Sol–gel synthesis and characterization of Co-doped LSGM perovskites

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Abstract

One of the major requirements for the development and commercialization of low-cost SOFCs is the reduction in the operating temperature. One of the methods to reach this aim is the use of solid electrolytes which exhibit superior ionic conductivity at intermediate temperatures (IT, *T* < 800 °C). Among these ionic conductors, doped LaGaO₃ materials show high oxide ionic conductivity in the 600–800 °C range. These perovskites are usually prepared by time- and energy-consuming solid state reaction. In this paper, La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂O₂.₈ (LSGM) and La₀.₈Sr₀.₂₀Ga₀.₈Mg₀.₂₋ₓCoₓO₃₋ₓ (LSGMC) powders containing different amounts of Co (x = 0.05, 0.085 and 0.10) were prepared from precursors synthesised by citrate sol–gel method. The precursors were calcined at 1000 °C (10 h) and dense high-purity pellets were obtained by pressing (300 MPa) and sintering in air at 1475 °C (5, 10 and 20 h). Sintered pellets of LSGM and LSGMC contained very small amounts (<1%) of SrLaGa₃O₇ and SrLaGaO₄, respectively, as detected by X-ray diffraction (XRD) and by the combined use of scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The data clearly showed the feasibility of sol–gel methods to produce Co-doped LSGM perovskite type oxides.

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1. Introduction

Oxygen ion transport in ceramic oxide materials has attracted considerable interest due to the promising electrochemical applications such as solid oxide fuel cells (SOFCs). In this field, LaGaO₃-based perovskites are known to have superior oxygen ion conducting properties over a broad range of oxygen partial pressures.

The incorporation of divalent cation dopants to form La₁₋ₓSrₓGa₁₋ₜMgₜO₃₋ₓ (often termed LSGM, where *k* = (*z* + *y*)/2), gives rise to highly mobile oxygen vacancies. As a consequence, the resulting ionic conductivities of LSGM at 700 °C is about four times larger than that of conventional yttria-stabilized zirconia (YSZ) electrolyte, and it is apparent that a significant decrease in the SOFC operating temperature would be an important practical advance. Following the initial discovery, numerous experimental studies have been carried out on LSGM materials, which also include the effect of transition-metal doping. It is generally believed that doping with a transition metal cation is undesirable for the 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 in LaGaO₃-based perovskites, although hole conduction was detected at high oxygen partial pressures. Nevertheless, Yamada et al. demonstrated that the Co-doped LSGM (LSGMC) can be used as an electrolyte for SOFCs operating at 770 °C. The 1-kW stack they tested had a fuel electrode that consisted of a mixture of NiO and Ce₀.₈Sm₀.₂O₂₋ₓ (SDC) and a Sm₀.₅Sr₀.₅CoO₃₋ₓ (SSC) cathode.

LSGM materials are usually prepared by conventional solid state reactive firing, although new powder production techniques, such as ultrasonic spray pyrolysis, combustion synthesis and sol–gel method have been used. Tas and co-workers have studied the preparation of LSGM powders by Pechini method, which is a versatile sol–gel method that proceeds via the formation of a polymeric resin using citric acid and ethylene glycol.
ovskite is rather difficult.\(^{13}\) Even sol–gel methods, which ensure the formation of polymeric precursor resins where cations are expected to be uniformly dispersed at an atomic scale, can give rise to LSGM materials containing, at the end of the preparation process, small amounts of undesired phases such as La\(_2\)Sr\(_2\)Ga\(_5\)O\(_{12}\) and MgO.\(^{19}\) Majewski et al.\(^{17}\) 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 mixed oxide route or Pechini method. Schulz and Martin.\(^{23}\) reported the sol–gel synthesis of pure La\(_{0.8}\)Sr\(_{0.2}\)Ga\(_{0.8}\)Mg\(_{0.2}\)O\(_{2.8}\). However, to get a pure perovskite phase, they performed a very long (120 h) firing treatment at 1400 °C of the uniaxially pressed multiphase precursor, thus resembling typical conditions of time-consuming solid state reactive sintering.

Given the promising properties of Co-doped LSGM (LSGM\(_{C}\)) electrolytes for the development of intermediate temperature (IT) SOFCs, in the present paper we continue our previous work on sol–gel synthesis of dense LSGM ceramics\(^{19}\) and for the first time, in accordance to the knowledge of the authors, we describe the synthesis of LSGMC electrolytes by sol–gel method.

