# Thermoluminescence of Mn doped ZnO Nanoparticles

Binapani Goswami, Ranjit Singha

**Abstract**

Undoped and 2wt%, 4wt%, 6wt% Mn doped ZnO nanoparticles were synthesized by using Chemical Co-precipitation method. X-ray diffraction data revealed the formation of hexagonal wurtzite phase of mean crystallite sizes 26.64 nm, 21.66 nm, 23.60 nm and 22.31 nm respectively obtained by Scherrer formula for undoped and Mn doped ZnO nanoparticles of different concentrations. Thermoluminescence studies of the nanoparticles of the above samples show TL peaks in three regions occurring around 346-361, 404 and 424-428 Kelvin. The thermal activation energy(E) of the peaks calculated by using CGCD technique are found to be 0.54 eV, 0.7eV and 0.83 eV respectively, with the first peak following nearly second order kinetics while the other two follow nearly first order kinetics. This result is in close agreement with those obtained by Chen's Peak shape method

**Index Terms**— CGCD- Computerised Glow Curve Deconvolution, chemical co-precipitation , doping, FOM, order of kinetics, peak shape method,, thermal activation energy (E), thermoluminescence(TL), X-ray diffraction, ZnO nanoparticles

## 1 Introduction

THERMOLUMINESCENCE (TL) is the phenomenon in which substances like semiconductors or insulators, irradiated with radiations like X-rays, γ-rays etc. emit light when it is heated gradually. This emission is due to the thermally induced recombination of charges (electrons and holes) at the luminescent centers.[1]. The light emitted by a thermoluminescent material is described by a 'glow curve', a curve drawn between emitted light intensity and temperature. The shape and position of the glow curve can be used to evaluate various important parameters of the trapping states viz. the thermal activation energy (E) or the trap depth below the conduction band, order of kinetics (b), frequency factor (s) etc [2]. Thermoluminescent materials popularly called phosphors are widely used in dosimetry for ionizing radiation and in many more fields.

ZnO being an efficient optical material is expected to show a good thermoluminescence behavior. The aim of the present investigation is to study the thermoluminescent charecteristics of ZnO nanoparticles when doped with transition elements.

## 2 Materials And Methods

### 2.1 Preparation of ZnO and Mn Doped ZnO nanoparticles

To prepare undoped ZnO nanoparticles 100ml solution each of 0.05M zinc acetate dihydrate [Zn(CH3COO)2,2H2O] and 0.4M Sodium hydroxide in deionized water were prepared and mixed together by constant stirring at $70^0$C for 30 minutes with the help of a magnetic stirrer. During this, 2wt% PolyVinylPyrolidone (PVP) i.e. 2gm PVP in 100ml deionized water at $70^0$C was added drop wise to the above mixture. The precipitates which get formed are separated from the solution by filtration, washed several times with deionized water and absolute ethanol and then dried in atmosphere for several days to obtain ZnO nanoparticles in powder form. For Mn doped ZnO nanoparticles with Mn content 2wt%, 4wt% and 6wt% of 0.05M Zinc acetate dihydrate, 0.05M Zinc acetate dihydrate and required amount of Manganese acetate tetra hydrate in 100ml deionized water were mixed together and stirred at $70^0$C for 2 hrs. 0.4M Potassium hydroxide solution in 100ml deionized water at same temperature was prepared and added drop wise to the above solution. The precipitate which gets formed were separated from the solution by filtration, washed several times with distilled water and absolute ethanol and then dried in atmosphere for several days to obtain Mn doped ZnO nanoparticles.

### 2.2 Characterization

The prepared samples were irradiated at room temperature by X-rays from a copper target for 20 minutes, operated at 30 KV and 8 mA and TL is recorded with TLD reader (NUCLEONIX-TL 1009I). The XRD (Brukar D8) and TEM (Model JEOL, JEM-2100) measurements were carried out at IASST, Gorchuk and SAIF, NEHU respectively.

