Unveiling point defects concentration in transition metal oxide thin films is essential to understand and eventually control their functional properties, employed in an increasing number of applications and devices. Despite this unquestionable interest, there is a lack of available experimental techniques able to estimate the defect chemistry and equilibrium constants in such oxides at intermediate-to-low temperatures. In this study, the defect chemistry of a relevant material such as La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ (LSF) with ($x$ = 0.2, 0.4 and 0.5 (LSF20, LSF40 and LSF50 respectively) is obtained by using a novel in situ spectroscopic ellipsometry approach applied to thin films. Through this technique, the concentration of holes in LSF is correlated to measured optical properties and its evolution with temperature and oxygen partial pressure is determined. In this way, a systematic description of defect chemistry in LSF thin films in the temperature range from 350 °C to 500 °C is obtained for the first time, which represents a step forward in the understanding of LSF20, LSF40 and LSF50 for emerging low temperature applications.

1. Introduction

Transition metal oxides thin films have been largely investigated in different strategic research fields such as electronics, solid state ionics, and ionotronics due to their wide variety of fascinating functional properties.[1,2] In this family of materials, point defects, imperfections, and higher dimensional extended defects are known to severely impact the overall functional properties.[3,4] As a matter of example, oxygen vacancies were shown to enhance oxygen conductivity in oxide–ion electrolytes[5] or to boost oxygen incorporation and catalytic activity in mixed ionic electronic conductors (MIECs)[6,7] while weakening electronic and magnetic order in ferromagnetic oxides.[8] Besides, the presence of heterogeneous and homogenous interfaces in thin films was shown to drastically impact defect concentrations in such layers, which gives rise to deviations from bulk defect chemistry and, eventually, to new and unexpected properties.[9–11] Therefore, the knowledge and quantification of the chemical reactions that dominate the defect concentration in oxide thin films (i.e., defect chemistry) is essential for understanding the material behavior and for engineering their properties. This is especially relevant at intermediate-to-low temperatures (below 500 °C), where a high electrochemical activity and the nanometric dimensions of the thin films allow the point defect equilibrium with the environment,[12] hampering the use of the high temperature defect chemistry model from the bulk counterpart.

A paradigmatic example of the large effect of point defects on the functional properties of transitional metal oxides can be found in the La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ (LSF) model family. LSF compounds crystallize in a perovskite ABO$_3$ structure and find application in many renewable energy technologies, such as solid oxide fuel cells (SOFC).[13] or electrochemical and photoelectrochemical water splitting.[14,15] In LSF, the substitution of trivalent La by divalent Sr gives rise to the generation of electronic holes and/or oxygen vacancies for electronic compensation, depending on the electrochemical equilibrium with the oxygen partial pressure of the environment. Interestingly, both point defects were found to be strongly correlated to many functional properties of LSF. For instance, the increase of holes concentration was found responsible for a large modification of the electronic structure,[16] affecting not just the electronic and magnetic transport properties[17] but also the oxygen evolution properties in aqueous media.[15] Meanwhile, oxygen vacancies were shown to take part into the rate-limiting step of oxygen incorporation at high temperature.[18] For these reasons, the development of a reliable and flexible in situ method for tracking the point defects of LSF thin films on any substrate and environment is fundamental for tailoring their properties.
Although many different techniques are available for the measurement of the defect concentration in bulk oxides (e.g., thermogravimetry, coulometric titration, and more), the reduced mass and thickness of thin films pose severe challenges in their applicability to nanometric-thick layers. The majority of in situ methods available for deducing oxygen equilibrium mechanisms in oxides thin films are based on an indirect probe of point defects, that is, a physical property dependent on one or more defects is measured as a function of the oxygen activity and the defect equilibrium is obtained by fitting a defect chemistry model. For instance, the measurement of the electrical conductivity as a function of oxygen partial pressure (i.e., Brower analysis) is expected to follow the behavior of the majority charge carrier (electrons or holes), which can then be used to fit a proper defect chemistry model to obtain the equilibrium constants. The major drawback of the Brower method is the charge carrier mobility may also vary with the oxygen partial pressure, giving rise to a non-trivial interdependence difficult to untangle. Another common method for getting insights into the oxygen nonstoichiometry of thin films is measuring the lattice parameters by X-ray diffraction (XRD), since a unit-cell expansion is commonly observed in oxygen deficient oxides. Nevertheless, challenges in the application of bulk atomic lattice refinement models and the presence of substrate-induced misfit strain hinder the exact quantification of the point defect concentration, making XRD a suitable method mainly for a qualitative analysis of the oxygen deficiency. The measure of the chemical capacitance as a function of oxygen partial pressure is also a very interesting method to extract the defect chemistry of oxide thin films. In this technique, electrochemical impedance spectroscopy (EIS) is performed to extract the chemical capacitive contribution of the electrodes, which can be related to the defect species involved in the oxygen incorporation by the application of a proper defect chemistry model. The main advantage of the method is the possibility of modeling the defect chemistry in situ and under real electrochemical conditions (i.e., under electrochemical bias), which was used, for instance, to get mechanistic information about the relationship between bulk point defects and oxygen incorporation and evolution reactions. Nevertheless, the measurement of chemical capacitance by EIS is problematic at low temperature, where the high polarization resistance (in parallel to the chemical capacitance) shifts the impedance to very low frequencies, increasing the error associated to the measurement.

