

Spectroscopic And Electrical Properties Of Strontium - Doped Lanthanum Manganite Thin Films For SOFC

B. S. Kamble, V. J. Fulari, R. K. Nimat

Abstract: Strontium-doped lanthanum manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ -LSM) has received much attention in recent years. Most studies have concentrated on thin film samples at low temperatures. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) has proved to be efficient cathode material for solid oxide fuel cell (SOFC). In the present work the strontium-doped lanthanum manganite ($\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3-\delta}$) were synthesized by spray pyrolysis technique in the thin film form on alumina substrate which was characterized by X-ray diffraction, scanning electron microscopy. The spectroscopic properties such as IR, FT-Raman have been studied. The temperature dependence resistivity and Dielectric constant was carried out at different frequencies. Film thickness measurement was carried out by using surface profilometer. X-ray diffraction results clearly indicated that sintered LSM at 900°C for 2 hours show the formation of single phase solid solution with perovskite like structure. Crystalline size has been calculated by SEM microscopy. Resistivity of LSM thin film decreases as absolute temperature increases and Dielectric constant suddenly decreases at low frequency and became constant as frequency increases. The film thickness is about 200 nm and roughness of the sample is 4000\AA .

Keywords: Spray Pyrolysis, Cathode, LSM, SOFC.

1. Introduction:

The power generation by clean, efficient and eco-friendly is the biggest challenge for scientists and engineers. The Solid oxide fuel cell (SOFC) technology offers efficient green power generation [1]. It is cost efficient, cheap, clean energy and power source. Solid Oxide fuel cells convert chemical energy of a fuel gas directly into electrical energy [2]. The power generated by fuel cells is efficient, environmentally clean and without combustion of fuel. A fuel cell consists of two electrodes, namely the cathode (air electrode) and the anode (fuel electrode) respectively, the oxygen reduces at cathode and the fuel oxidizes at anode [3]. The two electrodes are separated by the electrolyte which is a dense ceramic layer which transports oxygen ions from the cathode to the anode. The SOFCs are operated at high temperatures up to 600°C - 1000°C and are based on well established component systems [4]. Strontium-doped lanthanum manganite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) has been utilized as a cathode for SOFC because of its high electrochemical activity for oxygen reduction and good chemical stability and compatibility with YSZ electrolyte [5-6]. The use of LSM is inapplicable for a low-temperature SOFC, however, due to its low oxygen ion conductivity and high activation energy.

The strontium doped lanthanum manganite $\text{La}_{1-x}\text{M}_x\text{MnO}_3$, where, M=Alkaline earth metal, plays the attention as electrode (Cathode) for solid oxide fuel cell. The Strontium doped lanthanum manganite perovskite has high electrical conductivity, good thermal and chemical compatibility and also have electro catalytic ability [7]. The LSM thin films for their application as cathode for SOFC were synthesized by Chemical Spray pyrolysis. The Spray pyrolysis technique is cost effective technique. It requires a simple equipment to deposit thin films of various materials under atmospheric conditions as compared to other techniques. It is one of the most suitable techniques to control the particle size, shape, compositional and phase homogeneity of the particles [8].

2. Experimental:

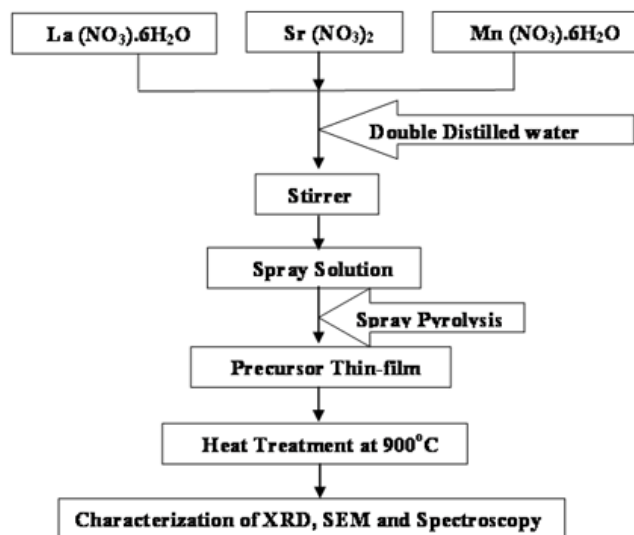


Fig.1 Flow-chart for synthesis of LSM

The Lanthanum Strontium Manganite (LSM) thin films were deposited on alumina substrate by using Chemical Spray Pyrolysis technique. The basic principle used in chemical spray pyrolysis technique is that, a very small droplet of the

