

Structural, optical and magnetic properties of Co(Cobalt) doped SnO₂ nanoparticles by one step method

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Cobalt doped SnO₂ nanoparticles were prepared for different molar concentration 2%, 4% & 6% of Co by Chemical co precipitation method. The prepared samples were characterized by X-ray diffraction (XRD), UV-visible absorption spectra, Photoluminescence (PL), High Resolution transmission electron microscopy (HRTEM) and Vibrating sample magnetometer for their Structural, Optical and Magnetic Properties. The doping concentration of Co induces crystal phase, crystallite size, lattice distortion, optical and magnetic properties were investigated. XRD Results showed that Co²⁺ replaces Sn⁴⁺ in the crystal lattice of SnO₂, which enhanced the growth of crystallite size and suppressed the transformation from anatase to rutile phase due to lattice distortion produced in SnO₂. The UV absorption studies concluded the band gap of Co doped SnO₂ nanoparticles decreased from 3.79 eV to 3.62 eV in visible region. PL spectra exhibit only a broad emission peak in the range of 420 nm to 540 nm and excitation is observed at the wavelength of 385 nm. New energy levels are not formed in the band structure to produce new emission due to Co doping and also indicates that the substitution of Co²⁺ ions for Sn⁴⁺ ions without the formation of other additional energy levels. Due to increasing Co concentration in SnO₂, the emission energies are decreasing the peak intensities. An efficient method for inducing the ferromagnetic behavior from increasing the Co concentration from 2% to 6% was known from the magnetization versus magnetic field (M-H) curves at room temperature of the Co doped SnO₂ samples. The dominant magnetic interaction between Co ions, and hence, the ferromagnetic behaviour increases for increase in Co²⁺ doping concentration. Consequently, to achieve the good ferromagnetic character in these materials, the concentration of Co dopant has to be properly optimized.

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1. Introduction

Nano sized metal oxide materials gained attraction in recent years due to their large surface area, unusual adsorptive properties, surface defects and fast diffusivities[1]. The structural properties of these materials play a crucial role in amending their optical, electrical, magnetic and catalytic properties making them compatible for solar cells, gas sensors, LED, Opto electronic devices [2]., The tin oxide is a stimulating IV–VI group n-type semiconductor among the metal oxide semiconductors, which have high potential applications [3]. It has a wide band gap of (E_g = 3.6 eV) and it produced ferromagnetism of diluted magnetic semiconductors (DMSs) doped with transition metal ions. The ferromagnetism of DMSs is significantly increased due to their

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imminent applications in spintronics, nanoelectronics, nanophotonics, magnetoelectronics, and microwave devices [4]. The chemical and mechanical stability of tin oxide is used in oxidation catalysis, gas sensing, transparent conducting oxides and optoelectronic devices [2-5]. The optical properties of SnO₂ nanostructures can be enhanced due to the impurity doping, coating with surfactants and annealing. Introduction of dopants in the parent system is one of the most dynamic methods to modify the characteristics of the materials. The addition of the transition metal dopants increases the surface area of SnO₂ and also modified by their grain size and crystallinity. The properties of impurity doped SnO₂ nanoparticles are recognized for their applications in magnetic and optical devices which are dependent on both the composition and synthesis methods of the materials. Among the different methods of preparation of transition metals doped SnO₂ nanoparticles, the precipitation method can control the grain size, crystalline phase, particles morphology and surface chemistry of the products [6]. In the present work, pure and different mol % of transition metal ion (Co) doped SnO₂ nanoparticles were prepared by the chemical co precipitation method. Furthermore, the modifications in the properties of SnO₂ could be made by doping it with transition metal ions or rare earth ions. The Co ions can improve the structural stability of SnO₂, its flexible capacity and properties. The Sn ions within the crystal lattice can be completely or partially replaced by them. The prepared Co doped SnO₂ samples has been characterized by XRD, SEM, HRTEM, UV absorption, PL and VSM for their structure, morphology, composition, optical and magnetic properties.

