Chapter: 2

Preparation and Characterization Techniques

In this chapter, the fundamentals and the theory behind the experimental techniques used in the present work are briefly described. It begins with the brief introduction to the methods used for the synthesis of nanoparticles and thin films followed by characterization techniques used for investigating different properties of prepared samples.
2.1. Synthesis of Nanoparticles

There are various methods known for the synthesis of metal oxide nanoparticles such as solid-state reaction [2.1], hydrothermal method [2.2], co-precipitation [2.3], sol gel [2.4] etc. In the present work, two types of wet chemical methods were used for the synthesis of transition metal (TM) doped SnO$_2$ nanoparticles which are discussed as follows.

2.1.1. Citrate-gel synthesis route

The most attractive advantages of this method include processing at low temperature, mixing at the molecular level and fabrication of novel materials. This process involves various steps:

i) **Mixing of required reagents:** Dissolving high purity (99.9% ‘AR’ grade) nitrates or chlorides into deionized water with appropriate stoichiometric mixtures and mixing it with citric acid aqueous solution in 1:1 M ratio.

ii) **Formation of Gel:** The above solution was kept on magnetic stirrer at 60°C with constant stirring until the gelation starts and the solution becomes viscous and the transparency of the solution is lost.

iii) **Drying of Gel:** The gel formed was dried at 100°C for 19 hours followed by grinding for half an hour. The powder formed was heated for 36 hours at 400°C to remove any organic material present. The rate of heating and cooling was maintained same, *i.e.* 1°C per minute and was finally ground for half an hour.

iv) **Pelletization:** This is achieved by using die-press technique in which a die of proper shape was filled with calcined powder and pressed using hydraulic pressure of 5 tons. In our case, pelletization was carried out using a circular shaped dye of 12 mm and 10 mm diameter. The thickness of the pellets were maintained ~ 1 to 4 mm. Silver coating was done on opposite faces of the pellet to make it as a parallel plate capacitor of DMS material as a dielectric medium and for resistivity measurements contacts were made using silver.
paste on the same face. Figure 2.1 shows the flow chart used for the preparation of samples.

![Flow chart used for the preparation Sn_{1-x}TM_xO_2 nanoparticles.](image)

**Figure 2.1:** Flow chart used for the preparation Sn_{1-x}TM_xO_2 nanoparticles.

### 2.1.2. Solution combustion method

Solution combustion method (SCS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of nanosized materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers and fuels. This process not only yields nanosized oxide materials but also allows uniform doping of trace amounts of rare-earth and transition impurity ions [2.5].
Figure 2.2: Flow chart used for the preparation of SnO$_2$ nanoparticles.

The various advantages of adopting combustion synthesis route are:

i) Self-purifying feature due to high temperature involved.

ii) The possibility of obtaining products in the desired size and shape.

iii) Simple and cost effective.

iv) Homogenous and very fine crystalline nanopowders without the intermediate decomposition and calcination steps which other conventional synthesis route require.

The fuel used was citric acid (C(OH)(COOH)(CH$_2$.COOH)$_2$.H$_2$O) and the precursor material used for the synthesis was stannous chloride (SnCl$_2$.2H$_2$O). Citric acid possesses a high heat of combustion and thus plays an important role of organic fuel and
it provides a platform for redox reaction to occur between the reactants during the course of combustion. Around 3 grams of sample obtained using solution combustion method was kept for further characterization, the rest as-synthesized SnO$_2$ nanoparticles were annealed at 500-1300 °C for 2 hours, in ambient conditions and later characterized using different techniques. Figure 2.2 shows the flow chart used for the preparation of samples.

2.2. **Thin Film Deposition**

Thin film deposition holds a major key for technological applications ranging from razor blade coatings to quantum-well lasers. Continuous demand improved quality and sophistication for solid state devices has resulted in a rapid evolution of deposition technology. Also, thin films offer better fundamental understanding of materials which leads to expanded applications and new design of devices that incorporate these material ions [2.6]. Pure and doped SnO$_2$ thin films can be deposited by various techniques including chemical vapor deposition (CVD) [2.7-2.8], magnetron sputtering [2.9], thermal evaporation [2.10] and pulse laser deposition (PLD) [2.11]. However, among the various techniques PLD has superiority over other techniques in terms of ease of thickness control, reasonable deposition rate, preservation of stoichiometry of films and is generally deposited at low substrate temperature. In the present work, SnO$_2$ thin films were deposited on Quartz substrate using pulse laser deposition (PLD) technique. This technique is among the best technique for thin film deposition and is briefly described below.

