Defect Chemistry and Surface Oxygen Exchange Kinetics of La-Doped $\text{Sr}(\text{Ti,Fe})\text{O}_{3-\alpha}$ in Oxygen-Rich Atmospheres

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Abstract:

The mixed ionic and electronic conductor $\text{Sr}(\text{Ti,Fe})\text{O}_{3-\alpha}$ (STF) exhibits fast oxygen surface exchange kinetics, of interest for gas sensors, gas separation membranes, and solid oxide fuel/electrolysis cell electrodes. Prior work has demonstrated the potentially key role that electron concentration and Fermi level may play in controlling these kinetics. In the present work we investigate the effect of A-site donor doping with La on the electron concentration, Fermi level, and overall defect chemistry of STF. Bulk $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$ (LSTF, $0 \leq x \leq 0.5$) samples were fabricated by solid state processing, and their corresponding thin films were deposited by pulsed laser deposition. Defect chemistry was investigated by applying thermodynamic defect chemical modeling to optical absorption and electrical conductivity measurements in oxidizing conditions (N_2/O_2 mixtures). Good agreement between experiments and the model for $[\text{La}] < [\text{Fe}]$ was achieved, indicating compensation of donors by an increase in oxygen and

electron concentrations, increase in Fermi level, and decrease in oxygen vacancy and hole concentrations. Upon increasing the La content to the point where $[La] > [Fe]$, both the model and experiments are consistent with compensation of La by cation (e.g., Sr) vacancies, once the oxygen content saturates. The corresponding surface exchange kinetics of the LSTF films, measured by AC-impedance spectroscopy, show a decrease in the oxygen exchange coefficient with increasing donor concentration. Taken together the results suggest that the oxygen exchange kinetics of donor-doped STF are not limited by electron transfer, but rather by the low oxygen vacancy and/or hole concentrations.

1. Introduction

$Sr(Ti,Fe)O_{3-\alpha}$, in the $SrTiO_3 - SrFeO_{2.5}$ perovskite solid solution, exhibits mixed ionic and electronic conductivity¹ in addition to rapid oxygen surface exchange kinetics², and is therefore promising as an oxygen sensor³, gas separation membrane⁴, and oxygen electrode⁵ for solid oxide fuel/electrolysis (SOFC/SOEC) cells. The intermediate $SrTi_{0.65}Fe_{0.35}O_{3-\alpha}$ (STF35) composition exhibits many orders of magnitude higher conductivity than the $SrTiO_3$ end-member¹ and higher phase stability than the $SrFeO_{2.5}$ end-member⁶. In addition STF35 exhibits a unique temperature-independent resistance in lean burn conditions, making it the composition of choice for automotive gas sensing³.

In each of the aforementioned applications, more rapid oxygen surface exchange kinetics are sought – either for faster sensor response times or lower electrode overpotentials in solid oxide cells. A large air electrode resistance, originating in sluggish oxygen exchange kinetics and owing to the high activation energy of the surface exchange process, is a major contributor to SOFC efficiency losses at low temperatures⁷. The oxygen exchange process has been shown to consist of adsorption, dissociation, and incorporation steps, with charge transfer taking place at one or more of these steps⁸. To improve the overall reaction rate, the rate-determining step must be identified and mitigated. Previous investigations into thin film STF demonstrated a correlation between the activation energy for surface exchange and the energy difference between the conduction band minimum (E_C) and the Fermi level (E_F), which was controlled by varying the Fe concentration⁹. For strongly p-type systems such as STF35 in air, where the

Fermi level is significantly ($> 3kT$) below the conduction band, the concentration of electrons in the conduction band (n) also depends exponentially on this energy difference, $E_C - E_F$:

$$n = N_c \exp\left(-\frac{E_C - E_F}{kT}\right) \quad \text{with } N_c = 2 \left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \quad (1)$$

where N_c is the effective density of states in the conduction band, k is Boltzmann's constant, T is temperature, m_e^* is the effective mass of an electron, and h is Planck's constant. These results therefore suggested a key role of electron transfer from the conduction band of STF to the adsorbed oxygen, taking place in the rate-determining step. Based on this model one expects that facilitating electron transfer should lower the activation energy for oxygen exchange. For example, our group previously demonstrated that partial substitution of Ba for Sr lowered the band gap and reduction enthalpy with a simultaneous decrease in activation energy for surface exchange¹⁰. Additionally, illumination with light having energies larger than the band gap has been used to enhance surface exchange kinetics for dilute Fe concentrations in $\text{SrTiO}_3\text{:Fe}^{11}$, consistent with the key role of electron transfer, though for $[\text{Fe}] > 0.3$ (e.g. STF35), other factors, such as oxygen incorporation into vacancies, have also been suggested by these authors to limit surface exchange¹².

