Supporting Information

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Detailed MW program for the synthesis of α-$La(IO_3)_3$, $La(IO_3)_3(H_2O)$ and $La(IO_3)_3HIO_3$

The MW program used for the synthesis of the different lanthanum iodate polymorphs was composed of 3 steps: a first dwell at 800 W for 3 min, followed by a second dwell at 850 W for 5 min, and finally a last dwell at 600 W whose duration was adjusted to change the maximal synthesis temperature (**Figure S1**). If the temperature and pressure are too close to the limiting conditions of the MW oven (T_{limit} = 280°C and P_{limit} = 80 bar), the MW power are automatically adjusted (**Figure S2**). After the third dwell, the MW program was then stopped, allowing the temperature (and pressure) to decrease down to room temperature (resp. 1 bar) within 20 min.

The temperature and pressure inside the MW oven depend on the quantity of HIO_3 introduced. For the precipitate resulting from a $[La^{3+}]$:$[IO_3^-]$ molar ratio of 1:20, the temperature (resp. pressure) inside the reactor reaches 180°C (resp. 30 bars) at the beginning of the third dwell (**Figure S1**), whereas for a molar ratio of 1:3 the temperature is already at 230°C at the beginning of the third dwell and the pressure at 78 bars, leading to an automatic MW power adjustment to remain in the operating conditions of the equipment (maximal pressure = 80 bars) (**Figure S2**).

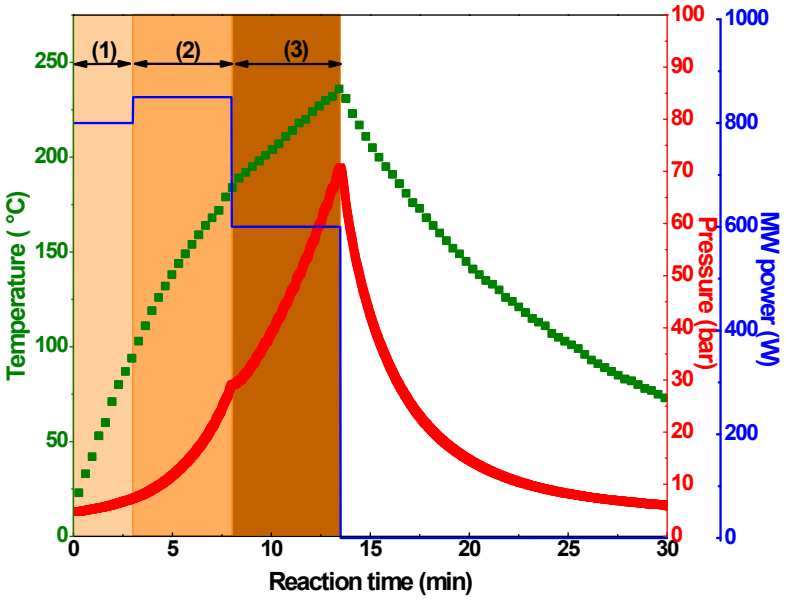
(1)
(2)
(3)
Temperature (°C)
Pressure (bar)
MW power (W)
Reaction time (min)
0
50
100
150
200
250
0
10
20
30
40
50
60
70
80
90
100
0
200
400
600
800
1000
0
5
10
15
20
25
30

Figure S1: *A typical MW program (blue) and associated temperature (green) and pressure (red). The program is composed of 3 steps: (1) a 3-min dwell at 800 W, (2) a 5-min dwell at 850 W and (3) a dwell at 600 W with variable durations. The indicated temperature and pressure were obtained when heating the precipitate resulting from mixing $LaCl_3 \cdot 6H_2O$ and HIO_3 in a molar ratio 1:20.*

