CHAPTER 3

INVESTIGATIONS ON SINGLY DOPED CERIA

3.1 INTRODUCTION

Solid Oxide Fuel Cell (SOFC) mainly focuses on Yttria-Stabilized Zirconia (YSZ) ceramics due to rapid oxygen ion diffusion in nature at higher temperature ranges. These ZrO$_2$ based electrolyte requires high operating temperatures of 800–1000°C in order to maintain high oxygen ionic conductivity (Minh & Takahashi 1995, Janina Molenda 2006, Mridula Biswas et al. 2011).

To reduce the operating temperature and to increase their conductivity at lower temperature range (500–800°C) compared with YSZ, some novel oxygen-ion conductors including CeO$_2$, Bi$_2$O$_3$- and LaGaO$_3$-based oxides have been extensively investigated (Jennifer et al. 2006, Krok et al. 2006, Tatsumi Ishihara et al. 2006, Weimin Guoa et al. 2010). Intensive researches were being carried out to reduce the operating temperature there by reducing the cost of material and cell fabrication by reducing the operating temperature of SOFC between 500-800°C.

Pure CeO$_2$ has low thermal resistance and low textural stability, which is not high enough to meet the requirements of high temperature applications. Hence pure ceria is generally not preferred.

Ceria-based solid solutions have been regarded as being the most promising electrolytes for intermediate temperature SOFC (IT-SOFC). Ceria (CeO$_2$) doped with rare earth metals as electrolyte materials showed higher
ionic conductivity at relatively lower temperatures (500°C) to that of Yttria Stabilized Zirconia (YSZ) (Sossina & Haile 2003). The catalytic behavior is reduced due to the higher temperature which is due to the increase in the surface area. The grain growth can be controlled and their conductivity can be increased relatively by doping the ceria with different metal ions and their structural stability can also be increased. (Muthukkumaran et al. 2004).

There were reports on the metal dopants and rare earth dopant on the host lattice of ceria, in which ceria site is replaced with a wide range of rare-earth ion dopants (e.g. Y\(^{3+}\), La\(^{3+}\), Gd\(^{3+}\), Sm\(^{3+}\) and Yb\(^{3+}\)) by which the ionic conductivity can be increased (Dudek & Molenda 2006, Zhang Hong et al. 2007, Fei Ye Toshiyuki Mori et al. 2007, Mamoune et al. 2012, Mingfei Liu et al. 2012, Souza et al. 2010).

In the present work Ce\(_{1-x}\)Mg\(_x\)O\(_2\) and Ce\(_{1-x}\)Sc\(_x\)O\(_2\) with a metal loading of x = 0, 0.5, 0.1, 0.15 and 0.2 have been synthesized by co-precipitation method. A simple co-precipitation technique is employed in the present case due to their cost effectiveness in the resultant product formation and uniform particle size distribution of the synthesized samples (Godinho et al. 2007).

The Ac impedance technique, a powerful tool was used to analyze the electrical properties of ceramic ionic conductors (Ross Macdonald 1992). From the impedance results obtained it was noted that 10 mol% of Magnesium doped ceria and 10 mol% of Scandium doped ceria has the highest ionic conductivity compared to other dopant concentrations. The conductivity of the nanocrystalline form of ceria increased due to the increase in surface to volume ratio at nano regime (Toshiyuki Mori & John Drennan 2006, Soofin Cheng & Feng-Yun Wang 2004, Costa & Muccillo 2008).
Reports have been published on the ionic conductivity of Magnesium doped Ceria (Soofin Cheng & Feng-Yun Wang 2004) and Scandium doped Zirconia (Costa & Muccillo 2008). So far, there is no report on the ionic conductivity of ceria doped with Scandium. Hence, in the present study Ion dynamic analysis of Scandium doped Ceria has been reported and compared with Magnesium doped Ceria.

