Research Article

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Study on Electrical conductivity and Activation Energy of doped Ceria nanostructures

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Abstract: $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) nanocrystalline materials are prepared by a solid state reaction method. The synthesized nano crystalline solid solutions have cubic fluorite structure as evident from XRD patterns. The materials are qualitatively analyzed by FTIR. The morphology, size and shape of grains etc. are identified from the SEM images. The grain size of GDC is smaller than that of SDC. The better morphology is obtained for GDC. Hence, this is electrically characterized. The activation energy is calculated from the slope of Arrhenius plot (showing variation of conductivity with temperature).

Keywords: solid electrolyte, solid state reaction, XRD, SEM, morphology, ionic conductivity, activation energy

1 Introduction

Cerium oxide (ceria) is one of the important functional materials with high mechanical strength, thermal stability, excellent optical properties, appreciable oxygen ion conductivity and oxygen storage capacity [1]. Ceria has far-reaching applications in mechanical polishing of microelectronic devices, as catalyst for three-way automatic exhaust systems and as additive in ceramics and phosphors. Ceria has been widely selected as a novel electrolyte material for intermediate temperature solid oxide fuel cells. Research on fuel cells has drawn attention due to their tremendous impact on many aspects of our life, environment and economy. Fuel cells are energy conversion devices which convert chemical energy directly into electrical energy and heat by the electrochemical combination of fuel with oxidant. Of the different types of fuel cells that differ in electrode, electrolyte, fuel, oxidant and operating temperature, the solid oxide fuel cells (SOFC) are prominent candidates for power generators. SOFC systems developed so far require high operating temperature which limits their commercialization. Thus research is going on to reduce the operating temperature of SOFC that require solid electrolyte, major component of SOFC, with high ionic conductivity even at low or intermediate temperatures (~600°C-800°C). Samarium doped ceria (SDC) and gadolinium doped ceria (GDC) exhibit higher conductivity than YSZ at 700°C [2, 3]. Apart from that it is possible to obtain power densities as high as 1 W/cm from anode-supported SDC fuel cells at 600°C using hydrogen as the fuel and air as the oxidant. The advantage of operating SOFC in low temperature regime is the reduction in the auxiliary component costs and the enhancement in the thermomechanical stability of the SOFC system. The doped ceria has enhanced electrical properties depending on various factors such as particle size, structural characteristics, morphology, etc. [4]. Ceria-based solid solutions have been widely identified as novel electrolytes for intermediate temperature solid oxide fuel cells (SOFC) [5, 6].

In the present study, gadolinium doped ceria and samarium doped ceria are prepared by solid state reaction method. The synthesized materials are structurally characterized using XRD, FTIR and SEM techniques. Since good morphology is obtained for GDC sample, it is electrically characterized using electrochemical impedance spectroscopy.

2 Materials and methods

Analytical grade starting materials (purity 99.9%), CeO_2 and Gd_2O_3 were weighed in stoichiometric proportions and mixed in an agate mortar with acetone to obtain homogeneity to prepare $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC). Stoichiometric amounts of CeO_2 and Sm_2O_3were weighed and the powder was ground well to obtain $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC). Both powder samples were calcined at 800°C for 2 h and pelletized using a hydraulic press by applying a pressure of 2.5 MPa. These pellets were sintered at 1200°C for 10 h.

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The phase purity and crystal structure of the calcined samples were studied by the diffraction of Cu-Kα_1 X-rays (XPERT-PRO) in an angular range of 20° - 90° with step-size 0.016711°. FTIR spectroscopy (SHIMADZU) was used to determine various bonds present in the calcined samples. SEM technique (BRUKER) was utilized to find the surface morphology and amount of grain-growth in the samples. The ac impedance study of the nanocrystalline pellet was carried out using impedance spectroscopy with SOLATRON 1250. The activation energy for bulk conduction was determined from the conductivity-temperature diagram.