A very promising family of methods for tracking point defects in oxides thin films are UV-visible optical characterization techniques. As recently reviewed by Buckner et al., point defects strongly modify the electronic band structure of many oxides, giving rise to unique changes of optical properties that can be tracked by optical methods. Although UV-visible techniques cannot directly probe the concentration of point defects, by measuring the evolution of the dielectric properties of the thin film by in situ Brower analysis, it is possible to indirectly achieve a quantification of the defect chemistry of the material, similar to the measurement of the electronic conductivity but without the limitation of a non-constant charge carrier mobility. In this regard, optical transmission was used to quantify the defect concentration and the kinetics of oxidation/reduction of many different oxides thin films, such as Pr doped ceria and La and Fe-doped SrTiO . However, the use of a transmission mode entails a non-trivial drawback, since the substrate must be transparent to light; what limits the application of this technique to specific cases or to limited photon energy windows. Finally, it was recently shown that Raman spectroscopy can also be used for tracking the oxygen non-stoichiometry of SrTi Fe O thin films.

Taking into consideration the benefits and limitations of the previous methods, an in situ ellipsometry technique is proposed here for quantifying the defect chemistry of LSF with x = 0.2, 0.4 and 0.5 (LSF20, LSF40 and LSF50, respectively) thin films through the measurements of optical conductivity. Ellipsometry is an optical spectroscopic technique based on the measure of the variation of polarization of a light beam reflected on a thin film sample. It is a non-destructive technique that can be used to measure many structural and optical characteristics of a thin film, such as optical constants and thickness, independently on the optical properties of the substrate. In this work, ellipsometry spectra are acquired under different electrochemical conditions and as a function of temperature (T = 350–525 °C) for LSF20, LSF40 and LSF50 thin films grown on Yttria-stabilized Zirconia (YSZ) substrates. The low energy transition of LSF optical conductivity is straightforwardly related to the concentration of electronic holes, which is then measured for different equivalent oxygen partial pressures generated by ion-pumping in an electrochemical cell. In this way, the defect chemistry of LSF thin films is unveiled in an unprecedented low temperature range, demonstrating the great capabilities of the in situ ellipsometry approach. Moreover, the results show the importance of non-dilute interaction among point defects in LSF thin films, largely influencing the energetics of the oxygen equilibrium reaction.

