

Variation In Structural and Magnetic Properties With Zn Concentration in of $\text{SnZnO}_{3\pm\Delta}$ nano Particulates

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ABSTRACT

In present scenario, the metal oxide materials have numerous applications and properties at nano scale i.e. 1-100 nm scale particles. The peculiar behavior of these particles at nano scale might be due to their large surface to volume (S/V) ratio and quantum confinement effect at this scale. The advances of materialistic properties at nano scale have numerous applications in the field of electronics, opto-electronics, super-conductivity, medical and defence sector. In present work, the various concentration Zn doped SnO_2 nano particles were synthesized via advanced chemical method and thereafter, calcined the samples at fixed 600°C for 2 hours for optimum crystallinity. The X-ray diffraction data reflects that all the samples have rutile tetragonal crystalline in nature and calculated crystallite size were in range 15 nm to 25 nm and reveals that crystallite size decrease with addition of ZnO initially up to 5% Zn concentration. The IR peaks at position 1058 cm^{-1} and 466 cm^{-1} are might be due to O-Sn-O and O-Zn-O vibrations respectively. The VSM data of samples revealed that Zn doped SnO_2 nanocomposites (NCs) are ferromagnetic in nature.

Keywords: ZnO/ SnO_2 nanocomposites, XRD, FTIR, VSM.

INTRODUCTION

The properties of materials show key function with size and shape of materials specially at nano scale [1,2]. The novel applications of materials depend upon morphology, size and crystallinity of materials. The nanomaterials have significant applications in the field of electronics, energy harvesting, balancing of ecological systems, semiconducting and optoelectronic field etc. The oxides of metal such that SnO_2 , ZnO, MgO and MnO_2 etc. have key role in the fabrication of gas sensors, super capacitor and electrode formation of cells due to its semiconducting nature and surface area [3]. Among metal oxides, SnO_2 NPs is proving its strong candidature especially in above mentioned fields and might be futuristic material of optoelectronic devices. Moreover, the bulky SnO_2 materials have optical band gap 3.68 electron volt [4,5] whereas the band gap is highly dependent on crystallite size at nano scale. The zinc oxide (ZnO) is well known for their semi conducting, gas sensing properties and photo catalytical actions [6-8]. The above-mentioned properties of SnO_2 and ZnO create the knee interest of researcher to synthesize and characterize the Zn doped SnO_2 NCs at different concentration of Zn at fixed calcination temperature $600^\circ\text{C}/2$ hrs. The novel materials may have approachable applications in the field of MRI, magnetostatics etc. [9-12]

EXPERIMENTAL

2.1 Method of Preparation

Pure SnO_2 NPs and Zn doped SnO_2 NCs samples were synthesized using chemical co-precipitation protocol. All the chemicals used in this study were analytical in grade (99.99% pure) and not to be purified at laboratory scale. In present work, the appropriate concentration of $\text{SnCl}_2 \cdot 5\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 5\text{H}_2\text{O}$ were mixed in 100 ml doubly deionized water (DDW) along with 10 ml fresh Alovera planted extract and resulted white color spongy solution was obtained. The 2.0 M NaOH solution of concentration was added drop wise so that pH of solution gradually increases and precipitates were achieved at pH value 9.0. The precipitated solutions were kept for ageing process about 24 hrs. and precipitates were uniformly settle down at the bottom of beaker. The precipitated solutions were filtered with Hoffman filter paper and thereafter, washed multiply with ethanol and doubly deionized water. The washed wet cake was put in microwave oven at 100°C for two seatings with duration 20 minutes each for dehydration of samples. The resulted dried cakes were distributed in four silica crucibles and heated for 2 hours in furnace at 200°C , 400°C , 600°C & 800°C respectively. The calcined samples were grinded in agate mortar for 2 hours and resulted fine powders were used for further characterizations purpose.

2.2 Characterization Techniques/Tools specifications

The crystallinity of samples has been examined through Perkin Elmer Diffractometer with Cu wavelength $\lambda=1.5406 \text{ \AA}$ radiation within diffraction angle range of $2\theta=10^\circ-80^\circ$. The IR study of samples have been done via IR spectrometer with use of KBr as standard transmittance rate in the wave number range 400cm^{-1} to 4000 cm^{-1} . The magnetic properties of samples have been examined through Vibrating Sample Magnetometer in the range of external field ± 1.5 Tesla at CIL, CEERI Pilani a segment of CSIR laboratory of India. The morphology of particles has been studied at nanoscale with the help of scanning of samples through field effect FESEM instrument. The results of above studies are given in subsequent section of paper.

