



Determination of Optical Band Gap Energy of Wurtzite ZnO: Ce Nanocrystallites

George Varughese^{1*}, P. W. Jithin¹ and K.T. Usha²

¹Department of Physics, Catholicate College, Pathanamthitta, Kerala-689 645, India.

²Department of Chemistry, St. Cyrils College Adoor, Kerala-691529, India.

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Aim: Determination of optical band gap energy of ZnO:Ce nanocrystallite and effect of doping on the optical band gap energy also probed.

Materials and Methods: ZnO:Ce nanoparticles are synthesized by Chemical precipitation route using 1 molar solutions of Zinc Acetate and Sodium Hydroxide at 60°C. Then 1 molar percentage (1.72 gm) of Cerium oxide is added with the above solution and stirred well using magnetic stirrer. Four-five drops Tri Ethyl Amine (TEA) are added as capping agent to control agglomeration. The characterization of sample was studied by XRD, FESEM, FTIR, EDAX and TEM. The UV-Vis spectrometer was used to study the Optical properties of nanopowder

Results and Discussion: From the XRD techniques the crystallite size of ZnO nanopowder was determined as 13.83 nm at 150°C which increased to 16.13 nm at temperatures 180°C. FESEM showed nanoparticle of average size 13-50nm and nano clusters have size of 1µm. EDAX data is found as Zinc oxide with 99.4% and Cerium 0.6%. TEM confirm the formation ZnO:Ce nanoparticle and it has an average size about 25nm, Some nanorods with average diameter of 40 nm and length of about 290 nm were also observed. The UV absorption spectra for bulk ZnO, nanoparticles of ZnO displayed excitonic peaks at 375 nm and 369 nm respectively. The present study found absorption edge at 372 nm for ZnO:Ce nanoparticle.

*Corresponding author: Email: gvushakoppara@yahoo.co.in;

Conclusion: The UV Absorption spectra showed red shift towards 372 nm due to doping with Cerium and blue shifted relative to Bulk ZnO. From the absorption spectra optical band gap is determined as 3.32 eV. It was found that energy band gap E_g decreases with doping of Ce. The analysis of optical properties shows that ZnO:Ce is promising dielectric material and has potential application in optoelectronic devices .

Keywords: Semi conductor; nanomaterials; zinc oxide; doping; optical properties.

1. INTRODUCTION

Zinc Oxide, a typical II-VI compound semiconductor, with direct band gap of 3.2 eV at room temperature and 60meV as excitonic binding energy, is a very good luminescent material used in displays, UV-Vis laser, solar cell components, gas sensors and varistors [1]. Zinc oxide is an excellent Ultraviolet absorber, antibacterial agent, a transparent electro conductive and piezoelectric material. ZnO has been used in solar cells, transparent electrodes, and LED's. This nanomaterial is a promising candidate for nano-electronics and photonics [1,2]. It is a possible material to observe coherent emission without population inversion induced by Bose- Einstein condensation at the lower polariton band [3]. ZnO is more resistant to radiation and uses in the areas as piezoelectric, ferroelectric and ferromagnetic [4]. ZnO: Ce is hexagonal in symmetry with Space group $P6_{3mc}$ and Lattice parameters [2] $a = 3.253 \text{ \AA}$, $b = 3.253 \text{ \AA}$, $c = 5.209 \text{ \AA}$. The stable structure of ZnO is wurtzite [1]. A substantial effort is made on utilizing such properties in new generation of short wavelength photonic devices [4]. In order to get better photo catalytic activity, the incorporation of rare earth ion doping is essential and that will enhance the photo current response and the separation of electron hole pairs under UV illumination [5]. Since CeO₂ has a band gap of $\sim 3\text{eV}$ and shows the fascinating properties that are similar to that of ZnO. The mixture of both materials have been used for the probing of highly efficient Photo catalysis [6]. The dopant sites defects induced by the doping have strong impact on the structural and optical properties of Ce doped ZnO [7]. In this investigation we report optical property studies of ZnO:Ce and the effect of dopant Ce ion in ZnO nanoparticle on optical band gap energy. The ZnO is reported to be a direct band gap material [8].

