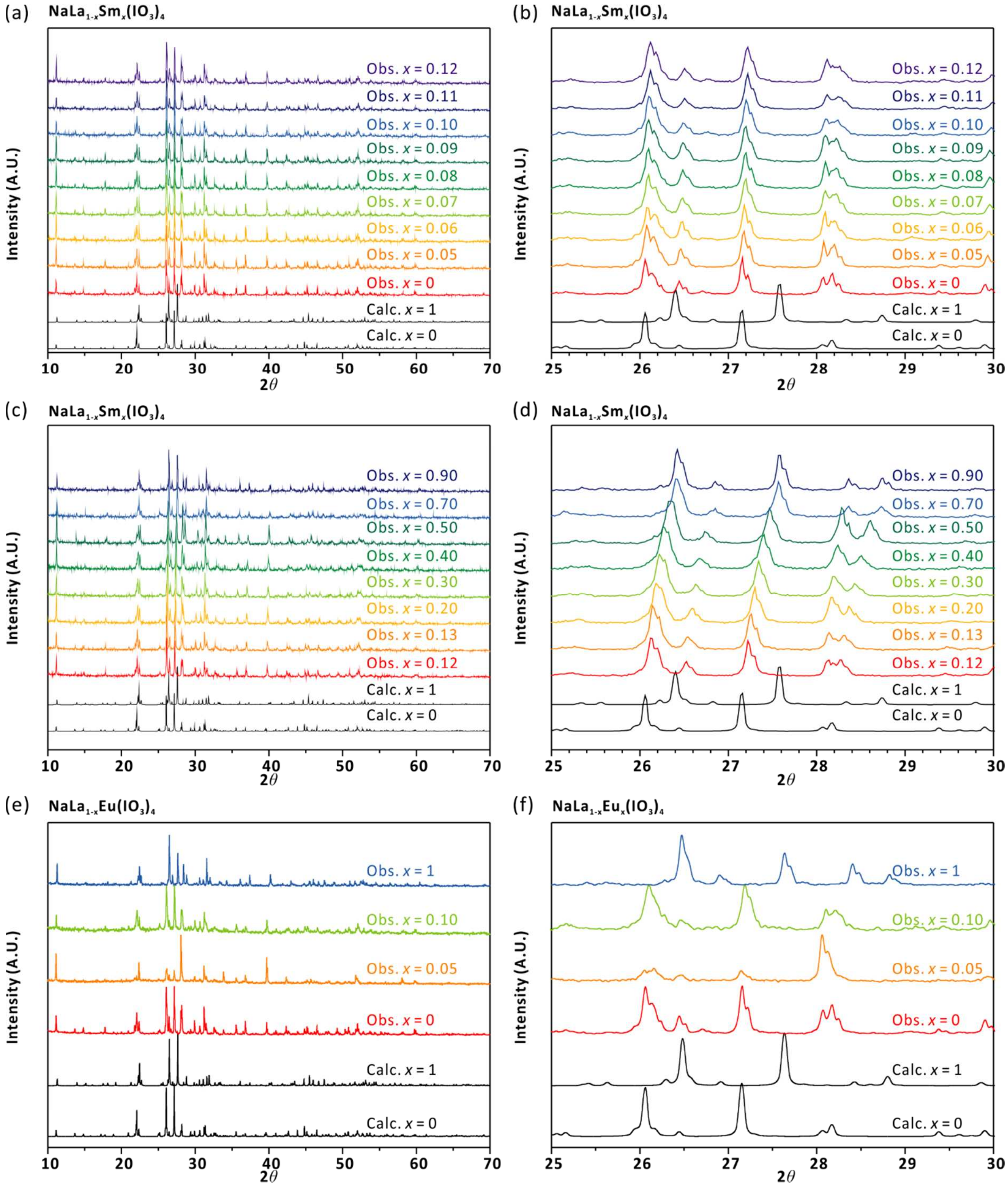

Figure S5. PXRD patterns for $NaLa_{1-x}Sm_x(IO_3)_4$ and $NaLa_{1-x}Eu_x(IO_3)_4$ ($0 \le x \le 1$).

