Structural and morphological study of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O synthesized by sol-gel wet chemical precipitation route

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Abstract. Transition metal substituted Zinc oxide (ZnO) has drawn a great deal of attention due to its excellent properties. Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O sample synthesized was by Sol-gel wet chemical precipitation route at temperature 350°C. The crystallinity and the structure of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O was determined by X-ray diffraction by Cu-K$_\alpha$ radiations operated at 40kV and 35mA in the range of 20° to 80°. The pattern gets indexed in wurtzite (hexagonal) structure with lattice constants a=b= 3.2525Å and c= 5.2071Å and approves the single phase material with no impurity. The values of particle size assessed by Debye Scherer's (DS) formula lie in the range of 13nm to 33nm indicating the nano-crystalline nature of the sample. The morphological analysis of the sample was performed by Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) measurements. The observed size of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O nanoparticles by TEM micrograph exhibits the similar trend with the size calculated by Debye-Scherer formula. TEM image show the irregular shape of the nanoparticles and particle size lies in the range of 10-35nm. Similar to SEM image, the slight agglomeration of the nanoparticles have been observed from TEM.

1. Introduction
Semiconducting nanoparticles are of tremendous interest now-a-days for fundamental as well as applied research because the properties of the materials change significantly when the particle size reaches bulk to nano size range. Semiconducting nanoparticles are one of the key player in the industrially important materials due to size-dependent properties like alteration in the optical properties and variation of the energy gap. Zinc oxide is an excellent n-type semiconductor with a extensive direct band gap and great exciton binding energy [1, 2]. “3d” transition metal substituted ZnO material, has been of great interest for industrial applications like Optoelectronics, UV- light emitting diodes, Chemical sensors, piezoelectric devices. For Optoelectronic field, it is important to tune the optical band gap which can be done by way of doping, with various “3d” transition metal [3-7]. Doping with transition metals offers generation of dilute magnetic semiconductors (DMS) into nonmagnetic semiconductors. Dietl’s reported the room temperature ferromagnetism of transition metal doped ZnO and it can be used for “spintronics” devices [8, 9]. Transition metals which contain unpaired electron or have partially filled d- states, are responsible for materials to exhibit magnetic behaviour. This property makes them for use as non-volatile switching elements [8, 9]. Over last decades, most of the research efforts were made to Mn and Co doped ZnO. Very less studies were reported for Mn and Fe doped ZnO [10]. Co-doped Mn and Fe in ZnO nanostructures may contribute the local magnetic moments and enhancement of the charge carrier density. ZnO nanoparticle can be synthesized on a
large scale at low cost by simple-solution methods, such as chemical precipitation [11] and gel combustion method [12]. The sol-gel technique permits mixing of the chemicals at microscopic level, thus reducing the possibility of undetectable impurity phase [13] also have the numerous benefit over other synthesizing processes like use of simple apparatus, low cost, environment friendly and reliability. In this paper, we report on the structural and morphological study of \( \text{Zn}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O} \) synthesized by sol gel wet chemical precipitation method.

