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Reduction of $\text{Ln}_2\text{Ti}_2\text{O}_7$ layered perovskites: a survey of the anionic Lattice, Electronic Features, and Potentialities

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Abstract

The reduction of the layered perovskites $\text{Ln}_2\text{Ti}_2\text{O}_7$ (LnTO, with lanthanide Ln= La, Pr, Nd) was studied with the aim to shift the UV photocatalytic activity for water splitting in the visible range by Ti^{3+} donor doping. For all phases, after reduction by CaH_2 , the absorbance is extended beyond the UV-vis region, giving rise to a gap-like edge in the mid-infrared at $\sim 0.4\text{eV}$ with a dark coloration of the samples. When the precursor with Ln= La was reduced under high temperature H_2 flow, we found a progressive nanotexturation down to 300 nm, which is responsible for a degree of Ti^{3+} segregation at the surface. Magnetic measurements, thermal analysis and powder neutron diffraction (PND) reveal that the sample reduced by both routes have a similar amount of anion vacancy with $\delta = 0.27$ (in $\text{La}_2\text{Ti}_2\text{O}_{7-\delta}$). It represents a limited topotactic reduction stage, prior to the reconstructive reduction into $\text{La}_5\text{Ti}^{+3.8}\text{O}_{17}$ observed in more severe reducing conditions. For the sample reduced by CaH_2 , a minor amount of hydride appears to be incorporated (~ 0.02 H per FU), with a $\text{Ti}^{3+}\text{---H}^-$ bonding observed by HYSCORE electron paramagnetic resonance (EPR) and density functional theory (DFT) calculations. Preliminary electrocatalysis tests show a promising anodic activity for water splitting hydrogen evolution with a voltage onset as low as 0.6V vs. RHE.

Introduction

Herein, the recent incorporation of significant amounts of hydride anions in the $\text{BaTiO}_{3-x}\text{H}_x$ perovskite ($x \leq 0.6$) by CaH_2 reduction at moderate temperature¹ was a source of inspiration for further studies, in trying to diversify the host systems for reduction of Ti^{4+} into mixed valence $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxyhydrides. Similar reduction for ATiO_3 epitaxial thin films (A= Ca, Sr, Ba) led to metallic $\text{ATi}(\text{O,H})_3$ phases,² while for a low hydride content a semiconducting state can also be reached.³ We recall that upon reduction of Ruddlesden-Popper (RP) phases, $\text{Ca}_{n+1}\text{Ti}_n\text{O}_{3n+1-\delta}$, under flowing H_2 also gives metallicity even with tiny oxygen deficiency ($\delta < 0.001$) which provides activated electrons from the conduction band.⁴ This ability for tuning the bandgap in mixed $\text{Ti}^{3+}/\text{Ti}^{4+}$ RP systems in a controlled manner offers promising potentials for various photo-electronic properties.

An extra opportunity is given to the $\text{A}_n\text{B}_n\text{O}_{3n+2}$ series ($n = \text{integer}$)^{5, 6} composed also of perovskite-like blocks separated by A cations. The perovskite layer n extends from 2 to 6 and $n \rightarrow \infty$ corresponds to the three-dimensional standard perovskite ABO_3 . For lanthanide (Ln) titanates, the increase of n from 4 ($\text{Ln}_2\text{Ti}^{4+}_2\text{O}_7$) to 5 ($\text{Ln}_5\text{Ti}^{3.8+}_5\text{O}_{17}$) and then to $n \rightarrow \infty$ ($\text{LnTi}^{3+}\text{O}_3$) is accompanied by a progressive reconstructive titanium reduction. The $n= 4$ member ($\text{Ln}_4\text{Ti}_4\text{O}_{14}$, i.e. $\text{Ln}_2\text{Ti}_2\text{O}_7$) cover two structural types depending on the Ln ionic radius. The layered perovskite structure is thermodynamically stable for Ln= La, Pr, Nd ($r_{\text{XII}} =$

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3 1.36 -1.27 Å). Although the pyrochlore structure is preferred for smaller Ln^{3+} ions, the layered
4 perovskite (ferroelectric) structure can be extended up to $\text{Gd}_2\text{Ti}_2\text{O}_7$ by substrate constraints in
5 epitaxial thin films.⁷ At the pyrochlore side, the CaH_2 reduction for small A^{3+} ions (e.g. Y, Lu,
6 Yb) topochemically leads to reduced pyrochlore $\text{AB}_2\text{O}_{7-\delta}$ with an A/B anti-site disorder and
7 phase separation.^{8, 9} For bigger A^{3+} ions (e.g. Sm, Eu), the transformation into ABO_3
8 perovskite was reported,⁸ while more recent investigation of the reduction for Eu indicated
9 the formation of perovskite oxyhydrides $\text{EuTiO}_{3-x}\text{H}_x$ ($x \leq 0.3$).¹⁰ To the best of our knowledge,
10 no significant result has been obtained for layered perovskites. $\text{La}_2\text{Ti}_2\text{O}_7$ is a ferroelectric
11 compound well known for its high Curie-temperature, spontaneous polarization and dielectric
12 constant ($T_c \sim 1500$ °C, $P_s \sim 5 \mu\text{C}\cdot\text{cm}^{-2}$, $\epsilon \sim 42-62$).¹¹ Tuning the gap of this compound while
13 conserving the non-centrosymmetry is challenging. Undoped $\text{La}_2\text{Ti}_2\text{O}_7$ has a wide bandgap
14 of 3 - 4 eV, the magnitude of which depends on its microstructure,¹² and it exhibits
15 photocatalytic activity under UV irradiation. This material can also be used for H_2 generation
16 by water splitting¹³ for the degradation of volatile organic compounds¹⁴ and the
17 photoreduction of metal ion such as Cr (IV).¹⁵ A further reduction of the gap into the visible
18 light region is highly demanded and in fact this could be achieved by Rh^{3+} , Fe^{3+} , Cr^{3+} doping
19 leading to H_2 evolution from aqueous-methanol solution due to unfilled 3d localized levels in
20 the gap.^{16, 17, 18} Recently, it has been experimentally demonstrated that nitrogen-doped
21 $\text{La}_2\text{Ti}_2\text{O}_7$ nanosheets showed both significant visible light but also enhanced ultraviolet
22 photocatalytic activity.¹⁹ Here, first principle calculations suggest that both N^{3-} host and
23 oxygen vacancies act to narrow the bandgap by creation of a continuum band at the top of
24 the valence band. Apart from aliovalent doping, introduction of only a small Ti^{3+} content in
25 $\text{La}_2\text{Ti}_2\text{O}_7$ has been reported using a combustion synthesis route.²⁰ In our work, the LTO
26 bandgap engineering was provided by using either solid hydride or H_2 gas as reducing
27 agents. Although both routes provided a maximal ratio of ca. 4 % of oxygen vacancies upon
28 topochemical reduction, contrasted microstructures have been obtained. This aspect will be
29 discussed on the basis of the structure ability to accommodate anionic vacancies in that
30 context. In addition, the weak H^- incorporation using the solid route was analyzed by means
31 of pulsed EPR, giving microscopic insights into the Ti---H bonding nature. Besides, precise
32 characterizations of the reduced LTO forms and preliminary aptitudes for electro catalytic
33 water splitting are demonstrated.

