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The impact of Mn nonstoichiometry on the oxygen mass transport properties of $La_{0.8}Sr_{0.2}Mn_yO_{3\pm\delta}$ thin films

Francesco M Chiabrera^{1,*}⁽ⁱ⁾, Federico Baiutti¹⁽ⁱ⁾, Jacqueline M Börgers²⁽ⁱ⁾, George F Harrington², Lluís Yedra³, Maciej O Liedke⁴⁽ⁱ⁾, Joe Kler², Pranjal Nandi³, Juan de Dios Sirvent¹⁽ⁱ⁾, Jose Santiso⁵, Miguel López-Haro⁶, José J Calvino⁶, Sonia Estradé³, Maik Butterling⁴, Andreas Wagner⁴⁽ⁱ⁾, Francesca Peiró³, Roger A De Souza²⁽ⁱ⁾ and Albert Tarancón^{1,7}⁽ⁱ⁾

- ¹ Department of Advanced Materials for Energy Applications, Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 08930 Sant Adrià del Besòs, Barcelona, Spain
- ² Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany
- ³ Laboratory of Electron Nanoscopies (LENS), Micro-Nanotechnology and Nanoscopies for electrophotonic Devices (MIND), Department of Electronics and Biomedical Engineering and Institute of Nanoscience and Nanotechnology (IN2UB), University of Barcelona C/Martí i Franquès 1, Barcelona 08028, Spain
- ⁴ Helmholtz-Zentrum Dresden-Rossendorf, Institute of Radiation Physics, 01328 Dresden, Germany
- ⁵ Catalan Institute of Nanoscience and Nanotechnology, ICN2, CSIC and The Barcelona Institute of Science and Technology (BIST), Campus UAB, Bellaterra, Barcelona, Spain
- ⁶ Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Uni-versidad de
- Cádiz, Campus Rio San Pedro, Puerto Real, Cádiz, 11510, Spain
- ⁷ ICREA, Passeig de Lluis Companys 23, 08010 Barcelona, Spain
- ⁶ Author to whom any correspondence should be addressed.

E-mail: fchiabrera@irec.cat

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Abstract

Oxygen mass transport in perovskite oxides is relevant for a variety of energy and information technologies. In oxide thin films, cation nonstoichiometry is often found but its impact on the oxygen transport properties is not well understood. Here, we used oxygen isotope exchange depth profile technique coupled with secondary ion mass spectrometry to study oxygen mass transport and the defect compensation mechanism of Mn-deficient $La_{0.8}Sr_{0.2}Mn_yO_{3\pm\delta}$ epitaxial thin films. Oxygen diffusivity and surface exchange coefficients were observed to be consistent with literature measurements and to be independent on the degree of Mn deficiency in the layers. Defect chemistry modeling, together with a collection of different experimental techniques, suggests that the Mn-deficiency is mainly compensated by the formation of La_{Mn}^{\times} antisite defects. The results highlight the importance of antisite defects in perovskite thin films for mitigating cationic nonstoichiometry effects on oxygen mass transport properties.

1. Introduction

Perovskite oxide thin films offer a unique platform for the investigation and the engineering of the functional properties, relevant for a variety of energy and information technologies [1]. In perovskite oxides (ABO₃), ionic defects are known to profoundly impact the overall functionalities [2]. Oxygen vacancies are a characteristic example, whose presence allows oxygen to diffuse in the perovskite lattice and strongly influences electronic and magnetic transport properties [3, 4]. Other important types of defects often present in perovskite thin films are those associated with cation nonstoichiometry (i.e. A/B site ratio different from 1). Cationic defects may be intentionally present or simply generated by a deficient stoichiometry transfer of the cationic species, characteristic of several thin film deposition techniques. In the particular case of pulsed laser deposition (PLD), cation deviations from the target stoichiometry can be introduced by a preferential ablation of some species [5], by plasma-background interactions [6] or by selective reevaporation [7]. While oxygen deficiency can be easily compensated by annealing the samples in oxidizing conditions, large cation

nonstoichiometries cannot be modified after growth, impacting the overall functional properties of these oxides in the same fashion as a dopant or impurity.

Cation non-stoichiometry has been found to be at the basis of many interesting phenomena of perovskite oxide thin films. The presence of cationic defects may give rise to non-centrosymmetric distortions, facilitating the appearance of spontaneous ferroelectric polarization. This phenomenon was for instance observed in SrTiO₃ [8–10], in PbZrO₃ [11] and in YFeO₃ [12] thin films. Deviation from the cation stoichiometry may also enhance or abate the electronic and magnetic order. B-site deficiency in La_{1-x}Sr_xMn_yO_{3±δ} strongly hinders the metal–insulator transition and the ferromagnetic order [13, 14], while A-site deficiency is known to be beneficial for electronic transport [15]. The difference of A- and B-site non-stoichiometry originates from the central role of Mn atoms in the electronic transport properties [13]. In SrTiO₃, both A and B site vacancies produce a negative effect on electronic conductivity [16, 17]. However, robust magnetic order can also be stabilized in the presence of cationic nonstoichiometry, as found for antisite defects at the interface between LaAlO₃/SrTiO₃ [18] and in the presence of Ti–O vacancy clusters in SrTiO₃ [19].

