

OPTICAL BAND GAP ENERGY DETERMINATION OF ZINC OXIDE NANOSTRUCTURES DOPED WITH GADOLINIUM IONS

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Abstract: Zinc Oxide is an extensively studied group II-VI semiconductor with optical properties that permits stable emission at room temperature having immense application in sensors, field emission and photonic devices. It exhibits a wide variety of morphologies in the nano regime that can be grown by tuning the growth habit of the ZnO crystal. ZnO nano materials with an average particle size of 15-27 nm are synthesized by the reaction of zinc acetate and sodium hydroxide solution under hydrothermal conditions. The UV absorption spectra revealed the absorption at wavelength <370 nm indicating the smaller size of ZnO nano particle. ZnO doped with Gadolinium nanoparticles have been synthesized by precipitation method. The absorption spectra have been obtained by UV-Vis spectrometer to find the optical band gap and the obtained values have been found to be in the range 2.94 eV. It was found that energy band gap E_g decreases with doping of Gd.

Introduction

ZnO nanoparticles have wide application. Zinc Oxide is an excellent ultraviolet absorber and antibacterial agent. ZnO has been used in solar cells, transparent electrodes, and blue/ UV light emitting devices. ZnO nanomaterials are promising candidates for nanoelectronic [1, 2] and photonics. Compared with other semiconductor materials, ZnO has higher exciton binding energy (60 meV), is more resistant to radiation and is multifunctional with uses in the areas as piezoelectric, ferroelectric and ferromagnetic.[3-5] ZnO based semiconductor and nanowire devices are also promising for the integration on a single chip. It possess with the large direct band gap (3.37eV) [6]. The stable structure of ZnO is wurtzite, in which four atoms of oxygen in tetrahedral coordination surround each atom of Zinc. Zinc oxide is also used in Adhesives, transparent rubber, photo-copying, food can linings, UV resistant plastics [3, 4], cosmetics and drugs, batteries, matches, agricultural. Ferromagnetic ZnO nanostructures are regarded as an excellent material for short wavelength magneto-optic device since it has wide band gap [14]. These studies enable the use of magnetic ZnO nanowires as nanoscale spin based devices. Obtaining

room temperature ferromagnetic spin polarized transport in ZnO nanostructures will greatly advance future research as spin based nanoscale devices [15]. Gadolinium is a material having large magnetic moment. They have application fuel cells in which they exhibit ionic conductivity. Hence this work is focusing on the variation of band gap energy with doping.

Experimental:

Material and Methods: ZnO nanoparticles are prepared by chemical precipitation route using Zinc acetate solution and sodium hydroxide solution and Gadolinium Nitrate solution. The precipitate obtained is washed with double distilled water, acetone and ethanol and filled with Grade 1 filter paper. The filtrate is placed in the furnace at 60 °C. The process is repeated for 120,180 and 200°C. The orientation and crystallinity of the powder were studied using Rigaku DMAX diffractometer using Cu -K α radiation monochromatised with a graphite crystal and high temperature attachment in θ -2 θ geometry. The surface topography and microstructure were studied using Field Emission Scanning Electron Microscopy (FESEM) with the instrument SEM, JEOL, JSM-67001. FTIR spectroscopy uses Nicolet (Impact 410) FTIR Michelson interferometer to produce an interferogram. Energy Dispersive X-ray Spectrum Analysis (EDX) was used to determine percentage composition of Gd in ZnO. Transmission electron microscopy (TEM) was performed by JEOL 1010, TEM operating at an accelerating voltage of 100keV. In this investigation, The UV measurements were done with UV spectrometer JASCO V-550 in the wavelength range of 200 nm to 850 nm

Table 1. Particle size of ZnO:Gd

Tem. °C	FWHM	$\beta \times 10^{-3}$	2 θ	θ	Partic Size L nm
120	0.53	9.24	36.2	18.1	15.78
180	0.369	6.04	31.7	15.83	22.41

200	0.301	5.25	34.48	17.190	27.663
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Results and discussions

Perker Elmer Lamda 25 UV-Vis spectrometer was used to study the optical properties of nanopowder. FTIR spectroscopy uses Michelson interferometer to produce an interferogram. Energy Dispersive X-ray Spectrum Analysis (EDX) was used to determine percentage composition of Gd in ZnO.