2.2.1. **Pulse Laser Deposition (PLD) technique**

Pulse laser deposition (PLD) or the laser ablation deposition (LAD) is a versatile technique and is being routinely used to deposit a wide range of materials. This technique was first used by Smith and Turner [2.12] in 1965 for the deposition of semiconductors and dielectric thin films and was later established in 1987 due to the work of Dijkkamp and coworkers [2.13] on high temperature semiconductors [2.14]. Since then this deposition technique has been intensively used for depositing thin films of all kind of oxides, nitrides or carbides and also for preparing metallic systems and even polymers. In this technique, a high power laser ($10^6$ – $10^8$ W) is used to evaporate target for the
surface. Excimer lasers such as XeF ($\lambda = 352$nm); XeCl ($\lambda = 308$nm); KrF ($\lambda = 248$nm); KrCl ($\lambda = 222$nm); ArF ($\lambda = 193$nm); and F$_2$($\lambda = 157$nm) are commercially available and can be used for thin film deposition. The incident laser is in the form of pulses of typical duration of 20 ns. Because of such a short duration of pulse, tremendous power (~10 - 100 MW/pulse) is delivered to the target. These lasers generate non equilibrium evaporation which leads to the congruent evaporation of target material because it penetrates only a thin surface layer on the target for a few tens to nanoseconds. A typical schematic of the PLD technique set up is shown in figure 2.3.

Figure 2.3: A schematic view of pulse laser deposition set up.

Pulse laser is focused on the target using a set of lenses. The target is put in ultra-high vacuum (UHV) chamber where the beam is incident on it at an angle of 45°. The substrate is put opposite to the target and the luminous plane of material evaporated from
Chapter 2 ------- Experimental and Characterization Techniques

the target, in direction perpendicular to the target surface, gets deposited on the substrate. The substrate is usually heated with the help of heater during deposition to obtain crystalline films. The laser pulse energy is in the range of 0.01 - 2 J and the repetition frequency is from 1 - 20 Hz. For every material there is a threshold laser fluence (laser pulse energy per unit area of the target) above which the material evaporates perpendicular to its surface in the form of luminous/plasma plume [2.15]. This plasma plume contains various excited atoms, molecules, ions and neutral species. This plasma expands quickly away from the target towards the substrate where the adiabatic expansion of plasma at the surface of the heated substrate takes place and leads to the growth of the desired thin film. While PLD is recognized to transport the stoichiometry from the target to the film, there are several parameters which immensely influence the growth and properties of thin films. These parameters are laser energy density falling on the surface of the target, ambient background pressure during and after deposition, pulse repetition rate, temperature of the substrate, choice and orientation of the substrate itself, target to substrate distance etc. Laser energy density is a vital factor, which affects the properties of films. If the energy density is low, the complex target molecules do not evaporate congruently; if very high droplet kind of particles is deposited on the substrate.

In the present work, thin films were prepared from a single phase SnO\textsubscript{2} target (1 inch diameter) onto quartz substrate of tetragonal rutile SnO\textsubscript{2} target. The target was sintered in air at 900 °C for 12 hours using SnO\textsubscript{2} powder synthesized by citrate-gel method. The substrates were cleaned by an Ar\textsuperscript{+} sputtering gun and then annealed at 550 °C for 15 minutes before deposition. The target was ablated by a KrF excimer laser (Lambda Physik, LEXtra 200, Göttingen, Germany) operating at a wavelength of 248 nm and a frequency of 10 Hz. The energy density on the target was 350 mJ and the duration of every excimer laser pulse was 34 ns. The laser beam was focused through an ultraviolet grade fused silica window using an ultraviolet grade fused silica lens on the target rotating at a rate of 15 rpm. The base pressure prior to laser ablation was about 1×10\textsuperscript{-6} mbar and the working pressure of the chamber during laser ablation was about 2×10\textsuperscript{-6} mbar. The ablated material was collected on a Quartz surface, which was mounted on a substrate holder 3 cm away from the target. All deposition processes were carried out at ambient temperature. The thickness of as-deposited SnO\textsubscript{2} thin films was about 150 nm.
Finally, the samples were annealed at different temperature ranging from 600 °C to 900 °C for 1 hour with 100 °C variation per sample respectively.

