

Optical Studies of Ni and Fe doped Tin Oxide Nanoparticles by Co-precipitation Method

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Abstract – Pure, Ni and Fe doped Tin Oxide (SnO_2) nanoparticles were synthesized by simple co-precipitation method. The structural, chemical and optical properties of the samples were analyzed using X-ray diffraction (XRD), UV-visible spectroscopy, FT-IR and Photo Luminescence Studies. SnO_2 crystallites were found to exhibit Tetragonal Rutile structure. Ni and Fe doped SnO_2 nanoparticles revealed that the metal ions substituted in the Sn lattice. A significant red shift in the UV absorbing band edge was observed with the doped Ni and Fe contents. The FT-IR analyses confirmed the incorporation of Ni and Fe in the synthesized powder.

Key Words: Tin Oxide, XRD, UV-Vis Absorption, FT-IR, PL Studies

1. INTRODUCTION

Among the various important categories of the functional materials like, polymers, magnetic, dielectric and semiconductors, the ferromagnetic semiconductors are emerged as attracting materials and driven a considerable attention in the recent years [1-2]. Tin oxide (SnO_2) is one of the most intriguing materials to be investigated today. This is because SnO_2 is a well-known n-type semiconductor with a wide band gap of 3.6-3.8 eV [3-5], and for its potential application in transparent conductive electrode for solar cells, a gas sensing material for gas sensors, transparent conducting oxide electrodes, photochemical and photoconductive devices in liquid crystal display, gas discharge display, lithium-ion batteries, etc., [6-10]. Co-precipitation [11] is a suitable chemical method in a nanoparticles synthesis because it does not require high pressure and temperature, impure materials are eliminated by filtration and repeated washing and cost effective method. In the present study, SnO_2 nanoparticles were synthesized by co-precipitation method and ultrasonic wave agitation was used to homogenize nanoparticles size.

2. EXPERIMENTAL ANALYSIS

2.1 Synthesis

For the preparation of pure, Ni and Fe doped SnO_2 nanoparticles, co-precipitation method have been adopted. The following analar grade precursors, 1.5 mM of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1.5 mM of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ and 1.5 M of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were taken to release Ni, Fe and Sn respectively. The aqueous solutions were taken in atomic weight percentage ratio to prepare doped SnO_2 nanoparticles. De-ionized water was taken as solvent for the preparation electrolyte. The solution was stirred for 2 hours using hot plate with a magnetic stirrer. Then, ammonium hydroxide (NH_4OH) was added into the solution (drop by drop), with stirring, until pH 9 was reached. The each doped solutions were then kept at room temperature for one day to complete the aging process. The resultant solution was washed several times with ethanol and double distilled water and dried in oven keeping the temperature at 100°C for 6 hrs. These precursors were ground in an agate mortar and pestle for 30 minutes to obtain fine powder. These powders were placed in an alumina crucible at sintering temperature as 500°C for 2 hrs in a furnace and brought the furnace to room temperature at the rate of 50°C per hour to get the annealed powder sample of pure and doped SnO_2 .

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Analysis

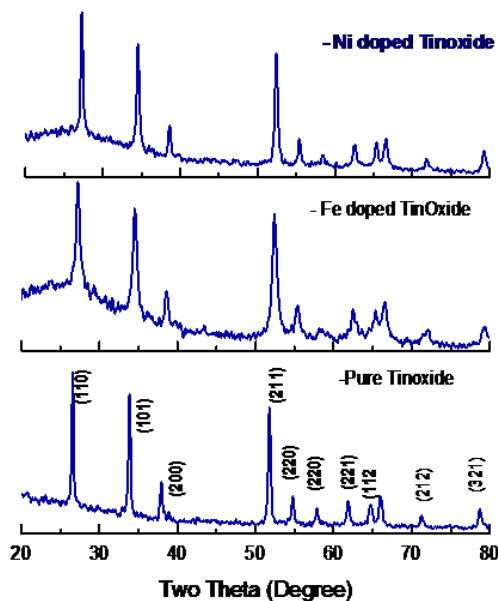


Fig.1: XRD patterns of (a) Pure (b) Fe and (c) Ni doped SnO₂ nanoparticles.

Table 1: Crystallite size and lattice parameters of pure, Ni and Fe doped SnO₂ nanoparticles.

