Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 7270–7277

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microstructure and electrical conductivity of fast fired Sr- and Mg-doped lanthanum gallate

S.L. Reis*, E.N.S. Muccillo

Energy and Nuclear Research Institute – IPEN, PO Box 11049, S. Paulo 05422-970, SP, Brazil

Received 25 November 2015; received in revised form 12 January 2016; accepted 13 January 2016
Available online 22 January 2016

Abstract

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ solid electrolytes were consolidated by fast firing aiming to investigate the effects of the sintering method on densification, microstructure and ionic conductivity. Powder mixtures were prepared by solid state reaction at 1250 and 1350 °C for 12 h, and fast fired at 1450 and 1500 °C temperatures for 5 and 10 min. The content of impurity phases was found to be quite low with this sintering method. Relatively high density (> 90% of the theoretical value) and low porosity (< 1.5%) were readily obtained for powder mixtures calcined at 1250 °C. The activation energy for conduction was approximately 1 eV. Specimens fast fired at 1450 °C for 10 min with a mean grain size of 2.26 μm reached the highest value of total ionic conductivity, 22 mS cm^{-1}, at 600 °C.

Keywords: A: Sintering; C: Electrical conductivity; D: Perovskites; E: Fuel cells

1. Introduction

Lanthanum gallate with partial substitutions by Sr and Mg, $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ has received considerable attention as a promising solid electrolyte for solid oxide fuel cells operating at intermediate temperatures (600–800 °C), owing to its singular electrical and electrochemical properties [1–7]. Among the several compounds formed by varying the strontium and the magnesium contents, that with $x=0.1$ and $y=0.2$ exhibits a perovskite type crystalline structure with orthorhombic symmetry and has been thoroughly investigated [1, 8, 9]. $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, hereafter named LSGM, exhibits high ionic conductivity (0.17 S cm^{-1} at 800 °C) and ionic transport number of approximately 1 in a wide range of oxygen partial pressures [1].

The LSGM compound is usually prepared by the solid state method, comprising the mixture of the starting reagents followed by high temperature reaction and conventionally sintered. The product material frequently contains minor amounts of secondary or impurity phases, such as $LaSrGaO_4$, $LaSrGa_3O_7$, $La_4Ga_2O_9$ and MgO [10–12]. The thermodynamic stability and the electrical conductivity of La- and Ga-containing impurity phases and of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ have already been investigated [13]. Based on the obtained results, it has been proposed that the ideal sintering temperature should be relatively high (1500 °C) to obtain good densification and because the solubility of strontium and magnesium is maximum at such high temperature, although the relative density seldom exceeds 95% [13]. Moreover, it was suggested the use of a fast cooling rate from the sintering temperature to preserve, as much as possible, the phase composition obtained at high temperature [13].

Relatively few studies may be found, on modified thermal cycles with fast heating and cooling rates during sintering of LSGM. The spark plasma sintering (SPS) technique was found suitable for obtaining LSGM specimens with density in excess of 90% at relatively low temperatures (1200–1300 °C) [14,15], and the use of high pressures allowed for full densification [16]. In addition, the SPS technique was effective to produce

*Correspondence to: Center of Materials Science and Technology, Energy and Nuclear Research Institute – IPEN, PO Box 11049, S. Paulo 05422-970, SP, Brazil. Tel.: +55 11 31339203.
E-mail address: shirley.reis@usp.br (S.L. Reis).

http://dx.doi.org/10.1016/j.ceramint.2016.01.121
0272-8842/

LSGM specimens with grain sizes smaller than 1 μm and with negligible (about 2% or less) impurity phases. In those studies the LSGM powder was synthesized by chemical methods, which are known to give rise to low content of impurity phases. Good densification (~98% of relative density) was also obtained by rapid solidification with CO_2 laser using LSGM powder prepared by the mixing of oxides method [17]. The reported total (grain plus grain boundary) electrical conductivity of LSGM at 600 °C varies considerably from 0.007 [14] to 0.027 S cm^{-1} [17]. Those relatively low values were attributed to the significant blocking of charge carriers at grain boundaries, due to the small grain sizes [14].

Another method applying fast heating and cooling rates, known as fast firing, was originally proposed for obtaining high densification and fine grain materials for ceramics exhibiting high activation energy for densification compared to that for grain growth [18, 19]. In this method, the green compact is heated at a fast rate up to a high temperature, usually higher than that of conventional sintering remaining for short time, and then, it is fast cooled down to room temperature. The fast firing method has been applied to several ceramic materials such as Al_2O_3, $BaTiO_3$, yttria-doped zirconia, manganese-doped ceria and Al_2O_3–TiC composite [18–22]. The main issues of this method of sintering were recently reviewed [23].

