



## Structural and Photoluminescence properties of Magnesium doped ZnO Nanoparticles

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### Abstract

Undoped Zinc oxide (ZnO) nanoparticles as well as ZnO nanoparticles doped with Magnesium (Mg) were synthesized by wet chemical precipitation method using Zinc acetate and Magnesium acetate in Ethylene glycol and distilled water medium. 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. Luminescence properties are discussed by probing the Photoluminescence properties of undoped zinc oxide (ZnO) nanoparticles as well as ZnO nanoparticles doped with Magnesium at different doping concentrations.

**Keywords:** ZnO:Mg, nanoparticles, ethylene glycol, photoluminescence.

### 1.0 INTRODUCTION

Owing to a direct wide band gap (3.37 eV), large exciton binding energy (60 meV), and superior conducting properties based on oxygen vacancies, the wurtzite-structured Zinc oxide (ZnO) has become one of the most promising materials for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region and transparent conducting and piezoelectric materials for fabricating solar cells, electrodes, and sensors.<sup>[1-6]</sup> It is well known that among the wide band gap semiconductors, addition of dopants often induces dramatic changes in their electrical and optical properties. 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.<sup>[1]</sup> By doping with wider band-gap material<sup>[7]</sup>, the band gap of ZnO nanoparticles can be tuned for manufacturing light-emitting devices operating in a wider wavelength region. ZnO is an ideal material for UV emission; but the intensity of UV emission is weak. However, doping with Group II elements (Cd, Mg) may modulate the value of the band gap and increase the intensity of UV emission<sup>[8]</sup>. Mg-doped ZnO nanostructures are very interesting owing to their unique optical properties.

In this work, the Mg doped ZnO (ZnO:Mg) nanoparticles were synthesized by a simple and low-cost wet chemical precipitation method. The structural and PL properties of the ZnO:Mg nanoparticles were discussed in detail with the investigation of the effect of magnesium doping and

annealing on the structural and optical properties of ZnO nanoparticles.

### 2.0 EXPERIMENTAL

#### 2.1 Synthesis

2gms of Zinc acetate and appropriate amount of Magnesium acetate to make the desired doping percentage was dissolved in 50ml distilled water. 150ml Ethylene glycol was added to the above solution. 6gm Urea was then added to the above solution. The solution was heated on a round bottom flask fitted with condenser and the temperature was maintained at 140°C for 2 hours. The precipitates formed were collected by centrifugation after washing with Methanol and finally with distilled water. The precipitates were dried at around 80°C to 100°C for 24 hours. The samples were finally annealed at different temperature for 2 hours.

#### 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<sub>α</sub> radiation. 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(a) shows XRD spectra of ZnO:Mg nanoparticles with different Mg concentrations (0, 1, 3, 5, and 10 at%)

annealed at the temperature of 700°C for 2 hours. The sample with 0 at% correspond with the undoped ZnO. XRD spectra show peaks at positions in agreement with the standard JCPDS file for ZnO (Card No. 36-1451,  $a = b = 3.249 \text{ \AA}$  and  $c = 5.206 \text{ \AA}$ ) and can be indexed as the hexagonal wurtzite structure of ZnO.

Since the ionic radius of  $\text{Mg}^{2+}$  (0.066 nm) is smaller than that of  $\text{Zn}^{2+}$  (0.074 nm) the decreasing of the lattice constant implies the substitution of Mg to Zn in the studied samples [10, 11]. Table 2 gives the crystallite size of nanoparticles along with the positions of (101) XRD peak of the 5 at% Mg doped ZnO:Mg nanoparticles annealed at different temperatures. It is also observed here that the (101) peaks

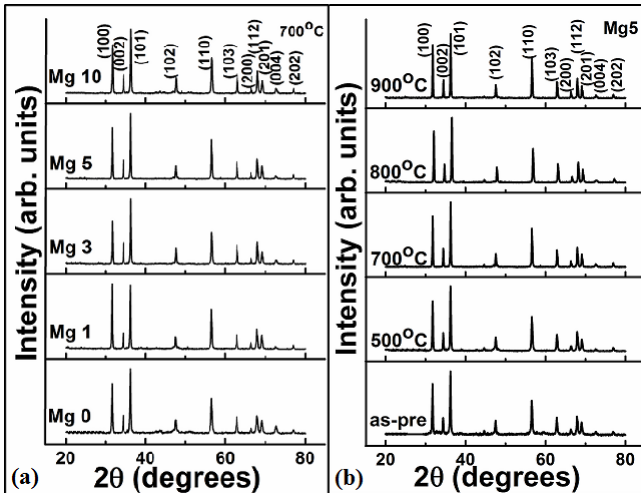


Fig. 1: XRD spectra of (a) ZnO:Mg at diff. Mg doping (b) 5 at% Mg doped ZnO:Mg at diff. temp.

