Investigation of the system (1-x) $La_{0.83}Sr_{0.17}Ga_{0.83}Mg_{0.17}O_{2.83}$ -x $La_{0.8}Sr_{0.2}MnO_3$ ($0 \leq x \leq 1$)

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Abstract

La(Sr)Ga(Mg)O_3 and La(Sr)MnO_3 are interesting materials for applications in the field of Solid Oxide Fuel Cells (SOFC), respectively as electrolyte and cathode materials. Composites formed by mixing La(Sr)Ga(Mg)O_3 and La(Sr)MnO_3 have proven to reduce the cathodic overpotential in single cells with yttria-stabilized zirconia and La(Sr)Ga(Mg)O_3 electrolytes; the assessment of the reactivity and diffusion between the two phases is relevant in view of the application in fuel cells. In this work, mixtures of LSGM and LSM were prepared, with emphasis on LSGM-rich compositions, and sintered at 1300 °C. Relative densities of the samples vary in the range 85-89%, and are consistent with previous literature reports for samples fired at 1300 °C. The total conductivity is about $2 \cdot 10^{-2}$ S cm^{-1} at 800°C for samples with 1 % and 5 % LSM; the low relative densities and the small grain size of the samples with respect to LSGM sintered at 1500°C may account for the low conductivity. Present results were compared with those obtained through EDX analysis and electrical measurments on LSGM thick films sandwiched between LSM electrodes. In both experiments there is not any evidence of the formation of new phases.

Keywords: LSGM, Composites (B), Electrical conductivity (C), Perovskites (D), Fuel Cells (E)

1. Introduction

Sr- and Mg-doped $LaGaO_3$[1,2] (LSGM) is attractive as electrolyte material for application in Solid Oxide Fuel Cells (SOFC), due to its high oxigen ion conductivity at intermediate temperatures (600-800 °C) compared to yttria-stabilized zirconia (YSZ). Sr-doped $LaMnO_3$ (LSM) mixed ionic-electronic conductor is successfully applied as cathode material in YSZ-based fuel cells, while it shows higher overpotentials if coupled with LSGM electrolyte[3]. Recently, mixtures of LSGM and LSM have been proposed as composite cathodes for application with both YSZ[4] and LSGM[5] electrolytes showing better performances than LSM alone. Nevertheless, several authors report the occurrence of cations interdiffusion between LSM and LSGM during both the sintering step at

elevated temperatures and after firing at temperatures suitable for operation in an Intermediate Temperature SOFC (IT-SOFC) [5,6,7,8], but disagreements remain on the extension of the diffusion layer and about the effects of diffusion on the cathodic properties. In this work we investigated the micro-structural features and the electrical behaviour of mixtures of $La_{0.83}Sr_{0.17}Ga_{0.83}Mg_{0.17}$ - $La_{0.8}Sr_{0.2}MnO_3$ fired at 1300°C; the results obtained for the mixtures were compared with those obtained studying the interface of two screen-printed thick films of both materials.

2. Experimental

$La_{0.83}Sr_{0.17}Ga_{0.83}Mg_{0.17}$ was synthesised via a sol-gel route. The appropriate amounts of the salts $La(OCOCH_3)_3$ (Sigma Aldrich, 99.9%), $Sr(OCOCH_3)_2$ (Sigma Aldrich, 99.995%), $Ga(NO_3)_3$ (Sigma Aldrich, 99.9%), $Mg(OCOCH_3)_2$ (Sigma Aldrich, 99.999%) were dissolved in water. The solution was heated to 60 °C and NH_4OH was slowly added until the pH reached the value of 9 and precipitation occurred; the suspension was then cured for several hours under continuous stirring. The solvent was evaporated on a thermal plate. The remaining water was removed by heating at 130 °C for 12 h. The powders were calcined at 1200 °C for 6 h and finally sintered at 1480 °C for 12 h, in air. $La_{0.8}Sr_{0.2}MnO_3$ (LSM) was produced by the common solid state route; La_2O_3, $SrCO_3$ and $MnCO_3$ (Sigma Aldrich, 99.9%) were mixed in an agate mortar and heated in air at 600 °C for 3 h and at 1350 °C for 6 h in air with intermediate regrinding.