3.2 EXPERIMENTAL

3.2.1 Synthesis of Nanocrystalline Form of Pure Ceria, Mg Doped Ceria and Sc Doped Ceria

A co-precipitation method was used to prepare pure Ceria, Magnesium doped Ceria and Scandium doped Ceria. Required quantities of Cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O) (99.99%, Himedia), Magnesium nitrate hexahydrate (Mg(NO$_3$)$_3$·6H$_2$O) (99%, Himedia) and Scandium nitrate hexahydrate (Sc(NO$_3$)$_3$·6H$_2$O) (99%, Himedia) were used as starting materials. All the chemicals were of analytical grade and were used as purchased.

For pure ceria, Cerium nitrate hexahydrate was dissolved in 80% ethylene glycol/water mixed solvents and for Magnesium doped ceria, 0.1M of Cerium nitrate hexahydrate and 0.1M of Magnesium nitrate hexahydrate were mixed according to the desired molar ratio of Ce$_{1-x}$Mg$_x$O$_2$ with a metal loading of $x =$0, 0.5, 0.1, 0.15 and 0.2. For Scandium doped ceria, 0.1M of Cerium nitrate hexahydrate and 0.1M of Scandium nitrate hexahydrate were mixed according to the desired molar ratio of Ce$_{1-x}$Sc$_x$O$_2$ with a metal loading of $x =$0, 0.5, 0.1, 0.15 and 0.2. All the components were dissolved in distilled water using a magnetic stirrer at 80°C with a stirring rate of 500 rpm. Ammonium hydroxide (NH$_4$OH) was added drop-wise to this mixture; precipitates were formed until pH10, the mixed solution being stirred
continuously until the reaction is completed in about 12 hours after which the precipitates were centrifuged and washed with water and ethanol multiple times. The synthesized powders were then dried and calcinated at 800°C for about 24 hours in air atmosphere to obtain nanocrystalline form of pure and doped ceria.

These nanocrystalline forms of powders were then subjected to different characterization techniques to test its phase identification. The powders were then ground and was then cold pressed isostatically under 4000 kg/cm$^2$ to form pellets with 0.1 cm thickness and 1.0 cm diameter which was further sintered in air at 1500°C for 2 hours. These pure and doped ceria pellets were then used for electrical measurements.

### 3.2.2 Characterization of Singly Doped Ceria

The crystallinity and phase analysis of the pure ceria, Magnesium doped ceria and Scandium doped ceria compositions of sintered samples were identified by X-Ray Diffraction (XRD) analysis by using Philips X-ray diffractometer PW 1830. The crystalline sizes of the powders were estimated by the line broadening analysis, using the reflection planes. The specific surface area evaluation of the powders was measured by the one-point Brunauer-Emmett-Teller (BET) technique. The Archimedean method was used to determine the apparent density of the studied samples. The Vickers Hardness (HV) and fracture toughness (K$_{IC}$) were determined by the Vickers indentation method. The morphology and composition of the nanocrystalline form of the samples were subjected to Scanning Electron Microscopy (SEM) using a JSM-6335F, JEOL microscope. The electrical properties of the samples were investigated by ac impedance spectroscopy in the temperature range of 500°C and at the frequencies from 50Hz to 5MHz using an impedance analyzer HIOKI 3532.
3.3 RESULTS AND DISCUSSIONS

3.3.1 Powder XRD and BET Analysis for Singly Doped Ceria

The crystallinity and phase analysis of the prepared nanocrystalline pure ceria, Magnesium doped ceria and Scandium doped ceria samples were examined by powder XRD and BET analysis. The crystalline size of the powders was estimated by the line broadening analysis, using the reflection plane. The specific surface area of the powders was measured by the one-point BET technique. The Archimedean method was used to determine the apparent density of the studied samples. The Vickers Hardness (HV) and fracture toughness (KIC) were determined by the Vickers indentation method.

Powder XRD patterns of doped ceria samples Ce$_{1-x}$Mg$_x$O$_2$ and Ce$_{1-x}$Sc$_x$O$_2$ with a metal loading of x =0, 0.5, 0.1, 0.15 and 0.2 are shown in Figure 3.1 and 3.2 respectively.

