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Structural, Optical and Magnetic Investigation of Ni, Co and Mn doped SnO_2 Nano particles Synthesized by Chemical Co-precipitation.

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Abstract

Pure and transition metal dopednano-crystalline $Sn_{1-x}TM_xO_2$ (x = 0.0, 0.05, TM = Ni, Co and Mn)were synthesized in aqueous solution by chemical Co-precipitation technique. X- ray diffraction (XRD), high resolution transmission electron microscope (HR-TEM), electron diffraction,UV – visible absorption spectroscopy and room temperature magnetization measurements were performed to investigate the structural and microstructural, morphology, optical and magnetic properties of pure and doped samples. The structure calculations revealed that Co and Ni atoms have been incorporatedin the SnO_2hostlattice.For Mn, the XRD analysis detected that SnO phase was formed instead during the synthesis process.HRTEM and XRD studies indicated that the particle size is in the range of quantum dot size except for Mn. For optical measurement, the quantum confinement effect was suggested to be the dominant reason for the great increase of the optical bandgap with respect to the bulk material. Magnetization measurements revealed that all doped samples were ferromagnetic in nature. Well defined strong hysteresis loop was detected for Co doped SnO_2 nanoparticles. It was suggested that the ferromagnetism is intrinsic in origin.It is not due to ferromagnetic metal clusters nor due to the presence of additional ferromagnetic phases. The strong ferromagnetic signal especially for Co doped SnO_2makes it a candidate for spintronic applications.

Keywords

Doped SnO_2 nanoparticle - chemical co-precipitation -HRTEM -ferromagnetism.

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1. Introduction

The study of diluted magnetic semiconductor (DMS) is being carried out since last few decades.Apart from the present day applications in the field ofspintronics, they are interesting to the physics community due to the rich variety of phenomena andphysics they exhibit [1-4]. Preparation of single phase diluted magnetic semiconductor,devoid of any secondary phases or metallic clusters, is abig challenge. Even if thematerial is a single phase, the magnetism in these systems hasalways been controversial and the debate on the originand the mechanism of ferromagnetism is far from over [5].

Many reports are available on room temperature ferromagnetism (RTFM) in various transition metal doped oxides, but no reports have clearly explained the origin of ferromagnetism. It may be intrinsic or due to the presence of hidden secondary phases of ferromagnetic metal clusters or their ferromagnetic oxides[6-8].

Recently, The RTFM has been actively investigated in the transition metal incorporated TiO_2[9-13], ZnO[14-18], CuO[19] etc. These oxides doped with TM is characterized by the large sp-d exchange interaction between the magnetic ions and the band electrons[20]. In fact, maintaining sufficiently high optical transparency in these oxides (optical gap width > 3 eV), gives rises for new applications with these semiconductors.

Among the other known metal oxide semiconductors, SnO_2 is a very interesting oxide material with a wideband gap. Its higher optical transparency,chemical stability, metal like conductivity and easy doping make it avery attractive material for optoelectronic devices, catalysis and gassensing applications. In the nano-scale form TM-dopedSnO_2 is reported to demonstrate more interestingstructural and magnetic properties[21].

In this work, we report ferromagnetism in chemically synthesized, single phase, Co, Ni and Mn doped tin oxide nanoparticles. The structural, microstructural andoptical properties of the prepared

$Sn_{1-x}TM_xO_2$have also been investigated.

2. Experimental Details

$Sn_{1-x}TM_xO_2$(TM = Ni, Co and Mn) and (x = 0, 0.05) nanoparticle systemwas synthesized by the Co-precipitation method. All the reagants used are of analytical grade (sigma Aldrich 99.9 %) and handled without further purification. Aqueous solutions of precursors $SnCl_2.2H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $C_4H_6MnO_4$(1M) were separately prepared in distilled water as pre stoichiometric ratio and stirred for 4 hours. Sodium hydroxide (NaOH) was added drop wise under constant stirring to maintain the chemical homogeneity until the white precipitates were obtained.The Phvalue was controlled to equal 7. After 30 minutes of stirring the precipitate was washed several times with de-ionized water to remove chlorine and other ionic impurities formed during the synthesis process. The washed precipitates were filtered out separately and dried in an oven at 50 C for 24 hours. The obtained product were grounded, collected carefully and then annealed at 400 C for 2 hours to obtain ($Sn_{1-x}TM_xO_2$) nanoparticle system. Structural investigations by XRD were carried out using Cu-kα radiation (λ = 1.5418 A°)using a Philips x◌Pert MPP diffractometer with agoniometer type Pw 3050/10.A transmission electron microscope (TEM) modelTecnai G20,Super twin, double tilt with applied voltage: 200 KV and magnification range up to 1,000,000 x and Gun type LaB 6 Gun, was used to identify the microstructure and surface morphology.The magnetization as a function of the applied magnetic field was measured at room temperature by employing a vibrating sample magnetometer (VSM) model Lake Shore 7410with an applied field of 301T. An optical absorption study of the prepared system was also performed usinga spectrophotometermodel JASCO – V-670.

