Influence of Cd substitution and temperature on dielectric properties of SnO₂

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Abstract. The temperature dependence of dielectric properties of Cd-doped SnO₂ nanoparticles has been carried out successfully in the temperature range 30 to 300 °C at specific frequencies. The dielectric constant of pure and Cd-doped SnO₂ sample at selected frequency increases with increasing temperature. The loss tangent of pure and doped materials has also been examined. Ac conductivity of Cd incorporated SnO₂ samples increases with increasing temperature. Further, the activation energies at different frequencies for all samples have been estimated.

Keywords: Cd-doped SnO₂, temperature dependent dielectric properties, dielectric relaxation, activation energy.

1. Introduction:
Doping of the impurity elements in host metal oxide semiconductor nanomaterials such that TiO₂, SnO₂, NiO, CuO, ZnO etc. has been a topic of discussion and considerable task for implementation from last two decades. The reason for this interest shown by a number of the researcher is the effective and noteworthy change in the physical properties of nanostructures when doped with the other elements. For example, I khan et al.[1] depicts that the Mn content has a great impact on the trend and the magnitude of magnetic and dielectric properties of ZnO. Siddiqui et al.[2] explored that Al content strongly influences the temperature dependent dielectric parameters of Al-doped NiO nanostructures. Among all metal oxides, tin oxide (SnO₂), a wide band gap semiconductor, seemed to be very interesting material because of its tailorable electrical, dielectric and magnetic properties. For the case, It has also been reported that the magnitude of dielectric constant and the saturation magnetization of SnO₂ increases with increasing concentration of Zn[3]. It has been seen that the electrical polarization decreases and the ac conductivity increase with increasing Co content in (Zn, Co) co-doped SnO₂[4]. In a further investigation, it has been clarified that Co substituent advances the dielectric constant, dielectric loss and ac conductivity of SnO₂[5]. The enhanced dc resistivity of (Mn, Co) co-doped SnO₂ has also been discussed in the latest report[6]. Its mutable electrical and dielectric properties mark it a very pertinent material for gas sensing applications[7–9]. Thus, the inspection of the influence of the Cd concentration on the temperature dependent dielectric properties of SnO₂ may have great advantages in improved future applications.
A number of the chemical routes like sol-gel, reverse-micelle, hydrothermal, precipitation etc. have been used to synthesize host and doped nanocrystalline metal oxide semiconductors[10,11]. Precipitation route, among all the synthesis process, seemed the easiest way to prepare nanoparticles. Therefore, In the present paper, we have made an attempt to explore the temperature dependent dielectric properties of Cd-doped SnO2 nanoparticle synthesized by very convenient precipitation route. The variation in dielectric constant, dielectric loss, ac conductivity and ac activation energies of Cd-doped tin oxide nanoparticles have been studied using LCR meter. Further, the influence of the Cd content on these dielectric parameters of SnO2 at a high and low temperature is monitored and argued.

Figure 1. The real part of dielectric constant as a function of temperature

2. Sample preparation and characterization:
Pure and Cd-doped SnO2 samples were prepared through precipitation route by using AR grade SnCl2.2H2O and CdCl2 as initial precursors. Details of synthesizing technique and the results of some
characterization techniques such as X-ray diffraction measurement (XRD), Transmission electron microscopy (TEM), Diffused reflectance spectroscopy (DRS), Room temperature dielectric properties (RTDP) etc. have been discussed in an earlier report[12]. In the current study, the temperature dependent dielectric response for the same samples has been determined by using LCR meter (Agilent 4285A) at six specific frequencies (75kHz, 100 kHz, 500 kHz, 1 MHz, 2 MHz, 4.5 MHz). In order to investigate the dielectric properties as a function of temperature for pure and Cd-doped samples through aforementioned LCR meter, small circular pellets of approximately 1-2 mm thickness and 10.2 mm diameter with silver coated were made in order to design circular parallel plate capacitor symmetry.

Figure 2. The imaginary part of dielectric constant as a function of temperature

3. Results and discussion:
It had been reported earlier[12] that all the samples exhibited polycrystalline tetragonal symmetry. The average crystallite or particle size of SnO$_2$ diminished for initial 1% doping of Cd and was found to be in increasing order with increasing concentration of Cd for Sn$_{1-x}$Cd$_x$O$_2$ samples (x= 0.01, 0.03, 0.05,
The optical band gap of pure and doped materials was found between 3.76 eV and 3.97 eV. From the room temperature dielectric analysis it was recognized that the dielectric constant falls down and ac conductivity rises with frequencies for all the samples. Ac conductivity of the pure SnO$_2$ was found small compared to that of doped samples at room temperature.

