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Phase composition, densification and electrical conductivity of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ consolidated by the two-stage sintering method

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Abstract

The influence of the method of sintering on densification, phase assemblage and electrical conductivity of Sr- and Mg-doped lanthanum gallate was investigated aiming to optimize the sintering process of this solid electrolyte. Powder mixtures were prepared by solid state reactions, and the sintering of green compacts was carried out by the two-stage method varying the temperature of the first stage (T_1) and the isothermal temperature (T_2) and time (t_2) profile. The type and content of predominant impurity phases depend on specific parameters of the sintering process. In the first stage of sintering, the content of impurity phases, such as $LaSrGaO_4$ and $La_4Ga_2O_9$, decreases with increasing temperature. The relative density of sintered specimens reaches 99% whenever T_1 is 1500 °C. The mean grain size varies from 1.45 to 4.9 μm. At 600 °C the electrical conductivity attains 12 mS cm^{-1} for T_1 1400 °C and T_2 1350 °C for 5 h, with activation energy of approximately 1 eV.

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

1. Introduction

Lanthanum gallate with partial substitutions by strontium and magnesium has been extensively investigated over the last two decades because of its high ionic conductivity (170 mS cm^{-1} at 800 °C), negligible electronic conductivity, and good chemical stability in a wide range of oxygen partial pressures (1–10^{-22} atm) [1,2]. Doped lanthanum gallate is a promising ceramic material for application as solid electrolyte in solid oxide fuel cells operating at intermediate temperatures (600–800 °C) [2,3]. The main disadvantage of this solid electrolyte is related to secondary or impurity phases, usually detected in sintered materials regardless the method of preparation.

$La_{1-x}Sr_xGa_yMg_{1-y}O_{3-\delta}$ compositions prepared by solid state reactions may exhibit impurity phases, mainly $La_4Ga_2O_9$, $LaSrGaO_4$, $LaSrGa_3O_7$ and MgO [4–7]. The total amount of these phases is known to vary according to several factors, including the Sr content. Among the most investigated compositions, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, hereafter named LSGM, is known to contain comparatively small fractions of impurity phases.

Recently, special attention has been given to the sintering of LSGM by non conventional methods. Liu et al. [8] synthesized the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ compound by the combustion method and the consolidation of bulk specimens was carried out by spark plasma sintering. The main results show that high relative densities (~95%) along with low contents of impurity phases were obtained after sintering at 1300 °C, with electrical conductivity of approximately 7.5 mS cm^{-1} at 600 °C. Zhang et al. [9] prepared the same compound by the rapid solidification method and obtained LSGM specimens with 98% of relative density and high electrical conductivity (about 27 mS cm^{-1} at 600 °C). In a previous work we have synthesized nanopowders of LSGM by the cation complexation technique; bulk specimens were obtained by fast firing at 1400–1500 °C for 5 and 10 min. The relative density of the sintered specimens was only 90%, but the content of impurity phases was negligible [10].

In 2000, Chen and Wang [11] proposed a new method of sintering, named two-stage sintering (tss), that allowed for

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obtaining yttria with high density and fine grain size. In that method, the green compact is heated up to a high temperature (T_1) at which it remains for a short (or null) holding time (t_1). Subsequently, the compact is fast cooled down to a specific temperature (T_2) for a long holding time (t_2). To improve the overall process, sufficiently high T_1 is chosen such that the compact reaches 75–85% of relative density in the first stage of sintering [12]. This method has been applied with success for sintering a number of functional ceramics such as Al_2O_3, ZnO, $BaTiO_3$, Si_3N_4, SiC, $Ca_3MgSi_2O_8$ and yttria-stabilized zirconia [13–22]. In all these studies, the main purpose was to obtain high densification along with negligible grain growth in the second stage.

In this work, LSGM powder was prepared by solid state reactions and the sintering of compacts was accomplished by the two-stage sintering method, aiming to evaluate the final densification and the electrical conductivity of the solid electrolyte. Other objective was to investigate the effect of the sintering method on phase evolution of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$.