3. Resultsanddiscussion

3.1. Structural and Microstructural Analysis

3.1.1. XRD analysis

The x-ray diffraction patterns of $Sn_{1-x}TM_xO_2$samples are shown in Fig. (1). Applying the search match program, no diffraction lines were found forSn, Ni, Co or Mn elements. Only one pure phase of $SnO_2$was detected for pure SnO_2 and Ni doped sample according to the specific ICDD card number (04-008-8133) confirming the formation of tetragonal structure with space group P42/mnm and lattice parameter a = 4.7421A^o and c = 3.1901A^o.Adding the Co atom into SnO_2enhances the formation of a minor phase of SnOtogether with the major phase as shown in Fig. (1-c) and table (2).For $Sn_{0.95}Mn_{0.05}O_2$ sample only one major phase of SnO was formed during the synthesis process as given in table (2). The specific ICDD card number (04-008-7670) confirming the formation of tetragonal structure for the SnO Phase with space group P4/nmm and lattice parameter a = 3.8036A^o and c = 4.8385A^o. This SnO phase is characterized by sharp diffraction lines i.e. more ordering crystalline structure asshown in the XRD pattern of Fig.(1-d).

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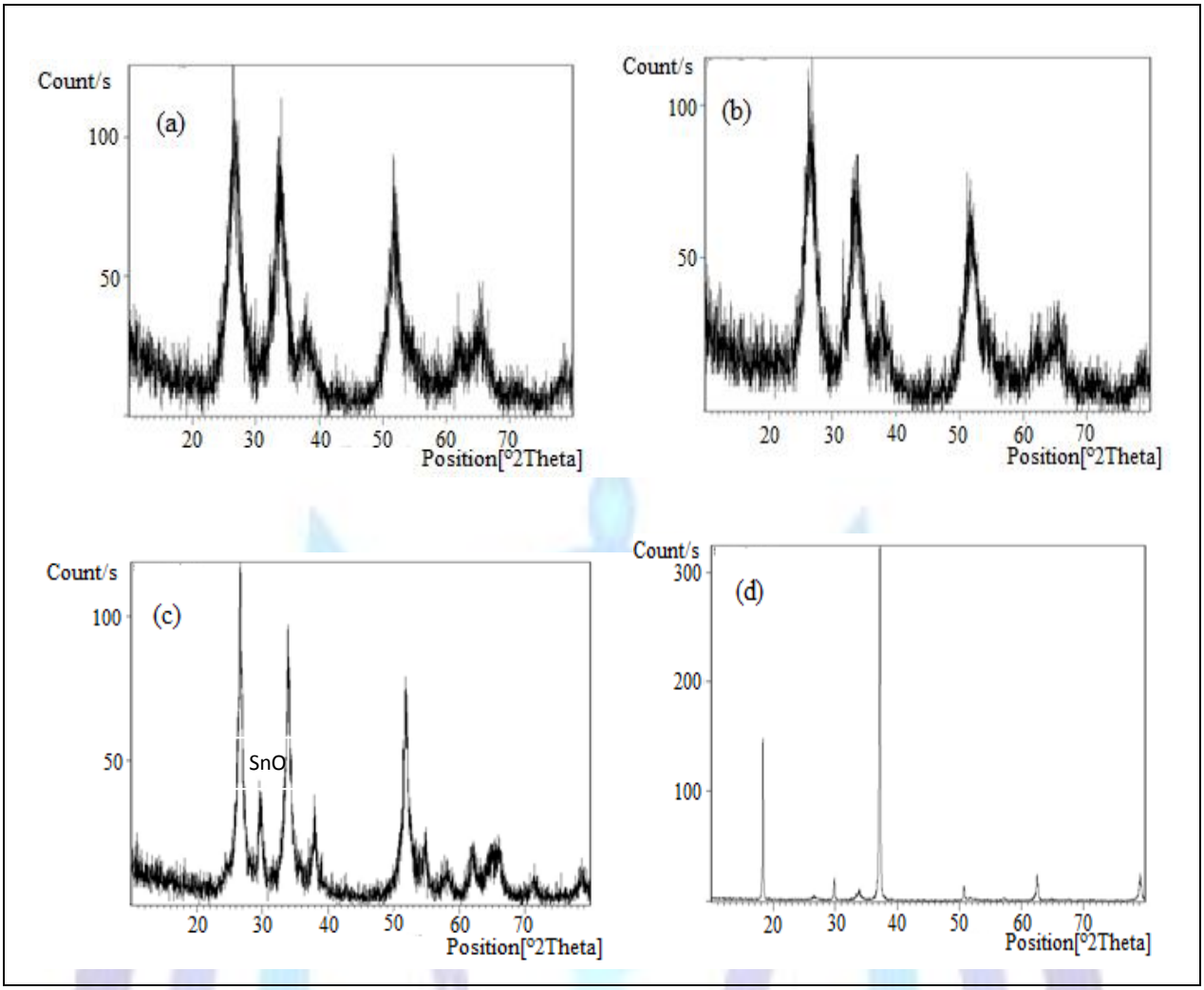