![Powder XRD patterns](image)

Figure 3.1 X-ray diffraction patterns of (a) JCPDS of Pure CeO$_2$, (b) Ce$_{0.95}$Mg$_{0.05}$O$_2$, (c) Ce$_{0.9}$Mg$_{0.1}$O$_2$, (d) Ce$_{0.85}$Mg$_{0.15}$O$_2$ and (e) Ce$_{0.8}$Mg$_{0.2}$O$_2$
Figure 3.2 X-ray diffraction patterns of (a) JCPDS of Pure CeO$_2$, (b) Ce$_{0.95}$Sc$_{0.05}$O$_2$, (c) Ce$_{0.9}$Sc$_{0.1}$O$_2$, (d) Ce$_{0.85}$Sc$_{0.15}$O$_2$ and (e) Ce$_{0.8}$Sc$_{0.2}$O$_2$

The XRD patterns are in accordance with the data in the JCPDS (Joint Committee on Powder Diffraction Standards) card no.81-0792 of a cubic phase CeO$_2$.

It is clearly evident from the XRD pattern that only the peaks correspond to the ceria alone is found and that, the absence of any other secondary phases of the dopants does not reflect in the spectrum.

The Crystallite (D) is estimated using the Debye Scherrer’s formula:

$$D = \frac{0.94\lambda}{\beta_2\cos \theta} \quad (3.1)$$
where $\lambda$ is the wavelength of the X-ray and $\beta_{2\theta}$ is the full width at half maximum of the corresponding peak of the XRD pattern.

Table 3.1 Unit cell parameters, Crystallite size and BET specific surface measurements of Mg doped ceria and Sc doped ceria

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit Cell parameters (Cubic A)</th>
<th>Crystallite size ($D_{hkl}$, nm)</th>
<th>Surface Area ($D_{BET}$, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Ceria (CeO$_2$)</td>
<td>5.412</td>
<td>29.8</td>
<td>30.8</td>
</tr>
<tr>
<td>Ce$<em>{0.95}$Mg$</em>{0.05}$O$_2$</td>
<td>5.472</td>
<td>17.9</td>
<td>18.7</td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Mg$</em>{0.1}$O$_2$</td>
<td>5.585</td>
<td>14.3</td>
<td>16.2</td>
</tr>
<tr>
<td>Ce$<em>{0.85}$Mg$</em>{0.15}$O$_2$</td>
<td>5.385</td>
<td>19.0</td>
<td>19.9</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Mg$</em>{0.2}$O$_2$</td>
<td>5.252</td>
<td>21.9</td>
<td>23.0</td>
</tr>
<tr>
<td>Ce$<em>{0.95}$Sc$</em>{0.05}$O$_2$</td>
<td>5.482</td>
<td>22.1</td>
<td>23.9</td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Sc$</em>{0.1}$O$_2$</td>
<td>5.510</td>
<td>18.3</td>
<td>19.8</td>
</tr>
<tr>
<td>Ce$<em>{0.85}$Sc$</em>{0.15}$O$_2$</td>
<td>5.397</td>
<td>23.7</td>
<td>25.8</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Sc$</em>{0.2}$O$_2$</td>
<td>5.247</td>
<td>24.9</td>
<td>26.0</td>
</tr>
</tbody>
</table>

The data presented in Table 3.1 indicates a decrease in the crystallite size of doped ceria solid solutions with increasing concentration of Magnesium and Scandium up to 10% after which the crystallite size increases.
The consistency of sizes determined by X-ray diffraction analysis and BET specific surface measurements suggests that the powders are composed of isometric and not agglomerated crystallites.

The average crystallite size of pure Ceria is about 29.8 nm and that of Ce$_{0.9}$Mg$_{0.1}$O$_2$ and Ce$_{0.9}$Sc$_{0.1}$O$_2$ ranges from 14.3-21.9 nm and 18.3-24.9 nm respectively.

3.3.2 SEM Analysis for Singly Doped Ceria

The surface morphology and chemical composition of Ce$_{1-x}$Mg$_x$O$_2$ and Ce$_{1-x}$Sc$_x$O$_2$ with a metal loading of $x$ =0, 0.5, 0.1, 0.15 and 0.2 which were observed and analyzed by SEM are shown in Figure 3.3. SEM micrographs clearly show the obtained powders are of nanosize particles with a uniform size distribution. From the observation, it can be seen; the surface morphology of pure CeO$_2$ is nearly spherical in shape and is dispersed well.