RESULTS AND DISCUSSION

3.1 XRD data analysis

The Zn(5%,10%,15%) doped SnO_2 NCs calcined at $600^\circ\text{C}/2$ hrs. have been scanned through X-Rays over the range of angle $2\theta=10^\circ$ to 80° . The comparative analysis of XRD data of Zn(5%,10% &15%) doped SnO_2 NCs in graphical representation were shown in along with SnO_2 pure calcined at $600^\circ\text{C}/2$ hrs. in figure no.1 as under:

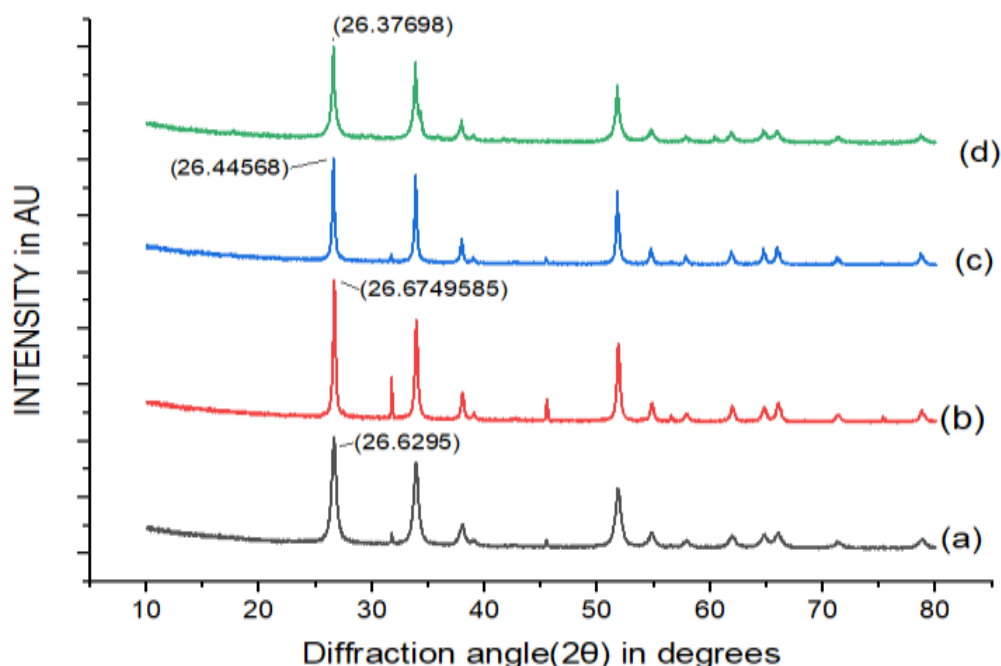


Figure 1: The XRD Spectrum of samples calcined at temperature $600^\circ\text{C}/2$ hrs of (a) pure SnO_2 & SnO_2 -ZnO nanocrystalline with Zn concentration (b) 5% Zn

(c) 10% Zn (d) 15% Zn

The above figure shows that the positions of most intense peaks were more or less same. However significant changes were recognised in intensity of XRD pattern i.e. intensity initially increases for 5% of Zn concentration and then decreases with further rise of Zn dopant concentration beyond the limit of 5% which might be due to crystalline defect promened at small Zn concentration such as 5% then intensity gradually increases with rise of Zn concentration beyond 5% which might be due to availability of Zn^{2+} ions in Sn^{2+} lattice and higher oxidation of Zn ions respectively. Whereas, the FWHM values initially decrease up to 5% of Zn concentration and the similar pattern was observed in FWHM(β) i.e. β value for Zn 5% (0.005radian) and then Zn10%(0.007 radian), Zn15%(0.008radian) respectively, increase with further rise of Zn dopant concentration beyond the limit of 5%. The various peaks of different intensity were exhibited at 2θ position $26.63^\circ, 26.67^\circ, 34.02^\circ, 38.00^\circ, 45.46^\circ, 51.70^\circ, 54.80^\circ, 57.92^\circ, 61.90^\circ, 65.88^\circ, 71.36^\circ, 75.48^\circ$ in which observed peaks at position $2\theta= 26.79^\circ, 26.67^\circ, 34.02^\circ$ and 51.70° were analogous to JCPDS CARD 88-0287 of SnO_2 [13]. Whereas, the additional peaks at position $38.00^\circ, 45.46^\circ, 54.80^\circ, 57.92^\circ, 61.90^\circ, 65.88^\circ, 71.37^\circ, 75.48^\circ$ were analogous to JCPDS 01-079-2205[14-16] of ZnO nano-crystalline. The XRD pattern reflects that Zn^{2+} ions were well incorporated in SnO_2 tetragonal rutile structure and no more phase change occurred in structure of SnO_2 . The crystallite sizes of various samples were estimated via Debye Scherrer formula i.e.

