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Optical properties of Ln₂Ti₂O₇ (with Ln = La to Lu) thin films grown on (110)-SrTiO₃ substrates by Pulsed Laser Deposition

Alexandre Bayart¹, Jean-François Blach¹, Marielle Huvé¹, Florent Blanchard¹, Pascal Roussel¹, Rachel Desfeux¹, Sébastien Saitzek^{1,}*

¹ *Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et Chimie du Solide (UCCS), F-62300 Lens, France*

Abstract

Ln₂Ti₂O₇ thin films with Ln=La to Lu were successfully grown on (110)-SrTiO₃ substrates by pulsed laser deposition. **The microstructure and optical properties of the entire Ln₂Ti₂O₇ series were investigated by X-Ray Diffraction, Atomic Force Microscopy, Scanning Transmission Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy and Spectroscopic Ellipsometry.** For large ionic radii (i.e. Ln³⁺ = La³⁺ to Eu³⁺), the monoclinic/layered-perovskite structure is obtained with epitaxial growth. For smaller ionic radii (i.e. Ln³⁺ = Tb³⁺ to Lu³⁺), the cubic/pyrochlore structure is privileged. We have also observed the growth of a Gd₂Ti₂O₇ polymorphic phase between the stability limit of the two previously described structures. The optical band gap increases when the ionic radius of Ln³⁺ decreases. Refractive index (n) and extinction coefficient (k) have been calculated over a wavelength range of 260 to 1500 nm. **The low value of the extinction coefficient indicates that these materials are transparent in the visible range and can therefore be used in electro-optics systems in the case of the layered-perovskite structure and more widely as emitting materials in solid-state lasers optically pumped.**

Corresponding author:

Sébastien SAITZEK,

¹Université d'Artois, Unité de Catalyse et de Chimie du Solide, UCCS,
Équipe Chimie du Solide, CNRS-UMR 8181, Faculté des Sciences Jean Perrin,
F-62300 LENS, France

Phone: +33 / 321791732, Fax: +33 / 321177955, E-mail: sebastien.saitzek@univ-artois.fr

1. Introduction

Since the last few decades, layered-perovskites, with the $A_nB_nO_{3n+2}$ general formula, are widely studied for their multifunctional properties [1],[2],[3]. These oxides possess a wide range of composition due to many possible combinations on A- and B-site of cations. Usually, A-site is occupied by a cation with a large ionic radius (lanthanides or actinides) and B-site is occupied by a cation of smaller size (transition metals) [1],[4],[5]. In this work, we are particularly interested in the lanthanum titanates ($Ln_2Ti_2O_7$) compounds, which belong to this large $A_nB_nO_{3n+2}$ series where $n=4$. $Ln_2Ti_2O_7$ oxides crystallize in two structural forms which depend on the ionic ratio $r(Ti^{4+})/r(Ln^{3+})$ [5]. For a ratio greater than 1.78 (i.e. $Ln=La$ to Nd), oxide crystallizes in a layered-perovskite with monoclinic structure and have piezoelectric [6],[7] and ferroelectric properties [8],[9] with a high Curie temperature [10],[11]. For a ratio smaller than 1.78 (i.e. $Ln=Sm$ to Lu), the compound crystallizes in a cubic/pyrochlore structure. All of these $Ln_2Ti_2O_7$ oxides can be employed in **photo-electrochemical systems as a photo-catalyst** (e.g. for the water-splitting [12],[13], for the **photo-degradation** of organic pollutants [14],[15],[16] and/or **for the photo-reduction of inorganic ions in water, like for example the reduction of Cr(VI) to Cr(III)** [17]). A photocatalyst, such as $La_2Ti_2O_7$, requires the use of an excitation energy in UV domain. Current research is therefore focused on reducing this energy in order to obtain an active photocatalyst under visible excitation. In this respect, the improvement of the absorption towards the visible range can be done according to several ways, for example, with : i) the formation of nano-composites oxide/metallic nanoparticles such as $Au/La_2Ti_2O_7$ [18] or $Ag@AgCl/La_2Ti_2O_7$ [19]; ii) the reduction [20] or the nitridation [21],[22] of oxide in order to decrease its optical band gap or iii) the realization of visible-light-driven n/p heterojunction such as $LaCrO_3/La_2Ti_2O_7$ [23], $CuO/La_2Ti_2O_7$ [24] or $g-C_3N_4/La_2Ti_2O_7$ [25].