2. Experimental details

A basic procedure to synthesize particles was employed, on the lines of the “Co-Precipitation” method which contains dissolving a salt precursor in water to precipitate the hydroxide form with the help of a base [14-15]. The focus was on preparing pure transition metal doped Zinc oxide. The Zinc chloride (\( \text{ZnCl}_2 \)), Manganese chloride (\( \text{MnCl}_2\cdot4\text{H}_2\text{O} \)), Iron chloride hexa hydrated (\( \text{FeCl}_3\cdot6\text{H}_2\text{O} \)) were used without further purification. The precursors were mixed in 100 ml water in desired proportions. Solutions were stirred for half an hour with a magnetic stirrer to get homogeneous solution. Citric acid anhydrous (\( \text{C}_6\text{H}_8\text{O}_7 \)) was added to the solution. After an hour of stirring, 10ml ethylene glycol (\( \text{C}_2\text{H}_4\text{O}_2 \)) added and pH was maintained at 1.5 with continued stirring. Liquid ammonia was added drop wise with constant monitoring of the pH value to bring it to 7. Extra precaution was taken while adding liquid ammonia, as an overdose may render the entire solution useless for the purpose of the experiment. The solution was further stirred for another 30 minutes after adding ammonia, attaining the right pH, at a temperature of 60°C. The solution was then poured on to a watman filter paper to extract the precipitate from the sol. The precipitate (gel) was then gently scraped from the filter paper, and then washed several times with distilled water and ethyl alcohol. Washed gel was dried in hot air oven at 110°C for two hours and then cooled and ground using agate mortar and pestle, to get a fine powder. A final heating was done in a muffle furnace at 350°C for a period of two hours, before subjecting the sample to analytical measurements. Structural characterization is performed using a Panalytical 'X' pert MPD X-ray diffractometer with Cu-Kα radiation (\( \lambda = 0.15418 \) nm) operating at 40 kV and 35 mA for 2θ values ranging from 20° to 80°. Surface morphologies and structural details of sample have been carried out using SEM (Carl Zeiss make and Model No. EVO18) and TEM (FEI make and model no. TECNAI T20S TWIN).

3. Results and discussions

3.1. XRD analysis

The diffraction pattern, Figure 1, shows that the sample \( \text{Zn}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O} \) is polycrystalline with wurtzite (hexagonal) structure having preferred orientations along (100), (002) and (101) planes and showing the growth of \( \text{ZnO} \) crystallites along different directions [16]. No other phases except that for \( \text{ZnO} \) is detected, indicating that the doping of Mn and Fe does not alter the Wurtzite (hexagonal) structure of \( \text{ZnO} \). The peaks intensity is sharp and narrow, confirming that the sample is of good quality with perfect crystallinity and fine grain size. The lattice parameters “\( a \)” and “\( c \)” are calculated for plane (100) and (002) of the sample. The values of lattice parameters are \( a=b=3.2525 \) Å and \( c=5.2071 \) Å. The values are slightly higher than those of reported for \( \text{ZnO} \) polycrystalline powder (\( a=3.249 \) Å, \( c=5.206 \) Å) in reference [17].

The slightly increasing value of lattice parameters is due to the smaller ionic radii of \( \text{Zn}^{2+} \) (0.74Å) ions than \( \text{Mn}^{2+} \) (0.80Å) ions and comparable to \( \text{Fe}^{2+} \) ions [18] and secondly, the oxygen vacancy associated with nanoparticles [19]. The advanced structural parameter ratio \( c/a=1.60 \) is resulting due to hexagonal close packing. The standard value of the \( c/a \) ratio for the Wurtzite structure is about 1.63. It is known that when the bonding character is more ionic, the \( c/a \) ratio moves to the ideal values [20]. There is a good concurrence between obtained values and the standard one which indicates that \( \text{Mn}^{2+} \) and \( \text{Fe}^{2+} \) ions are able to substitute the \( \text{Zn} \) ions in the \( \text{ZnO} \) lattice without any effect on overall crystal structure. The obtained volume (\( V \)) = 47.7Å³ of unit cell in \( \text{Zn}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O} \) is more than that of pure \( \text{ZnO} \), due to increase of the lattice parameters “\( a \)” and “\( c \)” [21, 22]. The Atomic packing fraction (APF) = 0.755 was calculated using the XRD data. The APF of particles is found to be nearly 75.5% in hexagonal structure, which is slightly more than the reported value 74% for \( \text{ZnO} \) [22]. The bond length (\( L \)) =
1.996 Å for Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O is calculated. It is known that ionic radius of O$^{2-}$ is 1.38Å and ionic radius of Zn$^{2+}$ is 0.74Å consequently, the length of the Zn-O bond is 2.12Å [18, 23, 24]. The small value of bond length indicates the presence of the structural defects or oxygen vacancies in our sample. The importance of the broadening of peaks indicates grain refinement along with the large strain coupled with the powder.

