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Structure study of manganese doped zinc oxide

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ABSTRACT

The present study deals with some physical properties of Diluted magnetic semiconductor (DMS) (Zn1-xMnxO) (0 % ≤ X ≤ 10%). The system has been synthesized in the nano form by co-precipitation method. Nanostructure features of the prepared samples have been investigated by X-Ray diffraction (XRD) and scanning electronic microscopy (SEM). Analysis of XRD patterns show that all prepared samples exhibit crystalline nature belong to the hexagonal wurtzite structure of space group C6v=p63mc (JCPDS 89-1397). The dependence of particle size D on the Mn content. The particle size increase almost linearly with Mn content up to 2%,was considered then it exhibits almost constant value up to 5%. A sharp increase in D is observed by going from 5% to 6%. All compositions exhibit, particle size D less than 100nm, so all the prepared samples lay in the nano range, The Particle size vary from 56.78 for pure ZnO to 94.61 at 6%Mn concentration. The particle size was calculated by two methods Scherer and Williamson hall methods. The two methods give different value of particle size, which is most likely due to the fact that both are approximate equations. However, both equation show that the particle size increases by increasing Mn content

Keywords: Mn doped ZnO , DMS , Spintronic , Nanomaterial's , ZnO

I. INTRODUCTION

Diluted magnetic semiconductors (DMS) are one of the most promising candidates for spintronic application. Developing (DMS) is an essential step toward the realization of spintronic devices where both the charge and the spin of the electrons are manipulated. However, the mechanism governing the magnetic interactions in these materials challenges understanding of magnetism in solids. This challenge mainly lies in the complex interplay between magnetic ions of the DMS and the intrinsic and extrinsic defects of the host materials. Another contributing factor is the inhomogeneous distribution of the doped magnetic ions in the host materials, which leads to the un intentional formation of hetrostructures and secondary phases, which adversely affect the magnetic properties of DMSs. Transition metal doped Zno semiconductor prepared in nano form are found to be a one of the best candidates for spintronic applications.

In present study work, synthesis of pure and transition metal (Mn)-doped Zno nanostructures, nanoparticles and Nano rods have been carried out by co precipitation method. Various characterization techniques have been used to study of synthesized nanostructures, as DMS material. The characterization techniques include XRD, SEM.

II. METHODS AND MATERIAL

The (Zn1-x Mnx O)(X=0%,1%,2%,3%,4%,5%,6%.) Series of polycrystalline samples were prepared by precipitation method using starting materials (Zn acetate) and (Mncl2). The desired amounts of starting materials required for each composition were weighted. Then dissolution in 5 ml in de ionizing water and mixed thoroughly, stirring 2 for hours and deride at 80 Co for 3 days. Finally, has been calcinated at 400 Co for one day, the samples were quenched to room temperature and grinded.

TABLE I. The list of starting chemicals used in this study

Chemical name	**Formula**	**Grade, %**	**Molecular weight ,g/mol**
Zinc acetate dehydrate	$Zn(C_2H_3O_2)_2.6(H_2O)$	98.5	219.498
Manganese chloride dehydrate	$MnCl_2.6(H_2O)$	97	197.90
De ionizing water	H_2O		

The samples were examined by X-RAY diffraction using (BRUKER D8 ADVANCE GERMANY) equipped with a cu X-ray tube with CuKα radiation source (λ=0.15406 nm) at a power of 1600 w (40kV and 40 mA). The patterns used for line profile analysis were recorded by varying 2θ from 10o to 80o. The samples were used in the form very fine homogeneous powder.

Diffraction peaks can be compared to known diffraction pattern through the JCPDS (joint committee on powder diffraction standard) database collected via the "PCPDFWIN" software. Zno Nano crystal sizes were estimated from XRD measurements and determined by scanning electron microscope (SEM)

III. RESULTS AND DISCUSSION

Obtained XRD spectra of the investigated system are shown in figure (1). Analysis of XRD patterns show that all prepared samples exhibit crystalline nature belong to the hexagonal wurtzite structure of space group C6v=p63mc (JCPDS 89-1397).The calculated lattice parameters are listed in table (2).

