CHAPTER 2
EXPERIMENTAL TECHNIQUES
2.1. **Introduction**

In this thesis preparation of various ceramic oxides and investigation of their electrical properties are focused. In this chapter, different types of preparation methods are briefly discussed. The conventional solid state, gel combustion methods were used to prepare ceramic oxides, while polyol route was adopted for preparation of metal nanomaterials. The prepared materials have been characterized by several analytical techniques, like X ray diffraction (XRD), Raman spectroscopy, FT-IR Spectroscopy, Scanning Electron Microscopy and Mössbauer spectroscopy. The functional properties of the prepared materials have been investigated by using Impedance Analyzer. The salient principle and scope of different experimental methods used are also discussed in this chapter.

2.2. **Synthesis methods**

Preparation of materials is the foremost aspect followed in material research. It is well known that the method of preparation is often selected depending on the nature of desired materials and their final applications. The preparation methods can be grouped as either high temperature ceramic methods or low temperature soft chemical methods. Each preparation method has certain advantage and disadvantage and thus adoption of a judicious preparation method is solely dependent on the desired products. Some of the adopted general methods of preparation of materials are explained below.

2.2.1. **Solid-state reaction route**

The solid-state process is a primitive, most conventional and widely used method to prepare polycrystalline ceramic oxide materials. It involves the mechanical mixing of the stoichiometric amounts of solid constituents (oxides/carbonates), repeated grindings and annealing at elevated temperatures, generally over a long
duration [73]. The formation of product and progress of the reaction is based on the diffusion of ions in solid state, which is an inherently slow process. The temperature chosen for the solid state reaction mainly depends upon the melting point of the solid reactants. Moreover, the ceramic oxides are high melting solids and hence, the reaction rate becomes extremely slow at lower temperature. Being the solid state reaction is a diffusion controlled process, the reaction rate follows a parabolic rate law as given below.

\[ \frac{dx}{dt} = k \cdot x^{-1} \]  

[2.1]

Where, \( x \) is the concentration of product (thickness of the product layer), \( t \) is the time and \( k \) is a constant. Since the reactants are mostly high melting refractory solids, only at high temperature ions can jump off from their normal lattice sites and diffuse through the crystals. Compared to solution processing, the solid state reaction occurs from a heterogeneous medium and thus they depend on several factors of the reactants. At a particular temperature, the reaction rate is fast in the initial stage and then progressively become slower due to the increasing barrier product layer in between the reactants which hinders the direct interaction of the two reacting solids. Usually, the solid state reactions are carried out by grinding the reactants to make a thoroughly mixed mixture of component solids. It can be mentioned here that the reaction rate depends to a large extent on the particle size of reactants, the degree of homogenization achieved on mixing and the intimacy of contact between the grains as well as annealing temperature. The area of contact between the reacting solids (their surface area) is also an important factor for enhancing the reaction of solids. The particle size of the reactants thus plays an important role in the solid state reactions, as
the decreasing the size, increases the surface area and hence increases the reactivity of the reactant particles. In order to increase the surface area, the reactants are crushed into finer powder. Further to increase the area of contact, the mixture of reactants are usually pressed into pellets. Most commonly, the repeated grinding and pelletizing after a heat treatment is essential for completion of the reaction. This is to bring fresh surfaces in contact and also to reduce the sizes of the reactant powders. Though the desired composition and phase can be managed by such solid state reactions, the process is often energy intensive and time consuming.

2.2.2. Soft chemical routes

Soft chemical routes are based on controlled chemistry of reactant ions. The problem of reactant heterogeneity of solid state reaction can be avoided by these soft chemical methods, as prefect homogeneity at molecular level is achieved in solutions state. The soft chemical methods employ a solvent medium from which, the required product can be isolated by precipitation, solvent evaporation etc. In the present work, two different soft chemical routes have been employed to prepare polycrystalline ceramic materials and metal nanoparticles. A detailed description of each of these synthesis methods is given as follows.

i. **Gel combustion method:**

Gel-combustion is an exothermic redox reaction between an oxidant viz., metal nitrate and a fuel such as citric acid, glycine, etc. The final product obtained by the combustion process has highest degree of phase purity and improved powder characteristics like, higher surface area, narrow size distribution of nanoparticles and better sinterabilty. In this thesis, nanocrystalline powder samples were prepared by gel-combustion process by using glycine as the fuel. Glycine (NH$_2$CH$_2$COOH) is a
zwitter ion forming compound having a carboxylic acid group at one end and amino group at the other end [74]. It is a low cost fuel which effectively complexes the metal ions of varying ionic sizes, preventing their selective precipitation. The powder properties such as crystallite size and surface area of the combustion-synthesized nano powders can be altered by changing the fuel content with respect to the oxidant. The amount of the fuel in the combustion reaction is fixed on the basis of principle of propellant chemistry [75]. According to the principle of propellant chemistry, for a stoichiometric redox reaction between a fuel and an oxidizer, the ratio (\(\varphi\)) of net oxidizing valence of metal nitrate to net reducing valency of fuel should be unity [76]. In such case the ratio of oxidizing-to-reducing valencies is called as stoichiometric ratio. The oxidant-to-fuel ratio less than that of stoichiometric ratio is termed as the fuel-deficient ratio and any ratio greater than this is termed as fuel-rich ratio. This oxidant-to-fuel ratio is an important parameter for gel combustion process as it governs the exothermicity of the combustion reaction and hence the flame temperature which thus governs the powder properties of final product. The typical chemical processes of a gel combustion reaction are explained below.

(a) Gel formation and combustion

The first step of the gel combustion is gel formation. In this step, the nitrate/oxy nitrate salts of the metals of interest, in a required molar ratio, are mixed together in an aqueous medium to produce a transparent mixed metal-nitrate solution. Nitrates present in the reaction medium fulfill the requirement of oxidant by providing the oxygen for combustion of the fuel. Appropriate amount of suitable fuel (glycine, citric acid or urea) is then added to this mixed metal nitrate solution. The aqueous solution of fuel and oxidants is then dehydrated on a hot plate (at about 353-373 K)
which transformed to a viscous liquid (hereafter termed as gel). A pictorial representation of the gel formation step is depicted in Fig.2.1a. It may be noted that the thermal dehydration process is rather an important step, because any excess water left behind would lead to a sluggish combustion, deteriorating the phase purity and powder quality. The formation of the transparent viscous gel depends on the nature of the fuel, its amount and pH of the starting solution.

Fig.2.1: Steps involved in the gel-combustion method; (a) gel formation (b) auto ignition.

