EFFECT OF Sr²⁺DOPING ON THE STRUCTURAL, THERMAL, DIELECTRIC AND ELECTRICAL PROPERTIES OF La_{1-x}Sr_xCo_{0.50}Fe_{0.50} O₃ {0.1 ≤ x ≤ 0.4} CATHODE FOR SOFCS

Manokamna^{1,✉}, Surinder Paul¹, A. Singh², K. L. Singh³, G. Bhargava¹ and A. P. Singh¹

¹Department of Applied Sciences, IKGPT University, Kapurthala-144601(Punjab) India

²Department of Physics, GNDU, Shri Amritsar-143006(Punjab) India

³Department of Applied Sciences, DAV Institute of Engg. And Tech., Jalandhar-144002(Punjab) India

✉Corresponding Author: manokamna12333@gmail.com

ABSTRACT

Solid solutions of perovskite La_{1-x}Sr_xCo_{0.50}Fe_{0.50}O₃; {0.1 ≤ x ≤ 0.4} ceramic material have been synthesized by solid-state route. Diffraction technique XRD has been used for structural analysis and results confirm single phase as well as crystalline behavior of the perovskite. The morphology has been investigated by scanning electron microscopy which undoubtedly indicates a decrease of granule size by Sr²⁺doping. Archimedes principle used to calculate the density which is observed to be decreasing with Sr²⁺ substitution and also is in good agreement with the microstructure. Thermogravimetric analyzer and dilatometer have been used to study the thermal properties which indicate a reduction of Co/Fe near 600°C or above consequently generate the oxygen vacancies in the prepared material and thermal expansion coefficient value decreased with Sr substitution. The impedance, as well as dielectric properties, has been studied at dissimilar temperatures as well as the frequency which affirm the non-Debye relaxation nature of the prepared cathode perovskite. The electrical conductivity value has been investigated to be larger than 100 S/cm, which recommends it to be an appropriate material for the cathode of solid oxide fuel cells.

Keywords: Fuel Cell, Perovskite, Cathode, XRD, TEC, Dielectric Constant

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INTRODUCTION

The exhausts of fossil fuel sources make it a necessity to locate clean and feasible alternative energy sources. Solid oxide fuel cell (SOFC) is a striking optional energy source due to its reasonable inexpensiveness and elevated efficiency.¹⁻⁴ Material fabricates SOFCs play a very important role to achieve such high efficiency and therefore, in the procession of such material perovskite proved its role as a significant cathode material of SOFCs.⁵ However, few issues limit the usefulness of these materials which include electrochemical performance as its electrical conductivity decreased with temperature reduction and nonequality of thermal expansion coefficient with the electrolyte.⁶⁻⁷ The introduction of element P can considerably decrease the resistance of polarization toward ORR.⁸⁻⁹ Magnetic insulators LaFeO₃ have antiferromagnetic ordering and with appropriate ion substitution, it is suggested to be the cathode of SOFCs.¹⁰ In lanthanum ferrite (LaFeO₃), Fe³⁺ ion has 3d⁵ stable electronic configuration and Sr substituted LaFeO₃ cathodes show hopeful performance regarding the stability and power density at 750°C.¹¹⁻¹³ Due to excellent oxygen diffusivity, La_{1-x}Sr_xCoO_{3-δ} has a striking electrode activity and shows marked dissociation ability towards O₂ molecules.¹⁴ But due to the large quantity of Co increase the coefficient of thermal expansion (TEC) and consequence may be crack in the electrolyte or delaminating the cathode/electrolyte interface.¹⁵ To eliminate these issues we decided to substitute Sr²⁺ at A site using varying content to form the charge inequity and consequently increase conductivity. Another approach is to balance the unequal charge by the creation of O₂ vacancies on substitution of Co at B side with fixed concentration. Therefore in the present work La_{1-x}Sr_xCo_{0.50}Fe_{0.50} O₃ (0.1 ≤ x ≤ 0.4), solid solutions have been prepared by solid-state process and samples are characterized for thermal, structural, dielectric as well as electrical measurements.

EXPERIMENTAL

Bulk material of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$, where x varies from 0.1 to 0.4 was prepared by the solid-state method. Raw powders of SrCO_3 , La_2O_3 , CoO and Fe_2O_3 (pure 99.9%, Sigma Aldrich) were used in a stoichiometric ratio to prepare the samples. The mixed powders were milled for 6 hours by using balls of zirconia oxide and acetone as solvent. Ball milled powder was mixed further thoroughly by using pestle and agate mortar for 2 hours in wet medium and then sieved using a 70-mesh sieve. Ground prepared powder was then exposed to calcination conventionally at 1200°C temperature for twelve hours. Obtained calcined powder was further mixed with 2wt % PVA used for proper binding. Pellets of 1mm thickness and 10 mm diameter were prepared. Prepared pellets were further sinter conventionally at 1400°C temperature for two hours for proper grain growth and densification of the samples.