![PureCeO$_2$](image)

*Figure 3.3: SEM micrograph of pure CeO$_2$.*
Ce$_{0.95}$Mg$_{0.05}$O$_2$

Ce$_{0.9}$Mg$_{0.1}$O$_2$

Ce$_{0.85}$Mg$_{0.15}$O$_2$

Ce$_{0.8}$Mg$_{0.2}$O$_2$

Ce$_{0.95}$Sc$_{0.05}$O$_2$

Ce$_{0.9}$Sc$_{0.1}$O$_2$
The substitution of Magnesium or Scandium in ceria resulted in reduced particle size. These reduced particle size greatly influences the conductivity nature due to the reduced hopping distance of the ionic motion. Further, the reduction of particle size with Magnesium or Scandium doping resulted in decrease of grain boundary resistance which is discussed in impedance analysis.

3.3.3 Mechanical Strength Analysis for Singly Doped Ceria

Mechanical properties are also important for ceria-based materials, serving as solid oxide electrolytes, suitable for use in solid oxide fuel cells. The determined values of hardness $HV$, fracture toughness $K_{lc}$, bending strength ($Bs$) of the materials are listed in Table 3.2.
Figure 3.4  Influence of doping on fracture toughness of Mg doped ceria and Sc doped ceria

Figure 3.5  Influence of grain size on fracture toughness of Mg doped ceria and Sc doped ceria
In figure 3.4, $K_{IC}$ measurements revealed an increase in fracture toughness with increasing in Mg or Sc concentration in solid solutions for $x = 0-0.10$. For further higher concentrations a rather small decrease was observed, which could be attributed to the presence of small amounts of closed porosity in the investigated samples. The effect of grain size on the fracture toughness of the samples is presented in Figure 3.5 in order to compare the influence of microstructure on the changes in the fracture toughness.
toughness of doped ceria based solid solutions. From the figure, one can observe an increase in fracture toughness with decrease in grain size.

Table 3.2 presents other mechanical properties (hardness and flexural strength) which are important in the usage of doped ceria as a solid electrolyte in SOFC. A comparison of the data indicates improvement of the mechanical characteristics on doping Mg and Sc up to 10% after which the mechanical properties slightly declines.

The determined values of hardness HV or fracture toughness $K_{IC}$ indicate that all these doped ceria based materials exhibited slightly higher values for hardness and toughness compared to pure ceria.

3.3.4 Thermal Expansion Coefficient for Singly Doped Ceria

The solid oxide fuel cell mainly consists of an anode, cathode, solid electrolyte and inter-connect and it can be regarded as a typical example of composite materials. The thermal expansion coefficients of electrolyte and electrodes should match, to avoid micro-cracks in between them for the operation of SOFC device at high temperatures. The thermal expansion data of $Ce_{1-x}Mg_xO_2$ and $Ce_{1-x}Sc_xO_2$ with a metal loading of $x = 0, 0.5, 0.1, 0.15$ and $0.2$ obtained in the temperature range $30-800°C$ in air is shown in Figure 3.6.
The thermal expansion depends on the electrostatic forces within the lattice, which depends on the concentration of positive and negative charges and their distances within the lattice. The thermal expansion increases due to the decrease in attractive forces. Thermal expansion of a lattice is characterized by a steady thermal expansion coefficient ($\alpha$), for a certain structure and fixed oxygen to metal stoichiometry. The thermal expansivity (TE) can be calculated from the expansion curves using the following expression as:

$$\alpha \Delta T = \frac{dL}{L} \Delta T$$  \hspace{1cm} (3.2)$$

where, $\alpha \Delta T$ is the average of TE in the temperature range of $\Delta T$, $dL$ is the change of the sample length in $\Delta T$ and $L$ is the original length of the sample. The slope of thermal expansion curves for all the compositions are increased with temperature. The thermal expansion coefficients (TEC) are calculated from the thermal expansion curves and values are listed in Table 3.3.
Table 3.3 Thermal expansion co-efficient of Mg doped ceria and Sc doped ceria