The obtained gel is further heated at a higher temperature (473-523K) where the combustion reaction is initiated or triggered. The very high exothermic decomposition of the fuel-oxidant precursor generated during the combustion reflects in the form of flame or fire and this processes is termed as auto-ignition (shown in Fig.2.1b). The auto-ignition is a very short-lived phenomenon as the flame persists for only about few (5-10) seconds. At this stage, the exothermic decomposition of fuel-oxidant results in a large voluminous powder. During the auto-ignition, gaseous products are evolved which dissipate the heat and fragment the product particle. Thus, the solid residual products are obtained as ultra-fine powders of oxide ceramics. However, the resultant product may be the desired phase, or semi-decomposed precursor having a
considerable amount of carbonaceous residue, depending on the nature and amount of fuel used.

(b). **Advantages of the gel combustion process**

1. Preparation of the precursor in the first step prevents the random redox reaction between a fuel and an oxidizer by the formation of homogeneous gel precursor. Thus, the possibility of local variations in the characteristics of the combustion-synthesized powders is very low.

2. As fuel and oxidant decompose, the final product does not require any special processing of the precursor such as washing etc.

3. Even though the time for which auto-ignition exists is very small, i.e. only for few seconds, most often the heat of combustion or flame temperature generated within this time is sufficient to produce the required phase. Hence, the combustion technique can be considered as time saving low temperature synthesis, which is not highly energy intensive.

(c). **Precautions and limitations**

Although the combustion process is known for its simplicity, few precautions are necessary while performing the experiments.

1. It is always advisable to perform the combustion process in a wide mouthed apparatus, with large volumes to avoid poor heat dissipation and for easy liberation of the gaseous products. Narrow opening container may lead to an explosion, due to the large swelling of viscous precursor and also the large volume of gaseous products eliminated, in addition, to the high exothermicity.
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2. Combustion is a vigorous and spontaneous process wherein large amount of heat is released in a very short duration. Hence there must be an arrangement for safe ventilation which facilitates safe release of the gaseous products.

ii. **Polyol method:**

Polyol method is a very promising technique for the preparation of magnetic nanoparticles. In polyol process, polyalcohol not only acts as a solvent, but also as a mild reducing agent. When coupled with a base, it acts as a perfect medium for the reduction of metal salt precursors. In this polyol method the precursor salts are dispersed in a liquid polyol. The suspension is then heated up to reflux. During the polyol reaction, inorganic reactant precursor reacts with diols or alcohols, forming an intermediate which are reduced to form metal nuclei, and then metal nanoparticles. The nanoparticles obtained in the polyol method have surface adsorbed glycols and thus reduces the hydrolysis of fine metal nanoparticles which often occurs in the aqueous reaction process. Various polyols such as ethylene glycol, diethylene glycol, trimethylene glycol, propylene glycol and butylene glycol can be used in the polyol process. The polyol reaction can be followed by studying the a) Nucleation b) Surfactants c) Growth parameters. The adsorbed polymers on the surface of the nanoparticle lower the surface energy and develop a barrier for the aggregation of nanoparticles. Various polyols used for the reduction of metal salt precursors are shown in the Fig.2.2.
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The prepared materials have been thoroughly characterized prior to measurement of any of their properties. The phase and structural characterization of the materials have been carried out by powder XRD and vibrational spectroscopic methods, while morphological properties have been investigated using Scanning Electron Microscopic technique. Several supporting techniques, like Mössbauer, X-ray photoelectron spectroscopy (XPS) and Extended X-ray Absorption of Fine Structure (EXAFS) have been used to understand the local structure and oxidation states of various ions in certain system. In the following section the brief overview of the techniques use in this thesis work is explained.

2.3. Characterization techniques and instrumental details

The prepared materials have been thoroughly characterized prior to measurement of any of their properties. The phase and structural characterization of the materials have been carried out by powder XRD and vibrational spectroscopic methods, while morphological properties have been investigated using Scanning Electron Microscopic technique. Several supporting techniques, like Mössbauer, X-ray photoelectron spectroscopy (XPS) and Extended X-ray Absorption of Fine Structure (EXAFS) have been used to understand the local structure and oxidation states of various ions in certain system. In the following section the brief overview of the techniques use in this thesis work is explained.

2.3.1. XRD-technique

X-ray diffraction (XRD) was used for characterization as well as for detailed structural elucidation of the material. As the physical properties of solids (e.g., electrical, optical, magnetic, ferroelectric, etc.) depend on atomic arrangements of materials, determination of the crystal structure is important. The d spacing between

Fig. 2.2: Molecular structure of various polyols used for the reduction of metal salt precursors.
various planes in the unit cell of a crystal is of the order of wavelength of X-rays. Hence, XRD patterns are used to establish the atomic arrangement or structure of the materials. X-rays are produced when high-energy electrons, typically 30 keV, are bombarded at a metal target which is usually made of copper as shown in the Fig.2.3.

Fig.2.3: A typical block diagram of a powder XRD unit

From this it clear that the prime components of a powder diffractometer is the source of X-ray, usually called x-ray tube, and the sample chamber and a goniometer for measuring the angles followed by a x-ray detector for measuring the intensity of diffracted X-ray beam. Besides there are several slits to reduce the divergence of the incident and diffracted beam and monochromator are also used. The most common method to generate X-ray is by the Bremsstrahlung process, where high energy electrons strike the metal target getting slowed down. In addition, if the energies of incident electron have sufficiently energy, they can ionize the atoms of the target by knocking an electron from inner orbital of atoms. Such ionization process leaves a hole in the inner orbital. The electron from a higher energy orbit or shell will jump down to replace the lost electron and the excess energy is released as monochromatic X-rays. In the overall process of interaction of electron with atoms results in X-ray
spectrum which consist of white radiation of broad spectrum of wavelengths, and a number of fixed, monochromatic wavelengths. Normally for X-ray diffraction, monochromatic radiation is required. In case of Cu target a transition from the 2p orbital of L shell to the K shell produces a $K_\alpha$ ($\lambda = 1.5418$ Å) X-ray, while the transition from 3p orbital of M shell to the K shell produces a $K_\beta$ ($\lambda = 1.3922$ Å) X-ray. The $K_\alpha$ radiation is more intense than the $K_\beta$. Slight difference in energy for the 2 spin states causes the splitting of Cu $K_\alpha$ into $K_{\alpha 1}$ and $K_{\alpha 2}$. The more intensity $K_\alpha$ is used for the diffraction measurements and remaining unwanted radiations are filtered off by using Ni filter.

