



Processing of (La,Sr)(Ga,Mg)O₃ Solid Electrolyte

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Abstract. The preparation of La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ (LSGM) powders by the mixed oxide route requires significantly longer annealing times of about 60 h compared to the combustion synthesis and Pechini method which requires less than 6 h. In comparison to the mixed oxide route the soft chemical synthesis methods produce significantly smaller grain sizes after solid-state reactive sintering, which is due to the significantly shorter annealing times in order to achieve well crystallized ceramics. It is emphasized that at 1400°C in air single phase LSGM samples with the composition La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ could be prepared neither by the mixed oxide route nor the combustion synthesis or the Pechini method, but only at higher temperatures, for example 1500°C. Taking the results of the dilatometric studies for processing of LSGM ceramics into account, it is obviously that sinter temperatures of above 1300°C in air are required in order to prepare dense LSGM ceramics.

Keywords: (La,Sr)(Ga,Mg)O₃ solid electrolyte, processing

Introduction

Lanthanum gallate (LaGaO₃) ceramics that have been doped with strontium and/or magnesium are known to have superior oxygen ion conducting properties, [1–3] in comparison, for instance, to even yttria-stabilized zirconia electrolytes. The conventional “solid-state reactive firing” method was used in order to synthesize strontium and magnesium doped LaGaO₃ ceramics [1–4]. The promising electrode performance [5] and the mechanical properties [6–8] of these ceramics have been reported. Stevenson et al. [9] first used the technique of combustion synthesis [10–15] to successfully prepare strontium and magnesium doped LaGaO₃ powders. More recently, the combustion synthesis of strontium and magnesium doped LaGaO₃ ceramics has been used also for the manufacture of thin films of the same [16]. In contrast, a coprecipitation route (with NH₄OH addition) from an aqueous mixture of the acetates of lanthanum, strontium, and magnesium, as well as that of gallium nitrate, has been attempted by Huang et al. [17]. In a separate study, those researchers [18] also briefly mentioned the use of a sol-gel method for the synthesis of strontium- and magnesium-doped LaGaO₃ ceramic powders. Recently, Tas et al. presented a

detailed study of the preparation of Sr and Mg doped LaGaO₃ powder via the Pechini method [19].

For the processing of ceramic materials, for example bulk ceramics, thick films, and ceramic foils, the knowledge of the preparation of ceramic powders with controlled grain size is eminent. Using the conventional mixed oxide route slow reaction kinetics of the often μm-sized crystalline precursors powders could prohibit the formation of single phase material. Therefore, also wet chemical methods were studied. These methods provide a mixing of the elements at an atomic scale which is known to accelerate the reaction of the phase formation. Therefore, in this work the preparation of powders of Sr and Mg doped LaGaO₃ with the composition La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-x} (LSGM) by different methods is studied with respect to grain size and carbon and nitrogen content as well as phase purity.

Experimental

Mixed Oxide Route

Samples with the composition La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ were prepared using La₂O₃, SrCO₃, MgO, and Ga₂O₃

(Aldrich Chemie, purity >99%). The starting materials were mixed and homogenized in an agate ball mill. The powder were calcined at 1200–1400°C in air for 6 h. Subsequently, the powders were ground in a ball mill and sieved (mesh 63 μm). The powders were annealed at different temperatures (1100, 1250, 1400, 1500°C, heating rate: 5°C/min) in air. At 1500°C, the samples were annealed for 24 h and at the other temperatures for 24 to 60 h with intermediate regrinding by ball milling. Finally, the samples were furnace cooled to room temperature. In addition, a calcined powder was cold isostatically pressed at 625 MPa in order to form a cylindrical sample (length 8 mm, diameter 4 mm) and sintered at 1400°C in air for 60 h with intermediate regrinding and pressing.

Combustion Synthesis

With combustion synthesis the same sample ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$) was produced as with the mixed oxide route. However, the starting materials were $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Merck, Darmstadt, Germany), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.99%, Sigma, USA), Sr-acetate (99%, Merck) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Merck). The powders were prepared by a modified glycine-nitrate-process using urea as a fuel. For each sample, appropriate volumes were taken from defined aqueous stock solutions of the cation-nitrates (purity: 99.99%) and mixed corresponding to a 5 g yield of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ ceramics. The amount of urea added was calculated following a method proposed by Jain et al. [20] to have a complete combustion. For the present synthesis, solutions rich in fuel (combustion parameter $\Phi_e \approx 2$) were prepared. Excess water was slowly evaporated from each solution until gelation, before the mixtures were transferred into covered aluminum crucibles and placed into a box furnace. Thermal treatment was carried out in air using an one-step process by first bringing samples to the ignition temperature of about 250°C and subsequently to the annealing temperature, i.e., 600 to 1400°C with a heating rate of 5°C/min. All samples were furnace-cooled to room temperature.

