IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861,
PP 92-97
www.iosrjournals.org

Structural & Optical Properties of Co DOPED SnO_2 Nanoparticles Synthesised By Microwave Assisted Solvothermal Method

K. Gnanaprakasam Dhinakar[1], S. Meenakshi Sundar*[1]
[1] *PG & Research Department of Physics, Sri Paramakalyani College, Alwarkurichi- 627 412, Tamil Nadu, India.*

Abstract: *Cobalt doped Tin Oxide nanoparticles ($Sn_{1-x}Co_xO_2$, x = 0.01 – 0.04) are synthesized by microwave assisted solvothermal method. The as prepared samples are annealed with 550 °C for 1 h. The XRD pattern shows that the particles are in tetragonal crystalline structure and there is no secondary phase. The particle sizes are calculated as 14 – 19 nm. TEM images and the SAED pattern reveal the crystalline nature of the samples and confirm the particle size from XRD results. From the UV-Vis spectroscopy it has found out that the optical band gap of the samples increases with the dopant ratio. The functional group analysis made from FTIR spectrum.*

Keywords: *Co doped SnO_2, Microwave assisted synthesis, Optical properties, SnO_2 nanoparticles, Structural properties,*

I. Introduction

Among the other wide-band gap semiconductors, SnO_2 is one of the important materials because of its optical transparency, high carrier density, and wide-band gap, remarkable chemical and thermal stabilities. In recent years, considerable efforts are focused on the synthesis of magnetic impurity-doped SnO_2 materials in order to explore its diluted magnetic semiconductor (DMS) properties. The observation of giant magnetic moment in Co doped SnO_2 thin film has attracted attention as suitable DMOS material [1]. The room temperature ferromagnetism in SnO_2 system was reported by doping transition metals such as Co, Ni, Cr, Fe, Mn and Zn [2-3]. Apart from dopant induced ferromagnetism the annealed oxide semiconductor materials also exhibit the room temperature ferromagnetism due to the presence of oxygen vacancies [4]. The substitution of cobalt at the Sn site in the SnO_2 host matrix is responsible for the room temperature ferro magnetism (RTFM) [5]. Co was reported as an effective dopant for the densification of SnO_2. The addition of 0.5-2 mol% CoO into SnO_2 promotes the densification of this oxide up to >99.0% of the theoretical density. The Co^{2+} ions incorporating into SnO_2 crystallites have acted as an acceptor leading to the addition of oxygen vacancies into SnO_2, thus enhancing the densification rate of this oxide [6]. Cobalt ferrite has specific properties which have made it a suitable candidate for different applications and recently in medical science. The main reason for using the Co-ferrite for medical applications is its high magneto-crystalline anisotropy which originates from the spin–orbit (L–S) coupling at crystal lattices [7]. This work deals with the effect of Co doping on structural and optical properties of SnO_2 nanoparticles.