When X-ray interacts with the atoms in crystal they produce diffraction pattern. Schematic representation of the X-ray diffraction process is illustrated in Fig.2.4.

**Fig.2.4: Schematic diagram of X-ray Diffraction process in crystal.**

The X-ray (ray-1 of schematic-2.3 can interact with the upper part of the atomic planes and reflect with angle $\theta$, equal to its angle of incidence. The ray-2 can travel down to the inner layer of atoms and then reflects back at an angle $\theta$. In this process ray-2 travel extra distance equivalent to 2a. For this wave to be in phase with the wave
which reflected from the surface, the extra path difference should be a whole number multiple of wavelength. Therefore Bragg’s equation can be written as:

\[ n\lambda = 2d \sin \theta \]  

where, \( \lambda \) is the wavelength of the X-ray, \( \theta \) is the angle of the diffracted X-ray coming out of the crystal, \( d \) is the inter spacing between the planes.

### i. Powder XRD instrumental details

X-ray diffraction experimental setup consists of a source of X-rays and a detector for the detection of diffracted X-rays. X-rays are produced by bombarding high-speed electrons on a metal target in a sealed X-ray tube. It should be mentioned here that only a very small fraction of electron energy is used for the X-rays production and the rest is lost in heating the target element. During this process, the target element gets heated and hence, it requires a continuous cooling. The X-rays are emitted in all the directions and hence, slightly divergent X-ray beams are allowed to emit in a particular direction usually though a beryllium window (which allows to pass out the X-ray beam). The background and \( \beta \)-radiation are filtered using \( \beta \) filters, usually a thin plate of element with atomic number one to two unit below than that of the target element. The beam of X-ray passes through the soller and divergence slits and then fall on the sample. The fine grains of sample are generally spread uniformly over a rectangular area of a glass slide. The sample is adhered to the glass slide either using binders like collodion or grease or wax. The diffracted X-rays beams from the sample passed though several slits, like soller and receiving slits and then fall on a monochromator before detection. The monochromator separates out the fluorescent radiation as well as stray radiation scattered by the sample and gas molecules in the
sample chamber. The details of the typical X-ray spectra and the X-ray production and are explained in several monographs [77].

XRD can be used for several purposes, like 1) calculation of unit cell parameters, miller indices 2) identification of types of phases present in the material 3) to determine the phase purity of the sample 4) evaluation of the average crystallite size, etc.

ii. Lattice parameter determination

Theoretically, the lattice parameters are determined from the relationship between the distance, \(d\), of two adjacent net planes and the \((h k l)\) Miller indices of the reflection planes and is given by the equation

\[
\frac{1}{d^2} = \frac{k^2 \sin^2 \alpha + l^2 \sin^2 \beta + l^2 \sin^2 \gamma + 2hkl}{abc \cos \gamma - \cos \alpha - \cos \beta + 2 \cos \alpha \cos \beta \cos \gamma} \]

\[2.3\]

where, \(V = abc \) is the volume of the unit cell, \(a, b, c\), \(\alpha, \beta, \gamma\) are lattice parameters and \(h, k, l\) are the Miller indices. To solve crystal structures, quantitative measurements of intensity are necessary. Intensity of these diffracted beams depends on the atoms type and positions within a unit cell. The intensity of a diffracted beam, \(I_{hkl}\), can be expressed as:

\[
I_{hkl} \propto F^{2}_{hkl} \text{mALP} \]

\[2.5\]

\(F_{hkl}\) = structure factor, which can be written as;

\[
F_{hkl} = \sum n \exp \left[ 2\pi i(hx_n + ky_n + lz_n) \right] [-B_n \sin^2 \theta / \lambda^2] \]

\[2.6\]

Where,
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\[ f_n = \text{atomic scattering factor of the } n^{\text{th}} \text{ atom in the unit cell with the coordinates } (x_n, y_n, z_n). \] It is directly proportional to atomic number, \( Z \).

\[ m = \text{multiplicity factor the multiplicity factor takes into account the number of equivalent reflections that give rise to a single powder line.} \]

\[ L = \text{Lorentz factor} \]

The Lorentz factor is the correction for variation in the probability of a Bragg reflection occurring within a given diffraction angle. It corrects for the geometry of the diffractometer and is a simple function of \( \theta \) [78].

\[ A = \text{absorption factor.} \]

This factor accounts for absorption occurring within the sample, equating the proportion of incident and diffracted X-rays absorbed. The amount of radiation absorbed depends upon sample composition, diffraction angle and thickness, and varies according to the geometry of the diffraction method used.

\[ P = \text{polarization factor} \]

This factor corrects for the unpolarized nature of X-rays produced by the X-ray tube. Diffracted beams are more intense, when the electric field vector is parallel or anti-parallel to the sample and are weakest when perpendicular. This correction is also a simple function of \( \theta \).

\[ B_n = \text{isotropic temperature factor} \]

This accounts for the effect of thermal motion on intensity and is proportional to the mean square oscillations of the atoms, \( u_{iso} \)

\[ B_n = 8\pi^2 <u_{iso}^2>_n \] \[2.7\]

Another important method used to quantify each of the phases present is the Rietveld refinement method. Rietveld refinement analysis of X-ray powder diffraction data are used to refine structural parameters, such as atomic coordinates, occupancies, lattice
parameters, thermal parameters, etc. In the Rietveld refinement method experimental data are compared with theoretical line profile and intensity. The obtained theoretical proposed structure refined using a least-squares approach. Best fit model structure, achieved by adjusting parameters of the proposed structure, in order to minimize the difference between the experimental and calculated intensities.

iii. Determination of the average crystallite size

In order to determine crystallite size, XRD method is one of the simpler and best methods which can be used in the range of 2-100 nm. The diffraction peaks of the nano materials are broadened. The broadening of the Bragg peaks is due to the development of the lower crystallite size and internal strain. If the studied crystals are free from defects and micro-strains, peak broadening can be attributed to average crystallite size and diffractometer characteristics. From the broadness XRD peaks, the average crystallite size can be calculated by using Scherer’s relation.

\[
D = \frac{0.9 \lambda}{\beta \cos \theta} \text{ or } K \frac{\lambda}{\beta \cos \theta}
\]  

[2.8]

Where, \( \lambda \) is wavelength of X-ray, \( \beta \) is FWHM in radian, \( \theta \) is the Bragg angle and \( K \) is the Scherer constant. \( D \) is the crystallite size.

