Chapter 5

Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.0 \leq x \leq 0.36$)

5.1 Introduction

Zinc Oxide (ZnO) nanostructures are of great interest due to their unique physical, chemical properties as well as spintronic [1] and optoelectronic device application [2] due to wide energy band gap (3.37 eV) and large exciton binding energy (60 meV). Among the II-VI semiconductors, although cadmium Selenide and cadmium Telluride has shown to be promising in solar cell applications, but they are toxic and harmful to the environment. With an increasing awareness of green and clean energy, ZnO based nanostructures are more suitable candidates for cost-effective and environmentally friendly applications [3, 4]. Physical properties of ZnO nanoparticles can be tailored by introducing the dopant element [5]. Doping of transition metal (TM) ions in the ZnO has lead to enhancement of the energy band gap, optical, electrical and magnetic properties [6-8]. The TM ions have several advantages as a dopant that makes easy to incorporate into ZnO crystal structures and induced the magnetic as well as optical properties [9, 10]. Especially, a significant attention has been recently given to investigate the effect of doping elements such as (V, Cr, Fe, Co, Ni) on its electrical, optical and magnetic properties of ZnO nanoparticles [11]. Furthermore, many theoretical and experimental evidences suggested that ZnO doped with transition metals is a promising host semiconductor material exhibiting ferromagnetism when doped with transition metal [12]. However, the source of ferromagnetic behaviour is not very well clear in these ZnO nanocrystals [13]. In order to understand the source of ferromagnetism at room temperature in dilute magnetic semiconductor material some theories and mechanism [161]
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were reported in the literature. The first theory was proposed by Dietl et al. [14], which was based on carrier–mediated mechanism and the second theory was proposed by Coey et al. [15] which was based on bound magnetic polarons (BMP) model. The main basis of this model is the presence of charge defect content which holds the electrons to cause the super exchange interaction between two metal ions. Furthermore, it was a spin-split band theory in which shallow donors controlled the magnetic moment of dopants in n-type wide band gap DMSs. It is worthy to mention that in case of DMSs, the kind of carriers, their mobility and density provide an opportunity to manipulate the ferromagnetic properties. Based on the prediction of Dietl et al., considerable effort has been focused on achieving reliable ZnO-based DMS with a Curie temperature well above room temperature by doping with transition metals, especially Mn and Co. According to these theoretical calculations, room-temperature ferromagnetism is the stable phase for a p-type doped Zn$_{1-x}$Mn$_x$O with 5 % Mn and $3.5 \times 10^{20}$ holes/cm$^3$.

Although, many preparation methods have been used to produce high quality Mn-doped ZnO nanoparticles, the obtained results are contradictory. Antiferromagnetic behavior was observed in Zn$_{0.64}$Mn$_{0.36}$O films prepared by pulsed laser deposition and polycrystalline ZnO: Mn powder samples [16, 17]. Paramagnetic properties were reported for Zn$_{0.93}$Mn$_{0.07}$O films prepared by magnetron sputtering [18]. Both the presence and the absence of ferromagnetism have been reported in Mn-doped ZnO thin films [19-21]. In bulk system the same contradictions are observed [22]. Recently, Garcia et al. [23] have reported that the presence of ferromagnetism with a coexistence of Mn$^{3+}$ and Mn$^{4+}$ in manganese oxides via a double-exchange mechanism. In both of these cases, manganese oxides with diffused Zn are considered to be responsible for the ferromagnetism. Recently, Ferromagnetism was observed in insulating ZnMnO, n-type ZnMnO, and p-type ZnMnO. However, the absence of ferromagnetic ordering in Zn,
MnO was also reported [20, 24-27]. Recently, it is understood that free carrier are the necessary for room temperature ferromagnetism [28]. The differences in the reported results are due to different preparation methods and the environment, since the properties of ZnO are sensitive to the preparation conditions.

The control of chemical composition, purity, morphology, and particle size is very important to obtain suitable metal-ions doped ZnO powders for their desired applications. A number of synthesis methods have been devoted to the fabrication of transition metal doped ZnO nanoparticles and thin film, such as auto combustion method [29], ball milling method [30], co-precipitation method [31], hydrothermal process [32], solid state reaction method [33]. Among these synthesis methods, we have adopted sol-gel auto combustion synthesis method for preparation of Mn$^{2+}$ doped ZnO nanocrystalline material. In the literature, the synthesis of ZnO/TiO$_2$ nanopowders obtained by sol-gel auto combustion method is reported [34]. The sol-gel auto combustion method is widely used by many researchers and has many advantages over the other methods. The advantages of this method are (i) fast heating rate and short reaction time (ii) the reagents are mixed at the molecular level (iii) high product purity and crystallinity (iv) fine particle size and narrow particle size distribution (v) it is easy to control stoichiometry (vi) dopants can be easily introduced into the final product (vii) simple equipment and preparation process (viii) low processing time (ix) low external energy consumption (process initiates at low temperatures) and multiple steps are not involved [35]. Solution combustion synthesis is an effective technique for the preparation of nanoscale material. The sol-gel auto combustion method is unique to obtain high porosity and high surface area to volume ratio fine particles. The method is best on the principle that once the reaction is started with low temperature an exothermic reaction occurs that becomes self-sustaining for a certain time interval. ZnO is a
multifunctional material and the solubility of transition metal in it is relatively high. Doping is one of the effective ways to modify the properties of ZnO material for desired application. Structural, optical and magnetic properties of ZnO materials can be changed with doping of transition metal ions. Among the transition metal ions, manganese is considered as a potential candidate because of its variable oxidation state, large solubility limit in ZnO matrix. To our knowledge, the effect of higher doping of Mn\(^{2+}\) ions on the structural, morphological, optical, dielectric, electrical and magnetic properties of ZnO nanoparticles has not been reported in the literature.

In the present work the ZnO nanoparticles with Mn substitution have been synthesized by using sol-gel auto combustion technique by optimizing the metal nitrate to citric acid ratio as 1:1. The influence of manganese substitution on the structural, morphological, optical, electrical, dielectric and magnetic properties of ZnO has been investigated and the results are presented in this chapter.

