Research Paper

Structural and Transport Properties of Strontium-doped Lanthanum Manganite Thin Films as Cathode for SOFC Application

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Abstract—In the current research paper strontium-doped lanthanum manganite (LSM) material in thin film with 0.10, 0.20, and 0.30 mol % strontium (Sr) was synthesized by spray pyrolysis technique (SPT). The thin film was sintered at 900 ℃, it had been characterized by XRD, FESEM for surface morphological analysis, and X-ray photoelectron spectroscopy. The Dielectric constant was measured with temperature variation. The Warburg impedance measurement was carried out with frequency variation in the range 100Hz-5MHz at room temperature. XRD results confirmed that the LSM perovskite phase was formed. Impedance study showed that with increasing strontium polarization resistance decreases.

1. Introduction

In recent times solid oxide fuel cells (SOFC) is used as a high-efficiency energy conversion device [1-2], commutable, and with minimum pollution [3]. But the operating temperature of SOFC is up to 300 ℃– 600 ℃ [4]. The SOFC cathode material in the bulk form is hindered due to the high operating temperature of SOFC. The reduction of operating temperature to 300 ℃– 600 ℃ is the major hurdle for the commercialization of SOFC [5]. For satisfactory performance of SOFC, the polarization resistance i. e. cathodic became the substantial factor that affects the efficiency of SOFC [6-7]. Cathode materials are having mixed ionic and electronic conduction which offers excellent electrochemical performances for SOFC [8]. Several research groups have synthesized LSM thick film material and electrode microstructure controlled by the thickness of the film [9]. To achieve a low operating temperature of the fuel cell the cathode material has a lower thickness and more porosity. In the current research, it is trying to synthesize the more porous LSM thin films and study the various characteristics. The porous electrode cathode is used in the fuel cell. So thin films have been synthesized by using SPT. The LSM cathode material is synthesized in thin film form on the alumina substrate and sintered at 900OC for 2 hours for desired phase formation. After thermal treatment, thin films had been characterized by XRD, FESEM, EDAX XPS, dielectric constant, and electrochemical impedance spectroscopy.

2. Related Work

To increase the efficiency of SOFC, it is essential to reduce its operating temperature. For that purpose, many research groups have been working on LSM thin film as cathode materials. A lot of studies have been reported in the literature regarding LSM cathode materials [10, 11].

3. Experimental Method

3.1 Materials and Methods
The SPT was used to synthesize the LSM thin films. The chemicals used in this synthesization are. Nitrates of Lanthanum (La $(NO_3).6H_2O$), Strontium ($Sr(NO_3)_2$) and Manganese (Mn $(NO_3)_3.6H_2O$) respectively. All the reagents were procured from S. D. Fine Chem. without further purification.

3.2. Synthesis of LSM thin films
The precursor solution was formed by dissolving the above chemicals in water with appropriate quantity. This precursor solution was used for spray using a spray nozzle by spraying 3 ml per minute on Al_2O_3 substrates with the help of a hot plate with a temperature of 225 ℃. There is the liberty to control the stoichiometry of precursor solution which is the benefit of the spry pyrolysis system. Due to the pyrolytic decomposition of these metallic salts of LSM thin films were formed. The strontium material was added by maintaining a suitable concentration. The pure phase of the material was achieved by sintering at 900 ℃ for two hours.

3.3. Physical Properties measurement

For XRD was used to confirm the phase formation of prepared material using Rigaku mini flex 600 X-ray diffractometer by cu-k-α radiation having wavelength 1.5406 Å. After sintering the films were then characterized by morphological properties. Microstructure of LSM film by using a field emission scanning electron microscope. Using HIOKI LCR - Q meter actual impedance was calculated with respect to frequency. Phase angle was measured simultaneously and from this data, real and imaginary impedance was calculated with respect to frequency. A special instrument was designed and fabricated for the purpose of connecting the electrodes to the L-C-R meter. Chemical composition and surface examination were done by XPS.

