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# Synthesis and Characterization of ZnO and Mn-Doped ZnO Nanoparticles

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**Abstract:** ***Zinc oxide and Mn- doped Zinc oxide nanoparticles has gained a lot of attention from the scientists and researchers to undergo this research interest due to its various applications in optoelectronic devices, chemical sensors, solar cells and photocatalyst. However, the doping efficiency was influenced by the strong tendency of the Mn dopant ions to segregate at the nanoparticles surfaces. Zinc oxide and Mn-doped Zinc oxide particles were successfully synthesized by wet chemical co-precipitation method using Zinc acetate dihydrate and sodium hydroxide as a precursor materials. Ethanol was used as a solvent for homogeneity of the solution and helps to make a stoichiometric solution in order to obtain Zinc oxide and Mn-doped Zinc oxide nanoparticles. The highy stable colloidal ZnO and Mn-doped Zinc oxide nanoparticles have been prepared at room temperature. The sample were characterized by X-ray diffraction(XRD), Fourier Transform Infra red spectroscopy(FTIR) and the band gap measured by UV-Visible reflectance. In the XRD pattern of samples, there is no change in the wurtzite structure which could indicate no Mn-related secondary phases were observed for the doped ZnO Samples upto 15% of Mn-doping. The band gap of Mn doped Zinc oxide is smaller than the undoped ZnO band gap. The result of characterization shows 15% Mn-doped ZnO has the lowest particle size. Moreover the calculated band gap of 10% ZnO is lower than others*.**

**Keywords:** ZnO nanoparticles, XRD, FTIR, UV-VIS Spectroscopy

## 1. Introduction

Nanotechnology and nanoscience is about controlling and understanding matter on the sub-micrometer and atomic scale. Exploiting advances in scientific measurement at this scale and the ability to manipulate material at this scale, scientists and engineers have found ever increasing uses for Nano-sized metals, polymers, and ceramics to create new functional materials, better coatings, better fluid flow, and a host of other improvements to everyday components and manufactured goods and systems. It involves the manipulation of atoms and molecules to create new products and improve the existing ones. Nanotechnology is multidisciplinary field of research dealing with objects that have dimensions up to a few hundreds of nanometers. A motivation of nanoscience is try to understand how materials behave when sample sizes are close to atomic dimension. Recent day trend of research is towards the fabrication of materials and devices at the nano scale so that their properties can be tailored to different applications. The most revolutionary consequences can be excepted if the most valuable properties of nanoparticles, their electronic properties, are exploited. As a broad definition we categorize nanomaterials as those which have structured components with at least one dimension less than 100 nm. Materials that have one dimension in the nanoscale are layers, such as thin films or surface coatings. Materials that are nanoscale in two dimensions include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids and quantum dots.

Zinc oxide has been a subject of interest for the scientists and the industry for decades. ZnO is often called a II-VI semiconductor because zinc and oxygen belong to the 2nd and $6^{th}$ groups of the periodic table.It has good transparency, high electron mobility, wide bandgap, strong room temperature luminescence. It is a versatile material that has found applications in a variety of areas such as photo catalysis, sensors, piezoelectric transducers, solar cells, transparent electrodes and electroluminescent devices, gas sensing devices. Manganese (II) acetate is the chemical compound with the formula Mn $(CH_3COO)_2$. It is used as a desiccant, a catalyst, and as fertilizer. There are several solution based routes are available for the preparation of ZnO nanoparticles such as solvothermal, hydrothermal,sol-gel,micro-emulsion, vapour phase ..transport process, precipitation, RF magnetron sputtering,etc.In the present work,an attempt has been made to synthesis ZnO and Mn-doped ZnO nanoparticles by wet chemical co-precipitation method. Zinc oxide due to its versatility and multifunctionality creates attention in the research field related to its applications. A wide number of synthesis techniques also been developed by which ZnO can be grown in different nanoscale forms and thereby different novel nanostructures can be fabricated with different shapes ranging from nanowires to nanobelts and even nanosprings. Many fine optical devices can be fabricated based on the free-exciton binding energy in ZnO that is 60 meV because large exciton binding energy makes ZnO eligible to persist at room temperature and higher too. Since ZnO crystals and thin films exhibit second- and third-order non-linear optical behaviour, it can be used for non-linear optical devices. Third-order non-linear response has recently been observed in ZnO nano crystalline films which make it suitable for integrated non-linear optical devices. Generally,the advantage of tuning the physical property of these oxides like zinc oxide becomes the root cause for the synthesis of smart application device. The electrical, optical, magnetic, and chemical properties can be very well tuned by making permutation and combination of the two basic structural characteristics they possess these cations with mixed valence states, and anions with deficiencies(vacancies). Thus, making them suitable for several application fields such as semiconductor, superconductor, ferroelectrics, and magnetic. DSSCs is an optoelectronics device that converts light to electrical energy via charge separation in sensitizer dyes