RESULTS AND DISCUSSION

Structural Analysis and Physical Properties

X-ray powder diffraction (XRD) of the samples was carried out by x-ray diffractometer from Shimadzu Maxima 7000 (Japan) at room temperature. X-rays of wavelength (λ) $1.54 \text{ \AA}$ were used to obtain the diffraction pattern with a 0.02° degree step size, range 20° to 80° and speed of two degrees/minute. XRD patterns are given away in Fig.-1. The elevated intensity and pointed crystalline peaks recognized that the prepared samples were well crystallized. X'Pert High Score Plus software was used to analyze the XRD data. All the peaks present in XRD patterns were indexed according to crystal structure cubic, Pm-3m space group and its number is 221. In the XRD pattern, no one crystalline peak left unidentified which recognized that the solid solution was very fine crystallized in the solo phase. The different parameter belongs to crystallography are showing in Table-1.

Fig.-1: XRD Patterns of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.1 \leq x \leq 0.4$) Perovskites

Table1: Crystallographic Parameters of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.1 \leq x \leq 0.4$) Perovskites

Composition	Lattice Parameters	Cell Volume $V (\text{\AA}^3)$	Volume (Occupied)	Volume (Specific Free)
	$a = b = c (\text{\AA})$			
$\text{La}_{0.90}\text{Sr}_{0.10}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	3.88	58.411	40.531	0.30611
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	3.83	56.181	40.759	0.27451
$\text{La}_{0.70}\text{Sr}_{0.30}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	3.78	54.010	40.987	0.24112
$\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	3.79	54.439	41.215	0.24291

Microstructure

A scanning electron microscope was used to determine the surface morphology as well as the average grain size of the prepared perovskite samples. The SEM micrographs of prepared solid solutions are shown in Fig.-2. The grains are very well attached because of the good sintering of the material. The grains are

randomly oriented, non-uniform and the size of the grains is observed to be decreasing with Sr doping at the A- site of perovskite samples. Values of average grain size are given in Table-2.

Fig.-2: Micrographs of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.1 \leq x \leq 0.4$) Solid Solutions

Density

Archimede's method was used to determine the density (experimental) of the material. Density (theoretical) was obtained by using the following equation:

$$\rho = \frac{W_a}{W_a - W_l} \times \rho_{\text{liquid}}$$

Where W_l and W_a are the weight of prepared pellets in fluid and air respectively. ρ and ρ_{liquid} is the density of prepared pellet and density of the used fluid respectively. The density of the material lowered with the increasing Sr concentration in the material. Density, grain size, and tolerance factor are given in Table-2.

Table-2: Calculated Density, MeanGrainSizes as well as Tolerance Factor of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.1 \leq x \leq 0.4$).

Samples	Density			MeanSize of Grain (μm)	Deviation (size)	Tolerance factor
	Density ($d_{\text{Theoretical}}$) (g cm^{-3})	Density ($d_{\text{Experimental}}$) (g cm^{-3})	$[d_{\text{Experimental}}/d_{\text{Theoretical}}]$ (%)			
$\text{La}_{0.90}\text{Sr}_{0.10}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	5.8782	5.683	96.679	0.54	0.24	0.730
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	5.71997	5.646	98.706	0.50	0.26	0.731
$\text{La}_{0.70}\text{Sr}_{0.30}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	5.56351	5.544	99.649	0.24	0.21	0.732
$\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$	5.40878	5.335	98.635	0.19	0.16	0.732

Thermo-gravimetric Analysis

The thermo-gravimetric analysis (TGA) of the sintered pellet was obtained in an air atmosphere at a heating rate 5°C per minute with a temperature range of 50°C to 800°C with Al_2O_3 powder were used as reference material. Thermogravimetric analysis curves of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ceramic for $x = 0.1$ and 0.4 are shown in Fig.-3. TGA curves initially show sharp weight loss up to temperature 200°C - 300°C .