4. Results and Discussion

4.1 XRD:

LSM thin films sintered at 900OC for 2 hours are shown in Fig. 1 by the X-ray diffraction pattern. The increased sharpness of the characteristic diffraction lines due to LSM implies further improvement in the crystallinity with an increase in the strontium content. The diffraction lines match with JCPDS data (file No. 047-0444) corresponding to trigonal-like perovskite crystal having an R3C space group. The crystal structure study showed that the unit cell is rhombohedral having a hexagonal lattice parameter [12, 13]. After calculating FWHM crystallite size is found by using the Scherer formula, where K is constant and is taken as 0.9, λ = 1.5406 Å. The estimated average size of LSM nanomaterial is 276 nm.
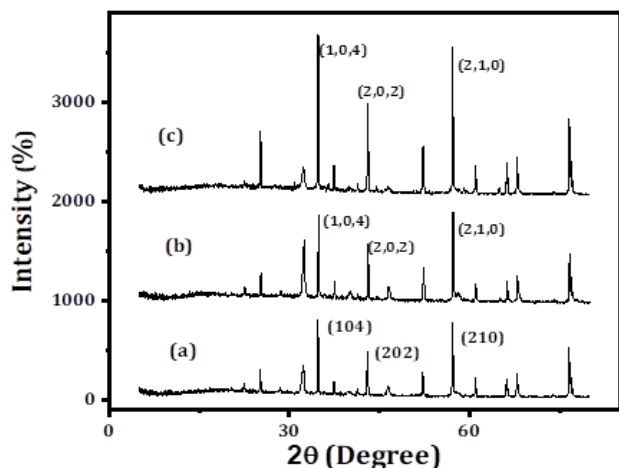

Fig. 1 XRD pattern of LSM a) X = 0.1, b) X = 0.2, c) X = 0.3

4.2 Field emission scanning electron micrograph (FESEM):-

Fig.2 exhibits the FESEM microscopy of the surface of LSM samples. The thin films prepared by the spray pyrolysis method seem to be a mushy or spongy microstructure and have excellent size distribution as well as separate the particle. It was clearly seen that particles have different dimensions and shapes [14]. It was observed that thin films had uniform porous and adhered with the substrate. The microstructure of LSM samples is shown the beginning of growth with aggregation of grains and well-developed pores [15]. As it is seen that the sample sintered at 900 °C has particles with globular shapes and also strontium content has been increased and grain size has been decreasing. It is found that as the percentage of strontium increases the volume of the unit cell decreases and particle size reduces [13]. Due to the thin and porous film oxygen can diffuse into the triple-phase boundary, resulting in much higher catalytic activity.
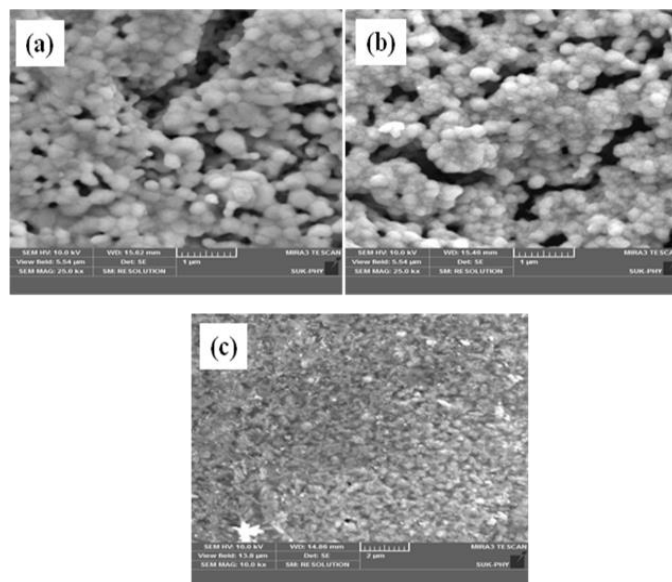

