Structural, Thermal and Electrical Properties of La$_{0.80}$Sr$_{0.20}$MnO$_3$ Cathode of SOFCS

Manokamna$^{1,a)}$, S. Paul$^1$, A. Kumar$^2$, D.K. Sharma$^3$, K.L. Singh$^4$, G.Bhargav$^1$ and A. P. Singh$^1$

$^1$Department of Applied Sciences, I.K.G.P.T.U, Jalandhar-144001, (Punjab) India
$^2$Department of Physics, Swami Premanand Mahavidyalaya, Mukerian (Punjab) 144211 India
$^3$Department of Physics, GGMSC, Jammu-180001, (J &K) India
$^4$Department of Applied Sciences, DAVIET, Jalandhar-144001, (Punjab) India
$^a$manokamna12333@gmail.com

Abstract: La$_{0.80}$Sr$_{0.20}$MnO$_3$ perovskite material is synthesized by conventional solid state reaction method. Raw materials in stoichiometric ratio are ball milled with use of zirconium oxide balls for six hours. Calcined powder is pelletized and then sintered by use of conventional furnace at 1400°C for 2 hours. Sintered pellets are characterized for study of density, phase identification, crystalline size, microstructure, electric and thermal properties. Crystalline size of the as prepared sample is found to be 52 nm. Thermo-gravimetric analysis shows weight loss in the material. Thermal expansion coefficient of the prepared sample is 8.45×10$^{-6}$ °C$^{-1}$. Observed value of activation energy for LSM is 0.18 eV which indicate the electronic conductive behavior of the prepared sample and can be used as cathode of SOFCs.

Keywords: Solid Oxide Fuel Cell, Cathode Material, XRD, TEC, Conductivity.

INTRODUCTION

For the development of any society one of the important factors is production of energy and in the present time the main challenge is to fulfill the futuristic demand of energy. Fuel cell plays an important role for clean, secure, sustainable energy with low pollution. Among all types of fuel cells, solid oxide fuel cells (SOFC) convert chemical energy in to electric energy without combustion as an intermediate step, offer the highest energy efficiency and the greatest fuel flexibility [1-2]. The cathode of SOFC is a thin porous layer on the electrolyte where oxygen reduction takes place. Perovskite materials have been widely used as cathode materials in SOFCs [3]. High electronic and ionic conductivity, adequate porosity, matched thermal expansion coefficient, high catalytic activity for the oxygen reduction reaction and chemical compatibility with the other contacting components under operating conditions is important factor of cathode material for maximum efficiency of SOFCs [4-5]. In recent years, great efforts have been devoted to develop low or intermediate temperature SOFCs (IT-SOFCs) operating at 500–800 °C. Lanthanum strontium manganite (LSM) and Lanthanum strontium cobalt ferrite (LSCF ) are the important candidates for cathode material for high temperature solid oxide fuel cell (SOFC) which meets many requirements in terms of porosity, electrical conductivity and thermal expansion [6-8]. LSM belongs to perovskite crystal general formula of ABO$_3$ that is electron-conductive. In the present work solid state approach is used to synthesis the LSM. Sintering studies have been carried out for the calcined powder. Sintered powder was characterized for its crystalline size,density,thermal properties, electrical conductivity and microstructure.
EXPERIMENTAL

La_{0.80}Sr_{0.20}MnO_3 synthesized by conventional solid state reaction method. Lanthanum oxide (La_2O_3), manganous oxide (MnO_2), strontium carbonates (SrCO_3) with 99.9% purity in stoichiometric ratio is ball milled for 6 hours by use of Zirconium oxide balls of size (1.8-1.0) mm for synthesis of La_{0.80}Sr_{0.20}MnO_3. Mixed solution is filtered and dried in air tight room. Precursor powder is further calcinated at 950°C for 12 hrs in conventional furnace. Calcinated LSM powder is ground in an agate mortar and a pestle for 1 hour and then pelletized with use of 4% PVA into circular discs by applying 12 kN/cm^2 pressures, which is further sintered by use of conventional furnace at 1400°C for 2 hours.

RESULTS AND DISCUSSION

X-ray diffraction

Synthesized sample is characterized by X-ray powder diffraction (XRD) for phase identification and crystalline size. D8-Advance Bruker-axe X-ray diffractometer at room temperature using a PANalytical X'Pert PRO system is used for X-ray powder diffraction (XRD). The wavelength of incident X-rays is 1.54 Å. The diffraction patterns are collected in the range of 20–80 °C with step size 0.02 and scan rate 2°/min. Diffraction patterns of the calcined powder and sintered pellet of La_{0.80} Sr_{0.20} MnO_3 are shown in Fig. 1. Below temperature 950°C LSM show additional peaks of La_2O_3 identified by ICDD card no. 01-089-4016. Sintered pellet at 1400°C single phase is formed with crystal structure Rhombohedral having space group R-3c identified by ICDD card no. 01-089-4461. Crystalline size of the as-prepared sample is calculated by using scherrer formula which is found to be 52 nm. William Hall plots shown in Fig. 2 show tensile strain which indicate that unit cell is expended.