Sintered LSGM and LSM powders were mixed in an agate mortar in the proportions listed in table 1, and pressed in a 13 mm pellet die at 460 MPa per 30 s with 2 wt% of organic binder (Polyethileneglycol - PEG 8000). The compacted powders were sintered at 1300 °C for 2 h with a 5 °C/min ramp; the experimental densities were measured using the Archimedean method. Cell parameters estimated from X-ray powder patterns were used for the calculation of the theoretical densities of pure LSGM and LSM. The mixture rule was applied for the calculation of relative densities of composites. Electrical characterisation was performed by the impedance spectroscopy technique (IS), in air in the temperature range 300-900 °C; thick Pt layers were deposited on both faces of the pellet as electrodes and fired at 900°C. Morphology and microstructure of the composites was investigated by scanning electron microscopy (SEM) on polished sections of the samples.

3. Results and discussion

3.1 Phase composition

In Fig 1 XRD pattern of the M05 sample annealed at 1300 °C 2 h is reported together with the diffraction patterns of the starting LSGM and LSM powders; LSM powders are found to be fully single phase, while a small amount of the melilite-type compound $LaSrGa_3O_7$ (JPCDS PDF # 45-0637, see peak at 2θ=29.911 °) is present, in addition to the perovskite phase, in the LSGM powders. LSGM cell parameters, refined with space group *Imma* using the software Topas P[9], are a = 5.5283(3), b = 7.8197(5), c = 5.5510(8), cell volume 240 Å^3, density = 6.648 g/cm^3; LSM is *R-3c*, a = b = 5.5144(2) c = 13.3630(7) γ = 120 °, cell volume 352 Å^3, density = 6.557 g/cm^3. There is evidence from the XRD pattern neither of new phases growth nor of peaks shift or broadening, which would indicate the formation of a solid solution.

3.2 Relative densities

Since doped $LaGaO_3$ is known to sinter completely at temperatures above 1400 °C, it is easily expected that the relative densities of the samples would not reach the theoretical values. $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ sintered at 1300 °C is known to produce samples with relative densities of around 85%[10], which agrees with the values obtained in this work, summarised in Table 1.

3.3 Microstructure

In Fig. 2a an artificially coloured SEM Micrograph of the 5% LSM sample is reported, in which orange areas are associated with the presence of Mn and blue ones with Ga concentration; small aggregates of LSM particles are well dispersed into the LSGM matrix; also large pores are visible as black areas. EDX analysis at the interfaces between particles were not reliable due to unfavourable morphology of the sample and thus are not reported. At bigger magnification (Fig. 2b) it can be seen the small grain size of the electrolyte (few microns on average) and the LSM aggregates (indicated by the arrow). No relevant differences in morphology and grain growth were noted between M01 and M05 composites.

3.4 Impedance Spectroscopy

The results of I.S. measurements of M01 and M05 are given in Fig.3 as conductivity vs. inverse temperature data. The samples exhibit nonmetallic behavior, consistent with thermally activated hopping conductivity. The total conductivities of M01 and M05 are one order of magnitude smaller than that measured for M00 sintered at 1500°C, and are similar to that observed by Cong et al.[11] for pure LSGM sintered at 1400°C. The significant smaller conductivity of the composites arises because their relative density is 86-89%, due to the lower preparation temperature (1300°C). In Fig.3 are also shown the conductivity vs. inverse temperature data of LSGM thick films sandwiched between LSM electrodes[12]. The effect ascribed to the migration of Mn cations

from LSM electrode material to LSGM electrolyte previously reported at LSGM/LSM interface is not significant for composites with small amount (1-5wt%) of LSM.

4. Conclusions

Mixtures of LSGM electrolyte and LSM were prepared and sintered at 1300°C; porous samples with 86-89% relative densities were obtained. The dispersion of 1% and 5% LSM into the electrolyte matrix did not show measurable harmful effects on the electrical conductivity, which was similar to values found in literature on LSGM samples sintered at 1400°C. Further work is ongoing to investigate compositions richer in LSM.