In the present work, La is introduced as an A-site donor dopant in this strongly p-type perovskite (in oxidizing conditions) with the goal of increasing the Fermi level and electron concentration, potentially even converting it to an n-type material. This paper, building on our preliminary work on $(\text{La,Sr})(\text{Ti,Fe})\text{O}_{3-\alpha}$ (LSTF)¹³, reports the influence of La on the defect chemistry of STF35, including the concentrations of key defects for surface oxygen exchange – oxygen vacancies and electrons, and also holes, which govern the electronic conductivity of STF35 in oxidizing conditions. Trends in these concentrations upon increasing the concentration of La are studied by defect thermodynamic modeling as well as by experimental optical and electrical characterization. We also introduce the measured surface exchange kinetics of La-doped STF35 thin films as they relate to the above defect chemistry.

To our knowledge this may be the first work investigating the defect chemistry of a perovskite transitioning from p-type towards n-type behavior with a non-dilute multivalent cation. Yoo and co-workers recently addressed this topic for relatively dilute acceptor (Mn on Ti) and donor (Y on Ba) concentrations in co-doped BaTiO₃, which transitioned from p-type to n-type behavior in oxidizing conditions upon increasing the donor-to-acceptor ratio¹⁴. In the present work, the large concentration of multivalent B-site cation (Fe) is expected to form a band and participate in electronic conduction¹⁵ (as opposed to isolated states in the dilute case). In addition the role of cation vacancies is considered in the present work. The resulting different approach to defect modeling of an otherwise similar system may therefore be of broader interest, relating to other ambipolar conducting perovskites with non-dilute doping levels.

2. Approach

2.1. Defect Modeling

The approach to modeling the effect of La doping in STF35 is based on a defect model established by Kuhn, Rothschild, and co-workers for undoped STF35, using electrical conductivity measurements¹⁵ and oxygen stoichiometry data from thermogravimetric analysis¹⁶. First this defect model for STF35 will be described, and then the modifications upon introducing a donor dopant will be presented.

Owing to the large Fe concentration, STF is considered as a solid solution between SrTiO₃ and SrFeO_{2.5}, and thus the reference state for the defect model is defined as SrTi_{1-x}Fe_x³⁺O_{3-x/2}. Oxygen deficiency and excess relative to this composition are accommodated by oxygen vacancies and oxygen “interstitials” (in the latter case, oxygen ions occupy structural vacancies in the reference compound). The concentration of “oxygen sites,” defined by the reference state, is given as (3-x/2)*[STF], while that of “interstitial sites” (i.e., structural vacancies) is (x/2)*[STF], with [STF] the volumetric concentration of STF formula units (~1.685 x 10²² cm⁻³). These two sites are considered structurally non-equivalent¹⁵. The

oxygen super-stoichiometry relative to the reference state, in the formula unit $\text{SrTi}_{1-x}\text{Fe}_x^{3+}\text{O}_{3-x/2+\delta}$, is then given as:

$$\delta = \frac{[O_i''] - [V_O^{\bullet}]}{[STF]} \quad (2)$$

where O_i'' and $V_O^{\bullet}$ are doubly charged oxygen interstitials and oxygen vacancies, written using Kröger-Vink notation. Brackets denote concentration. The anion disorder is described by the anion Frenkel reaction below and the following corresponding equilibrium, or mass action, equation.

$$K_f'(T) = \frac{[O_i''] [V_O^{\bullet}]}{[O_O^x] [V_i^x]} = K_f^{0'} \exp\left(\frac{-G_f'}{kT}\right) \quad (4)$$

where K_f' , G_f' , O_O^x , and V_i^x are a temperature dependent equilibrium constant, the Gibbs free energy for the reaction, oxygen ions on an oxygen site, and vacant interstitial sites, respectively. Due to the small impact of vibrational entropy, G_f was previously considered equal to H_f (the enthalpy for the reaction)¹⁵. Oxygen vacancies are also generated through the reduction reaction, which is followed by the corresponding equilibrium equation.

$$K_{red}'(T) = \frac{[V_O^{\bullet}] \cdot n^2 \cdot pO_2^{1/2}}{[O_O^x]} = K_{red}^{0'} \exp\left(\frac{-H_{red}'}{kT}\right) \quad (6)$$

where n , pO_2 , and H_{red}' are the concentration of electrons, partial pressure of oxygen, and enthalpy of reduction, respectively. Note, primes are attached to the mass action and enthalpy terms to distinguish them from values derived earlier in References 15 and 16, as described below and in Table 1. The intrinsic electronic disorder is given by the following equations, assuming the effective densities of states for the valence and conduction bands (N_v and N_c , respectively) remain approximately constant.

$$null \rightleftharpoons p + n \quad (7)$$

$$K_i(T) = np = N_v N_c \exp\left(\frac{-E_g}{kT}\right) \quad (8)$$

where p and E_g are the hole concentration and band gap, respectively.