2.3. CHARACTERIZATION TECHNIQUES

2.3.1. X-Ray Diffraction (XRD)

The German Physicist, Von Laue in 1912 was the first who took up the problem of X-ray diffraction (XRD) with the reason that, “if crystals were composed of regularly spaced atoms which might act as scattering centers for X-rays, and if X-rays were electromagnetic waves of wavelength about equal to the interatomic distances in crystals, then it should be possible to diffract X-rays by means of crystals” [2.16]. Today, X-ray diffraction [2.17] is a routine technique for the characterization of the materials. A rich variety of information can be extracted from the XRD. This is an appropriate technique for all forms of samples, i.e. powder and bulk as well as thin film. Using this technique, one can get the information regarding the crystalline nature of a material, nature of the phase present, lattice parameters and grain size [2.18]. From the position and shape of the lines, one can obtain information regarding the unit cell parameters and microstructural parameters (grain size, micro strain, etc.), respectively. In case of thin films, the change in lattice parameters with respect to the bulk gives the idea about the nature of strain present in the system.

Figure 2.4: Geometrical illustrations of crystal planes and Bragg’s law.
The interaction of X-ray radiation with crystalline sample is governed by Bragg’s law, which depicts a relationship between the diffraction angles (Bragg angle), X-ray wavelength, and interplanar spacing of the crystal plane. According to the Bragg, the X-ray diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in figure 2.4.

The path differences introduced between a pair of waves travelled through the neighbouring crystallographic planes are determined by the interplanar spacing. If the total path difference is equal to \( n\lambda \) (\( n \) being an integer), the constructive interference will occur and a group of diffraction peaks can be observed, which give rise to X-ray patterns. The quantitative account of Bragg’s law can be expressed as:

\[
2d_{hkl} \sin \theta = n\lambda
\]  

(2.1)

where \( d \) is the interatomic spacing for a given set of \( hkl \) and \( \theta \) the Bragg angle of the planes, \( \theta \) is the angle between the incident/diffracted beam and the sample surface as shown in the figure 2.5.

![Figure 2.5: Schematic illustrating XRD basic set-up.](image-url)
The intensity of powder diffraction peaks is in principle determined by the structural factor $F_{hkl}$ as expressed in equation (2.2), which depends on the crystal structures including relative positions of atoms in the unit cell, types of unit cells and other characteristics such as thermal motion and population parameters.

$$F_{hkl} = \sum_{i=1}^{n} g^i t^i(s) f^i(s) \exp[2\pi i(hx^i + ky^i + lz^i)]$$

(2.2)

where $f^i(s)$ is the atomic scattering factor, $g^i$ is the population factor of $i$th atom, $t^i(s)$ is the temperature factor, $hkl$ are the Miller indices, and $xyz$ are the fractional coordinates of $i$th atom in the unit cell. In addition to the primary structural factors, the intensity of diffraction is dependent on other factors, which are not only relevant to sample effects such as its shape and size, grain size distribution, etc., but also on the instruments including detector, slit and/or monochromatic geometry. In this work, the identification of the phases and the measurement of lattice parameter of $\text{Sn}_{1-x}\text{TM}_x\text{O}_2$ ($\text{TM} = \text{Fe, Co}$) nanostructures and $\text{SnO}_2$ thin films were carried out using XRD; it was performed using Bruker D8 Advance X-ray diffractometer at Inter University Centre (IUC) Indore. The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on silicon strip technology (Bruker Lynx Eye detector) and using Rikagu X-ray diffractometer at Aligarh Muslim University (AMU), Aligarh, with CuKα ($\lambda = 1.54187\text{Å}$) radiation at room temperature was employed and operated at an applied voltage of 30 kV and filament current of 40 mA. The operating voltage and filament current were increased to 40 kV and 50 mA respectively in case of nano samples to reduce the background and to ensure single phase nature of the samples. The phase identification for all the samples reported in this report were performed by matching the peak positions and intensities in XRD patterns to those patterns in the JCPDS (Joint Committee on Powder Diffraction Standards) database [2.19]. The diffraction method is based on the effect of broadening of diffraction reflections associated with the size of the particles (crystallites). All types of defects cause displacement of the atoms from the lattice sites. M.A. Krivoglaz in 1969 [2.20] derived an equation for the intensity of the Bragg reflections from a crystal defect, which enabled all the defects to be derived conventionally into two groups. The defects in...
the first group only lower the intensity of the diffraction reflections but do not cause the reflection broadening. The broadening of the reflections is caused by the defects of second group. These defects are micro-deformations, inhomogeneity (non-uniform composition of the substance over their volume) and the small particle size. The size of nanomaterials can be derived from the peak broadening and can be calculated by using the Scherrer equation (2.3), provided that the nanocrystalline size is less than 100 nm.

