

# Densification of LSGM electrolytes using activated microwave sintering

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## Abstract

Lanthanum gallate doped with alkaline rare earths (LSGM) powders were densified using an activated microwave sintering process for developing a dense stable electrolyte layer for applications in intermediate temperature-solid oxide fuel cells (IT-SOFCs). Due to heat generation in situ, the process of sintering gets activated with faster kinetics compared to a conventional sintering process. The effect of various microwave process parameters on the microstructure and phase formation was studied. The sintered pellets were characterized using scanning electron microscopy-energy dispersive analysis (SEM-EDAX), and X-ray diffraction (XRD). The density of LSGM pellets microwave sintered at 1350 °C for 20 min is greater than 95% theoretical density with a fine grained microstructure (~2–3 μm) and without the presence of other phase(s).

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## 1. Introduction

Conventional solid oxide fuel cells (SOFCs) are based on yttria-stabilized zirconia (YSZ) electrolytes. Although the conventional YSZ electrolyte has the adequate electrolyte domain and ionic conductivity above 700 °C, the electrolyte layer becomes ineffective and unattractive at lower temperatures [1] due to a significant increase in the bulk resistance. Because of higher ionic conductivity at lower temperatures, several doped (with gadolinia, samaria, etc.) ceria-based electrolyte materials have been considered for lower temperature applications (500–700 °C). However, there remains a concern about oxygen loss from the crystal lattice in the fuel atmosphere and resulting structural instability during thermal cycling operation (lattice expansion and contraction). Perovskite oxides of type ABO<sub>3</sub> have stable crystal structures and furthermore, a large number of oxide ion vacancies can be introduced into the lattice by the partial substitution of cation A or cation B with lower valence cations. Lanthanum gallate, LaGaO<sub>3</sub> perovskites with proper substitutions have proven electrolyte domain and high oxygen ionic conductivity at lower temperature [2]. Fig. 1 compares the conductivities of various solid electrolytes [1].

Ionic conductivity of lanthanum gallate has been further improved by substituting divalent acceptor cations at A-sites/B-sites of the perovskite [3]. Ishihara et al. reported that simultaneous substitutions of Sr<sup>2+</sup> in the A-sites and Mg<sup>2+</sup> in the B-sites increase the conductivity substantially [4]. Feng and Goodenough reported that Sr- and Mg-doped lanthanum gallate (LSGM) has higher conductivity values at lower temperatures as compared to YSZ materials [5]. Petric and Huang corroborated these results further [6]. Skowron et al. [7] have shown that, oxygen vacancies are ordered into planes at low temperature and become disordered at 500–600 °C. This corresponds to the observed decrease in activation energy since disordered vacancies are more mobile where as ordered vacancies act as traps. The conductivity exhibits a maximum as a function of Mg concentration (or oxygen vacancy concentration) for a given temperature. As the temperature is increased, more vacancies can be disordered and therefore a higher concentration of Mg yields better conductivity.

The thermal expansion of LSGM has been reported to be 11–12 ppm/K, a good match with the standard Sr-doped LaMnO<sub>3</sub> (LSM) cathode material. Unlike YSZ, LSGM is chemically compatible with other perovskite cathodes, including LaCoO<sub>3</sub> substituted with Sr and Fe (LSCF).

In spite of its excellent combination of properties for intermediate temperature applications, existing processing techniques for LSGM remain inadequate for producing stable