Upon introducing a donor dopant, the electroneutrality equation is given by

$$2[V_O^{\bullet\bullet}] + p + [La_{Sr}^{\bullet}] = 2[O_i^{\prime\prime}] + n + m[V_{cat}^{m'}] \quad (9)$$

where $La_{Sr}^{\bullet}$ and $V_{cat}^{m'}$ are La dopants on Sr sites and cation vacancies with a negative charge of m , respectively. Here, La is assumed to be soluble in STF35 in the composition range studied (complete replacement of Sr with La in SrTiO₃ has previously been demonstrated for samples cooled from 1350 °C in air¹⁷, and all bulk samples in the present work were single phase by XRD) and ionized. It is apparent from eq. 9 that La dopants can be compensated for not only by electrons, but also by $O_i^{\prime\prime}$ and $V_{cat}^{m'}$. For example, La doping in bulk SrTiO₃ has been shown to generate Sr vacancies ($V_{Sr}^{\prime\prime}$) in oxidizing conditions (rather than Ti vacancies as in BaTiO₃)¹⁸, and Moos has experimentally determined energetic terms associated with formation of Sr vacancies in La-doped SrTiO₃ via a partial Schottky reaction¹⁹:

where SrO_{RP} represents rocksalt layers of SrO within the perovskite as in Ruddlesden-Popper phases. The partial Schottky mass-action relationship is written as:

$$K'_{PS} = \frac{[V_O^{\bullet\bullet}][V_{Sr}^{\prime\prime}]}{[O_O^{\times}][Sr_{Sr}^{\times}]} = K_{PS}^{0'} \exp\left(\frac{-E'_{PS}}{kT}\right) \quad (11)$$

It is also possible to describe cation vacancy formation through doping reactions, e.g., as shown in eq. 12;

however, precipitation of a La-rich second phase is not observed in the present work. Alternatively, cation vacancies may be “frozen in” from processing in a more energetic condition than that used for property measurements. The main differences upon use of other cation-generating reactions are the pO₂

dependence of cation vacancies, and their concentration, which affects the concentrations of other defects. The effect of cation vacancy concentration on defect concentrations is shown in the results section.

Because of the large amount of donor dopant used here, constraints on the numbers of acceptor species (V_{Sr}'' or O_i'') that can be generated to charge-balance the La donor must be implemented. Thus, the following site balance equations are introduced.

$$[O_O^x] = [\text{oxygen sites}] - [V_O^{\bullet}] = \left(3 - \frac{x}{2}\right) [STF] - [V_O^{\bullet}] \quad (13)$$

$$[V_i^x] = [\text{structural interstitial sites}] - [O_i''] = \left(\frac{x}{2}\right) [STF] - [O_i''] \quad (14)$$

$$[Sr_{Sr}^x] = [Sr \text{ sites}] - [V_{Sr}''] = [STF] - [La_{Sr}] - [V_{Sr}''] \quad (15)$$

It should be noted that site balance terms are accommodated in this revised model while previously, in References 15, 16, and 19, $[O_O^x]$, $[V_i^x]$, and $[Sr_{Sr}^x]$ were considered constants and incorporated into the pre-exponential factors. One therefore expects changes in the pre-exponential and/or energetic terms as derived from previous calculations. The energy terms in eqs. 4, 6, and 8 were determined by fitting the same TGA data used for the initial STF35 model¹⁶. This approach does not allow for a precise determination of the partial Schottky energy in eq. 11, since cation vacancies were not found to contribute significantly to the measured non-stoichiometry of undoped STF35. E'_{pS} was instead estimated from the experimental data in the present work and compared to the value reported by Moos¹⁹ for $SrTiO_3$ with assumed constant $[O_O^x]$ and $[Sr_{Sr}^x]$. Values for pre-exponential and energy terms are given in table 1 (see results section). Using eqs. 4, 6, 8, 9, and 13-15, the concentrations of all the defects can be calculated for different concentrations of La doping. It is noted that activity coefficients have been assumed to be unity, as is common practice, despite such large concentrations of defects.