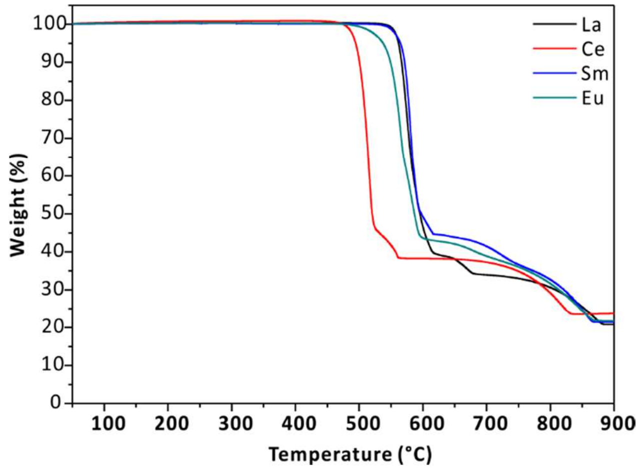

Figure S6. TGA diagrams for $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

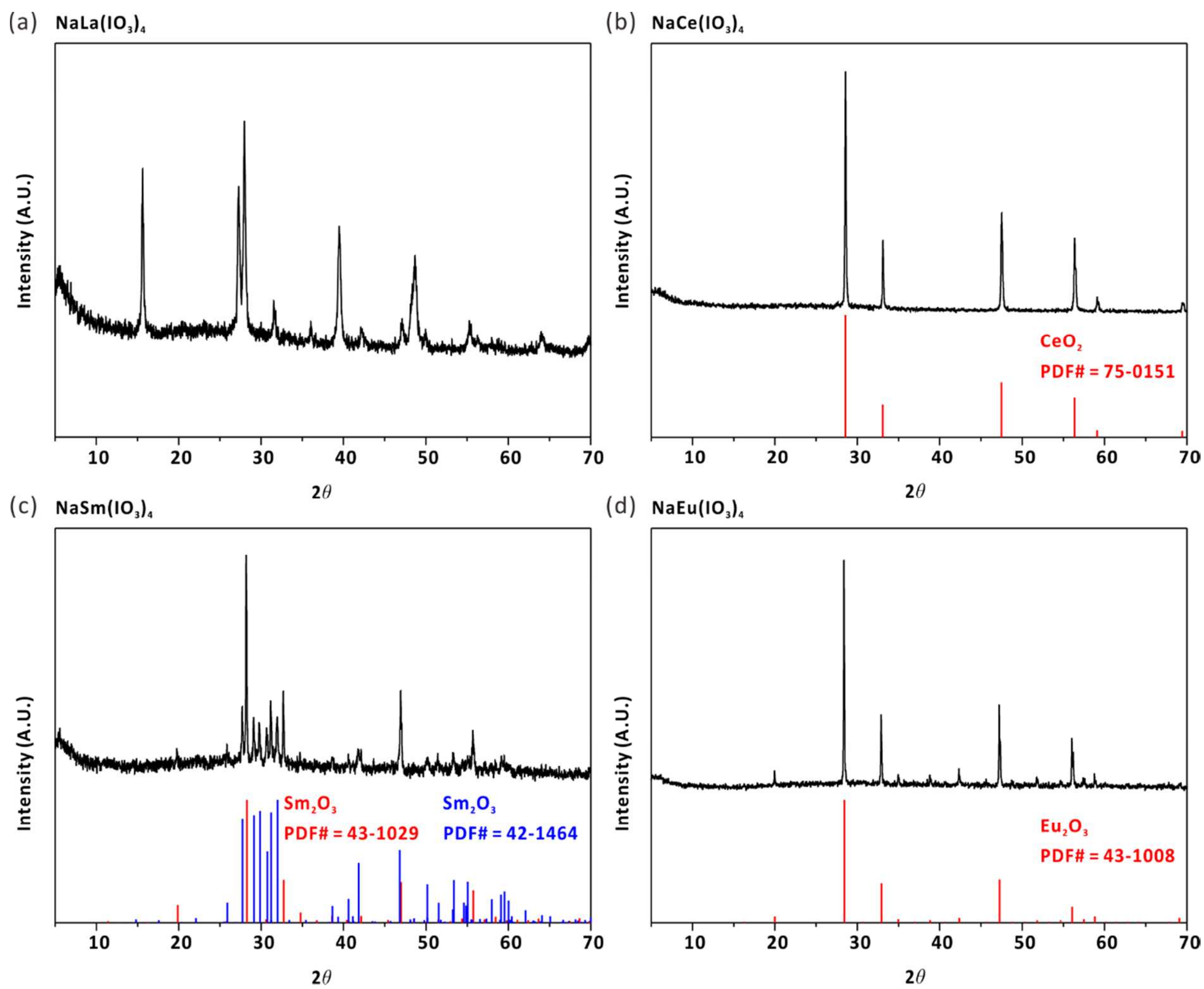

Figure S7. PXRD patterns of the calcined products of $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

