A Microstructural Study of Doped-$LaGaO_3$ ($La_{0,9}Sr_{0,1}Ga_{0,8}Mg_{0,2}O_{2,85}$) Produced by an Autocombustion from a Gel-Like Precursor

Karl Traina[1], Cesar M. Steil[2], Christophe Bossuot[3], Jean-Paul Pirard[3], André Rulmont[1] and Rudi Cloots[1]

[1]University of Liege, Inorganic Chemistry Laboratory Chemistry Institute, B6 Sart-Tilman, BE-4000 LIEGE / Belgium

[2]Laboratoire de Cristallochimie et Physicochimie du Solide, UPRES A 8012, ENSCL et USTL, BP 108, FR-59652 Villeneuve d'Ascq Cedex / France

[3]Laboratoire de Génie Chimique, B6a, Université de Liège BE-4000 Liège / Belgium

Abstract

Polycrystalline dense samples of lanthanum gallate doped with strontium and magnesium ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ or LSGM) were prepared using a novel gel precursor synthesis method. This consists in preparing a LSGM precursor from a freeze-dried Agar-Agar gel. After the freeze-drying step, the dry residue is put in an oven at 120°C where autocombustion occurred. The as-produced powders are then calcined.

Investigations are made to follow both structural and microstructural evolutions from the dry residue to the end product. The effect of the temperature evolution was examined by thermogravimetric analysis, X-ray diffraction, environmental scanning electron microscopy, and specific surface area analysis. Dilatometric curves and density measurements have been also performed on the sintered products.

Advantages of this method are the ability to control the size distribution and to obtain high density materials without any milling step and thus, avoiding any contamination coming from the grinding medium.

Introduction

Within the space of a few years and in order to enhance electrical performances of solid oxide fuel cell in the intermediate temperature field, a lot of investigations were made on doped $LaGaO_3$ perovskite. Therefore, several properties like structure (X-ray, electronic or neutron diffraction), microstructure (electronic microscopy), electrical behaviour (as well as for electrolyte or electrode components) were studied. Nevertheless, in most cases, the accession to a desired compound with good electrical properties needs the use

of an appropriate synthesis method. Although many different synthesis processes have been proposed [solid state route (1-5), sol-gel preparation (3, 6-7), gel method (7-10) and autocombustion or combustion procedure (11-13)], to control simultaneously crystallographic phase formation of a desired compound and microstructural properties of corresponding powder (essentially grain size and distribution) remains still problematic.

By considering first the presence of four different cations in the end-product, the formation of the desired compound requires for the different precursors homogeneity distribution at the molecular level in order to avoid secondary phases formation. By-products generally require high temperature heat treatment for getting long range ion diffusion processes leading finally to the desired stoichiometry. As a consequence, starting from an homogeneous distribution for the different cations in solution, a nearly pure crystallographic phase can be obtained if high temperature is reached as fast as possible. The second issue to be considered is to prepare a desired compound with control of grain size and distribution in order to obtain in fine high density values up to 95% of the theoretical density ones.

However the high temperature heat treatment generally required to produce the desired compound is accompanied by a grain coarsening process and increased porosity not satisfactory for getting highly dense products. A milling step is then required to reduce grain size. Unfortunately, such a process often introduce chemical contamination coming from the milling medium. Furthermore a crystallographic phase modification may occur leading to an amorphous phase when grain size is less than one micron. In order to avoid such a milling step, a new synthesis method was proposed.

The final goal is to develop a new procedure allowing the synthesis of a polycrystalline powder compound with the desired phase composition and appropriate microstructure. In the first part of this paper, the synthesis of a new precursor gel is presented. Different heat treatments have been applied in order to get the appropriate precursor powder. Results of microstructural characterisations are presented in the second part of this paper.

Experimental procedure

Precursors preparation and synthesis of final compounds

The precursor gel was prepared by dissolving gradually 40g of Agar-Agar powder in 775ml stirred hot water (95°C). For the preparation of aqueous solutions of metallic cations, $La(NO_3)_3.6H_2O$ (99,9% REO, Alfa Aesar), $Sr(NO_3)_2$ (p.a. Acros) and $Mg(NO_3).6H_2O$ (p.a. Acros) are used. Gallium nitrate was prepared from a concentrated nitric acid attack on metallic gallium (99,9% ABCR). The obtained solution was heated in Teflon oven to evaporate the

excess of nitric acid. The so-obtained gallium nitrate was dissolved in water quantitatively in a volumetric flask.

