

La(OH)₂I(H₂O): Closing a Gap in Rare Earth Hydroxide Halide Structural Chemistry

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UCl₃ type La(OH)₂I can be stabilized by additional water molecules during a hydrothermal synthesis from hydroiodic acid and lanthanum carbonate hydrate at 453 K to form La(OH)₂I(H₂O). The new rare earth (*RE*) hydroxide halide hydrate crystallizes monoclinically, space group *C2/m* with lattice parameters of $a = 19.691(3)$, $b = 4.136(1)$, $c = 6.286(1)$ Å, $\beta = 108.45(1)^\circ$ and $V = 485.6(2)$ Å³, $wR2 = 0.0695$, 648 F^2 values and 32 variables. La centered, distorted, tricapped, trigonal prisms formed by iodide, (OH⁻)- and (H₂O) groups are connected *via* common edges in [001]-direction and common faces in [010]-direction to built up a zigzag like layered arrangement. Hydrogen bonding between the water molecules and iodide ions of adjacent La(OH)₂I layers stabilize the UCl₃ related structure, which was only observed for the lighter homologues La(OH)₂X ($X = \text{Cl}, \text{Br}$) so far. DTA/TG and IR measurements substantiated the occurrence of (H₂O)- and (OH⁻)-groups and semiquantitative EDX analyses proved a 1:1 composition for La:I in La(OH)₂I(H₂O).

Key words: Rare Earth Elements, Hydrates, Hydrogen Bonding, Hydrothermal Synthesis

Introduction

The structural variety of ternary and multinary rare earth hydrates containing simple or complex ions has been studied in the past decades [1–3]. Today only one rare earth (*RE*) hydroxide halide hydrate with nominal composition 1:2:1:1 has been mentioned in literature. La(OH)₂Br(H₂O) was postulated beside La(OH)₂Br · 1.5(H₂O) as one product of the hydrolysis reaction of LaOBr with water vapour [4]. The thermal decomposition of these materials was discussed but no proper structure determination was given by the authors. If one tries to find further quasi quaternary 1:2:1:1 *RE* hydroxide hydrates only one compound has been structurally characterized. La(OH)₂NO₃(H₂O) was prepared by controlled thermal decomposition of La(NO₃)₃ · 6H₂O. The crystal structure of La(OH)₂NO₃(H₂O) [5] could be determined by a Rietveld analysis and the thermal properties were observed by temperature dependant powder X-ray diffraction and thermogravimetry. Unfortunately, all synthetic routes to prepare these materials, that are hydrolysis of LaOBr or dehydration of LaNO₃ · 6H₂O lead to microcrystalline materials only.

In the field of *RE* hydroxide halides two different structure types are known to date, the monoclinic

RE(OH)₂X and the hexagonal *RE*₇(OH)₁₈X₃ type. The *RE*(OH)₂X structure ($X = \text{F}^-, \text{Cl}^-, \text{Br}^-$) can be derived from the UCl₃ [6] type. Focusing on the number of materials being characterised a drastic decrease can be observed from $X = \text{F}^-$ to Br^- . The preparation, crystal structure and thermal decomposition of *RE*(OH)₂X (trivalent *RE* = La–Ho; $X = \text{F}^-, \text{Cl}^-$) compounds has been studied by many groups, mainly focusing on the chlorides [7–12]. In case of $X = \text{Br}$ the amount of barely characterized materials is limited to the trivalent *RE* elements La, Ce and Pr only [13]. *RE*(OH)₂I does not exist so far and non stoichiometric phases of the general composition *RE*(OH)_{2–y}X_y (trivalent *RE* = Sm–Gd; $X = \text{I}^-, \text{NO}_3^-$; $y = 0.33$ and 0.4) have been reported instead [14, 15]. Since today, no structure model was given for any *RE* hydroxide iodide of the *RE*(OH)_{2–y}X_y type.

The *RE*₇(OH)₁₈X₃ structure type can be found with the early *RE* elements. Most of the *RE*₇(OH)₁₈X₃ type materials containing trivalent *RE* elements have been characterised from microcrystalline samples (*RE* = La, Pr; $X = \text{I}^-$; *RE* = La–Gd; $X = \text{Br}^-$ and *RE* = La; $X = \text{Cl}^-$) [15]. Only one single crystal structure determination of a *RE* hydroxide iodide, that is La₇(OH)₁₈I₃ [16], is performed for the complete *RE* hydroxide io-

Table 1. Crystallographic data for La(OH)₂I(H₂O) at 173 K.