2. MATERIALS AND METHODS

2.1 Synthesis and Characterization

ZnO:Ce nanoparticles are prepared by chemical precipitation route using 1 molar solutions of Zinc acetate and Sodium hydroxide at 60°C. One molar percentage (1.72 gm) of rare earth element Cerium oxide solution is mixed with the above solution using magnetic stirrer. The precipitate obtained is washed with double distilled water and acetone many times and filtered well. Four-five drops Tri Ethyl Amine (TEA) was added as capping agent to control agglomerations. After centrifugation the precipitate obtained is placed in the furnace and calcinated to 150 and 180°C. The samples are powdered well in the crucible. The X-ray diffraction spectrum of the nano powder was carried out using Rigaku DMAX diffractometer with Cu -K α radiation monochromatised with a graphite crystal. The morphology and atomic percentage of elements in ZnO: Ce material was deliberated using Field Emission Scanning Electron Microscopy (FESEM) and Electron Dispersive X-ray Analysis (EDAX) with a Hitachi Model s-3000H Electron microscope. Fourier Transform Infrared spectroscopic (FTIR) studies was conducted using Nicolet (Impact 410) FTIR Michelson interferometer. The Transmission electron microscopy (TEM) was performed by JEOL 1010, TEM operating at an accelerating voltage of 100keV. Perker Elmer Lamda 25 UV-Vis spectrometer was used to study the Optical properties of nanopowder.

3. RESULTS AND DISCUSSION

3.1 Determination of Particle Size from XRD Pattern

The XRD pattern, Fig. 1, consists of sharp intense peaks of ZnO:Ce which confirms the good crystalline nature of ZnO and peaks originated from (100), (002), (101), (102), (110), (103), (112), (201), (200) and (202) reflections of hexagonal ZnO [4,5]. The XRD techniques are

widely used for the particle size determination and structure determination of nanoparticles. The patterns are compared with JCPDS file No:80-0075 comparing the observed data with the JCPDS file. In XRD no peaks are identified to represent Ce due to the small percentage of Ce incorporated into the lattice matrix of ZnS. Only a lattice strain can be observed. Due to doping there will not be significant change in the structure of ZnS, whereas disappearance of certain peaks and a shift in the peak position on the 2-theta scale were observed. Also intensities of the peaks are decreased relate to the undoped Zinc oxide. The peaks are found to be broadened. The disappearance of peaks was due to small change in crystalline structure or crystalline phase. The small shift in peak position and decrease in the intensity on doping are due to change in electron density or might be due to point defects. The presence of long range stain field associated with doping causes line broadening and decrease in peak intensity.

The degree of crystallinity of nanoparticles increases with annealing temperature. The percentage of lattice contraction with annealing temperature can also be studied using X-ray diffraction pattern. Particle Size, can be calculated by the formula [4,7], Debye-Scherrer's formula

$$D = K\lambda / \beta \cos \theta \quad (1)$$

$K = 0.89$, λ the X-ray wavelength = 0.154095 nm, β the full width at half maximum and θ the half diffraction angle. The crystal sizes of ZnO:Ce nano particles synthesized at 150 and 180°C were calculated from FWHM and tabulated in Table 1.

From the Fig.1(a-b) it was found that the crystallite size of ZnO nanopowder was 13.83 nm at 150°C which increased to 16.13 nm at temperatures 180°C. From the above study, it is observed that there is a continuous increase in the particle size with temperature. The increase in the particle size is due to the amalgamation of the smaller particles into larger particles [9] is a result of solid state diffusion.

