The Effects of Mn Doping on the Structural and Optical Properties of ZnO

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$\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.00, 0.01, \text{ and } 0.05$, respectively) was synthesized by using solid state reaction method. The structural properties were characterized by using X-ray diffraction and scanning electron microscopy. Optical properties were investigated by UV-visible spectroscopy. X-ray diffraction patterns indicate that all samples have hexagonal wurtzite structure without any impurity phases. The diffraction intensity increases and the peak position shifts to a lower 2θ angle with Mn concentration. The lattice parameters a and c , the volume of unit cell increase with Mn content indicating that Mn^{2+} ions go to Zn^{2+} ions in ZnO lattice. The grain size increases with Mn doping while the microstrain and dislocation density decrease. UV-vis spectra of the samples show that undoped ZnO sample has an energy band gap E_g of 3.34 eV. The optical study indicates a red shift in the absorbance spectra and a decrease in the band gap E_g with Mn content. This decrease of band gap may be attributed to the influence of dopant ions. The morphology and grain distribution of ZnO samples were analysed by scanning electron microscopy. The particle sizes are higher in doped samples when compared to the undoped sample and the surface roughness increases with Mn content. The grains are closely, densely packed and pores/voids between the grains increase with Mn content.

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1. Introduction

Zinc oxide (ZnO) is a II–VI semiconductor with wide direct band gap energy (3.37 eV) at room temperature, that is suitable for short wavelength optoelectronic applications and it has a large exciton binding energy (60 meV). Due to its properties like low cost, non-toxicity, abundance in nature, suitability to doping, ZnO has got wide device applications in different areas such as ultraviolet light-emitters, gas sensors, piezoelectric transducers, and solar cells [1–15].

ZnO has a hexagonal wurtzite structure belonging to the space group $P6_3mc$ with the lattice parameters of $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$. One can simply describe the structure of this material as a number of alternating planes composed of tetrahedral coordinated O^{2-} and Zn^{2+} ions, stacked interchangeably along the c -axis. The tetrahedral coordination in ZnO results in noncentral symmetric structure and consequently piezoelectricity and pyroelectricity [16].

Many methods have been employed to optimize the optical, electrical, and magnetic properties of ZnO materials, and among them doping is considered as one of the most effective approaches. Thus, doping is used in order to change the band gap energy of ZnO, either by narrowing the band gap or by introducing energy levels in the band gap of semiconductor materials [17–25]. 3d transition metal (TM) ions such as Ti, V, Mn, Fe, Co, Ni, and Cu are generally preferred to substitute for the

cations of the host semiconductors. Among different TM doping to ZnO, Mn has the advantage owing to its high moment, relatively small ionic radii difference between Mn^{2+} and Zn^{2+} , and its exactly half-filled 3d orbitals which makes its incorporation easier into the ZnO lattice. Electronegativity and ionic radius are the two frequently considered factors that may have impact on doping ions into ZnO. Since the electronegativities and ionic radii of Mn^{2+} (1.55, 80 pm) are close to those of Zn^{2+} (1.65, 74 pm), it is expected that these metal ions can occupy the lattice Zn^{2+} positions in ZnO [26–32].

The objective of this work is to investigate the influence of doping different concentrations of Mn on the structural and optical properties of ZnO prepared by solid state reaction method. The solid state reaction is chosen because of its reproducibility and sufficient final product for further measurements. The structural characteristics were studied by X-ray diffraction (XRD), the morphological features were studied by scanning electron microscope (SEM), and optical properties were investigated by UV-visible spectroscopy (UV-vis).

2. Experimental

Samples of nominal compositions $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.00, 0.01, \text{ and } 0.05$ referred as Mn0, Mn1, and Mn5, respectively) were synthesized via solid state reaction method. The stoichiometric amounts of starting powders ZnO and Mn_2O_3 were mixed and ground, followed by calcination at 450 °C for 8 h. After cooling, the resulting material was reground and pelletized. Finally, pellets of 10 mm diameter were prepared using press and sintered at 900 °C for 12 h.