Empirical formula	La ₁ I ₁ O ₃ H ₄
M [g mole ⁻¹]	317.8
Crystal system	monoclinic
Space group	<i>C2/m</i> (no. 12)
Lattice parameters [Å, °]	<i>a</i> = 19.691(3) <i>b</i> = 4.136(1) <i>c</i> = 6.286(1) β = 108.45(1)
Cell volume [Å ³]	485.6(2)
<i>Z</i>	4
Temperature [K]	173
$\rho_{x\text{-ray}}$ [g cm ⁻³]	4.35
Absorption correction	numerical
μ [mm ⁻¹]	15.0
Min/max transmission	0.073/0.431
<i>F</i> (000)	536
Crystal size [mm ³]	0.35 × 0.20 × 0.05
Diffractometer	IPDS I
Radiation	Mo-K α
Wavelength [Å]	0.71073
Monochromator	graphite
No. of reflections	3594
No. of independent reflections	648
Reflections <i>I</i> > 3 σ (<i>I</i>)	615
Refinement program	Jana2000 [21]
<i>R</i> _{int}	0.0399
<i>R</i> 1 (<i>I</i> > 3 σ (<i>I</i>))	0.0237
<i>wR</i> 2 (<i>I</i> > 3 σ (<i>I</i>))	0.0685
<i>R</i> 1 (all)	0.0258
<i>wR</i> 2 (all) = for all reflexes	0.0695
Max./min. residual electron density [e Å ⁻³]	1.20/−1.59

vide structure family. Obviously this structure type is favourite if large ions like iodide or early *RE* cations are concerned as the counterparts in the *RE* hydroxide halides.

Herein we report the preparation, single crystal structure determination and thermal decomposition of La(OH)₂I(H₂O) and discuss the general consequences on *RE* hydroxide halide structural chemistry.

Results and Discussion

Semi-quantitative EDX analysis of La(OH)₂I(H₂O) reveal a 1:1 composition of lanthanum and iodine. Oxygen has been detected as the only additional element. IR spectra substantiate the occurrence of (H₂O)- and (OH)-groups in La(OH)₂I(H₂O) featuring stretching and bending modes in the expected regions. Combined DTA/TG and X-ray powder diffraction data of La(OH)₂I(H₂O) show a non reversible two step reaction with the loss of two equivalents of H₂O. LaOI with PbFCl structure was identified as the final product after the dehydration [17, 18]. The intermediate product of this decomposition has not been determined jet. All

Table 2. Atomic coordinates and isotropic displacement parameters [Å²] for La(OH)₂I(H₂O) at 173 K. O_{H2} (water molecule); O_{Hx} (OH) groups. All atoms on 4*i*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U _{iso}
La	0.2969(1)	0	0.8015(1)	0.0083(2)
I	0.4198(1)	1/2	0.6654(1)	0.0154(2)
O _{H2}	0.5813(3)	0	0.8606(7)	0.021(2)
O _{Ha}	0.1924(2)	0	0.9412(6)	0.011(1)
O _{Hb}	0.2736(2)	0	0.3853(6)	0.011(1)

Table 3. Selected bond distances [Å] for La(OH)₂I(H₂O) at 173 K.

2 × La–I	3.490(1)	La–O _{H2}	2.654(4)
La–O _{Ha}	2.479(5)	2 × La–O _{Ha}	2.593(2)
La–O _{Hb}	2.509(4)	2 × La–O _{Hb}	2.559(2)

Table 4. Selected donor-acceptor (D–A) interactions [Å] of hydrogen bridges for La(OH)₂I(H₂O) at 173 K.

