Effect of Calcination Temperature on Pure Cerium Oxide Nanoparticles by Precipitation Method

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Abstract – Cerium oxide is the most exciting rare earth element for researchers in the field of catalysis. Cerium oxide also known as ceria is produced by various methods chosen by the desired properties of the product. Cerium oxide is an important functional material which contributes to a wide range of applications. In the present study, pure CeO_2 nanoparticles were synthesized using chemical co-precipitation method. The size of pure CeO_2 nanoparticles before and after calcinations were estimated by powder X-ray diffraction (PXRD) pattern and it was revealed that pure CeO_2 crystallizes into cubic phase. The photoluminescence (PL) spectroscopy study shows the prominent UV emission peak occurs at 320nm. The chemical structural information of the synthesized as nanoparticles was studied by Fourier transform infrared (FTIR) spectroscopy.

Index Terms – Co-Precipitation method, PXRD, UV-DRS, FESEM, PL, FTIR.

1. INTRODUCTION

During the last few years, synthesis of nanostructured oxide materials have attracted considerable attention because of their extremely fascinating and useful properties, which can be exploited for a variety of structural and non-structural applications. They can be subdivided into nanoparticles, nanofilms and nanocomposites. Rare earths are the fourteen lanthanides along with scandium and yttrium. It is well recognized that rare-earth oxides have wide range of applications in many fields like electronics [1], bio-sensors [2], drug delivery [3], agriculture [4], pharmaceutical and medical [5]. Among the rare earth oxides, cerium oxide or ceria (CeO_2) finds enormous applications in catalysts/catalyst supports [6-7], oxygen ion conductors in solid oxide fuel cells [8-10], electrochemical oxygen pumps [11], UV absorbents [12], fluorescent materials [13] and amperometric oxygen ion monitors because of its high oxygen ion conductivity [14]. Earlier reports reveals that CeO_2 nanoparticles have been prepared by sol-gel processing [15-16], sonochemical synthesis [17], a thermal decomposition process [18], hydrothermal synthesis [19], a polymeric precursor route [20], etc. Its high abundance combined with excellent catalytic activity for a variety of reactions makes cerium the element of choice for the automotive industry enabling the catalytic conversion of the exhaust system of automobiles. In many of the above processes, the main objective is the synthesis of phase pure CeO_2 based materials for various applications. The objective of the present research is the synthesis of CeO_2 nanoparticles by the chemical co-precipitation process. Also the samples are characterized using PXRD, UV, FESEM, PL, FTIR and EDAX analysis.

2. MATERIALS AND METHODS

All the chemicals used in the experiments were analytical reagent grade and used without further purification. All the aqueous solutions were prepared using double distilled water. In the present work, pure CeO_2 nanoparticles are synthesized by chemical co-precipitation method.

2.1 EXPERIMENTAL DETAILS

0.01M CTAB and 1M of cerium nitrate were dissolved in 50 ml of double distilled water and the solution was kept under constant stirring at room temperature using magnetic stirrer for one hour. Cerium nitrate solution was added drop wise in the CTAB solution. 2M of sodium hydroxide was dissolved in 50 ml of distilled water and was heated upto 60 °C. After completely dissolving the solution of cerium nitrate and CTAB, this solution is added drop wise to the beaker containing the hot NaOH solution and immediately white precipitate of CeO_2 nanoparticles are formed. Then the produced nanoparticles were washed out for 10 times using distilled water and ethanol. Then it is dried in hot air oven for about 100 ºC for few hours until the water evaporates. The dried sample is calcined at 600 ºC in muffle furnace. The as-prepared sample CeO_2 is finely powered in agate mortar. The synthesized CeO_2 nanoparticle sample is pale yellow in color.

3. RESULTS AND DISCUSSION

3.1. Powder X-ray Diffraction Analysis (PXRD)

The powder X-ray diffraction pattern of pure Cerium oxide nanoparticles was obtained using a XPERT-PRO diffraction system using the CuKα radiation of wavelength 1.5406 Å. The type of the scan used is continuous and range from 20º to 80º and the rate is 0.05.