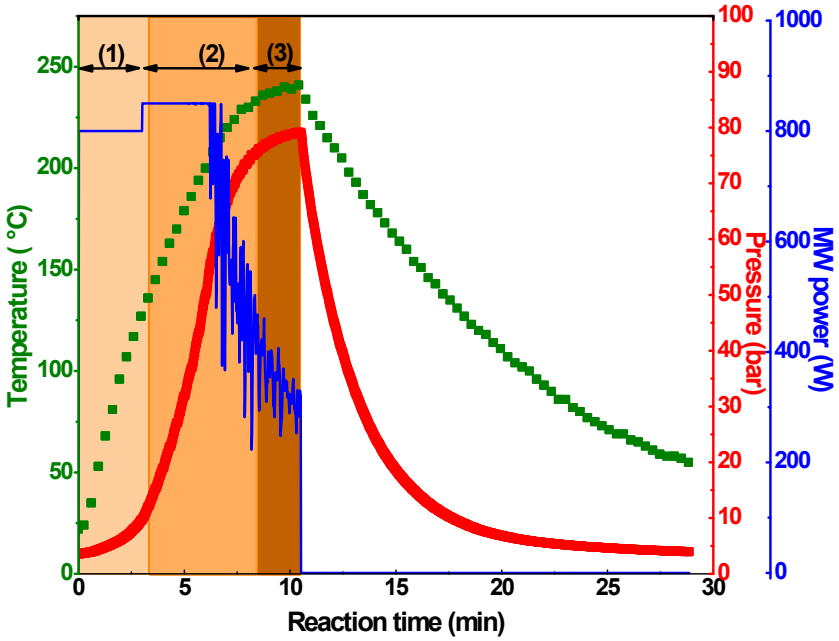

Figure S2: *MW program (blue) and associated temperature (green) and pressure (red) obtained when heating the precipitate resulting from mixing $LaCl_3 \cdot 6H_2O$ and HIO_3 in a molar ratio 1:3. Note that the MW power of the second dwell is kept lower than the programmed one so that the pressure remains below the operating limit of the oven (80 bars).*

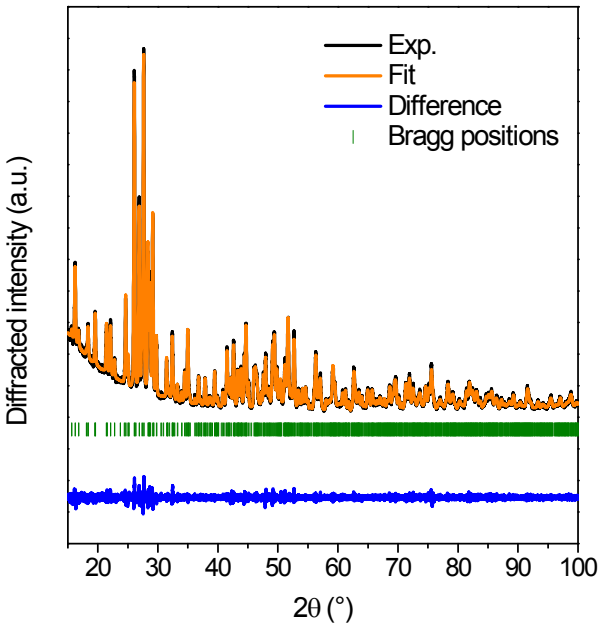

Figure S3. *Powder XRD pattern of $La(IO_3)_3(H_2O)$ refined via the LeBail method, in the $P2_1/n$ space group. The refined cell parameters are a = 7.195(1) Å, b = 13.261(2) Å, c = 9.808(1) Å, β = 100.275(6)° , V = 920.8(4) Å^3 and the reliability factors are R_p = 12.5 ; R_{wp} = 13.7; R_{exp} = 8.26 et chi² = 2.76.*

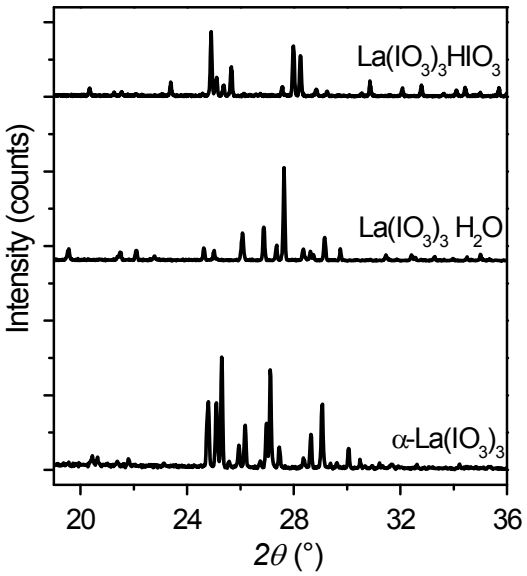

Figure S4. PXRD patterns of $La(IO_3)_3(H_2O)$, $La(IO_3)_3(HIO_3)$ and α-$La(IO_3)_3$, in (18-36°) 2θ range showing the main peaks of each phases.

