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Ce induced Structural and Optical Properties of Ce Doped Zno Nanoparticles

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Abstract: Ce-doped ZnO nanoparticles with different Ce-doping concentrations (0, 0.96, 1.96, 2.52, and 3.12 at.% of Ce) were prepared by the chemical co-precipitation method. XRD studies confirm both undoped and Ce-doped ZnO nanoparticles exhibited wurtzite structure with average grain size in the range of 17-23 nm and are in agreement with TEM analysis. EDS confirms the presence of Ce in Ce-doped ZnO nanoparticle. From FTIR studies, the lower shift of Zn-O stretching peak in Ce-doped ZnO nanoparticles confirm the incorporation of Ce into ZnO matrix. UV-Vis. DRS measurements indicated a red shift in optical band gap with Ce-doping. PL spectrum demonstrated enhanced violet and blue emissions for 0.96at. % and green emission for 1.96 at. % in Ce- doped ZnO nanoparticles.
Keywords: Cerium, Zinc Oxide, Structural Properties; PL, DRS.

1. Introduction and Experimental:

In recent decades, semiconducting oxide nanostructure based research stimulating more attention. Among the II-VI group semiconductors ZnO nanostructure receives greater scientific interest in the field of optoelectronics due to wide band gap (3.3 eV) [1,2,3]. ZnO exhibits different morphologies like nanowire, nanobelts, nanorods, nanoparticles etc. In order to control the morphology of ZnO crystals, organic additives, such as PVP, PEG, SDS and CTAB [4, 5], were commonly introduced into the reaction system to manipulate the nucleation and growth. The optical, luminescence and catalytic properties arises from the availability of the shielded 4f levels with only one electron in the 4f state, Ce^{3+} [6].

In the present work, pure and Ce doped ZnO nanoparticles were prepared by chemical co-precipitation method. Zinc acetate, cerium chloride hexahydrate were the starting materials with 99.9% purity and were dissolved in Ethanol- di-water (50-50 %) and stirred for 1/2 hour until to obtained clear solution. In the experimental procedure Polyvinylpyrrolidone (PVP) as a surfactant and NaOH solution was added in order to fix the pH-9. This Solution was transformed to hot bath of temperature 90^{o}C and stirred rigorously for 12 hours until fine precipitation is formed. The as formed precipitation was washed 4 times with di-water and dried at 80^{o}C for 24 hours.

The structural, morphology and size of the particle were investigated by X-ray diffraction (XRD) measurements (D8 Advance, Bruker, Germany) and Transmission electron microscopy (TEM) of JEM-100CX. The compositions of the prepared samples were analyzed through energy dispersive spectroscopy (EDS) using Oxford Inca Penta FeTX3 EDS instrument. The functional groups analysis was carried out by FTIR. Diffuse reflectance spectra (DRS) studies were carried out using Cary-5E UV-VIs-NIR lambda-950 spectrometer. Photoluminescence spectra were recorded in the wavelength range of 380-800 nm using FP-8500, JASCO Spectrofluorimeter.

2. Results and Discussion:

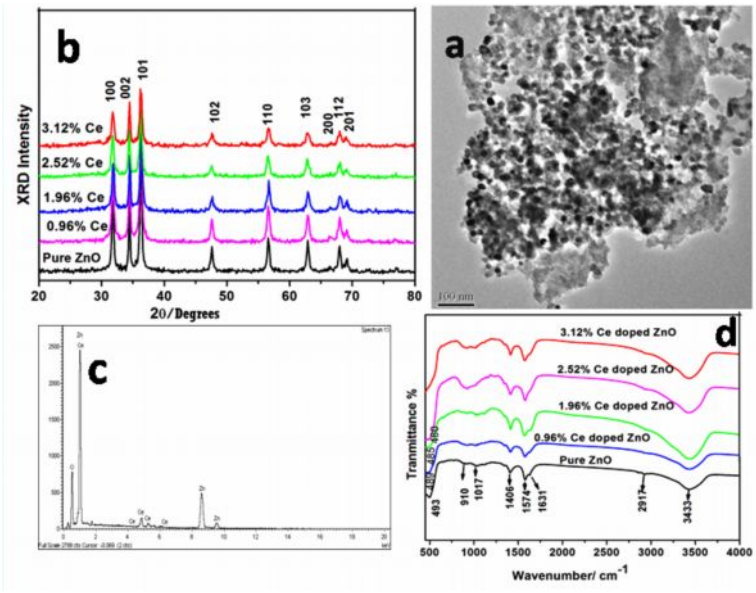

Figure 1. As-synthesized (b) XRD pattern (a). Typical TEM image and (c) EDS spectrum 2.52% of Ce-doped ZnO (d) FTIR spectrum of Ce-doped ZnO nanoparticles.