51 **Experimental and techniques**

52 *Synthesis:* Powder samples of $\text{La}_2\text{Ti}_2\text{O}_7$ (LTO), $\text{Nd}_2\text{Ti}_2\text{O}_7$ (NTO) and $\text{Pr}_2\text{Ti}_2\text{O}_7$ (PTO) were
53 prepared by solid state synthesis from a stoichiometric mixture of high purity binary oxides.
54 As starting reagents, La_2O_3 (1.629 g, 99.9%, Alfa Aesar), Nd_2O_3 (1.522 g, 99.9%, Reacton),
55 Pr_6O_{11} (1.702 g, 99.9% Alfa Aesar) and TiO_2 (0.799 g, 99%, Fluka) were used. After grinding
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3 in an agate mortar, the mixture was calcined in an alumina crucible in air at 1350°C for a total
4 time of 170h (50h + 48h + 72h) with intermediate grinding steps in ethanol. The reduction via
5 the hydride route was then conducted by grinding $\text{La}_2\text{Ti}_2\text{O}_7$ (0.2889 g), $\text{Nd}_2\text{Ti}_2\text{O}_7$ (0.2946 g)
6 or $\text{Pr}_2\text{Ti}_2\text{O}_7$ (0.2906 g) with CaH_2 (0.15 g), so as to have a molar Ti/H ratio of 1/3, in a glove
7 box. The powder was then flame-sealed in an evacuated Pyrex or silica tube (15 cm^3) at
8 pressures below 1.10^{-2} Bar. The tubes were then heated at 550°C during 72h, reiterating the
9 process until the powder turns black. Then, the product has been washed several times with
10 a 0.1M NH_4Cl /methanol solution to remove excess CaH_2 and CaO and dried in an oven at
11 100°C.
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17 The reduction via the hydrogen route was performed by firing $\text{La}_2\text{Ti}_2\text{O}_7$ under flowing pure
18 hydrogen gas in a tubular furnace during 12h at a temperature of 1000°C. The furnace was
19 then switched off to rapidly cool the sample while preserving the hydrogen flow. This
20 treatment was found to allow the best compromise between reduction and non-
21 decomposition. Caution: for both treatments, using solid CaH_2 or H_2 flow, particular safely
22 rules must be respected to avoid contact with air.
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27 *Diffraction:* X-ray diffraction (XRD) patterns were collected using a Bruker AXS D8 Advance
28 X-ray diffractometer (radiation $\text{Cu K}\alpha = 1.5418\text{\AA}$) equipped with a fast detector type LynxEye
29 using a copper anticathode and a secondary beam monochromator. The scanning rate was
30 0.02° with the step time adapted for each sample. XRD data were also collected on the
31 Synchrotron 11-BM beamline at the Advanced Photon Source (APS, Argonne National
32 Laboratory) with a wavelength of $\lambda=0.4137\text{\AA}$. High-resolution Powder Neutron Diffraction
33 (PND) experiment was carried out at the ILL on the 3T2 diffractometer, $\lambda = 1.22\text{\AA}$.
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39 *Elemental Analysis:* the Elemental Analysis for the quantification of C, H and N contents in
40 LTO, LTO- H_2 and LTO- CaH_2 samples were made on a HPLC analysis using a Chiralpak AD
41 column (hexane/*i*PrOH = 90/10, flow = 0.8 ml/min).
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44 Transmission electron Microscopy (TEM) experiments were carried out on a FEI Tecnai
45 G220 microscope operating at an accelerating voltage of 200 kV equipped with a LaB_6
46 crystal. Prior to TEM observations, samples were deposited from ethanolic solution onto
47 holey-carbon copper grids.
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51 *TPD/TCD and Thermal analysis:* The amount of adsorbed hydrogen of the $\text{La}_2\text{Ti}_2\text{O}_7$ - CaH_2
52 phase was evaluated by TPD using a Micromeritics Autochem 2920 apparatus coupled with
53 a mass spectrometer Omnistar. 100 mg of the reduced phase was outgassed under a helium
54 flow of 40 mL min^{-1} , while being heated from room temperature to 1023 K with a heating rate
55 of 40 K min^{-1} before cooling to room temperature under He. Thermogravimetric analysis
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(TGA) on $\text{Ln}_2\text{Ti}_2\text{O}_7$ after the hydridation treatment was carried out using a TGA 92-1600 SETARAM analyzer under flowing recomposed air (20% O_2 and 80% N_2) or pure Argon, from room temperature to 1000 °C, upon heating and cooling.

Infrared Spectroscopy: Infrared analysis was carried out using a Perkin–Elmer Spectrum 2 instrument equipped with a single reflection diamond module (ATR). IR spectra were recorded in the 400–4000 cm^{-1} range with a 4 cm^{-1} resolution.

XPS measurements: X-ray photoelectron spectroscopy (XPS) experiments were performed using an AXIS Ultra DLD Kratos spectrometer equipped with a monochromatized aluminum source (Al K_{α} = 1486.7 eV) and charge compensation gun. All binding energies were referenced to the C 1s core level at 285 eV. Simulation of the experimental photo peaks was carried out using a mixed Gaussian/Lorentzian peak fit procedure according to the software supplied by CasaXPS.

Magnetic measurements: The magnetic characterizations $M(H)$ and $\chi^{-1}(T)$ were performed using a MPMS SQUID-VSM (Quantum Design) magnetometer in a temperature and field range of 1.8–300 K and 0–5 T, respectively. The temperature dependence variation of the magnetization was carried out under various magnetic fields after cooling the sample in a field (FC: field cooling) or in zero field (ZFC: zero field cooling).

EPR measurements: X-band measurements were performed at 4 K with a Brüker ELEXYS E580 equipped with a cryofluid-free cryostat. Continuous wave (CW) spectra were recorded using respectively 1mW microwave power and 5G of amplitude modulation. In a HYSCORE (hyperfine sublevel correlation spectroscopy) experiment, characterized by the four pulse sequence $\pi/2-\tau-\pi/2-t_1-\pi-t_2-\pi/2-\tau$ -echo, the first part ($\pi/2-\tau-\pi/2$) of the sequence creates nuclear coherences (coherent superpositions of m_I states) in each $m_S = \pm 1/2$ state. The π pulse transfers each nuclear coherence from one m_S state to the other, and the last $\pi/2$ pulse transfers all nuclear coherences to the electron coherence (coherent superposition of $m_S = \pm 1/2$ states) for detection.

Density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP).²¹ The calculations were carried out within the generalized gradient approximation (GGA) for the electron exchange and correlation corrections using the Perdew-Wang (PW91) functional and the frozen core projected wave vector method.^{22, 23} The full geometry optimizations on the three studied models (1- precursor oxide, 2- oxyhydride and 3- lacunar) were carried out using a plane wave energy cutoff of 550 eV and a set of $5 \times 3 \times 7$ k-points. All structural optimizations converged with residual Hellman-Feynman forces on the atoms smaller than 0.03 eV/Å. The relaxed structures were used for calculations of the electronic structure. In that purpose, we employed a plane wave energy

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3 cutoff of 400 eV, an energy convergence criterion of 10^{-6} eV and a set of $10 \times 6 \times 14$ k-points
4 for all models. For the oxyhydride and the lacunar models (presence of Ti^{3+}), we employed
5 GGA+U calculations (DFT plus on-site repulsion U)²⁴ in order to describe the electron
6 correlation associated with the 3d states of Ti. An effective on-site repulsion value $U_{\text{eff}} = U - J$
7 = 3 eV was used.
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14 Results and Discussion