2. Preparation

The chemicals were used in this present work are of analytical grade and used without further purification. In all the synthesis steps de-ionized water was used. SnO₂ nano particles doped with three different concentration of Co 2%, 4% and 6%, were prepared by chemical co-precipitation method. The precursors for dopant and host were cobalt nitrate hexahydrate Co(NO₃)₂.6H₂O and tin chloride (SnCl₂.2H₂O) respectively. The solution was prepared using tin chloride (SnCl₂.2H₂O) and cobalt nitrate hexahydrate Co(NO₃)₂.6H₂O in distilled water to make 0.3 M solution and to increase the pH of the solution for the precipitate formation, aqueous ammonia (NH₄OH) of 0.4 M was added to the solution. The source materials were weighed according to the stoichiometry as per the target composition 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 3h at room temperature till fine brown coloured precipitate was formed. Using the same method, 2%,4 % and 6% Co doped SnO₂ samples have been prepared. The solution obtained was centrifuged at 3000 rpm for 10 minutes. The yellow coloured precipitate was filtered out separately and washed with de-ionized water during the precipitation process. The obtained product was placed in oven at 100°C for 8h.

3. Results and discussion

In the XRD spectra of Fig. 1, composition evolution of crystalline phases for the system of different mol concentration of 2%, 4% and 6 % Co doped SnO₂ nano particles were illustrated. All the diffraction peaks were perfectly indexed to the rutile SnO₂ structure (JCPDS card, No.41-1445). There was no shift for the diffraction peaks of Co-doped SnO₂ and no impurity phase correlated with Co was observed. The effective growth of the nanostructure in the X-direction is clearly indicated by the peak orientations in the planes (110), (101), (200), (211), (220), (002), (310), (112), (301), (202) and (321). The average grain size of all the samples was calculated using the Scherrer equation and were tabulated. From the table1, the results show that the average grain sizes kept as 16–21 nm with increasing the Co-doping concentration from 2%, 4% to 6%. The chemically precipitated powders synthesized using dilute solutions of precipitating agent (NH₄OH) provide finer powders with grain size increasing from 11 to 17 nm, respectively. When the dopant Co concentration with SnO₂ is increased, the grain size also increases, due to the replacement of Sn with Co ions in the sites[7].

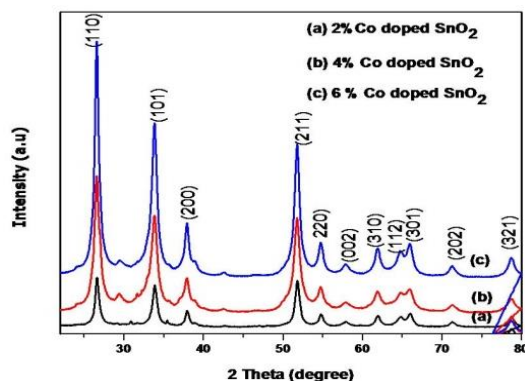


Fig. 1. XRD Pattern of (a) 2% Co doped SnO₂ (b) 4% Co doped SnO₂ (c) 6% Co doped SnO₂.

Table 1. Structural parameters of (a) 2% Co doped SnO₂ (b) 4% Co doped SnO₂ (c) 6% Co doped SnO₂.

S.No	Samples	Lattice Parameters (Å)		Grain Size (nm)
		A	C	
1	2% Co doped SnO ₂	4.685	3.184	16
2	4% Co doped SnO ₂	4.674	3.173	18
3	6% Co doped SnO ₂	4.663	3.161	21

It is notable that there is no diffraction peak corresponding to cobalt oxide or other impurity phases which indicates that Co is well dispersed within the SnO₂ lattice. It is also observed that with increase in Co content, the peak position shifts to larger angle, with changes in lattice parameter values. Due to the smaller crystallite size of SnO₂ nano particles, all the doped samples have a clear peak broadening. The obtained crystallite sizes of the samples and the lattice parameters are given in Table 1. The grain size is found to increase with increase in cobalt concentration. The surface stresses and surface defect dipoles are the phenomena governing the change in lattice parameters as the grain size is increased. It is obvious that the specific surface area shifts towards higher values with the increase in Co concentration [8]. The intensity of XRD peaks increases, as the Co content increases. The average crystallite size also increases with increase in cobalt concentration (Table 1) due to the replacement of some of the Sn⁴⁺ ions by Co²⁺ ions in SnO₂ lattice. The ionic radii of Sn⁴⁺ ion (0.069 nm) is smaller than the dopant Co²⁺ ion (0.072) nm [9]. The portion of the metal oxide forms stable solid solutions with SnO₂ and the metal oxide ions occupy the regular lattice site in SnO₂.

