

Structural Properties of Mn Doped Zinc Oxide Nanopowders by Chemical Co-Precipitation

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ABSTRACT

Nanocrystalline tin oxide (SnO₂) was synthesized using stannic chloride pentahydrate (SnCl₄·5H₂O) as a precursor in aqueous medium by chemical co-precipitation method. The influence of sintering temperature on the crystalline structure was studied. X-ray diffraction studies reveal that all powders exhibit tetragonal crystal structure. It is observed that crystallinity and crystallite size increases with sintering temperature. Various absorption bands viz. Sn-O, O-Sn-O and O-H are observed from the FTIR study. The compositional analysis of SnO₂ nanoparticles is studied using X-ray photoelectron spectroscopy (XPS). The symmetric spin orbit splitting of Sn 3d_{5/2} ground state and Sn 3d_{3/2} excited states is observed in XPS with sintering temperature while O 1s is recognized with O-2 state.

Keywords: Chemical co-precipitation, Tin oxide, XRD, crystallite size, FTIR, XPS.

I. INTRODUCTION

In this fast-paced world, nanotechnology has created a new industrial revolution globally and becomes a major topic in recent material research fields. Many countries have invested in nanotechnology due to its small in size with huge immense potential. It is well known and widely applied in many areas such as in nano finishing of functional textiles, biomedical, electronics, batteries, solar cells, chemical coatings and so forth. Nanotechnology creates structures that have excellent properties by controlling atoms and molecules, functional materials, devices and systems on the nanometer scale by involving precise placement of individual atoms of the size around 1 nm to 100 nm.

Mn- doped Zinc oxide nanoparticles has increased a lot of attention from the scientists and researchers to undergo this research interest due to its various applications in photocatalyst, chemical sensors, solar cells and optoelectronic devices. However, the doping efficiency was influenced by the strong tendency of the Mn dopant ions to segregate at the nanoparticles surfaces. The Mn doping transition metals in ZnO give the best results because Mn has the highest magnetic moment and has the most stable polarization regions. Some Zn can be substituted with Mn ions which can provide ferromagnetic properties [1-2]. Many studies have been conducted to produce ZnO including in the form of powder and film [3]. In general, Mn substitution into ZnO can be formed in the system of Zn_{1-x}Mn_xO. Regarding the synthesis of nanoparticles, many experts due to its excellent

properties compared to other methods have chosen precipitation. Mn is preferred for the doping of ZnO due to the d electron of Mn can easily overlap with the ZnO's valence band as compared with other transition element. There are various studies shown that Mn doped semiconductors have influenced the physical, chemical and structural properties of undoped ZnO nanoparticles. For example, the optical properties of undoped ZnO nanoparticles especially on the tuning of the band gap can be greatly improved at the nanoscale by Mn doping. Practically, among other traditional synthetic methods, coprecipitation provides a simple route with low cost for large-scale production. Furthermore, such method also does not need expensive raw materials. Actually, the term "doped" is used to modify the optical or magnetic properties of the host by adding impurities ions against the host lattice (Figure 1).

In this paper, we report the effect of Mn dopant concentrations (1 to 5 at %) on the structural properties of Mn-doped ZnO nanoparticles.

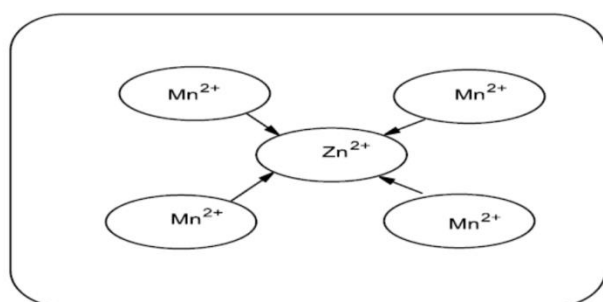


Figure 1: Mn-doped ZnO nanoparticles

II. EXPERIMENTAL:

Zinc oxide nanoparticles are synthesized using the wet chemical co-precipitation method. The precursors used in the synthesis ZnO are Zinc acetate dihydrate having purity 99%. The preparation conditions were carefully controlled. Double distilled water was used for solution preparation. Solution pH, considered using the relation between pH and concentrations of both the solutions was adjusted to neutral by adding aqueous ammonia to preserve the

hydroxide phases of Zn and Mn. The homogeneous solution was prepared by thoroughly mixing both the solutions. White gelatinous precipitate formed, was filtered using Whatmann filter paper No. 17. The precipitate was washed thoroughly until traces of Cl were removed. It was further dried at ambient temperature and sintered at different temperatures within 400°C for 6h in air atmosphere.

