International Research Journal of Multidisciplinary Science & Technology
Volume: 02 Issue: 01 | January -2017 www.irjmrs.com ISSN: 2455-930X

INVESTIGATION OF STRUCTURAL, SURFACE MORPHOLOGY AND MAGNETIC STUDIES OF Mn-DOPED SnO_2 NANOPARTICLES

M.Umadevi [1], M.Saravanakumar[2], K.Rathina[3]

[1]*Department of Physics, Sri Parasakthi College for Women, Courtallam, India.*

[2]*Department of Physics, SVS College of Engineering, Coimbatore, India.*

[3]*Department of Physics, Kumaraguru College of Technology, Coimbatore, India.*

ABSTRACT

The Mn doped SnO_2 were found to have an average crystallite size lying in the range of 3.7- 4.3 nm. The observed average crystallite size of Mn doped SnO_2 nano particles are found to decrease with the increase in Mn doping concentration. Absorbance spectra of Mn doped SnO_2 nano particles show an ultraviolet edge around 327–343 nm, and the band gap energy has been observed to decrease from 3.79 eV to 3.61eV with increasing the Mn concentration. The SEM images of the prepared Mn doped (2% , 4% and 6%) SnO_2 samples show clearly the formation of nano clusters and it has been observed that the grains have aggregated to form clusters. The chemical compositions of the prepared samples have been studied using the energy dispersive X-ray analysis. From the HRTEM images the inter planar distance have been determined using lattice fringes of Mn doped SnO_2 nano particles and are found to be 0.31 nm. The obtained inter planar spacing values correspond to the (110) plane of rutile phase SnO_2.

Keywords: **XRD, Structural parameters, SEM, Magnetic Properties.**

1. INTRODUCTION

Oxide based diluted magnetic semiconductors have been attracting passionate interest to the current researchers due to their potential applications in Spintronics .The materials can exploit both charge and spin degrees of freedom of electrons to create new functionalities beyond conventional semiconductors[1].The most common approach to drive a semiconductor ferromagnetic is that of diluted magnetic semiconductors (DMSs), which is obtained by doping a non-magnetic semiconductor with a few atomic percent of transition metal (TM) elements (V, Cr, Mn, Fe, Co, Ni and Cu) [2] . Recently, magnetic semiconductors have been studied extensively with the doping of magnetic transition metal ions (Co, Mn, Cr and Ni) for multidisciplinary magneto electronic devices. Further the dilute magnetic semiconductors with high T_c is needed for real life advanced Spintronics device fabrication technology. For DMS application it is crucial to avoid magnetic precipitation in host semiconductor oxide [3]. So, desire of semiconductor nano particles without any magnetic impurity is required. Indeed, we should chose alternative non-magnetic transition metal ions as the dopants due to their intrinsic non magnetic nature, its precipitates do not contribute magnetically with semiconductors. In this view among the elements of Mn will be most suitable non-magnetic transition metal ions with good conductor of heat and electricity [4]. Furthermore, ion radius of Mn is smaller as compared to other transition metals and it can be easily substituted by Mn into any semiconductor oxide [5]. Already few reports had been published elsewhere with room temperature ferromagnetism at various semiconductor oxides. Further to evolve the intrinsic magnetism it is needed to study with different host matrix both bulk as well as thin layers. Among the various host semiconductor oxides for dilute magnetic semiconductors a unique structural featured ZnO, SnO_2 and TiO_2 have been received a great research interest [6]. It is cleared that synthetic conditions, temperature, particle size and micro structure of the semiconductor oxides also greatly influences on the magnetic and optical behavior. Therefore, it is not worthy to control the material structure using different synthetic route to obtain the desired property.

Considerable research has been concentrated on the development and synthesis of Mn- doped Tin oxide phases that would exhibit room temperature ferromagnetism (RTFM). Several groups have reported on the magnetic properties of Mn- doped thin films [7-9] and on SnO_2 nanocrystals [10], which show room temperature ferromagnetism. Nanocrystalline samples are important subjects for investigation, as they are prepared under equilibrium conditions. In this paper, the experimental results obtained from Mn-doped SnO_2 nanocrystalline samples were prepared and characterized. Secondly, in order to improve the magnetic property in SnO_2, Mn were introduced into the system. Different concentration (2%,4%,6%) Mn doped SnO_2 samples were prepared by chemical co precipitation method.

