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Investigations on structural and electrical properties of calcium substituted LSGM electrolyte materials for IT-SOFC

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Abstract

Strontium and magnesium doped lanthanum gallate, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM) and a few compositions of calcia (CaO) incorporated LSGM, $La_{(0.9-x)}Ca_xSr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$; $x \leq 0.10$, were prepared by conventional solid state ceramic route. The X-ray diffraction patterns showed orthorhombic LSGM phase along with a few impure secondary phases. SEM micrograph depicted fairly dense grain morphology of the system. The textural properties were also found to be quite suitable for solid oxide fuel cell electrolyte applications. The electrical conductivity of the systems was measured in the frequency range 20 Hz to 1 MHz and temperature range 300–800 °C. The total conductivity of the system was found to first increase up to $x=0.05$ and thereafter it decreased for higher concentrations of the dopant. A small amount of calcia (upto $x=0.05$) scavenges the intergranular secondary impure phases resulting in a significant increase in grainboundary conduction. The presence of extra secondary phases in the higher compositions has been attributed to decrease in electrical conductivity.

Keywords: LSGM; IT-SOFC; XRD; Grain and grainboundary conductivity

1. Introduction

Solid oxide fuel cell (SOFC) is an electro-chemical conversion system that converts chemical energy directly into electrical energy with high efficiency [1,2]. For successful operation of an SOFC, the ionic conductivity of electrolyte material should be high enough. Yttria stabilized zirconia (YSZ), one of the promising electrolyte materials, has been reported to show high oxygen ion conductivity only above 800 °C [3–5]. Therefore, it becomes imperative to operate SOFC above 800 °C. The high operating temperature of SOFC puts major constraints over commercialization of this system. However, it is desired that the electrolyte should exhibit high oxygen ion conductivity at intermediate temperatures (in the range of 500–800 °C). This has led researchers to investigate for alternative materials for fuel cell technology [6]. Doped ceria (Sm/Gd doped CeO_2) and doped Bi_2O_3 with fluorite structure have been proposed as a few traditional electrolyte materials for intermediate temperature-SOFC (IT-SOFC). Bi_2O_3 showed high ionic conductivity at intermediate temperatures. However, it is easily reducible and reported to change into bismuth metal at an oxygen partial pressure of $\sim 1.0 \times 10^{-8}$ Pa and at temperature 600 °C [7]. Ceria also has been reported to depart from its ideal stoichiometry (reduces from Ce^{4+} to Ce^{3}) accompanied by electronic conductivity at higher temperatures and in reducing atmospheres [8,9]. In recent years, developments of electrolytes with non-fluorite structures have gained much interest. In 1994, Ishihara et al. [10] investigated a new $LaGaO_3$ based material that incorporates Sr and Mg in the $LaGaO_3$ host matrix i.e. $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM). At the same time, Feng and Goodenough [11] also reported LSGM as an electrolyte material for IT-SOFC. LSGM shows high ionic conductivity comparable to YSZ in the intermediate temperature range. This electrolyte also possesses negligible electronic conductivity at temperatures below 800 °C and over a broad range of oxygen partial pressure from $pO_2=1$ to $\sim 10^{-22}$ atm and shows a stable performance over a long operating period [12]. Its superior ionic conductivity and

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chemical properties make it a new generation electrolyte material for IT-SOFCs. This also results in a better performance of the cell [13]. However, it is difficult to synthesize pure LSGM phase. Most of the reports on LSGM show that it contains a few minor secondary phases along with LSGM phase [14–17]. Djurado et al. [18] pointed that the presence of impurity phases or secondary phases decreases the conductivity of LSGM greatly. Therefore, various synthesis techniques and approaches have been employed to obtain pure LSGM phase and to improve its electrical performance [14–20]. There are a few dopants, when introduced into the LSGM; they improve the electrical conductivity and also the stability [21]. The electrical properties of LSGM were also modified by partial substitution on the Ga site by transition metals like Cr, Mn, Fe, Co, and Ni. It has been reported that a few transition metals doping (like Co, Ni, Fe etc.) on Ga site in LSGM have significantly improved electrical conductivity and the performance of the system [22–27]. Nevertheless, so far to the best of our knowledge, no effort has been made to dope a substituent at La site in the LSGM. In this paper, we have tried to investigate the effect of the calcium (alkaline earth metal) doping into the LSGM at La site. In the present study, the electrical properties of Ca doped LSGM system, $La_{(0.9-x)}Ca_xSr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LCSGM) have been probed employing impedance analysis technique. The structural and textural properties of the LCSGM system have also been investigated employing XRD, SEM, particle size analyzer and BET techniques (N_2 adsorption).

