Neutron structural characterization and transport properties of oxidized and reduced $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (M=Mn, Fe) perovskites: Possible electrode materials in solid-oxide fuel cells

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Neutron structural characterization and transport properties of *oxidized and reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn, Fe}$) perovskites: Possible electrode materials in solid-oxide fuel cells

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Oxygen-stoichiometric $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn, Fe}$) perovskites and the corresponding *reduced* specimens, of $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ composition, have been prepared and characterized by x-ray diffraction and neutron powder diffraction (NPD), in complement with thermal analysis, electrical conductivity, and thermal expansion measurements. NPD data show that these perovskites are all orthorhombic, space group *Pbnm* (No. 62). The total reduction of M^{3+} to M^{2+} in the *reduced* phases is accompanied with the occurrence of oxygen vacancies, which was confirmed by thermogravimetric analysis (TGA). Above room-temperature, these phases undergo two structural phase transitions studied *in situ* from NPD data; the former to a tetragonal (*I4/mcm*) structure, and the second one to a cubic (*Pm-3m*) phase. All the oxides display a semiconductor-like behavior with a maximum conductivity value of $15 \text{ S}\cdot\text{cm}^{-1}$ for the *oxidized* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ phase at 850°C . The measured thermal expansion coefficients perfectly match with the values usually displayed by solid-oxide fuel cell (SOFC) electrolytes. The obtained results present these perovskites as alternative electrodes for SOFCs. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4798364>]

I. INTRODUCTION

Materials with perovskite-like structure are receiving great attention due to their huge range of possible applications; these oxides are widely used as functional materials in ferroelectric, thermoelectric, magnetoelectronic devices, and in solid oxide fuel cells (SOFC). Their unique properties derive from an unmatched chemical flexibility in spite of their relatively simple crystal structure.¹ The reduction of stoichiometric phases into novel oxygen hypo-stoichiometric oxides is a powerful tool for the development of new materials with original magnetic or transport properties.² Moreover, the stabilization of transition-metal perovskites with an adequate concentration of oxygen vacancies under reducing atmosphere can also be of application in new mixed electronic-ionic conductors for energy-conversion devices such as solid oxide fuel cells or oxygen separation membranes.

Titanium perovskite oxides RTiO_3 ($\text{R} = \text{rare earth}$) and $\text{R}_{1-x}\text{M}_x\text{TiO}_3$ (Refs. 3–5) ($\text{R} = \text{La, Nd, Gd, Er, and Y}$; $\text{M} = \text{Ba}^{2+}, \text{Sr}^{2+}, \text{K}^+, \text{and Na}^+$) have been the topic of numerous recent studies. RTiO_3 compounds can be viewed as distorted perovskites with orthorhombic structure (GdFeO_3 -type). The substitution of aliovalent cations for R leads to changes in the properties; for instance, in the stoichiometric LaTiO_3 , the substitution of divalent ions (Ba^{2+} and Sr^{2+}) for La^{3+} results in novel transport and magnetic

properties,^{6–8} whereas substitution of Na^+ , i.e., $\text{La}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ produces paraelectricity.⁹ In the field of SOFC, despite the high electronic conductivity, Sr-substituted LaTiO_3 exhibits low electrocatalytic activity for fuel oxidation.^{10,11} However, it is possible to improve the activity through a high level of substitution of an alternative M first-row transition metal at the Ti site.

The formation of $\text{R}(\text{M,Ti})\text{O}_3$ ($\text{R} = \text{rare earth}$; $\text{M} = \text{metal transition}$) may be feasible either for trivalent M and Ti ions (having in mind that Ti^{3+} ions are difficult to stabilize) or with a combination of divalent M and tetravalent Ti ionic states, under the appropriate atmosphere during the high-temperature synthesis.¹² It is also possible to form ALaMTiO_6 , where A is an alkaline earth or their solid solution and the ionic states of M and Ti are trivalent and tetravalent.¹³ For $\text{M} = \text{Mn}$, previous studies of Alvarez-Serrano *et al.* have reported 50% substitution of Mn ions for Ti in $\text{Sr}_{0.5}\text{La}_{0.5}\text{MnO}_3$.¹⁴

The introduction of $\text{M} = \text{Fe}$ in $\text{R}(\text{M,Ti})\text{O}_3$ may also be appealing since the end-member perovskite RFeO_3 orthoferrites present a good chemical stability in both reducing as well as oxidizing atmosphere¹⁵ as well as high electrical conductivity (in suitably Sr-doped samples).^{16–18}