15 In order to explore the different possibilities of topotactic reductions, layered perovskite
16 $\text{Ln}_2\text{Ti}_2\text{O}_7$ compounds were reacted either by mixing with solid CaH_2 or NaH , or flowing H_2
17 (100%). The reactivity with metal hydride was tested with variation conditions using the
18 following parameters: time (72 h to 144 h), temperature (350 °C to 650 °C) and stoichiometry
19 between the hydride and the pristine compound (H/Ti ratio of 1 to 6). Using NaH , depending
20 on the temperature and reaction time, we obtained either unreacted compounds, either
21 decomposed binary oxides. The highest temperature and/or hydride reactant amount lead to
22 partial or complete decomposition of the phase into binary oxides (La_2O_3 , TiO_2),
23 amorphization and formation of phases such as $\text{La}_5\text{Ti}_5\text{O}_{17}$ or $\text{La}_4\text{Ti}_3\text{O}_{12}$. This result highlights
24 the further reconstructive reduction into the $n = 5$ $\text{A}_n\text{B}_n\text{O}_{3n+2}$ mentioned in the introduction.
25 Figure S1a shows selected XRD patterns after various reaction conditions. In order to
26 analyze the topochemical accommodation of vacancies keeping the original LnTO crystal
27 structure, the best selected synthesis parameters were 550 °C, 144 h and use of CaH_2 with a
28 H/Ti ratio of 3. So we could obtain reduced phases as shown by drastic color changes
29 leading to nearly single phase with limited loss of crystallinity. Using a hydrogen flow, the
30 temperature was increased until the color darkens significantly. From our screening, the ideal
31 conditions are $T = 1000$ °C and $t = 12$ h. The phase could be partially/fully decomposed at
32 higher temperature. A surficial decomposition responsible of the color change could not be
33 excluded at this stage. The respective samples will be denoted LTO- CaH_2 and LTO- H_2 in the
34 following.
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47 *Physico-chemical features upon reduction:* Analysis of the diffraction patterns of the
48 parent (LTO) and reduced phases (LTO- H_2 and LTO- CaH_2) (Figure 1) indicates a loss of
49 crystallinity dependent on the reduction pathway. The Bragg peaks of the different samples
50 follow the same extinction rules and show the conservation of the symmetry of LTO after
51 reduction, as confirmed for LTO- CaH_2 after PND data treatment. For LTO- CaH_2 , the splitting
52 of the peaks typical of the monoclinic lattice (space group $\text{P}112_1$) is observed using the
53 synchrotron radiation. The lattice parameters and diffracting particle β_{size} were determined
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3 after XRD-profile fitting using the Cox-Hasting function implemented in the Fullprof suite.²⁵
4 The instrumental profile was determined using a LaB₆ standard.
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7 Table 1 gives the refined lattice parameters for various samples and radiation sources.
8 The evolution between LTO and LTO-CaH₂ is minor while only LTO-H₂ shows a detectable
9 cell contraction. However this latter should be considered with precaution, taking into account
10 the relative evolution of the microstructure. Indeed, the *as-prepared* LTO (white powder)
11 particle size was refined to $\beta_{\text{size}} = 5474(8) \text{ \AA}$ (i.e. $\sim 5500 \text{ \AA}$), in agreement with a well
12 crystalline submicronic powder, see fig.1a. LTO-CaH₂ which is black, shows a strong size
13 broadening effect for all peaks leading to a crystal size of $833.6(8) \text{ \AA}$, (fig1.b). It validates the
14 fragmentation of initial particles under the CaH₂ treatment, see the TEM image (fig. 1d). The
15 peak broadening sometimes reported for oxyhydride perovskites¹⁰ often results from the H
16 distribution. In reduced LTO, the inhomogeneous distribution of vacancies/H is also probable
17 but the fragility of the LTO structure during the reduction process is the main driving
18 parameter for the nanometrization due to a limited accommodation of vacancies. We recall
19 that most stable reduced phases exist via reconstructive transformations, maybe already on
20 the run. Note that a partial decomposition into La₅Ti^{3.8+}O₁₇ (n= 5 octahedra perovskite
21 layers) and RP La₄Ti₃O₁₂ was detected in more aggressive conditions, see fig. S1. It proves
22 that prior to the reconstructive reduction, the topochemical reduction is allowed while the
23 structure suffers instability and local decomposition. All electron diffraction patterns obtained
24 for reduced LTO samples show evidence for superposition of disoriented domains due to this
25 drastic size reduction, see Figure S1b. It is such that the searching of eventual n= 5 inter-
26 grown domains by HREM was not possible. Then, as discussed later about magnetic
27 properties, a certain degree of surficial segregation of reduced species is expected.
28 Additionally, the refinement is imperfect, due to diffuse shoulder at the bottom of some peaks
29 and asymmetric broadening that occurs at high or low angles depending on the reflections.
30 This effect is clearly evidenced on the high resolution XRD data (synchrotron radiation,
31 11BM, Argonne Laboratory, $\lambda=0.414 \text{ \AA}$) as shown by blue arrows on the figure 1e by drastic
32 asymmetric broadening effects that we did not attempt to model. The diffuse shoulder should
33 arise from an uneven distribution of diffracting particle sizes and the asymmetric broadening
34 presumably indicates local intergrowth defects between distinct perovskite blocks, commonly
35 found after reduction, see the reduced RP Nd₄Ni₃O₈ prepared under flowing hydrogen.²⁶
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54 This type of irregular intergrowth of the layers has also been reported after the
55 reduction La₃Ni₂O_{7-x} into La₃Ni₂O_{6.35}.²⁷ Here again, the observation of n= 5 octahedra thick
56 blocks (La₅Ti₅O₁₇ with intrinsic Ti³⁺ distribution) in more reducing conditions comfort the
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defected state of LTO-CaH₂. After treatment under H₂ gas flow at 1000°C, the broadening of XRD peaks is intensified. It results in a pale blue nano powder with an average size of 294.2(7) Å (~300 Å), see fig.1c, d. However the peaks preserve a symmetrical shape excluding a significant phase transformation into related members of the A_nB_nO_{3n+2} series.

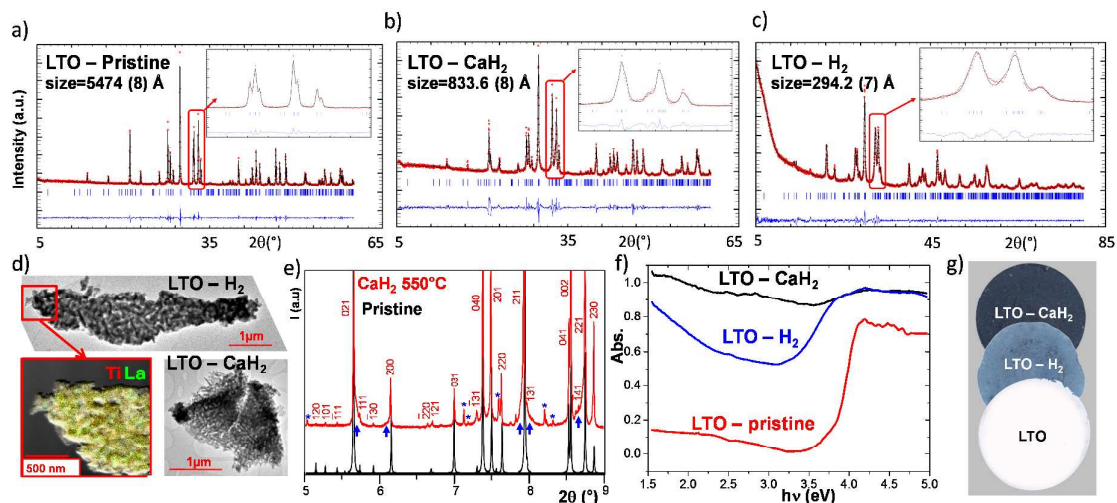


Fig 1: (a,b,c) Profile fitting and crystal size for LTO, LTO-CaH₂ and LTO-H₂ with a progressive broadening of XRD peaks. The refined lattice parameters are $a=7.8120(1)$ Å, $b=13.0144(2)$ Å, $c=5.5472(1)$ Å, $\beta=98.6318(8)^\circ$; $a=7.8159(5)$ Å, $b=13.0064(9)$ Å, $c=5.5480(3)$ Å, $\beta=98.5866(3)^\circ$ and $a=7.8076(3)$ Å, $b=12.9914(6)$ Å, $c=5.5299(3)$ Å, $\beta=98.551(3)^\circ$ respectively. d) nano-fragmentation observed from with Ti/La EDS mapping for CaH₂ showing the homogeneous composition. e) Synchrotron XRD data (Argonne Source 11BM, $\lambda = 0.42$ Å) with asymmetric broadening pointed by blue arrows. f) UV-Vis absorption curves for the LTO-series. g) Color variations after reducing treatments.

Besides the size reduction, the color changes show major modifications of the electronic structure, analyzed hereafter by the UV/vis spectroscopy (Figure 1g). LTO shows a bandgap of 3.63eV, from the Tauc plot after Kubelka-Munk transformation $(\alpha hv)^{1/2}$ for indirect bandgap (LTO case), see Fig. 1f. For the pale-blue LTO-H₂, in addition to the reminiscence of the original transitions, the absorption is extended to the visible light region due to the formation of Ti³⁺ extra electrons in defect levels. The estimated bandgap is reduced to 2.02 eV from Tauc plots, see fig.1f. For the dark-colored LTO-CaH₂, a quasi-continuous absorption is observed in the UV-vis range which is typical of highly reduced titanates such as TiO_{2-x}²⁸ or BaTiO_{3-x}²⁹. Similarly to what has been reported for aliovalent doped Ti_{1-x}M_xO_{2-δ}, electron-doping populates defect levels below the conduction band and shifts the bandgap edge deep into the forbidden gap (Urbach tail).³⁰ Similar effects have been observed after treating Nd₂Ti₂O₇ (NTO) and Pr₂Ti₂O₇ (PTO) with CaH₂. Their UV-Vis spectra (pristine phases and after CaH₂ treatment), are given in Figure S2. Here again, the *as-prepared*

