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Grain boundary Fe-doping effects in LSGM

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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.

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, $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (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.

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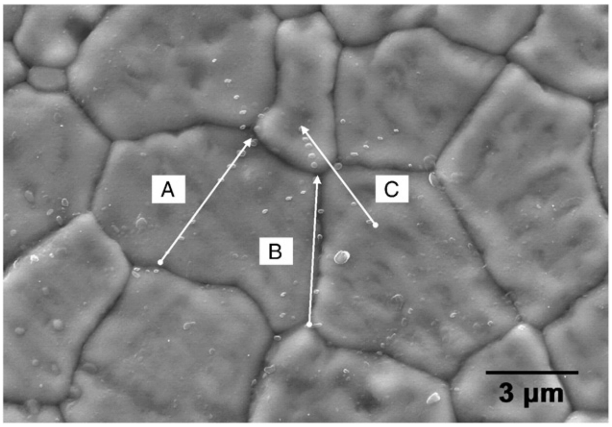

Fig. 1. SEM micrograph of one Fe-doped LSGM sample obtained after three impregnation cycles of 1 h each at 1550 °C. The white spots are due to the prolonged action of the EDS. Arrows A, B and C indicate the directions along which the Fe/Ga concentration ratios were studied (see Fig. 2).

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 (A, B and C), 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

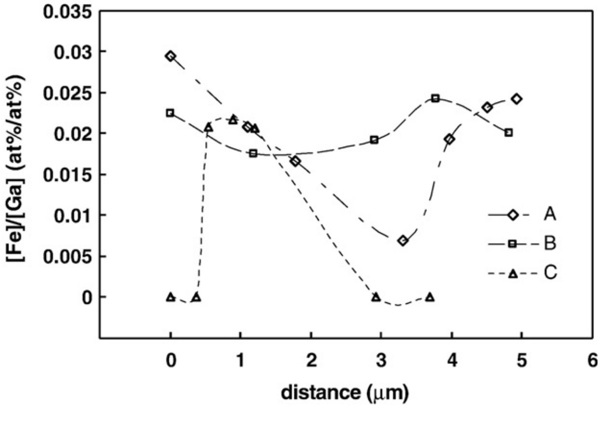

Fig. 2. Fe/Ga concentration ratio along the A, B and C directions (arrows) shown in Fig. 1: A — across the grain; B — along the grain boundary region; C — across one grain boundary. Lines shown for visual guidance only.

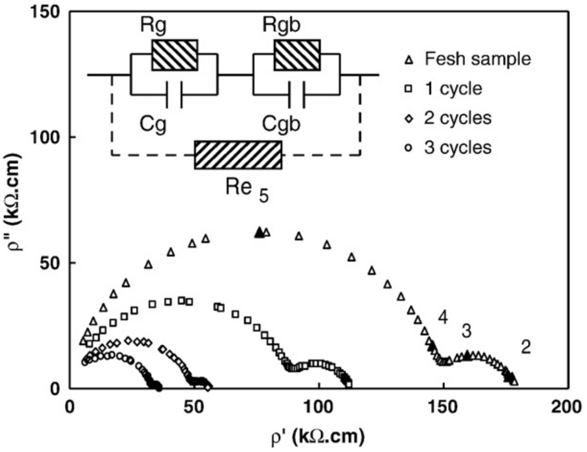

Fig. 3. Impedance spectra in air, at 250 °C of one LSGM sample, fresh and after several impregnation cycles of 1 h at 1550 °C. Numbers close to filled data points indicate the logarithm of the measuring frequency. The equivalent circuit used to simulate the cell performance, where R_e stands for the electronic resistance of the Fe-doped region pathway, is shown as inset.

