

Photoluminescence properties of undoped and doped ZnO Nanoparticles S Dorendrajit Singh¹ and N Surajkumar Singh^{1, 2}

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Abstract

Luminescence properties are discussed by probing the Photoluminescence properties of undoped zinc oxide (ZnO) nanoparticles as well as ZnO nanoparticles doped with Terbium (Tb) at different doping concentrations. Various methods were employed to synthesize Zinc Oxide (ZnO) nanoparticles of different particle sizes. In one case, a low temperature Chemical Precipitation Method is employed for synthesis of ZnO nanoparticles. The particles are synthesized in Isopropanol medium with Diethanolamine (DEA) as capping agent. This procedure were followed for the synthesis of Tb doped ZnO nanoparticles using Zinc acetate and Terbium nitrate at different doping percentages of Tb. The prepared nanoparticles were characterized with X-ray diffraction (XRD). The XRD patterns show the pattern of typical ZnO nanoparticles and correspond with standard XRD pattern as given by the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 36-1451 showing hexagonal phase structure. The size dependence of the PL emission are elaborately discussed. PL intensity was enhanced due to Tb^{3+} doping and it was decreasing at higher concentrations.

Keywords: ZnO, nanoparticles, diethanolamine, photoluminescence, wet chemical method

1.0 INTRODUCTION

Zinc oxide (ZnO), which is a direct band gap semiconductor with a wide band gap of 3.37 eV having a large excitonic binding energy of 60 meV, at room temperature, good piezoelectric characteristics, chemical stability and biocompatibility, suggest a host of possible practical applications, notably in the areas of ultraviolet/blue emission devices for the fabrication of optoelectronic devices, solar cells, electrodes, and sensors [1-6]. During the last few years, ZnO has been synthesized and used as the cathode material for field emission [7-9]. So ZnO nanostructures were studied extensibly owing to their potential applications in nano-devices and optical materials [10-15]. In order to design the electrical, optical and magnetic properties of ZnO for the practical applications, the control of shape and crystal structure are very important, and the synthesis of novel nanostructures is highly desired [1]. However, it has been realized that tuning the band gap only by changing the morphology or size of nanocrystals is not well suited for some applications such as fluorescent imaging and nano-electronics [16, 17]. Doping ZnO with selective element has become an important route for enhancing and controlling its optical, electrical, and magnetic performance, which is usually crucial for their practical applications [1]. Rare earth (RE) ions incorporated into ZnO nanoparticles result in remarkable changes in the optical properties of ZnO [10, 18]. Of many RE ions, Tb^{3+} ion is an important dopant element for green emission band [10, 19]. ZnO: Tb^{3+} nanoparticles are assumed to be new type of green phosphor with interesting Photoluminescence (PL) properties [1,19]. In this work, various methods were employed to synthesize Zinc Oxide (ZnO) nanoparticles of different particle sizes in order to discuss in detail the size dependence of PL emission. Following one of the methods, Tb doped ZnO nanoparticles were synthesized. The PL emission of ZnO: Tb^{3+} nanoparticles are also discussed and they show emissions related to the intra 4f transitions of Tb^{3+} ions.

2.0 EXPERIMENTAL

2.1 Synthesis

ZnO nanoparticles were synthesized by five different methods. The first method is a Chemical precipitation method of synthesis using Zinc acetate in Isopropanol and Distilled Water medium with Diethanolamine (DEA) as capping agent at 60 °C. The synthesis was performed at different molarities of Zinc acetate. The synthesized ZnO nanoparticles were named A1, A2, A3, A4, A5 and A6 for further characterization and analysis. The second method is again chemical precipitation using Zinc acetate in Ethylene Glycol (EG) and Distilled Water medium with EG as capping agent. The samples are named as A. The third



method is Sol – gel synthesis using Zinc nitrate, Citric acid and Ethylene Glycol in the ratio of 1:5:20 mol%. The gel obtained is dried and finally annealed at 500 °C for 2hours to get the nanoparticles. Samples are named - N.

In the fourth method, the synthesis was performed by the same method as in the 1^{st} method but without the presence of any distilled water in order to see any possible influence of the presence of water in the earlier synthesis both in reaction mechanism as well as the size of the nanoparticles. In this method of synthesis where no water was present, the solution containing the reactants was heated at 60 °C for 1 to 2 hours until complete dissolution of the solvents. No precipitation was observed during this time. The clear sol was finally kept for aging at room temperature and precipitates were formed in 7 to 10 days. The sample so synthesized without water was named NA.

