

Synthesis and characterization of Mn doped ZnO nanomaterial

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Abstract: Mn doped ZnO particles have been synthesized using a chemical co-precipitation method. Characterization was carried out by XRD, FTIR, UV and PL Spectroscopy. The average crystallite sizes of the samples were calculated by using Debye- Scherrer's formula and were found to be in the nanoscale. In addition to this XRD results also indicate no extra impurity or secondary phases are observed. As the Mn doping increases the optical band gap decreases for the range of Mn doping reported 2.65 eV for Undoped ZnO and 2.97eV for Mn doped ZnO.

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1. Introduction

Studies on ZnO based diluted magnetic semiconductors (DMSs) have received much attention in the recent years after Sato et al. first predicted that ZnO doped with 3d transition metal ions such as V, Cr, Fe, Co, and Ni may exhibit ferromagnetism [1-4]. Dietl et al. also predicted that Mn doped p-type ZnO should be ferromagnetic above room temperature [5]. Based on these predictions, several experimental investigations have been carried out by different researchers on ZnO based DMSs [6] [7]. There are many studies reported on ZnO based DMSs on thin film samples fabricated using different techniques, as well as on polycrystalline materials synthesized by different methods. It is generally believed that the origin of ferromagnetism in such transition metal doped ZnO is carrier induced. No ferromagnetic ordering has been observed for Cr to Cu doped ZnO thin film samples down to 3 K in the earlier studies made by Jin et al. in 2001 [8]. From studies on thin film samples, Fukumura et al. showed a 36% solubility of Mn in ZnO, with strong antiferromagnetic ordering [9]. However, recently Coey et al. found room temperature ferromagnetism in some of these transition metal ion doped ZnO thin films [10]. In fact, in a very recent report, Hong et al. showed that Zn site defects in ZnO thin films give rise to room temperature ferromagnetism, and there is no role for the doped transition metals such Mn and Fe in introducing magnetism in the ZnO lattice [11]. One of the approaches to drive a semiconductor ferromagnetic is to introduce magnetic ions like Mn, Cr, Co and Fe into non-magnetic semiconductors [12, 13, 14]. In these ferromagnetic semiconductors, a part of the lattice is made up of substitutional magnetic atoms. Hence they are called diluted magnetic

semiconductors (DMS). In recent years there has been an extensive research towards introducing ferromagnetic property at room temperature in semiconductors to realize a new class of spintronic devices such as spin valves, transistors, spin light emitting diodes, magnetic sensors, non-volatile memory, logic devices, optical isolators and ultra-fast optical switches. The potential advantages of spintronic devices will be higher speed, greater efficiency, and better stability, in addition to the low energy required to flip a spin. Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability, is a multifunctional material [15-16]. ZnO nanoparticles were synthesized by different methods. It is confirmed that the various applications of ZnO nanoparticles depend upon the control of both physical and chemical properties such as size, size disparity, shape, surface state, crystal structure, organization onto a support, and dispensability [17-22]. This has led to the development of a great variety of techniques for synthesizing the compound.

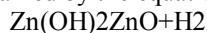
2. Experimental Work

From the studies it is found that there are generally five methods of synthesizing Undoped ZnO and Mn-doped ZnO nanoparticles namely sol-gel, solvothermal reaction with microwave heating, solid state reaction, hydrothermal and chemical precipitation. Here we have used chemical precipitation method. If silver nitrate solution is poured into a solution of sodium chloride, a chemical reaction occurs forming a white precipitate of silver chloride. When potassium iodide solution reacts with lead nitrate solution, a yellow precipitate of lead

iodide is formed. Precipitation may occur if the concentration of a compound exceeds its solubility (such as when mixing solvents or changing their temperature). Precipitation may occur rapidly from a supersaturated solution. In solids, precipitation occurs if the concentration of one solid is above the solubility limit in the host solid, due to e.g. rapid quenching or ion implantation, and the temperature is high enough that diffusion can lead to segregation into precipitates. Precipitation in solids is routinely used to synthesize nanoclusters. An important stage of the precipitation process is the onset of nucleation. The creation of a hypothetical solid particle includes the formation of an interface, which requires some energy based on the relative surface energy of the solid and the solution. If this energy is not available, and no suitable nucleation surface is available, supersaturation occurs. Zinc oxide nanoparticles were synthesized by chemical precipitation method using Zinc Chloride and Sodium Hydroxide as precursors. The concentration ratio between the Zinc chloride and sodium hydroxide was determined using the chemical equation formula shown below:



Hence, 0.4M aqueous methanol solution of zinc chloride was kept under constant stirring using magnetic stirrer to completely dissolve the zinc chloride and 0.8M aqueous methanol solution of sodium hydroxide was also prepared in the same way and kept under stirring. The speed of stirring the Zinc chloride was increased after its complete dissolution and 0.8M aqueous solution of sodium hydroxide was added for 20mins in drops. The colorless solution obtained after complete addition of addition of NaOH was allowed to be under constant stirring for 2hrs and later sealed and kept overnight. After the whole process Zinc hydroxide with some unknown impurities assumed settled at the bottom and the excess mother liquor obtained on top was removed. The remaining solution was centrifuged for 5mins and the precipitate obtained was washed five times with deionized water and methanol to remove the by products which were bound with the Zinc hydroxide and then dried in air atmosphere. After drying Zn(OH)₂ is completely converted to into ZnO explained by the equation below:



Synthesis of Mn-doped ZnO Nanoparticles

For synthesis of the ZnO nanoparticles first we have to take two materials that are precursor one is of zinc precursor and other is of Oxygen. For synthesis of the Mn doped ZnO, Zinc Sulfate and Manganese sulfate and NaOH were used. When the particle

growth is started and they are starting to form, a capping agent must be added that stop further growth of the particle. If the capping agent is not added then particle continuously growth and does not remain in the nanometer range. To keep the particle size in the range of nanometer range capping agent must be added. We were used Ethylene Glycol as capping agent. Analytical grade materials were used for the synthesis of ZnO: Mn nanoparticles. [ZnSO₄.7H₂O] (0.2 M), [MnSO₄. H₂O] (0.2M) and NaOH (1M) are used as the starting material for the synthesis of Mn doped zinc oxide nanoparticles. First we have weighting the starting material according to their molarity in the solution. ZnSO₄.7H₂O and MnSO₄. H₂O were dissolved in 30 ml distilled water under stirring at room temperature for 30 min both solutions were prepared separately. Then these solutions are mixed during continuously stirring, An aqueous solution of NaOH was slowly added to the mixture under constant stirring until the pH of the solution reached to 10. During adding of NaOH solution, precipitation was start. After adding of NaOH, 10 ml EG was added immediately. The final solution was then stirred for 20 hours at room temperature, so that homogeneity can be maintained. The reaction mixture was centrifuged to get the precipitate out, before the washing of sample pH was above the 10 then sample was washed several times until the pH was 7. After washing we have dried sample at 1500C. The sample thus obtained in the powder form to make fine particles we have grinded it and then it was calcined at 400°C for 3 h in the muffle furnace.

3. Result and discussion:

Data collection and structure solution:

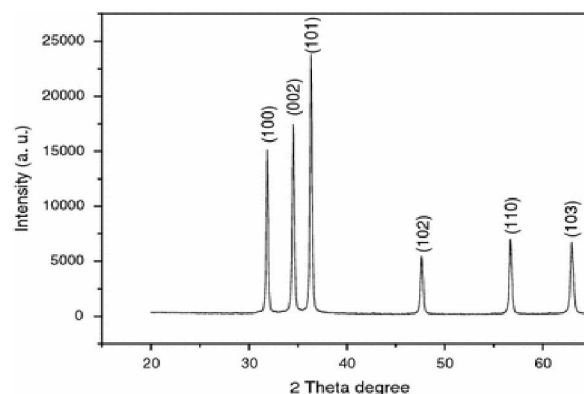


Fig – 2 XRD Spectra of Undoped ZnO nanoparticles

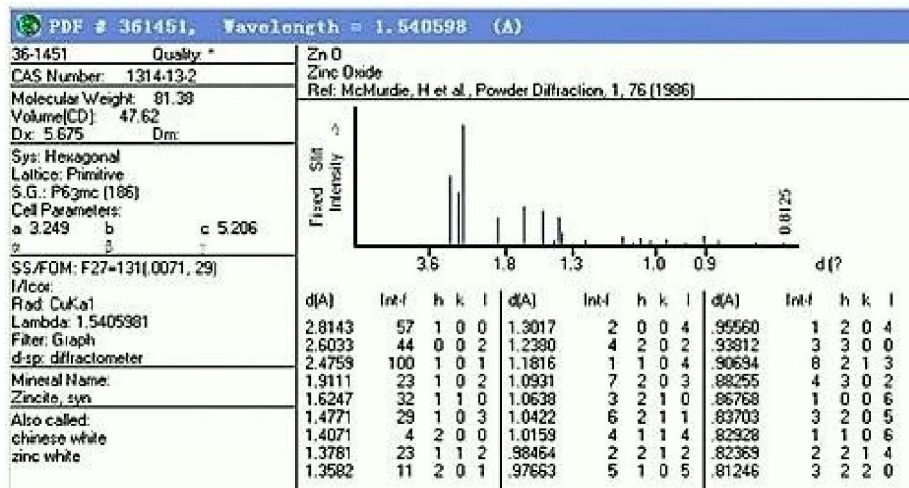


Fig – 1 XRD reference data for ZnO wurtzite JCPDS No. 36-1451

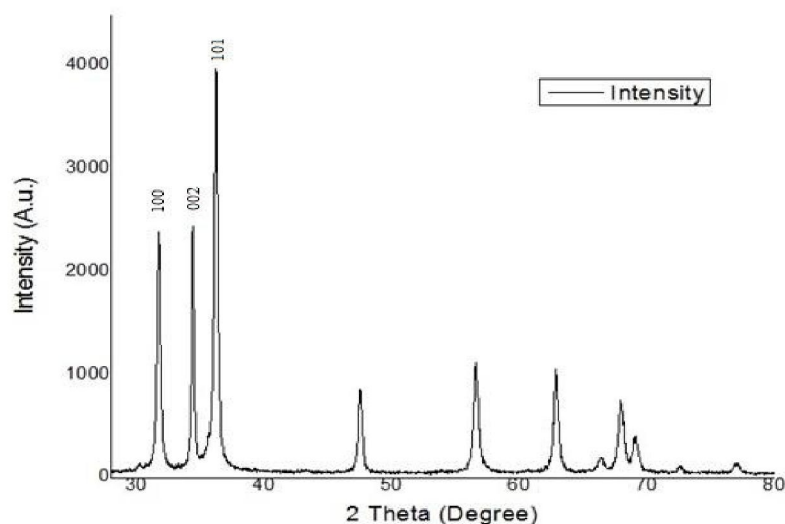


Fig – 3 XRD Spectra of Mn doped ZnO nanoparticles

We have taken Undoped ZnO and Mn doped ZnO and calculated their different parameters.

a. Crystallite Size: The X-ray diffraction of the samples were recorded by an X-ray diffractometer with a CuK α radiation ($\lambda = 1.54060 \text{ \AA}$) in a range of 2θ from 300 to 800. The top three peaks are only produced at 2θ ranging from 300 to 380 which further corresponds to the crystal planes (100), (002) and (101) for Mn doped ZnO and for Undoped ZnO, CuK α radiation ($\lambda = 1.54060 \text{ \AA}$) in a range of 2θ from 200 to 700. The top three peaks are only produced at 2θ ranging from 300 to 380 which further corresponds to the crystal planes (100), (002) and (101) as of Mn doped. The broadening of the diffraction peak in the xrd pattern indicates the formation of the

nanocrystallinity. Using Debye- Scherrer formula, the crystalline size of the sample was calculated from full width at half maxima of XRD pattern shown in Fig 2 and Fig 3. The average nanocrystallite size is calculated by the formula,

$$D = 0.9 \lambda / \beta \cos \theta \quad \dots \text{Eq (2)}$$

Where λ is the wavelength of the incident ray, θ is the Bragg's angle and β is the full width at half maxima [23-27].

b Non Uniform Strain:

We have also studied the change in non-uniform strain (η) with particle size using the Hall equation,

$$\beta \frac{\cos \theta}{\lambda} = \frac{1}{t} + 2\eta \frac{\sin \theta}{\lambda} \dots \text{Eq (3)}$$

where, 'λ' is the wavelength of x-ray used for scattering experiment and 't' is the particle size and β is the line broadening.

c. Dislocation Density: The dislocation density (δ) which represents the amount of defects in the sample is calculated using the relation.