Fig.(1, a - d): The X–ray diffraction patterns for the prepared nanoparticlesystem(a) SnO_2, (b) $Sn_{0.95}Ni_{0.05}O_2$ (c) $Sn_{0.95}Co_{0.05}O_2$and(d) $Sn_{0.95}Mn_{0.05}O_2$.

Applying the Win-fit program the resulting apparent crystallite size D_β(nm) and D_F(nm) and root mean square strain <eg> from single line analysis are given in table (1,2) . The data revealed that the size of the quantum dots of SnO_2 (2.7-2.9 nm) increases to (4.6-5.2 nm) as Ni was added. For Co and Mn bigger crystallite size were detected (13.9-14.4 nm and 26.2-28.2 nm respectively).

Table (1): Apparent crystallite size D_β(nm) &D_F(nm) from single line analysis for thepreparedSnO_2 and $Sn_{0.95}Ni_{0.05}O_2$ nanoparticle samples.

SnO_2			$Sn_{0.95}Ni_{0.05}O_2$		
single line analysis of SnO_2 phase			single line analysis of SnO_2 phase		
hkl	D_β(nm)	D_F(nm)	hkl	D_β(nm)	D_F(nm)
110	2.4	2.6	110	3.9	4.4
101	1.8	2.1	101	4.1	4.6
111	1.5	1.8	200	4.9	5.4
211	5.3	5.4	112	5.7	6.2
221	3.2	3.5			
301	2.2	2.4			
Average	2.7	2.9	Average	4.6	5.2

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Table (2): Apparent crystallite size D_β(nm) &D_F(nm) for single line analysis for the prepared$Sn_{0.95}Co_{0.05}O_2$ and $Sn_{0.95}Mn_{0.05}O_2$ nanoparticle samples.

$Sn_{0.95}Co_{0.05}O_2$			$Sn_{0.95}Co_{0.05}O_2$			$Sn_{0.95}Mn_{0.05}O_2$		
single line analysis of SnO_2 phase			single line analysis of SnO phase			single line analysis of SnO phase		
hkl	D_β(nm)	D_F(nm)	hkl	D_β(nm)	D_F(nm)	hkl	D_β(nm)	D_F(nm)
110	14.8	15.1	101	13.6	13.9	001	30.6	31.4
101	13.8	14.1				101	26.9	28.7
200	15.1	15.3				002	27.8	32.0
211	13.9	14.2				112	20.8	21.9
220	14.1	14.5				103	25.1	26.9
002	17.7	18.9				Average	26.2	28.2
310	12.1	12.3						
301	14.1	14.3						
202	10.1	11.4						
Average	13.9	14.4						

3.1.2. HRTEM Analysis

The HRTEM images for the system under study are shown in Fig. (2, a - d). It is clear from figures that spherical shaped nanoparticles have been formed in the un-doped and transition metal ion doped SnO_2. The size, estimated from individual nanocrystals for SnO_2 and $Sn_{0.95}Ni_{0.05}O_2$ is in the quantum dot range 3.37- 5.85 and 3.31 – 4.97 nm respectively. For Co and Mn doped SnO_2, the crystallite size increases to 16.8- 18.3 and 28.2 – 30.4 nm respectively. These values are in good agreement with those determined from the XRD analysis. Similar results for the particle size in undoped and SnO_2 doped samples were also reported [22-24].