Pechini Method [21]

With this method the same starting materials were used as with the combustion synthesis. Stoichiometric amounts of nitrate stock solutions corresponding to a

5 g yield of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ ceramic were first mixed together in a 50 mL-capacity glass beaker to obtain a total solution volume of ~ 25 mL. A mixture of 60 wt% citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7$, 99.9%, Merck) and 40 wt% ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99%, Merck) was then added (molar ratio of “citric acid-to-total cations” being kept constant at 1.88) to this cation solution. This solution was homogenized by stirring at room temperature for 1 h. The resulting clear solution was then evaporated (in 3 h) on a hot plate until first a clear yellow gel, then a dark brown resin, formed. The obtained resins (following overnight drying in an oven at 100°) were scraped off from the beakers with a spatula, then ground by hand using an agate mortar/pestle, and finally calcined isothermally for 6 h in air over the temperature range of 200° to 1400° with a heating rate of 5°C/min. Finally, the samples were furnace cooled to room temperature.

Characterization

The phase constitution of the powders was analyzed, as a function of temperature, using a powder X-ray diffractometer (D-5000, Siemens GmbH, Karlsruhe, Germany) with monochromated $\text{Cu K}_{\alpha 1}$ radiation (40 kV, 30 mA, scan rate of 0.2° 2 θ /min).

The residual C and N contents of the uncalcined and calcined powders were determined by the method of combustion-IR absorption (CS-800, Eltra GmbH, Neuss, Germany). ICP-AES analyses were also performed to obtain quantitative elemental information (JY-70Plus, Jobin Yvon S.A., Longjumeau, France) on the samples. Morphology of the powders was monitored by scanning electron microscopy (DSM 982-Gemini, Zeiss GmbH, Oberkochen, Germany).

The bulk densities of some of the green and sintered samples were measured by the Archimedes method following the ASTM C372-73 standard [22].

Dilatometry

A dilatometer run (VIS 401, Bähr GmbH, Bremen, Germany) was performed using a cylindrical sample of LSGM powders (length: 8 mm, diameter: 4 mm) which were prepared by the mixed oxide route and cold isostatically pressing at 625 MPa. The annealing rate was maintained at 10°C/min up to 500°C, and subsequently, at 3°C/min up to 1450°C in air.

