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ORIGINAL ARTICLE

Synthesis of Cerium doped Zinc oxide nanoparticles by aqueous precipitation method and study on the structural and optical properties

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Abstract

Objectives: To understand the effect of impurity element doping; especially rare earth (Ce) ions on structural and optical properties of ZnO. **Method:** Co-precipitation method is used to prepare nanoparticles of pristine ZnO and ZnO doped with cerium. This method is found to be very useful in preparing nanoparticles of very low size. The property of the samples is studied by different characterization techniques such as Powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FESEM), UV-visible (UV-Vis) spectroscopy, photoluminescence (PL) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. **Findings:** XRD studies reveal the crystallographic data which tells that the prepared ZnO is of hexagonal wurtzite phase with size of 35 nm. Crystallite size and unit cell volume increase with cerium doping. FESEM study shows the formation of nanoparticles. FTIR study shows the position of different stretching and bending modes present in the sample. It confirms the position of metal-oxygen bond. Photoluminescence and UV-VIS spectra show the interesting optical properties of Ce-ZnO. The PL spectra show the presence of UV excitonic emission and visible defect emissions along with emissions due to dopant. Upon Ce doping, ZnO shows a new peak around 645 nm ascribed to the transition related to dopant level. Enhancement in emission in visible-red region of ZnO with Ce doping will be useful in preparation of LED.

Keywords: ZnOCe; Optical study; Photoluminescence; Co-precipitation

1 Introduction

Nanotechnology is one of the interesting branches of modern science which has scope in many fields for designing of products for human use[(1)]. Nanomaterials are used in medicine, transport, food packaging, electronics and space technology showing better efficiency in comparison to conventional materials[(1)]. Zinc oxide is one such material which has tremendous applications in the above fields[(2–4)]. It has some novel physical

and chemical properties which enhances its applicability. It is a wide band gap semiconducting material which finds its use in opto-electronics. The band gap of ZnO is 3.37 eV with high excitonic binding energy (60 meV) [2–4]. It has also high breakdown strength. Due to these properties, ZnO is largely used in electronic, photonic, sensing devices as well as for high-frequency applications. ZnO is also used in materials used for varistors, transparent conductors and transparent UV-protection films. The wide band gap of ZnO is responsible for its applicability as a potential material for fabricating light emitting diodes (LEDs), laser diodes (LDs) and detectors [2,4].

Researchers have used many chemical methods for the preparation of nano ZnO in different size and shapes. Some of these methods are hydrothermal, sol-gel, co-precipitation, chemical vapour deposition, sputtering and pulsed laser deposition [4]. Chemical methods are very simple and cost effective for the preparation of nanomaterials. ZnO in different forms such as; nanoparticles, nanorods, nanowires, nanoflower, nanobelt, nanocolumn, nanoboat etc. have been prepared by different chemical methods [5,6]. Co-precipitation is a very simple and novel synthesis procedure to prepare ZnO in the above forms and widely used by many scientists/researchers. These methods are also used for doping of different materials into semiconductor nanoparticles like ZnO to enhance its structural and optical properties. Impurity or dopants like rare earth elements are very crucial for enhancing the emission properties of ZnO. The availability of 4f electrons which are involved in the spectroscopic transition leads to novel emissive properties when embedded in hosts like ZnO [7]. In the present work, we have doped Ce into ZnO to study its role in governing the structural/optical properties of ZnO. Cerium can exist as Ce^{4+} or Ce^{3+} and have the greatest chance to modify the band structure of ZnO.

2 Materials and Method

Precursor materials of Zinc and cerium ions such as, zinc acetate ($Zn(CH_3COO)_2.2H_2O$) and cerium nitrate ($Ce(NO_3)_3.6H_2O$) of analytical grade were procured from M/s Sigma Aldrich and used for synthesizing ZnO and Ce doped ZnO. These salts were dissolved in double distilled water and continuously stirred. A magnetic stirrer was used for this purpose. Liquid ammonia solution (25%) was added to the above solution drop-wise to get precipitation. The pH of the solution was measured in the range of 8.5 to 10.5 before and after the process of precipitation. The precipitates were centrifuged and collected for washing with water and acetone. The samples were dried at 100° C overnight. In this process pristine ZnO and cerium doped ZnO were prepared. The chemical reactions taking place during the process can be enumerated as given below:

$NH_3+H_2O \rightarrow NH_3.H_2O \rightarrow NH_4^{+}+OH^{-}$

$Zn(CH_3COO)_2 \rightarrow Zn^{2+} + 2CH_3COO^{-}$

$Zn^{2+} +2OH^{-} \rightarrow ZnO+H_2O$

$Ce(NO_3)_3.6H_2O \rightarrow Ce^{3+}+3NO_3^{-}+6H_2O$

$Ce^{3+}+4OH^{-} \rightarrow CeO_2+2H_2O+e^{-}$

$NO_3^{-} +H_2O+2e^{-} \rightarrow -NO_2^{-}+2OH^{-}$

The structural and phase studies were carried out by using a powder x-ray diffractometer (M/s Panalytical, X pert Pro). The surface morphology was studied by a FESEM (ZEISS Supra) and FTIR patterns were recorded by a Perkin-Elmer spectrometer. Room temperature photoluminescence measurement was taken by a Fluormax-4 spectrometer made by M/s Perkin-Elmer.

