

# The Calcinations Temperature Dependent Structural and Optical Behaviour of ZnMnO<sub>3-Δ</sub> Nanocrystalline

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The materialistic particles have remarkable technological application at size of nano scale (1-100 nm). The metal such as zinc and manganese have enhanced properties in field of Optical, Magnetic, Electrical and Biogenic field because of valence d-orbital electrons with great efficiency. In present work, the researcher synthesized pure ZnO and 10% Mn doped ZnO nanoparticles via microwave irradiated chemical co-precipitation protocols and then as synthesized samples were calcined at 200, 400 & 600 °C for 2hrs. The powdered sample of pure and ZnO and Mn doped ZnO were examined through XRD, FTIR, FESEM and HRTEM characterization tools. The XRD results indicates that wurtzite crystalline were in formation with crystallite size increase with increase of calcinations temperature. The intensity of absorption was increases with increase of calcinations temperature 200, 400 & 600 °C for 2hrs. The IR absorption peak at about 403, 404, 413cm<sup>-1</sup> & 638, 658, 669 cm<sup>-1</sup> were assigned to O-Zn-O and O-Mn-O vibration of ZnO & MnO<sub>2</sub> respectively. The morphological studies of particles were examined by electron microscopic tools FESEM and HRTEM. The magnified images of MnO/ZnO sample indicates that single phase hexagonal structure was formed and morphology of ZnO pure particles were spherical whereas, MnO/ZnO calcined at 600 °C 2hrs were 2D nanosheet occurrence in nature. The photoluminescence (PL) study of various samples concluded that newer material has primary excitation energy level at about 303, 305, 307nm and secondary exciton energy level 471, 474, 477nm whereas, the emissive transition occurred at position 661, 665, 668nm for 10% Mn doped ZnO crystalline calcined at 200, 400 & 600 °C for 2 hrs respectively. The newer calcined materials have remarkable properties in field of optoelectronics as the material have optical band gap at about 1.8 eV to 1.90 eV respectively and may have provoked application in field of herbicide and bactericidal applications in presence of sunlight.

**Keywords:** ZnO; MnO/ZnO; XRD; FTIR; PL; HRTEM; FESEM

## 1 Introduction

Zinc oxides with nanoscale sizes have drawn more attention due to their peculiar characteristics such as wide band gap, strong room-temperature luminescence, high electron mobility and remarkable transparency<sup>1</sup>. Zinc oxide (ZnO) is commonly referred to as an II-VI semiconductor because both oxygen and Zinc are found in the II and VI groups of the periodic table<sup>2</sup>. At room temperature, ZnO exhibits a significant exciton binding energy of 60.0 MeV<sup>3</sup>, a considerable band gap of 3.3 eV<sup>4</sup> and an optically active wurtzite structure<sup>5</sup>. Zinc oxide is key material for making lasers<sup>6</sup>, UV light emitting diodes<sup>7</sup>, gas sensors<sup>8</sup>, transducers<sup>9</sup>, UV protection coatings<sup>10</sup>, variable transistors<sup>11</sup> and transparent conductors of electricity<sup>12</sup>. It is widely acknowledged that adding appropriate dopants such as MnO<sub>2</sub> can

improve the functionality of semiconductor nanostructures<sup>13</sup>. The researcher considered these aspects and chosen Mn as the dopant material because of multi d-orbital valence electron and colourful properties in field of optoelectronic and biogenic area<sup>14</sup>. Moreover, the material properties and its functionality are highly dependent on method of synthesis, thermo dynamical conditions applied during synthesis protocols and size of synthesized /calcined nano crystalline<sup>15</sup>. In present work, the various samples of ZnO pure and Mn incorporated ZnO nanocrystalline were synthesized via microwave irradiated chemical co-precipitation method. The colour of newer MnO/ZnO samples were transform from ZnO pure white colour to light Gray in nature and intensity of coloured samples increases with increase of dopant concentration.

The various samples of pure ZnO and MnO (10%) doped ZnO calcined at 200, 400 & 600 °C for 2 hrs

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respectively were studied through employing XRD, FTIR, FESEM, HRTEM, PL characteristics tools. The results of various studies were discussed in respective section/subsection of this paper as under. However, the current study reflects that newer material have  $Mn^{2+}$  tailored optical band gap in visible light spectrum and remarkable purposed futuristic applications in field of optoelectronics and photo induced applications.

