Supporting Information

$[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga, In): metal iodate-selenate nonlinear optical materials with hexagonal tungsten oxide-type topology

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Table S1. Selected bond lengths (Å) and the calculated total BVS values for $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga **1**, In **2**).

1		**2**	
Ga(1)-O(1)	1.944(2)	In(1)-O(1)	2.121(3)
Ga(1)-O(1)#1	1.944(2)	In(1)-O(1)#1	2.121(3)
Ga(1)-O(2)	1.922(2)	In(1)-O(2)	2.094(3)
Ga(1)-O(2)#4	1.922(2)	In(1)-O(2)#4	2.094(3)
Ga(1)-O(3)	2.000(7)	In(1)-O(3)	2.162(8)
Ga(1)-O(4)	2.067(7)	In(1)-O(4)	2.205(8)
BVS (Ga)	3.20	**BVS (In)**	3.23
I(1)-O(3)	1.807(6)	I(1)-O(3)	1.797(8)
I(1)-O(3)#1	1.807(6)	I(1)-O(3)#1	1.797(8)
I(1)-O(3)#2	1.807(6)	I(1)-O(3)#2	1.797(8)
BVS (I)	5.10	**BVS (I)**	5.24
Se(1)-O(4)	1.646(7)	Se(1)-O(4)	1.635(9)
Se(1)-O(4)#3	1.646(7)	Se(1)-O(4)#3	1.635(9)
Se(1)-O(4)#4	1.646(7)	Se(1)-O(4)#4	1.635(9)
Se(1)-O(5)	1.616(11)	Se(1)-O(5)	1.606(15)
BVS (Se)	6.00	**BVS (Se)**	6.17
O(1)-H(1)	0.7920	O(1)-H(1)	0.8353
O(2)-H(2)	0.8196	O(2)-H(2)	0.8565

Symmetry transformations used to generate equivalent atoms: #1 -x+y, -x, z; #2 -y, x-y, z; #3 -x+y, -x+1, z; #4 -y+1, x-y+1, z.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga **1**, In **2**).

1				
Atom	**x**	**y**	**z**	**U(eq)**
Ga(1)	1673.0(9)	3346.0(17)	5086.1(10)	8.1(2)
I(1)	0	0	2785.4(8)	9.6(2)
Se(1)	3333.33	6666.67	7214.3(11)	8.0(3)
O(1)	-1245(5)	1245(5)	5490(5)	10.8(12)
O(2)	757(10)	5379(5)	4779(6)	11.5(13)
O(3)	1283(5)	2566(10)	3476(6)	13.3(13)
O(4)	2097(5)	4194(10)	6744(6)	12.6(13)
O(5)	3333.33	6666.67	8556(9)	15(3)
O(1W)	-3333.33	3333.33	6861(15)	47(5)
2				
Atom	**x**	**y**	**z**	**U(eq)**
In(1)	1675.9(6)	3351.7(12)	5118.0(9)	10.33(19)
I(1)	0	0	2758.4(9)	14.9(3)
Se(1)	3333.33	6666.67	7299.9(13)	12.3(4)
O(1)	-1243(6)	1243(6)	5635(6)	13.7(17)
O(2)	714(12)	5357(6)	4711(6)	17.7(18)
O(3)	1189(6)	2379(12)	3431(7)	21.1(19)
O(4)	2194(6)	4388(13)	6831(6)	22(2)
O(5)	3333.33	6666.67	8615(12)	20(4)
O(1W)	-3333.33	3333.33	6940(20)	89(10)

Table S3. The assignments of the infrared absorption peaks for $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga, In).

IR peak (cm^{-1})	Assignment
3700-3200	O-H stretching bands
1637	H-O-H bending mode
1130-950	v_3 asymmetric stretching of Se-O
950-823	v_3 asymmetric stretching of I-O
823-670	v_1 symmetric stretching of I-O
630-400	v_4 asymmetric bending of Se-O and v_2 symmetric bending of I-O

Table S4. Calculated dipole moments for GaO_6, IO_3, and SeO_4, as well as net dipole moment for a unit cell in $[Ga(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$.

