



Effect of sintering time on structural, microstructural and chemical composition of Ni-doped lanthanum gallate perovskites



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ABSTRACT

This work reports the effect of two different sintering times, 6 and 48 h on the structural, microstructural, and chemical features of Ni-doped $\text{La}_{0.90}\text{Sr}_{0.10}\text{GaO}_{3.00-\delta}$. Independently of the sintering time, $\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{1-x}\text{Ni}_x\text{O}_{3.00-\delta}$ (where $x=0.10$, and 0.20 (mol)) presents a rhombohedral symmetry with a lattice volume that decreases when NiO dopant increases. Besides the perovskite, $\text{LaSrGa}_{3.00}\text{O}_{7.00}$ (nominal composition) is present as second phase in all cases. When the samples are doped with NiO, the peaks of this second phase are shifted with respect to the peaks of the pure phase. These shifts suggest that this second phase could admit some Ni ions in its structure. According to the XRD patterns, the amount of the latter phase is larger when sintering time is increased. Electron probe microanalysis (EPMA) indicated that the matrix of the samples sintered for 6 h is constituted by a perovskite with an experimental composition very close to the nominal one. However, when the samples are sintered for 48 h the matrix of each sample is constituted by two perovskites; both with compositional deviations with respect to their nominal one. In particular, a significant Sr depletion compensated by a La increment in the A site is observed. Those compositional deviations could be mainly due to the diffusion of the cations in the bulk and/or from the bulk to the surface of the samples. That diffusion can favour the formation, not only, of a second perovskite with a different composition in relation with the first one formed, but also, the formation of second phases. In addition, a very slight broadening of Bragg peaks of the perovskites sintered for 48 h is observed by XRD and can be related to the presence of two different perovskites in each sample according to EPMA results.

By BSEM and EPMA analyses $\text{La}_{4.00}\text{Ga}_{2.00}\text{O}_{9.00}$ (nominal composition) is also observed as second phase when samples are treated for 48 h.

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1. Introduction

Sr- and Mg-doped LaGaO_3 (LSGM) has been found to be an excellent oxide-ion conductor over a broad range of oxygen partial pressures ($1\text{--}10^{-22}$ atm) at low temperatures [1,2]. At 700°C , for instance, its ionic conductivity is around 4 times higher than that of the conventional yttria stabilized zirconia (YSZ). LSGM is an ideal candidate not only as an electrolyte but also as an electrode for intermediate temperature solid oxide fuel cells (IT-SOFCs) given the flexibility to substitute ions on either the A or B sites to enhance its ionic or electronic conductivity. In addition, for catalytic purposes, a mixed ionic and electronic conducting (MIEC) electrode is preferred over a pure electronic conductor, due to the expansion of the triple phase boundary for oxygen reduction to the whole surface of the mixed conductor.

Solid solutions of the gallate can be expected to exhibit a high degree of mixed conductivity. In this respect, Ni-doped lanthanum gallate perovskites could be a good alternative. The electrical effect of Ni as a B site dopant in $\text{La}_{0.90}\text{Sr}_{0.10}\text{GaO}_{3.00-\delta}$ on the electrical properties has also been studied by different authors [3–6]. Furthermore, the chemistry of the perovskites and the presence and chemistry of any second phases in the LSGM perovskites has not been studied in depth. Both the phase purity and the microstructure of materials depend on synthetic procedure and processing and, in addition the synthesis of a single phase perovskite is rather difficult in this quaternary system.

Although knowledge of the phase diagrams that represent the thermodynamic equilibrium of heterogeneous multicomponent systems is essential to understanding the fundamental materials aspects that underlie the preparation of single-phase or controlled multiphase ceramics, the phase relationships of the La_2O_3 , SrO, Ga_2O_3 , and NiO have not been studied yet to the best of our knowledge. In relation with the $\text{La}_2\text{O}_3\text{--Ga}_2\text{O}_3$ binary system, we have found one study that reports two binary compounds, LaGaO_3 and $\text{La}_4\text{Ga}_2\text{O}_9$ [7].