Moreover, it has been reported that $La_2Ti_2O_7$ can also act as excellent hosts for integration

of lanthanides ions in order to produce luminescent materials [26],[27],[28]. Or even, these phases possess a great ability for the realization of immobilization matrices of highly active nuclear wastes (lanthanides substitution by actinides) [29],[30].

Concerning optical properties, Z. Wang *et al.* [31] have recently proposed an overview on the recent development of $A_2B_2O_7$ oxides as transparent ceramics. Among these compounds, the $A_2Hf_2O_7$ and $A_2Zr_2O_7$ oxides are the most studied and only a few studies are available on $A_2Ti_2O_7$ oxide. Thus, it has been reported that $Y_2Ti_2O_7$ ceramics with an excess amount of Y exhibited ~50 % transmittance at 1100 nm [32] or that $Lu_2Ti_2O_7$ ceramics prepared by spark plasma sintering presented a very good transmittance in the NIR domain with 72% transmittance at a wavelength of 2000 nm (40 % transmittance at 550 nm) and high refractive index (2.57 at 632.8 nm) [33]. For thin films, studies are still much more scarce and to the best of our knowledge only one study has been performed by spectroscopic ellipsometry on the $La_2Ti_2O_7$ thin films [34].

All the properties described above make these oxides multifunctional materials particularly interesting to study. Recently, we have shown that the stability limit can be extended by constraints on epitaxial films prepared by sol-gel associated with the spin-coating technique on a substrate (110)-oriented $SrTiO_3$ [35]. This helped highlight new ferroelectric metastable phases such as $Sm_2Ti_2O_7$ [36]. Similarly, ferroelectricity can be induced to films with a geometrically frustrated pyrochlore structure. Indeed, the loss of symmetry induced by the epitaxial growth can lead to the emergence of new properties. One can cite the example of $La_2Zr_2O_7$ deposited on (110)-oriented $SrTiO_3$ [37].

There are several synthesis routes for $Ln_2Ti_2O_7$ thin films (Ln =Lanthanide) such as sol-gel associated with spin-coating technique [38],[39],[40], metal-organic decomposition methods [41], spray pyrolysis process [42], RF sputtering [43] and pulsed laser deposition [44],[45],[46].

In this work, we present the synthesis optimization of thin films on the complete series of Ln = La to Lu via the Pulsed Laser Deposition (PLD) technique. The stability limit of layered-perovskite structure onto (110)-oriented SrTiO₃ substrates has been highlighted. Studies on optical properties of Ln₂Ti₂O₇ thin films are scarce or even non-existent for some compositions. We therefore propose a full study on this series in order to determine the optical gaps and the optical indices, and to correlate them with the structural properties related to the nature of the Ln³⁺ cation.

2. Experimental section

Ln₂Ti₂O₇ thin films were deposited on (110)-oriented SrTiO₃ single-crystal substrates (Crystal GmbH, Germany). All substrates were firstly ultrasonically cleaned in acetone then in ethanol for 5 minutes. Each substrate was attached to a heater plate using silver paste.

Ln₂Ti₂O₇ target was synthesized using a classical solid-state reaction route. A stoichiometric mixture [1:2] of precursor compounds: Ln₂O₃ with Ln=La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Lu (99.9% STREM CHEMICAL) and TiO₂ (99.9% GERAC), were ground in ethanol during 20 min. All oxides Ln₂O₃ being hygroscopic, they must undergo a thermal pre-treatment at 800°C to obtain the correct stoichiometry (except for Pr₂Ti₂O₇, where Pr₆O₁₁ (99.9% STREM CHEMICAL) was used as precursor, also with a thermal pre-treatment). The ground powders were afterward packed in alumina crucible and calcined, under air, at 1100°C during 12 hours.

After this first step, the powders were re-ground, and then placed in an uniaxial press to produce 1 inch diameter PLD targets. Finally, these pellets were sintered at 1250°C during 12h. X-Ray patterns, realized on the pellets, confirmed the presence of the expected monoclinic phase, with no impurities.