3.2 Fourier Transform Infrared Spectrum Analysis

FTIR spectrum, see Fig. 2, of ZnO:Ce has been shown that as particle size decreases, increase in frequency for the bond (blue shift) is observed in nanoparticles relative to the undoped ZnO. The comparative study of Vibrational modes of doped and undoped ZnO is presented in the Table 2. The stretching frequency of ZnO is observed at 489.12 cm^{-1} . Here a blue shift is observed in that frequency i.e., that frequency change may be due to quantum confinement.

Three intense bands were centered at 1386.15 cm^{-1} , 1042.54 cm^{-1} and 2822 cm^{-1} and are attributed to the stretching vibrations of C = O, C = C and C-H groups in acetate species, which suggests its presents as adsorbed species in the surface of nanoparticles. The broad absorption peak centered at 3376.66 cm^{-1} and 1506.97 cm^{-1} corresponds to O-H stretching, indicating the existence of water molecule occluded in the surface of nanoparticles and H-O-H deformation. The peak observed at 832.64 cm^{-1} and 599.23 cm^{-1} might be due to the presence of Ce-O stretching vibration [10] and Ce^{3+} doped ZnO respectively [11].

3.3 Scanning Electron Microscopy (SEM)

The Morphology of the nanostructure of ZnO:Ce, obtained after 4hrs of reaction, was studied using a Hitachi Model s-3000H Field Emission Scanning Electron Microscope (FESEM). The orientational growth of nanocrystal in water is higher [6]. Spear shaped morphology is observed in the micrograph of ZnO:Ce. The SEM pictures see Fig. 3, showed distinguished self aligned prismatic and rod like morphology. The Scanning Electron Microscopic image showed nanoparticles of average size 13-50 nm. In SEM measurement the grain size are measured. The particle size is calculated by taking the noticeable grain boundaries. While in XRD, measurements are taken from the crystalline area that diffracts the X-ray waves. Thus the particle size measurement of capped ZnO:Ce using XRD was found to be smaller than that with SEM measurement [12].