2. Results and Discussion

2.1. Microstructural and Morphological Analyses

LSF thin films with different Sr concentration (LSF20, LSF40, and LSF50) were prepared by Pulsed Laser Deposition (PLD) on top of gadolinium-doped ceria (CGO)-coated YSZ (001) substrates. The CGO layer (~10 nm) was deposited on YSZ substrates as a barrier to prevent the formation of secondary phases at the LSF/YSZ interface. Figure 1a shows the XRD patterns of the as-deposited multilayers. The LSF20 thin film shows a pseudo-cubic polycrystalline structure with two main orientations along the (h00) and (hk0) directions, while LSF40 and LSF50 films present a single (h00) preferential orientation. The increase of the Sr content in the LSF layers gives rise to a shrinkage of the out-of-plane lattice parameter, as shown by the progressive shift toward higher angles of the (100) diffraction peaks in Figure 1b. This contraction of the unit cell with the Sr content is consistent with literature data (see Figure S1, Supporting Information), and is associated to a subsequent partial oxidation of the Fe ions, being the ionic radius of the Fe smaller than the one of the Fe . The structural differences among the samples are also confirmed by the surface topography measured by atomic force...
Electronic holes strongly modify the optical absorption and the bandgap of the LSF family.\cite{16,32,36} Although this effect is well documented in literature, to the best knowledge of the authors, a direct relationship between hole concentration and optical features is still lacking. For this reason, as a first step, here we study the optical properties of LSF thin films at room temperature by spectroscopic ellipsometry. In order to remove all the oxygen vacancies and observe the true effect of electronic holes on the optical absorption, the samples were fully oxidized by electrochemical method at 400 °C (see Experimental Section for more details). Under these conditions, the concentration of holes in the films is entirely determined by the Sr content and the electronic equilibrium can be written as:

\[
\left[ S_{\text{Fe}}^{\text{L}} \right] = \left[ Fe_{\text{e}}^{\text{L}} \right] = x
\]

(1)

Where \( \left[ S_{\text{Fe}}^{\text{L}} \right] \) and \( \left[ Fe_{\text{e}}^{\text{L}} \right] \) are the concentration of Sr and localized electronic holes represented according to the Kröger–Vink notation. Moreover, LaFeO\(_3\) (LFO) thin films with no formal concentration of holes (\( x = 0 \)) were also measured for comparison. The resulting optical conductivity spectra measured at room temperature are shown in Figure 2c (please, refer to Section S2, Supporting Information, to see the ellipsometry raw data and the description of the five-Lorentzian oscillators model employed in the fitting process\cite{31}). Observing the optical conductivity, one can clearly note that increasing the hole doping leads to strong modifications of the optical properties of the material, consisting in an increase of spectral weight of the low energy transitions around 1 and 3 eV (named A and B, respectively) and a decrease of the high energy features around 4.5 eV (labelled C). These results are in good agreement with previously reported works, which deeply analyzed the origin of optical transitions in the LSF system by means of different spectroscopy techniques.\cite{15,31,37–38} According to these studies, the parent LFO presents a semiconductor structure in which the valence band is mainly composed by hybridized O 2p–Fe eg orbitals and the conduction band by empty minority spin Fe t2g states, while changing the Fe oxidation state in LSF through Sr doping introduces new intra-bandgap states, as depicted in Figure 2c. The exchange of electrons between all these bands has been directly correlated to the A, B, and C features observed in the optical conductivity spectra (Figure 2c). More specifically, transition A corresponds to the electron promotion from the valence band to the intra-bandgap states induced by hole doping while transition B and C are assigned to the transfer of electrons from O 2p–Fe eg orbitals to Fe t2g states and from deeper electronic states toward the empty minority spin Fe eg orbitals,\cite{39} respectively. In the energy range considered, the
Sr doping mainly affects the optical transitions indirectly by modifying the concentration of holes in the system (appearance of new Fe intra-bandgap electronic states, Figure 2c) and not directly, since available Sr electronic states are far from the Fermi level.\[16,32,36\]