III. RESULTS AND DISCUSSION:

Figure 2 & 3 shows the XRD patterns of undoped and 10 at % Mn-doped ZnO nanocrystalline powder. The sharp intense peaks of ZnO confirms the good crystalline nature of ZnO and the diffraction peaks can be indexed to a hexagonal wurtzite structured ZnO [4]. Furthermore, compared with the undoped ZnO, introduced manganese ions shift the diffraction peaks to higher angles by 0.17°. Such changes are indeed to be expected if Mn ions replace Zn ions in the lattice, as the Mn ions have smaller ionic radii (0.66Å) than Zn ions (0.74Å). The shift degrees indicate decrease of lattice parameters. From Fig. 2 one can observe that the intensity of (101) diffraction plane increased slightly than that of pure ZnO [5].

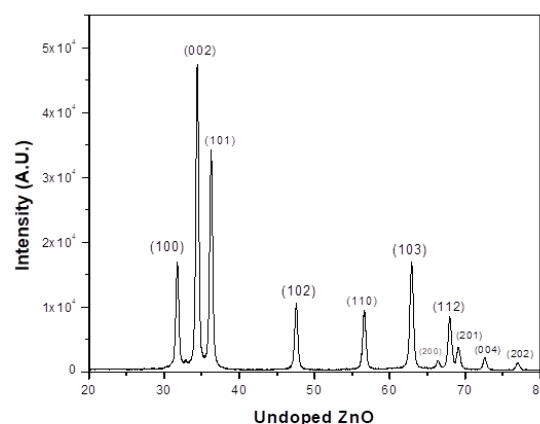


Fig. 2 XRD patterns of undoped ZnO nanocrystalline powder.

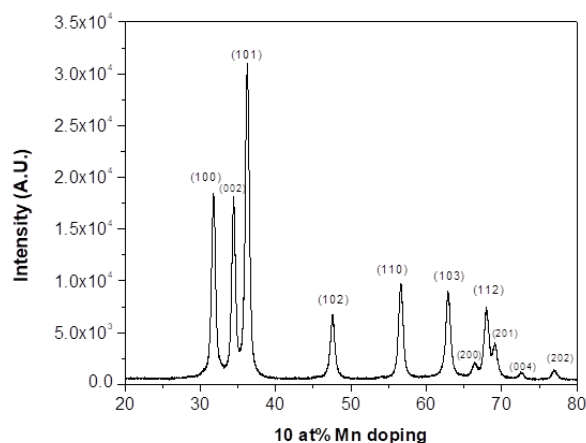


Fig. 3 XRD patterns of 10 at % Mn-doped ZnO nanocrystalline powder.

The crystallite size 'D' is calculated using Scherrer's formula,

$$D = 0.94\lambda / \beta \cos\theta$$

Where D is the crystallite size, β is the broadening of the diffraction line measured at half of its maximum intensity (rad) FWHM and λ is the x-ray wavelength (1.5405Å). It is seen that as doping increases the crystallite size increases up to 10 at% and tends to decrease afterwards as shown in Fig. 4.

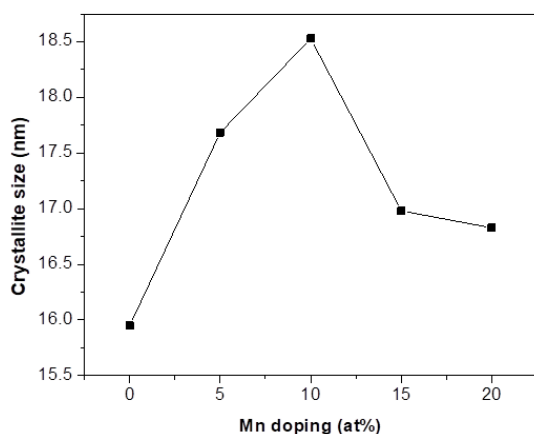


Fig. 4 Variation crystallite size with Mn doping.

