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Influence of Copper doping on Structural, Morphological and Optical Properties of ZnO Nanoparticles

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Abstract: In this work pure and Copper doped ZnO (CZO) Nanoparticles were synthesized by sol-gel process. The influence of Cu doping on Structural, Morphological, Compositional and optical properties of ZnO Nanoparticles were analyzed by performing various studies using X Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible Optical absorption and Photoluminescence (PL) Spectroscopic Characterizations. XRD is used to determine structural properties of Nanopowders.SEM images show morphology of Nanopowders. An FTIR spectrum is used to specify functional groups. Optical properties were analyzed from UV-Visible optical absorption and PL characterizations. The results proved Cu incorporation into ZnO lattice modified properties of pure ZnO. Sol-gel method utilized for fabrication is simple, low cost, environmental friendly. As synthesized nanoparticles can further utilized for fabrication of Sensors, Solar Cells, LED etc.
Keywords: Nanoparticles, Optical Absorption ,Scanning Electron Microscopy, X Ray Diffraction, Zinc oxide.

Introduction

Nanomaterials are tunable by size, shape, structure and or composition. Advances in the synthesis of well-defined nanomaterials have enabled control over their unique optical, electronic, and chemical properties stimulating tremendous interest across a wide range of disciplines[1]. Since the intrinsic characteristics and relevant applications of nanoparticles are closely related to their size, shape, and surface properties, great efforts have been devoted to the controlled synthesis of nanoparticles. The properties of nanoparticles (such as gold and silver) can thus be tailored by altering their physical geometries. Numerous publications have addressed the unique properties exhibited by variously metal nanoparticle shapes, including ZnO nanospheres , nanorods, nanoprisms ,nanocubes, and nanowires. The optical properties, including optical resonance wavelengths, extinction cross-section, relative contribution of scattering to the extinction, can be tuned for different applications. Spherical nanoparticles offer resonance wavelengths in the visible region, while nanoshell and nanorod resonances are shifted into the Near Infrared (NIR) region. Moreover, nanoshells and nanorods optical properties are enhanced by altering the core-shell radius and aspect ratio, respectively.

Due to the Advancement of material technology over the past decade Wide band gap semiconductors emerged as UV sensitive they are implemented in optoelectronic, sensors, transducers and biomedical applications[2]. Group II-VI nanoscale semiconductors recognized for their unique optical and electronic properties and also due to their vast potential applications in optoelectronic devices ,solar cells ,biological labelling etc. ZnO is widely used for optoelectronic and luminescence devices due to its remarkable luminescence properties due to their wide direct band gap of 3.44 eV, large exiton Binding energy 60 meV. strong luminescence in green white region of the spectrum making suitable for phosphor applications[3,8].

ZnO are replaced by magnetic ions. Generally, when 3d TM ions are substituted for the cations of the host, their electronic structure is influenced by the strong 3d orbital's of the magnetic ion and the p orbitals of the neighboring anions , hence leads to change in structure and optical properties of ZnO[4].Many researchers reported Cu2+ concentrations reveal some shifting in the peak positions compared to that of the pure ZnO.(P.D sahare .Vipin kumar ,2013) , The incorporation of Cu+2 in the place of Zn2+ provoked an increase in the size of nanocrystals as compared to undoped or pure ZnO (Ruby chauhan et al,2010) The presence of Cu in the ZnO lattice as Zn substitution indicated by an in- crease in lattice parameter values (Mergoramadhayenty Mukhtar,2012), Cu dopant introduces significant Red shift in PL spectra (Arindam ghosh et al 2014) . The crystalline size of Copper doped Nanoparticles of 11 nm is revealed by XRD The optical transmittance of the UV – VIS measurements indicates that the Pure ZnO and Cu doped ZnO nanoparticles have a band gap energy of 4.9 eV and 15.86eV (V.Kalaisevi et al,2015). Dopant studies are still in progess. Extensive research is being undertaken by the researchers in Cu doped ZnO to improve the performance of opto electonic device applications.