The X-ray diffractogram of the pure CeO_2 is depicted in Fig.1. The PXRD pattern shows that the crystal structure of pure CeO_2 nanoparticles before calcination is cubic (face centered) and the diffraction data are in good agreement with the JCPDS file No: 81-0792. The high intensity peaks observed at (111), (200), (220), (311), (400), (331) corresponding to $2\theta = 28.59°$, 33.21°, 47.44°, 56.27°, 76.92°.

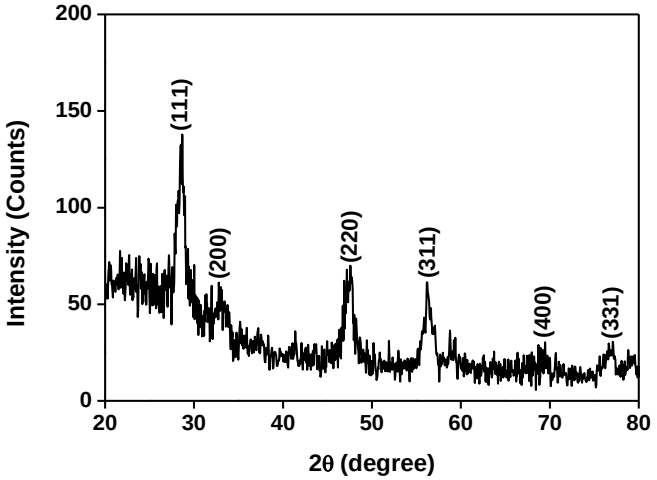


Fig.1. PXRD pattern for pure CeO_2 nanoparticles before calcination

The d-spacing values obtained from XRD data of the as-prepared pure CeO_2 nanoparticles before calcination are identified with the JCPDS file No: 81-0792 and their respective h k l and relative intensity values are presented in Table.1.

Table.1. d-spacing values for pure CeO_2 nanoparticles before calcinations

S.No	2θ (degree)	d-spacing (Å)		h k l	Relative intensity (%)
		Observed	JCPDS		
1.	28.5979	3.1214	3.1248	1 1 1	100
2.	33.2117	2.6976	2.7062	2 0 0	15.98
3.	47.4497	1.9161	1.9135	2 2 0	49.54
4.	56.2732	1.6348	1.6319	3 1 1	46.82
5.	76.9211	1.2395	1.2416	3 3 1	16.04

Fig.2 shows the PXRD pattern of pure CeO_2 nanoparticles calcined at 600° C. The peaks are very broad, polycrystalline in nature and observed at (111), (200), (220), (311), (400), (331) corresponding to 2θ = 28.66°, 33.07°, 47.41°, 56.40°, 59.03°, 69.28°, 76.74°. Girija et al. [21] have reported similar assignments to the broadened peaks obtained for pure CeO_2 nanoparticles.

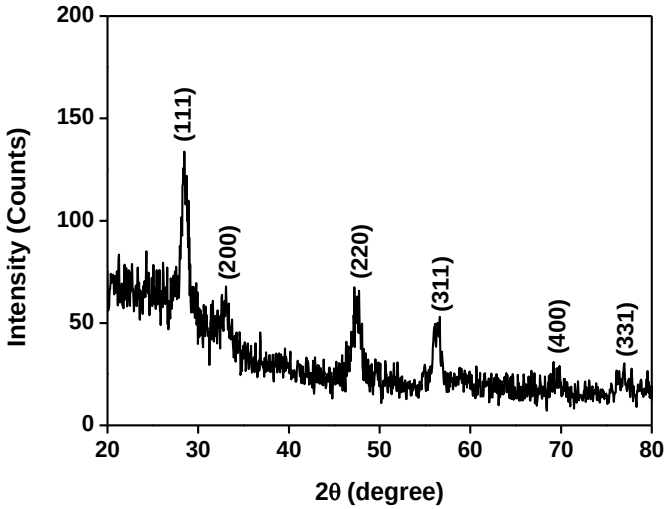


Fig.2. PXRD pattern for pure CeO_2 nanoparticles calcined at 600 ºC

The d-spacing values obtained from XRD data of the as-prepared for pure CeO_2 nanoparticles calcined at 600 °C are identified with the JCPDS file No: 81-0792 and their respective h k l and relative intensity values are presented in Table.2.