The Co²⁺ doping in SnO₂ produces crystal defects around the dopants and the charge imbalance arising from this defect changes the stoichiometry. Table 1 shows the obtained crystallite size of the samples in the range of 11 nm - 17 nm calculated by Scherer's relation. It is observed that the crystallite size increases with increasing the dopant Co concentration. This implies that Co ions get accommodated at the Sn site without changing the rutile structure of Co doped SnO₂ nano particles.

The morphology was further investigated by SEM. From the SEM studies, Co doped solvents mediated tin oxide nanoparticles are spherical and ellipsoidal morphology as Shown in Fig. 2 a,b and c. Moreover, some of the particles were aggregated. During the process of rutile SnO₂ nanoparticles formation, the gel structure was maintained in this preparation method. It shows that homogeneous and well-dispersed spherical nanoparticles and some of them partially aggregated in the form of irregular shaped tin oxide nanoparticles. The presence of spherically elongated crystals indicates that the growth of the SnO₂ crystal is followed by the grain rotation induced grain coalescence mechanism. Comparing the SEM patterns, we can clearly observe the anisotropic growth trend of the spherical and some aggregated SnO₂ nanoparticles with the presence of Co ions in the precursor, which are well consistent with those of XRD.

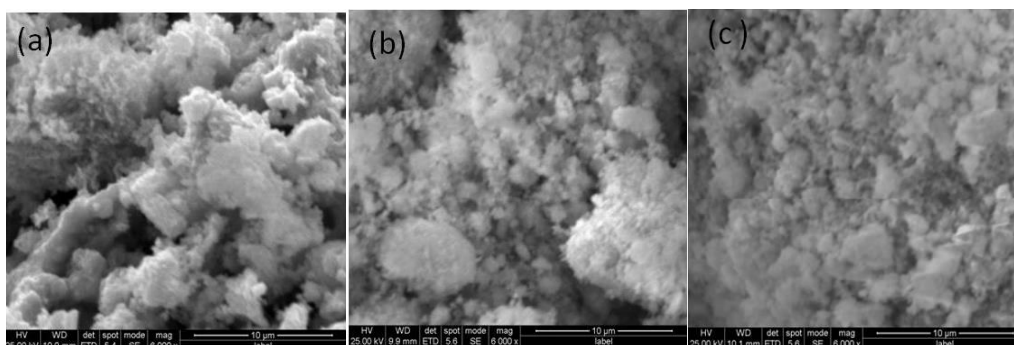


Fig. 2. SEM images of Co doped SnO_2 , (a) 2% Co doped SnO_2 (b) 4% Co doped SnO_2 (c) 6% Co doped SnO_2 .

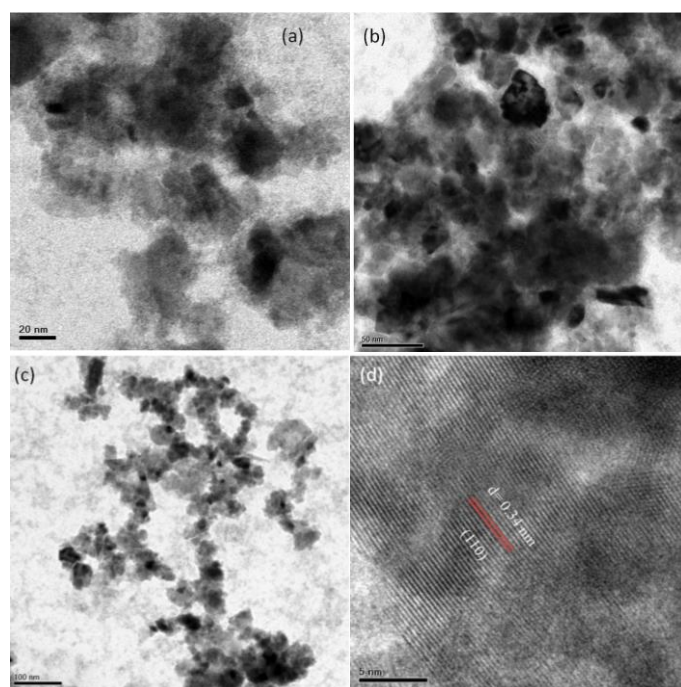


Fig. 3. HR-TEM images of the 4% Co doped SnO_2 nano particles.