### 5.2 Experimental technique

#### 5.2.1. Synthesis of Zn\(_{1-x}\)Mn\(_x\)O (0.00 \(\leq x \leq 0.36\)) nanoparticles

Nanocrystalline Zn\(_{1-x}\)Mn\(_x\)O (\(x = 0.00, 0.06, 0.12, 0.18, 0.24, 0.30\) and \(0.36\) mol) samples were synthesized by a sol-gel auto combustion method. All of the chemical reagents used in our experiments were of analytical grade and utilized as received without further purification. Zinc nitrate hexahydrate Zn (NO\(_3\))\(_2\).6.H\(_2\)O, 98 %, Sigma-Aldrich), Manganese nitrate hexahydrate (Mn (NO\(_3\))\(_2\).6H\(_2\)O, 99 %, Sigma-Aldrich), and Citric acid monohydrate (C\(_6\)H\(_8\)O\(_7\).H\(_2\)O, 99.57 % Merck) were used. All the reagents were dissolved in double distilled water. Citric acid was used as a fuel. The fuel ratio was taken according to stoichiometries proportion of metal nitrate to oxidizer ratio (1:1). In a typical synthesis of Zn\(_{1-x}\)Mn\(_x\)O samples, the appropriate proportion of Zn(NO\(_3\))\(_2\).6H\(_2\)O, Mn(NO\(_3\))\(_2\).6H\(_2\)O and C\(_6\)H\(_8\)O\(_7\).H\(_2\)O were completely dissolved in a minimum amount of
double distilled water to get the aqueous solution. The aqueous solution was then stirred for about 1 h in order to mix the solution uniformly. The mixed solution was evaporated to dryness by heating at 90° C on a hot plate with continuous constant stirring and finally formed a very viscous gel. The viscous gel was ignited by increasing temperature up to 200 °C and the loose powder of the samples was obtained. Finally, the burnt powder was sintered at 600 °C for 6 h to obtain manganese substituted zinc oxide nanoparticles. The resulting powders of undoped and manganese doped ZnO powder were white in colour. All the samples were ground for a half an hour and were prepared as best nanopowders. The typical synthesis images of Zn$_{1-x}$Mn$_x$O ($x = 0.00$, 0.06 mol) nanoparticles have been shown in Fig. 5.1(a). A flowchart of sol-gel auto combustion synthesis method for undoped and Mn doped ZnO nanoparticles are shown in Fig. 5.1 (b). The chemical reaction of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles is shown in Fig. 5.1 (c).

### 5.2.2. Characterization techniques

The crystalline nature and the phase identification of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles were examined through X–ray powder diffraction analysis (XRD) technique using (Model: Xpert PRO MPD) with Cu-Kα radiations ($\lambda = 1.5405$ Å) operated at a voltage of 45 kV and current of 40 mA. The grain size and surface morphology of the prepared nanoparticles was studied by scanning electron microscopy (ZEISS Ultra FE-SEM) technique. The stoichiometries proportion of the constituent ions was examined through the energy dispersive X-ray analysis (EDAX) technique. In order to study the accurate size and crystalline characteristics of prepared nanoparticles transmission electron microscopy (TEM, Philips CM-200, Operating voltages: 20-200 kV, Resolution: 2.4 Ao) and selected area diffraction (SAED) techniques were used respectively. Fourier transform infrared spectroscopy (FT-IR) spectra of all the samples
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5.3 Results and discussion

Structural analysis

5.3.1. X-ray diffraction (XRD)

The X–ray diffraction patterns of all synthesized Zn$_{1-x}$Mn$_x$O (0.0≤x≤0.36) nanoparticles are shown in Fig. 5.2 (a-d). X-ray diffraction analysis revealed that all the diffraction peaks in the XRD pattern well match with the standard pattern of pure ZnO (JCPDS: 36-1451). From the analysis of XRD pattern of undoped and Mn doped ZnO nanoparticles revealed the formation of hexagonal wurtzite structure. It is evident from Fig. 5.2 (d) that a small amount of impurity peaks in the form of Mn$_3$O$_4$ is present. The impurity peak of Mn$_3$O$_4$ has been observed for sample x = 0.36 mol. This result indicated that the doping
The limit of Mn in ZnO samples is below 0.3 mol. Similar reports are available in the literature [36, 37]. The careful analysis of the expanded XRD patterns in the 30°–37° 2θ region, shown in Fig. 5.3, clearly shows that there is a significant shifting and broadening in (100), (002) and (101) peaks position toward higher 2θ value relative to that of pure ZnO with increasing of Mn²⁺ content. The variation of the 2θ position of XRD patterns which indicate that the lattice parameters of ZnO changes very slightly with Mn²⁺ doping, due to the differences of ionic radii of Mn²⁺ (0.83 Å) and Zn²⁺ (0.72 Å) [38, 39]. From the analysis of Fig. 5.4, it is found that the diffraction peak intensities decreases with an increase in Mn²⁺ content in ZnO matrix, which indicates that the dopant Mn²⁺ ions are substituted in the inner lattice of Zn²⁺ ions. Fig. 5.5 shows the variation of full width at half maxima of most intense peak and the average crystallite size with Mn²⁺ content and co-relation between them. Average crystallite size of nanoparticles was calculated from the Debye-Scherrer’s equation [40].

\[
D = \frac{0.90 \lambda}{\beta \cos \theta}
\]  

where, \( \lambda \) is the X-ray wavelength (1.540 Å), \( \beta \) is the full width half maximum of the most intense peak, \( \theta \) is the Bragg’s angle position.

The increase of the full width at half maxima of the diffraction peak reveals that the crystallite size decreases with increase in Mn²⁺ content. The average crystallite size of pure ZnO nanoparticles was found to be as 17 nm, and it is found to be decreased with increase in Mn²⁺ content, and represented in Table 5.2. The reduction in the average crystallite size is mainly due to the distortion in the host (ZnO) lattice by foreign impurity introducing that decrease the nucleation and growth rate of ZnO nanoparticles [41]. The substitution of Mn²⁺ ion in an interstitial position would affect the content of the interstitial Zn, oxygen and Zn vacancies. The observation of small changes of 2θ
values in diffraction peaks and peak broadening is due to the increase of micro strain in nanoparticles and decrease size of the nanoparticles. The structural change obtained from the diffraction peaks illustrates the incorporation of Mn\textsuperscript{2+} ions into the ZnO lattice, which indicates that the crystal structure has no obvious change up to x = 0.30 mol by Mn\textsuperscript{2+} doping because after doping of Mn\textsuperscript{2+} in ZnO show secondary phase (Mn\textsubscript{3}O\textsubscript{4}). The micro strain can be calculated using the equation [42].

\[ \varepsilon = \frac{\beta \cos \theta}{4} \] (2)

The lattice parameters of the hexagonal wurtzite structure undoped and Mn\textsuperscript{2+} doped ZnO nanoparticles were calculated from the using equation [40, 42].

\[ \frac{1}{d^2} = \left[ \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right) \right] \] (3)