II. Synthesis Method

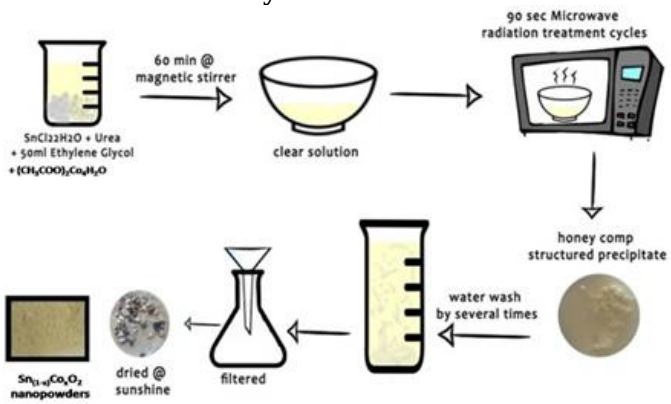

Fig. 1 Synthesis flow chart of Co doped SnO_2 nano particles

The cobalt doped SnO_2 ($Sn_{(1-x)}Co_xO_2$) ($0.01 \geq x \leq 0.04$) nanoparticles are synthesized by microwave assisted solvothermal method. Fig. 1 shows the flow chart of the synthesis method of Co doped SnO_2 nanoparticles. The precursors used for the synthesis of $Sn_{1-x}Co_xO_2$ are analytical grade tin (II) chloride, Cobalt II Acetate, urea as a catalyst and ethylene glycol as a solvent. Initially at room temperature, tin (II) chloride, Cobalt II Acetate and urea were dissolved in ethylene glycol by constant stirring for 90 minutes in a magnetic stirrer. The microwave power was set to 650 watts and operated at the rate of 2 minutes per cycle and cooled between the intervals until the precipitate was formed. The resulting precipitate was washed with double distilled water and dried. Again, the dried powders were washed with acetone annealed at 550 ºC for 1 hour in air atmosphere to remove unwanted organic substances present if any.

Characterization Techniques

XRD pattern were recorded using X-ray diffractometer (Bruker D8 Advance XRD) equipped with Cu target of step size 0.02° and 2θ degree ranging from 20° to 80° to determine the crystal structure. The field emission scanning electron microscopy (FESEM) images were obtained from FEI- QUANTA – FEG 250 instrument. Transmission electron microscopy (TEM) images were obtained to reveal the morphologies of the samples and selected area electron diffraction (SAED) patterns were recorded from 200kV TECNAI G^2 Transmission electron microscope. The functional group analysis was carried out fromFTIR spectrum recorded using Bruker Vertex 70 spectrometer. The UV-Vis absorption spectrum for all the samples was taken using Shimadzu UV-2550 spectrophotometer. The electrical and dielectric properties were studied using Solartron 1260 impedance set up. For electrical measurements two electrodes were formed by applying silver paste on both sides of the pellet and the measurement were carried out at room temperature in the frequency range of 1 kHz to 1 MHz.

III. Results And Discussion

3.1 XRD Spectrum Analysis

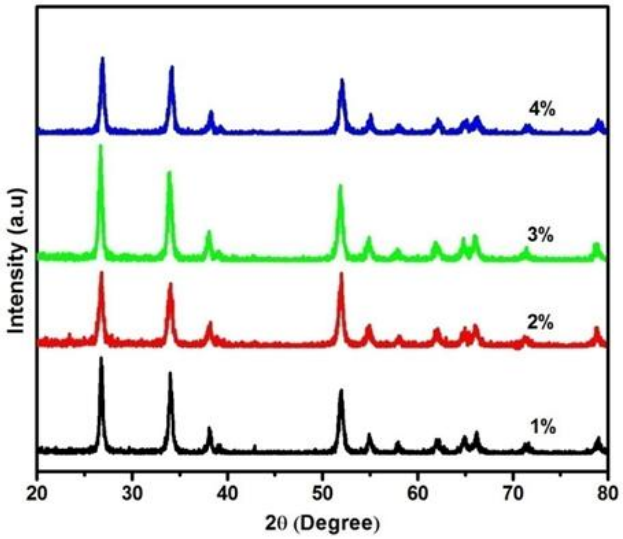

Fig. 2 XRD patterns of $Sn_{(1-x)}Co_xO_2$ ($0.01 \geq X \leq 0.04$) nanoparticles

The XRD patterns of the Cobalt doped SnO_2 nanoparticles are shown in Fig. 2. The major peaks are appeared at 26.7º, 34.06º, 38.02º, 52.01º, 55.05º, 57.89º, 62.05º, 64.89º, 66.21º, 71.48º and 78.68º. All the peaks are having good agreement with JCPDS card no 88-0287 (space group $P4_2$-mnm) and it confirm that the particles are in tetragonal crystal structure. There are no other peaks related to either cobalt or cobalt oxides. It confirms that the cobalt was doped into the host SnO_2 lattice. The intensity of the diffracted peaks and crystallite size showed decrease with increase in Co doping concentration. The average particle size calculated using the well known Scherrer's formula presented in equation (1)