The investigation of the microstructure of 4% Co doped SnO_2 nano crystalline powder was done with High-resolution transmission electron microscopy. The Co (4%) doped SnO_2 was dissolved in acetone for high resolution transmission electron microscopy analysis. The solution was sonicated for 30 minutes. The images of Co doped with SnO_2 seen through the high-resolution transmission electron microscope are shown in Fig. 3(a, b and c) respectively. Fig. 3 (a) shows the presence of closely-packed agglomeration of the nano particles in the mesoporous structure. This accumulation of nano particles creates narrow channels that may serve as electronic injection membranes. The size of the nano particles is extremely uniform as seen from Fig. 3 (b). Lattice fringes and the interplanar distance is measured to be 0.34 nm shown in the Fig. 3 (c and d). The obtained interplanar spacing values correspond to the (110) plane of rutile phase SnO_2 .

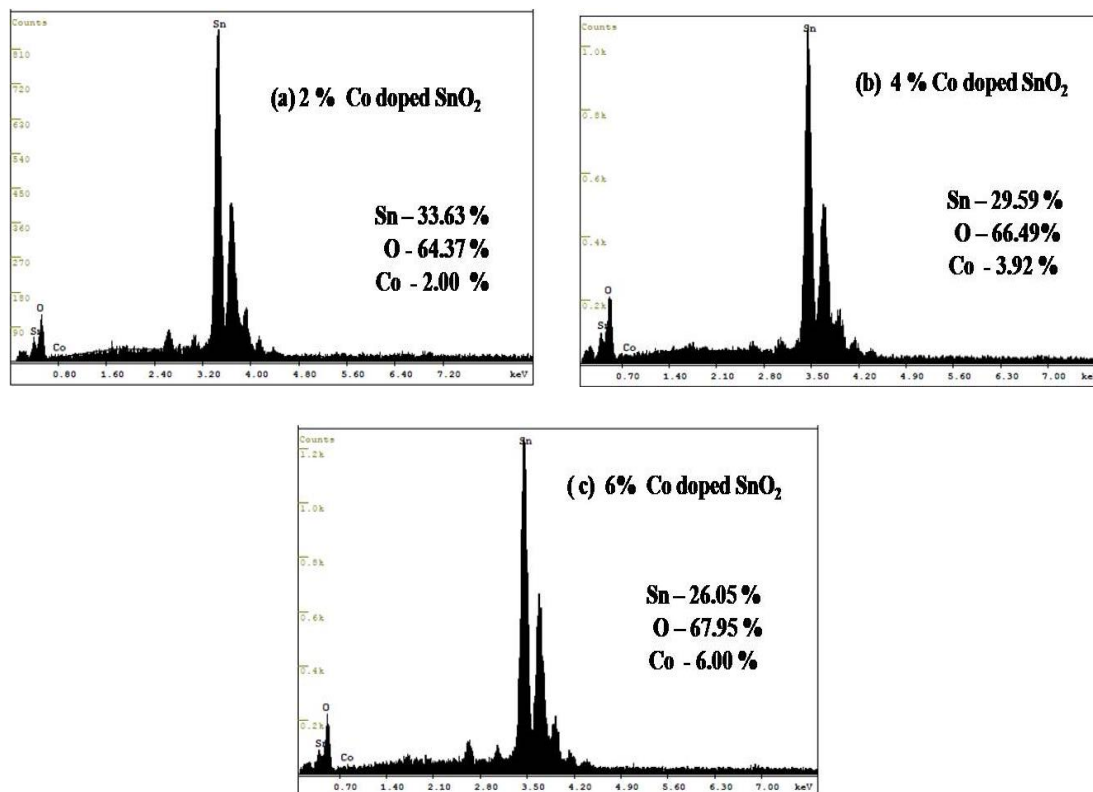


Fig. 4. EDAX Spectra of (a) 2% Co doped SnO₂ (b) 4% Co doped SnO₂ (c) 6% Co doped SnO₂.

