Optical and dielectric studies on tin(iv) tungstate nanoparticles

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Abstract. Tin(IV) tungstate nanoparticles in the form of disc were synthesized by a novel chemical coprecipitation method. Surface morphology and particle size of the synthesized materials were analysed using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). SEM image shows disc like appearance of the nanoparticles. The particle size obtained was found to be ~20nm. Optical absorption for this material arises due to O$_2p$ W$_5d$ charge transfer in the tungstate structure. The energy band gap determined using optical absorption spectrum shows that it is a direct band gap semiconductor. The extent of disorder determined using Urbach plot was found to be 0.00176 meV. The material showed intrinsic Photoluminescence around 468nm when excited by UV light of 275nm. The variation of dielectric permittivity in the frequency range 316 Hz to 3.16 MHz was studied. The temperature dependence of dielectric permittivity was also studied in the frequency range 10Hz and 32 MHz. The compound exhibit a high dielectric constant at room temperature ($\varepsilon_r>10^3$) for frequencies 10Hz and ($\varepsilon_r>10^5$) for frequencies 3.2x10$^7$ Hz. It posses lower dielectric loss ie, ~0.1 at 10 Hz to ~3 at 3.2x10$^7$ Hz. The material is very attractive for potential application provides its losses can be minimized.

1. Introduction
Nanodielectrics are the subject of study related to dielectric phenomena of nanoscale materials having morphology of particles, sheets, wires, tubes etc. These materials have enormous scope in power electronics industry, as gate electrodes, capacitors, sensors, electrochemical transducers, fuel injectors for automobile engines etc [1,2,3,4]. The dielectric properties and electrical transport in nanostructured materials differ from micron sized materials due to increase in interfacial atoms or ions and sinking of large amount of defects at or near the grain boundaries. The interfaces of the nanoparticles act as capacitor, thus changing the dielectric permittivity of the materials [5].

Nowadays, there is constant effort for miniaturization of electronic components, which demands the search for new materials with high dielectric constant [6]. The studies on the effect of frequency in the dielectric behavior and ac conductivity give valuable information about the conduction phenomena in nanostructured materials. In this paper, we report the dielectric properties of tin(IV) tungstate nanoparticles synthesized by chemical co-precipitation method. The microstructure and morphological characterizations were carried out using SEM and AFM. The optical absorption spectrum of the material was used to determine the optical energy band gap and the Urbach energy which defines the extent of disorder in the material. The frequency dependence of dielectric properties in the frequency range 316 Hz to 3.16 MHz was studied.
2. Experimental

Tin(IV) tungstate nanoparticles were synthesized and characterized by chemical coprecipitation method as reported earlier [7]. The microstructure of the prepared tin(IV) tungstate was investigated by scanning electron microscopy (JOEL model JSM-6390LV Instrument). The morphology of the nanocrystallites were analysed by AFM taken using NTEGRA (NT MDT) NSG 10 model AFM instrument by contact mode. The absorption spectrum of the tin(IV) tungstate nanoparticles was recorded at room temperature using SHIMADSU UV-2550 UV-Vis spectrophotometer in the wavelength range 200-800 nm. The photoluminescence spectrum of the material was recorded using Fluorolog Spectrophotometer using UV radiation of 275nm excitation wavelength and emission was recorded in the range 300-550nm. The dielectric permittivity measurements were carried out using HIOKI 3532-50 LCR Hi tester in the frequency range 316 Hz to 3.16 MHz.

3. Results and Discussion

3.1 Microstructure Analysis

The microstructural aspects of the nanoparticles of tin(IV) tungstate studied by SEM using an accelerating potential of 25kV is shown in Figure 1. In this case, the particles appear as agglomerates made of tiny crystals of nanodimension. The aggregation of nanoparticles occurs during synthesis and processing and this result in the development of discs. The morphology obtained by AFM shown in Figure 2 reveals the nanosized formation of the prepared material and the particles are more or less spherical in shape. The particle size obtained is ~20 nm.

3.2 Optical Studies

Figure 3 shows the optical absorption spectrum of tin(IV) tungstate nanoparticles in the UV-Vis range. The absorption increases almost vertically when the wavelength is below 240 nm. The characteristic absorption arises due to the $\text{O}^{2p}_{2p} \rightarrow \text{W}^{5d}_{5d} \text{O}^{2p}_{2p}$ charge transfer in the tungstate structure.