Name of the Sample	Crystallite Size (nm)	Lattice parameters (Å)	
		a = b	c
SnO ₂	35	4.7371	3.1905
Ni doped SnO ₂	21	4.6246	3.1363
Fe doped SnO ₂	17	4.6279	3.1379

Fig.1 shows the XRD patterns of pure, Ni and Fe doped SnO₂ nanoparticles calcinated at 500°C for 2 hrs. The XRD patterns revealed that all the samples possess tetragonal rutile structure (JCPD File. Nos. 00-041-1445 and 01-070-6995) and the crystallographic space group (P4₂/mnm) 136. The broadening of the Bragg peak is due to the occurrence of smaller in crystallite size. The decrease in the crystallite size of doped samples when compared to pure is due to the decrease in the crystallinity of the doped samples [12]. A slight shift is observed in the unit cell parameters which indeed indicate that the doped atoms

might be substituted into the lattice sites of parent atoms [13]. The crystallite size of the Ni and Fe co-doped SnO₂ samples were calculated by the Debye-Scherrer's equation which is given by $d = k\lambda/(\beta \cos\theta)$, where 'k' is the shape factor, 'λ' is the wavelength of x-rays used, β is the full width at half maximum of the prominent Bragg peak and θ is the Bragg angle. Crystallite size and lattice parameters of pure, Ni and Fe doped SnO₂ nanoparticles are shown in the Table 1.

3.2 UV-Vis. Analysis

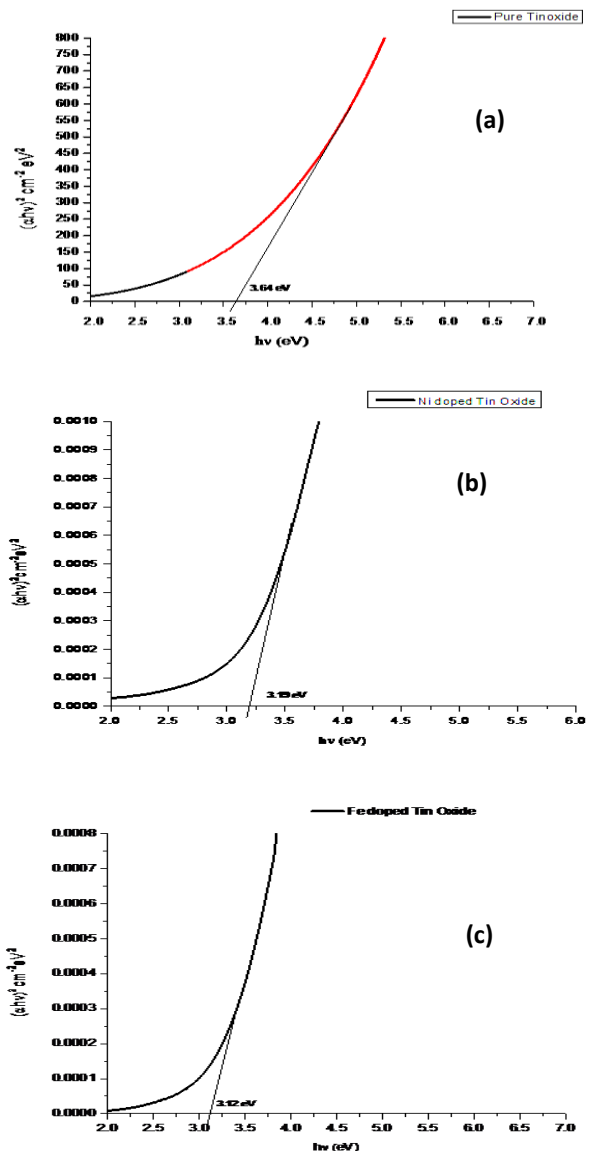


Fig.2: Tauc's plot of (a) Pure (b) Ni and (c) Fe doped SnO₂ nanoparticles.

Fig. 2 shows that the direct optical energy band gap (E_g) of the samples can be determined by the X-axis intercept of the straight-line portion of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$). The estimated band gap energy of pure SnO_2 is ~ 3.64 eV, while, the band gap energy of the Ni and Fe doped compound found as 3.19 and 3.12 eV. The observed band gap energy of pure SnO_2 nanoparticles is quite higher than the band gap energy of bulk SnO_2 (3.6 eV). The optical absorption edge of the spectrum of pure is sifted to blue wavelength and for doped sample is shifted to red wavelength with respect to the bulk (3.6 eV). The broad blue emission is due to the electron transition mediated by defect levels in the band gap. A significant decrease in band gap is observed with respect to doped samples. The decrease in the band gap energy may be due to the accumulation of donor energy levels of TM ions in the actual band gap of SnO_2 .