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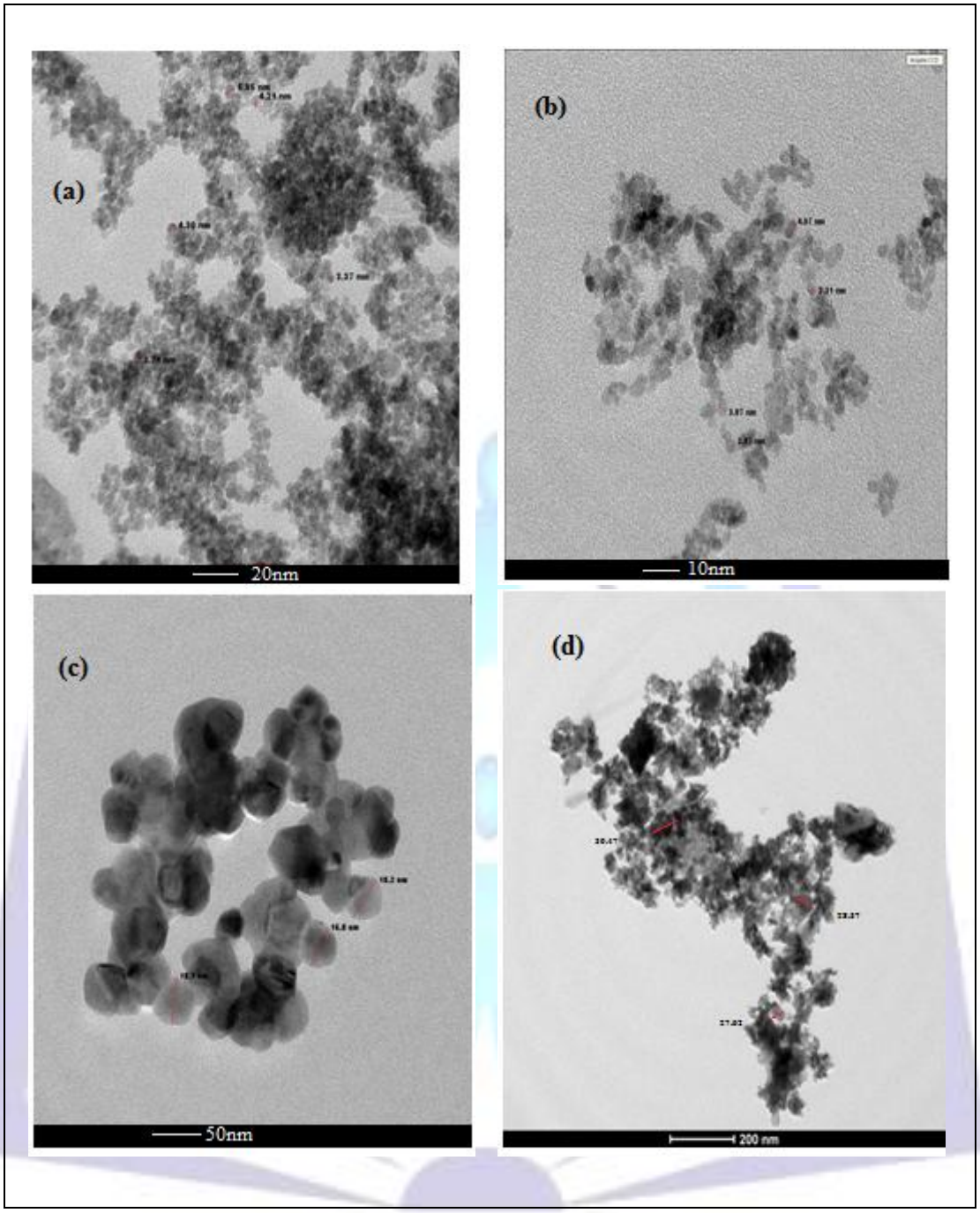

Fig. (2, a –d): The HRTEM images for the prepared nanoparticle system (a) SnO_2, (b) $Sn_{0.95}Ni_{0.05}O_2$, (c) $Sn_{0.95}Co_{0.05}O_2$ and(d) $Sn_{0.95}Mn_{0.05}O_2$.

The selected area electron diffraction (SAED) patterns of the samples under study are shown in Fig. (3, a - d) for the prepared SnO_2, $Sn_{0.95}Ni_{0.05}O_2$, $Sn_{0.95}Co_{0.05}O_2$ and $Sn_{0.95}Mn_{0.05}O_2$.These patterns show that all crystalline rings can be indexed to a rutile type tetragonal crystal structure.