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3 compounds display the expected bandgaps, (3.73 eV for NTO and 2.99 eV for PTO), while
4 the absorption is continuous in the full UV/visible range, after reduction by hydrides. We also
5 observe the occurrence of $f \rightarrow f$ electronic transitions from the paramagnetic Nd^{3+} and Pr^{3+}
6 ions. For the three hydrides, clues for low energy electronic transitions at 0.43 eV (i.e. 3500
7 cm^{-1}) are found on IR spectra after comparison with the pristine phases, see figure 2.
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9 Although the transmission step for the three LnTO-CaH_2 samples should be interpreted with
10 precaution, it could picture the gap narrowing by donor/shallow levels at the bottom of the
11 conduction band. It suggests a narrow-gap semiconducting behavior, although we have not
12 been able to measure a reasonable electric conductivity on densified pellets (compacity
13 ~68%). Both blocking grain boundaries and inhomogeneities of the distribution of vacancies
14 may be involved.
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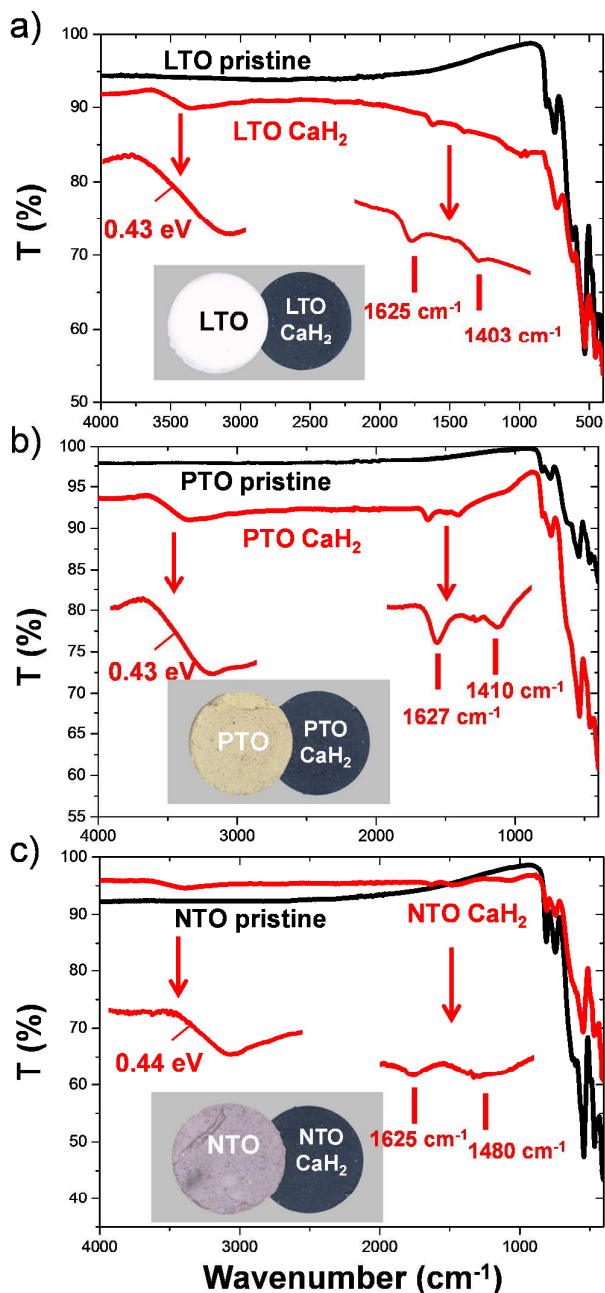
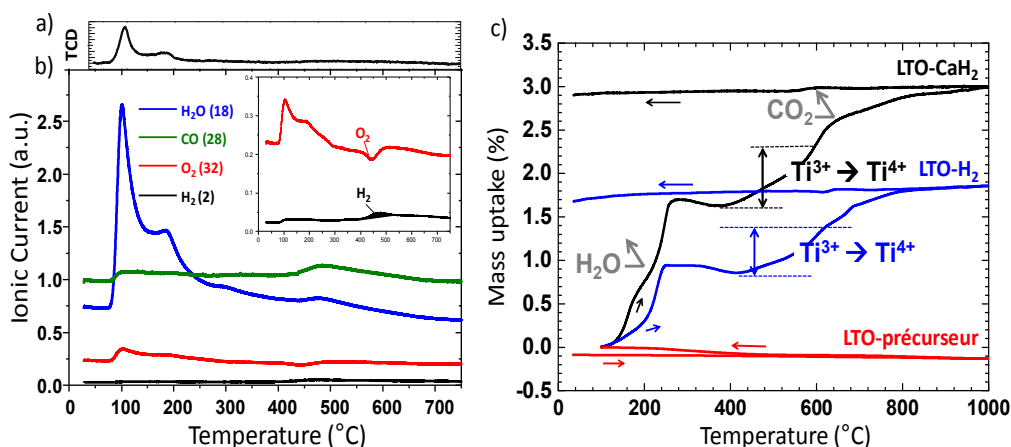


Figure 2 : Infrared spectra for a) LTO and LTO-CaH₂. b) PTO and PTO-CaH₂. c) NTO and NTO-CaH₂. The zoom in red highlights the gap-like edge at ~0.4 eV and extra band due to partial hydridation (see text).

Hydrides against vacancies: Focusing on the LTO based compounds, besides the reduction rate, one important insight concerns the incorporation or not of hydrides ions in LTO-CaH₂, especially taking into account the existence of fourteen independent oxygen positions in the monoclinic LTO crystal structure, with specific reactivities towards H⁺. Although LTO-CaH₂ was washed/stirred in NH₄Cl/methanol and dried in oven, its preliminary TGA under flowing

argon (see figure S3) shows an important mass loss (>13%) until 650°C. This mainly stems from residual solvent absorbed on the nanosized grains. Around $T = 400^\circ\text{C}$, a second step is assigned to the removal of various surficial species, including a weak but undoubtful H_2 peak ($m/e=2$) detected by mass spectrometry. The second abrupt mass loss around 650°C corresponds to the departure of the carbonate species ($m/e=44$). To remove most of the solvent and undesirable species, samples were heated overnight at 100°C in secondary vacuum. After combustion in a commercial elementary analyzer chamber, a significant decrease of the carbon and hydrogen content was observed, reaching values close to those for the pristine LTO and LTO- H_2 , see Table S4. Thus, the contamination by surficial carbonates is significant, and emphasized by nanostructures. Similarly the nitrogen-absorption is rather important in any cases (wt% between 0.64 and 0.94). For LTO- CaH_2 the amount of hydrogen possibly associated to hydride is hard to distinguish due to residual water and solvent traces. It was accurately estimated by temperature programmed desorption (TPD) using a thermal conductivity detector (TCD), coupled with mass spectrometry under flowing Ar, see Figure 3a, b. For LTO- CaH_2 , the TCD signal shows first the water removal ($m/e=18$) between 100°C and 250°C in good agreement with the preliminary TGA. The broad desorption above 440°C is assigned to CO and/or N_2 ($m/e= 18$) and a later H_2 ($m/e= 2$) removal. At this temperature the system also absorbs the residual oxygen impurity of the He flow (< 0.1 ppm). The quantification of hydrogen was performed after injection of 5 pulses of hydrogen and calibration of both TCD and mass spectroscopy signals (see Supplementary S5). The integration and scaling of the hydrogen peak gives coherent but very weak released hydrogen (H_2) amount of 0.00357 mmol/g (TCD) and 0.00319 mmol/g (mass spectroscopy), see the inset of Figure 3b. It leads to the formula $\text{La}_2\text{Ti}_2\text{O}_{7-x}\text{H}_{0.02}$. The HYSOCORE-EPR study presented below unambiguously confirms the accommodation of hydride anions in the lattice, even if weak.



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3 *Fig 3: a) Temperature programmed desorption for LTO-CaH₂ under flowing Ar : a) TCD*
4 *signal. b) Mass spectrometry results for various m/e signals. The zoom in the inset shows*
5 *above 400°C the H₂ removal together with the residual O₂ consumption. c) TGA under air*
6 *of the LTO precursor, LTO-CaH₂ and LTO-H₂ with their attribution.*
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10 Ti-H bonds are also validated by the IR spectra given figure 2. Weak bands appear after
11 hydridation at 1403 cm⁻¹ for LTO, 1480 cm⁻¹ for PTO and 1410 cm⁻¹ for NTO. According to
12 literature, these bands may correspond to the antisymmetric stretching vibration of the Ti-H-
13 Ti bridges expected around 1450 cm⁻¹.³¹ The complete absence of any absorption in the
14 2000 cm⁻¹ region of the spectra of LnTO-CaH₂ plays against the presence of terminal Ti-H
15 bonds, i.e. externally to the perovskite blocks.²⁴ This is in agreement with the preferred
16 location of the Ti³⁺ ions in the blocks, discussed later from our DFT modeling. Finally, another
17 peak independent of the Ln³⁺ nature appears at 1625 cm⁻¹ for the three phases. It may be
18 assigned to N-H bending modes, possibly resulting from residual ammonium after the
19 methanol/NH₄OH washing stage.
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24 It proves a minor H⁻ incorporation compared to the recent perovskite oxyhydrides, e.g.
25 BaTi(O,H)₃^{2,32}, CaTi(O,H)₃, SrTi(O,H)₃ and the related solid solutions³³ and EuTi(O,H)₃.¹⁰ In
26 these phases the maximal reported H ratio is shown in Figure 4 as a function of the Ti-Ti
27 distance, which proves a certain correlation. The average Ti-Ti distance of the LTO
28 compound is situated in the same range (d_{Ti-Ti}= 3.926 Å), leading to a foreseen plausible
29 hydridation of 0.278 H⁻ per formula unit. However, in LTO the mean Ti-Ti bond distance
30 results from a number of discrete values between 3.86 and 4.14 Å due to the complex crystal
31 structure, but the reason for such a low hydridation ratio remains open. A number of key-
32 parameters should influence, such as the exact experimental conditions or the
33 microstructural features of the unreacted phase. However, focusing on structural arguments,
34 two main parameters may be responsible for the blocked H⁻ diffusion in LnTO by comparison
35 with other titanate oxyhydrides. a) Its fragility versus topochemical reduction taking into
36 account reconstructive reduction in other layered terms, e.g. La₅Ti^{+3.8}O₁₇. b) Bordering Ti³⁺ in
37 the layered structure are not favored, as deduced from our DFT simulations which limit the
38 reduction ratio. c) The strongly constrained character of all Ti-O-Ti angles in LTO (142° to
39 174°) compared to cubic or pseudo-cubic phases (~180°) in which the overlapping with
40 hydrogen s states via σ-bonds may be a limitation. These parameters may offer a predicting
41 vision of the realization or not of hydridation in other next target phases.
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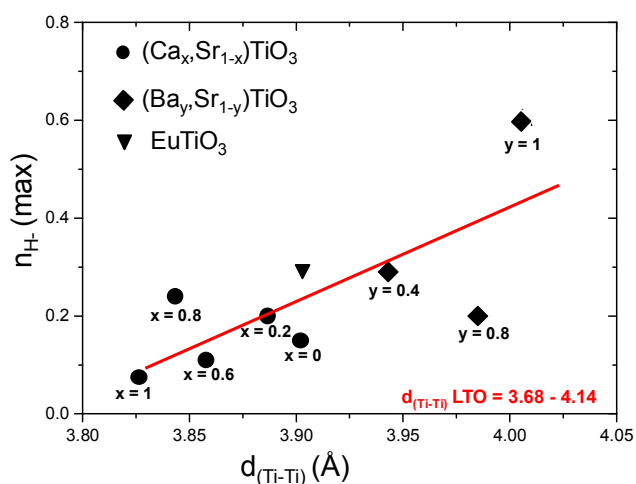