2.2. Experimental

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4 Fabrication of $\text{Sr}_{1-y}\text{La}_y\text{Ti}_{1-x}\text{Fe}_x\text{O}_{3-x/2+\delta}$ ($y = 0, 0.1, 0.2, 0.35, 0.5$; $x = 0.35$) thin films on single
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6 crystal 8 mol% and 13 mol% Y_2O_3 -stabilized ZrO_2 substrates (MTI Corp., Richmond, CA, USA and Keri
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8 Optoelectronic Technology Co. Ltd., Dalian, China, (001) orientation) and single crystal Al_2O_3 substrates
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10 (MTI Corp., (0001) orientation) was performed by pulsed laser deposition (PLD), using conditions
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12 described previously.¹³ Targets for PLD were fabricated by a solid state process; powders of dried La_2O_3 ,
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14 Fe_2O_3 , SrCO_3 , and TiO_2 were ground together, uniaxially pressed, then isostatically pressed at 300 MPa,
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16 and sintered in air at 1425 °C for 6 h with heating and cooling at 5 °C/min. Compositions of the targets
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18 were found to agree with the desired composition, within error, by X-ray fluorescence measurements
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20 (EDX-800, Shimadzu Corp., Japan). The single phase perovskite structure of all the targets was observed
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22 by X-ray diffraction (RINT 2200 Ultima III diffractometer, Rigaku Corp., Tokyo, Japan). Film growth
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24 rates/ thicknesses were evaluated *ex situ* by X-ray reflectivity (X'Pert Pro, PANalytical), profilometry (P-
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26 16 surface profilometer, KLA-Tencor, Milpitas, CA, USA), and scanning electron microscopy (S-5200
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28 FE-SEM, Hitachi, Japan). Out-of-plane lattice parameters and the extent of texturing of the thin films
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30 were evaluated by X-ray diffraction (X'Pert Pro, PANalytical) with $\text{Cu K}\alpha_1$ radiation at 1.540 Å. Peak
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32 positions were fit using the program CMPR²⁰. Lattice parameters were estimated by normalizing the film
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34 peak position to that of the substrate and using the substrate lattice parameter reported by the
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36 manufacturer.
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43 Optical absorption of ~200 nm thick films using light with wavelengths from 200-2000 nm was
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45 measured using a V-670 spectrophotometer (Jasco Analytical Instruments, Easton, MD, USA) at room
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47 temperature in air. Absorption of the YSZ substrate was subtracted using a separate measurement of an
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49 uncoated substrate. Prior to the measurements, the films were annealed in air at 500 °C for 6 h and cooled
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51 at 5 °C/ min in air for oxidation after deposition. In-plane conductivity of as-deposited films on Al_2O_3
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53 substrates was determined from 2-point AC-impedance spectroscopy measurements (Alpha-A Frequency
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55 Analyzer, Novocontrol Technologies GmbH & Co. KG, Montabaur, Germany) over the frequency range
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57 1 MHz to 0.01 Hz from room temperature up to 500 °C and in N_2/O_2 gas mixtures with oxygen partial
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pressures ranging from $\sim 10^{-5}$ atm (N_2) to ~ 1 atm (O_2) with a total flow rate of 100 sccm. The electrodes for these measurements were interdigitated Pt, deposited by sputtering over a shadow mask. The impedance spectra were modeled with a resistor in parallel with a constant phase element, using Boukamp's Equivalent Circuit program²¹, and the conductivity was determined from the resistance using the following equation:

$$\sigma = \frac{d}{Rtl(n-1)} \quad (24)$$

where d is the distance of the gap between adjacent electrode fingers (~ 150 μm), R is the measured resistance, t is the film thickness (50-150 nm), l is the length of the fingers (0.55 cm), and n is the total number of fingers (20, counting both electrodes). Bulk conductivity of a $Sr_{0.5}La_{0.5}Ti_{0.65}Fe_{0.35}O_{3-\alpha}$ PLD target was also evaluated by impedance spectroscopy at 800 °C, with porous Au paste (TR-1301 paste, Tanaka Kikinzoku Kogyo K.K., Japan) painted on each face of the pellet for electrodes. Conductivity was corrected for porosity using Maxwell's dilute limit approximation²².

Measurements of thin film cathode area-specific resistance (ASR) were performed on asymmetrical cells with porous Ag (Dotite D-550 paste, Fujikura Kasei Co., Ltd., Japan) as a counter electrode, the YSZ substrate as an electrolyte, ~ 100 nm-thick La-STF thin films as the cathodes, and a thin layer of porous Au as the current collector (TR-1301 paste, Tanaka Kikinzoku Kogyo K.K., Japan). The cross-plane impedance of these cells was measured by AC-impedance spectroscopy, as described above, after heating each cell to 600 °C in a flowing $N_2/O_2/H_2O$ mixture with $pO_2 = 0.21$ atm and $pH_2O = 0.012$ atm, at 5°C / min and holding for 30 min before making the measurement. In this way the thermal history of each sample and the gas environment, both important variables in the performance of La-STF thin film cathodes, were kept the same. In this case the impedance spectra were modeled as described in ref. 9. When current collection is adequate and the thickness of the film is considerably less than the critical length for diffusion vs. surface exchange-limited kinetics (calculated as >200 μm for STF35 at

<700 °C²³), the electrical surface exchange rate coefficient (k_q) can be determined from the measured resistance corresponding to the low frequency impedance arc:

$$k_q = \frac{kT}{4q^2 R A c_0} \quad (25)$$

where q is the electronic charge, R is the measured resistance of the low frequency arc, A is the cathode area (considered to be the area covered by the film on the substrate owing to minimal surface roughness and highly dense films), and c_0 is the volumetric concentration of oxygen in the film, i.e., $[O_O^x] + [O_i'']$.