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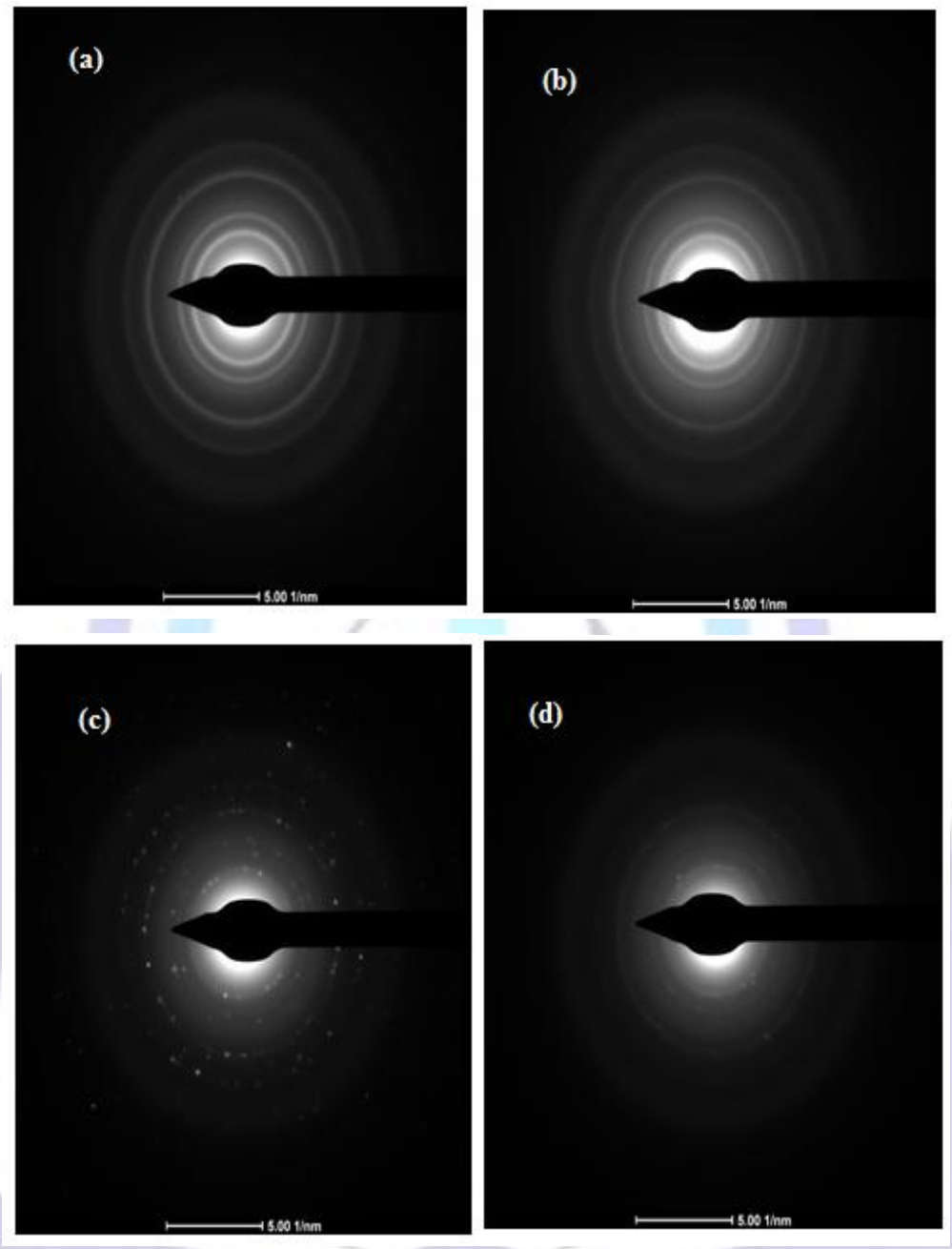

Fig. (3, a –d): The SAED patterns for the preparednanoparticle systems

(a) SnO_2, (b) $Sn_{0.95}Ni_{0.05}O_2$, (c) $Sn_{0.95}Co_{0.05}O_2$ and(d) $Sn_{0.95}Mn_{0.05}O_2$.

3.2. Magnetic studies

To probe the magnetic properties of ($Sn_{1-x}TM_xO_2$) nanoparticle system, where x = 0 and 0.05 and TM = Ni,Co and Mn, the field dependent magnetization curves (M-H) taken at room temperature with applied magnetic field ranging from -15KG to 15KG were measured.As given in Fig. (4), it is clear thatthe undoped SnO_2 nanoparticles exhibit the diamagnetic behavior with a negative magnetic susceptibility. This may be due to the 4+ valance state of Tin (Sn^{4+}) favouring $4d^{10}$ electronic configuration of Sn in SnO_2 and, hence, there is no unpaired d electrons in the materials for any kind of ferromagnetic ordering. Partial substitution of Ni and Mn ions for Sntransformed it from diamagnetic state to a weak ferromagnetic ordering state with a very narrow hysteresis loop and a small value of corecivity (Hci) as shown in table (3).

The room temperature magnetization of Co-doped SnO_2 showed significant hysteresis at room temperature, reflecting a good ferromagnetic ordered state (Fig. 4). The ferromagnetic behavior of Co-doped SnO_2 shows a hysteresis loop at low magnetic field followed by a linear increase in magnetization at higher fields. A high corecivity (Hci)of ~544.29G was recorded. This type of linear behavior might be attributed to the magnetic moment associated with the conduction electrons[25]. It has been suggested that room- temperature ferromagnetism results from the magnetic coupling between oxygen vacancy (V_0) centers at the surface of the nanoparticles[26-28].