$$D = \frac{k\lambda}{\beta \cos \theta}$$

in formulation, the used notations have their as usual standard scientific meanings. The calculated D values in nm were tabulated in table no.1 as under:

Table No. 1: XRD data of ZnO/SnO₂Nano crystallines calcined at 600°C for 2 h with different concentration of Zn

Sr No.	Sample	Peak position(2θ) (In degree)	FWHM (In radian)	Size (in nm)
1.	SnO ₂ Pure Nps	26.63	0.009	14.76
2.	Zn (5%)/SnO ₂	26.67	0.005	26.36
3.	Zn (10%)/SnO ₂	26.44	0.007	20.92
4.	Zn (15%)/SnO ₂	26.37	0.008	16.71

The above tabular data reflects that crystalline size of Zn doped SnO₂ gradually decrease with rise of Zn concentration (5% to 15%) in SnO₂NCs. However, SnO₂ pure crystalline have lesser size as compared to Zn doped samples which might be due to lesser ionic radii of Sn⁺² (69 pm) than of Zn⁺² (74 pm).

3.2 IR Spectroscopic data analysis

The purity of powdered calcined samples of Zn/SnO₂ NCs were examined through scanning of samples with E.M. radiation in IR region 4000 cm⁻¹ to 400 cm⁻¹. The IR spectrum pattern is helpful tool and provide finger print of samples and their graphical representation were explored in figure no.2 as below:

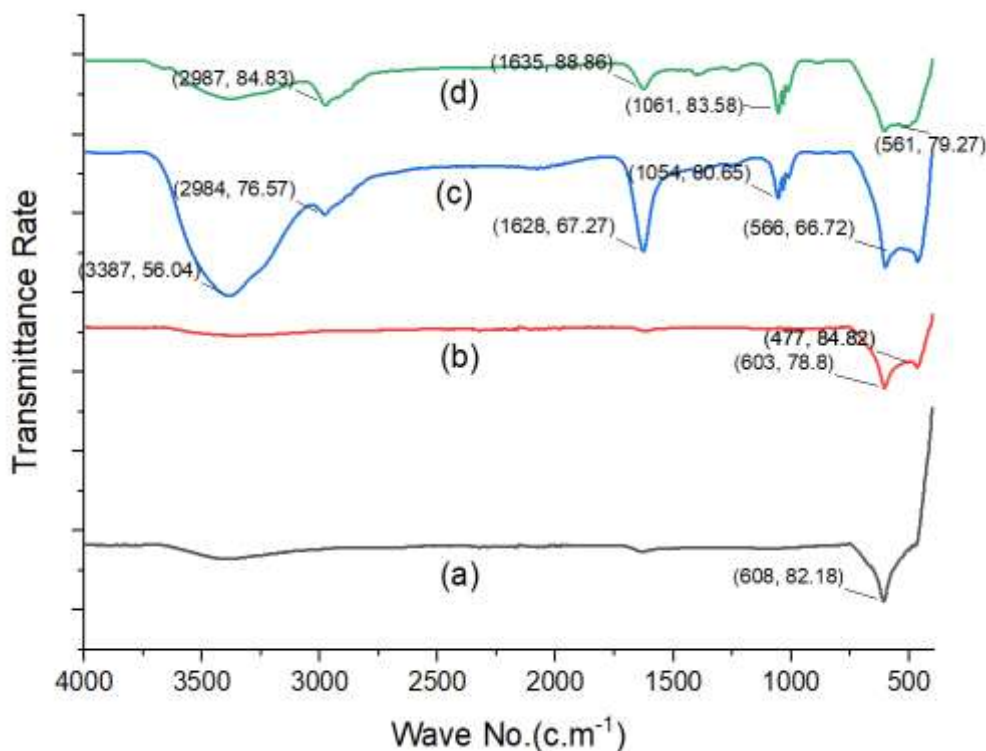


Figure No.2: IR Spectrum of calcined samples of SnO₂-ZnO nanocrystalline with Zn concentration (a) pure SnO₂ (b) Zn(5%) (c) Zn(10%) (d) Zn(20%) at calcination temperature 600°C for 2 hrs respectively

The IR spectrum of above-mentioned data shows that as usual broad band were appeared in all the graphs at about 3500 cm⁻¹, 3100 cm⁻¹ and 1650 cm⁻¹ respectively and signifies the presence of O-H vibrations of water molecules present in the atmosphere of samples. Moreover, metal oxide peaks were observed at about 608 cm⁻¹, 603 cm⁻¹, 566 cm⁻¹, 561 cm⁻¹ and 477 cm⁻¹ respectively. The peak exhibited at position 608 cm⁻¹ may be assigned by O-Sn-O molecule vibration whereas peak positioned at 477 cm⁻¹ be assigned to O-Zn-O vibrations of ZnO molecules. The study shows that a newer peak positioned at 560 cm⁻¹ and 566 cm⁻¹ were might be due to O-Zn-O-Sn-O vibrations of SnO₂-ZnO NCs. The IR spectrum results of samples were in accordance with XRD results and proved the candidature of researcher.

