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Sol–gel synthesis, X-ray photoelectron spectroscopy and electrical conductivity of Co-doped (La, Sr)(Ga, Mg)$O_{3-\delta}$ perovskites

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Abstract

$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2-x}Co_xO_{3-\delta}$ (LSGMC) powders containing different amounts of Co ($x = 0.05$ and 0.085) were prepared by a citrate sol–gel method. The powders were used to prepare highly phase-pure LSGMC sintered pellets with controlled composition and fractional densities larger than 95%. For the first time, LSGMC materials were subjected to X-ray photoelectron spectroscopy (XPS) characterization. XPS data confirmed the presence of the dopants in the material and allowed to identify two different chemical states for Sr^{2+} and oxygen, both related to the oxygen-deficient perovskite structure of LSGMC. The conductivity of LSGMC sintered pellets containing different amounts of Co ions in the B sites of the perovskite lattice was assessed by electrochemical impedance spectroscopy (EIS) in the 250–750 °C temperature range. Conductivity values and apparent activation energies were in good agreement with previously published data referring to materials with same composition, but prepared by solid-state route. Therefore, the physicochemical and electrochemical characterization clearly demonstrated the ability of sol–gel methods to produce high-purity Co-doped LSGM perovskites, which represent promising solid electrolytes for intermediate-temperature SOFCs.

Keywords: Powders-chemical preparation; Sol–gel processes; Mixed ionic-electronic conductivity; Perovskites

1. Introduction

Solid oxide fuel cells (SOFCs) offer a highly efficient power generation system. One of the major requirements for the development and commercialization of low-cost SOFCs is the reduction of the operating temperature. One of the ways to reach this aim is the use of solid electrolytes exhibiting superior ionic conductivity at intermediate temperatures ($T < 800$ °C). Among these ionic conductors, doped $LaGaO_3$ materials show high oxide ion conductivity in the 600–800 °C range. The incorporation of divalent cation dopants to form $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM, where $\delta = (x + y)/2$), gives mobile oxygen vacancies. As a consequence, the resulting ionic conductivity of LSGM at 700 °C is about four times larger than that of conventional yttria-stabilized zirconia (YSZ) solid electrolyte.[1–3] Following the initial discovery,[1–5] numerous experimental studies have been carried out on LSGM materials, which also include the effect of transition-metal doping.[6–11] It is generally believed that doping with a transition-metal cation is undesirable for an ionic conductor due to the appearance of n- or p-type conduction. However, it was found that the oxide ion conductivity was also improved by doping Co for Ga site of $LaGaO_3$-based perovskites,[7] although hole conduction was detected at high oxygen partial pressures.[7,11] Yamada et al.[12] demonstrated that the application of Co-doped LSGM as electrolyte in SOFCs greatly improves the power density of the cell at intermediate temperatures.

LSGM materials are usually prepared by time- and energy-consuming solid-state reaction,[1,2] although new powder production techniques have been used. Aldinger and coworkers[13,14] have studied the preparation of LSGM powders by the Pechini method, which is a versatile sol–gel method that proceeds via the formation of a polymeric resin using citric acid and ethylene glycol.[15] However, sol–gel methods can give LSGM materials containing small amounts of undesired phases such as $SrLaGa_3O_7$, $SrLaGaO_4$[13] and MgO.[16] Majewski et al.[14] showed that sintering temperatures as high as 1500 °C were necessary to prepare pure $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ ceramics by using mixed oxide route or Pechini method. Schulz and Martin[17] reported the sol–gel synthesis of pure $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ electrolyte. However, to get a pure perovskite, they performed a very long (120 h) treatment at 1400 °C of the uniaxially pressed

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multiphase precursor, i.e. typical conditions of solid-state reaction. Given the promising properties of Co-doped LSGM (LSGMC) electrolytes for the development of intermediate-temperature (IT) SOFCs, we continued our previous work on sol–gel synthesis of dense LSGM ceramics[16] and present the physicochemical and electrical characterization of LSGMC electrolytes prepared by sol–gel method.