For the purpose of investigating LSF’s defect chemistry, transition A was analyzed in more detail since this feature is correlated with the concentration of holes in the doped system.\[40,41\] For this analysis, the contribution of the transition A to the total spectra was deconvoluted (see Section S2, Supporting Information) showing a linear relationship between the associated maximum of the optical conductivity and the concentration of holes in the system (Figure 2b and inset). This linear relationship holds also at high temperature, although a different slope is observed due to the effect of temperature on the electronic band structure\[39\] (see Figure S4, Supporting Information). Moreover, the fully reduced LSF50 samples ([Fe\text{\textsuperscript{3+}}] = 0) shows an optical spectra similar to the LFO layer and no low energy transition A (see Figure 1a), confirming that electronic holes are at the origin of the changes observed in the optical properties. It must be noted here that the linear relationship found here may not hold if LSF films present misfit strain, structural defects or other phenomena able to modify both the electronic band structure and the energetics of oxygen incorporation in layers. Moreover, grain boundaries or dislocations could introduce local modification of the electron holes concentration, introducing uncertainties in the quantification of the optical conductivity (see Section S3, Supporting Information for the discussion about the effects of homogeneity of the thin films and its effects on the ellipsometry parameters). Nevertheless, the strong experimental and theoretical relationship between transition A and the electron holes in LSF suggest that ellipsometry may be used to track the defect chemistry of LSF thin films.

2.3. In Situ Ellipsometry Measurements as a Function of Temperature and Equivalent $pO_2$

We then investigated the variation of optical conductivity in LSF thin films under real electrochemical conditions. In particular, it is possible to measure the material under test as an electrode of an electrochemical cell. If this cell is employed as an oxygen pump against the material, a wide range of oxygen partial pressures can be covered by simply applying a voltage bias.\[23,27,42\]

In this work, Ag/YSZ/LSF electrochemical cells were fabricated and afterwards measured in a special setup with electrical probes and a heating stage designed for in situ/operando spectroscopic ellipsometry analysis (Figure 3a inset and Experimental Section). As depicted in the inset of Figure 3a, DC voltage bias ($\Delta V$) was applied between the LSF layer and the silver counter electrode both in anodic ($\Delta V > 0$) and cathodic ($\Delta V < 0$) modes. In cathodic mode, the voltage forces the gaseous oxygen to be reduced and incorporated into the LSF while, in anodic mode, the cell operates in reverse way, incorporating oxygen at the thin films’ surface. This electrochemical bias also modifies the oxygen chemical potential of the LSF layer, varying the equivalent oxygen partial pressure experienced by the material ($pO_2^\text{eq}$) according to the Nernst potential (the reader is strongly encouraged to see Section S5, Supporting Information, where a detailed discussion of the estimation of the $pO_2^\text{eq}$ and the fulfillment of required homogeneous oxygen chemical potential in the LSF layers is presented).

Figure 2. a) Optical conductivity spectra of the fully oxidized LFO, LSF20, LSF40, and LSF50 thin films measured by spectroscopic ellipsometry at room temperature. b) The deconvoluted optical conductivity of the low energy transition A. The inset shows the linear relation between the maximum optical conductivity and the hole concentration in the LSF system at room temperature and 400 °C. c) Sketch of the LSF electronic band structure and main optical transitions.\[31,32,36,39,40,53\]
In situ spectroscopic ellipsometry measurements of LSF thin films were then carried out under different electrochemical bias, that is, equivalent oxygen partial pressures, as a function of temperature ($T = 350–525 \, ^\circ\mathrm{C}$). Figure 3a shows the optical conductivity of the LSF50 samples at 400 \, ^\circ\mathrm{C} for different equivalent $p\text{O}_2$ (refer to section S5, Supporting Information, for the ellipsometry raw data). One can note that, decreasing the oxygen partial pressure, a gradual decrease of spectral weight of transition A and B takes place, along with an increase of transition C, giving rise to a radical change of optical properties of the LSF thin film, which also changes color from black to almost transparent. The variation of optical conductivity lowering the $p\text{O}_2$ is similar to the behavior observed in the fully oxidized samples when decreasing the Sr content (see Figure 2a), indicating that the electronic holes progressively deplete in the LSF thin film. This hypothesis is also supported by the evolution of the low energy transition A (Figure 3b), gradually reducing the spectral weight of the hole-induced empty states above the Fermi level.$^{[32]}$ It must be noted here that all the measurements were perfectly reversible and reproducible (see Figure S6, Supporting Information). This means that the changes observed in the in situ measurements entirely originate by the variation of hole concentration and not by structural features (i.e., micro voids, cracks) that would lead to a strong non reversible behavior.