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The crystalline structure of the samples was characterized by using X-ray diffractometer in 2θ range of 20–80 degrees. The phase and crystal parameters of all samples were identified by XRD using Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). For all samples, the major diffraction peaks can all be indexed to the hexagonal wurtzite structure of ZnO crystal with reference to Joint Committee on Powder Diffraction Standards (JCPDS) file No. 36-1451. The optical properties of the samples were characterized using ultraviolet-visible spectrometer (UV-vis). UV-vis absorption spectra of the samples were recorded in the wavelength range of 200 to 800 nm. The band gap of undoped and Mn doped ZnO were determined by ultraviolet (UV) absorption spectra recorded. The surface morphology and grain size of the samples were studied by employing a SEM.

3. Results and discussion

Figure 1 shows XRD patterns of undoped and Mn doped samples for different Mn concentrations of the form $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.00, 0.01, \text{ and } 0.05$). All samples have hexagonal wurtzite structure without any additional impurity phases and no other peaks were observed. This may be attributed to incorporation of Mn ion into Zn lattice site rather than interstitial ones. The pattern can be indexed for diffractions from the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes of the wurtzite crystals corresponding to ZnO and very close to the standard data of undoped ZnO ($a = 3.2488 \text{ \AA}$, $c = 5.2061 \text{ \AA}$, space group $P6_3mc$, 186, JCPDS data Card no. 36-1451).

Fig. 1. XRD patterns of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.00, 0.01$ and 0.05) samples.

The lattice parameters a and c were determined using Eqs. (1) and (2) used for hexagonal systems [33]:

$$a = \frac{\lambda}{\sqrt{3} \sin \theta} \sqrt{h^2 + hk + k^2}, \quad (1)$$

$$c = \frac{\lambda}{2 \sin \theta} l, \quad (2)$$

where λ is the wavelength, θ is the Bragg angle of diffraction peaks, and h, k, l are the Miller indices. The volume of wurtzite unit cell for hexagonal system of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ was determined using Eq. (3):

$$V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c, \quad (3)$$

where V is the lattice volume, a and c are the lattice constants [34]. Table I presents the lattice parameters a and c and the unit cell volume (V) obtained from XRD patterns. Both lattice parameters and the cell volume V increase with Mn content. The lattice parameters are found as $a = 3.2500(1) \text{ \AA}$, $c = 5.2030(11) \text{ \AA}$, and $a = 3.2493(8) \text{ \AA}$, $c = 5.2023(11) \text{ \AA}$ in Mn1 and Mn5 samples, respectively, whereas in undoped ZnO sample $a = 3.2487(8) \text{ \AA}$, $c = 5.1989(22) \text{ \AA}$ (Fig. 2). The obtained cell volume of the wurtzite phase of the samples are $47.59 \text{ \AA}^3$, $47.57 \text{ \AA}^3$ and $47.52 \text{ \AA}^3$ for Mn1, Mn5, and undoped ZnO samples, respectively, which may be caused by the decrease of defects consistent with the crystals improvement due to Mn doping. The increase of the lattice parameters with Mn concentration may be attributed to the larger ionic radius of Mn^{2+} ($0.80 \text{ \AA}$) compared to that Zn^{2+} ($0.74 \text{ \AA}$), hence leading to a lattice expansion. Lattice parameters a and c decrease slightly while concentration of Mn increases from 0.01 to 0.05, which might indicate the start of formation of secondary phase in the samples and a decrease in the defect concentration (oxygen vacancies). However, for Mn content $x = 0.05$, no additional peaks could be detected in XRD. Similar trends have been reported in the literature [26–28].

Fig. 2. Variation of lattice parameters with Mn concentration.

