Synthesis and Characterization of La$_{0.70}$Ca$_{0.30}$MnO$_3$ System for Solid Oxide Fuel Cell Applications

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Abstract. La$_{0.70}$Ca$_{0.30}$MnO$_3$ system has been prepared by solid state reaction method for cathode of solid oxide fuel cell applications. The structural studies have been investigated by X-Ray diffraction method and the experimental results have confirmed that the prepared system has been well crystallized into single phase, crystal structure is orthorhombic and size of the particle has been calculated to be 0.35 µm. The surface morphology has been studied by scanning electron microscopy which confirmed that grain sizes are irregular, non uniform and randomly oriented. Archimedes principle has been used to investigate the density of the prepared material. Thermal properties of the system confirmed its stability at high temperature and thermal expansion coefficient well matched with other cell components. The dielectric as well as impedance properties have been investigated at different ranges of temperature and frequency. Electrical conductivity of the prepared system has been found to be more than 100 S/cm as well as obtained value of activation energy signifies that the synthesized system is suitable for cathode of solid oxide fuel cell applications.

Keywords: solid oxide fuel cell, X-Ray diffraction, density, thermal expansion coefficient, activation energy

1. Introduction

Solid oxide fuel cell (SOFC) represent one of the sustainable, clean alternate non conventional energy sources and versatile way of power production by converting the chemical energy from fuel directly into electric energy. SOFCs work at higher value of temperatures in comparison to other fuel cells [1-3]. Because of clean, portable and renewable character of the hydrogen, it can be considered as the next generation energy carriers [4, 5]. SOFCs are one of the chief sources of generation of hydrogen. In addition to this its efficiency arrives at sixty percentages and reaches at eighty percentages on heat recovery [6, 7]. Cathode is one of its components which is a conducting electrode and play a vital role in increasing the efficiency of the SOFCs. The main requirement of the cathode of SOFCs includes its adequate conductivity preferably more than 100 S/cm and its compatibility of thermal expansion coefficient (TEC) along with neighbouring components like electrolyte and anode [8]. High temperature working condition of SOFCs limits the properties of cathode and hence affects the overall efficiency of the cell [9-11]. In recent years a variety of mixed ionic and electronic cathode has been developed which prove their potential when SOFCs worked at intermediate temperature range [12, 13]. Metal doped LaCO$_3$, LaMnO$_3$ and LaFeO$_3$ perovskite oxide are commonly used inexpensive cathode material for SOFC. However at low temperature their electrochemical performance being affected [14]. Calcium is another reported pronouncing element for doping result in to elevated
electrical conductivity in addition to thermal expansion compatibility among YSZ electrolyte [15-17]. Therefore in this work calcium is substituted in LaMnO₃ system to study the structural, thermal, dielectric and conductive properties in order to use LaMnO₃ as cathode component of solid oxide fuel cell.

2. Experimental

Laₐ₀.7₀Ca₀.₃₀MnO₃ prepared by solid state reaction method. Calcium carbonates (CaCO₃), Lanthanum oxide (La₂O₃), Manganese oxide (MnO₂) from sigma Aldrich and 99.9% pure has been taken in stoichiometric ratio. Acetone has been used as solvent and this mixture has been further milled with zirconium oxide balls for 6 hours. Dried precursor powder further has been calcinated conventionally at 950°C for twelve hours and pellet of 1mm diameter has been prepared. Pellets have been conventionally sintered 1400°C for 2 hours.

3. Results and Discussion

3.1 X-ray diffraction and Density

The as-prepared La₀.7⁰Ca₀.₃₀MnO₃ solid solution has been characterized by X-ray diffraction and the obtained patterns at 1400°C has been shown in figure 1. X-rays of wavelength equal to 1.54 Å, range 20°–80°, size of step 0.02 degree as well as speed limit of 2 degree per minutes have been used to obtain the XRD diffraction patterns. The crystal structure of the as prepared perovskite is orthorhombic and has been well crystallized, moreover recognized by sharp crystalline peaks. None of the peak remain unassigned which confirm that sample is synthesized in single phase. Crystalline size has been determined by scherrer formula and found to be 0.35 μm.
Figure 1. X-ray diffraction patterns of La$_{0.70}$Ca$_{0.30}$MnO$_3$ system sintered at 1400°C.