In this work pure and Cu doped ZnO nanoparticles were synthesized using sol-gel process .Sol gel method is preferred as it can produce nanopowders with a high chemical homogeneity, purity and with a Simple, Economic and Environmental friendly characteristics[5,9]

Experimental Procedure

Materials

Zinc Chloride (ZnCl2),Sodium Hydroxide (NaOH), Copper Nitrate Cu $(NO_3)_2$. And Ethanol All chemicals used are of Analytical grade. The chemicals were bought from commercial market and used without further purification

Experimental Procedure

Pure and Cu doped ZnO Nanopowders were synthesized by Sol gel process. To synthesize Pure ZnO nanoparticles 0.2 M aqueous ethanol solution of ZnCl2 was prepared under constant stirring of $ZnCl_2$ using magnetic stirrer for one hour. 0.2 M aqueous ethanol solution of NaOH was also prepared in the same way with stirring of one hour. After complete dissolution of ZnCl2, NaOH aqueous solution was added to Zinc chloride solution under high speed constant stirring, drop by drop (slowly for 15 min) touching the walls of the vessel. The solution was strongly stirred for 2 hours. White precipitate was obtained within the solution. The beaker sealed and the solution was allowed to settle for overnight and further, the supernatant solution was separated carefully. The remaining solution was centrifuged for 10 min, and the precipitate was removed. Thus, precipitated ZnO NPs cleaned repeatedly with deionised water and ethanol to remove the unwanted impurities bound with the nanoparticles. The washed precipitate then dried in an oven at about 60◦C.After drying Zn (OH)2 is completely converted to into ZnO explained by the equation below[6,7].

For the synthesis of Cu doped ZnO nanoparticles (CZO) the same procedure was repeated by adding Aqueous solution of Copper Nitrate Cu(NO3)2.5H2O to the Zinc Nitrate solution to serve as a do pant source

Results and Discussions

X Ray Diffraction (XRD)

XRD is a primarily used technique to obtain structural features of nanopowders including crystal structure, size, shape, internal stress and average spacing between the layers. Figure 1.1 and Figure 1.2 represent XRD spectrum of Pure and Cu doped ZnO Nanopowders synthesized using Sol-gel process. Various diffraction peaks are observed in the spectra of Pure and Cu doped ZnO Nanopowders. The Line broadening of the peaks indicate synthesized particles in the Nanoscale range. In the spectra of pure ZnO diffraction peaks appear at 32.265°, 37.243°, 46.499°, 47.818°, 57.07°, 62.69°, 67.64° and 75.85° respectively. In spectra of Cu doped ZnO diffractions peaks appear at 12.789°,16.786°,29.298°,31.838° ,35.406°,34.345°,38.861°,39.270° and 45.452° respectively. The intense diffraction peaks keenly indexed as hexagonal wurtzite structure of ZnO. No other peaks related to impurity are observed in spectra. No change in the crystalline structure was detected due to Cu doping which suggests that the majority of the Cu atoms were in the ZnO wurtzite lattice The mean crystalline size was calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye-Scherer formula represented below in Equation 1and The Stokes and Wilson formula given in Equation (2) were used to calculate the strain induced broadening of the Bragg's diffraction peak[8].

$D = 0.9\ \lambda / (\beta_{h,k,l} \cos\theta)$ ------------- (1)

Where D is the average crystalline diameter, λ is the wave-length in angstrom, β is the line width at half – maximum and θ is the Bragg angle.

$$\varepsilon = \frac{\beta\ h,k,l}{4\ Tan\theta} \quad \text{--------------- (2)}$$

The average crystalline size and lattice strain calculated from most intense peak of XRD spectra is found be 23.8 nm and 0.0055 in the case of pure ZnO and 20.28 nm and 0.0071nm in the case of Cu doped ZnO Nanopowders[9].