A precise volume of this solution and weights of other nitrate salts were placed in an Erlenmeyer. The quantities were chosen in a molar ratio to finally obtain the following desired stoichiometry $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (denoted LSGM12). Water was added to obtain a total volume of 225ml. Then, the aqueous nitrates solution was added to the Agar-Agar solution. The obtained solution is stirred a few minutes before pouring it in a 2 litres crystallizer and cooled down to room temperature overnight.

The formed gel is then cut in six pieces which are put in three beakers (two pieces per one beaker). Those are placed in a refrigerator at –77°C during two hours. After that, the gel was freeze-dried during 3 days.

The heat treatment was made in three steps. First, the freeze-dried gel is placed in a Teflon oven programmed to reach 120°C at a rate of 3°C/min. We observed that an autocombustion processes immediately in mass around 70°C. This comes presumably from an oxydo-reduction reaction between Agar-Agar reactant (reducing agent) and nitrates (oxidant agents). For eliminating all formed gases (CO_2, NO_2), the so-obtained black coloured gel residue is held two hours in the oven at 120°C. After this, in a second step, the so-called precursor of LSGM12 was mixed in a coffee grinder before being calcined at 570°C during 12 hours. After that, the powder colour is white. Then, this white powder was directly introduced in a furnace preheated at 650°C (sample 1) and 1200°C (sample 2). This heat treatment consists in the third step of the thermal cycle. Calcined powders were analysed by X-ray diffraction, scanning electronic microscopy, and specific surface area measurements.

A cylinder was prepared from sample 2 for dilatometric measurements. The cylinder was prepared by pressing uni-axially the powder at 500bar followed by an isostatic pressing at 1800bar. The cylinder dimensions were 5mm in diameter and 5,01mm in length. A disc was also prepared for granulometric analysis but only uni-axial pressing at 500bar was done. The dimensions were 5mm in diameter and 2mm in thickness. After dilatometric analysis, density measurements were made on the sintered cylinder by the Archimedes method.

Characterisations

In order to understand how microstructure and structure evolve with temperature, different characterisation techniques were used.

The decomposition of the intermediate products was monitored by thermogravimetric analysis and differential scanning calorimetry (Netzsch STA 449C) under air atmosphere at a rate of 5°C/min up to 1400°C.

XRD powder patterns were collected at room temperature for phase characterisation on a Siemens D5000 diffractometer (Cu Kα source) in a flat plate geometry. Data were recorded from 10 to 80° 2Θ-range with 0.04° step. Environmental scanning electronic microscopy (Philips ESEM XL30 FEG) was used to observe the morphology and particle size of the synthesized powders, fractured and etched samples. According to the samples, accelerating voltage of the electron beam was used between 10 and 15kV.

Specific surface area of the calcined powder was measured by BET (Brunauer-Emmett-Teller) isotherm technique (sorptomatic 1990 – CE Instrument) with nitrogen adsorption.

The particles size distribution of sample 2 (powders calcined at 1200°C), using a Malvern – Mastersizer 2000 – Hydro 2000S apparatus, was analysed in two steps. In the first step, a few hundred milligrams of the powder was suspended in several millilitres of water. This suspension was then placed a few seconds in an ultrasonic bath (Transsonic TS 540 Elma, 35kHz - 77W) before doing measurements. The second step consists in putting a prepared disc (see experimental procedure) in several millilitres of water before doing measurements. The disc broke up itself in ultrasonic bath without any prior milling.

The shrinkage of this material during sintering process was analysed by dilatometric measurements monitored by a LINSEIS LN75 dilatometer. Measurements were made from room temperature to 1450°C with a heating ramp of 5°C/min. A dwell of 2 hours was made at this temperature before cooling down to room temperature. All the measurements were made under air atmosphere.

The bulk density was measured by the Archimedes method in n-butanol on a cylinder sintered at 1450°C.

