

# Lanthanum Gallate Based Electrolyte Materials for Solid Oxide Fuel Cell Application

Ramesh Chandra Biswal

## Abstract

Primarily four different synthesis routes, viz. precipitation, hydrothermal, Pechini and glycine nitrate process (GNP) were used to synthesize LSGM. The materials, thus obtained were heat treated following different time-temperature schedules (calcinations and sintering) to obtain dense, phase pure LSGM. The qualitative and quantitative phase analyses were done by XRD followed by Rietveld analysis. Structural, morphological, elemental, thermal and electrical properties of the specimens were analyzed by TEM, SEM/ FESEM, BET, EDX, TG-DTA, TMA, XPS, FTIR and Impedance spectroscopic (IS) analyses.

XRD analysis of LSGM materials synthesized by precipitation and GNP routes showed presence of few secondary phases like  $\text{La}_4\text{Ga}_2\text{O}_9$  and  $\text{LaSrGaO}_4$ , respectively, even after adopting various heat treatment schedules. Similarly, for hydrothermal and Pechini method, secondary phases like  $\text{LaSrGaO}_4$ ,  $\text{La}_4\text{Ga}_2\text{O}_9$  and  $\text{LaSrGa}_3\text{O}_7$  were observed when powders were calcined at  $1000^\circ\text{C}$ . But, calcinations at high temperature significantly reduced the secondary phases and single phase LSGM was obtained in hydrothermal route after calcining at  $1400^\circ\text{C}$  for 8 h. However, in case of Pechini method, all the secondary phases were eliminated following a particular four-step controlled heat treatment schedule at  $1400^\circ\text{C}$  for 8 h.

Impedance spectroscopic analysis at different temperatures was done to access the anionic conductivity and the corresponding activation energy of these materials. The Nyquist plots obtained from IS revealed diffused semicircular type arcs with non-zero high frequency intercept and these plots were modeled by Zsimp win software with (RQ)(RQ) as equivalent circuit. Due to phase purity, ionic conductivities measured for LSGM synthesized by hydrothermal (0.019 S/cm) and Pechini methods (0.032 S/cm) were found to be much higher than that of LSGM synthesized by precipitation and GNP routes. However, a significant conductivity difference was observed between hydrothermal and Pechini and was attributed to the difference in respective crystallite sizes (of LSGM). Compared to the existing best known literatures about LSGM materials obtained by similar/different processing routes, the conductivity value reported in the present work was found to be higher for LSGM synthesized by Pechini method.

The role of secondary phases was also studied extensively by systematical heat treatment (which will create different amount of secondary phases) of derived LSGM. The quantitative phase estimation was done by Rietveld analysis. A perfect correlation between microstructure (observed under SEM and TEM) and ionic conductivity was established. It was corroborated that presence of pores/secondary phases, which were preferentially segregated at the grain boundaries (GB), made it (GB) thicker and thus enhanced the space charge layer causing a higher GB resistance. This lead to an overall decrease in ionic conductivity.

Since LSGM synthesized by Pechini method gave highest conductivity, the subsequent multiple/co-doping was adopted to synthesize phase pure LSGM (and its derivatives) by this method only. It was found that when LSGM was co-doped with Ba<sup>2+</sup> and Sr<sup>2+</sup> at La-site (LSBGM) by judicious stoichiometric alteration, the system not only stabilizes the desired perovskite structure, but also eliminates the complexity of synthesis route or processing techniques. An extensive Rietveld analysis showed that unit cell of LSBGM was bigger compared to LSGM. Tolerance factor (t) calculation showed higher lattice symmetry in LSBGM compared to LSGM, which is well supported by XPS analysis. Additionally, the optimized structural parameters calculated by density functional theory (DFT) supported the experimental findings. Interestingly, derived LSBGM showed the highest ionic conductivity (0.046 S/cm) which is ~ 44% higher than the LSGM synthesized by similar/different routes reported in literatures. This increase in conductivity might be due to the overall reduction in O<sup>2-</sup> ion migration energy (activation energy ~ 1.02 eV), an increase in free volume (~ 0.4%) and/or increase in structural symmetry (t = 0.9652). In a similar way, co-doping of Co<sup>2+</sup> or Ni<sup>2+</sup> along with Mg<sup>2+</sup> at Ga-site stabilized the LSGM structure and single perovskite phase was easily obtained. With these dopings, both bulk and GB conductivities were increased leading to overall conductivity enhancement (~ 21%) in Co-doped LSGM (0.039 S/cm). But, the conductivity was reduced in Ni-doped LSGM (0.024 S/cm) and showed some electronic conductivity in the restricted oxygen atmosphere. Thermal expansion co-efficient of the LSGM and co-doped LSGM are in the range of 11-13 × 10<sup>-6</sup> /K which suggests that these materials are very much compatible with the perovskite type anode or cathode materials for better performance compared to fluorite based systems.

**Keywords:** *SOFC; LSGM; Rietveld analysis; Impedance spectroscopy; Pechini method*