Synthesis of Superfine Powders Using Sol-Gel Technique

Shivaji S Anarthe, Priyanka K Gadhave, Pradeep M Dighe

Abstract - Non-magnetic semiconductor from column II-VI or III-IV type is doped by transition metal ion. In current study we have doped Mn in ZnO. The concentration of Mn or Co is varied using the relation Zn1-xMnxO, thus variation in 'x' gives variation in concentration. To achieve the concentration variation Zinc acetate and Manganese acetate were taken in stoichiometric amount .Then the grown samples were subjected to x-ray diffraction studies for structural characterization. The average crystallite size was also estimated by measuring full width at half maxima of the intense diffraction peaks in all the compositions using Scherrer formula. Further SEM technique was employed to explore the distribution of particles in the materials. The analysis of diffraction peaks revealed the presence of wurtzite (hexagonal) structural phase in all compositions. It was observed that the samples synthesized with sol-gel route have smaller crystalline sizes (225 nm) as compared to the corresponding samples synthesized with solid–state reaction method (245 nm), but it was also found that the samples synthesized with citrate-gel path have smaller crystallite sizes (50 nm). The EDX show the amount of Mn doped on ZnO is slightly lower than the theoretical value.

Keywords - 1.Sol-gel technique, 2.doping, 3. Particle size, 4. X-ray diffraction

I. INTRODUCTION

The diluted magnetic semiconductors (DMSs) have attracted much attention recently because in these materials new functions can be added by transporting and controlling various types of spin states. In DMS materials, a non-magnetic semiconductor is doped with magnetic ions. These materials have resulted in the emergence of a new field of semiconductor spin-electronics involving the use of spin states inside semiconductor materials. Among these materials Mn doped II–VI and III–V semiconductors have been extensively studied [2, 3]. However, the Curie temperatures (Tc) of these materials have been limited to 140 K, which is far too low for practical device applications [1-4]. A theoretical prediction, by Dietl et al. [5], that hole–mediated Mn-doped ZnO and GaN can achieve Curie temperatures well above the room temperature initiated intense experimental work on a variety of doped diluted magnetic semiconductors. Subsequently, the values of Tc above room temperature were reported in Co-doped TiO_2 [6, 7], ZnO [8, 9] and Mn-doped GaN.

ZnO, an II-VI compound semiconductor with a wide band gap of about 3.4 eV, is an attractive material for applications in optical devices such as blue-, violet-, and UV- light emitting diodes (LEDs) and laser diodes (LDs). ZnO is also a strong piezoelectric material. Thus, transition metal doped ZnO has the potential to be a highly multifunctional material with coexisting magnetic, semiconducting, electromechanical and optical properties.

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A number of workers have therefore investigated the ferromagnetic properties of Mn-doped ZnO in the last few years. The samples have been synthesized in the bulk and thin film forms and a wide range of magnetic properties including room temperature ferromagnetism have been reported [10-14]. For example, thin films of $Zn_{1-x}Mn_xO$ (x=0.1 and 0.3) grown on Al_2O_3 substrates by laser MBE are reported to show a Tc value in the 30-40 K range by Jung et al. [14], whereas the films of similar compositions have been reported to exhibit spin-glass behavior with a strong antiferromagnetic exchange coupling by Fukumura et al. [15]. Y. M. Kim et al. reported Tc ~ 39 K in $Zn_{0.8}Mn_{0.2}O$ films prepared by sol gel method [16]. Similar, widely varying results have been reported on bulk samples also. For example, Han et al. observed a ferrimagnetic phase transition in the case of $Zn_{0.95}Mn_{0.05}O$ sample processed at 1170 K and it was attributed to the presence of the impurity spinel phase namely $(Mn,Zn)Mn_2O_4$ in the system [17]. Similar observation was obtained by J. H. Li et al. [18] in sol-gel derived $Zn_{1-x}Mn_xO$ samples sintered in nitrogen atmosphere at 900°C. P. Sharma et al. observed room temperature ferromagnetism in low temperature processed bulk and thin films of Mn-doped ZnO [10]. Recently, Chen et al. [19] have studied the effect of sintering temperature and atmosphere on the magnetic properties of Mn-doped ZnO. They observed ferromagnetic interaction in the samples sintered in Ar atmosphere below 700°C and found that ferromagnetic property disappeared when samples were sintered in air. From the above discussions it is clear that the ferromagnetism in Mn-doped ZnO is not well established. It also appears that processing parameters that affect the magnetic properties of the samples are not well optimized, particularly for the bulk samples. Also the variations of Tc and magnetization with concentration of Mn in the bulk samples have not been established very well. Under this scenario, the present investigation on the synthesis, structural and magnetic properties of bulk Mn-doped ZnO has been undertaken to explore the effect of processing parameters and concentrations of Mn ions in the samples on these properties. The samples in the bulk form were synthesized with the nominal compositions Zn1-xMnxO (x= 0.02, 0.05, 0.10, 0.15) by solid-state reaction and sol-gel methods. In both cases samples were sintered in air at ~ 700°C. The structural characterization of all the samples by XRD revealed the presence of wurtzite (hexagonal) crystal structure identical to the parent compound (ZnO).