### Table 1

Nominal composition, sintering cycle, shrinkage and density of LSGM and Co-doped LSGM sintered pellets

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal composition</th>
<th>Sintering cycle</th>
<th>Shrinkage (ΔR/R(_0)) (%)</th>
<th>Density (g/cm(^3))</th>
<th>Theoretical density (g/cm(^3))</th>
<th>Fractional density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSGM</td>
<td>La(<em>{0.8})Sr(</em>{0.2})Ga(<em>{0.8})Mg(</em>{0.2})O(_{2.8})</td>
<td>1475 °C (20 h)</td>
<td>14.6</td>
<td>5.75</td>
<td>6.43(^{26})</td>
<td>89.1</td>
</tr>
<tr>
<td>LSGMC(_{0.05})</td>
<td>La(<em>{0.8})Sr(</em>{0.2})Ga(<em>{0.8})Mg(</em>{0.1})Co(<em>{0.1})O(</em>{3})</td>
<td>1475 °C (20 h)</td>
<td>17.7</td>
<td>6.51</td>
<td>6.65(^{27})</td>
<td>97.9</td>
</tr>
<tr>
<td>LSGMC(_{8.5})</td>
<td>La(<em>{0.8})Sr(</em>{0.2})Ga(<em>{0.8})Mg(</em>{0.115})Co(<em>{0.085})O(</em>{3})</td>
<td>1475 °C (20 h)</td>
<td>17.3</td>
<td>6.40</td>
<td>6.66(^{27})</td>
<td>95.8</td>
</tr>
<tr>
<td>LSGMC(_{8.5})</td>
<td>La(<em>{0.8})Sr(</em>{0.2})Ga(<em>{0.8})Mg(</em>{0.115})Co(<em>{0.085})O(</em>{3})</td>
<td>1475 °C (5 h)</td>
<td>17.3</td>
<td>6.37</td>
<td>95.4</td>
<td></td>
</tr>
<tr>
<td>LSGMC(_{8.5})</td>
<td>La(<em>{0.8})Sr(</em>{0.2})Ga(<em>{0.8})Mg(</em>{0.115})Co(<em>{0.085})O(</em>{3})</td>
<td>1475 °C (10 h)</td>
<td>17.7</td>
<td>6.43</td>
<td>96.3</td>
<td></td>
</tr>
<tr>
<td>LSGMC(_{8.5})</td>
<td>La(<em>{0.8})Sr(</em>{0.2})Ga(<em>{0.8})Mg(</em>{0.115})Co(<em>{0.085})O(</em>{3})</td>
<td>1475 °C (20 h)</td>
<td>16.9</td>
<td>6.22</td>
<td>6.54(^{27})</td>
<td>95.1</td>
</tr>
</tbody>
</table>

2. Experimental

The powders were synthesized using the following starting materials: La\(_2\)O\(_3\) (99.9% pure, Aldrich), SrCO\(_3\) (99% pure, Carlo Erba), MgO (99% pure, Carlo Erba), Co (99.9% pure, Aldrich) and a fresh solution of Ga(NO\(_3\))\(_3\)·\(_n\)H\(_2\)O (99.9% pure, Aldrich). The approximate value of \(n\) in the formula of gallium nitrate was estimated by using thermogravimetric analysis (TG/DTA, Netzsch STA 409). Then a solution containing about 0.1 g/L of gallium nitrate was prepared and standardized by ICP. Before weighing, MgO and La\(_2\)O\(_3\) were fired at 1000 °C overnight to decompose carbonate and hydroxide impurities. Stoichiometric amounts of solid powders were dissolved in HNO\(_3\)·H\(_2\)O = 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, in which the cations were expected to be statistically distributed in chelate complexes. The formed gel was further heated until solid foam was formed. The foam was then ground and dried at 200 °C overnight. The obtained 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 so that all remaining organic residuals were decomposed. The powders were ground in an agata mortar and then uniaxially pressed at 300 MPa into a 13 mm diameter cylindrical die. Pellets with 1–2 mm thickness were sintered in air at 1475 °C for 5–20 h, with a heating rate of 10 °C/min. The shrinkage of the pellets, ΔR/R\(_0\), was determined by measuring the final diameter of each sintered pellet, being 13 mm the initial green diameter (R\(_0\)). The density of the pellets was determined by Archimedes’s technique.

![Fig. 1. TG/DTA curves of the LSGM (panel a) and LSGMC\(_{8.5}\) (panel b) foams obtained by sol–gel citrate synthesis and previously dried at 200 °C overnight. The TG/DTA curves of the other powder precursors with different Co contents were similar to the one shown in panel b.](https://example.com/fig1.png)
Table 1 summarizes nominal composition, sintering treatment and density of the pellets. LSGM refers to La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ material. LSGMC$_{z}$ refers to doped La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$Co$_x$O$_{3-\delta}$ materials, where $z = 100x$ represents the mole percent of cobalt ions in B sites of the perovskite, substituting Mg$^{2+}$. Three different Co levels were studied, with $x = 0.05$, 0.085 and 0.10. The LSGM material was prepared and characterized for sake of comparison.

