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Effect of Aliovalent Substitution on sol-gel Derived SnO_2 Nanoparticles

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Abstract—*Nano-crystalline metal oxides have drawn attention due to their exceptionally brilliant properties due to large surface area, small grain size, quantum confinement effect etc. which varies with the size and shape of metal oxide. Lanthanum doped tin oxide nanoparticles and lanthanum and zinc co-doped tin oxide nanoparticles were successfully synthesized by sol gel method. The precursor materials used were tin tetrachloride, lanthanum nitrate, zinc nitrate, and ethylene glycol. Nanoparticles formed from this method were calcined at 600 ^{0}C/2h to get the crystalline powder. Using XRD pattern, the average crystalline size of metal doped tin oxide nanoparticles were determined and compared with tin oxide nanoparticles. UV-VISIBLE absorption spectrum was recorded and found the absorption of sample at a particular wavelength value. One of the most fascinating and useful aspects of nanomaterial's is their optical properties. Applications based on optical properties of nanomaterial's include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photo catalysis, photo electrochemistry and biomedicine. With the SnO_2 semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles.PL emission spectra were recorded for the pure SnO_2, La doped SnO_2, La-Zn doped SnO_2 samples. A dominant PL peak was observed at 685nm in these samples.*

Keywords*: Metal oxides nanoparticles, structural refinement, optical properties.*

1. INTRODUCTION

Metal oxide semiconductors (MOS) have become a potential member emerging technologies. In recent times, SnO_2 represents a key aspect of technological application because it exhibit interesting optical, electronic, optoelectronic and biological characteristics [1]. SnO_2 conform n-type semiconducting behavior to wide energy band gap ~3.6eV[2, 3]. SnO_2 attains several crystal structure rutile (P42/mnm), pyrite-type (Pa3), CaCl2-type (Pnnm),a-PbO2-type (Pbcn), fluorite-type (Fm3m) [4-8]. But the most stable phase at room temperature is cassiterite tetragonal rutile phase. The simultaneous appearance of conductivity and transparency becomes a unique feature of SnO_2, amongst the Group IV elements of the periodic table. In nanomaterial's, high surface area to volume ratio is measure of number of atoms appear on the surface i.e. more reactive sites are present on the surface. The dual valence state of Sn governs the surface properties which facilitates the transition of the compositions and changes Sn^{4+} to Sn^{2+} depending upon the chemical potential of oxygen [9]. The oxygen vacancies concentration is difficult to control due to dual valency of Sn in non-stoichiometric pure SnO_2. Many reports are available on conductivity of the thin films of modified SnO_2 [10-12]. In optoelectronic devices, the concentration of doped SnO_2 carriers is nearly $10^{20}cm^{-3}$. The optical activity alters the light constants from near infrared to visible region at these carrier concentrations [13, 14]. To introduce electron degeneracy the doping mechanism is adopted. It is well established that group V increases the conductivity and group III decrease the conductivity of SnO_2. The optimum dopant concentration lies in a range of 0.4% to 3% as it decreases the resistivity initially but increase with higher doping concentration [15]. Kilic et al. reported the first principal calculation study on transparent conductivity of SnO_2 and they have calculated the formation of energies and electrical properties with different levels of defects like oxygen interstitials, oxygen vacancies, Sn antisites and Sn interstitials [16]. In this report, we have carried out the structural and photoluminescence studies of pure and aliovalent substituted SnO_2 solgel derived nanoparticles.

2. EXPERIMENTAL

The un-doped and co-doped tin oxide nanoparticles were synthesized by the sol gel method. All reagents of analytical grade were used without any further purification. Tin tetrachloride (98%) and ethylene glycol obtained from the LobaChem and lanthanum nitrate, zinc nitrate and iron nitrate chloride from the Aldrich, used as precursor materials. Solution of tin tetrachloride in ethylene glycol was prepared by dissolving appropriate amount of tin tetrachloride in ethylene glycol under vigorous stirring at 80 degree Celsius

until colourless and transparent solution is obtained. First 3.5773g of $SnCl_4.5H_2O$ was dissolved in 100ml of ethylene glycol and then the solution was stirred without heating for 30 minutes till the solution become transparent and then kept on heating with stirrer at 80^0C for six hours till the solution reduces to 2/5 of its original volume. The solution was heated to 120 degree Celsius and kept at the temperature to evaporate water and hydrochloride (HCl). A gel is formed which is of dark brown colour, when the solvent was completely removed.. After drying of the solution at 600 degree Celsius the powder thus formed. The specimens were characterized by using X-ray diffractometer. The GSAS suite of Rietveld refinement were used for analysis of X-ray diffraction(XRD) data.

Reagents used- Tin tetrachloride, ethylene glycol, lanthanum nitrate, zinc nitrate, iron nitrate

3. RESULTS AND DISCUSSION.

Fig. 1 shows the X-ray diffraction patterns of pure SnO_2 (S1), $Sn_{0.95}La_{0.05}O_2$ (S2) and $Sn_{0.92}La_{0.02}Zn_{0.06}O_2$ (S3)] annealed at 600°C. The diffraction pattern was recorded between scanning angles over a range 20 ≤2θ ≤90. It is clear from the figure that there exist no extra peaks in the diffraction patterns which suggests that the doping of La (5%) and La (2%), Zn (6%) do not alter the crystal structure of SnO_2. Rietveld refinement method has been employed to determine the crystalline structure of all the samples. All the compositions (S1, S2 and S3) exhibit rutile tetragonal structure with a space group P42/mnm (No. 136). The ball structure with refined data for pure SnO_2 is displayed in Fig. 2. The refined structural parameters are given in Table 1. The unit cell volume of S2 and S3 is slightly higher as compared to S1. The ionic radii of La^{3+} (0.104 nm) is greater than that of Sn^{4+} (0.069 nm), which can be the reason for the increment of the cell volume. Due to the difference between the ionic radii and also due to charge neutrality, there occurs structural rearrangement which results in structural distortion. It suggests that the lattice distortion is mainly due to difference between the ionic radii of the dopant ions, which can significantly affect the other properties related to anisotropy of the crystalline compounds.

