CHAPTER 3

ELECTRICAL, OPTICAL AND HIGH PRESSURE STUDIES
OF Mn-DOPED SnO$_2$ NANOPARTICLES

3.1 INTRODUCTION

Tin dioxide (SnO$_2$) is an attractive n-type wide bandgap ($E_g = 3.6$ eV at 300 K) semiconductor. It has been a rutile-type tetragonal structure. Numerous investigations have been performed on the pure and doped SnO$_2$. Electronic structure of the material is responsible for most of its observable properties. The atomic surface geometries, driven by the energy minimization of the electronic configuration, present a variety of structures in different materials. This is due to lower symmetry at the surfaces as compared with the bulk. These surface phenomena include relaxation, reconstruction and even larger rearrangements like surface diffusion or reactions with the gas atmosphere. In the case of ionic compound materials these phenomena may appear to be exceptionally strong and have to be included in a proper calculation of the electronic structure (Rantala et al 2000).

Figure 3.1 shows, the rutile-type crystal structure of SnO$_2$. Rutile has tetragonal $4hD^{14}$ symmetry. It is a non-symmorphic crystal with two formula units per unit cell. Atomic positions are determined by the c/a ratio and the internal parameter $u$ (Wyckoff 1963). The cations are at $(0\ 0\ 0)$ and $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ and are surrounded by a distorted octahedron of anions at $\pm(\ u\ u\ 0)$ and $\pm(\frac{1}{2} + u, \frac{1}{2} - u, \frac{1}{2})$. Each cation has two anions at $d_1 = (2)^{1/2}ua$ and four at $d_2 = [2(\frac{1}{2} - u)^2 + (c/\ 2a)^2]^{1/2}a$. These bond lengths are equal if $u$ takes the
special value: \( u^* = \frac{1}{4} [1 + \frac{1}{2} (c/a)^2] \). The octahedral coordination is ideal if \( (c/a) = 2u = 2 - (2)^{1/2} \).

Tin dioxide (SnO\(_2\)) is an ionic compound, which is generally used in gas sensing applications due to its environment dependent surface chemistry. The ‘oxygen chemistry’ at the grain surfaces of the porous SnO\(_2\) material is strongly dependent on the surrounding gas atmosphere and it is reflected in the easily measurable electric conductance (Lantto and Golovanov 1995).

It possesses many unique chemical, electronic and optical properties. It is advantageous in several applications, such as solar cells, catalysis and gas-sensing applications (Vaishanv et al 2006, Hays et al 2005, Heo et al 2004). It is essential to have a deep understanding of crystal structure, surface area, grain boundary and impurity effect of pure and doped SnO\(_2\) powder (Hongyan Miao et al 2003). However, crystalline materials have a dispersion of permittivity of a frequency independent behaviour at low frequency region and it exhibits a frequency dependent behaviour at higher frequencies. The universal behaviour of the ac conductivity has been extensively studied for various materials like ionically conducting glasses, amorphous semiconductors, electron conducting polymers, ionically conducting polymers, transition metal oxides. Among these, SnO\(_2\) often employed for ac conductivity studies in crystalline form (Roling 1998, Padma and Mahadevan 2008, Chandra Bose et al 2003).

Size dependent properties are one of the essential aspects to explore the novel characteristics of the materials. In particular, the electrical properties of nanoscaled materials have attracted much interest in recent years because of its unique size dependent nature. Moreover, the grain property and grain boundary effect lead to the variation of conducting nature in materials (Maity et al 2006, Radheshyam Rai et al 2006). Impedance spectroscopy is one
of the essential tools to identify the electrical properties of a material as a function of frequency. Many methods have been employed for producing SnO$_2$ nanoparticles. Amongst, chemical method yields nanocrystalline samples with uniform size, high quality and chemical homogeneity by controlling the physical and chemical parameters (Ararat Ibarguen et al 2007, Chandradass and Ki Hyeon Kim 2010).

![Figure 3.1 Crystal structure of SnO$_2$](image)

Manganese combined with other elements is widely distributed in the Earth’s crust. Manganese is second only to iron among the transition elements in its abundance in the Earth’s crust; it is roughly similar to iron in its physical and chemical properties but is harder and more brittle. Wide variety of compounds formed by manganese, the most stable occur in oxidation states +2, +6, and +7. These are exemplified, respectively, by the manganous salts (with manganese as the Mn$^{2+}$ ion), the manganates (MnO$_4^{2-}$), and the permanganates (MnO$_7^{4-}$). As in the case of titanium, vanadium, and chromium, the highest oxidation state (+7) of manganese corresponds to the total number of 3d and 4s electrons. Manganese in oxidation state +7 is powerfully oxidizing, usually being reduced to manganese in the +2 state. The
intermediate oxidation states are known, but, except for some compounds in the +3 and +4 states, they are not particularly important.

