Nanostructure and Magnetic Properties of Nickel Doped Zinc Oxide Nano-Powders Prepared by Coprecipitation Method

M.Mohsen^{*}, E.Gomaa^{*}, E.Hassan Aly^{*}, M.Essam^{**}, M.M. ElOkr⁺

*Phys. Dept. Faculty of Science, Ain Shams University, Cairo, Egypt.
 * Phys. Dept. Faculty of Science, Al-Azhar University, Cairo, Egypt.
 ** Phys. Dept. Faculty of Engineering, Modern Academy, Cairo, Egypt.

The $Zn_{1-x}Ni_xO$ ($0 \ge x \ge 0.1$) system have been synthesized in nanoform by coprecipitation method. Nanostructure features of the prepared samples have been investigated by X-Ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD data reveal that the prepared sample are crystalline and belongs to space group P6₃mc. The estimated average crystallite size is ranging between 62 nm and 96 nm in agreement with TEM measurements. This also confirmed the nanostructure nature of all samples. The variation of lattice parameters and internal strain, that have been deduced from XRD data, has shown that the solubility limit of NiO in ZnO does not exceed 5% .At 7% and 10% Ni-doped ZnO samples reveal the presence of secondary peaks due to NiO in the XRD spectra. Hysteresis loop curves have been obtained. The saturation magnetization M_s suggests the presence of ferromagnetic behavior, the latter decreases with increasing Ni contents. It is supposed that the presence of Ni-Ni ion interaction suppress the ferromagnetic ordering due to the formation of Ni clusters at high Ni content larger than 7%.

1. Introduction

Recently, enhanced interest in the search of ferromagnetic order in diluted magnetic semiconductors (DMS). It has attracted significant attention with a focus on the study of their spin transport properties. This is because of many possibilities for potentially interesting device applications such as spin filters, spin transport media [1,2] as well as enabling materials in the emerging field of spintronics [3]. Magnetic characteristics have been widely studied theoretically and experimentally in ZnO doped with transitional metals [4-10]. It is well established that one of the best candidates is ZnO which is a direct wide band gap semiconductor with a hexagonal (Wurtzite) crystal structure.

It is observed that the synthesis method play a principle role in determining the magnetic properties of Ni doped ZnO [11]. Although some groups found room temperature ferromagnetism in Ni doped ZnO [9], yet other groups exhibit paramagnetic behavior. On the other hand and according to same theoretical studies high curie temperature (T_c) ferromagnetism can be realized with ZnO doped with transition metals [11]. Some experimental investigations have shown that it is possible to raise the T_c of Fe-, Co- or Ni-doped ZnO [12-14].

Accordingly, it is of interest to study the nanostructure and magnetic properties of $Zn_{1-X}Ni_XO$ systems prepared by Coprecipitation method, which may enhance our basic knowledge for the development of semiconductor based spintronic devices.

Experimental

 $Zn_{1-x}Ni_xO$ (X=0, 0.01, 0.03, 0.05, 0.07, 0.1) series of polycrystalline samples were prepared using $ZnCl_2$ and $NiCl_2$ as starting materials. Stoichiometric amounts of starting materials required for each composition were mixed thoroughly and calcinated at 600 C° for 6 hours following several cycles of quenching and grinding. The obtained powders are pressed into pellets of 5 gram by weight and 10 mm diameter with thickness 0.5cm at a pressure of 4 tons / cm².

The reaction can be demonstrated as follow:

 $(ZnCl2_6H_2O)_{1-X} + (NiCl_2_6H_2O)_X + 2NaOH \longrightarrow Zn_{1-X}Ni_X(OH)_2 + 2NaCl + 6H_2O$ $Zn_{1-X}Ni_X(OH)_2 \xrightarrow{heat} Zn_{1-X}Ni_XO$

where X= 0, 0.1, 0.3, 0.5, 0.7, 0.10

2. Results and Discussion

2.1. X-Ray Diffraction (XRD)

The XRD patterns of pure ZnO and Ni-doped ZnO samples are shown in **Fig. (1)** the prepared samples (X=1%, 3%, 5%, 7%, 10%). All samples are polycrystalline in nature having all the peaks corresponding to wurtzite structure of ZnO [14]. with space group P6₃mc. This indicates formation of substitutional solid solution of NiO in ZnO. This can be understood because it is known that Zn has an atomic radius of 0.74 A° and forms a stable oxidation state of 2, and Ni has an atomic radius of 0.69 A°[15] which is close to that of zinc. For $X \ge 7\%$ the diffraction peaks of NiO start to appear. The peak intensity of NiO increase

with the increase of Ni concentration, this is most likely due to the formation of Ni clusters [11]. The tendency to form clusters of metallic Ni or NiO especially at higher concentrations (>5%) indicates that Ni does not incorporate in ZnO matrix and precipitates as secondary phase, such as NiO. The average crystallite size (**D**) of the samples is determined using Williamson Hall analysis, according to the relation:

$$\Box \cos \Theta = (D / \lambda) + 2\varepsilon \sin \Theta$$
 (1)

where \Box = Full width at half maximum (FWHM) of the peaks in XRD spectrum ε = internal strain

By drawing \Box Cos Θ as a function of Sin Θ (in radians), (D) can be deduced for each samples.