Fig 4: Plot of the maximal quantity of hydride inserted ($n_{H^-} (max)$) versus the average distance Ti-Ti for several perovskite titanates: $BaTiO_3$ ^{2, 32}, $CaTiO_3$, $SrTiO_3$ and the associated solid solutions³³ and $EuTiO_3$ ¹⁰.

A rough estimation of the titanium redox can be deduced from the TGA under air for LTO- CaH_2 and LTO- H_2 by analogy with TGA under argon, see Fig. 3b. For the pristine compound, no mass change was detected. For reduced compounds, we note the preliminary water loss already observed by TPD. It reaches ~1.5% for LTO- CaH_2 . Above 400°C, the mass uptake is assigned to Ti^{3+} oxidation until the inflexion at ~600°C, this latter being assigned to the removal of carbonate species. Then for both LTO- CaH_2 and LTO- H_2 the oxidation steps (w% ~ 0.7) corresponds to ~0.2 oxygen, i.e. $La_2Ti_2O_{6.8}$ for the two samples.

Neutron Diffraction: This ratio was confirmed by powder neutron diffraction (3T2 diffractometer, LLB, Saclay France). Here the preparation of one single batch (for homogeneity reasons) of ~2g of LTO- CaH_2 leads to the presence of the $La_5Ti_5O_{17}$ secondary phase further refined to a weight ratio of 10.1(6) %. The main anion sub-stoichiometry $La_2Ti_2O_{7-\delta}$ was refined to $\delta=0.27(1)$ starting from the LTO model³⁴ (space group $P112_1$). After refinement of atomic coordinates, isotropic thermal parameters have been restrained equal for each chemical nature, due to the large number of independent atoms (i.e. four La, four Ti and fourteen O positions). It was not possible to locate the minor amount of H anions, while oxygen sites O3 to O8 show significant deviation from full occupancy. In the last refinement stage, their occupancies (= 91(1) %) have been restrained equal for the six concerned sites leading to the formula $La_2Ti_2O_{6.73}H_{-0.02}$. The calculated vs. experimental PND diffractograms ($\chi^2=2.55$, $R_{Bragg} LTO-CaH_2 = 5.06\%$, $R_{Bragg} La_5Ti_5O_{17} = 6.69\%$) are shown in Figure 5. The refined atomic coordinates, occupancies and thermal parameters are listed in Table 2.

Atomic distances are presented in Table S6. It is striking that only the central atoms of the perovskite blocks forming Ti-O-Ti bridges in the *ab* plane are deficient which denotes a certain anisotropy in the topochemical depletion process before the structure collapsing. It is also noteworthy that external atoms at the interlayer edges are not concerned by reduction, see Figure 6a.

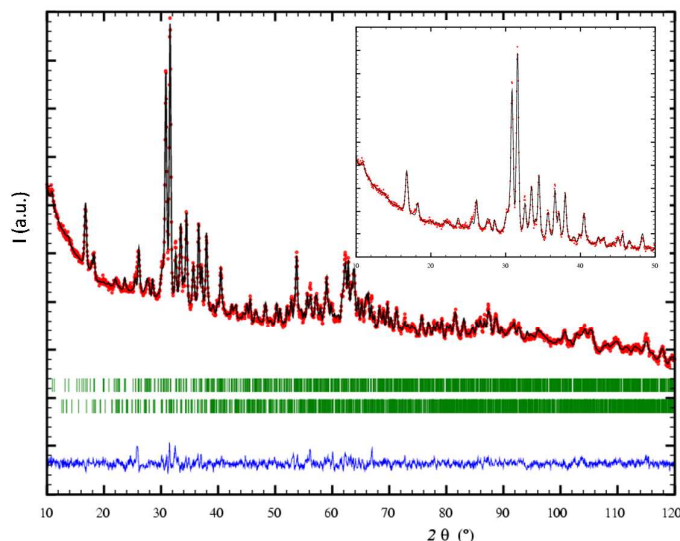


Fig 5: experimental (red) calculated (black) and difference (blue) PND pattern for LTO-CaH₂ with Bragg contributions of two phases (green) : La₂Ti₂O_{6.73} (top), La₅Ti₅O₁₇ (bottom). The inset shows a zoom of the 10-50° range.

Magnetic Properties: Quantification of Ti³⁺ was achieved by magnetic analysis of LTO-CaH₂ and LTO-H₂. The magnetization versus external field *M*(*H*) shows predominant paramagnetism (Brillouin function shape) with similar amplitudes, see Figure 7a. Typically, *M*(*H*) of both compounds show very close moments in the main thermal range (~0.35 μB at 5 Tesla and *T*=2K) which indicates similar paramagnetic contributions. However, their accurate interpretation is complicated owing to the nanosize of the studied sample and the presence of a weak parasitic ferromagnetic (FM) component highlighted on the low field region at 2 K, 25 K, 100 K and 300 K on the Figure 7b.

Indeed for both compounds, *M*(*H*) shows the opening of a small hysteresis loop at all temperatures, accompanied with a remanent moment which slightly increases on cooling. This nonzero magnetization called FM_{nano} hereafter was already observed and discussed for nanometric BaTiO₃³⁵ and PbTiO₃³⁶ with similar amplitudes as in the title compounds. In agreement with theoretical calculations³⁷, it was assigned to extrinsic surficial oxygen vacancies leading to Ti³⁺ or Ti²⁺ FM interactions. Then in both LTO-CaH₂ and LTO-H₂ it indicates a certain segregation of reduced species at the surface, together with the nanometrization upon reduction, leading to intrinsic weak ferromagnetic component.

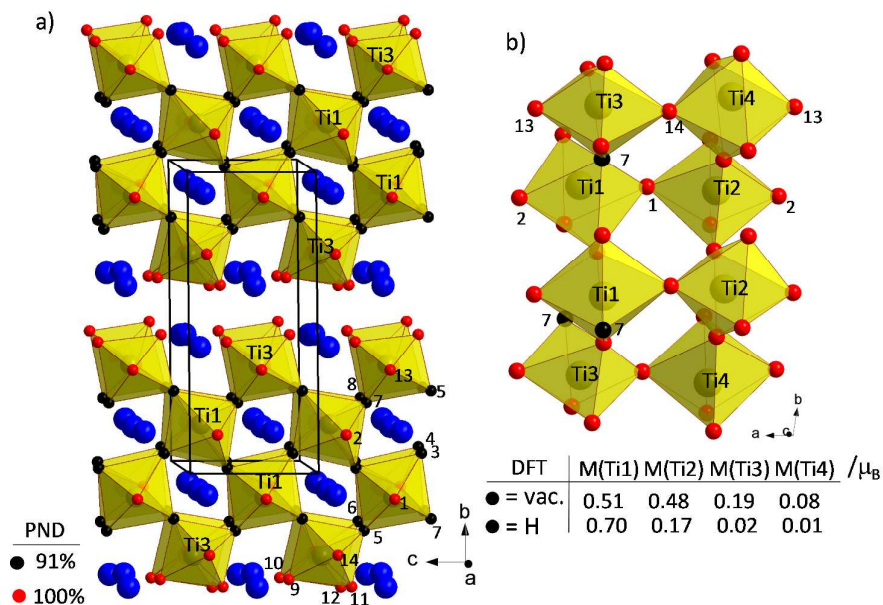


Fig 6: a) Crystal structure and atom labels for LTO-CaH₂ refined from PND data. Black and red atoms correspond to partially occupied and fully occupied oxygen positions. b) Fragment of the structure used for DFT calculations with O7 (black) replaced by vacancies or H ions. The local moment on each Ti sites is given at the bottom.