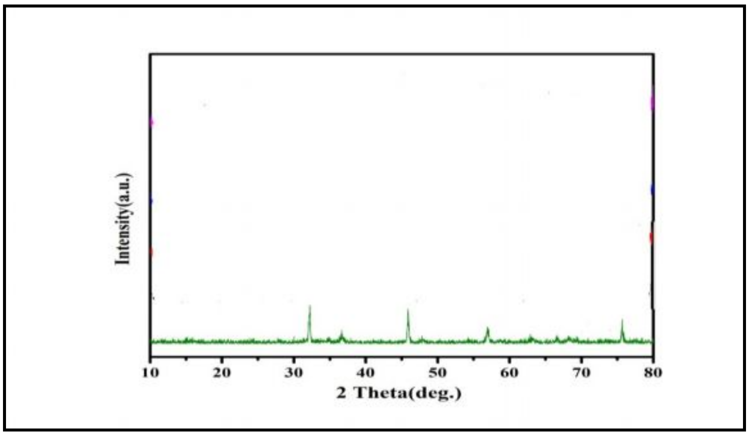

Figure 1.1: XRD spectra of Pure ZnO Nanoparticle

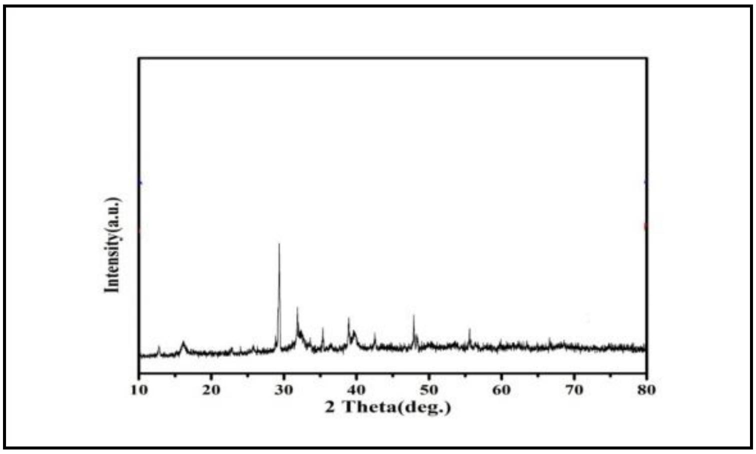

Figure 1.2: XRD spectra of Copper Doped ZnO Nanoparticle

From spectra it is clear that no impurity peaks were observed in the spectra of pure and Cu doped ZnO Nanopowders. This shows that Cu2+ ion successfully occupy the lattice site rather than interstitial one. This is due to the fact that ionic radius of Cu2+(0.73Å) is very close to that of Zn2+(0.74Å),due to which Cu can easily penetrate into ZnO crystal lattice. From XRD data it was clear that the incorporation of Cu in to ZnO lattice decreases in the crystalline size, which further improves structural properties of nanopowders[10]

Scanning Electron Microscopy (SEM)

SEM is a remarkably versatile technique that can be used to obtain information about the surface topography and composition. Figure 2.1 and Figure 2.2 represent SEM micrographs of Pure and Cu doped ZnO Nanoparticles observed at different magnifications synthesized using Sol-gel Process. From micrographs it was observed that Pure ZnO Nanopowders represent the formation of Spherical, Triangular and cube like morphology but by copper doing remains almost rod like morphology. This indicates Cu doping influences strongly on morphology of ZnO nanoparticles[11]

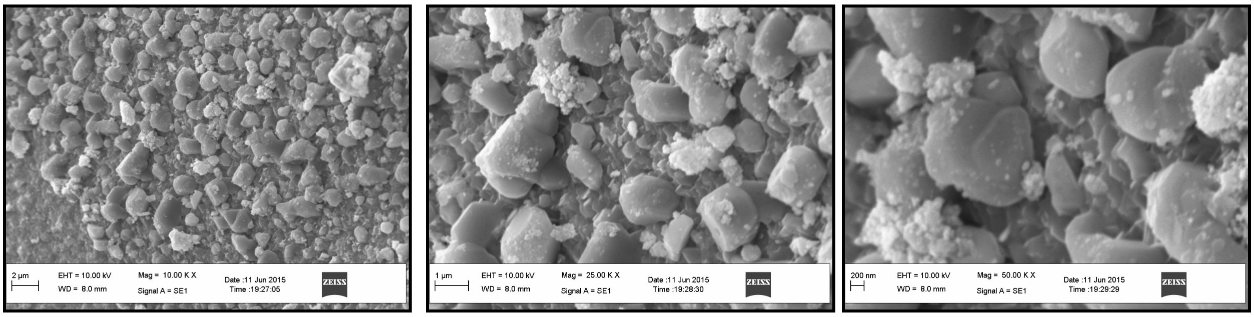

Figure 2.1: SEM pictures of ZnO Nanoparticles observed at different magnifications