The fifth method is again Chemical precipitation and similar to the second method but here Zinc chloride has been used. Samples are named as C1, C2 and C3. Now we adopted the fourth method to synthesize Tb doped ZnO nanoparticles using required amounts of Zinc acetate and Terbium nitrate to obtained desired percentages of doping concentrations of terbium on ZnO.

2.2 Instrumentation

The samples were characterized for crystal phase identification by powder X-ray diffraction (XRD) using X'Pert PANalytical X-Ray Diffractometer with Cu-K_a radiation. Compositions of the synthesized nanoparticles were quantified by energy-dispersive analysis of X-ray energy-dispersive (EDAX) using X-ray (EDX) spectrometer attached to scanning electron microscope (SEM), FEI Quanta 250. The morphology and particle size of the samples were examined with transmission electron microscopy (TEM) by using JEOL JEM-2100. Photoluminescence measurements were taken on a LS 55 PerkinElmer fluorescence spectrophotometer with a Xenon lamp as excitation source at room temperature.

3.0 RESULT AND DISCUSSIONS

3.1 X-Ray Diffraction

Figure 1 shows the XRD spectra of the nanoparticle. Figure 1(a) is the spectra for the samples synthesized by various methods selecting one each from each of the methods. Figure 1(b) shows the XRD spectra of the Tb doped ZnO nanoparticles at different Tb doping concentrations. XRD spectra show peaks at positions in agreement with the standard JCPDS file for ZnO (Card No. 36-1451, a = b = 3.249 Å and c = 5.206 Å) and can be indexed as the hexagonal wurtzite structure of ZnO. The size of the nanoparticles were estimated by Debye-Scherrer's equation [20].

Where *d* is the crystallite size, λ is the wavelength of radiation used, θ is the Bragg angle and B is the full width at half maxima (FWHM).



Fig. 1: XRD spectra of (a) undoped ZnO (b) ZnO:Tb

Table 1 shows the size and crystal parameters of the nanoparticles selecting one sample each from the samples prepared by various methods.

Table 1. Particle size and Crystal parameters:

Sample	Size d (nm)	a (Å)	c (Å)	V (Å cube)
A4	49.13	3.25	5.22	47.97
NA	15.39	3.25	5.22	47.97
C1	34	3.23	5.19	47.14
N	28.55	3.24	5.20	47.57
A	33	3.25	5.20	47.69

The crystallite sizes of the ZnO:Tb nanoparticles were found to be 15.4 nm for the undoped ZnO and 17.4 nm, 18.8 nm, 16.7 nm, and 14 nm for ZnO:Tb³⁺ nanoparticles with Tb³⁺ doping concentrations of 0.52, 1.25, 1.51 and 3.40 atomic % respectively.

3.2 Transmission Electron Microscopy (TEM)

A TEM image showing the morphology and size distribution of ZnO sample NA (i.e., for the smallest particle size obtained in the present study) is shown in figure 2 (a). The sample was uniform with well distributed spherical particles with a size below 18 nm. This is consistent with estimated grain size (15.39 nm) from XRD peak broadening. TEM images for sample N giving average size of 29 nm, sample A3 giving average size of 31 nm, sample A with average size 33 nm, sample C1 having average size 34 nm and sample A4 giving average size of



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Fig. 2: TEM images of ZnO nanoparticles for sample (a) NA (having mean size 18 nm), (b) N (29 nm), (c) A3 (31 nm), (d) A (33 nm), (e) C1 (34) and (f) A4 (50 nm).



Fig. 3 TEM images of (a) undoped sample (NA) and (b) 1.51 atomic % ZnO:Tb.

50 nm are shown in figure 2 (b), (c), (d), (e) and (f) respectively. Figure 3(a) again show the TEM image of sample NA together with that of 1.51 atomic % Tb^{3+} doped samples giving a size range from 16 nm to 32 nm which is also consistent with the value (16.7) calculated from XRD.

3.3 Photoluminescence study

Photoluminescence properties of ZnO nanoparticles were studied by taking both the excitation and emission spectrum. Figure 4 shows the excitation spectra (a) of the



Fig. 4 Excitation spectra of ZnO nanoparticle synthesized by (a) 1st method and (b) by different methods.

samples synthesized by the 1st method and (b) of samples synthesized from different methods, taken in the excitation range from 200nm to 350nm by monitoring emission at 383nm. Three peaks are observed at 240nm, 256nm and 280nm. These wavelengths were used as excitation wavelengths for further study of emission spectra.