In the present work, a Philips 1710 diffractometer and rotating anode based X-ray diffractometer (Rigaku, Japan) were mostly used for the characterization process. Philips-1710 diffractometer is based on the Bragg-Brentano reflection geometry. The Cu K\( \alpha \) emissions from sealed tube are used as the incident beam. In the former set up, the diffracted beam is monochromatized with a curved graphite single crystal. The Philips (PW-1710) diffractometer has a proportional counter (Argon filled) for the
detection of X-rays where as rotating anode diffractometer has scintillator detector. The X-ray tube rating was maintained at 30 kV and 40 mA in both units.

2.3.2. X-ray photoelectron spectroscopy (XPS)

The basic components of XPS are X-Ray source, sample stage and electron analyser combined with detection system as shown in the Fig.2.5. XPS measurements are conducted in ultra-high vacuum (UHV). Interaction of sample with X-rays of sufficient energy emits the photoelectrons. Electron analyser measures the kinetic energy of the emitted electron. There is also a detector which measures the number of photo electron emitted.

![Fig.2.5: Schematic diagram of a XPS unit [79(a)]](image)

When X-ray of energy higher than 1 keV exposed on the sample, electrons are liberated from the specimen sample by photoemission process. For each and every element, there will be a characteristic binding energy associated with each atomic orbital. In photoemission process, atom absorbs the photon energy $h\nu$, results the ejection of the core level electron. The characteristic parameter for the electron is its binding energy. The relation between these parameters is given by Eq. (2.9)

$$E_B = h\nu - E_K - W \quad [2.9]$$
Where, $E_B$ and $E_K$ are the binding and the kinetic energy of the emitted photoelectron respectively, $W$ is the spectrometer work function and $hv$ is the photon energy. The excitation by X-rays may also cause electronic energy transitions within the atom that leads to emission of Auger electrons, which also appear in the spectra. The Auger electrons are not the main concern of XPS. The electrons emitted in XPS process contain information regarding electronic structure, chemical oxidation state and atomic composition. Thus, the XPS can provide the information on the shell structure. Since electrons emitted from atoms lying in layers deeper within the material have small chance for reaching the surface and being detected. Hence, this technique provides information about the atoms present within few uppermost atomic layers.

Since each element have different electronic binding energies, XPS can be used for elemental analysis. The binding energy of an electron is influenced by chemical environment around and oxidation state of the concerned atoms, the photo electrons from atoms of different binding states appear as generate, i.e. slightly shifted peaks. As a rule, binding with elements of higher electronegativity will shift the peaks to higher binding energy values and atoms with higher oxidation state shift the peak to higher binding energy values. Therefore, the technique is also useful for analyzing chemical bonding.

### 2.3.3. X-ray absorption spectroscopy

X-rays have sufficient energy to eject a core electron from an atom. Thus, X-ray intensity is decreased while transmitting though a material. Absorption of X-ray in a material depends on the elements present in it and energy of the incident X-rays.

The number of X-ray photons that are transmitted through a sample can be written as

$$I = I_0 e^{-\mu(E)t}$$

[2.10]
\[\mu(E)t = -\ln \frac{I}{I_0}\]  

[2.11]

Where, \(I = \) intensity transmitted through the material, \(I_0 = \) X-ray intensity hitting the material, \(\mu(E) = \) absorption coefficient, \(t = \) thickness of material the beam is passing through.

\(\mu\) depends strongly on X-ray energy \(E\), atomic number \(Z\), density \(\rho\) and atomic mass \(A\);

\[\mu \approx \rho Z^4/AE^3\]  

[2.12]

The plot of the mass absorption coefficients of matter against the incident X-ray energy or wavelength is called X-ray absorption spectrum (XAS). XAS gives the information about electronic and structural properties of a particular element in a material. Usually X-ray absorption spectroscopy (XAS) measures the variations in the X-ray absorption coefficients at energies near and above an X-ray absorption edge of an element, the total spectrum can be broken into two categories [79(b)];

1) XANES = X-ray Absorption Near-Edge Spectroscopy

2) EXAFS = Extended X-ray Absorption Fine Structure

i. **Extended X-ray Absorption of Fine Structure (EXAFS)**

The photoelectrons emitted from an atom due to the interaction of incident X-ray beam are scattered back by the surround atoms. The interference of the electron wave of the emitted and back scattered electrons interferes with the incident X-ray wave which results in a variation in the X-ray absorption pattern of the atom. When the electron waves of the outgoing and backscattered electrons are in phase, which happens with the X-ray having energy similar to absorption edge, the absorption of X-ray is maximum and appeared as a local maximum in the X-ray photo absorption spectra [79b]. At higher X-ray energy, the photoelectron has greater kinetic energy
and thus a shorter wavelength, resulting in destructive interference and a local minimum in photo absorption cross section. The physical origin of EXAFS is thus related to the electron scattering process and hence can provide information on the atomic species, arrangements of atoms and the bonding mechanisms. The schematic of EXAFS instrument is shown in Fig.2.6.

![Schematic diagram of an EXAFS instrument](image)

**Fig.2.6: Schematic diagram of an EXAFS instrument [79(e)]**

The synchrotron X-ray source is generally used in EXAFS, which gives the full range of X-rays and a monochromator uses the Braggs diffraction condition to select the particular energy. The monochromatic X-rays are then allowed to pass through the sample, which absorbs some of the incident electrons. The transmitted and incident X-ray fluxes are monitored, by gas ionization chambers.

In the present thesis certain XANES experiments have been carried out to ascertain oxidation states. The absorption experiments were carried out in transmission mode at the EXAFS beam line (BL-9) at the INDUS-2 synchrotron source at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.

### 2.3.4. Vibrational spectroscopy

The vibrational spectroscopy is the most widely used spectroscopic technique for characterization of structural and in particular the local structure around an atom in a material. Mainly these methods are based on the interaction of electromagnetic

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radiation with the different vibrational energy level in a molecule and thus they belong to molecular spectroscopy branch of spectroscopy.

In molecule, the total energy can be given as sum of all contributing components as given below

\[ E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} + E_{\text{tran}} + E_{\text{spin}} + E_{\text{nucl}}. \]  

[2.13]

Interaction of electromagnetic radiation with a molecule can result in transition between various quantized energy states. The resonance between energy states of a molecule and electromagnetic wave occurs when energy of electromagnetic radiation \((h\nu)\) matches to the difference between initial and final quantized energy states of molecule \((\Delta E)\) [80]

\[ \nu (\text{Hz}) = \frac{c}{\lambda} \]  

[2.14]

Where, \(c\) = velocity of light, while the \(\lambda\) and \(\nu\) are wavelength and frequency of electromagnetic radiation, respectively.