Fig.2 The images FESEM of LSM a) X=0.10, b) X = 0.20 and c) X = 0.30

4.3 Elemental analysis (EDS):

The EDS spectra for variation of strontium content are shown in Fig. 3. All EDS spectra reveal no extra peaks and reflected the presence of all constituents. In all LSM samples, the standard peak position for La, Sr, Mn, and O were exactly matched. This divulged that the elemental composition of all the LSM samples did not contain any unfamiliar element. Hence elemental analysis shows almost the same as the calculated stoichiometry. Thus, the samples investigated for elemental analysis showed same the estimated stoichiometry.
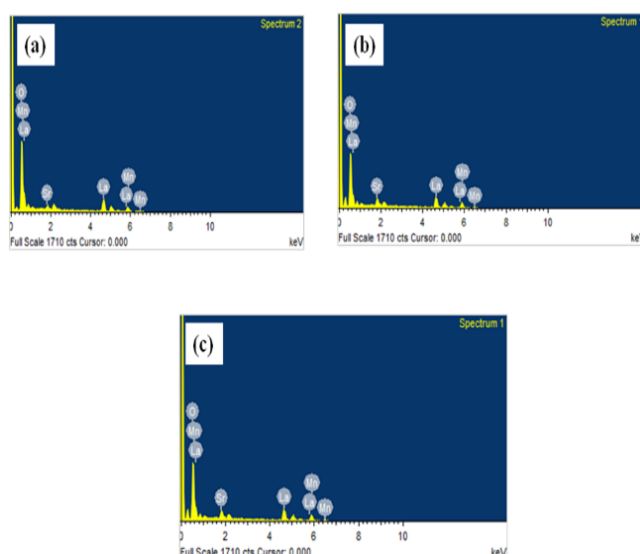

Fig. 3. EDAX spectrum of LSM a) X = 0.10, b) X = 0.20 and c) X = 0.30

Table 1. EDS Data

Element	Weight %			Atomic Weight%		
	0.1	0.2	0.3	0.1	0.2	0.3
La	49.26	53.05	56.89	15.84	17.01	18.60
Sr	2.44	3.42	6.02	1.25	1.74	3.12
Mn	26.24	20.22	13.42	21.34	16.86	11.09
O	22.06	23.30	23.67	61.58	64.86	67.19
Total	100.00	100.00	100.00	100.01	100.00	100.00

4.3 XPS Analysis of LSM thin films:

XPS gives detailed cognition of the oxidation state of each element, from the chemical composition near the surface area and the binding energy at the particular level. [16]. The XPS of LSM thin films deposited on alumina substrate is shown in Fig. 4. The peaks for La (3d) state are observed. The corresponding binding energy was also reported at 834 eV and 851 eV. The spin-orbit splitting i.e., Energy difference ΔE between the 3d5/2 level is approximately 17 eV [17].

The Sr spectrum is shown in Fig. 5(b). The strontium 3d spectrum reveals the coupling of 3d3/2 and 3d5/2 spin orbits, which is responsible for a doublet state. The first was doublet at 133.6 eV with a separation of 1.7 eV between the Sr 3d3/2 and 3d5/2 which are required to fit the Sr 3d spectrum. The binding energies around 133.6 eV and 135 eV were addressed to Sr 3d5/2 and Sr 3d3/2 [18]. The peak observed at 133.6 eV arises due to perovskite lattice-bound Sr and at 135 eV was attributed to Strontium surface because of Strontium on the surface of LSM thin films [19]. The Sr peaks did not seem to change or shift as the depth increased and it showed that the chemical state of Sr has unchanged.

In Fig. 5 (c) Mn 3P1/2 and 3P3/2 doublet of LSM exhibited a shift of 1 eV towards lower binding energy. But in high binding energy region shift was observed at about 8 eV for 2P1/2 and 2P3/2 doublet. Mn 2P and 3P doublet provide strong evidence to show the presence of Mn2+ ions and thus electron-doped state was formed.

Three contributions to the Oxygen (1s) signal have related to the binding to each of the three elements of the compound. From this spectrum, Mn – O component was located at about 529 eV, the La-O component at about 531 eV, and Sr – O at about 531.7 eV.

