MODIFICATION OF STRUCTURAL, THERMAL, ELECTRICAL AND DIELECTRIC PROPERTIES OF La$_{0.7}$Sr$_{0.3}$Fe$_x$Mn$_{1-x}$O$_3$ \{x=0.2 AND 0.3\} WITH Fe DOPING FOR CATHODE APPLICATION IN SOFCs

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ABSTRACT

La$_{0.7}$Sr$_{0.3}$Fe$_x$Mn$_{1-x}$O$_3$ for (x=0.20 and 0.30) compound was modified by substituting Fe at Mn site in order to study different physical properties for its use as the cathode of SOFCs. The solid-state method was used to synthesize the material. The single crystallized phase was observed by X-ray diffraction and the size of the particle was observed to be in micrometer. Micrographs obtained from scanning electron microscope indicate a decrease in grain size with Fe doping. Density was calculated by Archimedes Principle and calculated values indicate increases in density with Fe substitution. Thermal expansion coefficient (TEC) observed by dilatometer decreased with Fe doping and thermogravimetric analysis showed weight gain by the compound with the rise in temperature. Impedance spectroscope recognized the non-Debye relaxation behavior of the compounds. Fe- substitution enhanced the conductivity and decreased the activation energy. Investigated parameters indicated that the prepared perovskite compounds are suitable for cathode application in SOFC.

Keywords: Perovskite, Cathode, SOFC, TGA, Crystalline, dielectric constant

INTRODUCTION

Solid oxide fuel cell (SOFC) is a type of fuel cell that commonly works at a high value of the temperature of almost 800°C or more than it. These cells are the most attractive alternative non-conventional energy sources because of their comparatively high efficiency. In current years, an enormous attempt was applied to fabricate SOFCs that can be operated at intermediate temperature 600°C to 800°C.\cite{1,2,3,4} However, electrode kinetics falls on reducing the operating temperature, which consequences in huge interfacial polarization resistances and reduces its efficiency. The cathode electrode is one of the components of SOFCs, which play an important role in gaining the desired efficiency. Therefore, the material of cathode must fulfill several requirements in which conductivity is most important and must be greater than one hundred Siemens per centimeter under oxidizing environment, thermal expansion, as well as chemical compatibility among adjoining components.\cite{5,6,7} In literature Strontium doped LaMnO$_3$ (LSM) compounds are inexpensive and reported as the best perovskite ceramic compound for using cathode of SOFCs. However, its electrochemical performance decreased below 800 °C temperature. To overcome this drawback La, as well as Mn, is replaced by different substituent metals.\cite{8,9} Doping of Sr$^{2+}$ at La-site on of LaMnO$_3$ perovskite creates charge inequality which can be remunerated by oxidation or reduction of Mn metal as well as doped metal in place of Mn -site. This process increases the electronic conductivity inside the material.\cite{10,11} For that reason, in this work, Sr$^{2+}$ in fixed quantity is substituted by the side of La site of LaMnO$_3$ to create charge imbalance and Fe doped at Mn site to compensate the charge, which
results in electron conduction in the perovskite compound. Increased electronic movement consequently increased the efficiency of SOFCs.

**EXPERIMENTAL**

The solid-state reaction method was used to prepare bulk material of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ for $(0.20 \leq x \leq 0.30)$. Raw material $\text{La}_2\text{O}_3$, $\text{Mn}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$ and $\text{SrCO}_3$ in the form of powders belonging to Sigma Aldrich (purity 99.90%) were taken stoichiometric ratio. Mixed powers were taken in a container and ball milled for twenty-four hours with the help of zirconia balls in acetone media. Precursor powders were further mixed for two hours with a mortar pestle. Powders were further calcined for twelve hours at 1200°C. Polyvinyl alcohol, two percent by weight, was also mixed with calcined powder for suitable binding. After that, pellets of the mixed powder were prepared by using a hydraulic press. Samples were subsequently sintered for 2.00 hours at 1400°C. Sintered pellets were then characterized to determine the different physical properties of the material.

**RESULTS AND DISCUSSION**

**Structural Analysis**

XRD pattern of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ for $(0.20 \leq x \leq 0.30)$ of as-prepared compounds were obtained by using X-Ray diffraction characterization technique and shown in Fig.-1. Patterns were obtained by using an X-Ray of wavelength 1.54 Å, temperature range 20–80 °C, step size 0.02 and scan rate 2°/minute. Sharp peaks confirm the crystalline character and the absence of an unidentified peak confirms the single phase of the material. The structural parameters were then studied by the use of $R-3c$ hexagonal space group and 167 group number. Calculated parameters were tabulated in Table-1.

