Synthesis characterization and dielectric studies of morphologically controlled ceria nanostructures

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ABSTRACT

The present work examines the dielectric property of ceria nanostructures of two different morphologies. Morphological characteristics and crystalline nature of the structures were analysed by electron microscopic analysis and powder X-ray diffraction analysis. Nanosized particles of cubic and spherical morphologies were obtained with average particle sizes 16 nm and 20 nm respectively. Dielectric studies showed a more dielectric dispersion of the materials at low frequency region that attains a temperature independent constant value at high frequencies. The a.c. electrical conductivity of the systems was also measured from the permittivity values and dielectric loss factor.

KEY WORDS: Ceria nano systems, hydrothermal synthesis, dielectric property, loss tangent factor.

1. INTRODUCTION

Semiconductors possess electrical conductivity intermediate to that of metals and insulators. Recently, semiconducting metaloxides offer a great promise for a wide range of electronic and technological applications. Semiconducting rare earth oxides contribute much to these areas due to their unique properties such as high chemical stability and high relative permittivity. The conduction mechanism in semiconductors mainly occurs via electron hopping or band type mechanism (Hannay, 1960).Cerium oxide (ceria, CeO_2) an n-type semiconductor, is one of the rare earth oxides possessing all the aforesaid properties and has a close lattice match with silicon. The defects and oxygen vacancies present in the cubic fluorite structure make it a good n-type semiconducting material (Santha and Sebastian, 2004).Oxygen ion conductivity increases in accordance with the vacancies created by the missing anions in the lattice. Pure ceria orits modified form (doped with other divalent or tetravalent cations) is a promising candidate for various applications including gas sensors, electrode material for solid oxide fuel cells, oxygen pumps, oxygen buffer, electronic ceramics, heterogeneous catalysis, antioxidants etc. (Riccardi, 2009; Moseley, 1992; Pan, 2008; Das, 2007). Solid oxide fuel cells operating at low temperature are a hot topic of research, where the search for suitable electrolyte material for this purpose is in full swing. The conductivity of doped ceria systems has been extensively studied and has attracted much attention as an important electrolyte material for intermediate temperature solid oxide fuel cells (Souza, 2012). For optimizing the existing electrolytes, studies are being done to know the influence of grain shape and size on the electrochemical properties of materials. Ceria performs as a mixed ionic electronic conductor at high temperatures due to its easily exchangeable tri and tetravalent oxidation states (Ce^{4+}/ Ce^{3+}).

$$2\,Ce^{4+} + O^{2-} \longrightarrow 2\,Ce^{3+} + 1/2\,O_2 + V_{oxy}$$
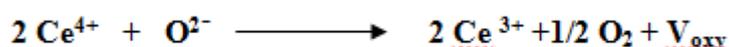
At high temperatures ($> 600^oC$), Ce^{3+} acts as localized negative charge or polaron, where hopping mechanism prevails rather than band type conduction. In the hopping type mechanism, the charge carrier can move from tri positive cerium state to the tetra positive state by a thermally activated polaron through ceria sublattice. But at low temperatures the conduction occurs via the movement of O^{2-} ions to the di positively charged oxygen vacancy. Upon increasing the temperature ionic and electronic conductivities together contribute to the total conductivity of the system (Zaghib, 2009).

On reducing the grain size of the semiconducting material into nanoregime, its optical and electrical properties are altered dramatically due to the large surface to volume ratio of nanoparticles. Some specific properties can be selectively controlled by tuning the size, morphology and composition of the material. The unusual dielectric property of nanostructured materials is very important and also attractive for their potential application as capacitors, memory devices and sensors. It is a well-known fact that space charge polarization and rotational polarization have a decisive role in determining the dielectric behavior of nanoscale materials (Indulal and Raveendran, 2010). Earlier reports revealed that the electrical conductivity is appreciably influenced by the grain size, homogeneity in grains, porosity and the grain structure. Fabrication into nanodimension generally lowers the ionic conductivity. However the exact reason for the decreased conductivity at the nanoscale is still unknown (Acharya and Singh, 2014). Studies on the effect of frequency in the dielectric behavior and ac conductivity give valuable information about the conduction phenomenon in semiconductor nonmaterials. In the

present study, ceria nanostructures are prepared via ammonia assisted hydrothermal route and ethylene glycol mediated route. The impact of the morphology of nanoceria on the dielectric property is investigated in detail.