A. Determination of Particle Size

XRD, (Fig.1), is a genuine tool to test the phase of a material, ie, whether it is crystalline or amorphous. 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. The patterns are compared with JCPDS file No: 80-0075. The degree of crystallinity of nanoparticles increases with annealing temperature. Particle Size, can be calculated by the formula[4,7] Debye- Scherrer's formula

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

$K=0.89$, λ the X-ray wavelength =0.154095 nm, β the full width at half maximum and θ the half diffraction angle. The crystal size of ZnO:Gd nano particle calculated from FWHM was tabulated in Table 1. 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 merging of the smaller particles into larger ones.[8] and is a result of potential energy difference between small and large particles and can occur through solid state diffusion.

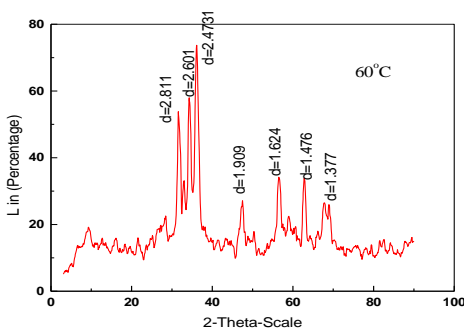


Figure1.XRD of ZnO:Gd annealed at 60°C

B. Scanning Electron Microscopic image of ZnS:Gd

The Scanning Electron Micrographs of ZnO:Gd nanomaterials synthesized under aqueous medium was carried out by Scanning Electron Microscope [Model LEO 1430 VP] operated with an accelerating potential of 15kV to 29kV. The orientation growth of ZnO:Gd crystal

in water is higher. The SEM of ZnO:Gd (Fig.2) exhibit spherical morphology.

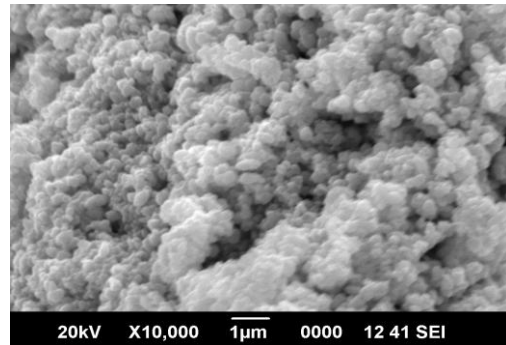


Figure 2. SEM spectra of ZnO:Gd

The formation of good spherical structure proved the formation of quantum dots (QD). It shows that the average particle size of the nanoparticle in the range 15nm to 28 nm and the large particle size labeled in the figure is the length of nanoclusters formed due to the agglomeration of nanoparticles in the aqueous medium.

C. Electron Dispersive Spectrum of ZnO :Gd nanoparticles

In Electron Dispersive Analysis X-ray spectrum, (Fig.3) each of the peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the spectrum. An EDS spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. For example, 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. About 97.22% of Zn²⁺ ion and about 2.19% Gd ion by mass are present in the sample.

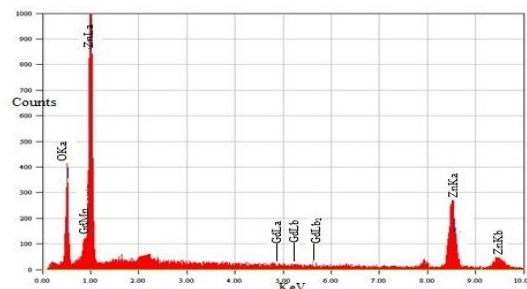


Figure 3. EDAX spectrum of ZnO:Gd

D. Fourier Transform Infrared Spectrum Analysis

FTIR spectrum, Fig. 4, the bands at 416.35 cm⁻¹ is assigned to the stretching vibrations of Zn-O. The stretching frequency of bulk ZnO is 424 cm⁻¹. Three intense bands were centered at 1384.34 cm⁻¹, 1041.54

cm^{-1} and 1556.58 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 absorbed species in the surface of nanoparticles.

