

# Investigation on Mg and Sc co-doped Ceria electrolyte for IT-SOFC

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**Abstract** - Nanocrystalline form of pure ceria (CeO<sub>2</sub>) and metal (Mg or Sc) doped ceria was attempted for 10 mol %. Also, Mg and Sc co-doped ceria with Ce<sub>1-x</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>x</sub>O<sub>2</sub> (x=0-0.24) was prepared as an electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs) by co-precipitation method. The synthesized different compositions of pure and doped nanocrystalline powders were then subjected to powder X-ray diffraction (XRD) for phase and structural identification. All the nanocrystalline samples were found to be ceria based solid solutions of fluorite type structures. A.C. impedance spectroscopy measurements in the frequency range of 50Hz to 5MHz was carried out to study the grain, grain boundary and ionic conductivity of doped ceria samples in the temperature range of 400-600°C. The sample Ce<sub>0.84</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.16</sub>O<sub>2</sub> composition showed highest ionic conductivity i.e., 1.923 x 10<sup>-2</sup> S/cm at 500°C. Its morphology and composition was investigated using scanning electron microscopic analysis (SEM) and energy dispersive X-ray spectrometry (EDS) and conductivity behavior was compared with those of pure ceria and singly doped ceria electrolytes namely Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub>. The impedance analysis reveals that the sample Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> was found to have higher ionic conductivity compared to Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> in the temperature range of 400–600°C. The co-doped ceria showed a much higher conductivity in air at 500°C in comparison to that of singly doped ceria. Therefore, these co-doped ceria are also the more ideal electrolyte materials for IT-SOFCs. Nyquist plot shows the major contributions were due to the grain boundary resistance contributions which accounts for the higher ionic conductivity in case of the dopants. These dopant effect on the ceria is discussed in detail.

**Keywords:** Electrolyte; Co-Precipitation method; Co-Doped ceria; X-ray Diffraction; Scanning Electron Microscopy; Energy-dispersive X-ray spectrometry; Impedance analysis.

## I INTRODUCTION

Solid oxide fuel cells (SOFCs) have fascinated substantial attention for distributed power sources due to its high efficiency and low emission of pollutions to the environment. They are energy conversion devices which produce electricity directly from the chemical conversion of a fuel gas and an oxidant through an electrochemical reaction [1],[2]. Solid oxide fuel cell mainly focuses on yttria-stabilized zirconia (YSZ) ceramics as electrolytes due to its low electronic and high ionic conductivities. It has high chemical stability under reducing and oxidizing atmospheres, moderate mechanical properties and comparatively low production costs [3],[4].

Yttria-stabilized zirconia electrolyte requires high operating temperatures of 800–1000°C in order to retain high oxygen ionic conductivity. However, at such high operating temperatures there are some problems like thermal mismatch between cell components, chemical instability and selection of materials. Hence, the operating temperature of SOFC has to be lowered to eliminate these problems. Lowering the operating temperature down to around 400–600°C would result in an increase in the cell stability and allow one to use cheaper materials for cell fabrication [5].

In order to reduce the operating temperature and to increase the ionic conductivity at lower temperature range (400–600°C), some novel oxygen-ion conductors including CeO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub> and LaGaO<sub>3</sub> based oxides have been extensively investigated to be used as electrolytes for SOFC [6]. Ceria doped with alkaline or rare earth materials showed higher ionic conductivity in the temperature range 400–600°C. When alkaline, rare earth and transition elements such as La, Pr, Nd, Sm, Gd, Dy, Er, Yb, Ca, and Y are doped into ceria, they become partially substituted in the crystal structure of ceria which considerably improves the oxygen ionic conductivity compared to YSZ electrolytes [7]-[9]. Gd or Sm doped ceria have been regarded as the most promising electrolytes for intermediate temperature solid oxide fuel cells [10]-[13]. The main downside of ceria-based electrolytes, complicating their commercial application, is an increased electronic conduction under low oxygen partial pressure accompanied by reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>. It has been reported that reduction of ceria can be neglected at lower temperatures around 400–600°C. However, such low temperature operations are not suitable for singly doped ceria due to higher electrical resistance. Structural modifications of ceria-based solutions has to

be made by co-doping of the elements to increase the oxide ionic conductivity of ceria-based electrolytes in the intermediate temperature range of 400-600°C. Ceria co-doped with Lanthanides and other divalent or trivalent elements depending on chemical composition have generally improved ionic conductivities. Studies [14]–[23] show that co-doped ceria could improve the ionic conductivity of SOFC than singly doped ceria.