In this context, recently we have prepared and characterized $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Ti}_{0.5}\text{O}_3$ oxide, in both *oxidized* and *reduced* phases,¹⁹ which have been described as possible symmetrical electrodes for SOFCs, based upon their mixed electronic and ionic conductivities. These oxides are stable in both, oxidizing and reducing conditions, as required for symmetrical electrode materials. In the present work, we

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describe the structure and properties of $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn}, \text{Fe}$) oxides. A structural characterization from neutron powder diffraction (NPD) data at room and high temperature was carried out in order to examine the crystal structure and the possible phase transitions of the perovskites. The characterization has been completed with thermal expansion, electrical conductivity measurements, and thermal analysis (TA), in order to evaluate their potential use as electrode materials in SOFCs.

II. EXPERIMENTAL

$\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn}, \text{Fe}$) oxides were prepared as polycrystalline powders from citrate precursors obtained by soft-chemistry procedures. Stoichiometric amounts of La_2O_3 (pre-dried at 900°C), $\text{Sr}(\text{NO}_3)_2$, MnCO_3 , $\text{C}_2\text{FeO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{TiC}_{10}\text{H}_{14}\text{O}_5$ were dissolved in citric acid and some drops of nitric acid in order to favor the dissolution of the rare-earth oxide. The solution was then slowly evaporated, leading to organic resins that contain a homogeneous distribution of the involved cations. The formed resins were dried at 120°C and decomposed at 600°C for 12 h in air. All the organic materials and nitrates were eliminated in a subsequent treatment at 800°C in air, for 2 h and a final treatment at 1000°C for 12 h gave to rise to the pure oxygen-stoichiometric perovskite phases. The *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ oxides were prepared by treating the *oxidized* phases under a 5% H_2 /95% N_2 flow (60 ml min^{-1}) at 800°C for 6 h in alumina boats.

The initial characterization of the products was carried out by x-ray diffraction (XRD) with a Bruker-axs D8 Advanced diffractometer (40 kV, 30 mA), controlled by a DIFFRACT^{PLUS} software, in Bragg-Brentano reflection geometry with Cu K_α radiation ($\lambda = 1.5418\text{ \AA}$) and a PSD (Position Sensitive Detector). A filter of nickel allows the complete removal of Cu K_β radiation. For the structural refinement, NPD patterns were carried out with two different diffractometers, D1A and D2B at the Institut Laue-Langevin, Grenoble, with $\lambda = 1.910$ and $1.594\text{ \AA}$, respectively; the patterns were collected at 25 (D2B), 500, 600, and 900°C (D1A). About 2 g of the samples were contained in a vanadium can at room temperature; the counting time was 2 h per pattern in the high-intensity mode. The patterns at high temperature for the *oxidized* samples were contained in a quartz tube open to the air atmosphere; in contrast, the *reduced* phases were contained in a vanadium tube and placed in the isothermal zone of a furnace with a vanadium resistor operating under vacuum ($\text{P}_{\text{O}_2} \approx 10^{-6}\text{ Torr}$). The NPD data were analyzed by the Rietveld method²⁰ with the FULLPROF program.²¹ A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, and isotropic thermal factors for all the atoms. The coherent scattering lengths for La, Sr, Mn, Fe, Ti, and O were 8.24, 7.02, -3.73 , 9.45, -3.438 , and 5.803 fm , respectively.

Thermal analysis was carried out in a Mettler TA3000 system equipped with a TC10 processor unit. Thermogravimetric

(TG) curves were obtained in a TG50 unit, working at a heating rate of $10^\circ\text{C min}^{-1}$, in a reducing $\text{H}_2(5\%)/\text{N}_2(95\%)$ flow of 0.31 min^{-1} ; about 50 mg of sample was used in each experiment.

Measurements of the thermal expansion coefficient (TEC) and electrical conductivity required the use of sintered pellets of 6 mm of diameter, heated in air at 900°C for 12 h; the *reduced* specimens were finally treated in a 5% H_2 flow at 800°C for 4 h. The obtained density is around 90%–95%. Thermal expansion of the sintered samples was performed in a dilatometer Linseis L75HX1000, between 100 and 900°C either in oxidizing (air) or reducing (H_2 5%) atmosphere. The electrical conductivity was measured between 200 and 950°C in the required atmosphere, by the four-point method in bar-shaped pellets (10 mm large $\times$ 3 mm width $\times$ 3 mm) under *dc* currents between 10 and 200 mA. The currents were applied and collected with a Potentiostat-Galvanostat AUTOLAB PGSTAT 302 from ECO CHEMIE.