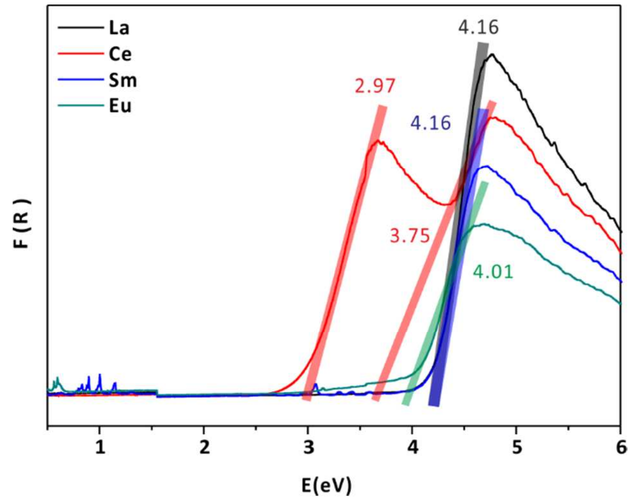

Figure S8. UV-Vis diffuse reflectance spectra for $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu).

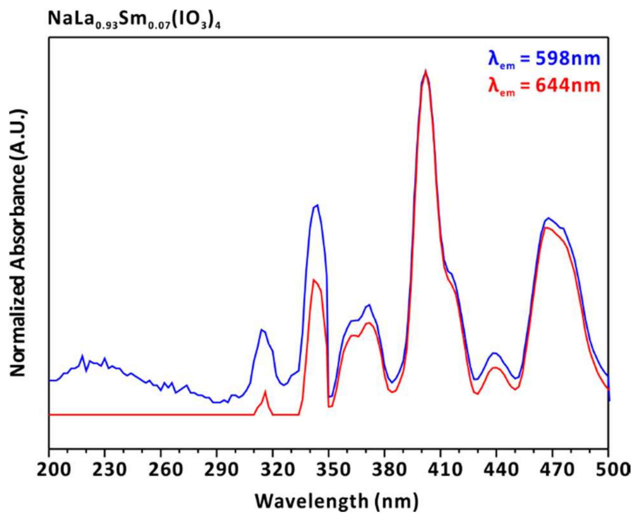

Figure S9. Excitation spectra of $NaLa_{0.93}Sm_{0.07}(IO_3)_4$ for 598 nm (blue) and 644 nm (red) emissions.

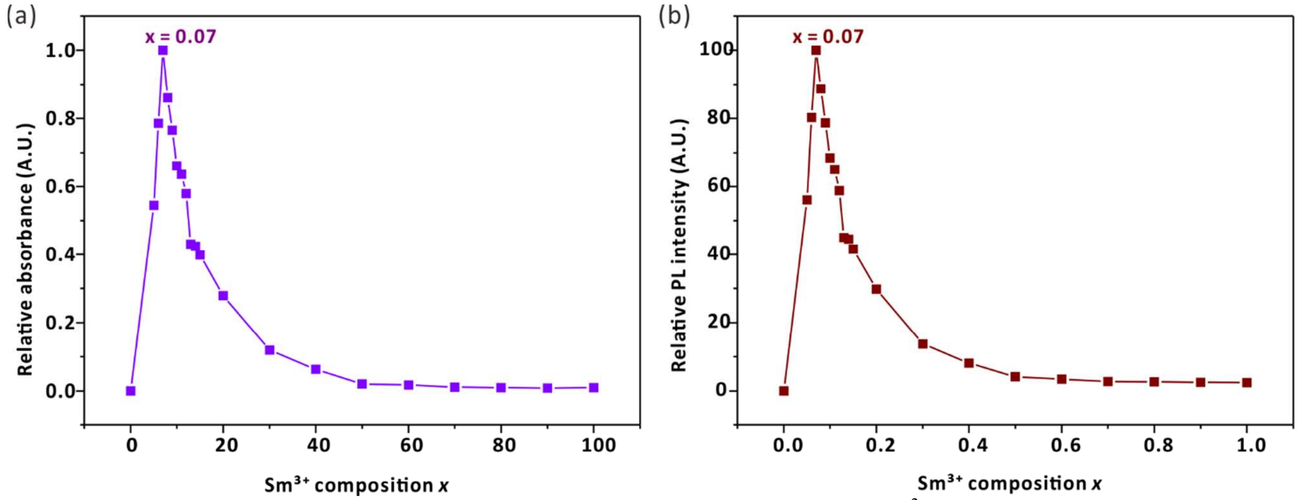

Figure S10. Plots of PL intensities for $NaLa_{1-x}Sm_x(IO_3)_4$ as a function of Sm^{3+} concentration ((a) excitation and (b) emission).