$$\delta = 1/D^2 \dots \text{Eq (4)}$$

where D is the average crystallite size where λ is the X-ray wavelength (here λ = 1.54060 Å) and θ is the Bragg's angle.

d. Average Strain: The average strain of the nanoparticles is calculated using following equation

$$\varepsilon = \beta/4 \tan \theta \dots \text{Eq (5)}$$

where ε = Average strain, β = FWHM, θ = Bragg's Angle,

Calculation Table 1 for Undoped ZnO		
Sr. No	Properties	Value
1.	Crystallite Size (nm)	21
2.	FWHM(degree)	36.236
3.	Non Uniform Strain	0.0745
4.	Dislocation Density δ (lines/m ²)	2.26x10 ¹⁵
5.	Average Strain	17.498

Calculation Table 2 for Mn doped ZnO		
Sr. No	Properties	Value
1.	Crystallite Size (nm)	27
2.	FWHM(degree)	36.736
3.	Non Uniform Strain	0.03
4.	Dislocation Density δ (lines/m ²)	1.365x10 ¹⁵
5.	Average Strain	13.776

PL Spectroscopy

The photoluminescence intensity depends strongly on Mn concentrations. Intensity is maximum for low concentrations of Mn and further it can be decreased together with the broadening of the FWHM (Full Width at Half Maximum) as a function of Mn content. The higher concentration of Mn induces a high density of defects, which acts as non-radiative recombination centres and reduces the intensity of emitted light [28-30].

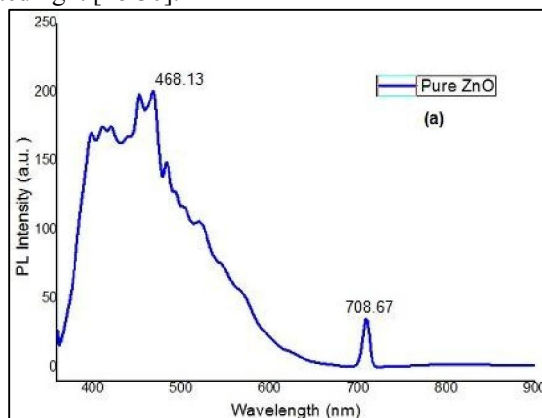


Figure 4. PL for pure ZnO phase

The energy gap is calculated using the equation for photon energy in terms of eV and μm.

$$\lambda = 1.24/E_g \mu\text{m} \dots \text{Eq (12)}$$

and is found to be 2.65 eV for Undoped ZnO and 2.97eV for Mn doped ZnO.

FTIR Spectroscopy:

The FTIR spectrum of Undoped ZnO and Mn doped ZnO at room temperature is shown in below figure 5 and 6. These spectrums shows the IR absorption due to the various vibration modes.