absorbed on a wide band gap semiconductor, which is different to conventional cells[23]. One important difference between conventional and dry sensitized solar cell is that they are epitomized by silicon p-n junction solar cells. The demand for zinc oxide based dye-sensitized solar cell is due to its low fabrication cost.

## 2. Methods and Materials

**Materials**

Zinc acetate dihydrate, Sodium hydroxide, Isopropyl alcohol, Manganese acetate, Ammonium hydroxide, ethanol and distilled water was used in all experiments.

**Synthesis of ZnO nanoparticles**

Zinc oxide nanoparticles are synthesized using the wet chemical co-precipitation method. The precursors used in the synthesis ZnO are zinc acetate dihydrate having purity 99%. The need for surfactant is fulfilled by the use of manganese acetate tetrahydrate which also possesses 99% purity. Isopropyl alcohol and ammonium hydroxide takes care for the homogeneity and pH value of the solution and helps to make a stoichiometric solution to get Zinc oxide nanoparticles. Firstly, in a 250ml conical flask 100 ml of Isopropyl alcohol is added with 6.67gm(0.6mole) of zinc acetate dihydrate and dropwise ammonia is added with continuous stirring to get a homogeneous solution. After addition of Isopropyl alcohol and the solution is prepared which is subjected to continuous stirring to get a homogeneous solution. Now the two solutions are mixed together in 500ml beaker and drop wise of 100 drops ammonium that is about 2ml and continuous stirring for 30 minutes results a homogeneous solution. 100ml of Isopropyl alcohol is mixed with 6.76 gm(0.6mole) of Sodium hydroxide pellets with constant stirring for 30 minutes and drop wise addition of ammonium hydroxide. The homogeneous solution obtained is kept for 2-3 hrs. Simultaneously, as per the molar calculation for zinc oxide 6.67gm of zinc acetate di-hydrate is mixed with 100ml ammonium hydroxide is added by fixing the ph 12 with continuous stirring for 1-2 hrs. Then the solution is left for 30 minutes which results in the formation of white bulky solution. The solution is then washed 8-10 times with distil water and ethanol and filtered in a filter paper. The sample was allowed to dried, to remove the water which yields the corresponding precursor. Then, the prepared samples are placed in the middle of a muffle furnace in silica crucible. The precursor was then calcined at $600^0$ C for 1 hour toobtain ZnO powder. The final particle is collected and grained and preserved in a air tight container. Thus the pure Zno nanoparticles are obtained by wet chemical co-precipitation method .

**Synthesis of Mn-doped ZnO nanoparticles**

Zinc oxide nanoparticles are synthesized using the wet chemical co-precipitation method. The precursors used in the synthesis ZnO are Zinc acetate dihydrate having purity 99%. The need for surfactant is fulfilled by the use of Manganese acetate tetrehydrate which also possesses 99% purity. Isopropyl alcohol and ammonium hydroxide takes care for the homogeneity and pH value of the solution and helps to make a stoichiometric solution to get Zinc oxide nanoparticles. Firstly, in a 250ml conical flask 100 ml of Isopropyl alcohol is added with 6.67gm of zinc acetate dihydrate and dropwise ammonia is added with continuous stirring to get a homogeneous solution. After addition of 100 drops ammonium that is about 2ml and continuous stirring for 30 minutes results a homogeneous solution. 100ml of Isopropyl alcohol is mixed with 6.76 gm of Sodium hydroxide pellets with constant stirring for 30 minutes and dropwise addition of ammonium hydroxide. The homogeneous solution obtained is kept for 2-3 hrs. Simultaneously, as per the molar calculation for zinc oxide 6.67gm of zinc acetate di-hydrate is mixed with 100ml of Isopropyl alcohol and the solution is prepared which is subjected to continuous stirring to get a homogeneous solution. Now the two solutions are mixed together in 500ml beaker and drop wise ammonium hydroxide is added by fixing the ph 12 with continuous stirring for 1-2 hrs. Then the solution is left for 30 minutes which results in the formation of white bulky solution. To the above solution, 0.02gm of manganese acetate tetrahydrate and the mixture was stirred until zinc acetate dihydrate and manganese acetate tetrahydrate mixed and dropwise ammonium hydroxide is added with continuous stirring for 30 minutes to get a homogenous solution .The solution is then washed 8-10 times with distil water and ethanol and filtered in a filter paper. The sample was allowed to dried, to remove the water which yields the corresponding precursor. Then, the prepared samples are placed in the middle of a muffle furnace in silica crucible. The precursor was then calcined at $600^0$C for 1 hour to obtain 5% Mn doped ZnO powder . The final particles is collected and grained and preserved in a air tight container. Thus the 5% manganese doped zinc nanoparticles are obtained by wet chemical co-precipitation method.