2. EXPERIMENTAL

2.1. Sample preparation: Ceria nanostructures for dielectric study were fabricated via two different synthetic routes. The variation in experimental conditions resulted in the formation of different morphologies.

2.2. Preparation of sample 1 (S1) through hydrothermal routeusing ammonia as the precipitant: Ceria nano particles were synthesized via following our own procedure (Renuka, 2015). Briefly, cerium nitrate hexahydrate (99.9 % purity Sigma Aldrich) is dissolved in 120 mL of deionized water and the nitrate solution was simultaneously precipitated using ammonia (SRL extra pure) at a pH~10. The precipitated solution without aging was transferred into a 200ml air tight stainless steel vessel and was kept at 130ºCfor 24 hours. The precipitate collected was dried at 110ºC in an air oven and was calcined at 500ºC for 3 hours to obtain ceria nanocubes.

2.3. Preparation of sample 2 (S2) through Ethylene glycol mediated route: In this procedure, cerium nitrate hexahydrate (Sigma Aldrich), Urea (Merck) and Cetyl tri methyl ammonium Bromide (CTAB, Sigma Aldrich) were added to 150mL ethylene glycol (Merck) and the mixture was heated with stirring at 180ºC for one and half hour. The reaction mixture was then cooled to room temperature, precipitate was centrifuged and washed with ethanol followed by drying at 110ºC. Calcination at 450ºC for 2 hours resulted in spherical ceria nanoparticles.

2.4. Characterization of the samples: The morphology of the samples was observed through electron microscopic techniques(SEM and TEM)on SEM – JSM 848 instrument and Philips CM 200 transmission electron microscope respectively. Crystallinity and average particle size of the samples were identified from powder X-ray diffraction analysis and Scherrer formula. RigakuMiniflex600 Diffractometer (Cu$K\alpha$ radiation) equipped with a rotating anode was used for this purpose. Fourier Transform Infrared Spectroscopic analysis on Jasco FTIR-4100 model gives the information about the structural vibrations present in the cubic fluorite structure of ceria. Micromeritics Gemini surface area analyzer served the purpose of surface area measurement through N_2 adsorption study of the samples.

The dielectric permittivity of nano sized ceria structures were evaluated from the observed capacitance values in the frequency range50 Hz to 40 kHz. For this purpose nanoceria cylindrical pellets having diameter 1.1 cm and thickness of 0.06 cmwere prepared using hydraulicpress. Complex impedance parameters (i.e., capacitance, dissipation factor, impedance phase angle parameters) were measured with a computer controlled impedance analyzer. HIOKI- LCR, Hi-Tester, Model-P8532-50, Japan impedance analyzer was used for this purpose. The relative permittivity (dielectric constant) of the prepared ceria samples were calculated using the equation, $\varepsilon_r = \dfrac{C.d}{\varepsilon_0.A}$, where C is the capacitance, d the thickness of the cylindrical pellets, ε_r the relative permittivity- a dimensionless quantity, ε_0 permittivity of free space and A the area of cross-section of the sample pellets.By knowing the value of dielectric constant, the electrical conductivity of the samples can be evaluated using the expression, $\sigma_{ac} = \omega\varepsilon_0\varepsilon_r tan\delta$, where $tan\delta$ be the tangent loss factor.