The energy dispersive X-ray analysis has been carried out to know about the chemical composition of the prepared samples. The EDAX spectra of Co doped SnO₂ nanoparticles are shown in Figures. In the Figure 4 (a), (b) and (c) there are peaks for O, Co respectively and a relatively sharper peak for Sn. Qualitatively, it can be predicted that oxygen deficiency is there in the samples, which in turn, makes these nanoparticles as n-type semiconductors. However, a quantitative chemical analysis has to be done for providing proper explanation for this. During the crystallization of samples, the oxygen species get de-absorbed and trapped electrons are released, which corresponds to the increase in number of oxygen vacancies[10]. The atomic percentages of Sn, O and Co elements present in the prepared 2%, 4% and 6% Co doped SnO₂ powder is found from the EDAX analysis. The composition of 2% Co doped SnO₂ nano particle is Sn = 33.63 at %, O = 64.37 at % and Co = 2 at %. The 4% Co doped SnO₂ nano particle has a composition of Sn = 29.59 at %, O = 66.49 at % and Co = 3.92 at % and 6% Co doped SnO₂ nano particle has a composition of Sn = 26.05 at %, O = 67.95 at % and Co = 6 at %.

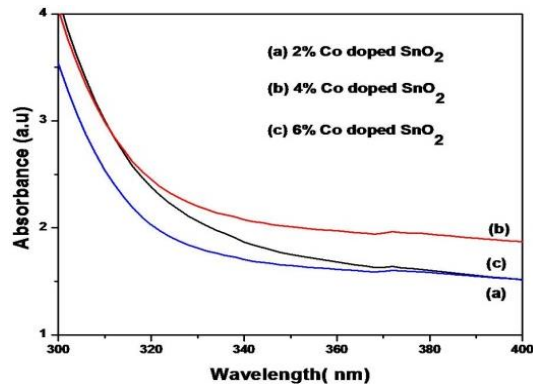


Fig. 5. Absorption spectra of (a) 2% Co doped SnO_2 (b) 4% Co doped SnO_2 (c) 6% Co doped SnO_2 .

Table 2. Band gap of (a) 2% Co doped SnO_2 (b) 4% Co doped SnO_2 (c) 6% Co doped SnO_2 .

S.No	Samples	Absorption Edge wavelength (nm)	Bandgap (eV)
1	2% Co doped SnO_2	327.16	3.79
2	4% Co doped SnO_2	337.27	3.68
3	6% Co doped SnO_2	343.05	3.62

The absorption spectra of Co doped SnO_2 is shown in the Fig. 5 and the spectra has a sharp absorption edge around 327 nm (3.7eV) for 2% Co doped SnO_2 which corresponds to the band gap (E_g) of bulk tetragonal SnO_2 (3.6eV). The 4% and 6% Co doped SnO_2 have the absorption edges at 337 nm and 343 nm. The band gap (E_g) is found to be reduced from 3.79 eV to 3.62 eV with increasing Co dopant concentration from the table 2. Such a decrease of the band gap (E_g) is induced by transition metal (Co and Mn) doping in SnO_2 . It has been ascribed to the sp-d exchange interactions between the band electrons and the localized d electrons of the transition metal ions substituting for Sn ions.

The band gap energy decreases with increasing Co^{2+} dopant concentration which may be attributed to the absorption of trapped electrons and d-d transitions of dopant Co^{2+} ions respectively [11]. Furthermore, in all absorption spectra, corresponding to Co_3O_4 no typical peak was detected because, only Co^{2+} ions are substituted for Sn^{4+} ions rather than creation of oxide impurities.

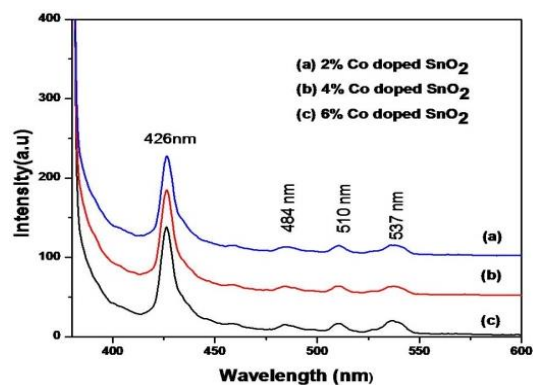


Fig. 6. PL Emission spectra of (a) 2% Co doped SnO_2 (b) 4% Co doped SnO_2 (c) 6% Co doped SnO_2 .