II. EXPERIMENTAL

In the present investigation, Zinc Acetate and Manganese Acetate in stochiometric amount added with citric acid. In this solution Nitric acid in double amount is added. This solution is then heated in waterbath to get foamy precursor. This foamy precursor is then heated in furnace at 400^0C for two hours, so that we get black fluffy mass. This further sintered at 800^oC and we form the

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sample in pellete form. The samples were synthesized with the nominal compositions $Zn_{1-x}Mn_xO$ (x= 0.01, 0.03, 0.05, 0.10) by Citrate-gel methods. The samples were sintered in air at ~ 400^0C for 4 h in air and thereafter it was furnace cooled. After cooling the resulting material was reground. Finally the powder was sintered at 800°C in air for 18 h followed by furnace cooling.

The crystal structure of the samples synthesized in the present work was studied by using X-ray diffractometer (XRD - BRUKER D8) employing Cu-Kα radiation. The surface and grain size were estimated by employing a Scanning Electron Microscope (SEM - LEO 435VP).

III. DATA ANALYSIS

The as grown samples with various compositions of Zn and Mn were subjected to X-ray diffraction studies for gross structural characterization. The typical X-ray diffraction patterns of the samples synthesized with nominal compositions $Zn_{1-x}Mn_xO$ (x= 0.01, 0.03, 0.05, 0.10) by the Citrate gel method are shown in figure 1.

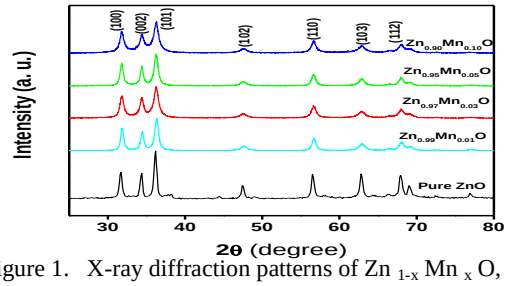
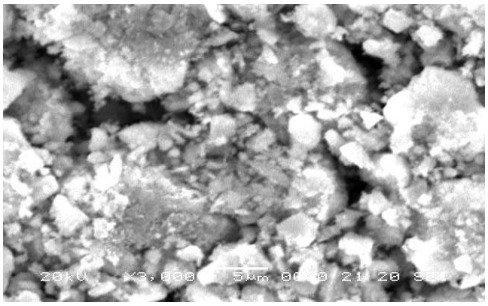
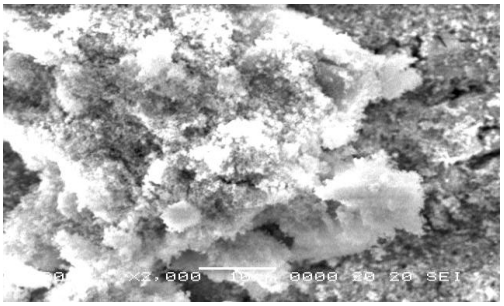


Figure 1. X-ray diffraction patterns of Zn $_{1-x}$ Mn $_x$ O, synthesized by the Citrate gel method.

