EFFECT OF Sr$^{2+}$ DOPING ON THE STRUCTURAL, THERMAL, DIELECTRIC AND ELECTRICAL PROPERTIES OF La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$O$_3$ \{0.1 ≤ x ≤ 0.4\} CATHODE FOR SOFCs

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ABSTRACT

Solid solutions of perovskite La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$O$_3$ \{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 Sr$^{2+}$ doping. Archimedes principle used to calculate the density which is observed to be decreasing with Sr$^{2+}$ 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

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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{6-7} The introduction of element P can considerably decrease the resistance of polarization toward ORR.\textsuperscript{8-9} Magnetic insulators LaFeO$_3$ have antiferromagnetic ordering and with appropriate ion substitution, it is suggested to be the cathode of SOFCs.\textsuperscript{10} In lanthanum ferrite (LaFeO$_3$), Fe$^{3+}$ ion has 3d$^5$ stable electronic configuration and Sr substituted LaFeO$_3$ cathodes show hopeful performance regarding the stability and power density at 750°C.\textsuperscript{11-13} Due to excellent oxygen diffusivity, La$_{1-x}$Sr$_x$CoO$_{3-δ}$ has a striking electrode activity and shows marked dissociation ability towards O$_2$ molecules.\textsuperscript{14} But due to the large quantity of Co increase the coefficient of thermal expansion (TEC) and consequence may be crack in the electrolyte ordel aminating the cathode/electrolyte interface.\textsuperscript{15} To eliminate these issues we decided to substitute Sr$^{2+}$ 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 O$_2$ vacancies on substitution of Co at B side with fixed concentration. Therefore in the present work La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$O$_3$ (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 $\text{SrCO}_3$, $\text{La}_2\text{O}_3$, $\text{CoO}$ and $\text{Fe}_2\text{O}_3$(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 a 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 1400degree 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 ($\lambda$) 1.54 Å 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 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.

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

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.

**Density**

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

\[ \rho = \frac{W_a}{W_a - W_l} \times \rho_{liquid} \]

Where \( W_l \) and \( W_a \) are the weight of prepared pellets in fluid and air respectively. \( \rho \) and \( \rho_{liquid} \) 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>
<thead>
<tr>
<th>Samples</th>
<th>Density (d_{theoretical}) (g cm(^{-3}))</th>
<th>Density (d_{experimental}) (g cm(^{-3}))</th>
<th>[d_{experimental}/d_{theoretical}] (%)</th>
<th>MeanSize of Grain (μm)</th>
<th>Deviation (size)</th>
<th>Tolerance factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{0.90}\text{Sr}</em>{0.10}\text{Co}<em>{0.50}\text{Fe}</em>{0.50}\text{O}_3 )</td>
<td>5.8782</td>
<td>5.683</td>
<td>96.679</td>
<td>0.54</td>
<td>0.24</td>
<td>0.730</td>
</tr>
<tr>
<td>( \text{La}<em>{0.80}\text{Sr}</em>{0.20}\text{Co}<em>{0.50}\text{Fe}</em>{0.50}\text{O}_3 )</td>
<td>5.71997</td>
<td>5.646</td>
<td>98.706</td>
<td>0.50</td>
<td>0.26</td>
<td>0.731</td>
</tr>
<tr>
<td>( \text{La}<em>{0.70}\text{Sr}</em>{0.30}\text{Co}<em>{0.50}\text{Fe}</em>{0.50}\text{O}_3 )</td>
<td>5.56351</td>
<td>5.544</td>
<td>99.649</td>
<td>0.24</td>
<td>0.21</td>
<td>0.732</td>
</tr>
<tr>
<td>( \text{La}<em>{0.60}\text{Sr}</em>{0.40}\text{Co}<em>{0.50}\text{Fe}</em>{0.50}\text{O}_3 )</td>
<td>5.40878</td>
<td>5.335</td>
<td>98.635</td>
<td>0.19</td>
<td>0.16</td>
<td>0.732</td>
</tr>
</tbody>
</table>

**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 \( \text{Al}_2\text{O}_3 \) 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 \( \text{LaFeO}_3 \) 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 La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$O$_3$ for $x$ belongs to 0.1 and 0.4 at temperatures 200 degrees and 800 degrees is $15.4 \times 10^{-6}$ and $13.7 \times 10^{-6}$ 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. 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$^{4+}$.

Dielectric Properties

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

$$\varepsilon_r(\omega) = \varepsilon'(\omega) - i\omega \varepsilon''(\omega)$$

Where $\varepsilon'(\omega)$ be dielectric constant (real component) which is in phase using field applied and $\varepsilon''(\omega)$ be the imaginary component of dielectric constant which is in quadrature using field applied. $\varepsilon_r = \varepsilon_r/\varepsilon_0$ ($\varepsilon_0$ is the dielectric permittivity in free space) furthermore, $\omega$ be angular frequency. The temperature-based $\varepsilon'$, as well as $\varepsilon''$ with respect to frequency of applied field at dissimilar temperature values, are shown in Fig.-5 as well as Fig.-6 respectively. Both $\varepsilon'$, as well as $\varepsilon''$ curves, are fitted using the Cole-Cole model given below which represents a relaxation model inured to express dielectric relaxations. Exponent $\alpha$ 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 $\alpha$ - values above zero signifying the non-Debye relaxation nature of the system.
In the lower region of frequency both $\varepsilon'$ (real) and $\varepsilon''$ (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. 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 $\varepsilon'$ in addition to $\varepsilon''$ 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.

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

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

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

Fig.-6: Variation of Imaginary Component $\varepsilon''$ with respect to Frequency of La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$O$_3$ (0.1≤ x≤ 0.4) Perovskite
Table-3: α–Parameter Values at Dissimilar Temperature of La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$O$_3$ ($0.1 \leq x \leq 0.4$) Perovskite

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>LSCF-0.10</th>
<th>LSCF-0.20</th>
<th>LSCF-0.30</th>
<th>LSCF-0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon'$</td>
<td>$\varepsilon''$</td>
<td>$\varepsilon'$</td>
<td>$\varepsilon''$</td>
</tr>
<tr>
<td>60</td>
<td>0.412</td>
<td>0.034</td>
<td>0.391</td>
<td>0.042</td>
</tr>
<tr>
<td>120</td>
<td>0.365</td>
<td>0.028</td>
<td>0.423</td>
<td>0.012</td>
</tr>
<tr>
<td>180</td>
<td>0.85</td>
<td>0.013</td>
<td>0.384</td>
<td>0.094</td>
</tr>
<tr>
<td>240</td>
<td>0.846</td>
<td>0.035</td>
<td>0.412</td>
<td>0.101</td>
</tr>
</tbody>
</table>

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.

Therefore, decreasing the value of $Z'$ with increasing both frequency and temperature indicates enhancement of electrical conductivity. $Z'$ merges in a region of high frequency show that material has a reduction of barrier properties. 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.

Electrical Properties

The conductivity of the prepared samples has been calculated using formula $G(H) = \sigma ac$, where $G$ be the conductance, $\sigma ac$ 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 La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$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, Co$^{3+}$/ Fe$^{4+}$ ions reduce to Co$^{2+}$/Fe$^{2+}$/ 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.
La$_{1-x}$Sr$_x$Co$_{0.50}$Fe$_{0.50}$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$^{-6}$ $^\circ$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.
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.

REFERENCES


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