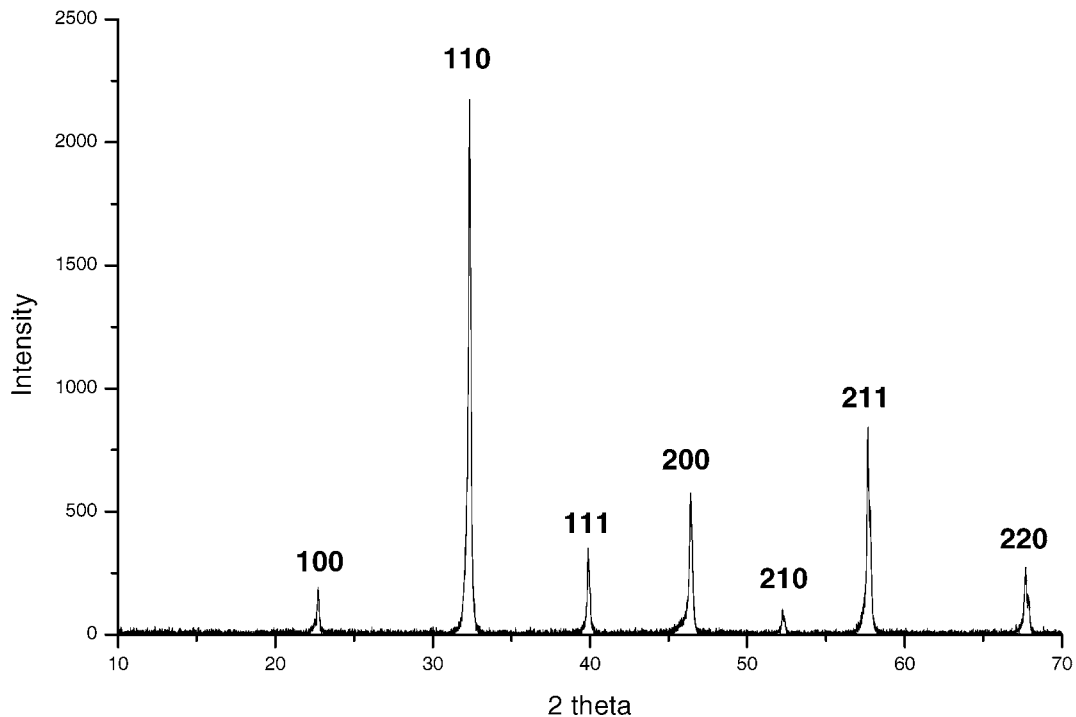


Fig. 1. XRD pattern of cubic LSGM powder prepared via the mixed oxide route at 1500°C in air. Miller indices are given for reflections attributed to cubic LSGM [4].

Results

Mixed Oxide Route

Using the mixed oxide route, after 24 h at 1400°C La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ powders consist of a high content of LSGM and about 5 vol% of LaSrGa₃O₇. Even longer annealing times, for example 60 h, do not result in phase pure LSGM samples. However, increasing the firing temperature from 1400°C to 1500°C removes the secondary phases. LSGM annealed at 1500°C has found to be cubic confirming the results of [4] (Fig. 1).

At temperatures below 1400°C, the compound La₂SrO₄ has often been observed in the powder (Fig. 2). Due to the hygroscopic character of this phase, pressed samples of that powder swell during storing. However, the phase disappears when the powder is annealed at 1400 to 1500°C for 48 h with intermediate regrinding.

Micrographs of the pressed sample sintered at 1400°C for 60 h show that the ceramic has a grain size of 20 to 50 μm (Fig. 3). Density measurements by the Archimedes method give a value of 95% of

the theoretical density. Carbon analysis of the powder prepared at 1400°C reveals a carbon content of about 0.2 wt%.

Combustion Synthesis

After combustion, powders exhibit hard agglomerates with a porous nano-structured morphology which in most cases is X-ray amorphous (Fig. 4). They show a high tendency to coarsening and crystallization at temperatures as low as 600°C, when annealed for at least 1 : 30 h. At temperatures below about 600°C the powders remain amorphous determined by XRD. Beside La₂O₃, LaOOH, and LaSrGa₃O₇, LSGM starts to crystallize at temperatures of about 800°C. With increasing temperature the volume content of LSGM significantly increases. At temperatures of above 1200°C, the sample consists only of LSGM and LaSrGa₃O₇ which has been reported to be in thermodynamic equilibrium [23, 24]. Therefore, it is not possible to distinguish, whether in the prepared powder LaSrGa₃O₇ is metastable or represents thermodynamically stable conditions at temperatures above 1000°C in air. The

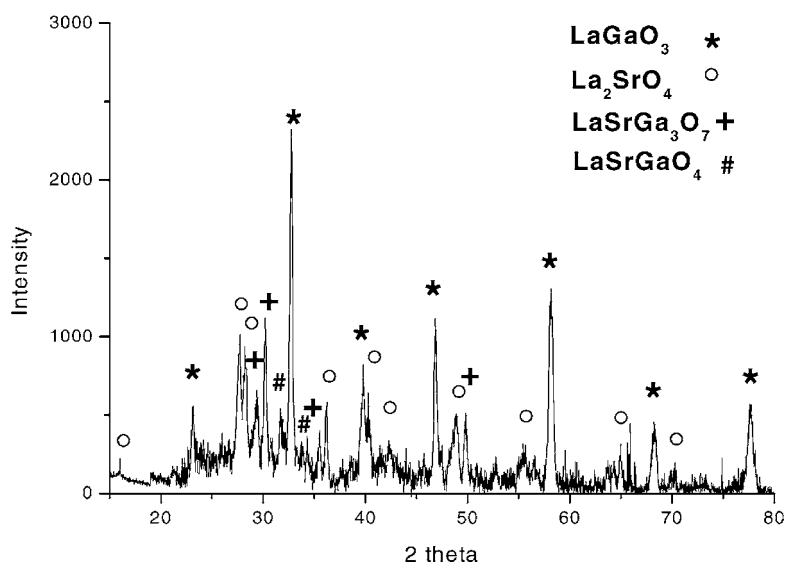


Fig. 2. XRD pattern of a LSGM sample prepared by the mixed oxide route calcined at 1200°C in air.