$[Ga(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (Z = 2)				
Polar unit	Dipole moment (D = Debyes)			
	total magnitude	x-component	y-component	z-component
$Ga(1)O_6$	0.827	(±0.004)×3	(±0.079) ×3	(0.823)×6
$I(1)O_3$	13.891	0×2	$\pm 8.824\times10^{-6}$	13.891×2
$Se(1)O_4$	0.162	0×2	$\pm 8.994\times10^{-5}$	(-0.162)×2
Net dipole moment (a unit cell)	32.396	0	0	32.396

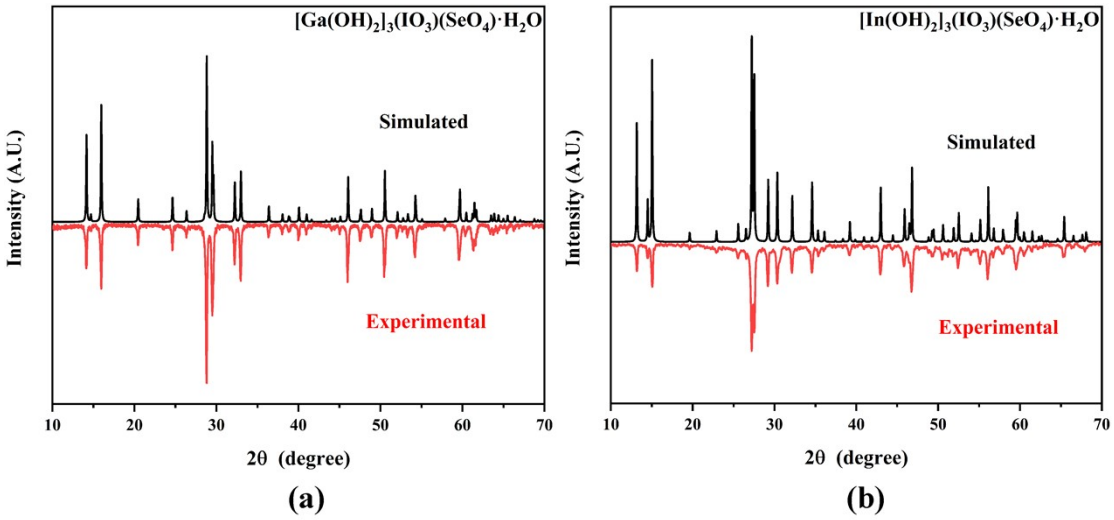

Figure S1. Simulated and experimental powder X-ray diffraction patterns of $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)).

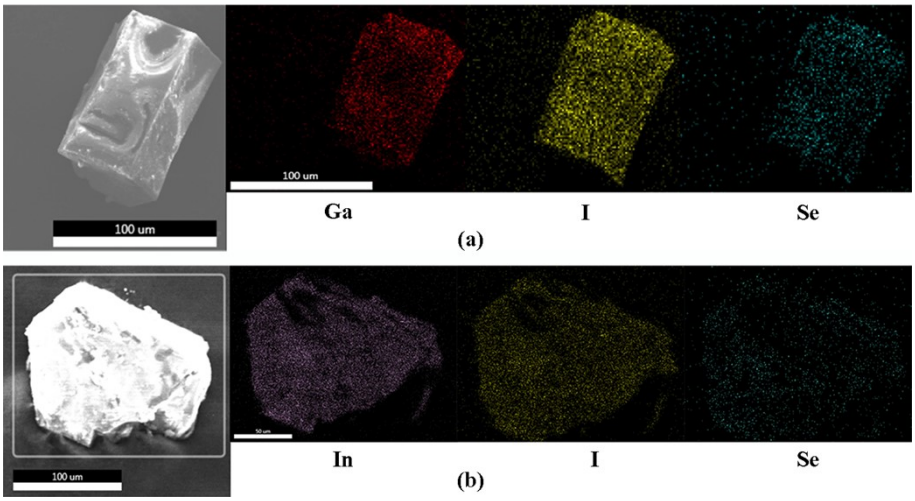

Figure S2. SEM images and their elemental distribution maps of $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)).

