



PHYSICS

## PREPARATION AND STUDIES OF CERIUM DIOXIDE( $\text{CeO}_2$ ) NANOPARTICLES BY MICROWAVE-ASSISTED SOLUTION METHOD

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### Abstract

In this paper, synthesis and characterization of cerium dioxide ( $\text{CeO}_2$ ) or ceria nanoparticles are presented. Nanoparticles of cerium dioxide were synthesized by solution method using a microwave oven. The precursor used to prepare the nanoparticles of  $\text{CeO}_2$  was ammonium ceric nitrate. The precursor was dissolved in de-ionized water and pH value of the solution was adjusted to be at 12 using sodium hydroxide and the solution was kept on the microwave oven to synthesize the ceria nanoparticles. Synthesized yellow precipitate was filtered, washed and annealed and the sample was subjected to various characterization techniques like XRD, FTIR, SEM, TG/DTA, UV-visible absorption studies, conductivity studies and the results are presented and discussed.

**Keywords:** Cerium dioxide; nanoparticles; microwave-assisted method; Characterization; XRD; SEM; FTIR; TG/DTA

### Introduction

Cerium dioxide or ceria ( $\text{CeO}_2$ ) is an important and interesting rare-earth oxide, which has multiple applications such as electrolyte materials of solid oxide fuel cells [1], Ultraviolet blocking materials [2], in the field of catalysts[3], Chemical Mechanical Polishing (CMP) [4] and oxygen gas sensors [5] and so on. It has a fluorite-like cubic structure in which each cerium site is surrounded by eight oxygen sites in face-centered cubic(FCC) arrangement and each oxygen site has a tetrahedron cerium site. Recently, a variety of methods based on wet chemical routes have been extensively employed to synthesize of  $\text{CeO}_2$  nanoparticles like precipitation [6-9], hydrothermal[10,11], sol-gel method[12], microemulsion method[13] and other methods. Among all the methods, microwave-assisted solution method is a simple and inexpensive method to prepare nanoamaterials. Microwave is electromagnetic radiation with frequency range of 0.3-300 GHz and corresponding wavelength from 1 mm to 1000 mm. In the microwave irradiation region, the frequency of the applied irradiation is low enough so that the dipoles have time to respond to the alternating electric field and therefore respond to rotation. This method has been successfully applied for the preparation of a variety of nano-sized inorganic materials [14-17]. Compared with conventional heating, microwave heating has an advantage of high efficiency and rapid formation of nanoparticles with a nano-size distribution and less agglomeration. The fundamental mechanism of microwave heating involves agitation of

polar molecules or ions that oscillate under the effect of an oscillating electric field. In the presence of an oscillating field, particles try to orient themselves. This constant re-orientation creates friction and collisions between molecules, thus producing heat[18]. In this work, cerium dioxide nanoparticles were prepared by microwave-assisted solution method. The aim of this paper is to report the preparation of cerium dioxide nanoparticles by solution method using a microwave oven and also to present the obtained results from various studies.

### Experimental Procedure Synthesis

All chemicals used in this work were Analytical Reagent(AR) grade and used without further purification. In the synthesis of  $\text{CeO}_2$  nanoparticles, the precursor like ammonium ceric nitrate  $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$  was used and sodium hydroxide (NaOH) was used to adjust the pH value of the solution. Initially, 10 g of ammonium ceric nitrate was dissolved completely in de-ionized water and the pH value was adjusted to be 12 using sodium hydroxide solution. The mixture solution was stirred well using a magnetic stirrer for about 1 hour with a stirring rate of 1000 rpm. Then the prepared mixture solution was kept in a microwave oven (900 W, 2450 MHz., Onida, India) at a temperature of 50 °C for about for 30 minutes. When the ammonium ceric nitrate is treated with sodium hydroxide, the hydrolysis process takes place and the products like sodium nitrate, ammonium hydroxide and cerium hydroxide are formed. During the reaction,

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one proton( $H^+$ ) is removed from cerium hydroxide due to polar nature of water and this leads to the formation of hydrated cerium dioxide. Synthesized pale-yellow precipitate was filtered and washed with de-ionized water twice. Annealing of the synthesized powder at  $130^\circ\text{C}$  in air for 2 h results in the formation of  $\text{CeO}_2$  nanoparticles.