![XRD Patterns of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$](image1.jpg)

**Table-1: Lattice Parameter and Volume of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ for $x=0.20$ and $0.30$ Compounds**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter</th>
<th>Ratio</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}<em>{0.7}\text{Sr}</em>{0.3}\text{Mn}<em>{0.8}\text{Fe}</em>{0.2}\text{O}_3$</td>
<td>5.589</td>
<td>13.536</td>
<td>2.421</td>
</tr>
<tr>
<td>$\text{La}<em>{0.7}\text{Sr}</em>{0.3}\text{Mn}<em>{0.7}\text{Fe}</em>{0.3}\text{O}_3$</td>
<td>5.588</td>
<td>13.533</td>
<td>2.421</td>
</tr>
</tbody>
</table>

**Morphology and Density**

Morphologies of the present material were obtained via Scanning Electron Microscope (SEM). Non-uniform, randomly oriented grains of the compounds were confirmed by SEM and shown in Fig.-2. Images showed that the obtained grains are extremely well linked with each other and showed that samples were very well sintered. Archimedes principle of liquid displacement was used to find out the density. The conductivity of the ceramic material is good when its density is good; therefore, density plays an imperative role in attaining the desired necessity of cathode for SOFCs. Density for $x=0.20$ composition is found to be 3.91 g/cm$^3$ and for $x=0.30$ is 4.47 g/cm$^3$, which confirmed that density increased with Fe addition. The average grain size for $x=0.20$ composition is found to be 2.14 μm and for $x=0.30$ be 2.18 μm, which showed that the size of the grain is also increased with Fe modification. $\text{Sr}^{2+}$ on La site suppresses the grains necking because of reducing in grain boundary movement, consequently decreasing the grain size.$^{12}$ Replacement of $\text{Fe}^{3+}$ may raise the mobility moreover improve the grain
dimension. The rise of the mean grain dimension involved in micrographs is in exceptional harmony with the obtained value of density.

Fig.-2: SEM Images of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ for (a) Sample with $x = 0.20$ and (b) Sample with $x = 0.30$

**Thermogravimetric Analysis**

The thermal stability of as-prepared ceramic compounds was determined by thermogravimetric analysis (TGA). The effect of heat on the change of weight all over the sintering process was analysed via TGA and curves obtained between 50 °C to 800 °C are revealed in Fig.-3. Up to temperature 350 °C there was a sudden loss in weight because of the presence of moisture in the samples. Above 350°C and up to 800°C temperature, weight gain showed in the material which was also increased with Mn replacement by Fe in the as-prepared compounds.

Fig.-3: Thermo Gravimetric Analysis Curves of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ for (a) Sample with $x = 0.20$ and (b) Sample with $x = 0.30$

**Thermal Expansion Coefficient**

The thermal expansion coefficient (TEC) is a significant parameter of the cathode electrode because TEC mismatching with other component produces thermal stress and decreases the performance of SOFCs. Dilatometer was used to determine the thermal expansion coefficient (TEC) of the material. Variation of $dL/L_0$ showing in thermal expansion curves with temperature increase up to 800 °C, showing in Fig.-4. Thermal expansion coefficient from 50°C to 800°C temperature range of for compositions $x = 0.20$ and 0.30 were obtained to be $11.26 \times 10^{-6}$ °C$^{-1}$ and $11.08 \times 10^{-6}$ °C$^{-1}$, respectively, which showed that Fe substitution reduces the TEC value.

Fig.-4: Thermal Expansion Curves of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ for Composition (a) Sample with $x = 0.20$ and (b) Sample with $x = 0.30$
Charge imbalance produced via the Sr adding at La site as well as Fe at Mn site of the LaMnO$_3$ create a reduction of Mn$^{4+}$ and Fe$^{4+}$ to Mn$^{3+}$ and (Fe$^{2+}$ or Fe$^{3+}$) produce O$_2$ vacancies or oxidation of Mn$^{3+}$ and (Fe$^{3+}$ or Fe$^{3+}$) to Mn$^{4+}$ and Fe$^{4+}$ at Mn site initiate annihilation of oxide vacancy in sintered material formed this thermal change aroused inside the as prepared compounds.\textsuperscript{13-15}

**Dielectric Constant**

Frequency variation consequence on dielectric constant can be observed by their relative dielectric permittivity in a complex form which is given by subsequent relation:

$$\varepsilon_r[w] = \varepsilon' [w] - i\varepsilon'' [w]$$

Here, $\varepsilon_r$ be $\varepsilon/\varepsilon_o$, $\varepsilon'$ represent a real component, $\varepsilon''$ represent an imaginary component of dielectric constant and $\varepsilon_o$ represent permittivity in free space. The change in $\varepsilon'$ and $\varepsilon''$ are exposed in 05 and 06 figures, respectively. Nonexistence of any peak suggested almost zero dielectric loss; consequently, polarizations were fully dominated by hopping mechanism.\textsuperscript{16} It is undoubtedly confirmed from the graphs that $\varepsilon'$ and $\varepsilon''$ increased by Fe addition at Mn site of the as prepared compound. This enhancement might be caused by the participation of polarization of interface and does not arise due to the polarization of dipolar kind. High dielectric constant in the lower region of frequency and vice versa in both $\varepsilon'$ and $\varepsilon''$ confirmed lag of switching signal of dipolar orientation plus filtering out an amount of polarization among the overall polarizability.\textsuperscript{17}