3. Results

Energetic and pre-exponential terms in the present defect model, compared to the previous model for undoped STF35, are shown in table 1. As mentioned, in the previous model^{15,16} and in the work by Moos incorporating Sr vacancies¹⁹, $[O_O^x]$, $[V_i^x]$, and $[Sr_{Sr}^x]$ were considered constants and incorporated into the pre-exponential terms, whereas the new model takes into account site balance (eqns. 13-15).

Table 1: Values of terms in the defect models for undoped and donor-doped STF35

Undoped	Donor Doped, Modified Model
$K_i^0 = 3.57 \times 10^{43} \text{ cm}^{-6}$	$K_i^{0*} = K_i^0$
$E_g \text{ (thermal)} = 1.38 \text{ eV}$	$E_g' = E_g$
$K_f^0 = [O_O^x]_{\text{ref}} [V_i^x]_{\text{ref}} = 1.53 \times 10^{44} \text{ cm}^{-6}$	$K_f^{0*} = K_f^0 / [O_O^x]_{\text{ref}} [V_i^x]_{\text{ref}} = 1$
$G_f = 0.52 \text{ eV}$	$G_f' = 0.48 \text{ eV}$
$K_{\text{red}}^0 = 3.93 \times 10^{70} \text{ cm}^{-9}$	$K_{\text{red}}^{0*} = K_{\text{red}}^0 / [O_O^x]_{\text{ref}} = 8.27 \times 10^{47} \text{ cm}^{-6}$
$H_{\text{red}} = 3.89 \text{ eV}$	$H_{\text{red}}' = H_{\text{red}}$
Negligible cation vacancy concentration	$K_{\text{PS}}^{0*} = 3 \times 10^{44} \text{ cm}^{-6}$
	$E_{\text{PS}}^* = 2.5 \text{ eV}$
	$K_{\text{PS}}^{0*} = K_{\text{PS}}^0 / [O_O^x]_{\text{ref}} [Sr_{\text{Sr}}^x]_{\text{ref}} = 3.74 \times 10^{-1}$
	$E_{\text{PS}}' \approx 1.5 \text{ eV}$

* Values from ref. 19 for constant $[O_O^x]$ and $[Sr_{\text{Sr}}^x]$ in the pre-exponential factor

The concentrations of all relevant point defect species as a function of La content in air at 600 °C, predicted using the energetic terms from table 1, are shown in figures 1a and 1b for two different partial Schottky formation energies. As expected, introduction of La increases the concentrations of all species with relative negative charges and lowers the concentrations of defects with relative positive charges. The

more significant changes observed near $[La_{Sr}'] = 0.35$ represent a transition from a condition where $[La_{Sr}'] < [Fe]$ or $[La_{Sr}'] < [\text{total oxygen interstitial sites}]$ to one where $[La_{Sr}'] > [Fe]$ or $[La_{Sr}'] > [\text{total oxygen interstitial sites}]$. Compensation of La_{Sr}' by V_{Sr}'' (and to a lesser extent, electrons) increases sharply once $[O_i'']$ has reached the maximum amount. For $E'_{pS} = 2.5$ eV (figure 1a), a transition from p-type to n-type electronic behavior is expected as the La content is increased, given the orders of magnitude greater n as compared to p with similar mobilities previously derived for these charge carriers¹⁶. On the other hand, for a decreased $E'_{pS} = 1.5$ eV (figure 1b), the transition to n-type behavior is suppressed due to the larger number of V_{Sr}'' compensating defects. Similarly $[V_O'']$ is higher in the latter case, again owing to the lower E'_{pS} .

Alternatively, a non-equilibrium high concentration of V_{Sr}'' may have formed during processing and subsequently frozen-in during measurements due to very slow Sr diffusion; an example of this situation is shown in figure 1c, where defect concentrations in a $Sr_{0.5}La_{0.5}Ti_{0.65}Fe_{0.35}O_{3-\alpha}$ composition are shown for different fixed $[V_{Sr}'']$. In figure 1d, the change in the energy difference, $E_C - E_F$, in air at 600 °C, calculated from the electron concentrations in figures 1a-b with eq. 1 is shown. It can be seen, in each case, that an increase of the Fermi level is expected upon La doping, though higher cation vacancy concentrations lead to smaller changes in Fermi level.