\[
t = \frac{K_{hkl} \lambda}{(L)_{vol} \cos \theta}
\]  

(2.3)

where \( t \) is the average crystalline dimension perpendicular to the reflecting phases, \( \lambda \) the X-ray wavelength, \( K \) the Scherrer constant which equals 0.9 for spherical particles, whose value depends on the shape of the particle (crystallite, domain) and on diffraction reflection indices \( (hkl) \), and \( (L)_{vol} \) the volume-weighted average column length, \( i.e. \), the number of reflecting planes times their effective distance ‘\( d \)’. For spherical particle \( (L)_{vol} \) equals 0.75\((D)_{vol}\), where \( D \) is the grain diameter.

The Scherrer’s formula is quite satisfactory for small grains (large broadening) in the absence of significant microstrain. A micro strain describes the relative mean square deviation of the lattice spacing from its mean value. Based on the crystallize size dependence of the strain it is reasonable to assume that there is a radial strain gradient, but from X-ray diffraction only a homogeneous, volume-averaged value is obtained. The effective lattice strain was calculated using Williamson Hall (W-H) equation [2.21] as shown in equation 2.4

\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{t} + \frac{\eta \sin \theta}{\lambda}
\]  

(2.4)

where \( \beta \) is full width at half maxima (FWHM), \( 2\theta \) is the Bragg angle, \( \lambda \) is wavelength of X-ray used (Cu K\(_a\) in this case), \( D \) is the crystallite size and \( \eta \) is effective strain in the lattice. A plot is drawn with \( \sin \theta / \lambda \) along the X-axis and \( \beta \cos \theta / \lambda \) along the Y-axis. From the linear fit to the data, effective lattice strain \( (\eta) \) was estimated from the slope of and the reciprocal of the intercept gives the crystallite size \( (t) \).
2.3.2. Raman Spectroscopy

The Raman Effect, named for the Nobel Prize work by Sir Chandrasekhara Venkata Raman in 1928 [2.22] is an optical analysis technique that measures the intensity of inelastically scattered light over a range of frequencies. Figure 2.6 shows schematic illustrating Raman set-up. When monochromatic light is incident on a material, most of the light is elastically scattered (Rayleigh scattering) and a small part of the scattered light is inelastically scattered (Raman scattering). The source of inelastic scattering can be due to the transitions between the various states in the materials induced by the incident radiation. The transition can be rotational, vibrational, electronic or a combination. Most of the transitions observed in solids by Raman spectroscopy are vibrational. Raman spectroscopy can be used for the study of gases, liquids and solids, both crystalline and amorphous. In this technique, the spectra are obtained as plots between the intensity of the inelastically scattered light and the shift in the wavenumber of the incident radiation. Each peak corresponds to one or more symmetry-allowed Raman active vibrational modes of the solid.