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spray solution reaches to the hot substrate leads to the pyrolytic decomposition of the solution which forms the adherent thin films in the presence of air as neutral gas^[9]. The stoichiometric amounts of precursor $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ metallic salts were dissolved in double distilled water and stirred with magnetic stirrer for 15 minutes, which was further used to deposit LSM thin films on alumina substrate at 250°C . The solution flow rate was maintained as 3ml/min, the nozzle to substrate distance was kept 20 cm, optimized to obtain pin-hole free, crack free and dense thin films. The post deposition annealing conditions to be chosen were two hours at 900°C in air. The crystal structures of the sintered LSM thin films were studied by X-ray diffraction (Bruker X-Ray Powder diffractometer) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and the morphology was probed by Jeol Scanning Electron Microscope (SEM). The thickness of spray deposited LSM thin films was determined using a fully computerized AMBIOS MAK XP-1 surface profiler with 1 \AA vertical resolution. Dielectric constant was measured by using LCR meter. D.C. resistivity was carried out by two probe resistivity setup.

3. Results and Discussion:

3.1 XRD studies

Fig. 2(a) XRD pattern for as-deposited multilayered thin film at optimized individual deposition conditions which shows amorphous structure, but the sample sintered at 900°C for two hours demonstrated the existence of perovskite type structure. The phase formation takes place after sintering at 900°C as compared to asdeposited LSM thin film. The XRD pattern of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3-\delta}$ perovskite nanostructures show characteristic peak of the perovskite phase. The XRD patterns are in good agreement with the standard data for hexagonal symmetry with $a=b=5.533 \text{ \AA}$ and $c=13.22 \text{ \AA}$. The crystallite size was determined by the broadening of the diffraction peak at particular angle using Scherrer's formula. The crystallite size was calculated for diffracted peaks and they are between 180-200 nm showing nanocrystalline natures of the films.

