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Structural and Dielectric Properties of Ti doped SnO_2 nanocrystals

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ABSTRACT
Pure Tin oxide (SnO_2) and titanium doped tin oxide nano crystals are synthesized by co-precipitation method. The structural and dielectric properties are characterized by using XRD, SEM and dielectric measurement techniques. XRD analysis shows that pure and Ti doped SnO_2 possess tetragonal rutile type structure. The SEM image depicts the surface morphology. The EDAX analysis confirms the elemental composition. Frequency dependence dielectric measurements are observed at 300K. The dielectric constant and dielectric loss decreases with increase in frequency. The ac conductivity is also determined.

Key words- ac conductivity, dielectric constant, dielectric loss,

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I. INTRODUCTION

The physical and functional properties of nano sized crystals differ greatly from the bulk and attract scientific and industrial applications. Tin oxide nano crystals is a wide band gap semiconductor used as functional material for optoelectronic devices, conductive electrodes [1], transparent coatings due to its good conductivity [2], transparency in the visible spectrum, dye sensitized solar cells [3], transistors [4], optical sensors [5], gas sensors [6,7], alcohol sensors [8,9], formaldehyde sensors [10], super capacitor applications [11,12]. The optical band gap of SnO_2 is 3.6 eV, and it possesses high specific capacity. It possesses good cycle performance, large reversible capacities, excellent rate performance, low discharge potential, etc., and so they are used as an anode material in rechargeable lithium-ion batteries [13].

The addition of impurity ions to the host crystal brings out change in the structure, morphology, optical, electrical magnetic properties etc. The morphology of nano particles affects both physical and chemical properties because of the change in surface area [14]. The doping of transition metal ions like Mn, Co and Fe creates a change in optical, magnetic and electrical characteristics due to the sp-d exchange interactions of the metal ions and the band electrons of the SnO_2 crystal [15,16]. In the present article Ti doped SnO_2 nano particles were synthesized by co-precipitation method and an effort has been taken to study the electric and dielectric properties.

II. MATERIALS AND METHODS

2.1 Preparation of samples

Tin oxide nano crystals are synthesized using a co-precipitation method with AR grade stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) and de-ionized water as solvent. The pH of the solution is maintained as 3 by adding aqueous NaOH (precipitating agent) drop wise. The solution thus obtained is stirred thoroughly for five hours using magnetic stirrer to form a homogenous mixture. White gelatinous precipitate is formed. The precipitate is filtered using whatmann filter paper and washed several times with de-ionized water until the effluent pH is neutral and then with ethyl alchohol to remove Cl traces. The precipitate is then calcined at 170^0C in hot air oven.

2.1.1. Preparation of Ti doped SnO_2Nano Powder

For the preparation of Titanium doped SnO_2 nano powder, 0.02M, 0.06M and 0.1M of titanium dioxide salt (TiO_2) was added to the 1M tin chloride solution and the pH is balanced as 3. The mixture was stirred well constantly for 5 hours using magnetic stirrer. The procedure adopted to prepare nano structured pure SnO_2 was used to obtain Ti doped SnO_2 nano crystals.

2.2. Characterization

The synthesized nano crystals, pure and Ti doped tin oxide nano crystals are characterized by diffractometer system, XPERT-PRO using CuKα radiation (K-Alpha = 1.5406Å) for the structural analysis and also to determine the crystallite size variation for the dopant. The surface morphology was investigated using EVO18 (CARL ZEISS) scanning electron microscope (SEM). The elemental analysis is carried out using AMETEK EDAX. The capacitance (Cp) and loss tangent of the samples are measured in the frequency range 50 Hz to 2MHz using LCR meter at temperature 300 K.

III. RESULT AND DISCUSSION

3.1. X-ray Diffraction Analysis

The determination of crystallite size and phases were carried out using X'Pert Pro X-ray diffractometer (CuKα target, =1.5406 Å). XRD data were collected in the 2theta range of 20°–80° and the diffraction pattern of pure and titanium doped SnO_2 were shown in Fig.1. The diffraction peaks are broad due to the nano size and the peaks were in harmony with JCPDS card no: 41-1445. The diffraction peaks show the tetragonal rutile structure [17]. The cell parameters a, c and cell volume V of the synthesized samples were calculated using the formula

$$1/d_{hkl}^2 = (h^2+k^2)/a^2 + l^2/c^2$$

Where, h,k,l were miller indices and d_{hkl} is the distance between two consecutive planes (m=1) with plane index (hkl). The unit cell volume of the tetragonal system are also calculated using the formula $V = a^2c$ [18]. The crystalline size, D, was estimated from the peak width with the Scherrer's formula:

$$D = (K\lambda) / (\beta\cos\theta_B)$$

Where, λ is the X-ray wavelength, β is the full width half maximum (FWHM) of a diffraction peak, θ_B is the Bragg's angle and K is the Scherrer's constant [19, 20]. The lattice parameters, cell volume, and average crystalline size of the pure and titanium doped tin oxide nano particles are given in table1. The lattice parameters of the synthesized Ti doped samples vary from the pure SnO_2. This variation is due the incorporation of Ti^{4+} ions into the SnO_2 crystal system. The number of unit cell in the crystallite is calculated using the relation $n = 3.14*D^3/ 6V$ where, D is the crystallite size, V is the volume of the crystal and the calculated values are tabulated in table1[21].