In this work, we focus on the impact of B-site deficiency on oxygen mass transport properties (i.e. oxygen diffusivity and surface exchange coefficient) of $La_{0.8}Sr_{0.2}Mn_yO_{3\pm\delta}$ (LSM_y), a material relevant for diverse applications, such as solid oxide fuel cells and electrolyzers, supercapacitors [20] and resistive switching [21]. The defect chemistry of bulk LSM is strongly dominated by cation vacancies, which give rise to the oxygen hyper-stoichiometry observed in oxidizing conditions [22, 23]. Moreover, cation vacancies were also observed to impact the oxygen diffusion of structural defects, such as grain boundaries and dislocations, known for presenting large enhancements of oxygen diffusion and incorporation compared to the bulk [24, 25]. Indeed, we previously showed that the grain boundaries of polycrystalline LSM_v thin films are characterized by a modification of site occupancy for both oxygen and cations stoichiometry [26]. Moreover, this local nostoichiometry can be tuned by the overall Mn/(La + Sr) ratio in the layers, offering a way to further enhance its electrochemical properties for large Mn deficiencies [Mn/(La + Sr)<0.9]. Also, faster oxygen transport along dislocations was recently proposed to originate from an accumulation of (negative) cation vacancies at the dislocation core, giving rise to a space charge accumulation of (positive) oxygen vacancies, and thus boosting the oxygen diffusivity [27]. Indeed, cation defects have been experimentally observed near the strained region of the dislocations [28]. However, the impact of cation nonstoichiometry on the oxygen mass transport properties of LSM_{ν} is not fully understood, even in the bulk case. This is particularly true for B/A<1 (Mn deficiency), which, although it was observed to enhance the electrochemical properties of Mn-deficient grain boundaries [26], is not commonly studied in bulk form due to the formation of secondary phases at typical sintering temperatures [29, 30]. For these reasons, this study deals with the bulk oxygen transport properties and defect-compensation mechanisms of Mn-deficient LSM $_{\nu}$.

Cation nonstoichiometry, and in particular B-site deficiency, is therefore expected to alter the atomic landscape for the diffusion of oxygen vacancies and, depending on the defect compensation mechanism, the concentration of oxygen vacancies in the system. Indeed, different types of compensation mechanisms have been reported in the literature concerning B-site deficient perovskites. In bulk samples, small deviations from stoichiometry are generally associated to the formation of cation vacancies [22, 30]. However, in thin films, beside the formation of cation vacancies [13, 31], also other type of point defects were observed, such as antisite defects [11, 12, 18, 32] or extended faulting planes (resembling a Ruddlesden–Popper phase) [33–35]. Excluding the formation of extended defects or secondary phases, the formation of B-site vacancies $(v_{Mn}^{\prime\prime\prime})$ or antisite defects (La_{Mn}^{\times}) in LSM_y thin films may produce quite different effects on both the oxygen vacancy diffusivity (D_v) and on the concentration of oxygen vacancies $[v_0^{\circ\bullet}]$). Indeed, oxygen diffusivity (D_0) in perovskite oxides is known to be directly affected by both these parameters, as:

$$D_{\rm O} = D_{\rm v} \cdot \frac{\left[\mathbf{v}_{\rm O}^{\bullet}\right]}{\left[\mathbf{O}_{\rm O}^{\times}\right]},\tag{1}$$

(where $[O_O^{\circ}]$ is the concentration of oxide ions sitting on the oxide-ion site). Regarding the variation of D_v with B/A ratio, molecular dynamics (MD) simulations indicated that various types of cation defects have substantially different effects on the oxygen vacancy diffusivity [36]. Mn and La vacancies were found to severely hinder D_v , due to an increase of the activation energy for oxygen vacancy migration in the surroundings of these point defects. In contrast, the oxygen-vacancy diffusivity in the presence of antisite defects was found to behave very similarly to the stoichiometric reference, with almost no change in the activation energy of ionic hopping [36]. Another important difference between $v_{Mn}^{\prime\prime\prime}$ and La_{Mn}^{\times} is that the former is negatively charged while the latter is formally neutral. This means that $(v_{Mn}^{\prime\prime\prime})$ would necessarily require the formation of positive defects (Mn $_{Mn}^{\bullet}$ and v_0^{\bullet}) for charge compensation, potentially promoting oxygen diffusivity (see equation (1)). Altogether, the overall effect of Mn-deficiency is unclear.

In order to investigate the effect of Mn-deficiency on the oxygen mass transport properties and the compensation mechanism of bulk LSM, we deposited a series of epitaxial LSM_y thin films with variable Mn content by PLD. Oxygen diffusivity and surface exchange coefficients were measured by oxygen isotope exchange depth profile technique coupled with secondary ion mass spectrometry (IEDP-SIMS). The measurements revealed that diffusivity does not substantially vary with Mn-deficiency and retains its bulk properties. The results are discussed by considering the defect chemistry models of cation vacancies $v_{Mn}^{\prime\prime\prime}$ and of antisite defects La_{Mn}^{\times} in Mn-deficient LSM_y.

