

Processing of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ by mechanical activation

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Abstract

This work reports on a first attempt to obtain $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ga}_{0.90}\text{Mg}_{0.10}\text{O}_{3-\delta}$ ceramics by mechanical activation of La_2O_3 , SrO , Ga_2O_3 and MgO precursors. The mechanical activation of the powder precursors was carried out by dry grinding in a planetary ball mill. Dense ceramics were obtained from these activated powders after sintering at a maximum of 1450°C for 4 h in air. Samples obtained by a conventional ceramic route were also prepared, but the sintering temperature was 100°C higher. Preliminary impedance spectroscopy data show similar grain conductivities for both materials. However, a significant degradation is observed on ageing the LSGM prepared by the conventional solid state route. This degradation is not present in the material prepared from the mechanically activated precursors.

1. Introduction

Feng and Goodenough¹ and Ishihara *et al.*² and reported that the perovskite LaGaO₃, when suitably doped with strontium and magnesium (La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-α}), exhibit a conductivity several times higher than Y₂O₃-doped ZrO₂, comparable with that of Gd₂O₃-doped CeO₂, and an ionic transport number close to unity within large ranges of oxygen partial pressure and temperature. Since then, a large amount of work has been dedicated to study these promising solid electrolytes.

The most commonly used method to obtain lanthanum gallate-based electrolytes is the conventional ceramic route, which consists in mixing the starting materials, followed by solid state reaction at high temperature³⁻⁵. The drawbacks associated to the high temperature needed for the solid state reaction to occur include large particle size and limited degree of chemical homogeneity. The phase purity and microstructure of these materials strongly depends on the synthesis of the powders and the ceramics processing and, as a matter of fact, the synthesis of a pure single phase material is rather difficult^{5,6}. Small amounts of undesired phases such as LaSrGa₃O₇ and LaSrGaO₄ are detected even in materials prepared by chemical solutions methods, which can provide products of fine and homogeneous particles^{7,8}.

The synthesis via mechanochemical reactions, using a high-energy ball mill, has proven to be versatile to obtain different kinds of materials, namely oxides⁹⁻¹². The high-energy milling makes the activated powder more reactive as a consequence of the fracture of the grains and defects generated during grinding, which leads to a higher internal energy and reduces the thermal barrier for any subsequent reaction¹³.

The aim of this work is to obtain La_{0.95}Sr_{0.05}Ga_{0.90}Mg_{0.10}O_{3-δ} (LSGM) ceramics by mechanical activation of oxide precursors and compare this material with the LSGM

prepared by the conventional solid state route. A preliminary impedance spectroscopy study is presented.

2. Experimental

Powders of $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ga}_{0.90}\text{Mg}_{0.10}\text{O}_{3-\delta}$ (LSGM) were prepared from mixtures of stoichiometric amounts of high purity lanthanum (Merck), gallium (Aldrich), magnesium (Panreac) and strontium, oxides. The SrO was obtained after calcining SrCaO_3 (Merk) at 1100°C during 30 min. Six grams of the oxides, previously mixed in absolute ethanol, were mechanically activated in a planetary ball-mill (Retsch Centrifugal Ball-Mill Type S-1/2) using a Nylon container and zirconia balls with a diameter of 10 mm. The ball to powders weight ratio was 10:1. The mechanical activation was performed at ~ 380 rpm in air during several hours up to a maximum of 60. Grinding was interrupted at regular time intervals for cooling down the container and collect samples for X-ray diffraction analyses (X'Pert MPD Philips diffractometer with CuK_α X-radiation) to monitor structural modifications. A sample from the powder mixture activated during 60 h was also analysed by thermogravimetric (TGA) and differential thermal (DTA) analyses, and *in situ* high temperature X-ray powder diffraction (HTXRD).

The information gathered by TGA/DTA and HTXRD analyses was used to design an appropriate sintering curve (Fig. 1) in order to prepare ceramics in a single thermal treatment in which both synthesis and sintering took place. The main objective was to retain the small grain size of the activated precursors.