2. Experimental procedure

$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2-x}Co_xO_{3-\delta}$ (LSGMC) powders with two cobalt concentrations ($x = 0.05$ and 0.085) were synthesized using the following starting materials: La_2O_3 (99.9% pure, Aldrich), $SrCO_3$ (99% pure, Carlo Erba), MgO (99% pure, Carlo Erba), metallic Co (99.9% pure, Aldrich), and a fresh solution of standardized $Ga(NO_3)_3 \cdot xH_2O$ (99.9% pure, Aldrich). Before weighing, MgO and La_2O_3 were fired at 1000 °C overnight to decompose carbonate and hydroxide impurities. Stoichiometric amounts of solid powders were dissolved in $HNO_3{:}H_2O = 1{:}1$ and then the proper amount of Ga^{3+} solution was added at room temperature. Citric acid was added in the molar ratio 2:1 with respect to the total amount of cations. Heating this solution at 80–90 °C under stirring yielded a gel, where the cations were expected to be statistically distributed in chelate complexes. The formed gel was heated further until solid foam was formed. The foam was then ground and dried at 200 °C overnight. The dried resin was ground, slowly heated (0.5 °C/min) to 450 °C, held at this temperature for 2 h and then heated up to 1000 °C at 10 °C/min and held at this temperature for 24 h. This pre-calcination step was required (i) to decompose all remaining organic residuals and (ii) to form Ga-containing phases thus avoiding the formation of Ga_2O_3 that could decompose to Ga_2O and O_2 at high sintering temperatures.[18] In fact, following this calcination step (24 h at 1000 °C), both perovskite phase and small quantities of $SrLaGaO_4$ and $SrLaGa_3O_7$ were formed.[19] The powders were then ground in an agate mortar and then uniaxially pressed at 300 MPa using a 13 mm cylindrical die. The pellets were sintered in air at 1475 °C for 5, 10 or 20 h, with a heating rate of 10 °C/min. The density of the sintered pellets was determined by Archimede's technique.

Table 1 summarizes nominal compositions, sintering treatments and the density of the pellets. $LSGMC_x$ refers to $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2-x}Co_xO_{3-\delta}$ materials, where x represents the fraction of cobalt ions that substitute Mg^{2+} in the B sites of the perovskite. Two different Co concentrations were studied ($x = 0.05$ and 0.085). Phase purity of calcined powders and of sintered pellets was determined by X-ray diffraction (XRD, Philips X'Pert Pro, Cu Kα radiation) at room temperature.

In the case of $LSGMC_{0.085}$ materials, pellets sintered at 1475 °C for 5, 10 and 20 h were analyzed by X-ray photoelectron spectroscopy (XPS). XPS spectra were acquired using a Leybold Heraeus LHS10 spectrometer equipped with an EA11 electron energy analyzer. The excitation source was Al Kα radiation ($h\nu = 1486.6$ eV). The analyzer operated in the fixed-analyzer transmission (FAT) mode with constant pass energy of 50 eV. The binding energy (BE) values were referred to the Fermi level of the electron energy analyzer. The spectrometer was calibrated with respect to Au $4f_{7/2}$ (BE = 83.8 eV). Binding energies were calibrated with respect to the C 1s component at 285.0 eV, attributable to carbon-based contaminants at the sample surface.[20] The error in the determination of the binding energies was ±0.2 eV.

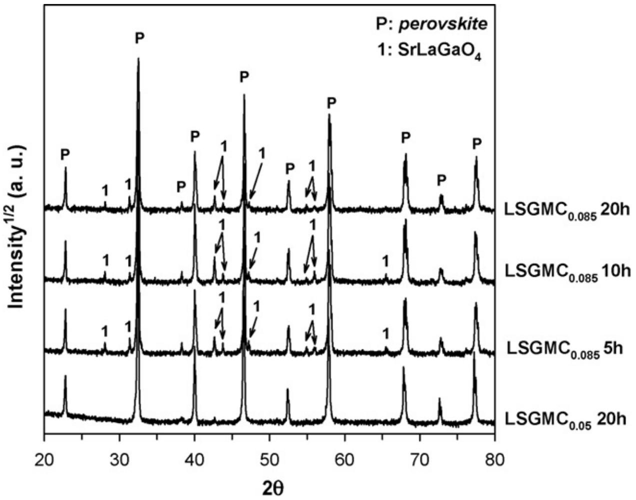

Fig. 1. XRD patterns of $LSGMC_{0.05}$ pellets after 20 h sintering at 1475 °C and of $LSGMC_{0.085}$ pellets obtained after 5, 10 and 20 h sintering at the same temperature.