Figure 1 (b) shows the XRD spectra of 5 at% ZnO:Mg nanoparticle samples annealed at different temperatures. The size of the nanoparticles were estimated by Debye-Scherrer's equation [9].

$$d = \frac{0.9\lambda}{B \cos \theta} \dots\dots\dots (1)$$

Where  $d$  is the crystallite size,  $\lambda$  is the wavelength of radiation used,  $\theta$  is the Bragg angle and  $B$  is the full width at half maxima (FWHM).

The lattice parameters extracted from XRD data and crystallite size of nanoparticles along with the positions of (101) XRD peak are given in tables 1 and 2. As can be seen from the table 1, the (101) peaks of ZnO:Mg moves from 36.22° to 36.34° as the Mg content increased to 10 at% and the corresponding lattice parameters extracted from XRD data changed from 5.210 Å to 5.1907 Å for the lattice parameter  $c$ .

Table 1: Lattice parameters of ZnO:Mg at various at% of Mg

Mg %	(101) Peak position	Size D (nm)	a (Å)	c (Å)
0%	36.2296	35.50	3.2463	5.210
1%	36.2176	43.23	3.2534	5.2117
3%	36.3047	39.83	3.2451	5.1964
5%	36.2696	42.44	3.2487	5.2047
10%	36.3407	34.06	3.2463	5.1907

Table 2: Lattice parameters of 5 at% ZnO:Mg at diff. temp.

Temp	(101) Peak position	Size D (nm)	a (Å)	c (Å)
as-pre	36.2207	36.03	3.2523	5.2117
500°C	36.2555	38.75	3.2499	5.2047
700°C	36.2696	43.22	3.2487	5.2047
800°C	36.5725	42.45	3.2193	5.1959
900°C	36.2879	45.25	3.2463	5.1977

shifted their position from 36.22° to 36.28° as the annealing temperature increases to 900°C. The shifting of the peak position to higher angles and decreasing values of the lattice parameters in the table 2 indicates more substitution of  $\text{Zn}^{2+}$  ions by  $\text{Mg}^{2+}$  ions as the samples are annealed at higher temperatures. However the increase of calculated crystallite sizes from 36.03 nm to 45.25 nm shows that there is size agglomeration with increase of annealing temperature.

### 3.2 Photoluminescence study

PL is very sensitive to the quality of crystal structure and to the presence of defects. The band-to-band excitation of ZnO promotes electrons from the valence band to the conduction band, leaving holes in the valence band. The holes migrate from the valence band to deep levels and recombination occurs between electrons from either the conduction band or shallow donor levels and trapped holes on deep levels [12,13].

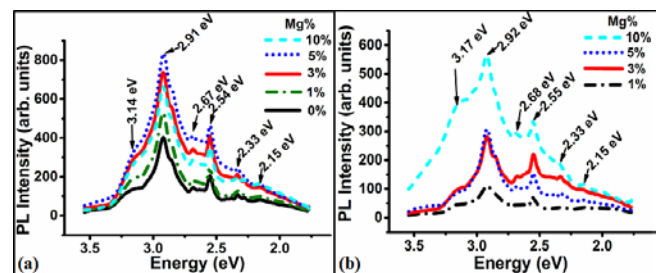


Fig. 2 Emission spectra of (a) as-prepared ZnO:Mg (b) 700°C annealed ZnO:Mg.

Figure 2(a) shows the PL emission spectra of ZnO:Mg nanoparticles, at different Mg doping percentages, taken when excited with 238 nm source. Emission peaks are observed at 3.14 eV, 2.91 eV, 2.67 eV, 2.54 eV, 2.33 eV

and 2.15 eV and the intensity is found to be increasing as the Mg at% increases upto 5 at% then it decreases for 10 at%. Figure 2 (b) shows the PL emission of the ZnO:Mg samples annealed at 700°C. It is seen that the intensity increases as the Mg content increases upto 10 at%. As to explain the PL emission mechanism of the nanoparticles, Gaussian deconvolution were performed on the above emission curves of figure 2 and representative deconvoluted peaks and convoluted curves were shown in figure 3.

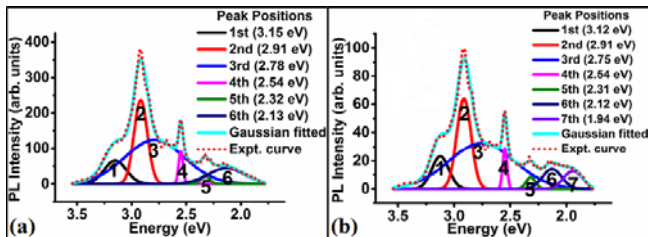


Fig. 3 Gaussian deconvolution of PL emission spectra for (a) as-prepared ZnO (b) 700°C annealed 1 at% ZnO:Mg.