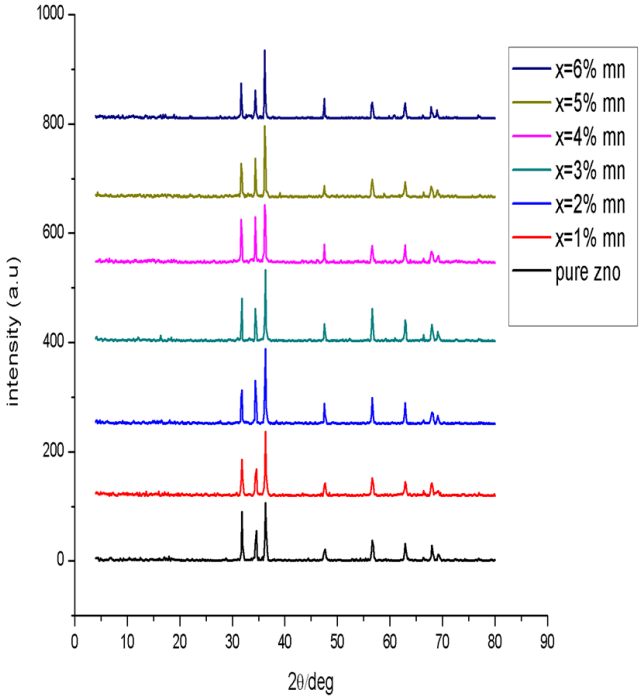

Figure 1: shows XRD pattern of all prepared samples (Zn1-xMnx O)

TABLE 2. The XRD data for the prepared samples

content mn %	2θ	hkl	d_{hkl}	structure	lattice parameters (A)			V (A)
					a	c	c/a	
0	31.85	(100)	2.8074	hexagonal	3.2448	5.997	1.84818787	54.6799121
	34.511	(002)	2.59679					
1	31.827	(100)	2.80938	hexagonal	3.2465	5.9981	1.84755891	54.7472625
	34.504	(002)	2.59729					
2	31.769	(100)	2.81441	hexagonal	3.2504	6.0084	1.84851095	54.9731152
	34.444	(002)	2.60173					
3	31.793	(100)	2.81234	hexagonal	3.248	6.0081	1.84978448	54.8892233
	34.445	(002)	2.60161					
4	31.732	(100)	2.8176	hexagonal	2.55	6.0172	2.35968627	55.0875099
	34.391	(002)	2.60556					
5	31.736	(100)	2.81725	hexagonal	3.2512	6.0156	1.85027067	55.0660868
	34.401	(002)	2.60487					
6	31.707	(100)	2.81976	hexagonal	3.252	6.0207	1.85138376	55.1398974
	34.371	(002)	2.60705					

Law manganese content samples(X=1,2,3and4 %Mn) exhibit XRD pattern similar to that of pure ZnO. On the other hand samples of x= 5 and 6 % Mn show new weak peak at 2θ~= 32, the latter is related the phase ($ZnMn_2o_4$) of tetragonal structure (JCPDS 71-2499) and having the indexes (103). The percentage of ($ZnMn_2o_4$) in 5% Mn sample is 3.9% and in 6%, Mn sample is 12.3%. This result indicated that the solubility limit of Mn in ZnO is 4%Mn.which in good agreement with data obtained by **Young Yeal song, et all. [3] and Ndia Febiana Djaja [5] .[1-5]**