This weight loss may occur due to loss of the moisture present in samples as well as carbonate change into oxides. Above 300°C the weight change is comparably small. In the perovskite material creation of oxygen vacancies at high temperatures may be the reason for weight loss. Weight change rose because of charge imbalance occurs in the prepared material on Sr^{2+} substitution at A -site which is compensated by a reduction of Co/Fe substituted at B -site of the LaFeO_3 perovskite material.^{16,17}

Thermal Expansion Coefficient

Mismatching of TEC with another component of the cell gives rise to thermal stresses and reduces cell performance. $\Delta L/L_0$ versus temperature curves for all the compositions of prepared materials up to

temperature 800 °C are shown in given Fig.-4. The calculated value of TEC of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ for x belongs to 0.1 and 0.4 at temperatures 200 degrees and 800 degrees is 15.4×10^{-6} and 13.7×10^{-6} per degree Celsius respectively. The main cause of lowering or raising TEC is gain or loss of lattice oxygen of the oxides at high value of temperature and also the existence of superstructure in addition to the ordering of O_2 vacancies may be the cause of change in TEC because potential energy well becomes more symmetric with the high-quality ordering of oxygen vacancies.¹⁷⁻¹⁸ In prepared material with Sr doping the TEC, value is decreased which shows that reduction of Co takes place at a high value of temperature which gives rise to the formation of O_2 vacancies in the solid because of larger radii (ionic) of Co^{3+} as compare to Co^{4+} .

Fig.-3: TGA Curves of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($x = 0.1$ and 0.4) Solid Solutions

Fig.-4: Thermal Expansion Curves of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($x = 0.1$ and 0.4) Solid Solutions

Dielectric Properties

Relative dielectric permittivity is the function of frequency, expressed by the subsequent relation:

$$\epsilon_r[\omega] = \epsilon'[\omega] - i\omega \epsilon''[\omega]$$

Where $\epsilon'[\omega]$ be dielectric constant (real component) which is in phase using field applied and $\epsilon''[\omega]$ be the imaginary component of dielectric constant which is in quadrature using field applied. $\epsilon_r = \epsilon / \epsilon_0$ (ϵ_0 is the dielectric permittivity in free space) furthermore, ω be angular frequency. The temperature-based ϵ' , as well as ϵ'' with respect to frequency of applied field at dissimilar temperature values, are shown in Fig.-5 as well as Fig.-6, respectively. Both ϵ' , as well as ϵ'' curves, are fitted using the Cole-Cole model given below which represents a relaxation model inured to express dielectric relaxations.¹⁹ Exponent α , be a parameter that is inured to depict varied spectral shapes. When $\alpha = 0$, the Cole-Cole model represents Debye behavior and confers stretched relaxation. On the other hand $\alpha > 0$, signifying that systems moving towards non-Debye nature. Table-3 indicates that the exponents, all α - values above zero signifying the non-Debye relaxation nature of the system.

$$\varepsilon' = \varepsilon_{\infty} + \frac{(1 + \sin \frac{\alpha\pi}{2} (\omega\tau)^{(1-\alpha)}) (\varepsilon_0 - \varepsilon_{\infty})}{(1 + (\omega\tau)^{2(1-\alpha)} + 2 \sin \frac{\alpha\pi}{2} (\omega\tau)^{(1-\alpha)})}$$

$$\varepsilon'' = \frac{(\omega\tau)^{(1-\alpha)} \cos \frac{\alpha\pi}{2} (\varepsilon_0 - \varepsilon_{\infty})}{(1 + (\omega\tau)^{2(1-\alpha)} + 2 \sin \frac{\alpha\pi}{2} (\omega\tau)^{(1-\alpha)})}$$

In the lower region of frequency both ε' (real) and ε'' (imaginary) incessantly decrease concerning frequency by the side of all value of temperature and nearly show a linear behavior in the area of elevated frequency. This kind of behavior is incredibly well described by the dipolar relaxation phenomenon.²⁰ In the lower frequency region, all forms of the polarizations ionic, electronic, dipolar and space charge contribute their role and result in the highest polarizability. In the area of elevated frequency both ε' in addition to ε'' drop back the switching signal of orientation like dipolar, which further consequences around linear variation in that region because of filter out few polarizations among the overall polarizability. This variation perhaps rose due to polarization like interfacial and does not belong to polarization like dipolar.