According to the non-linear $\chi^{-1}(T)$ plot for LTO-CaH₂, its paramagnetic contribution of $\chi(T)$ was fitted using data collected at 200 Oe, 1 kOe and 3 kOe between 300 K and 75 K using a modified Curie-Weiss law: $\chi = C/(T - \theta) + \chi_0$. Here, C and θ have their usual meanings while χ_0 takes into account both the diamagnetic and FM_{nano} contributions. χ_0 is expected weak compared to the paramagnetic response and was roughly approximated to be temperature independent. It yields three comparable μ_{eff} values between 0.73 and 0.80 μ_{B}/FU (i.e. 0.18-0.22 Ti³⁺/FU assuming 1.70 μ_{B} per Ti³⁺ ion, see the EPR section below). As expected both the calculated θ and χ_0 values depend on the applied field as long as FM_{nano} is not saturated. Most reliable results are expected at H= 3 kOe, leading to $\theta = -30.4$ K and $\chi_0 = 1.9 \cdot 10^{-4}$ emu/mol (i.e. $1.02 \cdot 10^{-4}$ μ_{B}/FU at 3 kOe). At 75 K, an abrupt jump of the susceptibility occurs, below which the ZFC/FC divergence is pronounced. This transition is not understood yet but its amplitude suggests intrinsic spin correlations. Uncompensated or canted spin domains may occur in Ti³⁺ rich domains of the nano-scaled phase. We cannot exclude the contribution of a minor unidentified phase with ferromagnetic correlations in order to explain the susceptibility jump.

Apart from its FM nano component, $\chi(T)$ for LTO- H_2 shows a predominant paramagnetic susceptibility with minor ZFC/FC divergence. The interpretation of the high temperature magnetism is complicated by the weak experimental χ values dominated by the competition between FM_{nano} and χ_{dia} with similar amplitudes, see $M(H)$ at 300 K on Figure 7a. This competition is such that it was not possible to extract a reasonable μ_{eff} value from the high temperature data. Assuming predominant paramagnetism in the 2-200 K range for $H=1\text{ kOe}$, the fit using $\chi = C/(T - \theta) + \chi_0$ gives $\mu_{\text{eff}} = 0.22 \text{ Ti}^{3+}/\text{FU}$, $\theta = -6.7 \text{ K}$ and $\chi_0 = 7.10^{-4} \text{ emu/Oe.mol}$ (i.e. $1.2 \cdot 10^{-4} \mu_B/\text{FU}$ at 1 kOe).

In conclusion, both compounds show very comparable paramagnetic contributions from Ti^{3+} ions in relatively good agreement with the priority established $La_2Ti_2O_{-6.8}H_\delta$ formula, if one takes into account the surficial Ti^{3+} species involved in FM_{nano} . However, the repartition of Ti^{3+} ions is plausibly most homogeneous in LTO- CaH_2 (size $\sim 835 \text{ nm}$) with strongest AFM exchanges between them compared to highly divided LTO- H_2 (size $\sim 295 \text{ nm}$). In the later, the surficial Ti^{3+} amount is expected biggest with more enhanced inhomogeneities between the core and the surface.

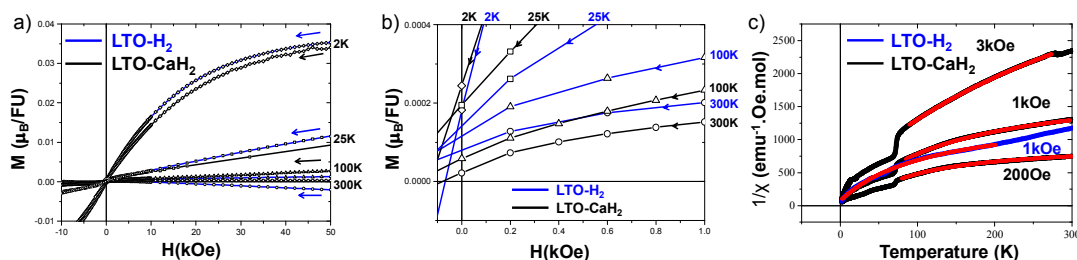


Fig 7 a) $M(H)$ magnetization plots for LTO- H_2 (blue) and LTO- CaH_2 (black) on decreasing the applied field. The high-field region shows similar magnetization at 2 K, while for LTO- H_2 the variation is dominated by diamagnetism at 300 K. b) Zoom of the low field region with evidences of weak remanent moments and their variations versus T . c) inverse susceptibility $\chi^{-1}(T)$ at 200 Oe, 1 kOe and 3 kOe (black) with their fit in the HT region (red). $\chi^{-1}(T)$ at 1 kOe for LTO- H_2 fitted in the LT region (red).

Electronic Structure: DFT optimizations of the precursor $La_2Ti_2O_7$ and of two modified models were carried out.²¹ The models correspond to an oxyhydride and a lacunar phase, respectively, in which the oxygen site O7 is replaced by an H atom ($La_2Ti^{+3.75}_2O_{6.5}H_{0.5}$) or an anionic vacancy ($La_2Ti^{+3.5}_2O_{6.5}$), see Fig 6b. Both modified models preserve the initial symmetry. The O7 site was selected because it was found partially occupied after our PND refinement. The minor structural changes between the reported LTO structure and the relaxed one validate our method, focusing on the Ti-Ti distances, see Fig S7. The two modified models give an opportunity for locally probing the effect of oxygen substitution and

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3 charge repartition through the analysis of DFT-calculated local moments and projected DOS
4 for each Ti site (1 to 4). The main DOS topology is similar for the three phases, see Figure
5 8a-c, while the anionic modifications lead to the filling of empty Ti1 *d* states (and Ti2 *d* states
6 in a lower extend) at the bottom of the conduction band (CB) giving total or partial Ti³⁺
7 character on these two sites. This is highlighted in Fig 8d, e in the oxyhydride case. On the
8 opposite, Ti3 and Ti4 have their *d* levels empty in the CB with no spin polarization in
9 agreement with a Ti⁴⁺ states. The projected DOS for all Ti sites in LTO and its two modified
10 forms is given Figure S8. Finally it turns out that the Ti⁴⁺ → Ti³⁺ reduction appears on sites
11 directly in the vicinity of the H⁻ anion or vacancy (Ti1) with an induced moment on next
12 connected site (Ti2) within the perovskite block rather than on its edges, see Figure 6b.
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18 For La₂Ti₂O₇, the calculated gap is 2.6 eV. For the virtual La₂Ti₂O_{6.5}H_{0.5} oxy-hydride, the H *s*
19 states are found in the VB, while they are unmixed with the newly occupied Ti *d* states at the
20 bottom of the CB. GGA+U with U= 3eV opens a gap of ~ 0.3 eV for the oxy-hydride while the
21 lacunar phase remains metallic. Compared to the real reduction rate on several O sites, our
22 models are exaggeratedly reduced and fully ordered. They give only trends for the new band
23 structure. It is clear that partial and disordered vacancies lead in real to a distribution of
24 occupied levels in the forbidden band, well compatible with the experimental UV-vis and IR
25 spectral features.
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31 Structurally, one main feature results from the replacement of O7 by vacancies or a H atom,
32 see Figure 6b. In both cases it leads to the increase of the concerned Ti-X-Ti bridge
33 distance, for instance Ti1-O7-Ti3 evolves as follows: 3.75 Å_(oxide) → 3.89 Å_(oxyhydride) → 3.98 Å
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(lacunar). Based on this observation, the PND structure of the reduced phase might be correlated. Although not straightforward for all, some of the distances evolution refined by PND, with respect to the experimental stoichiometric phase, can be rationalized: Ti2-O6 (90%occ.)-Ti4 and Ti2-O8 (90% occ.)-Ti4, 3.75 Å → 4.08 Å and O8, 3.69 Å → 4.04 Å.