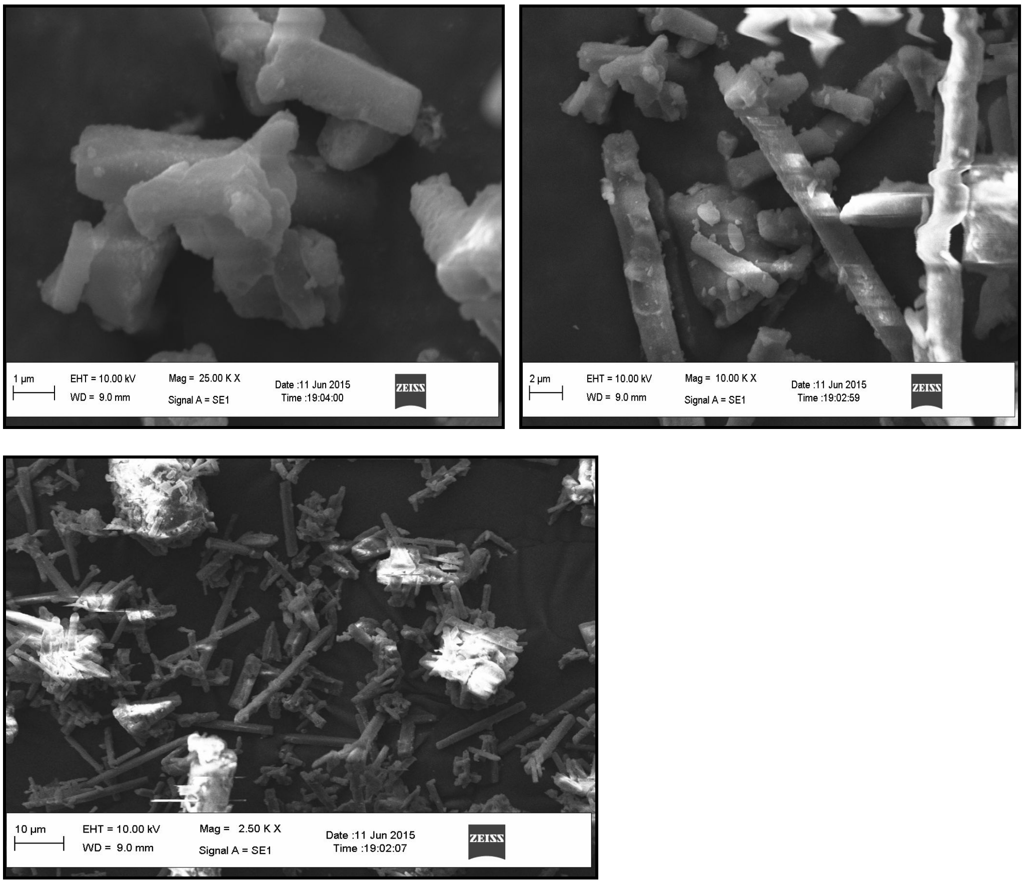

Figure 2.1: SEM pictures of Cu doped ZnO Nanoparticles observed at different magnifications

Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is a simple and reliable technique which is widely used to identify the functional groups present in the sample. Figure 3.1 and Figure 3.2 represent FTIR spectra of Pure and Cu doped ZnO

Nanopowders. The FTIR spectra were recorded in the range of 400–4000 cm−1. The position and number of absorption bands not only depend on crystal structure and chemical composition but also on crystal morphology[12]. The strong absorption peaks observed at 3448.467 in Pure ZnO and 3481.4526, 3326.678 in Ni-ZnO attributed to the presence of hydroxyl group (O-H stretching).The peaks observed near 1613.28 in Pure ZnO and 1627.358 in Cu-ZnO revealed the presence of O-C-O. The peaks observed at 1381.388 in Pure ZnO and 1381.386 cm-1 in Cu –ZnO are attributed to the symmetric and asymmetric C=O stretching vibration modes. It is very important to identify that Cu doping affects the spectra In Figure 4.1 the Zn-O band is observed at 455 cm-1and Figure 4.2 below 700 cm^{-1} many peaks are observed attached to Zn-O which assigned as Cu-O stretching mode. This is due to the presence of Cu ion in the doped sample. A small hump observed at 2043.09 in Figure 4.1 due to the C-H stretching. Various shifts observed in the spectra might be due to the Cu incorporation[13].