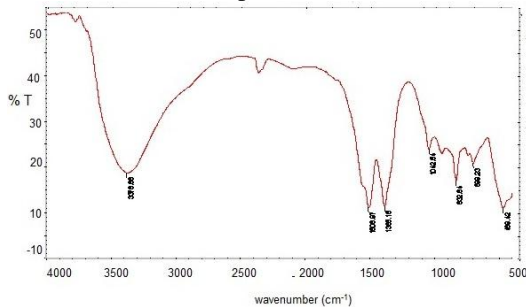


Figure 4. FTIR spectrum of ZnO: Gd

The band centered at 3423.61 cm^{-1} and 1626.40 cm^{-1} corresponds to O-H stretching and bending frequencies of H_2O , indicating the existence of water occluded in the surface of nanoparticles [9]. The peak observed at 825.80 cm^{-1} may be the presence of some impurities in the Zinc Acetate or Zinc Oxide nanoparticle

E. Transmission Electron Microscopy of ZnO:Gd

The transmission electron micrograph of the ZnO:Gd sample is given in fig.4The figure clearly indicates the morphology

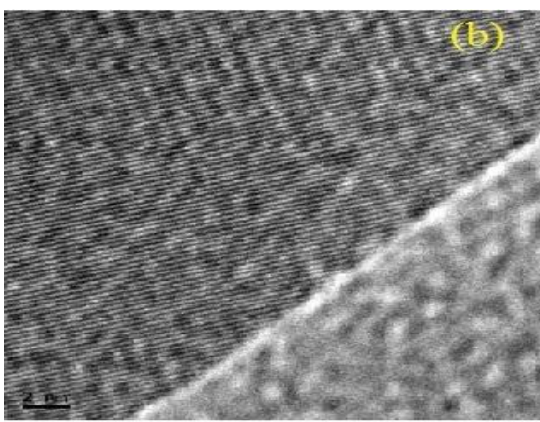
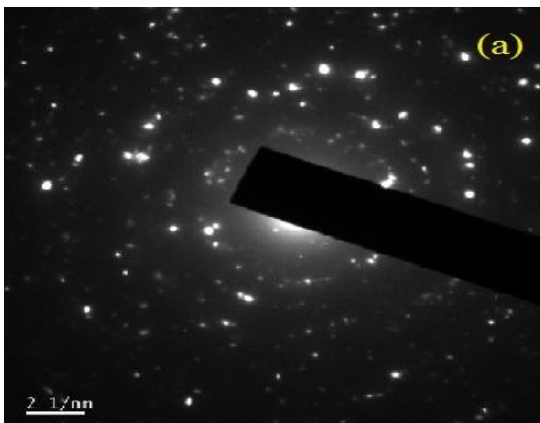


Figure 5(a-b).TEM images of ZnO:Gd quantum dots of the particle to be roughly spherical and homogeneous. The distribution of the particle obtained from the TEM is depicted in the Fig.5(a).The bright field TEM image

shown in the Fig 5(a) revealed that the size of the particle synthesized ZnO:Gd quantum dots were around 2-5 nm . Further high resolution study shown in fig 5(b) revealed that the lattice fringes of the particle run in the same direction across the whole structure, indicating that the single quantum dots possessed good crystallinity. Most of the quantum dots are less than 5nm.

E. UV Absorption Spectra of ZnO:Gd nanoparticle

Energy band gap studies of these materials have been reported using absorption spectra [5,6]. The [fig.6] depicts the optical absorption spectrum of ZnO:Gd nanopowder prepared under aqueous conditions. The UV visible spectra for ZnO:Gd nanoparticle synthesized in aqueous media exhibited excitonic absorption feature at 200 nm.