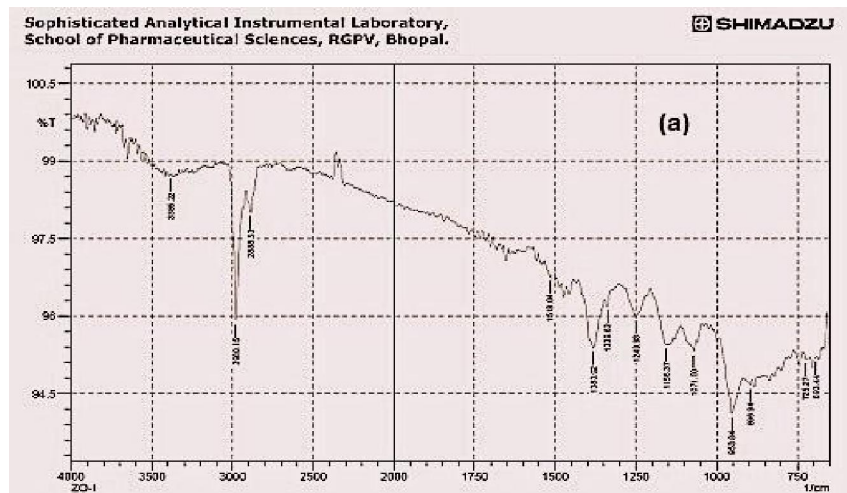


Fig – 5. FTIR of Undoped ZnO

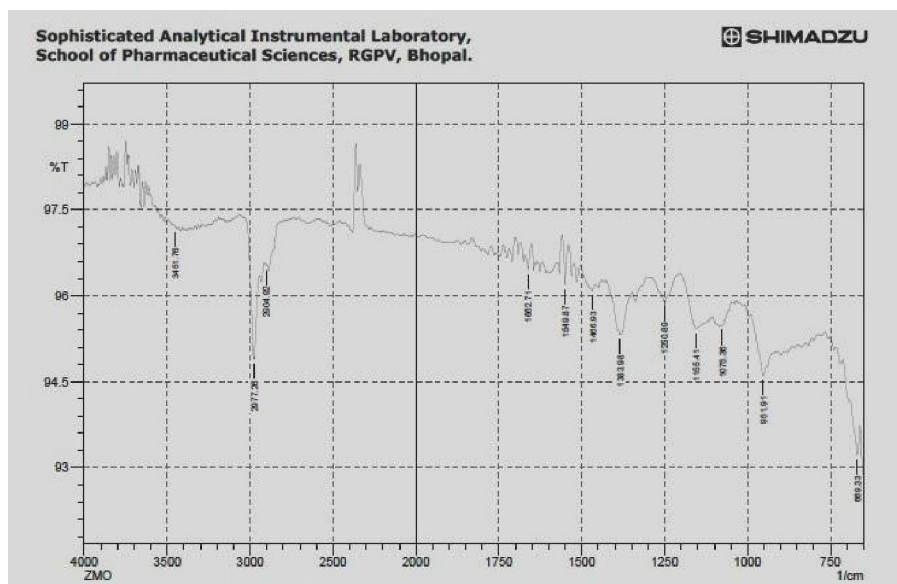


Fig – 6 FTIR of Mn doped ZnO

UV-Vis Spectroscopy:

UV-Vis spectra of undoped and Mn doped ZnO observed in the 200-800nm range. Before the UV Characterization we have dissolve 10mg of each sample in the 50ml DI separately to form a monodispersed solution. After this each sample was sonicated for 30 min. Both samples are not having any peak in the visible region. A UV-Vis spectrum is used for the band gap calculation but it requires the

wavelength at which spectra start to take off. But it is difficult to obtain take off wavelength manually, so we have only information about the peak wavelength where absorption is highest and value of the absorption. Undoped ZnO has the peak absorbance of 1.143 at the wavelength 372nm [31]. Manganese doped ZnO has highest absorbance of 0.747 at the wavelength 376nm. Shown in fig 7 and 8.

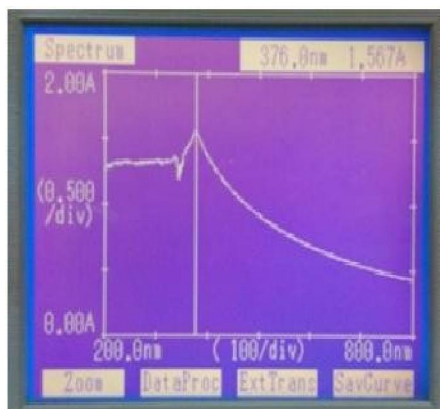


Fig – 7 UV spectroscopy of Undoped ZnO

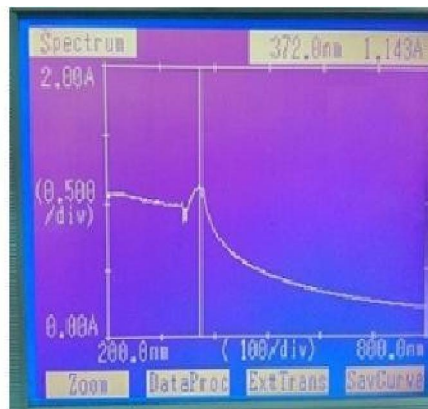


Fig – 8 UV spectroscopy of Mn doped ZnO

4. Conclusion

To summarize, we have prepared Pure and Mn doped ZnO by chemical precipitation method. The Mn-doped ZnO system is very promising due to its wide bandgap of ZnO host material and due to its high solubility of Mn atoms in ZnO matrix. Mn-doped ZnO has also attracted much attention because of disagreements about the existence and the origin of room-temperature ferromagnetism. Crystallite size for Undoped and Mn doped ZnO is found to be 21 nm

and 27 nm respectively. Energy gap for Undoped and Mn doped ZnO is found to be 2.65 eV and 2.97 eV respectively.

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