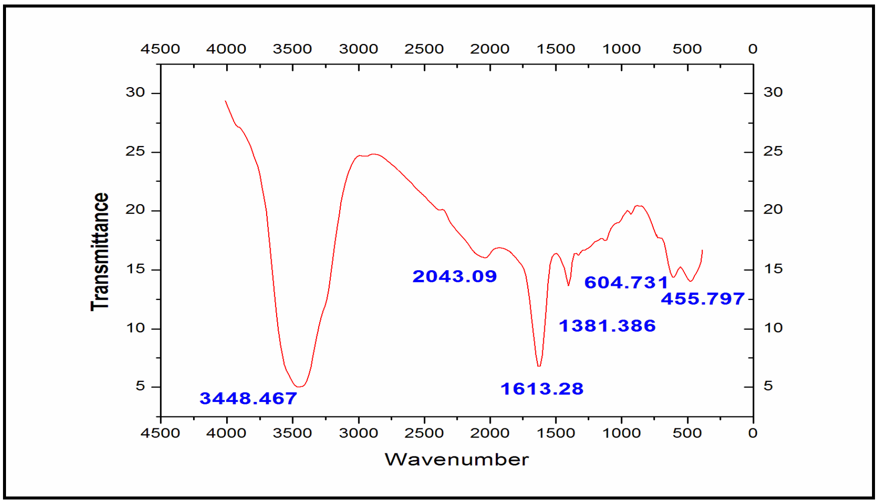

Figure 3.1: FTIR spectra of Pure ZnO Nanoparticle

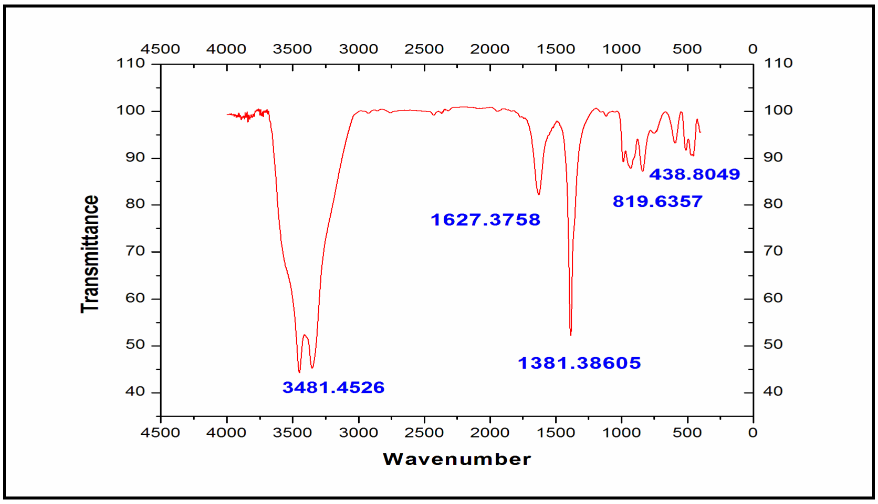

Figure 3.1: FTIR spectra of Cu doped ZnO Nanoparicles

UV-Visible optical Absorption Spectroscopy

The spectroscopy with high performance used mainly for quantitative determination of compounds that absorb UV radiation at characteristic wavelengths in the Electromagnetic spectrum[14]. Figure 4.1 and Figure 4.2 represent absorption spectra of pure and Cu doped ZnO Nanopowders recorded in the range 200-800 nm. From Spectra,an exitonic absorption peak around 210 nm with a little shift can be observed in the pure and doped ZnO. It can also be seen clearly from Figures 4.1 and 4.2 undoped ZnO nanopowders show little absorbance around 350 nm in the Visible region where as Cu doped ZnO particles have little higher absorbance compared to pure ZnO .

The direct band gap energy (Eg) of Nanoparticles obtained from Taus relation. $\alpha h\nu = A(h\nu - Eg)^m$ Where α is absorption coefficient given by α = 2.303 log (T/d) (d is the thickness of the sample and T is the transmission), hν is the photon energy. Energy band gap is found to be 3.81 eV in the case of pure ZnO and 3.858 eV in the case of Cu doped ZnO Nanoparticles. It shows that bandgap of nanoparticles is higher than that of bulk ZnO. Significant increase in Band gap is observed by doping with Cu .The Eqn. (1) obtained from using the effective mass model evaluates the particle size (r, radius) as a function of peak absorbance wavelength (p) for monodispersed ZnO nanoparticles,

$$r(\mathrm{nm}) = \frac{-0.3049 + \sqrt{-26.23012 + \dfrac{10240.72}{\lambda_p(\mathrm{nm})}}}{-6.3829 + \dfrac{2483.2}{\lambda_p(\mathrm{nm})}}$$