3. RESULTS AND DISCUSSIONS

3.1. Powder X-ray diffraction analysis: Powder X-ray diffraction is an ideal technique that gives information about the crystallinity of materials. The powder XRD patterns of the two ceria nanostructures are provided in Figure 1. The sharp well defined peaks show that S1 is highly crystalline in nature. The major peaks are observed at 2θ values28.71, 33.24, 47.64, 56.48, 59.23 and 69.53 degrees. Intense peak at 28.71 arises from the (111) crystal plane of cubic ceria with lattice parameter, a= 0.54 nm. From the X-ray diffraction analysis it is clear that S2 is amorphous in nature, as well defined peaks were lacking in the diffraction pattern. Average crystallite size of S1 sample calculated by Scherrer formula, was found to be 18.6 nm.
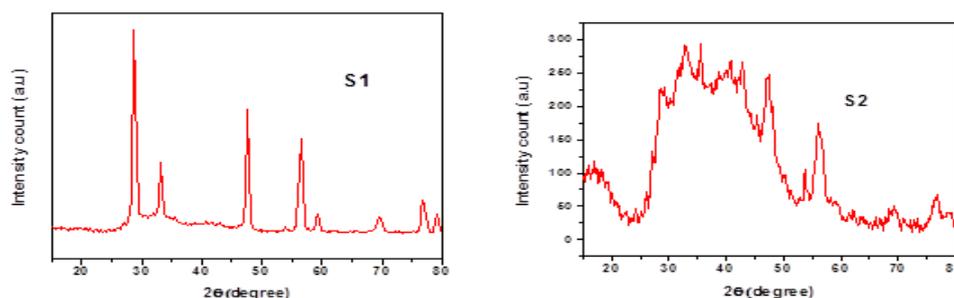

Fig.1.XRD patterns of ceria nanostructures

3.2. Fourier Transform Infrared Spectroscopic analysis: Fourier Transform IR patterns of samples 1& 2 are given in Figure 2. The IR bands below 1000cm^{-1} confirm the presence of CeO_2 in the prepared systems. The intense band at 3435cm^{-1} corresponds to the stretching vibration of physisorbed water on ceria surface. The band at 1620 cm^{-1} signifies the stretching mode of hydroxyl group.
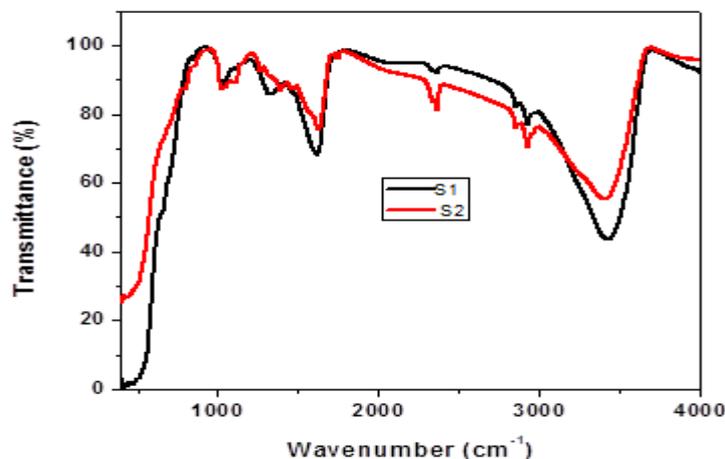

Fig. 2. Fourier Transform IR spectra of S1 and S2

3.3. Electron Microscopic Analysis (SEM and TEM): Electron microscopic images of sample 1 and sample 2are provided in Figures3 and 4, in the respective order. Agglomeration of individual particles was confirmed from the scanning electron microscopic images. When compared to S2, the extent of inter particle porosity was higher for S1. The transmission electron microscopic images give a clear idea about the average particle size and morphology of the prepared systems. Cubic particles and spherical particles of size 16 nm and 20 nm, respectively were envisaged from the images of S1 & S2 samples respectively. Particle size observed from TEM images are in consistence with that calculated using Scherrer formula. Surface area values obtained through BET nitrogen adsorption study were respectively 66 m^2/g and 58 m^2/g for S1 and S2samples.
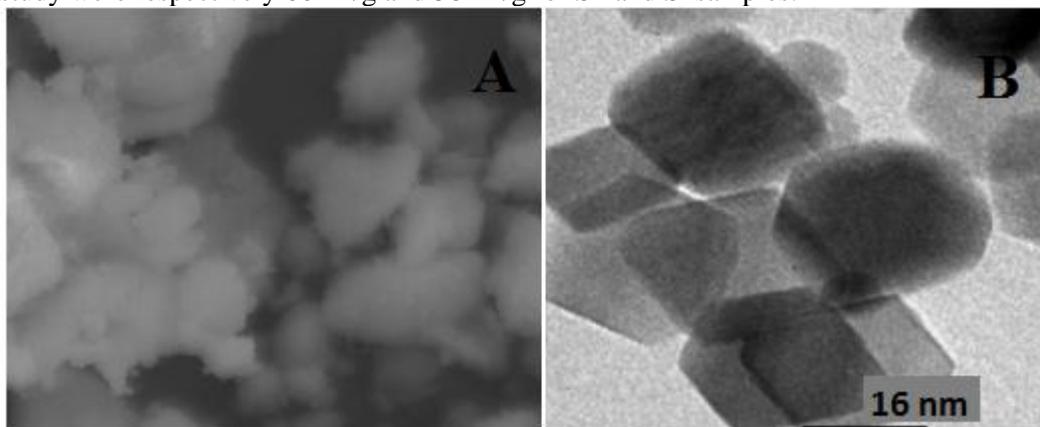