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

Where λ, β and θ are the wavelength of X-ray used, full width at half maximum and Bragg's angle respectively. The average particle sizes for different Co doping ratios are tabulated in Table.1. The crystallite size decreases with increasing Co doping concentration and this may be due to the small ionic radii of Co^{2+}(0.79

Å) when compared to Sn^{4+}ion(0.83 Å) [8-10]. The lattice parameters and unit cell volume are also calculated using the equation represented in (2)

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (2)$$

Where h, k, l is lattice plane index and d is the distance between two consecutive planes. Table.1. Expose that the particle size values are decreasing as a function of dopant ratio [11].

Tabe. 1 Structural parameters of Co doped SnO_2 nanoparticles

Co Dopant ratio	Grain size D nm	Tetragonal structure lattice parameters (a.u)		Unit Cell Volume ($Å^3$)
		a,b (a = b)	c	
1%	19.04	4.7912	3.2170	73.849
2%	18.79	4.7893	3.2239	73.946
3%	18.42	4.7904	3.2219	73.934
4%	14.75	4.7824	3.2193	73.632

3.2. SEM IMAGES & EDAX

Fig. 3 (a-d) shows the SEM images of $Sn_{1-x}Co_xO_2$ (x = 0.02, 0.03) nanoparticles. Fig. 3 (a, b) are SEM images of $Sn_{0.98}Co_{0.02}O_2$ with 10,000 X and 1, 00, 000 X magnification respectively. One can see the clustered spherical granules of different sizes. Fig.3 (c, d) is SEM images of $Sn_{0.97}Co_{0.03}O_2$ with 10,000 X and 1, 50, 000 X magnification respectively. It also exposes clearly that the particles are spherical shaped clustered granules.