Two carbon (1s) peaks are present in the sample. The first was present at 286.2 eV which produce due to atmospheric hydrocarbons. The second peak was present at 279.8 eV. This energy corresponds to another atmospheric hydrocarbon peak and to carbonate.
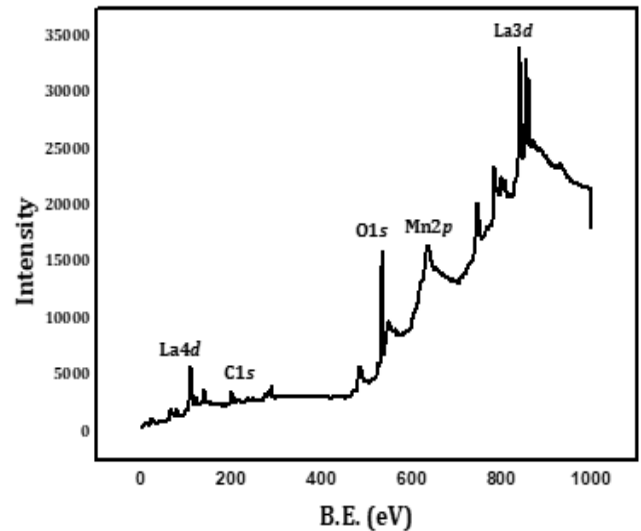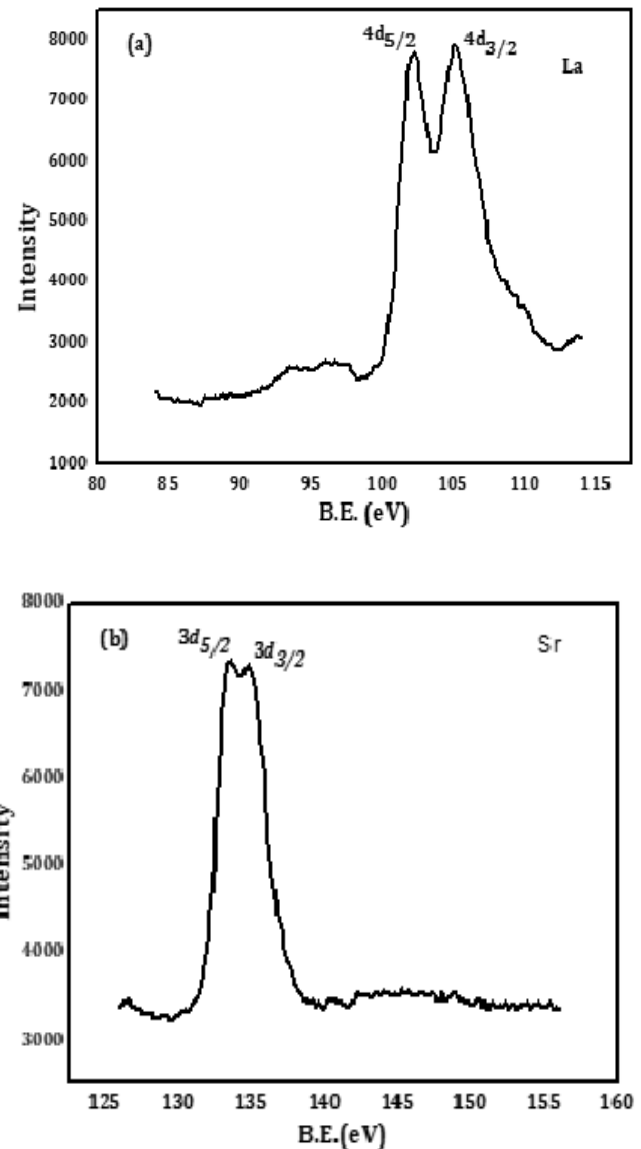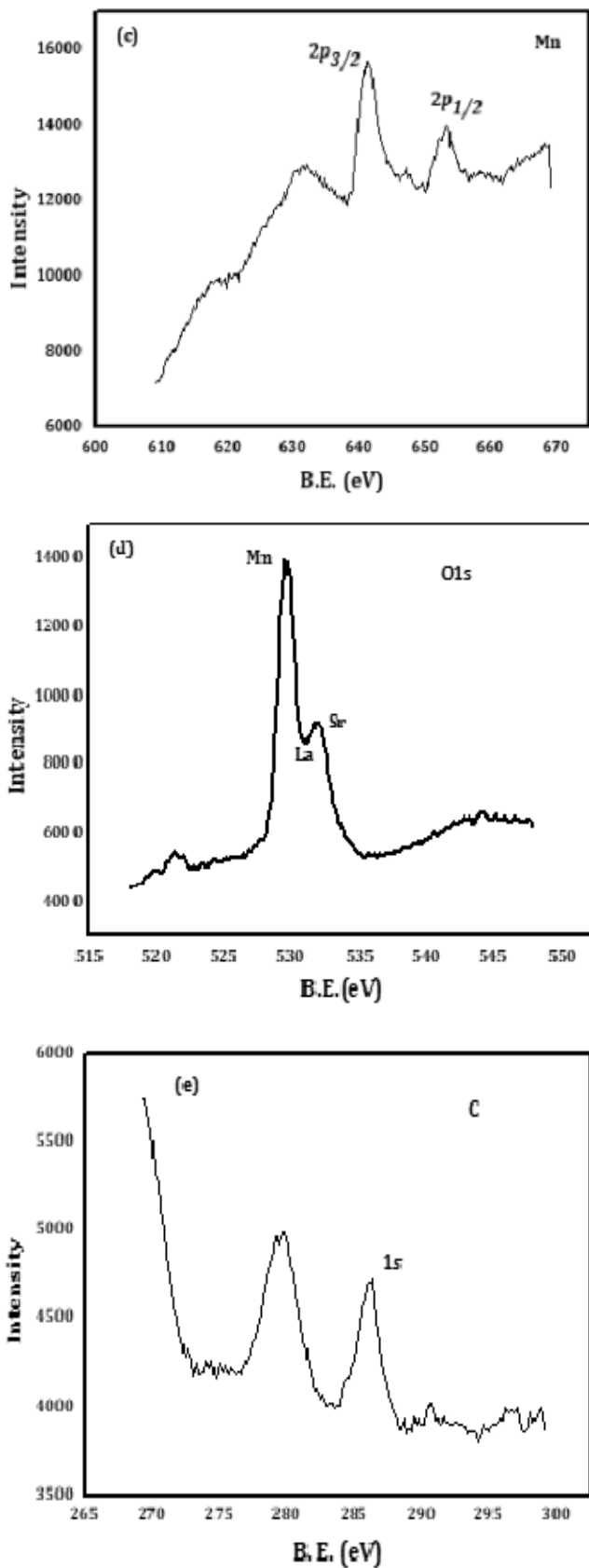