Results and Discussion

Using the precursor powder obtained after autocombustion, calcination temperature was determined from thermal analysis curves (TGA – DSC). It can be observed (figure 1) that final degradation temperature occurs at about 650°C. Unfortunately, when XRD powder patterns were recorded (figure 2 – curve b) for a sample calcined at this temperature, it was observed that crystallisation of some intermediate phases (not identified) has already started. Generally, these impurities appear before the formation of the desired phase (4, 7, 11, 13) and their elimination needs a higher temperature heat treatment. Therefore, in order to prevent their formation, we preferred to prepare a powder calcined at 570°C. At this lower temperature, XRD powder pattern (figure 2 – curve a) confirms that any crystallized phase was still formed. Consequently, this powder prepared at 570°C will be used to prepare sample 1 and 2.

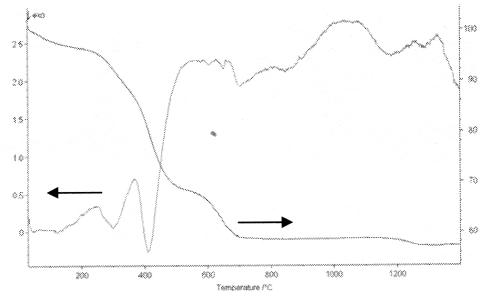


Figure 1 Thermogravimetric analysis and differential scanning calorimetry of the precursor obtained after autocombustion in an oven at 120°C.

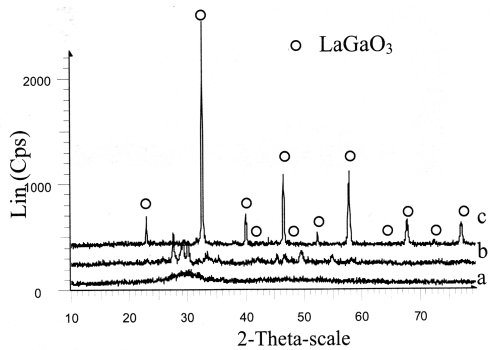
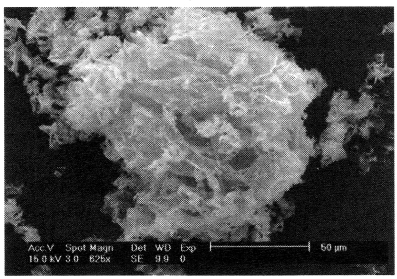
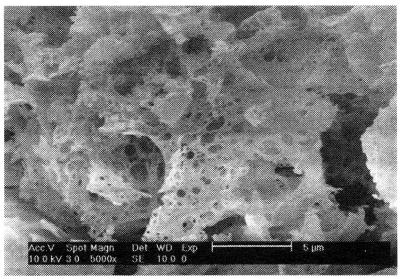


Figure 2 X-ray diffractogram of a) powder calcined at 570°C, b) sample 1 and c) sample 2

For sample 1, same results as before (figure 2 – curve b) have been reported. Curve c on figure 2 shows the XRD powder pattern of sample 2 where only a little peak corresponding to the $LaSrGaO_4$ phase, located at 31,44 2Θ-degree can be observed, all others reflection peaks correspond to the LSGM12 perovskite phase.

Similarly, in order to investigate how the microstructure of LSGM12 precursor powder evolves with increasing temperature, the prepared powders will be analysed simultaneously by scanning electronic microscopy (figures 3) and specific surface area measurements.





Figures 3 Electronic micrograph of a) powder obtained after autocombustion process and after a grinding step - b) powder calcined at 570°C. Holes apparition in the microstructure are observed

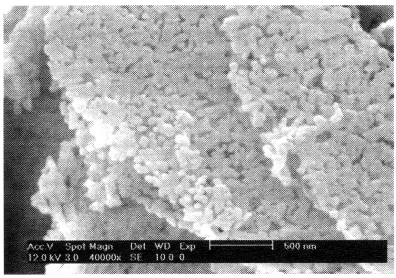


Figure 3 c) Electronic micrograph of sample 1. Crystallites emergence can be observed.

