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Synthesis of Cerium doped Zinc oxide nanoparticles by aqueous hydrothermal method and study of their properties

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ABSTRACT

A new and simple method to synthesize stable and crystalline pure phase Cerium doped Zinc oxide nanoparticles has been developed using glycerol as a structure directing agent and cerium nitrate $Ce(NO)_3.6\ H_2O$ as a dopant. Cerium doped Zinc nanoparticles are prepared by hydrothermal technique, calcinated at 350^0C and characterized by using the x-ray diffraction(XRD), scanning electron microscopy(SEM), electron dispersive X-ray spectrometry(EDS), UV-visible spectrophotometry and FTIR spectroscopy. The results indicate that the synthesized powders are nanocrystalline Ce doped Zinc oxide with cubic structure.

Keywords: Cerium oxide, hydrothermal method, Zinc oxide, nanoparticles

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INTRODUCTION

Recent works have focused on the designed synthesis and exploration of applications of binary oxide films or powders, such as TiO_2 –CeO_2, [1]TiO_2-ZnO,[2] TiO_2-SiO_2[3] and TiO_2-WO_3,[4] which were considered to be effective semiconductors , advanced materials , heterogenous catalysts and catalyst supports. Recently Zinc oxide materials have attracted much interest due to their wide applications for various devices transducers, transparent conducing electrodes, gas sensors and as a catalysts[5,6,7] because of their abundance and inexpensiveness. Many studies have been conducted on the sintering of several doped Zinc Oxide systems, such as Sb doped ZnO[8,9],Bi doped ZnO[10],Mn doped ZnO[11] and Al doped ZnO[12,13]. ZnO and CeO_2 were also used as components of heterogenous catalysts or catalysts supports for catalytic oxidation reactions[14,15], though reports on the synthesis and applications of coupled bicomponents ZnO-CeO_2 materials are scerce. The properties of the materials are greatly affected by their morphologies , wide range of metal oxide with different morphologies providing great opportunities for the discovery of new properties and potential uses have been synthesized via different methods . Among these methods hydrothermal approach [16,17] has great advantages in synthesizing metal oxide crystals through relative low temperature and simple equipment , which makes the method more suitable and economic for large scale production.Therefore in this communication we have reported a new and simple low-temperature hydrothermal process for preparation of Ce doped ZnO nanoparticles and study of properties of these nanoparticles.

MATERIALS AND METHODS

The chemicals used are of reagent grade purity. In a beaker 0.2 M zinc nitrate and cerium nitrate were mixed under vigorous stirring for two hours. P^H was adjusted to 11 by adding anhydrous Na_2CO_3. The glycerol was also added to the beaker in order to control the morphology of crystal. The product obtained was separated by decantation, washed with de-ionized water and ethanol to remove ions possibly remained in product. The product was dried in oven at 80^0 C for three hours.

X-ray diffraction (XRD) study of the synthesized product was carried out by using Philips model PW-3710 x-ray diffractometer with Cr *k ά=2.28 A°* . Scanning electron microscopy (SEM) observation was performed with a JEOL JSM-6360 scanning electron microscope . Electron dispersive X-ray spectrometry(EDS) was used for elemental analysis of these nanoparticles. To estimate the band gap, UV-vis spectrum of the product was obtained by using UV3600Shimadzu UV-vis spectrophotometer. A Perkin-Elmer Spectrum100 Fourier transform infrared spectrometer (FTIR) was used for IR study of these nanoparticles. The TGA-DSC measurements were carried out using SDTQ600V20.9 Build 20 themogravimetric analyser.

RESULTS AND DISCUSSION

3.1 TGA-DSC analysis:

TGA-DSC analysis of these nanoparticles heated at the rate 10^0c / minute from 30 to 350^0C, is given in figure 1 .The DSC curve shows that thermal decomposition of cerium doped ZnO nanoparticle below 350^0C occurs at an endothermic peak and this peak at 264^0C is ascribed due to thermal decomposition of zinc carbonate and formation of crystalline ZnO[18].