Fig. 4 XPS Spectrum of LSM Thin Film

Fig.5 XPS spectrum of a) La, b) Sr, c) Mn, d) O, e) C

3.4 Dielectric Constant:-

Fig. 6 exhibits the dielectric constant which varies w. r. t. the temperature of LSM thin films. The temperature varied from

300 K (room temperature) to 600O K. It was observed that LSM samples showed sharp transition, which was characteristic of phase transition at 500O K. The Curie temperature (Tc) i.e., transition temperature was found to be 500 K. The dielectric constant value increases and reaches a maximum and then decreases. This was due to accumulation charges at the grain boundaries of LSM particles.

As shown from the graph temperature increases the dielectric constant increases. This is because, at low temperatures, the dipoles cannot orient themselves. As the temperature increased, the dipoles were easily oriented, which tended to increase of dielectric constant value. The rate of increase of dielectric constant (ε') with temperature was found to highest for sample crystallized with increased strontium content. Initially, the dielectric constant slowly increasing with an increase in temperature [20, 21] because of the growing effect of dipole polarization and ionic polarization, which comes into play as relaxation time. If the temperature was further increased by approximately up to 500 K, relaxation time decreased, and the random vibrations of the molecules are added, it became less susceptible, and because the molecules are oriented with field direction dielectric constant decreases [22].
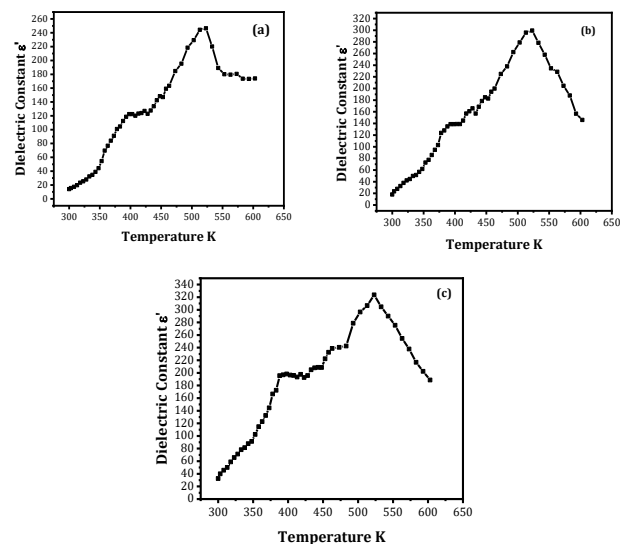