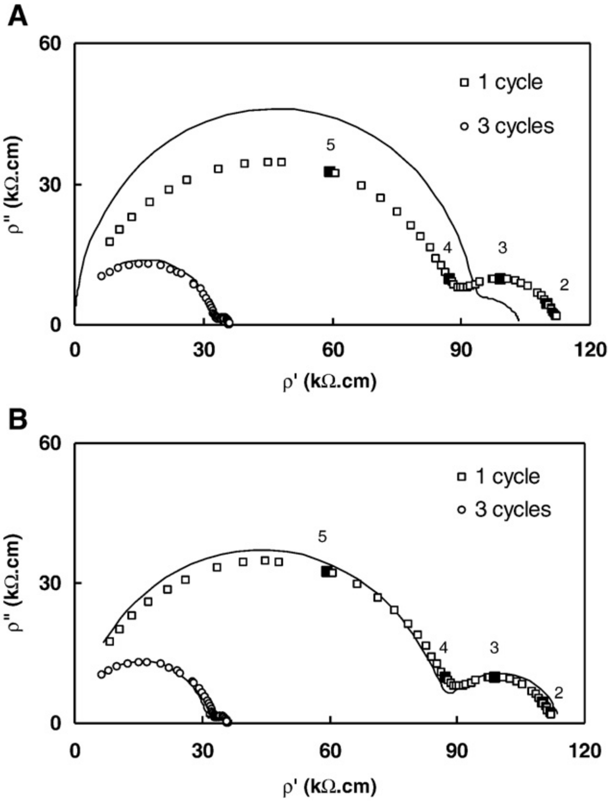

Fig. 4. Impedance spectra of one LSGM sample after one and three impregnation cycles, and the corresponding fit (solid lines) to the equivalent circuit described in Fig. 3: A — only R_e is adjusted; B — both R_e and R_g are adjusted.

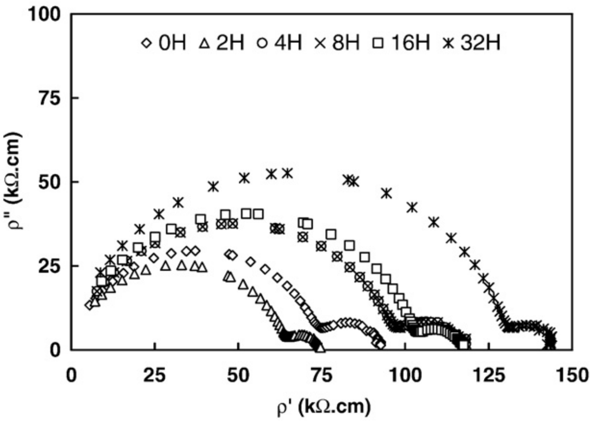

Fig. 5. Impedance spectra in air, at 250 °C, of one LSGM sample impregnated with Fe, after ageing at 1550 °C for several periods of time (without any source for Fe). The ageing grain time is shown in the figure caption.

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, since the semicircles were slightly depressed. According to Bernard Boukamp's notation [12], this circuit may be represented as (R_gQ_g) ($R_{gb}Q_{gb}$), where R_i are resistors, Q_i 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 $C=R^{(1-n)/n}\text{Q}^{1/n}$.

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_g. The improvement in the quality of data fit is obvious (Fig. 4B). Considering the small magnitude of the grain boundary arc, also likely to be influenced by the Fe-impregnation process, no further attempts were made to optimise the fit with a variable R_{gb}. Lastly, if the central region of the pellet behaved as pure LSGM, the total cell electrical response would be dominated by this region ("electron blocking"), preserving the relative magnitudes of the grain and grain boundary arcs. All these arguments are in favour of the adopted model.

The impregnated samples were also annealed in air for several hours (without source for Fe) and the electrical response studied as previously (Fig. 5). Except for the set of results obtained after 2 h of annealing (presumably corresponding to unidentified experimental error), both the bulk and the grain boundary resistance increase with ageing time. This is the opposite of the trend observed when the fresh sample was impregnated with successive cycles. In the absence of a source for Fe, the Fe present in the grain boundary region vanished due to Fe diffusion to inner grain layers. The localized region with high electronic conductivity was destroyed. This trend would be hardly explained if the starting material had Fe homogeneously dispersed throughout the bulk grain and grain boundaries.

4. Conclusions

Heterogeneous ceramics based on $La_{0.95}Sr_{0.05}Ga_{0.90}Mg_{0.10}O_{3-\delta}$ 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

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