![Raman set-up schematic](image)

*Figure 2.6: Schematic illustrating Raman set-up.*

Raman activity is a function of the point group symmetry of a molecule and the space group symmetry of a crystalline solid. However, the symmetry of the crystal is embodied in its crystallographic point group [2.23]. Raman measurements can provide
information like the strength of interatomic and intermolecular bonds, the mechanical strain in a solid, the composition of multicomponent matter, the degree of crystallinity and the effects of pressure and temperature on phase transformations. When a photon is incident on a solid, the inelastically scattered photon can have the frequency lesser or greater than the frequency of the incident photon, the corresponding scatterings are known as Stokes or anti-Stokes Raman scattering, respectively. When electron excited by the incident photon is in the ground state and returns back to the same state then the electron is elastically scattered and this is called Rayleigh scattering, but if it returns to some excited state, as shown in figure 2.7, then it loses some energy to the system and the scattered photon has frequency lower than that of the incident photon, this gives rise to Stokes lines. If the system is initially in an excited state and then the incident photon excites it to some higher excited state, the electron can return back to the ground state with the scattered photon having energy larger than the incident photon, this is the origin of anti-Stokes lines. Statistically, most of the electrons will be in ground state at room temperature, Stokes lines have higher intensities as compared to the anti-Stokes lines.

![Figure 2.7: Schematic diagram showing the different scattering possibilities.](image)

Here, $v_{\text{inc}}$ and $v_{\text{sc}}$ represent the frequency of the incident and scattered photon respectively.
The major components of a Raman facility include:

- i) Source of radiation.
- ii) Optics for illuminating the sample and collecting the Raman scattered radiation.
- iii) A spectrometer for dispersing the Raman scattered radiation.
- iv) Device for measuring the intensity of the Raman scattered light.
- v) Set of components that control the polarization of the incident radiation and monitor the polarization of the Raman scattered radiation for polarized Raman scattering measurements.

The sample is illuminated using monochromatic light from a laser and the scattered light is collected using suitable collection optics. The light is then passed through the spectrometer and the Raman spectra are obtained. In the collected light, the dominant contribution is from Rayleigh scattering. Because of imperfections in the gratings and mirrors within the spectrometer, a portion of the Rayleigh scattered light is present in the Raman spectra in the range of 0 to 200 cm\(^{-1}\). Although the fraction of the Rayleigh scattering in this region is very small, it can overshadow the Raman spectra as the intensity of Rayleigh component is very high. Thus, the Raman peaks in this region can be observed only when the Rayleigh scattered light is strongly reduced. For this purpose, a notch filter is used; it removes the Rayleigh scattered radiation (as well as Brillouin scattered light and Mie scattering from dust particles). In this study, the Raman spectra for the samples were collected at room temperature using Renishaw in Via Raman microscope with Ar ion laser excitation of 514 nm in backscattering geometry at Inter University Accelerator Centre, New Delhi.

### 2.3.3. Fourier Transform Infrared Spectroscopy (FTIR)

The foundations of modern FTIR were laid in the latter part of the nineteenth century by Michelson [2.24] and Lord Raleigh who recognized the relationship of an interferogram to its spectrum by a Fourier transformation [2.25]. It was not until the advent of computers and the fast Fourier algorithm that interferometry began to be applied to spectroscopic measurements in the 1970s. The basic optical component of
Fourier transform spectrometers is the Michelson interferometer shown in simplified form in figure 2.8, heated element or a glow bar is collimated and directed onto a beam splitter, creating two separate optical paths by reflecting 50% of the incident light and transmitting the remaining 50% [2.26].

![Figure 2.8: Schematic illustrating FT-IR set-up.](image)

In one path the beam is reflected back to the beam splitter by a fixed position mirror, where it is partially transmitted to the source and partially reflected to the detector. In the other leg of the interferometer, the beam is reflected by the movable mirror that is translated back and forth while maintained parallel to itself. The movable mirror rides on an air bearing for good stability. The beam from the movable mirror is also returned to the beam splitter where it, too, is partially reflected back to the source and partially transmitted to the detector. Although the light from the source is incoherent, when it is split into two components by the beam splitter, the components are coherent and can produce interference phenomena when the beams are combined. The light
intensity reaching the detector is the sum of the two beams. The two beams are in phase when $L_1 = L_2$. When $M_i$ is moved, the optical path lengths are unequal and an optical path difference $\delta$ is introduced. If $M_i$ is moved a distance $x$, the retardation is $\delta = 2x$ since the light has to travel an additional distance $x$ to reach the mirror and the same distance to reach the beam splitter. In the present work, the *Fourier transform infrared spectroscopy* (FT-IR) spectra were recorded in the range 400 to 4400 cm$^{-1}$ using (Thermo Scientific, Nicolet-8700) at Aligarh Muslim University.