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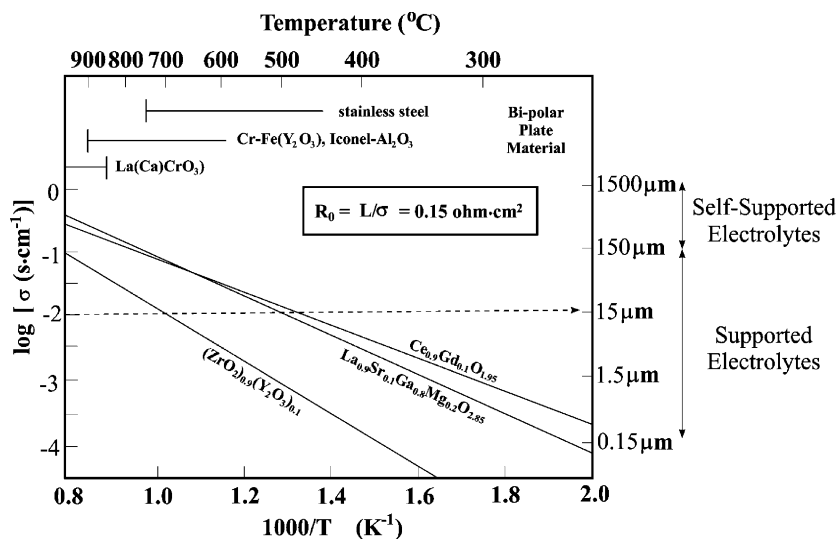


Fig. 1. A comparison of ionic conductivities of potential electrolyte materials for IT-SOFC applications [1].

electrolyte structures. The synthesis of LSGM powders of suitable composition and their sintering is a major hurdle in the future development of these materials. Initial development of these materials utilized conventional solid-state reactions of various constituent oxides [8,9]. This process is tedious because the procedure requires firing the ingredients at high temperature, regrinding and followed by final sintering at a very high temperature (typically 1470–1500 °C) for 15–35 h. This is because there are hard agglomerates in the powder and they require long soaking times to produce high density. Co-precipitation [10] and sol-gel techniques [11] have been tried. Alternatively, LSGM can be synthesized by a variety of reactive processes (e.g. spray pyrolysis, Pechnie Process or Glycine Nitrate Process). Tas et al. [11], Majewski et al. [12] and Tao et al. [13] used both the Pechnie Process and the Glycine Nitrate Process. Maric et al. [14] used a spray pyrolysis technique to synthesis the LSGM powders. The Glycine Nitrate synthesized LSGM powders were also densified by Stevenson et al. [15] and Baskaran et al. [16]. It is generally believed that in spite of the use of advanced chemical processing techniques, the sintering of LSGM needs high temperatures, albeit at a significantly lesser soaking period. Due to the high temperature exposure, general features of the resulting microstructure may not be desirable. First, the grain size is large (approximately 10–20 μm). Second, secondary phases such as SrLaGa<sub>3</sub>O<sub>7</sub> and La<sub>4</sub>Ga<sub>2</sub>O<sub>9</sub> are often detected along the grain boundaries. These microstructural features deteriorate both mechanical as well as electrical properties of LSGM.

Thus, LSGM materials may serve as effective electrolytes for intermediate temperature-solid oxide fuel cells (IT-SOFCs) operating between 500 and 700 °C in view of their conductivity at those temperatures and compatibility with electrode materials. However, sintering the powders using conventional procedures yields a large grained material with undesirable phases. The presence of these phases

affects the cells from proper functioning. Hence, sintering of LSGM powders is an important step towards the fabrication of electrolytes.

In this work, an activated sintering process is reported for fabricating dense LSGM electrolytes. The present effort utilizes microwaves as an activated sintering technique. It is expected that this will result in high density while retaining fine grain structure without the formation of undesirable phases. A short exposure at moderate temperature reduces the energy costs with desirable properties.

## 2. Experimental procedure

LSGM powders were prepared by the method used by the glycine nitrate auto-ignition process [15,16]. The powders were characterized by X-ray diffraction (XRD; Siemens D5000) technique, using with Cu K $\alpha$  radiation at 40 kV and 30 mA in the range  $2\theta = 12\text{--}60^\circ$ . Scanning electron microscopy (SEM; Leo 1530, 30 kV) was carried out to ascertain the powder morphology and the extent of agglomeration of the solid combustion residues. Subsequently, the as-synthesized powders were cold isostatically pressed (Iso-Spectrum CP2-60) at 25 ksi pressure for 10 min and the resulting green compacts were subjected to sintering in an industrial microwave furnace (Microwave Materials Technology, Knoxville, TN). The system as shown in Fig. 2 has a variable-power output magnetron source capable of operating from 0 to 3 kW at 2.45 GHz. The samples were placed within a box, constructed out of Al<sub>2</sub>O<sub>3</sub> fiberboard. The fibers are low density and insulating but not significantly absorptive at the operating frequency. The box also contains strips of dense SiC to act as susceptors. The gap between the sample and the susceptors were filled with an alumina fiber blanket. Different microwave input powers were used namely, 1.5, 1.75, 2.0 and 2.25 kW with duration

