Frequency Dependent Dielectric Response in Sr doped SnO$_2$ Nanoparticles

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Abstract. In this work, we have investigated the structural and dielectric properties of Sr doped SnO$_2$ nanoparticles synthesized via sol-gel process. Single phase tetragonal rutile structure of Sr doped SnO$_2$ nanoparticles (NPs) have been examined by X-ray diffraction. No impurity peak has been detected which signifies the purity of the prepared sample. Average crystallite size has been calculated using Scherrer’s formula and found to be 10.3 nm. Dielectric measurements have been carried out in the frequency range of 75 kHz to 5 MHz using LCR meter. Dielectric constant and loss both decrease with increase in frequency while increased in ac conductivity is observed with frequency such behaviour can be explained using Maxwell- Wagner two-layer model.

1. Introduction
Nanomaterials are much profound and functionally active due to their smaller size and large aspect ratio in comparison to the bulk material in micrometer range. Metal oxides nanomaterials have got considerable attention owing to their exceptional properties arising from their large surface area, quantum confinement effect, high annealing, etc. These properties also depend on the local structure and size of the particle. Since, the passionate research on the wide band gap semiconductor oxide nanomaterials from last few decades, still tin oxide (SnO$_2$) is a very good candidate for research. The direct gap value for bulk SnO$_2$ is 3.6 eV and its nanostructure has very high relative permittivity at low frequency [1] and can have practical application in various fields such as large energy storage material [2], highly energy storing capacitor [3], conductive film [4], dynamic RAM [5], and fabricating transparent thin film transistors [6]. With the use of appropriate dopants, the electrical, magnetic and optical properties of semiconducting oxides can be tuned. Still, the dielectric properties of the alkaline earth element doped SnO$_2$ have been less investigated.

Although, electrical properties of SnO$_2$ have significance from the industrial point of view. Non-stoichiometry, mainly defects/oxygen vacancies, makes it conducting. Oxygen vacancies and tin interstitials can be generated easily in SnO$_2$ due to its lesser formation energy as a results SnO$_2$ exhibited high electrical conductivity [7]. Electrical parameters dielectric constant and charge carrier concentration can be enhanced by the use of suitable dopants. Typically, F as an anion and Sb as a cation were previously studied for improving the conductivity of SnO$_2$ [8].
2. Synthesis Method
Sn\textsubscript{1-x}Sr\textsubscript{x}O\textsubscript{2} (x = 0.02) NPs have been synthesized via the sol–gel process. In this process, the required amount of SnCl\textsubscript{2}.2H\textsubscript{2}O and Sr (NO\textsubscript{3})\textsubscript{2} precursors were dissolved in 80 ml double distilled water to make precursor solution and stirred for 20 min. Then, 30 ml ethylene glycol was dispersed into the precursor solution. After 30 min stirring, aqueous ammonia solution was added to above solution until the pH becomes 8 under constant stirring. A white product was obtained, further the obtained solution again stirred at 80 °C for 2 h to get homogeneous sol. In order to dry the solution, sol was kept in an oven at 100 °C for 24 h. The dried powder ground for 30 min then calcined in air at 550 °C for 4 h and cooled up to room temperature to get crystalline Sr doped SnO\textsubscript{2} NPs. The structural properties of sample has been characterized by using Miniflex (Rigaku) II X-ray diffractometer with Cu-K\textsubscript{α} radiations (\(\lambda = 1.5406 \text{ Å}\)) at scan rate of 2°/min in 2θ in the span of 20-80°. Dielectric behavior of the solid sample has been studied from the frequency 75 kHz to 5 MHz with the help of LCR meter (Agilent 4284A).

3. Results and Discussion
3.1. Structural Analysis
XRD patterns of 2% Sr doped SnO\textsubscript{2} NPs has been recorded in the 20 range of (20° to 80°) and shown in figure 1(a). All the Bragg’s reflection are well indexed to rutile structure of SnO\textsubscript{2} with space group (P42/mnm), which is well matched with the standard XRD data (JCPDS No. 41-1445). No impurity peaks or other strontium-related phase are observed within the detection limit of XRD. In order to calculate crystallite size, two methods are used i.e. Scherrer [9] and Williamson-hall method (W-H) [10]. Scherrer and W-H equations are given by the following Eq. (1) and Eq. (2), respectively.