In a previous work, we consolidated chemically synthesized powders of LSGM by fast firing [24]. The 90% dense specimens showed negligible impurity phase contents, but relatively low electrical conductivity probably due to limited densification. However, for practical applications, high relative density (≥ 92% of the theoretical value) and suitable electrical conductivity are required. Therefore, in this work, the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ compound was prepared by solid state reaction, and green compacts were fast fired at high temperatures aiming to establish sintering parameters for obtaining high densification along with reduced amounts of impurity phases. The effect of the sintering method on the electrical conductivity of LSGM was investigated by impedance spectroscopy measurements.

2. Experimental procedure

2.1. Material preparation

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ compound was prepared by the conventional solid state reaction method with La_2O_3 (99.9%, Alfa Aesar), $SrCO_3$ (P. A., Vetec), Ga_2O_3 (99.9%, Alfa Aesar) and MgO (P. A., Vetec) as starting materials. The lanthanum precursor was heat treated at 1000 °C for 3 h prior to use. The starting materials were mixed together in the stoichiometric ratio and calcined at 1250 °C and 1350 °C for 4 h. These temperatures were selected from a previous study [25]. The calcination step was repeated twice with intermediate deagglomeration in an agate mortar to improve the mixing of the powder particles and, consequently, the reaction among the several components. After 12 h of calcination the powder mixture was attrition milled for 1 h in a teflon jar with zirconia balls (ϕ 2 mm) in alcoholic medium. The dried mixture was uniaxially and isostatically (200 MPa) pressed into pellets (ϕ 10 mm and 2–3 mm thickness) without any binder material. Green pellets were introduced in a pre-heated (1450 or 1500 °C) tubular furnace (Lindberg, BlueM). After 5 or 10 min. of isothermal treatment, the pellets were pulled out of the furnace and quickly cooled down in air to room temperature. These experiments were repeated a number of times to ensure reproducibility.

2.2. Characterization methods

The crystalline structure of fast fired pellets was characterized by X-ray diffraction, XRD (Bruker-AXS, D8 Advance) in the 20–80 ° 2θ range with Cu K_α radiation ($\lambda = 1.5405$ Å), and 0.05° step size with 2 s counting time. The main impurity phases were identified with the corresponding ICDD files: 24-1208 ($LaSrGaO_4$), 37-1433 ($La_4Ga_2O_9$) and 45-0637 ($LaSrGa_3O_7$). The XRD patterns were normalized for the most intense reflection of the orthorhombic phase for comparison purpose, once the amount of impurity phases was not quantified. The sintered density was determined by the immersion method with distilled water and compared to the theoretical density (6.67 g cm^{-3}, ICSD 51-288). The porosity of fast fired pellets was estimated according to ASTM C20-00.

The main microstructural features of sintered pellets were studied by field emission scanning electron microscopy, FESEM (FEI, Inspect F50). The mean grain size, G, was determined by the intercept method on a large population of grains. Electrical conductivity measurements were carried out by impedance spectroscopy (HP 4192A) in the 5 Hz–13 MHz frequency and 280–420 °C temperature range, respectively. Silver paste was painted onto parallel surfaces of the pellets and fired at 400 °C to act as electrode. The impedance diagrams were normalized for pellet dimensions for comparison purpose, and the collected data were analyzed in impedance mode with special software [26].

3. Results and discussion

3.1. Structure and microstructure

Fig. 1 shows XRD patterns of LSGM recorded after each processing step for powders calcined at 1250 °C. The diffraction pattern of the powder mixture (PM) is included as reference. After the first calcination step, the diffraction pattern displays the main reflections of LSGM with orthorhombic symmetry according to ICSD 51-288, along with $La_4Ga_2O_9$ (3) and $LaSrGa_3O_7$ (4) as impurity phases, and unreacted La_2O_3 (1) and Ga_2O_3 (2). The most intense reflection, in this pattern belongs to the gallium-rich phase $LaSrGa_3O_7$. The reflections of the LSGM phase attain high intensity after the second calcination step, whereas the fraction of the $LaSrGa_3O_7$ decreases. The reflections of the starting powders are no longer observed after 8 h of calcinations at 1250 °C. In addition, a low intensity reflection belonging to $LaSrGaO_4$ (5) phase is also detected. The third calcination step promotes further