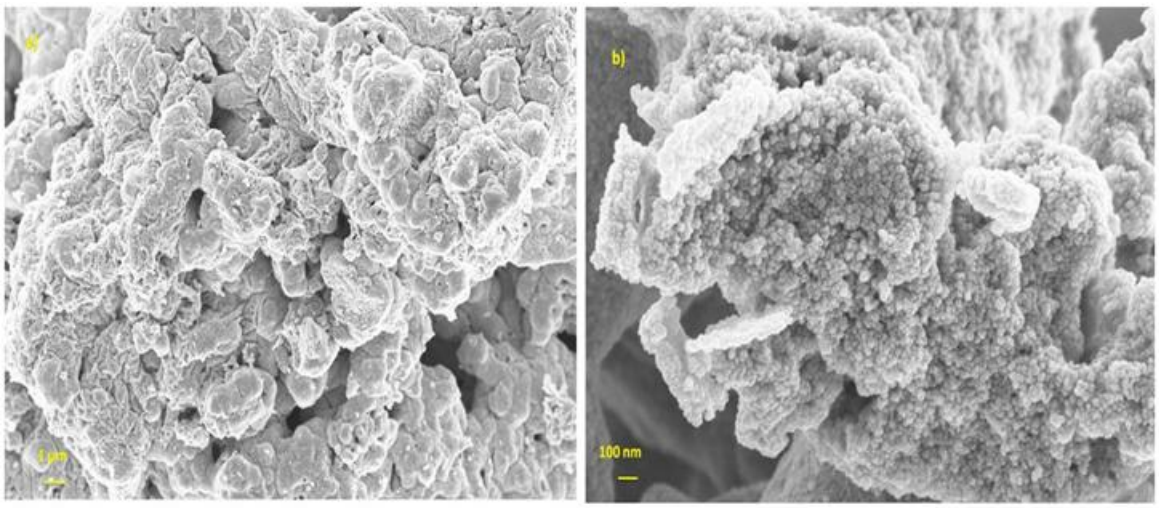

Fig. 3 (a, b) SEM images of 2% Co doped SnO_2 nanoparticles

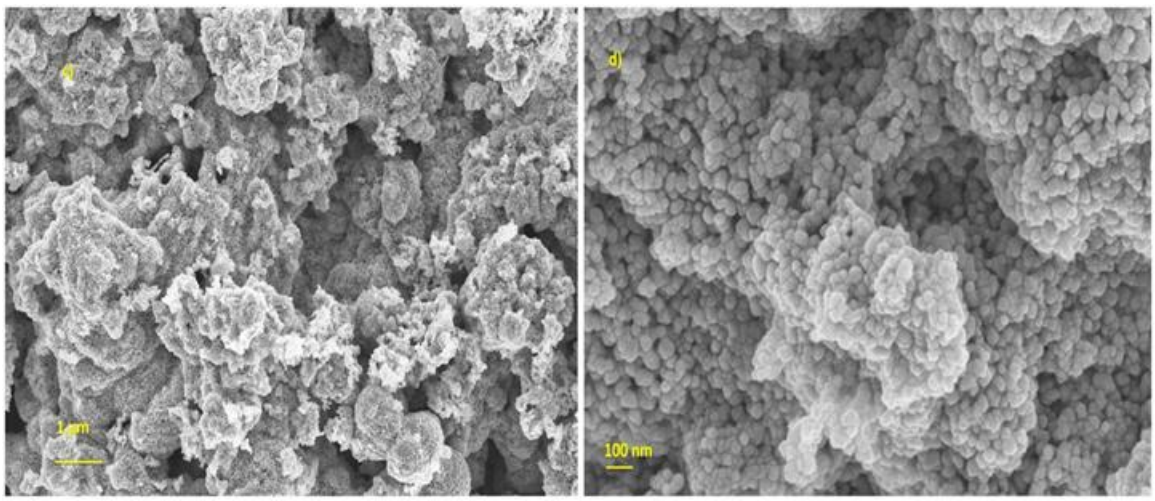

Fig. 3 (c, d) SEM images of 3% Co doped SnO_2 nanoparticles

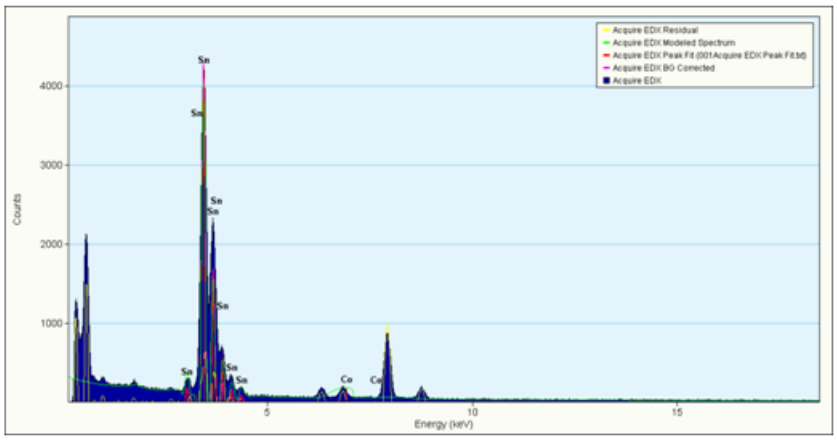

Fig. 4 EDAX picture of 2% Co doped SnO_2 nanoparticles

Fig. 4 depicts EDAX spectra of 2% and 3% Co doped SnO_2 nanoparticles, this clearly shows the existence of Co ions in doped sample and confirms the successful doping of Co in SnO_2.