The paper focuses on the preparation of nano powders of pure ceria, singly and co-doped ceria materials by co-precipitation method in the  $\text{CeO}_2\text{-Mg}_2\text{O}_3\text{-Sc}_2\text{O}_3$  systems as well as on investigation of the properties essential for the application of ceria-based materials as oxide electrolytes for SOFC. 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 [24]. The practical aim of this research was to obtain a co-doped ceria based material which could be applied as an electrolyte for solid oxide fuel cell working at the temperature range of 400–600°C.

So far, there is no report on the ionic conductivity of Mg and Sc co-doped ceria. Hence, in the present study  $\text{Mg}^{2+}$  and  $\text{Sc}^{3+}$  co-doped ceria materials were prepared by co-precipitation method and characterized with different dopant concentrations to identify proper electrolyte composition for SOFC application. The effect of co-doping on structure and conductivity was studied in comparison to singly doped ceria of the same elements. As a result higher conductive electrolytes were found.

## II EXPERIMENTAL

Co-precipitation method was used to prepare nano powders of pure ceria, Magnesium or Scandium doped Ceria and Magnesium and Scandium co-doped ceria with different dopant concentrations. Required quantities of Cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) (99.99%, Merck), Magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (99%, Merck) and Scandium nitrate hexahydrate ( $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) (99%, Merck) were used as starting materials. All the chemicals were of analytical grade and were used as purchased.

### II.1. Synthesis of nano powders of pure, singly and co-doped ceria materials in the $\text{CeO}_2\text{-Mg}_2\text{O}_3\text{-Sc}_2\text{O}_3$ system

The reagents were mixed in distilled water in order to prepare pure  $\text{CeO}_2$ , singly doped ceria with formula  $\text{Ce}_{0.9}\text{M}_{0.1}\text{O}_2$  (M=Mg or Sc) and co-doped ceria-based materials with the formula  $\text{Ce}_{1-x}(\text{Mg}_{0.5}\text{Sc}_{0.5})_x\text{O}_2$  (x=0-0.24). For pure ceria,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 80% ethylene glycol/water mixed solvents and for Mg or Sc doped and co-doped ceria, 0.1M of Cerium nitrate hexahydrate, 0.1M of Scandium nitrate hexahydrate and 0.1M of Magnesium nitrate hexahydrate were prepared and mixed in distilled water according to the desired molar ratios using a magnetic stirrer at 80°C with a stirring rate of 500 rpm. Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was added drop-wise to this mixture until precipitates were formed at pH10, the mixed solution being stirred continuously and the reaction was 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 the samples. 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<sup>2</sup> to form green pellets using a stainless steel die with 0.1 cm thickness and 1.0 cm diameter which was further sintered in air at 1500°C for 2 hours at a programmed heating rate to form dense pellets. These pure, singly doped and co-doped ceria pellets were then used for electrical measurements.

### II.2. Characterization techniques

The phase analysis of the pure ceria, Mg or Sc doped ceria and Mg and Sc co-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 sintered pellets were polished, thermally etched and gold coated for analyzing the morphology and composition of the prepared samples using a Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectrometry (EDS) JSM-6335F, JEOL microscope. For conductivity measurement, Ag paste was brushed onto both sides of the dense pellet, and then sintered at 800°C for 30 min to form Ag electrodes. Pt leads were attached to the electrodes using Ag paste and were sintered again at 800°C for 30 min. Impedance was measured in static air using the two probe method by ac impedance spectroscopy at constant temperature between 400-600°C at frequencies from 50Hz to 5MHz using an impedance analyzer HIOKI 3532. In this study, the conductivity measured in air was treated as the oxide ionic conductivity only (>99.5%) and the electronic conductivity being negligible.