Conventional LSGM samples were also prepared by the conventional ceramic route using the same initial raw materials mixed in ethanol with zirconia balls in a Teflon container. The mixture was dried, calcined at 1100°C for 12 h, and again ball-milled and dried. The resultant powder was pressed into pellets with a diameter of 10 mm and sintered at 1550°C for 4 h with constant heating and cooling rates of 5 K/min.

The ceramics prepared by the two methods were characterised by impedance spectroscopy (HP 4284A impedance analyser) at frequencies in the range from 20 Hz to 1 MHz and applying an alternative signal of 100 mV. The measurements were carried out in air at temperatures from 200°C to 500°C in order to distinguish the grain from the grain boundary impedances. The evolution of both contributions to the overall impedance was studied in samples annealed at the maximum sintering temperature for 4, 16, 32 and 40 hours (1450°C and 1550°C for mechanically activated and conventional ceramics, respectively). Platinum electrodes were painted onto the surface of the samples and calcined at 1000°C for 10 min to ensure the necessary electrical contacts. Fresh electrodes were applied before every measurement.

3. Results

The powder XRD pattern shown in Fig. 2 show that single phase $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ga}_{0.90}\text{Mg}_{0.10}\text{O}_{3-\delta}$ can be obtained at 1200°C. This represents a significant decrease in the temperature necessary to promote the solid state reaction of formation of the perovskite oxide and must be a direct consequence of the higher reactivity of the activated powders. The mechanochemical approach thus seems promising to the synthesis of lanthanum gallate-based materials.

The benefits arising from the higher reactivity of these powders are extended to the sintering behaviour since ceramics with densification levels higher than 90% of the theoretical density could be obtained at a temperature about 100°C lower than that needed for the material prepared from non-activated precursors. It should be noticed that a systematic study of other factors influencing the mechanochemistry of the system (nature of precursors, the type of mill, rotation velocity of the mill, balls to powder ratio, etc.) is fundamental for further improvements.

Fig. 3 shows preliminary impedance spectra obtained at 300°C for the non-activated (A) and activated samples (B) annealed for different periods of time. The spectra reveal two semicircles which can be ascribed to the grain interior impedance, at higher frequency, and to the grain boundary, at the lower frequency. The grain boundary resistive contribution (R_{gb}) is clearly lower than that of the grain (R_g), in the case of the conventional ceramics (Fig. 3A). Moreover, both R_g and, particularly, R_{gb} increase with increasing annealing time. This may suggest a degradation of the microstructure, probably linked to the existence of chemical inhomogeneities.

On the contrary, for the activated ceramics (Fig. 3B), the initial value of R_{gb} is considerably higher than R_g but it decreases to a much lower value after annealing; R_g remains nearly unchanged under the same conditions. The initially high R_{gb} is likely to result from a large grain boundary density since these ceramics are expected to partially retain the small grain size of the milled precursors (typically in the nanometer range). The increase of the sintering time will certainly lead to larger grains and, thus, to the decrease of the amount of resistive grain boundaries in the ceramic body. The results presented in Arrhenius coordinates in Figs. 4 and 5 show that the aforementioned trend

spans over the entire measuring temperature range where the separation between the grain and grain boundary contribution is possible (250-400°C).

Tentative simple arguments have been put forward to interpret the results, but they still lack further experimental support. The systematic characterisation of the microstructure by scanning electron microscopy, transmission electron microscopy and analytical techniques such as energy dispersion spectroscopy are now object of our attention.