Figure 1. Predicted equilibrium defect concentrations at 600 °C in air for different concentrations of La in $(\text{Sr},\text{La})\text{Ti}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$ (a) using the partial Schottky reaction with $E'_{\text{PS}} = 2.5$ eV and (b) with a lower $E'_{\text{PS}} = 1.5$ eV. In (c) the defect concentrations are shown for different “frozen-in” $[V_{\text{Sr}}'']$ in $\text{Sr}_{0.5}\text{La}_{0.5}\text{Ti}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$. In (d) the resulting energy difference between the conduction band minimum and the Fermi level is shown for the cases in (a) and (b).

Figure 2 shows that the LSTF films grown on YSZ are strongly (110) oriented, without significant evidence of other orientations. The large lattice mismatch with the substrate suggests a polycrystalline morphology (confirmed by SEM) consisting of highly textured (110)-oriented grains. From figure 2b, it can be seen that the film peak position shifts to lower 2θ values with increasing La

concentration, indicating an expansion of the lattice out-of-plane. The corresponding out-of-plane lattice parameters are 3.912, 3.916, 3.917, 3.928, and 3.940 Å for [La] = 0, 0.1, 0.2, 0.35, and 0.5, respectively. Since the radius of La [1.36 Å] is smaller than that of Sr [1.44 Å]²⁴, the lattice expansion upon La doping may indicate a reduction of Fe⁴⁺ to the larger Fe³⁺ species, which is consistent with the decrease in hole concentration in figure 1 and the optical absorption results described next.

Figure 2. (a) X-ray diffraction patterns of (Sr,L)Ti_{0.65}Fe_{0.35}O_{3-α} films on single crystal 8 mol% YSZ substrates. (b) Corresponding position of film peak in 2θ as a function of La content.

In STF the optical absorption is sensitive to the valence state of Fe, as there are absorption features at characteristic energies corresponding to the presence of Fe⁴⁺ or Fe²⁺, while Fe³⁺ is optically

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4 inactive²⁵. These optically active centers can be used to derive the defect equilibria and corresponding
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6 oxygen vacancy content of oxides, as demonstrated previously using absorption studies of $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$
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8 thin films²⁶ and STF single crystals²⁷. As shown in figure 3a, the room temperature optical absorption of
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10 LSTF films on YSZ in air decreases with increasing La content, ultimately appearing to saturate for $[\text{La}]$
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12 $\geq [\text{Fe}]$. The inset of figure 3a shows the associated color change of powders with increasing La contents.
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14 This trend is further confirmed by the thin film absorption at specific energies corresponding to Fe^{4+}
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16 absorption²⁵ (figure 3b). Decreasing absorption is consistent with a decreasing concentration of Fe^{4+} as La
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18 is added and then it remaining at a low value once there is more La than Fe. The results are also consistent
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20 with the decreasing hole concentration (related to Fe^{4+} concentration) with La addition predicted by the
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22 defect model (figure 1). Interestingly, no additional absorption that could be attributed to electrons (e.g.
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24 free carrier absorption or Fe^{2+} absorption²⁵) is observed in these oxidized films, suggesting that high
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26 electron concentrations are not generated even under donor doping conditions. The absorption associated
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28 with the presence of Fe^{4+} has been attributed to charge transfer, e.g., from the O 2p levels deep in the
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30 valence band into the $\text{Fe}^{3+/4+}$ levels at the top of the valence band²⁸. The disappearance of the absorption
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32 would then correspond to a filling of the $\text{Fe}^{3+/4+}$ levels as all the Fe reduces to the Fe^{3+} state, indicating a
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34 rise in Fermi level, again consistent with the defect model.
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Figure 3. Optical absorption coefficients of $(\text{Sr,La})\text{Ti}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$ thin films with thickness of ~ 200 nm, (a) as a function of light energy, (b) at energies characteristic of Fe^{4+} absorption. Substrate absorption has been subtracted.

In figure 4a the measured in-plane electrical conductivity (σ) of LSTF thin films containing different amounts of La, on Al_2O_3 (0001) substrates, is shown as a function of oxygen partial pressure at ~ 390 °C. The positive dependence of $\log(\sigma)$ on $\log(p\text{O}_2)$, with a slope between $1/4$ and $1/6$, is characteristic of p-type electronic conductivity, even for the highest La contents. As previously shown in figure 1a, the defect model with a relatively high value (2.5 eV) for E'_{FS} predicts a significant drop in hole concentration and a transition to n-type conductivity once the La concentration exceeds the Fe

concentration, neither of which are observed in the measured conductivity data to the extent expected. Instead the model, using a lower partial Schottky energy of 1.5 eV (as in figure 1b), yields hole concentrations in reasonable agreement with the conductivity changes shown in figure 4a, assuming a constant mobility of $\sim 2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This mobility value is smaller than expected based on the high temperature results for bulk samples in ref. 15, possibly suggesting trapping at this lower temperature. The predicted hole concentrations are the solid lines superimposed in figure 4a. In figure 4b the electrical conductivities measured as a function of temperature in air are shown. The activation energies (in the low temperature range) are observed to increase when the La concentration per formula unit is 0.35 or higher, and again the magnitude of the conductivity decreases with increasing La content at all temperatures in this range.