Table.2. d-spacing values for pure CeO_2 nanoparticles calcined at 600 ºC

S. No	2θ (degree)	d-spacing (Å)		h k l	Relative intensity (%)
		Observed	JCPDS		
1.	28.6645	3.1143	3.1248	1 1 1	100
2.	33.0714	2.7087	2.7062	2 0 0	31.02
3.	47.4102	1.9176	1.9135	2 2 0	64.48
4.	56.4026	1.6313	1.6319	3 1 1	62.28
5.	59.0305	1.5648	1.5624	2 2 2	12.02
6.	69.2893	1.3561	1.3531	4 0 0	7.27
7.	76.7414	1.2419	1.2416	3 3 1	17.06

The grain size can be calculated from the diffracted beam using the Debye Scherrer formula

$D=K\lambda/\beta\cos\theta$

The dislocation density is found out using the formula

$\delta= 1/D^2$ lines/sq.m

The average grain size and dislocation density of the as-prepared CeO_2 nanoparticles before and after calcinations are given in Table.3.

Table.3. Average Grain Size and Dislocation density of the as-prepared samples

S. No.	Nanoparticles	Average Grain Size (nm)	Dislocation Density $x10^{15}$(lines/m^2)
1	Pure CeO_2before calcination	13.202	3.5465
2	Pure CeO_2calcined at 600°C	13.5530	3.1799

The PXRD patterns of as-prepared ceria nanoparticles showed the same crystalline structure for all the synthesis conditions used. The entire peak scan be well-indexed to a pure cubic structure of CeO_2 with lattice constant 'a' is 5.4124 Å and cell volume is 158.55 (Å) ^{3} which is in good agreement with the JCPDS file for CeO_2 (JCPDS 81–0792).

Table.4. shows the comparison of standard and observed Lattice Parameters & Unit Cell Volume. The lattice parameter and unit cell coincides well with that of the JCPDS values as reported by Jasmine Ketzial et al. [22]. A slight increase in the lattice constant for the samples before and after calcinations is obtained.

Table 4. Comparison of standard and observed Lattice Parameters and Unit Cell Volume

Materials	Lattice Parameters (Å)		Unit Cell Volume $(Å)^3$	
	Observed	JCPDS	Observed	JCPDS
Pure CeO_2 before calcination	5.4051	5.4124	157.9115	158.55
Pure CeO_2 after calcination	5.4136	5.4124	158.6584	158.55

3.2 UV-DRS Studies

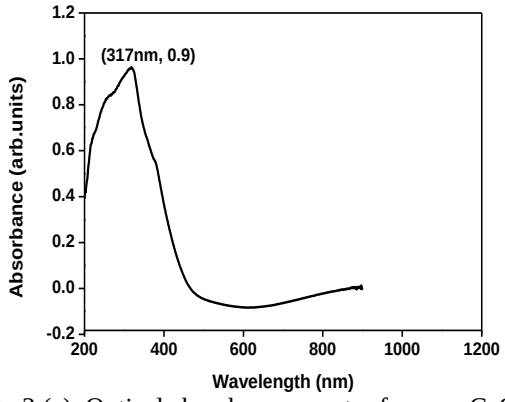


Fig.3 (a). Optical absorbance spectra for pure CeO_2 nanoparticles before calcinations

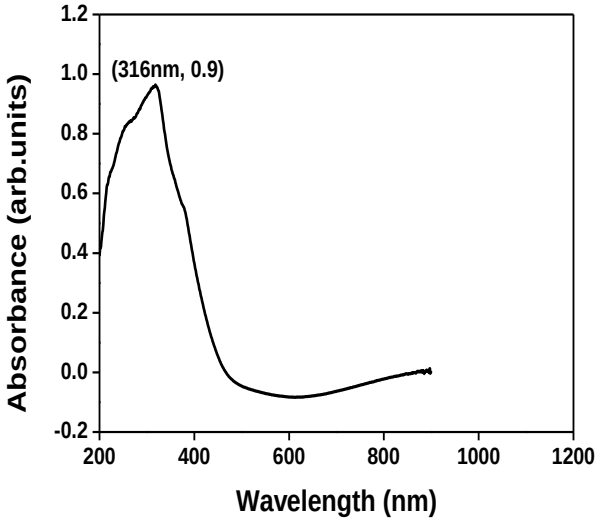


Fig.3 (b). Optical absorbance spectra for pure CeO_2 nanoparticles calcined at 600 °C

