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Photoluminescence Studies on Nanocrystalline Pure and Cr Doped Tin Oxide Powder

M.Saravanakumar*[1], S.Agilan[2], N.Muthukumarasamy[2], V.Rukkumani[3], A.Marusamy[2], P. Uma mahshwari[4], A.Ranjitha[2]

[1]Department of Physics, SVS College of Engineering, Coimbatore, India.
[2]Department of Physics, Coimbatore Institute of Technology, Coimbatore, India.
[3]Department of Electronics and Instrumentation, Sri Ramakrishna Engineering College,Coimbatore, India.
[4]Department of Physics, Indian Institute of Science, Bangalore, India

*Corres.author : saranspectra@gmail.com
Fax # 04222321332; Telephone #9942095222

Abstract : Nanocrystalline pure tin oxide (SnO2) and Cr doped SnO2 powders have been synthesized by a low temperature chemical precipitation method. As-prepared and heated powders were characterized by XRD, SEM and luminescence studies. The confirmation of rutile tetragonal structure of particle size 4.3 nm and 14.3 nm has been calculated of by XRD. The change in the particle's size with the Cr concentration shows that the increasing crystallite size with Cr doping nano particles. SEM images explain the washed powders morphology was almost spherical in shape and agglomerate. UV–vis absorption spectral studies showed a peak at 330 nm and 359 nm of pure and Cr doped SnO_2 respectively. A Photoluminescence (PL) study was measured at an excitation wavelength of 385 nm for as-prepared and annealed powders; it showed a broad emission peak at 426 nm for all powders.
Keywords : Pure and Cr doped SnO_2, XRD,SEM, UV and PL.

Introduction

Nano materials are great insert in the recent year due to the promising technological application in various fields. Among these materials, tin oxide (SnO_2) is a very important material, due to its attractive properties like optical transmittance, uniformity, low resistivity, mechanical hardness, stability to heat treatment and piezoelectric behaviour [1-2]. The recent intense research interests in nanosized particles of metals and semiconductors have been mainly attributed to the so-called quantum size effect,i.e., the size-tunable materials properties. For semiconductornanoparticles, this is distinctly reflected in the rather significant band gap structure that is size-sensitive,and might be manifested by the varied luminescence characteristics [3–5].

These properties make SnO_2 a suitable candidate for device such as for gas sensor application, Li- ion batteries, photovoltaic, super capacitor, Light emitting diode, display devices and solar cell [6-7].

SnO_2 thin film has been prepared by various techniques such as RF magnetron sputtering [8-9], electron beam evaporation [10], sol gel coating [11], chemical vapour deposition [12], etc. Among them Chemicl precipitation method is very simple technique for the growth of SnO2 due to its simplicity and low cost. In comparison of other techniques which required to maintains atmospheric pressure. As well as the physical and chemical properties of SnO_2 nano particles

the addition of some metal ions as impurities is expected to play an important role in changing the charge carriers concentration of the metal oxide matrix, catalytic activity, the surface potential, the phase composition, the size of crystallites, and so on [14-15]. In literature we have found that Cu [16], Fe [17], Mn [18], Sb [19], Co [20] and Cr [21] were doped to improve the properties of SnO_2. In the literature, no one has reported the deposition of $Cr_xSn_{1-x}O_2$ nano powder by Chemical precipitation method. The Cr^{3+} has ionic radius of 0.67Å, which is close to the ionic radius of Sn^{+4} that is 0.71Å. Therefore replacement of Sn by Cr does not change in lattice constants and crystal structure. It is possible to change the band gape by doping SnO_2 with suitable ratio of Cr. In this study, we have grown SnO_2 nano particles with a concentration of 2% Cr and study the effect of Cr doping on the structure and optical properties of the growth using X-ray diffraction (XRD), EDAX, UV-Vis transmission spectroscopy and Photoluminosense (PL).

Result and Discussion.