3 Results and discussion

The diffractograms of prepared gadolinium-doped ceria, samarium-doped ceria along with the host ceria (CeO_2) are shown in Figure 1. It is clear from the patterns that the prepared samples have cubic fluorite structure and pure single phase. Gd^{3+} and Sm^{3+} ions are perfectly substituted into the ceria lattice. The absence of extra peaks confirms the purity of the synthesized samples.

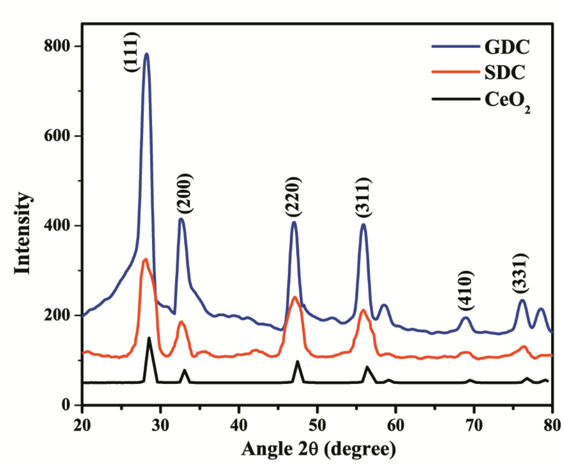

Figure 1: XRD patterns of Ceria, GDC and SDC

The broad peaks in the XRD patterns suggest the nanocrystallinity of the samples. The most prominent peak is observed for (111) plane, which is the characteristic of cubic fluorite structure (JCPDS file no: 75-0162). The peaks in both patterns are slightly shifted towards lower angles than the undoped ceria nanocrystallites, as in many similar substitutions. The addition of larger Gd^{3+} in place of Ce^{4+} ion expands the lattice, which is in accordance with Vegards law and hence leads to higher conductivity [7].

The crystallite size is determined using the Scherrer equation [8, 9]. The lattice parameter for the prepared samples is calculated using the equation for simple cubic structure and are tabulated in Table 1 attached at the end of the manuscript.

Table 1: Crystallite size and lattice parameter of the prepared samples

Sample	Crystallite size D (nm)	Lattice parameter a (Å)
CeO_2	16.67	5.459
GDC	11.22	5.472
SDC	15	5.473

The FTIR spectra of the calcined sample are shown in Figure 2. The band below 800 cm^{-1} shows the presence of Ce-O bond stretching modes [10]. The band below 550 cm^{-1} is due to Gd-O bond vibrations [11].

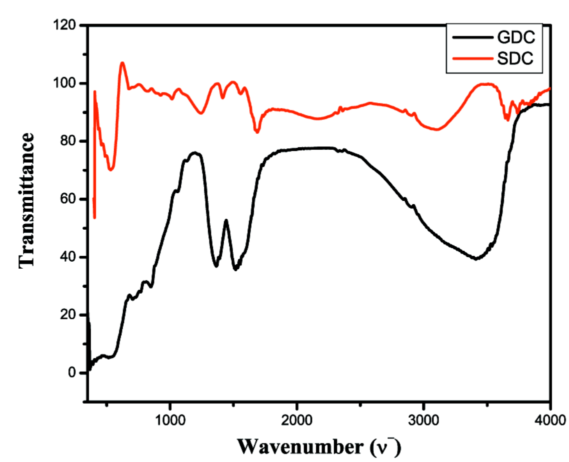

Figure 2: FTIR spectra of GDC (black) and SDC (red)

The broad band near 3300 cm^{-1} and band at 1650 cm^{-1} are mainly due to the hydroxyl group stretching vibration [12]. The band near 1450 cm^{-1} is due to C=O stretching mode [10]. The presence of water in the spectrum indicates the moisture-absorbing nature of solid state reaction samples. For SDC sample, the band centered at 675 cm^{-1} arises due to Ce-O vibrations. The band centered at 1033 cm^{-1} corresponds to Sm-O bond [13].

