

# Mn-DOPED ZnO NANOCRYSTALLINE WERE PREPARATION, UNDER ANALYSIS AND ELEMENTAL APPLICATION

## Abstract

Doped Zn oxide is use full to various field of material science. Nanocrystalline pure and Mn doped metal oxide (ZnO) with large amount of energy required and present in mass defect .It is also used as diluted magnetic semiconductors. pure ZnO and Mn bind in ZnO metal oxide has been synthesized with 2 mol% of Mn content by co-precipitation method I will be studied the structural, chemical and optical properties of the samples by using X-ray diffraction (XRD), energy dispersive x-ray (EDX) analysis. The impact of annealing on structural, optical and, it ware confirmed that the eight layered film shows high crystalline quality, having the prominent (002) peak which is the characteristic peak for the c-axis oriented wurtzite ZnO structure. Again, the morphology of the eight layered sample showed hexagonal shaped grains reflecting the basic unit cell structure. Hence, for the preparation of Mn doped ZnO films, eight layered thickness films annealed at 500°C in open air has been used. The effect of hybrid and open air annealing on the structural and optical properties has been investigated. Due to good crystallinity and enhanced photoluminescence behavior, open air annealing was carried out for the preparation of all doped ZnO nanocrystals.

## Keywords

Zinc Oxide (ZnO) Nanocrystalline, Mn- doped ZnO, Properties of Mn doped ZnO, Powder X-ray diffraction, Optical and Magnetic Properties, Application

## Introduction

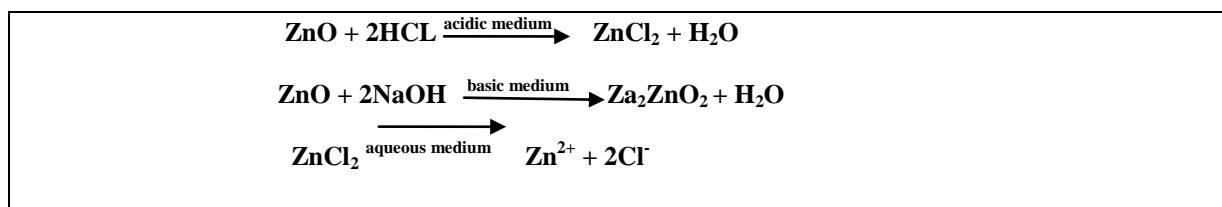
### Nanoparticles:

A solid particle in the range of 1-100 nm is called nanoparticles. Different types of nanoparticles are ZnS, CdS, MnO, CdTe e.t.c. These nanoparticles are affect in physical properties. Therefore, nanoparticles are chemically reactive in nature and affect their strength or electrical and magnetic properties and also be arranged into layers on surfaces and hence activity, relevant to a range of potential applications such as catalysts. They have varied applications such as cosmetics, textiles, paints and drug chemistry.

### Zinc Oxide Nanoparticle:

Zinc oxide (ZnO) is a one type of ambient metal oxide nanoparticle, it is very important in materials science. On the other hand, ZnO is a white colour powder that is an insoluble in water and its suspension could not be electrostatically stabilized in the preset pH (7.2 – 12) and due to formation of unstable Colloidal practices zinc hydroxide. It is widely used as an additive in numerous materials ceramics, lubricants, batteries, cement, glass etc. ZnO is a wide-band gap semiconductor of the II- VI semiconductor group. Most applications exploit the reactivity of the oxide as precursor to other zinc compounds. For materials science applications, zinc oxide have high refractive index, high electrically conductivity, binding energy , antibacterial and UV protection properties. It is universally known that zinc oxide nanoparticles are antibacterial and inhibit the growth of microorganisms by permeating into the cell membrane. Since zinc oxide is an amphoteric in nature, it react with both acids and alkali giving Zn (II) ions.

Scheme -1 ( Ambient nature of zinc Oxide& there reaction )



### Doped Oxide:

Doped oxides have significant physical and chemical properties which are often, sharply improved by combining them in different proportions for making their alloy or compounds or nanocrystals. Doped oxides nanocrystals hold promise for a wide variety of applications if dopant –induced properties can be appropriately harnessed. X-ray photo electron spectroscopy analysis indicated that doped metal is distributed throughout the nanocrystal. On the other hand, Elemental composition analysis, shift and intensity changes in the x-ray diffraction peaks and electronic absorbance spectroscopy suggest that the guest cations are substitution doping in the host matrix.