Fig. (1): XRD Pattern for all samples.

Fig. (2) Demonstrates the increase of average crystallite size **(D)** and the microstrain. The crystallite size increase with Ni concentration from 62 nm at 1 % concentration to 96 nm at 7% then remains constant **(Table 1)**. It is to noted that the value of **(D)** at 7% and 10% is equivalent to the corresponding **(D)** value of undoped ZnO indicating that the solubility limit of NiO in ZnO is at 5%.



Fig. (2): Average crystallite size versus Ni concentration in Zn1-xNixO system: x=0; x=1%; x=3%; x=5%; x=7% and x=10%.

Ni Concentration	Particle Size (nm)	
0	95.7	
1%	62.4	
3%	84.4	
5%	89.7	
7%	95.3	
10%	95.3	

Table (1): Variation of Particle size with Ni concentration.

This result is confirmed by studying the dependence of lattice parameters (a) and (c) on Ni concentration Fig. (3). It is observed that (a) and (c) values decrease reaching a minimum at 5% Ni concentration. At 7% Ni concentration, a sharp increase in the lattice parameter (c) towards its initial value is observed indicating more reduction in the internal strain in (c) lattice parameter compared to (a) parameter.

Table (2) shows the calculation of the internal strain (ε) as a function of Ni concentration using the relation (1). Fig. (4) shows maximum internal strain at 5% Ni concentration, which explains the minima in (c) and (a) parameters. At higher concentrations a decrease in internal strain is observed thus explaining the increase in (c) and (a) parameters.



Fig. (3): Lattice parameters variation with Ni concentration.

Ni	EWIN	O (rad)	Internal strain=
Concentration			FWHM / 4 Tan Θ
0	3.3 x 10 ⁻³	0.631	0.075
1%	3.2 x 10 ⁻³	0.631	0.073
3%	3.8 x 10 ⁻³	0.631	0.086
5%	4.2 x 10 ⁻³	0.631	0.095
7%	3.5 x 10 ⁻³	0.584	0.079
10%	3.5 x 10 ⁻³	0.584	0.079
		O(rad)	
Ni	EWIN	O (rad)	Internal strain=
Ni Concentration	FWHM	O (rad)	Internal strain= FWHM / 4Tan O
Ni Concentration O	FWHM 3.3 x 10 ⁻³	θ (rad) 0.631	Internal strain= FWHM / 4Tan O 0.075
Ni Concentration 0 1%	FWHM 3.3 x 10 ⁻³ 3.2 x 10 ⁻³	θ (rad)0.6310.631	Internal strain= FWHM / 4Tan O 0.075 0.073
Ni Concentration 0 1% 3%	FWHM 3.3 x 10 ⁻³ 3.2 x 10 ⁻³ 3.8 x 10 ⁻³	 θ (rad) 0.631 0.631 0.631 	Internal strain= FWHM / 4Tan O 0.075 0.073 0.086
Ni Concentration 0 1% 3% 5%	FWHM 3.3 x 10 ⁻³ 3.2 x 10 ⁻³ 3.8 x 10 ⁻³ 4.2 x 10 ⁻³	 φ (rad) 0.631 0.631 0.631 0.631 	Internal strain= FWHM / 4Tan 0 0.075 0.073 0.086 0.095
Ni Concentration 0 1% 3% 5% 7%	FWHM 3.3 x 10 ⁻³ 3.2 x 10 ⁻³ 3.8 x 10 ⁻³ 4.2 x 10 ⁻³ 3.5 x 10 ⁻³	 Φ (rad) 0.631 0.631 0.631 0.631 0.584 	Internal strain= FWHM / 4Tan 0 0.075 0.073 0.086 0.095 0.079

Table (2): demonstrates the variation of internal strain with Ni concentration.

2.2. Transmission electron microscopy (TEM)

Figure (5a, b, c, d) shows the TEM pictures for different Ni concentrations. (TEM) pictures for all samples reveal that nano-structure nature in agreement with XRD data



Fig. (4): Internal strains versus Ni concentration.

Figure (5a) shows the presence of pure ZnO in form of nano rods or nano spheres well separated with large intergranular spacing. By increasing the Ni content, deformation occurs in the initial shape which may be related to incorporation of NiO inside ZnO lattice, where different shapes of nano structures are observed (5c, d) up to 5% Ni concentration (solubility limit). At 7% and 10% Ni content (5e, f) the Intergranular spacing decreases due to formation of Ni clusters in agreement with XRD data, which has shown increase in the peak intensity of the NiO secondary phase.