Fig.-5: Variation of Real Component ε' Concerning Frequency of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.1 \leq x \leq 0.4$) Perovskite

Fig.-6: Variation of Imaginary Component ε'' with respect to Frequency of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.1 \leq x \leq 0.4$) Perovskite

Table-3: α -Parameter Values at Dissimilar Temperature of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.1 \leq x \leq 0.4$) Perovskite

Temperature (°C)	LSCF- 0.10		LSCF- 0.20		LSCF- 0.30		LSCF- 0.40	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
60	0.412	0.034	0.391	0.042	0.417	0.045	0.451	0.083
120	0.365	0.028	0.423	0.012	0.366	0.024	0.348	0.097
180	0.85	0.013	0.384	0.094	0.384	0.016	0.376	0.084
240	0.846	0.035	0.412	0.101	0.348	0.023	0.643	0.091

Impedance Spectroscopy

The real component Z' , as well as imaginary component Z'' of impedance w.r.t. frequency for $x=0.10$ and 0.40 samples in temperature range 60°C to 240°C, is shown in Fig.-7. From the graph, it is revolved that Z' has a large value at the lesser value of temperature moreover also with increasing frequency, its magnitude decreases which confirm that the prepared material show typical negative temperature coefficient of resistance.²¹

Fig.-7: Variation of Z' (real) and Z'' (Imaginary) Vs Frequency $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($x=0.1$ and 0.4) Perovskite

Therefore, decreasing the value of Z' with increasing both frequency and temperature indicates enhancement of electrical conductivity.^{22,23} Z' merges in a region of high frequency show that material has a reduction of barrier properties.^{24,25} The decreasing character of Z'' with enhancing both frequency and temperature confirm the fall of the resistive nature of the material. Peaks broadening on increasing the temperature revolves that the prepared samples show temperature based electrical relaxation occurrence and in the region, soaring frequency, merging of Z'' curves indicate the disappearance of polarization raised due to space charge.^{26,27}

Electrical Properties

The conductivity of the prepared samples has been calculated using formula $G\left(\frac{l}{A}\right) = \sigma_{ac}$, where G be the conductance, σ_{ac} be the ac conductivity, l be thickness and A be the cross-sectional area of the pellets. Electrical conductivity variation relating to temperature at dissimilar frequencies from 25°C temperature to 600°C temperature of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($x=0.1$ and 0.4) samples is exposed in Fig.-8. It is undoubtedly found from the graph that with enhance in temperature as well as frequency conductivity continuously increases. The maximum value of the conductivity is 156.44 S/cm as well as 189.80 S/cm for $x=0.1$ and 0.4 respectively, which also shows that the Sr modification increases the conductivity.

At a high value of temperature, $\text{Co}^{3+}/\text{Fe}^{4+}$ ions reduce to $\text{Co}^{2+}/(\text{Fe}^{2+}/\text{Fe}^{3+})$ ions and result in the generation of oxygen vacancies in the materials. As the Sr doping has been enhanced in the material, there may be the extra probability of reduction of ions and creation of O_2 vacancies in the prepared

material which future becomes the cause of raising the conductivity of the material. Grain size, grain boundaries and defects of the material play an especially important part in the conductivity of the material.

Fig.-8: Variation of Conductivity with respect to Temperature of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$;($x = 0.1$ and 0.4) Perovskite

Also, alkaline earth metals cations form ordered oxygen vacancies clusters in materials by acting like nucleating sites which can make them engaged for conduction.^{28,29} At a low value of temperatures, some extra energy is required for the dissociation of formed clusters for making the ions mobile. Therefore, the net activation energy of the material is the sum of dissociation as well as migration energy. On another side, the energy required at a high value of temperature is only for ions mobility inside the material and consequently, total activation energy is connected to migration energy which is always less than the value of activation energy at low temperature.^{30,3} The activation energy of the material has been obtained by the Arrhenius fit of electrical conductivity relating to temperature and shown in Fig.-9.

Fig.-9: Arrhenius Curves ($\ln \sigma$ vs. $1000/T$) of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ for ($x = 0.1$ and 0.4) Solid Solutions

Activation energy value calculated for $x=0.10$ sample is 0.23 eV and for $x=0.40$ sample its value is 0.21 eV which also confirm that with Sr substitution, energy value decreases. The activation energy value of the material is established to be in superior agreement with the results of the obtained value of the conductivity.

CONCLUSION

$\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ ($0.10 \leq x \leq 0.40$) perovskite ceramic material has been synthesized via solid-state method. The XRD confirms the cubic structure and single phase of the material. The obtained micrographs confirm that mean grain size constantly falls with rising Sr^{2+} substitution which in excellent agreement with the density value of the material. TGA graph shows the reduction of the material which causes the weight loss of the material. TEC value falls with Sr substitution and lies in the range $(13.7-15.4) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for $x=0.10$ to 0.40 . The dielectric constant is large at low frequency and has a low value at

high frequency. The impedance analysis established the non-Debye relaxation conduct of the samples. The electrical conductivities at unlike temperatures and frequencies have been increased with increasing Sr^{2+} content in the material.

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