References

- ¹Feng, M., Goodenough, J.B., A superior oxide-ion electrolyte, *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 663-672.
- ²Ishihara, T., Matsuda, H., Takita, Y., Doped LaGaO₃ Perovskite Type Oxide as a New Oxide Ionic Conductor, *J. Am. Chem. Soc.*, 1994, **116**[9], 3801-3803.
- ³Huang, P., Petric, A., Superior oxygen ion conductivity of lanthanum gallate doped with strontium and magnesium, *J. Electrochem. Soc.*, 1996, **143**[5], 1644-1648.
- ⁴Huang, K., Tichy, R.S., Goodenough, J.B., Superior perovskite oxide-ion conductor; Strontium- and Magnesium-doped LaGaO₃: II, ac Impedance spectroscopy, *J. Am. Ceram. Soc.*, 1998, **81**[10], 2576-2580.
- ⁵Djurado, E., Labeau, M., Second phases in doped lanthanum gallate perovskites, *J. Eur. Ceram. Soc.*, 1998, **18**, 1397-1404.
- ⁶Gorelov, V.P., Bronin, D.I., Sokolova, J.V., Nafe, H., Aldinger, F., The effect of doping and processing conditions on properties of La_{1-x}Sr_xGa_{1-y}Mg_yO₃, *J. Eur. Ceram. Soc.*, 2001, **21**, 2311-2317.

⁷Tas, A.C., Majewski, P.J., Aldinger, F., Chemical preparation of pure and strontium - and/or magnesium-doped lanthanum gallate powders, *J. Am. Ceram. Soc.*, 2000, **83**[12], 2954-2960.

⁸Polini, R., Pamio, A., Traversa, E., Effect of synthetic route on sintering behaviour, phase purity and conductivity of Sr- and Mg-doped LaGaO₃ perovskites. *J. Eur. Ceram. Soc.*, 2004, **24**, 1365-1370.

⁹Mi, G., Saito, F., Suzuki, S., Waseda, Y., Formation of CaTiO₃ by grinding from mixtures of CaO or Ca(OH)₂ with anatase or rutile at room temperature, *Powder Technology*, 1998, **97**[2], 178-182.

¹⁰Zhang, Q., Saito, F., Mechanochemical synthesis of lanthanum aluminate by grinding lanthanum oxide with transition alumina, *J. Am. Ceram. Soc.*, 2000, **83**[2], 439-441.

¹¹Algueró, M., Alemany, C., Jiménez, B., Holc, J., Kosec, M., Pardoet, L., Piezoelectric PMN-PT ceramics from mechanochemically activated precursors, *J. Eur. Ceram. Soc.*, 2004, **24**, 937-940.

¹²Castro, A., Jiménez, B., Hungría, T., Moure, A., Pardo-Castro, L., Sodium niobate ceramics prepared by mechanical activation assisted methods, *J. Eur. Ceram. Soc.*, 2004, **24**, 941-945.

¹³Hungría, T., Hungría, A.B., Castro, A., Mechanochemical synthesis and mechanical activation processes to the preparation of the Sr₂(Sr_{n-1}Ti_nO_{3n+1}) Ruddlesden-Popper family, *J. Solid State Chem.*, 2004, **177**, 1559-1566.

Figure captions

Fig. 1. Sintering curve used to obtain ceramics from mechanically activated precursors

Fig. 2. X ray diffraction pattern of the activated powders collected *in situ* at 1200°C (the * peaks correspond to the platinum)

Fig. 3. Impedance spectra at 300°C of conventional **A)** and mechanically activated **B)** LSGM ceramics annealed for different periods of time (frequency decreases from 1MHz in the first point in the left down to 20 Hz)

Fig. 4. Temperature dependence of the electrical conductivity for grain (G) and grain boundary (GB) of conventional LSGM ceramics annealed for different periods of time

Fig. 5. Temperature dependence of the electrical conductivity for grain (G) and grain boundary (GB) of LSGM ceramics obtained from mechanically activated precursors annealed for different periods of time