### III. RESULTS AND DISCUSSIONS

#### III.1. Powder XRD analysis

The crystallinity and phase analysis of the prepared nanocrystalline Mg or Sc doped and co-doped ceria samples were examined by powder XRD analysis. Powder XRD patterns of pure CeO<sub>2</sub>, Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> are shown in Fig.1. The XRD pattern is in accordance with the data in the JCPDS card no.81-0792 of a cubic phase CeO<sub>2</sub>.

The particle size (D) is estimated using the Debye Scherrer's formula:

$$D = \frac{0.94\lambda}{\beta_{2\theta} \cos \theta}$$

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. The average crystallite size of pure Ceria is about 17 nm and that of Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> and Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> was found to be 23 nm and 25 nm respectively. It is clearly evident from the XRD pattern that only the peaks correspond to the ceria alone and that the absence of any other secondary phases of the dopants does not reflect in the spectrum. Hence these single phase ceria and doped ceria were used for further characterization techniques to test its electrical properties.

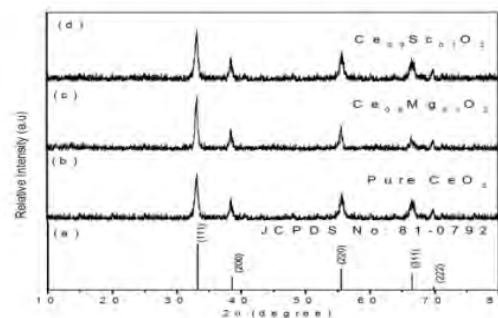


Fig.1. XRD patterns of (a) Pure CeO<sub>2</sub> (b) Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and (c) Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub>.

The XRD pattern samples of Ce<sub>1-x</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>x</sub>O<sub>2</sub> (x=0-0.24) is shown in Fig.2. The diffraction pattern is in accordance with the data in the JCPDS card no.01-081-0792 of a cubic phase CeO<sub>2</sub>. It can be seen that the samples contain only a cubic fluorite structure. It is clearly evident from the XRD pattern that the entire sample crystallizes in cubic phase and thus only the peaks corresponding to ceria alone were found. There are no secondary phases of the dopants and hence the electrical phenomena would result only due to the single phase nature of the ceria alone. The secondary phases would not contribute to the conductivity due to its complete absence.

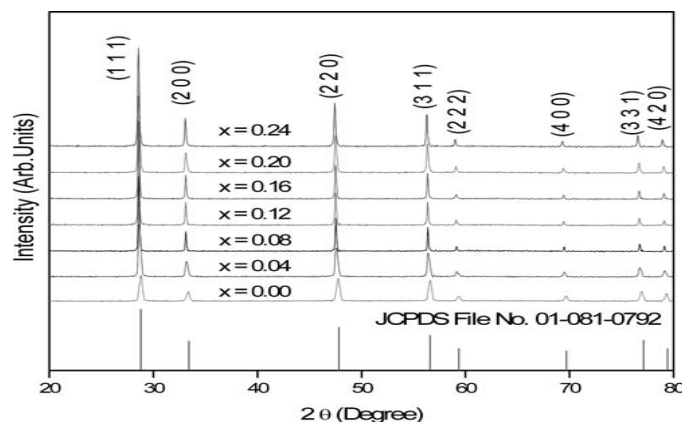


Fig.2. XRD patterns of Ce<sub>1-x</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>x</sub>O<sub>2</sub> (x=0-0.24) system.

The data in table.1 show that, the particle size ranges for pure and doped ceria varies between 17 to 35 nm. The consistency of particle sizes determined by X-ray analysis suggests that the powders were composed of isometric and rather weakly agglomerated crystallites. Further observations of all the powders allow us to state that no distinct differences in morphology were present. As the percentage of dopant increases, it is clear from the below table that the unit cell parameter increases gradually. The full-width half maximum (FWHM) of the XRD peak decreases as the dopant concentration increases.

