

# EFFECT OF SINTERING TEMPERATURE ON THE IONIC CONDUCTIVITY OF SAMARIUM DOPED CERIA ELECTROLYTE FOR SOLID OXIDE FUEL CELL.

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**ABSTRACT:** *The present work is dealt with the investigation to explore the structural properties and ionic conductivity of sintered Samarium Doped Ceria Oxide (SDC) powder, which could be used as electrolyte for Solid Oxide Fuel Cells. The SDC powder was prepared by co-precipitation method and sintered at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C for four hours. The structural analysis is done with the help of XRD and FTIR. The XRD spectra show the increasing crystallite size of Ceria with sintering temperature and higher value of lattice parameter than standard. Whereas, FTIR spectra describe the effect of sintering temperature on chemical bonding and existence of ceria content by Ce-O peaks. Two Probe Impedance Spectroscopy spectra show the maximum ionic conductivity at low measuring temperature that was 650 °C. The fabricated SDC powder could be used as an electrolyte for SOFCs in temperature range from 550 °C to 650 °C.*

## 1. INTRODUCTION

Nowadays, just due to maximum efficiency and environment friendly behavior as well as fuel flexibility, which can produce electrical power at both small and large scale, solid oxide fuel cells (SOFCs) have appealed great consideration [1-4].

SOFC is an electrochemical conversion scheme that based on a solid electrolyte, which creates current accurately from fuel oxidation at high temperature (800 °C- 1000 °C) [1]. It resides of three constituents known as, an anode, an electrolyte and a cathode. The electrochemical responses are taken place at the anode and cathode. The fuel is fed to the anode flank; on the other hand the oxidant (often air or oxygen) is served to the cathode. The only difference between the batteries and fuel cells is that in distinct with the batteries, fuel cells can produce electricity with the stream of fuel to electrodes while no storing of electricity is occurred in them [5,6].

High temperature SOFCs have an advantage that they show good ionic conductivity. Beside it, they have many disadvantages i.e. fuel cell deprivation issue, incompatibility of thermal expansion co-efficient, difficulties in technology and high cost. To overcome these issues, many latest materials have become viable to reduce the operating temperature of SOFCs by fresh researchers [7-8].

The SOFCs that will operate at low or intermediate temperature should have maximum ionic conductivity through electrolyte and increasing reactive activity at electrodes. Each component of SOFCs has importance to enhance the efficiency. So, for the advancement of SOFCs to low or intermediate temperature, a noteworthy work has been consumed for the development of electrolyte and electrodes materials [9-10].

There are many solid oxide electrolyte materials developed to show the good ionic conductivity i.e. Ytria Stabilized Zirconia (YSZ), Scandia Stabilized Zirconia (ScSZ) and Samarium doped Ceria (SDC) [3]. The most commonly practiced electrolyte material is YSZ, which can sustain at both oxidizing and reducing atmosphere with good linkage with electrode materials. YSZ electrolyte is shown good ionic conductivity at high temperature but not at low or

intermediate temperature. For low temperature SOFCs (650 °C), SDC (ceria based electrolyte) is used to show the high ionic conductivity [1-4].

The ionic conductivity is still improving to enhance the overall cell recital. The fabrication and dispensation has great influence on cell performance [14, 15]. Many synthesis methods have been developed for ceria based electrolytes i.e. glycine-nitrate process, sol-gel process, solid state reaction and carbonate co-precipitation method. All methods are shown low densification and low conductivity at low temperature except carbonate co-precipitation method [4]. In terms of thermal and mechanical stability, grain boundary, purity and porosity, the synthesize conditions should have great effect on the resulted ionic conductivity and activation energy of solid electrolyte powder [2].

In this work, we studied for the first time the effect of varying sintering temperature from 300 °C to 700 °C with 100 °C increment for four hours, on the properties of fabricated SDC powder via co-precipitation method. This evaluation is also done to explain the possible advantages of the usage of carbonate co-precipitation on cost, compatibility and enactment as well as the sintering temperature effects on the improvement of ionic conductivity, crystallinity, crystallite size and thermal stability of fabricated SDC electrolyte powder.

## 2. MATERIALS AND METHOD

The  $Ce_{0.8}Sm_{0.2}O_{1.9}$  (SDC) powder was fabricated via Coprecipitation method.  $Ce(NO_3)_3 \cdot 6H_2O$  and  $Sm(NO_3)_3 \cdot 6H_2O$  were dissolved in distilled water in a stoichiometric ratio and appropriate amount of precipitating agent  $Na_2CO_3$  added in the prepared solution. The suction filtration method was used for the filtration of final mixture and dried for one hour at 100°C in the furnace. The dried powder was crushed into fine powder. The milled powder was divided into five samples. Each sample was sintered at 300°C, 400 °C, 500 °C, 600 °C and 700°C for 4hours. Colour variation was also observed in all samples from pale yellow to tea pink when sintering temperature was increased.