<table>
<thead>
<tr>
<th>Composition</th>
<th>TE/10⁻⁶ °C⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>Pure Ceria (CeO₂)</td>
<td>10.89</td>
</tr>
<tr>
<td>Ce₀.₉₅Mg₀.₀₅O₂</td>
<td>11.57</td>
</tr>
<tr>
<td>Ce₀.₉Mg₀.₁O₂</td>
<td>11.65</td>
</tr>
<tr>
<td>Ce₀.₈₅Mg₀.₁₅O₂</td>
<td>11.18</td>
</tr>
<tr>
<td>Ce₀.₈Mg₀.₂O₂</td>
<td>11.35</td>
</tr>
<tr>
<td>Ce₀.₉₅Sc₀.₀₅O₂</td>
<td>10.97</td>
</tr>
<tr>
<td>Ce₀.₉Sc₀.₁O₂</td>
<td>11.12</td>
</tr>
<tr>
<td>Ce₀.₈₅Sc₀.₁₅O₂</td>
<td>11.06</td>
</tr>
<tr>
<td>Ce₀.₈Sc₀.₂O₂</td>
<td>10.41</td>
</tr>
</tbody>
</table>

The values of thermal expansion coefficients of all the compositions are in the range of 10.41×10⁻⁶/°C to 12.73 × 10⁻⁶/°C. It is noticed that the change of TE is very small. Hence the doped ceria samples can be used as possible electrolyte material for IT-SOFC applications.

3.3.5 Impedance Analysis for Singly Doped Ceria

A.C impedance analysis is an important technique to investigate the electrical properties of solid electrolytes. The ionic conductivity can be
influenced by the grain and grain boundary which in turn modifies the electrode contribution. The high frequency semi-circle corresponds to grain resistance (Rg) and grain boundary resistance is reflected in intermediate frequency semi-circle and that the low frequency incomplete arc corresponds to electrode resistance (Re).

In addition to the overall conductivity, one can also obtain information about electrode processes, and in the case of polycrystalline materials, the separate contributions of the bulk crystal lattice (grain interior) and grain boundaries.

The real (z’) and imaginary components (z”) of the impedance (z) were determined by measuring the amplitude and phase angle (θ) of the current. By plotting -Z” versus Z’, one obtains Nyquist plot, where each arc in the plot represents a distinct process whose time constant is sufficiently separated from the others over the range of measurement frequencies. The left most x-intercept of the arc is the resistance of the sample, from which conductivity values can be determined.

The typical plots obtained for Ce$_{1-x}$Mg$_x$O$_2$ and Ce$_{1-x}$Sc$_x$O$_2$ with a metal loading of x =0, 0.5, 0.1, 0.15 and 0.2 measured at a temperature of 500°C are shown in Figure 3.7 and 3.8.
Figure 3.7  Impedance spectra in Nyquist- plots of Mg doped ceria samples at 500°C

Figure 3.8  Impedance spectra in Nyquist- plots of Sc doped ceria samples at 500°C
From Figures 3.7 and 3.8 it can be noted that the composition with 10 mol% of Magnesium and 10 mol% of Scandium respectively has the highest ionic conductivity when compared to the other samples.

Impedance spectroscopy measurements enable one to determine the bulk ($\sigma_b$) and grain boundary ($\sigma_{gb}$) conductivities. The samples show semicircular arcs in the plot between real and imaginary impedance. The first arc at higher frequency (left) is attributed to the contribution from grain interior and the second one (right) to the grain boundary. The impedances were found out from the individual semicircles and the grain interior and the total conductivity (grain interior and grain boundary) were evaluated.

The impedance data shows depressed semicircles, due to the bulk and grain boundary effects. The circular fitting of the complex impedance plot has been done by using the programme EQ developed by Boukamp which yields the value of ‘n’ used to find the depression angle from the formula $(1-n) (\pi/2)$.

The associated capacitance value for the semicircles has been calculated using the formula $\omega RC = 1$. The capacitance value is found to be in the order of pF, and therefore they have been attributed to a conduction process through the bulk and the grain boundary of the material.