Sintered pellets were observed by field emission gun scanning electron microscopy (FEG-SEM, Leo Supra 35) and their chemical composition was assessed by energy dispersive X-ray spectroscopy (EDS, Oxford Inca 300). Electrical conductivities were measured by electrochemical impedance spectroscopy (EIS) with an EGG 6310 spectrometer between 0.1 and 100 kHz. The amplitude of the signal was 20 mV and the electrode material was sputtered platinum.

3. Results and discussion

Fig. 1 shows the XRD patterns of the pellets after sintering at 1475 °C. No secondary phases could be detected in the sintered $LSGMC_{0.05}$. However, in $LSGMC_{0.085}$ pellets small amounts of electrically insulating 214 phase ($SrLaGaO_4$) were detectable, even after 20 h of sintering.

These results were in agreement with previously published XRD patterns of $La_{0.8}Sr_{0.2}Ga_{0.85-x}Mg_{0.15}Co_xO_{3-\delta}$ materials synthesized by conventional solid-state route, which showed small amounts of 214 phase in samples containing 10 or 20 mol% Co and no secondary phases in LSGMC pellets doped with 5 mol% Co.[21]

SEM micrographs of LSGMC pellets sintered for 20 h are shown in Fig. 2. Equally dense microstructures were observed also for $LSGMC_{0.085}$ pellets sintered for 5 or 10 h, thus confirming that all samples exhibited a high density and a negligible amount of residual porosity.

XPS spectra of La 3d, Sr 3d, Ga 2p, Mg 1s, Co 2p and O 1s regions were analyzed for $LSGMC_{0.085}$ sintered pellets. The spectra were very similar for all the samples and Fig. 3 shows the results for $LSGMC_{0.085}$ pellet subjected to 20 h sintering ($LSGMC_{0.085}$_20).

Table 1
Nominal composition, sintering cycle, and density of sintered pellets

Sample	Nominal composition	Sintering cycle	Density (g/cm^3)	Fractional density (%)
LSGMC$_{0.085}$_5	La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.115}$Co$_{0.085}$O$_{3-\delta}$	1475 °C (5 h)	6.40	95.8
LSGMC$_{0.085}$_10		1475 °C (10 h)	6.37	95.4
LSGMC$_{0.085}$_20		1475 °C (20 h)	6.43	96.3
LSGMC$_{0.05}$	La$_{0.80}$Sr$_{0.20}$Ga$_{0.80}$Mg$_{0.15}$Co$_{0.05}$O$_{3-\delta}$	1475 °C (20 h)	6.22	95.1

The core and satellite peaks of La 3d$_{5/2}$ and La 3d$_{3/2}$ were separated by 3.9 eV and the binding energy of the La 3d$_{5/2}$ core level was 833.5 eV, a value in good agreement with those reported previously for La$_{0.8}$Sr$_{0.2}$CoO$_3$.[22,23]

Sr 3d band showed multiple components. A careful fitting procedure allowed identifying four components, namely two 3d$_{5/2-3/2}$ doublets with 1.79 eV splitting between 3d$_{5/2}$ and 3d$_{3/2}$ peaks, a value in excellent agreement with literature data.[24,25] The 3d$_{5/2}$ peaks were at 133.9 and 132.0 eV, respectively. Therefore, these components could not be attributed to SrCO$_3$ (133.2 eV). The first and most intense 3d$_{5/2}$ component (at 133.9 eV) is attributable to Sr^{2+} in the perovskite lattice, being its BE comparable to those measured in similar perovskite structures.[23,27] The BE of 3d$_{5/2}$ weaker component (at 132.0 eV) was close to that of SrO$_{1-\delta}$ suboxide (132.2 eV, Ref. 28). Therefore, we infer that this component could be attributed to Sr^{2+} ions surrounded by vacancies in the oxygen-deficient perovskite structure.