The calculated lattice parameters ‘a’ and ‘c’ of undoped and Mn\textsuperscript{2+} doped ZnO nanoparticles are listed in Table 5.1. The lattice parameters a and c are found increases with increase in Mn content in ZnO nanoparticles because of higher ionic radius of Mn\textsuperscript{2+} ions (0.83 Å) in comparison to the Zn\textsuperscript{2+} ions (0.72 Å). However, the lattice parameter c linearly increase up to 0.36 mole with increase in Mn content, whereas lattice parameter ‘a’ linearly increase up to x = 0.30 mol and sudden decreases for x\geq0.30, it may be due to the doping limit of Mn or due to Mn\textsuperscript{3+} and Mn\textsuperscript{4+} brings. A similar behaviour of lattice parameter has been reported for Mn doped ZnO system by Duan L. B. et al. [37]. The variations of lattice parameter with Mn\textsuperscript{2+} content have been shown in Fig. 5.6. The volume of the unit cell was calculated using the equation [41].

\[ V = \frac{\sqrt{3}}{2} a^2 c \] (4)

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where, V is the volume of the hexagonal unit cell, ‘a’ and ‘c’ are lattice parameter. It was found that the volume of the unit cell increases with increase of Mn$^{2+}$ doping level, the obtained values of volume of unit cell present sample is displayed in Table 5.2.

The X-ray density was determined using the equation [43].

$$\rho_x = \frac{nM}{N_AV} \quad (5)$$

where, $n$ is the number of atoms per unit cell, M is the molecular weight, $N_A$ is the Avogadro’s number and V is the volume of the unit cell.

Fig. 5.7 shows the variation of X-ray density and the volume of the unit cell with Mn$^{2+}$ content. From Fig. 5.7, it is seen that the X-ray density decreases with increase in Mn$^{2+}$ content. The behaviour of X-ray density is attributed to the fact that decreases of volume of unit cell and molecular weight of the samples. The values of X-ray density and volume of the unit cell are tabulated in Table 5.2. The X-ray density decreases and volume of unit cell increases with the increase in Mn$^{2+}$ content. It means that Mn$^{2+}$ ions go to the Zn$^{2+}$ site in ZnO structure [44]. The values of X-ray density has been found suddenly change, when $x \geq 0.30$ mol. It may be due to the solubility limit of Mn$^{2+}$ ions in ZnO nanoparticles i.e. $\approx 0.30$ mol. The atomic packing fraction was calculated using the equation [42].

$$APF = \frac{2\pi a}{3\sqrt{3}c} \quad (6)$$

where, a and c are the lattice parameters. The values of atomic packing factors (APF) are listed in Table 5.1. It is found that values of atomic packing factor increase with increase in Mn content, it may be due to the decreases of voids in the samples. The atomic packing factor of bulk ZnO nanomaterials is about 74 %. But in our result the atomic packing factor is 75 % in hexagonal wurtzite structure. It means that APF in nanocrystals are slightly larger than that of bulk nanomaterials. It may be due to the size effect in the
nanocrystalline samples. The variation of atomic packing factor, it suggests that homogeneous substitution of Mn$^{2+}$ ions in the Zn$^{2+}$ site of ZnO hexagonal wurtzite structure.

The bond length of undoped and doped ZnO nanoparticles has been calculated using the following equation [41].

\[ l = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2} \]  \hspace{1cm} (7)

where, a and c are lattice constant, u is the positional parameter.

The Zn-O bond length is obtained from lattice parameters ‘a’ and positional parameters ‘u’ in the wurtzite structure and has been tabulated in Table 5.1, which has been observed that ‘bond length (l) increases with the increase in Mn$^{2+}$ content up to 0.30 mol, it may be due to the effect of replacement of Mn$^{2+}$ ions in ZnO. It has been also observed that there is a strong correlation between the c/a ratio and positional parameter ‘u’ which is shown in Fig. 5.8. The values of c/a and u are given in Table 5.1.

**Morphological analysis**

**5.3.2. Scanning electron microscopy (SEM)**

The surface morphology of Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.30) nanoparticles was observed by scanning electron microscopy (SEM). The SEM images of undoped and Mn$^{2+}$ doped ZnO nanoparticles are shown in Fig. 5.9 (a-f). From the SEM images analysis, it can be seen that the surface of synthesized nanoparticles appear to be nearly spherical and uniform, circular in shape. From the SEM images, it has been also observed more agglomeration appears from x = 0.12 to 0.30 mol. This may probably be related to the kinetic equilibrium process where the high content of Mn dopants could be nucleated.
with oxygen ions by itself and form bigger particles. As a conclusion, a lower dopant content of Mn-doped ZnO nanoparticles showed lower agglomeration and well ordered than the higher Mn dopant content. Besides the spherical crystals, several voids and pores are observed in all images because of the escaping gases during combustion reaction. The average grain size obtained through linear intercept method, which was found to be in the range 74-33 nm. The specific surface area and the surface area to volume ratio were determined from obtained grain size value. The obtained values of grain size, specific surface area and surface area to volume ration are listed in Table 5.3.

5.3.3. Energy dispersive X-ray analysis (EDAX)

The chemical compositions of the synthesized Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.30) nanoparticles were measured by Energy dispersive X-ray analysis (EDAX) spectrometer. The EDAX spectra for all samples are shown in Fig. 5.10 (a–f). EDAX spectra of undoped ZnO nanoparticles only Zn and O ions are detected, as shown in Fig. 5.10 (a). The analysis of Mn doped ZnO nanoparticles EDAX spectra indicated the presence of Zn, O and Mn as well as with small amount of Carbon (C) peaks. The appearance of carbon peak at the 0.289 KeV in EDAX spectra, due to the carbon tape pasted on copper grids, while measuring of EDAX spectra on the instrument. All EDAX plots give the evidence of Zn$^{2+}$, Mn$^{2+}$ and O$^{2-}$ ions with proper ratio confirming the desired stoichiometric composition. The relative atomic compositions for each sample are illustrated in Table 5.3. EDAX results suggest that the Mn$^{2+}$ ions are proper substituting in the ZnO lattice.

5.3.4. Transmission electron microscopy (TEM)

The transmission electron microscopy is an important technique for the particle size determination. Typical TEM micrograph and their corresponding selected area diffraction patterns (SAED) of prepared nanoparticles are shown in Fig. 5.11 (a-d) and (e-h) respectively. It indicates that the shapes of the nanoparticles are approximately
spherical. In addition, Fig. 5.12 (a-d) also shows a small agglomeration is also present in nanoparticles and this result agrees with SEM image. The SAED pattern confirms that the prepared nanoparticles are wurtzite structure single crystalline in nature. The selected area electron diffraction (SAED) pattern consists of nine concentric sharp rings, which corresponded to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) of the diffraction of the ZnO, which good match with the standard hexagonal wurtzite structure of ZnO.