#### **Mn- doped ZnO:**

“The term Mn- doped ZnO” has come from the adding ions against host lattice. The Mn atoms replace few Zn atom and occupy the position in ZnO nanocrystal. The doping with 3d transition metal Mn highly effect in surface area and less amount of the particle size of ZnO nanoparticles. Mn is preferred for the doping of ZnO due to the fact that the d electron of Mn at  $t_{2g}$  level can easily overlap with the ZnO’s valence bond as compared with other transition elements.

#### **Properties of Mn doped ZnO:**

The properties of Mn doped ZnO are significant due to two types of important properties such as optical and magnetic properties. The optical band gap of the ZnO:Mn increases with the decrease of doping concentration. The transmission range of Mn doped ZnO nanoparticles in the visible light range is more than about 88%. The samples with low doping concentration (1-3% of Mn) exhibit paramagnetic and ferromagnetic behaviors.

### Requirement of Preparation in Mn-ZnO Nanocrystalline

Table-1

Materials Name	Formula	Company Name
Manganese :acetate tetra-hydrate	$(\text{CH}_3\text{COO})_2 \text{Mn} \cdot 4\text{H}_2\text{O}$	MERK
Zinc acetate di-hydrate	$\text{Zn} (\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	SIGMA – ALDRICH
Sodium lauryl sulphate	$\text{CH}_3 (\text{CH}_2)_{10} \text{CH}_2\text{O}-\text{SO}_2\text{Na}$	SIGMA – ALDRICH
Sodium hydroxide	NaOH	SIGMA – ALDRICH
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	SIGMA – ALDRICH
Distilled water	$\text{H}_2\text{O}$	SIGMA – ALDRICH

Table-2:

Calculation	Compound Molecular weight
Zinc (II) acetate di-hydrate	219.498g/mol
Manganese (II) acetate tetra-hydrate	173.026g/mol
Sodium hydroxide	39.997g/mol
Water	18.01528g/mol
Sodium lauryl sulfate	288.372g/mol

Table-3

Materials Required	Amount
Zinc (II)	0.5g
Manganese (II)	0.01g

NaOH +EtOH	125ml
C <sub>2</sub> H <sub>5</sub> OH	100ml
Polymer	0.4g
H <sub>2</sub> O	1ml