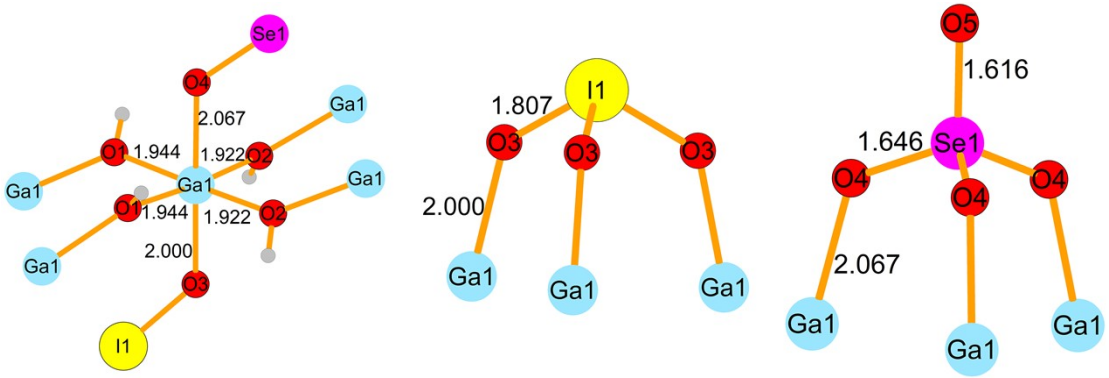

Figure S3. The coordination geometries around the Ga^{3+}, I^{5+} and Se^{6+} ions in $[Ga(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$.

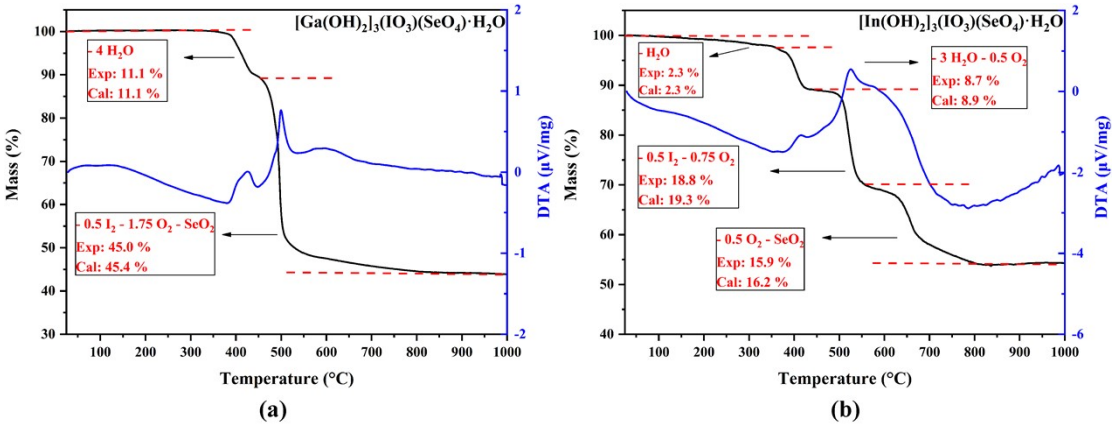

Figure S4. TGA and DTA curves of $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)) under the N_2 atmosphere.

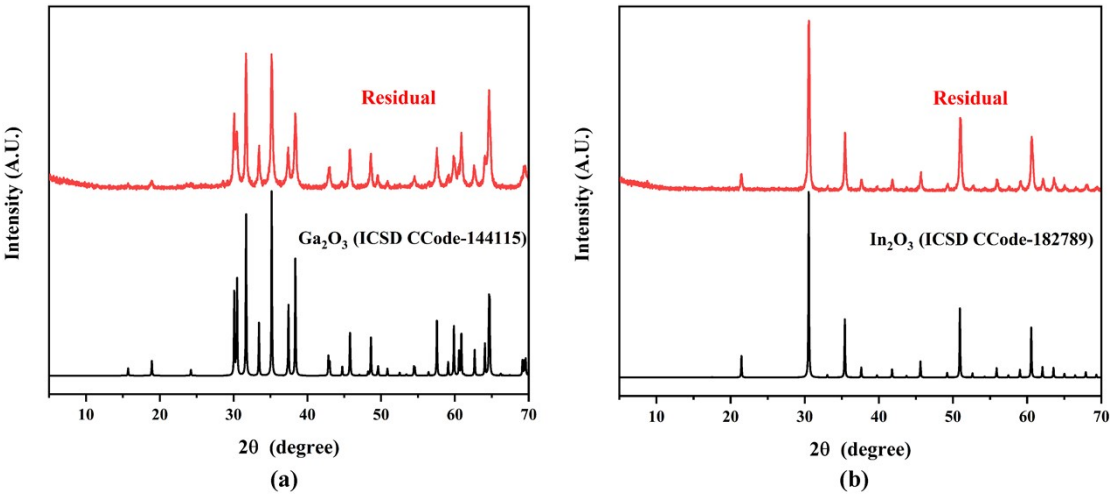

Figure S5. The powder X-ray diffraction patterns of the residuals of $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)) after decomposition at 1000 °C.