2. Methods

LSM thin films were deposited by PLD on SrTiO₃ (001) single crystal substrates (Crystec GmbH). A large area PLD system (PVD Systems—PLD 5000) equipped with a 248 nm KrF excimer laser was used (Lambda Physics—COMPex PRO 205). The thin films were deposited at 700 °C with an energy fluence of 1 J cm⁻¹ per pulse, a frequency of 10 Hz and a substrate-target distance of 95 mm. An oxygen background pressure of $pO_2 = 2.6 \times 10^{-2}$ mbar was used for growing highly Mn-deficient thin films ($y \sim 0.85$), while $pO_2 = 6.6 \times 10^{-3}$ mbar was employed for obtaining nearly stoichiometric LSM layers ($y \sim 1.00$). LSM_y thin films with variable Mn/(La + Sr) ratio were grown by combinatorial PLD on SrTiO₃ (001), see figure 1(a). Following the procedure developed in our previous works [26, 37], the control of cationic stoichiometry was achieved by an alternate deposition of Mn-deficient LSM and Mn₃O₄. The thickness of the LSM and Mn₃O₄ layers deposited per-cycle was optimized for achieving an *in-situ* synthesis of the perovskite phase at the deposition temperature (T = 700 °C) [26, 38]. The set of LSM_y thin films deposited by combinatorial PLD (cPLD) presents the overall recipe ((LSM_{0.85})₆₆ + (Mn₃O₄)_z)₆₀, where z is the number of Mn₃O₄ pulses per cycle, 66 pulses of LSM corresponds to ~1 nm and the total number of cycles was set for having an overall thickness of ~60 nm, as measured by ellipsometry and confirmed by SIMS. The samples were *in-situ* annealed in 0.3 mbar of oxygen at 700 °C to compensate oxygen deficiency in the layers.

The Mn/(La + Sr) ratio of the thin films was measured by energy-dispersive x-ray analysis (EDS) in a ZEISS AURIGA equipment. In order to increase the sensitivity of the technique to the cationic species contained in the thin films, the EDS analysis was performed on samples deposited on Si (001) substrates. The cationic composition of LSM thin films on STO and Si is expected to be comparable, as observed in previous publications [6] and confirmed by the similar evolution of lattice parameter (see section 3.1). The error associated with the EDS measurement was fixed at 3% for each element to take into account possible uncertainties related to the data acquisition and data processing (the measurement variability on the same sample was less than 2%). X-ray diffraction (XRD) analysis was carried out in a four-angle goniometer diffractometer with a monochromatic Cu K α_1 radiation source (X'Pert Pro MRD, Malvern-Panalytical) which was used for measuring the $\theta/2\theta$ scans and the reciprocal space maps (RSM) of certain reflections in the films. The surface topography of the thin films was measured by atomic force microscopy (AFM) in a Park System (XE 100 Park System Corp.) and analyzed by Gwyddion software. The thickness and the optical properties of the LSM $_{\gamma}$ thin films were obtained by spectroscopic ellipsometry (UVISEL, Horiba scientific) and fitted using DeltaPsi2 software from Horiba scientific. The measurements were performed in the energy range from 0.6 to 5.0 eV with an angle of incident light beam of 70°. The LSM_v dielectric properties were simulated with a series of five Lorentzian oscillators, while the optical properties of the SrTiO₃ were measured from a pristine substrate [39-41]. The fitting model consisted in a tri-layer structure composed by the substrate, the LSM_y thin film and a 0.5 nm top-layer of 50% LSM_y and 50% air, to take in account the roughness of the thin films [37].

A thin cross-sectional lamella for transmission electron microscopy (TEM) of the sample with lower Mn/(La + Sr) ratio was prepared in a Thermo-Fischer Scios 2 Dual Beam FIB SEM and observed in a JEOL 2100 TEM at 200 kV in high resolution mode and in an aberration corrected Titan³ Themis (FEI) working at 200 kV in high angle annular dark field (HAADF) and differential phase contrast image acquisition modes. The oxygen column position determination was performed with Atomap software [42].

Variable energy positron annihilation lifetime spectroscopy (VEPALS) measurements were performed at the monoenergetic positron source beamline at Helmholtz-Zentrum Dresden-Rossendorf in Germany [43]. Positron annihilation lifetime data is recorded using a digital data acquisition system, consisting of a CeBr3 scintillator coupled to a Hamamatsu R13089-100 PMT. Data processing is evaluated using a SPDevices ADQ14-DC-2X digitizer with 14-bit vertical resolution, 2 GS s⁻¹ horizontal resolution. The overall VEPALS beamline has a time resolution of about 0.230 ns [44].

Oxygen IEDP-SIMS was used to determine the oxygen tracer diffusivity and surface exchange coefficient of the layers. The ¹⁸O isotope exchange was performed at 650 °C for 3540 s (for y = 0.85 and y = 1.00) and 4000 s (for y = 0.88, y = 0.94 and y = 0.99). Isotope profiles in the exchanged samples were measured by time of flight-secondary ion mass spectrometry (ToF-SIMS) on a ToF-SIMS IV machine fitted with a

ToF-SIMS.5 analyzer (IONTOF, Münster, Germany). Secondary ions for ToF analysis were generated by raster scanning a beam of 25 keV Ga⁺ over 80 μ m × 80 μ m; for sputter etching of the surface, a beam of 1 keV Cs+ ions was raster scanned over 300 μ m × 300 μ m; a beam of low-energy electrons was used for charge compensation. Negative secondary ions were recorded with a ToF cycle time of 50 μ s. Crater depths were determined post-analysis by interference microscopy. Each sample was probed at multiple locations (at least three) to ensure the reproducibility and to estimate the error of the measurement.