The expanded XRD patterns of the 34–35 2θ region are shown in Fig. 3. The 2θ degrees of the ZnO (002) diffraction peak is slightly shifted from 34.49 to 34.45 , indicating the replacement of Zn^{2+} by Mn^{2+} . It can be inferred that the increase in lattice parameters a and c , when compared to undoped sample, causes this shift.

TABLE I

Lattice parameters a and c , unit cell volume, lattice distortion c/a , positional parameter u and Zn-O bond length L of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.00, 0.01$ and 0.05) samples

Sample	Lattice parameters			c/a	u	Zn-O bond length L [Å]
	a [Å]	c (Å)	Volume [Å ³]			
Mn0	3.2487(8)	5.1989(22)	47.52(3)	1.6003	0.38016	1.97640
Mn1	3.2500(1)	5.2030(5)	47.59(1)	1.6009	0.38006	1.97740
Mn5	3.2493(3)	5.2023(11)	47.57(1)	1.6010	0.38004	1.97706

TABLE II

Peak position (2θ), FWHM, crystallite size D , strain ε , dislocation density δ and APF of (002) plane of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.00, 0.01$ and 0.05) samples

Sample	hkl (002)			$\varepsilon (\times 10^{-3})$	$\delta \times 10^{-3} [\text{nm}^{-2}]$	APF [g/cm ³]
	Peak distance (2θ)	FWHM	Crystallite size [nm]			
Mn0	34.49	0.225	41	3.163	0.59	0.75561
Mn1	34.44	0.206	45	2.899	0.49	0.75531
Mn5	34.45	0.217	43	3.054	0.54	0.75525

Fig. 3. Comparison of the expanded XRD patterns with different compositions of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.00, 0.01$ and 0.05) in the $34\text{--}35^\circ$ 2θ regions.

Zn-O bond length (L) for all samples was determined using the following Eq. (4):

$$L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2}, \quad (4)$$

where a , c are the lattice parameters and u is the positional parameter of the wurtzite structure. u is a measure of the amount by which atom is displaced with respect to the next along the c -axis. For wurtzite structure, u is given as [35–38]:

$$u = \frac{a^2}{3c^2} + 0.25. \quad (5)$$

The calculated Zn-O bond length (L) values are summarized in Table I. The bond length (Zn-O) increases slightly with Mn content which causes a small crystal distortion in crystal structure. Bond lengths (L) were obtained as 1.97740 Å in Mn1, 1.97706 Å in Mn5, and

1.97640 Å in Mn0 samples, which is a similar trend observed for lattice parameters a and c and agrees with Zn-O bond length in the unit cell. It is also known that ionic radius of O^{2-} is 1.21 Å, ionic radius of the Zn^{2+} is 0.74 Å, and consequently the length of the Zn-O bond is 1.95 Å. The values obtained are slightly higher and indicate the presence of the structural defects, especially oxygen vacancies [39].

The oxygen positional parameter (u) calculated for Mn0, Mn1, and Mn5 samples are 0.38016, 0.38006, and 0.38004, respectively. It is worth mentioning that in a stoichiometric wurtzite structure, the c/a ratio is 1.633 [40]. All samples showed a significantly smaller c/a ratio and this might indicate the presence of oxygen vacancies V_{O} and extended defects.

Atomic packing fraction (APF) was determined using Eq. (6):

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

where a and c are the lattice parameters [41]. The value of APF for all samples are listed in Table II. The values of APF decrease with increasing Mn content, this may be due the increment of voids in the samples. The APF of bulk hexagonal ZnO materials is about 74%, but in this study the APF of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nanoparticles is nearly 75% in hexagonal structure. This could be due to substitutional effect of Mn.

The average crystallite size was estimated by measuring full width at half maximum of the intense diffraction peaks in all the compositions using the Scherrer formula

$$\lambda D = \frac{K}{\beta \cos \theta}, \quad (7)$$

where D is a grain size, K is the constant, considered to be 0.9, λ is the wavelength of used X-ray ($\lambda = 1.5406$ Å), β is the full width at half maximum (FWHM), and θ corresponds to the intense (002) peak position [42, 43].