3.2 XRD analysis:

Figure 2 shows the XRD pattern of calcined sample at 350^0C for 3 hours. This pattern corresponds to peaks of (111), (100), (002), (101), (102), (110), (103), (200), (112), (201). Polycrystalline nanoparticles with a hexagonal wurtzite structure (zincite, JCPDS 36-1451) and cubic structure CeO_2 from the JCPDS(No.75-0390) card. In the view of the valency of Ce^{3+} in the cerium nitrate hexahydrate,there is shift of valency in the course of nanoparticle formation which is in agreement with the literature[19]. The average grain size of Ce doped zinc oxide is calculated by Deby-Scherrer equation to the half intensity width of (101) peak.

$$d = 0.9\lambda / \beta\cos\theta$$

where λ is the wave length of Cr k ά=2.28 A°, β is the caliberated half intensity width of the selected diffraction peak (degrees) and θ is the Bragg's angle (half of the peak position angle).From this equation the average size of Ce doped zinc oxide nanoparticle was estimated to be 35 nm.

3.3 SEM and EDS analysis:

The SEM micrographs of cerium doped ZnO synthesized by hydrothermal method shows spherical morphology(Figure 3).The elemental analysis of the sample was carried out by using enengy dispersive X-ray spectrometer(EDS) and is shown in figure 4.The EDS result clearly shows that cerium has been doped in to ZnO crystal lattice and no metallic Zn or Ce exists in Ce doped ZnO nanoparticles..The cerium ions doped into the ZnO crystal may be responsible for the observed morphology of the nanoparticle and it also minimizes the surface energy of these nanoparticles.

3.4 UV-visible and IR analysis:

UV-visible absorption spectra of Ce doped ZnO calcined at 350^0C is shown in figure 5.This spectra shows maximum absobancy in the range 270nm to 360 nm. From this spectra the band gap energy for the sample was computed by using following realation.

$$\alpha\ (h\nu)=A(h\nu-E_V)^{m/2}$$

A plot of $(\alpha\ (h\nu))^2$ against $h\nu$ (Figure 6) will give slope=A^2 and intercept=E_VA^2.The ratio of intercept to slope gives the band gap energy. The band gap energy was found to be 2.9 eV which is less in comparison with band gap energy of undoped ZnO nanoparticles[20].

FTIR spectra of Ce doped ZnO nanoparticle is given in figure 7. It shows characteristic Zn-O, O-Ce-O stretching frequencies at 560 cm^{-1} , 717 cm^{-1} and 855 cm^{-1}respectively.