The same procedure is repeated again to obtain 10% and 15% manganese doped zinc oxide nanoparticles by adding 0.05 gm and 0.08 gm of manganese acetate tetrahydrate in 6.67 gm of zinc acetate dihydrate. These nanoparticles are subjected to various studies.

## 3. Results and Discussion

**1.Structural Properties**

**Phase *confirmation***

**Fig.1** shows the X-ray diffraction patterns of the Pure ZnO and different Mn content. For pure ZnO five diffraction peaks at 2θ = $31.71^0$, $34.34^0$, $36.19^0$, $56.55^0$ and 62.81° corresponding to (100), (002), (101), (102), (110) and (103) crystal planes of hexagonal phase Structure are observed. The positions of the five peaks are coinciding with the values obtained in the JCPDS card.

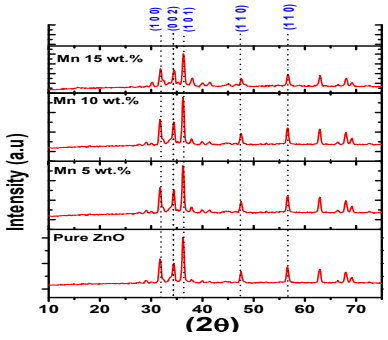
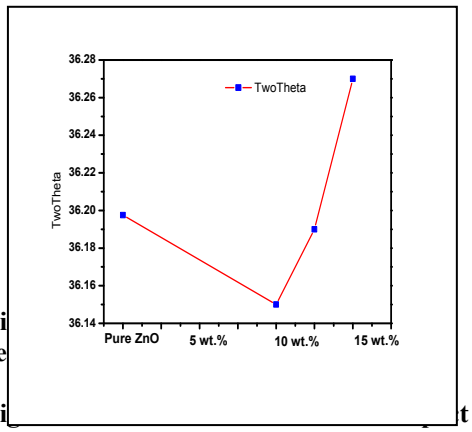



**Figure.**
**Mn Do**

For the ZnO with Mn content of 5 wt.%, the diffraction peaks are found at the angles of 2θ = 31.67$^0$, 34.29$^0$, 36.15$^0$, 56.47$^0$ and 62.74° corresponding to (100), (002), (101), (102), (110) and (103) ZnO reflections as shown in the fig.1. Similar peaks are observed in Mn doped ZnO nanoparticles

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**to Mn content in ZnO**

prepared using chemical vapour deposition by Shuang *et al*., **[1]** and sol gel process by Xiaolu Yan *et al*., **[2]**. It was found that for various samples, the phase wurtzite structure is formed. With the increased Mn content of 5 wt.%, the diffraction peaks of ZnO small shifting to lower angles as shown in the Fig.2 . This causes to increases of lattice constant arising from the replacement of more zinc atoms in the ZnO lattice by Mn. With further the increasing Mn content from 10 to 15 at.% , only hexagonal ZnO phase is present with large variation of two theta.

***Lattice Parameter***

The lattice parameter of various phases of ZnO is determined by using Unit Cell program as shown in the Fig .3 The calculated lattice parameter is well coincide with standard values a = 3.249 Å and c = 5.205 Å as per standard JCPDS pattern. For pure ZnO lattice parameter value is obtained 3.233 Å and showed increasing trend from 3.223 Å to 3.24734 Å for Mn content from 5 to 10 wt.%. The ionic radius of Zn2+ is 0.60 A°, and that of Mn2+ is 0.66 A°, for four-fold coordination [3]. Hence, Mn incorporation will lead to an expansion of the ZnO lattice. Furthermore small decreased trend were found at 15wt.% of Mn.