3. Magnetic Properties

The B-H curves for the investigated samples are shown in Fig. (6). It should be mentioned that all doped samples exhibit ferromagnetic character, because the observed saturation magnetization, which varies in the range from 0.009 to 0.0135 (emu/gm). The estimated values of coercive and remainant fields were found to be composition dependent. The dependence of both on Ni concentration is shown in Fig. (6). The magnetization value decreases by increasing Ni content till 7% Ni then starts to increase, this clearly shown in Fig.(7). In such cases two possible interaction mechanisms ferro and anti ferromagnetic. The observed behavior depends on the state of energy terms

(singlet and triblet). The energy of interaction between 2 atoms having spin S_1 and S_2 is given by:

 $\mathbf{E} = -\mathbf{J} \mathbf{S}_{\mathbf{i}} \mathbf{S}_{\mathbf{J}}$

where \mathbf{J} = the exchange coupling constant.



Fig. (5): TEM pictures of Zn1-xNixO system

a) for pure Zinc Oxideb) for 1% conc. Of NiO in ZnO Latticec) for 3% conc. Of NiO in ZnO Lattice

d) for 5% conc. Of NiO in ZnO Lattice e) for 7% conc. Of NiO in ZnO Lattice f) for 10% conc. Of NiO in ZnO Lattice



Fig. (6): Hysteresis curve of Zn1-xNixO system.



Fig. (7): Magnetization of Zn1-xNixO system.

It is well established that in case of super exchange interaction, i.e.: interaction through the magnetic ion enhance anti ferromagnetic mechanism. However, if the magnetic ions make an angle $(\pi/2)$ with the non bridging diamagnetic ion, the ferromagnetic interaction can be observed.

Inspection of the present data allows us to conclude that the latter condition is satisfied in the present case.

Obtained results show the decrease of magnetization by increasing Ni content, i.e.: it reduces the ferromagnetic interaction.

In the present case the super exchange interaction enhance the ferromagnetic interaction, by increasing the Ni content, the number of Ni ions which exhibit super exchange interaction decrease and then reduce the ferromagnetic interaction.

4. Conclusion

Ni doped ZnO nanoparticles (1%, 3%, 5%, 7% and 10%) have been prepared by coprecipitation method.

XRD patterns revealed that the samples are polycrystalline having wurtzite structure of ZnO, with the presence of a NiO by concentration higher than 5% a secondary phase of NiO is observed.

From XRD data, the average crystallite size is found to increase with Ni concentration from 62 nm to 96 nm. The variation of lattice parameters and internal strain with Ni content suggested that 5% is the solubility limit of NiO into ZnO. This result is also confirmed by TEM pictures.

The saturation magnetization values suggest the presence of ferromagnetism, which decrease with Ni concentration due to the antiferromagnetic interaction between Ni-Ni ions thus reducing the ferromagnetic ordering in agreement with Mohapatra et al. [11].

Acknowledgment

The authors acknowledge the support of IAEA for providing the 22 Na source.

References

- 1. H. Ohno, Science, 281, 951 (1998).
- Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumuru, M.Kawasaki, P. Ahmet, T.Chikyow, S.Koshihara and H.Koinuma, *Science*, 291, 854 (2001).
- 3. S.Das Sarma, Am. Sci, 89, 516 (2001).

- 4. T. Dietl, H. Ohno, and F. Matsukura, Science, 287, 1019 (2000).
- 5. K. Sato and H. Katayama-Yoshida, *Physica*, E10, 251 (2000).
- 6. S.J. Pearton, D.P. Norton, K.Ip, Y.W. Heo, and T. Steiner, *J. Vac. Sci. Technol.*, **B22**, 932 (2004).
- 7. C. Liu, F. Yun, and H. Moroc, J. Mater, Sci., 16, 555 (2005).
- R. Janisch, P. Gopal, and N.A. Spaldin, J. Phys.: Condens. Matter, 17, R657 (2005).
- **9.** P.K. Sharma, R.K. Dutta, A.C. Pandey, S.Layek, and H.C. Verma, *J. Magn, Magn. Mater*, **321**, 2587 (2009).
- 10. H. Katayama-Yoshida, K. Sato, T. Fukushima, M. Toyoda, H. Kizaki, V. A. Dinh, and P. H. Dederichs, *Phys. Status Solidi*, A **204**, 15 (2007).
- J. Mohapatra, D.K. Mishra, S.K. Kamilla, V.R.R. Medicherla, D.M. Phase, V. Berma, S.K. Singh, *Phys. Status Solidi*, B 248, No. 6, 1352-1359 (2011).
- 12. K.Sato, H.Katayama-Yoshida, Phys. Stat. Sol., (B)229, 673 (2002).
- 13. Y.Uspenskii, E.Kulatov, H.Mariette, H.Nakayama, H.Ohta, J. Magn, Magn Mater., 258-2, 248 (2003).
- 14. K.Sato, H.Katayama-Yoshida, Semicond. Sci. Technol., 17, 367 (2002).
- 15. JCPDS 36-1451, H. McMurdie, Powder Diffract., 1, 76 (1986).