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  
(1)

\[
\frac{\beta \cos \theta}{\lambda} = \frac{k}{D} + \frac{\eta \sin \theta}{\lambda}
\]  
(2)

Where D is crystallite size, \(\eta\) is the effective strain, \(\theta\) is the glancing angle, k is shape constant (k = 0.9) and \(\beta\) stands for full width at half maxima (FWHM). From the linear fit of W-H plot as displayed in figure 1(b), the intercept on Y-axis is comes out to be 0.0137.

![Figure 1. (a) X-ray diffraction pattern of Sn\textsubscript{0.98}Sr\textsubscript{0.02}O\textsubscript{2} NPs](image)

![Figure 1. (b) W-H plot Sn\textsubscript{0.98}Sr\textsubscript{0.02}O\textsubscript{2} NPs](image)
The average crystallite size of Sn_{0.08}Sr_{0.02}O_{2} NPs is found to be 10.3 nm and 11.2 nm using Scherrer’s formula as well as (W-H) method, respectively.

3.2. Dielectric properties

In an ac field dielectric constant becomes complex and is given by

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

(3)

Where $\varepsilon^*$ is the complex dielectric constant, $\varepsilon'$ is the real part of dielectric constant which signifies the stored energy in the capacitor and $\varepsilon''$ is the imaginary factor of dielectric constant, which explains the energy dissipation in the material.

The imaginary part can be determined as

$$\varepsilon'' = \varepsilon'\tan\delta$$

(4)

figures 2(a, b) show the frequency dependent real and imaginary part of dielectric constant of 2% Sr doped SnO$_2$ NPs. One can observed from the figure that the both part of dielectric constant decreases as frequency of applied field increases. The reduction in dielectric constant with frequency is fast when frequency is low and falls slowly in high frequency region and achieved almost constant value such frequency independent nature can be understood in the light of Koop’s assumptions based on Maxwell- Wagner model [11]. The large values of electrical permittivity in the low frequencies region may be clarified considering the interfacial space charge polarization because of inhomogeneous dielectric structure.

The ac conductivity $\sigma_{ac}$ of prepared nanoparticles can be obtained using the given equation

$$\sigma_{ac} = 2\pi f_0 \varepsilon_0 \varepsilon''$$

(5)

Where $f$, $\varepsilon_0$ and $\varepsilon''$ are the linear frequency of the applied field, free space permittivity and imaginary factor of relative permittivity, respectively.

![Figures 2](image)

*Figures 2.* Variation of real (a) and imaginary (b) part of dielectric constant with frequency at room temperature.

The dielectric constant is found to be decrease with the increase in applied frequency of ac field and become frequency independent in the high frequency region as clearly displayed in figure 3(a). It is noticed that at higher frequencies the dielectric losses have low values since motion of domain wall is suppressed and magnetizing force try to change dipole rotation. It is also noticed from the plot that the higher dielectric loss occurs in the low frequency region. This trend occurs at the cost of space charge polarization in the lower frequency regime which can be understood by the Shockley-Read mechanism. Sample exhibits a loss peak in the frequency range confirming the presence of hopping resonance. This peak arises when tunnelling frequency of local charge carriers become almost equivalent to that of the external ac field [12].
Figure 3. (a) Variation of dielectric loss and (b) ac conductivity as a function of frequency at room temperature.

The ac conductivity of Sr doped SnO$_2$ NPs with respect to frequency is shown in figure 3(b). In our case the ac conductivity increases as frequency rises such behaviour occurs when hopping of charge carriers occurs between ions of the elements having more than one valence state that are randomly distributed with in the lattice sites.

4. Conclusion

Single phase Sr-doped SnO$_2$ NPs have been prepared successfully via chemical sol–gel process. The XRD spectrum shows the tetragonal rutile structure. No extra phase was detected in XRD plot. The frequency dependent dielectric behaviour of synthesized sample was shown as normal behaviour, both the relative permittivity and dielectric loss were found to be decrease with the increase in ac frequency which was described by the Maxwell–Wagner model. The ac conductivity is found to increase as applied frequency rises. The higher dielectric constant would makes it a promising materials for energy storing device.

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