Fig 6. Dielectric Constant as a function of the temperature of LSM thin films
a) X = 0.10, b) X = 0.20, c) X = 0.30

Fig. 7 depicts the plot of dielectric constant versus frequency. The capacitance value of the LSM thin films was determined with respect to frequency using an LCR-Q meter and calculate the dielectric constant from the following equation,

$$\varepsilon' = \frac{\varepsilon}{\varepsilon o}. \tag{1}$$

where, ε - permittivity of the material and $\varepsilon0$ – permittivity of free space. It is related to polarization in that particular LSM material.

It is found that the dielectric constant attends higher value at low-frequency regions because of the space charge polarization at the grain boundary interfaces [23]. Because of

dielectric relaxation, the dielectric constant decreases as the frequency and due to the usual dielectric dispersion further, it remains constant.
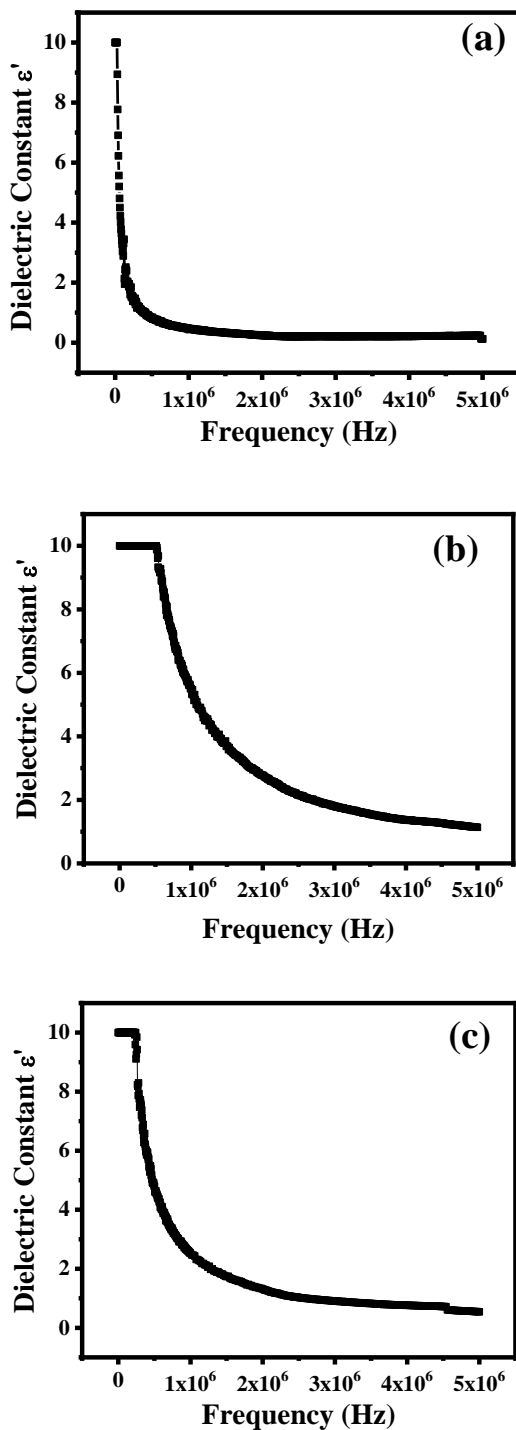

Fig. 7. Dielectric Constant as a function of the frequency of LSM thin films a) X = 0.10, b) X = 0.20, c) X = 0.30

4.5 Impedance spectroscopy:

How the grain and grain boundary is contributed is identified by the impedance spectroscopy technique. The most appropriate tool for determining the impedance of a material is the Cole-Cole plot. Fig.8 shows one of the typical impedance spectra. In all spectrums, there is the presence of one semicircle in the Cole-Cole plot which shows Debye-type relaxation [24]. The grain contributes ion found at high frequency, grain boundaries at middle frequency, and electrodes at low frequency [25].