The principal industrial compounds of manganese include several oxides. Manganous oxide, or manganese monoxide is used as a starting material for the production of manganous salts, as an additive in fertilizers, and as a reagent in textile printing. It occurs in nature as the green mineral manganosite. It also can be prepared commercially by heating manganese carbonate in the absence of air or by passing hydrogen or carbon monoxide over manganese dioxide. The most important manganese compound is manganese dioxide, in which manganese is in the +4 oxidation state, and the black mineral pyrolusite is the chief source of manganese and all of its compounds. It is also widely used as a chemical oxidant in organic synthesis. Manganese dioxide is used as the cathode material in electric dry cells. It is produced directly from the ore, although substantial amounts are also prepared synthetically. The synthetic oxide is prepared by decomposition of manganous nitrate; by reaction of manganous sulfate, oxygen, and sodium hydroxide; or by electrolysis of an aqueous solution of manganese sulfate.

Pure manganese produced electrolytically is used mostly in the preparation of nonferrous alloys of copper, aluminum, magnesium, and nickel and in the production of high-purity chemicals. Practically all commercial alloys of aluminum and magnesium contain manganese to improve corrosion resistance and mechanical properties. Manganese has been a very good optical property, doped with metal oxides, composites then significantly improved their optical properties (Shinde et al 2006, Li et al 2009). It has been doped with some metal oxide and metal sulfides then gives a very good magnetic property. In low temperature, Mn-doped material behaves a ferromagnetic nature (Ma et al 2006). Mn-doped materials are improved their electrical, dielectric properties. Now a days, manganese dopant material used in lithium
batteries for storage devices (Zhang and Oyanagi 2008). In this chapter, Mn-doped with SnO$_2$ nanoparticles then electrical, optical, dielectric, high pressure properties were investigated.

3.2 EXPERIMENTAL DETAILS

This chapter describes the synthesis and electrical, optical and high pressure studies of Manganese (Mn) doped SnO$_2$ nanoparticles. The samples were prepared through the simple co-precipitation method. The associated structural, electrical, optical, dielectric and high pressure electrical resistivity studies of the nanoparticles as a function of dopant concentrations have been systematically studied. X-ray powder diffraction reveals that all samples have the tetragonal system of SnO$_2$ and the lattice parameter analysis indicated the dopant ions may be substitute into the lattice position of the parent atom. In addition of the dopant atoms result the enhanced optical, electrical, dielectric and high pressure studies.

Pure and Mn-doped SnO$_2$ nanoparticles were prepared by co-precipitation method. Pure SnO$_2$: 0.1 M SnCl$_2$.2H$_2$O dissolved in deionized water was used as precursor solution. Precipitation was done by slowly adding 8 M aqueous ammonium solution until pH value reaches 10 with constant stirring, followed by repeated washing with de-ionized water to remove the by-products. After filtration, the precipitate was washed several times and dried in an oven at 80°C for 12 hrs. The dried precursor was calcined at 600°C for 3 hrs in air atmosphere. Manganese doped SnO$_2$: The requisite amount of the starting raw materials SnCl$_2$.2H$_2$O and MnCl$_2$.4H$_2$O were weighed depending on the percentage of dopant (4 mol %, 6 mol % and 8 mol %) and dissolved into deionized water. The precipitation was achieved by slowly adding aqueous ammonium solution (8 M) with the constant stirring until the pH value reaches 10. The final product was washed several
times with deionized water to remove any possible by-products. The filtrate was initially dried at 80°C for 12 hrs and calcined in the temperature range of 600°C for 3 hrs in air atmosphere.

3.3 RESULTS AND DISCUSSION

3.3.1 Structural and Morphological Analysis

Figure 3.2 shows the X-ray powder diffraction patterns of pure and Manganese doped SnO$_2$ nanoparticles. All the diffraction peaks are well assigned to the tetragonal system of SnO$_2$ with a standard reference pattern (JCPDS # 41-1445). It is noteworthy that no diffraction peaks corresponding to Mn oxides and it indicates that increase the dopant concentration of Mn the peak shifted towards the higher angle. The observation of peak broadening is due to the occurrence of smaller crystalline size of SnO$_2$ nanoparticles. As the Mn content increases, the intensity of XRD peaks decreases and which shows the degradation of crystallinity. This means that Mn doping in SnO$_2$ produces crystal defects around the dopants and the charge imbalance arisen from this defect changes the stoichiometry of the materials (Tian et al 2008).