**Fig.3.Microscopic images of sample 1, SEM (A) and TEM (B)**
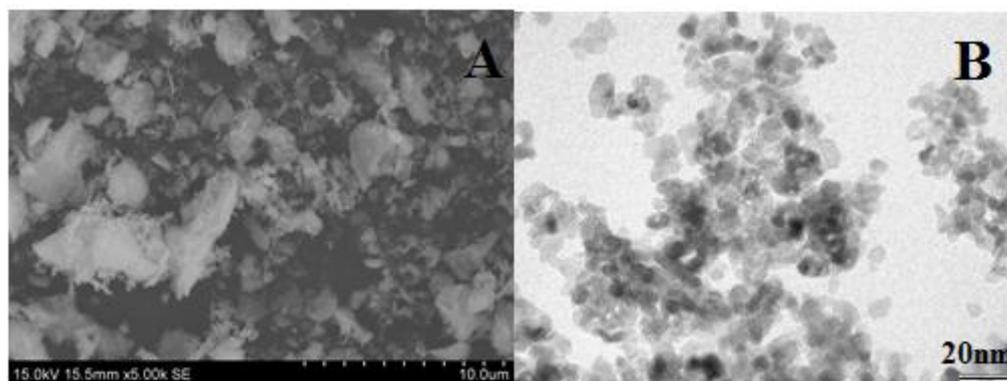
Fig.4.SEM (A) and TEM (B) images of sample 2

3.4. Dielectric studies: The variation of dielectric constant value of the two systems with frequency is evaluated from the observed capacitance values in the frequency range of 50 Hz to 40 KHz at 150°C (Figure 5a). The observed dielectric property is frequency dependent which can be explained on the basis of Maxwell-Wagner model. In the low frequency region both the systems show dielectric constant or permittivity of high values. The dielectric constant values of S1 and S2 samples were179 and242, respectively at 50 Hz for a given temperature of 150°C.High dielectric constant value ofS2 when compared to S1 may be attributed to the grain size effect. Some of the earlier researchers have noticed the high dielectric constant value of ceria nanoparticles synthesized via ethylene glycol assisted route (Ho, 2005). Various studies showed that the synthesis procedures can influence the physical and chemical properties of materials. The dielectric behavior of the nanostructured materials is determined by various types of polarization such as space charge and rotational polarization occur within the system. Generally, the extent of polarization present in the system decreases with the increase of frequency. From the present study it is observed that dielectric constant decreases with increase in frequency and beyond a certain frequency limit cerium ions cannot follow the alternating field leading to a constant value of permittivity (Kaur, 2012). Nanoceria possessing low value of dielectric constant and loss factor value at higher frequencies has a key role in the fabrication of materials for ferroelectric, electro ceramic, photonic and electro optic devices (Priyanka, 2014).