Optical analysis

5.3.5. Fourier transforms infrared spectroscopy (FTIR)

Fourier transforms infrared absorption measurement technique was employed to conform the wurtzite structure formation and also used to obtain information about the chemical bonding in a material. It is used to identify the elemental constituents of a material. FTIR measurements of all the samples were performed in the wave number range from 400 to 4,000 cm\(^{-1}\) using the KBr method at RT as shown in Fig. 5.12. The absorption peaks are observed between 1536 cm\(^{-1}\) and 1515 cm\(^{-1}\) corresponding to asymmetric and symmetric stretching of the carboxyl group (C=O) [45]. The broad absorption peak shows the presence of O-H stretching mode of H\(_2\)O in the ZnO nanocrystals around 3403 cm\(^{-1}\) for pure ZnO, 3396 cm\(^{-1}\), 3389 cm\(^{-1}\), 3409 cm\(^{-1}\), 3409 cm\(^{-1}\), 3398 cm\(^{-1}\) and 3389 cm\(^{-1}\) for (x= 0.06, 0.12, 0.18, 0.24, 0.30 and 0.36) respectively [46, 47]. The absorption peaks observed between 2348 cm\(^{-1}\) and 2307 cm\(^{-1}\) is because of the existence of O-C-O molecule in the atmosphere [48, 49]. The main absorption band of Zn-O stretching, vibration at 460 cm\(^{-1}\), 475 cm\(^{-1}\), 481 cm\(^{-1}\), 488 cm\(^{-1}\), 495 cm\(^{-1}\), 509 cm\(^{-1}\) and 516 cm\(^{-1}\) for 0.00, 0.06, 0.12, 0.18, 0.24, 0.30 and 0.36 respectively [50-54]. There is a slight change in the band position observed due to the substitution of Mn\(^{2+}\) content. The band positions are slightly shifted towards higher frequency with increase in Mn\(^{2+}\) substitution in ZnO
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All assignments of FTIR spectra are listed in Table 5.4. From the FTIR study it is confirmed that Mn$^{2+}$ ions are substituted into the ZnO system synthesized by auto combustion technique.

5.3.6. UV-Vis absorption spectroscopy

UV–Vis absorption spectroscopy is one of the important techniques to explore the optical properties of semiconductor nanoparticles. The absorbance of nanoparticles is expected to depend on several factors such as size of nanoparticles, energy band gap and oxygen deficiency and structure of nanoparticles, surface roughness and impurity centers. The optical absorption spectra were recorded in the wavelength region of 300-600 nm. The UV-Visible absorption spectrum as a function of wavelength is shown in Fig. 5.13. From the observation absorption spectra, it is clear that the absorption wavelength varies according to the change in doping content. The optical band gap of the nanopowders was determined by using the Tauc relation [55] as given below.

$$\alpha h\nu = B (h\nu-E_g)^n$$  \hspace{1cm} (8)

where, $\alpha$ is the absorption coefficient ($\alpha = 2.303$), $B$ is a constant, $h$ is the planks constant, $\nu$ is the photon energy and $E_g$ is the optical energy band gap and the value of $n = 1/2, 1, 3/2$ and 2 is depending on the nature of the transition responsible for absorption and $n = 1/2$ for direct band gap semiconductor. The optical energy band gap ($E_g$) is estimated from the intercept of the linear region in the curve of a plot of $(\alpha h\nu)^2$ on the Y-axis verses photon energy ($h\nu$) on the X-axis as shown in Fig. 5.14. The variation of the optical energy band gap with change in doping content of Mn$^{2+}$ ions have been shown in the Fig. 5.15. In our result, it is found that the absorption edge shifts towards higher wavelength (red shift), when the doping content of Mn$^{2+}$ increases. This indicates that the energy band gap of ZnO material decreases with increase in Mn$^{2+}$ content from $x = 0.00$ to 0.30 mol. It may be due to sp-d spins exchange interaction between the s-p band...
electrons and localized d electrons of transition metal ions, it has been theoretically explained using the second-order perturbation theory [56-58]. The s-d and p-d exchange interaction gives rise to a negative and a positive correction to the conduction band and the valance band energies respectively and lead to narrowing of the band gap. Moreover, the narrowing of band gap is due to many-body effects on the conduction band and valence band [59]. The many-body effects that can shrink the band gap originate from the electron interaction and impurity scattering. It has been attributed to the merging of an impurity band into the conduction band, thereby shrinking the band gap. In our result, additionally, the sudden variation has been observed in absorption edge and their corresponding energy band gap value, when $x \geq 0.30$ mol. It may be due to the solubility limit of Mn$^{2+}$ ion in ZnO lattice structure. Our experimental result suggests that a red shift of the absorption edge in higher wavelength. It indicates that confirm the substitution of Mn$^{2+}$ ions in the ZnO lattice structure. Similar result has been also reported in the literature [60-62]. The absorption edge and corresponding energy band gap are tabulated in Table 5.5.

5.3.7. Photoluminescence spectroscopy (PL)

Photoluminescence spectroscopy is used to study the luminescence properties of ZnO nanocrystals. Fig 5.16 depicts the PL spectra of undoped ZnO and Mn doped ZnO nanocrystals that are measured at room temperature. Strong UV-emission peaks from 386 nm to 402 nm are observed for all samples and can be assigned as a near-band–edge excitonic emission, whereas the defect-related emission (green or yellow emission) is not observed. Near-band–edge excitonic emission (NBE) peak around 382 nm is naturally found in ZnO nanostructures because of the near band edge excitonic emission as the energy corresponding to this peak is almost equal to the band gap energy of ZnO [63, 64]. The photoluminescence emission values are tabulated in Table 5.5. The intensity of
the UV emission undergoes change after Mn doping, while a slight shift of the peaks are found toward the higher wavelength following the substitution of Mn$^{2+}$ ions. The peak intensity of the NBE emission increases with the increase of Mn concentration. The increase of NBE emission intensity indicates that the incorporation of Mn$^{2+}$ ion into ZnO nanoparticles may suppress some non-radiative recombination of free excitation that is near band edge emission.