The crystalline sizes were estimated from the Scherrer’s relation (Taylor 1961). It indicates that increase the dopant concentration of Mn, the average crystalline size also increased. The lattice parameters were determined using the XRDA software for all prepared samples. Furthermore, the peak position shifts to higher angle with the increase in Mn content, revealing the changes in lattice parameter values. A slight variation in the unit cell parameters is observed with an increase in dopant concentration, which indeed indicates that the doped atoms substitute into the lattice sites of parent atoms. Table 3.1 shows the obtained crystallite size of the samples calculated by Scherrer’s relation. It indicates that crystallite size increases with the
increasing the dopant concentration of Mn. The lattice parameter decreases with the increasing the dopant concentration of Mn.

Figure 3.2  X-ray powder diffraction patterns of pure and Mn-doped SnO$_2$ nanoparticles (CuK$_\alpha$ radiation is used)

FTIR spectrum of pure and Mn-doped SnO$_2$ nanoparticles is shown in Figure 3.3. There are three peaks observed at around 671 cm$^{-1}$, 1628 cm$^{-1}$, 3460 cm$^{-1}$ for pure SnO$_2$ nanoparticles. The peak at 671 cm$^{-1}$ can be assigned to the stretching vibration of the O–Sn–O bond formed by oxolation reactions. A weak bond at 1628 cm$^{-1}$ is attributed to the deformation mode of OH groups. The peak at 3460 cm$^{-1}$ corresponds to the OH vibrational mode (Xiong et al 2003). The formation of OH bond due to presence of atmospheric hydroxyl radicals. It has also been attributed that, the increase in Mn content causes the small shift in wavenumber to lower region.
Table 3.1 Summary of pure and Mn-doped SnO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle Size (nm)</th>
<th>Lattice parameters (Å)</th>
<th>Bandgap value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>Pure SnO$_2$</td>
<td>11</td>
<td>4.722</td>
<td>3.172</td>
</tr>
<tr>
<td>4mol% Mn/SnO$_2$</td>
<td>12</td>
<td>4.660</td>
<td>3.144</td>
</tr>
<tr>
<td>6mol% Mn/SnO$_2$</td>
<td>13</td>
<td>4.668</td>
<td>3.198</td>
</tr>
<tr>
<td>8mol% Mn/SnO$_2$</td>
<td>14</td>
<td>4.673</td>
<td>3.150</td>
</tr>
</tbody>
</table>

Figure 3.4(a) and 3.4(b) shows the SEM images of 4 mol%, 8 mol% Mn-doped SnO$_2$ nanoparticles respectively. It is observed that the particles are spherical in shape and uniformly dispersed on the surface. There are small agglomerated particles and this might be due to the lower calcination temperature.

Figure 3.3 FTIR spectra of pure and Mn-doped SnO$_2$ nanoparticles
3.3.2 Optical Absorption Analysis

The optical properties of pure and Mn-doped SnO$_2$ samples were characterized by UV-vis diffuse reflectance spectroscopy. Figure 3.5 shows the UV-vis absorption spectra of pure and Mn-doped SnO$_2$ nanoparticles. It is observed that the absorption edge shifts towards the higher wavelength side with the increase in dopant concentration. The bandgap ($E_g$) was determined by extrapolating the rising part of the absorption peak. The estimated bandgap values for pure and Mn-doped SnO$_2$ nanoparticles were tabulated in Table 3.1. A significant decrease in bandgap is observed with respect to increase in doping concentration.
Figure 3.5  UV-vis absorption spectra of pure and Mn-doped SnO$_2$ nanoparticles