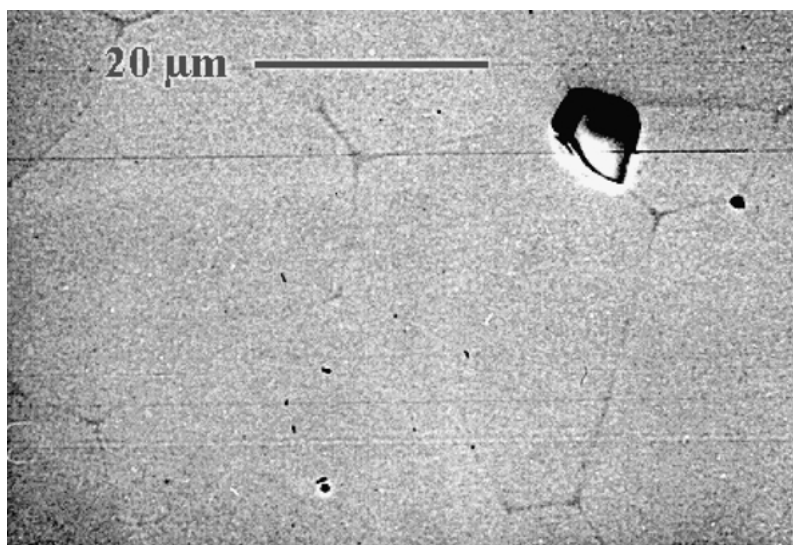


Fig. 3. Micrograph of a LSGM ceramic made of LSGM powder at 1400°C in air prepared via the mixed oxide route.

formation of La_2SrO_4 at temperatures below 1400°C is not observed.

At temperatures of 1400°C, the powders were found to contain about 5 vol% of $\text{LaSrGa}_3\text{O}_7$ (Fig. 5). Single phase products were prepared by annealing at temperatures of 1500°C. Residual carbon analysis reveal that the powders contain about 0.01 wt% carbon after

annealing at 1400°C. With decreasing annealing temperatures the carbon content increases significantly (Fig. 6). The nitrogen content of the powders annealed at 1400°C were analyzed to be 0.34 wt%. SEM images of the powder compacts annealed at 1400°C for 3 h show well crystallized grains of LSGM with a grain size of 2 to 4 μm (Fig. 7).