Figure 4. In-plane electrical conductivity of $(\text{Sr},\text{La})\text{Ti}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$ films on Al_2O_3 (0001) substrates, (a) as a function of oxygen partial pressure at 390 °C, with expected hole concentrations from the defect model (with $E'_{PS} = 1.5$ eV) superimposed, and (b) as a function of temperature in air.

For comparison to the thin films and the defect model, steady-state electrical conductivity for bulk $\text{Sr}_{0.5}\text{La}_{0.5}\text{Ti}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$ as a function of oxygen partial pressure at 800 °C was measured and is shown in figure 5 along with data for bulk $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$ from ref. 3. Hole and electron concentrations predicted from the defect model (either $E'_{PS} = 1.5$ eV, as for the thin films, or fixed $[V''_{Sr}] = 0.15[La'_{Sr}]$) are superimposed as dashed lines and solid lines, respectively. At this higher temperature, the bulk pellet appears to exhibit a transition from p-type to n-type behavior upon decreasing the oxygen partial pressure, albeit with very small slopes in this transition range, of +0.02 between air and pure O_2 and -0.07 between 0.1% O_2 and pure N_2 . The experimental crossover point between the different electronic regimes ($\sim 10^{-1.8}$ atm) agrees well with the defect model, assuming similar mobilities for electrons and holes ($\sim 5 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, in agreement with the value reported for holes at this temperature previously for STF35¹⁶). The decrease of the conductivity in the $[La'_{Sr}] = 0.5$ sample vs. the case with no La doping appears to match more closely with the model where the cation vacancy concentration is fixed with respect to oxygen partial pressure.

Figure 5. Electrical conductivity of bulk STF35 ($[La'_{Sr}] = 0$; diamonds), from Ref. 3, and $\text{Sr}_{0.5}\text{La}_{0.5}\text{Ti}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\alpha}$ ($[La'_{Sr}] = 0.5$; filled circles) measured in the present study at 800 °C as a function

of oxygen partial pressure. Superimposed lines indicate defect concentrations calculated from the model with $E'_{PS} = 1.5$ eV (dashed lines for $[La] = 0.5$), with fixed $[V''_{Sr}] = 0.15[La'_{Sr}]$ (solid lines for $[La] = 0.5$), or for STF35 where the magnitude of E'_{PS} has little effect on defect concentrations (dashed-dotted lines).

The influence of La on thin film LSTF area-specific resistance and corresponding oxygen surface exchange rate at 600 °C in 0.21 atm O₂ with 0.012 atm H₂O obtained from impedance spectra as described in the experimental section, is shown in figure 6. Under these conditions La is seen to systematically increase the ASR and correspondingly worsen the oxygen surface exchange kinetics.

Figure 6. Area specific resistance (squares) and corresponding electrical oxygen surface exchange coefficients (triangles) of (Sr,La)Ti_{0.65}Fe_{0.35}O_{3-α} thin film cathodes at ~600 °C in 0.21 atm O₂ with 0.012 atm H₂O.

4. Discussion

4.1 Thin film conductivity

As expected, La doping suppresses the p-type conductivity and quenches the optical absorption from holes, i.e., Fe⁴⁺. Despite large fractions of donor dopant, n-type behavior was not observed for the thin films. Instead, donor dopants appear to be largely compensated by, first, oxygen interstitials, and second, cation vacancies with increasing La content. For lower La concentrations ($[La'_{Sr}] < [Fe]$), where the concentration of cation vacancies appears to remain low, changes in cation vacancy formation

energetics have very little effect on the concentrations of other defects. In this more dilute regime, the defect model may be considered more quantitatively accurate since the previously established energetic terms from the STF model largely dictate the behavior of the system, yielding good agreement to experimental thin film conductivity data. In this case, La doping is largely compensated by the mechanisms that are active in undoped STF: creation of O_i'' , with annihilation of $V_O^{\bullet}$ and holes. By contrast, for high La concentrations ($[La_{Sr}] > [Fe]$), the “intrinsic” defect compensation mechanisms of STF approach saturation given a finite number of structural oxygen interstitial sites to fill. In this non-dilute regime, the more energetically costly cation vacancies begin to form in significant concentrations. Increasing the cation vacancy concentration in the calculations (figure 1) results in a much more significant change in the concentrations of other defects, for example causing a transition from predominantly n-type behavior in oxidizing conditions to p-type behavior.