2. Experimental

A few compositions of calcia doped LSGM system, $La_{(0.9-x)}Ca_xSr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LCSGM), with $x=0.0$, 0.02, 0.05, 0.07 and 0.10, were synthesized via solid state ceramic route. An appropriate amount of constituent oxides, having purity greater than 99.5% were mixed in a planetary ball mill for six hours at 150 rpm using acetone as mixing media. The dried mixed powders were calcined at 1300 °C for 12 h in air. A few drops of 2% solution of polyvinyl alcohol (PVA) were added to the powder as a binder. The calcined powders were ground, mixed and pelletized at 100 kg/cm^2. The pellets were sintered at 1400 °C for 12 h. After sintering, the samples were furnace cooled to room temperature. A few pellets were crushed into fine powder. The phase-purity, structure, and lattice parameters of the samples were determined using X-ray powder diffraction technique (Rigaku Miniflex II desktop) with Cu-Kα radiation ($\lambda \approx 1.54$ Å) at room temperature. Microstructural image of the polished surface of pellet samples were taken with the help of a Scanning Electron Microscope (Quanta 200 FESEM). The density of the pellets was measured by the Archimedes method. The particle size distribution of LCSGM powders was investigated with the help of a particulate size analyzer (ANKERSMID, CIS-50, USA). BET surface area and porosity of the samples were measured by Micromeritics (ASAP 2020) Surface Area and Pore Size Analyzer using adsorption–desorption isotherms of nitrogen. For the electrical characterizations, sintered pellets were polished and coated with a high temperature Ag-paint on both sides. The paint was matured after firing at 750 °C for 20 min. Electrical conductivity of the silver coated pellet were measured by Wayne Kerr (6500 P Series) LCR meter in the temperature range 300–800 °C using two-probe method. Polished pellet samples were placed between the electrodes of the sample holder and then kept into a furnace to record the data from the automated data acquisition software.

3. Results and discussion

3.1. Crystal structure

In the present discussion, the system $La_{0.9-x}Ca_xSr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ is designated as LCSGM and the compositions with $x=0.00$, 0.02, 0.05, 0.07 and 0.10 of this system are assigned as LCSGM00, LCSGM02, LCSGM05, LCSGM07 and LCSGM10, respectively. For example, LCSGM07 represents the composition $La_{0.83}Ca_{0.07}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$. Fig. 1 shows the powder X-ray patterns of all the compositions alongwith Rietveld refinement by taking LSGM system as the reference phase at room temperature. The peak shape was assumed to be pseudo-Voigt functions. The background of each profile was approximated by a 12-parameter polynomial. The R_{wp} (weighted-pattern factor) and S (goodness-of-fit) parameters were used as numerical criteria of the quality for the fit of calculated to experimental diffraction patterns. XRD patterns reveal the orthorhombic LSGM phase (space group, *Pnma*) along with presence of minority secondary phases like $LaSrGaO_4$ (JCPDS file no. 24-1208), $LaSrGa_3O_7$ (JCPDS file no. 45-0637) and $La_4Ga_2O_9$ (JCPDS file no. 53-1108), as indicated in Fig. 1.

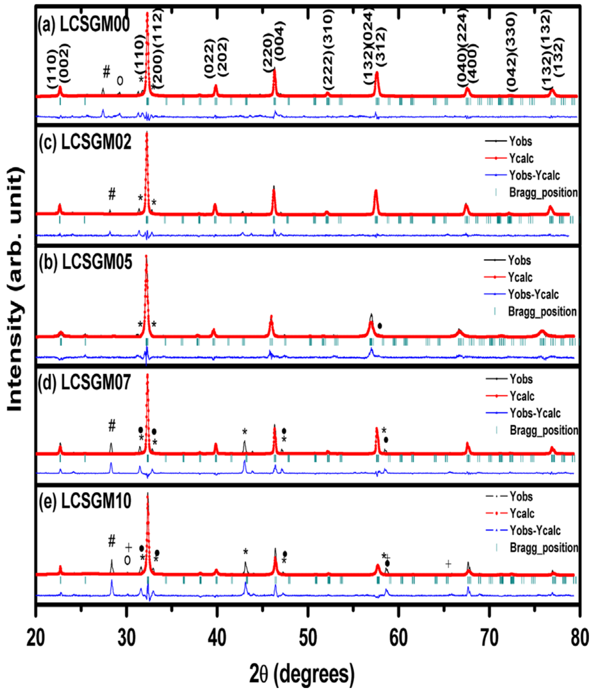

Fig. 1. Powder X-ray Rietveld refinement patterns of the system $La_{(0.9-x)}$-$Ca_xSr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ for (a) $x=0.00$, (b) $x=0.02$, (c) $x=0.05$, (d) $x=0.07$ and (e) $x=0.10$ sintered at 1350 °C. Secondary phases are indicated by the symbols (#) for $La_4Ga_2O_9$, (✻) for $LaSrGaO_4$, (o) for $LaSrGa_3O_7$, (●) for $CaLaGaO_4$ and (+) for $LaCaGa_3O_7$.