Figures

Fig.1

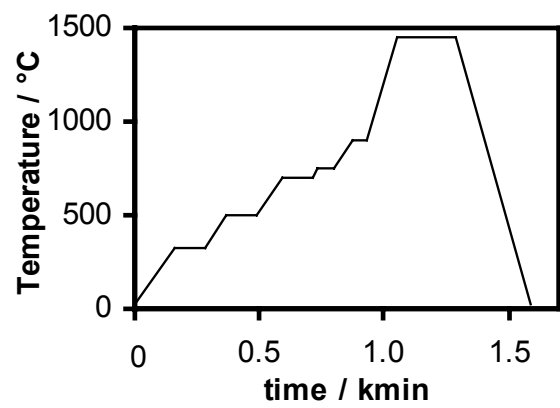


Fig.2

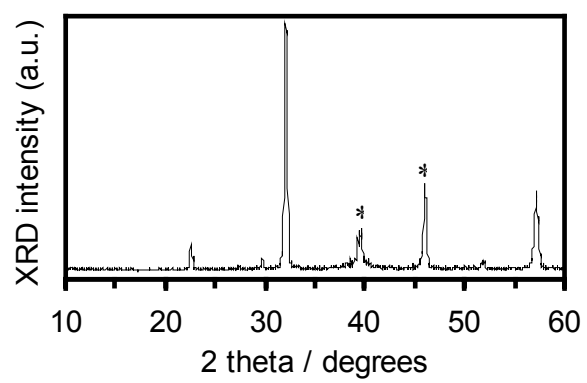


Fig. 3

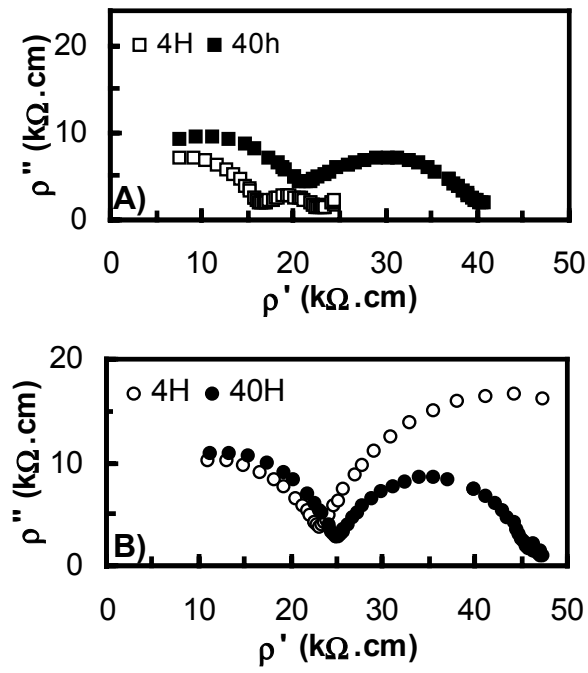


Fig. 4

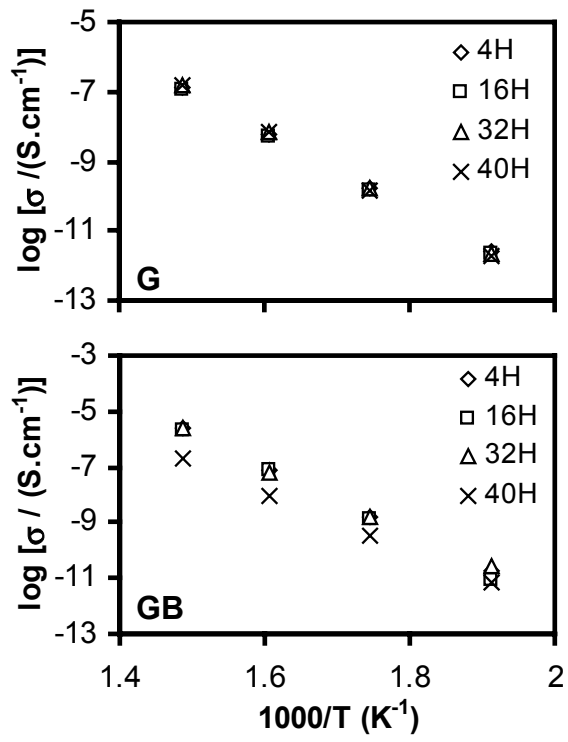


Fig. 5