In this study, we set some instrumental parameters at (conditions determined in previous work for $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{Pr}_2\text{Ti}_2\text{O}_7$ and $\text{Nd}_2\text{Ti}_2\text{O}_7$ thin films on SrTiO_3 substrate [7][46]): depositions were carried out with a Compex Pro 102 deposition system using a KrF excimer laser operating at a wavelength of 248 nm. The laser was pulsed at a rate of 3 Hz with an energy density of 2 J/cm^2 and the target-substrate distance was fixed at $d = 45 \text{ mm}$. All films were deposited for 4000 pulses.

The structural characterization of the films was performed using a Rigaku SmartLab High Resolution X-Ray Diffractometer (HR-XRD) equipped with a 9 kW rotating anode X-ray generator ($\lambda\text{K}\alpha_1=1.54056 \text{ \AA}$). The X-Ray beam was made parallel with cross-beam optics and monochromatized with a double Ge (220) monochromator. In this study all the (ω - 2θ) scans were performed in the range of $10^\circ - 80^\circ$, with a step size of 0.01° and a speed of $3^\circ/\text{min}$. The rocking-curve technique (ω scan) was also employed to evaluate the mosaic spread of the films.

The Scanning Transmission Electron Microscopy (STEM) images and the Energy Dispersive Spectroscopy (EDS) mapping were obtained with a FEI TITAN Themis 300. The TEM samples are prepared using the Focused Ion Beam (FIB) technique.

Analyses by Atomic Force Microscopy (AFM) were carried out in air at room temperature using a modified commercial microscope (Multimode, Nanoscope V, Bruker). Topography was imaged in contact mode with a silicon nitride ultralever tip.

Spectroscopic Ellipsometry measurements were performed at room temperature using a phase-modulated ellipsometer (UVISEL HR460 from Horiba Scientific) at wavelengths ranging from 260 to 1500 nm with 2 nm interval. An incidence angle of 70° was used for all measurements.

The raw signal measured by Spectroscopic Ellipsometry has the following form:

$I(t) = I_0 + I_s \sin(\delta(t)) + I_c \cos(\delta(t))$, where $\delta(t)$ is the phase shift of a modulator. In our

experimental configuration, the value of I_0 , I_C and I_S are related to the ellipsometric angles (Δ , Ψ) by the following relations: $I_0 = 1$, $I_S = \sin 2\Psi \sin \Delta$, $I_C = \sin 2\Psi \cos \Delta$. The ellipsometric angles Δ and Ψ are related to the complex reflection coefficients of polarized light (R_p and R_s for respectively a polarization parallel and perpendicular to the plane of incidence) by the following relation $\rho = \frac{R_p}{R_s} = \tan \psi e^{i\Delta}$. For each sample, the measured spectrum was analyzed using an appropriate fitting model based on sample structure. For that, we created a model with the same number of layers (substrate, film layers, roughness). For each layer, we defined a thickness and the refraction index (in the case of the roughness layer, the refractive index was calculated by using the effective medium theory). This model allows the calculation of the ellipsometric angles ψ and Δ . The unknown parameters (refractive indices, thicknesses) were determined by finding the global minimum of a merit function χ^2 (Levenberg-Marquardt algorithm) which compare the ellipsometric angles obtained by the model with the measurements [47]:

$$\chi^2 = \min \sum_{i=1}^n \left[\frac{(\Psi_{th} - \Psi_{exp})_i^2}{\sigma_{\Psi,i}^{exp}} + \frac{(\Delta_{th} - \Delta_{exp})_i^2}{\sigma_{\Delta,i}^{exp}} \right] \quad (1)$$

Where n is the number of measured Ψ and Δ pairs, $\sigma_{\Psi,i}^{exp}$ and $\sigma_{\Delta,i}^{exp}$ are the standard deviations of $\Psi_{exp,i}$ and $\Delta_{exp,i}$. All fitting steps were performed using the Delta-Psi Horiba software.