These plots are beneficial to determining the dominant impedance of the samples. Ohmic resistance and total electrode polarization resistance also called Warburg impedance were calculated from impedance spectra. The ionic resistance of the electrolyte layer of the cell means ohmic resistance (Ro). It is calculated from high-frequency intercept on impedance spectra. One of the significant factors is electrode polarization resistance (Rp) which was calculated by taking the difference between the intercept of the low and high-frequency region of the spectra with Z'. These Warburg impedance values were determined, which are exhibited in summary form in table 2. It was found that the Warburg impedance decreased with increasing Sr^{2+} concentration.
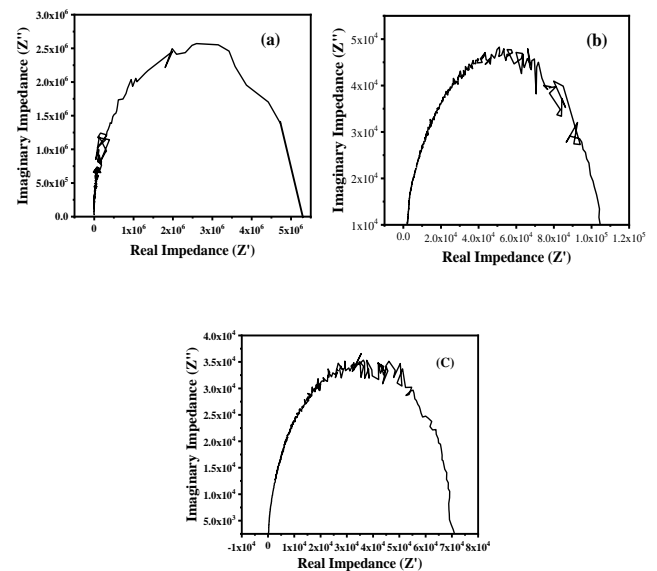

Fig.8. Nyquist plots for LSM thin films a) X = 0.10, b) X = 0.20, c) X = 0.30

Table 2. Polarization resistance determined from impedance spectra

Strontium Concentration	Polarization Resistance (R_p)
0.10	$55 \times 10^5 \ \Omega \ cm^2$
0.20	$1.5 \times 10^5 \ \Omega \ cm^2$
0.30	$0.7 \times 10^5 \ \Omega \ cm^2$

5. Conclusion and Future Scope

The XRD study shows LSM thin films have been exhibiting a single LSM phase formed by sintering at 900OC for 2 hours. The effect of Sr^{2+} ion concentration on crystal structure was investigated. The addition of strontium in LSM produced considerable modifications in the morphological, and

structural properties. The microstructure of LSM films has been revealed by FESEM and agglomerate has been formed by particles like spherical shape. FESEM study showed that the porous morphology of LSM thin films which is apposite to pass ions through the cathode electrolyte interface in SOFC. It has been found that the addition of strontium doping materials had a significant effect on their microscopic composition and specific surfaces. EDAX study showed that metal-metal ratios perfectly match as required. It also elucidates the degradation mechanism of SOFC perovskite cathode region near the surface. The binding energies of the strontium-substituted constituent elements of LSM were confirmed from XPS. The valence states of LSM thin films were studied by XPS. Dielectric constant decreases with increasing frequency is because of the presence of interfacial polarization. The impedance measurement elucidates the substitution Sr^{2+} concentration. The Warburg impedance of the material was approximately calculated from the Cole-Cole plot. Due to an increase in the strontium content, polarization resistance decreases and manifestly indicates A. C. conductivity increases. Thin films with low polarization resistance are more suitable cathode materials for miniature SOFC to reduce operating temperature.

Data Availability: Related data will be made available on request.

Conflict of Interest: No conflict of interest declared by the author.