(D–A)			
2 × O _{H2} –I	3.633(4)	2 × O _{H2} –I	3.664(4)
2 × O _{H2} –I	3.894(4)	O _{Ha} –I	3.753(3)
O _{Ha} –I	3.802(5)		
2 × O _{H2} –O _{Ha}	2.936(5)	O _{Ha} –O _{Hb}	2.743(5)
2 × O _{Ha} –O _{Hb}	3.132(5)	2 × O _{Hb} –O _{Hb}	2.839(4)
2 × O _{Ha} –O _{Ha}	2.985(4)		

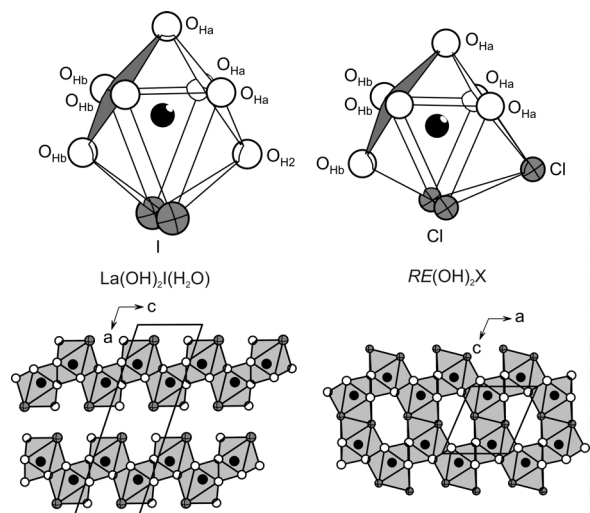


Fig. 1. La-coordination in La(OH)₂I(H₂O) and *RE*(OH)₂X (example Nd(OH)₂Cl [28]) (*d*(La–X)_{max} = 3.5 Å). La is nine-fold coordinated to form distorted, tricapped, trigonal prisms. Insertion of a water molecule separates the La(OH)₂I layers.

the phase analytical experiments and thermal analyses correspond perfectly with the postulated composition.

Colourless La(OH)₂I(H₂O) is monoclinic, space group *C2/m* (No. 12) with *Z* = 4 units per unit cell and lattice parameters of *a* = 19.691(3), *b* = 4.136(1),

$c = 6.286(1) \text{ \AA}$, $\beta = 108.45(1)^\circ$ and $V = 485.6(2) \text{ \AA}^3$ at 173 K. The structure was solved by direct methods [19] from Lorentz-, polarisation- and absorption corrected data. Positional and displacement parameters of all La, I and O atoms were refined by least squares methods against F^2 values using the Jana 2000 program package [20]. The positions of the H atoms could not be detected reliably neither by an unrestricted nor a restricted refinement and were therefore rejected. Selected crystallographic data are summarized in Tables 1–3. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-416012, the name of the author and citation of the paper.

Lanthanum is ninefold coordinated by six (OH)-groups ($d(\text{La}-\text{O}_{\text{Ha,b}}) = 2.479(5)$ to $2.559(2) \text{ \AA}$) one H₂O molecule ($d(\text{La}-\text{O}_{\text{H}_2\text{O}}) = 2.654(4) \text{ \AA}$) and two I ions $d(\text{La}-\text{I}) = 3.490(1) \text{ \AA}$ in the form of a distorted tricapped trigonal prism (see Fig. 1). The position of the water molecule was derived from structure chemical considerations like the La-O distances, anisotropic displacement parameters and coordination spheres around the O positions. La-polyhedra are connected *via* common edges in [001]-direction and common (O_{Ha})-(O_{Hb})-I-faces in [010]-direction to built up a zigzag-like layered arrangement.

A comparable ninefold coordination is common for trivalent lanthanum in an oxygen or mixed oxygen/halogen environment and can also be found in other lanthanum hydrates like (H₃O)La(SO₄)₂ · 3H₂O [21], La(CH₃SO₃)₃ · 2H₂O [22], [La₂Cl₃(OAc)₂(H₂O)₇]Cl [23] or the hydrated RE halides RE(H₂O)₉I₃ ($RE = \text{La}^{3+} - \text{Ho}^{3+}$) [24].

From a topological point of view the crystal structures of REOX, RE(OH)₂X ($X = \text{halide}$) and La(OH)₂I(H₂O) are closely related to each other. A stepwise formalism can be postulated to derive the La(OH)₂X structure directly from the PbFCl type REOX structure. In a first step one has to break RE-X bonds in the REOX structure type (Fig. 2 (1)) to achieve the desired RE-halide substructure motive as shown in Fig. 2 (2). After a protonation of the O²⁻-group and insertion of one additional (OH) group, necessary to balance the charge of the remaining cation substructure, one has to perform an anti-parallel translation of the La/OH part leaving the halides on their positions (Fig. 2 (4)). As a result one ends up with the UCl₃ related RE(OH)₂X structure. The translation process of the La/(OH) substructure can be correlated