The electrical conductivity ($\sigma$) of the prepared sample pellets were determined from the usual Arrhenius expression:

$$\sigma T = \sigma_0 \exp \left[ - \frac{E}{kT} \right]$$  \hspace{1cm} (3.3)
Where, $\sigma_0$ is the pre-exponential factor, $E$ is the apparent activation energy for conduction, $k$ is the Boltzmann constant and $T$ is the absolute temperature.

The above equation gives a straight line between $\ln \sigma$ and $T$, the slope of which is $[-Ea/K]$. The total electrical conductivity is calculated as a sum of bulk and grain boundary conductivities.

Figure 3.9  Arrhenius plots of the total electrical conductivity for Mg doped ceria samples at 500°C
Figure 3.10  Arrhenius plots of the total electrical conductivity for Sc doped ceria samples at 500°C

A typical plot between logarithmic conductivity and temperature of the samples are shown in the figures. Figure 3.9 and 3.10 shows Arrhenius plots of the total electrical conductivity ($\sigma_T$) of samples Ce$_{1-x}$Mg$_x$O$_2$ and Ce$_{1-x}$Sc$_x$O$_2$ with a metal loading of $x = 0, 0.5, 0.1, 0.15$ and $0.2$.

The respective values of the conductivities of pure CeO$_2$, and doped ceria samples at 500°C are given in Table 3.2.
The smaller grain size reduces the hopping distance of ionic motion and thereby has a great influence on conductivity properties. The reduced particle size of Magnesium doped ceria and Scandium doped ceria up to 10mol% doping resulted in decrease of bulk and grain boundary resistance resulting in higher ionic conductivity compared to pure ceria.

Table 3.4 Electrical conductivity (σ) of Mg doped ceria and Sc doped ceria at 500ºC

<table>
<thead>
<tr>
<th>Composition</th>
<th>σ(S/cm), 500ºC</th>
<th>Ea, eV</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Grain Boundary</td>
<td>Bulk</td>
</tr>
<tr>
<td>Pure Ceria (CeO₂)</td>
<td>6.92×10⁻⁵</td>
<td>1.21×10⁻⁶</td>
<td>0.90</td>
</tr>
<tr>
<td>Ce₀.₉₅Mg₀.₀₅O₂</td>
<td>6.12×10⁻³</td>
<td>5.03×10⁻³</td>
<td>0.88</td>
</tr>
<tr>
<td>Ce₀.₉Mg₀.₁O₂</td>
<td>6.23×10⁻³</td>
<td>5.24×10⁻³</td>
<td>0.86</td>
</tr>
<tr>
<td>Ce₀.₈₅Mg₀.₁₅O₂</td>
<td>6.19×10⁻³</td>
<td>5.12×10⁻³</td>
<td>0.90</td>
</tr>
<tr>
<td>Ce₀.₈Mg₀.₂O₂</td>
<td>6.15×10⁻³</td>
<td>5.06×10⁻³</td>
<td>0.93</td>
</tr>
<tr>
<td>Ce₀.₉₅Sc₀.₀₅O₂</td>
<td>5.57×10⁻³</td>
<td>4.21×10⁻³</td>
<td>0.91</td>
</tr>
<tr>
<td>Ce₀.₉Sc₀.₁O₂</td>
<td>5.71×10⁻³</td>
<td>4.32×10⁻³</td>
<td>0.89</td>
</tr>
<tr>
<td>Ce₀.₈₅Sc₀.₁₅O₂</td>
<td>5.62×10⁻³</td>
<td>4.25×10⁻³</td>
<td>0.93</td>
</tr>
<tr>
<td>Ce₀.₈Sc₀.₂O₂</td>
<td>5.53×10⁻³</td>
<td>4.18×10⁻³</td>
<td>0.95</td>
</tr>
</tbody>
</table>
The conductivities from the grain interior and the grain boundaries were calculated based on the impedances measured. The sample $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ and $\text{Ce}_{0.9}\text{Sc}_{0.1}\text{O}_2$ shows higher conductivity when compare to other Magnesium doped ceria and Scandium doped ceria samples.

The bulk resistance of Magnesium doped ceria has been found to be low compared to the Scandium doped ceria. The bulk resistance values of the samples indicate the higher ionic conductivity for the sample $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ compared to $\text{Ce}_{0.9}\text{Sc}_{0.1}\text{O}_2$.

