Grain boundary Fe-doping effects in LSGM

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Received 13 July 2007; received in revised form 21 January 2008; accepted 26 January 2008

Abstract

The electrical properties of La$_{0.95}$Sr$_{0.05}$Ga$_{0.90}$Mg$_{0.10}$O$_{3-\delta}$ (LSGM) were modified by selective doping of the grain boundaries, using LaFeO$_3$ screen-printed layers and annealing at high temperature to promote Fe diffusion into LSGM. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analyses showed that iron was mainly located along the grain boundaries with the bulk grain composition almost unchanged. Impedance spectra showed a significant increase in the total conductivity for the Fe-doped samples, the effect being greater for the grain boundary contribution. The formation of a parallel pathway for electronic conduction along the grain boundaries explains these effects. Ageing of these samples at high temperature, after removal of the Fe source, showed a steady shift to the original LSGM behaviour, due to dilution of Fe throughout the samples.

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Keywords: Lanthanum gallate; Grain boundary; Mixed conductor; Impedance spectroscopy

1. Introduction

Mixed ionic and electronic conductors can be used in several electrochemical applications, namely as oxygen separation membranes [1]. Perovskites with the B-site partly occupied by transition metals are common examples of such materials [2–4]. The optimisation of the properties of these materials is usually achieved by doping. As an example, La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ (LSGM), one excellent oxygen ion conductor, can be easily transformed into a mixed conductor by substitution of Ga by a transition metal like Fe [5].

Mixed conducting composites may also be obtained by combining one ionic conducting phase with one electronic conductor [6,7]. Heterogeneous materials may also occur as a core-shell type microstructure, in which one component (core) is surrounded by the other (shell) [8,9]. In recent years we have developed mixed conductors by selective grain boundary doping of LSGM [10], exploiting the known preferential diffusion of Fe along grain boundaries [11]. This work presents new results on LSGM-based ceramics changed by Fe-impregnation of grain boundaries.

2. Experimental procedure

Dense samples of La$_{0.95}$Sr$_{0.05}$Ga$_{0.90}$Mg$_{0.10}$O$_{3-\delta}$ (LSGM) were prepared via the conventional ceramic route starting from high purity oxides and carbonates. The precursors were wet-milled, dried and calcined at 1100 °C, again wet-milled and dried. Disk-shaped pellets, about 1 mm thick, were sintered at 1550 °C for 4 h. The room temperature powder X-ray diffraction pattern could be indexed in the Imma orthorhombic space group. The samples had a density greater than 93% of the theoretical value. Samples for SEM and EDS analyses were prepared following the usual procedures.

After polishing, the pellet surfaces were screen-printed with LaFeO$_3$ and annealed in air at 1550 °C to promote the diffusion of Fe through LSGM. The duration of each annealing cycle was 1 h. Another set of samples was obtained after impregnation with Fe by annealing at high temperature, without the Fe source. These results will be described as ageing.
The electrical properties of all ceramic samples were studied by impedance spectroscopy in air between 250 and 500 °C. Fresh platinum electrodes were applied before each measurement and gently removed before subsequent thermal treatments. After Fe-impregnation, removal of the screen-printed layers before electroding was also mandatory. These procedures, strongly based on manual skill, might explain slight deviations from general tendencies.

3. Results and discussion

The SEM microstructure shown in Fig. 1 was obtained after three impregnation cycles of 1 h each, at 1550 °C. The grain size remains nearly unchanged throughout the impregnation cycles and is fairly large (in the range 5–10 μm). Results on the Fe/Ga atomic percentage ratio obtained from EDS spectra, collected along the small arrows shown in Fig. 1, are shown in Fig. 2. In case A, the Fe/Ga ratio shows maximum values close to the grain boundary region. In case B, always along the grain boundary area, the Fe/Ga ratio is high and almost constant. In case C, the peak in the Fe/Ga ratio coincides with crossing the grain boundary. All these results show that iron is present mostly at the grain periphery and that the thickness of the iron containing region hardly exceeds 1 to 2 μm. The dark colour evidenced throughout the pellets cross-section, indicated that the impregnation was effective in the entire pellet thickness. However, the Fe concentration at a distance of about 100 μm from the surface was below EDS detection limits. All these comments...
indicate that the overall Fe-content was well below typical values with known impact on LSGM bulk electronic transport properties [5].

The impedance spectra in air, at 250 °C, for one sample, before and after Fe-impregnation, are shown in Fig. 3. The fresh sample spectrum shows the usual high and low frequency arcs, which may be ascribed to the bulk and grain boundary, respectively. The spectra were thus fitted to an equivalent circuit comprising a series association of two resistors in parallel with constant phase elements and the subscripts \( g \) and \( gb \) refer to bulk grain and grain boundary, respectively. The indexes that account for the depression of the semicircles are \( n_g \) and \( n_{gb} \). The true capacitances associated with each semicircle are \( C = R (1 - \alpha) \alpha Q^1/2 \).

The amplitude of both semicircles (\( R_g \) and \( R_{gb} \) values) decreases with increasing number of impregnation cycles. Moreover, the effect is greater for the grain boundary contribution. The microstructural characterization and impedance spectroscopy results suggest a fairly simple model consisting of one ionic conductor grain bulk surrounded by mixed conducting grain boundaries. Starting from the already depicted equivalent circuit, this additional contribution can be described by adding one parallel electronic branch to the pure ionic conductor, as shown in the inset in Fig. 3. \( R_e \) is the electronic resistance corresponding to this electronic branch.

This circuit was used to fit the impedance spectra of LSGM ceramics, including variable \( R_e \) but constant bulk and grain boundary parameters, the latter corresponding to those of the fresh sample (Fig. 4A). The solid lines in this figure reveal the best but modest fit at 250 °C. This means that this simple model is not enough to account for the observed changes.

The parameter \( n \) (for the grain) drops about 10% after consecutive impregnation cycles, typical of increasingly depressed arcs. This seems to be due to formation of inner and outer regions within the grain with different Fe-contents. The co-existence of different defects and defect associates explains the broader range of polarisation phenomena observed in the grain bulk. Based on this, a second attempt to fit experimental data involved also a variable \( R_e \). The improvement in the quality of data fit is obvious (Fig. 4B).

4. Conclusions

Heterogeneous ceramics based on La\(_{0.95}\)Sr\(_{0.05}\)Ga\(_{0.90}\)Mg\(_{0.10}\)O\(_{3–δ}\) were obtained using LaFeO\(_3\) as source for Fe. The diffusion of this species into LSGM occurs preferentially along the grain boundaries. The combined study of these samples by EDS analysis and impedance spectroscopy revealed that iron doping leads to a significant increase in electronic conduction along the grain boundary region. Ageing of these samples at high temperature, without source for Fe, showed that this effect could be cancelled by dilution of Fe throughout the entire sample. The effectiveness of grain boundary doping as a strategy to obtain mixed conductors was demonstrated.

Acknowledgements

Work supported by project POCl/CTM/59727/2004 (FCT, Portugal), and the NoE FAME (CEC, Brussels). E. Gomes would like to thank PRODEP for funding (4/5.3/PRODEP/2000).

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