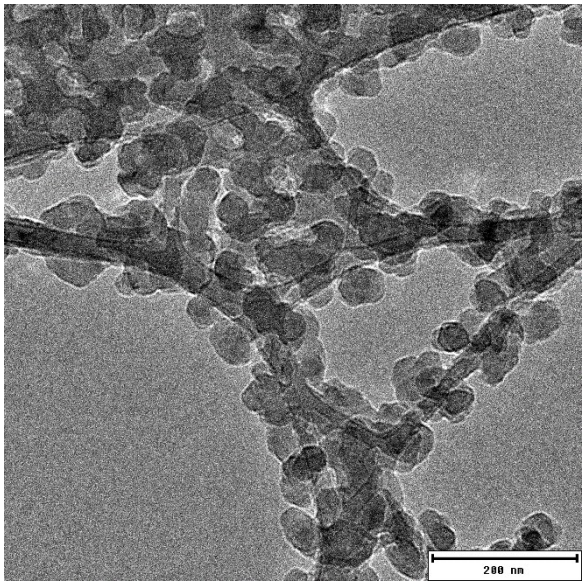

Figure S5. Low-temperature Transmission Electron Microscopy image of α-$La(IO_3)_3$ nanocrystals with 50 nm mean size.

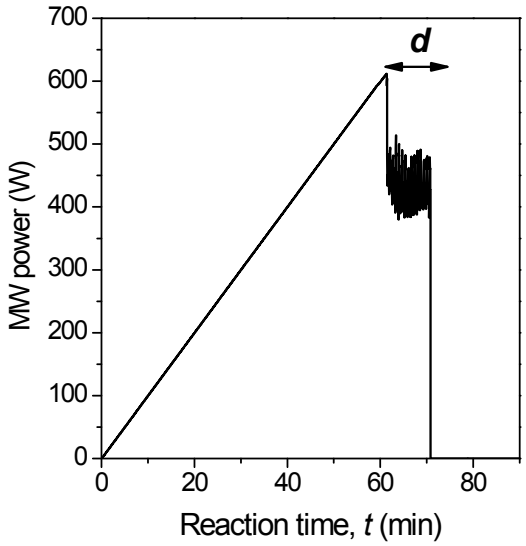

Figure S6. *MW program applied to $La(IO_3)_3(H_2O)$ dispersed in water. At t = 60 min, the temperature reaches 250°C. This temperature is kept constant for different durations, d, leading to $La(IO_3)_3(H_2O)$ for d = 1 s, $La(IO_3)_{2.66}(OH)_{0.33}$ for d = 7 min and α-$La(IO_3)_3$ for d = 10 min.*

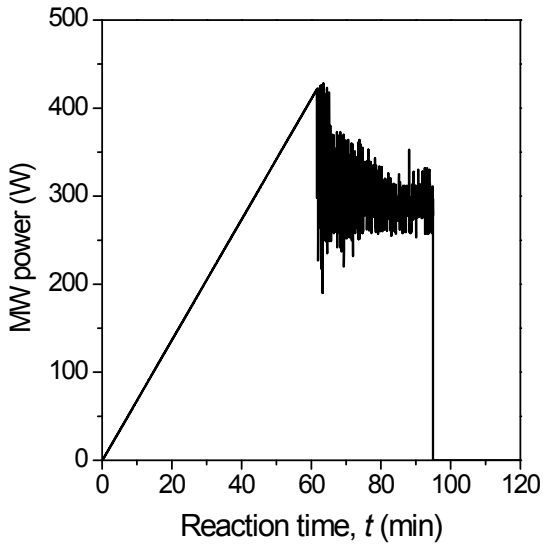

Figure S7. *MW program applied to the mixture $La(IO_3)_{2.66}(OH)_{0.33}$ + HIO_3 in water. At t = 60 min, the temperature reaches 250°C.*

Table S1. *Crystal data for $La(IO_3)_3(H_2O)$, $La(IO_3)_{2.66}(OH)_{0.33}$, α-$La(IO_3)_3$, β-$La(IO_3)_3$, γ-$La(IO_3)_3$*

	$La(IO_3)_3(H_2O)$	$La(IO_3)_{2.66}(OH)_{0.33}$	α-$La(IO_3)_3$	β-$La(IO_3)_3$	γ-$La(IO_3)_3$
M (g mol^{-1})	681.6	609.7	663.6	663.6	663.6
Crystal system	Monoclinic	Trigonal	Monoclinic	Monoclinic	Monoclinic
Space group (n°)	$P2_1/n$ (14)	$P3c1$ (158)	Cc (9)	$P2_1$ (4)	$P2_1/c$ (14)
***a* (Å)**	7.1916(1)	10.2208 (4)	12.492(1)	7.2539(4)	7.3427(9)
***b* (Å)**	13.2584(1)		7.072(1)	8.5360(5)	8.684(1)
***c* (Å)**	9.8098(1)	12.9586 (10)	27.727(3)	13.5018(7)	13.741(2)
***β* (°)**	100.2409(1)		102.1(1)	97.499(2)	99.913(8)
***V* (Å^3)**	920.369(2)	1172.35 (10)	2396.0(5)	828.9(1)	863.0(4)
Z	4	6	12	4	4
***D$_x$* (g cm^{-3})**	4.92	5.192	5.519	5.32	5.11