**Fig.-5:** Real Part of Dielectric Constant Vs Frequency of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ for (a) Sample with $x = 0.20$ and (b) Sample with $x = 0.30$

\varepsilon’ and $\varepsilon''$ graphs are fitted by means of Cole-Cole equations, recognized as relaxation model communicate dielectric relaxations, by way of an exponent $\alpha$, identified as parameter inured to express different spectral shapes.\textsuperscript{18}

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

Obtained values of \( \alpha \) shown in Table-2 were obtained to be more than zero, recognizing that material follows non-Debye relaxation behavior.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( \varepsilon' )</th>
<th>( \varepsilon'' )</th>
<th>( \varepsilon' )</th>
<th>( \varepsilon'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.06332</td>
<td>0.09</td>
<td>0.1154</td>
<td>0.102</td>
</tr>
<tr>
<td>100</td>
<td>0.04213</td>
<td>0.087</td>
<td>0.0916</td>
<td>0.098</td>
</tr>
<tr>
<td>150</td>
<td>0.01560</td>
<td>0.063</td>
<td>0.0529</td>
<td>0.075</td>
</tr>
<tr>
<td>200</td>
<td>0.0098</td>
<td>0.057</td>
<td>0.0380</td>
<td>0.067</td>
</tr>
<tr>
<td>250</td>
<td>0.0015</td>
<td>0.051</td>
<td>0.0250</td>
<td>0.052</td>
</tr>
</tbody>
</table>

**Impedance**

Impedance \( Z' \) (part real) vs impedance \( Z'' \) (part imaginary) variation of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) for \( 0.20 \leq x \leq 0.30 \) with respect to frequency from 50°C to 250°C temperature range are shown in figure number 07 and 08 respectively. The magnitude of \( Z' \) was obtained to be high at a small value of temperature and reduced with increase in frequency, consequence into negative temperature coefficient of resistance of the present prepared material. Fall in \( Z' \) caused an increase in electrical conductivity. Both \( Z' \) and \( Z'' \) merge in higher frequency values, causing a drop in barrier properties and disappearance of polarization caused by space charge respectively.

**Electrical Conductivity**

A major requirement of the cathode of SOFCs is its conductivity of more than 100 S/cm. An impedance analyzer was used to find out the conductivity of the sintered pellets of the material. Conductivity at various frequency values and temperature (50°C - 600°C) for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) for composition \( x = 0.2 \) and \( x = 0.3 \) are given in Fig.-9. The highest calculated conductivity for sample \( x = 0.2 \) and \( x = 0.3 \) were
found to be 104.56 S/cm and 114.23 S/cm respectively. Fe modification also increased the conductivity of the material.

Activation Energy (Ea)
Arrhenius plots (ln σ w.r.t. 1000/T) of La_{0.7}Sr_{0.3}Mn_{1-x}Fe_{x}O_{3} for composition x equal to 0.2 and 0.3 are tabulated in Fig.-10. The activation energy (Ea) was determined after Arrhenius curve fitting and its value was determined to be 0.143 eV for x= 0.2 compositions and 0.108 eV for x=0.3 composition, respectively of perovskite compounds. As the Mn was replaced by Fe, the value of Ea decreased, which confirmed the electronic conduction increased in the prepared materials. Decrease value of Ea on Mn replacement by Fe was also major evidence which confirmed the enhancement of conductivity of the compound.

CONCLUSION
A solid-state reaction route was used to prepare bulk material of La_{0.7}Sr_{0.3}Mn_{1-x}Fe_{x}O_{3} for (0.20 ≤ x≤ 0.30). The XRD found a single-phase, hexagonal structure and solid crystalline nature of the material. SEM confirmed average grain size incessantly increases by Fe doping which is moreover in fine harmony with a density of present perovskite. TGA confirmed weight gain, which proved that prepared material attained stability with temperature. The calculated value of the thermal expansion coefficient was found to be 11.26×10^{-6} per °C and 11.08×10^{-6} per °C for x=0.20 and 0.30 composition, respectively, which lie in the required range of TEC for the cathode of SOFCs. The dielectric constant was observed to be large at a small frequency and showed linear behavior at a higher value of frequency. The impedance spectroscopy defined that material show non-Debye relaxation behavior. The material showed a negligible dielectric loss. The electrical conductivity was found to be increased and activation energy decreased with Fe substitution. Maximum conductivity was found to be 114.23 S/cm for x=0.30 sample. Activation energy calculated to be 0.143 eV and 0.108 eV for x=0.20 and 0.30 respectively which confirm conductivity rise with Fe substitution. Therefore, as per the requirement of the cathode of SOFCs, the prepared material is observed to be the appropriate material proposed for cathode application in SOFCs.

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