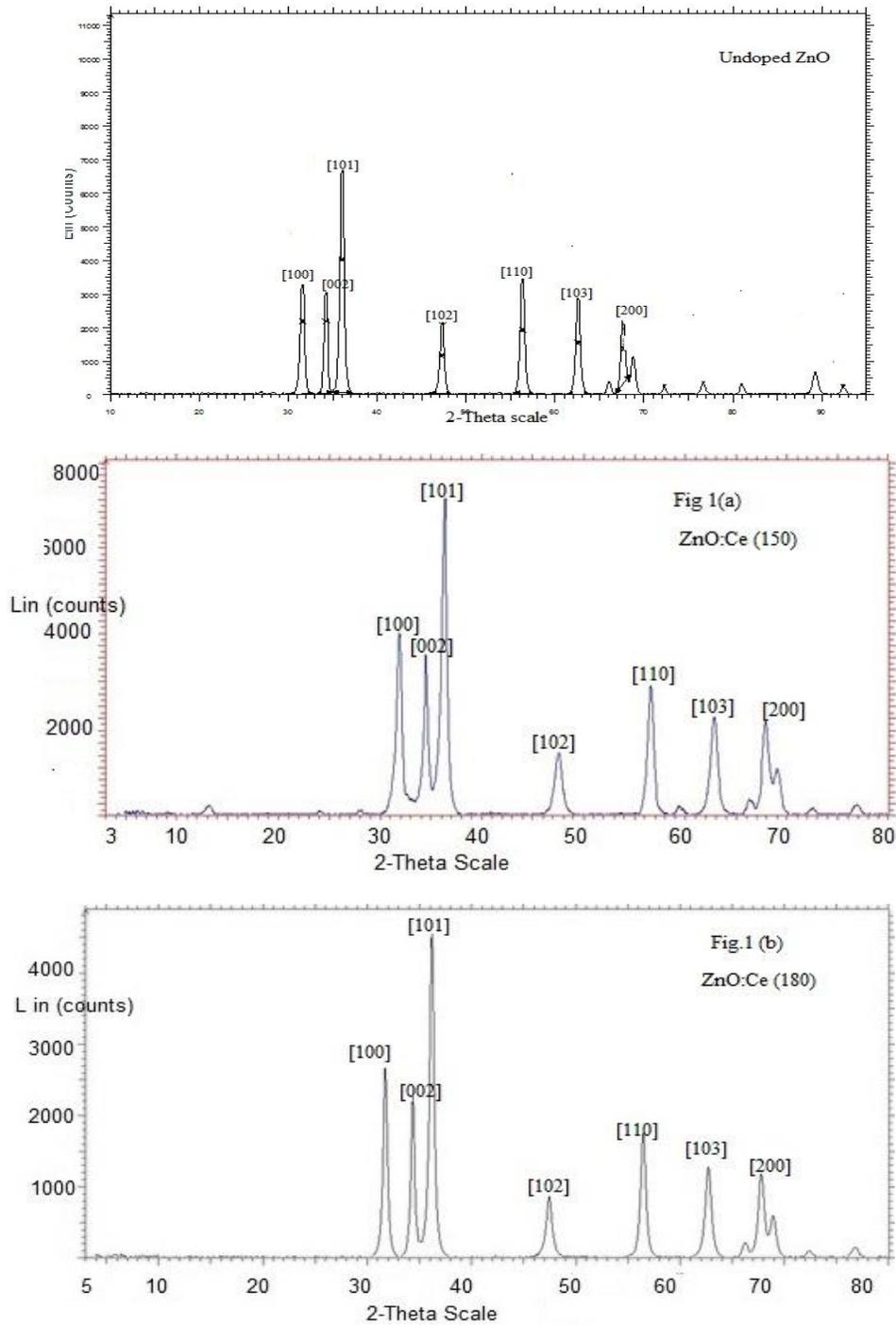


Fig. 1(a-b). XRD patterns of ZnO: Ce nanoparticles at 150 and 180°C

Table 1. Variation of Grain size of ZnO:Ce with temperature

Temperature °C	FWHM	$\beta \times 10^3$	2θ	θ	Particle size(D) nm
150	0.653	11.39	56.64	28.32	13.83
180	0.560	9.768	56.515	28.257	16.13

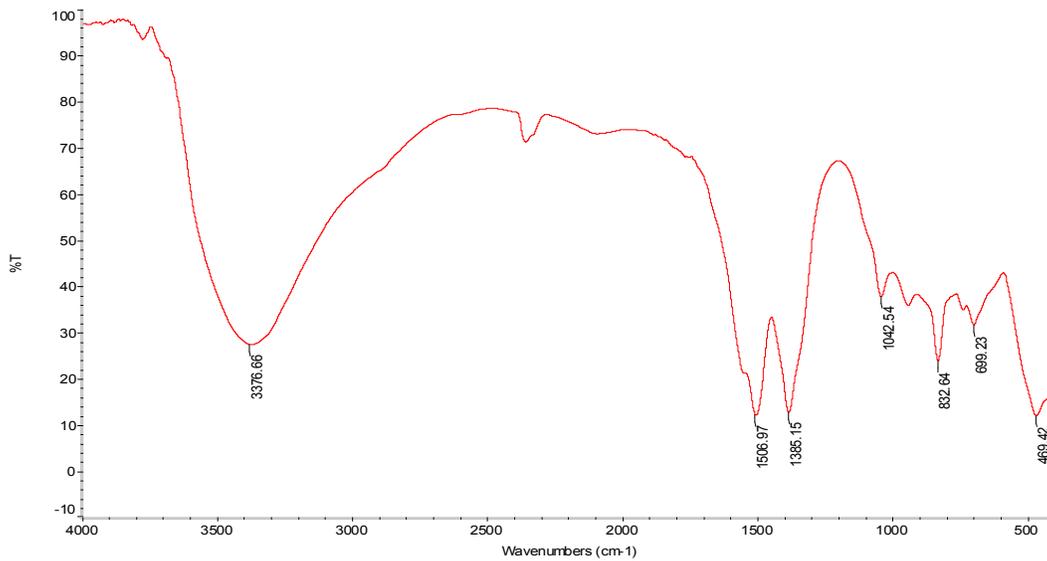


Fig. 2. Fourier Transform Infrared Spectrum of ZnO:Ce nanorods after calcination at 600°C for 4 hours