Motivated by the linear relation found in the previous section between transition A and the hole concentration in the LSF system, the maximum of the optical conductivity of A was plotted as a function of the oxygen partial pressure (Brouwer diagram), see Figure 3c. The behavior found is in agreement with the diluted defect model developed by Mizusaki et al.$^{[43]}$ in which the holes progressively decrease their concentration following the oxygen incorporation reaction:

$$\text{VO} + \frac{1}{2} \text{O}_2 + 2\text{Fe}^{3+} \leftrightarrow 2\text{Fe}^{4+} + \text{O}_2$$

(2)

With diluted equilibrium constant ($K_{\text{ox}}^{\text{di}}$):

$$K_{\text{ox}}^{\text{di}} = \frac{[\text{Fe}^{3+}]^{2} [\text{O}_2]}{(p\text{O}_2)^{\frac{1}{2}} [\text{Fe}^{4+}]^{2} [\text{V}^{\text{O}}]}$$

(3)

Here $[\text{Fe}^{3+}]$, $[\text{V}^{\text{O}}]$, $[\text{Fe}^{4+}]$, and $[\text{O}_2]$ refer respectively to the concentration of Fe$^{3+}$, oxygen vacancies, Fe$^{4+}$ holes, and oxygen ions written according to the Kröger–Vink notation. Note that considering both the range of oxygen pressure and the temperature conditions in this work, the concentration of Fe$^{2+}$ electrons are expected to be negligible.$^{[23,43]}$ so that the electronic equilibrium in the LSF system can be simplified to:

$$[\text{Sr}] = 2 [\text{V}^{\text{O}}] [\text{Fe}^{3+}]$$

(4)

Equations (3) and (4) can be used to fit the evolution of hole concentration with the $p\text{O}_2$ found by spectroscopic ellipsometry, see Figure 3c. The diluted model well describes the experimental data for the LSF50 sample, endorsing the possibility of optically measuring in situ the concentration of holes in the system under real operation conditions. It is interesting to note here that ellipsometry is also very sensitive to the thickness of the layers and may therefore be used for tracking the expansion of temperature ($T = 350–525 \, ^\circ\mathrm{C}$).
study the defect concentration of oxides in systems where the optical properties (electronic structure) are not modified upon oxygen reduction, simply by tracking their chemical expansion/contraction.[44]

The point defect concentration as a function of equivalent $pO_2$ was then measured with the same procedure for LSF thin films with different Sr content. Figure 4 shows the evolution of the electronic holes in the layers obtained by fitting the maximum of optical conductivity at 400 °C. One can note that, decreasing the Sr concentration, the dilute model starts to fail in describing the hole concentration, especially at intermediate $pO_2$, where the films are constantly more reduced than expected. In other words, increasing the hole concentration of the oxygen incorporation becomes progressively more difficult, giving rise to a less steep growth of $[Fe^{3+}]$.

Similar non-ideal behaviors were reported in literature for other oxides, such as La$_{1-x}$Sr$_x$CrO$_3$ (LSCr),[45] La$_{1-x}$Sr$_x$CoO$_{2.67}$ (LSCO),[46,47] SrFeO$_{3.6}$[48] Ba$_{1-x}$La$_x$FeO$_{3}$[49] and are commonly described considering the Gibbs free energy of incorporation reactions (Equation (2)) defined by a standard term ($\Delta G_{ex}^{id}$ constant for any $pO_2$) and an activity term ($\Delta G_{ex}^{cv}$), as:

$$\Delta G_{ex} = -RT \ln (K_{ex}) = \Delta G_{ex}^{id} + \Delta G_{ex}^{cv}$$  (5)

