

# Structural and optical properties of Cerium oxide nanoparticles

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## Abstract

*Ceria (CeO<sub>2</sub>) is a technologically important rare earth material because of its unique properties and various engineering and biological applications. The structural features and optical properties of the nanoparticles were determined in depth with X-ray powder diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), UV-Vis absorption spectroscopy (UV), Photoluminescence spectroscopy (PL) and EDAX. The average crystallite size was estimated from the XRD pattern using Debye Scherrer equation as about 8.92 nm. The Cell volume, dislocation density are calculated. Lattice parameters were also determined and it is verified by Williamson- Hall plot. The EDAX analysis shows the chemical compositions of nanoparticles. The UV-visible absorption spectroscopic measurement results showed that the products had conspicuous quantum size effects. The absorption spectrum indicates that the nanostructured CeO<sub>2</sub> has a wide band gap of 4.26 eV and the photoluminescence spectra shows a strong band at 360 nm and so it has promising application in optoelectronic materials.*

**Keywords:** Precipitate, XRD, Band gap, Photoluminescence, Metal Oxide

## 1. Introduction

Nanostructured metal oxides have attracted considerable attention from many researchers due to their diversity of applications in various technological fields of science and technology [1-4]. These nanostructured metal oxides have unique physical and chemical properties, which are significantly different from their bulk counterparts [5, 6]. In particular, cerium oxide is a promising material which shows a potential application in gas sensors [7], fuel cells [8], solar cells [4] and as a coating material [9]. Several studies have been reported on the size dependent properties that can increase the attention due to size induced changes in physical and chemical properties [10, 11].

In the present study, we employed the precipitation method to prepare the nanometer- sized cerium oxide ultrafine particles. The structural features and optical properties of the ceria

nanoparticles were determined in depth with X-Ray powder diffraction (XRD), UV-Vis spectroscopy, PL spectroscopy, FESEM and EDAX.

## 2. Materials and methods

### 2.1 Materials

All chemicals such as ammonium cerium nitrate, urea, ammonia and ethanol were of analytical grade and purchased from Merck.

### 2.2 Experimental Procedure

A modified precipitate method has been used for the fabrication of CeO<sub>2</sub> nanoparticles. In typical procedure, 0.25% of cerium ammonium nitrate was dissolved in 50 ml deionized water and stirred to get transparent solution. Then, 0.75% of urea was dissolved in 50 ml deionized water. Add ammonium cerium nitrate solution drop wise in urea solution under vigorous stirring. Upon adding the ammonia solution, precipitation of Ce (OH)<sub>4</sub> occurred. Excess ammonia solution was added drop wise until a solution of pH 10 was achieved, obtaining a gray colored precipitate. After stirring a pale yellow precipitate of Ce (OH)<sub>4</sub> was obtained and it was subsequently washed several times with deionized water and centrifuged to remove residual reactants. Moreover the dried samples are calcined at 500 °C for 2 hours. The synthesized CeO<sub>2</sub> nanoparticles are pale yellow in color.