## 3 RESULTS AND Discussions

### 3.1 Structural Study

Figure 1 and figure 2 show the previously reported X-ray diffraction pattern and TEM micrograph of the prepared undoped and Mn doped ZnO nanoparticles [3]. Diffraction peaks confirm the formation of hexagonal wurtzite phase of ZnO. No additional peaks which may belong to impurity phases are observed which implies that the doping amount is within the solubility limit. Crystalline sizes as calculated by Scherer formula is within the range 26-20nm.

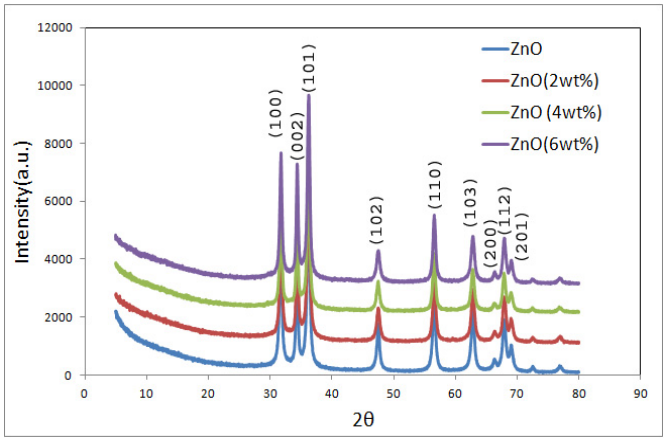


Fig.1. XRD spectra of ZnO and Mn doped ZnO nanoparticles which reveal the hexagonal wurtzite phase of ZnO without any additional impurity peak.

TEM images shown in figure 2 are found to be in agreement with the XRD results and show particles with diameters within the range 20-26 nm but the particles are without any definite shape.

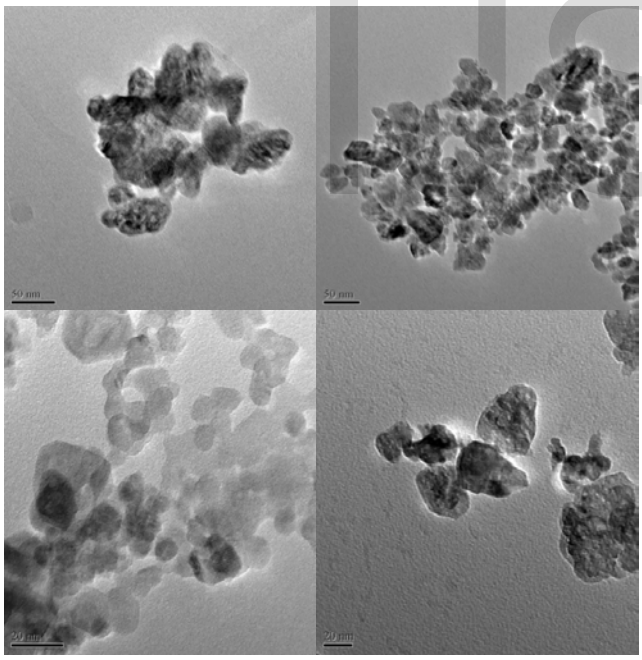

Fig.2. TEM images of ZnO and Mn doped ZnO nanoparticles.