Figure 3 (a) is the deconvolution of the as-prepared undoped (0 at%) ZnO nanoparticle. It is found that the emission curve can be fitted well with six bands. As shown in Figure 3 (a), the first deconvoluted peak at 3.15 eV (393 nm) correspond to the near band edge (NBE) emission. Generally, oxygen vacancy ( $V_O$ ) and interstitial zinc ( $Zn_i$ ) are donors, while zinc vacancy ( $V_{Zn}$ ) and interstitial oxygen ( $O_i$ ) are acceptors in ZnO. Among these point defects, only  $Zn_i$  is a shallow donor and the corresponding defect level could be located slightly below the conduction band-edge. Lin et al. [14] pointed out that the energy gap from the  $Zn_i$  level to the valance band is about 2.9 eV. Zeng et al. [15] experimentally assigned the violet shoulder at 415 nm in ZnO nanoparticles to  $Zn_i$ . In our work, an emission around 2.91 eV (426 nm) is likely associated to an electron transition from a shallow donor level of  $Zn_i$  to top level of valance band [15], also this peak shift to the lower energy with increasing Mg content and this shifting will again depicted well in the figure 4.

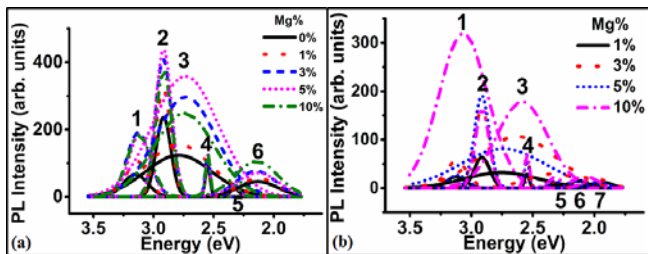


Fig. 4 Gaussian deconvoluted peaks of PL emission spectra for (a) as-prepared ZnO:Mg and (b) 700°C annealed ZnO:Mg.

The broad emission band centered at blue region around 2.78 eV (446 nm) can be attributed to the transition from extended  $Zn_i$  states, which are slightly below the simple  $Zn_i$  state, to the valance band [15]. The fourth peak at 2.54 eV (488 nm), is assumed to be commonly originated from recombination of the photoexcited holes with the electrons occupying the singly ionized oxygen vacancies [13]. The green emission at 2.32 eV (534 nm) and 2.13 (582 nm) is more preferably attributed to the various ionisation states of  $V_O$  [16].

Figure 4 shows the complete plots of the all Gaussian deconvolution components for the PL emissions of the samples for different Mg concentrations. Figure 4 (a) is for the as-prepared samples and (b) is for the 700°C annealed samples. The peak positions are observed to be shifting to the lower energy side as the Mg concentration increases.

#### 4.0 CONCLUSION

Mg doped ZnO nanoparticles were synthesized using wet chemical precipitation method. XRD characterization of the samples show the samples can be identified as having hexagonal wurtzite phase. Intensity of PL increases with increase of Mg doping concentration upto 5 at% in as-prepared samples and then decreases as the concentration increases to 10 at%. When the ZnO:Mg samples were annealed at 700°C, the intensity increases with the Mg doping concentration upto 10 at%.

#### References:

1. A. K. Mishra, et al., J Appl Phys, 102 (2007) 103514.
2. S. Maensiri, et al., J Crys Growth, 289 (2006) 102.
3. R. N. Gayen, et al., Indian J Pure & Appl Phys, 49 (2011) 270.
4. N. Pandey, et al., Indian J Pure & Appl Phys, 50 (2012) 260
5. H. Zhou, et al., Appl Phys Lett, 80 (2002) 210
6. S. Hong, et al., Appl Phys Lett, 83 (2003) 4157.
7. L. Kumari, et al., Ceram Int, 35 (2007) 3355.
8. O. Ohotomo et al, Appl Phys Lett, 72 (1998) 2466.
9. P. K. Sharma, et al., J Coll Int Sc, 345 (2010) 149.
10. X. Long, et al., Chi Phys B, 19 (2010) 027202.
11. F. K. Shan, et al., J Appl Phys, 95 (2004) 9.
12. R. Kripal, et al., Spectrochim Acta A, 79 (2011) 1605.
13. T. P. Rao., et al., J Alloy Compd, 541 (2012) 495.
14. B. X Lin, et al., Appl Phys let, 79 (2001) 943.
15. H. B Zeng, et al., Adv Func Mater, 20 (2010) 561.
16. W. W. Zhong, et al., Appl Surf Sci, 257 (2011) 9318.