**Electrical properties**

**5.3.8. D C electrical resistivity**

ZnO is a well-known n-type binary semiconductor material. Its electrical conductivity at room temperature is associated with intrinsic defects (zinc interstitial and oxygen vacancy), which can lead to shallow donor in ZnO. However, there is a contradictory opinion amongst different authors for room temperature intrinsic conduction of ZnO. Intrinsic defects may be responsible for room temperature electrical conductivity [65]. On the other hand, Zinc interstitials to be the main cause of electrical conductivity of ZnO. Recently, researchers have studied ZnO nanoparticles doped with metals ion divalent and trivalent can result in the formation of an n-type semiconductor, and can influence the optical and electrical properties significantly [66, 67].

The resistance of pellets of samples was measured using two point probe method within the temperature range of 300-493 K and the obtained value of resistance was used to calculate the resistivity using the following equation [68].

$$\rho = \frac{RA}{h}$$  \hspace{1cm} (9)

where, $R$ is the resistance and $A$ is the area of the pellet, $h$ is the thickness of pellet.

The variations of electrical resistivity with temperature for all Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles are shown in Fig. 5.17. From the Fig. 5.17, it is seen that resistivity
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5.3.9. Dielectric properties

The dielectric constant ($\varepsilon'$) was calculated using the equation [73].

$$\varepsilon' = \frac{Cd}{\varepsilon_0A}$$  \hspace{1cm} (10)

where, C is the capacitance in Farad, d is the thickness of the pellet in meter; A is the cross sectional area of the flat surface of the pellet and $\varepsilon_0$ is the permittivity of the free space. The variation of dielectric constant ($\varepsilon'$) with frequency of Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles is shown in Fig. 5.18. From this Fig. 5.18, it is seen that the dielectric constant initially decreases rapidly at low frequency, whereas at higher frequency dielectric constant, slowly decreases, which shows that frequency independent behaviour. Similar behaviour of dielectric constant is also observed by several other investigators [74-76].

The dielectric properties of nanoparticles are dependent on several factors, including the method of preparation, chemical composition and grain structure and size. In the present sample the observed behavior of dielectric constant may be due to the particle size effect. The observed dielectric dispersion curve can be explained on the basis of Koop’s theory [77], which is based on the Maxwell–Wagner model for the heterogeneous double
structure [78, 79]. According to this model, a dielectric medium is assumed to be made of two layers, one is more conducting and other is poor conducting the more conducting layer due to grains and poor conducting layer due grain boundaries. Under the application of external electric field, the charge carriers can easily move the grains, but are accumulated at the grain boundaries. This process can produce large polarization and high dielectric constant. The small conductivity of grain boundary contributes to the high value of dielectric constant at low frequency. The higher value of dielectric constant can also be explained on the basis of space charge polarization due to inhomogeneous dielectric structure. The in-homogeneities present in the system may be porosity and grain structure. The polarization decreases with the increase in frequency and then reaches a constant value due to the fact that beyond a certain frequency of external field the hopping between different metal ions (Zn$^{2+}$, Mn$^{2+}$) cannot follow the alternating field. The largest value of dielectric constant at lower frequency is due to the predominance of the effect like oxygen vacancies, grain boundary defects, etc. [78], while the decrease in dielectric constant with increase in frequency is natural because of the fact that any species contributing to polarizability is found to show lagging behind the applied field at higher and higher frequencies [80].

The dielectric loss factor ($\varepsilon''$) was determined using the equation [81].

$$\varepsilon'' = \varepsilon' \tan \delta \quad (11)$$

where, $\varepsilon'$ is the dielectric constant and $\tan \delta$ is the dielectric loss tangent.

The variation of dielectric loss factor ($\varepsilon''$) as a function of frequency at room temperature for all the compositions is shown in Fig.5.19. It is evident from Fig. 5.19 that the dielectric loss factor decreases with increase in frequency and at higher frequency; it remains almost constant in similar manner to that of dielectric constant ($\varepsilon'$). According to Hudson high values for dielectric loss factor ($\varepsilon''$) at lower frequencies are
observed due to impurities, crystal defects and moisture [82, 83]. A similar variation of dielectric loss vs. frequency was also observed in the literature [75].

The dielectric loss tangent (tan \( \delta \)) was determined using the relation [84].

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]  

(12)

where, \( \varepsilon'' \) is dielectric loss and \( \varepsilon' \) is the dielectric constant. The dielectric loss tangent (\( \tan \delta \)) represents the energy dissipation. It is considered to be caused by domain wall resonance. At higher frequencies the losses are found to be low since domain wall motion is inhibited and magnetization is forced to change the rotation. Fig. 5.20 shows the variation of dielectric loss tangent (\( \tan \delta \)) as a function of frequency at room temperature. It is observed that \( \tan \delta \) decreases with the increase in frequency for all the composition which may be due to the space charge polarization. According, to relation \( \tan \delta \) is proportional to the imaginary part (\( \varepsilon'' \)) of dielectric constant, so exhibits similar dispersion behavior. It is also noticeable that dielectric loss tangent is greater for pure ZnO material, but it decreases when Mn\(^{2+}\) is incorporated into ZnO and gradually decreases in the high frequency regime. Hence, we can suggest that these Mn doped samples show the capability to be used in high frequency device applications.

It is evident that the dielectric constant, dielectric loss and dielectric loss tangent decreases with an increase in the Mn\(^{2+}\) content. Iwauchi et al. [67] have pointed out that there is a strong relationship between the conduction mechanism and the polarization mechanism. The polarization of space charge may be occurring due to the electron displacement when an electric field is applied to the sample. Therefore, dielectric constant, dielectric loss and dielectric loss tangent would be expected to decrease by increasing Mn\(^{2+}\) content ‘\( x \)’. Similar results also were observed in other literature [85, 86].
Magnetic properties

5.3.10. Vibrating sample magnetometer (VSM).

The magnetic properties of Mn$^{2+}$ doped zinc oxide nanoparticles were carried out with the help of vibrating sample magnetometer (VSM) technique. Fig. 5.21 (a-d) shows the field–dependent magnetization curve of Mn$^{2+}$ doped ZnO nanoparticles at room temperature. From the analysis of the M-H curve of undoped (ZnO) sample, it can be seen that the undoped sample shows clear diamagnetic behavior [87-90]. The perfect linear (M-H) curve nature of Mn$^{2+}$ doped ZnO sample, indicate the absence of ferromagnetic and exhibit paramagnetic nature at room temperature [26, 91, 92].