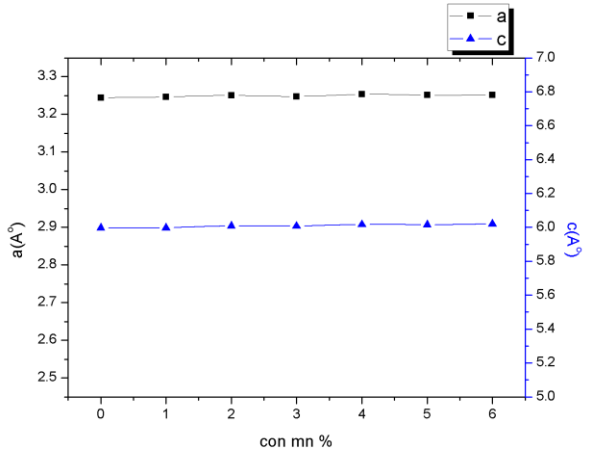

Figure 2: the lattice parameter a and c with Mn content a and c values show linear dependence on Mn concentration

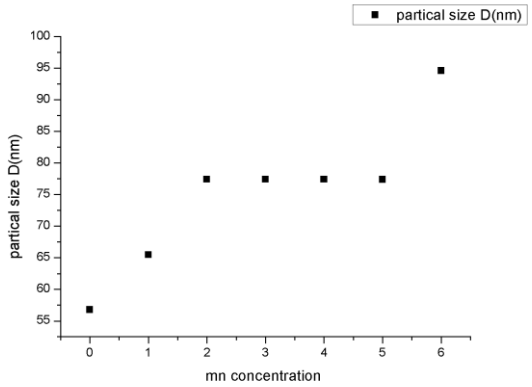

Figure 3: variation of particle size with Mn content

The lattice parameters of the prepared samples are listed in table (2). The dependence of particle size D on the Mn content is shown in fig 5.it is observed that the particle size increase almost linearly with Mn content up to 2% , then it exhibit almost constant value up to 5%. A sharp increase in D is observed by going from 5% to 6%. All compositions exhibit, particle size D less than 100nm, so all the prepared samples lay in the Nano range. The Particle sizes vary from ~ 56 at pure ZNO to~ 94 at 6%MN concentration.

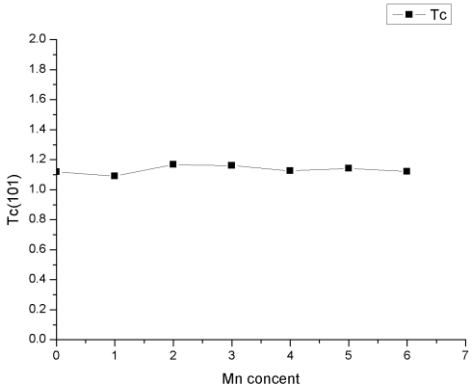

Figure 4: the texture coefficient with Mn content

The obtained data were used to calculate the texture coefficient (Tc) according to equation (1) [6, 7]. The plan (101) was used to calculate (Tc) fig (4) show the variation of the value of Tc with Mn concentration. The obtained data reveal that the dependence of Tc on Mn content is almost constant. However, it is established that Tc (hkl) increases the preferential growth of the crystallite in the direction perpendicular to the (hkl) plane. [6.7]

$$TC(hkl)=\frac{I(hkl)}{Io(hkl)}\left[\frac{1}{n}\sum_{n=1}^{n}\frac{I(hkl)}{Io(hkl)}\right] \quad (1)$$

The particle size was calculated by two methods Scherer and Williamson Hall methods

Scherer method :

Scherer plot of $1/\beta_D$ against cosθ fig (5)

The crystallite size D was extracted from the slope of the fitting of data Fig. (5) **A.Khorsand Zak [10]**.

$$D=\frac{k\lambda}{\beta\cos\theta} \Longrightarrow \cos\theta=\left(\frac{k\lambda}{D}\right)\left(\frac{1}{\beta}\right) \quad (2)$$

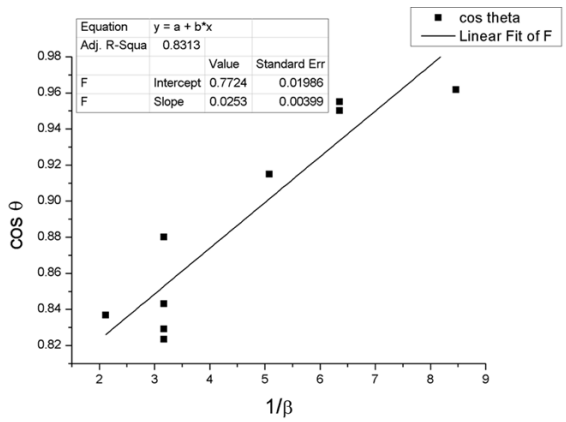

Figure 5: Scherer plot of ZnO.