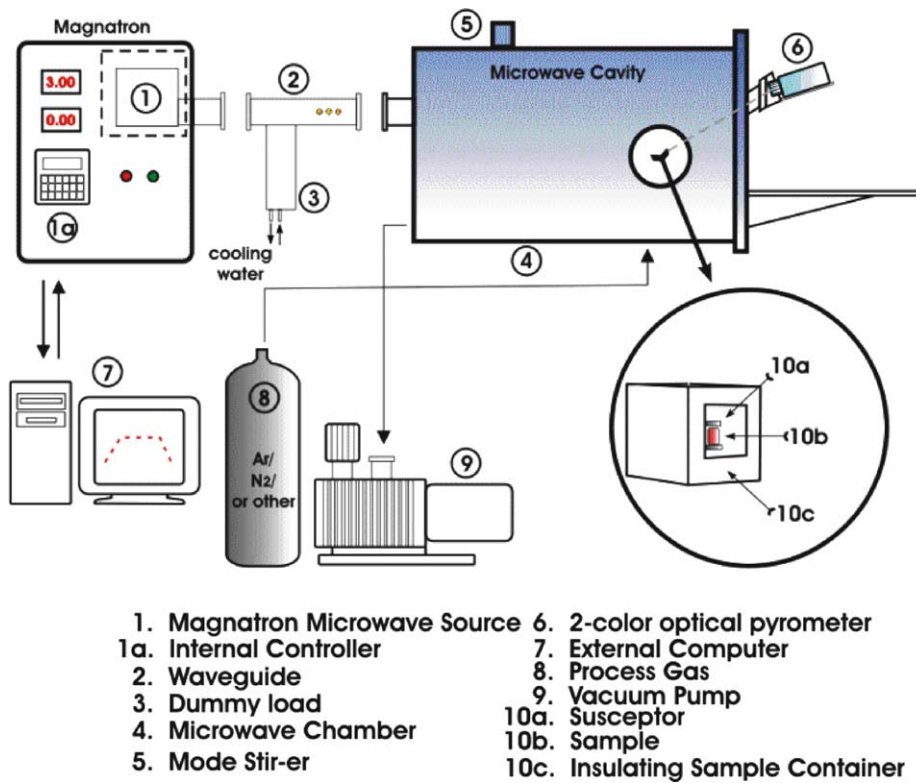


Fig. 2. A schematic of the microwave furnace.

time at these power levels of 20 and 30 min. All the sintered pellets were characterized by XRD and SEM-EDS (AM-RAY 1830, 10kV). The samples were sputter coated with graphite prior to their SEM analysis.

### 3. Results and discussion

The XRD pattern of as-synthesized powder is shown in Fig. 3. The peaks in the pattern are comparable to lanthanum gallate (JCPDS 24-1102) with a minor shift of the peaks due a change in the lattice parameter because of the substitution. Fig. 4 shows the scanning electron micrograph of the

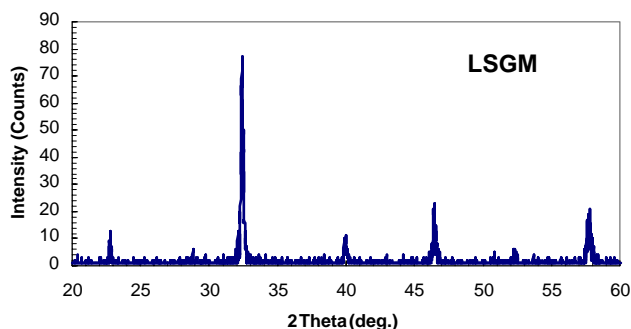


Fig. 3. XRD patterns of LSGM powder synthesized by glycine nitrate route.

as-synthesized powder. The average particle size is around 1.2  $\mu\text{m}$ .