In addition to the clear p-type behavior observed in thin films for all La contents, a slight irreversible decrease in p-type electrical conductivity was observed in some of the thin films after the isothermal measurements at ~ 390 °C and in the bulk sample after measuring at ~ 800 °C, while an irreversible decrease of conductivity was found upon heating the $Sr_{0.5}La_{0.5}Ti_{0.65}Fe_{0.35}O_{3-\alpha}$ film above 500 °C (figure 4b), each of which is consistent with (but not conclusive of) a gradual decrease in a non-equilibrium cation vacancy concentration towards a lower equilibrium value. This result indicates that the energetic values derived for V_{Sr}'' formation in the present case may be influenced by non-equilibrium $[V_{Sr}'']$.

On the other hand, other factors could explain the electrical behavior of thin films and bulk samples without needing to invoke the presence of cation vacancies. P-type behavior could also, hypothetically, be maintained in air across the same range of La concentrations by changing other energetic terms; e.g., a gradual (though large) increase of the reduction enthalpy from 3.9 eV to 4.7 eV as La is added up to $[La_{Sr}] = 0.5$ suppresses the transition to n-type behavior in these conditions. It is also possible that lower concentrations of La exist in the thin films than expected, though preliminary energy-

dispersive spectroscopy analysis of the thin films (from the surface in the SEM and a cross-section in TEM) compared with bulk samples does not support this conclusion. Finally, bulk conductivity behavior of the $[La_{Sr}] = 0.5$ (confirmed by X-ray fluorescence) sample is also suggestive of a high cation vacancy concentration.

4.2 Thin film vs. bulk

The thin films and bulk $[La_{Sr}] = 0.5$ sample exhibited different dependencies of the electrical conductivity on oxygen partial pressure. For the thin film samples, the data were best fit with a model that allows the cation vacancy concentration to equilibrate with respect to oxygen partial pressure within the time frame of the measurements, despite the low measurement temperature. In fact it was not possible to match both the magnitude changes of the conductivity upon doping and their oxygen partial pressure dependence to a model where the cation vacancy concentrations were fixed during the measurement. For the bulk sample, on the other hand, the data were best fit with the model where cation vacancy concentration is fixed with respect to oxygen partial pressure, despite the higher measurement temperature. It is unclear why the kinetic barrier to forming/annihilating cation vacancies might be lower in thin films, although there are numerous aspects of the micro-, crystal-, and defect- structures that differ vs. bulk samples. 1) Cation mobilities may be modified vs. bulk, given the predominant influence of surface/gas, substrate/film, and internal grain boundary interfaces and the possibility of lattice strain/crystal structure anisotropy. 2) Owing to the high energy, non-equilibrium processing technique, different cation vacancy species vs. those found in bulk samples could be formed in the thin film samples during the PLD process. For example, though Sr vacancies are calculated to have a lower formation energy and appear to predominate in bulk donor-doped $SrTiO_3$, Ti vacancies have been observed in $SrTiO_3$ films prepared by PLD under certain conditions²⁹. 3) The in-plane conductivity measured using electrodes on top of the films may have been dominated by a surface layer with different chemistry than the bulk of the film. Sr enrichment is well-known to occur in STF, and it is possible that Sr-rich phases may precipitate at the surface in concentrations not detectable by X-ray diffraction.

5. Summary and Conclusions

Defect chemical modeling, combined with structural, optical, and electrical measurements of thin film and bulk samples were applied to study changes in the defect chemistry of STF upon donor doping with La in oxygen-rich conditions, with particular attention to factors that may influence the oxygen surface exchange rate. The main changes that take place in STF upon La doping in oxidizing conditions include filling of structural oxygen “interstitial” sites, decreasing oxygen vacancy concentration, decreasing hole concentration, and rising electron concentration and Fermi level. The extent to which electrons form and the Fermi level rises is dependent upon the number of other compensating defects that form, where large concentrations of cation vacancies may be responsible for the persistent p-type behavior of thin films even with large donor dopant concentrations and the shallow dependence of conductivity on oxygen partial pressure for bulk samples. Such defect chemical changes are consistent with the decline in oxygen exchange rate measured for the thin film samples in oxidizing conditions, since oxygen vacancies are necessary defects for oxygen incorporation and holes are important for in-plane conductivity and current collection. Therefore for moderate or high concentrations of donor dopant, one expects oxygen exchange not to be limited by electron transfer.

Finally it should be noted that, in equilibrium, the compensation of donors by cation vacancy formation has an oxygen partial pressure dependence, given by the partial Schottky reaction, and that one expects a transition to electronic compensation of the donor for lower oxygen partial pressures.

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