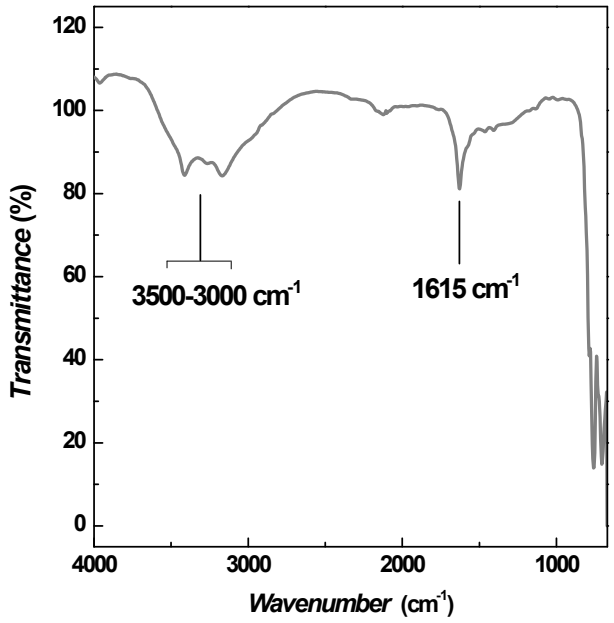

Figure S8. FTIR spectrum of $La(IO_3)_3(H_2O)$.