#### 3.1. Effect of microwave power

The effect of microwave power was studied at different input power levels (1.5–2.25 kW). Fig. 5 shows the XRD pattern of the samples sintered at various microwave powers. All the samples showed single-phase LSGM compositions. Fig. 6 shows the variation of density with microwave power.

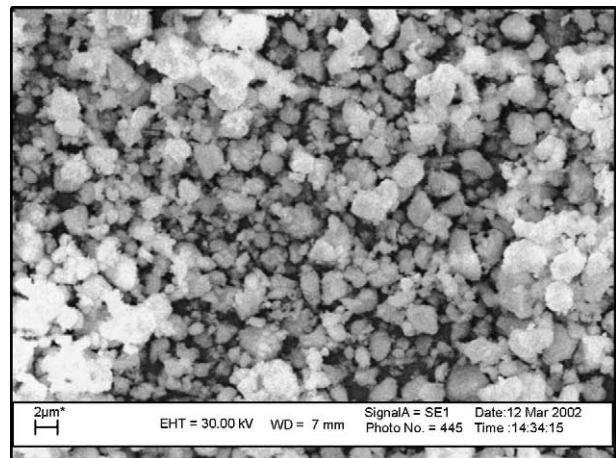


Fig. 4. Scanning electron micrograph of as-synthesized LSGM Powder, showing an average particle size of 1.2  $\mu\text{m}$ .

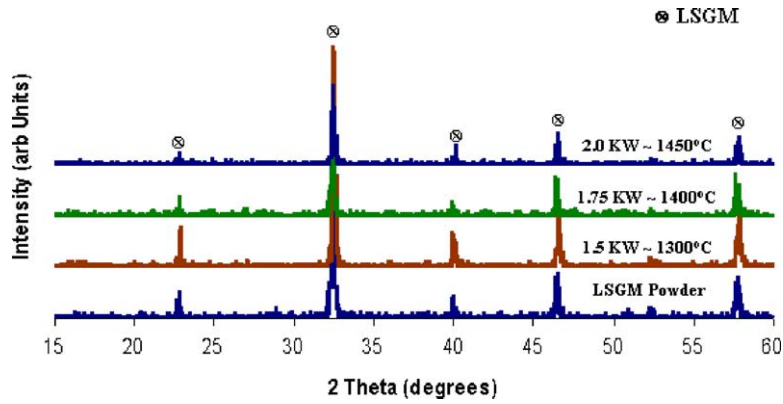


Fig. 5. XRD patterns of microwave sintered samples at various power levels. Input power was varied from 1.5 to 2.0 kW (1300–1450 °C).

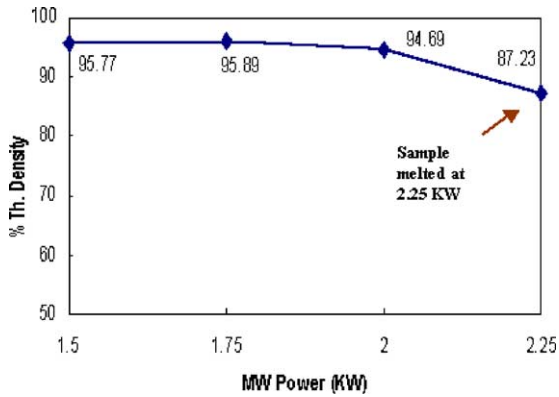


Fig. 6. Density of microwave sintered LSGM samples at various power levels.