The XPS spectra for gallium unambiguously confirmed the Ga^{3+} state, with a BE value of the Ga 2p$_{3/2}$ level at 1116.8 eV. The BE of the weak Mg 1s core level peak at 1304.2 eV is close to that previously reported for Mg^{2+} in LSGM by Shkerin et al.[27] The Co 2p$_{3/2}$ signal gave a distorted peak at 779.9 eV, in good agreement with the BE of Co^{3+} ions in LaCoO$_3$ and La$_{1-x}$Ca$_x$CoO$_3$ perovskites.[23,29] Pure CoO and Co$_3$O$_4$ exhibit a 2p$_{3/2}$ peak centred at 780.4 and 780.1 eV, respectively.[20,29] Therefore, different oxidation states of Co ions could not be discriminated since binding energies are similar.[26] The presence of Co^{2+} should be assessed by satellite peaks in the 785–788 eV range.[26,30] However, due to the low Co concentration (∼2 wt.%) in LSGMC$_{0.085}$ and the consequent low intensity of the Co 2p signal, the lack of satellite peaks in our spectra did not allow to exclude the presence of divalent cobalt in our sintered materials.

Fig. 4 shows the O 1s core level spectrum of the LSGMC$_{0.085}$_20 sintered pellet. The spectrum showed a doublet feature with the peak energies at 528.9 and 531.6 eV. The full widths at half maximum (FWHM) of the two components were 1.6 and 2.6 eV, respectively. The sharper component at lower binding energy is typical of O^{2-} ions.[24] The nature of the other component at larger binding energy has been studied extensively by Imamura et al.[31] These authors assigned the larger binding energy component (at 531.5 eV) to O$_2$ species that are molecularly adsorbed in the subsurface regions of oxygen-deficient perovskite-type compounds during the cooling period after calcination. This adsorbed oxygen is presumably incorporated in the material along grain boundaries, because oxygen deficiency is not large enough to accommodate a negatively charged dioxygen molecule.

The conductivity in air of LSGMC$_x$ materials with $x \leq 0.085$ is expected to be mostly ionic at high temperatures with a transport number of oxide ions larger than 0.8 at $T \geq 600$ °C.[7] Furthermore, Ishihara et al.[7] showed that the electrical conductivity of LSGMC$_{0.085}$ at higher temperatures was almost independent of the oxygen partial pressure. Therefore, it was decided to carry out the electrical characterization of Co-doped LSGM materials in air and at temperatures up to about 800 °C.

The results of the total electrical conductivity measurements are reported in Fig. 5 in the form of Arrhenius plots. LSGMC$_{0.085}$ exhibited larger electrical conductivities than LSGMC$_{0.05}$ due to the larger cobalt concentration. The total conductivity of LSGMC$_{0.05}$ and LSGMC$_{0.085}$ at 615–620 °C, i.e. at typical operating temperatures for IT-SOFCs, were 0.024 and 0.057 S cm^{-1}, respectively. These values were larger than those of yttria-stabilized zirconia (YSZ, 8.1×10^{-3} S cm^{-1} at 700 °C)[32] and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ (0.020–0.043 S cm^{-1} at 600–650 °C).[3,7]

At high temperatures the ionic conductivity, σ_{ion}, is predominant[7] and Khorkounov et al.[21] showed that the ionic conductivities at 700 °C and 900 °C of La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.15}$Co$_{0.05}$O$_{3-\delta}$ sintered pellets prepared by