Fig. 5 Emission spectra of ZnO nanoparticles synthesized by the 1st method at different excitation wavelengths.



The emission spectra of various samples had been studied to observe its dependence on the size of the particles as well as on the excitation wavelengths. Figure 5 shows the emission spectra, taken in the wavelength range of 350nm to 600nm, of the samples synthesized by the 1st method at different excitation wavelenmgths. Figure 5(a). shows the emission spectra of sample A1 (having size 40nm) giving emission peaks at 387nm, 415nm, 479nm and 525nm. Intensity of emission increases as the excitation wavelength. Then the Intensity decreases when excited with 300nm and two other peaks at 420nm and 460nm are observed. It is found that intensity of emission increases as the excitation wavelength increases until it becomes highest when excited with 280nm wavelength. Figure 5(b) is for the sample A2 (having size 43nm), giving similar emission pattern as to sample A1. Figure 5(c), (d), (e) and (f) are for sample A3 (size 31nm), sample A4 (size 49 nm), sample A5 (size 42 nm) and sample A6 (size 31 nm) respectively. Sample A4 having highest particle size (49nm) shows most intense UV emission and lower intensity visible emissions. Sample A3 having lowest particle size (31nm) shows lowest intensity and shoulder like peak at UV, but higher intensity for the visible emissions thereby indicates the presence of intrinsic defects. Very sharp peak at UV (NBE) shows high purity and finer crystalline quality.



Fig. 6 Emission spectra of (a) ZnO nanoparticles synthesized by the 1st method and (b) nanoparticles from different methods when excitated with 280 nm wavelength.

Figure 6(a) shows emission spectrum taken in the wavelength range of 350nm to 600nm when excited by 280 nm wavelength only for the samples shown in figure 5 and figure 6(b) shows the emission for the samples obtain from different methods of synthesis when the excitation was done by 280 nm wavelength. Emissions peaks at 383nm, 387nm, 415nm, 416nm, 480nm and 525nm were observed. The fluorescence at 383 nm to 387 nm corresponds to the characteristic near band edge (NBE) emission. The violet luminescence (415, 416 nm) has been assigned to electronic transitions from Zn_i level to the valence band corresponding to shallow level emissions (SLE) [21-23]. Deep level emissions (DLE) band had also been identified and at least two different defect origins (V $_{o}$ and V $_{Zn})$ with different optical characteristics were claimed to contribute to this deep level emission [21]. The energy level corresponding to anion vacancies (V_{Zn}) are situated 2.7 eV below the conduction band is found to be in agreement with the 460 nm emission in the blue region [22].



Fig. 7 PL emission spectra ZnO nanoparticles having same size exhibiting similar pattern. (a). for pair of samples having size 31 nm, (b). for pair of samples having size 34 nm, (c). for pair of samples having size 40 nm.

Among the samples of ZnO nanoparticles synthesized using different methods, we find three pairs of samples having same particle size, namely, samples A3 and A6 having size 31nm, samples C1 and C3 having size 34nm and samples A1 and C2 having size 40nm. Interestingly these nanoparticles having same size show emission peaks at same positions and very similar pattern of intensity variation. These facts establish the size dependence of PL spectra. Figure 7 show these similar patterns in the emission spectra for each pair.



Fig. 8 Gaussian deconvulation of PL emission spectra.

In order to demonstrate the size dependence of the PL emission, deconvulation were performed on the spetra taken with the 280 nm excitation wavelength, shown in



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figure 6(b), for the samples having different particle sizes as obtained from different synthesis methods. The PL emission is very well fitted with three to four Gaussian peaks. The Gaussian fitting of the emission spectra are shown in figure 8 (a) to 8 (f). The emission spectra of sample NA having lowest particle size is found to fitted well with three Gaussian peakscentred at 416 nm, 487 nm and 528 nm. The emission spectra of sample A4 having the highest particle size is also found to fitted with three peaks which are centered at 381 nm, 406 nm and 478 nm. The central position of the Gaussian components were observed to be changing along with the variation in the emission intensity. The variation of the first peak position is depicted in figure 9 (a).



Fig. 9 (a) First Gaussian components and (b) variation of Max. Int. and peak position with the variation in the size.

As the size of the nanoparticles decreases from 49 nm to 15 nm, the peak position changes from 382 nm to 385 nm with decreasing in emission intensity and as the position further changes from 385 nm to 416 nm, the emission intensity again increases. So the size dependence of the UV peak in the PL emission of the ZnO nanoparticles is well demonstrated in this experimrnt. The figure 9 (b) further show the plot of the variation of maximum intensity and peak position as the particle size changes.