3.3.3 Impedance Analysis

The electrical behavior of SnO$_2$ nanoparticles has been studied over a wide range of frequencies at room temperature using ac technique of complex impedance spectroscopy. This technique is widely used to separate the resistive and capacitive components of electrical parameters and hence provides a clear picture of the features of the material. When the impedance data of materials having capacitive and resistive components is plotted in a complex plane plot it appears in the form of a sequence of semicircles representing electrical phenomenon due to bulk (grain) material, grain boundary and interfacial phenomenon. Generally, the grains are effective in high frequency region while the grain boundaries are effective in low frequency region. Thus the semicircle appearing in the high frequency region corresponds to grain contribution while in low frequency region corresponds to the grain boundary contribution (Diaz-Flores et al 2003). The electrical
characteristic of a material is exhibited by the appearance of semicircular arcs in Nyquist plots. Figure 3.6 shows the complex impedance plots of pure and 4mol%, 6mol%, 8mol% Mn-doped SnO$_2$ nanoparticles. It is evident that all the samples show single semicircular behavior, which suggests the predominance of grain boundary resistance over the grain resistance in these samples. It is observed that, the diameter of the semicircle increases with the increase in dopant concentration referring to pronounced decrease in electrical conduction. Based on the semicircle, the resistance $R$ and capacitance $C$ are determined from the diameter and frequency of the semicircle-maximum respectively. Otherwise, increase in dopant level cannot enhance the electrical conductivity of the material at the nanoscale level. At higher frequency region the semicircle is attributed to the grain property of the materials, which may be due to the parallel combination of resistance and capacitance of the materials. However, the electrical response of material can be broadly depends on the structure, composition, particle size and impurities (Smilja Markovic et al 2009, Irvine et al 1990, Byeon et al 1997).

![Complex impedance plots of pure and Mn-doped SnO$_2$ nanoparticles](image)

Figure 3.6 Complex impedance plots of pure and Mn-doped SnO$_2$ nanoparticles
3.3.4 AC Conductivity

Figure 3.7 shows the electrical ac conductivity of pure and Mn doped SnO$_2$ nanoparticles with frequency at room temperature. The ac conductivity increases with the increase in frequency for all compositions. Total conductivity of the system is given by $\sigma = \sigma_0(T) + \sigma(\omega, T)$. Here, first term on R.H.S is dc conductivity which is independent of frequency. The second term is pure ac conductivity due to the electron hopping between the metal ions. It has been observed that ac conductivity gradually increases with the increase in frequency of applied ac field because the increase in frequency enhances the electron hopping frequency. It can also be seen from the Figure 3.7 that ac conductivity decreases with the increase in dopant concentration. It may be attributed to the fact that the dopants of Mn$^{+3}$ introduce the defect ions (such as tin interstitials and oxygen vacancies) in SnO$_2$ system. These defects tend to segregate at the grain boundaries due to the diffusion process resulting from sintering and cooling processes. Thus, the increase in dopant concentration increases the concentration of defect ions which facilitates the formation of grain boundary defect barrier leading to the blockage of flow of charge carriers. This in turn decreases the conductivity of the system (Ameer Azam et al 2010).

Figure 3.7 AC conductivity of pure and Mn-doped SnO$_2$ nanoparticles with frequency at room temperature
3.3.5 Dielectric Constant

Figure 3.8 shows the dielectric constant of pure and Mn doped SnO$_2$ was measured as a function of frequency at room temperature, which describes the dissipated energy. It can be seen from Figure 3.8 that the dielectric constant decreases with the increase in frequency and becomes almost constant at high frequencies. The dielectric constant is decreases with increasing the Mn dopant Concentration. The dielectric constant has been suddenly dropped at lower frequencies. This behavior can be explained using Maxwell–Wagner interfacial model (Prodromakis and Papavassiliou 2009). According to this model, a dielectric medium is considered to be composed of double layers, well conducting grains which are separated by poorly conducting grain boundaries. Under the application of external electric field, the charge carriers can easily migrate the grains but are accumulated at the grain boundaries. This process can produce large polarization and high dielectric constant. The higher value of dielectric constant can also be explained on the basis of interfacial/space charge polarization due to inhomogeneous dielectric structure. The inhomogeneties present in the system may be porosity and grain structure. The polarization decreases with the increase in frequency and then reaches a constant value due to the fact that beyond a certain frequency of external field the hopping between different metal ions (Sn$^{+4}$, Sn$^{+2}$, Mn$^{+3}$ and Mn$^{+4}$) cannot follow the alternating field. It has also been observed that the value of dielectric constant decreases with the increase in Mn dopant. It may be due to the small dielectric polarizability of manganese ions compared to tin ions (Shannon 1993). Hence, as the dopant concentration increases more tin ions will be substituted by manganese ions and thereby decreasing the dielectric polarization, which in turn decreases the dielectric constant.
3.3.6 Dielectric Loss