The oxygen mass transport parameters (i.e. tracer oxygen diffusivity, D^* and surface exchange coefficient, k^*) of LSM_y thin films were obtained by fitting the tracer fraction profiles ($f({}^{18}\text{O}) = [{}^{18}\text{O}]/([{}^{18}\text{O}] + [{}^{16}\text{O}])$) with the semi-infinite diffusion equation [45] and by finite element model (FEM). The FEM simulations were performed by COMSOL Multiphysics to address the impact of fast dislocation and subsurface diffusivity on the bulk D^* and k^* . The 2D axial symmetric geometry of the model is based on previous works [24, 38, 46] and consists in a small cylinder with fast diffusivity (D^*_{d}) embedded in a larger cylinder with slower one (D^*), simulating an equivalent threading dislocation running through the film's depth (Dislocation model, see figure S4(a) of the supporting information). The width of the dislocation is fixed at 1 nm. The effect of fast subsurface diffusion is taken in account by considering a 2 nm thick region beneath the surface with different diffusivity D^*_{s} (Dislocation + subsurface model, see figure S4(b) of the supporting information). Fick's second law of diffusion with a convective-type boundary condition on the sample surface was then solved by FEM method. The external $f({}^{18}\text{O})$ and the exchange time was set equal to the experimental exchange conditions, while an initial $f({}^{18}\text{O})$ equal to the natural ${}^{18}\text{O}$ abundance was considered. Triangular elements were employed for meshing. The fitting procedure was based on a parametric sweep study of the oxygen transport parameters [24].

3. Results and discussion

3.1. Structural and chemical characterization of LSM_v thin films

 LSM_{ν} thin films were deposited by PLD on SrTiO₃ (001) substrates. In order to achieve a variable y = Mn/(Sr + La) ratio in the layers, we took advantage of the plasma-background interactions in PLD chamber to control the transfer of Mn from the target to the thin films. It was indeed demonstrated that oxygen pressure during the deposition largely influences the cation composition of the layers, due to a preferential scattering of lighter species (Mn) to higher angles compared to heavier ones (La, Sr) [5–7, 13]. This phenomenon is particularly relevant at intermediate deposition pressures $(10^{-2}-10^{-1} \text{ mbar})$ and for the large substrate-target distances used in LA-PLD, while at low pressure and in vacuum the reduction of plasma-background interactions promotes a stoichiometric transfer [6]. Following this idea, LSM thin films were deposited at 2.6×10^{-2} mbar (see section 2 for more details). EDS analysis revealed a large Mn deficiency ($y = 0.85 \pm 0.03$) and a stoichiometric transfer of Sr/(Sr + La), in agreement with our previous results [26, 37]. Although the deposition pO_2 is an effective strategy to modify the cation ratio in the layers, a precise control of the cation ratio is challenging, due to sudden variation of stoichiometry in the intermediate pressure range [6]. In order to achieve a more precise control over the B/A ratio for a series of intermediate compositions of LSM_y, we deposited a series of thin films by cPLD, see figure 1(a). This technique is based on the alternate deposition of Mn-deficient LSM (deposited under the intermediate pO_2 conditions aforementioned) and Mn_3O_4 (see Methods for more details) [26, 37]. EDS analysis of the thin films revealed that the Mn/(Sr + La) ratio progressively increased with increasing the Mn_3O_4 pulses, ranging from $y = 0.88 \pm 0.03$ (z = 2) to $y = 0.99 \pm 0.03$ (z = 10), see figure 1(b). Finally, state-of-the-art stoichiometric LSM was also deposited for comparison by conventional PLD in the low pO2 regime $(6.6 \times 10^{-3} \text{ mbar})$, obtaining nearly stoichiometric transfer ($y = 1.00 \pm 0.03$). Therefore, the samples deposited with the different strategies presents a variable Mn/(La + Sr) from 0.85 to 1.

Fully oriented pseudo-cubic structure was obtained for all the compositions under study by XRD analysis. Increasing the Mn deficiency, a progressive increase of the out of plane lattice parameter is observed, highlighted in the high resolution $\theta/2\theta$ scans of the (002) reflections by a shift towards lower angles, see figure 1(c). RSM maps around (103) reflections show that the LSM_y thin films are coherently grown on the STO substrate and confirm the out-of-plane expansion observed by $\theta/2\theta$ scans, see figures 1(f) and (g). For intermediate compositions, the LSM_y layers present a splitting of the 103 Bragg peak along Q_x, sometimes found in manganite epitaxial thin films due to the appearance of orthorhombic or rhombohedral twin domains [47, 48] or to lattice modulations [49] (see figure S1 in supporting information). AFM images of the Mn-deficient (y = 0.85) and stoichiometric (y = 1.00) LSM thin films show an atomically flat surface, highlighting the good quality of the layers despite the cationic deficiency (see figures 1(d) and (e)).