Crystallite size of samples was determined using the peak (002) of ZnO particles and is tabulated in Table II. The average crystallite size for all samples, which was determined from the broadening FWHM of the ZnO peaks of the XRD patterns using the Scherrer formula, was found as 41, 45, and 43 nm for $x = 0.00, 0.01$, and 0.05 samples, respectively.

The dislocation density, defined as the length of dislocation lines per unit volume of the crystal, were calculated by equation $\delta = 1/D^2$, where D is average grain size of the samples [44].

Strain (ε) was determined using Eq. (8) [45]:

$$\varepsilon = \beta/4 \tan \theta. \quad (8)$$

As illustrated in Table II, the crystallite size of the samples increases while the dislocation density and lattice strain decrease with Mn doping. The decrease in the strain indicates a decrease in the concentration of lattice imperfections. Since these intrinsic quantities are a measure of the dislocation networks, the decrease in both quantities indicates the formation of better quality samples.

UV-visible absorption spectra of all the samples $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ with composition $x = 0.00, 0.01$, and 0.05 are shown in Fig. 4. All samples exhibit a strong absorption maximum below 400 nm, which may be linked to the electronic transition of electrons from valence band to conduction band. The absorption maximum of the doped samples shift to higher wavelengths (lower energy) and the absorbance increases with Mn concentration. The change in the absorption peak due to doping indicates that there is a change in the band structure.

Fig. 4. UV-visible absorption spectra of undoped and Mn doped ZnO samples.

Absorption edges for the semiconductors indicate the threshold of charge transition between the highest filled band and the lowest empty band. The optical band gap was determined using Eq. (9) [46–48]:

$$\alpha h\nu = B(h\nu - E_g)^n, \quad (9)$$

where α is the absorption coefficient ($\alpha = 2.303A/t$, where A is the absorbance and t is the thickness of the sample, $t = 1$ mm), B is a constant which is related to the effective masses associated with the bands, h is Planck's constant, ν is the photon frequency ($h\nu = 1240/\text{wavelength}$), and E_g is the band gap energy. The value of $n = 1/2, 3/2, 2$ or 3 depending on the nature of the electronic transition responsible for absorption, which is $1/2$ for direct band gap material and 2 for indirect band gap material. ZnO has a direct band gap, and thus in the equation $n = \frac{1}{2}$.

Fig. 5. $(\alpha h\nu)^2$ versus $h\nu$ for undoped and Mn doped ZnO samples.

The energy band gap E_g of the samples were evaluated by plotting $(\alpha h\nu)^2$ versus photon energy $h\nu$ graphs which is shown in Fig. 5. E_g of all samples were estimated by using the intercept of the linear portion of the curve $(\alpha h\nu)^2$ to $y = 0$. Linearity of the plots indicates material's direct band gap nature [49]. The calculated E_g of the samples are listed in Table III. From the Table, it was observed that the value of E_g in the undoped ZnO is ≈ 3.34 eV which is lower than its typical value of 3.37 eV [50]. The lower band gap of the undoped ZnO might be caused by the number of point defects (vacancies and interstitials of Zn and O) [51]. E_g of the Mn1 and Mn5 samples are 3.08 and 3.28 eV, respectively. It is clear that the optical band gap decreased or shifted to lower energy with Mn concentration. The noticed red shift in the band gap is due to Mn doping in ZnO. A similar narrowing of band gap was also observed in other studies [41, 52]. The observed decrease in energy band gap of the Mn doped ZnO is related to the shrinkage effect of the optical energy band gap. Moreover, the red shift of the band gap could be mainly due to the $sp-d$ exchange interactions between the d -electrons associated with the doped Mn^{2+} ions and the sp electrons of the valence and conduction bands. The interaction leads to corrections in the energy bands, and thus it can be seen that the conduction band is lowered and the valence band is raised causing the band gap to narrow [53]. The change

in the value of E_g depends on several factors such as grain size, carrier concentration, lattice strain, etc. Variation of the band gap and crystallite size of samples with respect to Mn concentration is shown in Fig. 6. As seen from the figure, the band gap of the samples decreases as the crystal size increases.