Williamson Hall methods

Strain – induced broadening arising from crystal imperfections and distortion are related to micro deformation by ε =β/ tanθ

$$B\cos\theta = \left(\frac{k\lambda}{D}\right) + (4\sin\theta) \qquad (3)$$

The estimating of particle size is the dependence of (B cosθ) against (4sin θ).[8-10]

These plots allow the estimation of micro deformation showing fig (6)

This is most likely due to the lattice shrinkage that was observed in the calculation of lattice parameters. The results of the uniform deformation model (UDM) analysis for the ZnO are shown in figure (6)[10]

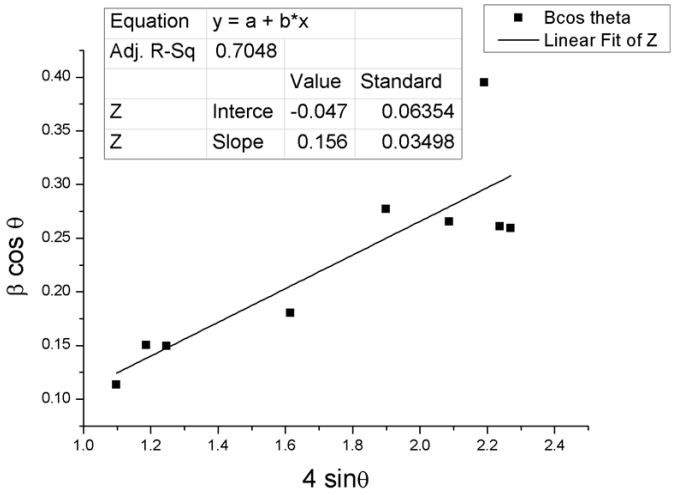

Figure 6: The W-H analysis of ZnO assuming UDM fit to the data

TABLE 3

The geometric parameter of prepared ZnO nanoparticles

Scherer method	**Scherer approximation**		**UDM**		**SEM**	
D nm	D nm	ϵ*10^3	D nm	ϵ*10^3	Math vol	Valid vol
56.77	17.9	0.025	29.50	0.156	51.23	69.23

It is clear The two methods give different particle size , which is most likely due to the fact that both are approximate equations , However both equation show that the particle size increases by increasing Mn content

Morphology study

The morphology of the prepared Mn doped Zno samples nanoparticles was examined using scanning electron microscopy (SEM) figure 7 shows the surface morphology of the samples using image processing (image J)software .