Fig. 10 Schematic Energy level diagrams of various defect levels responsible for the observed emissions in ZnO nanoparticles.

Now figure 10 shows the schematic energy level diagram of the corresponding defect levels in the ZnO nanoparticles responsible for the observed emission peaks. The energy level from the interstitial zinc Zn_i energy level to the

valence band and conduction band to the antisite oxygen O_{Zn} defect energy level is 2.9 eV and 2.38 eV respectively and they are consistent with the energy level of the blue emission (2.98 eV) and green emission (2.38 eV) in this study. The energy level corresponding to anion vacancies (V⁻_{Zn}) are situated 2.7 eV below the conduction band. Energy levels for neutral oxygen vacancy V₀ and singly ionized oxygen vacancy V⁺₀ are 2.57 eV and 2.36 eV respectively from the valence band [20-27]. These levels are responsible for the various emissions at the visible region.

Now Figure 11 (a) shows the emission spectra of ZnO:Tb³⁺ nanoparticles, at different percentages of Tb doping concentrations, taken in the wavelength range of 350 nm to 700 nm at 240 nm excitation wavelength. Figure 6(b), 6(c) and 6(d) shows the emission spectra when the excitation was done by 255 nm, 285 nm and 344 nm wavelengths respectively. The doped samples show emission peaks centred at 405 nm, 420 nm, 445 nm 484 nm and 530 nm for all the Tb concentrations. The peak intensity for the doped samples increased up to 1.25 at % of Tb³⁺, beyond that it decreases as the concentration of doping increases.



Fig. 11 PL Emission at different Tb concentrations taken with excitation wavelength (a). 240 nm, (b). 255 nm, (c). 285 nm and (d). 344 nm.

This may be due to the concentration quenching of the Tb^{3+} ions. So, the optimum dopant concentration is found to be 1.25 at % in this study. The peaks at 405, 420 and 445 are attributed to different defects associated with the host lattice. The bluish green and green emission peaks at 460, 484 and 530 arise from Tb^{3+} 4f-4f transitions [10, 28, 29,30]. Figure 12 presents a schematic drawing for possible mechanisms of electron transitions to illustrate the mechanism of excitation and emission process according to the results in this work. When the ZnO:Tb³⁺ nanoparticles are excited by the 240 nm line of a Xe lamp, the process of



electronic transitions occur from the valence band (VB) to an exciton band [10].

Excited states ZnO CB $^{5}D_{3}$ III ⁵D₄ 240 400-700 nm I E mu E Surface states 460 389 530 184 VB

Fig. 12 Schematic drawing for possible mechanisms of electron transitions to illustrate the mechanism of excitation and emission

And then a series of nonradiative process is performed, which are denoted by the dotted lines in the figure. Then they are trapped at surface states of particles and consequent recombination from surface states to VB results in a broadband emission. These excited carriers are also trapped at Tb^{3+} centres and leads to the characteristic emission peaks of Tb^{3+} which are being denoted by solid lines in the diagram [28]. The emission at 460 nm is originated from Tb^{3+} 4f-4f transition ${}^{5}D_{3} - {}^{7}F_{3}$ [29]. The emission at 484 nm and 530 nm are assigned to be originated from ${}^{5}D_{4} - {}^{7}F_{6}$ [31, 32] and ${}^{5}D_{4} - {}^{7}F_{5}$, respectively.^[10] The emission at 490 nm is also assigned to ${}^{5}D_{4} - {}^{7}F_{6}$ of Tb^{3+} .^[33] The other peaks at 405, 420 and 445 nm probably originate from defect state such as Zn and oxygen interstitials and oxygen vacancies.^[24, 34, 35]

4.0 CONCLUSION

ZnO nanoparticles in different sizes were successfully synthesized. Smaller size particles give stronger visible emissions and weaker UV emissions. Larger size particles give weaker visible emissions and stronger UV emissions. PL spectra are dependent on particle size. There is quenching of emission intensity as the Tb doping concentration increases and the optimum dopant concentration is found to be 1.25 at % in this study. The Tb³⁺ ions have an important effect on the UV emission of ZnO. In addition, the characteristic emissions of Tb³⁺ ions are observed. For all samples carrier relaxation from excited states of ZnO hosts to dopant result in the characteristic emission of Tb³⁺ ions.

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