3 Results and Discussion

3.1 X-Ray Diffraction Studies

XRD measurement gives useful information on the crystal structure and phase of the sample and has been carried out for all the samples. Pristine ZnO and Ce-ZnO are of crystalline nature and show hexagonal wurtzite phase as studied from the XRD patterns depicted in Figure-1. There exist nine diffraction peaks which are indexed as (100), (002), (101), (102), (110), (103), (200), (112) and (201) [8]. Among these peaks, the (101) diffraction peak has highest intensity both for ZnO and Ce-doped ZnO. Peaks corresponding to cerium are also detected in XRD pattern of Ce-ZnO. These are observed around 24, 26 and 41 degree along with some $Zn(OH)_2$ phase. The particle size of the samples is calculated by the Scherrer formula given by D = kl/bcosq. Here, the parameters like D is the size, l is the x-ray wavelength (1.5406 Å), b is the peak FWHM, q is the diffracting angle and k = 0.94 [8]. Lattice micro-strain is calculated using the formula; e = b/4tanq. With cerium doping, the value of crystallite size is found to be higher as compared to pristine ZnO (Table-1). The strain value also increases with doping along with unit cell volume. The data obtained from XRD measurement has been given in Table-1. Ce^{3+} ions may have substituted the Zn^{2+} ions in ZnO lattice leading to these results. The ionic radius of Ce^{3+} (1.03 Å) is much higher than that of Zn^{2+} (0.74 Å) [7]. This gives a clear picture about the influence of cerium doping on the structural properties of ZnO.

Table 1. Crystallographicparameters of ZnO and Ce doped ZnO obtained from XRD measurements

Sample	Size (nm)	Stain	Lattice Parameter			Bond Length (Å)	Unit cell volume (Å)
			a (Å)	C (Å)	u		
ZnO	36	0.0030	3.249	5.209	0.379	1.9355	47.2457
Ce-ZnO	17	0.0064	3.240	5.210	0.378	1.9883	47.2677

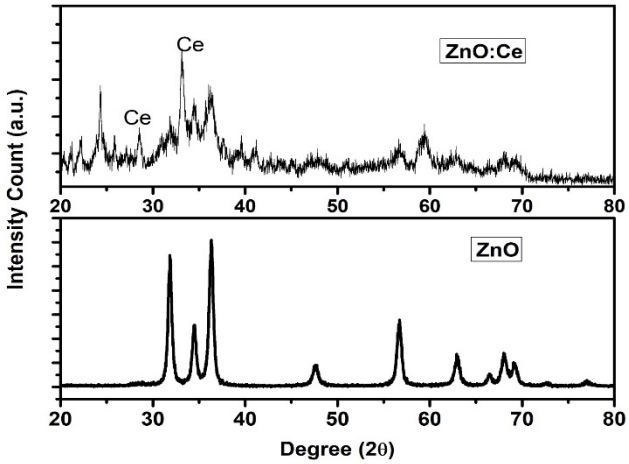

Fig 1. XRD patterns of ZnO and cerium doped ZnO.

3.2 FESEM Studies

The shape and size of a material collectively gives the information on the morphology which has been studied by FESEM measurement. Surface property of nanomaterials is an essential parameter in influencing the optical emission processes. The images obtained for Ce-ZnO have been shown in Figure-2. It shows the formation of flower-like structure of ZnO with Ce doping. The dopant incorporation in ZnO is also confirmed by EDAX measurement and given in the same figure.

3.3 UV-VIS absorbance Studies

The interaction of light in UV-VIS (300-700 nm) range on the sample (ZnO and Ce-ZnO) has been studied by recording the optical absorption spectrum. The nanopowders are made ready for measurement by dispersing them in acetone and filled in the quartz cuvette. Figure-3 shows the absorbance spectra of ZnO and Ce-ZnO. Both the spectra show a clear peak in the region (360-370 nm) which is the absorption band of ZnO. It is found at 362 nm for ZnO but shifts to 365 nm for Ce doped ZnO. This shift in the absorption peak may be due to cerium doping.