Samples sintered at 1.75 kW for 20 min showed maximum density of about 95% theoretical density. Fig. 7 shows the microstructure of the fractured surface of the sample sintered at 1.75 kW for 20 min. The fractured surface shows very little porosity. The average grain size is of the order of 2–3 μm. The grain size is obtained with a concomitant high density. This is compared to the density values reported by Baskaran et al. [16], and Stevenson et al. [15]. The sintered density of reaction-synthesized powders in [12] was significantly less with bimodal grain size. Tas et al. [11] reported a lower sintering rate for chemically processed powders without examining the cause. However, it is clear that chemically synthesized powders have better homogeneity yet they need to be sintered using an activated sintering technique to control the grain size and the formation of undesirable phases.

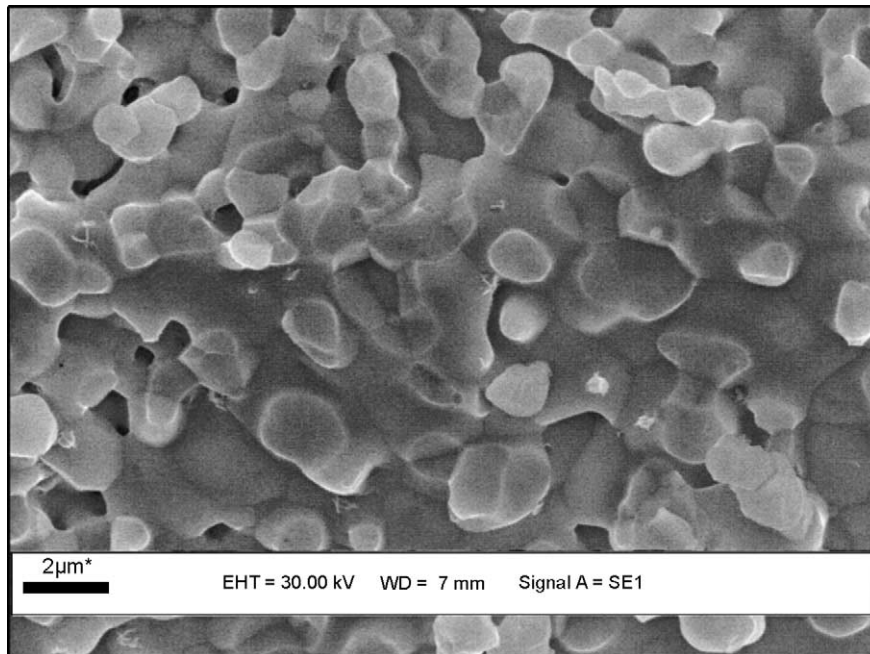


Fig. 7. LSGM sample sintered at 1.75 kW for 20 min.

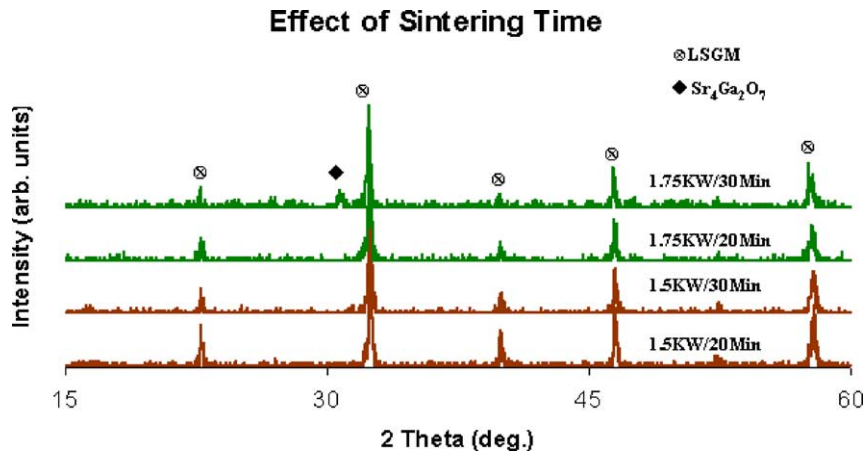


Fig. 8. XRD patterns of samples microwave sintered at two power levels (1.5 and 1.75 kW) and two sintering times (20 and 30 min).