Fig. 6. Variation of optical band gap and crystallite size with Mn concentration.

TABLE III

Variation of optical band gap of undoped and Mn doped ZnO samples

Samples	Band gap [eV]
ZnO	3.34
Zn _{0.99} Mn _{0.01} O	3.08
Zn _{0.95} Mn _{0.05} O	3.28

The surface morphology for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ with composition ($x = 0.00, 0.01$, and 0.05) samples was investigated using SEM and displayed in Fig. 7. The grains of the samples are homogeneously distributed, and the presence of hexagonal-like grains is observed in all samples. SEM images of the undoped sample revealed that grains are more closely packed and have smaller sizes when compared to the Mn doped samples. It is also observed that doped samples have a large grain structure and pores/voids between the grains increase with Mn concentration. Changes in the average particle size of the samples caused by doping are also studied by SEM. The average particle size is found to be 510 nm for undoped ZnO. For Mn doped ZnO, the average particle size is slightly higher (730 nm and 723 nm for Mn1 and Mn5, respectively) than the undoped ZnO which is in agreement with XRD results. SEM images of the samples show that the doped samples have rougher surface morphologies, and are illustrated in Fig. 8. These rough surfaces observed in the doped samples may arise from ionic radius differences of the Mn (0.80 Å) and Zn (0.74 Å) ions. It seems that by choosing a suitable doping concentration, the particle size and roughness may be controlled.

Fig. 7. SEM images of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ (a) $x = 0.00$, (b) $x = 0.01$ and (c) $x = 0.05$ samples.

Fig. 8. Roughness of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ (a) $x = 0.00$, (b) $x = 0.01$ and (c) $x = 0.05$ samples from SEM images.

4. Conclusion

In this work, the crystal structure of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ compound with $x = 0.00, 0.01$ and 0.05 synthesized by solid state reaction method was studied. The samples were characterized using XRD, UV-visible spectroscopy, and SEM.

The XRD data shows that all samples have hexagonal wurtzite structure. There were no extra peaks of manganese metal, oxides, or any impurity phases observed in any of the samples doped with Mn which indicates that all samples have single phase. The lattice parameters a and c , and unit cell volume increase with Mn content which may be attributed to slightly different ionic sizes of Zn and Mn ions. The grain size and atomic packing fraction were calculated from XRD data. It was found that grain size increases while atomic packing fraction (APF) decrease with Mn concentration. There was a slight shift of (002) peak towards lower diffraction angle for Mn doped samples, which provides an indirect evidence that Mn is incorporated into ZnO crystal lattice. The increase in oxygen positional parameter (u) indicates lattice distortion in the crystal structure. From UV-vis spectra of the samples, it was observed that undoped ZnO sample has an optical band gap of 3.34 eV. The optical band gaps of Mn1 and Mn5 decrease to 3.08 and 3.28 eV, respectively, indicating a red shift in the band gap. It can be inferred that the interactions between the d electrons of Mn^{2+} and the s and p electrons of the host ZnO bands leads to the red shift of E_g with Mn content. SEM micrographs indicate the presence of homogeneous grain distribution and well defined hexagonal-like grains. The undoped sample is closely packed and pores between the grains are very few. SEM micrographs also revealed that Mn doped samples have larger grain sizes when compared to the undoped sample. It was shown from SEM that the surface roughness increases with increase in particle size, which is due to the larger grains formation as well as an increase in the porosity of the samples. Thus, this study presents that adjusting the concentration of Mn^{2+} ions may help to control the optical and structural properties of ZnO nanocrystals.

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