The strain also calculated using following equation

$$\text{Strain} = \frac{a - a0}{a0} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

a- Calculated Lattice Parameter from XRD

$a_0$ - Standard Lattice Parameter (From JCPDS - 3.249 Å

**Figure 3.Lattice Parameter Vs Strain with respect to Mn content.**

The calculated strain values were showed decreasing trend Mn doped ZnO than Pure ZnO samples. For pure ZnO sample showed around 0.016 and further Mn content of 5 wt.% showed nearly -0.0070 values which indicates doped samples had compressive strain .Further 10 to 15 wt.% samples also found to be strain value and showed drastic increasing trend from -0.0027 to 0.0026 . Its confirmation result higher Mn doped in ZnO samples are had lower compressive strain than lower content of 5 wt. %.

***Crystallite Size***

**Fig.4 .**shows relation between the FWHM and Crystallite size of ZnO with increase in the content of Mn. The crystallite size calculated from the (001) ZnO peak by Scherrer‟s equation (2)

**Crystallite Size = 0.9λ/β C**… (2)

Where λ be a of wavelength of Cu kα (1.54A˚), β be the Full Width Height Maximum (FWHM) value, θ be the peak value

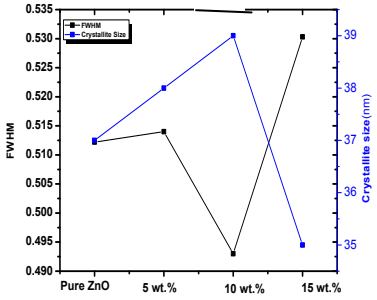


**Figure.4.** FWHM and crystallite size of Pure ZnO and Manganese Doped ZnO

The crystallite size of Mn doped ZnO is calculated using Scherrer's formula [2].For Pure ZnO sample FWHM value showed about 0.5122, contrary 5 wt% Mn doped ZnO the full width half maximum (β) were increased from 0.5122 to 0.5303. While for pure ZnO sample the crystallite size is 37 nm, it increases from 37 to 38 nm for the Mn content of 5 wt.% and to 39 nm for 10 wt.%, respectively. However, that the intensities of diffraction peaks decline as the Mn2+ ion concentration increases, i.e. the Mn doping within the sample causes the ZnO crystallinity to deteriorate. Since the intensity of diffraction peaks becomes weaker and the half-peak width becomes wider with the increase of dopant concentration, the Mn2+ ions inhibit the aggregation of ZnO nanoparticles and affect the crystallization of ZnO. For further increase of Mn that is 15 wt% Mn doped ZnO the (β) of the peaks become lower than other samples which implies crystallite size increases from 39 nm to 35nm.. At higher

content of Mn crystallite showed higher value than any other sample which implies that Mn may help to promote the growth ZnO at certain level of dopant content.

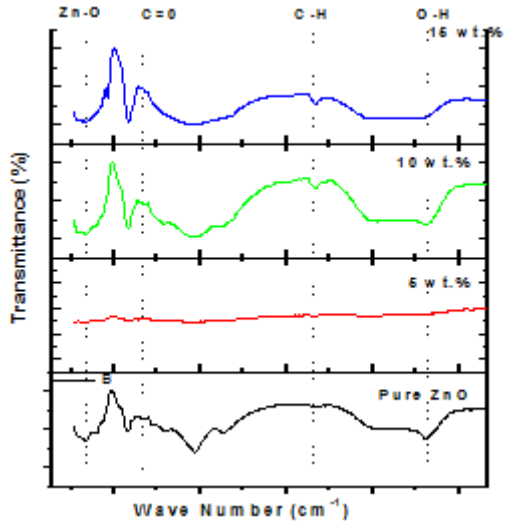


**Figure 5:** FTIR Spectrum of Pure ZnO and Manganese Doped ZnO

## 2. Fourier Transform Infrared Spectroscopy

Infrared spectroscopy gives the information on molecular vibration or more precisely on transition between vibration and absorption energy level. Absorption of radiation in the infrared region results in the excitation of bond deformation, either stretching or bending vibration occurs at certain quantized frequencies. The plot of absorption intensity verse wave number is referred to as the „infrared spectrum" compound