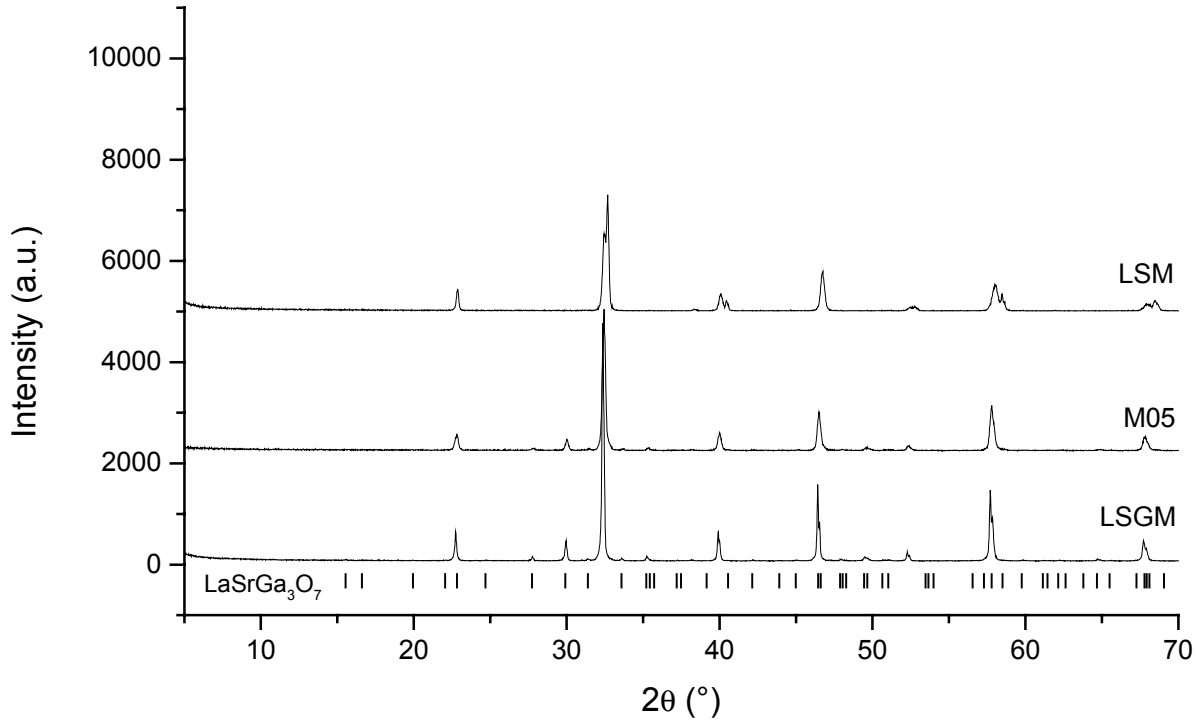
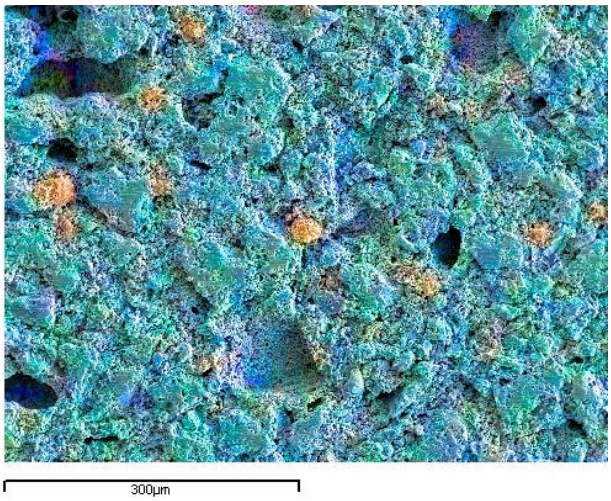