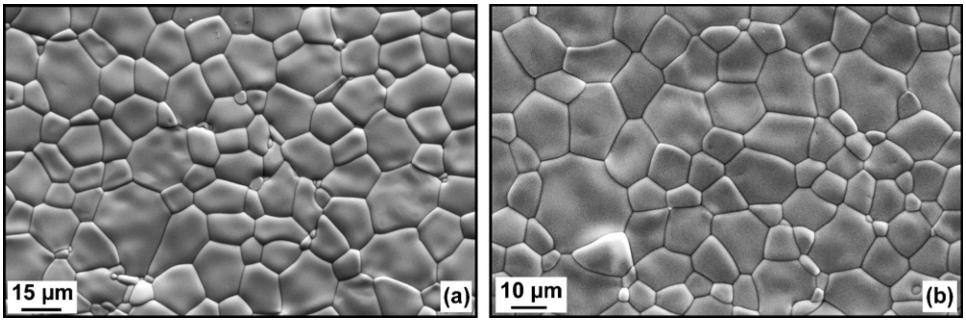

Fig. 2. SEM micrographs of pellets sintered for 20 h at 1475 °C: (a) LSGMC$_{0.05}$ and (b) LSGMC$_{0.085}$.

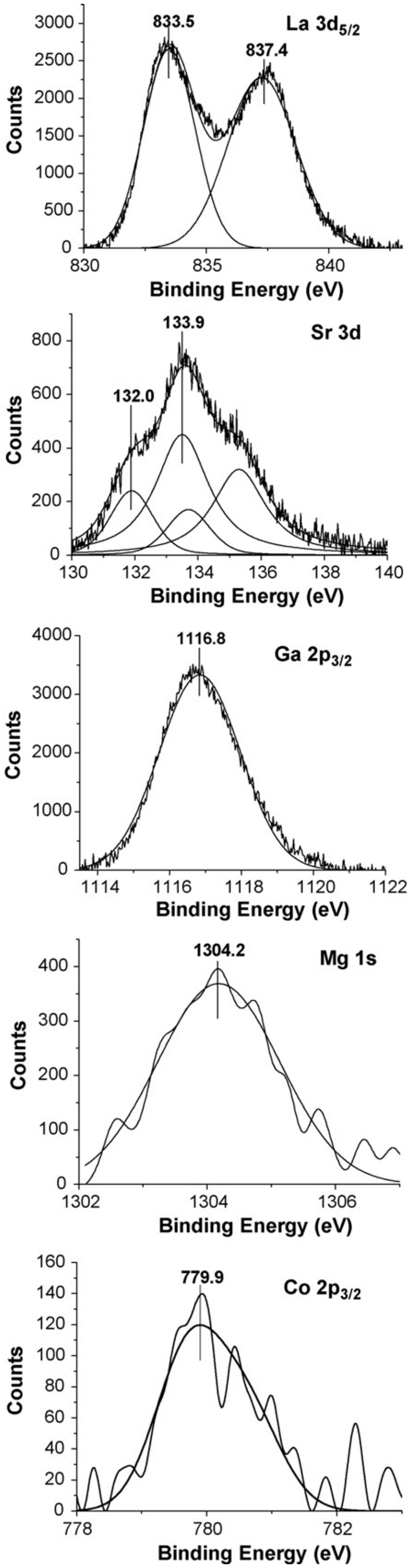

Fig. 3. XPS spectra of La $3d_{5/2}$, Sr $3d_{5/2}$, Ga $3p_{3/2}$, Mg 1s, Co $2p_{3/2}$ peaks of $LSGMC_{0.085}$ pellet sintered at 1475 °C for 20 h.

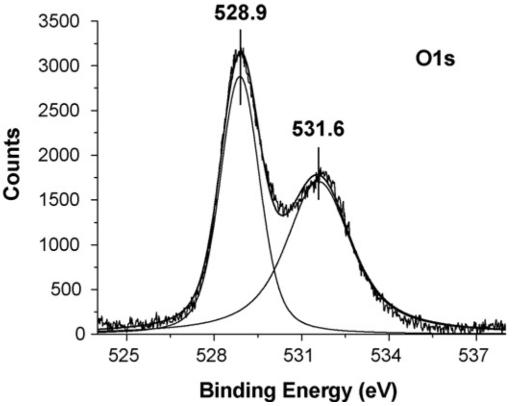

Fig. 4. O 1s core level of $LSGMC_{0.085}$ pellet sintered at 1475 °C for 20 h.