### 2.3.4. Field Emission Scanning Microscopy (FESEM)

FESEM is a versatile applied technique in material science which enables the investigation of specimen with a resolution down to the nanometric scale. It is used to get information about the topographical features, morphology, phase distribution, crystal structure, crystal orientation and the presence and location of defects. The basic principle of this technique is that an accelerated beam of mono-energetic electrons is generated by a field emission gun. The electron beam is accelerated through a high voltage (*e.g.*: 20 kV) and pass through a system of apertures and electromagnetic lenses to produce a thin beam of electrons. This beam is focused in a vacuum of $10^{-4}$ - $10^{-10}$ torr; the signal obtained from these types of electrons conveys information of the topology of the sample. Some of these electrons get scattered elastically (*i.e.* change the direction without change of energy) from the coulomb field of the nucleus where as some undergo inelastic scattering (with change in energy) from the electrons of the host atoms giving secondary electrons. The secondary electrons are collected by the detector for every position of the incident electron beam and are used to form an image. The signal is amplified and made to form synchronous image on the cathode ray tube. A camera is used to photograph the image or it may be digitalized and processed on a computer. The electron detector controls the brightness of the spot on the screen- as the detector sees more electrons from a particular feature, the screen brightness is increased. When there are fewer electrons, the spot on the screen gets darker. The magnification of the image is the ratio of the size of the screen to the size of the area scanned on the specimen [2.27]. A line diagram of typical FESEM is given in figure 2.9.
Essential requirement is that the samples should be conductive. Surfaces of non-conductive samples are rendered conductive usually by coating a thin layer of gold. The resolution and the depth of field of the image are determined by the beam current and the final spot size, which are adjusted with one or more condenser lenses and the probe forming objective lenses. The electrons interact with the sample from few nanometers to several microns of the surface depending on the beam parameters and the sample type. Electrons are emitted from the sample primarily as either backscattered or secondary electrons and detected by scintillation photomultiplier detector. Accordingly, there are two types of images, the secondary electron image (SEI) and backscattered electron image (BEI). The SEI is used mainly to image fracture surfaces and give a high resolution image. The BEI is used typically to image a polished section; the brightness of the SEI is dependent on the atomic number of specimen. The high energy electrons also cause electronic excitations of the atoms in the specimen. The excitation and de-excitation processes produce characteristic X-rays. The energy of each X-ray photon is
characteristic of the element which produced it. Therefore, the electron microscopy measurements also help us to analyze the elemental analysis of samples and are known as energy dispersive X-ray analysis (EDX). In the present work, morphological and microstructural features of SnO$_2$ based DMS and SnO$_2$ thin films were investigated with a FEI Quanta 200F FESEM at Indian Institute of technology (IIT) Roorkee.

2.3.5. Transmission Electron Microscopy (TEM)

TEM is a powerful and versatile technique used to characterize the microstructure of material with very high spatial resolution. In this technique, information about the morphology, crystal structure and defects, crystal phases, compositions and magnetic microstructure can be obtained by the combination of electro-optical imaging, electron diffraction and small probe capabilities. Here a beam of electrons interacts with the ultra-thin specimen as it passes through. An image is formed from the interaction of electrons transmitted through the specimen; the electron beam is focused by an objective lens and amplified by a magnifying (projector) lens and finally produce the desired image [2.28]. Figure 2.10 shows the cross sectional view of a typical transmission electron microscope. The wavelength (nm) of the electron in the incident beam is given by;

$$\lambda = \frac{h}{\sqrt{2mqV}}$$  

(2.5)

Where m and q are the electron mass and charge, h is Plank’s constant and V is the potential difference through which electrons are accelerated (expressed in kilovolts). Electrons interact much more strongly with matter than that of X-rays or neutrons with comparable energies or wavelengths. To get best results in electron microscopy thickness of the specimen should be comparable with mean free path of electrons, which is the average distance traversed by electrons between scattering events. Much thinner specimen exhibits too little scattering to provide useful image, and in thick specimen multiple scattering events dominate, making the image blurred and difficult for interpretation. Thick specimen can be studied by detecting back scattered electrons. The main part of the electron beam transmitted by the sample consists of electrons that have not undergone any scattering. The beam also contains electrons that have lost energy
through inelastic scattering with no deviation of their paths, and the electrons that have been reflected by various hkl crystallographic planes.