### Co-precipitation Method

Anion solution + Cat ion solution

↓  
Nucleation and Growth

↓  
Precipitation

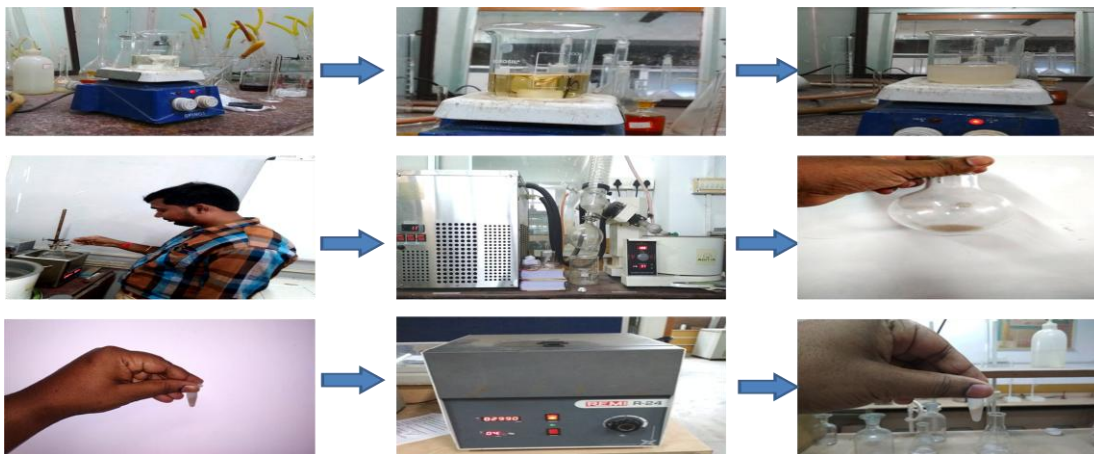
↓  
Filtration

↓  
Calcinations

### Experimental procedure

- 0.01g amount of manganese acetate tetra hydrates were dissolved in 1ml of water.
- Added 100 ml of Ethanol (C<sub>2</sub>H<sub>5</sub>OH).
- After vigorous stirring 2 hours.
- Then 0.5 g amount of zinc acetate di-hydrates were added and this mixture was heated at 50 °C to 60°C
- Then it was small amount of ice and 0.4 g polymer were added.
- The reaction mixture was stirred for 2 hours.
- Then hydrolyzed by the drop wise mixture (NaOH + EtOH = 125ml) under ultrasonic agitation for about 2 hours.
- This mixture solvent was removed by rotavapourization, then the resulting mixture was washed with water.
- Mn -ZnO Nanocrystals were precipitated out.
- These precipitates were centrifuged machine and dried in a vacuum for 10 hours and more.