The instrument-corrected broadening ($\beta_{hkl}$) corresponding to the diffraction peak of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O was estimated using the relation:

$$\beta_{hkl}^2 = \beta_{hkl \text{ measured}}^2 - \beta_{\text{instrumental}}^2$$

The particle size ($t_{DS}$) in the samples is estimated using Debye Scherer’s (DS) formula as in equation (1) [25-27].

$$t_{DS} = \frac{k\lambda}{\beta_{hkl \cos \theta}}$$

Where, $t_{DS}$ is the particle size, $k$ is the Scherer’s constant and is taken equal to 0.9, $\lambda$ (wavelength of CuK$\alpha$) is 0.15418 nm and $\beta_{hkl}$ is full width at half-maximum (fwhm) of X-ray diffraction peaks in radians and $\theta$ is angle of Bragg’s reflection.

Crystallite sizes along different crystallographic planes are presented in Table 1. The values of particle size lie in the range from 13 to 33nm indicating the nano-crystalline nature of the sample.

| Sample       | Particle size ($t_{DS}$) in nanometre | Gauss fitted fwhm (rad) |
|--------------|--------------------------------------|------------------------|
| Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O | (100) 0.0045, (002) 0.0047, (101) 0.0057, (102) 0.0082, (110) 0.0057, (103) 0.0098, (112) 0.0134 | 33, 32, 27, 19, 29, 17, 13 |

Due to massively defect clusters of the grain edge and imperfection free of grain interior, the nano-crystalline material usually grieves from structural strain [28, 29].

The average crystallite size and strain can be calculated by Williamson and Hall [W-H] plot [29], as shown in Figure 2, with different X-ray peaks taken into consideration. Depending on different $\theta$
positions the size and strain broadening analysis has been done using [W- H] relation as in equation (2):

\[ \beta_{hkl} \cos \theta = \frac{0.9\lambda}{\tau_{WH}} + 2\varepsilon \sin \theta \]  

(2)

Where, \( t_{WH} \) is the crystalline size and \( \varepsilon \) is lattice strain. Graph between \( \beta_{hkl} \cos \theta \) and \( \sin \theta \) is plotted and then a linear fit to the points is extrapolated to give the crystallite size and Lattice strain [26, 31]. From W-H plot particle size (\( t_{WH} \)) = 54 nm and strain (\( \varepsilon \)) = 0.0122 were observed. Strain might be due to the lattice shrinkage. The particle size obtained from DS formula closely fitted with those obtained by the W-H plot for the sample under tensile strain. The dislocation density (\( \rho \)), represents the length of dislocation lines per unit volume, and the amount of defects [32,33], here varies randomly between \( 9\times10^{-14} \) lines/m\(^2\) and \( 63\times10^{-14} \) lines/m\(^2\) for Zn\(_{0.9}\)Mn\(_{0.05}\)Fe\(_{0.05}\)O sample along each plane [Table 2]. The orientation parameter \( \gamma_{[hkl]} \) for the Zn\(_{0.9}\)Mn\(_{0.05}\)Fe\(_{0.05}\)O sample is obtained from the relative heights of all the peaks present in the pattern Table 2.

| Sample                  | Planes | (100) | (002) | (101) | (102) | (110) | (103) | (112) |
|-------------------------|--------|-------|-------|-------|-------|-------|-------|-------|
| Zn\(_{0.9}\)Mn\(_{0.05}\)Fe\(_{0.05}\)O |        |       |       |       |       |       |       |       |
| Dislocation Density (\( \rho \)) |       | \( 9\times10^{-14} \) | \( 10\times10^{-14} \) | \( 14\times10^{-14} \) | \( 28\times10^{-14} \) | \( 12\times10^{-14} \) | \( 35\times10^{-14} \) | \( 63\times10^{-14} \) |
| Orientation Parameter (\( \gamma_{[hkl]} \)) |       | 0.24  | 0.16  | 0.28  | 0.05  | 0.12  | 0.07  | 0.08  |
| Morphology Index (MI)    |       | 0.75  | 0.74  | 0.70  | 0.62  | 0.70  | 0.58  | 0.5   |