### 2.3 Characterization techniques

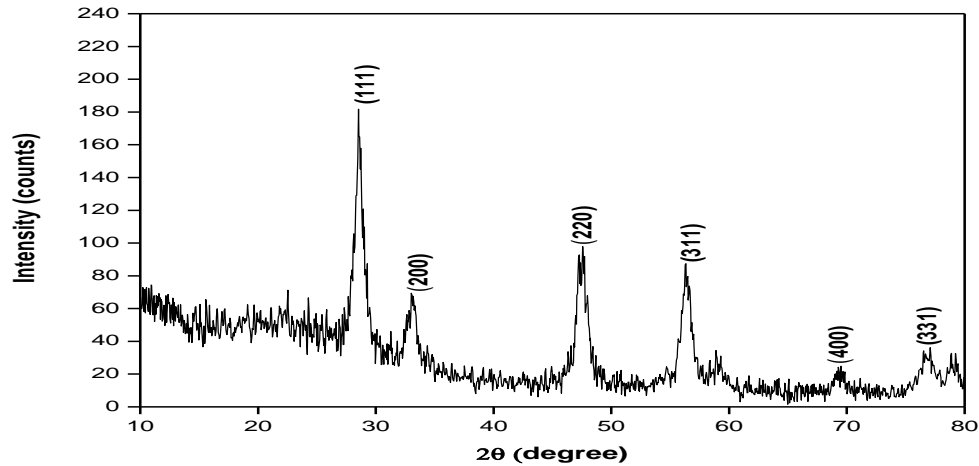
Phase identification of the as-prepared pure CeO<sub>2</sub> was carried out by a XPERT-PRO Diffraction system using the CuK<sub>α</sub> radiation of wavelength 1.5406 Å. A Field Emission Scanning Electron Microscopy (FESEM JSM-5600 LV (JEOL, Japan) was utilized to observe the morphology of the samples. The optical absorbance and band gap of the as-prepared pure CeO<sub>2</sub> nanoparticles were recorded using Hitachi U-2900 Spectrophotometer in the wavelength range 200–800 nm. Photoluminescence (PL) spectra were measured at room temperature with a spectrophotometer (Perkin Elmer L-55). The purity of the samples and the incorporation of the dopants are identified from EDAX.

### 3. Result and Discussion

#### 3.1. Structural properties

The structural characterization of the pure cerium oxide nanoparticles are carried out by X-ray Diffraction method. The XRD pattern reveals all of the major peaks of CeO<sub>2</sub> corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystallographic plane cubic fluorite structure as identified using the

standard data JCPDS Card No. **81-0792**. The intensities and positions of the peaks are in perfect agreement with the literature values. No peak of any other phase is detected indicating the high purity of the product. The broadening of the reflections in the diffractogram distinctly indicates the formation of nano-dimensional crystals. The average crystallite size is found out to be 8.9229 nm.



*Fig 1. XRD pattern for pure cerium oxide nanoparticles*

For cubic structure, the lattice constant ‘a’ is evaluated using the relation

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where, (h k l) are the Miller indices and d is the interplanar spacing.

The precise lattice parameters of pure CeO<sub>2</sub> are calculated by the Bradley-Jay and Nelson-Riley extrapolation methods that minimize the influence of systematic errors. Extrapolation against cos<sup>2</sup>θ is called Bradley- Jay method whereas extrapolation against {(cos<sup>2</sup>θ/sinθ)+(cos<sup>2</sup>θ/θ)} is called Nelson-Riley plot.

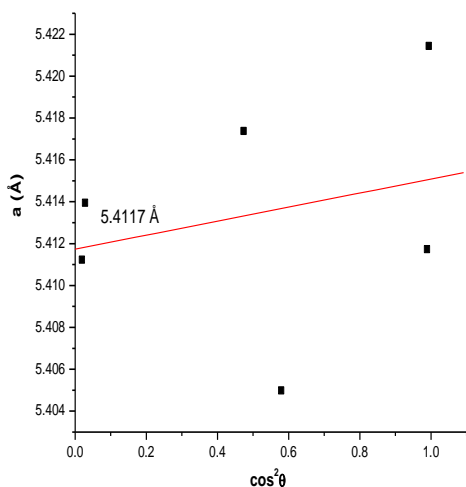


Fig 2. Bradley Jay plot

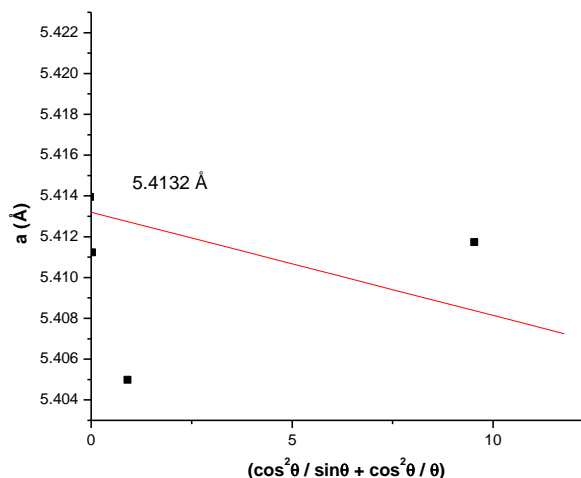


Fig 3. Nelson Riley plot

*Lattice parameters of CeO<sub>2</sub> nanoparticles*

sample	Lattice Parameter a (Å)				Unit Cell Volume (Å) <sup>3</sup>	
	Calculated	Standard (JCPDS)	Bradley Jay plot	Nelson Riley plot	Calculated	Standard (JCPDS)
Pure cerium oxide	5.41445	5.411	5.4117	5.4132	158.7316	158.46