Depending on the absorption region of electromagnetic radiation and energy state transition, different sorts of structural information can be obtained from such vibrational spectroscopy. When Infrared (IR) radiation interacts with the molecule or crystal lattice, transition between vibrational states of the atoms occurred by absorption of equivalent energies. These absorptions appeared as bands in the spectra which are generally presented in the unit wavenumber \(\nu\) in cm\(^{-1}\). The range of IR absorption spectra is 200-4000 cm\(^{-1}\). The wave number of absorbance can be calculated by the harmonic oscillator model.

\[ \nu = \frac{1}{2\pi c} \sqrt{f/\mu} \]  

[2.15]

Where \(c\) is the light velocity, \(f\) is the force constant in the atomic scale and spring constant for the macroscopic model and \(\mu\) is the reduced mass defined by
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\[ \mu = \frac{m_A m_B}{m_A + m_B} \quad [2.16] \]

Therefore, wavenumber of absorption is related to the force constant and reduced mass. Since the force constant is directly related to the chemical bond strength, the groups with stronger chemical bond and smaller the reduced mass \( m \) (mass effect) show absorption band at higher wavenumber. Assuming the molecule in the harmonic oscillator, the energy of vibrational levels can be written as below.

\[ E_v = \left( v + \frac{1}{2} \right) \hbar \omega \quad [2.17] \]

The allowed transitions in between levels are defined by selection rules. Selection rule for allowed transition is \( \Delta v = \pm 1 \).

Modern IR instruments are based on Fourier transformation method, where the signal to noise ratio is improved considerably. In the FTIR instrument, all the frequency are used simultaneously to excite the all the vibrational modes of different types of bonds present in the sample.

![Fig.2.7: Schematic diagram of FTIR instrument](81).

The construction of FT-IR instrument is based on Michelson interferometer and the typically ray sketch FT-IR is shown the Fig.2.7. The interferometer consists of a beam
splitter, a fixed mirror and a movable mirror that translates back and forth. A beam of IR emitted from the source is split into two parts by the beam splitter, one part is transmitted to the movable mirror and the other part is reflected to the fixed mirror. The fixed and moving mirrors reflect the radiations back to the beam splitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting a part of the beam passing to the detector and the second back to the source. The beam from the moving mirror has traveled a different distance than the beam from the fixed mirror. Thus, the outgoing beam to the detector is a combination of beams reflected from the fixed and moveable mirrors and hence, an interference pattern is created due to constructive and destructive interference of wavelengths depending on differences in the path traveled by the beams. This interference pattern is called an interferogram. This interferogram then goes from the beam splitter to the sample, where some energy is absorbed and some is transmitted to the detector. The detector reads the information of wavelengths simultaneously. To obtain the infrared spectrum, the detector signal is sent to the computer where time domain wavelength information is converted to wavelength versus intensity by an algorithm called a Fourier transform. The x-axis of FT-IR spectrum is typically displayed in “wavenumbers cm\(^{-1}\)”. This unit is a product of the Fourier transform algorithm operating on the interferogram and is the reciprocal of the actual wavelength of radiation measured in centimeters at a point in the infrared spectrum.

In the present thesis IR data was recorded using a Bomem MB102FTIR (model 610) equipped with a DTGS detector.
2.3.5. Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopy based on the interaction of monochromatic light with the electron cloud and bonds of a molecule. In such interaction, a part of the incident photon energy absorbed by the molecule and exited the molecule to a virtual energy state. As the molecule cannot remain within this virtual state, it relaxes to the ground state by emission of a photon whose energy is the same as that of the exciting radiation, which is elastic and known as Rayleigh scattering as shown in the Fig.2.8. There is no frequency shift in the emitted photon for Rayleigh scattering. However, if the molecule excitation or relaxation involves different energy levels then the frequency of scattered light is different from that expected in the elastically scattered process. This process is called Raman scattering. The emitted frequencies higher than elastically scattered frequency give anti stoke lines while those lower than elastically scattered frequency give stokes lines. The Raman spectra selection rule is analogues to the IR vibrational spectroscopy. It requires a changing induced dipole moment. Electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field [82].

\[
\frac{d\varepsilon}{d\varepsilon_0} \neq 0 \quad [2.18]
\]

From group theory, if a molecule has a center of symmetry, vibrations that are Raman active will be inactive in the infrared, and vice versa. Also the scattering intensity is proportional to the square of the induced dipole moments.
The energy of Raman mode depends on the crystallographic location of atoms in the crystal and their local coordination including cell parameters, bond angle and type of coordination polyhedra and hence explicitly explains the structure of molecule and crystal. It can also directly identify local vibrational modes that are related to configurations of impurities or vacancies. Thus, the Raman scattering has been widely used to study short range order in disordered structures, micro or nano crystals, mixed oxides, impurities-doped semiconductors, alloys or compounds, and ion-implanted crystals. More detailed information on the identity and the location of the isolated defects can be obtained by Raman spectroscopy. Thus, Raman scattering provides important information on disordered materials, which is often observed consequence of chemical substitution and ion irradiation etc.

Raman spectrometer consists of four major components as shown in the Fig.2.9.

1. Excitation source, which is generally a continuous-wave (CW) laser
2. Sample illumination and collection system
3. Wavelength selector

**Fig.2.8: Schematic presentation of Raman Scattering.**
(4) Detection and computer control/processing systems.

![Block diagram of Raman spectrometer.]

**Fig.2.9: Block diagram of Raman spectrometer.**

**i. Source:** To get high intensity signal the sources used in modern Raman spectroscopy should have high frequency as possible. Five of the most common lasers along with their wavelength (nm) used for Raman spectroscopy are; Argon ion (488 or 514.5 nm), Krypton ion (530.9 or 647.1 nm), Helium/Neon (632.8 nm), Diode laser (782 or 830 nm) and Nd:YAG (1064 nm).

**ii. Sample illumination and collection system:** Due to the lower intensity of the Raman scattering, the laser beam must be focused properly on to the sample. The focusing of laser can be achieved by small diameter of the laser beam (1 mm to few µm). Collection optics consists of an achromatic lens system with a collecting lens and a focusing lens. The light gathering power of a lens can be expressed as $F = \frac{f}{D}$, where $f$ is the focal length of the lens and $D$ is the lens diameter. The smaller the value of $F$, higher is the light gathering power.