The decomposition of the dried resins was monitored by simultaneous thermogravimetric and differential thermal analysis (TG/DTA, Netzsch STA 409) to select the proper thermal treatments to obtain the oxide powders. The analyses were carried out in air from room temperature to 1500 $^\circ$C with a heating rate of 5 $^\circ$C/min. Phase purity of calcined powders and of sintered pellets was determined by X-ray diffraction (XRD, Philips X’Pert Pro) at room temperature. Scans were taken with a 2$\theta$ step of 0.02$^\circ$ and using graphite-filtered Cu Kα radiation (40 kV, 40 mA).

The morphology of the powders as well as the microstructure of the sintered pellets was observed by field emission scanning electron microscopy (FE-SEM, Leo Supra 35). The grain size of sintered pellets was estimated by using the mean intercept method.$^{11}$ The chemical composition of the pellets was assessed by quantitative energy dispersive X-ray spectroscopy (EDS, Oxford Inca 300).

3. Results and discussion

Fig. 1 shows the TG/DTA curve of the LSGM (panel a) and of the LSGMC$_{8.5}$ (panel b) powder precursors. The TG/DTA curves of the other LSGMC precursors were quite similar to the one shown in Fig. 1b. TG curves showed a significant weight loss (>35 wt.%) due to the oxidative decomposition of organic residuals in the 200–450 $^\circ$C range, accompanied by large exothermic peaks in DTA curves. At approximately 500 $^\circ$C, another mass loss started, accompanied by exothermic effects, which could be attributed to the combustion of carbonaceous residuals. The rather sharp endothermic peak observed in the case of the LSGM precursor at about 1250 $^\circ$C, without any associated weight loss, was attributed to solid state reactions. It is worth noting that this endothermic peak was never observed in the TG/DTA curves of LSGMC precursors.

Fig. 2 shows the SEM micrographs of LSGM and LSGMC powders obtained after the firing treatment at 1000 $^\circ$C. The particle size of the powders was in the 50–300 nm range.

Fig. 3 shows the XRD patterns of LSGM and LSGMC powders. After calcination at 1000 $^\circ$C (24 h) the powders were found to contain the LaGaO$_3$-based perovskite phase (JCPDS card no. 83-566) and secondary phases such as LaSrGa$_3$O$_7$ (237, JCPDS card no. 86-1839) and LaSrGaO$_4$ (214, JCPDS card no. 83-1004). The relative amounts of these phases were estimated by measuring the ratio, $A_p/A_h$, of the total integrated intensities of the most intense XRD peaks of

![Fig. 2. SEM micrographs of different powders obtained by 24 h firing at 1000 $^\circ$C: (a) LSGM, (b) LSGMC$_{5}$, (c) LSGMC$_{8.5}$, (d) LSGMC$_{10}$. The composition of the samples is reported in Table 1.](image-url)
LaSrGa$_3$O$_7$ and LaSrGaO$_4$ over the integrated intensity of the (1 2 1) peak of the perovskite. Table 2 reports the $A_s/A_p$ ratios for all the powders. The LSGMC$_{8.5}$ and LGMC$_5$ powders exhibited a higher phase purity, being the $A_s/A_p$ ratio slightly larger than 20%, while the $A_s/A_p$ ratio for both LSGM and LSGMC$_{10}$ powders was around 40%.

In Table 1, the density of pellets obtained after powder pressing (300 MPa) and sintering at 1475 °C are reported. The data clearly showed that fractional densities larger than 95% were obtained for Co-doped LSGM pellets, while the fractional density of the LSGM pellet submitted to the same sintering cycle was lower, and around 90%. The larger sinterability of Co-doped samples cannot be ascribed to particle size effects. In fact, as shown in Fig. 2, all powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>$A_s/A_p$ (%)</th>
<th>Pellet</th>
<th>$A_s/A_p$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSGM</td>
<td>41.3</td>
<td>LSGM</td>
<td>0.82</td>
</tr>
<tr>
<td>LSGMC$_{10}$</td>
<td>37.4</td>
<td>LSGMC$_{10}$</td>
<td>0.94</td>
</tr>
<tr>
<td>LSGMC$_{8.5}$</td>
<td>20.6</td>
<td>LSGMC$_{8.5}$</td>
<td>0.93</td>
</tr>
<tr>
<td>LSGMC$_{10}$</td>
<td>20</td>
<td>LSGMC$_{10}$</td>
<td>0.40</td>
</tr>
<tr>
<td>LSGMC$_{20}$</td>
<td>24.3</td>
<td>Undetectable</td>
<td></td>
</tr>
</tbody>
</table>