3.3 TEM IMAGES

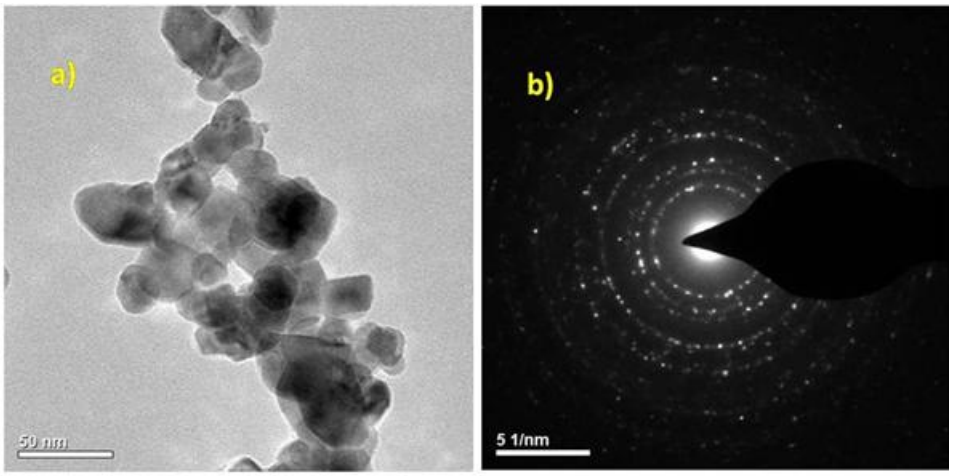

Fig. 5 (a, b) TEM Image & SAED pattern of 4% Co doped SnO_2 nanoparticles

Fig. 5 shows the TEM images of 4% Co doped SnO_2 nanoparticles. The TEM image exhibits that the particles are in spherical shape and they are clustered. This confirms the shape from SEM images. Fig. 8 shows the SAED pattern, and it reveals formation of rings. This shows that the particles are in good crystallinity and it has good agreement with the XRD pattern and the particle size values from XRD.

3.4. FTIR SPECTRUM

Fig. 6 shows the FTIR spectrum of different ratios of Co doped SnO_2 nanoparticles. There is a broad peak observed in the wavelength region 570 cm^{-1} - 630 cm^{-1}which are assigned to Sn-O-Sn, Sn-O vibrations [12]. The broad band appeared in the range of 3500 to 3200 cm^{-1} and the peak appeared in 2800 $cm^{-1}$are may be due to the vibration of water molecule. The peaks appeared at 2330 cm^{-1} 1608 cm^{-1} are related to the O-H stretching due to the absorbed water on the surface [13-14].There is a small shift occurs in the peak position. This is for the reason that there is a difference in bond length due to the replacement of Co ions in Sn site of the SnO_2 lattice.