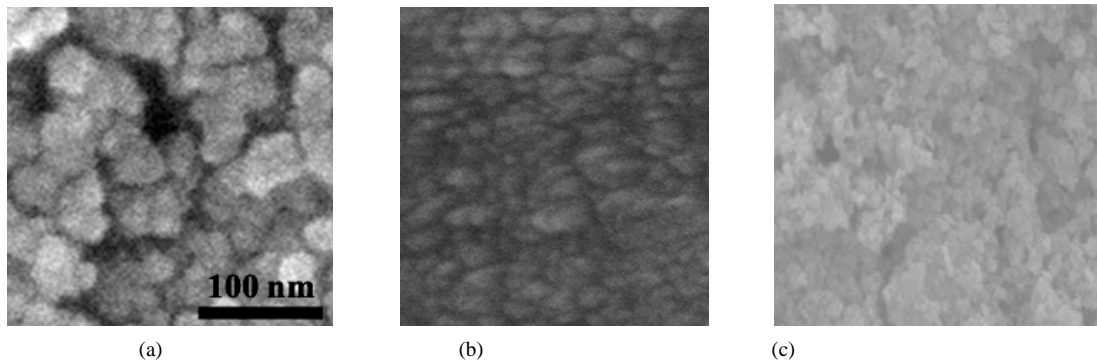
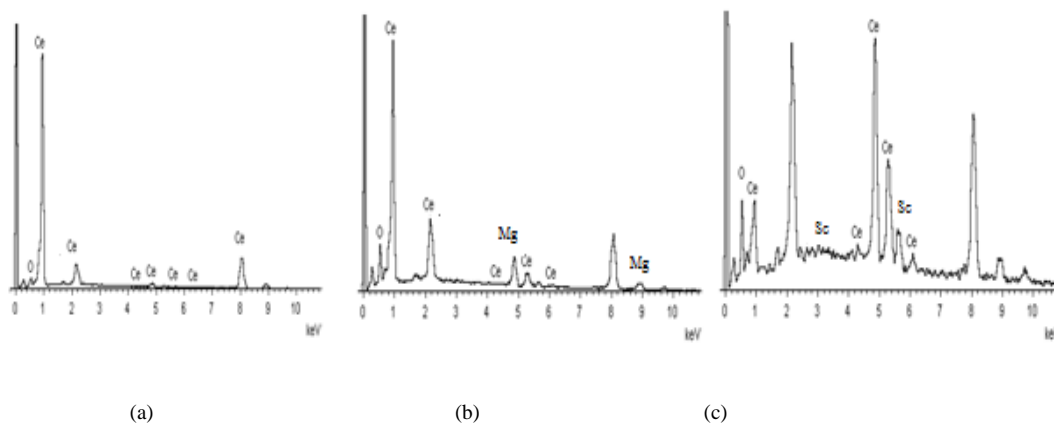
TABLE.I: Unit cell parameter and particle size of the samples determined by XRD measurements

Composition	Unit cell parameter (Cubic A)	Particle size d(hkl),nm
CeO <sub>2</sub>	5.585	17.1
Ce <sub>0.9</sub> Mg <sub>0.1</sub> O <sub>2</sub>	5.412	23.3
Ce <sub>0.9</sub> Sc <sub>0.1</sub> O <sub>2</sub>	5.510	25.4
Ce <sub>0.96</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.04</sub> O <sub>2</sub>	5.401	23.3
Ce <sub>0.92</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.08</sub> O <sub>2</sub>	5.437	25.8
Ce <sub>0.88</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.12</sub> O <sub>2</sub>	5.454	27.4
Ce <sub>0.84</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.16</sub> O <sub>2</sub>	5.471	29.9
Ce <sub>0.80</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.20</sub> O <sub>2</sub>	5.499	32.2
Ce <sub>0.76</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.24</sub> O <sub>2</sub>	5.512	35.8

