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Effect of Ti doping on the structural and optical properties of tin oxide nanoparticles

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Abstract: Pure and Ti doped tin oxide nanoparticles were synthesized employing a sol-gel method. The samples have been characterized by X-ray diffraction (XRD), Photo Luminescence (PL) and Fourier transform infrared spectroscopy (FT-IR). The X-ray diffraction reveals that all samples are pure rutile-type tetragonal phase and the average particle sizes was observed to vary from 10.6 nm to 7.8 nm as the Ti content was increased. Photo Luminescence shows, strong UV band located at 372 nm.

Keywords: Tin Oxide, sol-gel, Titanium doping.

Introduction:

Tin oxide (SnO_2), is a wide band gap n-type semiconductor (E_g = 3.6 - 3.8 eV) and one of the most widely used semiconducting oxides due to its chemical and mechanical stabilities. It is one of the potential materials for gas sensors, optoelectronic devices and negative electrodes for lithium batteries [1–4]. Recently, transition-metal doped tin dioxide has gained much attention due to the possibility of exhibiting room-temperature ferromagnetism. Many methods have been developed to synthesize SnO_2 nanoparticles, including homogeneous precipitation [5], hydrothermal route [6], solid state reaction [7], and sol-gel route [8]. The main purpose of the present research work is to synthesis Ti doped SnO_2 nanoparticles by sol gel because very few reports are available in this material.

Experimental details:

Tin oxide materials were prepared by the sol-gel method .All the reactants used were of analytical grade without further purification. The preparatory materials were Tin tetrachloride ($SnCl_4.5H_2O$, Sigma Aldrich) and 25% ammonia solution (NH_4OH, sigma Aldrich). Calculated amount of $SnCl_4.5H_2O$ solution was prepared by using deionised water and magnetically stirred it for 30 min. Then ammonia solution (25%) was added into the mixture under the controlled supply until the PH of the solution becomes 8 and constant stirring. After 2 hours of stirring, the sol was aged at room temperature for 5 days. The resulting gel was washed with ethanol and deionised water for several times to remove the by products Cl^- and impurities. The product was separated by using the high speed centrifuge at 10000 rpm for 20 min. the precipitate was then dried in a hot air oven at 100°C for 10 h. The dried precipitate was calcined in air at 450°C for 2 h in muffle furnace. The formation of SnO_2 nanoparticles in colloidal medium may occur as follows.

$$x(SnCl_4) + y(NH_4OH) \rightarrow x(Sn)^{+4} + 4x(Cl)^- + y(NH_4)^+ + y([OH])^-$$

$$y(NH_4)^+ + 4x(Cl)^- \rightarrow a(NH_4Cl)$$

$$x(Sn)^{+4} + y([OH])^- \rightarrow b(Sn(OH)_2)$$

$$b(Sn(OH)_2) \xrightarrow{heating} c(SnO_2) + d(H_2O)$$

For preparing $(Sn_{1-x}Ti_x)O_2$, calculated amount of Titanium tetra chloride ($TiCl_4$) was used to the above sol solution. Titanium doping ratio was the molar ratio of Ti to Ti+Sn, namely x. The crystalline structure of the samples were analyzed by X-ray diffraction (XRD) using a Xpert-Pro diffractometer and using the CuKα1 wavelength of 1.5406 Å. The Fourier transform infrared spectra (FT-IR) of the samples were recorded using a SHIMADZU-FTIR spectrometer.

Results and Discussion:

XRD:

Figure 1(a and b) shows the XRD paterrn of SnO_2 and $(Sn_{0.95}Ti_{0.05})O_2$ nanoparticles. XRD peaks at 2Ө =26.6°,33.9°,38°,51.8°,57.9°,65.2°,71.3°&78.7° were assigned to diffraction from the (1 1 0), (1 0 1), (2 0 0), (2 1 1), (0 0 2), (3 0 1), (2 0 2) and (3 2 1). The diffraction peak of the samples corresponds to rutile phase of SnO_2 (JCPDS card No:41-1445) with lattice constants of a=b=4.743Å and c=0.3198Å. The peak broadening and high background may arise due to the very narrow size distribution of the so formed nanoparticle.

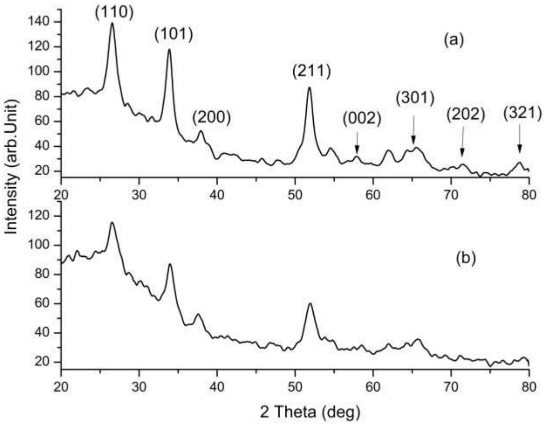


Figure 1 : XRD patterns of SnO_2 nanoparticles (a) and $(Sn_{0.95}Ti_{0.05})O_2$ nanoparticles (b)

The average crystalline size of the crystallites was calculated using the Debye-Scherrer's formula $d = k\lambda / \beta \cos\theta$ where d is the mean crystalline size, K is a grain shape dependent constant (0.9), λ is the wavelength of the incident beam, θ is a Bragg's reflection angle and β is the full width half maximum. The average size and lattice parameters of the synthesized particles were shown in Table 1.