The values obtained matched well with the JCPDS data. The precision obtainable with the Nelson-Riley extrapolation function is better than that obtained from the Bradley-Jay extrapolation function greater range of linearity and so it is useful when only a few high-angle reflections are present.

**3.2 Optical properties**

Using UV-Visible spectrophotometer absorption spectra of particles were recorded by dispersing the particles. The spectrum of nanostructure CeO<sub>2</sub> nanoparticles indicates that the pure cerium oxide nanoparticles exhibit maximum absorption peaks at 341 nm. Nanostructured CeO<sub>2</sub>

nanoparticles exhibit a strong absorption bands below 400 nm in wavelength at the UV region due to the charge-transfer transitions from oxygen 2p to cerium 4f which overturns the well-known f-f spin orbit splitting of the Ce 4f state. Also the spectrum of each sample shows that most of the UV light (200nm–350nm) is blocked allowing ceria nanoparticles to be used as a UV blocker. The absorbance spectra of all the samples thus show blue shift which is due to quantum confinement effect. The band gap energy calculated is larger than the bulk CeO<sub>2</sub> (E<sub>g</sub> = 3.19 eV). The results confirm that a blue shift has occurred.

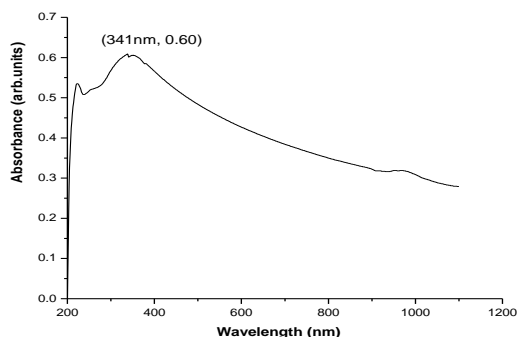


Fig 4. Absorption spectra of CeO<sub>2</sub>

Figure 6 shows the photoluminescence spectra of CeO<sub>2</sub> excited at wavelength 220 nm at room temperature. Upon excitation peak of wavelength 360 nm, a strong blue-green emission is observed from the Ce<sup>4+</sup> ions in CeO<sub>2</sub>. A significant enhancement in the emission band is observed in the spectrum of CeO<sub>2</sub>; this may be due to the change in particle size and the quantum size effect. This emphasizes the fact that the d electrons of cerium

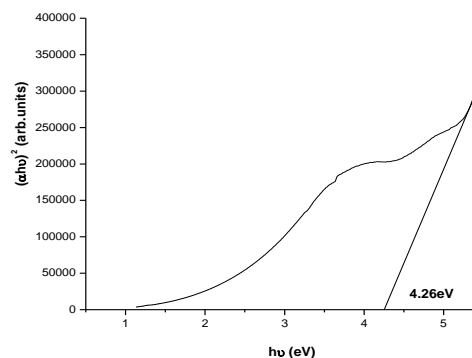


Fig 5. Tauc Plot of CeO<sub>2</sub>

couple differently to the lattice phonon in the cubic fluorite structure, leading to a higher Stokes shift. It exhibited a strong emission band near 360nm and a weak blue shoulder at about 491nm. This is attributed to surface defects (oxygen vacancies) which existed between the Ce 4f state and O 2p valence band. Other supplementary weak bands are detected at 376, 411, 440 and 520 nm.