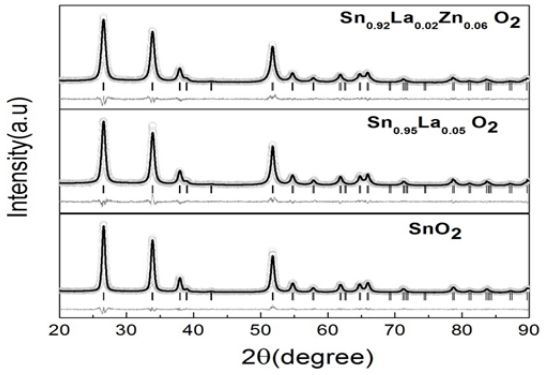

Fig. 1: XRD pattern of SnO_2, $Sn_{0.95}La_{0.05}O_2$ and $Sn_{0.92}La_{0.02}Zn_{0.06}O_2$ nanoparticles

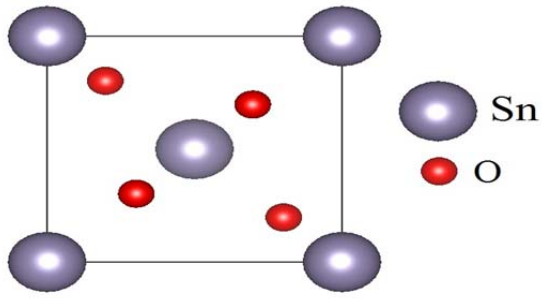

Fig. 2: Rutile tetragonal structure of pure SnO_2

Table 1: Refined structural parameter of SnO_2, $Sn_{0.95}La_{0.05}O_2$ and $Sn_{0.92}La_{0.02}Zn_{0.06}O_2$ nanoparticles

Sample	Lattice Parameter		Cell Volume	Refinement Parameter
	a	c		χ^2
SnO_2	4.740524	3.189022	71.6655	1.54
$Sn_{0.95}La_{0.05}O_2$	4.741791	3.186314	71.7429	1.68
$Sn_{0.92}La_{0.02}Zn_{0.06}O_2$	4.743148	3.188333	71.7293	1.55

PL emission spectra are recorded for SnO_2 (S1), $Sn_{0.95}La_{0.05}O_2$ (S2) and $Sn_{0.92}La_{0.02}Zn_{0.06}O_2$ (S3). The excitation wavelength was 312nm. The pure SnO_2 powder shows four strong PL broad band peaking at 344.76nm, 380.31nm, 400.31 and 425.08 under excitation at 312nm as shown in Fig3. La modified SnO_2 i.e. $Sn_{0.95}La_{0.05}O_2$ displays three excited bands at 364.87nm, 455.85nm and 681.24nm and $Sn_{0.92}La_{0.02}Zn_{0.06}O_2$ illustrates only one broad band peaked at 574.71nm.

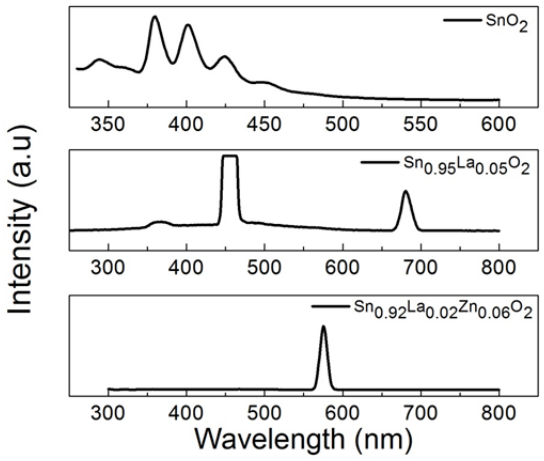

Fig. 3: PL spectra of SnO_2, $Sn_{0.95}La_{0.05}O_2$ and $Sn_{0.92}La_{0.02}Zn_{0.06}O_2$ nanoparticles

4. CONCLUSION

Nano-structured tin oxide nanoparticles and metal doped tin oxide nanoparticles were successfully prepared using sol-gel

method. The sol gel method of preparing the sample is very easy to control. Through the XRD pattern we can clearly identifies and confirms the crystalline phase of the composition. UV-VISIBLE absorption spectrum was recorded and found the absorption of sample at a particular wavelength value. PL analysis stated that a dominant PL peak was observed at 685nm in all the samples. The emission intensity increases on doping. Sol gel method was found to be an effective and economic route for the synthesis of pure and metal doped tin oxide nanoparticles having high degree of crystallinity, homogeneity and expected elemental composition.

5. SCOPE

Tin oxide can be used as a antibacterial agent. Its anticancer study will be carried out in coming months with cancer cell line. And its water purification capacity would be tested.

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