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In addition, NiGa₂O₄ occurs in the NiO–Ga₂O₃ system [8]. In the La₂O₃–NiO system, LaNiO₃ with a nickel ion valence 3⁺ exists below 800 °C, but a higher temperature decomposes into La_{n+1}NiO_{3n-1}, NiO and O₂. In addition, at 1200 °C in air the only stable phase is La₂NiO₄ [9].

Subsolidus equilibria in air in the La₂O₃–Ga₂O–NiO system were studied by Hrovat et al. [10] at 1300 °C and no ternary compound was found. Their preliminary results indicated that the solid solubility of nickel ions in lanthanum gallate can be described by the formula LaGa_{1-x}Ni_xO_{3-x/2} up to $x=0.05$, while no solid solubility of LaGaO₃ in NiO could be detected. Audinot et al. [11] found perovskites solid solutions with rhombohedral symmetry at 1350 °C in air for LaGa_{0.50}Ni_{0.50}O_{3- δ} and LaGa_{0.80}Ni_{0.20}O_{3- δ} .

According to Majewski et al. [12] the La₂O₃–SrO–Ga₂O₃ system exhibits complex phase relationships, including ternary oxides. For instance, at 1400 °C in air, four ternary phases, seven binary phases, and one liquid phase were found, together with SrO, La₂O₃, and Ga₂O₃. LaGaO₃ was in thermodynamic equilibrium with Ga₂O₃, La₄Ga₂O₉, and LaSrGa₃O₇. The authors found that the solid solubility of strontium, at that temperature, in LaGaO₃ was ~4 mol%, and that in La₄Ga₂O₉ was ~3 mol%. However, that solid solubility limit is still controversial in the literature. Matraszek et al. [13] found lower values than those determined by Majewski et al. [12] at the same temperature. Matraszek et al. [13] studied the relationships of La₂O₃–Ga₂O₃–MgO–SrO system in air. Solubility limits of Mg or Sr in the perovskite LaGaO₃ phase were determined at 1400 °C as 14 mol% for Mg and <2 mol% for Sr. In addition, the solubility of Sr in the La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2} perovskite phase increases up to about 20 mol% if Mg and Sr are added together. This system also exhibits complex relationships including ternary and quaternary oxides such as MgGaLa₃O₇, MgGa₁₁LaO₁₉, La₄Ga₂O₉, LaSrGa₃O₇, LaSr(Ga,Mg)O₄, and MgO.

Unfortunately, as was mentioned above the La₂O₃–SrO–Ga₂O₃–NiO quaternary phase diagram has not been outlined yet. However, all of this information about binary, ternary and the related quaternary systems gives us an idea of the complexity of the quaternary system La₂O₃–SrO–Ga₂O₃–NiO.

In this study, we report the effect of the sintering time on the structural, microstructural and chemical features for La_{0.90}Sr_{0.10}Ga_{1-x}Ni_xO_{3.00- δ} perovskites where $x=0.00, 0.10, \text{ and } 0.20$. These studies are significant previous to the evaluation of those materials as possible cathodes for IT-SOFCs.

2. Experimental

2.1. Materials preparation

The solid state reaction was used for the synthesis of La_{0.90}Sr_{0.10}Ga_{1-x}Ni_xO_{3.00- δ} with $x=0.00, 0.10, \text{ and } 0.20$ (mol). Stoichiometric amounts of La₂O₃ (analytical-reagent grade, Aldrich, Steinheim, Germany; pre-calcined at 1000 °C/6 h), SrCO₃ (analytical-reagent grade, Aldrich, Steinheim, Germany), Ga₂O₃ (analytical-reagent grade, Apollo Scientific Ltd., Cheshire, UK) and NiO (analytical-reagent grade, B.D.H. Lab. Supplies; UK) were mixed in acetone in an agate mortar and then calcined at 1000 °C for 6 h, sieved to 65 μm , ball-milled for 1 h, dried and sieved again to 65 μm . The resulting powders were uniaxially pressed at 1 t and isostatically pressed (300 MPa) into disks and sintered in air for 6 and 48 h, at 1500 °C for $x=0.00$, and at 1450 °C for samples containing Ni.