Figure1: TG-DTA profile of as-prepared Ce doped ZnO

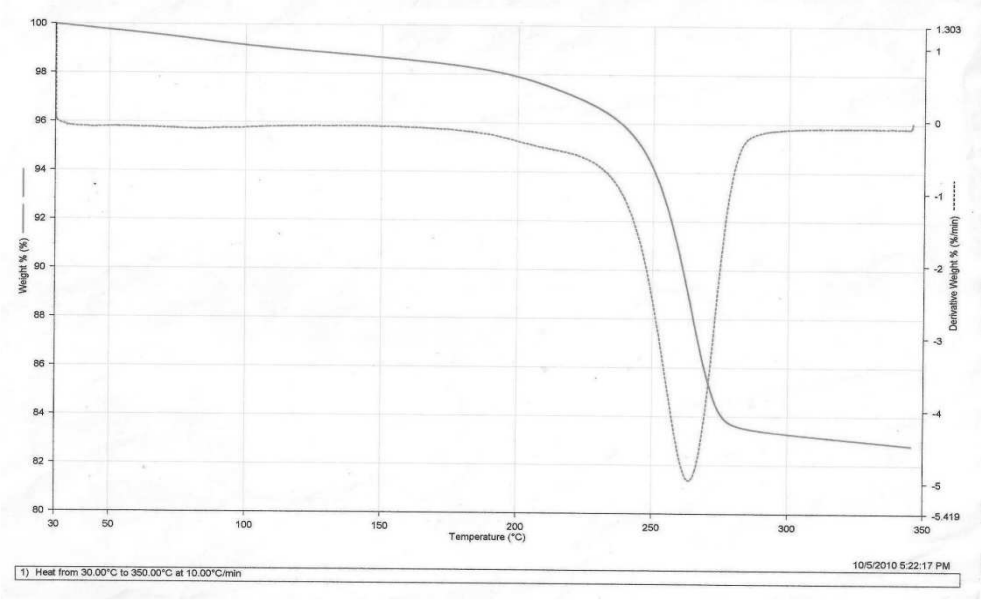


Figure 2 : XRD pattern of the Ce doped ZnO

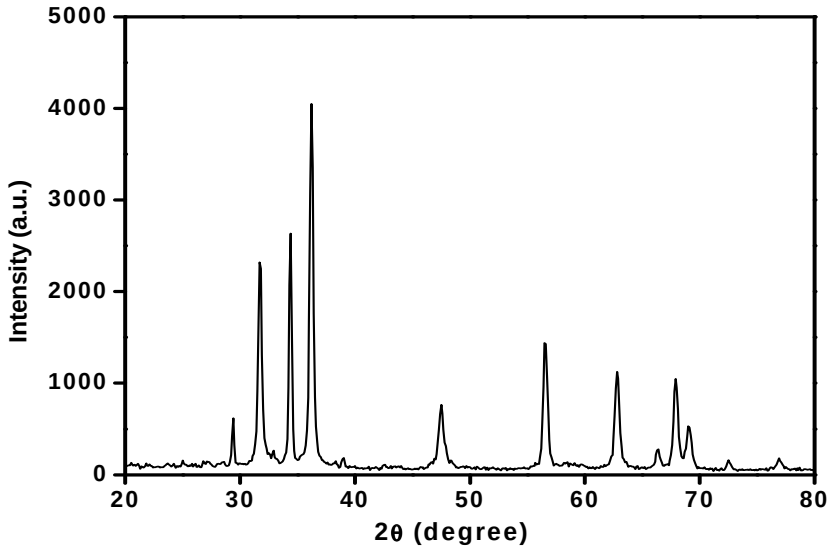


Fig.3: SEM micrograph of Ce doped ZnO

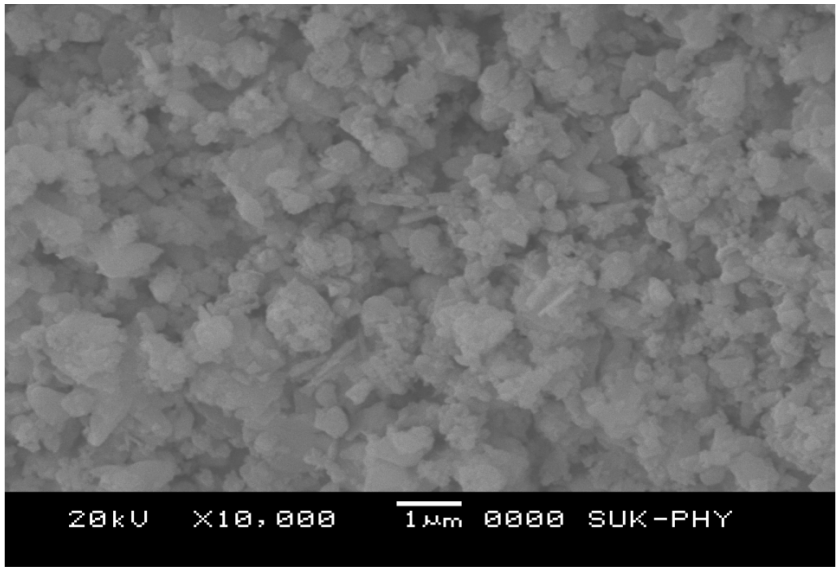


Figure 4: EDS spectrum of elements detected in the sample

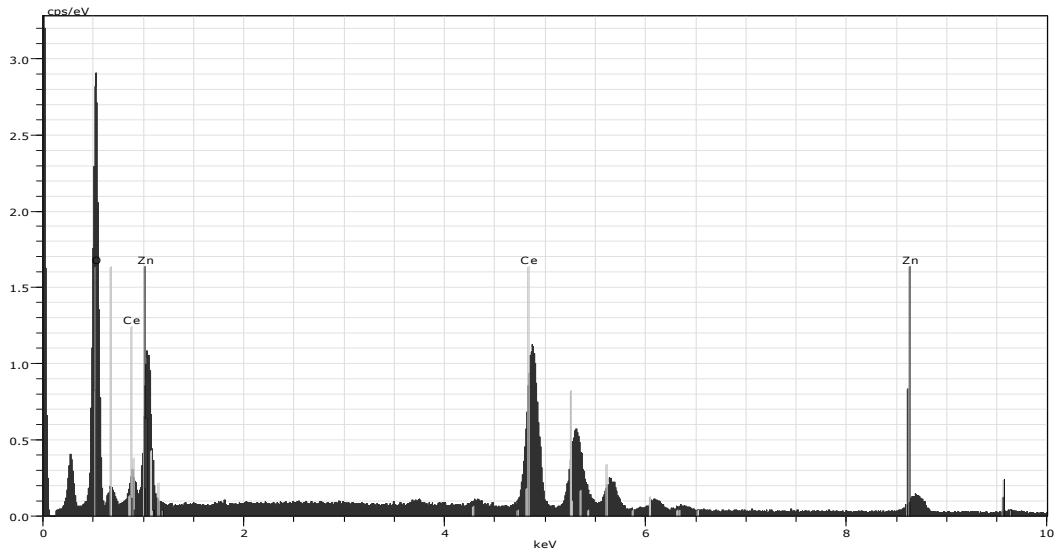


Fig. 5: UV-Vis absorption spectra of Ce doped ZnO

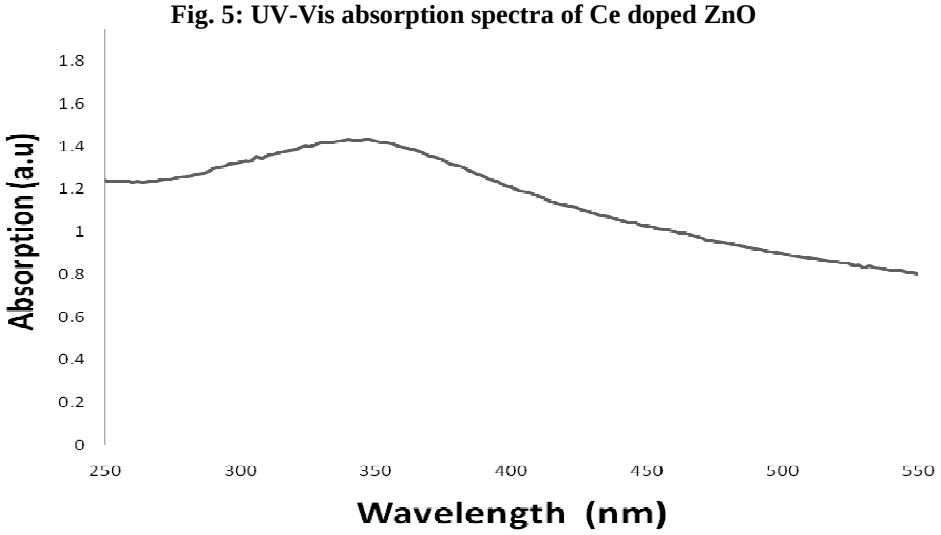


