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Influence of phase segregation on the bulk and grain boundary conductivity of LSGM electrolytes

D. Marrero-López [a,*], J.C. Ruiz-Morales [b], J. Peña-Martínez [c], M.C. Martín-Sedeño [d], J.R. Ramos-Barrado [a]

[a] Dpto. de Física Aplicada I, Laboratorio de Materiales y Superficies (Unidad Asociada al C.S.I.C.) Universidad de Málaga, 29071-Málaga, Spain
[b] Dpto. de Química Inorgánica, Universidad de La Laguna, 38200-La Laguna, Tenerife, Spain
[c] Dpto. de Química Inorgánica, Universidad Complutense de Madrid, 28040-Madrid, Spain
[d] Dpto. de Química Inorgánica, Universidad de Málaga, 29071-Málaga, Spain

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ABSTRACT

Electrolytes based on $La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) are difficult to synthesise as single phase materials and secondary phases of $LaSrGa_3O_7$ and $LaSrGaO_4$ are usually found at temperatures as high as 1400 °C. Dense LSGM ceramics with different amounts of these impurities were prepared from freeze-dried powders. These ceramics were studied by impedance spectroscopy to evaluate the influence of phase segregation on the bulk and grain boundary contributions to the ionic conductivity. The bulk and specific grain boundary conductivities of dense LSGM samples resulted to be nearly independent on the fraction of impurities. Furthermore, the ionic and electronic conductivities are not seriously affected by the presence of minor secondary phases.

1. Introduction

Electrolytes based on $LaGaO_3$ are promising alternatives to yttria-stabilised zirconia (YSZ) for intermediate temperature solid oxide fuel cells (IT-SOFCs) mainly due to their higher ionic conductivity [1–6]. These electrolytes exhibit negligible electronic conductivity and high stability over a wide range of oxygen partial pressures and temperatures compared with ceria-based electrolytes [7].

The highest oxide ion conductivity in this system was found for Sr- and Mg-codoped $LaGaO_3$ (e.g. $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$, denoted as LSGM). However, there are several drawbacks for the application of LSGM that should be overcome, such as: the segregation of secondary phases during the synthesis process (e.g. $LaSrGa_3O_7$ and $LaSrGaO_4$); the high sintering temperatures necessary to obtain dense ceramics; and volatilization of gallium oxide in the course of prolonged heat treatment at high temperatures [8–11].

The solid-state reaction method, commonly used in the synthesis of LSGM, requires sintering temperatures as high as 1500 °C with intermediate regrinding and thermal treatments. This leads to powders with large grain size and consequently poor sinterability to obtain dense electrolytes. In order to avoid these problems, several precursor routes have been used, such as Pechini method [12], regenerative solution route [13], citrate [14] and microwave [15], giving rise to pure $LaGaO_3$-based ceramics at 1400 °C. On the other hand, the sintering time necessary to obtain both a single phase and high densification was still longer than 5–8 h. Such sintering conditions render ceramic materials with large grain size and thus lower mechanical stability.

Alternative ceramic processing has also been used to improve the relative density of the LSGM materials, such as hot isostatic pressure and spark-plasma [16,17], although these methods seem to be unsuitable for large-scale use.

In a recent work [18], a freeze-drying method allowed obtaining dense LSGM ceramics at temperatures as low as 1250 °C. However, $LaSrGaO_4$ and $LaSrGa_3O_7$ impurities were detected at this temperature and a subsequent thermal treatment, between 1300 and 1400 °C, was necessary in order to obtain pure LSGM ceramics. The main advantage of freeze-drying method is that the sintering time was reduced to only 5–15 min compared to other methods previously reported [12–15].

Phase segregations are generally considered to have detrimental effects on the performance of the ceramic electrolytes; such impurities are preferentially distributed around the grain boundary and therefore its resistivity is expected to increase [19]. Indeed, $LaSrGa_3O_7$ and $LaSrGaO_4$ impurities, usually found during the synthesis of LSGM, are low conducting materials compared to LSGM. In this sense, several works demonstrated that the ionic and electronic conductivity of LSGM depends on the cation composition, the presence of minor secondary phases and the ceramic microstructure [20]. However, a detailed analysis of the effects produced by phase segregations on the grain interior and grain boundary conductivities in LSGM ceramics has been not extensively studied.

In this work, dense $La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_{3-x/2}$ ($x=0.1$ and 0.2) ceramics have been prepared at different temperatures between 1200

* Corresponding author. Tel.: +34 952137057; fax: +34 952132382.
E-mail address: damarre@uma.es (D. Marrero-López).

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Table 1
Sintering conditions, phase composition, and structural and microstructural parameters for $La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_{3-x/2}$ materials.

x	Sintering conditions	Impurities (wt.%)		V (Å^3)/Z	Relative density (%)	D_g (μm)
		$LaSrGaO_4$	$LaSrGa_3O_7$			
0.1	1200 °C/4 h	1.1	2.1	59.49 (2)	83	0.6
	1250 °C/4 h	1.0	1.8	59.56 (1)	98	1.0
	1300 °C/4 h	–	–	59.62 (2)	99	1.7
	1400 °C/4 h	–	–	59.63 (2)	100	4.4
	1500 °C/4 h	–	–	59.64 (1)	100	9.8
0.2	1300 °C/4 h	12.3	8.5	59.75 (1)	98	2.8
	1350 °C/4 h	5.5	3.0	59.84 (0)	99	4.6
	1400 °C/5 min	1.5	–	59.94 (1)	99	2.6
	1400 °C/15 min	–	–	59.89 (1)	100	3.4
	1400 °C/1 h	–	–	59.89 (1)	100	6.0
	1400 °C/4 h	–	–	59.92 (0)	100	7.8
	1500 °C/4 h	–	–	59.91 (1)	100	18.1

and 1500 °C using polycrystalline powders obtained from freeze-drying. These samples contain different amounts of secondary phases depending on the sintering temperature and Sr-content. Impedance spectra measurements were used to determine the bulk and grain boundary contributions of the overall conductivity as a function of the ceramic microstructure and impurity content. In addition, the ion-blocking and electromotive force methods were used to evaluate the ionic transport numbers.