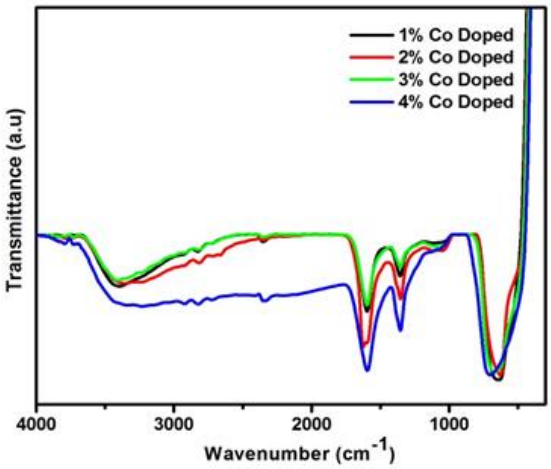

Fig. 6 FT-IR spectra of Co doped SnO_2 nano particles

3.5. BAND GAP ANALYSIS

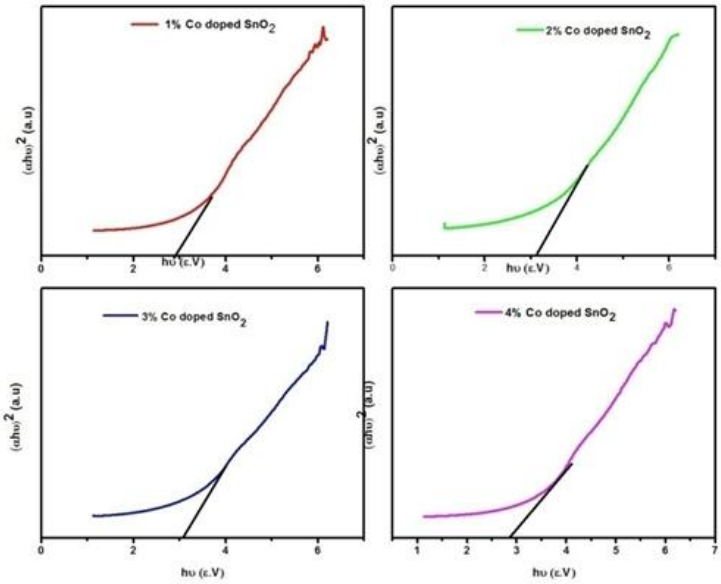

Fig. 7 Tau plot of Co doped SnO_2 nano particles

The optical band gap energy E_g of the Co doped SnO_2 nanoparticles are calculated from the UV-Vis spectrum. The relationship between the absorption coefficient (α) and optical band gap can be expressed as

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/n}$$

Where *A* is a constant and *h* is Planck's constant. The exponent *n* depends on the type of the transition, for direct allowed transition *n*=2, indirect allowed transition *n* = 1/2 and direct forbidden *n* = 3/2. For determining the band gap a plot between $(\alpha h\upsilon)^2$ and $(h\upsilon)$ is drawn and extrapolation of the linear part of the curve at α=0 gives E_g value. This plot is called as Tauc's plot. Fig. 10 shows the Tauc's plot for the Co doped SnO_2 nanoparticles. The band gap values are tabulated in Table 2. The band gap E_g value increases with the concentration of Co dopant ratio [16-17]. This behaviour shows the occurrence of additional electronic levels inside the band gap as a result of merging of Co into the SnO_2 lattice.

Table. 2 The band gap values for different Co doping ratios

Co doping Ratio	Band gap energy (eV)
1%	2.52
2%	2.65
3%	2. 67
4%	2.85

IV. Conclusion

The Cobalt doped Tin Oxide nanoparticles are synthesized successfully by microwave assisted solvothermal method. The XRD pattern reveals that there are no other peaks related to either cobalt or cobalt oxides. It confirms that the cobalt was doped into the host SnO_2 lattice. The average crystallite size is found to be 14 - 19 nm and the particle size decreases with doping ratio and this may be due to the small ionic radii of Co^{2+}. SEM and TEM micrograph shows that the particles are in tiny spherical shape and aggregate to form a clustered structure. The FTIR peaks shows a small shift in the peak position with the doping ratio and this may be due to the difference in bond length due to the replacement of Co ions in Sn site of the SnO_2 lattice. From Tauc's plot method the optical band gap energy of the Co doped SnO_2 nanoparticles are found. The values of band gap energy are increasing with increase in dopant ratio the values are varying from 2.52 eV – 2.85 eV.

References

[1]. Aditya Sharma, Abhinav Pratap Singh, P. Thakur, N. B. Brookes, Shalendra Kumar, Structural, electronic, and magnetic properties of Co doped SnO_2 nanoparticles, *Journal of Applied Physics. 107, 2010, 093918.*

[2]. Anees A. Ansari, J. Labis, M. Alam Shahid, M. Ramay N. Ahmad & Asif Mahmood, Effect of cobalt doping on structural, optical and redox properties cerium oxide nanoparticles, *Phase Transitions, 2015, 1*-12.