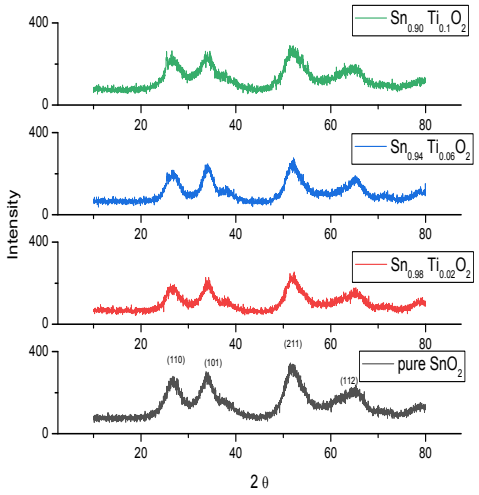


Fig.1 XRD pattern

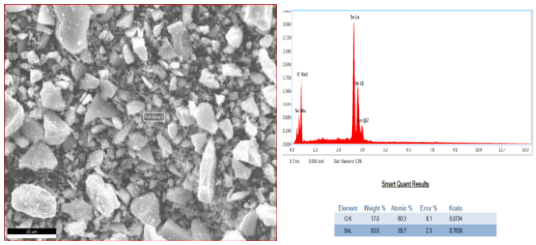
Samples	Lattice parameters A (Å)	Lattice parameters c (Å)	Cell Volume $V=a^2c$ $(Å)^3$	Crystallite size Nm	No. of unit cells in crystal	Dislocation density $=1/D^2$ Fermi
Pure SnO_2	4.70	3.16	69.9954	3.871	433	66.734
$Sn_{0.98}$ $Ti_{0.02}O_2$	4.69	3.15	69.6626	9.87	7223	10.265
$Sn_{0.94}$ $Ti_{0.06}O_2$	4.70	3.15	69.7645	13.80	19714	5.2509
$Sn_{0.90}$ $Ti_{0.1}O_2$	4.73	3.16	70.9821	18.38	45778	2.9601

Table:1 Lattice parameters

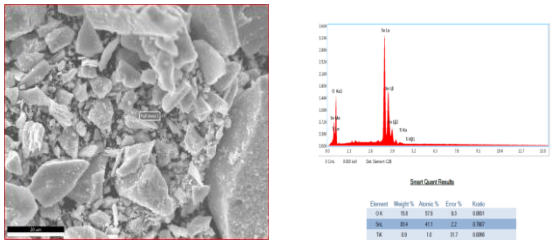
3.2. Morphological Analysis:

Fig.2 shows the SEM and EDAX images of pure and titanium doped tin oxide nanocrystals. In the case of pure tin oxide, tetragonal morphology is seen in the SEM image. As the dopant concentration increases, the tetragonal morphology transforms in to spherical. Pure and Ti doped tin oxide nano particles are stabilized in the tetragonal phase.

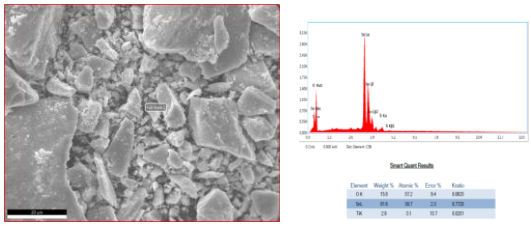
The EDAX spectrum confirms the presence of tin and oxygen of the synthesized compound which is shown in the Fig.2. The EDAX spectrum analyses very few impurities to be present and is due to repeated washing during the synthesis process. The intensity peak of oxygen is lower than that of Sn and this indicates that the oxygen atoms are desorbed. This corresponds to the increase in oxygen vacancies. The atomic weight percentages of Sn and O present in the pure SnO_2 nanocrystals are 36.4 mass% and 63.6 mass% respectively, which indicates that the synthesized SnO_2 powder is very close to the stoichiometry.



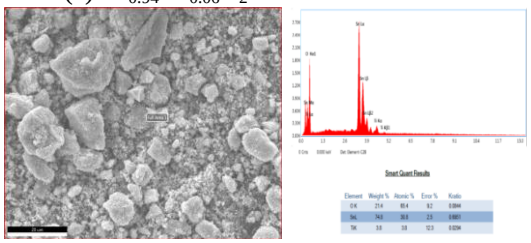
(a) Pure SnO_2



(b)$Sn_{0.98}Ti_{0.02}O_2$



(c) $Sn_{0.94}$ $Ti_{0.06}O_2$



(d) $Sn_{0.90}$ $Ti_{0.1}O_2$

Fig.2 SEM & EDAX images

The incorporation of Ti ions in the SnO_2 crystal lattice is confirmed by the corresponding peaks of EDAX spectra.