The FTIR spectra of Pure ZnO and Mn doped ZnO are given in Fig.5. There are two broad absorption bands in sample at wavenumber of about 1442 cm−1 due to C=O stretching mode. On increasing the Mn doped ZnO band showed sharp edges. The other two peaks observed at about 3240 and 3400 cm−1 belongs to vibrations of C–H and O–H, respectively. The effect of doping level in spectra, in the region 400–700 cm-1, is explained. Zn–O stretching modes are clearly presented in pure ZnO samples centered at about 492 cm−1 and a shoulder at 510 cm−1 . Moreover, the shoulder is clearly blue shifted with increasing Mn content. Otherwise, Zn–O absorption peaks are broadened in the range of 10 to 15wt.% respectively. The peak position of FTIR spectrum with respect to Mn content in ZnO is shown in the Fig 5

The peak position C=O, C–H, and O–H were shifted lower position from the original position with Mn doped sample in ZnO in the range of 5 to 15 wt.% as shown in the figure 6. However Zn–O absorption peaks shifted lower poistion which indicates the Mn replaced by Zn substitution atoms. Further Mn from 10 to 15 wt.% were increased band position which indicate Mn and Zn act as a metal oxide in the higher contents

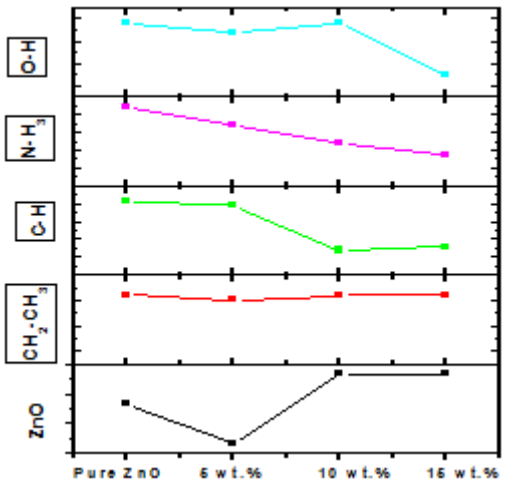


**Figure 6:** Peak shifting Mn Doped ZnO samples

## 3. Optical Studies

The optical transmittance of the Pure ZnO and Mn doped ZnO nanoparticle was determined by the spectrophotometer within the wavelength range of 200-2500nm. For the transmittance measurements, the nanoparticles were grown on quartz substrate and irradiated at a perpendicular angle of incidence with quartz glass as reference. The typical room temperature transmittance spectra for undoped ZnO and different concentration of Mn doped ZnO. The optical absorption coefficient (α) is evaluated from the transmission spectra using the relation

$$\alpha = -1/d \ln(T) \quad (1) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where d is the thickness of the film and T is the transmittance. The optical band gap was evaluated using the relation:

$$(\alpha h\nu)2 = A( h\nu - Eg) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where A is a constant, hν the photon energy, and Eg is the energy gap. The absorption coefficient was a function of photon energy for Pure ZnO and Mn doped ZnO sample.

**Table 1**

| *Sample* | *Band Gap (eV)* |
|---|---|
| Pure ZnO | 3.77 |
| 5wt.%Mn doped ZnO | 3.56 |
| 10 wt.%Mndoped ZnO | 3.4 |
| 15 wt.%Mn doped ZnO | 3.28 |

We obtained the band gap to be 3.77eV for undoped ZnO and it starts decreasing for 5 wt%, 10 wt% and 15 wt.% of Mn doped ZnO samples as 3.56eV, 3.4eVand 3.28eV as shown in the table 1. The decrease in Eg for increasing Mn content is attributed to the s-d and p-d interactions giving rise to band gap bowing and it has been theoretically explained using second-order perturbation theory [15].

## 4. Conclusion

ZnO sample containing transition metal Mn synthesized by wet chemical co-precipitation method correspond to a hexagonal structure similar to that of undoped ZnO. The XRD measurement suggests that Mn atoms substitute Zn sites in the crystals without changing the wurtzite structure, but with the lattice parameters varying slightly with the

extent of doping. We also observed on doping the grain size reduces drastically reducing to nano-scale i.e., doping hinders the grain growth . No secondary phases were observed for the simple synthesis process adapted in the present work for the doped ZnO samples upto 15 wt% of Mn doping. The FTIR analysis confirms the formation of ZnO and Mn doped ZnO. The UV-VIS-MNR measurements show the reduction in the band-gap upon Mn doping for concentration of Mn ≤ 15 wt.%

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## Author Profile

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