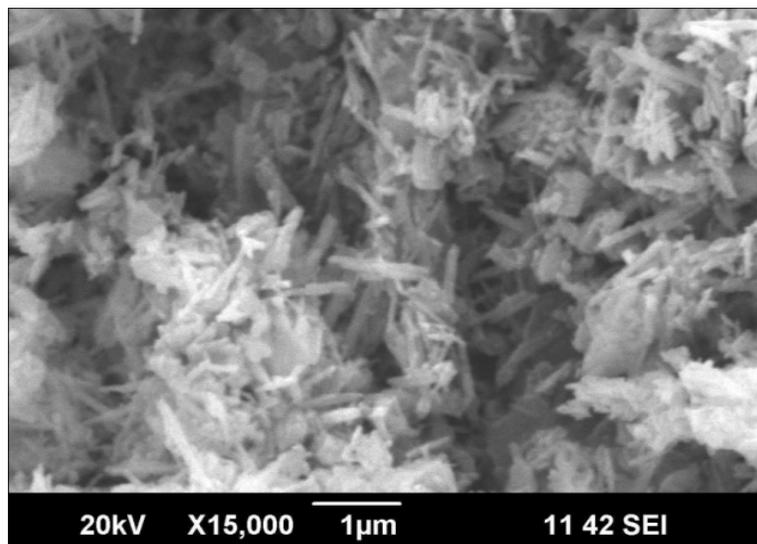


Fig. 3. SEM image of ZnO:Ce Nanorods under high magnification

3.4 Energy Dispersive Spectrum Analysis (EDAX)

EDAX is considered a relatively rapid and non destructive approach for surface analysis. Purity and composition of the sample is studied by EDAX. It is often used to survey surface analytical problems and elemental analysis. The higher a peak in a spectrum, the more concentrated the element is in the sample.

The dried powder samples were analyzed on EDX. The observed peaks reveals the presence of Zn and O₂ confirming the formation of pure ZnO. The average atomic percentage ratio of ZnO was 43.97:56.33. A peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak. High intensity peaks for Zn, O₂ and minor peaks for Ce. Other peaks

correspond to C and Silicate, which are due to sputter coating of glass substrate on the EDX stage and were not considered in elemental analysis. The EDAX, see Fig. 4, of ZnO:Ce nanoparticle is plotted using the recorder and The atomic percentage of elements present in the sample is presented in the Table 3. The EDAX data has shown Zinc Oxide with 99.4% and Cerium 0.6%. *i.e*, very small percentage was incorporated in to the ZnO matrix due to incompatible size of the impurity atom.

Table 2. Comparison of vibrational modes of undoped and Ce³⁺ doped ZnO

ZnO (cm ⁻¹)	ZnO:Ce (cm ⁻¹)	Vibrational modes
3480	3376.66	OH
2820	2822	C-H Stretching
1319	1386.15	C=O Stretching
1119.15	1506.97	HOH deformation
1050	1042.54	C=C
	832.64	Ce-O stretching vibrations
	599.23	Ce ³⁺ Doped ZnO
480.27	489.12	Stretching frequency of ZnO