The microstructure and topography of GDC and SDC pellets are shown in Figure 3a and b. The grains are well formed and are non-uniform in size. Small amount of

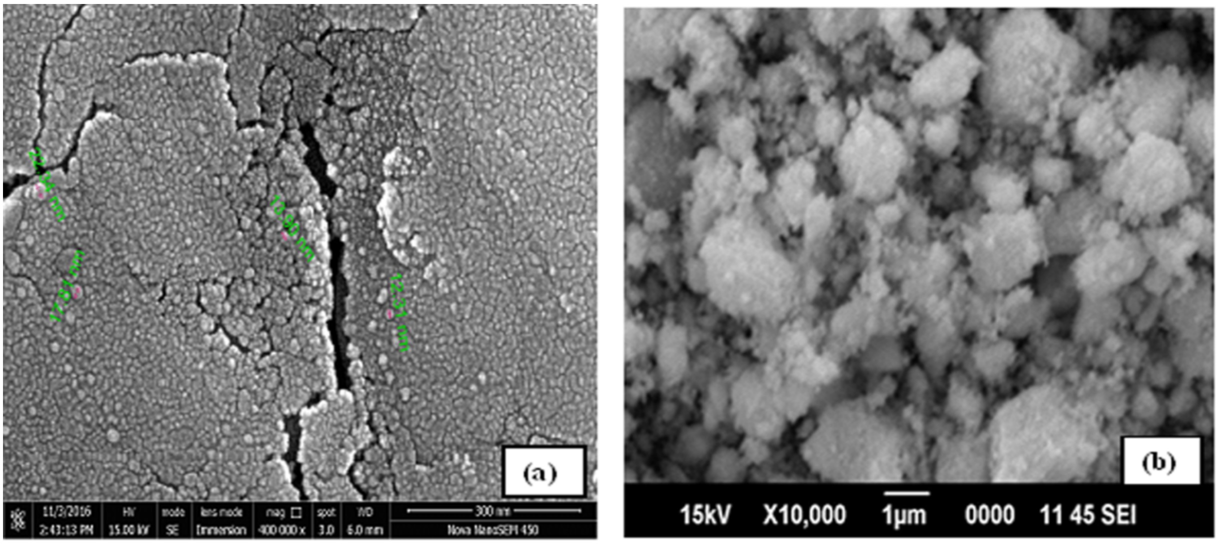

Figure 3: Scanning electron micrographs of (a) GDC and (b)SDC

porosity is seen in the micrographs. The sintered GDC pellet has a density of about 90% of theoretical value. The surface of sintered GDC pellet is smoother than that of the sintered SDC pellet. GDC has comparatively better surface morphology than the SDC pellet. The grain growth can be increased by increasing the sintering temperature [14, 15]. The amount of porosity or the size of pores may be decreased by increasing the sintering temperature. This process contributes to higher ionic conductivity in solid oxide electrolytes. The grain size of the GDC pellet sintered at 1200°C for 10 h is about 10 to 22 nm, whereas the grain-size of SDC pellet is about 120 to 200 nm. Since the surface to volume ratio of GDC sample is very large, it may produce higher electrical conductivity than SDC sample. So the electrical study is restricted to GDC sample alone. Energy dispersive spectrum of the GDC sample in Figure 4 clarifies the elements present in the sample. EDS works on the principle that every element has a different atomic structure, which gives a unique set of peaks on its electromagnetic emission spectrum. The EDS spectra show that there are no impurities present in the samples.