Figure 2.10: Cross sectional view of a typical transmission electron microscope.

For producing bright image the aperture is inserted so that it allows the main un-deviated transmitted electron beam to pass. The bright field image is observed at the detector or viewing screen. If the aperture is positioned to select only one of the beams reflected from a particular hkl plane, the result is the generation of a dark field image at the
viewing screen. A technique called image processing can be used to increase the information obtained from a TEM image, and enhance some features that are close to the noise level. If the image is Fourier-transformed by highly efficient technique called fast Fourier transformation, then it provides information similar to that in the direct diffraction patterns. In this work, TEM analysis was done at Sophisticated Instruments Facility (USIF) AMU, using JEOL JEM 200.

2.3.6. Dielectric Studies

In the present work, the dielectric, ac conductivity and impedance measurements have been carried out as a function of composition and frequency (42Hz - 5MHz) using HIOKI-36532-50 HI-TESTER LCR meter. The SnO$_2$ based DMS material was pelletized using a circular shape dye of 10mm and 12mm diameter. The thickness of pellets was ~1 to 3 mm. For dielectric and ac impedance measurements, silver paste was coated on the opposite faces of the pellet to make parallel plate capacitor geometry and SnO$_2$ based DMS material as the dielectric material. For taking dielectric measurements of SnO$_2$ thin films, Au/SnO$_2$/Au sandwich type structure was deposited on quartz substrate to make parallel plate capacitor geometry and SnO$_2$ thin films.

Bauerle [2.29] was the first to use this technique in 1969 to separate bulk from interfacial properties in polycrystalline ceramics. In complex impedance diagrams (Nyquist or Cole–Cole plot) the imaginary part of the impedance $Z''(\omega)$ is plotted against the real part of impedance $Z'(\omega)$. The response of an ideal parallel circuit of resistance $R$ and capacitance $C$ is a semicircle centered on the real axis. $R$ is determined from the diameter of the semicircle, whereas $C$ is calculated from the frequency of semicircle maximum. Impedance spectroscopy is ideal for investigating the electrical response of dielectric materials as a function of frequency. It is a powerful technique for unraveling the complexities of materials, whose properties and applications depend on the close control of structure, composition, ceramic texture, dopants (or defects) and dopant distribution, which functions by utilizing the different frequency dependence of constituent components for their separation. The impedance analysis of a material is based on an idealized circuit model with discrete electrical components. The analysis is
mainly accomplished by fitting the impedance data to an equivalent circuit, which is representative of the material under investigation. It has been among the most useful investigation techniques since the impedance of grains can be separated from the other sources of impedance, namely grain boundaries and electrode effects [2.30]. When the grain boundary resistance is larger than the resistance of bulk, two semicircles are often obtained in Cole-Cole plot. Deviations from ideal semicircles have been attributed to the distribution of relaxation times arising from the micro-structural inhomogeneity or disorder in the samples [2.31]. Figure 2.11 shows the systematic diagram of LCR meter.

![Figure 2.11: Schematic diagram of the LCR meter setup.](image)

A sine wave signal was fed to the input terminal (T₁) of the LCR meter and the sample from the signal generator (SG) terminal. The output (T₀) measured the output signal from the sample, which was voltage drop across a standard resistance of 1kΩ. LCR then automatically analyzed the signals from T₁ and T₀ to give phase difference (θ) between the input and out signals, i.e., Z' and Z". The complex impedance plot is obtained after plotting Z" versus Z'. When an ac voltage \( V = V_0 e^{j\omega t} \) is applied across the sample, the current that flows across the sample is given by:

\[
i = j\omega CV = \frac{j\omega (\varepsilon' - j\varepsilon'')Ae_0V}{d} \tag{2.6}
\]
2.3.7. Resistivity measurement

The dc electric resistivity measurements were performed using four probe technique due to its familiar gain of avoiding the contact resistance over two probe technique [2.32].