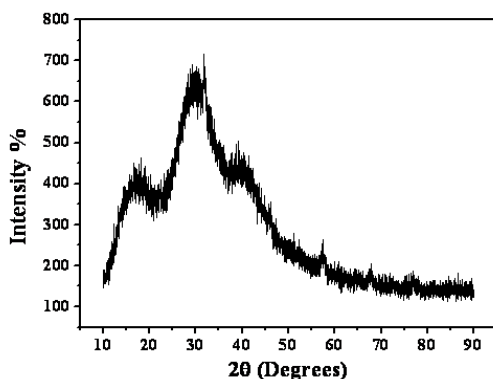


Fig. 2 (a) The XRD of LSM thin films asprepared

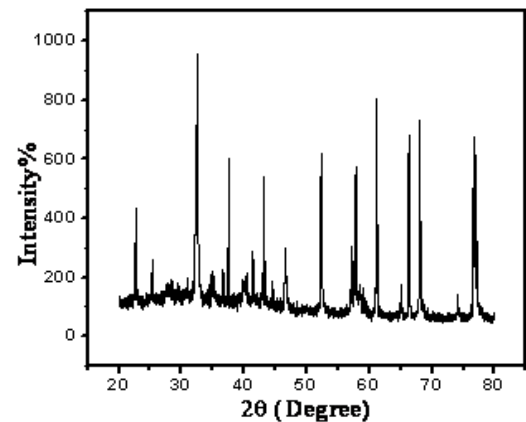


Fig. 2(b) The XRD of LSM thin film sintered at 900°C

3.2. Scanning electron micrograph and FE-SEM:

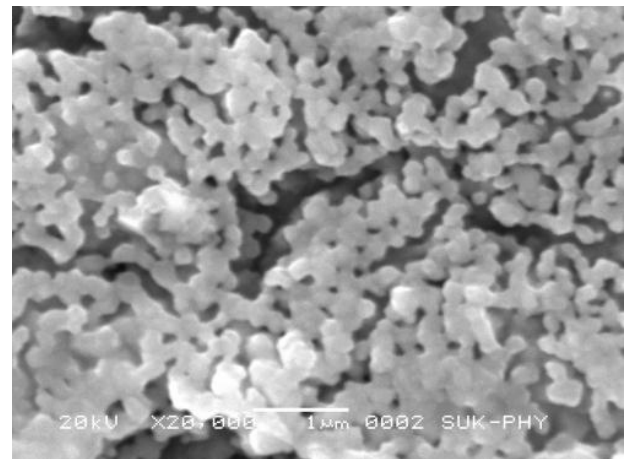


Fig. 3 The FE-SEM image of LSM thin films sintered at 900°C .

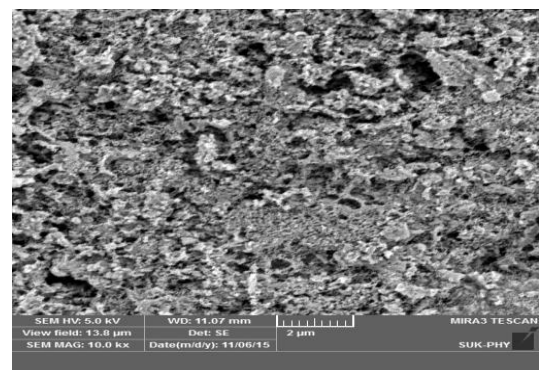


Fig.4) The FE-SEM of LSM

The typical SEM photograph of the surface of LSM film is shown in Fig.3. The grains are quite uniform in size and porous morphology composed by the many crystallites of Lanthanum Strontium Manganite^[3]. The porous morphology of LSM which is applicable as cathode for solid oxide fuel cell. Since the porosity of cathode is necessary in order to pass oxygen molecules at cathode-electrolyte interface^[10]. The crystallite size from sintered sample is approximately

200 nm. The electrode (cathode) thin film showed a structure with a more porosity and well-necked particles which provide the gas transportation for the reaction at the electrodes in SOFC [11]. Fig.4 shows the FESEM image of LSM thin film. The nanoparticles prepared by spray pyrolysis have a porous structure like spongy and a good size distribution which is applicable for SOFC. The film thickness is about 200 nm and roughness of the sample is 4000\AA .

3.3 Fourier transforms Raman and infrared spectroscopy:

Raman spectroscopy is very powerful technique to study soft modes and structural phase transitions. Fig.5 shows FT-Raman spectrum of LSM thin film. It shows pronounced bands at 557cm^{-1} , 807cm^{-1} , 1099cm^{-1} , 1912cm^{-1} and 2128cm^{-1} . These peaks have been arising from LSM. The band observed at 557cm^{-1} characteristic of orthorhombic LSM was found. The band denoted at 1099cm^{-1} is associated to the stretching and bending of MnO_6 octahedra.