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The origin of ferromagnetism in Ni, Co and Mn doped SnO_2 could be attributed to oxygen deficiency, formation of TM related secondary phases and metallic TM clusters. No magnetic phases of TMO_2 and no metallic TM clusters were detected by XRD analysis. Hence, one can conclude that the ferromagnetic character observed for the TM doped SnO_2 is not due to any additional magnetic phase but it is only caused by TM doping. The appearance of ferromagnetism with Mn as a dopant can be attributed to the presence of secondary phases, since nearly all of the possible Mn – based binary and ternary oxide candidates are anti-forromagnetic with a Néal temperature far below room temperature [29]. The XRD analysis and electron diffraction have not revealed any Mn – O phases for the present case. This ferromagnetism may be a result of the interaction of the Mn d orbital with the sp orbital of SnO_2. K. Gopinadhan et.al.have reported according to structural and optical investigation that $Sn_{1-x}Mn_xO_2$forms a random alloy as Mn ions are incorporated irregularly in SnO_2lattice [30].

Some Mn ion separations into the SnO_2 lattice may be less than others; hence an anti-ferrmagnetism may occur locally reducing therefore the overall magnetization. This may give account for the low value of correcivity (Hci) measured for the present study (59.28G). Similar interpretation can be also given for Ni doped SnO_2, because if Ni atom pairs come closer sufficiently, the super-exchange interaction is expected between the TM atoms. This may lead to an anti-ferromagnetic type interaction leading to the moderate values ofMs and Mr.Previous results reported similar data for Ni concentration higher than X = 0.03 [21]. It is likely that, the room temperature ferromagnetism in Ni, Co andMn doped SnO_2 samples is intrinsic to the material.

As seen from Fig.(4) and table (3)The ferromagnetic signal is greatly enhanced for Co doped SnO_2 as a strong well defined hysterysis loop was detected. The highest saturation magnetic moment of 56.63×10^{-3}(emu/g) and corrcieve field of 544.29 G may be due to the substitution of $Co^{2+}$with Sn^{4+}which favours an increase of oxygen vacancies available for electron trapping and hence increase in saturation magnetic moment. Such substitution may increase the local hole concentration, hence the local density of states at the Fermi level giving rise to the double exchange interaction, consequently an increase of ferromagnetism.

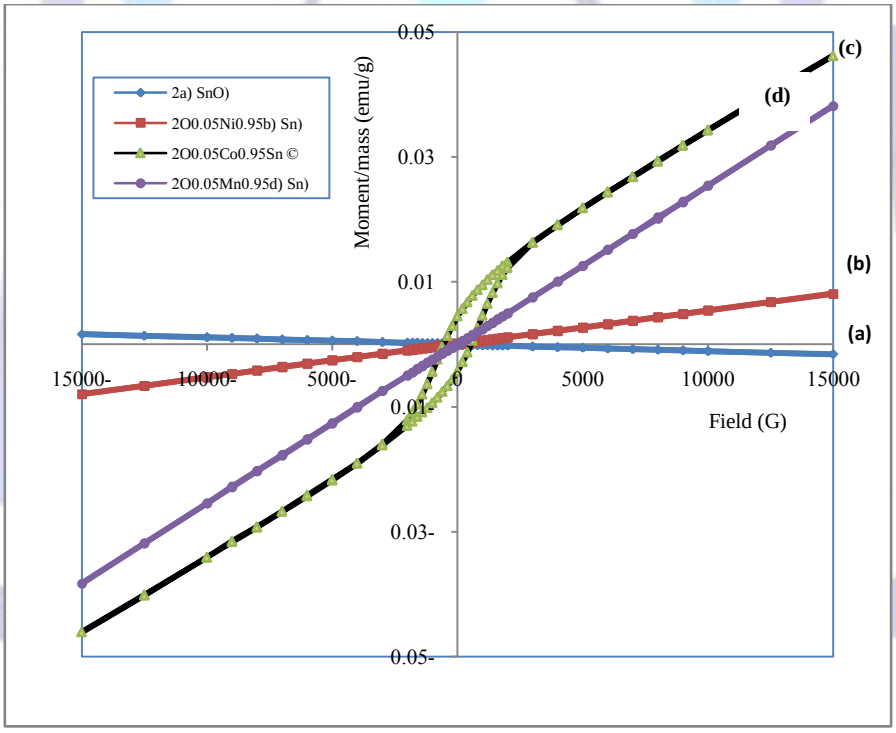

Fig. (4) The hystrysis loops of the prepared $Sn_{1-x}TM_xO_2$system.

Table (3): The magnetic parameter Ms, Mr, Mr/Ms and Hci for the nanoparticlesystems under study.