2.2. Characterisation

2.2.1. Structural characterisation

Phase identification was performed by XRD at room temperature on the powders and the sintered pellets using a Phillips

PW1710 diffractometer (Amsterdam, The Netherlands), equipped with a graphite monochromator, using CuK α radiation, a step width of 0.02° $2\theta_{\text{min}}^1$ and a counting time of 10 s. Silicon cleaved along (1 1 1) was used as an external standard.

The lattice parameters of the perovskites were determined using a least-squares fitting method.

2.2.2. Microstructural and chemical characterisation

The microstructure of the sintered samples was analysed on polished (down to 1 μm) and thermally etched surfaces (1440–1490 °C for 6 min, heating and cooling rates of 10 °C/min) by means of field-emission-gun scanning electron microscopy (FEG-SEM) analyses (Hitachi S-4700 type I, Tokyo, Japan).

The chemistry of the perovskites (major phase) and the second phases were analysed on sintered and polished samples by field-emission-gun-scanning electron microscopy with X-ray energy-dispersive spectrometry (FEG-SEM-XEDS) and backscattered scanning electron microscopy (BSEM). The latter assisted by electron probe microanalysis (EPMA) using a beam size of 1 μm and conventional standards with a JEOL Superprobe JXA-8900 M (Tokyo, Japan) electron probe microanalyser with 5 wavelengths dispersive X-ray spectrometers (WDS), attached to the Zeiss DSM400 microscope. Quantitative analysis was conducted using the ZAF (atomic number, absorption, fluorescence) correction software following the Microspec WDX-3PC programme. The composition of each phase was averaged over 20 spot analyses and its accuracy was of 1 wt%. The quantitative analysis of the phase compositions can be carried out accurately in a small area 1–2 μm in lateral size.

3. Results and discussion

3.1. Structural characterisation

The XRD pattern of La_{0.90}Sr_{0.10}GaO_{2.95} samples sintered for 6 h and polished (Fig. 1a) indicated that the main phase present has the GdFeO₃-type orthorhombic perovskite structure, iso-structural with LaGaO_{3.00- δ} (JCPDS 24-1102) and the XRD patterns have been indexed in accordance with that scheme (Miller indexes are included in Fig. 1a according to JCPDS 24-1102). The second phase found corresponds to LaSrGa_{3.00}O_{7.00} (JCPDS 45-0637). When sintering time is 48 h a similar XRD pattern is observed (not shown here), although the intensity of the peaks for the second phase is higher which means that a larger amount of that phase is present. The XRD patterns of polished La_{0.90}Sr_{0.10}Ga_{0.90}Ni_{0.10}O_{2.90} sample after sintering for 6 and for 48 h are shown in Fig. 1b and c, respectively. These figures indicated that the main phase present in all cases is a perovskite with a rhombohedral symmetry (Miller indexes are included in Fig. 1b and c according to JCPDS 33-0711). When $x=0.10$, the second phase detected also corresponds to LaSrGa_{3.00}O_{7.00} (for 6 and 48 h) and the peaks of this second phase are shifted with respect to the peaks of the pure phase. These shifts suggest that this second phase could admit some Ni ions in its structure. In addition, an increment of the intensity of the peaks of the second phase is also observed when sintering time is 48 h, indicating that a larger amount of that phase is present. For $x=0.20$ a shift of the peaks for the perovskite with respect to those of $x=0.10$ is also observed. It suggests that it could admit more Ni ions than that for $x=0.10$ into its structure. LaSrGa_{3.00}O_{7.00} is also detected for $x=0.20$ and the shift of the peaks with respect to the pure phase is also produced.

Thus, when Ni is introduced into the orthorhombic lattice perovskite a change in symmetry is produced. Doping with nickel resulted also in decreasing perovskite cell volumes (Table 1(a) and (b)). According to the lattice volume values found in this study, for

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