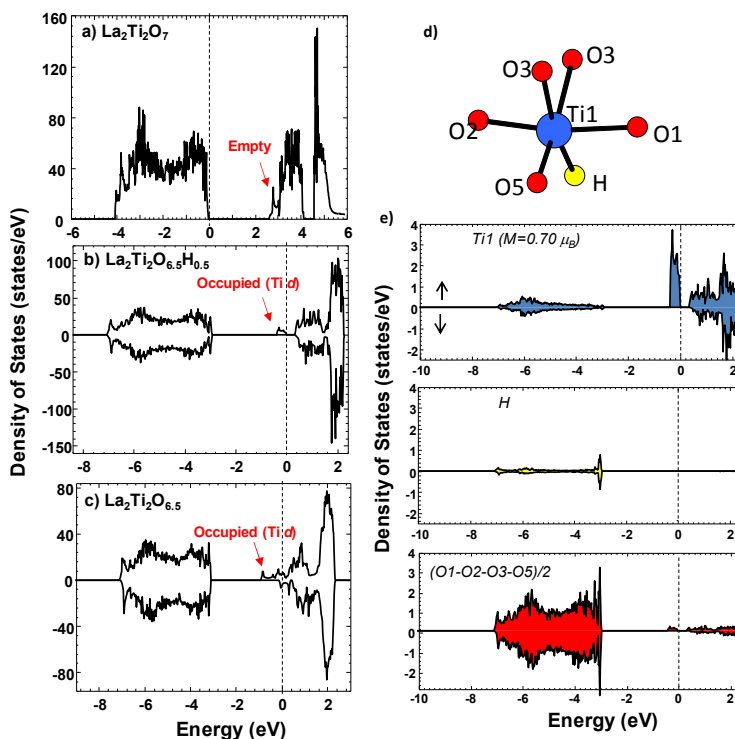


Fig 8: total density of states (GGA+U) for a) $\text{La}_2\text{Ti}_2\text{O}_7$ ($U=0$) b) $\text{La}_2\text{Ti}_2\text{O}_{6.5}\text{H}_{0.5}$ ($U=3\text{eV}$) c) $\text{La}_2\text{Ti}_2\text{O}_{6.5}$ ($U=3\text{eV}$) with evidence of occupied defect levels at the bottom of the CB and opening of a gap for the oxyhydride. d) Ti1 case with weak overlapping between oxygen p states and Ti^{3+} paramagnetic levels contrarily to H s levels which show no magnetic character.

The Ti-H bonding scheme: Further insights on the Ti^{3+} paramagnetic species and their possible couplings with ^1H nuclear spin were analyzed by EPR spectroscopy at 4 K. LTO- CaH_2 displays a continuous-wave (CW) X-band EPR spectrum with an axial g tensor, $g_{xy}=1.95$ and $g_z=1.91$, characteristic of an $S=1/2$ Ti^{3+} species with almost quenched spin-orbit coupling ($g_s=2$, $g_j=0.8$), Fig 9-inset. It is in excellent agreement with the effective moment generally reported for this cation, i.e. $1.70 \mu_B$ weakly lower than the spin only approximation ($1.74 \mu_B$) due to the negative LS contribution responsible for the weak anisotropic magnetism of this ion.

Two dimensional pulsed EPR experiments were performed to probe the nuclear environments of Ti^{3+} moieties. The (+,+) quadrant of the HYSCORE spectrum recorded at g_{xy} of the CW X-band is shown Figure 9. Along the diagonal, we can observe the nuclear Larmor frequencies with the first one centered at 1.95 MHz, the ^{139}La ($I=7/2$) Larmor frequency. It is assigned to the hyperfine coupling with ^{139}La multi-quanta transitions. A pair of cross-peaks centered at the ^1H Larmor nuclear frequency, i.e. 13.7 MHz is also revealed. The hyperfine coupling strength can be estimated from the width of the HYSCORE signals along the antidiagonal, i.e. 8 MHz which at first sight suggests Ti-H Fermi contact. Here, the Ti^{3+} ($3d^1$)-

H(s^2) bond involves σ -overlapping with empty d levels of the titanium centers. A significant electronic delocalization of the single electron probe is plausible and would largely dominate the dipolar coupling with the ^1H nuclear spin. We estimate that 0.5% of electronic transfer would justify by its own the 8MHz hyperfine coupling.

The calculations of the $\text{La}_2\text{Ti}^{3.75}\text{O}_{6.5}\text{H}_{0.5}$ give informative parameters about the Ti-H electronic exchange, see Fig. 8 d, e. Focusing on the magnetic Ti1 site ($M = 0.7 \mu_B$) despite direct Ti-H bond, the newly occupied d states from the bottom of the CB do not interact with H s states, separated by $\sim 3\text{eV}$. It is confirmed by the local moment on H calculated to $0.02\mu_B$ (i.e. $\sim 0.02\%$ of delocalization) which excludes any electronic transfer between the magnetic electron and the H site, even in our exaggerated hydrided model. It is such that the dipolar contribution with the ^1H nuclei is expected predominant. Assuming a point to point dipole approximation, the 8MHz corresponds to an electron-H distance of 2.14 \AA , very close to the expected Ti^{3+} -H distance. Finally, it is most plausible that the hyperfine coupling have both contributions in significant amount, for instance 25 % (2MHz) from Fermi contact in good agreement with the H quasi-null local moment and 75% (6MHz) from dipolar interaction would correspond to Ti-H distance of 2.3 \AA . To the best of our knowledge, despite the recent discovery of a large variety of transition metal oxyhydride, this result makes our study the first preliminary characterization of the Ti-H electronic partition.

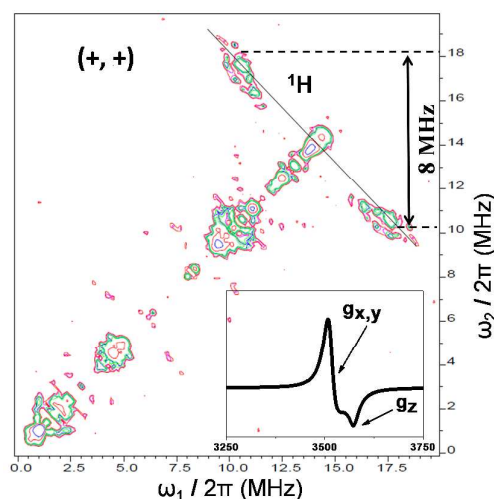


Fig 9: (+,+) quadrant of the Two-dimensional EPR HYSCORE spectra recorded at 5 K of LTO-CaH_2 . It was recorded at $g_{xy} = 1.95$ of the Ti^{3+} species. The X-band EPR spectrum is shown in the inset.

Catalytic performances: Due to its favorable bandgap and donor-doped character, $\text{La}_2\text{Ti}_2\text{O}_7$ has a high photocatalytic activity for overall water splitting under UV irradiation with high quantum yields.³⁸ Optimization of its morphology¹³ and surface³⁹ area greatly improves its

performances, while (Fe-Cr) co-doping to $\text{La}_2\text{Ti}_2\text{O}_7$ narrows its bandgap, giving rise to an efficient hydrogen production under solar irradiation¹⁸. Here, the efficient photocatalytic hydrogen production and the high photocurrent in the co-doped $\text{La}_2\text{Ti}_2\text{O}_7$ originate from the optimized combination of the physical–chemical properties, namely, the small bandgap and the low recombination rate of photoelectron–holes. Thus, according to its extended optical absorbance and nanometric morphologies, LTO- CaH_2 deserves attention as a photocathode for water-splitting. Especially, the mid-infrared bandgap, E_g of ~ 0.4 eV reported above, makes it possible to reach efficiencies higher than 10% in a tandem device, if combined with a photoanode with a band gap between 0.4 eV and 2.3 eV. Its photoelectrochemical performances have been evaluated using a three electrode cell upon linear sweep voltage in pH 7 potassium phosphate solutions. In this preliminary study, a rough layer (ca. 300 μm thick) of LTO- CaH_2 was pasted on a FTO (Fluorine doped Tin Oxide) substrate using a commercial glazing and heated at 400°C under flowing argon leading to mechanically stable FTO/LTO- CaH_2 interface. It is probable that the nanotexturation of the precursor is mainly responsible for the good adherence and mechanical integrity of the layer. As shown Figure 10a, the hydrogen evolution reaction current begins at the very low value 0.6 V vs. RHE in the dark for our ~ 500 nm thick mesoporous film, corresponding to a remarkable shift of ~ 1 V vs. RHE compared to recent results reported by Paracchino *et al.* for an optimized photocathode^{40, 41}. This very favorable onset potential makes the LTO- CaH_2 photoelectrode potentially compatible with previously reported photoanodes, such as n- BiVO_4 ⁴² or n- WO_3 ⁴³ in a complete PEC tandem cell for water splitting. At 0 V vs. RHE, the current density is as high as $-4 \mu\text{A}/\text{cm}^2$ in absence of any optimization of the layer. Upon illumination, the onset potential does not evolve, a small change is observed at high potential. The stability of $\text{La}_2\text{Ti}_2\text{O}_7$ photocathode was tested by cycling the electrode between +0.6 V to -0.6 V. After several cycling (typically ~ 10 cycles), an evolution of the J-E curve is observed, corresponding to an evolution of the samples under these conditions. Typically, the peak around 0.4 eV may correspond to Ti^{4+} reduction into Ti^{3+} . Post-mortem XRD analysis confirms a partial decomposition into Ti_2O_3 , Ti_6O_{11} and orthorhombic TiO_2 during the reduction process, see Fig. 10b. However, we note a considerable increase by two decades in the photocurrent after phase degradation. This high activity could be related to the formation of heterojunction $\text{TiO}_x/\text{LaTi}_2\text{O}_{7-\delta}$ that might be performant for water-splitting. The formation of in-situ junctions might be also an attractive pathway to explore for improved photocurrent. Another route consists in the addition of a thin TiO_2 barrier to improve the stability of the electrode by avoiding parasitic reactions and degradation.