Figure 3. The behavior of loss tangent of pure and Cd-doped SnO$_2$ with temperature

The complex dielectric constant $\varepsilon^*$ of the material is calculated by using the following equations:

$$\varepsilon^* = \varepsilon' - j \varepsilon''$$  \hspace{1cm} (1)

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A}$$  \hspace{1cm} (2)

$$\varepsilon'' = \varepsilon' \tan \delta$$  \hspace{1cm} (3)
Where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary contributions to the complex dielectric constant corresponds to the stored and dissipated energy respectively in the materials. $\tan\delta$ is the dielectric loss tangent, $C_p$ is the capacitance of the parallel plate capacitor, $d$ is the thickness of the pellet, $A$ is the area of the pellet and $\varepsilon_o$ is permittivity of free space ($8.854 \times 10^{-12} \text{F/m}$).

Ac conductivity of the material was evaluated by the expression:

$$\sigma_{ac} = \varepsilon_o \varepsilon' \omega \tan\delta$$

Here $\omega = 2\pi f$ is the angular frequency of the applied ac electric field.

The temperature dependence of the real and imaginary part of the dielectric constant for pure and Cd assimilated SnO$_2$ samples have been studied and shown in figure 1 and figure 2. It is observed from figure 1 and 2, at low temperature the dielectric constant exhibits very small dependence on the temperature even at high temperature regime it increases with the temperature. It may be due to the enhanced electron hopping in the materials on the absorption of extra thermal energy (provided by the high temperature) by the electrons[13]. This enhanced electronic hoping may lead to an increment in the dielectric constant of the materials at high temperature. But at low temperature region (just above room temperature) the results are just contrary. Khan et al.[1] reported that the increasing dielectric permittivity with increasing temperature may be due to lattice expansion, increased molecular mobility, and the excitation of the charge carriers present in the nanoparticles. Further, the increase in dielectric constant with temperature is observed more rapid at low frequencies viz. dielectric constant increases more quickly with temperature and the numerical values of dielectric constant is quite high at low frequencies for all the samples. Since the dielectric constant of the materials is strongly correlated to the four type of polarizations namely interfacial, ionic, dipolar (rotational) and electronic, and at high frequencies the contribution of interfacial and dipolar polarizations inhibited, the rapid increase in the dielectric constant at low frequencies with the increasing temperature may be the results of dominating dipolar and interfacial polarization. It is because this two polarizations (interfacial and dipolar) have a strong dependence on the temperature and frequency as well[3]. The interfaces of the nanomaterials have a large number of defects. On applying alternating electric field the charge carriers present in the material may be trapped by these defects and can evolve the number of electric dipoles which in turn increases the interfacial (space charge) polarizations[2]. At high temperature, the rotation of these dipoles becomes easier signifying the high polarization and hence high dielectric constant. At high frequencies, the contribution to the dielectric constant comes from ionic and electronic polarizations only which are independent of temperature. This will in turn display very small dependency of dielectric constant on the temperature at high frequencies. In 7% Cd-doped SnO$_2$ sample, a relaxation peak at high temperature in the dielectric constant is observed (figure 1 and 2) i.e. the dielectric constant of 7% Cd-doped SnO$_2$ increases until it attains a maximum value and decreases. Since the number of defects and number of charge carriers increases with doping and temperature, this relaxation peak at high temperature may be explained by Rezlescu model[14] which tells that the contribution to the electric polarization by positive and negative charge carriers are temperature dependent. The decrease in relaxation peak intensity at high frequencies may be assigned to the lack of polarization (small permittivity) which is very obvious as the frequency increases.

Temperature dependent loss tangent, which signifies the variation of dielectric loss (electrical energy loss) with temperature in the dielectric medium, is shown in figure 3. It is obvious that the increasing loss tangent with increasing temperature as the dielectric loss strongly depends on the disordering in the materials which may be the result of increasing temperature leading to an expansion in the lattice and creation of some oxygen or metal vacancies. The rapid increase of loss tangent with increasing temperature at low frequencies can be explained by Shockley read mechanism in terms of space charge polarization[15]. According to which the capturing of the surface electron increases with the temperature which leads to an increment in the loss tangent in the high temperature region at low frequencies[16]. The similar trend of dielectric loss for pure sample and highly doped (7% Cd) sample is observed. The dielectric loss of 1% Cd-doped SnO$_2$ is observed to be highest in magnitude compared to other samples.
at a specific temperature and specific frequencies which is consistent with the smallest crystallite or particle size. The dielectric loss arises in the medium when the polarization lags behind the applied ac electric field which may be caused by originated imperfections or defects. Smallest the crystallite size will enhance the imperfections like grain boundaries as a consequence of which loss tangent increases. Relaxation peaks in the dielectric loss vs temperature graphs 1%Cd, 3%Cd and 5%Cd doped SnO\textsubscript{2} samples may be assigned to the matching of the jumping or hoping frequency of the charge carriers (electrons) and the frequency applied alternating electric field. The shifts of the relaxation peaks in the aforementioned samples are often assigned to the change of the rate of the hopping of the charge carriers (electrons)[17].