Author's Contribution: The corresponding author, B. S. Kamble collected the experimental data, and the data was discussed with. U. M. Chougale. So both authors have contributed experimentally and theoretically.

References

[1] Da Silva, F.S.; de Souza, T. M. International Journal of Hydrogen Energy, Vol. 42, pp. 26020-26036, 2017

[2] Huang, K; Goodenough, John. B. Solid Oxide Fuel Cell Technology: Principles, Performance and Operations, Woodhead Pub. Ltd, Cambridge U. K. 2009

[3] T-L Wen, D. Wang, M. Chen, H. Z. Zhang, H. Nie, W. Huang Solid State Ionics, Vol.148, pp. 513-519, 2002

[4] U. P. Muecke, K. Akiba, A Infortune, T. Salkus, N. V. Stus, L. J. Gauckler, Solid State Ionics, Vol. 178, pp. 1762-1768, 2008

[5] J. R. Smith, A. Chen, D. Gostovic, D. Hickey, D. Kundinger, D. Ketal Solid State Ionics, Vol.180, pp. 90-98-, 2009

[6] E. P. Murray, T. Tsai, S. A. Bernett Solid State Ionics, Vol. 110, pp. 235-243, 1998

[7] T. Tsai, S. A. Bernett, Solid State Ionics, Vol. 93, pp. 207-243, 1998

[8] J. H. Kim, G. M. Choi 2000 Solid State Ionics, Vol. 130, pp. 157-168, 1997

[9] J. Piao, K. Sun, N. Zhang, S. XU Journal of Power Source,s Vol.175, pp. 288-295, 2008

[10] K. Miyoshi, T. Miyamae, H. Jwai, M. Saito, M. Kishimoto, H. Yoshida, Journal of Power Sources, Vol. 315, pp. 63-69, 2016

[11] M. Vigneshwar, K. Sakthipandi, S. Sankarrajan, International Journal of Engineering Research and Technology, Vol. 3, pp. 13-19, 2014

[12] B. S. Kamble, V. J. Fulari, R. K. Nimat, IOSR Journal of Applied Physics, Vol. 8, pp. 66-71, 2016

[13] A. M. Turky, M. M. Rashid, A. M. Hassan, E. M. Elanggar, M. Bechelany, Royal Society of Chemistry, Vol. 19, 2017

[14] E. Squizzato, C. Sanna, A. Glisenti, P. Costamagna, Energies, Vol.14, 3602, pp. 1-13, 2021,

[15] K. R. Nagde Macromolecular Symposia, 392, pp. 1-8, 2020

[16] M. Anwar, M. A. S. Abdul, U. M. Khan, M. Hasan, A. H. Khoja, A. Muchtar, Materials., Vol. 15, 2540 pp. 1-23, 2022

[17] P. Decorse, E. Quenneville, S. Poulin, M. Meunier, A. Yelon Journal of Vaccum Science & Technology A, Vol. 19, pp. 910-915, 2001

[18] Q. H. Wu. M. Liu, W. Jagegermann, Materials Letters Vol. 59, pp. 1980- , 2005

[19] Z. Cai, M. Kubieck, J. Fleig, B. Vildiz, Chemistry Materials Vol. 24, pp. 1116-1127, 2012,

[20] B. M. Tereev "Electrical and Radio Engineering Materials" MIR Publishers, Moscow. Pp. 0-390, 1980

[21] A. R. Blythe "Electrical Properties of Polymers" Cambridge University Press, Moscow, pp. 0-200, 1989

[22] B. S. Kamble, V. J. Fulari, R. K. Nimat, International Journal of Scientific Research in Physics and Applied Sciences, Vol. 6, pp.115-117, 2018

[23] S. Devikala, P. Kamraj, M. Arthanareeswari Chemical Science Transition Vol. 2, pp. S129-S134, 2013

[24] N. H. Al-Hardan, M. J. Abdullah A. Abdul Aziz International Journal of Hydro. Energy, Vol. 35, pp.4428-4434, 2010

[25] S. Roy, S. B. Mujumdar, "Synthesis and Characterization of multiferroic composite thin films", Ph. D. Thesis, IIT Kharagpur, India, 2014.

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