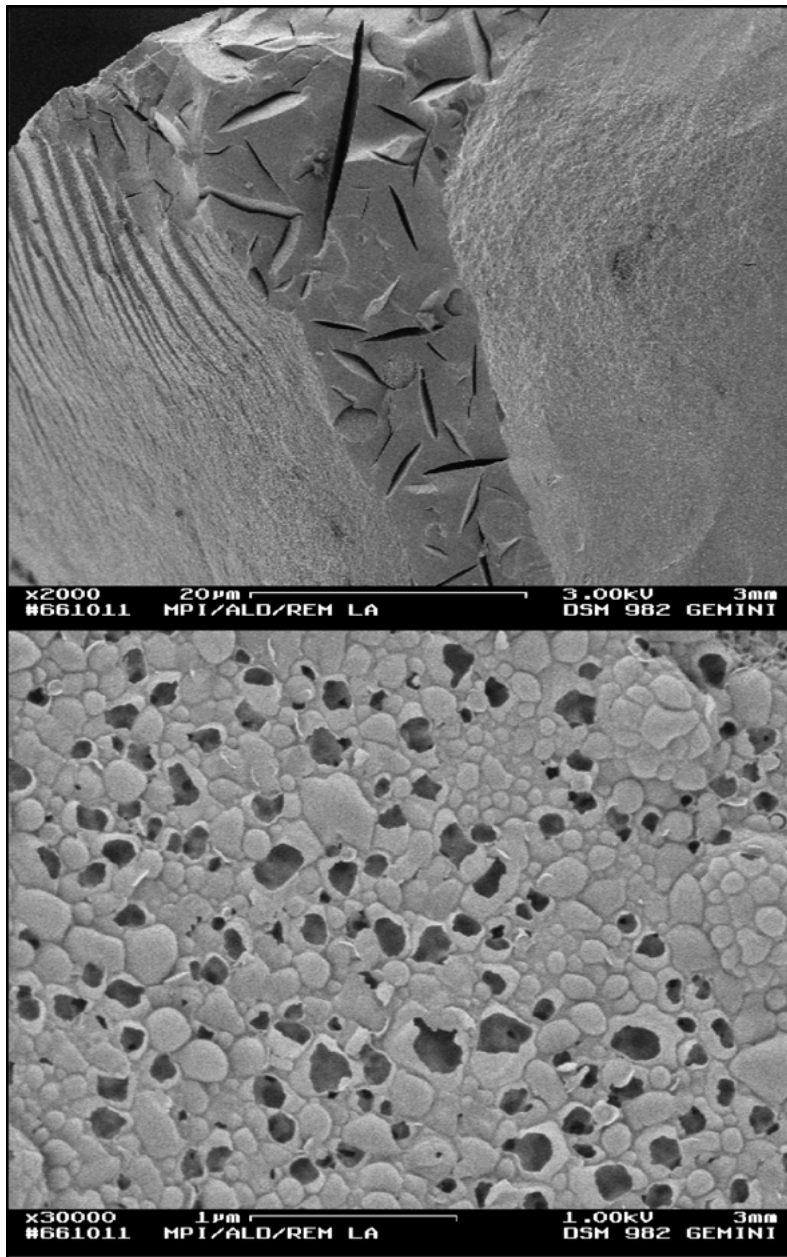


Fig. 4. Micrograph of a hard agglomerate with nano structured morphology (top). Below: blow up of the agglomerate showing nano sized grains and pores (black).

Pechini Method [21]

LSGM resins calcined for 6 h at 500° were found to be X-ray amorphous (Fig. 8). After calcination at 700°C for 6 h, LaOOH and LaSrGa₃O₇ were observed to be the

first two phases to crystallize. LSGM was first observed to crystallize after calcination at 850° for 6 h. Precursor powders consisted of a mixture of four or five phases over the calcination temperatures of 850 to 1000°C. Even after calcination at 1400°C for 6 h, the powders

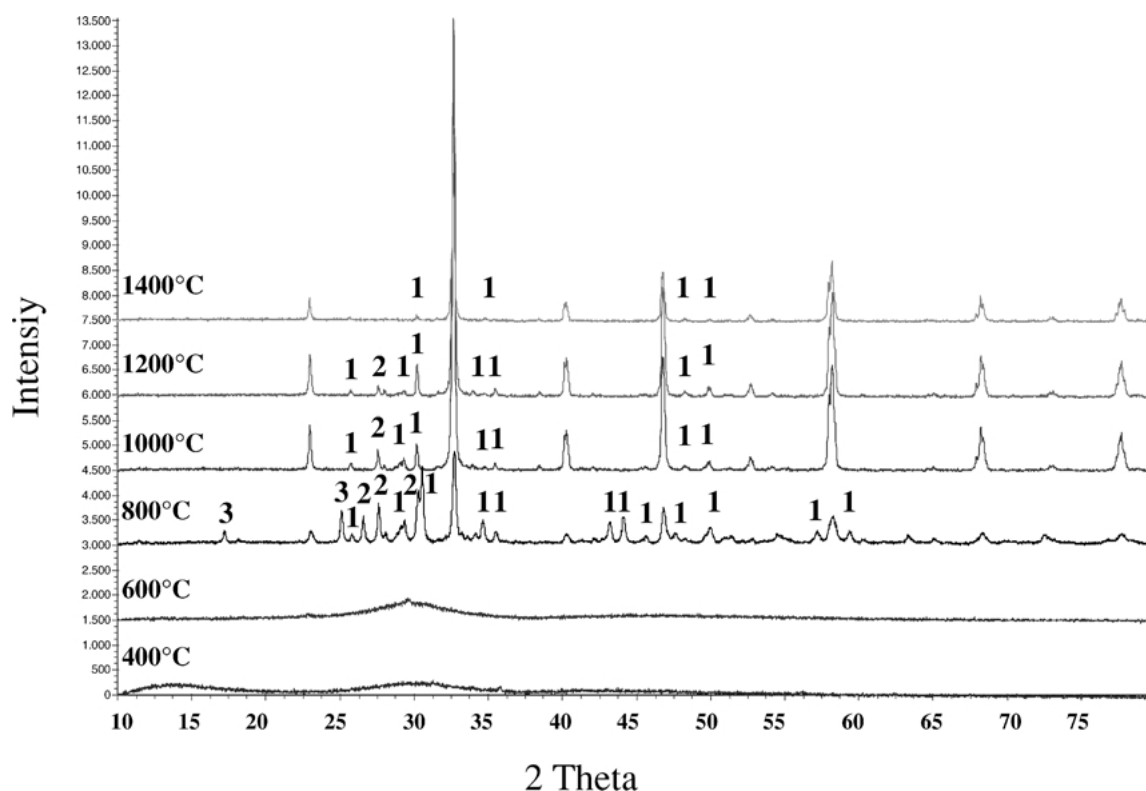


Fig. 5. XRD patterns of LSGM powders prepared by the combustion synthesis and annealed at different temperatures. (1) $\text{LaSrGa}_3\text{O}_7$; (2) LaOOH ; (3) La_2O_3 . All other reflections are attributed to LSGM.