**iii. Wavelength selector:** Both prism, grating monochromator and spectrographs have been used extensively for measuring Raman spectra. Monochromators are still mainstay in this instrumentation.
iv. **Detector:** There are two different ways to detect and record Raman lines. The simple way is to gather the scattered light emerging through a glass window at the end of the Raman sample tube. Modern spectrometers have photomultiplier tubes which can do direct measurements and automatic scanning of a spectrum. The spectrum produced by the monochromator is passed through a slit which allows a narrow wavelength region to pass through which is focused on to a photomultiplier type detector. This detector employs an amplifier and a recorder to provide Raman spectrum. Modern Raman spectrometers uses CCD based detector for efficient and fast data acquisitions.

Raman spectroscopic measurements were carried out by using the Linkam variable temperature stage (Model-TS 1500) in back-scattering geometry. Scattered light was analyzed by using a home built 0.9 m single monochromator, coupled with an edge filter and detected by a cooled CCD.

**2.3.6. Thermo-gravimetric Analysis (TGA)**

Thermo-gravimetry or Thermo-gravimetric Analysis (TGA) measures the weight changes associated with thermally induced transitions. It uses a highly sensitive thermo-balance to measure the change in weight while heating or cooling the sample [83]. In TGA weight changes of a sample is being continuously recorded over a period of time under controlled heating rate in a specified atmosphere. The schematic diagram of TGA is shown in the Fig.2.10. A plot of mass change versus temperature ($T$) is referred as thermo-gravimetric curve. The TGA curve for the single decomposition consists of two characteristic temperatures, one the lowest temperature at which the onset of a mass change can be detected by thermo balance operating under particular conditions and other is the final temperature ($T_f$) at which the
particular decomposition completes. The difference $T_f - T_i$ is called as reaction interval. Thus, the resulting thermogravimetric curve (change in weight versus temperature) provides information about the thermal stability and also about the composition of any intermediate compounds that formed and also composition of the residue, if any.

Fig.2.10: Schematic diagram of thermo-balance

In present thesis the TGA experiments were performed, using a SETARAM simultaneous TG/DTA instrument, Model 92-16.18, on the part of the dried gel precursors in the flowing air atmosphere with the heating rate of 10°C/min. Precursor (sample) and reference material (alumina) were placed in two identical platinum crucibles. The weight loss of the sample as a function of temperature was monitored with the help of a thermo-balance whereas difference in temperatures between sample and reference material, as well as sample temperature was monitored simultaneously using two thermocouples.
2.3.7. Scanning Electron Microscopy (SEM)

Electron microscopy has become important for all types of materials as it can be used to get the substantial information about the structure-property correlation including morphology, crystallographic defects, composition of phases and estimation of the crystallite size etc. Due to limited resolution, the above stated information cannot be obtained by optical microscopy. It mainly involves the interaction of the electrons with the sample. In the present thesis, Scanning Electron Microscopy (SEM) was used to study the morphology of sintered pellets. The principle and experimental particulars of SEM technique is given below.

**Interaction of electron beam with specimen**

![Interaction of electron beam with specimen](image)

*Fig.2.11: Depiction of different phenomena occurring on interaction of electron beam with material.*

The scanning electron microscope (SEM) is one of the most versatile techniques used for the examination and analysis of the microstructure morphology and chemical composition characterizations. In which an electron beam is focused on the material and the signals resulting from the interaction of the beam with the surface
are recorded. Various interactions of electron beam with specimen are shown in the
Fig.2.11. These interactions can be divided into two major categories elastic
interactions and inelastic interactions. Elastic scattering results a change of direction
without change of energy of electron. Such interactions are characterized by a wide-
angle directional change of the scattered electron. In inelastic scattering, the electrons
undergo changes in direction as well as energy. The outgoing electrons in an electron-
sample interaction process considered in electron microscopes are three general types,
viz. secondary electrons (SE), back-scattered electrons (BSE) and transmission of
electrons. If the incident electrons are scattered through an angle of more than 90°
they are called backscattered electrons (BSE). The inelastic scattering occurs through
the varieties of interaction of incident electrons and atom of the sample, where
substantial amount of energy of the electron is transferred to the atoms of sample. The
excitation of the electrons by ionization process of atoms of sample leads to the
generation of secondary electrons (SE) and energy of these secondary electrons are
typically below 50 eV [84(a)].

In a typical scanning electron microscope, a well-focused electron beam is
incident and scanned over the sample surface by two pairs of electro-magnetic
deflection coils as shown in the Fig.2.12. Usually secondary (SE) and/or backscattered
electrons (BSE), are collected by a detector and the resulting signal is amplified and
displayed on a TV screen or computer monitor. The main components of a typical
SEM are electron column, scanning system, detector(s), display, vacuum system and
electronics controls. For SEM measurements sample should have the following
requirements.
(1) The sample to be probed by SEM should be vacuum compatible. Electrons, being charged particles, require vacuum environment for traversing without any change in their number and density. Thus, the sample should be able to withstand vacuum of $\sim 10^{-6}$ Torr, is required for SEM applications. Placing the sample in vacuum avoids their scattering by gas molecules, improving the measurements.

(2) The sample to be analyzed should be electrically conducting; otherwise there is a charge buildup on the sample due to accumulation of impinging electrons. This gives rise to the jumping of beam and makes the beam unstable. The surfaces of non-conductive materials are thus made conductive by coating with a thin film of gold or platinum or carbon.

The secondary electrons have low energies, so only those close to the surface can be detected. Besides the morphology, other information like elemental composition can be obtained from the analyses of the characteristic X-rays emitted by the excitation of inner shell electrons. The composition of the material can be
evaluated by Energy Dispersive X-ray spectroscopy (EDS) attachment to the SEM. Back-scattered electrons gives information about composition due to the Z-contrast, i.e. dependence of the number of back-scattered electrons to atomic number of atoms. Thus, back-scattered electrons can be used to determine local atomic number contrast, enabling distinction between different phases in the material. The technique is routinely used to study the microstructure evolution (grain size, porosity, etc.) of the sintered crystalline samples.

The technique was used to study the microstructure evolution (grain size, porosity, etc.) of the sintered samples. The instruments used in this thesis work were a mini SEM model SNE 3000M and scanning electron microscope (Zeiss, Germany). Conductive copper/gold coating was applied on the sintered samples using 6” d.c. sputtering unit, model 6-SPT, manufactured by M/s. Hind High Vacuum, Bangalore.