Archimedes principle has been used to measure the density of the as-prepared La$_{0.70}$Ca$_{0.30}$MnO$_3$ system and tabulated in table 1. Calculated value of specific free volume as well as tolerance factor is also given in the table 1.

| Sample         | Theoretical density $d_{th}$ (g/cm$^3$) | Experimental density $d$ (g/cm$^3$) | Specific free volume $(d/d_{th})$ % | Tolerance factor |
|----------------|------------------------------------------|-------------------------------------|----------------------------------|-----------------|
| La$_{0.70}$Ca$_{0.30}$MnO$_3$ | 5.12                                      | 4.16                                | 81.25                             | 0.821           |

3.2 Scanning Electron Micrograph

The SEM micrograph of prepared La$_{0.70}$Ca$_{0.30}$MnO$_3$ has been shown in figure 2. The grains have been formed of non-regular in size and shape which are evidently observable from the image. Average grain size is found to be in well agreement with the XRD results. Average grain size is observed to be near 0.35 µm which is in well agreement with size calculated from XRD analysis.
3.3 Thermal Properties

Thermo-gravimetric analysis (TGA) and Thermal expansion coefficient (TEC) has been used to study the thermal properties if the as prepared material. Material used as cathode of SOFCs must be thermally stable in order to avoid electrolyte cracking or delaminations at interface of electrodes. Thermo-gravimetric analysis (TGA) and thermal expansion coefficient (TEC) graphs has been shown in figure 3 (a) and 3 (b). Consequence of heat on weight change is analyzed by thermo-gravimetric analysis (TGA) technique. At low temperature due to loss of moisture there is a sharp weight drop and above 350°C temperature material start gaining stability. This is because of oxidation at high temperature of Mn present at B site of ABO$_3$ perovskite [18, 19]. Dilatometer is used to investigate the TEC of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ sample and therefore obtained value is found to be 10.9 x 10$^{-6}$°C$^{-1}$.

Figure 3. (a) Thermo-gravimetric analysis (TGA) and (b) Thermal expansion coefficient (TEC) curves of La$_{0.7}$Ca$_{0.3}$MnO$_3$ perovskite material.
3.4 Dielectric properties

The dielectric properties in the La_{0.70}Ca_{0.30}MnO_3 has been studied by impedance spectroscopy. At different temperature, \(\varepsilon'\) (real) and \(\varepsilon''\) (imaginary) dielectric constant with respect to variation in frequency has been given in figure 4 (a) as well as 4 (b) respectively. The graphs undoubtedly expose that with rising frequency (low frequency region), both \(\varepsilon'\) (real) and \(\varepsilon''\) (imaginary) continually decreases while in higher frequency together shows approximately linear behavior. At low frequency maximum polarizability arise due to dipolar, ionic, electronic and space charge while at high frequency dielectric constant \(\varepsilon'\) (real) and \(\varepsilon''\) (imaginary) lags behinds the switching signal of dipolar orientation result into linear variation. Figure 4 (c) and 4 (d) has been show variation of part \(Z'\) of impedance and part \(Z''\) of impedance with respect to frequency respectively. Continuous decrease in \(Z'\) with temperature and frequency give rise to negative temperature coefficient of resistance (NTCR) in the sample. The merging of impedance \(Z''\) vs. frequency values curves bear out the disappearing of polarization (space charge) [20].

![Figure 4](image)

**Figure 4.** Variation of (a) dielectric constant \(\varepsilon'\) (real), (b) \(\varepsilon''\) (imaginary), (c) real part \((Z')\) of impedance and (d) imaginary part \((Z'')\) with respect to frequency.
3.5 Electrical Properties

Electrical conductivity Value at diverse frequencies range for La$_{0.70}$Ca$_{0.30}$MnO$_3$ up to 600°C has been shown in figure 5. Graph moreover explains that conductivity improved with temperature as well as frequency. The maximum calculated conductivity value has been found to be 103 S/cm at 600 °C and activation energy calculated by using Arrhenius fitting is 0.19 eV.

![Graph](image.png)

**Figure 5.** Variation of (a) conductivity with temperature at different frequencies and (b) activation with respect to temperature

4. Conclusions

La$_{0.70}$Ca$_{0.30}$MnO$_3$ perovskite material has been prepared by solid state reaction method. X-Ray diffraction confirmed that the prepared system has been well crystallized into single phase, crystal structure is orthorhombic and size of the particle is calculated to be 0.35 µm. The surface morphology has been studied by scanning electron microscopy which confirmed that grains are non uniform, randomly oriented and density of the prepared material is found to be 4.16 g/cm$^3$. TEC of the material is found to be 10.9 ×10$^{-6}$ °C$^{-1}$ in addition to this material show weight gain above 350°C. The dielectric constant lowered with temperature as well as frequency and also material showing negligible dielectric loss. Electrical conductivity has been found to be 103 S/cm at 600 °C and activation energy 0.19 eV signifies that the synthesized system is suitable to be used as cathode electrode of solid oxide fuel cell.

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