Further, for pure ceria, the total electrical conductivity is lower than that of sample $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ by near one order of magnitude. The higher total electrical conductivity of sample $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ when compared to pure ceria and $\text{Ce}_{0.9}\text{Sc}_{0.1}\text{O}_2$ is probably due to smaller particle size of $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ sample.

Based on the above results, the ionic conductivity of $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ and $\text{Ce}_{0.9}\text{Sc}_{0.1}\text{O}_2$ was compared with that of pure ceria. The plots obtained for Pure $\text{CeO}_2$, $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ and $\text{Ce}_{0.9}\text{Sc}_{0.1}\text{O}_2$ measured at temperature of 500$^\circ$C are shown in Figure 3.11 and Figure 3.12.
Figure 3.11  Impedance spectra in Nyquist- plots for Pure CeO$_2$, Ce$_{0.9}$Mg$_{0.1}$O$_2$ and Ce$_{0.9}$Sc$_{0.1}$O$_2$

Figure 3.12 Arrhenius plots of the total electrical conductivity of Pure CeO$_2$, Ce$_{0.9}$Mg$_{0.1}$O$_2$ and Ce$_{0.9}$Sc$_{0.1}$O$_2$

From Figure 3.11 and Figure 3.12 it can be noted that the composition Ce$_{0.9}$Mg$_{0.1}$O$_2$ has the highest ionic conductivity when compared to pure CeO$_2$ and Ce$_{0.9}$Sc$_{0.1}$O$_2$ and also the ionic conductivity of Ce$_{0.9}$Sc$_{0.1}$O$_2$ is higher when compared with pure CeO$_2$. 
3.4 CONCLUSION

Ce\textsubscript{1-x}Mg\textsubscript{x}O\textsubscript{2} and Ce\textsubscript{1-x}Sc\textsubscript{x}O\textsubscript{2} with a metal loading of x = 0, 0.5, 0.1, 0.15 and 0.2 had been prepared by co-precipitation method. The composition Ce\textsubscript{0.9}Mg\textsubscript{0.1}O\textsubscript{2} had the highest ionic conductivity among the other Mg doped ceria samples. Ce\textsubscript{0.9}Mg\textsubscript{0.1}O\textsubscript{2} was compared with Ce\textsubscript{0.9}Sc\textsubscript{0.1}O\textsubscript{2} sample which also has the highest ionic conductivity among the Scandia doped ceria samples. The ionic conductivity of both these samples was also compared with that of pure ceria.

Single phase cubic natured ceria was obtained for all the samples. Particle size calculation from the XRD pattern reveals that the synthesized powders were of nanocrystalline in nature. SEM micrograph of the pure and doped ceria sample confirms the nanocrystalline nature and that the synthesized powders possess uniformly distributed spherical powders.

The impedance analysis reveals that the samples Ce\textsubscript{0.9}Mg\textsubscript{0.1}O\textsubscript{2} and Ce\textsubscript{0.9}Sc\textsubscript{0.1}O\textsubscript{2} was found to have more higher ionic conductivity compared to pure ceria and that the ionic conductivity of the sample Ce\textsubscript{0.9}Mg\textsubscript{0.1}O\textsubscript{2} has a higher conductivity than that of Ce\textsubscript{0.9}Sc\textsubscript{0.1}O\textsubscript{2} at 500°C.

It was found that the electrical conductivity, fracture toughness and flexural strength of the investigated materials increases with the doping concentration and reaches a maximum for Ce\textsubscript{0.9}Mg\textsubscript{0.1}O\textsubscript{2} and Ce\textsubscript{0.9}Sc\textsubscript{0.1}O\textsubscript{2}. Contrary to mechanical properties, the electrical conductivity of ceria-based electrolytes can be improved simply by controlling the grain size. The obtained values of electrical conductivity and energy activation for Ce\textsubscript{0.9}Mg\textsubscript{0.1}O\textsubscript{2} and Ce\textsubscript{0.9}Sc\textsubscript{0.1}O\textsubscript{2} show that the prepared materials are a promising solid electrolyte for IT-SOFC systems.