### 2.3.8. Mössbauer spectroscopy

Mössbauer spectroscopy is one of the best techniques for identifying the electronic or magnetic structure such as its valence, spin state, or magnetic moment of the Mössbauer active atom. Mössbauer setup consists of the source, the absorber (sample) and the detector. The γ-ray emitted by the source pass through the sample and transmitted γ-rays are detected by radiation detector. The Mössbauer drive oscillates the source so that the incident γ-rays hit the absorber with a range of energies due to the doppler effect as shown in the Fig.2.13. Sometimes it is also possible to keep source stationary and oscillate the sample, as is done with synchrotron Mössbauer instrument. The technique belongs to nuclear spectroscopy, where nuclei in atoms undergo a variety of nuclear energy level transitions with the emission or absorption of gamma rays. These nuclear energy levels are influenced by their surrounding
environment and hence they appear as a change or split of these energy levels. These changes in the energy levels can provide information about the arrangement of the surrounding atom within a system. But there are two major obstacles in obtaining this information, one is the 'hyperfine' interactions between the nucleus and its environment are extremely small, and another is the recoil of the nucleus when the gamma-ray is emitted or absorbed prevents resonance.

For the analyses of emission and absorption of gamma rays by atoms in solids following three different situations need to be considered.

1) When atom in a solid emits a gamma ray, it recoils. The recoil energy can be calculated as:

\[ E_r = \frac{E_\gamma^2}{2M} \]  

Where, \( E_\gamma \) is the gamma ray energy and \( M \) is mass of the recoiling atom. If the recoil energy is large compared to the binding energy of the atom in the solid, the atom will be completely dislodged from its lattice site.

2) If the recoil energy is larger than typical energies of lattice vibration but less than the binding energy, the atom dissipates the recoil energy by heating the surrounding solid.
3) If the calculated recoil energy is smaller than the phonon energies, it is possible for the atom to emit or absorb rays without recoiling. This is called as the Mössbauer effect.

Mössbauer effect can be detected in isotopes with very low lying excited states. Similarly, the resolution is dependent upon the lifetime of the excited state. These two factors limit the number of isotopes that can be used successfully for Mössbauer spectroscopy, the most commonly used isotope in Mössbauer spectroscopy is $^{57}$Fe. In a Mössbauer experiment, a source and absorber with the same isotope of an atom are used [85]. The emitting $^{57}$Fe results from electron capture phenomena in a $^{57}$Co radioactive source, as shown in Fig.2.14.

![Diagram of Mössbauer decay](image)

**Fig.2.14:** Decay scheme of $^{57}$Co to $^{57}$Fe (E.C. denotes electron capture) [86].

### i. Magnetic splitting

Since Fe has cubic structure, no quadrupole splitting in the absorber is observed. The resonances are due to magnetic splitting of the $^{57}$Fe nuclear levels which arise from the interaction of the nuclear magnetic dipole moment with the magnetic field due to its own electrons. The ground state of $^{57}$Fe in a magnetic field $B_z$ splits into two energy levels, which gives rise to the 14.4 keV gamma ray. Further,
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Each state is split into 2I+1 magnetic sublevel and allowed transitions must satisfy \( \Delta m = 0, \pm 1 \) selection rule as shown in the Fig.2.15. The energy difference between magnetic sublevels is \( \Delta E = g \mu_N B \), where, \( \mu_N \) is a nuclear magneton and the g factor is different for different levels and B is the magnetic field.

![Diagram of magnetic splitting of nuclear levels](image)

**Fig.2.15: Magnetic splitting of nuclear levels. (Nuclear Zeeman Effect) [86].**

ii. **Isomer shift or chemical shift**

The nucleus in an atom is always surrounded and penetrated by the electronic charge with which it interacts electrostatically. A nucleus in the excited state is larger than a nucleus in the ground state, so the nucleus in the excited state will have a larger overlap with the s-electron than when in the ground state. This will decrease the energy of the excited state relative to the ground state and any difference in the s-electron environment between the source and absorber produces a shift in the resonance energy for the transition. This shifts the whole spectrum positively or negatively depending upon the s-electron density, and sets the centroid of the spectrum.
iii. **Electric quadrupole splitting**

This splitting arises from the interaction between the gradient of the electric field at the site of the nucleus of the source and/or absorber and the quadrupole moment of the source or absorbing nucleus. This splits the nuclear energy levels as shown in the Fig.2.16.

![Diagram showing quadrupole splitting for 3/2 to 1/2 transition](image)

**Fig.2.36: Quadrupole splitting for 3/2 to 1/2 transition [86].**

Mössbauer spectra (MS) at room temperature were recorded with a conventional spectrometer (Nucleonix Systems Pvt. Ltd., Hyderabad, India) operated in constant acceleration mode in transmission geometry with $^{57}$Co source in Rh matrix of 50 mCi. The calibration of the velocity scale was done by using an enriched $^{57}$Fe metal foil. The isomer shift values are relative to Fe metal foil (= 0.0 mm/s)

2.3.9. **Electrical measurements**

i. **Impedance spectroscopy:**

Impedance spectroscopy is a valuable electrochemical technique that can be used to characterize electrical properties of any material and its interface. Impedance
measurement is a sensitive indicator of wide varieties of chemical and physical properties, such as oxide ion conduction, diffusion, corrosion in materials. The basis of impedance spectroscopy involves the analysis of the impedance (resistance to alternating current) of the observed system with respect to the applied frequency and applied signal potential.

Electrochemical Impedance Spectroscopy (EIS) measures the response of the system with the application of a periodic small amplitude ac signal. The measurements carried out at different ac frequencies provide the information about the total opposition to the flow ac current in a circuit or in a substance. The net opposition is termed as impedance and thus the measurement is generally named as Impedance Spectroscopy. Such responses to ac field contain information about bulk conduction, ionic transport, grain boundary conduction, electrolyte-electrode interfaces and dynamics of bound or mobile charges etc. In impedance measurements, the resistance to the flow of the charges can be measured by measuring the current of the system with the applied potential.

From the fundamentals of AC theory, a pure sinusoidal voltage can be expressed as \( E(t) = E_0 \exp (j\omega t) \), where \( t = \) potential at time \( t \), \( E_0 = \) amplitude of the signal, \( \omega = \) radial frequency. The relationship between radial frequency \( \omega \) (radians per second), and frequency \( f \) (hertz) is described by, \( \omega = 2\pi f \). The output current of the system can be written as the \( I(t) = I_0 \exp (jwt+\Phi) \) where \( I_0 = \) amplitude \( \Phi = \) phase difference. The value of \( \Phi \) is positive when the voltage is leading the current, and is negative when the voltage is trailing the current.