3.4 FTIR Studies

To understand the vibrational properties of ZnO before and after doping, the FTIR measurements are performed and illustrated in Figure-4. The existence of all the functional groups in a sample can be confirmed by the unique and characteristic absorption of IR radiation by the sample [9,10]. The IR light in the form of energy lets the bonds present in a molecule to bend and stretch that can be recorded in IR spectrum. The spectra recorded by us are in the range of 4000–400 cm^{-1}. Both the spectrum for pristine and doped ZnO has shown many bands which has been assigned to different vibrations as given below.

Band around 3000–3600 cm^{-1}: ascribed to –OH groups [10]

Band around 1350 cm^{-1}: ascribed to N–O stretching modes [10]

Band around 910 cm^{-1}: ascribed to stretching vibrations of N–H groups [10]

Band around 600–400 cm^{-1}: ascribed to metal-oxygen vibrational modes [10]

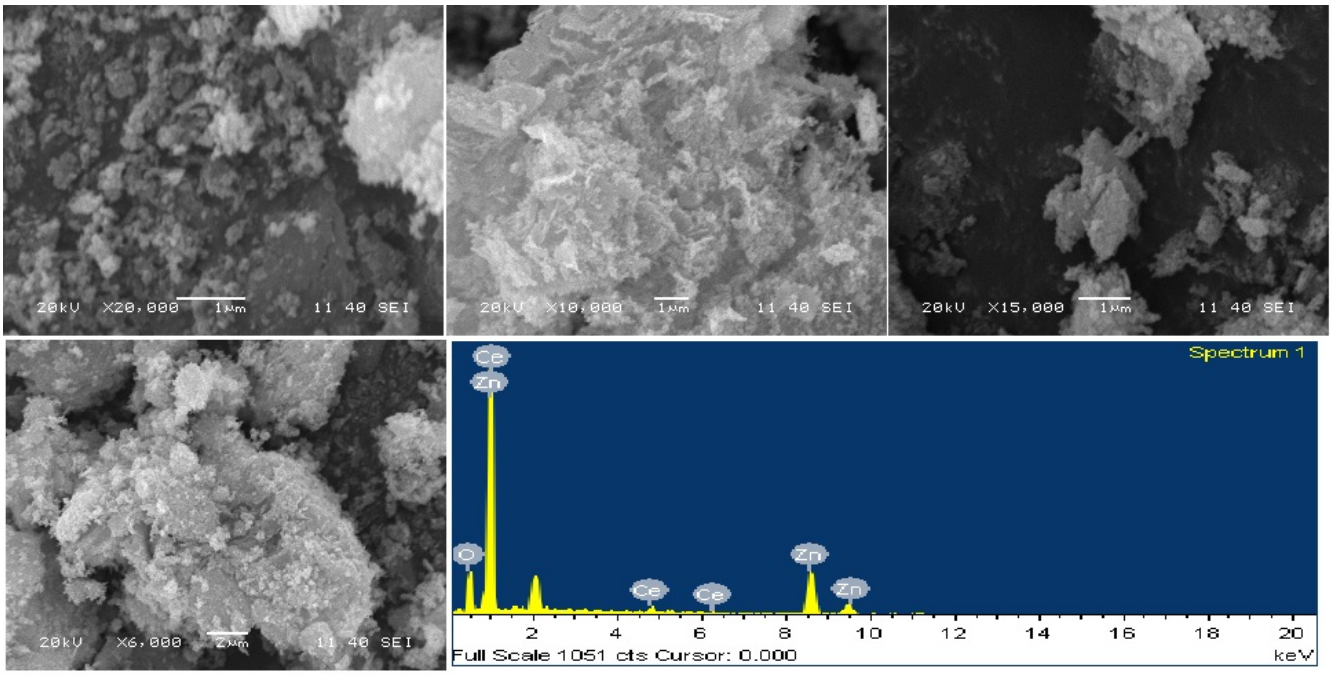

Fig 2. FESEM images and EDAX pattern of Cerium doped ZnO.