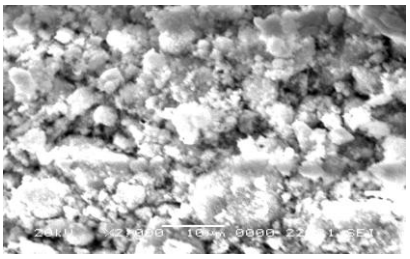
Grain Size is determined using Debye- Scherer's formula
Grain Size = 0.94 λ / B½* cos(θb)
λ -wavelength of x-ray (1.542 A°)
B½ - full width at half maximum of the diffraction peaks
λ b - Bragg's angle in degrees



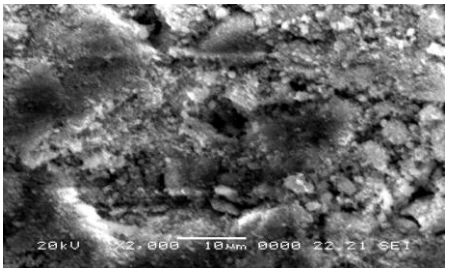
a) Zn $_{0.90}$ Mn $_{0.10}$ O



b) Zn $_{0.99}$7Mn $_{0.01}$ O



c) Zn $_{0.97}$ Mn $_{0.03}$ O

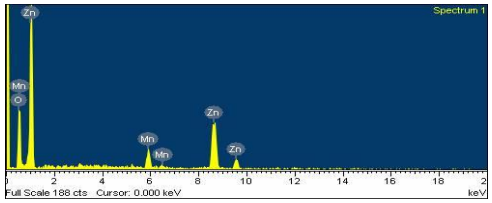


d) Zn $_{0.95}$ Mn $_{0.05}$ O

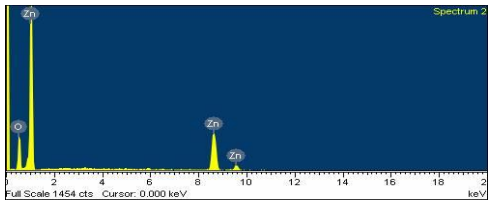
Figure 2. Scanning Electron Micrographs of Zn $_{1-x}$ Mn $_x$ O samples synthesized by Citrate gel method.

IV. EDX CHARACTERIZATION

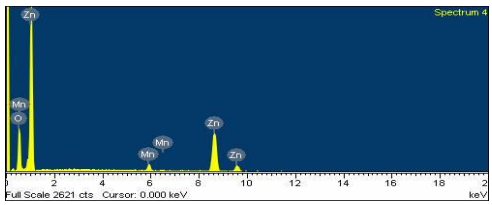
Sample 1: - Zn $_{0.90}$ Mn $_{0.10}$ O



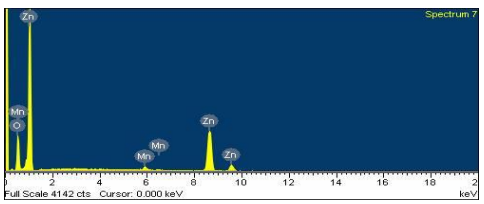
Sample 2: - Zn $_{0.99}$ Mn $_{0.01}$ O



Sample 3: - Zn $_{0.97}$ Mn $_{0.03}$ O



Sample 4: - Zn $_{0.95}$ Mn $_{0.05}$ O



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%Mn(Theoretical)	%Mn (EDX)	Crystallite size(nm)
1	0.91	9
3	2.95	15
5	5.74	30
10	8.59	11

V. CONCLUSION

In the Citrate gel method Mn doped ZnO [25,26,27] samples of nominal compositions $Zn_{1-x}Mn_xO$ (x=0.01, 0.03, 0.05, 0.10) synthesized by the citrate gel reaction, from the structural characteristics of the samples explored by XRD of pure and Mn doped ZnO system it is confirm that system having complete phase formation with Wrutzite (Hexagonal) crystal structure. Showing absence of Mn and Mn-O peak confirming substitution of Mn atoms on Zn site. All samples are prepared from citrate gel method sherror formula gives rise to average particle size of all particles is of the order ~ 16 nm. The EDX show the amount of Mn doped on ZnO is slightly lower than the theoretical value.

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