3.3 FT-IR Analysis

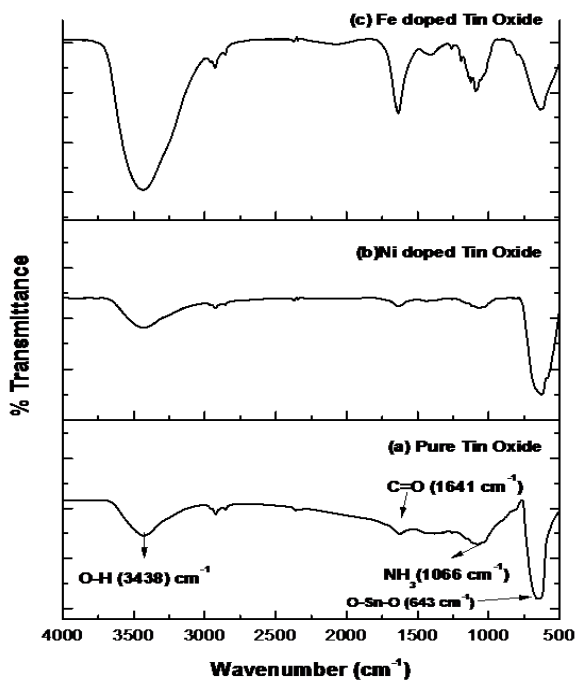


Fig -3: FT-IR spectra of (a) Pure (b) Ni and (c) Fe doped SnO_2 nanoparticles.

Figure 3 shows the FTIR spectrum of pure and Ni and Fe co-doped SnO_2 nanoparticles. At 1641 cm^{-1} and 3438 cm^{-1} indicates the presence of C=O and OH functional groups respectively [14]. The absorption band at 643 cm^{-1} is associated with the antisymmetric O-Sn-O stretching mode of the surface bridging oxide formed by the condensation

of the adjacent surface hydroxyl groups, which is in close agreement with the reported literatures [14, 15]. The peak at 1066 cm^{-1} is attributed to the NH deformation of ammonia [15, 16]. The above studies confirmed the formation of the tin oxide powder.

3.4 PL Analysis

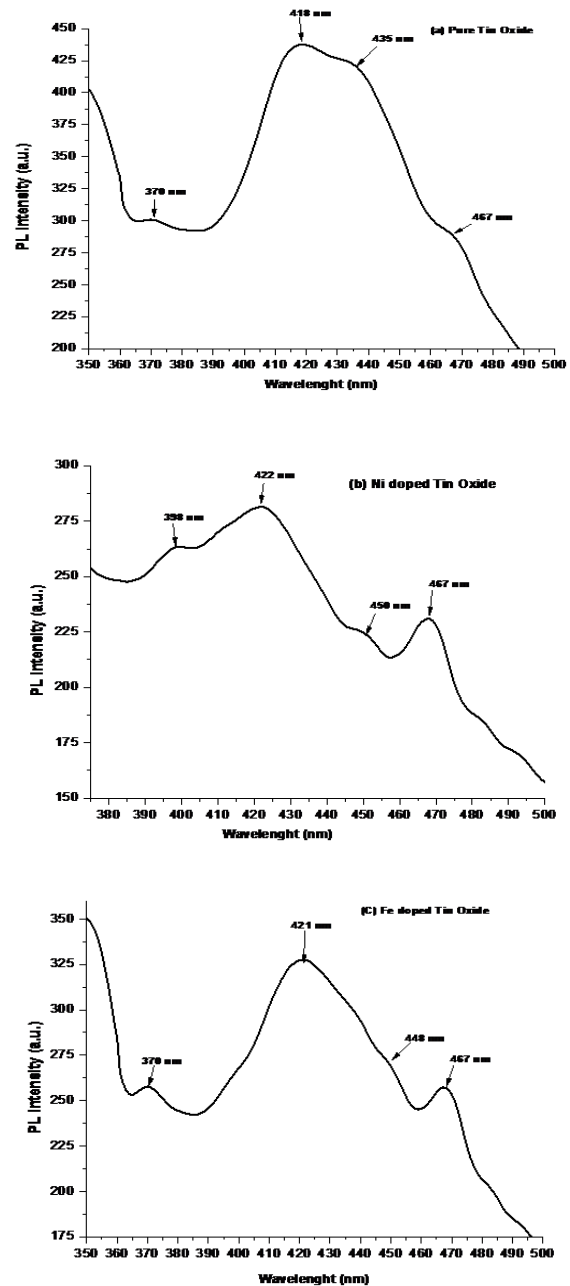


Fig.4: PL spectrum of (a) pure SnO_2 (b) Ni and (c) Fe doped SnO_2 nanoparticles.

The fig. 4 shows the PL spectra of pure SnO₂ nano emission bands at 370 nm, 418 nm, 435 nm, 467 nm and for Ni doped SnO₂ emission bands at 369 nm, 421 nm, 448 nm, 467 nm and for Fe doped SnO₂ emission bands at 370 nm, 422 nm, 450 nm, 467 nm. The blue emission peak at 467 nm is possibly attributed to the electron transition, mediated by defect levels in band gap, such oxygen vacancies or tin interstitials [17, 18]. The luminescence for doped samples is associated with the recombination of many more electrons and holes trapped at the surface of the SnO₂ nanoparticles.