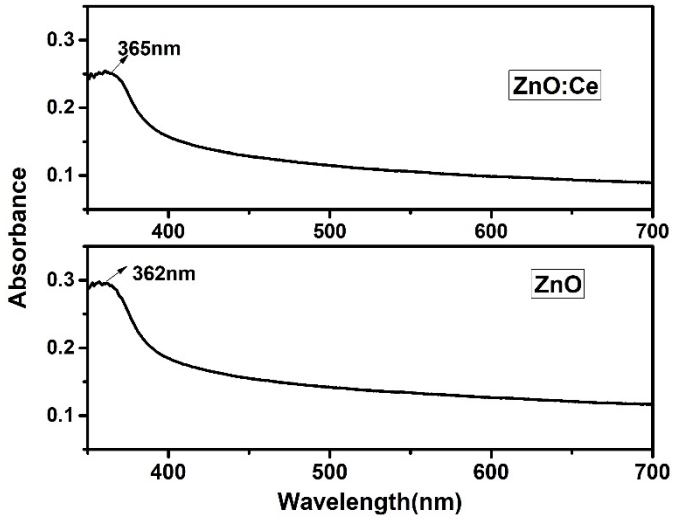

Fig 3. UV-Vis absorption spectra of ZnO and cerium doped ZnO

3.5 Photoluminescence Studies

Photoluminescence measurements have been performed by exciting samples with light and recording the emission spectrum. These spectra for ZnO and Ce-ZnO have been shown in Figure-5. The spectrum for ZnO shows the excitonic emission around 400 nm and defect emissions around 430, 460 and 570 nm with excitation of light of 350 nm[11–13]. The PL spectrum for Ce-ZnO also shows the excitonic emission of ZnO[12,13]. It also shows two clear and sharp peaks around 520 nm and 640 nm. The peak in the green region may be due to the presence of oxygen vacancies[13]. The red emission in Ce-ZnO is assigned to the transition related to the dopant.

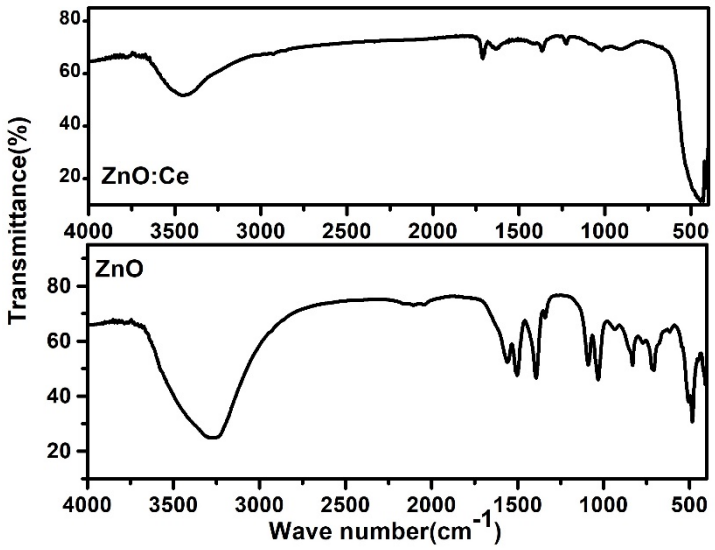

Fig 4. FTIR spectra of ZnO and Cerium doped ZnO.

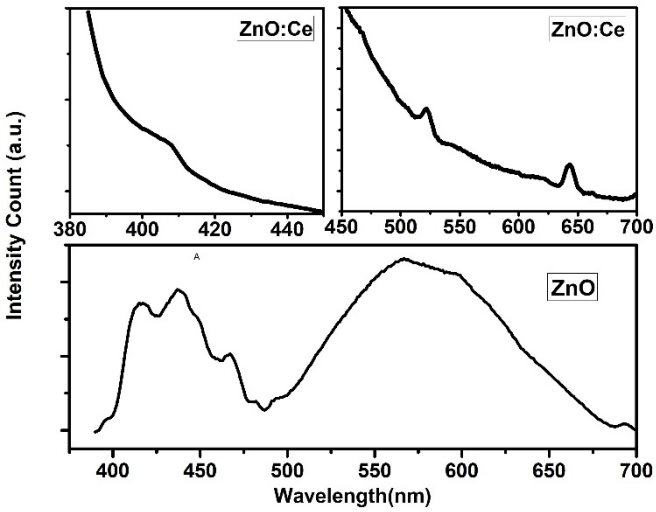

Fig 5. PL spectra of ZnO and Cerium doped ZnO.

4 Conclusion

The present study deals with the synthesis of rare earth (Ce) ion doped ZnO nanopowder by chemical precipitation method. Study is also carried out to understand the structural and optical property of pristine and doped ZnO. XRD measurements show the nanopowders have size in nano range and cerium doping increases the size, strain and unit cell volume of ZnO. The FESEM measurement shows the morphology of the doped sample to be flower like. UV-VIS absorbance spectra confirm the absorption band of ZnO in the region around 360 nm which shifts with cerium doping. FTIR spectra depicts the existence of different stretching and bending vibration along with metal-oxygen bond in the sample. The Pl spectra show the excitonic emission along with defect emission of ZnO. With cerium doping, emissions in the red region is observed.

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