Optical response of the ceria nanoparticles have been investigated using Hitachi U-2900 Spectrophotometer. Fig.3 (a) & (b) shows the absorbance spectra of the as-prepared pure CeO_2 nanoparticles before and after calcinations. Before calcinations, it was noticed that the strong absorption band at low wavelength occurs at 317 nm. After calcination at 600°C, the strong absorption band at low wavelength is observed at 316 nm.

Fig.4 (a) & (b) show the Tauc plot for the pure CeO_2 nanoparticles before and after calcination in which the curves of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) are drawn. The optical band gap for the pure CeO_2 nanoparticles before and after calcination has been calculated as 3.32 eV and 3.33 eV respectively.

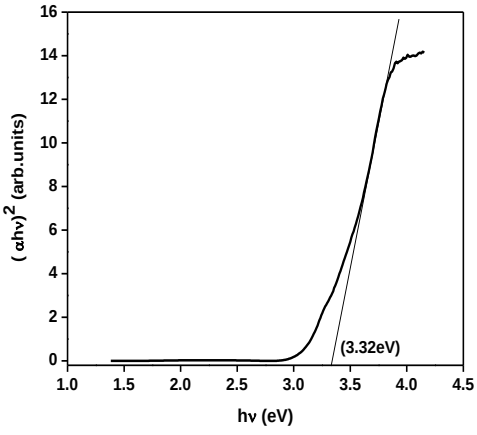


Fig.4 (a). Tauc plot for pure CeO_2 before calcinations

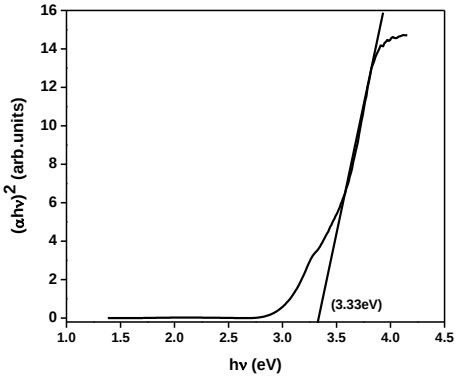


Fig.4 (b). Tauc plot for pure CeO_2 nanoparticles calcined at 600 °C

3.3 Photoluminescence Studies

Photoluminescence Spectroscopy for the pure cerium oxides are carried out using Gary-Eclipse fluorescence spectrophotometer at a scan rate of 600 nm. Fig.5.depicts the photoluminescence (PL) emission spectrum. From the spectrum it was observed that the maximum excitation peak for pure CeO_2 nanoparticles calcined at 600 ºC is at wavelength of 491 nm.

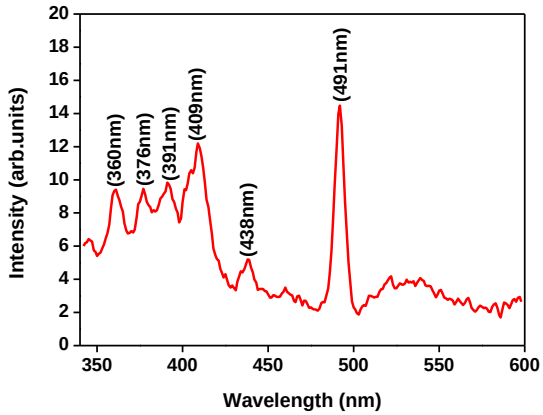


Fig. 5. PL excitation spectrum of pure CeO_2 nanoparticles calcined at 600 ºC at an emission wavelength of 320 nm

3.4 EDAX Analysis

The chemical composition of as synthesized pure CeO_2 nanoparticles was investigated by Energy Dispersive X-ray (EDAX) analysis. The EDAX analysis of the pure CeO_2 nanoparticles shows the presence of Cerium (Ce) and Oxygen (O) elements. No other impurities are added. It shows the purity of the samples.