2 EXPERIMENTAL DETAILS

All chemicals used in the present work were of analytical grade and used without further purification. De-ionized water was used in all the synthesis steps. SnO_2 nano particles doped with three different concentration of Mn, 2%, 4% and 6%, were prepared by chemical co-precipitation method. The precursors for dopants and host were manganese acetate tetra hydrate ($(CH_3COO)_2$ $Mn.4H_2O$) and tin chloride ($SnCl_2.2H_2O$) respectively. The solution was prepared using tin chloride ($SnCl_2.2H_2O$) and manganese acetate tetra hydrate ($(CH_3COO)_2$ $Mn.4H_2O$)) in distilled water to make 0.3 M solution and aqueous ammonia (NH_3 OH) of 0.4 M was added with the solution to increase the pH of the solution for the precipitate formation. The source materials were weighed according to the stoichiometry as per the target compositions and were dissolved in distilled water to make 0.3M solution. Aqueous solution of ammonia was added drop wise to the solution of tin chloride precursor under continuous stirring for 3hr at room temperature till fine precipitate was formed. Using the same method, we have repeated the procedure for various concentrations of $SnCl_2.2H_2O$ for molar values of 0.4 and 0.5 M respectively. The solution obtained was centrifuged at 3000 rpm for 10 minutes. The precipitate was filtered out separately and washed with de-ionized water to remove the unnecessary impurities formed during the precipitation process. The obtained product was placed in oven for 8h at 60°C.

X-ray diffraction studies have been carried out using PANalytical x-ray diffractometer. Elemental composition of the prepared samples has been studied using Energy dispersive analysis of X-rays (EDAX, Thermo-Noran system Six). The optical properties have been studied using absorbance spectrum recorded using spectrophotometer (JASCO V-570). Photoluminescence emission spectrum has been recorded using Cary Eclipse spectrophotometer.

3. RESULT AND DISCUSSION

3.1 STRUCTURAL PROPERTIES

Figure 1 shows that XRD pattern of Mn doped SnO_2 nanoparticles having Mn doping concentration of 2%,4% and 6%. All the diffraction peaks were indexed and found to match with the JCPDS standard (No. 88-0287) data of rutile-type tetragonal structure of SnO_2. The diffraction peaks are observed to be shifted towards higher angles with increase in Mn content which indicates that Mn ion has substituted for Sn site without changing the rutile structure. Lattice constant values were calculated from the XRD peak positions and are shown in table 1. Lattice parameters are observed to decrease with the increased Mn content in the nano particles. The change in the lattice constants may be due to smaller ionic radius of Mn^{3+} (0.65 Å) when compared to Sn^{4+} (0.69 Å) as reported by [1]. From the diffraction pattern is observed that the intensity ratio decreases with the Mn addition into SnO_2 and it indicates that the presence of manganese in the SnO_2 matrix and changes the structure factor, because the atomic scattering factor for Mn is almost half the value for Sn (

Table 1: Strucutral parameters of (1) 2% Mn Doped SnO_2 (2) 4% Mn Doped SnO_2 (3) 6% Mn Doped SnO_2

S.No	Samples	Lattice parameters (Å)		Grain Size (nm)
		a	c	
1	2% Mn doped SnO_2	4.765	3.761	3.79
2	4% Mn doped SnO_2	4.760	3.76	3.86
3	6% Mn doped SnO_2	4.755	3.759	4.31

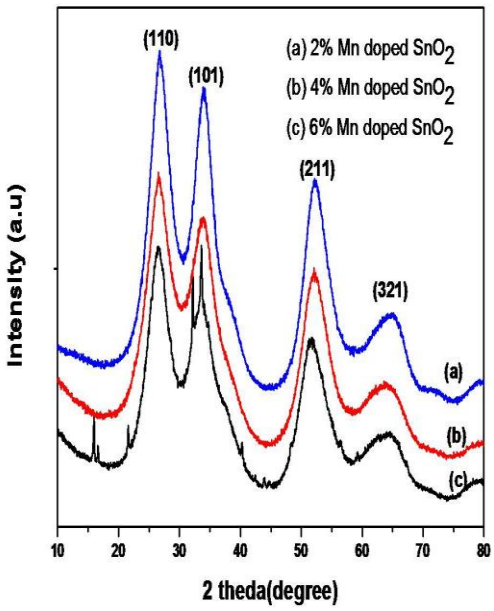


Figure. 1 XRD Pattern of (a) 2% Mn Doped SnO_2 (b) 4% Mn Doped SnO_2 (c) 6% Mn Doped SnO_2