The $A_s/A_p$ values represent the ratio of the total integrated intensities of the most intense XRD peaks of secondary phases over the integrated intensity of the (1 2 1) peak of the perovskite phase.
had particles whose sizes were few hundreds of nanometer. Therefore, we infer that Co-doping enhanced oxygen ion mobility and reduced the dopant-vacancy binding energy,22 thus favouring the overall ion mobility at high temperatures. Mobility and reduced the dopant-vacancy binding energy, 22 had particles whose sizes were few hundreds of nanometer. The experimental values were determined by quantitative EDS analyses.

Fig. 4 shows the XRD patterns of the pellets after 20 h sintering at 1475 °C. The data clearly showed that the relative amounts of secondary phases considerably decreased after sintering. In fact, in all samples the A/La ratio was lower than 1%. In particular, no secondary phases could be detected by XRD in the case of LSGMC5 sintered pellet, thus indicating that high purity Co-doped LSGM electrolytes can be prepared by sol–gel citrate method. The decrease of Sr-containing secondary phases confirmed our previous findings.19 This might be attributed to decomposition of 214 and 237 phases and subsequent solid state reactions occurring at the sintering temperature, which were promoted by the intimate contact of the particles in pressed compact. The effect of sintering time on both fractional density (Table 1) and phase purity (Table 2) was studied for the LSGMC5,1 samples. The results pointed out that dense LSGMC5,1, ceramics with very high phase purity was obtained after 5 h sintering.

Fig. 5 shows the SEM micrographs of LSGM and Co-doped LSGM pellets after 20 h sintering. The average grain size of pellets LSGM3 and LSGM5 was in the 11–19 μm range. To check the chemical composition and homogeneity of Co-doped sintered pellets, we performed spot EDS microanalyses of several grains for each LSGM sample. The results of the quantitative EDS analyses are reported in Table 3 and showed a very good agreement between the experimental stoichiometric indexes and the nominal ones.

4. Conclusions

The sol–gel citrate method is clearly suitable for preparing dense and high purity Co-doped LSGM (LSGM) sintered pellets with controlled composition. Sintering cycles performed at 1475 °C and as short as 5 h were sufficient to obtain pellets with fractional density larger than 95% and with less than 1% secondary phases (LaSrGa3O7 and LaSrGaO4). No Co-containing phases were detected neither in the powder nor in the sintered pellets and this fact suggested that Co2+ ions were easily incorporated in the B sites of the perovskite lattice. The data clearly showed the feasibility of sol–gel methods to produce Co-doped LSGM perovskite type oxides, which represent promising solid electrolytes for IT-SOFCs.

References

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Table 3

Nominal and experimental stoichiometric indexes of Co-doped sintered pellets (Table 1)

<table>
<thead>
<tr>
<th>Element</th>
<th>La</th>
<th>Sr</th>
<th>Ga</th>
<th>Mg</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSGMC5</td>
<td>0.80</td>
<td>0.20</td>
<td>0.80</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>LSGMC20</td>
<td>0.84 ± 0.02</td>
<td>0.16 ± 0.02</td>
<td>0.83 ± 0.02</td>
<td>0.13 ± 0.02</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>LSGMC2</td>
<td>0.80</td>
<td>0.20</td>
<td>0.80</td>
<td>0.115</td>
<td>0.085</td>
</tr>
<tr>
<td>LSGMC8.5</td>
<td>0.87 ± 0.04</td>
<td>0.13 ± 0.03</td>
<td>0.86 ± 0.02</td>
<td>0.065 ± 0.02</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>LSGMC10</td>
<td>0.80</td>
<td>0.20</td>
<td>0.80</td>
<td>0.115</td>
<td>0.085</td>
</tr>
<tr>
<td>LSGMC5</td>
<td>0.83 ± 0.02</td>
<td>0.17 ± 0.02</td>
<td>0.82 ± 0.04</td>
<td>0.09 ± 0.02</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>LSGMC2</td>
<td>0.83 ± 0.02</td>
<td>0.17 ± 0.02</td>
<td>0.82 ± 0.04</td>
<td>0.09 ± 0.02</td>
<td>0.08 ± 0.01</td>
</tr>
</tbody>
</table>

The experimental values were determined by quantitative EDS analyses.

The nominal and experimental stoichiometric indexes and the fractional density (Table 1) and phase purity (Table 2) were studied for the LSGMC5 samples. The results pointed out that dense LSGMC5,1,11 ceramics with very high phase purity was obtained after 5 h sintering.


