Structural and Optical properties of Mn doped ZnO Nanoparticles

Teny Theresa John, K. R. Priolkar* and P. R. Sarode
Department of Physics, Goa University, Taleigao Plateau, Goa - 403206
*Email: krp@unigoa.ac.in

Abstract
Mn-doped ZnO nanoparticles prepared by Chemical Bath Deposition (CBD) with substituent fraction ranging from x= 0.01 to x=0.05 are characterized structurally and optically using X-Ray Diffraction (XRD), UV-Vis Absorption and Fourier Transform Infrared Spectroscopy (FTIR). The unique feature of the sample preparation is the low temperature processing. The band edge shows a red shift on higher doping concentration. FTIR spectra reveal a transition of Mn$^{4+}$ state to Mn$^{2+}$ state on increasing doping concentration.

INTRODUCTION
Recently there has been intense searching for ferromagnetic ordering in doped, dilute magnetic semiconductors focusing on possible spin-transport properties, which has many potentially interesting device applications. One natural way of incorporating magnetism into a non magnetic semiconductor of II-VI or III-V type is to substitute transition metal ions for the nonmagnetic ions of the semiconductor. One material which shows particular promise for yielding a suitable ferromagnetic semiconductor is ZnO. Stimulated by the theoretical predictions of room temperature ferromagnetism in DMSs by Dietl et al [1] many systems of ZnO:TM (TM = Mn, Co, Ni, V, Cr etc) have been synthesized by different methods and extensively studied, but controversial results are reported. The first observation of ferromagnetism above room temperature for dilute (< 4%) Mn doped ZnO was reported by P. Sharma et al [2]. In light of all controversies, we have undertaken a detailed study of Zn$_{1-x}$Mn$_x$O samples. In this paper, we combine XRD, UV-Vis absorption and FTIR for structural and optical properties of Mn doped ZnO.

EXPERIMENT
For synthesis CBD method has been chosen because it is cost effective, requires only low temperature processing and allows homogeneous dispersion of dopants. The ammonium zincate bath used for the deposition of ZnO is prepared by adding ammonium hydroxide (30% ammonia solution) to an aqueous solution of zinc acetate ([CH$_3$COO]$_2$Zn.2H$_2$O) with constant stirring. At first a white precipitate of zinc hydroxide (Zn(OH)$_2$) appears. On further addition of ammonia, the precipitate dissolves forming the (NH$_4$)$_2$ZnO$_2$ bath. The final reaction that leads to the formation of ZnO from ammonium zincate bath is

\[(NH_4)_2ZnO_2 + H_2O \rightarrow ZnO + 2 NH_4OH \ldots \] (1)

An excess of alkali is required to have a stable ammonium zincate bath. The bath was kept at 70°C. The precipitate which formed was separated from the solution by filtration and dried in the oven at 50°C. It was then pressed into pellets and annealed at 160°C for 1 hr on hot plate prior to structural characterization. For Zn$_{1-x}$Mn$_x$O required quantity of aqueous solution of manganese acetate is added with stirring to the zinc acetate solution prior to the addition of ammonia so that the x value varies as 0.01, 0.02, 0.03 and 0.05. The samples thus prepared are named as Mn$_0$ (undoped), Mn$_{0.01}$, Mn$_{0.02}$,Mn$_{0.03}$ and Mn$_{0.05}$ respectively.

RESULTS AND DISCUSSION
The x-ray diffractogram of the synthesized powder with Rietveld refinement is shown in Fig.1.

![XRD pattern of undoped and Mn doped ZnO nanoparticles.](image)

Figure 1 XRD pattern of undoped and Mn doped ZnO nanoparticles. Rietveld refinement of undoped sample is also shown. *denotes impurity peaks.

XRD pattern of nanosized undoped ZnO shows reflections of pure hexagonal wurtzite structure (space group...
The lattice parameters obtained \((a = b = 3.251(1) \, \text{Å} \) and \(c = 5.208(8) \, \text{Å})\) match well with the reported values \([3]\). The unit cell volume was calculated to be 47.68 \(\text{Å}^3\). A few impurity peaks have grown on doping Mn, which correspond to different phases of zinc manganese oxide. As the amount of Mn increases, the x-ray peak width increases up to Mn_0.02 and then decreases. Evolution of lattice parameters and cell volume, as obtained from Rietveld refinement, with \(x\) is shown in Fig. 2. The cell parameters and volume decreases linearly with \(x\) from \(x = 0\) to \(x = 0.02\) and then increases. Grain size as obtained from Williamson-Hall plot also shows similar variation. The value decreases from 47 nm (Mn_0) to 28 nm (Mn_0.02) and then increases (51 nm for Mn_0.05) on further doping.

Optical absorption spectra are recorded in the wavelength region 300-900 nm. The band gap of sample Mn_0 is found to be 3.2(4) eV.

Two new bands appear at around 625 cm\(^{-1}\) (for all Mn doped samples) and 450 cm\(^{-1}\) (for Mn_0.01 and Mn_0.02 only). From the spectra recorded for pure MnO\(_2\), it is seen that the band at around 450 cm\(^{-1}\) corresponds to MnO\(_2\) phase. On increasing Mn concentration (Mn_0.03 and Mn_0.05) this band disappears. This is perhaps because of transition from Mn\(^{3+}\) to Mn\(^{2+}\) state with increasing Mn doping. Such a transition is also seen in the behaviour of cell parameters and cell volume. An abrupt increase in cell parameters and volume beyond 2% Mn doping can be attributed to ionic sizes of Zn\(^{2+}\) (0.60 Å), Mn\(^{4+}\) (0.39 Å) and Mn\(^{2+}\) (0.66 Å). Substitution of Mn in 4+ state at lower Mn doping results in a decrease while nearly equal cell volumes of Mn_0.03, Mn_0.05 and undoped ZnO indicate Mn to be in 2+ state.

**CONCLUSION**

Undoped and Mn-doped ZnO nanoparticles were prepared using chemical bath deposition with lattice parameters varying with the extent of doping. Incorporation of Mn into ZnO lattice is obvious from the optical absorption and FTIR studies. FTIR measurements predict a possible Mn\(^{3+}\) to Mn\(^{2+}\) transition in the doped samples which is supported by the variation in lattice parameters and cell volume. Further confirmation studies are going on.

**REFERENCES**


**ACKNOWLEDGEMENTS**

Authors thank DST, Govt. of India for funding under the project.