Figure 3 shows the TL glow curves of X-irradiated undoped ZnO nanoparticles and ZnO doped with 2wt%, 4wt% and 6wt% of Mn. Apparently it looks that there is a peak around 360 K and another at around 428 K. However on close observation and analysis of the glow curves it is observed that there are three peaks occurring in total. Peak I occurring in the region 346-361 K, Peak II at around 404 K and Peak III in the region 424-428 K as shown in figure 4 (A-D). The average values of thermal activation energies of the peaks are found to be 0.54eV, 0.7 eV and 0.83 eV with corresponding values of b=1.9, 1.2 and 1.3 for peak I, II and III respectively. The CGCD of the glow curves using Kitti's equation resolve the curves into following components as shown in Fig 4 (A-D): (A) Undoped ZnO nanoparticles sample gives peaks at 361 and 405 K having thermal activation energies 0.54eV and 0.7 eV with b=1.9 and 1.25 respectively; (B) 2wt% doped sample gives peaks at 356 and 404 K having thermal activation energies 0.54eV and 0.7eV with b=1.8 and 1.2 respectively; (C) 4wt% doped sample gives peaks at 355 and 424 K having thermal activation energies 0.54eV and 0.86eV with b=1.9 and 1.3 respectively, and (D) 6wt% doped sample gives peaks at 346 and 428 K having thermal activation energies 0.56eV and 0.8eV with b=2.0 and 1.3 respectively. The summary of the resolved peaks, their thermal activation energies and order of kinetics are given in table 1.

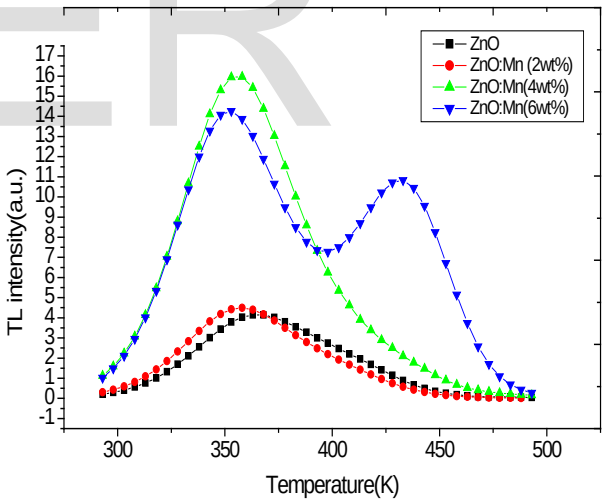


Fig. 3. TL glow curves of X-ray irradiated ZnO and Mn doped ZnO nanoparticles.

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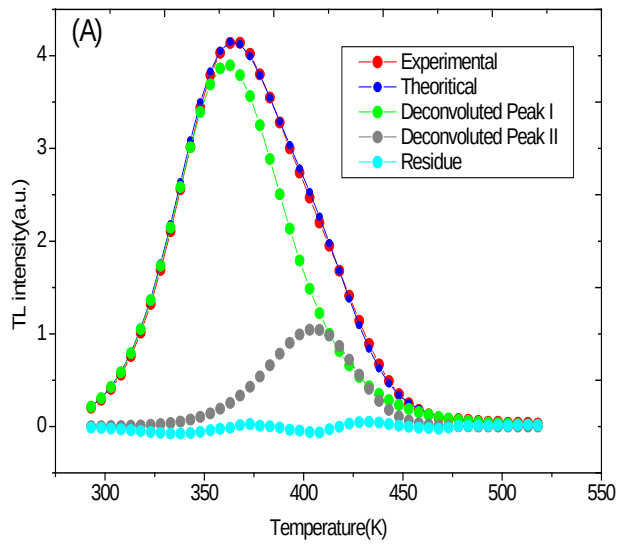


Fig 4(A). Deconvoluted glow curve of undoped ZnO nanoparticles showing the component peaks I and II with residue of curve fitting.

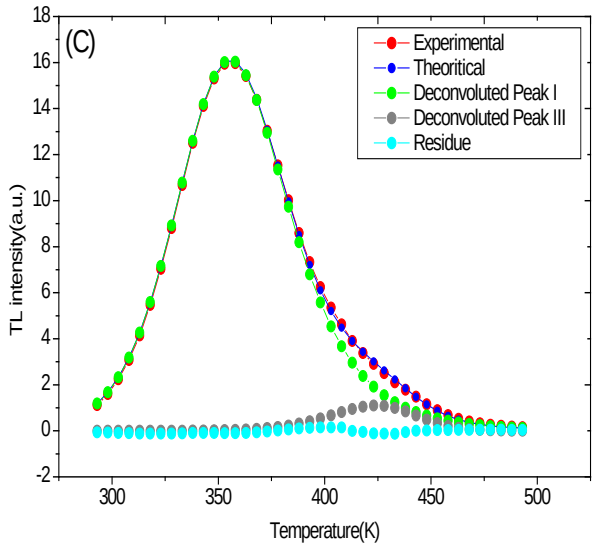


Fig 4(C). Deconvoluted glow curve of ZnO:Mn (4wt%) nanoparticles showing the component peaks I and III with residue of the curve fitting.