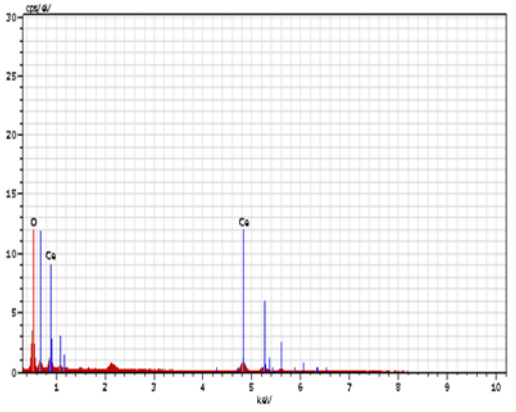


Fig.6(a). EDAX spectra for pure CeO_2 nanoparticles before calcinations

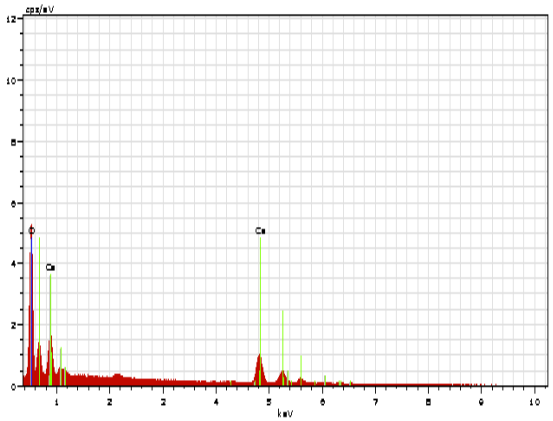
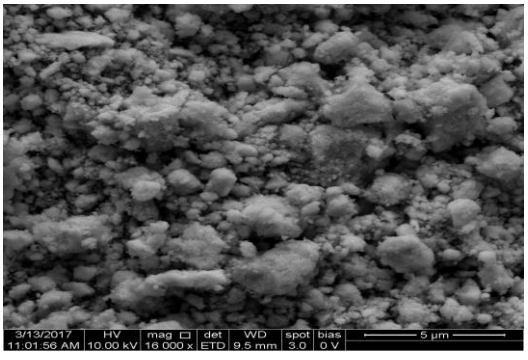


Fig.6 (b). EDAX spectra for pure CeO_2 nanoparticles calcined at 600 °C

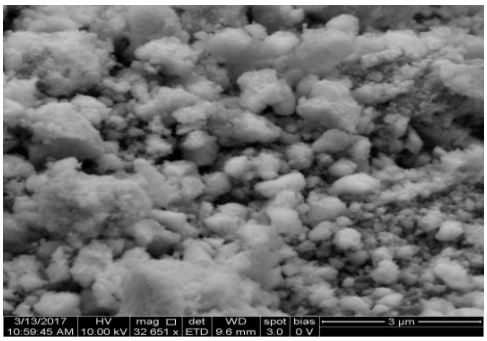
3.5 Studies on Morphology using FESEM

The morphology of CeO_2 nanoparticles were characterized by field emission scanning electron microscopy (FESEM) and investigated by FEI QUANTA – 200 microscopes.

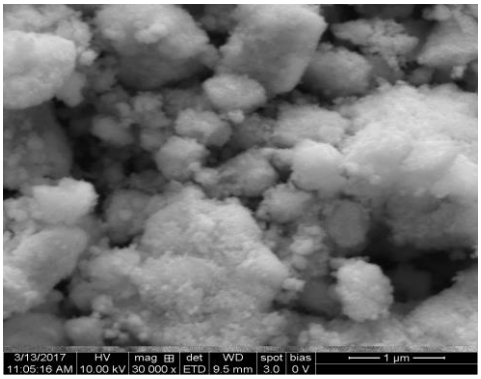
3.5.1 FESEM image of pure CeO_2 nanoparticles before calcinations