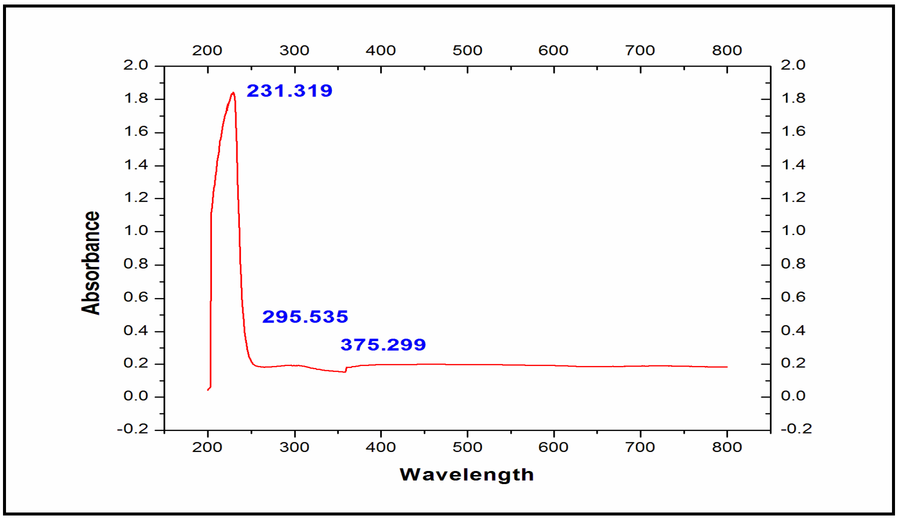

Figure 4.1: UV-Visible absorption Spectra of Pure ZnO Nanoparticles

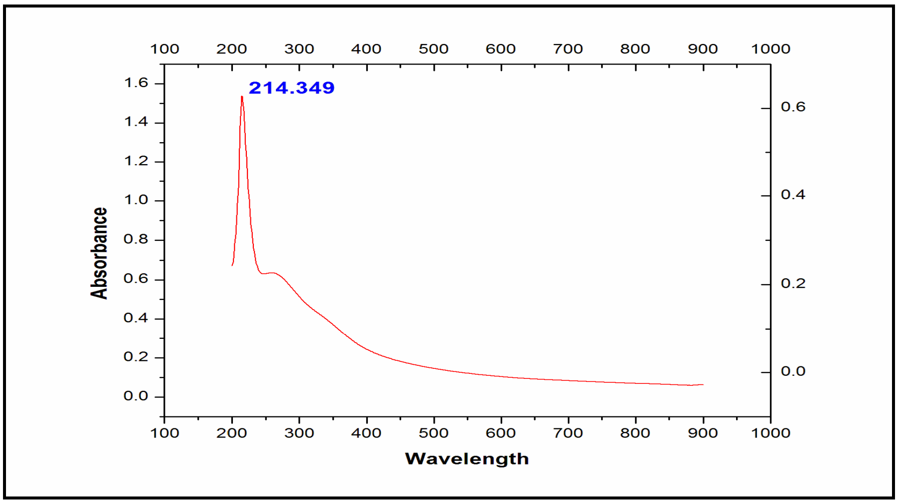

Figure 4.2: UV-Visible absorption Spectra of Cu doped ZnO Nanoparticles

For obtaining equation these values are taken me = 0.26 mo, mh = 0.59 mo, mo is the free electron mass, ε = 8.5, and Eg bulk = 3.3 eV. The prepared ZnO nanoparticles show peak absorbance at 372 nm which corresponds to average particle size of 5 nm

Photo Luminescence

Photoluminescence (PL) spectroscopy is a non-contact, non-destructive method of probing the electronic structure of materials. It is concerned with the emission of light after the optical excitation. Figure 5.1

and 5.2 represents PL spectra of undoped and doped ZnO Nanopowders. Basically ZnO Particles exhibit good Luminescence[15]. The spectra of undoped ZnO exhibits broad visible Luminescence around 350 nm which relates to blue emission in visible region of UV spectra. Cu doped ZnO Nanoparticles exhibit small high luminescence around 360 nm and small Intensity 378.326 in the UV region and three peaks in the visible region at 414.132nm,439.254nm and 519.241 nm that corresponds to Blue and green emissions. Cu doped ZnO when compared to pure ZnO contributes blue emission in the particles of ZnO.