III. RESULTS AND DISCUSSION

A. Crystallographic characterization

Oxidized $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}$) perovskites were obtained as well-crystallized powders. An apparently single-cubic structure phase was identified from laboratory XRD for all the samples as shown in Fig. 1; no impurity phases were detected.

A NPD study at room and high temperature was useful to investigate the structural details of the different samples synthesized. The NPD data at room temperature reveal superstructure reflections not observed by XRD for the *oxidized* and *reduced* samples. For all of them, the crystal structure was defined in the *Pbnm* space group (No. 62), $Z = 4$, as it was previously reported by Alvarez-Serrano *et al.* by NPD for $\text{M} = \text{Mn}$.¹⁴ La, Sr, and O1 atoms are located at $4c$ ($x, y, 1/4$) positions, M and Ti are distributed at random at $4b$ ($1/2, 0, 0$), and oxygen atoms O2 are located at $8d$ (x, y, z). The occupancy factors of oxygen atoms were refined in the final run. In some cases, the occupancy factors converged to values slightly higher than the unity, thus they were fixed to 1.00. A negligible oxygen deficiency was observed in the *oxidized* phases, meanwhile the *reduced* phases display a significant concentration of oxygen vacancies, located at the axial oxygen O1, yielding the following stoichiometries: $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{2.70(2)}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_{2.75(1)}$. The stoichiometries of the *reduced* phases reveal a reduction of the oxidation state of M^{3+} to M^{2+} , and also a partial reduction of Ti^{4+} to Ti^{3+} , which only appears in the Mn oxide. Figs. 2–4 illustrate the good agreement between the observed and calculated NPD patterns for the *oxidized* and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn}, \text{Fe}$); Table I summarizes the unit-cell, atomic, displacement parameters, discrepancy factors, interatomic distances, and angles after the Rietveld refinement of the crystal structures at room temperature.

The unit-cell parameters of the *reduced* phase are expanded with respect to the *oxidized* sample, as expected from the larger size of the reduced cations. The (M,Ti-O1)

FIG. 1. XRD pattern with Cu K α radiation for the *oxidized* and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn}, \text{Fe}$) perovskites.

bond-lengths at room temperature for the *oxidized* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ compare reasonably well with the expected values calculated as ionic radii sums, displaying values of 1.968(2) and 1.974(6) Å, respectively; meanwhile, the calculated values are 2.025 Å for both samples ($^{\text{VI}}\text{Mn}^{3+}$: 0.645 Å; $^{\text{VI}}\text{Fe}^{3+}$: 0.645 Å; $^{\text{VI}}\text{Ti}^{4+}$: 0.605 Å).²² It is remarkable to compare the (M,Ti-O) distances of the *oxidized* and *reduced* samples, which increase upon reduction; this is a consequence of the increase of the ionic size from M^{3+} (i.r. Fe/Mn: 0.645 Å) to M^{2+} (i.r. Mn: 0.83 Å; i.r. Fe: 0.78 Å), in addition to the partial reduction of Ti^{4+} (0.605 Å) to Ti^{3+} (0.670 Å). The Ti only presents a mixed valence state for $\text{M} = \text{Mn}$. This aspect will be discussed in more detail in Sec. III B.

The thermal evolution of the crystal structure was evaluated by NPD for the *oxidized* and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ perovskites; the data were collected *in situ* in a furnace at 500, 600, and 900 °C. The *oxidized* samples were contained in a quartz tube open to the air atmosphere and the *reduced* phases were contained in a vanadium tube and placed in the isothermal zone of a furnace with a vanadium resistor operating under vacuum ($\text{P}_{\text{O}_2} \approx 10^{-6}$ Torr). The NPD data show two structural transitions in the studied temperature range (25–900 °C), the first one from the orthorhombic $Pbnm$ at room temperature to the tetragonal $I4/mcm$ (No. 140) space group at 500–600 °C and the second one from the tetragonal $I4/mcm$ to the cubic $Pm-3m$ (No. 221) space group at 900 °C. The step from $Pbnm$ ($a^-a^-c^+$)