Density

Theoretical density (X-ray density) and measured density (d) of sintered sample is shown in table no.1. The high density of the material indicates the good sinterability. Moreover, relative values of conductivity and thermal expansion of samples does not affected by density due to negligible variation of d/dth (%) of the sample.

FIGURE.1: Diffraction patterns of the calcined powder and sintered pellet of La_{0.80} Sr_{0.20} MnO_3
Table 1: Theoretical densities, measured density, specific free volume and Tolerance factor of sintered La$_{0.80}$Sr$_{0.20}$MnO$_3$ Material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density</th>
<th>Experimental Density</th>
<th>(d/ d$_{th}$) %</th>
<th>Specific free volume</th>
<th>Tolerance factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.80}$Sr$</em>{0.20}$MnO$_3$</td>
<td>5.8</td>
<td>5.223</td>
<td>90.05%</td>
<td>0.357</td>
<td>0.78</td>
</tr>
</tbody>
</table>

FIGURE 2: William Hall analysis plots showing tensile strain at temperature 950°C and 1400°C

Microstructure

Morphology of the sample were studied using FEI Quanta 200F scanning electron microscope (SEM) equipped with EDAX detector. The scanning electron micrographs obtained from the fractured surface of the sintered pellets of La$_{0.80}$Sr$_{0.20}$MnO$_3$ and shown in Fig. 3. Material is quite porous clearly shown in SEM picture.

FIGURE 3: Scanning Electron Micrograph of La$_{0.80}$Sr$_{0.20}$MnO$_3$ perovskite

Thermal Properties

Sintered sample is characterized for thermal gravimetric measurements with a Netzsch DSC and Diamond Pyris TG (Perkin Elmer) using Al$_2$O$_3$ powder as reference material in argon atmosphere from 25°C to 900 °C at 10 °C/min heating rate, respectively. Thermogravimetric analysis (TGA), differential scanning calorimetric
(DSC/DTA) and thermal expansion coefficient (TEC) curves of LSM is shown in fig 4. With an increase in temperature below 350-400 °C there is sharp weight loss which may be due to the loss of moisture content present in the samples as well as loss of CO$_3^{2-}$ ions from the precipitate. Above 800 °C temperature TGA graph show that there is very small loss in weight and above this value of temperature material become stable. In the perovskite material creation of oxygen vacancies at high temperature may be reason of weight loss, which arises due to either oxidation or reduction of metal present at B site of the perovskite material and result in to creation of charge imbalance in the material [9-10]. DTA clearly show endothermic peak at temperature 300 °C which is corresponds to Neel’s temperature ($T_N$) and this type of peak arises due to antiferromagnetic to paramagnetic phase transition [11]. Dilatomer is used to calculate the thermal expansion coefficient (TEC) of the prepared sample and the obtained value of TEC is $8.45 \times 10^{-6}$ °C$^{-1}$.

**FIGURE.4:** Thermogravimetric analysis (TGA), differential scanning calorimetric (DSC/DTA) and thermal expansion coefficient (TEC) curves of LSM

### Electrical properties

Conductivity behavior of the samples are analyzed by use of Impedance spectroscopy in a frequency range of 0.1 Hz–32 MHz and from 300°C to 800 °C. Electronic conductivity of the material is calculated by use of relation

$$\sigma = \frac{l}{RA}$$
where \( l \) is thickness and \( A \) is cross-sectional area of gold sputtered pellet. Electronic conductivity of \( \text{La}_{0.80} \text{Sr}_{0.20} \text{MnO}_3 \) sintered at 1400°C is found to be 103 S/cm at 600°C and 135 S/cm at 800°C. The activation energy of the prepared sample is obtained by the Arrhenius fitting of conductivity with respect to temperature and shown in figure no. 5. Obtained value of activation energy for LSM is 0.18 eV which confirm the electronic conductive behavior of the prepared sample.

**CONCLUSION**

\( \text{La}_{0.80} \text{Sr}_{0.20} \text{MnO}_3 \) synthesized by conventional solid state reaction method which show rhombohedral structure, space group \( \text{R}-3c \) and crystalline size is found to be 52 nm. Material show tensile strain which indicate that unit cell is expended. The microstructural analysis shows good porosity of the material. TGA confirm creation of oxygen vacancies in the material at high temperature result in to weight loss of the material. DTA show antiferromagnetic to paramagnetic phase transition and TEC value is found to be \( 8.45 \times 10^{-6} \) °C\(^{-1}\). Highest value of conductivity of LSM is 135 S/cm. Observed value of activation energy for LSM is 0.18 eV which confirm the electronic conductive behavior of the prepared sample. Therefore the studied properties of the present prepared sample indicate that it can be used as cathode of SOFC.

**REFERENCE**