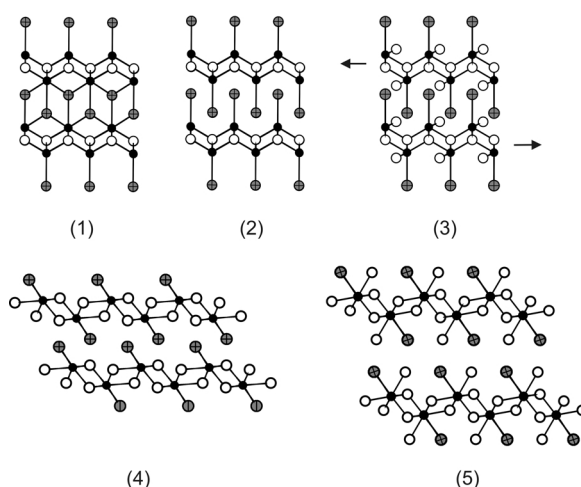


Fig. 2. Topological relations between the REOX ($X = \text{Cl}^- - \text{I}^-$), RE(OH)₂X ($X = \text{Cl}^-$, Br⁻) and La(OH)₂I(H₂O) structures. RE (black spheres), halogen (grey spheres, cross), oxygen positions (open spheres). The La(OH)₂I(H₂O) structure (5) can be derived from the LaOX structure (1–3) from the “intermediate” RE(OH)₂X structure (4). Arrows symbolize the necessary translation step from the LaOX to the RE(OH)₂X structure after insertion of an oxygen position.

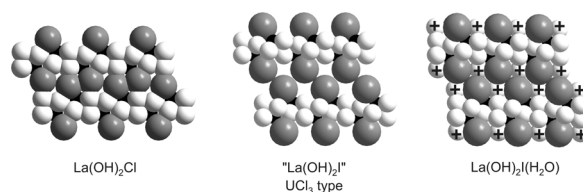


Fig. 3. Space-filling representations of La(OH)₂Cl [29], the UCl₃ related La(OH)₂I substructure and La(OH)₂I(H₂O). Views parallel [010]. Black spheres lanthanum, grey spheres halide, white spheres oxygen. Water molecules are marked by a cross.

to the development of the hydrogen bonding interaction in RE(OH)₂X. Hydrogen bonding of (OH) groups to halide ions of neighbored RE(OH)₂X layers was postulated as the essential interaction for the stabilisation of the layered RE(OH)₂X structure [8]. Finally an insertion of a water molecule (Fig. 2 (5)) leads directly to La(OH)₂I(H₂O).

This close relationship between the structure types forced us to examine the reason for the existence of a water stabilised RE(OH)₂I material with a UCl₃ related structure type instead of a water free one. A space-filling representation of the La(OH)₂Cl and La(OH)₂I(H₂O) structures (Fig. 3) based on ionic radii [25] in suitable coordination spheres of La³⁺, O²⁻, Cl⁻ and I⁻ and a comparison of the hydrogen bond-