FIG. 2. Comparison of the observed (crosses), calculated (solid line), and difference (at the bottom) NPD patterns for *oxidized* and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ at room temperature (25 °C), refined in the orthorhombic $Pbnm$ space group. The two series of tick marks correspond to the positions of the allowed Bragg reflections for the main phase and vanadium.

to $I4/mcm$ ($a^0a^0c^-$) involves the reduction of the freedom degrees of the octahedral tilting; in the last transition to $Pm-3m$ ($a^0a^0a^0$) the arysto-type is reached, in which the octahedra are perfectly aligned. This classic tendency has been observed in many perovskites, whose symmetry progressively increases with temperature, ending in the cubic arysto-type. This effect is due to a progressive increment of the tolerance factor of the ABO_3 perovskite, as A-O bonds expand faster than B-O bonds. Figs. 3 and 4 illustrate the good agreement between the observed and calculated NPD patterns for the *oxidized* and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ perovskite at different temperatures; Fig. 3 shows at low angles a large background that corresponds to the quartz tube (*oxidized* sample) and Fig. 4 shows a series of tick marks that correspond to the positions of the allowed Bragg reflections for vanadium (*reduced* sample). Table II summarizes the results obtained after the Rietveld refinement. The insets in Fig. 4 sketch the crystal structures observed upon heating from $Pbnm$ (orthorhombic) to $I4/mcm$ (tetragonal) and finally $Pm-3m$ (cubic).

As expected, the unit-cell of the *oxidized* and *reduced* $\text{M} = \text{Fe}$ oxides expands as the temperature increases

FIG. 3. Comparison of the observed (crosses), calculated (solid line), and difference (at the bottom) NPD patterns for *oxidized* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ at $T = 25, 500$, and 900°C . The series of tick marks correspond to the positions of the allowed Bragg reflections for the main phase.

(Tables I and II). Fig. 5 shows the volume expansion of the *oxidized* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ as a function of the temperature. The thermal evolution of the oxygen content was also studied by NPD for both phases. For the *oxidized* phase, the occupancy factors of the oxygen atoms do not seem to evolve with temperature; the oxygen content remains constant within the standard deviation, e.g., $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_{2.98(2)}$ at 900°C (Table II). Something similar happens to the *reduced* phases (Table II). Furthermore, there is an increase in the oxygen displacement factors, exhibiting values always higher than $3 \text{ \AA}^2$ from 500 to 900°C (Table II and Fig. 4).

B. TA

The thermal evolution of the samples was studied by recording thermogravimetric analysis (TGA) curves. Heating the stoichiometric $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($M = \text{Mn, Fe}$) in a $5\%\text{H}_2/95\%\text{N}_2$ flow leads to the reduction of the perovskites yielding the $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ deficient oxides (Fig. 6). The amount of released oxygen is always calculated from the weight loss between the weight sample at room

FIG. 4. Comparison of the observed (crosses), calculated (solid line), and difference (at the bottom) NPD patterns for the *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ at $T = 25, 600$, and 900°C . The two series of tick marks correspond to the positions of the allowed Bragg reflections for the main phase and vanadium. The insets show a view of the crystal structures at the different temperatures.

temperature and the weight sample at the minimum of the curve. Fig. 6 shows the thermal analysis curves obtained in $5\%\text{H}_2$, displaying the loss of $0.33(1)$ and $0.26(1)$ oxygen atoms in the $500\text{--}600^\circ\text{C}$ temperature range for $M = \text{Mn}$ and Fe , respectively. A thermal treatment of the *oxidized* phases in $5\%\text{H}_2$ flow at higher temperatures (900°C) shows the decomposition of the perovskites to the respective oxides. Therefore, the calculated stoichiometries for the intermediate perovskite phases are $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{2.67(1)}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_{2.74(1)}$. The calculated values are in good agreement with those obtained from the refinement of the oxygen occupancy factors from NPD data, which were shown Sec. III A. The thermal analysis confirmed the total reduction of M^{3+} to M^{2+} in both phases (responsible for 0.25 oxygen vacancies), and the partial reduction of Ti^{4+} to Ti^{3+} in the $M = \text{Mn}$ oxide, which exhibits an oxygen content below 2.75 per formula unit. From the obtained stoichiometry, $2.67(1)$, we can determine that 16% of Ti ions are reduced to the trivalent Ti^{3+} state. A thermal treatment of the resulting

TABLE I. Unit-cell, thermal parameters, selected distances (Å), and angles (°) for $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn, Fe}$) in the orthorhombic $Pbnm$ (No. 62) space group, from NPD at room temperature (25 °C). La, Sr, and O1 atoms at 4c (x,y,1/4) positions, M and Ti at 4b (1/2,0,0), and O2 at 8d (x,y,z).