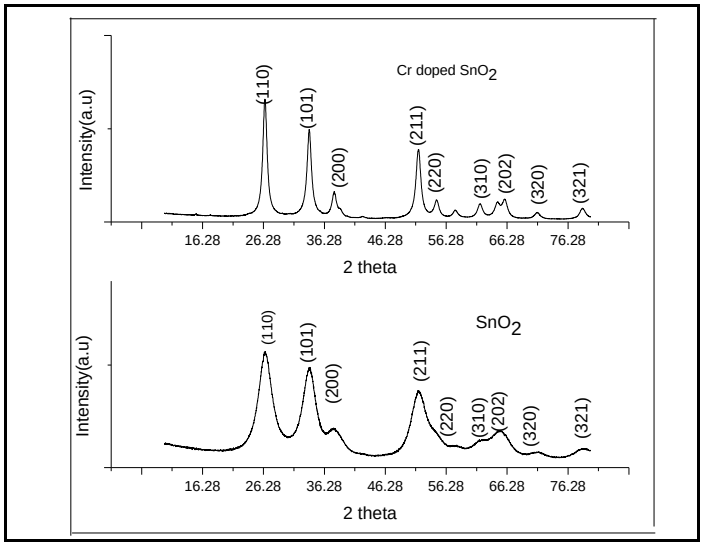

Fig.1 XRD Pattern of (a) Pure SnO_2 (b) 2% Mn Doped SnO_2 (c) 4% Mn Doped SnO_2 (d) 6% Mn Doped SnO_2

The structural properties of the undoped and 2% Cr doped SnO_2 nanopowders were investigated by powder XRD method. The XRD patterns (Fig. 1) of all the samples could be indexed to (JCPDS card no. 41-1445) the rutile-type phase of SnO_2 with a tetragonal unit cell which are consistent with the standard values for bulk SnO_2. No characteristic peaks of impurities, such as other forms of tin oxides, pure Sn or Cr oxides were observed within the detection sensitivity. All the peaks in the diffraction pattern are found to be characteristic of rutile tetragonal SnO_2 phase. The unit cell parameters were calculated from the known (h k l) values of the peaks (1 1 0) and (1 0 1) using the equation $\frac{1}{d^2} = \frac{(h^2 + k^2)}{a^2} + \frac{(l^2)}{a^2}$ the values are The observed shrinkage of the unit cell volume is consistent with the fact that the ionic radius and valence of Cr^{3+} (63 °A) is smaller than that of Sn^{4+} (74 °A).

The XRD results showed that the Cr^{3+} ions in corporate into SnO_2 lattice or replace Sn^{4+} sites without changing the rutile structure . The average crystallite size (D) was determined using the diffraction peaks of (110) and (101) from Scherer's formula

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{----------} \quad (1)$$

where K is the shape factor whose value is taken as 0.89, λ is the wavelength of Cu Ka radiation, and β is the corrected full width at half maximum (FWHM) of the diffraction peak and Q is the diffracting angle. The average crystallite sizes were found to be 4.3 and 14.3 nm and The lattice constants have been found to be a = 4.733 A ° and c = 3.161 A° for undoped SnO_2 and 2 wt% Cr doped SnO_2 nano particles respectively. These results indicate that the crystallite size of the Cr doped SnO2 nano particles depends on the Cr content, and that

the doping inhibits growth of crystalline grains of SnO_2. The particle size increases as the Cr concentration is increased.

The SEM micrographs of SnO_2 and Cr doped SnO_2 nanoparticles shows that surface morphology for the all samples are agglomerated. The agglomeration could be due to strong hydrogen bonding in the gel network, which is then difficult to remove in the subsequent stages. The agglomerate size is further increases on Cr concentration Fig.2 a, b. The Pure and 2 % Cr doped SnO_2 samples, on the contrary, show a better morphology of the samples, have finer particles at the same magnification.

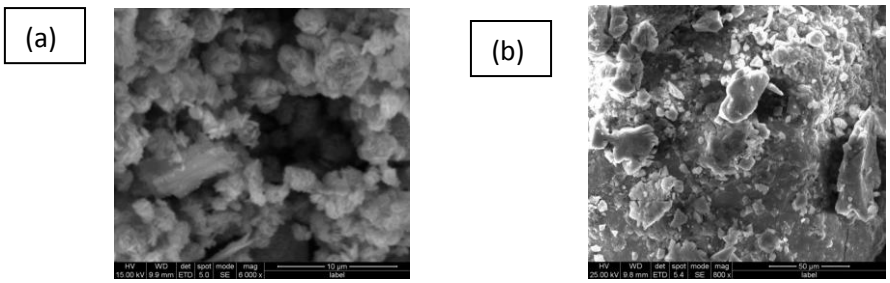

Fig. 2. SEM images of the (a) SnO_2 (b) 2% Cr doped SnO_2 nanoparticles

Fig. 3, it can also be observed that the absorption spectra have a red shift with addition of Cr, which is consistent with the effect of quantum confinement when the semiconductor particles are in nano scaled range . One of the main objectives of the present investigation is to clarify the effect of Cr^{3+} ions on the luminescence for the SnO_2 host.