![Figure 4. AC conductivity of pure and Cd-doped SnO\textsubscript{2}](image)

AC conductivity of all the samples as a function of temperature has been studied and shown in figure 4. The very typical semiconducting nature for all the samples is observed viz. ac conductivity of the materials rises with the increasing temperature. Since ac conductivity, in general, depends on the hopping or jumping of charge carriers (electrons) between ions of same elements present in more than one valence state in the crystal lattice, the number of charge carriers for hopping mechanism increases by getting thermal activation from increasing temperature. Further, it has been reported that the electrical
conductivity of the materials increases with frequencies when the hopping mechanism is dominating and decreases in the case of band conduction[1]. Usually, the total conduction in the material can be understood by the summation of band conduction and hopping conduction. The peak observed in the plot of ac conductivity in 7% Cd-doped SnO$_2$ may be attributed to a phase change of the sample from ferroelectric to paraelectric[1].

In order to estimate the ac activation energy of all the samples at specific frequencies, Arrhenius equation has to be followed:

$$\sigma_{ac} = \sigma_o \exp \left\{-\frac{E_a}{k_B T}\right\}$$ (5)

Here $E_a$ is the activation energy, $k_B$ is the Boltzmann constant ($8.61733 \times 10^{-5}$ eV/K) and $T$ is absolute temperature. A graph between $\ln\sigma_{ac}$ vs 1000/T has been plotted and displayed in figure 5. The slope of the least square fit line of the plot was used to evaluate the ac activation energy and tabulated in table 1.

The ac activation energies are found in the range of 0.245-0.332 eV for pure SnO$_2$, 0.013-0.088 eV for 1%Cd, 0.038-0.095 eV for 3%Cd, 0.011-0.039 eV for 5%Cd and 0.113-0.179 eV for 7%Cd doped SnO$_2$ samples. It is observed from table 1, the 7%Cd doped SnO$_2$ sample has the maximum values of ac activation energies among all the doped samples. The activation energy strongly depends on the mobility and transportation ability of the ions present in the materials. Thus the maximum activation energies for maximum (7%) doping concentration of Cd may be due to reduced ionic mobility prohibited by the defects and distortion which are produced by impurity ions in the crystal lattice[6]. The highest activation energy for pure SnO$_2$ may be assigned to the deficiency of immobile ions in the material.

**Table 1.** Activation energies of the pure and Cd-doped SnO$_2$ samples at different frequencies.

| Sample    | 75 kHz | 100 kHz | 500 kHz | 1 MHz | 2 MHz | 4.5 MHz |
|-----------|--------|---------|---------|-------|-------|---------|
| Pure SnO$_2$ | 0.329  | 0.277   | 0.288   | 0.255 | 0.245 | 0.332   |
| 1%Cd-SnO$_2$ | 0.088  | 0.058   | 0.045   | 0.033 | 0.018 | 0.013   |
| 3%Cd-SnO$_2$ | 0.038  | 0.038   | 0.089   | 0.094 | 0.094 | 0.095   |
| 5%Cd-SnO$_2$ | 0.013  | 0.011   | 0.018   | 0.015 | 0.033 | 0.039   |
| 7%Cd-SnO$_2$ | 0.179  | 0.156   | 0.167   | 0.142 | 0.150 | 0.113   |

4. Conclusion:

In the summary, the detailed temperature dependent dielectric properties of host and Cd-doped SnO$_2$ was investigated. Dielectric constant and dielectric loss of all the samples rose with temperature demonstrating the typical semiconducting behavior of the material. Enhanced dipolar and interfacial polarizations are found as the main contributors to the increasing dielectric constant with temperature in the materials. All the relaxation peaks in dielectric loss emphasize the frequency match between hopping and applied ac field. Ac conductivity of all the samples at specific frequencies is found to increase with temperature and the pure material display the maximum magnitude of activation energy.
Figure 5. ln\(\sigma_{ac}\) vs 1000/T plot to estimate activation energies at different frequencies
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