	Mn (oxid)	Mn (red)	Fe (oxid)	Fe (red)
a (Å)	5.5184(5)	5.5434(3)	5.5569(2)	5.5604(2)
b (Å)	5.4975(4)	5.5201(2)	5.5310(2)	5.5334(2)
c (Å)	7.7915(7)	7.8274(5)	7.8160(3)	7.8198(3)
V (Å ³)	236.37(3)	239.52(5)	240.22(1)	240.73(4)
La/Sr 4c (x,y,1/4)				
x	0.0042(3)	0.0082(1)	-0.0041(6)	-0.00096(6)
y	-0.0002(2)	-0.0051(2)	0.0046(2)	-0.0050(2)
B_{iso}	0.891(3)	0.852(1)	0.690(4)	0.650(2)
f_{occ}	0.500/0.500	0.500/0.500	0.500/0.500	0.500/0.500
Ti/M 4b (1/2,0,0)				
B_{iso}	0.636(3)	0.692(1)	0.527(2)	1.165(3)
Ti/M f_{occ}	0.500/0.500	0.500/0.500	0.500/0.500	0.500/0.500
O1 4c (x,y,1/4)				
x	0.0496(2)	0.0517(9)	0.0504(6)	0.04994(1)
y	0.5096(5)	0.4991(3)	0.5001(3)	0.5000(4)
B_{iso}	1.053(0)	1.062(1)	0.664(7)	0.399(3)
f_{occ}	1.000	0.851(2)	1.000	0.875(1)
O2 8d (x,y,z)				
x	-0.2543(3)	-0.2583(2)	0.7481(4)	0.74472(2)
y	0.2534(4)	0.2590(1)	0.2537(2)	0.2537(3)
z	0.01927(6)	0.02018(4)	0.02581(3)	0.02746(3)
B_{iso}	0.787(7)	1.207(2)	1.26(6)	1.471(4)
f_{occ}	1.000	1.000	1.000	1.000
Reliability factors				
χ^2	1.59	2.31	1.53	1.99
R_p (%)	4.49	2.32	4.72	4.72
R_{wp} (%)	5.62	3.01	6.05	5.91
R_{exp} (%)	4.51	2.28	5.28	6.49
R_B (%)	8.99	4.95	4.89	9.37
Distances (Å)				
$\langle \text{La/Sr-O1} \rangle$	2.759	2.761	2.779	2.781
Ti/M-O1 (x2)	1.968(2)	1.977(4)	1.974(6)	1.974(7)
Ti/M-O2 (x2)	1.949(4)	1.966(8)	1.978(2)	1.969(4)
(x2)	1.957(3)	1.961(8)	1.963(2)	1.980(2)
$\langle \text{Ti/M-O2} \rangle$	1.953	1.964	1.971	1.975
Angles				
Ti/M-O1-Ti/M	163.72(3)	163.33(2)	163.69(2)	163.83(9)
Ti/M-O2-Ti/M	171.0(8)	169.9(3)	168.2(8)	167.34(6)

reduced phases in oxidizing atmosphere (O_2) restores the oxygen-stoichiometric phases, confirming the required reversibility upon cycling in oxidizing-reducing atmospheres.