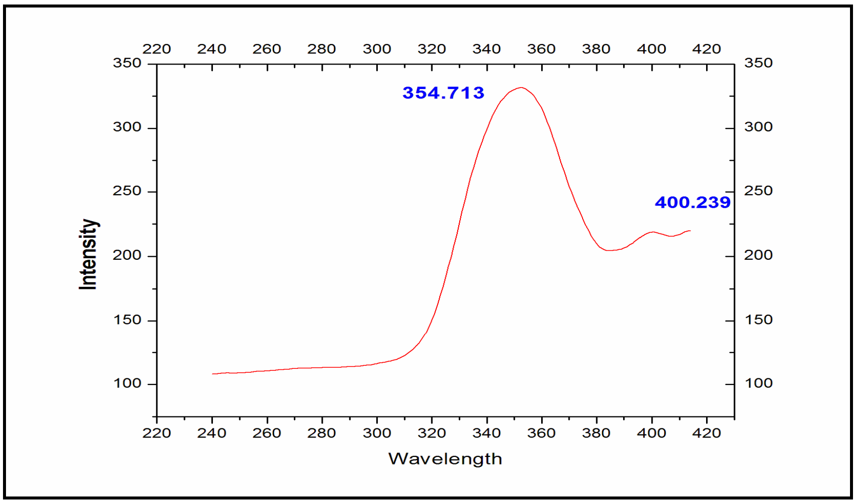

Figure 5.1: PL Spectra of Pure ZnO Nanoparticles

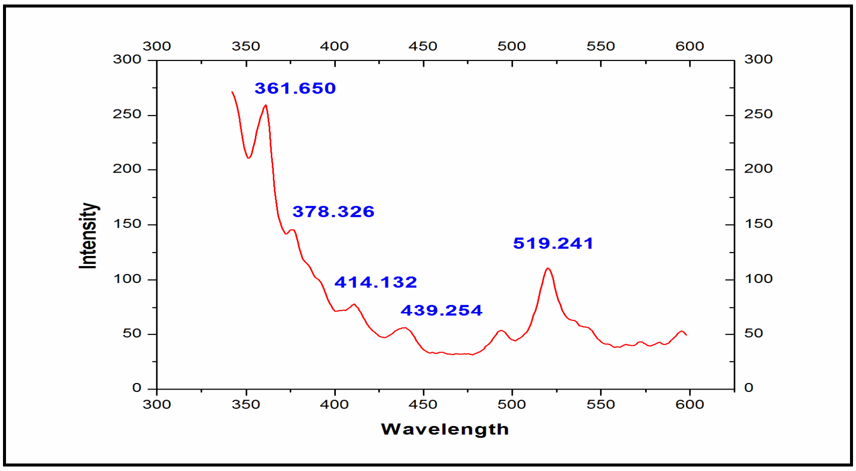

Figure 5.2: PL Spectra of Cu doped ZnO Nanoparticles

Conclusion

In this paper Pure and Cu doped ZnO Nanopowders were synthesized by Sol-gel method and further characterized using XRD, SEM, UV-Visible optical absorption and PL Characterizations. Structural, Morphological and optical properties of nanopowders were analyzed to compare the properties of pure and doped ZnO Nanoparticles. The structural analysis confirms formation of Wurtzite structure in both pure and doped samples. Increase in crystalline nature was observed by doping with copper. Particles of almost spherical in the case of pure and rod like in the case of Cu doped observed from morphological analysis in the case of Cu doped Nanoparticles. The structural properties of nanopowders were further confirmed from FTIR spectra. Optical properties reveal energy band gap of 3.81 eV in the case of Pure ZnO nanoparticles and 3.858 eV in the case of Cu doped ZnO Nanoparticles. ZnO Nanoparticles represent Luminiscence around 430 nm (Blue emission) where week Luminescence peaks around 440 nmand strong luminescence around 530 nm observed in the Doped ZnO Nanoparticles.It was very clear that The synthesized nanopowders with unique properties can further utilized in the Fabrication of optoelectronic devices .The Luminiscence resembles Usage of Nanopowders for Blue and Green emission LEDs.

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