According to X-ray diffraction pattern peak intensities decreases with an increase in Mn content in the ZnO lattice, variation of lattice parameter a and c with increase in Mn content in the ZnO lattice, variation of energy band gap with increase in Mn content in the ZnO lattice, all these variation indicates the dopant Mn$^{2+}$ ions are substituted in the inner lattice of Zn$^{2+}$ ions. Additionally, substitution of Zn ion Zn$^{2+}$ (0.72 Å) by Mn$^{2+}$ ions (0.83 Å) does not cause any significant change in the host (ZnO) lattice. Hence it is logical to assume that Mn goes into the ZnO lattice in the same oxidation state as Zn (i.e., 2+) with a tetrahedral coordination.

In order to understand the absence of ferromagnetic properties and exhibit of paramagnetic properties in the present Mn$^{2+}$ doped ZnO nanoparticles some possibilities were checked such as presence of secondary phase, presence of intrinsic defects, and presence of free carrier concentration . In the present Mn$^{2+}$ doped ZnO nanoparticles (for x = 0.06 to 0.30 mol), according to XRD results clearly indicate the absence of any other secondary phases in the region below 0.30 mol, which mean that Mn$^{2+}$ replaces Zn$^{2+}$ ions effectively without any Mn precipitation or secondary phase and thus, the possibility of secondary phase which is responsible for ferromagnetism can be ruled out. The obtained
VSM graph of Mn\(^{2+}\) doped ZnO nanoparticles shows the absence of ferromagnetic properties and presence of purely paramagnetic properties due to the incorporation of Mn\(^{2+}\), which supports no secondary phase detected in XRD pattern. In the present Mn\(^{2+}\) doped ZnO nanoparticles (for x = 0.36 mol), according to XRD patterns, we found traces of the secondary phase as Mn content in the sample increases above 0.30 mol, a new diffraction peaks starts appearing, which has been identified as impurity peaks of Mn\(_3\)O\(_4\) due to the solubility limit of Mn\(^{2+}\) ions in ZnO matrix. According to VSM and SQUID analysis, there is no indication observed of ferromagnetic behaviour, even though, secondary phase has been observed in the sample. Similar type of work has been reported in literature [93, 94] A. Sivagamasundari et al., [95] have reported that paramagnetism has been observed due to non availability of free carriers for Co\(^{2+}\) doped ZnO nanoparticles. Shi T. et al. [96] reported that cobalt is a neutral dopant atom which do not produce free carrier from X-ray absorption near edge structure (XANES) studies. Hence, non availability of free carriers is responsible for the observed paramagnetism in the prepared samples. According to recent experimental results, Alaria et al. [94] reported that pure paramagnetic behavior in Mn-doped ZnO synthesized by co-precipitation method was reported, where the absence of ferromagnetism was probably due to the lack of free carriers. In order to confirming and the existence of free carriers, we have studied the resistance of the Mn doped ZnO nanoparticles pellets at room temperature of all samples using LCR-Q meter, which is found to be very high in (M \(\Omega\) cm). This indicates to a very low carrier concentration in the present samples. The resistivity at room temperature of all sample are shown in Fig. 5.17. We were not able to determine the electron concentration at room temperature via Hall measurement on these samples, due to the very high resistance (~M \(\Omega\)). However, the resistance for undoped and Mn doped ZnO sample is still so high in the M\(\Omega\) magnitude, which means the
existence and creation of very low free carrier concentration. It is evident as very low free carrier concentration are available in the samples (x = 0.12 to 0.36 mol), hence paramagnetism was observed in our system. As, in most of the cases, the ferromagnetism is obtained due to the oxygen vacancies [97]. Recently, Ilyas U. et al. [98] reported that the ferromagnetism in oxides is due to the defects such as zinc vacancies (Vzn), oxygen vacancies (Vo), zinc interstitial (Zni) and oxygen interstitial (Oi). According to photoluminescence study, there is no indication has been observed of any intrinsic defects like oxygen vacancies (Vo) and zinc vacancies (Vzn) in the sample (from x = 0.00 to x = 0.36 mol). The possibility of oxygen vacancy can be ruled out and hence absence of ferromagnetic behaviour and presence of paramagnetic behaviour has been observed in the sample.

5.3.11. Superconducting quantum interference device magnetometer

In order to understand more detail the magnetic behavior of Mn^{2+} doped ZnO nanoparticles, we have recorded temperature dependent magnetization (M–T) curves of Mn^{2+} doped nanoparticles using superconducting quantum interference device magnetometer (SQUID) in the temperature range of 0 K-300 K. The zero fields cooled (ZFC) and field cooled (FC) M–T curves measured by applying a magnetic field of 112 Oe are shown in Fig. 5.22 (a–g). From the analysis of Fig. 5.22 (a–g), this shows that no ferromagnetism observed in the temperature range 0–300 K. The difference between ZFC and FC gives the net magnetization value. The magnetization increases with decreasing temperature and the drastic increase of the magnetization below 50 K with decreasing temperature can be attributed to the strong paramagnetism in Mn^{2+} doped ZnO nanoparticles. The rapid change of magnetization curve (ZFC and FC) below 50 K, it is an evidence of transition from diamagnetic phase to paramagnetic phase. Furthermore, ZFC and FC curve of Mn^{2+} doped ZnO nanoparticles merge into one and
another indicate that prepared samples are purely paramagnetic nature. Our results are analogous to those reported in the literature [91, 99, 100].

Finally, from the analysis of field dependent (M-H) and temperature dependent (M-T) magnetization, it can be concluded that prepared nanoparticles of pure ZnO show diamagnetic behaviour, while Mn$^{2+}$ doped ZnO nanoparticles ($x = 0.06$ to $0.36$ mol) show the purely paramagnetic nature due absence of secondary phase and absence of intrinsic defects as well as lack of free carriers concentration in Mn$^{2+}$ doped ZnO host lattice.

5.4 Conclusions

Pure and Mn$^{2+}$ doped ZnO nanoparticles have been successfully synthesized by sol-gel auto combustion route. Effect of Mn$^{2+}$ doping on the structural, optical, morphological, electrical, dielectric and magnetic properties in ZnO nanoparticles has been studied.

XRD results confirmed the prepared samples are in the nano-scale regime having a hexagonal wurtzite structure with single phase for ($x \leq 0.30$ mol), whereas for higher substitution of Mn$^{2+}$ ion ($x \geq 0.30$ mol) secondary phase Mn$_3$O$_4$ has been observed.

The variation of lattice parameters, X-ray density, and porosity, reduction in average crystallite size of Mn$^{2+}$ doped ZnO nanoparticles indicate that Mn$^{2+}$ ions have been successfully doped into the ZnO lattice.

SEM image revealed that the sample consists of nearly spherical shaped grains in nanometer sizes without any sign of phase segregation. The results of TEM and SAED confirmed the Mn$^{2+}$ doped ZnO nanoparticles are in nano regime and having good crystallinity respectively.