The complex impedance plots for GDC measured at intermediate temperatures are shown in Figure 5. The measured data are fitted with an equivalent circuit using EC lab software. The equivalent circuit consists of two RC parallel circuits connected in series to a resistor. Two arcs are seen at lower temperatures upto 450°C. The single semicircle at high temperatures indicates conduction either through the grains or the grain-boundaries. The respective capacitance values are used to differentiate it. The equivalent circuit shows capacitance values in nanofarad and in picofarad. The picofarad (pF) range of capacitance indicates conduction through the grains and nanofarad (nF) range that along the grain-boundaries [16]. The capacitance values for GDC at the intermediate temperatures lies in the nano farad range. Hence grain-boundary conduction dominates in sintered gadolinium doped ceria with increase in temperature.

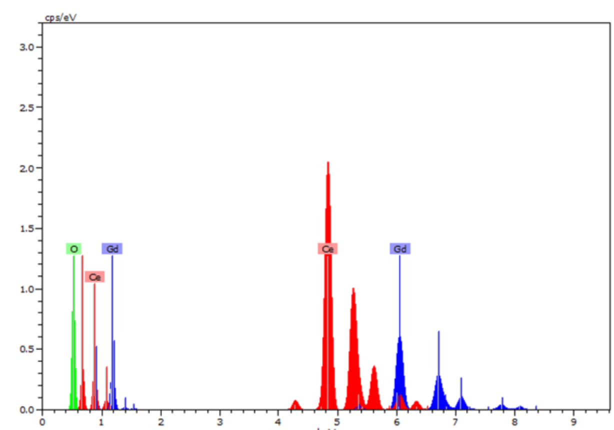

Figure 4: Energy dispersive spectrum of GDC

The sintered pellet with thickness 't' and radius 'r' with an impedance |Z| has an ac conductivity ,

$$\sigma = t/(\pi r^2 |Z|)$$

which in general increases with temperature.

The ac conductivity spectrum in Figure 6 shows the dc plateau with dispersion at higher frequencies for all temperatures. This obeys Jonscher's power law equation [16, 17]. As temperature increases, the dispersion frequency