According to Tauc relation, the absorption coefficient ($\alpha$) and the photon energy $h\nu$ are related as,

$$\alpha \propto (h\nu)^{1/n} = B(h\nu - E_g)$$

where $B$ is a constant, $E_g$ is the band gap, $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy. The values of $n$ for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions are respectively $\frac{1}{2}$, 2, $\frac{3}{2}$ and 3 [8,9,10]. The direct allowed band gap of this material is obtained by plotting a graph of $(h\nu)^2$ versus $h\nu$ as shown in Figure 4. The extrapolation of the straight line portion to the $(h\nu)^2 = 0$ axis gives the value of optical energy band gap which is found to be ~4.9eV.
The Urbach energy is commonly used to characterize the degree of disorder in amorphous and crystalline systems. The Urbach energy or band tails are developed in the material due to the potential fluctuations of energy levels in the material which extended into the band gap and thus show an exponential behavior. The band tails are characterized by band tail parameter, the Urbach energy ($E_u$), which is given by the inverse of the slope of $\ln \alpha$ versus $h\nu$ graph (Figure 5) at the lower energy region [11]. The value of $E_u$ for this material is found to be 0.00176 meV. This indicates that the material is disordered due to substitutional defects or oxygen vacancies. This results in the formation of large number of energy levels inside the band gap. This leads to the formation of large band gap in this material [12].

3.3 Photoluminescence Studies

As shown in Figure 6, the material exhibits photoluminescence spectra around 425-525nm up on excitation of the sample with UV radiation of wavelength 275nm. A blue broad emission band located at 468 nm (2.65 eV) is observed, and it is apparent that the broad peak is the result of the convolution of more than one emission lines. These lines arises from the self trapped and localized excitons of the tungstate group [13,14].

3.4 Frequency dependence of dielectric studies

Fig.6 PL of tin(IV) tungstate nanoparticles
Fig.7 Variation of dielectric constant and loss factor ($\tan \delta$) with log frequency
Fig.8 Variation of ac conductivity with log frequency of tin(IV) tungstate nanoparticles
The variation of dielectric constant ($\varepsilon'$) and the loss factor (tan $\delta$) with frequency measured in the range 316 Hz to 3.16 MHz at room temperature for tin(IV) tungstate nanoparticles as a function of log frequency at 300K is shown in Figure 7. The dielectric constant decreases with increase in frequency and remains almost constant at high frequency region. The dielectric constant and loss factor are found to be $1\times10^5$ and 5.2 respectively at 316 MHz. The high value of dielectric constant is because the nanocrystalline grains behave as nanodipoles under the application of voltage. Since the grains are nanometer ordered, the number of grains per unit volume increases and hence the dielectric constant increases [15]. The dielectric loss observed for this material is low compared to the high value of dielectric constant.

Figure 8 shows the variation of ac conductivity as a function of frequency. It is seen from the figure that the ac conductivity increases with increase in frequency. The increase in ac conductivity with increase in frequency is due to accumulation of charge carrier at the boundaries [16]. In most of the disordered solids, ac conductivity is directly proportional to frequency and it results from small polaron hopping [17]. The increase in frequency of the applied field enhances the hopping of charge carriers resulting in increase of conductivity and decrease of resistivity. At higher frequencies, ac resistivity decreases and remains constant because hopping can no longer follow the applied field [16].

4. Conclusion
Morphological studies of the tin(IV) tungstate were carried out using SEM and AFM. Optical study shows absorption characteristics of $O_2p\rightarrow W_{4d}$-$O_2p$ charge transfer in the tungstate structure. The UV-Vis spectrum analysis revealed that the material is a wide band gap ($E_g = 4.9\text{eV}$) direct transition semiconductor at room temperature. The exponential band tail in the compound is due to existence of defects or disorders. The photoluminescence spectra exhibited by this material as intense blue luminescence when excited by UV light of 275nm is a promising result for various scintillation applications. The material is found to have high value of dielectric constant with low dielectric loss. The material shows fairly high value of ac conductivity. The dielectric constant of tin(IV) tungstate shows only small variations with change in frequency and temperature in the high frequency region, which is desirable for technological applications.

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