## 2 Method of Preparation of pure ZnO & MnO/ZnO nanoparticulates (NPs)

Pure ZnO and Mn-doped ZnONPs were prepared through microwave irradiated chemical co-precipitation protocols. The chemicals used in study were Analytical reagents (AR) in grade and not purified further. The Hydrated salts of Manganese chloride and Zinc nitrate were starting ingredients that were weighed in stoichiometric ratios. In the current experiment, the appropriate concentrations of these ingredients were utilized into 100 ml doubly de-ionized water resulted white colour solution obtained. 2.0M NaOH solution were added drop wise as a precipitating agent and precipitate(ppts) were achieved at about pH=9.0. The solution was left to rest for a day following the completion of the reaction for ageing process. The samples were then regularly cleaned using a filtering technique with ethanol (Merck) and doubly-de-ionized water. Two cycles of 15 minutes of microwave treatment were applied to the cleaned NCS ppts. After that, the samples were distributed among three crucibles and calcined for a predetermined time (two hours) at 200, 400 & 600 °C to observe the impact of the calcined temperatures. The calcined samples were finely powdered after being crushed in an agate mortar for two hours. The fine powdered calcined samples were used for further characterization process and results of various studies were explored in next section of paper.

## 3 Result and Discussion

### 3.1 X-Ray Diffraction

The X-ray diffraction was employed to examine the structure and grain size of a variety of calcined samples. Copper  $CuK\alpha = 1.5406 \text{ \AA}$  was utilised as a X-ray source for investigating the diffraction pattern of calcined samples. A scanning rate of 57.3 minutes per second was maintained for the wide-angle diffraction i.e.  $2\theta=10^\circ-80^\circ$ . The as-synthesized/ calcined materials were identified as ZnO with Mn doped of the wurtzite phase by X-ray diffraction analyses.

Furthermore, as seen in Fig. 1, the intensity of the peaks increases as the temperature rises at a certain level.

At 200, 400 & 600 °C, the XRD pattern of distinct ZnO with dopant Mn (NPs) shows that the majority of the most intense peaks were found at the same position with large variation in FWHM and intensity of peak and a few additional peaks were also noticed and shown in bold. In the above Table 1, all peak positions are arranged.

The crystallite sizes of various samples were calculated using Debye Scherrer formula.

$$d = 0.89\lambda / \beta \cos \theta \quad \dots (1)$$

Equation 1 has all the variables in standard notation:  $\theta$  is the Bragg diffraction angle,  $\lambda$  is the wavelength and  $\beta$  is the full width at half-maximum (FWHM) of the diffraction peak. Scherrer's constant is 0.89. Due to doping of Mn in ZnO, size of nanoparticles increases as we can see in Table 2.

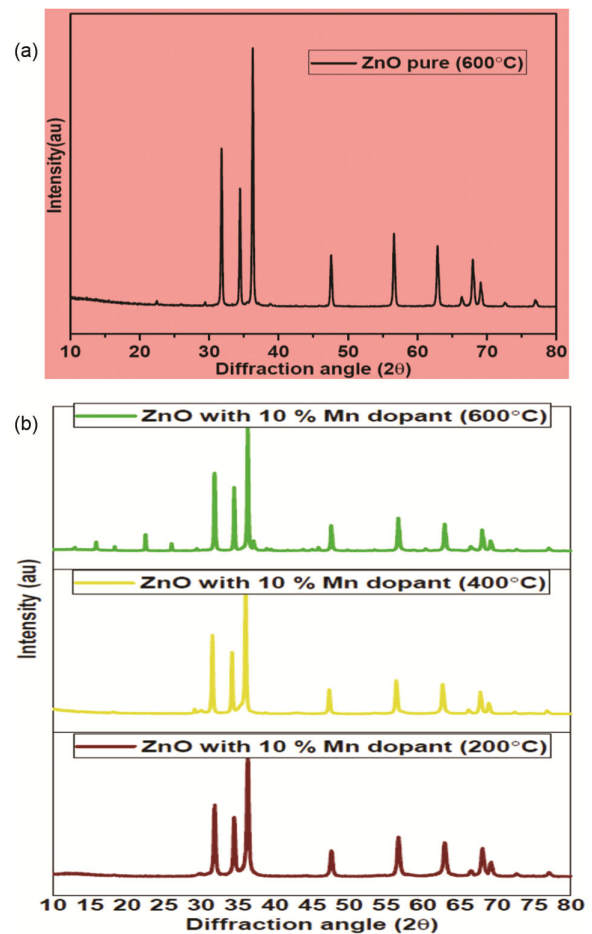


Fig. 1 — XRD pattern (a) Pure ZnO calcined at 600 °C /2hrs and (b) ZnO with 10% Mn dopant nano particulates calcined for 2hrs at temperature 200, 400 & 600 °C

Table 1 — Peak position of XRD of nano particulates of ZnO with Mn dopant.