3.5 SEM and EDX Analysis

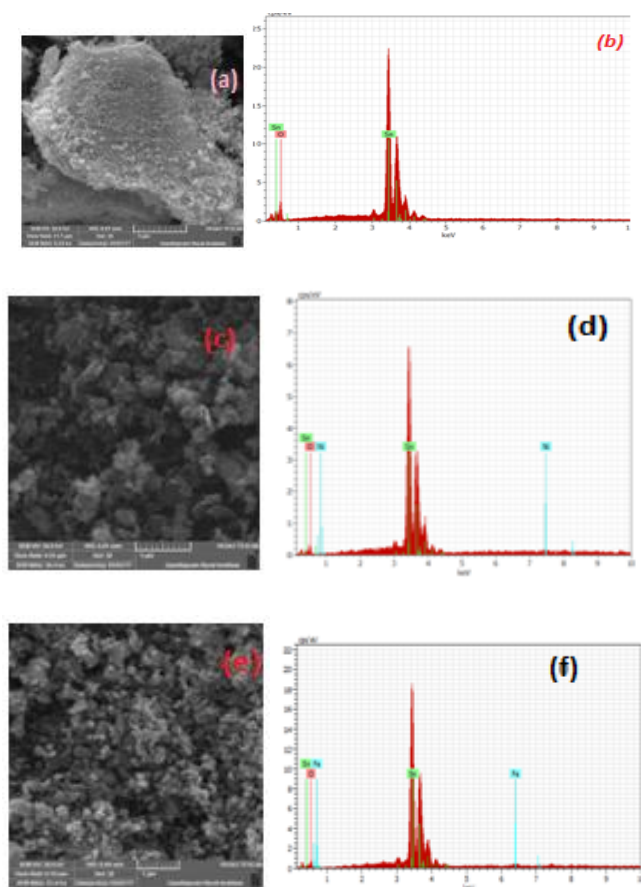


Fig.5: (a) SEM image and (b) EDX spectrum of pure SnO₂ nanoparticles, (c) SEM image (d) EDX spectrum of Ni doped SnO₂ nanoparticles, (e) SEM image (f) EDX spectrum of Fe doped SnO₂ nanoparticles

Table 2: Atomic Weight % of pure SnO₂ nanoparticles.

Element	AN	Series	unn.C [wt.%]	Norm.C [wt.%]	Atom.C [at.%]	(1 Sigma) [wt.%]
O	8	K-series	21.41	28.60	74.82	4.20
Sn	50	L-series	53.45	71.40	25.18	1.64
Total:			100.00	100.00		

Table 3: Atomic Weight % of Fe doped SnO₂ nanoparticles.

Element	AN	Series	unn.C [wt.%]	Norm.C [wt.%]	Atom.C [at.%]	(1 Sigma) [wt.%]
Sn	50	L-Series	72.50	89.39	54.60	2.22
O	8	K-Series	7.93	9.78	44.33	2.60
Fe	26	K-Series	0.67	0.82	1.07	0.07
Total:			81.00	100.00	100.00	

Table 4: Atomic Weight % of Ni doped SnO₂ nanoparticles.

Element	AN	Series	unn.C [wt.%]	Norm.C [wt.%]	Atom.C [at.%]	(1 Sigma) [wt.%]
O	8	K-Series	9.29	13.67	53.93	3.76
Sn	50	L-Series	58.47	86.02	45.74	1.86
Ni	28	K-Series	0.21	0.31	0.33	0.06
Total			67.97	100.00	100.00	

Figure 5 shows the typical morphology and Table 2, Table 3 and Table 4 shows the composition of Pure, Ni and Fe doped Tin Oxide nano particles. Fig.5 (a) shows the SEM morphology showing the presence of large spherical aggregates of small individual nanoparticles. In Fig.5(c), Ni and Fe co-doped SnO₂ SEM morphology shows spherical and nano rod aggregates of small individual nano particles. The presence of Sn, Ni and Fe is confirmed from the selective area EDX analysis. It can be verified from the results of change in cell dimension of XRD data and EDX shows that the Ni and Fe is successfully doped in the SnO₂.

4. CONCLUSIONS

Pure, Ni and Fe doped SnO₂ powders in nanometric dimensions were found by the co-precipitation method. The XRD pattern reveals the phase, structure and lattice parameters. The band gap energy of SnO₂ is promising for the application in optical device. The FT-IR studies confirm the presence of the Sn-O bond. The PL emission spectrum of the Pure and Ni & Fe co-doped SnO₂ nanostructures were observed in the strong visible region. It was attributed to the surfaced effects related to the oxygen vacancies. The SEM study confirms the presence of uniform

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grains in the synthesized powder. EDX reveals the presence of the elements, Sn, Co, Fe and O₂.

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