The expansion of the out-of-plane lattice parameter c_{pc} as measured by XRD is shown as a function of the cation ratio in figure 1(h), along with previous results obtained for Mn deficient polycrystalline and epitaxial thin films [26, 37]. Comparable behavior, that is, lattice expansion upon Mn decrease, is observed for all the



Mn/(La + Sr) ratio measured by EDS. (c) XRD patterns around the (002) diffraction peak showing a shift toward lower angles while decreasing y. AFM images (d) and (e) and RSM around the (103) reflections (f) and (g) of the LSM_y thin films with y = 0.85 and y = 1.00. (h) Expansion of the out of plane lattice parameter observed by XRD as a function of the Mn/(La + Sr) ratio. Results previously obtained for epitaxial [A] [37] and polycrystalline [B] [26] thin films on Si are also reported for comparison.

micro-structures under consideration, with a linear variation of lattice parameter per Mn deficiency equal to $\frac{c_{pc}(y)}{c_{pc}(y=1)} \sim 0.1 \cdot (1-y)$. Note however that, as far as the absolute c_{pc} values are concerned, the epitaxial LSM_y thin films on NdGaO₃ show an overall increase of the out-of-plane lattice constant due to the in-plane compressive strain imposed by the substrate [37]. Nevertheless, the similar trend observed despite the different micro-structure of the films indicates a direct relationship between the modification of the lattice parameters and the decrease of the Mn composition in the B-site, in agreement with previous reports on similar perovskite thin films (e.g. LaCrO₃ [32], NdNiO₃ [50], LaFeO₃ [31], and SrTiO₃ [16, 35, 51]).

In order to obtain precise insights into the microstructure of the films, a representative sample (y = 0.85) was comprehensively studied by TEM. Figures 2(a) and (b) shows the cross-section HAADF of the thin film. The layer presents a very ordered structure, with atomic contrast visible across the whole specimen despite the high level of nonstoichiometry. Figure 2(c) shows the fast Fourier transform (FFT) images of three characteristic regions of the film. In the subsurface region (inset 1), the FFT presents a clear cubic symmetry, belonging to the (1 0 0) and (0 0 1) zone axis. In the central part of the films, the FFT reveals the appearance of additional spots, related with (1/2 1/2 0) and (1/2 0 0) reflections, as shown respectively in insets 2 and 3 of figure 2(c). These superstructures are characteristic of an orthorhombic structure, originated by antipolar displacement of A-site cations and tilting of the oxygen octahedra (see figure S2 in supporting information for more details) [52, 53]. Overall, no structural defects nor secondary phases are visible in the film, confirming the fully epitaxial nature of the layer (see figure S3 in supporting information for more details). This result indicates that the Mn deficiency is compensated by point defects in the layers (e.g. v_{Mn}'' and/or La_{Mn}^{\times}) causing a progressive expansion of the out-of-plane lattice parameter, rather than by secondary phase formation.

We investigated the presence of cation defects by employing VEPALS measurements. Positron annihilation lifetime spectroscopy (PALS) is a technique able to detect the presence of point defects, which act as centers for the annihilation of positrons. Due to the positrons' positive charge, negative defects such as cation vacancies are easily detectable, while positive or neutral point defects (e.g. $v_0^{\bullet\bullet}$ and La_{Mn}^{\times}) generally present lower trapping effect [35, 54, 55]. Figure 3(a) shows the variation in positron lifetime measured for



Figure 2. (a) HAADF cross section image (a) and detail (b) of a Mn-deficient LSM_y thin films (y = 0.85). (c) FFT images of three different regions (highlighted as inset 1, 2 and 3), showing the presence of ordered lattice distortions characteristic of an orthorhombic structure.





different positron implantation energy (i.e. penetration depths) for the LSM_{ν} thin films. As a consequence of positron diffusion, for depths lower than about 30 nm ($E_p > 3$ keV) an increasing fraction of positrons annihilate with the substrate, which lowers and averages out the positron lifetimes. The most pure representation of the film related defect nanostructure is found in the range of $E_p = 2-3$ keV. The analysis of the VEPALS measurements revealed the presence of two major trapping sites, with lifetimes $au_1 \sim 200$ ps and au_2 ~ 300 ps. These defects are comparable with the defect annihilation times calculated in literature for $v_{Mn}^{\prime\prime\prime}$ and $v_{La}^{\prime\prime\prime}$ [54], see figure 3(a). An increase of τ_2 is observed for some compositions (y = 0.85 and y = 0.98); however, no clear trend emerges with the Mn/(La + Sr) ratio. This is probably originated by the presence of some defect clusters in the $v_{La}^{\prime\prime\prime}$ surroundings, which are known to increase the open volume and the positron lifetime [55]. The relative intensity of $v_{Mn}^{\prime\prime\prime}$ and $v_{La}^{\prime\prime\prime}$ related defects was obtained by averaging the central part of the films (highlighted in figure 3(a) by a green region) and plotted in figure 3(b) against the Mn/(La + Sr) ratio. Here it must be noted that the relative intensity extracted by PALS is not only function of the defect concentrations but also of the defect trapping coefficients, which are not necessarily equal for different defect types [54]. However, since 70%–90% annihilation events are associated with $v_{Mn}^{\prime\prime\prime}$ we can safely assume that the relative intensity reflects here the change in density of this particular defect type $(v_{Mn}^{\prime\prime\prime})$. Moreover, the ratio between $v_{Mn}^{\prime\prime\prime}$ and $v_{La}^{\prime\prime\prime}$ can be treated as quantitative as long as the experimental lifetimes lay in the vicinity of their theoretical discrete predictions, i.e. close to the specific values for given point defects. The slight deviations from these values can be explained by relaxations and in the case of lifetimes larger than the theoretical value for $v_{La}^{\prime\prime\prime}$ a complex of multiple vacancies is expected (see τ_2 in figure 3(a)). Hence, some insights into the concentration ratio of cation vacancies can be still drawn from the trend observed with varying Mn/(La + Sr) ratio. Figure 3(b) shows an overall flat tendency of the relative Mn intensity down to





y = 0.88, while the most Mn-deficient sample (y = 0.85) presents a ~15% increase. This behavior stands in contrast to Sr-deficient SrTiO₃ thin films, where a linear increase of the intensity of the Sr-vacancy component was observed upon increasing Ti/Sr ratio [35, 54]. The results suggest an almost constant v'_{Mn}/v'_{La} ratio, which may originate from a similar increase of v'_{La} and v''_{Mn} when reducing the Mn/(La + Sr) ratio or from the presence of an alternative mechanism for compensating the Mn-deficiency.