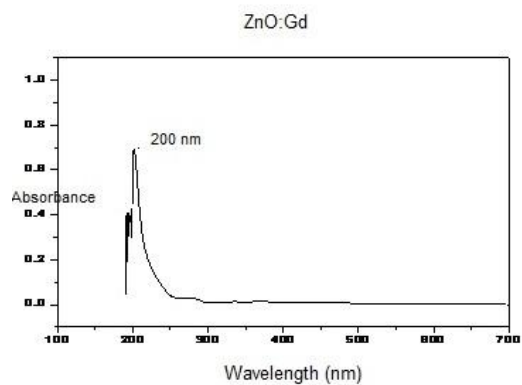


Figure.6 UV Absorption spectra of ZnO:Gd

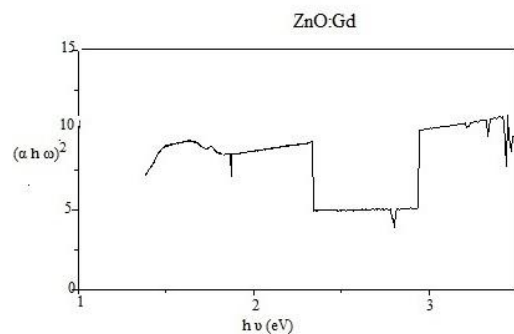


Figure.7 Tauc plot ZnO:Gd

Which is considerably blue shifted relative to the absorption of the bulk Cds indicating quantum size effect in the prepared nanosamples and is agree with result of direct band gap semiconductor nanocrystal for potential application [10,13].The material is reported as direct band gap material. The well defined maximum at 200 nm is assigned to the optical transition of the first excitonic state. Generally, the wavelength of the maximum exciton absorption decrease as the particle size decreases, as result of quantum confinement of the photogenerated electron hole pairs [12].

Energy band gap studies [5] of these materials have been reported using Tauc plot [Fig. 7]. For higher values of absorption coefficient, optical absorption

shows a power load dependence on photon energy [9, 10].

$$h \omega \alpha(\omega) = B(h\omega - E_g)^\gamma \quad (2)$$

where exponent γ can take values 2, 3, 1/2 and 3/2 for indirect allowed, indirect forbidden, direct allowed and direct forbidden transition respectively. E_g is the optical band gap. Optical energy gap is obtained by extrapolating the linear portion of the absorption spectrum to $h\omega = 0$. The energy band gap for ZnO:Gd is calculated as 2.97 eV. But the standard band gap energy for ZnO nanoparticle is 3.37 eV. Hence the value of band gap energy lies in the lower wavelength region, i.e. grain size decreases. When grain size changes band gap also changes. Srikant et al. [11] investigated the optical band gap ZnO single crystals at room temperature using a variety of optical techniques, change in band gap were due to the existence of a valence band-donor transition at 2.97 eV which can dominate the absorption spectrum when the bulk, as distinct from the surface, of a single crystal is probed. ZnO:Gd nanoparticle band gap values are lower than ZnO Nanoparticle (3.53 eV) because the magnetic properties of ZnO:Gd nanoparticle increases by doped Gadolinium and interaction potential become more strong in comparison with ZnO nanoparticle. By doping with Gd ions, the wavelength of absorption edge shift towards a higher wavelength compared to ZnO nanoparticle. This changes the band gap energy suggesting that there is direct energy transfer between semiconductor excited state and 3d levels of Gd^{2+} ions, that can be coupled by energy transfer process [16].

Conclusions

The size and crystal structure of ZnO doped with Gadolinium was studied using XRD. The XRD results indicated that the particle size of nano ZnO:Gd is much smaller as compared to that of pure ZnO and decreases with the gadolinium loading. From the XRD results, it is clear that as temperature increases, particle size also increases. The change in particle size causes 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 EDS spectrum identifies the presence of doped gadolinium ions in the material. SEM image confirms the morphology and size of the particle. The bright field TEM image shown revealed that the size of the particle as-synthesized ZnO:Gd quantum dots were around 2-5 nm. Further high resolution study revealed that the lattice fringes of the particle, indicating that the single quantum dots possessed good crystallinity. The UV Absorption spectra show a red shift towards 200 nm due to doping with Gadolinium. The Gadolinium doped ZnO is highly effective and can significantly enhance the photocatalytic degradation and magnetic properties. Doping with Gadolinium nitrate decreases the band gap energy of ZnO. These studies

enable the use of magnetic ZnO nanowires as nanoscale spin based devices.

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Biography

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