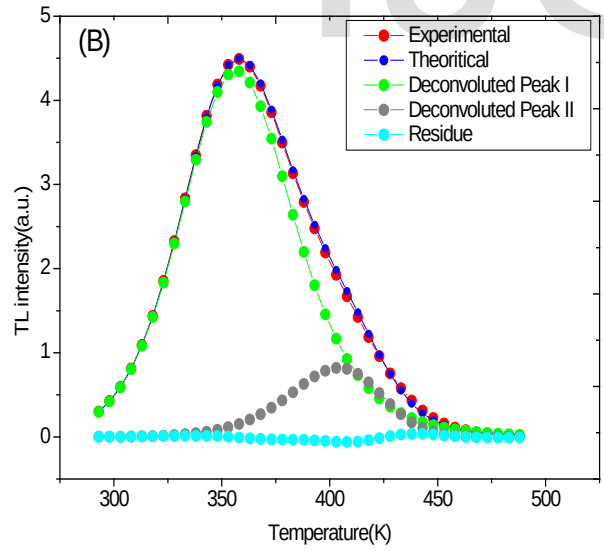


Fig 4(B). Deconvoluted glow curve of ZnO:Mn(2wt%) nanoparticle showing the component peaks I and II with residue of the curve fitting.

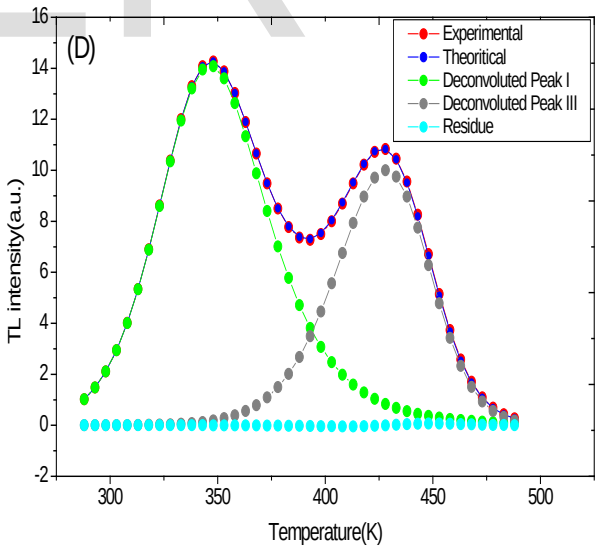


Fig 4(D). Deconvoluted glow curve of ZnO:Mn (6wt%) nanoparticle showing the component peaks I and II with residue of the curve fitting.

Chen's peak shape method [7] is also employed to determine different kinetic parameters like, activation energy (E), order of kinetics (b) etc. of the deconvoluted peaks. The values of E obtained are in close agreement with those obtained by CGCD and are summarized in table 1. The figure of merit (FOM) [8] of deconvolution for all the samples are found to be <1.9%, which shows a good agreement between experimental and theoretical data.