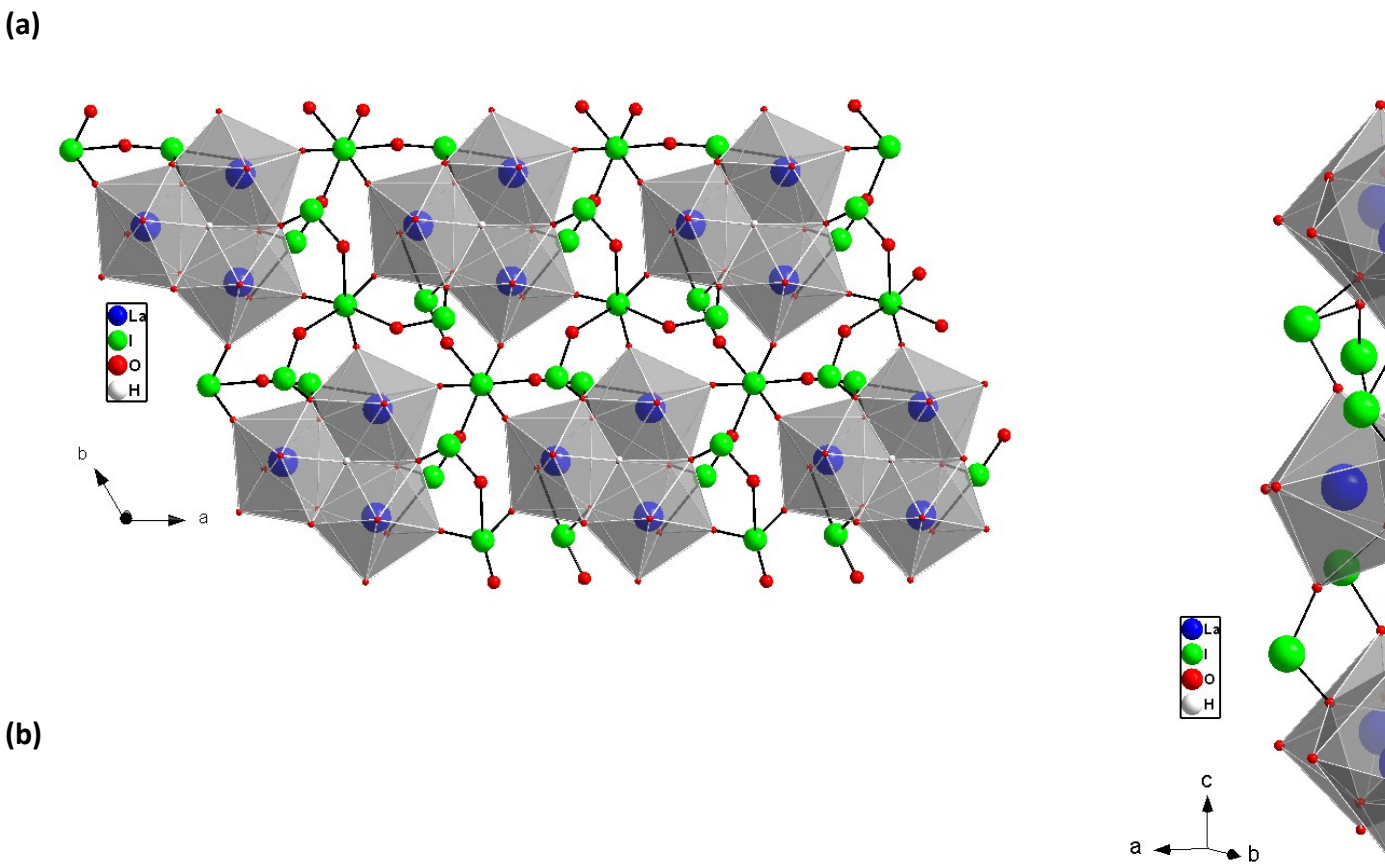

Figure S9. Representation of the $La(IO_3)_{2.66}(OH)_{0.33}$ structure showing the triangular $\{La_3\text{-}(\mu_3\text{-}OH)\}$ trinuclear entities in which lanthanum polyhedra share faces linked together by bridging iodates (a) in projection in the (001) plane and (b) along the [001] direction.

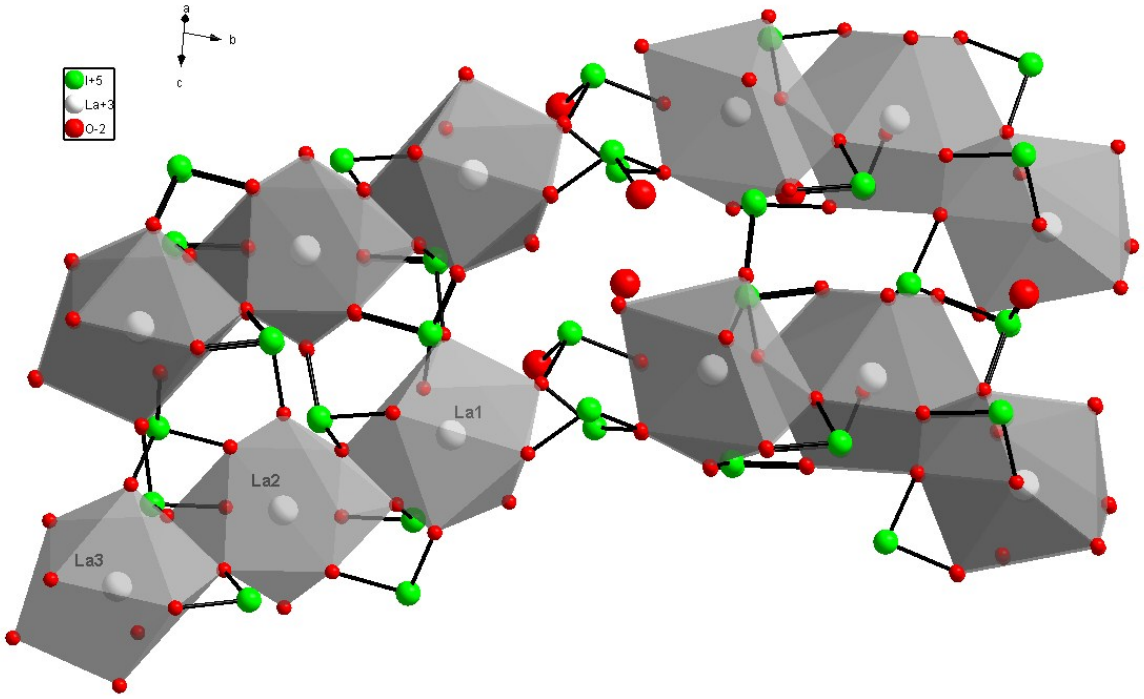

Figure S10. Representation of the chains of trinuclear lanthanum entities showing the almost linear arrangement of the polyhedra in the very compact crystal structure of α-La$(IO_3)_3$. The lanthanum polyhedra share edges and the trinuclear entities are linked together by bridging iodates.