Sample	Ms(emu/g)	Mr(emu/g)	Mr/Ms	Hci(G)
$Sn_{0.95}Ni_{0.5}O_2$	10.46×10^{-3}	95.217×10^{-6}	9.1029×10^{-3}	212.21
$Sn_{0.95}Co_{0.5}O_2$	56.629×10^{-3}	4.428×10^{-3}	7.8193×10^{-3}	544.29
$Sn_{0.95}Mn_{0.5}O_2$	49.756×10^{-3}	130.33×10^{-6}	2.61938×10^{-3}	59.287

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3.3. Optical Properties

Absorption spectroscopy was used to explore the energy band gap changes brought about by the presence of Ni, Co and Mn dopant in SnO_2nanocrystallite. The absorption spectra of pure SnO_2 and TM doped SnO_2 are given in Fig. (5).

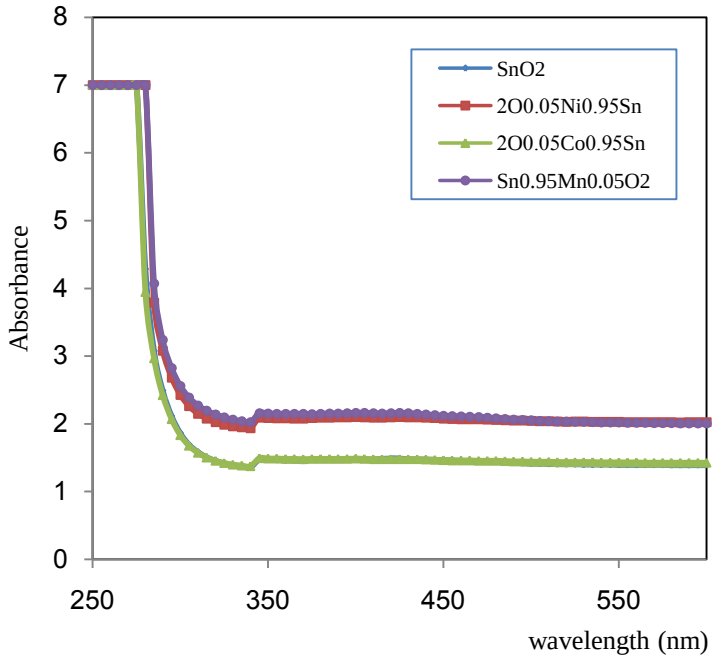
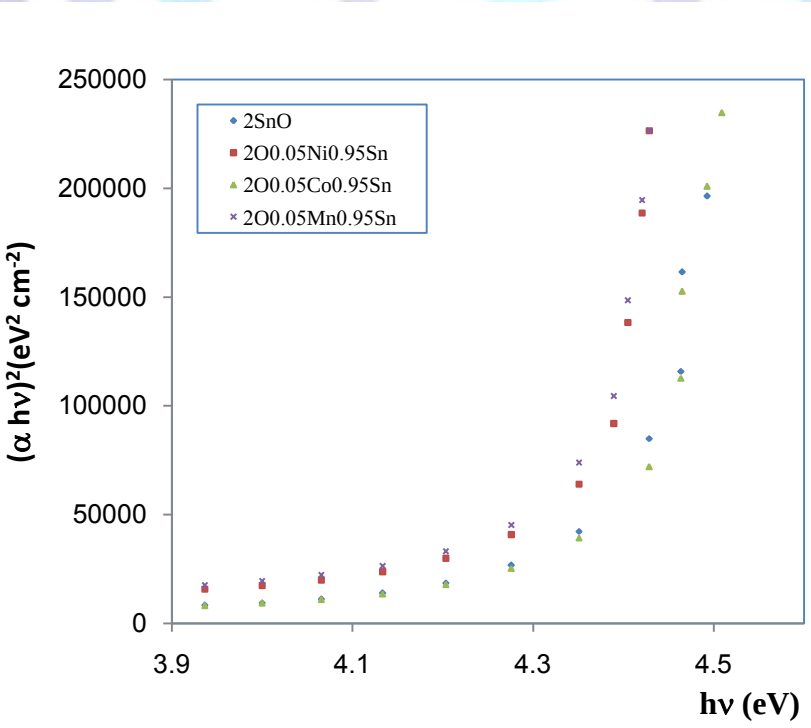


Fig. (5): Optical absorbance spectra of the prepared $Sn_{1-x}TM_xO_2$ Nanoparticle system.

The band gap width (Eg) was calculated according to Tauc's relation[31]. $\alpha h\upsilon = A (h\upsilon - Eg)^n$ (1)

Where α is the absorption coefficient, A is a constant and n = ½ for direct band gap transition. Eg is estimated from the extrapolation of the linear portion of the plot $(\alpha h\upsilon)^2$Vs. hυ as shown in Fig. (6). Values of Eg of the four samples are displayed in table (4) together with the particle size detected by XRD measurements.