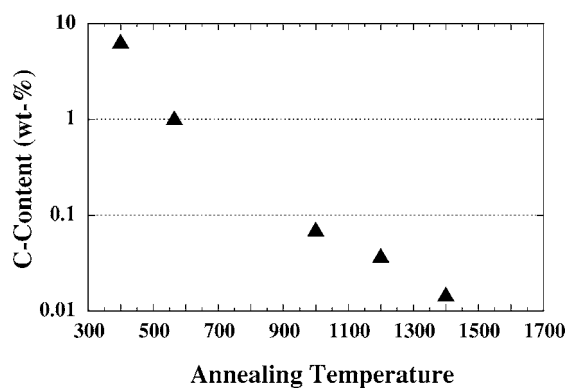


Fig. 6. Carbon content of LSGM powders prepared by the combustion synthesis and annealing at different temperatures.

were still not single-phase and contained about 5 vol% of the phases LaSrGaO_4 and $\text{LaSrGa}_3\text{O}_7$. The formation of La_2SrO_4 at temperatures below 1400°C was not observed.

The results of residual carbon analyses after annealing at different temperatures are shown in Fig. 9. The

carbon content decreases significantly with increasing temperature down to 0.014 wt% at about 1400°C . The nitrogen content of the 100°C -calcined precursor samples was found to be in the range of 1.05 to 1.2 wt%, but with increasing calcination temperatures (starting from 200°C) it decreases to levels below the reliable detection level (i.e., 0.01 wt%) of the equipment used. The fracture surface of a pellet of the powder which was cold isostatically pressed at 650 MPa and then annealed at 1400°C for 8 h in air show a final grain size of $\leq 2 \mu\text{m}$ (Fig. 10). The density of pellets of LSGM sintered at 1400°C in air is 85% determined by the Archimedes method.

Dilatometry

The result of the dilatometric investigation of a LSGM powder compact prepared by the mixed oxide route reveals a high shrinking rate at temperatures between 1300 and 1450°C in air (Fig. 11). At temperatures below 1200°C , no densification of the sample is observed.

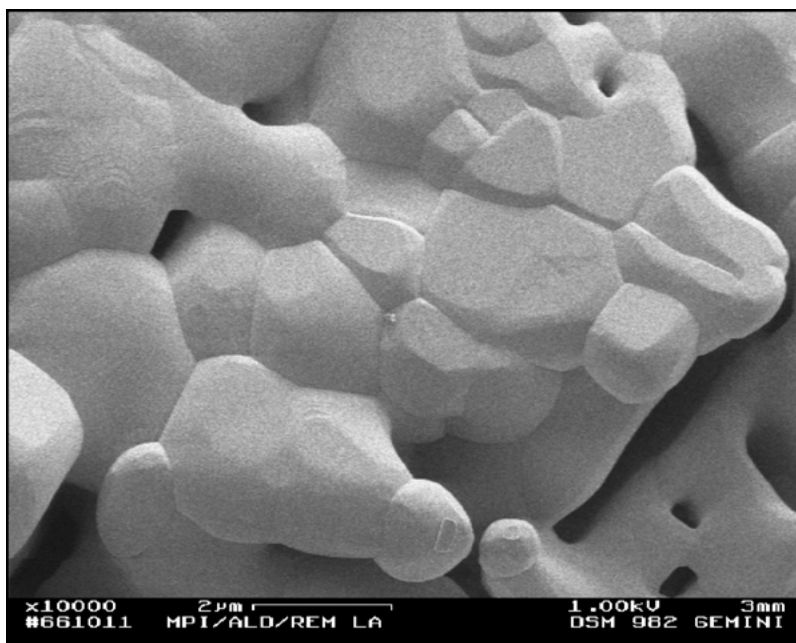


Fig. 7. Fracture surface of a powder compact prepared by the combustion synthesis and annealed at 1400°C in air.