Table 3. Composition of elements in ZnO:Ce sample

Sample	Element	Atomic percentage
ZnO:Ce	O	56.33
	Zn	43.07
	Ce	0.6

3.5 Transmission Electron Microscopy (TEM)

Fig. 5 (a, b) show typical TEM Images, after 4 hours photo development, of a single ZnO:Ce nanorods to confirm the crystal quality and growth direction. It is clear from TEM image that the end of the ZnO:Ce nanorod is sharp tip. TEM confirm the formation ZnO:Ce nanoparticle and it has an average size about 25nm, Some nanorods with average diameter of 40 nm and length of about 290 nm were also observed. TEM showed that the particles have nanometric prism like and rod like morphologies. The cross section of the one dimensional (1D) nanostructure include triangle, hexagonal and rectangle shapes. High Resolution Transmission Electron Microscopic (HRTEM) pattern indicates that the nanorods grow along the c-axis and it has standard hexagonal structure.

3.6 UV Absorption Spectra

3.6.1 Optical band gap energy from UV absorption spectra

Energy band gap studies of these materials have been reported using absorption spectra. The ZnO is reported to be a direct band gap material. When an electron sitting at the bottom of the conduction band recombines with a hole sitting at the top of the valence band, there will be no change in momentum value. Energy is conserved in the process by emitting photon. Direct band gap materials are capable of emitting photons by radiative recombination. So in order to have efficient LED's and optoelectronic devices one should choose material having direct band gap [13]. The Fig.6 (a-b) depict the optical absorption spectrum of undoped ZnO nanoparticle and ZnO:Ce nanopowder prepared under aqueous conditions. A size-dependent electron-hole exchange interaction is also responsible for it and has been reported [14]. The optical band gap energy can be computed using the relation where *h*, the Planck's constant, *c* velocity of light and λ_g wavelength corresponding to the absorption maximum.

$$E_g = h \nu_g = hc / \lambda_g \quad (2)$$

The UV absorption spectra for bulk ZnO, nanocrystallite of ZnO displayed excitonic peaks at 375 nm and 369 nm respectively [15]. The present study revealed that The UV visible spectra absorption edge is at 372 nm (3.32 eV) for nanocrystallite of Zinc Oxide doped with rare earth ion Cerium. The values are tabulated in the Table 4. It has displayed a red shift 5 nm for absorbance. It is found that after the Ce incorporation, a new localized band appears between the valence and conduction band, which corresponds to the majority spin of Ce- 4f states [16]. It is this localized band constructs a bridge between the valence and conduction state, which will improve the optical performance of ZnO. ZnO:Ce is a degenerate semiconductor. The strong correlation effect is very important for the 4f of the Ce atom in ZnO:Ce. The mismatch of the majority and minority spin of Ce-4f, Ce-5d state and the spin polarized holes in O-2p state induced by Ce doping leads to the presence of magnetic order for ZnO:Ce [17]. The analysis of optical properties shows that ZnO:Ce is promising dielectric material and has potential application in optoelectronic devices [18]. The

introduced dopant ions might shape a shallow energy level near valence band. Hence we assign the red shift to the defects and the probable shallower energy levels [19]. Therefore, the optical band gap of Ce doped ZnO is broader than that of undoped Zinc Oxide. Hence the value of band gap energy lies in the

higher wavelength region. The changes in band gap were due to the existence of a valence band-donor transition at 3.38 eV which can dominate the absorption spectrum when the bulk, as distinct from the surface, of a single crystal is probed.