**Picture-1 (preparation procedure, steps are followed by experimental process)**

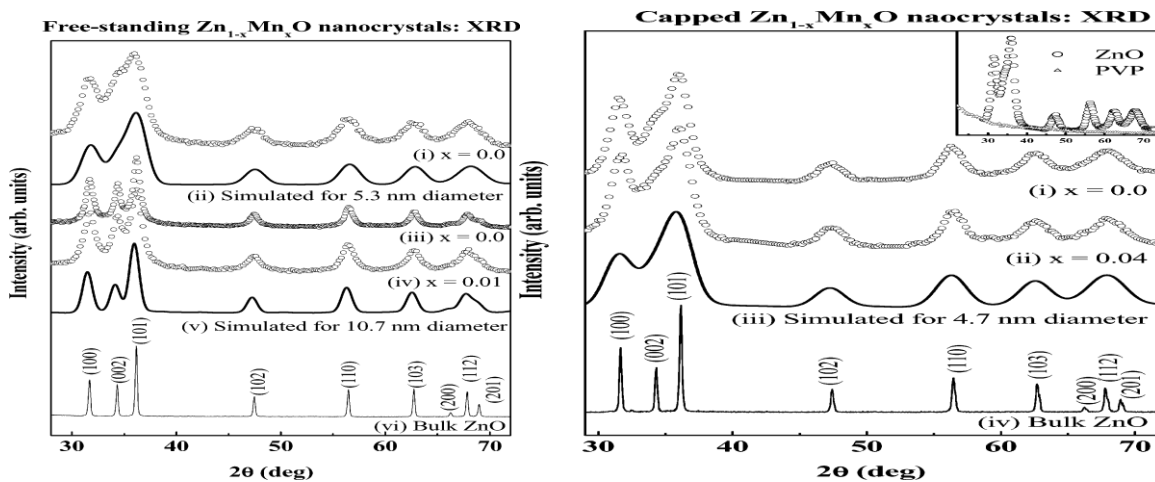


### Experimental Analysis

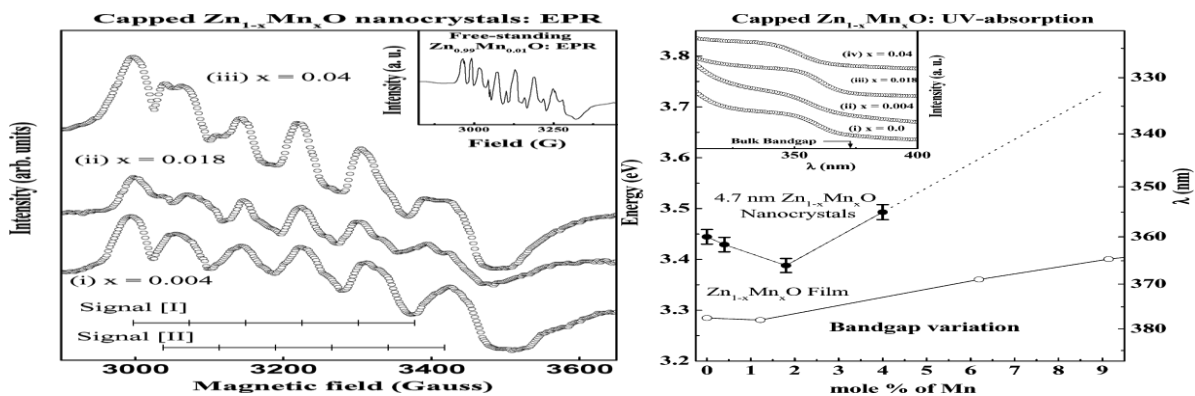
**1 Powder X-ray diffraction** patterns of free ZnO and Mn bined ZnO are shown in below. The characteristic peaks with high intensities corresponding to the planes (100), (002), (101) and lower intensities at (102), (110), (103), (200), (112) and (201) indicated the annealed product is of high- purity hexagonal ZnO wurtzite structure. It is evident from the XRD data that there are no extra peaks due to manganese metal, other oxides or zinc manganese phase, as indicating the samples are single phase. The Mn(II) was doped to the ZnO, No changing the wurtzite like structure at 500° to 550° C of 1hours 30minutives. The graph of the X- ray diffraction method was doped samples are slightly changes to left as compares to the free ZnO. This shows that small variation in the lattice parameters occurs as Mn concentration. In the sample increases, The result shows that the lattice constant of Mn doped ZnO were slightly larger than those of undoped ZnO, because ionic radius of Mn(II)(0.66) is larger than that of Zn(II)(0.60). The sample grain size was estimated below. The crystal size of undoped ZnO decreases on doping 1mol% of Mn and subsequent doping shows an increasing tendency below.

The sample grain size were calculated :

Samples	Grain Size (nm)
Free ZnO	19.21
1 mol% Mn doped ZnO	15.80
2 mol % Mn doped ZnO	17.66



**Fig-1** XRD method in samples are annealed in ambient air at 500° to 550° 1hours30 mints.. (a) free ZnO; (b) 1mol% Mn doped ZnO; (c) 2 mol% Mn doped ZnO.



**Fig- 2** Analysis of optical and Magnetic properties.

**Optical properties and Magnetic properties**

- UV- absorption spectra of free-standing ZnO and Mn-doped ZnO nanocrystals, both with an average diameter of 10.7nm.
- The band gap thus obtained for the ZnO nanocrystals corresponds to 3.38eV (367nm), indicating a blue shift of about 0.1eV compared to the bulk band gap of 3.3eV (373nm), due to confinement effect. Shows EPR spectra of the doped Nano crystal samples with different Mn concentrations. The EPR spectrum from the uncapped, free-standing Mn doped sample.

### **Theoretically Application**

- [1] This nanoparticles use on the polyester fabric dyes.  
 [2] It is used in semiconductor in Nanotechnology.  
 [3] It is used in the Cosmetics, Nutraceutical and Pharmaceutical industries.

### **Conclusion**

- Mn-doped ZnO nanocrystals have been synthesized by co-precipitation method with different type of manganese(II) compositions.
- ZnO nanocrystals containing transition metal Mn synthesized by a simple Co- precipitation process correspond to a hexagonal structure similar to that of un-doped ZnO
- As -synthesized ZnO and Mn-doped ZnO nanocrystals have a good crystal quality.
- ZnO and Mn-doped nanocrystals show diamagnetism at room temperature

### **Future work**

To study the structural behaviour of the undoped and doped ZnO samples Screening electron microscopy (SEM) and transmission electron microscope (TEM) can be used. As well as temperature dependent photoluminescence can be taken to know more about luminescence behaviour. To improve the nanostructure behaviour of the oxide, few suggestions are given below.

1. Samples could be prepared on different substrates like different polymer, solvent and materials the role of substrate matrix on the growth of nanocrystals could be investigated.
2. Sample doped with different dopants could be annealed at various temperatures and the variation in structural, optical and magnetic properties could be studied.
3. Using same precursors dip coating and spray pyrolysis methods could be employed to study the change in physical properties of the samples.
4. Using different precursors samples could be prepared with the addition of various dopants and their physical properties could be compared.
5. Electrical studies like I-V characterization, Hall measurement and impedance study could be carried out for the above prepared.

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