3.3 M-H data analysis

The magnetic properties of various calcined Zn concentration (5%, 10%, 15%) doped SnO₂NCs were studied via Vibrational Sample Magnetometer tools. The samples of Zn/SnO₂NCs were analyzed through applied magnetic field interval ±1.5 Tesla and corresponding intensity of Magnetization (M_H) were represented in graphical form. The various M-H graphs of samples shown in figure no. 3(a), 3(b), 3(c) and 3(d) respectively. The various M-H graphs were shown as under:

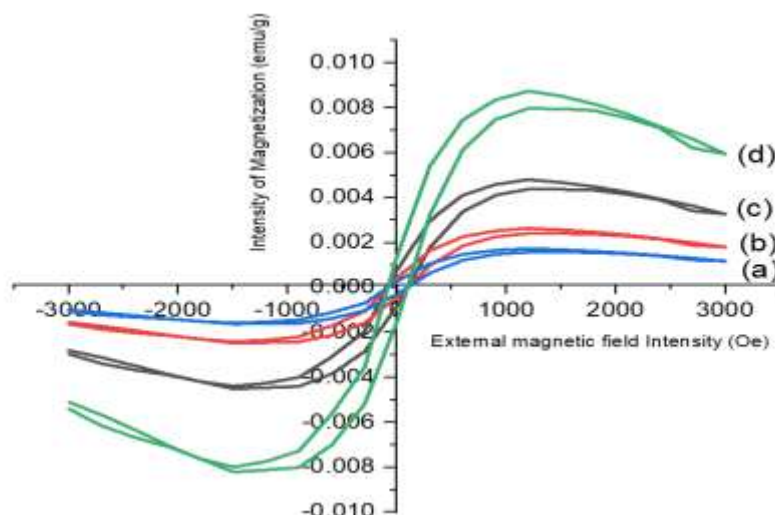


Figure 3: M-H curves of samples calcined at 600°C/2 hrs (a) SnO₂ pure and SnO₂-ZnO samples with Zn concentration (b) Zn (5%) (c) Zn(10%) (d) Zn(15%) respectively

The aforementioned M-H curve reflects that all the samples were ferromagnetic in nature at nanoscale with different scale of M and H values. However, the ferromagnetic character rise with rise of dopant concentration and the parametric study of samples was tabulated in table no. 2 as below:

Table 2- The parametric study of Zn doped SnO₂ nanocomposites calcined at 600°C /2hrs with different concentrations(0%,5%,10% &15%):

Sr No.	Sample calcined at temp	Ms. Saturation ($\times 10^{-6}$ emu/g)	Coercive (Hc Oe)	Remnant ($\times 10^{-6}$ emu/g)	Squareness Factor	M at Max Field ($\times 10^{-6}$ emu/g)	Energy Loss(Oe)	Saturation Applied H _s (Oe)
1.	SnO ₂ pure	1730	180.05	313.45	0.913	634	1.025	2999
2.	SnO ₂ / ZnO (5%)	2640	149.60	307.78	0.336	1015	1.025	2999
3.	SnO ₂ /ZnO (10%)	4800	87.19	609.92	0.239	2589	1.506	2999
4.	SnO ₂ /ZnO (15%)	8740	65.26	708.41	0.187	4781	1.103	2999

The above tabular data reflects that the magnetic behaviour of Dopant material increases with rise of Zn Dopant concentration and Zn(15%) doped material have remarkable remittance value 708.41×10^{-6} emu/g and may be the highlighted applications in the field of MRI and in fabrications of memory chips.

CONCLUSIONS

The various Zn doped SnO₂NCs were prepared with aloe-vera treated coprecipitation technique. The XRD data of samples explored that tetragonal rutile crystalline were in formation with size gradually decrease with rise of Zn concentration. The IR sharp peaks at 660 cm⁻¹, 608 cm⁻¹ and 471 cm⁻¹ confirmed the presence of O-Sn-O, Zn-O-Sn, O=Zn-O vibrations of SnO₂, SnO₂/ZnO zinc oxide molecule vibrations. The M-H graph concluded that all the crystalline samples were ferromagnetic in behaviors and magnetic behavior rise with Zn concentration and proposed futuristic materials for MRI applications or memory chip fabrications.

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