Samples	temp <sup>r</sup>	Peak position
ZnO with 10% Mn doping	200°C	31.87, 34.47, 35.96, 36.31, 47.60, 47.70, 56.58, 62.93, 63.05, 66.38, 68.04, 69.09, 69.23, 77.00
	400°C	29.19, 31.52, 34.18, 35.22, 35.49, 36.00, 36.33, 47.30, 56.36, 62.66, 66.12, 67.76, 68.88, 72.42, 76.78
	600°C	15.85, 18.36, 22.58, 31.91, 34.57, 35.59, 36.39, 37.15, 47.66, 56.71, 62.99, 68.08, 69.23

Table 2 — Crystalline size of nano-particulates of XRD samples

Samples	Temp <sup>r</sup>	Peak position(2 $\theta$ )	d-spacing	Intensity	FWHM	Crystalline size (nm)
ZnO (pure)	600°C	36.266	2.475	761	0.205	40.32
ZnO with 10% doping of Mn	200°C	36.31	2.472	701.80	0.286	28.90
	400°C	36.00	2.492	738.59	0.184	31.77
	600°C	36.31	2.472	823.14	0.220	37.58

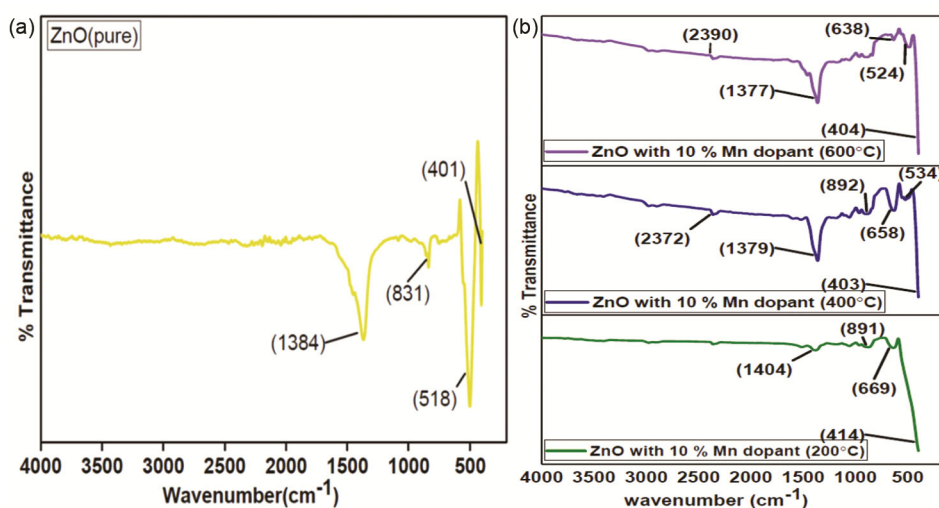


Fig. 2 — FTIR pattern (a) ZnO (pure) and (b) ZnO with 10% doping of Mn calcined for 2hrs at different temperatures

XRD data displays that the size of prepared nanoparticles is directly related to the calcined temperature and as the temperature rises, so does the size of the generated nanoparticles as reveal in Table 2. Particularly, at 200 °C (28.90 nm), 400 °C (31.77 nm) and 600 °C (37.58 nm).

### 3.2 FTIR spectrum analysis

The IR spectroscopy was used to determine the number of group present in various samples and it gave the Molecular vibration positions of respective molecules i.e. stretching or bending vibration occurs at specific quantized frequencies. The infrared spectrum is plotted as transmitted rate vrs. wave number. The effect of Mn doping levels in ZnO lattice were recorded in spectrum in range of 400 and 700  $\text{cm}^{-1}$ . The FTIR spectra of Zinc Oxide with Mn (10%) dopant are shown in Fig. 2. The edges of the Mn doped ZnO band became more prominent with an increase in doping concentration.

Pure ZnO samples exhibit distinct Zn-O stretching modes, with a shoulder and centre of approximately

401 and 518  $\text{cm}^{-1}$  respectively. Strong peaks were observed at 403  $\text{cm}^{-1}$ , 404  $\text{cm}^{-1}$  and 414  $\text{cm}^{-1}$ .