### Characterization techniques

Powder X-ray diffraction pattern of the as-prepared sample was obtained using an automated X-ray powder diffractometer (PANalytical) with nickel filtered, monochromated  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at 35 KV, 10 mA. The sample was scanned over the required range for  $2\theta$  values ( $10 - 80^\circ$ ). The crystalline phase of the sample was identified from the crystallographic parameters such as  $2\theta$ , relative intensity and hkl values. The morphology of the nanoparticles was examined by Scanning Electron Microscope (SEM) and the SEM image of the synthesized cerium dioxide nanoparticles was recorded using a Hitachi Scanning Electron Microscope. A Perkin Elmer UV-visible spectrophotometer was used to take the absorption spectrum in the 200-800 nm wavelength range at room temperature after the as-prepared ceria nanoparticles are dispersed in ethanol. DC electrical conductivity of the pelletized nanoparticles was calculated using a two-probe arrangement and a megohm digital meter. The resistance (R) of the sample was measured in the temperature range  $30-80^\circ\text{C}$  and the conductivity was determined using the relation  $\sigma_{ac} = d/(RA)$  where d is the thickness of the pellet, A is the area of cross section the pellet[19]. The infrared spectroscopy is effectively used to identify the functional groups of organic and inorganic samples. The Fourier Transform Infrared (FTIR) spectrum of the sample was recorded using JASCO FI-IR 460 spectrometer by KBr pellet technique in the range  $400-4500 \text{ cm}^{-1}$ . Thermo Gravimetric (TG) analysis and Differential Thermal Analysis (DTA) were carried out using Seiko thermal analyzer. Both TG/DTA analyses were carried out simultaneously in nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{minute}$  for temperature range of  $30-600^\circ\text{C}$ .

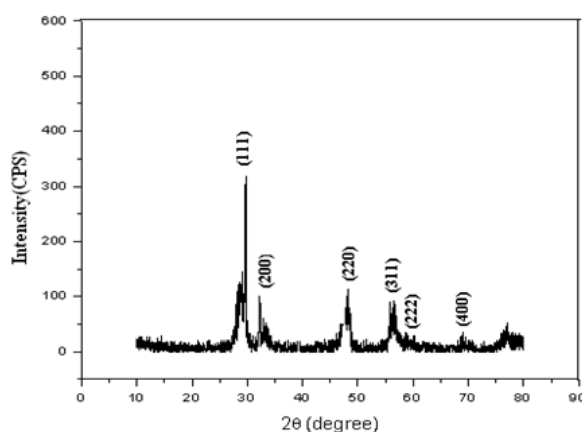
## Result and Discussion

### Powder XRD studies

Fig. 1 shows the powder XRD pattern of the as-prepared cerium dioxide nanoparticles. From this figure, the characteristic peaks are located at  $2\theta = 28.5, 33.9, 47.8, 56.2, 58.5$  and  $69.1^\circ$  and they correspond to (111), (200), (220), (311), (222) and (400) lattice planes, respectively. All the reflections of powder XRD pattern of the sample of this work were indexed using the INDEXING software package.

The lattice parameters from powder XRD data were found using the UNITCELL software package and the obtained values were found to be  $a = b = c = 5.416 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ . The obtained lattice parameters for ceria nanoparticles are observed to be in good agreement with the data reported in the literature (JCPDS43-1002). The powder XRD pattern of  $\text{CeO}_2$  nanoparticles shows broad peaks, which confirmed the formation of small-sized nanoparticles. The particle size of nanoparticles was determined using the Scherrer's relation  $d = (0.9 \lambda) / (\beta \cos \theta)$  where  $\beta$  is the full width at half maximum in radians,  $\lambda$  is the wavelength of X-rays used and  $\theta$  is the Bragg's angle[20]. For the various reflection peaks of the XRD pattern, the particle size was estimated and the average size of nanoparticles of the sample was found to be around 27 nm.

Fig.1: Powder XRD pattern for  $\text{CeO}_2$  nanoparticles



### FTIR studies

Fourier Transform Infrared (FTIR) spectrometer is the sophisticated instrument which can be used to identify the functional groups of samples of nanomaterials, crystals and other types of materials. When an infrared radiation is passed through a sample, certain percentage of intensity of the radiation would be absorbed by the sample and that will be indicated in the FTIR spectra. The absorption of IR radiation in the sample is due to stretching and bending vibrations. Depending on the material of the sample, absorption of IR radiation will occur at certain frequencies. An FTIR spectrum is recorded between percentages of transmittance (%T) and wave number of IR radiation. By observing the absorption bands or peaks in the wave number range  $400 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  of FTIR spectrum, one can ascertain the functional groups of the sample and hence the chemical formula and the sample can be identified. The FTIR pattern of cerium dioxide nanoparticles is shown in the Figure 2. The broad absorption band located around  $3400 \text{ cm}^{-1}$