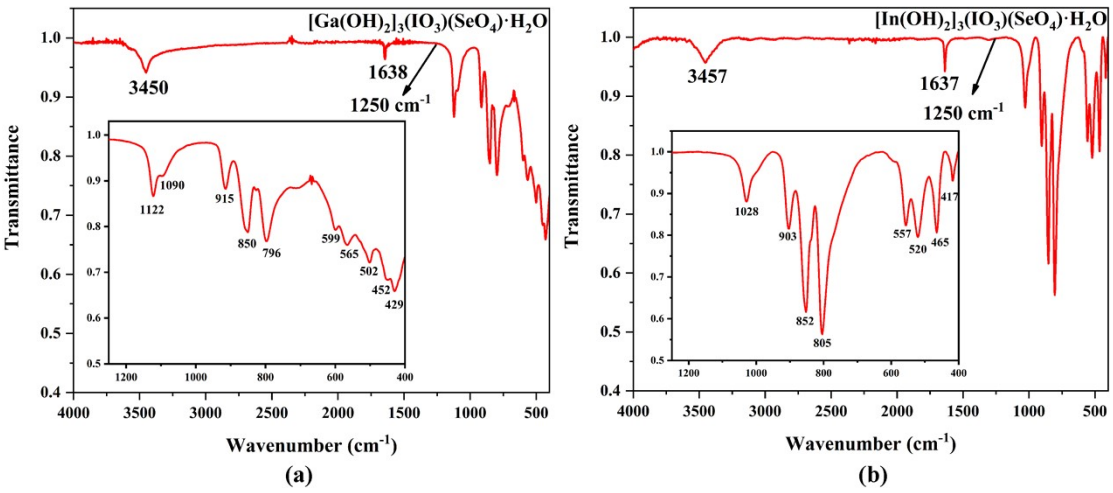

Figure S6. IR spectra for $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)).

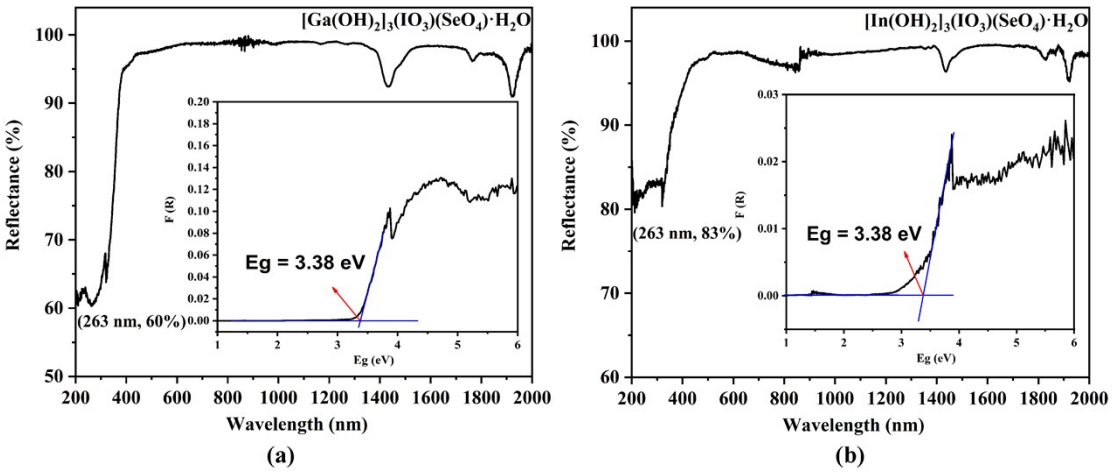

Figure S7. UV-vis-IR spectra of $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)).