C. Thermal expansion measurements

Aiming to determine the mechanical compatibility of our material with the other cell components, thermal expansion measurements were carried out in dense ceramics under different atmospheres. A dilatometric analysis was performed between 35 and 900 °C for several cycles; the data were only recorded during the heating runs. Fig. 7 shows no abrupt changes in the thermal expansion of both the *oxidized* and the *reduced* phases (except Mn) in all the temperature range under measurement. As we can see, the *reduced* Mn

phase presents two anomalies in the thermal expansion that corresponds to the two phase transitions, which are at 300 and 650 °C, confirmed by NPD data. The TEC measured under air atmosphere between 100 and 850 °C are $11.41 \times 10^{-6} \text{ K}^{-1}$ and $12.13 \times 10^{-6} \text{ K}^{-1}$ for Mn and Fe, respectively; the value for the *oxidized* Fe obtained from neutron diffraction data in the heating run is $9.40 \times 10^{-6} \text{ K}^{-1}$. On the other hand, the thermal expansion of the *reduced* phases shows values of $10.49 \times 10^{-6} \text{ K}^{-1}$ and $11.52 \times 10^{-6} \text{ K}^{-1}$ when heating the samples in $\text{H}_2(5\%)/\text{N}_2(95\%)$, very similar to those obtained for the *oxidized* perovskites. All the calculated values of the TEC are in the range of those usually displayed by SOFC electrolytes.

D. Electrical conductivity measurements

Fig. 8 shows the thermal variation of the electrical conductivity of the *oxidized* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn}$ and Fe) perovskites that present a semiconductor-like behavior in air atmosphere in all the temperature range. Both samples exhibit similar values at 200 °C, but the conductivity for $\text{M} = \text{Mn}$ increases significantly with temperature, whereas for $\text{M} = \text{Fe}$ it remains almost unchanged. The maximum values of conductivity obtained were 17 and 0.5 S cm^{-1} at 950 °C for $\text{M} = \text{Mn}$ and Fe , respectively; the values at the working temperature (650–850 °C) of a SOFC are also high and range between 10 and 15 S cm^{-1} for $\text{M} = \text{Mn}$. We speculate that, upon increasing temperature, Mn^{3+} is more easily reduced giving rise to a $\text{Mn}^{3+}/\text{Mn}^{2+}$ mixed valence, which allows the electronic hopping, whereas Fe^{3+} remains stable in all the temperature range; it seems to be more reluctant to be partially reduced, lacking the necessary mixed valence to favor the electronic motion.

The inset in Fig. 8 illustrates the electrical conductivity of the *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn}$ and Fe) perovskites, measured in a 5% H_2 /95% N_2 flow. These phases also display a semiconductor-like behavior, but with conductivity values much lower than those for the *oxidized* ones; for instance, the maximum value displayed is 0.10 S cm^{-1} at 900 °C for $\text{M} = \text{Mn}$. The $\text{M} = \text{Mn}$ *reduced* perovskite, which exhibits a $\text{Ti}^{3+}/\text{Ti}^{4+}$ mixed valence, presents higher conductivity than $\text{M} = \text{Fe}$ (with only Ti^{4+} valence) due to the electronic hopping between Ti^{3+} and Ti^{4+} adjacent cations (that takes place owing to the total cation disorder at the B position); in an ordered composition, the presence of M^{2+} ions should hinder the Ti^{3+} -O- Ti^{4+} conduction paths at large distance.

IV. SUMMARY AND CONCLUSIONS

In this work, we have prepared oxygen-stoichiometric $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M} = \text{Mn, Fe}$) perovskites, containing M^{3+} and Ti^{4+} , by soft chemistry procedures followed by thermal treatments in air. A topotactic reduction of the stoichiometric perovskites, in a reducing atmosphere, leads to oxygen-deficient phases with $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{2.70}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_{2.75}$ compositions, where M^{3+} is reduced entirely to M^{2+} , as shown by both neutron diffraction and thermogravimetric analysis. $\text{M} = \text{Mn}$ exhibits the creation of a greater number of oxygen vacancies with an oxygen

TABLE II. Unit-cell, thermal parameters, selected distances (Å), and angles (°) for the *oxidized* and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ in the tetragonal $I4/mcm$ (No. 140) and cubic $Pm-3m$ (No. 221) space group, from NPD at 500 to 900 °C.