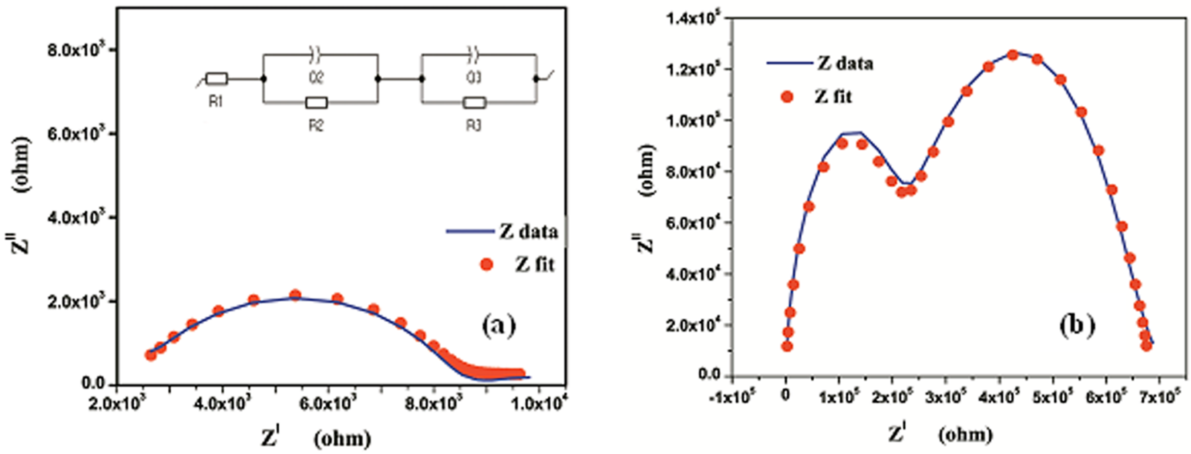

Figure 5: Nyquist plots of GDC at temperatures 500°C, and 350°C

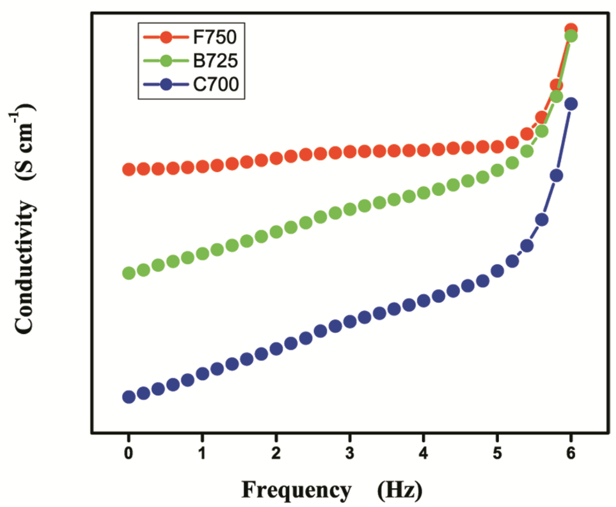

Figure 6: Variation of conductivity with frequency for GDC at different temperatures

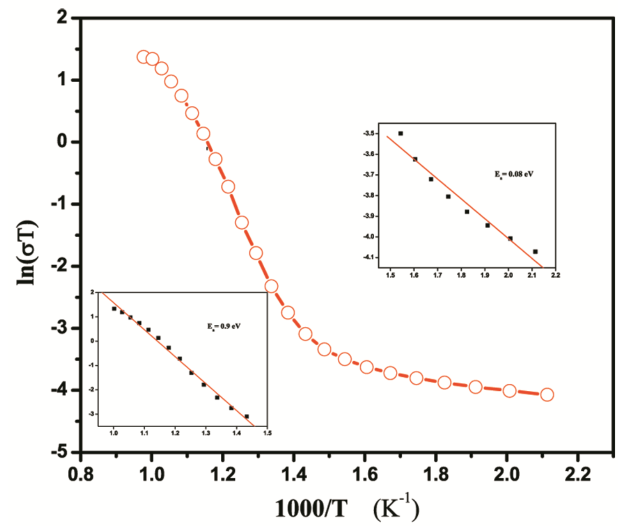

Figure 7: Arrhenius plot of GDC

shows a positive deviation towards higher values. This type of conductivity spectrum is the characteristic of a group of materials for which the conduction is mainly due to thermally activated hopping of ions through vacancies introduced in the lattice.

The temperature-dependent ionic conductivity of the samples obeys Arrhenius equation [18]. The Arrhenius plot is shown in Figure 7. It cannot be fitted with a single straight line, because of the nano-crystalline nature of the material. Two different straight lines - one in low temperature region and the other in high temperature region - are needed to fit the curve [19, 20] shown in Figure 7. The oxide ionic conductivity is found to increase with increase in temperature. The bulk activation energy of the GDC pellet for the high temperature region from the Arrhenius plot is 0.95 eV. The sample has a maximum ion conductivity of 3.865×10^{-3} Scm^{-1} at 750°C. Gadolinium doped ceria solid electrolyte has good mechanical strength and long-term stability even though the sintering temperature is low.

Thin films of the synthesized samples may have activation energy two or three powers less [20, 21]. Hence an increase in ionic conductivity can be expected at intermediate temperatures (~ 500 – 750°C).

4 Conclusions

Single phase pure nanocrystalline $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ materials are successfully synthesized by a solid state reaction method. The crystallite size obtained from XRD data is 11 nm and 15nm for GDC and SDC respectively. The trivalent dopants produce more oxygen vacancies and give high oxide ion conductivity in intermediate temperature range. The pellets of both samples show satisfactory surface morphology at the sintering temperature (1200°C for 10 h) and the grains have nanometer size. More conductivity is expected from GDC than from SDC since the GDC has higher surface to volume ratio. The conduction mechanism is mainly the hopping of thermally activated oxide ions with low bulk activation energy ~ 0.95 eV in the temperature range 500 – 750°C.

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