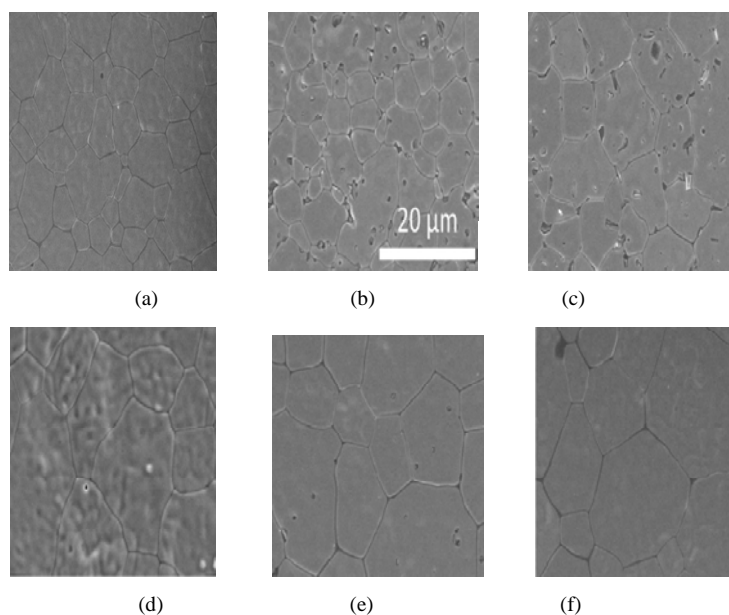
From the XRD pattern, we could observe that the lattice parameter of the pure ceria was found to be 5.585Å and that of Mg and Sc co-doped ceria Ce<sub>1-x</sub>(Mg<sub>0.5</sub> Sc<sub>0.5</sub>)<sub>x</sub>O<sub>2</sub> (x=0-0.24) ranges from 5.401Å to 5.512Å. This could well reflect in the peak shift of the XRD pattern. This is due to the difference in the ionic radii of magnesium and scandium with that of the ceria. Due to this difference, there is a difference in thermal expansion for each composition which gives rise to different unit cell parameters and thus increases the lattice volume [25].

### III.2. SEM and EDS analysis

The surface morphology and chemical composition of pure CeO<sub>2</sub>, Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> which were observed and analyzed by SEM and EDS are shown in Fig.3 and Fig.4. SEM micrograph clearly shows 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<sub>2</sub> is nearly spherical in shape and is dispersed well. EDS analysis shows the presence of Mg or Sc elements in the doped ceria samples.

Fig.3. SEM micrographs of (a) Pure CeO<sub>2</sub> (b) Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and (c) Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub>.Fig.4. EDS analysis of (a) Pure CeO<sub>2</sub> (b) Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and (c) Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub>.

The surface morphology of  $Ce_{1-x}(Mg_{0.5}Sc_{0.5})_xO_2$  ( $x=0-0.24$ ) was obtained using scanning electron microscopic (SEM) analysis as shown in Fig.5. All the compositions showed uniform grain growth when calcinated. The minor cracks appear along the surface due to the higher calcinations at  $500^\circ C$ .



a)  $Ce_{0.96}(Mg_{0.5}Sc_{0.5})_{0.04}O_2$  b)  $Ce_{0.92}(Mg_{0.5}Sc_{0.5})_{0.08}O_2$  c)  $Ce_{0.88}(Mg_{0.5}Sc_{0.5})_{0.12}O_2$   
 d)  $Ce_{0.84}(Mg_{0.5}Sc_{0.5})_{0.16}O_2$  e)  $Ce_{0.80}(Mg_{0.5}Sc_{0.5})_{0.20}O_2$  f)  $Ce_{0.76}(Mg_{0.5}Sc_{0.5})_{0.24}O_2$

Fig.5. SEM micrographs of Mg and Sc co-doped samples.

The substitution of Mg and Sc 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 Mg and Sc co-doping resulted in decrease of grain boundary resistance and increased ionic conductivity which is discussed in impedance analysis.

### III.3. Impedance analysis

A.C. impedance analysis is an important technique to explore the electrical properties of solid electrolytes and to study the grain, grain boundary and electrode contribution to the overall ionic conductivity. High frequency semi-circle corresponds to grain resistance ( $R_g$ ), intermediate frequency semi-circle corresponds to grain boundary resistance ( $R_{gb}$ ) and low frequency incomplete arc corresponds to electrode resistance ( $R_e$ ).