Overall, the structural and chemical analysis revealed that the Mn-deficient LSM_y thin films present a very well-ordered structure down to y = 0.85 and are therefore suitable for the measurement of bulk oxygen mass transport properties.

3.2. Oxygen mass transport properties of LSM_v thin films

Oxygen mass transport properties of LSM_{ν} thin films were measured by IEDP-SIMS. The samples were annealed at 650 °C in ¹⁸O enriched atmosphere to allow the tracer incorporation and diffusion in the samples (see section 2 for more information). Figure 4(a) shows the tracer fraction depth profiles obtained in the thin films with different Mn/(Sr + La) ratios. The profiles were first fitted with the semi-infinite solution of oxygen incorporation and diffusion for retrieving the oxygen diffusivity (D^*) and surface exchange coefficient (k^*) [45]. The model correctly reproduces the main features of the profiles except for the long tails, where a small but systematic difference in the tracer fraction was observed. This behavior is commonly explained in LSM thin films by the presence of dislocations or other types of 2D structural defects, which are known to provide a preferential pathway for oxygen diffusion in manganite perovskites, allowing the tracer to diffuse more deeply into the sample [27, 46]. In order to improve the fittings and to avoid uncertainties on the bulk coefficients, 2D FEM simulations based on previous works on fast diffusion in dislocations and grain boundaries were implemented [24, 38, 46, 56]. The model approximates a dislocation as a thin cylinder with enhanced diffusivity embedded in a larger cylinder representing the bulk properties (more details on the model can be found in section 2). The best-fit profiles obtained by FEM modeling show good agreement with the experimental data, see figure 4(a), allowing us to extract the bulk and dislocation D^{\dagger} and k^{\dagger} . Here, we mainly focus on the bulk parameters, the interested reader is referred to section S1 the supporting information for the evolution of the dislocation coefficients and a comparison between the models.



Figure 5. Linear and logarithmic Brouwer diagrams of the main defect species plotted as a function of pO_2 for stoichiometric LSM ((a) y = 1.00), Mn-vacancy model ((b) y = 0.85) and La-antisite model ((c) y = 0.85). Equilibration constants are derived for T = 650 °C from the values measured in bulk samples by Nowotny *et al* [23] For the La-antisite model an antisite equilibrium constant of $K_a = 0.05$ is considered.

The evolution of bulk diffusivity and surface exchange coefficients as a function of cation nonstoichiometry is shown in figures 4(b) and (c), respectively. The oxygen parameters present a flat trend, with no differences among the samples except for the most Mn deficient, which shows a small decrease of both D^* and k^* (a factor of ~3 and ~7, respectively). The coefficients extracted at the exchange temperature agree well with literature data for stoichiometric LSM bulk and thin films [57, 58]. Overall, Mn deficiency does not produce significant variation of oxygen mass transport properties in LSM_y thin film as a function of B/A content.

3.3. Discussion

As noted in the introduction, B-site deficiency in perovskite oxides may be explained by the formation of either B-site vacancies $(v_{Mn}^{\prime\prime\prime})$ or antisites defects (La_{Mn}^{x}) . These two mechanisms are expected to have radically different effects on the oxygen vacancy diffusivity and the oxygen-vacancy concentration. In the first case, the required 15% of cationic vacancies will give rise to a decrease of over four orders of magnitude of $D_{\rm v}$ compared to cation vacancy-free LSM (using vacancy diffusivity extrapolated by MD simulations [36]) while the presence of La antisites is expected to produce only minor changes on the oxygen vacancy diffusivity. This would be a first indication of the presence of antisite defects according to the small change in the oxygen diffusivity for Mn-deficient layers. Nevertheless, it is important to note that stoichiometric LSM is known to naturally present moderate concentration of cationic vacancies in oxidizing conditions (up to few percent) [22, 23]. That is, oxygen vacancy diffusivity of the stoichiometric sample may already be affected by cationic vacancies, which would decrease the relative negative impact of further Mn-deficiency on Dy. Additionally, due to the negative nature of cationic defects, one cannot exclude that an increase of v''' would originate a rise of $[V_0^{\bullet\bullet}]$ for charge compensation, mitigating the overall impact on the oxygen diffusivity (see equation (1)). In order to understand how $v_{Mn}^{\prime\prime\prime}$ and La_{Mn}^{x} may affect the oxygen vacancy concentration and which compensation mechanism better explain the results observed, different defect chemistry models were considered.

Figure 5(a) shows the reference case of the concentration of the main defect species against the oxygen partial pressure (pO₂) for stoichiometric LSM (y = 1.00) at 650 °C, in linear and logarithmic scale. The defect model, adopted from Poulsen [22], is based on three equilibrium reactions, *viz.* the oxygen incorporation reaction, the charge disproportionation reaction and the Schottky reaction, and on the charge and site balance equations (see section S2 in supporting information). The equilibrium constants were derived from the values measured in bulk samples by Nowotny *et al* [23] The behavior is almost entirely dominated by electron holes (Mn[•]_{Mn}), compensating the negative aliovalent doping and, at high pO₂, the cation vacancies generated for Schottky disorder.