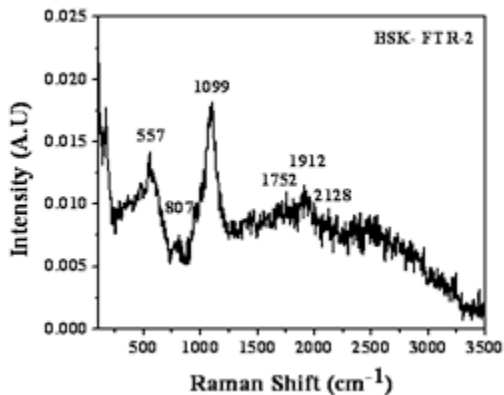


Fig.5 FT-Raman spectra of LSM

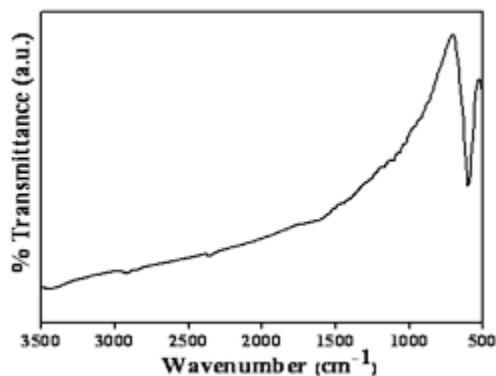


Fig.6 IR absorption pattern of LSM

IR spectroscopy is common spectroscopic technique used by organic and inorganic materials. IR analysis is to determine the chemical and functional groups in the sample. Different functional groups absorb characteristics frequencies of IR radiation. IR spectrum of LSM thin film was heat-treated at 900°C for 2 hours; the spectrum did not show any characteristics band of organic compounds in a range from 3500cm^{-1} to 500cm^{-1} as depicted in Fig.6.

According to the band observed at 600cm^{-1} which was ascribed to the metal-oxygen band, indicates the formation of the corresponding oxides [12-14].

3.4 D.C. Resistivity and Dielectric constant:

The resistivity as a function of temperature for 200nm LSM thin film is shown in Fig.7. Transport measurements were performed using conventional two probe method. The D.C resistivity decreases exponentially as temperature is raised. Resistivity linearly decreases with increase in temperature effects the semiconductor behavior of the LSM sample. The decrease in resistivity with increase in temperature is due to increase in thermally activated drift mobility charge carriers according to the hopping conduction mechanism [15]. The frequency dependence of the dielectric constant is shown in Fig.8. At low frequency dielectric increases and as frequency increases dielectric constant decreases up to frequency 10 kHz and then becomes constant.

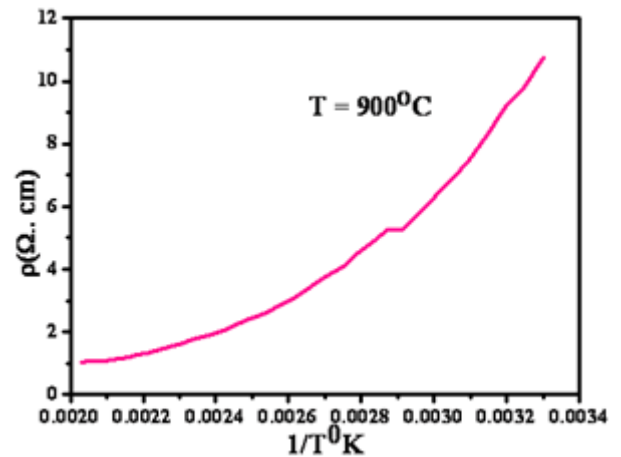


Fig.7 D.C. Resistivity Vs Temperature

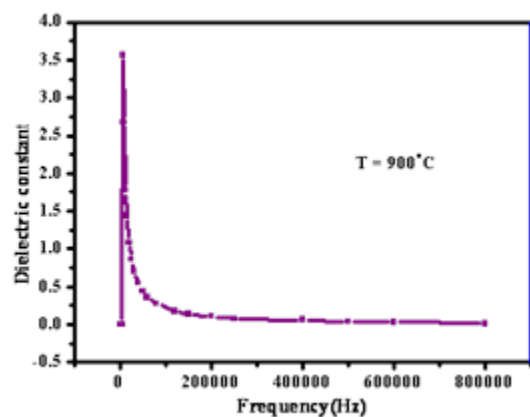


Fig.8 Dielectric constant Vs frequency

4. Conclusion:

The Spray Pyrolytic Synthesis of porous Lanthanum Strontium Manganite ($\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3-\delta}$) thin films as cathode for solid oxide fuel cell has been successfully synthesized. The crystallite size found to be 200 nm. The porous LSM thin films are usable as cathode for solid oxide fuel cell due to good oxygen reduction reaction at cathode. X-ray

diffraction results clearly indicated that sintered LSM at 900°C for two hours show the formation of single phase solid solution with perovskite like structure which were confirmed by IR analysis. Resistivity of LSM thin film decreases as temperature increases behaves as semiconductor property and Dielectric constant suddenly decreases at low frequency and became constant as frequency increases.

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