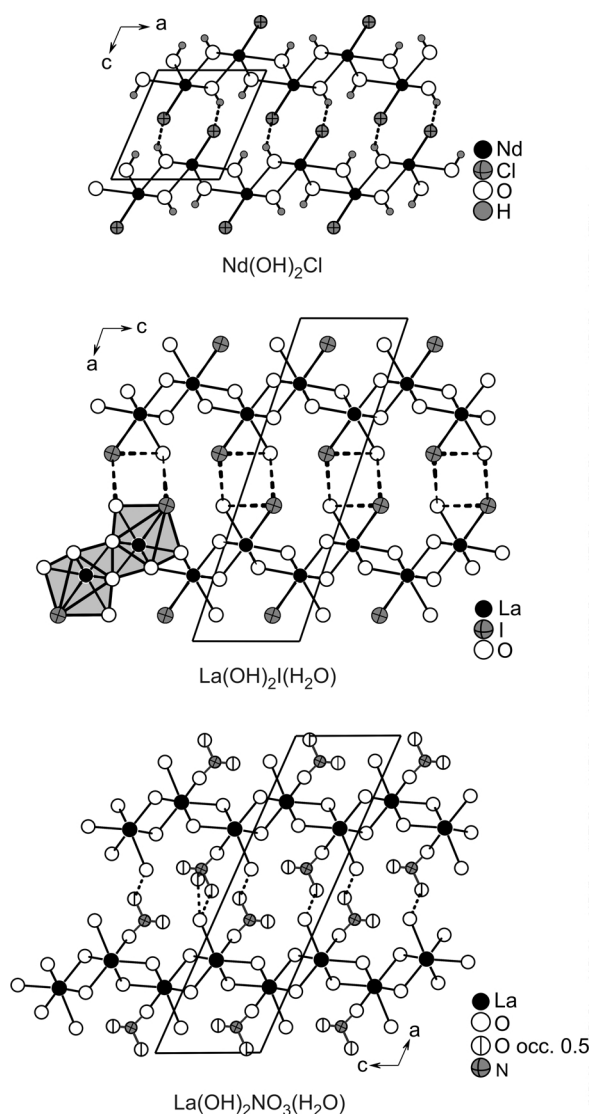


Fig. 4. Hydrogen bonding situation in the $RE(\text{OH})_2X$ ($X = \text{Cl}, \text{Br}$) structure type (example $\text{Nd}(\text{OH})_2\text{Cl}$, neutron diffraction data [28]) compared with $\text{La}(\text{OH})_2\text{I}(\text{H}_2\text{O})$ and $\text{La}(\text{OH})_2\text{NO}_3(\text{H}_2\text{O})$ [5]. Hydrogen bonding and donor-acceptor interactions are marked by dashed lines. In case of $\text{La}(\text{OH})_2\text{NO}_3(\text{H}_2\text{O})$ only one disordered NO_3 group is drawn for clarity.

ing situation illustrates two possible reasons for this finding. One is of course a stacking problem of the $[\text{La}(\text{OH})_2\text{I}]$ layers due to the size of the iodide ions. An analogous packing of interpenetrating $[\text{La}(\text{OH})_2\text{I}]$ layers, comparable to the layers in $\text{La}(\text{OH})_2\text{Cl}$, would directly lead to a very short I-I distance in neighbored layers, far below two times the ionic radius. As a re-

sult of this stacking situation the repulsion of the iodide ions tends to force a non-intercalated packing. Assuming this arrangement, one ends up with large and empty channels within the UCl_3 analogous “ $\text{La}(\text{OH})_2\text{I}$ ” substructure (see Fig. 3). Exactly at this position supposed to be the area of the important hydrogen bonding interaction between the donor (OH)-group and the acceptor halide position in a UCl_3 analogous $RE(\text{OH})_2\text{I}$ structure (Fig. 4). To our opinion the stacking problem, caused by the ion size of the iodide, in combination with the missing hydrogen bond interaction between the $[\text{La}(\text{OH})_2\text{I}]$ layers are the reasons for the destabilisation of a UCl_3 type $RE(\text{OH})_2\text{I}$ phase. The loss of the hydrogen bonding interaction of the postulated $RE(\text{OH})_2\text{I}$ structure is compensated by the addition of spacer molecules (water) to the empty channels, capable to create new inter- and intra-layer donor-acceptor interactions between the $[\text{La}(\text{OH})_2\text{I}]$ layers in $\text{La}(\text{OH})_2\text{I}(\text{H}_2\text{O})$ (Fig. 4). Donor-acceptor distances of $d(\text{O}_{\text{H}_2}-\text{I}) = 3.633(4)$ and $3.664(4)$ Å are in the same range than observed for other hydrogen bond stabilized materials like the maximally hydrated rare earth iodides e.g. $\text{La}(\text{H}_2\text{O})_9\text{I}_3$ [24, 26].

This assumption can also be substantiated by taking a closer look to the structural chemistry of isostructural $\text{La}(\text{OH})_2\text{NO}_3(\text{H}_2\text{O})$. If one compares the $\text{La}(\text{OH})_2\text{NO}_3(\text{H}_2\text{O})$ and $\text{La}(\text{OH})_2\text{I}(\text{H}_2\text{O})$ structures it becomes obvious that the same structure and bonding principles are realized and that the water molecule plays exactly the same role in the nitrate than in the iodide. Both the inter- and intra-layer donor-acceptor interactions to the nitrate group (see Fig. 4), bonded to lanthanum in a monodentate way, demands the rotation disorder of the nitrate group observed in this material.