The values of \( \gamma_{[hkl]} \) varies from 0.05 to 0.24 indicating random orientation. Larger orientation appears along the plane (101) in the sample [34, 35]. A XRD Morphology Index (MI) is derived from fwhm of XRD data. MI relates the fwhm of two peaks to its particle morphology. Generally, for highest fwhm peak, the MI is 0.5 because the MI is derived from the single peak. MI is obtained using equation (3).

\[ MI = \left[ \frac{\text{fwhm}_{H}}{\text{fwhm}_{P} + \text{fwhm}_{P}} \right] \]  

(3)

Where, \( \text{fwhm}_{H} \) is highest fwhm value obtained from peaks and \( \text{fwhm}_{P} \) is value of particular peak’s fwhm. The values of MI lie in the range of 0.50 to 0.75 and the details are presented in Table 2. It is correlated with the particle size (ranges from 13 to 33nm). It is observed that MI has linear relationship with particle size [36]. The result is shown in Figure 3.

**Figure 3.** Morphology index versus Particle size.

**Figure 4.** SEM image of the Zn\(_{0.9}\)Mn\(_{0.05}\)Fe\(_{0.05}\)O nanoparticles.
4. Morphological measurements

Scanning electron microscopy is used here to study the surface morphology of the Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O sample. Figure 4 SEM measurements shows the formation of cotton balls like structure of irregular shape and simultaneously agglomeration of particles seems to have occurred on the surface. SEM measurements shows the irregular shape of the nanoparticles and particle size lies in the nano range. TEM provides further insight into the morphologies and structural details of sample. Figure 5, shows the TEM image of the Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O nanoparticle. The observed size of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O nanoparticles by TEM micrograph exhibits the similar trend with the size calculated by Debye-Scherer formula. TEM images also show the irregular shape of the nanoparticles and particle size lies in the range of 10-35nm. Similar to SEM image, the agglomeration of the nanoparticles has been observed from TEM also. Figure 6, displays the electron diffraction patterns of the sample which shows that the Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O particles nature are crystalline. Seven fringe pattern corresponding to planes (100), (002), (101), (102), (110), (103), and (112) are consistent with the peaks observed in the XRD pattern [37]. Figure 7, shows the HRTEM image of the Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O nanoparticle. HRTEM pattern indicates that the Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O has standard hexagonal structure and grow along the c-axis [38].

![Figure 5. TEM image of the Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O.](image1)

![Figure 6. SAED image of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O.](image2)

![Figure 7. HRTEM pattern of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O.](image3)

5. Conclusions

The Sample Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O was synthesized successfully by Sol-gel wet chemical precipitation route. The crystal structure and morphological study of Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O sample were investigated at length. The Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O has wurtzite (hexagonal) crystal structure. The SEM image shows the clustering of particles occurred on the surface. TEM images show the irregular shape of the nanoparticles and particle size lies in the range of 10-35nm. HRTEM pattern indicates that the Zn$_{0.9}$Mn$_{0.05}$Fe$_{0.05}$O has standard hexagonal structure and grow along the c-axis.

6. References

[1] Gyu-Chul Yi, Wang C and Park W 2005 Semicond. Sci. Technolog. 20 S22.
[2] Zhang Q, Yu K, Bai Q W, Wang Q, Xu F, Zhu Z, Dai N and Sun Y 2007 Materials Lett. 61, 3890-3892.
[3] Nomura K, Ohta H, Ueda K, Kamiya T, Hirano M and Hosono H 2003 Science 300 (5623) 1269-1272.
[4] Yuzhen L, Guo L, Huibin X, Ding L, Chunlei Y, Jiannong W, Weiken G, Shine Y and Ziyu W 2006 J. Appl. Phys. 99 114302-114304.
[5] Ushio Y, Miyayama M and Yanagida H 1994 Sensor and Actuat. B 17 221-226.
[6] Ohtomo A, Tamura K, Kawasaki M, Makino T, Segawa Y, Tang Z K, Wong G K L, Matsumoto Y and Koinuma H 2000 Appl. Phys. Lett. 77 2204-2206.
[7] Pearton S J, Heo W H, Ivill M, Norton D P and Steiner T 2004 Semicond. Sci. Technol. 19, R59-R74.
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