Polarization effects that arise due to the defects and imperfections present in the system are responsible for the energy dissipation in the material. Dielectric loss with angular frequency studied for the two samples is shown in Figure 5(b). Dielectric loss values of S1 and S2 are 1.32 and 1.57 respectively at a frequency of 50 Hz. The low loss tangent values of our systems at a low frequency of 100 Hz compared to other reports indicate the possible application of these materials in the above mentioned areas. Absorption current formed in the nanostructured materials maybe due to the presence of defects, impurities and space charge formation in the lattice, which causes a dielectric loss in the sample (Priyanka, 2014). As the frequency of the applied signal increases, there observed a decreasing trend of dielectric loss due to the reduced absorption current. At lower frequencies more energy is required for the exchange of electrons between the cerium cations and hence loss is high. A sudden decrease in the loss factor is observed in the lower frequency region, which gradually approaches a constant value at high frequency. The almost constant value of the loss tangent at high frequency is due to the difficulty in electron exchange between Ce^{3+} and Ce^{4+}, because they cannot follow the applied ac frequency.
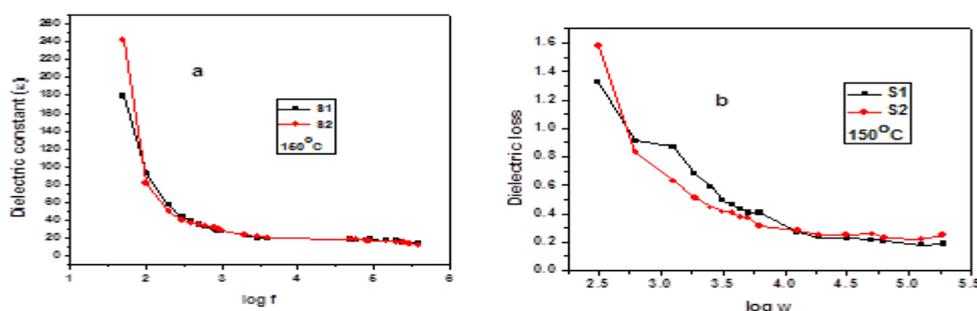
Fig.5.Dielectric behavior of S1 and S2 at 150°C. dielectric constant with logf (a), dielectric tangent loss with logw (b)
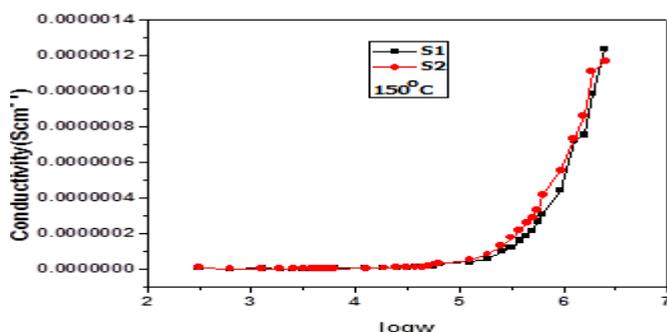
Fig.6.Electrical conductivity variation with frequency of prepared ceria nanostructures

The A.C. electrical conductivity of the synthesized samples at 150°C was evaluated from the obtained permittivity values (Figure 6). From the graph it is observed thatS1 and S2 show electrical conductivity values of $1.23 \times 10^{-6} Scm^{-1}$ and $1.163 \times 10^{-6} Scm^{-1}$ respectively. The A.C. conductivity increases with increase in frequency

that resembles a hopping type conduction mechanism. A small difference in conductivity value is noticed between the two ceria structures attained via two different synthetic routes. The grain size as well as the shape have decisive role in influencing the electrical conductivity. It is clear from the graph that S1 prepared through hydrothermal route using ammonia as the precipitant shows higher conductivity than S2 which may due to the increased number of oxygen vacancies and defects present in the system. It is established that the dielectric loss decreases with amount of defects which varies inversely with conductivity this is in accordance with our experimental observation also (Mei, 1995).

4. CONCLUSIONS

In this work we have successfully synthesized cubic and spherical ceria nanostructures with average particle size of 16 nm and 20 nm respectively. As a direct semiconductor rare earth oxide, ceria has versatile applications in various technological fields. The dielectric property variation of the prepared ceria systems with frequency was examined. Both ceria nanostructures possess high dielectric constant value in the lower frequency region and the value decreases with increase in frequency for a fixed temperature. The electrical conductivity and dielectric behavior show grain size dependent properties. Electrical conductivity measurements reveal that the system follows hopping type conduction mechanism.

5. ACKNOWLEDGEMENT

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