The Mn-vacancy model was calculated considering a Mn/(Sr + La)<1 (see section S2 in supporting information) [22]. Figure 5(b) shows the Brouwer diagram calculated for y = 0.85 and keeping the equilibrium reaction constants equal to the stoichiometric case. It is important to note that the assumption of unvaried equilibration constants may not be entirely correct, since oxygen incorporation reaction may be

affected by the increase of v''_{Mn} , similarly to what takes place increasing the aliovalent doping in LSM [23, 59]. Nevertheless, the general trend of the point defects is expected to be the same.

In comparison to the stoichiometric case, a substantial increase of positive defects (Mn_{Mn}^{\bullet} and $v_{O}^{\bullet\bullet}$) is observed for charge compensation, similarly to the effect of an increase of acceptor dopant concentration. Our previous analysis on polycrystalline LSM_{ν} samples revealed a constant Mn oxidation state for $0.85 \le y \le 1$ [37]. The evolution of optical absorption in LSM_y thin films also suggests no variation of the Mn oxidation state, see figure S7 in supporting information. In brief, the low energy optical transition in manganites is known to originate from intra-band Mn 3D transitions and to be very sensitive to the variation of Mn^{4+} concentration [40, 41, 60, 61]. The absorption spectra measured in the LSM_y thin films show a small decrease of the intensity of this transition, lowering the Mn content, mainly related to a decrease of the overall Mn concentration rather than to a variation of Mn oxidation state [31, 37]. A Mn oxidation state independent of the Mn/(Sr + La) ratio is therefore not consistent with the Mn-vacancy model. Additional inconsistencies come from the comparison between the $v_{Mn}^{\prime\prime\prime}/v_{La}^{\prime\prime\prime}$ ratio predicted by the model and the results observed by VEPALS (see figure 3(b)). In the Mn-vacancy model, Schottky equilibrium in the oxidized region determines a large suppression of La vacancies, which would give rise to a relative intensity of $v_{Mn}^{\prime\prime\prime}$ rapidly approaching 100% while decreasing the Mn/(Sr + La) ratio. This is not what is observed by VEPALS, where a rather constant intensity of cation vacancies was measured. These considerations suggest that Mn-vacancies are not the main compensation mechanism in our Mn-deficient LSM $_{\gamma}$ thin films.

The La-antisite model was developed to catch the point defects properties of LSM_y in the presence of La_{Mn}^{\times} . The model is based on the antisite reaction:

$$\mathbf{v}_{\mathrm{Mn}}^{\prime\prime\prime\prime} + \mathrm{La}_{\mathrm{La}}^{\times} \to \mathrm{La}_{\mathrm{Mn}}^{\times} + \mathbf{v}_{\mathrm{La}}^{\prime\prime\prime} \tag{2}$$

where an La_{Mn}^{\times} defect is formed by hopping of a La atom into $v_{Mn}^{\prime\prime\prime}$, generating a $v_{La}^{\prime\prime\prime}$. The equilibration constant of equation (2) is then defined as:

$$K_a = \frac{\left[\mathrm{La}_{\mathrm{Mn}}^{\times}\right] \cdot \left[\mathrm{v}_{\mathrm{La}}^{\prime\prime\prime}\right]}{\left[\mathrm{v}_{\mathrm{Mn}}^{\prime\prime\prime}\right] \cdot \left[\mathrm{La}_{\mathrm{La}}^{\times}\right]}.$$
(3)

The inclusion of the antisite equilibrium reaction into the Mn-vacancy model allows to calculate the effect of antisite defects in B-site deficient manganites (see section S2 in supporting information). Here, we only considered the presence of La_{Mn}^{\times} and not of Sr'_{Mn} , since the lower atomic radius of La atoms is expected to favor their migration into the small Mn-site compared to the larger Sr atoms. Nevertheless, the general trend described by the model would be maintained also in the presence of Sr'_{Mn} . Figure 5(c) shows the Brouwer diagram calculated for y = 0.85 for the case of La_{Mn}^{\times} being the main cationic compensation mechanism, corresponding to a $K_a = 0.05$. This value can be considered as an upper bound for the case in which cation nostoichiometry is fully compensated by antisites (the Brouwer diagram for lower K_a can be found in figure S8 of the supporting information). Interestingly, the diagram shows a concentration of point defects comparable to the stoichiometric sample. In other words, the inclusion of antisite defects strongly reduces the need of positive defects for charge compensation, allowing Mn_{Mn}^{\bullet} and $v_0^{\bullet \bullet}$ to remain the same as in stoichiometric LSM. The La-antisite model can therefore rationalize the constant Mn oxidation state observed upon decreasing the Mn/(La + Sr) ratio. Moreover, despite the large Mn deficiency, a similar concentration of $v_{La}^{\prime\prime'}$ and $v_{Mn}^{\prime\prime\prime'}/v_{La}^{\prime\prime'}$ ratio was observed increasing the Mn deficiency.