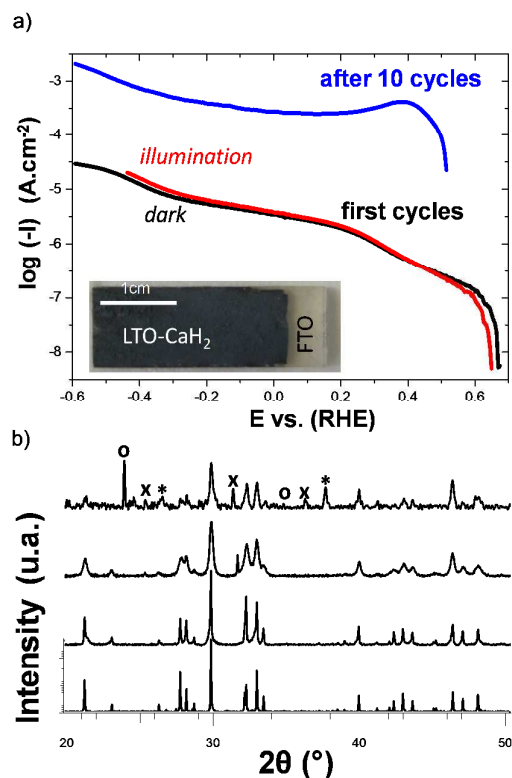


Fig 10: LTO-CaH₂ electrocatalysis for hydrogen evolution : a) Photocurrent density vs. the applied potential. First cycles in the dark (black) and under illumination (red). second test after 12 hours, in the dark (blue). A photography of the LTO film before catalytic test is also presented. b) XRD Characterization of (from bottom to the top): Pristine compound LTO ; LTO – CaH₂ ; LTO – CaH₂ film before first catalytic test ; LTO – CaH₂ after several catalytic tests, showing the partial decomposition into Ti₂O₃ (open circles), Ti₆O₁₁ (stars) and o-TiO₂ (crosses).

Conclusion

In this work, we investigated topochemically modified layered perovskite Ln₂Ti₂O_{7-δ} (Ln= La, Pr, Nd) compounds (LTO) after reduction using either solid CaH₂ (or NaH) or flowing H₂ (100%). Compared to three-dimensional titanate perovskites offering well-adapted potential for the formation of oxyhydrides, it is striking that a significant nanotexturation occurs which suggests a fragility of the 2D-LTO structure upon reduction. Our results validate a limited topotactic reduction stage, prior to the reconstructive reduction into La₅Ti^{+3.8}₅O₁₇ observed in more severe reducing conditions, and finally into the extreme LaTi⁺³O₃ polymorph. This observation may be related with the poor reducibility of titanium species located at the edge of the octahedral blocks (from our DFT simulations), which may act as a redox-barrier. However apart from Ti³⁺ segregation at the surface, responsible for extrinsic ferromagnetism, both reduction methods create a similar amount of oxygen vacancies close to 3%. It leads to

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3 a band gap reduction from LTO (3.63eV) to the dark colored LTO-CaH₂) via occupied defect
4 levels in the forbidden band. Similar effects are observed after treating Nd₂Ti₂O₇ and
5 Pr₂Ti₂O₇.
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7 Dealing with CaH₂ as the reducing source, the weak but sensitive incorporation of H
8 species in LTO-CaH₂ was estimated to La₂Ti₂O_{6.73}H_{-0.02}. The understanding of parameters
9 ruling out the hydridation appears complicated due to a number of key structural, electronic
10 and experimental parameters, but should help predicting best candidates toward hydridation.
11 However in LTO-CaH₂, the weak oxyhydride character gives the opportunity to probe the
12 nuclear environments of Ti³⁺ moieties which represents to the best of our knowledge, the first
13 preliminary characterization of the Ti-H electronic partition. The Ti-H covalence is mediated
14 by non-magnetic empty Ti *d* states and no significant electron transfer occurs between Ti³⁺
15 and the hydrogen *s* states. This result opens a broad field of investigation tuning the H
16 content in more standard oxyhydrides such as BaTi(O,H)₃ for which the high H content
17 (~20%) should reveal a hierarchy of Ti-H bond in the bulk. Finally the evaluation of LTO-
18 CaH₂ photoelectrochemical performances shows very promising performances, in that sense
19 that the hydrogen evolution reaction current starts as low as +0.6 V vs. RHE in the dark (shift
20 of ~1 V vs. RHE compared to recently optimized photocathodes). Although a fast
21 degradation of the layer was observed, it makes the LTO-CaH₂ photoelectrode potentially
22 compatible in a complete PEC tandem cell for water splitting. At 0 V vs. RHE, the current
23 density is as high as -4 μA/cm².
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34 **Supporting informations**

35 The supporting information is available free of charge on the ACS publication website. It
36 includes additional spectroscopic results, details of the DFT calculations and
37 crystallographic informations.
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Table 1: Comparison between reported powder XRD information for LTO and experimental PND information for LTO – CaH₂ (monoclinic system, space group: P112₁)

| | LTO Pristine Compound ³⁴ | LTO Pristine X-ray Tube | LTO CaH ₂ PND | LTO CaH ₂ Synchrotron | LTO H ₂ X-ray Tube |
|-------------------------|-------------------------------------|-------------------------|--------------------------|----------------------------------|-------------------------------|
| Unit cell (Å and °) | a = 7.800(3) | 7.8120(1) | 7.817(1) | 7.81618(1) | 7.8076(3) |
| | b = 13.011(4) | 13.0144(2) | 13.006(1) | 13.01244(3) | 12.9914(6) |
| | c = 5.546(2) | 5.5472(9) | 5.547(1) | 5.54834(1) | 5.5299(3) |
| | ̑ = 98.60(2) | 98.6318(8) | 98.673(2) | 98.6226(2) | 98.551(3) |
| Volume (Å) ³ | 556.51(34) | 557.59(1) | 557.44(2) | 557.930(2) | 554.67(3) |

Table 2: Atomic positions, site occupancies and anisotropic displacement parameters from Rietveld refinement on ND data of the LTO-CaH₂ compound.

| Atom | Wyck. | Occ. | x/a | y/b | z/c | Uiso |
|------|-------|----------|-----------|----------|----------|---------|
| La1 | 2a | 1 | 0.280(2) | 0.107(1) | 1/4 | 0.92(9) |
| La2 | 2a | 1 | 0.768(3) | 0.103(1) | 0.260(4) | 0.92(9) |
| La3 | 2a | 1 | 0.357(2) | 0.390(1) | 0.823(4) | 0.92(9) |
| La4 | 2a | 1 | 0.857(3) | 0.413(1) | 0.862(3) | 0.92(9) |
| Ti1 | 2a | 1 | 0.040 (6) | 0.121(2) | 0.771(7) | 0.2(1) |
| Ti2 | 2a | 1 | 0.506 (4) | 0.107(3) | 0.788(7) | 0.2(1) |
| Ti3 | 2a | 1 | 0.084 (5) | 0.320(2) | 0.325(6) | 0.2(1) |
| Ti4 | 2a | 1 | 0.578 (6) | 0.338(2) | 0.293(5) | 0.2(1) |
| O1 | 2a | 1 | 0.776(3) | 0.117(1) | 0.796(4) | 0.12(6) |
| O2 | 2a | 1 | 0.280(4) | 0.096(1) | 0.678(4) | 0.12(6) |
| O3 | 2a | 0.907(2) | 0.033(3) | 0.025(1) | 0.059(4) | 0.12(6) |
| O4 | 2a | 0.907(2) | 0.476(3) | 0.023(2) | 0.001(4) | 0.12(6) |
| O5 | 2a | 0.907(2) | 0.102(3) | 0.234(2) | 0.991(5) | 0.12(6) |
| O6 | 2a | 0.907(2) | 0.533(3) | 0.222(2) | 0.973(5) | 0.12(6) |
| O7 | 2a | 0.907(2) | 0.015(3) | 0.192(2) | 0.482(4) | 0.12(6) |
| O8 | 2a | 0.907(2) | 0.548(4) | 0.187(1) | 0.458(4) | 0.12(6) |
| O9 | 2a | 1 | 0.109(4) | 0.398(1) | 0.577(4) | 0.12(6) |
| O10 | 2a | 1 | 0.633(3) | 0.415(1) | 0.570(4) | 0.12(6) |
| O11 | 2a | 1 | 0.122(3) | 0.423(2) | 0.088(5) | 0.12(6) |
| O12 | 2a | 1 | 0.599(3) | 0.444(1) | 0.101(4) | 0.12(6) |
| O13 | 2a | 1 | 0.324(3) | 0.312(1) | 0.338(5) | 0.12(6) |
| O14 | 2a | 1 | 0.823(3) | 0.306(1) | 0.235(4) | 0.12(6) |

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TOC Graphic