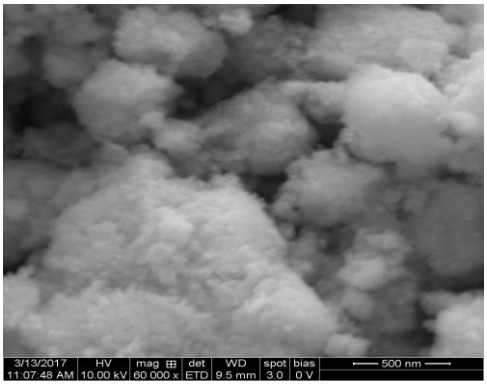
(a)



(b)



(c)

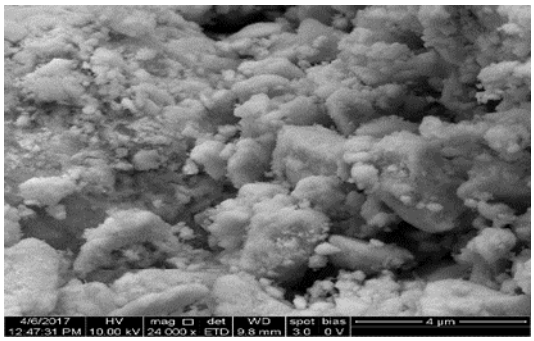


(d)

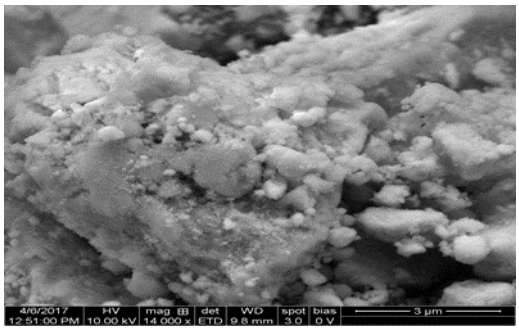
Fig.7.FESEM image of pure CeO_2 nanoparticles before calcination with magnification at a) 5 µm, b)3 µm, c) 1 µm, d) 500 nm

3.5.2 FESEM image of pure CeO_2 nanoparticles calcined at 600°C

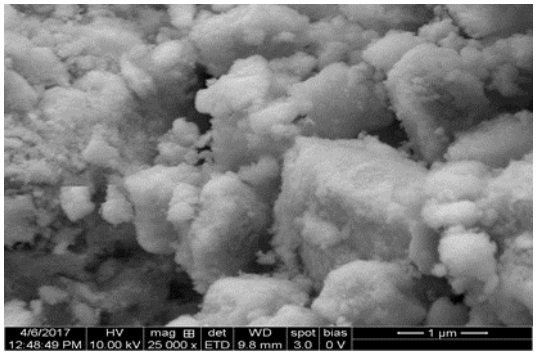
Fig.7 and Fig.8 represent the morphology of the as-synthesized pure CeO_2 nanoparticles before and after calcinations. Typical FESEM images of the CeO_2 nanostructures at different magnifications are shown. It is clear that for 500 nm magnification, the synthesized pure CeO_2 nanoparticles are spherical like structure.



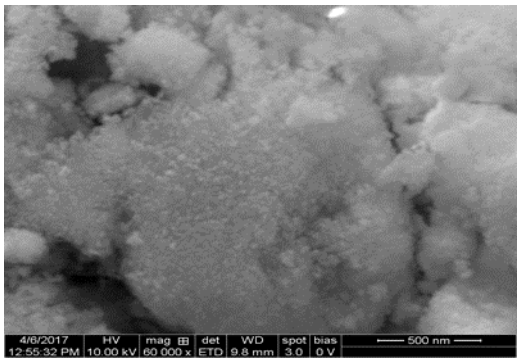
(a)



(b)



(c)



(d)

Fig.8.FESEM image of pure CeO_2 nanoparticles calcined at 600 °C with a magnification at a) 4 µm, b) 3 µm, c) 1 µm, d) 500 nm

3.6 FTIR Analysis

The FTIR spectra of the prepared CeO_2 nanoparticles were obtained using the KBr pellet method in the wave number range 400- 4000 cm^{-1} and are shown in Fig.9.

Comparing the FTIR peak of pure CeO_2 before and after calcinations, we can understand the chemical composition change as the broad band in Fig.9 (a) is narrowed in Fig.9 (b).