3. Results and Discussion

Structural investigations : As pointed out previously, the growth parameters required to obtain ferroelectric LnTO thin films with Ln=La, Pr, Nd were determined in previous work [7][46]. We highlighted the presence of a competition between a monoclinic ferroelectric phase (called α -phase) and a polymorphic phase with orthorhombic structure with $Ammm$ space group (called γ -phase) identified by S. Havelia *et al.* [48]. Recent studies show that the

stability limit of the layered perovskite family can be extended by epitaxial strain. In this work, we sought if possible to further extend the range of stability in $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films grown by PLD on (110)-oriented SrTiO_3 substrates. Figure 1. shows the XRD patterns of $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films grown on (110)-oriented SrTiO_3 substrates by PLD technique. The temperature selected for the film growth was fixed at 950°C for the entire series. We observe a structural evolution according to the size of the ionic radius. Indeed for the large ionic radii, (i.e. $\text{Ln}=\text{La}$ to Nd), only the layered perovskite structure/ monoclinic (α phase) is observed with the (00 l) orientation. When the size of the Ln^{3+} cation decreases (i. e. $\text{Ln}=\text{Sm}$, Eu), the layered perovskite is retained with the same orientation but with also a second phase identified as the cubic/pyrochlore phase of $\text{Ln}_2\text{Ti}_2\text{O}_7$ (Figure 1a). The proportion of this pyrochlore phase increases gradually as the ionic radius decreases. It is important to note that layered perovskite phases do not exist in bulk for $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Eu}_2\text{Ti}_2\text{O}_7$ compounds (under standard conditions of temperature and pressure). In our case, these phases are stabilized by the constraints effects due to the epitaxial growth of film on the substrate, as previously observed on $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films elaborated by sol-gel technique [35]. When the size of the cation is still decreasing (i.e. $\text{Ln} = \text{Gd}$), layered perovskites and pyrochlore phases disappear in favor of a γ phase, always with the (00 l) orientation, as seen on the $2\theta/\omega$ scan with the sudden displacement of the (00 l) reflections towards small 2θ angles. This γ phase has already been highlighted by Havelia et al. for $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films with $\text{Ln}=\text{Nd}$, Sm , Gd , Dy [48]. In a previous study performed by X-ray diffraction vs. temperature, we showed that the formation of this phase was governed by surface energy parameters (epitaxial growth on this type of substrate allows the stabilization of this phase) but also by kinetics parameters [35]. Thus, annealing of the $\text{Gd}_2\text{Ti}_2\text{O}_7$ layer at 950°C with a rate of $3^\circ\text{C}/\text{min}$ leads to the formation of the pyrochlore phase.

When size of the Ln^{3+} cation is further reduced (i.e. $\text{Ln} = \text{Tb}, \text{Dy}$), the γ phase decreases in favor of the pyrochlore phase, as expected (Figure 1b). For $\text{Ln} = \text{Ho}, \text{Er}$ and Tm , only the pyrochlore phase is observed with (011) preferential orientation. And finally, for the smallest Ln^{3+} cation (i.e. $\text{Lu}_2\text{Ti}_2\text{O}_7$), the pyrochlore phase is always present, but with (011) and (001) orientations.

As already discussed in the introduction, the phase with layered-perovskite structure presents interesting ferroelectric properties with a High Curie temperature ($T_c \approx 1500^\circ\text{C}$ in bulk for $\text{La}_2\text{Ti}_2\text{O}_7$) [11] [46][49] and a polarization vector mainly directed along \vec{b} -axis. It is thus interesting to know the epitaxial relations of the film with the substrate. For that, we recorded a pole figure at $2\theta = 33.7^\circ$. This particular value corresponding to the $\{-204\}$ reflection of $\text{Nd}_2\text{Ti}_2\text{O}_7$ (the lattice parameters of the bulk were used to determine this angle) was chosen for its strong intensity and its proximity to the (101) reciprocal node of STO. The results are given in figure 2 for the both observed and simulated ones. The analysis was performed by visual comparison of the measured enhanced pole densities with calculated spherical projections of SrTiO_3 and $\text{Nd}_2\text{Ti}_2\text{O}_7$ crystals, using the software STEREOPOLE [50]. The different poles observed can be simulated considering (00 l) oriented $\text{Nd}_2\text{Ti}_2\text{O}_7$ film (blue index) deposited on a (110) SrTiO_3 substrate (red index). Since only punctual poles are observed one can conclude the epitaxial growth. The epitaxial relationships deduced from this pole Figure are: $[001]_{\text{SrTiO}_3} // [100]_{\text{Nd}_2\text{Ti}_2\text{O}_7}$ and $[1-10]_{\text{SrTiO}_3} // [010]_{\text{Nd}_2\text{Ti}_2\text{O}_7}$.