corresponds to the O–H stretching vibration of residual water and hydroxyl groups, while the absorption band at 1630  $\text{cm}^{-1}$  is due to the scissor bending mode of associated water. The complex bands observed at about 1518, 1350, 1053  $\text{cm}^{-1}$  are due to unwanted residues in the sample. The band at 848  $\text{cm}^{-1}$  corresponds to metal–oxygen bond. The assignments for the absorption peak/bands for cerium dioxide nanoparticles are provided in the Table 1.

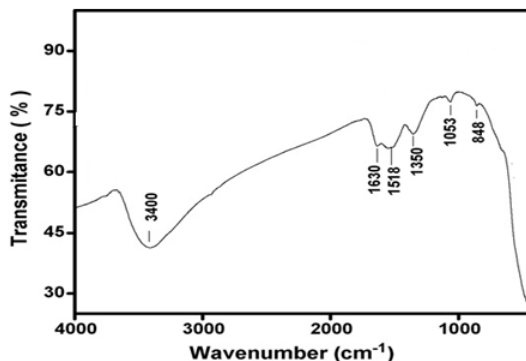


Fig.2: FTIR spectrum for the nanoparticles of cerium dioxide

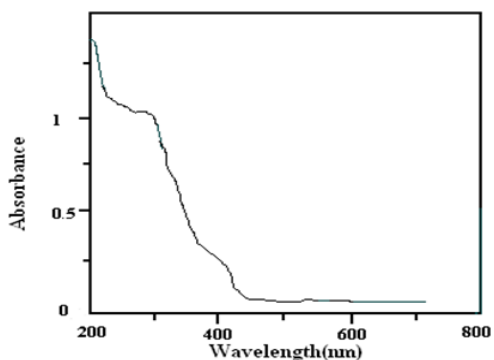
Table 1: Assignments for absorption bands/peaks of FTIR spectrum of cerium dioxide nanoparticles

Bands/peaks ( $\text{cm}^{-1}$ )	Assignments
3400	OH stretching
1630	OH bending
1518	$\text{CH}_2$ bond
1350	$\text{CH}_2$ bond
848	Metal-O bond

**UV-visible absorption spectral studies**

UV-visible absorption spectral study may be assisted in understanding electronic structure of the optical band gap of the material. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. The study of the absorption edge is important especially in connection with the theory of electronic structure, which predicts that the band structure is mostly affected near the band extreme [21]. UV-visible absorption spectrum of cerium dioxide nanoparticles dispersed in ethanol solution was measured and it is presented in the Figure 3. The spectrum shows a strong absorption band in the UV region due to the charge transfer transitions between the energy states. In the wavelength range 700-500 nm, no absorption was detected. The broadness of the absorption shoulder in UV region is attributed to the self-assembly of the nanoparticles and this is confirmed from SEM study.

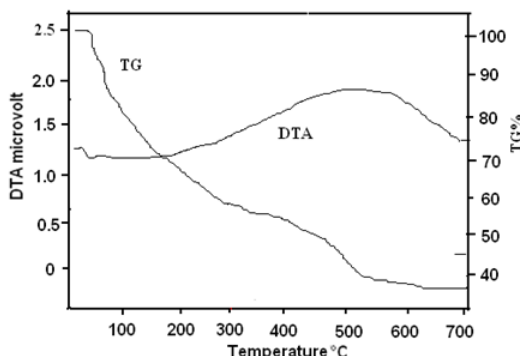
Fig.3: UV-visible absorption spectrum for  $\text{CeO}_2$  nanoparticles



**Thermal studies**

TG/DTA thermograms for as-prepared cerium dioxide nanoparticles are shown in the Figure 4. The TG curve shows the corresponding weight losses at the various stages. The shallow endothermic peak at 50  $^\circ\text{C}$  is due to the evaporation of absorbed moisture in the sample. The TG curve shows that there is a weight loss taking continuously up to 600 $^\circ\text{C}$ . The maximum weight loss is observed in the temperature range 100 $^\circ$  – 450 $^\circ\text{C}$ . From DTA curve, it is observed that there is a broad exothermic peak in the temperature range 450-600 $^\circ\text{C}$  which represents the decomposition of the sample.