solid-state route were 8 and 20 times larger, respectively, than the hole conductivity at the same temperatures and 1 bar oxygen partial pressure (σ_p^o). In the case of Co-doped LSGM, the total conductivity, σ_{tot}, can be expressed as a function of σ_{ion} and σ_p^o[21]:

$$\sigma_{tot} = \sigma_{ion} + \sigma_p^o p_2^{1/4} \qquad (1)$$

Our conductivity measurements were performed in air, where $p_{O_2}^{1/4} = 0.67$. Therefore, the ionic to hole conductivity ratios are expected to be even higher than those given in Ref. 21.

The high temperature activation energies for our $LSGMC_{0.05}$ and $LSGMC_{0.085}$ pellets were 0.62 and 0.45 eV, respectively, and in good agreement with previously published data.[7,21,33]

Ishihara et al.[7] found that the apparent activation energy for high temperature electrical conductivity of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2-x}Co_xO_{3-\delta}$ decreased with Co content in the B sites of the perovskite and was lower than that of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ materials (0.80 eV). Khorkounov et al.[21] also found a similar trend, with activation energies for ionic conductivities ranging from 0.51 to 0.68 eV. Therefore, although we did not measure the p_{O_2} dependence of conductivity, the good agreement of high temperature activation energies in Fig. 5 with activation energies for ionic conduction published in the literature confirmed the predominant ionic conductivity at high temperatures.

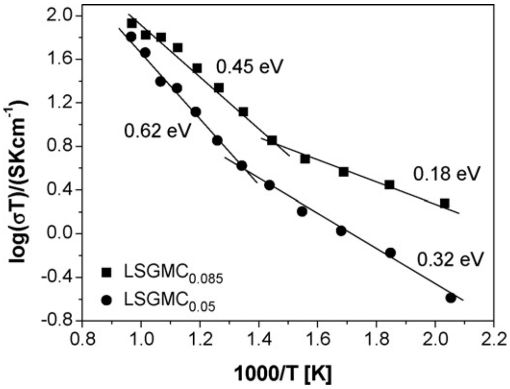

Fig. 5. Arrhenius plots of electrical conductivity of $LSGMC_{0.05}$ and $LSGMC_{0.085}$ pellets prepared by sol–gel method and sintered at 1475 °C (20 h).

The Arrhenius plots were linear also in the lower temperature region, but with significantly lower slopes (Fig. 5). This linearity, the conductivity values and the low apparent activation energies were consistent with electron hole conduction via a small polaron mechanism, which is common among oxides containing cations adopting different valences. According to Refs. 21,33 also the activation energies for electronic conduction decrease with increasing Co content. This fact might be attributed to the increased fraction of adjacent B-cation sites (in the ABO_3 structure) occupied by Co cations, so that conduction occurs increasingly by transfer of electrons between nearest neighbour sites instead of next-nearest neighbour sites.

4. Conclusions

The sol–gel citrate method allowed preparing dense and highly phase-pure Co-doped LSGM (LSGMC) sintered pellets with controlled composition. Sintering times as short as 5 h at 1475 °C were sufficient to obtain pellets with fractional density larger than 95% and with very small amounts of $SrLaGaO_4$. No other Co-containing phases were detectable by XRD and this fact suggested that Co ions were easily incorporated in the B sites of the perovskite lattice. XPS data confirmed the presence of all dopants in the material and two different chemical states for Sr^{2+} and oxygen, both related to the oxygen-deficient perovskite structure of LSGMC. The electrical conductivity values and the apparent activation energies were in good agreement with previously published data referring to materials with similar compositions, but prepared by solid-state reaction. In particular, oxide-ionic conductivity dominated at temperatures of interest for IT-SOFCs, while hole conduction via a polaron mechanism prevailed at lower temperatures.

The microstructure and electrical characterization clearly demonstrated the ability of sol–gel methods to produce Co-doped LSGM perovskite-type oxides, which represent promising solid electrolytes for intermediate-temperature SOFCs.

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