Using an excitation wavelength of 385 nm, the room temperature PL spectra of the Co doped SnO₂ samples were recorded and is shown in Figure 6. PL spectra exhibit only a broad emission peak in the range of 420 nm –540 nm. This implies that Co doping does not bring about new energy levels in the band structure to produce new emission. It also indicates that the Co²⁺ ions replaces Sn⁴⁺ ions without the formation of other additional energy levels. In all the samples, as the emission energies are lesser than the band gap (E_g), such emissions cannot be assigned to direct recombination of electrons in Sn⁴⁺ conduction band and holes in O²⁻ valence band, whereas it is usually related to the oxygen vacancies[12]. The concentration and distribution of the oxygen vacancies are also increased along with the local disorder influenced by the substitution of Co²⁺ ion for Sn⁴⁺ and charge imbalance in Co doped SnO₂. Therefore, the emission intensity is decreased, when there is an increase in Co concentration. It is understood that the Co substitutes at the Sn site in SnO₂ matrix with +2 charge state and does not form metallic clusters and other oxide phases. The intrinsic defects such as oxygen vacancies can also act as luminescent centers by formation of defect levels located inside the energy gap and trap electrons from the valence band. In oxide nano particles, oxygen vacancy is known to be the most common defect and usually acts as a radiative center in the luminescence [13].

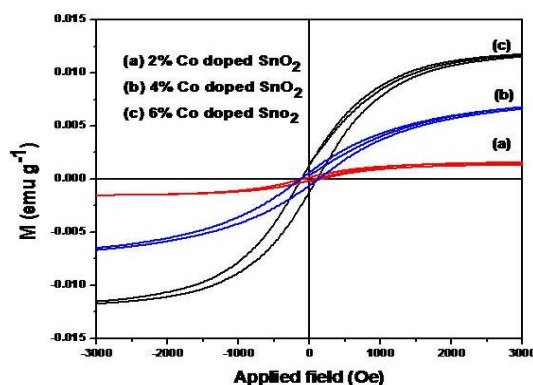


Fig. 7. Magnetisation curve of (a) 2% Co doped SnO₂(b) 4% Co doped SnO₂(c) 6% Co doped SnO₂.

The room temperature magnetization versus magnetic field (M–H) curves of the Co doped SnO₂ samples, shown in the figure 7 wherein the diamagnetic data of the background have been subtracted. Ferromagnetism of the samples at room temperature demonstrated by all the curves which exhibit clear hysteresis phenomenon. This has been earlier reported in nano crystalline SnO₂ samples doped with $\leq 5\%$ Co[14]. In our investigation, since the above structural characterizations have ruled out the presence of secondary phases including Co clusters in the prepared Co doped SnO₂ nano particles, the observed ferromagnetism should be the intrinsic in nature. The ideal SnO₂ surface has two characteristic surface sites: fivefold coordinated Sn⁴⁺ ions and twofold coordinated O²⁻ ions. Thus, the substitutional doping of Co²⁺ for Sn⁴⁺ introduces excessive negative charges in the lattice, making the system unstable in total charge. In order to maintain charge balance, an amount of O²⁻ ions need to escape from the lattice and form the oxygen vacancies. Oxygen vacancies tend to form near the Co ions. As a result, the substitutional doping of Co²⁺ for Sn⁴⁺ introduces redundant negative charges to the lattice, making the system unequilibrium in total charge. The localized spins of the Co ions interact with the charge carriers, which are bound to oxygen vacancies, resulting in a magnetic polarization and forms the bound magnetic polaron (BMP) [15]. A number of BMPs overlap and coalesce into an extended ferromagnetic domain, which ultimately create the long range ferromagnetic ordering in Co doped SnO₂ nano particles [16]. It is fascinating to note that with the increase in Co²⁺ molar concentration, the saturation magnetization (M_s) increases, as shown in Figure 7. The observed magnetisation and coercivity values are shown in Table 3. The changes in magnetic behavior indicates that the ferromagnetism is sensitive to surface modification occurring during the synthesis process, since the synthesis condition is identical for all the nano particles except the Co concentration. When the nano