Intensity (a.u.)
10000
8000
6000
4000
2000
0
LSM
M05
LSGM
LaSrGa3O7
10
20
30
40
50
60
70
2θ (°)

Figure 1

a)



b)

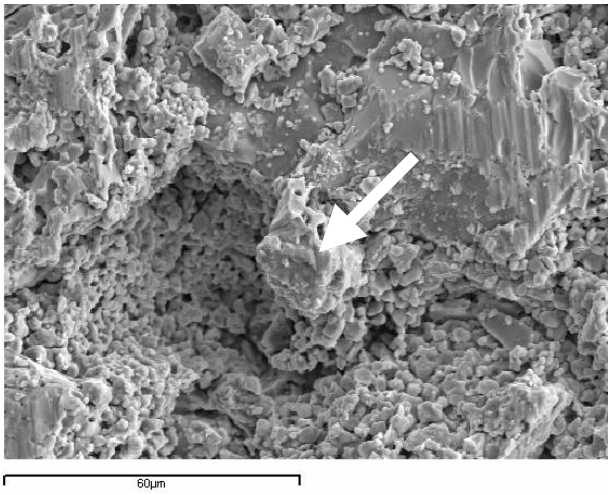


Figure 2

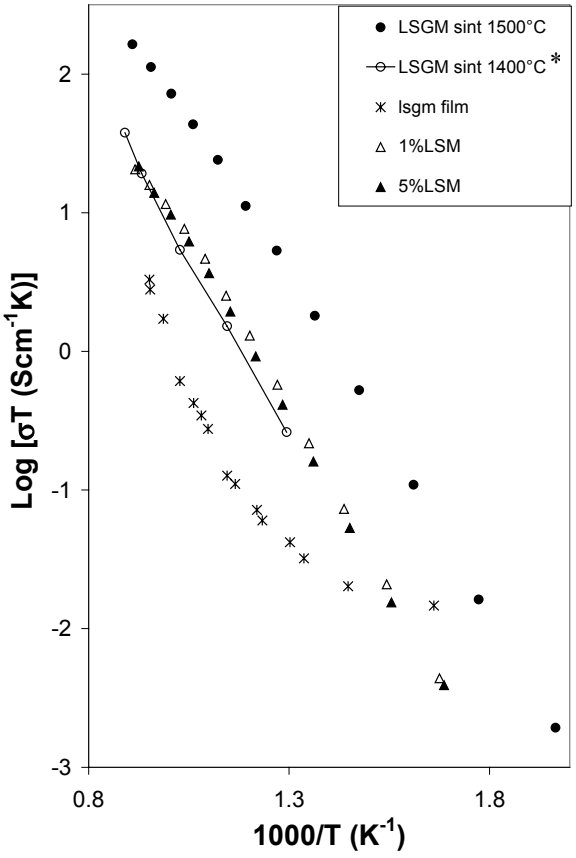

LSGM sint 1500°C
LSGM sint 1400°C *
lsgm film
1%LSM
5%LSM
Log [σT (Scm-1K)]
1000/T (K-1)
2
1
0
-1
-2
-3
0.8
1.3
1.8

Figure 3

Table 1. Samples compositions, relative density and electrical conductivities.

SAMPLE	LSGM wt%	LSM wt%	Relative Density (%)	σ at 800 °C (S/cm)
M00	100	-	92	$1.49 \cdot 10^{-1}$
M01	99	1	89	$2.18 \cdot 10^{-2}$
M05	95	5	86	$2.10 \cdot 10^{-2}$

Captions to Figures

Fig. 1: X-Ray powder diffraction patterns of LSGM (bottom), M05 (middle), LSM (top).

Fig. 2: a) artificially coloured SEM micrograph of M05 composite (orange indicate Mn, blue Ga); b) bigger magnification of the same sample.

Fig. 3: Arrenhius plot of the total electrical conductivity of composites M01 and M05, LSGM sintered at 1500 °C, LSGM sintered at 1400 °C (* data taken from reference[11]) and LSGM film.

5. References

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