These observations could be attributed to ZnO stretching vibration, which confirmed the wurtzite structure of prepared samples. Fig. 2 displayed peaks at 638, 658 and 669  $\text{cm}^{-1}$  could be caused by MnO's vibration mode<sup>16</sup>.

According to Fig. 2, red shift happened as temperature increased between 200 and 400 °C and blue shift happened as wavelength slightly increased at 600 °C. Table 3 provides the vibration frequency distribution of the corresponding modes for ZnO and MnO/ZnO nanoparticles.

### 3.3. FESEM Image Analysis

The calcined samples were shared with JEOL JSM-7610FPLUSEDs at LPU, Phagwara, Punjab. The FESEM images of Mn (10%) doped ZnO sample calcined at 600 °C /2hrs were shown in Fig. 3 and compared with ZnO pure sample calcined at 600 °C /2hrs as shown in Fig. 4 respectively. The perusal of images reveals that morphology of ZnO (pure) particles

Table 3 — Vibration frequency value of ZnO(pure) and Mn doped nanoparticle

ZnO (pure)	MnO/ZnO	Vibration/stretching modes
401, 518	420, 403, 507, 523	Zn-O
-	642, 660	Mn-O
828	856	Zn-O
-	1088	C-O stretching vibration
1393	1381, 1385, 1392	C=O symmetric stretching
-	2374	CO <sub>2</sub> molecule

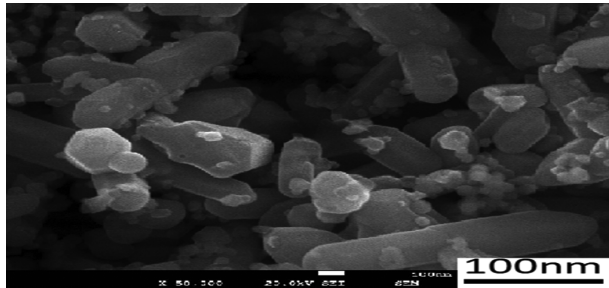


Fig. 3 — FESEM of ZnO(pure) nano particulates calcined for 2hrs at 600 °C

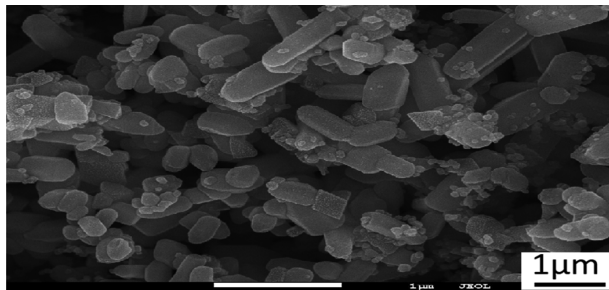


Fig. 4 — FESEM images of Mn doped ZnO nanoparticles calcined for 2hrs at 600 °C

changes from spherical to 2D nanosheet (MnO/ZnO) respectively. Moreover, The FESEM results cleared the formation of nano sized particles and also support the XRD and FTIR spectroscopic findings.

The FESEM images demonstrate that the Mn doping does not alter the hexagonal shape of the ZnO aggregates because Mn usually creates Zn<sub>1-x</sub>Mn<sub>x</sub>O by replacing the Zn<sup>2+</sup> sites of ZnO.

### 3.4 HRTEM Images Analysis

The morphology of Mn-doped ZnO (10%) nanoparticles calcined at 600 °C/2hrs has been examined through images created with a JEOL, JEM 2100 HRTEM in SAIF, PU, Chandigarh. The as-received images of pure ZnO and MnO/ZnO calcined for two hours at 600 °C were displayed in Figs. 5 & 6 respectively.

As seen in Fig. 5, shape of ZnO (pure) nanoparticles was sugar crystalline like cuboid at

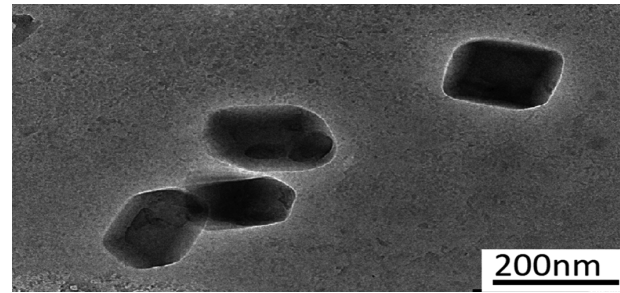


Fig. 5 — HRTEM of pure ZnO nano particulates calcined for 2hrs at 600 °C.

