Conductivity of La$_{0.95}$Sr$_{0.05}$Ga$_{0.90}$Mg$_{0.10}$O$_{3-\delta}$ obtained by mechanical activation

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Abstract

Dense ceramics of La$_{0.95}$Sr$_{0.05}$Ga$_{0.90}$Mg$_{0.10}$O$_{3-\delta}$ (LSGM) were obtained from La$_2$O$_3$, SrO, Ga$_2$O$_3$ and MgO precursors activated by dry grinding in a high-energy planetary ball-mill. Samples sintered at 1450$^\circ$C for 4 h have an average grain size of ca. 250 nm. This value increases to 5.926 m when the sample is annealed for 40 h at the same temperature. Samples prepared by a conventional ceramic route were also obtained with a grain size of 13.5 and 20.5 m, after sintering at 1550$^\circ$C for 4 and 40 h, respectively. Impedance spectroscopy data revealed similar grain conductivities for both materials. However, a significant degradation was observed on ageing the LSGM prepared by the conventional ceramic route, probably due to compositional alterations at the grain boundaries. This degradation was not present in the material prepared from mechanically activated precursors. Grain size effects on the electrical conductivity were analysed to determine the effective grain boundary conductivity and the brick-layer model is assumed to estimate the grain boundary thickness.

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1. Introduction

Feng and Goodenough$^1$ and Inihara et al.$^2$ reported that LaGaO$_3$, when doped with strontium and magnesium (La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$) exhibit a conductivity several times higher than Y$_2$O$_3$-doped ZrO$_2$, or comparable to that of Gd$_2$O$_3$-doped CeO$_2$, and an ionic transport number close to unity within large ranges of oxygen partial pressure and temperature. Since then, a large amount of work has been dedicated to study these promising solid electrolytes.

Usually, LaGaO$_3$-based electrolytes are obtained via the conventional ceramic route, which implies a high temperature treatment in the range 1400–1600°C. As a result, these samples have a large particle size and, most importantly, they are chemically inhomogeneous. Small amounts of undesired phases, such as LaSrGa$_3$O$_7$ and LaSrGaO$_4$, which contribute negatively to the electrical performance, are detected even in materials prepared by chemical solution methods, which can provide products of fine and homogeneous particles.$^3,4$

The synthesis via mechanochemical assisted reactions has proven to be versatile to obtain different kinds of materials, namely oxides.$^7,9$ The high-energy milling makes the activated powder more reactive as a consequence of the fracture of the grains and defects generated during grinding, which leads to a higher internal energy and reduces the thermal barrier for any subsequent reaction.

The aim of this work is to obtain La$_{0.95}$Sr$_{0.05}$Ga$_{0.90}$Mg$_{0.10}$O$_{3-\delta}$ (LSGM) ceramics by mechanical activation of oxide precursors and compare this material with the LSGM prepared by the conventional solid state route. Differences are discussed based on microstructural and impedance spectroscopy results.

2. Experimental

Powders of La$_{0.95}$Sr$_{0.05}$Ga$_{0.90}$Mg$_{0.10}$O$_{3-\delta}$ were prepared from high purity lanthanum (Merck), gallium (Aldrich),...
magnesium (Panreac) and strontium oxides. The SrO was obtained from SrCO$_3$ (Merk) calcined at 1100 °C for 30 min. Six grams of the oxides were dry ground in a planetary ball-mill (Retsch Centrifugal Ball-Mill Type S-12) using a nylon container and zirconia balls (Ø = 10 mm). The ball to powder weight ratio was 10:1. The mechanical activation was performed at ∼380 rpm in air during several hours with interruptions, at regular intervals, for cooling and collecting samples for X-ray diffraction analysis (X’Pert MPD Philips, Cu Ka radiation) to monitor structural modifications. A sample from the powder mixture activated for 60 h was also analysed by thermogravimetric (TGA) and differential thermal analyses (DTA), and in situ high temperature X-ray powder diffraction (HTXRD) (Fig. 1).

The information gathered by TGA/DTA and HTXRD was used to design an appropriate sintering curve in order to prepare ceramics in a single thermal treatment at a maximum temperature of 1450 °C for 4 h, with intermediate dwells at 320 °C (2 h), 500 °C (2 h), 700 °C (2 h), 750 °C (25 min) and 900 °C (1 h) for degas.

Ceramics with the same composition were prepared by the conventional ceramic route starting from the same raw materials. The mixture was dried, calcined at 1100 °C for 12 h and again ball-milled and dried. The resultant powder was pressed into pellets and sintered at 1550 °C for 4 h with constant heating and cooling rates of 5 K/min. This was the minimum temperature needed to ensure densification (>93%).

The ceramics prepared by the two methods were characterised by impedance spectroscopy (HP 4284A) at frequencies in the range 20–10$^5$ Hz with $V_{rms}$ = 100 mV. The measurements were carried out in air at temperatures from 200 to 500 °C. The evolution of the spectra was studied in samples annealed at the maximum sintering temperature for 4, 16, 32 and 40 h. Fresh platinum electrodes were applied before every measurement.

Images of the microstructure of the ceramics, thermally etched at a temperature 10% lower than the sintering temperature, were obtained by scanning electron microscopy (SEM) and subsequently analysed using a linear intercept method\textsuperscript{[10,11]} to obtain estimates of the average equivalent grain size.

![Image](image.png) **Fig. 1.** X-ray diffraction pattern of the activated powders collected in situ at 1200 °C (symbols (+) and (*) identify the secondary LaSrGaO$_7$ phase and the platinum from the support, respectively).
frequency \( f_{gb} \) is independent of geometry and reads:

\[
f_{gb} = \frac{1}{2\pi C_{gb} R_{gb}} = \frac{\sigma_{gb,\text{eff}}}{2\pi \varepsilon_0 \varepsilon_r}
\]

where \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F} \) is the permittivity of vacuum and \( \varepsilon_r \) is the dielectric constant of the bulk. Under these conditions, the impedance spectra collected at 300 °C of conventional (A) and mechanically activated (B) ceramics annealed for different periods of time (frequency decreases from 1 MHz in the first point in the left down to 20 Hz). Temperature dependence of the apparent grain boundary conductivity for ceramics obtained from (A) non-activated and (B) activated ceramics annealed at the maximum sintering temperature for different periods of time.
Fig. 5. Temperature dependence of the true grain boundary conductivity for ceramics obtained from mechanically activated precursors sintered for 4 h (○) and 40 h (■) (CGO data taken from reference). 13

conditions,

$$\sigma_{gb,eff} = \frac{2\pi f_{gb} \varepsilon_0 \varepsilon_r}{\delta_{fg}}$$

(2)

The $\sigma_{gb,eff}$ estimates shown in Fig. 5 were obtained through Eq. (2) using $f_{gb}$ values extracted from the impedance spectra and $\varepsilon_r = 25$ obtained by others. 12 It can be seen that $\sigma_{gb,eff}$ is slightly lower than estimates obtained for submicrometric Ga-substituted ceria, 13 and, moreover, that it is independent of the grain size. This means that the differences in $\sigma_{gb,app}$ are probably due to a grain size effect. Therefore, by assuming the simplest and well known brick-layer model for the electrical conduction of a polycrystalline ceramic, the grain boundary thickness $\delta_{fg} = 2\pi r_{gb} \sigma_{gb,eff}/\sigma_{gb,app}$ may be estimated to be $\approx 5$ nm, a reasonable value. Nevertheless, the validity of the brick-layer model should be confirmed on data collected from samples with various $G_{av}$ values.

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References