In the literature, it has been shown that the $\text{La}_2\text{Ti}_2\text{O}_7$ structure (which is isostructural to $\text{Nd}_2\text{Ti}_2\text{O}_7$) has a twinning [51]. In the tabulated monoclinic unit cell used in our work, the twinning operation corresponds to a mirror plane perpendicular to the \mathcal{C}^* direction giving two directions for the \mathcal{A}^* -axis (the angle between $\mathcal{A}^*_{\text{twin1}}$ and $\mathcal{A}^*_{\text{twin2}}$ is equal to $2(\beta-90^\circ)$) [51]. The presence of this twinning is also highlighted in the pole figure with the presence of the $\{-105\}$ reflection (figure 2.b). In a non-twinned structure, a single reflection should be

observed. While, in our case, two reflections are clearly visible. This can be explained by the presence of twinning in the $\text{Nd}_2\text{Ti}_2\text{O}_7$ structure, with two domains (I and II) related by a 180° rotation around the \vec{c} -axis.

Pole figures highlighted an epitaxial grown for LaTO, PrTO, NdTO, SmTO and EuTO films. Based on epitaxial relationships, using bibliographical references for LnTO materials listed in Table 1 and considering $a = 3.905 \text{ \AA}$ as lattice parameter for the STO substrate, we have calculated the LnTO/STO lattice/substrate mismatches (δ , δ') with the following relations [7]:

$$\delta = \frac{a_L - 2a_{STO}}{2a_{STO}} \quad \text{and} \quad \delta' = \frac{b_L - a_{STO}\sqrt{2}}{a_{STO}\sqrt{2}} \quad (2)$$

We observe a trend increasingly significant for mismatch when Ln^{3+} ionic radius decreases. This should result in an increase in mosaic spread of the films (increasing for La to Eu). To verify this behavior, we performed the rocking-curves on the (004) reflection for each film with layered perovskite structure. Figure 3 shows the evolution of the Full Width at Half Maximum (FWHM) as a function of ionic radius (Ln^{3+} in coordination VIII). The data used for the ionic radius are from ref [52]. However, we do not observe a gradual increase in the FWHM when the ionic radius decreases. In fact, the $\text{La}_2\text{Ti}_2\text{O}_7$ film does not follow the expected trend and nevertheless observed for other LnTO Films. Note that in a previous study, for films prepared by sol-gel a gradual increase is observed between La and Nd but the FWHM is much greater. To explain this phenomenon, two hypotheses can be made: i) using the PLD technique, the crystallization temperature required to obtain the LTO film with the optimum crystallization seems to be more important than for the rest of the LnTO family. In this respect, the film annealed at 1050°C reduces the FWHM to 0.202° (white square in Figure 3); ii) there may also be a difference in the matching structures between the substrate and the layer. Indeed, for $\text{La}_2\text{Ti}_2\text{O}_7$, the growth is carried with a compressive strain ($\bar{\delta} < 0$)

while for others it is performed with a tensile strain ($\bar{\delta} > 0$). It would be more complicated to compress the LTO cell in order to adapt to the substrate. The film would be more relaxed. This will be able to lead to a larger mosaic spread in $\text{La}_2\text{Ti}_2\text{O}_7$ layer. Nevertheless, based on the studies of K. B. Helean *et al.* [53] on the formation enthalpies of rare-earth titanates, the first hypothesis is the most likely. Indeed, these studies show: i) that formation enthalpies increase when the ionic radius of the lanthanide decreases (for example, these values are $-206.0 \text{ kJ.mol}^{-1}$ and $-115.4 \text{ kJ.mol}^{-1}$ for $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{O}_7$, respectively) and ii) that the critical amorphization temperature is linearly related to this enthalpy of formation. So, the crystallization temperature of $\text{La}_2\text{Ti}_2\text{O}_7$ is higher than that of $\text{Nd}_2\text{Ti}_2\text{O}_7$ (which is itself greater than $\text{Pr}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{O}_7$). Consequently, for $\text{La}_2\text{Ti}_2\text{O}_7$, this leads to a higher mosaic spread (more weakly crystallized for a similar substrate temperature). Moreover, the decrease of the FWHM with the annealing temperature also argues for a higher crystallization temperature for $\text{La}_2\text{Ti}_2\text{O}_7$.