In addition to this, there is a new peak seen at 1250 cm^{-1} in Fig.9 (b). This is a clear indication that the particle size of the CeO_2 is reduced to smaller size. Also, some other change has taken place at 2950 cm^{-1} in both the spectrum.

The broad absorption in the frequency band 3750-3000 cm^{-1} is assigned to O-H stretching from residual alcohols, water and Ce-OH. The absorption peak is observed at 3475 cm^{-1} for CeO_2 NPs. The CO_2 peaks are observed at 2358 cm^{-1} and 1394 cm^{-1} for CeO_2 NPs.

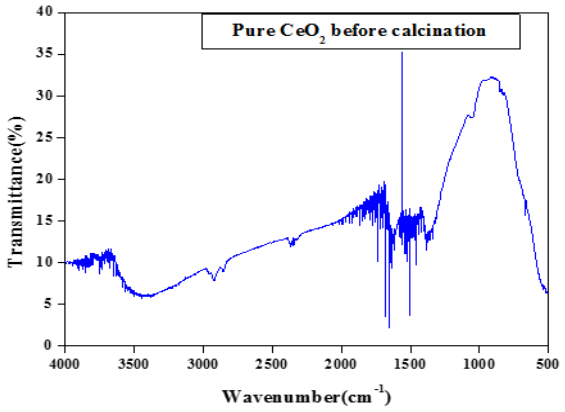


Fig.9. (a) FTIR spectra for pure CeO_2 nanoparticles before calcination

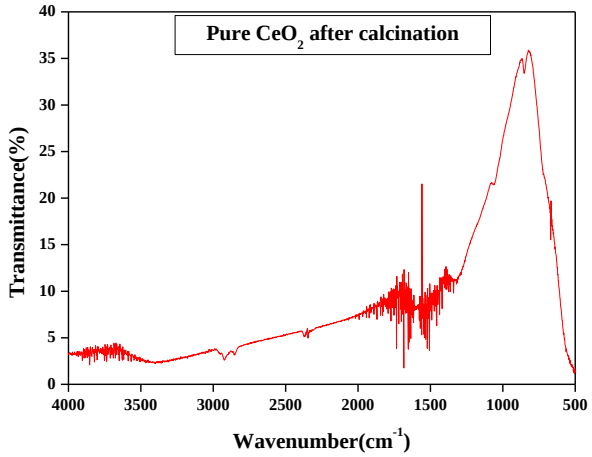


Fig.9.(b) FTIR spectra for pure CeO_2 nanoparticles calcined at 600 °C

4. CONCLUSION

In the present work, pure CeO_2 nanoparticles are synthesized by chemical co-precipitation process. The preparation process has advantages of simple technology, cheap, good yield, homogeneity, low temperature and short preparation cycle.

From the PXRD studies, it is obvious that the pure CeO_2 nanoparticles show a decrease in average grain sizes of the samples as the calcination temperature is increased. As the grain size increases, the dislocation density decreases. No other impurity peaks is seen, which confirms the purity of the as-prepared samples. The PXRD data of all the samples are in good agreement with the JCPDS file No.81-0792. It was observed that the pure CeO_2 samples exhibit cubic (face centered) crystal structure. The lattice constant and cell volume computed from the UNITCELL software agrees well with the standard values.

The absorbance characteristics of the samples are studied from the UV-DRS studies. UV absorption spectrum studies reveal that there is a blue shift in the samples. The Tauc plot shows that after the calcination there is increase in the band gap in all the samples, which causes blue shift. 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.

For the pure CeO_2 PL emission plots contain peaks centered on 330 nm. This is attributed to oxygen vacancies which existed between the Ce 4f state and O 2p valence band. PL spectra also support the blue shift nature.

The FESEM images show that the sample is composed of spherical nanosized particles. No other impurity peak is seen in the EDAX spectrum which confirms the purity of the prepared samples.

The FTIR spectral studies prove the chemical changes occurred during the process of calcination of as-prepared CeO_2 nanoparticles. Thus the synthesized particles confirm the reduction of particle size, enhancing its properties.

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