The activity term $\Delta G_{ex}^{cv}$ represents the deviation from the standard free energy of the ideal solution, which is the driving energy for the modification of the oxygen incorporation equilibrium (see Section S7, Supporting Information). A commonly employed model for describing non-dilute behavior in oxides was proposed by Mizusaki et al., who considered $\Delta G_{ex}^{cv}$ to be linearly proportional to the point defect concentration, as:[45]

$$\Delta G_{ex}^{cv} = b [Fe^{3+}]$$  (6)

In this work, we found that a quadratic approximation better fits the experimental data obtained ($\Delta G_{ex}^{cv} = b [Fe^{3+}]^2$), probably due to a non-negligible interaction between the point defect concentration (see Figure S11, Supporting Information). The fitting based on this model leads to a satisfactory description of the experimental data, see Figure 4. The ideal equilibrium constant $K_{ex}^{id}$ and quadratic non-ideal parameter $b$ obtained at 400 °C for the different thin films is shown in Figure 5a. In agreement with the literature, the oxidation constant progressively lowers increasing the Sr content, shifting the chemical equilibrium of Equation (2) toward a more reduced state. However, also the quadratic parameter $b$ is observed to present roughly the same behavior, rapidly decreasing with the Sr content, similarly to what was observed in LSCr.[45]

A comprehensive model for describing the physical origin of $\Delta G_{ex}^{cv}$ and its relation with the other point defects is still uncertain. Lankhorst et al. used a rigid band model formalism to interpret the variation of $\Delta G_{ex}^{cv}$ measured in LSCO.[46,47] In their model, the non-ideal behavior was explained by a rigid shift of Fermi level when increasing/decreasing the electron concentration, giving rise to a modification of the enthalpy of oxygen incorporation. For metallic and semi-metallic oxides, an alternative explanation based on hole degeneracy was also proposed, where the oxygen incorporation leads to the formation of delocalized and highly degenerated holes that modifies

![Figure 4. Dilute defect chemistry model (dash lines) and quadratic (solid lines) approximation of the concentration of the point defects (symbols) for the a) LSF50, b) LSF40, and c) LSF20 thin films as a function of equivalent oxygen pressure at 400 °C.](image-url)
and energy levels measured in previous works,\[16,36\] suggests that the concentration of oxygen vacancies is consistently higher than the one predicted by the ideal behavior, especially for the LSF20 thin film.

3. Conclusions

The defect chemistry of LSF thin films with different Sr content was studied by spectroscopic ellipsometry concluding that low energy transitions (=1eV) observed in the optical conductivity can be used for tracking the concentration of holes in the material. Moreover, using LSF as an electrode in an electrochemical cell coupled to an ellipsometer, this approach can be extended to calculate the concentration of holes as a function of temperature and oxygen partial pressure in a wide range from $10^{10}$ to $10^{17}$ bar. In this way, the defect chemistry of LSF20, LSF40, and LSF50 thin films was unveiled for the intermediate-to-low temperature range, not accessible with other techniques. The equilibrium constants extracted from the analysis of the optical constants variation shows a good agreement with the extrapolation from high temperature bulk measurements. Nevertheless, deviations from the dilute defect model are observed in the LSF layers, especially for low Sr contents, consisting in a less steep increase of hole concentration while oxidizing the sample. Overall, in this work, it was possible to push the current limits for the direct measurement of defect chemistry in LSF20, LSF40 and LSF50 thin films to lower values of temperature, which is crucial for a systematic description of transition metal oxides nowadays in the core of several emerging energy and information technologies.