2. Experimental

2.1. Synthesis

Polycrystalline powders of $La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_{3-\delta}$ ($x=0.1$ and 0.2) were prepared using the freeze-drying method as described in detail elsewhere [18]. The starting reactants were high purity oxides: La_2O_3 (99.99%), Ga_2O_3 (99.99%), MgO (99.99%), and $SrCO_3$ (99.999%) from Aldrich. Stoichiometric amounts of these reactants were mixed in an agate mortar, pressed into a pellet and fired at 1200 °C for 4 h.

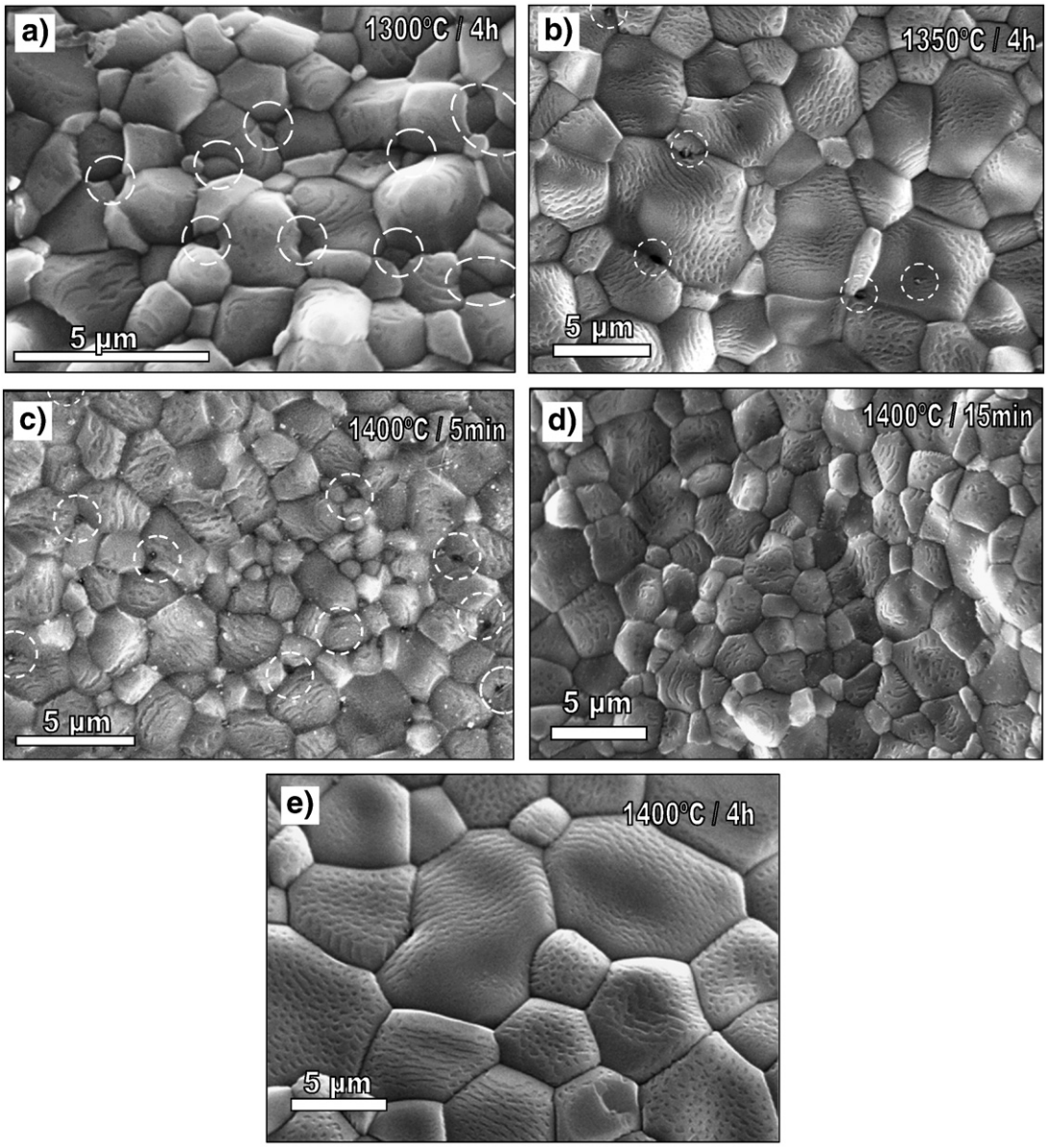

Fig. 1. SEM micrograph of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ prepared at different sintering temperatures: (a) 1300 °C for 4 h, (b) 1350 °C for 4 h, (c) 1400 °C for 5 min, (d) 1400 °C for 15 min and (e) 1400 °C for 4 h. The dashed circles show $LaSrGa_3O_7$ and $LaSrGaO_4$ impurities.