The FT-IR analysis confirmed the presence of Zn-O bond and substitution of Zn$^{2+}$ ions by Mn$^{2+}$ ions in the crystal lattice structure. The presence of functional groups and the chemical bonding due to Mn$^{2+}$ doping is confirmed by FT-IR spectra.
The optical energy band gap was found to decrease with increase in Mn$^{2+}$ ions concentration in ZnO matrix indicating a clear red shift.

The PL spectra of undoped ZnO and Mn doped ZnO nano-crystallites that are measured at room temperature. Strong UV-emission peaks from 386 nm to 402 nm are observed for all samples and can be assigned as a near-band–edge (NBE) emission, whereas the defect-related emission (green or yellow emission) is not observed.

The DC electrical resistivity has been investigated with the variation of the temperature, which shows the semiconducting nature of the samples. The dielectric parameters revealed normal dielectric behavior. The dielectric constant and dielectric loss decreases with increase in frequency and also dopant concentration, which has been well explained on the basis of Koop’s theory of space charge polarization in accordance with the Maxwell-Wagner two layer models. The detailed analysis of field dependent (VSM) and temperature dependent (SQUID) magnetic data of Mn$^{2+}$ doped ZnO nanoparticles, which revealed that the observed paramagnetic behavior at room temperature due to the absence of secondary phase, intrinsic defects and lack of free carrier concentration. From the above studies, it can be concluded that a high solubility limit of Mn$^{2+}$ substitution in the place of Zn has been achieved in these nanoparticles as compared to the earlier reported literatures. Even with high solubility limit of Mn$^{2+}$ ions in ZnO matrix, plots of temperature dependent magnetization of Mn$^{2+}$ doped nanoparticles shows the Curie temperature below room temperature and paramagnetic behaviour at room temperature. This confirms that prepared nanoparticles are not suitable for spintronic device application. Finally, it can be concluded that prepared samples show a good electrical and dielectric properties as well as worthy optical properties. These results make the prepared samples as promising candidates for high frequency device applications as well as optoelectronic device application.
Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

References


[184]
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles


Results and Discussions on $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ (0.00 $\leq x \leq$ 0.36) nanoparticles


Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles


Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles


Results and Discussions on $\text{Zn}_{1-x}\text{Mn}_x\text{O} \ (0.00 \leq x \leq 0.36)$ nanoparticles


Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 $\leq x \leq$ 0.36) nanoparticles

**Fig. 5.1 (a)** Typical synthesis images of Zn$_{1-x}$Mn$_x$O ($x = 0.00$ and $0.06$) nanoparticles by sol-gel auto combustion method.
Fig. 5.1 (b) Flowchart of sol–gel auto combustion synthesis method of Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles.
Results and Discussions on Zn\textsubscript{1-x}Mn\textsubscript{x}O (0.00 \leq x \leq 0.36) nanoparticles

Fig. 5.1 (c) Chemical reaction of Zn\textsubscript{1-x}Mn\textsubscript{x}O (0.00 \leq x \leq 0.36) nanoparticles by sol–gel auto combustion synthesis method
Fig. 5.2 (a) X-ray diffraction patterns of Zn$_{1-x}$Mn$_x$O ($x = 0.00, 0.06$) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 $\leq x \leq$ 0.36) nanoparticles

Fig. 5.2 (b) X-ray diffraction patterns of Zn$_{1-x}$Mn$_x$O (x = 0.12, 0.18) nanoparticles
Fig. 5.2 (c) X-ray diffraction patterns of Zn$_{1-x}$Mn$_x$O (x = 0.24, 0.30) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles

Fig. 5.2 (d) X-ray diffraction pattern of Zn$_{1-x}$Mn$_x$O (x = 0.36) nanoparticles

Fig. 5.3 Expanded view of (100), (002) and (101) plane of Zn$_{1-x}$Mn$_x$O (0.00≤x≤0.36) nanoparticles
Results and Discussions on $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($0.00 \leq x \leq 0.36$) nanoparticles

Fig. 5.4 Variation of peak intensity along (101) plane with Mn content ‘$x$’.

Fig. 5.5 Variation of full width half maxima (FWHM) and average crystallite size with Mn content ‘$x$’.
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ $x$ ≤ 0.36) nanoparticles

**Fig. 5.6** Variation of lattice parameter a and c with Mn content ‘x’

**Fig. 5.7** Variation of X–ray density and volume of the unit cell with Mn content ‘x’
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles

Fig. 5. Variation of c/a ratio and positional parameter ‘u’ with Mn content ‘x’
**Fig. 5.9 (a–f)** Scanning electron microscope images of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ $(0.00 \leq x \leq 0.30)$ nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

Fig. 5.10 (a–f) Energy dispersive X-ray analysis patterns of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.30$) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

Fig. 5.1 Typical TEM images (a-d) and their corresponding selected area electron diffraction (SAED) patterns (e-h) of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.18$) nanoparticles
Results and Discussions on Zn\textsubscript{1-x}Mn\textsubscript{x}O (0.00 ≤ x ≤ 0.36) nanoparticles

Fig. 5.12 FTIR spectra of Zn\textsubscript{1-x}Mn\textsubscript{x}O (0.00≤x≤0.36) nanoparticles

Fig. 5.13 UV–vis absorption spectra of Zn\textsubscript{1-x}Mn\textsubscript{x}O (0.00≤x≤0.36) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

**Fig. 5.14** $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

**Fig. 5.15** Variation of energy band gap with Mn content ‘$x$’
Results and Discussions on $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($0.00 \leq x \leq 0.36$) nanoparticles

**Fig. 5.16** Room temperature photoluminescence spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($0.00 \leq x \leq 0.36$) nanoparticles

**Fig. 5.17** Variation of DC electrical resistivity as a function of temperature with Mn content ‘x’
**Fig. 5.18** Variation of dielectric constant ($\varepsilon'$) with log (f) of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

**Fig. 5.19** Variation of dielectric loss ($\varepsilon''$) with log (f) of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles
Fig 5.20. Variation of dielectric loss tangent (tanδ) with log (f) of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ (0.00 $\leq x \leq$ 0.36) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles

![M–H plots of Zn$_{1-x}$Mn$_x$O (x = 0.00, 0.06) nanoparticles](image)

**Fig. 5.21 (a)** M–H plots of Zn$_{1-x}$Mn$_x$O (x = 0.00, 0.06) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles

Fig. 5.21 (b) M–H plots of Zn$_{1-x}$Mn$_x$O (x = 0.12, 0.18) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