In general, the total conductivity ( $\sigma_t$ ) of the elements co-doped with ceria is the sum of ionic conductivity ( $\sigma_i$ ) and electronic conductivity ( $\sigma_e$ ). The main contribution of the conductivity of ceria-based compounds in air is the ionic conductivity and contribution of the electronic conductivity is negligible. The real ( $Z'$ ) and imaginary components ( $Z''$ ) of the impedance ( $Z$ ) were determined by measuring the amplitude and phase angle ( $\theta$ ) 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 Pure  $CeO_2$ ,  $Ce_{0.9}Mg_{0.1}O_2$  and  $Ce_{0.9}Sc_{0.1}O_2$  measured at a temperature of  $500^\circ C$  are shown in Fig. 6. The impedance plot for co-doped ceria compositions of  $Ce_{1-x}(Mg_{0.5}Sc_{0.5})_xO_2$  ( $x=0-0.24$ ) is shown in Figure 7. 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.

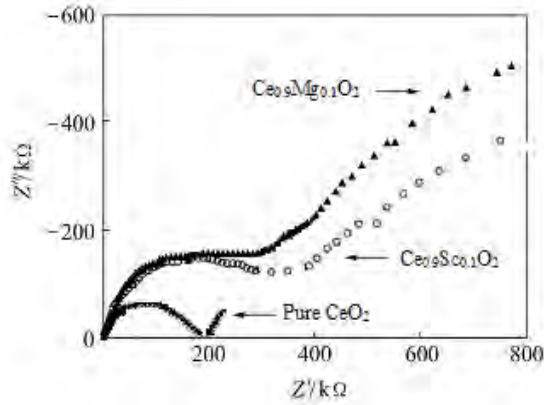
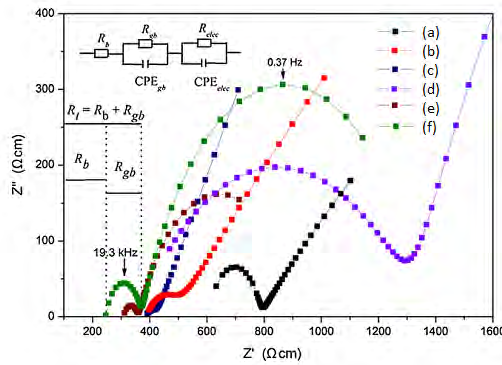


Fig.6. Impedance spectra in Nyquist- plots for CeO<sub>2</sub>, Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> at 500°C.



- a) Ce<sub>0.96</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.04</sub>O<sub>2</sub>
- b) Ce<sub>0.92</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.08</sub>O<sub>2</sub>
- c) Ce<sub>0.88</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.12</sub>O<sub>2</sub>
- d) Ce<sub>0.84</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.16</sub>O<sub>2</sub>
- e) Ce<sub>0.80</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.20</sub>O<sub>2</sub>
- f) Ce<sub>0.76</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.24</sub>O<sub>2</sub>

Fig.7. Impedance spectra in Nyquist- plots for Mg and Sc co-doped samples calculated at 500°C

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:

$$\sigma T = \sigma_0^{-E/kT}$$

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 respective values of the conductivities of all the samples at 500°C are given in Table.2. The total electrical conductivity is calculated as a sum of bulk and grain boundary conductivities. The ionic conductivity increases when the composition increases. For the composition of Ce<sub>0.84</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>0.16</sub>O<sub>2</sub> the sample possess maximum conductivity.

TABLE II. Electrical conductivity ( $\sigma$ ) of pure ceria and doped ceria samples at 500 °C