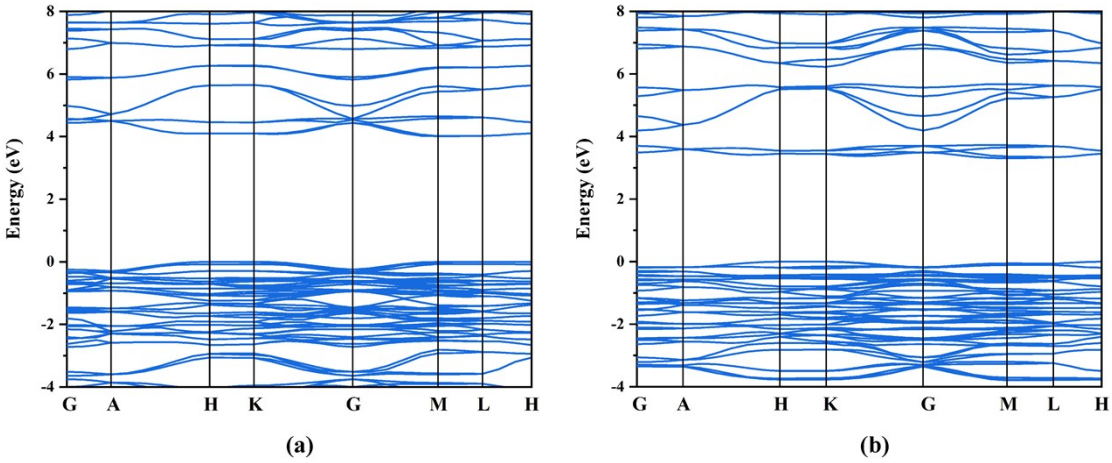

Figure S8. The calculated band structure of $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)).

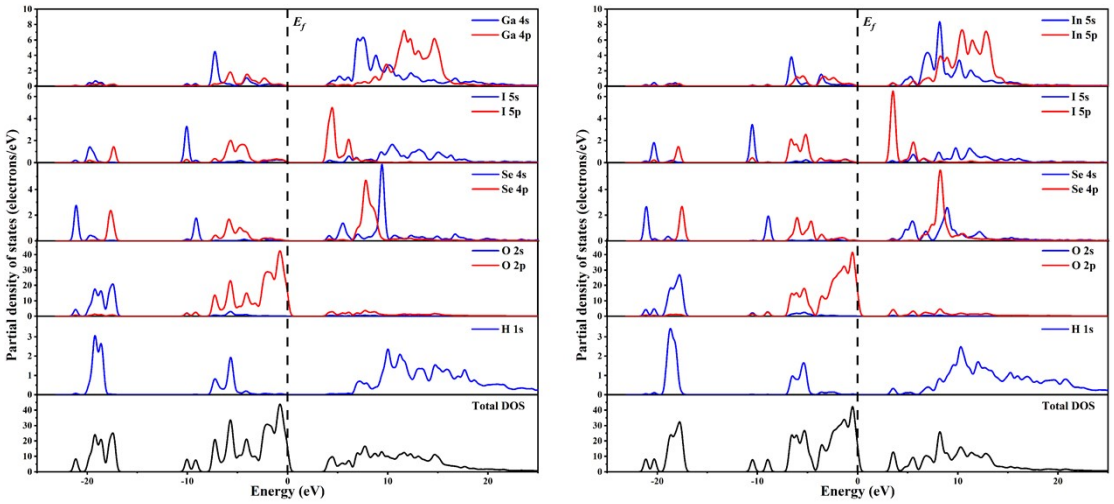

Figure S9. The partial and total density of states for $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)).

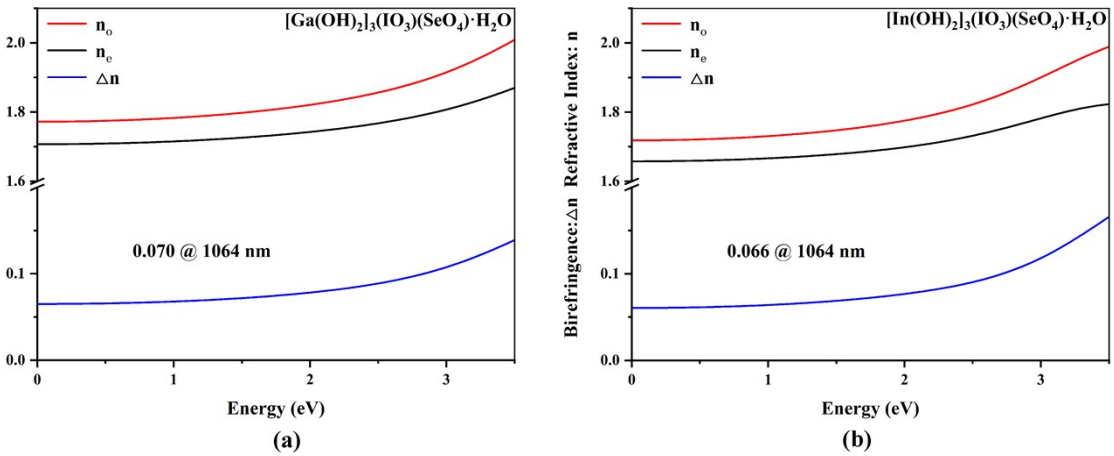

Figure S10. The calculated refractive indices for $[M(OH)_2]_3(IO_3)(SeO_4)\cdot H_2O$ (M = Ga (a), In (b)).