Fig. 6: Absorption spectra of sample by ploting (□h□))^2 vs h□

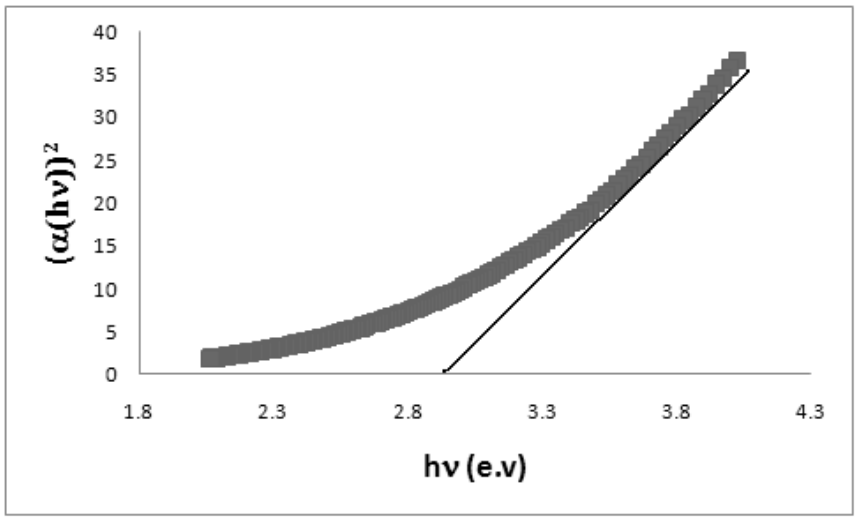
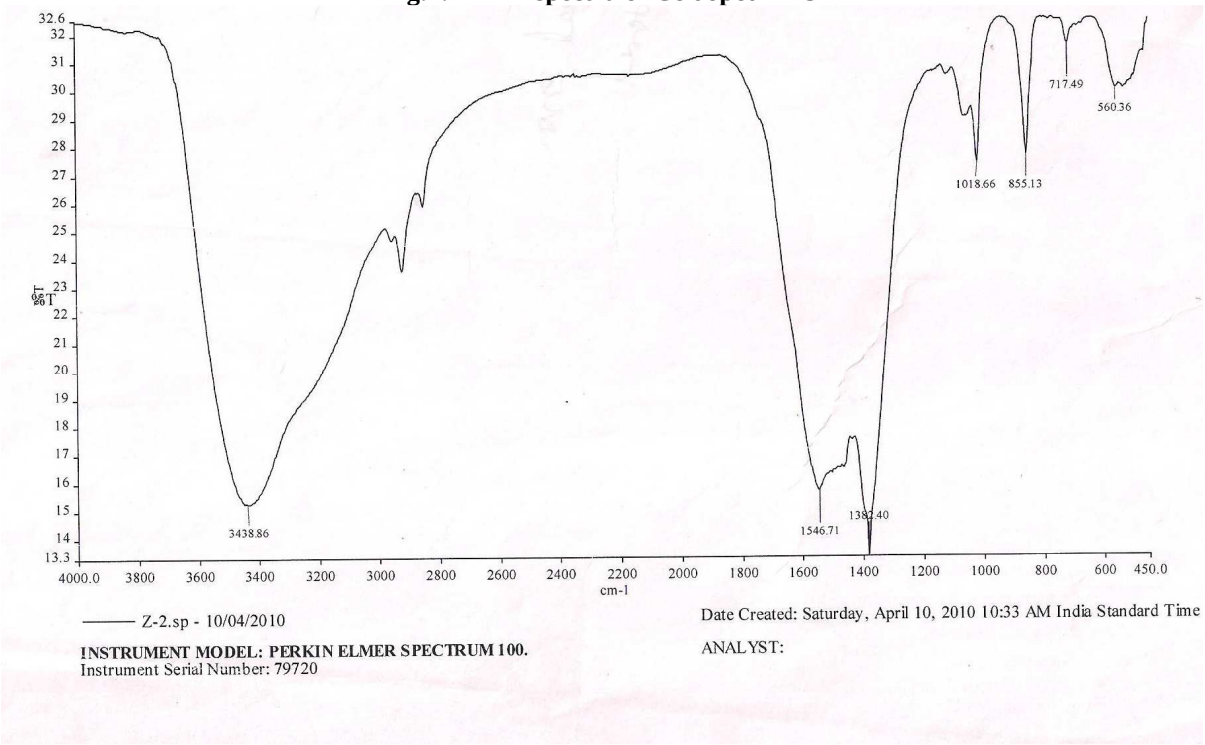


Fig.7: FT-IR spectra of Ce doped ZnO



CONCLUSION

A simple hydrothermal process with addition of ethylene glycol was used to synthesize Ce doped ZnO nanoparticles. Size of nanoparticles was found to be 35 nm and were formed by calcination at 350□C for 3 hours. The band gap energy was found to be 2.9 eV. EDS analysis of the nanomaterial confirms that the material is composed of Zn, O and Ce without any impurity. The synthesis route to Ce doped ZnO nanoparticles is promising for large-scale and low-cost production of this material. The result of UV-visible analysis shows that Ce doped ZnO powders have strong UV absorption ability between 270 nm to 360 nm.

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