Composition	$\sigma$ (S/cm), 500°C		Ea, eV	
	bulk	grain boundary	bulk	grain boundary
CeO <sub>2</sub>	6.92x10 <sup>-5</sup>	1.21x10 <sup>-6</sup>	0.90	1.01
Ce <sub>0.9</sub> Mg <sub>0.1</sub> O <sub>2</sub>	6.23x10 <sup>-3</sup>	5.24x10 <sup>-3</sup>	0.86	0.97
Ce <sub>0.9</sub> Sc <sub>0.1</sub> O <sub>2</sub>	5.71x10 <sup>-3</sup>	4.32x10 <sup>-3</sup>	0.89	1.00
Ce <sub>0.96</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.04</sub> O <sub>2</sub>	6.25x10 <sup>-3</sup>	9.85x10 <sup>-4</sup>	0.85	0.95
Ce <sub>0.92</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.08</sub> O <sub>2</sub>	4.41x10 <sup>-4</sup>	8.67x10 <sup>-4</sup>	0.83	0.94
Ce <sub>0.88</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.12</sub> O <sub>2</sub>	6.28x10 <sup>-3</sup>	5.26x10 <sup>-3</sup>	0.80	0.90
Ce <sub>0.84</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.16</sub> O <sub>2</sub>	6.31x10 <sup>-3</sup>	5.28x10 <sup>-3</sup>	0.75	0.86
Ce <sub>0.80</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.20</sub> O <sub>2</sub>	6.11x10 <sup>-3</sup>	5.08x10 <sup>-3</sup>	0.86	0.98
Ce <sub>0.76</sub> (Mg <sub>0.5</sub> Sc <sub>0.5</sub> ) <sub>0.24</sub> O <sub>2</sub>	5.21x10 <sup>-4</sup>	4.53x10 <sup>-4</sup>	0.91	1.02

Figure 8 shows Arrhenius plots of the total electrical conductivity,  $\sigma T$ , of samples sintered at 500°C. The above equation gives a straight line between  $\ln\sigma$  and T, the slope of which is  $[-E_a/K]$ . A typical plot between logarithmic conductivity and temperature of Pure CeO<sub>2</sub>, Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> are shown in the figure. The conductivities from the grain interior and the grain boundaries were calculated based on the impedances measured.

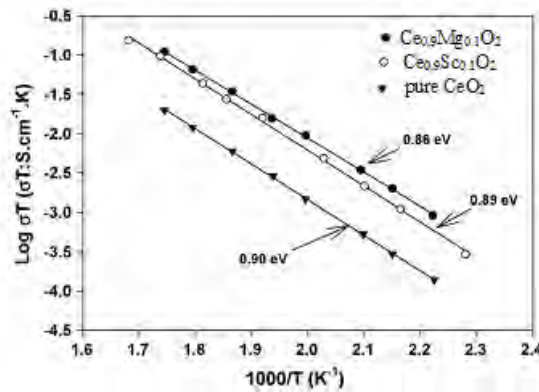
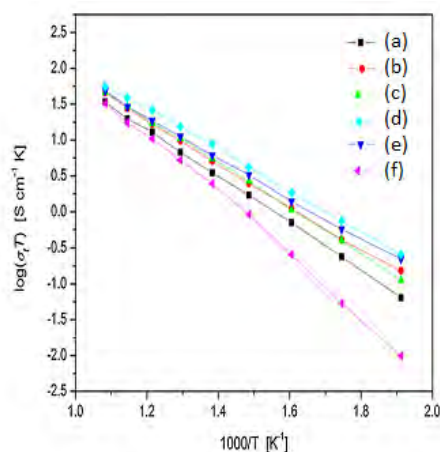


Fig. 8. Arrhenius plots of the total conductivity of CeO<sub>2</sub>, Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> and Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> at 500°C.

For pure ceria, the total conductivity is lower than that of sample Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> by near one order of magnitude. The higher total conductivity of sample Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> compared to pure ceria and Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub> is probably due to smaller particle size of Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> sample. 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 Mg or Sc doped ceria resulted in decrease of bulk and grain boundary resistance resulting in higher ionic conductivity compared to pure ceria. The bulk resistance of Mg doped ceria has been found to be low compared to the Sc doped ceria. The bulk resistance values of the samples indicate the higher ionic conductivity for the sample Ce<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> compared to Ce<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>2</sub>. Figure 9 shows the Arrhenius plots for the total conductivity,  $\sigma T$ , of samples Ce<sub>1-x</sub>(Mg<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>x</sub>O<sub>2</sub> (x=0-0.24) system measured at 500°C. The above equation gives a straight line between  $\ln\sigma$  and T, the slope of which is  $[-E_a/K]$ .