4. Experimental Section

Thin Film Deposition: LSF20, LSF40 and LSF50 thin films were deposited by PLD on 10 nm CGO/YSZ (001) substrates. Commercial pellets of LSF20 and CGO were used as target materials, while the pellets of LSF40 and LSF50 were prepared by solid state synthesis. For the home-made targets, first La$_2$O$_3$, SrCO$_3$ and Fe$_2$O$_3$ powders were stoichiometrically mixed in an agate mortar and heated up to 1250 °C for 12 h in air. Then, the synthesized LSF powder was uniaxially pressed into a one-inch pellet and sintered in air at 1300 °C for 12 h. All the layers were deposited employing a large-area system from PVD products (PLD-5000) equipped with a KrF-248 nm excimer laser from Lambda Physik (COMPex PRO 205). The LSF films were grown with an energy
fluence of 0.8 J cm\(^{-2}\) per pulse at a frequency of 10 Hz. The substrate was kept at 700 °C, in an oxygen partial pressure of 0.0067 mbar during the deposition and the substrate–target distance was set to 90 mm. The CGO barrier layer was deposited under the same conditions but at a temperature of 750 °C. All the thin films were deposited using a microfabricated Si mask that allowed the deposition of 2 mm x 3 mm rectangular layers at the centre of the 10 mm x 10 mm YSZ (001) substrates.

**Thin Film Characterization:** Microstructural characterization and phase identification were carried out by XRD in a coupled 0–2θ Bragg–Brentano configuration using a Bruker D8 Advanced diffractometer equipped with a Cu Kα radiation source. Cross-section image of the as-deposited film was characterized using a Scanning Electron Microscopy (SEM) (Zeiss Auriga) and elemental composition of the LSF thin films was analyzed using a SEM-coupled EDX Spectroscope (Zeiss Auriga). The analysis shows an Sr content of 0.17 ± 0.01, 0.34 ± 0.01, and 0.44 ± 0.01 for the LSF50, LSF40, and LSF20 thin films, respectively. Topography of the LSF thin films was characterized in non-contact mode by AFM of XE 100 model provided by Park System Corp.

**Electrochemical Characterization:** Silver paste was used on the backside of the YSZ substrate as counter electrode. For increasing the current collection, gold paste was painted on the 2 mm x 3 mm sides of the LSF thin films. On one corner of the YSZ electrolyte, a silver reference electrode was painted, which was used to check the potential applied across the YSZ electrolyte (see inset of Figure 3a). The measurements were carried out at intermediate temperatures (490 °C, 440 °C, 395 °C, and 350 °C) using a heating stage (Linkam instruments THMS350), which not only heats up the samples but also includes electrical contacts for in situ electrochemical measurements during the experiment. The LSF thin films were electrochemically analyzed by a staircase potential-electrochemical impedance spectroscopy (SPEIS) using a potentiostat from Biologic (model SP-150). A DC voltage bias from 0.3 V to −0.6 V was applied at a step of 0.05 V between the gold current collector and the back-side Ag counter electrode. Once the current was stabilized, the electrochemical impedance spectra were recorded with an AC voltage of amplitude 0.01 V in a range of frequency from 1 MHz to 0.1 Hz. All the experiments were carried out in atmospheric air.

**Spectroscopic Ellipsometry Measurements:** The optical constants of the LSF thin films were measured by spectroscopic ellipsometry employing an ellipsometer (UVISEL, Horiba scientific) in a photon energy range from 0.6 to 5.0 eV with an interval of 0.05 eV. The angle of incident light beam was 70°. The ellipsometry data were modeled and fitted using DeltaPsi2 software from Horiba scientific (see Supporting Information for the description of the fitting procedure). The ellipsometry measurements show the thickness of 94 ± 1 nm, 98 ± 1 nm, and 112 ± 1 nm for the LSF50, LSF40, and LSF20 thin films, respectively. In situ ellipsometry measurements were carried out during the electrochemical characterization after each voltage bias step. The ex situ optical conductivity of the fully oxidized LSF samples was obtained by heating the samples at 400 °C and applying a 0.3 V anodic bias across the YSZ electrolyte. The fully reduced ex situ optical conductivity of the LSF50 layer was instead obtained by applying −0.4 V cathodic bias at 400 °C. The temperature of the samples was then rapidly decreased continuously applying the anodic bias (assuring a fully oxidized state) down to room temperature, where the ellipsometry spectra were recorded.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

defect chemistry, in-situ, optical conductivity, spectroscopic ellipsometry, thin films

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