It is also interesting to note that with the finer microstructure, the mechanical properties are expected to be better. It is shown in reference [8,15,16], that LSGM materials are very brittle in nature. Drennan et al. reported an average strength value of 162–14 MPa at room temperature for a large grain sized material of average grain size 15–20  $\mu\text{m}$

[8]. Baskaran et al. reported an enhancement in mechanical properties with finer grain sized material [16]. This material was obtained with a certain amount of dopant level (i.e. with some microstructural tailoring). As opposed to that, in the present case, the microstructure was obtained with an activated microwave sintering technique carried out at a lower temperature and sinter time.

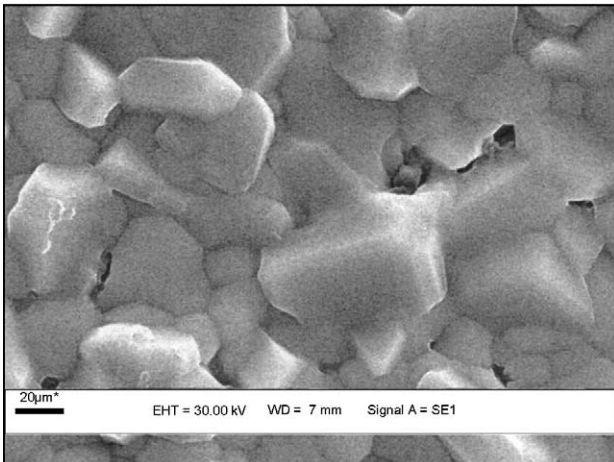
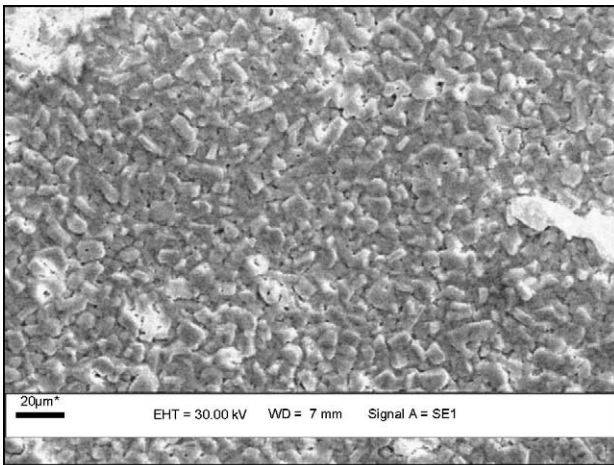


Fig. 9. Micrographs of LSGM sintered at 1350 °C for 20 min.

### 3.2. Effect of sintering time

The effect of microwave sintering time was studied by varying the sintering time from 20 to 30 min. Fig. 8 shows the XRD patterns of samples sintered at 1.5 and 1.75 kW for 20 and 30 min, respectively.  $\text{Sr}_4\text{Ga}_2\text{O}_7$  impurity peak was found in samples sintered at 1.75 kW for 30 min. Hence, prolonged sintering time will result in the appearance of residual phases in the material. Fig. 9 shows the high magnification fractured surface of sample sintered at 1.75 kW for 20 min. The fractured surface looks very dense with little or no porosity.

## 4. Conclusions

LSGM powders were sintered to high density ( $\sim 95\%$  of the theoretical density) using activated microwave sintering. Due to the heat generation in situ, the process of sintering is activated with faster kinetics compared to a conventional sintering technique. Conventional sintering for prolonged periods of time results in the appearance of undesirable secondary phases in the material and a reduction in density. We have shown here that, microwave sintering can alleviate that problem. The best results were obtained at 1.75 kW microwave power and 20 min sintering time. With an optimized sintering schedule, a fine grained microstructure without any undesirable phase can be obtained. Thus, microwave sintering can reduce processing time, while achieving mechanical reliability and desirable electrical characteristics.

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