NPD T (°C) Space group	$\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (oxidized)		$\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (reduced)	
	500 <i>I4/mcm</i>	900 <i>Pm-3m</i>	600 <i>I4/mcm</i>	900 <i>Pm-3m</i>
<i>a</i> (Å)	5.5697(6)	3.9589(1)	5.5697(5)	3.9587(1)
<i>b</i> (Å)	...	...	...	...
<i>c</i> (Å)	7.8749(2)	...	7.8749(2)	...
<i>V</i> (Å ³)	244.29(5)	62.048(3)	244.09(6)	62.039(4)
La/Sr	(0,1/2,1/4)	(1/2,1/2,1/2)	(0,1/2,1/4)	(1/2,1/2,1/2)
<i>B</i> _{iso}	1.63(2)	2.229(2)	1.45(2)	2.215(1)
<i>f</i> _{occ}	0.500/0.500	0.500/0.500	0.500/0.500	0.500/0.500
Ti/M	(0,0,0)	(0,0,0)	(0,0,0)	(0,0,0)
<i>B</i> _{iso}	1.95(2)	2.034(5)	1.87(2)	2.154(3)
Ti/M <i>f</i> _{occ}	0.500/0.500	0.500/0.500	0.500/0.500	0.500/0.500
O1	(0,0,1/4)	(1/2,0,0)	(0,0,1/4)	(1/2,0,0)
<i>B</i> _{iso}	3.22(3)	3.54(1)	3.35(3)	3.52(1)
<i>f</i> _{occ}	1.000	0.994(2)	1.000	1.000
O2	(x,x + 1/2,0)		(x,x + 1/2,0)	
<i>x</i>	0.2232(3)		0.2231(4)	
<i>B</i> _{iso}	1.73(1)		1.89(3)	
<i>f</i> _{occ}	1.000		1.000	
Reliability factors				
χ ²	1.69	3.20	2.29	2.94
<i>R</i> _p (%)	3.55	3.33	3.42	5.27
<i>R</i> _{wp} (%)	4.70	4.30	4.21	6.58
<i>R</i> _{exp} (%)	3.62	3.38	3.87	5.86
<i>R</i> _B (%)	4.01	4.09	4.56	4.53
Distances(Å)				
⟨La/Sr-O1⟩	2.7848(3)	2.7993(6)	2.7887(4)	2.7993(6)
Ti/M-O1(x2)	1.9687(4)	1.9794(6)	1.9718(5)	1.9794(6)
Ti/M-O2 (x2)	1.9785(2)		1.978(4)	
Angles				
Ti/M-O1-Ti/M	180.00(4)		180.00(6)	
Ti/M-O2-Ti/M	167.76(7)		169.71(16)	

content below 2.75, which implies the existence of $\text{Ti}^{4+}/\text{Ti}^{3+}$ mixed valence assuming that Mn cannot be reduced beyond the divalent state. For $\text{M}=\text{Fe}$, however, the reduction is limited exactly to the conversion from Fe^{3+} to Fe^{2+} .

FIG. 5. Thermal variation of (a) volume (left axis) and (b) isotropic displacement factor for O1 atoms (right axis), for the *oxidized* $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Ti}_{0.5}\text{O}_3$ from *in situ* NPD data.

The crystal structures of both, *oxidized* and *reduced* oxides, have been refined in the orthorhombic $Pbnm$ space group, assuming a random distribution of La and Sr at A positions and M and Ti at B sites of the perovskite. Two

FIG. 6. Thermal evolution of the stoichiometric-oxygen $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{M}=\text{Mn}, \text{Fe}$) perovskites in a 5% H_2 /95% N_2 flow.

FIG. 7. Thermal expansion determined by dilatometry for the *oxidized* and *reduced* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}$) perovskites.

FIG. 8. DC-conductivity as a function of temperature for the *oxidized* $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}$). The inset shows the dc-conductivity for the *reduced* samples.

structural transitions have been identified heating the $\text{M} = \text{Fe}$ phases up to 900°C ; the first transition, from the former symmetry to a tetragonal $I4/mcm$ structure below 500°C , and the second one to a cubic $Pm\bar{3}m$ phase between 600 and 900°C , accompanied with a gradual reduction of the octahedral tilting. The electrical characterization evidences a semiconductor behavior in all the samples displaying a maximum value of $15 \text{ S} \cdot \text{cm}^{-1}$ in the *oxidized* $\text{M} = \text{Mn}$. The thermal expansion coefficients span from 10.49 to $12.13 \times 10^{-6} \text{ K}^{-1}$ for the *oxidized* and *reduced* phases that perfectly match with the standard values of SOFCs electrolytes. The

reversibility of the reduction-oxidation of the oxides makes it possible the required cyclability of the cells; the phase transition is totally reversible and it is not expected to lead to cracking problems during the cell operation. All these features make the perovskites with $\text{La}_{0.5}\text{Sr}_{0.5}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}$ and Fe) composition to be considered as candidates for electrodes in SOFCs.

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