Table 1: Lattice Parameters and particle size of synthesized nanoparticles

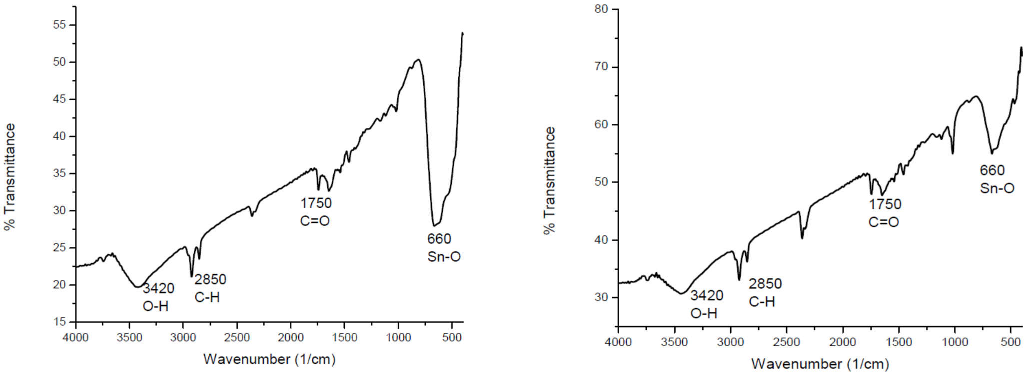
Sample	h k l	FWHM (deg)	d-Spacing (Å)	Grain size (nm)	Lattice Volume $(Å)^3$	Lattice constant	
						a (Å)	c (Å)
SnO_2	110 101	1 0.6	3.35422 2.64477	10.6	71.69	4.7436	3.1859
$(Sn_{0.95}Ti_{0.05})O_2$	110 101	2 1	3.35616 2.63783	7.8	71.66	4.7540	3.1707

Small changes in the line positions, intensity and broadening are observed between the samples SnO_2 and $(Sn_{0.95}Ti_{0.05})O_2$. Substitution of Sn^{4+} ions (ionic radius=0.71 Å) by the smaller Ti^{4+} ions (ionic radius=0.68

Å) slightly decrease the inter-atomic spacing and therefore expansion in lattice parameters is observed with Ti doping. Atomic scattering factor for Ti (Z=22) is almost half the value for Sn (Z=50) therefore, any substitution of Sn by Ti may lead to change in the structure factor of SnO_2 lattice, which will reflect in the change in XRD peak intensity ratios on Ti doping.

FTIR:

FT-IR spectra of SnO_2 and $(Sn_{0.95}Ti_{0.05})O_2$ nanoparticles were shown in Figure 2(a and b). Data collected are in agreement with XRD results. The narrow peaks at 660 cm^{-1} confirm the formation of crystalline SnO_2 phase and it was observed due to Sn-O vibration. The spectra exhibit also a common broad band around 3420 cm^{-1} due to the OH-stretching vibrations of free and hydrogen bonded hydroxyl groups. Importantly, XRD and FT-IR analyses suggest that no significant variation in the phase composition.



(a) **(b)**

Figure 2 : FTIR pattern of SnO_2 nanoparticles (a) and $(Sn_{0.95}Ti_{0.05})O_2$ nanoparticles (b)

Photo Luminescence:

PL spectrum of pure SnO2 nanoparticles with an excited wavelength at 260 nm is shown in figure 3. The emission band is composed of a strong UV band located at 372 nm. The UVemission band must be explained by a near-band-edge transition of wide band gap SnO2 nanoparticles, namely the free excitons recombination through an exciton-exciton collision process. The visible emission of SnO2 nanoparticles is related to the defect levels within the band gap of SnO2, associated with an oxygen vacancies or tin akthiin terstitials that formed during the synthesis process. For Ti doped SnO2 nanoparticles the change in intensity of UV band was observed.

In summary, the SnO_2 nanoparticles doped with Ti were synthesized successfully by the Sol-gel method. Based on XRD and FTIR studies, well crystalline Ti doped SnO_2 nanoparticles were formed with average particle size of 6.2 nm. Such a sample is useful for to make spintronic devices.

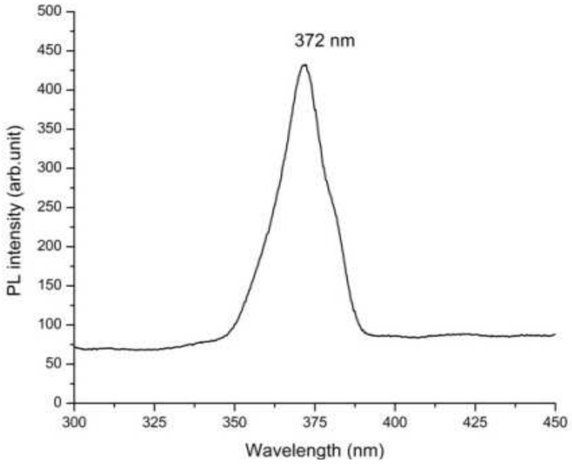


Figure 3: PL spectrum of SnO_2

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