3.3. Dielectric Studies

The variations of the capacitance and the dielectric loss factor of the Ti-doped SnO_2 nano particles in the frequency range from 50Hz to 2 MHz and at 300K temperature is measured using LCR meter. The 8 mm in diameter disc shaped pellet is used to find out the capacitance. The relative dielectric constant is the characteristic of nano crystals to allow the electric flux to pass through it. The relative dielectric constant of the samples is calculated using the relation [22]

$$\varepsilon_r = Cd/\varepsilon_0 A$$

where, C the capacitance, d is the thickness of the pellet, and A the area of cross section of the sample. ε_r is the relative permittivity of the material ε_0 is the permittivity of free space (8.854×10^{-12} F/m) and the variation of dielectric constant of all the pure and doped nanocrystals $SnO_2$with frequency are exhibited in Fig.3. It is clearly observed that the dielectric constant abruptly decreases with the increase in frequency at lower frequency range and becomes almost a constant after 100 Hz. The mechanism responsible for higher value of dielectric constant at low frequency is the space charge polarization and rotation polarizabilities [23]. Since SnO_2 is an n-type semiconductor, the oxygen vacancies which acts as holes and the oxygen ions forms the dipoles. At low frequencies, these dipoles align easily with the change in the applied electric field since the atoms reside in the grain boundaries and become electrically active due to charge trapping. Moreover, these dipoles rotate which in turn is responsible for the rotation direction polarization. As the concentration of Ti is increased, the crystallite size is increased and so the dielectric constant.

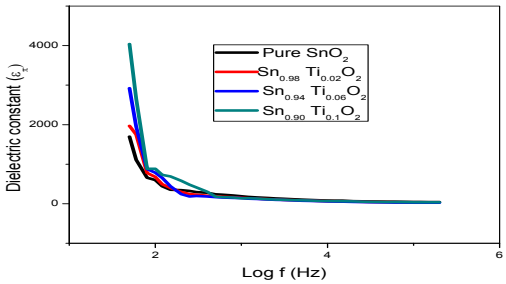


Fig.3 Dielectric constant

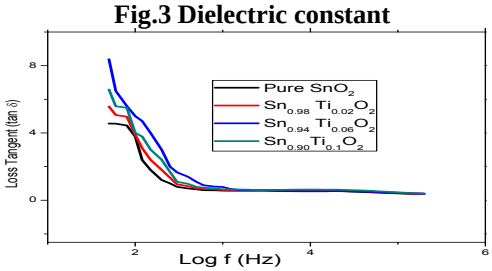


Fig.4 Dielectric loss

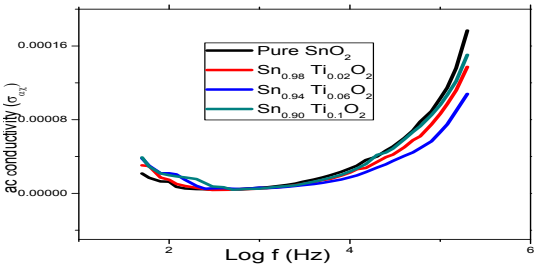


Fig.5 A.C. conductivity

The dielectric loss of the nano crystals is the energy loss when an electric field is applied across the material to be polarized and is in the form of heat. Loss tangent decreases with increase in frequency.

The ac conductivity of pure and Ti doped SnO_2 nanocrystals is calculated by using the relation:

$$\sigma_{ac} = \omega \tan \delta \, \varepsilon_0 \, \varepsilon_r$$

ω is the angular frequency and $\omega=2\pi f$, f is the frequency of applied electric field, $tan\ \delta$ is loss tangent from dielectric measurement, ε_r is the relative dielectric permittivity of the sample and ε_0 is the dielectric permittivity of vacuum (8.854×10^{-12} $C^2N^{-1}M^{-2}$)[24]. The ac conductivity increases with increase in frequency. Thus the synthesized samples can be used in high density energy storage materials [25].

IV. CONCLUSION

Pure and Ti doped SnO_2 nano particles were prepared by simple co - precipitation method. Structure and morphology of the synthesized nano particles were investigated by XRD and SEM. The Structural analysis depicts the tetragonal structure of the samples. The average crystallite size of pure SnO_2 was found to be around 3.871 nm. The crystallite size increases with increase in the concentration of Ti dopant. The dielectric studies of the pure and Ti doped samples reveals that the dielectric constant and dielectric loss decreases with increase in frequency. The ac conductivity of all the synthesized samples was calculated and the ac conductivity increases with the increase in the frequency. It is concluded that the synthesized samples can be a promising material for high density energy storage material.

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