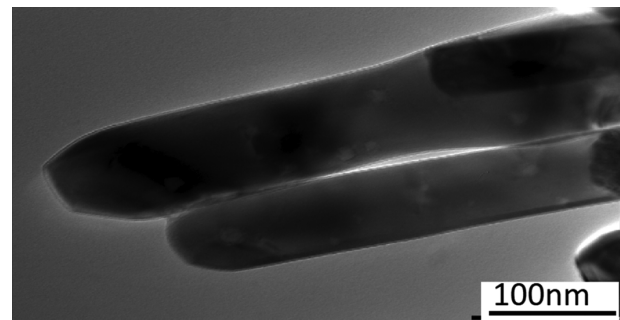


Fig. 6 — HRTEM images of Mn doped ZnO nanoparticles calcined for 2hrs at 600 °C

magnification rate of 200nm. The image also illustrated the formation of 2D nanosheet in morphology. The Mn(10%) doped samples calcined at 600 °C /2hrs were shown in Fig. 6.

It is evident from the image that the morphology of nano particulates resembles with flakes structure with consistent nano size in thickness. The perusal of image also signifies that 2-D nano sheets were may be helpful in formation of various type of gas sensors or biogenic sensors.

### 3.5 Photoluminescence (PL) study

The luminescence emission study was described the connections between particle size, morphological modifications, surface effects doping and luminescence-related defects present in samples. The photoluminescence spectra of MnO/ZnO NPs were done under room temperature conditions were shown in Fig. 7 in the range of 300 –700 nm respectively. The results of the photoluminescence (PL) spectrum of different calcined samples were concluded that the primary exciton energy level of newer materials is at about 303, 305, 307 nm while the secondary exciton energy level was occurred at about position 471, 474, 477 nm.

The 10% Mn doped ZnO crystalline calcined at 200, 400 & 600 °C for two hours have emissive

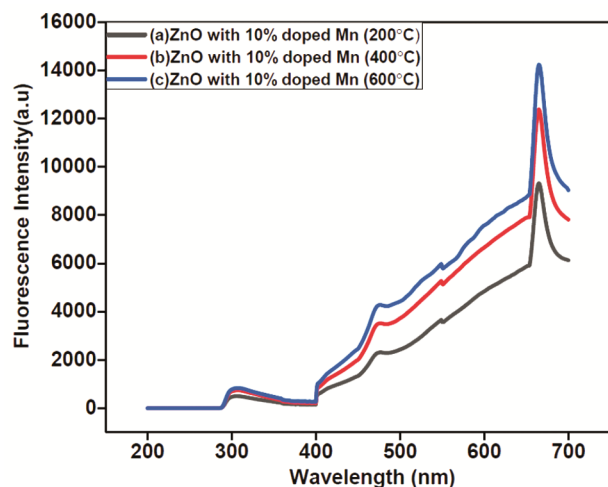


Fig. 7 — PL spectrum of 10% MnO/ ZnO NSM calcined for 2hrs at temperature (a) 200 °C (b) 400 °C and (c) 600 °C

transition occurred at about positions 661, 665, 668nm. The findings of PL study reveals that the optical band gap of the newer materials was lying in the range of 1.8 and 1.90 eV and make their importance in the field of optoelectronics and photo induced applications.

#### 4 Conclusion

The advanced Chemical co-precipitation protocols were utilized for preparations of pure ZnO and Mn doped ZnO nanoparticles. The XRD results concluded that crystallite size increases with Dopant  $Mn^{2+}$  concentration in ZnO lattice. The IR spectrum also exhibited vibrational peaks of O-Zn-O and O-Mn-O at position at about 403, 404, 413 $cm^{-1}$  & 638, 658, 669 $cm^{-1}$  respectively. The morphological analysis of particles was shows that 2-D nano sheets were in formation in HRTEM Image examination and sugar like cuboids crystalline were recognised in FESEM image of samples respectively. The photoluminescence (PL) studies of various samples concluded that primary excitation energy transitions were noticed at about 303, 305, 307nm and secondary exciton energy transitions were exhibited at about

471, 474, 477nm whereas, the emissive transition were seen at position 661, 665, 668nm for 10% Mn doped ZnO crystalline calcined at 200, 400 & 600 °C for 2 hrs respectively. The study approaches that the newer synthesized materials may have remarkable properties in field of optoelectronics or biogenic field such as herbicidal area as the material have optical band gap lying at about 1.8 eV to 1.90 eV respectively.

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