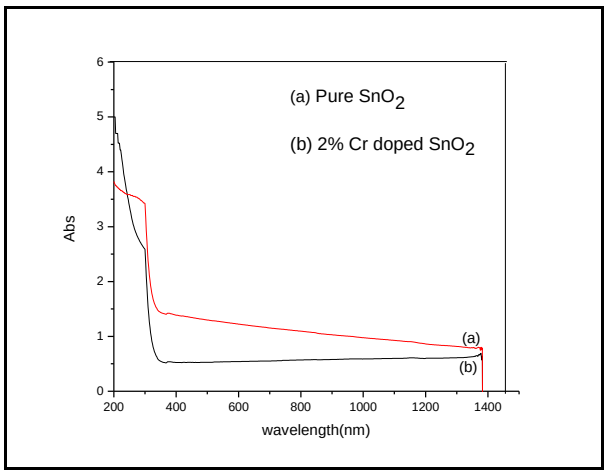

Fig. 3 Absorption spectra of (a) Pure SnO_2 (b) 2% Cr Doped SnO_2

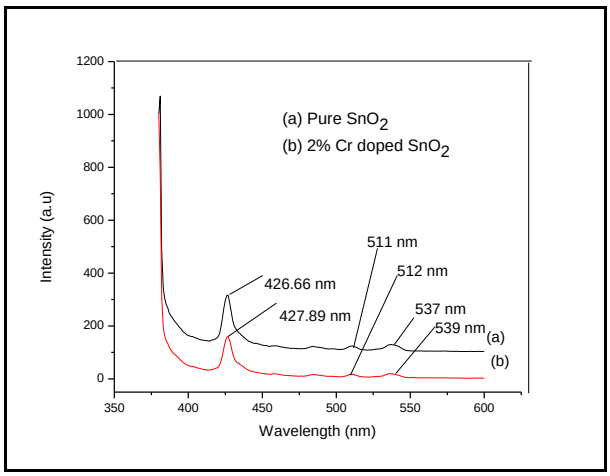

Fig. 4 Emission spectra of (a) Pure SnO_2 (b) 2% Cr Doped SnO_2

Fig. 4 shows the excitation and emission spectra of Pure and 2% Cr doped SnO_2 samples. The excitation spectrum shows one strong band at 385 nm (λ_{em} =426 nm), which is consistent with the results of absorption spectra. The emission spectrum presents two bands at 512 and 539 nm, respectively.From Fig.4, it can be observed that the addition of Cr^{3+} to SnO_2 host lattice can result in the increment of PL intensity of SnO_2 host, while the characteristic peaks of Cr^{3+} ions could not be collected, which differs from the behavior of Cr^{3+} in ZnS host. In pure SnO_2 host, the emission attributes to electron transition, mediated by defects levels in the band gap, such as oxygen vacancies, tin interstitials and so forth. Probably after introducing Cr^{3+} into the SnO_2 host, the defects still play a dominant role with respect to the luminescence processes.

Conclusion

Pure and Cr doped SnO_2 nanoparticles have been successfully prepared by chemical precipitation method. The structural and optical properties of Pure and Cr doped SnO_2 nano particles were studied using XRD ,SEM, Uv-Vis and PL. Cr substitution into the SnO_2 nano particles can be confirmed by the shifting of peaks in XRD patterns confirmed rutile teteragonal structure on grain size 4.3 nm and 14 nm and shrinkage the lattice constant with increasing Cr content. investigated by SEM, UV-Vis and PL studies. The concentration of Cr can affect the particle size; it increasing particle size are well presented for the as-synthesized samples. The shift in Eg could be attributed to the sp-d exchange interactions or increase in crystallite size. Photoluminescence emission exhibits a band at 385 nm. It is related to the recombination of electrons in singly occupied oxygen vacancies with photo excited holes in the valence band. Then the concentration of Cr affect the luminescence process, the emission resulting in the decrease in the oxygen vacancies, as revealed by the increase in luminescence at 426 nm.

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