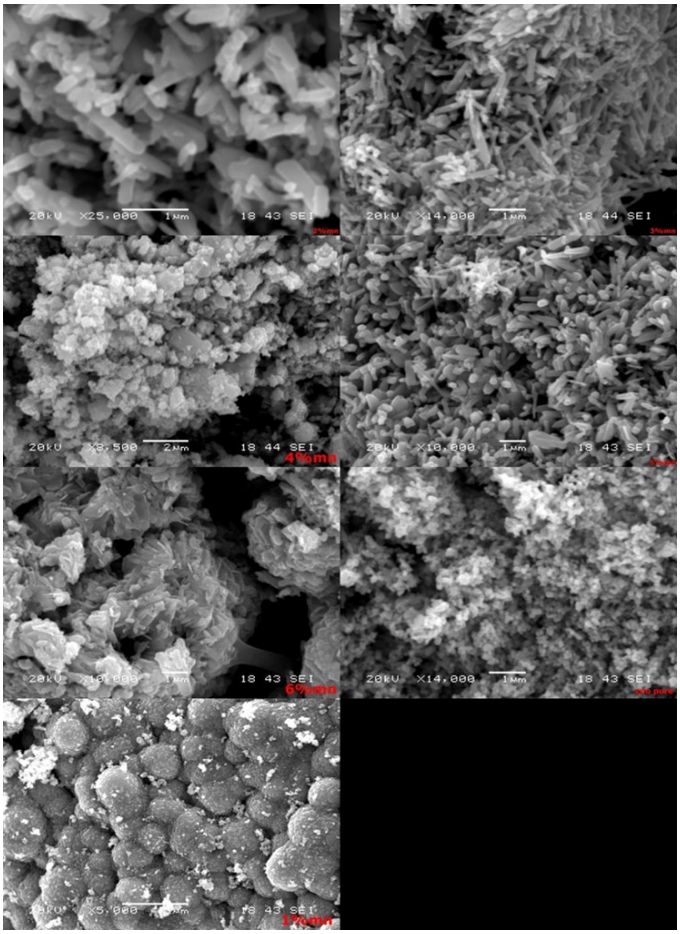

Figure 7: Show SEM image of pure zno and MN doped zno nanoparticles

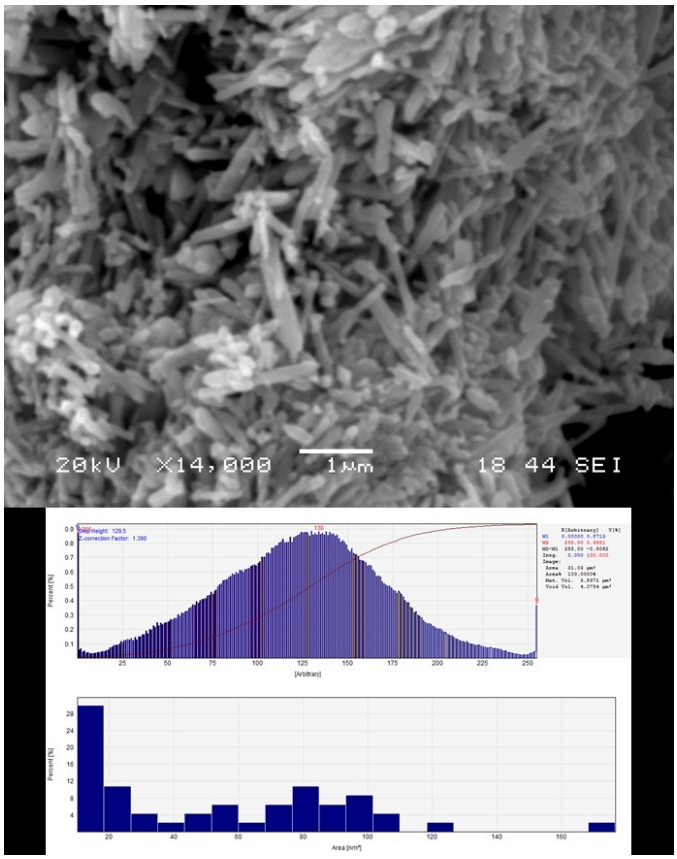

Figure 8: SEM image of 3%Mn dopd ZnO and size distribution histogram

IV. CONCLUSION

Mn doped ZnO were synthesized by co precipitation method and characterized by powered X-Ray diffraction and scanning electron microscopy (SEM) Analysis of XRD patterns show that all prepared samples exhibit crystalline nature belong to the hexagonal wurtzite of space group C6v=p63mc (JCPDS 89-1397) The dependence of particle size D on the Mn content increases by increasing Mn content , The particle size increase almost linearly with Mn content up to 2% , then it exhibit almost constant value up to 5%. A sharp increase in D is observed by going from 5% to 6% . All compositions exhibit, particle size D less than 100nm, so all the prepared samples lay in the Nano range, the particle size vary from 56.78 at pure ZNO to 94.61 at 6%MN concentration. The particle size was calculated by two methods Scherer and Williamson hall methods. ,The two methods give particle size , which is most likely due to the fact that both are approximate equations , However both equation show that the particle size increasing by increasing Mn content

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