When temperature was increased, some chemical and/or physical processes on investigated powders were observed. The first occurred in the temperature range from 120°C to 570°C, where a decrease of the specific surface area (table 1) and an important weight loss (see on figure 1) were observed. This is probably explained by a volume reduction of the powder caused by the

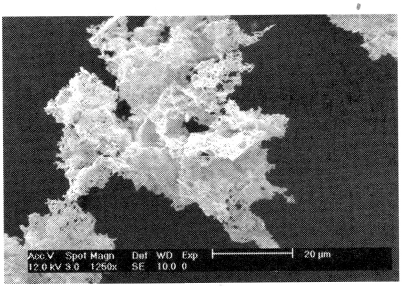
degradation of the residual carbonised compounds and by holes apparition in the bulk (see figure 3b).

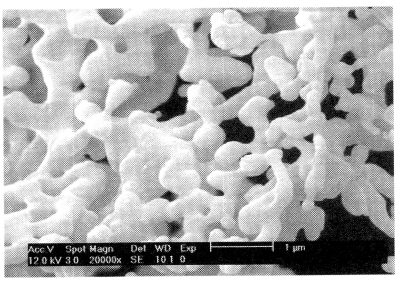
Table 1 Area specific surface

Temperature	After autocombustion	570°C	Sample 1 (650°C)	Sample 2 (1200°C)
Area specific surface (in m^2/g)	21	14	41,40	6

A second process seems to appear between 570°C and 650°C. On figure 3c, the emergence of the first crystallites corresponding to intermediate crystallographic phases observed on XRD patterns (see figure 2b) are visible. Concurrently this phenomenon can also explain the increase of specific surface area (see table 1).

A last process was observed beyond the temperature of 650°C (powder prepared at 1200°C). A grain growth process can be observed (see figure 3e). This is confirmed by a reduction of specific surface area measured on this sample (see table 1).





Figures 3d – 3e: Electronic micrograph of sample 2A.
Chain-like microstructure can be observed

In the following, additional characterisations have been made on powder synthesised at 1200°C (sample 2). As described in the experimental procedure, this powder was used to prepare a disc and a cylinder for particle size distribution and dilatometric measurements respectively.

When the prepared disc was observed by electron scanning microscopy (see figure 4), it appears that constitutive particles are disagglomerated. So, to confirm this observation, particles size distribution analysis was made on powder synthesized at 1200°C without uni-uniaxial pressure (sample 2A) and on the disc uni-uniaxially pressed (sample 2B).

For this purpose, both samples have been placed in an ultrasonic bath a few seconds before doing measurements. Graphical data are respectively reported on figure 5.

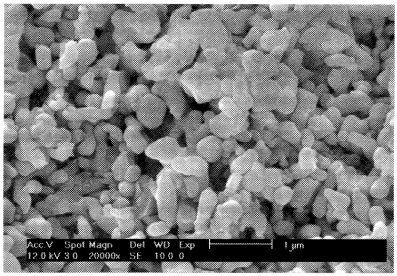


Figure 4 Electronic micrography of sample 2B. All particles seem to be disagglomerated by the pressing effect

The particle size distribution of sample 2A and 2B reported in figure 5 is comparable with typical sizes observed on figures 3d and 4 respectively. As described before, disc breaks up immediately in ultrasonic bath without any prior milling. This suggests that particles present inside the disc are really not agglomerated. Successive pressings on powder can eliminate the residual peak present on granulometric measurements made on the disc sample solution (arrow on figure 5). This peak results from agglomerated particles not broken yet.

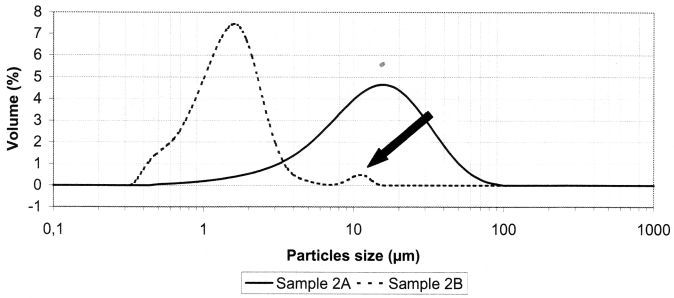


Figure 5 Particles size distribution of sample 2A (without uni-uniaxial pressure) and 2B (with uni-uniaxial pressure). Both samples underwent an ultrasonic treatment before measurement.