All the diffraction peaks shown in Fig.1 (b) have been indexed to a hexagonal wurtzite structure of ZnO with JCPDS No. 31-1451. The increase in FWHM suggests that Ce is incorporated into the ZnO matrix. The average grain size of the undoped and Ce doped ZnO was estimated to be in the range 17 -23 nm. The micro-strain [7] increased with Ce doped ZnO nanoparticles which may be due to the presence of defects and vacancies in the Ce–Zn–O lattice [8]. The precise analysis of TEM image (Fig. 1(a)) indicates the existence of well spherical shaped nanoparticles with sizes varying 12-20 nm which are compatible with the XRD values. The typical EDS spectra (Fig. 1(c)) Ce-doped ZnO nanoparticles confirms that the synthesized nanoparticles are Ce-doped ZnO nanoparticles are impurity free. The peaks appeared at 493 cm^{-1} in the FTIR spectra (Fig. 1(d)) for pure ZnO could be attributed to the metal oxygen (Zn-O) bonds. The peaks corresponding to Zn-O bonds shifted towards lower wavelength for Ce doped ZnO nanoparticles indicating the incorporation of Ce ions in the ZnO lattice.

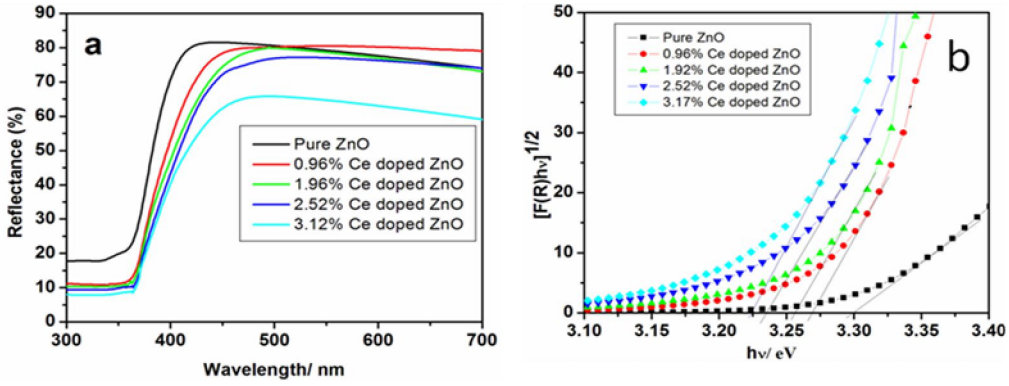

Figure 2. (a) UV-Visible Diffuse reflectance spectrum (b) Energy gap spectrum of as-synthesized pure and Ce-doped ZnO nanoparticles.

The absorption edge of all the Ce doped ZnO red shifts with as shown in fig. 2(a). The Figure 2(b) shows the band gap (hυ in eV) as a function of Kubelka- Munk function $[F(R)h\upsilon]^2$ [10]. The calculated band gap from the spectrum is 3.30eV, 3.269eV, 3.257 eV, 3.236 eV and 3.224 eV for undoped and doped Ce-ZnO nanoparticles respectively. In the PL spectra a broad and intensified green emission was observed at 554-558 nm along with narrow violet-blue emissions for undoped and Ce-ZnO nanoparticles. The absence of UV emission in the emission spectra may be due to non-radioative recombination of an excitons. The strong violet emission at 415 nm indicates that high-concentration of Zn vacancies and peak at 436 attributes to Zn interstitials[11] in addition to [OH^-] ions on the surface of ZnO [12] are also accountable. Broad band green emission at 554 nm due to oxygen vacancies.

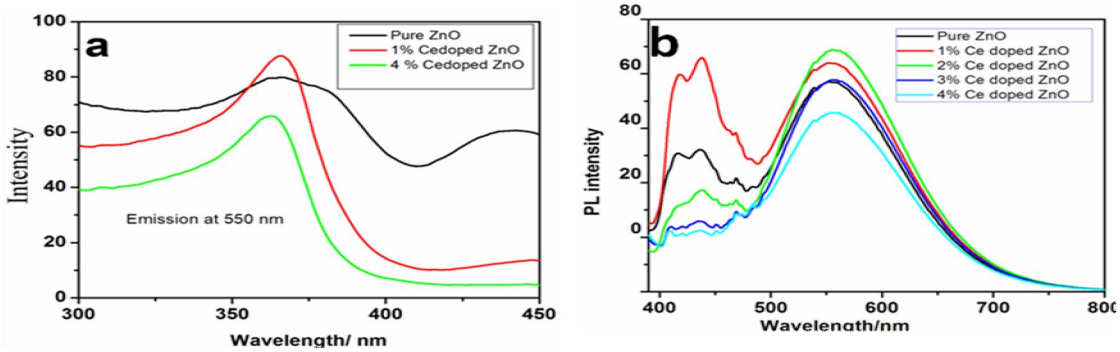

Figure 3. photoluminescence spectra of undoped and Ce-doped ZnO nanoparticles
(a) Excitation spectrum with emission wavelength 550 nm (b) Emission spectrum with excitation at 367 nm.

3. Conclusions:

Pure ZnO and Ce-ZnO nanoparticles have been synthesized successfully by chemical co-precipitation method. XRD analysis confirmed hexagonal wurtzite structure with average grain sizes 17-23 nm and the values are compatible with that obtained from TEM analysis. UV-DRS studies exhibit band gap narrowing for Ce doped ZnO nanoparticles. PL spectra of the 0.96 at % Ce-doped ZnO nanoparticles showed increased intensity in violet- blue at 417 nm and 437 nm respectively and enhanced green emission was observed for 1.96 at.% of Ce.

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