a)  $\text{Ce}_{0.96}(\text{Mg}_{0.5}\text{Sc}_{0.5})_{0.04}\text{O}_2$  b)  $\text{Ce}_{0.92}(\text{Mg}_{0.5}\text{Sc}_{0.5})_{0.08}\text{O}_2$  c)  $\text{Ce}_{0.88}(\text{Mg}_{0.5}\text{Sc}_{0.5})_{0.12}\text{O}_2$   
 d)  $\text{Ce}_{0.84}(\text{Mg}_{0.5}\text{Sc}_{0.5})_{0.16}\text{O}_2$  e)  $\text{Ce}_{0.80}(\text{Mg}_{0.5}\text{Sc}_{0.5})_{0.20}\text{O}_2$  f)  $\text{Ce}_{0.76}(\text{Mg}_{0.5}\text{Sc}_{0.5})_{0.24}\text{O}_2$

Fig. 9. Arrhenius plots for total conductivity of Mg and Sc co-doped samples at 500°C.

It can be seen from the figure that  $\text{Mg}^{2+}$  and  $\text{Sc}^{3+}$  co-doped ceria samples showed higher conductivities for the composition  $\text{Ce}_{0.84}(\text{Mg}_{0.5}\text{Sc}_{0.5})_{0.16}\text{O}_2$  than other co-doped concentrations and the conductivity is also higher than pure ceria and singly doped ceria i.e.,  $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$  and  $\text{Ce}_{0.9}\text{Sc}_{0.1}\text{O}_2$ . The total ionic conductivity of  $\text{Ce}_{1-x}(\text{Mg}_{0.5}\text{Sc}_{0.5})_x\text{O}_2$  increases upto dopant concentration ( $x=0.16$ ). After that, the total ionic conductivity decreases with increase in dopant concentration, which is related to the formation of local defect structures, which lowers the mobile oxygen vacancy concentration. Further, the total ionic conductivity of  $\text{Ce}_{0.84}\text{Mg}_{0.08}\text{Sc}_{0.08}\text{O}_2$  is  $1.923 \times 10^{-2} \text{ S/cm}$  (0.77 eV) at 500°C.

#### IV. CONCLUSION

Pure Ceria, 10 mol% Mg doped Ceria ( $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$ ) and 10 mol% Sc doped Ceria ( $\text{Ce}_{0.9}\text{Sc}_{0.1}\text{O}_2$ ) had been prepared by co-precipitation method. Single phase cubic natured ceria was obtained for both pure and doped ceria. The crystal structure, densification and ionic conductivity were studied. Magnesium and Scandium co-doped ceria samples with  $\text{Ce}_{1-x}(\text{Mg}_{0.5}\text{Sc}_{0.5})_x\text{O}_2$  ( $x=0.0, 0.04, 0.08, 0.12, 0.16, 0.20$  and  $0.24$ ) were also prepared by the co-precipitation process and were investigated. Particle size calculation from the XRD pattern reveals that the synthesized powders were of nanocrystalline in nature and that for pure it was around 17nm and for Sc or Mg doped ceria it was found to be 23 and 25 nm respectively. SEM micrograph of the pure and doped ceria confirms the nanocrystalline nature and that the synthesized powders possess uniformly distributed spherical powders. SEM images of the co-doped  $\text{Ce}_{1-x}(\text{Mg}_{0.5}\text{Sc}_{0.5})_x\text{O}_2$  pellets showed high dense ceramics and the results were consistent with relative density. EDX confirms the presence of Mg, Sc and Ce elements in the samples. All the sintered samples were of cubic fluorite-type ceria solid solutions. The ionic conductivity of pure  $\text{CeO}_2$  and singly doped ceria improved significantly with co-doping of Mg and Sc in the ratio of 1:1 at temperature 500°C. The contribution of grain boundary conductivity to the total conductivity is more compared to the grain conductivity at 500°C. The composition  $\text{Ce}_{0.84}\text{Mg}_{0.08}\text{Sc}_{0.08}\text{O}_2$  showed highest grain ionic conductivity.

The results presented in this paper indicate that magnesium and scandium co-doped ceria leads to enhance the electrolytic properties compared to singly doped ceria and this material seems to be a promising solid electrolyte for IT-SOFCs operating in the temperature range between 400-600°C.

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