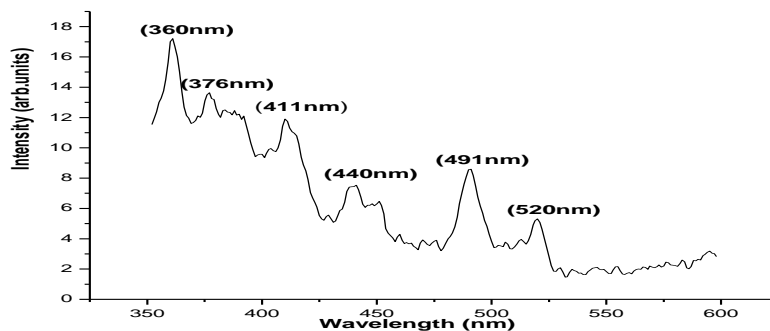
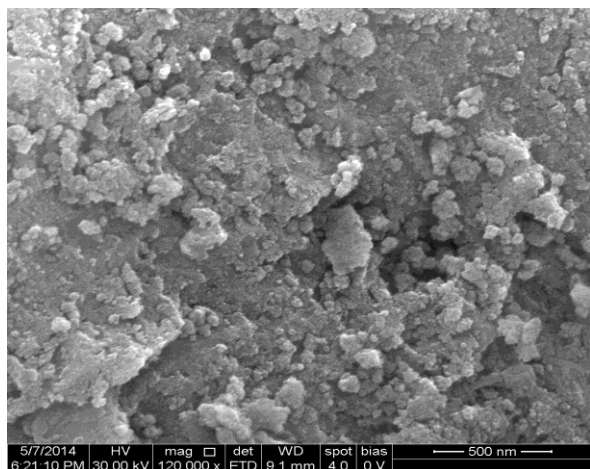


Fig 6. PL spectra of CeO<sub>2</sub>

### 3.3 FESEM AND EDAX

The morphology of CeO<sub>2</sub> nanoparticles have been investigated by FEI QUANTA – 200 microscope and the EDAX data is given.



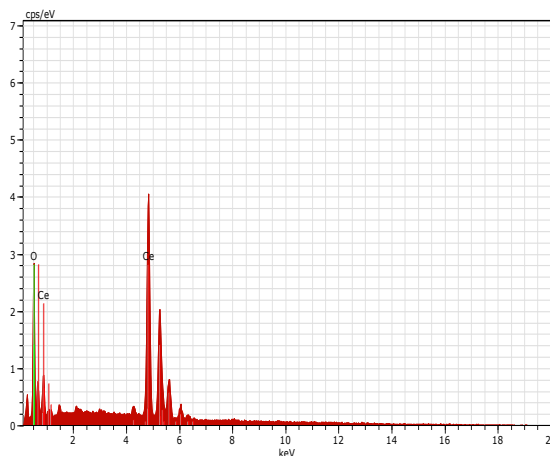
**Fig.7 FESEM image of CeO<sub>2</sub>**

The FESEM image shows that the sample of porous powders, are formed by the aggregation of nanosized particles. The as-prepared CeO<sub>2</sub> nanoparticles are spherical in shape with uniform size distribution.

As the particle size decreases, agglomeration will increase. Agglomeration of nanoparticles is a very common phenomenon that occurs because the nanoparticles tend to decrease the exposed surface in order to lower the surface energy and the smaller particle size results in stronger agglomeration. Ceria nanoparticles have a special property which causes agglomeration by minimizing the interface energy with the formation of a lattice matched ‘coherent interface’. The energy dispersive X-ray analysis of the cerium oxide nanoparticles shows the presence of cerium (Ce) and oxygen (O) elements. No other impurity peak is seen in the EDAX spectrum which confirms the purity of the as-prepared samples.

### Conclusions

In conclusion, the simple chemical method has been successfully employed for synthesis of cerium oxide nanocatalyst. Optical and structural properties were discussed. XRD studies show that as the grain size increases, the dislocation density decreases. No other impurity peaks is seen from



**Fig.8 EDAX Spectrum**

EDAX spectrum which confirms the purity of the as-prepared samples. UV absorption spectrum studies reveal that there is a blue shift. As the average grain size increases, the optical band gap decreases. Also the spectrum of each sample shows that most of the UV light (218 nm – 341 nm) is blocked allowing ceria nanoparticles to be used as an UV blocker.

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