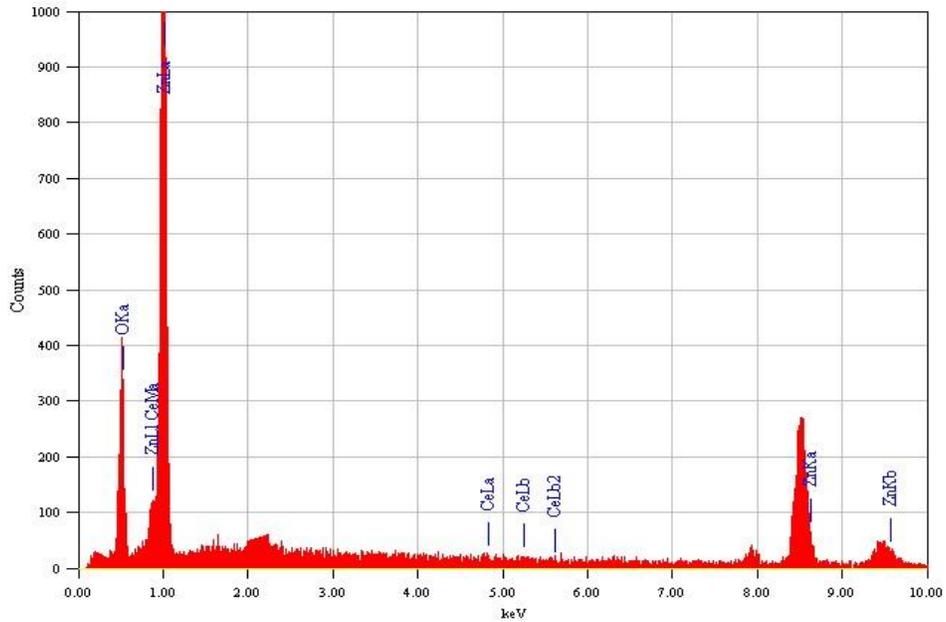


Fig. 4. Energy dispersive spectrum of ZnO:Ce nanorods

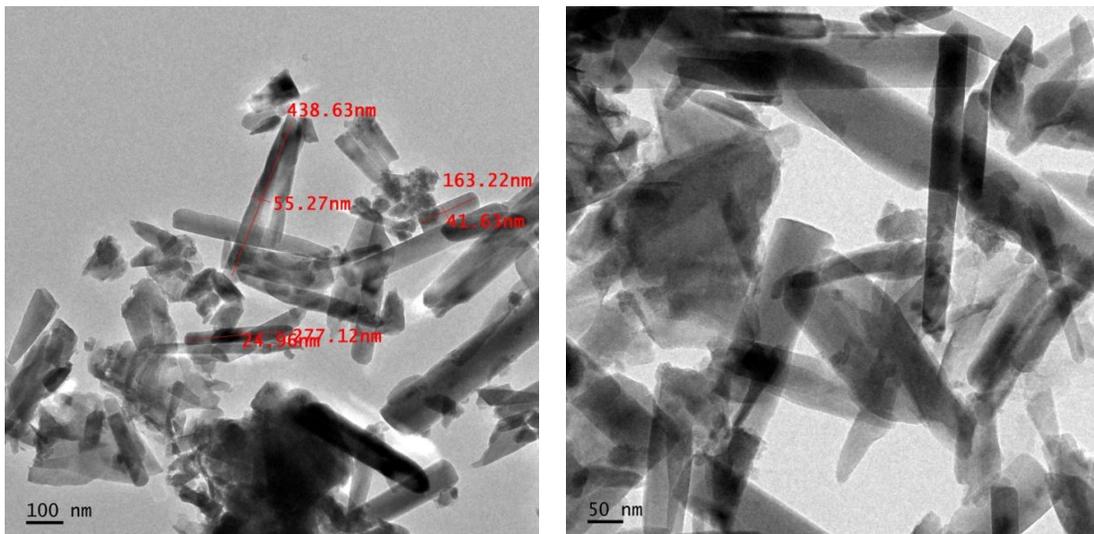


Fig. 5(a-b). TEM images of ZnO:Ce nanorods

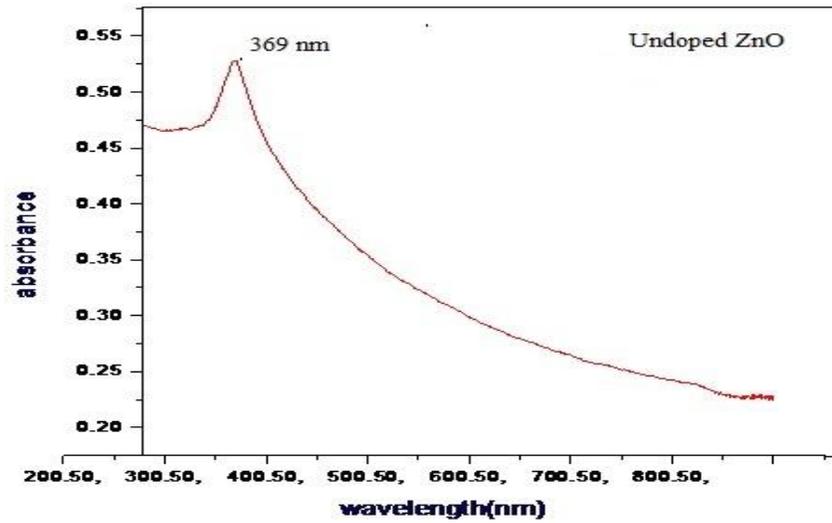


Fig. 6(a). UV spectrum of ZnO

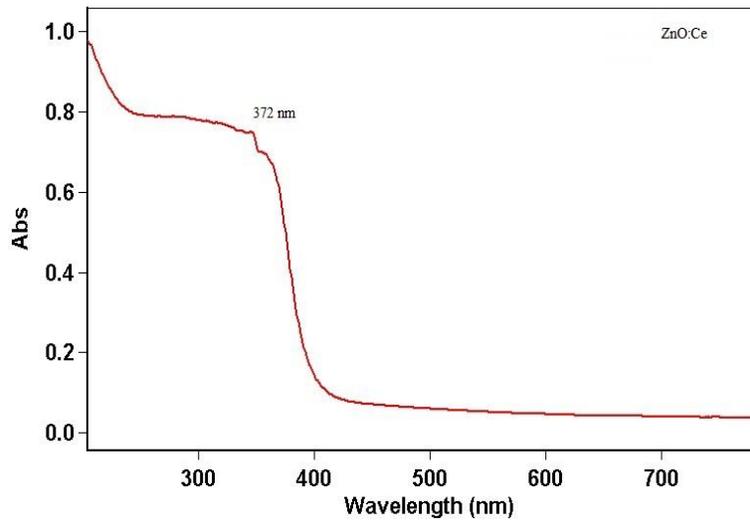


Fig. 6(b). UV Spectrum of ZnO:Ce nanorods

Table 4. Band gap energy of Bulk ZnO, undoped ZnO, doped ZnO nanoparticles, Blue/red shift observed

Sample material	Band Gap energy E_g (eV)	Wavelength maximum λ_{gn} (nm)	Blue shift w.r.t to bulk ZnO (eV)	Red shift w.r.t undoped ZnO nanoparticle(eV)
ZnO: Ce Nanomaterials	3.32	372	0.02	0.06
ZnO Nanomaterials	3.38	369		
ZnO Bulk material	3.3	375		

4. CONCLUSION

The size and crystal structure of ZnO doped with Cerium was studied using XRD. The XRD results indicated that the particle size of nano

ZnO:Ce is much small as compared to that of pure ZnO and decreases with the cerium loading. From the XRD results, it is clear that as temperature increases, particle size also increases. The change in particle size cause

large variation in the physical properties. High temperature XRD also confirmed that the nanoparticles were stable not only at room temperature but at high temperature as well. The UV Absorption spectra showed red shift towards 372 nm due to doping with Cerium. From the absorption spectra obtained by UV-Vis spectrometer the optical band gap is determined and found to be in the range 3.32 eV. It was found that energy band gap E_g decreases with doping of Ce. Doping of Ce changed the free carrier concentration in the ZnO nanoparticles. The analysis of optical properties shows that ZnO: Ce is promising dielectric material and has potential application in optoelectronic devices.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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