To conclude, the polynomial behavior of the curve, presented in Figure 3, is the result of two antagonistic phenomena. In part I, the curve evolution is dominated by the crystallization temperature and in part II, it is rather related to the increase of the lattice mismatch.

To calculate the optical indices, it is necessary to know the thickness of the synthesized films. In the case of layered-perovskite films, the thickness has already been measured at 60 nm in a previous study [7] performed by STEM-HAADF (Scanning Transmission Electron Microscopy – High Angle Annular Dark Field). In this paper, we carried out the same study on the pyrochlore phase. Figure 4 shows the STEM-HAADF images obtained on the $\text{Er}_2\text{Ti}_2\text{O}_7$ layer. The thickness of the layer is about 40 nm (Figure 4a). Far from the interface (Figure 4b), the [110] projection of the ordered pyrochlore structure is well superposed. The blue scale is related to the erbium density in the column perpendicular to the projection plane. The EDX mapping confirms the ordered position of the different atoms and in particular the

superposition of the Er and Ti sites in purple. One can notice a dark band, roughly equal to 4-5 Å along the interface (Figure 4a). EDX mapping indicates that this band is a disordered area of Ti. One can notice that near the interface the pyrochlore structure is not so well ordered on some cell unit before rearranging to grow in the direction [110], as indicated by X-rays patterns. Otherwise, no amorphous zone was observed in the layer and the EDX analyzes showed a good chemical homogeneity as showed by Figure 4.b.

The surface morphology of the films was characterized by AFM. The characteristic images of the three phases observed in this study are presented in Figure 5. we can observe a dense granular surface with small-rounded grains in all three cases (the topographic behavior is generalizable to all the compounds crystallizing in the same structure). For the α and pyrochlore phases, the surface morphology is quite close with rounded grains whose diameter is about 40 and 30 nm, respectively. While the root mean square roughness (R_{ms}) measured for 2 x 2 μm^2 scan area were found to be ~ 7 and 3 Å, respectively. In the case of γ phase, the observed grains have a much larger size about 90 nm. But, the R_{ms} calculated at 6 Å remains fairly close to that observed for the α phase.

Optical properties:

Optical characterization of these films were obtained by spectroscopic ellipsometry. In a first step, we determined the optical function of SrTiO₃ substrate by a measurement on a cleaned substrate. The optical function $\varepsilon(\omega)$, in this simple case, depends only on the incidence angle θ and the complex reflectance ratio ρ [54]:

$$\varepsilon(\omega) = \sin^2 \theta + \sin^2 \theta \tan^2 \theta \frac{(1-\rho)^2}{(1+\rho)^2}. \text{ Using this relation, we can extract the optical function}$$

of SrTiO₃ in the visible-NIR range (0.78 – 4.76 eV).

Afterward, this optical function was then inserted in a three layers model (Figure 6.a) for the modelling of ellipsometric spectra obtained on all samples: a semi-infinite STO substrate

covered by a dense layer of $\text{Ln}_2\text{Ti}_2\text{O}_7$, and a rough layer which can be represented as a $\text{Ln}_2\text{Ti}_2\text{O}_7$ matrix with holes filled by air (The taking into account of this layer is necessary to the model in order to report the roughness of the films highlighted by AFM analyses and of which this one can be more important on millimetric surfaces analysis) ; we used the Bruggeman [55] effective medium approximation for modeling this last layer.

As proposed by Dickerson *et al.* [34], we can use an absorbent Cauchy relation for the modelling of optical properties of $\text{La}_2\text{Ti}_2\text{O}_7$ thin film in the whole UV- Visible range. Moreover, the transparent Cauchy relation ($n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$, $k=0$) has been shown to produce good and easiest adjustments for $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films in their transparency range of the optical spectrum (below 3 eV for powder samples [56]). The modelling of our samples was then accomplished with two following steps:

In the first step, we created a model with a transparent Cauchy relation to perform the modeling in the 0.82 – 3.00 eV range. With this method, it was possible to find both the thickness values and Cauchy parameters. All samples were successfully analyzed (an example of fitting result can be shown on figure 6.b) by this method and the values of thicknesses (around 60 nm for layered perovskite samples) were compared to those measured by TEM on some samples, and found in good agreements.