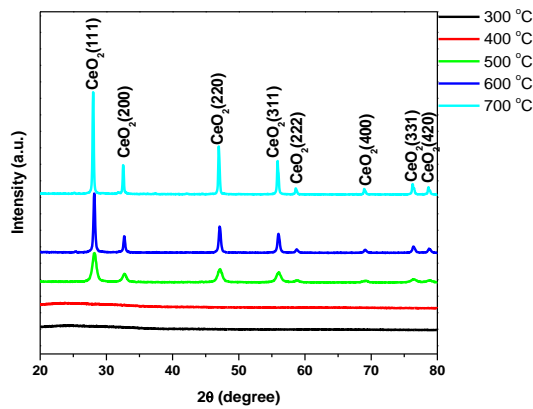


Figure 1: XRD spectra of five SDC samples sintered at varying temperature from 300 °C to 700 °C.

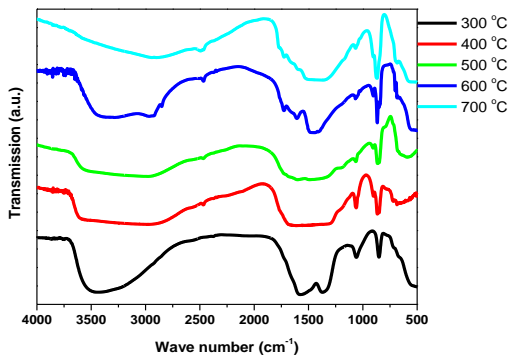


Figure 2: FTIR spectra of five SDC samples sintered at varying temperature from 300 °C to 700 °C.

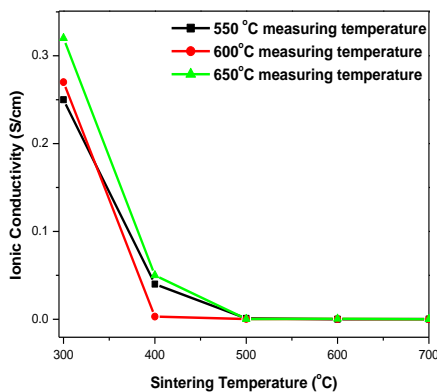


Figure 3: Ionic conductivity of SDC powders at varying measuring temperatures.

### 3. RESULTS AND DISCUSSION

#### X-ray Diffraction Analysis:

The XRD spectrum (Intensity versus  $2\theta$ ) of five SDC samples, which were sintered at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C for four hours is given in Figure 1. It was observed that all samples are single phase crystallite with cubic fluorite type structure of  $\text{CeO}_2$  except those two samples that sintered at 300 °C and 400 °C. The crystallite size ( $D_{\text{xrd}}$ ) of three samples, which were sintered at 500 °C, 600 °C and 700 °C is 144 Å, 312 Å and 450 Å respectively. The following Debye Scherer's equation was executed on (111) diffraction to intend the crystallite size.

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

For the similar (111) plane, the value of lattice constant ( $a$ ) was 5.54 Å, which is calculated by given equations

$$d = \lambda/2\sin\theta \quad (2)$$

$$a = d(h^2 + k^2 + l^2)^{1/2} \quad (3)$$

No peak was observed at 300 °C and 400 °C. At these temperatures the sample was showing more or less amorphous behavior. Conversely, at 500 °C to 700 °C, eight reflection peaks of Ceria were observed. At increasing annealing temperatures from 500 °C to 700 °C, the reflection peaks were become shriller and finer. That indicated the improvement of Crystallinity and increment of densification and crystallite size of sample [16]. The data obtained from XRD pattern of all samples arranged in table 1, which is listed below:

There was no availability of any secondary phase in the XRD spectra. No peak for Samarium and sodium carbonate is observed in the composite, which was the proof of complete doping of samarium contents at the lattice sites of Ceria and disposal of sodium carbonate in an amorphous form. From table 3.1, it can be easily observed that there is an inverse relation between dislocation line density and sintering temperature [17].

As sintering temperature was increasing along that, crystallite size was increasing but dislocation line density was decreasing. So, that was good for the increment of crystallinity due to removal of maximum defects in the lattice [18].

#### FTIR Analysis:

The FTIR spectra of all SDC samples sintered at varying temperature in the range from 4000 $\text{cm}^{-1}$  to 500 $\text{cm}^{-1}$  is shown in figure 2. The presence of Ce-O bond would be sited in the form of peaks and band from 800  $\text{cm}^{-1}$  to 1900  $\text{cm}^{-1}$  are shown in table 2. The FTIR peaks and band related to metal oxygen bond (Ce-O) are almost matched to that of viable powder and Ceria oxide particles [19-21].