[3]. Manikandan, D. and Murugan, R., Room temperature dilute magnetism in nanoscale Co and Zn co-doped SnO_2, *Superlattices and Microstructures, 89, 2016, 7-14.*

[4]. Amiri, S. and Shokrollahi, H., The role of cobalt ferrite magnetic nanoparticles in medical science, *Materials Science and Engineering: C, 33(1), 2013, 1-8.*

[5]. Bouaine, A., Brihi, N., Schmerber, G., Ulhaq-Bouillet, C., Colis, S. and Dinia, A., Structural, optical, and magnetic properties of Co-doped SnO_2 powders synthesized by the co precipitation technique, The *Journal of Physical Chemistry C, 111(7), 2007, 2924-2928.*

[6]. Zhang, T.S., Kong, L.B., Song, X.C., Du, Z.H., Xu, W.Q. and Li, S.,Densification behaviour and sintering mechanisms of Cu-or Co-doped SnO_2: A comparative study, *Acta Materialia, 62, 2014, 81-88.*

[7]. Amiri, S. and Shokrollahi, H., The role of cobalt ferrite magnetic nanoparticles in medical science. *Materials Science and Engineering: C, 33 (1) 2013, 1-8.*

[8]. K.Subramanyam, N.Sreelekha, G.Murali, G.Giribabu, R.P.Vijayalakhmi, Influence of Co Doping on structural and Optical properties of SnO_2 Nanoparticles, *International Journal of ChemTech Research, 6, 2014, 2051-2053.*

[9]. Structural and ferromagnetic investigation of the size effects in pure and Co doped SnO_2 nano particles, M. Saravanakumar, S. Agilana, N. Muthukumarasamya, *Int. J. Chem. Sci.: 13(2), 2015, 605-612.*

[10]. Yongvanich, N. and Maensiri, S., Synthesis of Cobalt-Doped SnO_2 Nanoparticles by Chemical Precipitation with Chelation. *Integrated Ferroelectrics, 156(1), 2014, 53-57.*

[11]. R, Malik, A., Hameed, S., Siddiqui, M.J., Haque, M.M. and Muneer, M., Influence of Ce Doping on the Electrical and Optical Properties of TiO_2 and Its Photocatalytic Activity for the Degradation of Remazol Brilliant Blue, *International Journal of Photo energy, 2013.*

[12]. Mariammal, R.N., Rajamanickam, N. and Ramachandran, K., Synthesis and characterization of undoped and Co-doped SnO_2 nanoparticles, *Journal of Nano-and Electronic Physics, 3(1), 2011, 92.*

[13]. Priyadharsini, C.I., Prakasam, A. and Anbarasan, P.M., Enhanced photoelectrical performance of DSSC by Co-doped SnO_2 nanoparticles. International Letters of Chemistry, Physics *and Astronomy, 12 2013.*

[14]. Stella, C., Soundararajan, N. and Ramachandran, K., Structural, optical, dielectric and magnetic properties of $Mn_{1-x}Co_xO_2$ nanowires. *Superlattices and Microstructures, 71, 2014, 203-210.*

[15]. Shan, L.T., Ba, D.C. and Han, X.B., First-Principles and Experimental Study on Cu Doped SnO_2 Structure, *Applied Mechanics and Materials Trans Tech Publications, 470, 2013, 35-38*

[16]. Bagheri-Mohagheghi, M.M. and Shokooh-Saremi, M., Electrical, optical, structural and thermo electrical characterization of n-and p-type cobalt-doped SnO_2 transparent semiconducting films prepared by spray pyrolysis technique. *The Physica B: Condensed Matter, 405(19), 2010, 4205-4210.*

[17]. Dalui, S., Rout, S., Silvestre, A.J., Lavareda, G., Pereira, L.C.J., Brogueira, P. and Conde, O., Structural, electrical and magnetic studies of Co: SnO_2 and (Co, Mo): SnO_2 films prepared by pulsed laser deposition. *Applied Surface Science, 278, 2013, 127-131.*