Due to the spongy aspect of the microstructure of sample 2 (see figure 3d), pressing effect probably causes a collapse of the structure giving free particles. To study the shrinkage evolution as a function of the temperature, dilatometric measurements were made on a cylinder. The dilatometric curve (figure 6) indicates that sintering process starts at 930°C. It is also visible from this curve

that a dwell made at 1450°C does not influence the sintering process. This step promotes certainly only a grain growth process. Bulk densities measured by the Archimedes method on sintered samples lye between 95 and 96% of the theoretical density value (6.68g/cm^3) (14).

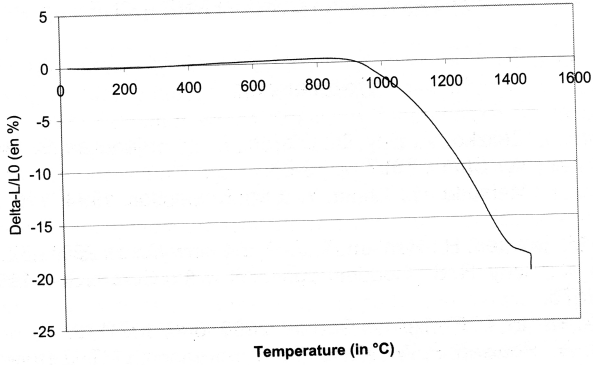


Figure 6 Dilatometric curve obtained at a rate of 5°C/min to 1450°C where a dwell was made during 2 hours.

Conclusion

The aim of this study was to demonstrate that it is possible to control phase crystallisation and microstructure by conducting synthesis under appropriate conditions. The method used starts from a new Agar-Agar nitrate gel combustion synthesis process which allows to separate the synthesis process from sintering ones. Advantages of this new experimental procedure to produce $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ powder can be divided into structural and microstructural parts:

- intermediate phase crystallisation described as "impurities" can be avoided by introducing gel precursors directly in a furnace preheated
- a well-defined single perovskite phase was obtained
- particles size distribution of LSGM12 can be controlled without any milling preventing introduction of any eventual chemical contamination

Acknowledgements

The autors express theirs thanks to CGRI (Commissariat Général aux Relations Internationales de la Communauté française de Belgique) for financial support . This project was performed as a part of CGRI – FNRS – CNRS agreement.

References

(1) Drennan, J.; Zelizko, V.; Hay, D.; Ciacchi, F. T.; Rajendran, S.; Badwal, S. P. S. *J.Mater.Chem.* **1997**, *7*, 79-83.
(2) Ishihara, T.; Matsuda, H.; Takita, Y. *J.Am.Chem.Soc.* **1994**, *116*, 3801-3803.
(3) Lerch, M.; Boysen, H.; Hansen, T. *J.Phys.Chem.Solids* **2001**, *62*, 445-455.
(4) Huang, K.; Tichy, R. S.; Goodenough, J. B. *J.Am.Ceram.Soc.* **1998**, *81*, 2565-2575.
(5) Azad, A. M.; Er, L. F. *J.Alloys Compd.* **2000**, *306*, 103-112.
(6) Tao, S. W.; Poulsen, F. W.; Meng, G. Y.; Sorensen, O. T. *J.Mater.Chem.* **2000**, *10*, 1829-1833.
(7) Huang, K.; Goodenough, J. B. *J.Solid State Chem.* **1998**, *136* , 274-283.
(8) Mathews, T.; Sellar, J. R.; Muddle, B. C.; Manoravi, P. *Chem.Mater.* **2000**, *12*, 917-922.
(9) Tao, S. W.; Wu, Q.; Zhan, Z.; Meng, G. Y. *Solid State Ionics* **1999**, *124*, 53-59.
(10) Schulz, O.; Martin, M. *Solid State Ionics* **2000**, *135*, 549-555.
(11) Cong, L.; He, T.; Ji, Y.; Guan, P.; Huang, Y.; Su, W. *J.Alloys Compd.* **2003**, *348*, 325-331.
(12) Mathews, T.; Sellar, J. R. *Solid State Ionics* **2000**, *135*, 411-417.
(13) Tarancon, A.; Dezanneau, G.; Arbiol, J.; Peiro, F.; Morante, J. R. *J.Power Sources* **2003**, *118*, 256-264.
(14) Gorelov, V. P.; Bronin, D. I.; Sokoloa, J. V.; Nafe, H.; Aldinger, F. *J.Eur.Ceram.Soc.* **2001**, *21*, 2311-2317.