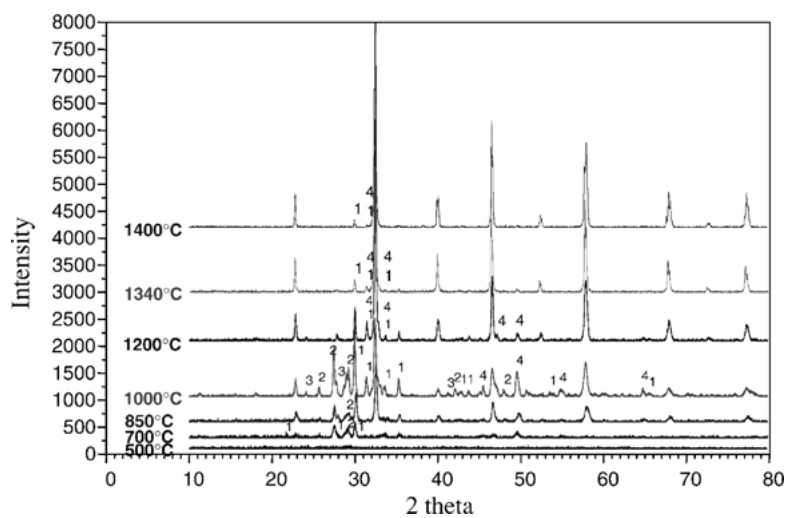


Fig. 8. XRD patterns of LSGM powders prepared by the Pechini method and annealed at different temperatures. (1) LaSrGa₃O₇; (2) LaOOH; (3) La₂O₃; (4) LaSrGaO₄. All other reflections are attributed to LSGM.

Discussion and Conclusion

The preparation of LSGM powders by the mixed oxide route requires significantly longer annealing times of about 60 h compared to that by the combustion synthesis and Pechini method [21], which both require less

than 6 h. This phenomenon is supposedly due to slow diffusion coefficients of the cations in the crystalline precursor material compared to those in the amorphous precursors.

At temperatures below 1400°C the compound La₂SrO₄ has been observed in the powders prepared

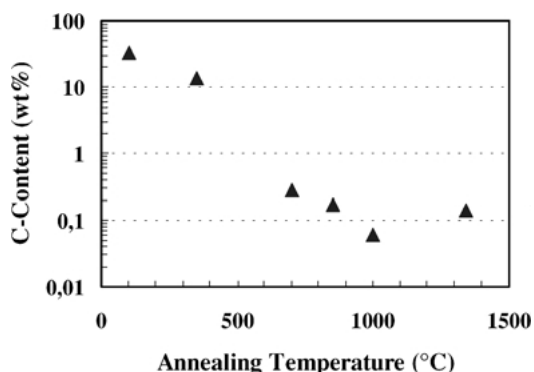


Fig. 9. Carbon content of LSGM powders prepared by the Pechini method and annealing at different temperatures.

by the mixed oxide route. From phase diagram studies in the system $\text{La}_2\text{O}_3\text{-SrO-Ga}_2\text{O}_3\text{-MgO}$ it is known that this phase is not in equilibrium with LSGM and therefore, indicate metastable conditions in the powders at temperatures below 1400°C [23, 24]. It is possible to decompose the phase by annealing the powder at temperatures of 1400 to 1500°C and intermediate regrinding. However, this treatment is very time consuming and it is recommended to avoid the formation

of this phase by calcining the powders at temperatures of 1400°C or above.

In comparison to the mixed oxide route, the soft chemical synthesis methods produce significantly smaller grain sizes after solid-state reactive sintering, which is due to the significantly shorter annealing time in order to achieve well crystallized ceramics, and hence, provides a clear advantage, for example for Wet-Powder- or Plasma-Spraying of $10\text{--}20\ \mu\text{m}$ thick LSGM films for applications as electrolytes of Solid Oxide Fuel Cells (SOFC's). In addition, the formation of the metastable phase La_2SrO_4 was not observed which indicates that thermodynamically stable conditions are attained much faster from the amorphous precursor. However, the measured density of the sintered pellets was found to be around 85% of the theoretical, owing to the presence of hard agglomerates in the green powders. This value is significantly lower compared to the density of 95% of sintered pellets prepared by the mixed oxide powder. A very low densification rate of chemically-prepared LSGM samples was also observed by Huang and Goodenough [18], and the data agree well with the values reported there.