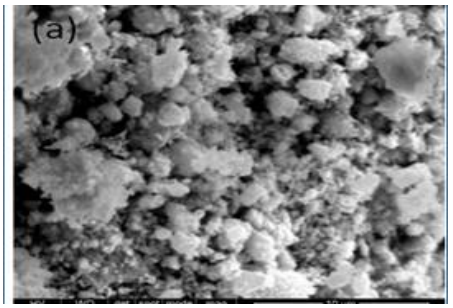
Atomic number of Mn is half that of Sn [11]. The crystallite size of Mn doped SnO_2 nano particles, determined from the full width at half maximum (FWHM) of the XRD peaks using the Scherrer's formula as function of the Mn doping concentrationis given in table 1. The samples have an average crystallite size lying in the range of 3.7- 4.3 nm.

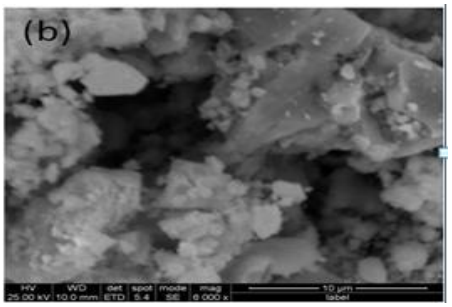
The observed average crystallite size of Mn doped SnO_2 nanoparticles is found to decrease with the increasing Mn doping concentration may be caused by decreasing in diffusion rate with the increasing of dopant. The reduction of the crystallite size suggests that the Mn ion replaces the Sn ion[12].

3.2. SURFACE MORPHOLOGY STUDIES

Figures. 2 (a), (b) and (c) shows the SEM images of the prepared Mn doped (2% Mn, 4% Mn and 6% Mn) SnO_2 samples. The SEM images show clearly the formation of nanoclusters. The grains have aggregated to form clusters. A SEM image suggests that the samples have uniform grain distribution. These images also shows that the particles are tend to agglomerate. It is well known that irrespective of preparation method used to obtain nano-oxides, there are some compelling evidence that crystallization does not follow a traditional nucleation and growth mechanism, more so in the case of increasing concentration of oxo-hydroxides to form metal oxides.

Figure 3 shows the magnetization curves of Mn doped SnO_2 powder samples. A very well-defined hysteresis loop was observed. The magnetization of Mn doped SnO_2 increases with Mn content (x = 2%), but when doping concentration increases to 6% saturation magnetization is decreased . The behavior of reduced ferromagnetism was exhibited in the sample with 6% Mn (Figure. 3 (c)). From table 2 the sample with lower Mn content (2%) showed the larger magnetization and with increasing Mn content (6%), the magnetization diminished. The saturation magnetization obtained from the Mn doped SnO_2 sample is more than fiftyfold larger than that of the pure SnO_2 powder sample.





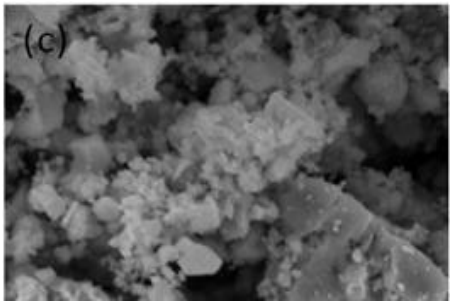


Figure. 2 SEM images of Mn doped SnO_2 (a) 2% Mn Doped SnO_2 (b) 4% Mn Doped SnO_2 (c) 6% Mn Doped SnO_2

Figure. 3 (a) shows the magnetization(M) as a function of the applied field (H) corresponding to the Mn doped SnO_2 sample. Ferro magnetization with such large coercivity of the loop and the large magnetization saturation in SnO_2 doped with non ferromagnetic element such as Mn is interesting and this finding proves that doping of small amount of transition metal in to non-magnetic oxides could induce room temperature ferro magnetization. However, this large value of the magnetization saturation is hard to attribute to any kind of impurities.