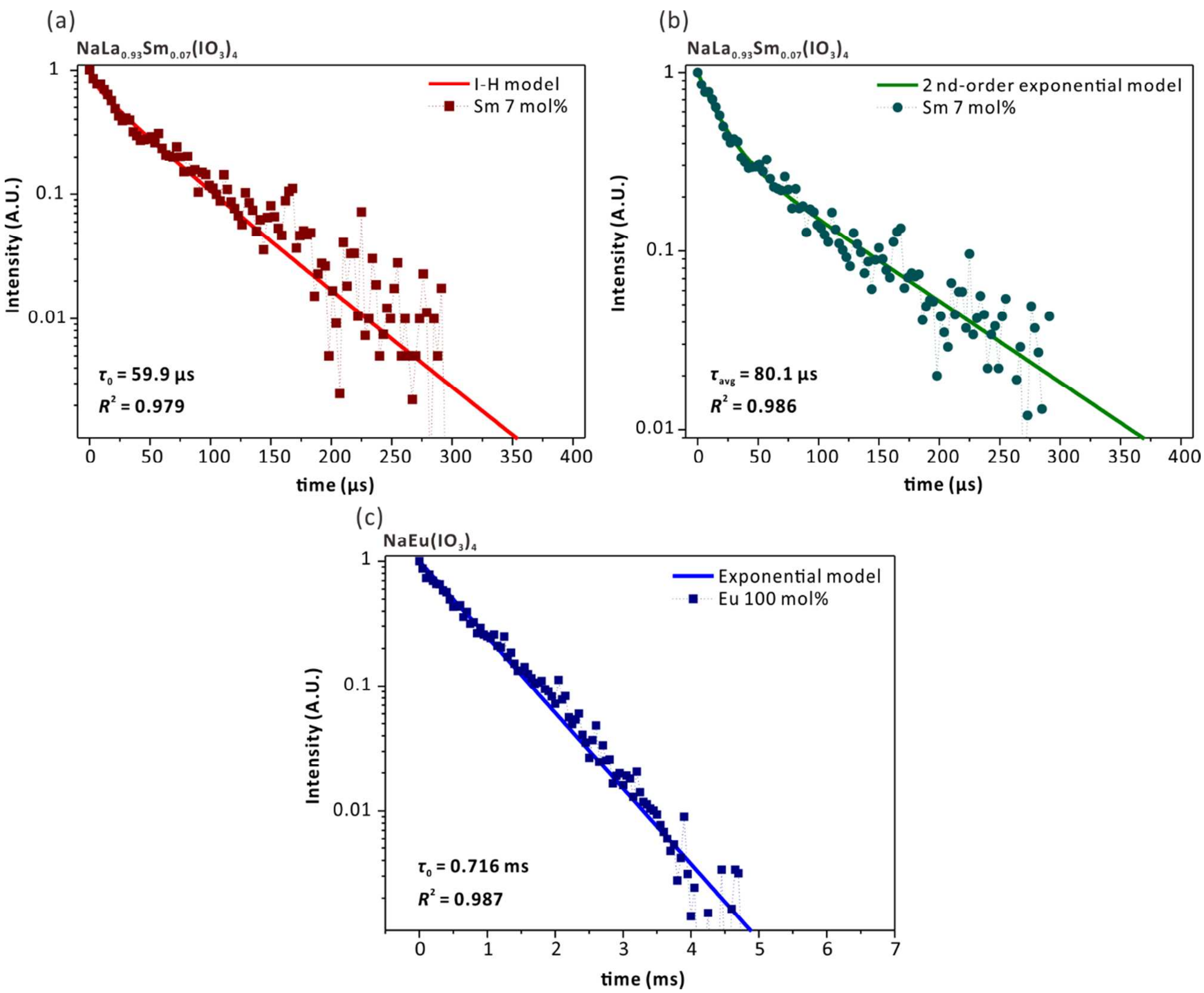

Figure S11. Decay curves of $NaLa_{0.93}Sm_{0.07}(IO_3)_4$ and $NaEu(IO_3)_4$.