With the increment of sintering temperature, the Ce-O peaks in FTIR spectrum become sharper and finer, showing the proper phase formation. That result was interlinked with the XRD analysis where crystallinity and crystallite size of Ceria showed linear relation with increasing temperature.

**Table 1: Structural properties of SDC powder from XRD spectra at varying sintering temperature.**

| Temperature (°C) | (h k l) | 2θ (degree) | Std.d-spacing (Å) | Cal.d-spacing (Å) | FWHM (Rad)            | Crystallite Size (Å) | DLD (m <sup>-2</sup> ) |
|------------------|---------|-------------|-------------------|-------------------|-----------------------|----------------------|------------------------|
| 500              | (1 1 1) | 28.29       | 3.12              | 3.20              | 0.01                  | 144                  | 4.82×10 <sup>15</sup>  |
| 600              | (1 1 1) | 28.29       | Std.a (Å)         | Cal.a (Å)         | 4.53×10 <sup>-3</sup> | 312                  | 1.02×10 <sup>15</sup>  |
| 700              | (1 1 1) | 28.29       | 5.40              | 5.54              | 3.14×10 <sup>-3</sup> | 450                  | 4.93×10 <sup>14</sup>  |

**Table 2: Identification of various vibrational modes of Samarium Doped Ceria (SDC).**

| Peaks/Band (cm <sup>-1</sup> )                           | Bonding   |
|--|---|
| 807, 850, 973, 1061,1069peaks and band from 1180 to 1811 | Stretching frequency of metal oxygen Ce-O bond.   |
| Band below 750   |   |
| strong absorption band from 2764 to 3713                 | O-H stretching frequency of aquatic and hydroxyl groups.  |
| Peaks at 2465 and 2840                                   | CH <sub>2</sub> stretching vibration  |
| peak at 1559   | stretching vibration of –COO <sup>-</sup> group   |
| peaks at 1422 and 895                                    | CO <sub>3</sub> <sup>2-</sup> group due to asymmetric stretching and out of plane bending vibrations respectively |
| peak at 1051 cm <sup>-1</sup>                            | sodium carbonate  |

That is another proof of formation of nanocrystalline ceria powders.

Moreover, it is also observed that strong absorption band of Hydroxyl group become weaker with increasing temperature but not completely disappeared probably due to some trapped Hydroxyl ions in the material [20].The peaks of organic compound (CH<sub>2</sub>-) may upsurge due to immersion of atmospheric CO<sub>2</sub>and OH- on the Ceria. The peak of –COO<sup>-</sup> group could be used as evidence that it is linked with the nanomaterials through bidentate coordination bonding. The peak of sodium carbonate(1051 cm<sup>-1</sup>) becomes extinct at high temperature.

**Two-Probe Impedance Spectroscopy Analysis:**

Figure 3 is illustrated the two probe impedance spectroscopy used to measure the conductivity of oxide ions of SDC powder. All five samples were investigated at 500 °C, 600 °C and 650 °C temperature. The ionic conductivity of all SDC samples decreases as the sintering temperature is increased. The conductivity of sample sintered at 300 °C is found highest among all due to presence of minimum crystallite size of Ceria, which did not affect the pores of conducting oxide ions of SDC electrolyte. The samples that sintered at high temperature such as 500 °C,600 °C and 700 °C, have minimum and constant behavior of ionic conductivity because of existence of large crystallite size of Ceria that become source of blockage of pores of conducting oxide ions. For the sample prepared at sintering temperature 300 °C, the ionic conductivity is found to be 0.25 S/cm, 0.28 S/cm and 0.33 S/cm at measuring temperatures 550 °C, 600 °C and 650 °C respectively. The investigated value of conductivity was more than those values which reported in literature [21].

**4. CONCLUSIONS**

The Co-precipitating method had been effectively proven for the synthesis of Ce<sub>0.8</sub> Sm<sub>0.2</sub> O<sub>1.9</sub> powder. The method was considered to be more useful, swift and efficient to govern the structural, optical and thermal properties of prepared powder. Crystallite Ceria, which had single phase was achieved after appropriate sintering. The average crystallite size of Ceria was calculated with the assistance of XRD spectra is 302 Å with cubic fluorite structure. FTIR study was concluded the existence of Ceria content, which demonstrated by Ce-O peaks. The excessive ionic conductivity observed at 650 °C measuring temperature that was 0.33 S/cm with the help of Two Probe Impedance Spectroscopy.

Hence, the synthesis method was very easy, less time consuming as well as economical for the fabrication of best electrolyte for SOFCs.

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