In a second step, we fixed the values of thicknesses obtained previously and we used the point by point inversion equations of ellipsometry to extract the optical properties (n and k) of $\text{Ln}_2\text{Ti}_2\text{O}_7$ materials for each photon energy in the whole optical range. An example of result can be shown on figure 7 in the case of $\text{La}_2\text{Ti}_2\text{O}_7$. It is worth to notice that the shape of these curves is similar to those obtained by numerical simulation by Sayede *et al.* [57].

Figure 8 shows the values of refractive index measured at 500 nm for all samples. These values are similar and close to 2.4; this result is in good accordance with the results of calculation performed by Sayede *et al.* [57] on $\text{Pr}_2\text{Ti}_2\text{O}_7$ and $\text{Ce}_2\text{Ti}_2\text{O}_7$ but is slightly higher

than the value ($n=2.1$) obtained by Dickerson *et al.* [34] on similar measurements performed on $\text{La}_2\text{Ti}_2\text{O}_7$ films but deposited on Si/SiO₂ substrates instead of STO. These samples are transparent at this wavelength and could thus be used for waveguide or electro-optical applications. Furthermore, as already pointed out, $\text{La}_2\text{Ti}_2\text{O}_7$ can serve as a host matrix for other lanthanide, such as Eu^{3+} , Er^{3+} , Sm^{3+} , Pr^{3+} ... , leading to the stabilization of phosphors emitting under both UV excitation (e.g. $\text{La}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$ [56], $\text{La}_2\text{Ti}_2\text{O}_7:\text{Sm}^{3+}$ [27], $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ [58]...) and NIR excitation, via an upconversion effect (e.g. $\text{La}_{1.9}\text{Er}_{0.1}\text{Ti}_2\text{O}_7$ [59]). Thus, combining these luminescence properties with the reported-here low values of the extinction coefficient, can be created optically pumped luminescent single crystals for applications in the field of lasers. The knowledge of the optical properties (n , k) allows also, using a Tauc plot [60], the determination of the optical band gap. Knowing that $\text{Ln}_2\text{Ti}_2\text{O}_7$ samples have a direct band gap behavior [57]. In that case, the Tauc plot (i.e. the plot of $(\alpha E)^2$ versus E where α and E are respectively the absorption coefficient and the photon energy) will lead to the determination of the band gap value by the intersection of the linear part of the curve with the energy axis. This procedure was applied for all samples and the results are represented on **Figure 8.a**). First, we can note that values are close to those already measured on $\text{Ln}_2\text{Ti}_2\text{O}_7$ powders [56] excepted for the pyrochlore phases where higher values are obtained. Secondly, we can note that the band gap value is almost constant in both structural domains observed with a larger band gap in the case of pyrochlore compared to the layered-perovskite. To conclude, these bands correspond to an absorption in the near UV range and these materials can be suitable for photocatalytic [61] and luminescence applications [56].

4. Conclusion

Lanthanide titanates thin films were grown on (110)- SrTiO_3 substrates by pulsed laser deposition. For $\text{Ln}_2\text{Ti}_2\text{O}_7$ with $\text{Ln}=\text{La}$ to Eu , epitaxial growth (with the following epitaxial

relations: $[001]_{\text{SrTiO}_3} // [100]_{\text{Ln}_2\text{Ti}_2\text{O}_7}$ and $[1-10]_{\text{SrTiO}_3} // [010]_{\text{Ln}_2\text{Ti}_2\text{O}_7}$) was obtained for monoclinic/layered-perovskite structure. It is important to note that in bulk, $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Eu}_2\text{Ti}_2\text{O}_7$ crystallize in a cubic/pyrochlore phase, whereas with the strains induced by the substrate in film, they crystallize in a monoclinic/layered-perovskite in thin films. Study of mosaic spreads shows an increase with increasing lattice mismatch excepted for $\text{La}_2\text{Ti}_2\text{O}_7$. This can be explained by i) the need for a higher crystallization temperature compared to other compounds and / or ii) the fact that the growth is achieved under compressive strains unlike other compounds. $\text{Ln}_2\text{Ti}_2\text{O}_7$ with $\text{Ln} = \text{Er}$ to Lu grow with cubic/pyrochlore structure, as expected in bulk. For these thin films, a preferential orientation in the (011) direction is observed. However, this decreases when the ionic radius decreases. For $\text{Gd}_2\text{Ti}_2\text{O}_7$, under the experimental conditions described, we have observed the growth of a polymorphic phase (γ phase) already described by Havelia *et al.* [48]. Optical properties of $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films were also studied by spectroscopic ellipsometry to determine the optical band gap, refractive index and extinction coefficient. We can notice an increase in the optical band gap when the ionic radius decreases with a significant evolution from 3.75 eV to 4.15 eV when passing through the pyrochlore structure to the layered perovskite structure. In addition, all films have similar characteristics in terms of refractive index and extinction coefficient. **Based on the optical properties described in this work, $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films of are promising candidates for various applications in the optical field. Indeed, we can cite here some examples: i) high refractive index optical elements applications; ii) The low values of k coupled to the ferroelectric properties of the layered-perovskite structure (ie $\text{Ln} = \text{La}$ to Eu), allow us to classify these oxides in the category of transparent ferroelectric materials. These materials have electro-optical properties due to their non-centrosymmetric structure (Pockels and Kerr effects) [62] which are the base of many optical systems such as switches, modulators, deflectors and demodulators for high-speed optical communications [63]. As such, the determination of the**