Thus, Mn can be distributed uniformly in the SnO_2 lattice in the dilute establishment .Even though some manganese oxide nano particles might be existing in the samples, they cannot be responsible for ferromagnetism observed at Room temperature. Based on the above discussion, the observed ferromagnetism must be related to the intrinsic defects in the SnO_2 lattice and the reaction of MnO_2 with SnO_2 prior to the final formation of the Mn-doped SnO_2 rutile. When increasing Mn content it induced the decreaseing ferromagnetic behaviour due to producing coupled spins [11]. Therefore, this significant enhancement of magnetization can be ascribed to the so-called F-centre exchange coupling, in which both oxygen vacancies and transition metal doping are involved [13].An oxygen vacancy in SnO_2 traps an electron to form F-centres, which with two Mn^{3+} constitutes a Mn^{3+}-x- Mn^{3+} group, where -x- denotes the oxygen vacancy. The electron trapped in the oxygen vacancy occupies an orbital which overlaps the d shells of both Mn neighbors . Based on Hund's rule and the Pauli's exclusion principle, spin orientations of the trapped electrons and the two neighboring Mn ions should be parallel in the same direction, thus ferromagnetic ordering is achieved.

Table 2 : Magnetic Properties of Mn doped SnO_2 nanoparticle

S.No	Samples	Coercivity (H_{ci}) (Oe)	Magnetization (M_s) emu/g	Retentivity (M_r) emu/g
1	2% Mn Doped SnO_2	126.82	13.898E-3	1.5097E-3
2	4% Mn Doped SnO_2	113.52	18.142E-3	1.8621E-3
3	6% Mn Doped SnO_2	30.895	72.093E-3	3.07E-04

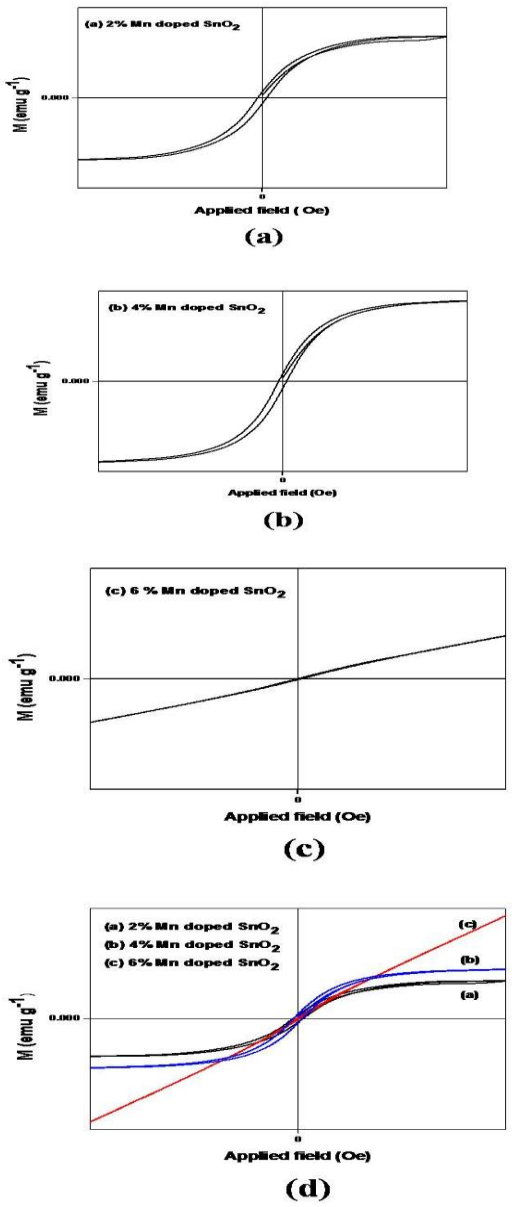


Figure.3 Magnetisation curve of (a) 2% Mn Doped SnO_2 (b) 4% Mn Doped SnO_2 (c) 6% Mn Doped SnO_2 (d) Comparison of 2%, 4% and 6% Mn Doped SnO_2