Conclusion

$\text{La}(\text{OH})_2\text{I}(\text{H}_2\text{O})$ can be described as a water filled variant of the UCl_3 like $RE(\text{OH})_2X$ structure. Hydrogen bonds between the water molecules and iodide ions of neighbored $[\text{La}(\text{OH})_2\text{I}(\text{H}_2\text{O})]$ layers play an important role to stabilise the new RE hydroxide halide hydrate. The water molecule can be regarded as a spacer between the $\text{La}(\text{OH})_2\text{I}$ layers filling up empty channels formed by repulsion effects of neighbored iodide ions. A combined IR- and DTA/TG investigation of the thermal properties revealed the formation of LaOI after a complete dehydration of $\text{La}(\text{OH})_2\text{I}(\text{H}_2\text{O})$.

Experimental Section

Preparation

Hydroiodic acid (Riedel de Haen, p.a., 54%) was distilled prior to use to remove the hypophosphoric acid added as a stabiliser. A titration of the freshly distilled, colourless acid resulted in a HI content of 53.8 weight-%. The acid can be stored for approx. 2 days without any significant decomposition.

La(OH)₂I(H₂O) can be prepared by a hydrothermal reaction of La₂(CO₃)₃ · x(H₂O) ($x \cong 3$; Chempur, 99.99 %), dissolved in semiconcentrated HI using evacuated quartz ampoules. 0.5 g La₂(CO₃)₃ · x(H₂O) was dissolved in semiconcentrated HI adjusting a final pH value of 5. The amount of HI is dependant on the water content of La₂(CO₃)₃ · x(H₂O) and therefore no exact volume is given. The preparation of La(OH)₂I(H₂O) is extremely sensitive to the pH value, the concentration of the La³⁺ and I⁻ ions and the reaction temperature. A dilution of the starting solution due to neutralisation reasons should be avoided. The solution was transferred to a silica ampoule, cooled down to liquid nitrogen temperature and evacuated to a pressure of approx. 10⁻³ bar. The sealed ampoule was heated in a home made autoclave to 453 K and kept at this temperature for 9 days, applying sufficient water pressure to the ampoule. Colourless La(OH)₂I(H₂O) was separated from the remaining solution, washed with water and ethanol and dried on air for 3 days. We found metal based yields up to 20%. La(OH)₂I(H₂O) can be stored in air for several weeks without decomposition.

Semiquantitative analyses

Electronmicroscopic measurements were performed using a DSM 950 microscope (Fa. Zeiss) fitted with a Link EDX detector system. Bulk material and single crystals of La(OH)₂I(H₂O) were prepared on graphite taps and mounted

on aluminium carriers. A total number of five analyses, neglecting the hydrogen atoms resulted in: calcd. La 20, I 20, O 60; found La 20(2), I 22(2), O 58(2) in at-%.

Thermal and X-ray powder diffraction analyses

DTA/TG measurements were performed using a SETARAM TG-DTA 92-16 at heating rates of 10 K min⁻¹ and applying a steady N₂ gas flow of 200 ml h⁻¹. The TG measurement of La(OH)₂I(H₂O) (8.289 mg, 0.026 mmol) between 298 and 873 K revealed a mass loss of 0.43 mg between 423 and 493 K and of 0.44 mg between 543 and 603 K (ideal value according to the mass loss of one equivalent of H₂O: 0.47 mg). An X-ray powder diffraction phase analysis (StadiP powder diffractometer, Fa. Stoe, 298 K, Cu-K_{α1} radiation, $\lambda = 1.54051 \text{ \AA}$, germanium monochromator, Si as external standard, linear 5° PSD) of the final product after the loss of two equivalents of water proved the formation of LaOI. We refined lattice parameters of $a = 4.155(3)$, $c = 9.23(2) \text{ \AA}$ and $V = 159.3(5) \text{ \AA}^3$ in good agreement to the values for LaOI reported in literature (space group *P4/nmm*; $a = 4.14$, $c = 9.13 \text{ \AA}$, $V = 156.7 \text{ \AA}^3$ [27]).

IR spectroscopy

IR spectra were recorded on an IFS 113V Fourier-Transform-Spectrometer (Fa. Bruker) between 4000 and 400 cm⁻¹ with a resolution of $\pm 2 \text{ cm}^{-1}$. Fine grained samples were run as KBr pellets.

IR(KBr, 298 K): $\tilde{\nu} = 3554 \text{ (OH)}$, 3523 (OH) , $3464 \text{ (OH}_2\text{)}$, $1630 \text{ (H}_2\text{O)}$, 683 (OH) , 541 (OH) cm^{-1} .

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