Fig.4: TG/DTA curves for the as-prepared cerium dioxide nanoparticles

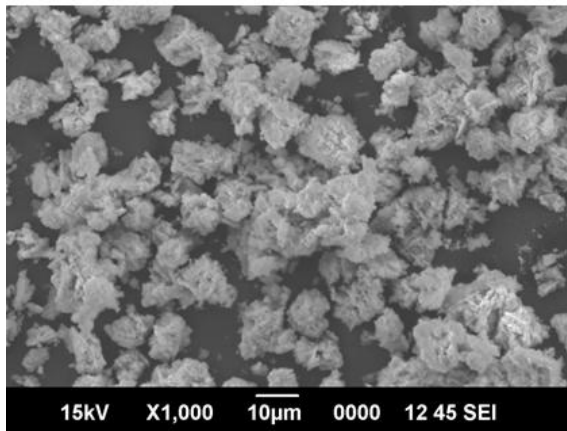


**SEM studies**

The morphology of nanoparticles is found using a Scanning Electron Microscope (SEM). The SEM image of the as-prepared cerium dioxide nanoparticles is presented in the figure 5. From the figure, it is

observed that most of particles are spherical and some are elongated in shape and these particles are observed to be agglomerated.

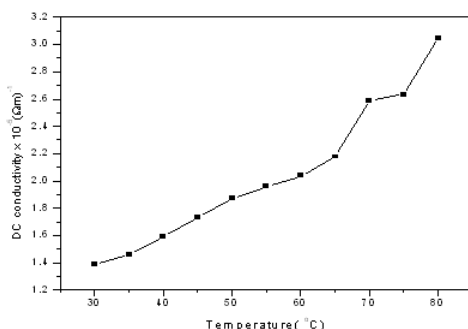
Fig. 5: SEM image of cerium dioxide nanoparticles



### DC Conductivity Studies

DC conductivity is the electrical conductivity of a sample when d.c. voltage is applied to the sample. Study on DC conductivity provides the electrical behaviour of the sample and from these studies, one could conclude that the sample is insulator, semiconductor or a metal. In this work, the DC conductivity ( $\sigma_{ac}$ ) of the pelletized form of cerium dioxide nanoparticles is measured using a two-probe arrangement and a digital multimeter. The measurements were taken for various temperatures ranging from 30–80 °C. The pellet is made using a hydraulic press by applying a pressure of 6 tonnes and opposite faces of pellet were electroded with a good quality graphite paint to obtain ohmic contact. Resistance (R) of the sample was measured directly and DC conductivity was determined using the relation  $\sigma_{ac} = d/(RA)$  where d is the thickness of the pellet, A is the area of cross section the pellet. A graph of DC conductivity ( $\sigma_{ac}$ ) versus temperature in centigrade was drawn for the pelletized sample of CeO<sub>2</sub> and it is depicted in the figure 6.

Fig.6: Variation of DC conductivity of pelletized nanoparticles of cerium dioxide with temperature



From the figure 6, it is noticed that DC conductivity increases with the temperature for the sample and the sample shows an insulating behaviour. When the

temperature is increased, there will be transition of charge carriers from valence band to conduction band and hence conductivity increases. Since number of electrons in the conduction band increases when the temperature is increased, the conductivity increases. Also due to small-size of particles in the sample, there will be easy transfer of charge carriers when the temperature is increased and hence conductivity increases [22].

### Conclusion

Nanoparticles of cerium dioxide have been prepared by microwave-assisted solution method using ammonium ceric nitrate as the precursor. Powder XRD studies reveal the crystal structure and nano-scale of the prepared CeO<sub>2</sub> particles. The morphology of the sample has been examined by SEM. The functional groups of the sample have been identified from FTIR studies. UV-visible absorption studies reveal the self-assembly of the nanoparticles. The thermal stability of the prepared sample has been examined by TG/DTA studies and the conducting nature of the pelletized form of cerium dioxide nanoparticles has been analyzed by conductivity studies.

### Acknowledgement

The supports extended in the research by RRL (Trivandrum), CECRI (Karaiyudi), M.K. University (Madurai) and St. Joseph's College (Trichy) are gratefully acknowledged. Also we thank authorities of Management of Aditanar College of Arts and Science, Tiruchendur, Infant Jesus College of Engineering and Technology, Tuticorin and MDT Hindu College, Tirunelveli for the encouragement given to us to carry out the research work.

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