More insights into the presence of La_{Mn}^{\times} can be drawn from the variation of the out-of plane lattice parameter observed by XRD for the Mn-deficient samples. Figure 6 shows the relative expansion measured for LSM_v thin films decreasing the Mn/(Sr + La). Results obtained for polycrystalline and compressive epitaxial LSM_{ν} thin films from our previous work are also reported [37]. As mentioned above, the expansion is comparable for all the different samples, suggesting a negligible influence of the substrate lattice strain. Since no secondary phases or extended structural defects were observed by TEM in the most Mn deficient thin film, the increase of out of plane lattice parameter can be rationalized by the presence of point defects, which are known to impact substantially the lattice structure of metal oxides [62]. Due to the larger dimensions of A-site atoms compared to B-site ones, La_{Mn}^{\times} can qualitatively explain the behavior observed [12, 32]. A simple hard sphere approximation model was considered to predict the relative expansion expected in the case of La-antisite defects (see section S3 of the supporting information) [62, 63]. The concentration of La_{Mn}^{\times} was extracted from the La-antisite defect model, considering that the decrease of Mn/(La + Sr) is entirely compensated by these defects. The results show a very good agreement with the experimental results, further supporting the presence of antisite defects in Mn-deficient LSM thin films, see figure 6. Regarding the Mn-vacancy model, the effect of $v_{Mn}^{\prime\prime\prime}$ is not easily predictable by a simple hard sphere approximation model. Indeed, as shown in figure 5(b), the concomitant increase of Mn valance and oxygen





vacancy concentration may have different effects depending on the defects arrangement [62]. In order to depict the effect of Mn vacancies on the lattice parameter of LSM, the results obtained by Ji *et al* [30] for Mn-deficient LSM polycrystalline powders are also presented in figure 6. In their work, the authors observed a small lattice contraction increasing the concentration of $v_{Mn}^{\prime\prime\prime}$ [30]. Lee *et al* also calculated by *ab initio* modeling a decrease of the lattice parameter in the presence of cationic vacancies [64]. These results support the presence of La_{Mn}[×] as main compensation mechanism in our LSM_y thin films.

It is also worth discussing the main differences observed between thin films and bulk LSM_y samples. The compensation mechanism based on v''_{Mn} that was found for bulk LSM_y powders gives rise to a minimum Mn/(La + Sr) ratio before the appearance of secondary phases, around y = 0.08 [30, 65]. This is not the case for thin films, for which much larger B-site deficiencies have been reported [12, 31, 32]. The origin of the difference between bulk and thin film samples is not clear and might originate from the lower synthesis temperature [29], the epitaxial strain effects imposed by the substrate [66] or the different growth conditions of thin film deposition techniques [32]. For example, the moderate reducing conditions of PLD deposition may favor the formation of La[×]_{Mn}, as observed by theoretical calculation in LSM [26] and in LaCrO₃ [32], while v''_{Mn} or secondary phases may form under the oxidizing conditions and higher temperatures usually used for the synthesis of bulk samples.

Overall, our results strongly suggest the formation of La-antisite defects as a compensation mechanism in Mn-deficient LSM epitaxial thin films. The presence of these defects explains well the constant oxygen diffusivity observed by SIMS in the LSM_y layers, La_{Mn}^{\times} having small or no effect on both $[v_0^{\bullet\bullet}]$ and D_v . It is worth noting that our results do not imply that modification of B/A ratio will always have a negligible effect on the oxygen mass transport properties of perovskite oxides. Variation of cation stoichiometry is known to take place in perovskite thin films in many different circumstances, such as structural defects [26, 67], strain relaxation [58, 68] or near free surfaces [69, 70]. For instance, cation segregation or exsolution were observed to generate regions with altered B/A ratio, which may affect the mobility and concentration of oxygen vacancies [71–73]. However, here we show that antisite defects may provide an efficient way to mitigate cationic nonstoichiometry effects on oxygen mass transport properties and that they should be considered when dealing with variation of the B/A ratio.

4. Conclusions

In this work, we studied the oxygen mass transport properties and the defect compensation mechanism of Mn-deficient LSM_y epitaxial thin films. Fully epitaxial layers with a variable and controlled Mn/(La + Sr) ratio were deposited by PLD. Oxygen diffusivity coefficient measured by IEDP-SIMS display a constant behavior with the Mn-content. The origin of this surprising result is investigated by defect chemistry modeling. Among the two different mechanisms proposed (cation vacancy $v_{Mn}^{\prime\prime}$ or antisite defects La[×]_{Mn}), only the presence of La[×]_{Mn} is compatible with the results observed by PALS, XRD and ellipsometry, provided

the absence of secondary phases as proved by TEM. A defect chemistry model and Brower diagrams for antisite compensation in Mn-deficient LSM is described. Overall, antisite defect generation is therefore proposed as an efficient way to mitigate the negative impact of cationic vacancy on the oxygen mass transport properties of LSM_v thin films.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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ORCID iDs

Francesco M Chiabrera © https://orcid.org/0000-0001-8940-2708 Federico Baiutti © https://orcid.org/0000-0001-9664-2486 Jacqueline M Börgers © https://orcid.org/0000-0001-8945-3142 Maciej O Liedke © https://orcid.org/0000-0001-7933-7295 Juan de Dios Sirvent © https://orcid.org/0000-0001-6999-7505 Andreas Wagner © https://orcid.org/0000-0001-7575-3961 Roger A De Souza © https://orcid.org/0000-0001-7721-4128 Albert Tarancón © https://orcid.org/0000-0002-1933-2406

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