2. Experimental

2.1. Sample preparation

The compound $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2-\delta}$ was prepared by solid state reactions starting with La_2O_3 (99.9%, Alfa Aesar), $SrCO_3$ (P.A., Vetec), Ga_2O_3 (99.99%, Alfa Aesar) and MgO (P.A., Merck). The La_2O_3 precursor powder was at first heat treated at 1000 °C for 3 h. Stoichiometric amounts of the starting reagents were mixed together and calcined at 1250 °C for 4 h. This calcination step was repeated twice with intermediate grindings. After calcination, the mixture was attrition milled for 1 h with zirconia balls (ϕ 2 mm) in alcoholic medium. The dried mixture was uniaxial followed by cold isostatic (200 MPa) pressing into pellets (ϕ 10 mm and 2–3 mm thickness). The sintering process was carried out in a box-type furnace (Lindberg BlueM) with heating and cooling rates of 10 and 30 °C min^{-1}, respectively.

In the first series of experiments, the sintering temperature T_1 was varied from 1250 to 1500 °C. Subsequently T_1 was fixed at 1400 or 1500 °C and T_2 varied from 1250–1450 °C with t_2 fixed a 5 h. In all experiments the holding time t_1 was null. This procedure is hereafter called TSS

2.2. Sample characterization

The apparent density of sintered specimens was determined by the immersion method with distilled water and compared to the theoretical density (6.67 g cm^{-3}, ICSD 51-288). Structure evaluation was performed by X-ray diffraction, XRD (Bruker-AXS, D8 Advance) with Cu K_α radiation (λ=1.5405 Å) in the 20–80° 2θ range, with 0.05° step size and 2 s counting time. Identification of impurity phases was performed according to the corresponding powder diffraction files: ICDD 24-1208 ($LaSrGaO_4$), ICDD 45-0637 ($LaSrGa_3O_7$) and ICDD 37-1433 ($La_4Ga_2O_9$). The amount of impurity phases was not quantitatively determined, but the XRD patterns were normalized for the most intense reflection of the orthorhombic phase, for comparison purpose.

Microstructure observations were performed by field emission scanning electron microscopy (FESEM, FEI, Inspect F-50). The mean grain size was estimated by the intercept method [23]. Electrical resistance measurements were carried out by impedance spectroscopy (HP 4192A) in the

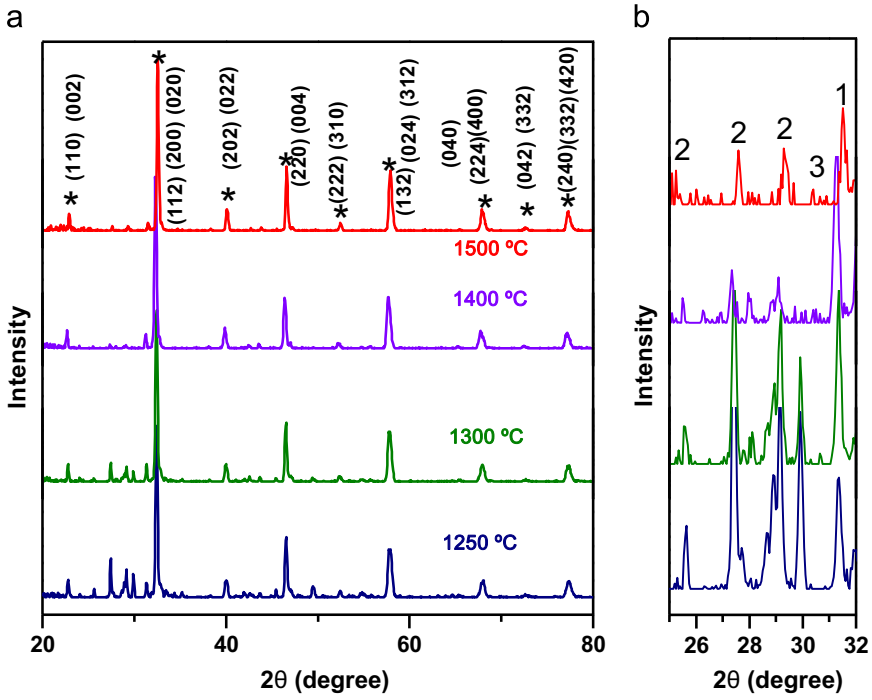

Fig. 1. XRD patterns of LSGM sintered by the TSS method with varying T_1 and null holding time in the (a) 20–80° and (b) 25–32° 2θ ranges. (*) LSGM, (1) $LaSrGaO_4$, (2) $La_4Ga_2O_9$ and (3) $LaSrGa_3O_7$.