Dielectric loss represents the energy dissipation in the dielectric system. Figure 3.9 shows the variation in dielectric loss factor with frequency at room temperature. It has been observed that dielectric loss decreases with the increase in frequency for all the compositions, which may be due to the space charge polarization. It can also be seen that dielectric loss decreases with the increase in dopant concentration and become very low value at high frequency region, which shows the capability of these materials to be used in high frequency device applications (Ameer Azam et al 2010).
Figure 3.9 Dielectric loss plot for pure and Mn-doped SnO$_2$ nanoparticles

3.3.7 High Pressure Electrical Resistivity

Figure 3.10 shows the high pressure electrical resistivity studies for pure and Mn-doped SnO$_2$ nanoparticles. The maximum pressure is applied up to 8 GPa. The observed relative resistivity value of the pure SnO$_2$ sample is decreases with increasing the pressure. The change in the electrical resistivity at lower pressures is larger while at higher pressures the decrease in resistivity is small. It indicates that increasing the pressure, the pure SnO$_2$ material goes to metallic nature. The dopant concentration of Mn increases the relative resistivity of the materials also increases. Compared to pure SnO$_2$, the relative resistivity of Mn dopant materials are very high. It indicates that increasing the dopant level of Mn, the relative resistivity increases with the increase of pressure. It is moreover, that the materials behaves an semiconducting property in increasing the pressure. It corresponds well to the anomalous
behavior in elastic constants under pressure. These results suggest that there remains a short-range order and local strain distributed throughout the sample, which results in the anomalous properties (Ishidate et al 1998, Mori et al 2002).

![Graph](image)

**Figure 3.10** Pressure induced electrical resistivity of pure and Mn-doped SnO$_2$ nanoparticles

### 3.4 CONCLUSION

It observed that it is possible to produce Mn-doped SnO$_2$ using co-precipitation method. Increasing the dopant level of Mn concentration, the crystallite size also increases. A slight variation in the unit cell parameters is observed with an increase in dopant concentration, which indeed indicates that the doped atoms substitute into the lattice sites of parent atoms. In impedance spectroscopy, all the samples show single semicircular behavior, which suggests the predominance of grain boundary resistance over the grain
resistance in these samples. It is observed that, the diameter of the semicircle increases with the increase in dopant concentration referring to pronounced decrease in electrical conduction. At higher frequency region the semicircle is attributed to the grain property of the materials, which may be due to the parallel combination of resistance and capacitance of the materials. However, the electrical response of material can be broadly depends on the structure, composition, particle size and impurities. The ac conductivity decreases with the increase in dopant concentration. It may be attributed to the fact that the dopants of Mn$^{3+}$ introduce the defect ions (such as tin interstitials and oxygen vacancies) in SnO$_2$ system. These defects tend to segregate at the grain boundaries due to the diffusion process resulting from sintering and cooling processes.

The dielectric constant has been suddenly dropped at lower frequencies. According to Maxwell–Wagner interfacial model, a dielectric medium is considered to be composed of double layers, well conducting grains which are separated by poorly conducting grain boundaries. Under the application of external electric field, the charge carriers can easily migrate the grains but are accumulated at the grain boundaries. This process can produce large polarization and high dielectric constant. The higher value of dielectric constant can also be explained on the basis of interfacial/space charge polarization due to inhomogeneous dielectric structure. The inhomogeneties present in the system may be porosity and grain structure. Therefore, the Mn dopant concentration increases more tin ions will be substituted by manganese ions and thereby decreasing the dielectric polarization, which in turn decreases the dielectric constant.

Dielectric loss of the pure and Mn-doped SnO$_2$ samples has been observed that decreases with the increase in frequency. It may be due to the interfacial/space charge polarization effect. In other words, the dielectric loss
is inversely proportional to frequency, which causes a reduction of dielectric loss with the increase in frequency. At higher frequencies, these materials exhibit a constant dielectric loss behaviour which suggests that these samples possess a lossless nature. This suggests that, these materials to be utilized in high frequency device applications. The high pressure electrical resistivities of pure and Mn-doped nanoparticles are investigated. The dopant concentration of Mn increases the relative resistivity of the materials also increases. Compared to pure SnO$_2$, the relative resistivity of Mn dopant materials are high. It indicates that increasing the dopant level of Mn, the relative resistivity increases with the increase of pressure. It is noteworthy, that the semiconducting property observed in increasing the pressure. It corresponds well to the anomalous behavior in elastic constants under pressure.