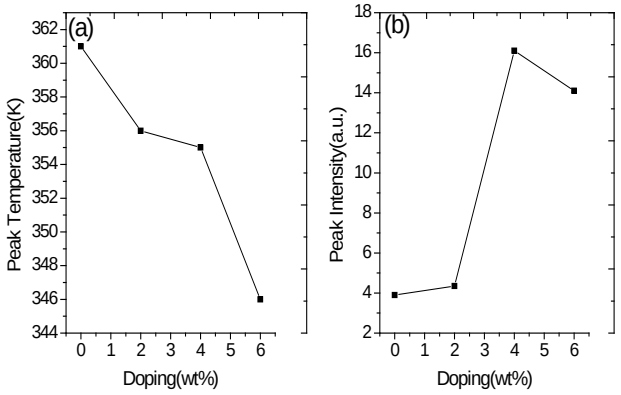


Fig.5. Plot of (a) Doping conc.Vs Peak temperature and (b) Doping conc.Vs Peak intensity of peak I of the glow curve of the nanoparticles.

In the work of Jagannatha Reddy et. al (2011) on TL of ZnO nanoparticles synthesized by combustion process, a single broad peak located at around 343°C is observed [4]. Recently V. R. Orante-Barron et. al. (2015) observed two peaks located at around 149°C and 308°C [5]. Thus the peak temperatures observed in our case are very much different from these observations. This disagreement may be due to the incorporation of Mn into the crystal as TL is very much sensitive to the presence of any kind of impurity in the crystal. In the glow curves the intensity is found to increase as the doping level increases but it decreases again in 6 wt% doped ZnO. The TL intensity of 4wt% Mn doped ZnO nanoparticle is almost four times that of the undoped and 2wt% Mn doped particles [Figure 4(b)]. This shows that a proper concentration of doping element can significantly enhance the TL emission. This enhancement can be attributed to the formation of traps. It has been seen in figure 4(a) that the glow peak I occurring in the region 346-361 shift from 361 to 346 K with increase of Mn doping concentration which is an indication that the second order kinetics (b=2) may be predominating the TL process [5]. The data in table 1 gives 'b' value nearly equal to 2, which is the value for second order kinetics. This supports the shifting of the peak I. towards lower temperature side.

## 4 Conclusions

ZnO nanoparticles both doped and undoped are successfully prepared by wet chemical synthesis process. Structural characteristics are studied by XRD and TEM. Synthesized nanoparticles are exposed to X-radiation and the TL emission is recorded. The peak temperature for peak I is found to shift towards lower temperature as the doping concentration is increased, indicates a non first order kinetics.In fact its b value obtained from CGCD and Peack shape method indicates nearly a second order peak. In this study on ZnO nanoparticles we observe TL maxima at different positions from those observed by earlier workers. It may be due to the generation of small component peak which is confirmed by CGCD technique. Also doping may play a significant role here as TL is highly sensitive to the presence of any impurity in the crystal.

TABLE 1
TL Parameters of ZnO and ZnO:Mn Nanoparticles

| SAMPLE | PEAK I (346-361 K) | | | | PEAK II (404 K) | | | | PEAK III (424-428) K) | | | | FOM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tm(K) | E(eV)(CGCD) | b | E′ (PS) (eV) | Tm | E (CGCD) | b | E′ (PS) (EV) | Tm | E (CGCD) | b | E′ (PS) (EV) | |
| ZnO(undoped) | 361 | 0.54 | 1.9 | 0.55 | 405 | 0.7 | 1.25 | 0.65 | | | | | 1.93% |
| ZnO (2wt% doped) | 356 | 0.54 | 1.8 | 0.56 | 404 | 0.7 | 1.2 | 0.68 | | | | | 1.13% |
| ZnO (4wt% doped) | 355 | 0.54 | 1.9 | 0.53 | | | | | 424 | 0.86 | 1.3 | 0.83 | 1.33% |
| ZnO(6wt% doped) | 346 | 0.56 | 2.0 | 0.56 | | | | | 428 | 0.80 | 1.3 | 0.82 | 0.26% |
| AVERAGE | | 0.54 | 1.9 | 0.54 | | 0.7 | 1.2 | 0.67 | | 0.83 | 1.3 | 0.83 | |

*Tm- Peak temp., E- Thermal activation energy (CGCD), b- Order of kinetics, E′(PS)- Thermal activation energy (Peak shape method) FOM- Figure of merit*

### 7.2 Acknowledgments

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