Conclusion

SnO_2 and Mn doped SnO_2 nanoparticles have been prepared at room temperature using chemical precipitation method without using catalysts, capping agent and surfactants. X-ray diffraction analysis reveals that undoped SnO_2 and Mn, doped SnO_2 nanoparticles exhibit rutile tetragonal structure without any impurity phase and the lattice constants of SnO_2 nano particles is observed to decrease slightly with increasing dopant (Mn) concentration. The grain size of undoped SnO_2 has been obtained as 5.20 nm (±0.1nm) and the grain size of 2% Mn, 4% Mn, 6% Mn doped SnO_2 has been found to be, 4.3 nm, 3.8 nm and 3.7 nm respectively. The grains have aggregated to form clusters .The magnetic studies carried out on the Mn doped SnO_2 samples suggest that Mn doped SnO_2 exhibits weak ferromagnetic behavior. The saturation magnetization obtained from the Mn doped SnO_2 sample is more than larger than that of the pure SnO_2 powder sample. SEM images shows the morphology of the prepared Mn, doped (2% 4% and 6%) SnO_2 samples. The SEM images Mn doped SnO_2 show clearly the formation of nanoclusters. The grains have aggregated to form clusters .

REFERENCES

[1] Tian, Z, Yuan, S, He, J, Li, P, Zhang, S, Wang, C, Wang, Y, Yin, S & Liu, L 2008, 'Structure and magnetic properties in Mn doped SnO_2 nanoparticles synthesized by chemical co-precipitation method', Journal of Alloys and Compounds, vol. 466, no. 1, pp. 26-30.

[2]Gopinadhan, K, Kashyap, SC, Pandya, DK & Chaudhary, S 2007, 'High temperature ferromagnetism in Mn-doped SnO_2 nanocrystalline thin films', Journal of Applied Physics, vol.102, no.11, pp.1135131-1135138.

[3]Sathyaseelan, B, Senthilnathan, K, Alagesan, T, Jayavel, R & Sivakumar, K 2010, 'A study on structural and optical properties of Mn-and Co-doped SnO_2 nanocrystallites', Materials Chemistry and Physics, vol. 124, no. 2, pp. 1046-1050.

[4] Sabri, N S, Deni, MSM, Zakaria, A & Talari, MK 2012, 'Effect of Mn Doping on Structural and Optical Properties of SnO 2 Nanoparticles Prepared by Mechanochemical Processing', Physics Procedia, Vol.25,no5,pp. 233-239.

[5] Fang, L, Zu, X, Li, Z, Zhu, S, Liu, C, Wang, L & Gao, F 2008, 'Microstructure and luminescence properties of Co-doped SnO2 nanoparticles synthesized by hydrothermal method', Journal of Materials Science: Materials in Electronics, vol. 19, no. 8-9, pp. 868-874.

[6]Gu, F, Wang, SF, Song, CF, Lü, MK, Qi, YX, Zhou, GJ, Xu, D & Yuan, DR 2003, 'Synthesis and luminescence properties of SnO 2 nanoparticles', Chemical Physics Letters, vol. 372, no. 3, pp. 451-454.

[7] Chun-Ming, L, Li-Mei, F, Xiao-Tao, Z & Wei-Lie, Z 2007, 'The influence of nickel dopant on the microstructure and optical properties of SnO2 nano-powders', Chinese Physics, vol. 16, no. 1, p. 95-99.

[8] Zhuang, S, Xu, X, Pang, Y, Li, H, Yu, B & Hu, J 2013, 'Variation of structural, optical and magnetic properties with Co-doping in Sn 1− x Co x O 2 nanoparticles', Journal of Magnetism and Magnetic Materials, vol. 327, no.1, pp. 24-27.

[9] Zhang, J & Gao, L 2004, 'Synthesis and characterization of nanocrystalline tin oxide by sol–gel method' Journal of solid state chemistry, vol.177, no.4, pp.1425-1430.

[10] Chiodini, N, Paleari, A, DiMartino, D & Spinolo, G 2002, 'SnO_2 nanocrystals in SiO_2: a wide-band-gap quantum-dot system', Applied physics letters, vol.81, no.9, pp.1702-1704.

[11] Fitzgerald, CB, Venkatesan, M, Douvalis, AP, Huber, S, Coey, JMD & Bakas, T 2004. 'SnO_2 doped with Mn, Fe or Co: room temperature dilute magnetic semiconductors', Journal of Applied Physics, vol.95, no.11, pp.7390-7392.

[12] Ahmed, S 2010, 'Room-temperature ferromagnetism in pure and Mn doped powders', Solid State Communications, vol. 150, no. 43, pp. 2190-2193.

[13]Coey, J, Venkatesan, M & Fitzgerald, C 2005, 'Donor impurity band exchange in dilute ferromagnetic oxides', Nature materials, vol. 4, no. 2, pp. 173-179.