Evaluation of the lattice parameters a, c as a function of Mn concentrations is shown in Fig. 5 & 6. As for Mn-doped nanocrystalline powder, the lattice parameters a & c calculated from the (101) a peak, the values of a & c are increases upto 10 at % doping and

further decreases. The calculated lattice parameter are higher than the standard JCPDS parameter for bulk ZnO, $a = b = 3.2498 \text{ \AA}$ and $c = 5.2060 \text{ \AA}$, respectively. Since the ionic radii of Zn^{2+} (0.74 Å) is smaller than that of Mn^{2+} (0.83 Å) and larger than that of Mn^{3+} (0.64 Å) [6].

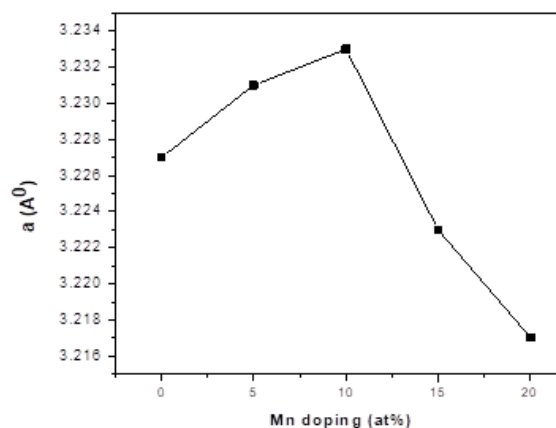


Fig. 5 Variation of lattice parameters 'a' function of Mn doping concentrations.

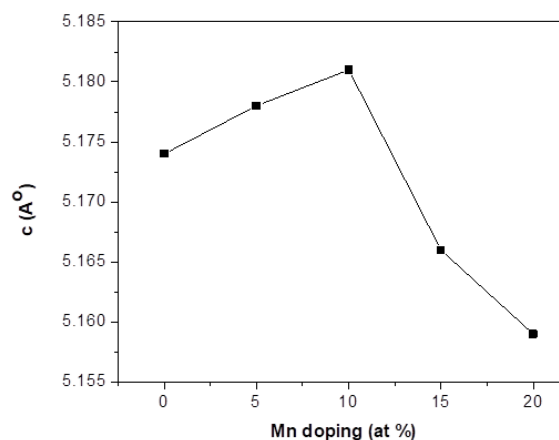


Fig. 6 lattice parameters 'c' as a function of Mn doping concentrations.

Fig. 7 shows the Williamson and Hall plot of our undoped as well as Mn-doped nanocrystalline ZnO particles. It is observed that the strain in Mn-doped samples decreases upto 10 at % Mn and further increases [7]. It is seen that more Mn content is introduced into the sample, the stronger tensile is, or more created compression stress. The change in structural properties of Mn-doped samples are due to

strain present in nanocrystals. The above study gives the idea of promising application of synthesized Mn-doped ZnO nanoparticles for optoelectronic devices.

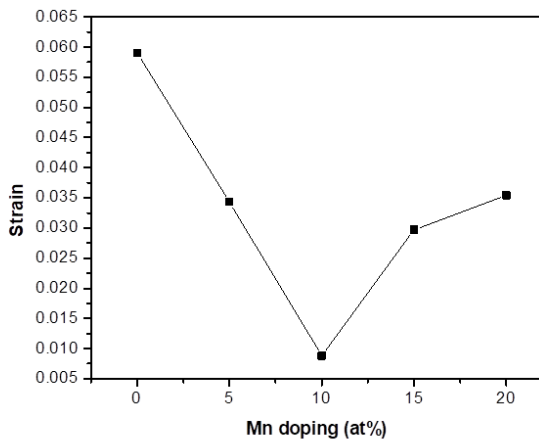


Fig. 7 Williamson and Hall plot of undoped as well as Mn-doped nanocrystalline ZnO nanoparticles.

IV. CONCLUSION

ZnO sample containing transition metal Mn synthesized by chemical co-precipitation method correspond to a hexagonal structure similar to that of undoped ZnO. The XRD measurement suggests that Mn atoms substitute Zn sites in the crystals without changing the wurtzite structure, but with the lattice parameters varying slightly with the extent of doping. XRD data showed that all the samples had a (002) preferential orientation perpendicular to the substrate. Crystallite size of the ZnO film was found to be decreased with Mn-doping. We also observed on doping the grain size reduces drastically reducing to nano-scale i.e., doping hinders the grain growth. No secondary phases were observed for the simple synthesis process adapted in the present work for the doped ZnO samples upto 20 at % of Mn doping.

V. REFERENCES

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