Fig. 5.21 (c) M–H plots of Zn$_{1-x}$Mn$_x$O ($x = 0.24, 0.30$) nanoparticles
Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

**Fig. 5.21 (d)** M‒H plots of Zn$_{1-x}$Mn$_x$O ($x = 0.36$) nanoparticles

**Fig. 5.22 (a)** Zero field cooling (ZFC) and field cooling (FC) M–T curves of Zn$_{1-x}$Mn$_x$O ($x = 0.00$) nanoparticles under a magnetic field of 112 Oe
Results and Discussions on Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles

**Fig. 5.22 (b)** Zero field cooling (ZFC) and field cooling (FC) M–T curves of Zn$_{1-x}$Mn$_x$O ($x = 0.06$) nanoparticles under a magnetic field of 112 Oe

**Fig. 5.22 (c)** Zero field cooling (ZFC) and field cooling (FC) M–T curves of Zn$_{1-x}$Mn$_x$O ($x = 0.12$) nanoparticles under a magnetic field of 112 Oe
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 $\leq x \leq 0.36$) nanoparticles

**Fig. 5.22(d)** Zero field cooling (ZFC) and field cooling (FC) M–T curves of Zn$_{1-x}$Mn$_x$O (x = 0.18) nanoparticles under a magnetic field of 112 Oe

**Fig. 5.22(e)** Zero field cooling (ZFC) and field cooling (FC) M–T curves of Zn$_{1-x}$Mn$_x$O (x = 0.24) nanoparticles under a magnetic field of 112 Oe
Results and Discussions on Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles

**Fig. 5.22 (f)** Zero field cooling (ZFC) and field cooling (FC) M–T curves of Zn$_{1-x}$Mn$_x$O (x = 0.30) nanoparticles under a magnetic field of 112 Oe.

**Fig. 5.22 (g)** Zero field cooling (ZFC) and field cooling (FC) M–T curves of Zn$_{1-x}$Mn$_x$O (x = 0.36) nanoparticles under a magnetic field of 112 Oe.

[216]
Table 5.1: Lattice parameters (a and c), c/a ratio, atomic packing fraction (APF), Bond-length (l) and positional parameter (u) of Zn$_{1-x}$Mn$_x$O (0.00 $\leq x \leq 0.36$) nanoparticles

<table>
<thead>
<tr>
<th>Conc. ‘x’ mol</th>
<th>Lattice parameters</th>
<th>Bond-Length (l) Å</th>
<th>Positional parameter (u)</th>
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<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>c/a ratio</td>
</tr>
<tr>
<td>0.00</td>
<td>3.2397</td>
<td>5.1964</td>
<td>1.6040</td>
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<td>0.06</td>
<td>3.2454</td>
<td>5.2011</td>
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<td>0.12</td>
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<td>5.2061</td>
<td>1.6024</td>
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<td>3.2504</td>
<td>5.2076</td>
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<td>1.6042</td>
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<td>0.36</td>
<td>3.2511</td>
<td>5.2289</td>
<td>1.6083</td>
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</table>
Table 5.2: Volume of unit cell (V), X-ray density (d), Crystallite size (D), and Micro strain (\(\varepsilon\)) of Zn\(_{1-x}\)Mn\(_x\)O (0.00 \leq x \leq 0.36) nanoparticles

<table>
<thead>
<tr>
<th>Conc. ‘x’ mol</th>
<th>Volume (V) (Å(^3))</th>
<th>X-ray density (d,) gm/cm(^3)</th>
<th>Crystallite size (D) nm</th>
<th>Micro strain ((\varepsilon)) (\times 10^{-3}) lines(^{-2})/m(^4)</th>
</tr>
</thead>
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<tr>
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<td>17.01</td>
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</tr>
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<tr>
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<td>11.78</td>
<td>2.01</td>
</tr>
<tr>
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<td>47.863</td>
<td>5.3866</td>
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Table 5.3: Elemental percentage from EDAX spectra and grain size, specific surface area (S), surface area to volume ratio (S/V) from SEM of Zn$_{1-x}$Mn$_x$O (0.00 $\leq x \leq 0.35$) nanoparticles

<table>
<thead>
<tr>
<th>Conc. ‘x’ mol</th>
<th>Zn$^{2+}$ at %</th>
<th>Mn$^{2+}$ at %</th>
<th>O$^{2-}$ at %</th>
<th>Grain Size (SEM) nm</th>
<th>Surface area m$^2$/gm</th>
<th>S/V ratio</th>
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<tr>
<td>0.00</td>
<td>50.00</td>
<td>—</td>
<td>50.00</td>
<td>59.40</td>
<td>17.64</td>
<td>0.3734</td>
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<tr>
<td>0.06</td>
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<td>0.18</td>
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<td>69.77</td>
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Table 5.4: FT-IR peaks and their assignments of Zn$_{1-x}$Mn$_x$O (0.00 ≤ x ≤ 0.36) nanoparticles.

<table>
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<tr>
<th>Assignments</th>
<th>Mn$^{2+}$ Concentration (‘x’ moles)</th>
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<tbody>
<tr>
<td></td>
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</tr>
<tr>
<td>Zn-O Stretching (cm$^{-1}$)</td>
<td>460</td>
</tr>
<tr>
<td>C=O Symmetric Stretching (cm$^{-1}$)</td>
<td>1522</td>
</tr>
<tr>
<td>O-C-O (cm$^{-1}$)</td>
<td>2313</td>
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<td>O-H band (cm$^{-1}$)</td>
<td>3403</td>
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</table>
Table 5. 5 Absorption edge ($\lambda_{\text{max}}$), energy band gap (Eg) from UV-Vis and near band edge emission (NBE) peaks values from PL of Zn$_{1-x}$Mn$_x$O ($0.00 \leq x \leq 0.36$) nanoparticles.

<table>
<thead>
<tr>
<th>Conc. ‘x’ mol</th>
<th>Absorption Edge (UV-Vis) ($\lambda_{\text{max}}$) nm</th>
<th>Energy Band gap (Eg) (eV)</th>
<th>Near Band Edge (NBE) nm</th>
</tr>
</thead>
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<tr>
<td>0.00</td>
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<td>384.47</td>
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<td>390.27</td>
<td>3.176</td>
<td>390</td>
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<td>395.09</td>
<td>3.138</td>
<td>391</td>
</tr>
<tr>
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<td>401.94</td>
<td>3.084</td>
<td>389</td>
</tr>
<tr>
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<td>418.56</td>
<td>2.962</td>
<td>392</td>
</tr>
<tr>
<td>0.36</td>
<td>409.48</td>
<td>3.027</td>
<td>395</td>
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