electro-optic coefficients of these oxides can be an interesting prosecution study to conduct. In addition, their high Curie temperatures ($T_c=1461^\circ\text{C}$ for $\text{La}_2\text{Ti}_2\text{O}_7$) [10], may allow use of such systems in extreme environments; iii) These oxides also constitute a good insertion matrix for other lanthanides and thus induce luminescence properties as described in the introductory part. These properties can be used in lighting systems (fluorophore lamps or as phosphors in UV light-emitting diodes). Indeed, the band gap of the layered-perovskite phases are suitable with commercial UV LED chips; iv) The low value of k in the visible range coupled with luminescence properties is very interesting for a potential use in solid-state lasers optically pumped.

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Figure Captions

Figure 1. XRD patterns of $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films grown on (110)-oriented SrTiO_3 substrates by PLD technique. The peaks with * correspond to the cubic pyrochlore phase.

Figure 2. Pole figure obtained at $2\theta = 33.8^\circ$. The blue crosses correspond to the calculated positions of NTO while the red ones correspond to the poles of the STO substrate. The following relationships can be deduced: $[001]_{\text{SrTiO}_3} // [100]_{\text{Nd}_2\text{Ti}_2\text{O}_7}$ and $[1-10]_{\text{SrTiO}_3} // [010]_{\text{Nd}_2\text{Ti}_2\text{O}_7}$.

Figure 3. Evolution of FWHM vs. the Ln^{3+} ionic radius obtained from the Rocking curves performed on the (004) reflections of LnTO thin films.

Figure 4. $\text{Er}_2\text{Ti}_2\text{O}_7$ on STO 110. a) HAADF image of a part of the substrate and the whole layer showing a dark zone at the level of the interface; b) enlargement of the image far from the interface and perfect superposition of the [110] pyrochlore structure. The scale of blue/red is proportional to the density of Er/Ti in the columns. EDX mapping confirming the superposition of Er and Ti sites in purple (sum of blue and red) for some columns; c) enlargement of the images at the interface showing a dark zone of about 5 Å and EDX mapping indicate a Ti rich dark area. One can notice a more disordered pyrochlore structure at this level.

Figure 5. Topography images ($2 \times 2 \mu\text{m}^2$) of (a) $\text{Pr}_2\text{Ti}_2\text{O}_7$ thin film (α phase), (b) $\text{Gd}_2\text{Ti}_2\text{O}_7$ thin film (γ phase) and (c) $\text{Lu}_2\text{Ti}_2\text{O}_7$ thin film (pyrochlore phase) deposited onto the (110)-oriented SrTiO_3 substrate.

Figure 6. a) Three layers model used for ellipsometric modelling; b) Example of results on I_s and I_c curves with the Cauchy relation for the $\text{La}_2\text{Ti}_2\text{O}_7$ film. The full and open circles represent the experimental and calculated datas, respectively.

Figure 7. Refractive index n (open circles) and extinction coefficient k (full circles) for $\text{La}_2\text{Ti}_2\text{O}_7$ thin film deposited on SrTiO_3 substrate.

Figure 8. Optical band gap (a) and refractive index at 500 nm (b) of $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films deposited on SrTiO_3 substrates.