(Fig.6): Tauc's plots of the prepared $Sn_{1-x}TM_xO_2$ nanoparticle system.

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The published Eg value of bulk SnO_2 is 3.6 eV[32]. The high Eg value given in table (4) can be attributed to quantum size effects in nano particles in accordance to the relation[33, 34].

$$Eg = Eg_b + \hbar^2 \pi^2 / 2 \mu r^2 - Ry^*(2)$$

where$Eg_b$is the energy band gap of the bulk, r is the particle radius, μ is the reduced mass and $Ry^*$is the Rydberg's energy. It could be suggested that the major reason for the blue shift in Egfor the nano-material is due to strong quantum confinement effects. As given in table (4) the prepared quantum dots SnO_2has a high value of Eg ~ (4.36eV).A value of 3.76 eVwas reported for SnO_2 with nano-size of ~ 26 nm prepared by mechanochemical processing[35], while a value of 4.07 eV was published for SnO_2 with average crystallite size in the range 4.78 nm stabilized with polyethylene glycol [23].

The decrease in the band gapenergy for Ni and Mn doped SnO_2 with respect to the undoped sample may be due to the accumulation of donor energylevels of TM ions in the actual band gap of SnO_2.

The value of the band tail width E_0 extended into the forbidden gap is calculated according to Urbach relation[32].

$$\alpha = \alpha_0 \exp (h\upsilon)/E_0 \quad (3)$$

The values of E_0extracted from Fig. (7) are given in table (4).

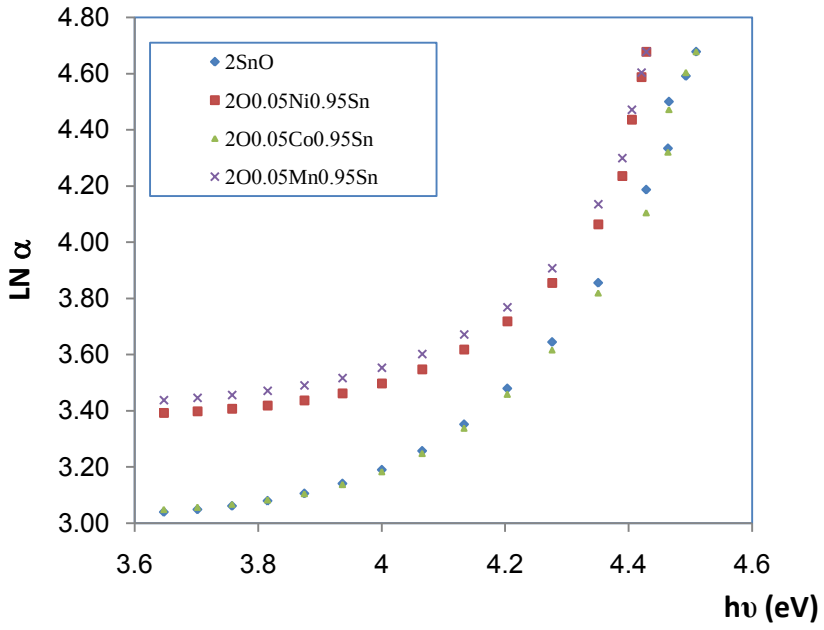

Fig. (7): The absorption coefficient of the prepared $Sn_{1-x}TM_xO_2$ nanoparticlesystem.

Table (4): The optical gap (Eg), the band tail width (E_0) and the particle size for the prepared $Sn_{1-x}TM_xO_2$nanoparticle system.

sample	(Eg) (eV)	E_0 (eV)	Particle size (nm)
SnO_2	4.36	0.222	2.7
$Sn_{0.95}Ni_{0.05}O_2$	4.28	0.244	4.6
$Sn_{0.95}Co_{0.05}O_2$	4.35	0.215	13.9
$Sn_{0.95}Mn_{0.05}O_2$	4.28	0.251	26.2

In spite of the nanocrystalline structure, some localized states are formed at the band edges. It is clear that, the band tail is more extended into the forbidden gap for Ni and Mn doped SnO_2 in consistent with the narrowing of their energy band gap.

Conclusion

Room temperature ferromagnetism is exhibited by doped $Sn_{1-x}TM_xO_2$ (x = 0,0.05, TM = Ni, Co and Mn,) synthesized by chemical copricipitation. XRD, electron diffraction in combination with magnetization study reveal that the

ferromagnetism is not due to any ferromagnetic phases. Optical measurements indicated a red shift in the absorption edge of Mn and Ni doped sample caused by the formation of donor energy levels inside the gap of SnO_2. The present study demonstrates that doping with 5 at % Co in SnO_2 nanomaterial gives rise to significant room temperature ferromagnetism ordering useful for spintronic applications.

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