particles are prepared in a surfactant environment, the surfactant molecules may be chemically absorbed on the particles. By increasing the Co doping concentration, the PL intensities of emission decreases gradually. Interestingly, the changes of the emission intensity depend on the surfactant concentration and it coincides with that of ferromagnetism [17]. The emission is ascribed to the oxygen vacancy. The intensity of emission is suppressed by the decrease of oxygen vacancies. It suggests that the introduction of the surfactant decreases the oxygen vacancies in the SnO₂ nano particles. Thus, it is confirmed that the enhanced ferromagnetism in the nano particles has been originated from the reduction of oxygen vacancies, which are induced by the surfactants. Meanwhile, the nano particles are found to absorb more surfactant molecules on the surface with increasing Co, which is accompanied by the increase in saturation magnetisation (M_s). It is strongly suggested that the surfactant modifies the oxygen vacancies which may be related with ferromagnetic divergence.

In the XRD pattern of the present study, however, no detectable Co or CoO phases could be observed. The systematic substitution of Co ions in the SnO₂ lattice is suggested by the decrease of intensities of Co related absorption bands in PL spectra and decrease of lattice constant values with increase in Co concentrations. These observations rule out the possibility of ferromagnetism due to unwanted Co precipitates in the samples. In the absence of any unwanted precipitates, the observation of ferromagnetism requires exchange interaction between free delocalized carriers and localized d-spins of Co ions. And therefore, for the observation of ferromagnetism, the presence of free carriers in the samples is a necessary condition. The presence of multi valence Co ions viz., Co²⁺ and Co³⁺ as well as valance centers made the availability of required free charge carriers(18). Further, the overall free charge carrier density due to annihilation of SnO₂ nano particles reduces with the increase of doping concentrations. As a result, the dominant magnetic interaction between Co ions, and hence, the ferromagnetic behaviour increases for increase in Co²⁺ doping concentration. Consequently to accomplish the good ferromagnetic character in these materials, the concentration of Co dopant has to be properly optimized.

Table 3. Magnetic Parameters of Co doped SnO₂ nano particles.

S.No	Samples	Coercivity (H_{ci}) (Oe)	Magnetization (M_s) emu/g (E^{-3})	Remanence (M_r) emu/g (E^{-3})
1	2% Co Doped SnO ₂	102.52	1.502	0.186
2	4% Co Doped SnO ₂	118.37	6.855	0.698
3	6% Co Doped SnO ₂	132.00	12.320	1.4678

4. Conclusion

The investigation of structural, Optical and magnetic properties of Co doped SnO₂ nanoparticles prepared by a simple chemical precipitation method has been done. The synthesized Co doped SnO₂ nanoparticles were in rutile phase with change in the lattice variation due to Co doping in Sn sites was revealed from the XRD studies. The scanning electron microscope and transmission electron microscope report the formation of nanoparticles with spherical agglomeration. High resolution TEM images clearly shows the lattice fringes by SAED pattern which specifies polycrystalline nature of rutile SnO₂. The optical properties of Co doped SnO₂ nanoparticles were carried out by UV and PL Studies.

The UV absorption of Co doped SnO₂ nanoparticles explained the blue shift of absorption spectrum. The reduction of bandgap is induced by the Co concentration in SnO₂. The PL spectra analysis provides evidence for the presence of oxygen vacancies in Co-doped SnO₂ samples. The increase of Co doping concentration, enhanced the intensity of peaks of the PL spectra at the wavelength 426nm, 484nm, 510nm and 537 nm. The magnetic measurement shows ferromagnetic behavior at room temperature in Co doped SnO₂ which has been invented Co ions in the oxygen vacancies. The coexistence of ferromagnetic phases due to oxygen vacancies was shown in the M-H curve of Co-doped SnO₂. Further, the decrease of intensities of Co related absorption bands in

PL spectra and decrease of lattice constant values with increase in Co concentrations suggests systematic substitution of Co ions in the SnO₂ lattice to increase the ferro magnetic property of Co doped SnO₂ nano particles.

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