According to Ohm's law, Impedance (\( Z \)) of the circuit at any frequency (\( \omega \)) can be represented by as.
\[ Z^* = Z_0 \exp(-j\Phi) \]

\[ Z^* = Z\cos\Phi - jZ\sin\Phi \]

\[ Z^* = Z' - jZ'' \quad \text{[2.20]} \]

Where, \( Z' \) is the real part of the impedance and is in phase,

\( Z'' \) is the imaginary part of the impedance and 90° out of phase.

\( j = \sqrt{-1} \), The phase difference \( \Phi \) can be expressed by 

\[ \Phi = \tan^{-1}\left(\frac{Z''}{Z'}\right) \]

Thus, the impedance for RC series circuit is given as

\[ Z = R + \frac{1}{i\omega C} = R - \frac{i}{\omega C}, \text{(where } i = \sqrt{-1}) \quad \text{[2.21]} \]

This means that, \( Z' = R \) and \( Z'' = -\frac{1}{\omega C} \).

For a parallel RC circuit, the real and imaginary components are given by

\[ Z' = \frac{R}{1 + (\omega RC)^2} \quad Z'' = -\frac{\omega R^2C}{1 + (\omega RC)^2} \]

A typical circuit containing a resistance and a capacitance in series and parallel are shown in Fig.2.17.

![Series and Parallel Circuit Diagram](image)

**Fig.2.17:** Series and parallel arrangement of resistance and capacitance.
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The impedance data is represented in the form of a complex impedance plot, where the x-axis shows the real component (Z') and y-axis shows the imaginary component (Z''). When plotted in the complex impedance plane for various frequencies (ω), a serial RC circuit will take the form of a spike, since R will be constant with ω. The graph representing the parallel RC combination is a semi-circle with its crest at a frequency \( \omega = 1/RC \) and intercepts on the Z' axis at zero and R. Thus, the resistance values are derivable from the circular arc intercepts on the real axis. Using the values of resistances and the geometry (length/thickness and cross-sectional area) of the sample, the conductivity (σ) can be determined.

In this work, the ionic conductivity was measured in air, by impedance spectroscopy analysis using Solartron Impedance/Gain-phase Analyzer (S1 1290, U.K) Novocontrol Alpha AN impedance analyzer (Novocontrol Technologies, Germany) and Quatro nitrogen cryosystem in the frequency range 0.1 Hz to 1 MHz and the data was recorded through software ZView-2 and ZPlot-2.

**Dielectric measurements**

The complex dielectric constant (\( \varepsilon^* \)) is expressed as

\[
\varepsilon^* = \varepsilon' - i \varepsilon''
\]  \[2.22\]

Where, \( \varepsilon' \) is the real part of \( \varepsilon^* \) and is equivalent to the measured dielectric constant, \( \varepsilon'' \) is the imaginary part of \( \varepsilon^* \)

\[
\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = 1/ [G i\omega \varepsilon_0 Z^*(\omega)]
\]  \[2.23\]

Where \( G = \) geometrical factor defined as \( A/l \)

\( A = \) Area and \( l = \) thickness of specimen

\( i = \sqrt{-1} \)
$$\omega = \text{angular frequency} = 2\pi f$$

$$\varepsilon_0 = \text{permittivity of free space} = 8.85 \times 10^{-14} \text{ F/cm}$$

The $\varepsilon'$ and $\varepsilon''$ were calculated from the complex impedance as below:

$$\varepsilon' = \frac{1}{\omega \varepsilon_0} \left[ \frac{Z' n^2 + Z'' n^2}{Z'' n^2 + Z'' n^2} \right]$$

$$\varepsilon'' = \frac{1}{\omega \varepsilon_0} \left[ \frac{Z' n^2 + Z'' n^2}{Z'' n^2 + Z'' n^2} \right]$$

The complex electric modulus $M^*$ is the reciprocal of the complex permittivity $\varepsilon^*$

$$M^* = \frac{1}{\varepsilon^*}$$

$$M^* = M' + jM'' \quad \text{[2.24]}$$

Where, $M'$ and $M''$ are, respectively, real and imaginary parts of complex electric modulus. The complex electric modulus spectra represent a measure of the distribution of ion energies in the structure.

Experimentally, dielectric measurements are usually made over a range of frequencies covering the audio frequency ($\sim 10^3$ Hz), radiofrequency ($\sim 10^6$ Hz) and microwave frequency ($\sim 10^9$ Hz). The response of a dielectric to an alternating electric field is plotted as Cole-Cole complex permittivity diagrams similar to complex impedance plots. In this thesis, dielectric measurements were carried out using a Solartron Electrochemical Interface (S1 1287, U.K) in the frequency range 0.1 Hz to 1 MHz.

### 2.3.10. Magnetic measurements

The instrument used to study the magnetic property of a material is called as magnetometer. In this study, Superconducting Quantum Interference Device (SQUID) magnetometer was used to investigate the magnetic properties.

A SQUID (Superconducting Quantum Interference Device) is the most commonly used device for measuring magnetic fields. A magnetometer developed...
using this device is known as SQUID magnetometer. It is used to characterize materials with highest detection sensitivity over a broad temperature range, using applied magnetic fields up to several Tesla. Schematic diagram of SQUID magnetometer is shown in the **Fig.2.18**.

![Schematic diagram of SQUID magnetometer](image)

**Fig.2.18: Schematic diagram of SQUID magnetometer.**

A SQUID magnetometer consists of three main parts viz.

1. **Superconducting magnet**: This is a solenoid made of superconducting wire. This solenoid must be kept at liquid helium temperature in a liquid-helium dewar. A uniform magnetic field is produced along the axial cylindrical bore of the coil. Currently, superconducting solenoids that produce magnetic fields in the range 5-18 Tesla are commercially available.

2. **Superconducting detection coil**: This is a single piece of superconducting wire configured as a second-order gradiometer. It is coupled inductively to the sample. This pick-up coil system is placed in the uniform magnetic field of the solenoidal superconducting magnet.
(3) SQUID: This device responds to a fraction of the flux quantum. The SQUID is usually a thin film that functions as an extremely sensitive current-to-voltage-converter.

Magnetic measurements are done in SQUID magnetometer by moving the sample through the second-order gradiometer. The magnetic moment of the sample induces an electric current in the pick-up coil system. A change in the magnetic flux in these coils changes the persistent current in the detection circuit. Thus, the change in the current in the detection coils produces a variation in the SQUID output voltage proportional to the magnetic moment of sample. SQUID magnetometers are versatile instruments that can perform both DC and AC magnetic moment measurements.

In the present thesis work, the temperature and field dependent magnetic properties of the samples were investigated by using SQUID magnetometer (Quantum Design, USA)