Figure 2.12: Schematic diagram of the cryostat and used ladder for four probe method setup.
In two probe arrangement each probe serves as a current and as a voltage probe. This gives rise to unwanted contact resistance $R_c$ at each metal probe semiconductor contact and spreading resistance $R_{sp}$ (due to resistance encountered by the current when it flows from the small metal probe into the semiconductor) under each probe. Therefore, the major problem in this method is the error due to the contact resistance of measuring leads, and thus resistance cannot be accurately measured. To overcome this problem, a collinear equidistant four probe method is used. In this technique the current is passed through outer probes and the voltage drop is measured across the inner two probes. Since voltage measuring devices draw negligible current or no current at all and they do not involve any of the current probes, and $R_c$ and $R_{sp}$ are negligible. In this work, the electric resistivity were measured using four probe low resistivity ohmic silver contacts in a linear geometry using high quality silver paste solution. Standard four probe detection method was then employed at Inter University Accelerator Center, New Delhi- India. Samples were mounted on the base of ladder as shown in figure 2.12, in the setup a calibrated PT100 temperature sensor is used near the sample on the copper plate for temperature measurement. A 50 W heater of Lake Shore has been inserted in the hole of the base of copper plate. The whole of this ladder is enclosed by removable stainless steel (SS) cup. When the dipstick cryostat is inserted inside the liquid nitrogen ($LN_2$) dewar, this cup kind of attachment is kept under rough vacuum using a rotary pump. There are ten electrical connections: four for sample, four for sensor and two for heater. Four shielded coaxial cables are for the electrical connections of the samples. These electrical connections travel through the thin SS tube which is about 1 meter in length. The temperature of the sample is controlled using the Lake Shore temperature controller (Model 340) and stabilized within ±50 mK. This setup is fully automated and program has been written using LabView software.

2.3.7. Vibrating Sample Magnetometer (VSM)

VSM is a scientific instrument invented by Simon Foner [2.33] at Lincoln laboratory MIT for measuring magnetic moment of the sample with high accuracy. It is based upon Faraday’s law according to which an e.m.f is induced in a conductor by time-varying magnetic flux. In VSM setup (figure 2.13) a sample magnetized is vibrated...
sinusoidally at small fixed amplitude with respect to stationary pick-up coils. Sample is kept in a uniform magnetic field and is made to vibrate perpendicular to the uniform magnetic field by a transducer assembly and an electrical signal induced in suitably located pick-up coils around the sample. This induces a voltage in the pick-up coils, which is vibrating at frequency \( f \) and is proportional to induced magnetic moment of the sample. Since the signal vibrating at frequency \( f \) is proportional not only to the magnetic moment of the sample but also to the vibration amplitude and frequency.

**Figure 2.13: Schematic block diagram for VSM the set up used in present work.**

Therefore, to get magnetic moment of sample, a comparison voltage induced in the same set of reference coils by a vibrating capacitor, which is being vibrated by the same transducer. This comparison voltage varies with vibration amplitude and frequency in the same manner, as that of the signal from the pickup coils placed near the sample. These two signals are applied to two inputs at a differential amplifier to cancel the effect of vibration amplitude and frequency. Thus, the signal at the output of the differential amplifier is only a function magnetic moment of the sample. This signal is then applied to a synchronous detector (lock-in amplifier), where it is compared with a reference signal.
and is also applied to transducer which oscillated the sample. The output signal is now proportional to the amplitude of the magneto moment. This signal is then amplified and used in two different ways. One part is fed back to the movable plate assembly of the vibrating capacitor and second part is applied to the output display circuits, where the amplitude of the moment is recorded. The effect of the feedback is to automatically adjust to required level to maintain the capacitor output signal at the same level as the pick-up coil signal [2.34]. In the present study, we have used VSM for the magnetization measurement of SnO$_2$ based DMS nanomaterial samples. The magnetization measurement was carried out using the VSM option of Quantum Design PPMS set up.
Chapter 2 ------ Experimental and Characterization Techniques

REFERENCES

2.24 A.A. Michelson, Phil. Mag. 31 (1891) 256.
2.27 Gringer (talk), http://en.wikipedia.org/wiki/File:Scheme_TEM_en.svg
2.34 Ghazala Anjum, Multiferroic properties of Mn doped La$_{0.8}$Bi$_{0.2}$FeO$_3$ system and effect of SHI irradiation, PhD thesis, AMU (2011).