With the preparation routines studied in this work, powders with low carbon contents were produced also carbon rich precursor materials, such as carbonates or

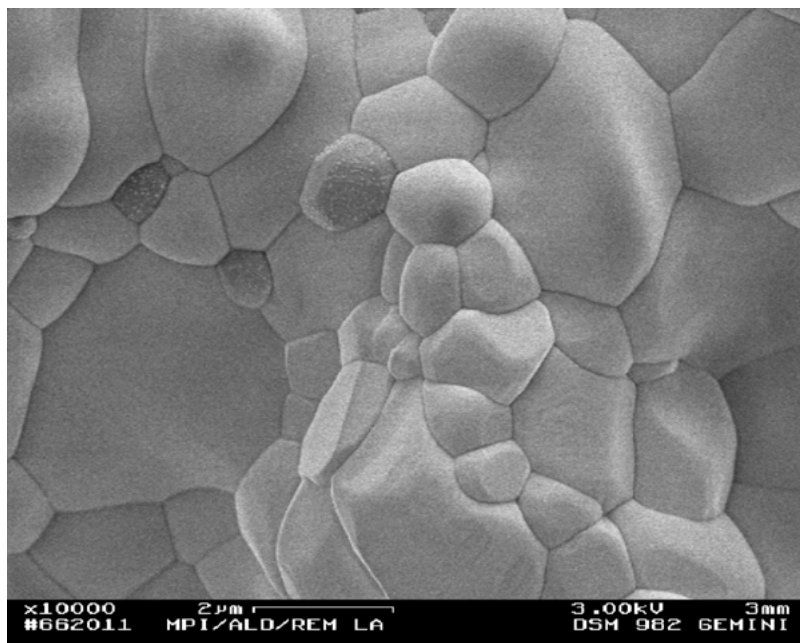


Fig. 10. Fracture surface of a powder compact of LSGM powder prepared by the Pechini method [21] and annealed at 1400°C in air.

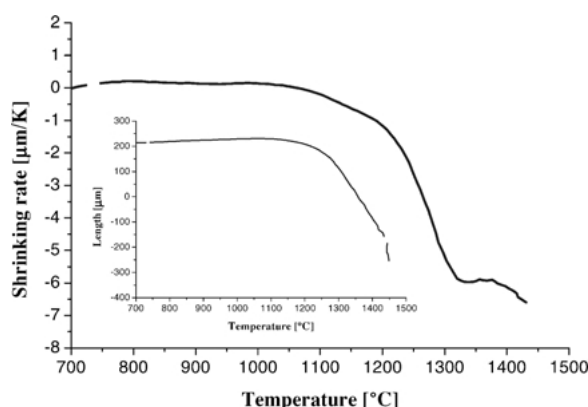


Fig. 11. Shrinkage rate of a LSGM powder compact prepared by the mixed oxide route at 1400°C in air. The insert shows the shrinking of the powder compact vs. temperature.

acetates, were used. This fact is of considerable interest, because residual carbon in the powders may affect the microstructure of LSGM ceramics, for example due to evaporation of CO₂ during annealing causing the formation of additional pores in ceramic materials or the change of the composition of the gas phase during plasma spraying.

Taking the results of the dilatometric studies into account, it is obviously that sintering temperatures of above 1300°C in air are required in order to prepare dense LSGM ceramics. However, as the studies show that quiet high amounts of second phases exist in the samples even at 1300–1400°C, sintering temperatures of 1450–1500°C are recommended.

It is emphasized that single phase LSGM samples with the composition La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ could be prepared neither by the mixed oxide route nor the combustion synthesis or the Pechini method [21] at 1400°C in air. The samples contain the compounds LaSrGa₃O₇ and/or LaSrGaO₄. Both compounds are known to be in thermodynamic equilibrium with LSGM at 1400°C in air. At higher temperatures, for example 1500°C, the samples are single phase. With respect to the XRD patterns of the powders prepared by the combustion synthesis and Pechini method [21], respectively, it is obviously that the volume content of LSGM increases with increasing temperatures. This observation indicates that the single phase region of LSGM continuously grows with increasing temperature and that at 1400°C

in air, the composition La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃ lies outside the homogeneity region of the LSGM phase, whereas, at 1500°C it appears to be inside the homogeneity region [24]. So, it is believed that the solid solubility of Sr and Mg in LaGaO₃ is temperature dependent and increases with increasing temperature up to 1500°C. Detailed studies of the extension of the homogeneity region of Sr and Mg doped LSGM are in progress.

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