

CHAPTER 2

CHARACTERIZATION TECHNIQUES AND INSTRUMENTATION

2.1 Introduction

Over the past several years, many techniques have been developed for studying the properties of ferrite nanoparticles. Different characterization of nanomaterials is performed at different levels. Some characterization methods are used to study the size, shape and morphology of nanostructures, whereas others are used to obtain details regarding the physical and chemical properties of the material. The structures of materials can be studied at various levels of sophistication including crystal structure, microstructure, atom-level structure and electronic structure. This chapter discusses in brief the various characterization techniques and analysis carried out to probe into the internal structure, surface morphology and optical, magnetic and electrical properties of the synthesized materials and their instrumental details.

2.2 Characterization techniques

The prepared samples in the present research work were characterized using powder X-ray Diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), High Resolution Transmission Electron Microscopy (HRTEM) with Selected Area Electron Diffraction (SAED), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDAX), Ultraviolet-Visible (UV-Vis) absorbance spectroscopy, Vibrating Sample Magnetometer (VSM) and dielectric analyser in order to study their structural, morphological, optical, magnetic and electrical characteristics.

From the XRD data, the lattice parameters namely lattice constant, volume of a unit cell, X-ray density, bulk density, porosity, hopping lengths, average crystallite size, specific surface area, dislocation density and microstrain are calculated. The phase identification is done by analysing the XRD data by comparing the interplanar distances and intensity values with the standard peaks using JCPDS files and peaks are indexed to the corresponding hkl planes. The shape and morphological characterization is done by TEM and SEM by analysing the images in detail. SAED is analysed in association with HRTEM to examine the crystallinity and EDAX analysis is done along with the SEM to confirm the composition of the nanoferrites. The absorptions in the FTIR spectra are analysed and designated to the corresponding characteristic vibrational modes of the material. Tauc's plot is plotted using the UV-Vis absorbance data to determine the band gap energy from which the refractive index and optical dielectric constant are calculated. The superparamagnetic behaviour and hence the magnetic parameters such as saturation magnetization, coercivity, retentivity, squareness ratio and magnetic moment are obtained from the hysteresis curve taken using VSM. The dielectric behaviour is studied from the variation of dielectric constant, dielectric loss and AC conductivity with frequency and temperature.

2.3 Instrumentation details

2.3.1 Powder X-Ray Diffraction

X-rays are electromagnetic radiation of exactly the same nature as light but of very much shorter wavelength about 1 Å. Max Von Laue in 1912, discovered that the crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. The PXRD is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural

properties of these phases. The intensities measured with XRD can provide quantitative, accurate information on the atomic arrangements at interfaces (e.g., in multilayers). It may be used to determine the structure, average particle size, unit cell dimensions and sample purity.

X-ray powder diffraction is based on the constructive interference of monochromatic X-rays and a crystalline material. These X-rays are generated when electrons moving at high speed are directed to a metal target; a small percentage of their kinetic energy is converted into X-rays. The X-rays emitted by the target consist of continuous range of wavelength and is called white radiation. The minimum wavelength in continuous spectrum is inversely proportional to the applied voltage, which accelerates the electron towards the target. If the applied voltage is sufficiently high in addition to the white radiation, the target also emits a characteristic radiation of specific wavelength and high intensity. The radiation emitted by a target includes both types of radiation. In spectroscopic notation, the characteristic radiations are named as K_{α} , K_{β} , K_{γ} etc. K_{α} radiation has high intensity and is commonly used for diffraction studies. The wavelength of this radiation for a typical copper metal target is 1.5406 Å. A beam of X-rays directed at a crystal interacts with the electron of the atom that constitutes the crystal.

The diffraction effect produced by the three dimensional grating provided by the crystal obeys Bragg's law. X-rays penetrate into the solid non-destructively and provides the information about the internal structure of solids. Crystal acts as a natural diffraction grating for the diffraction of X-ray beam incident upon it in all the directions. The X-rays are diffracted in accordance with the Bragg's law given by

$$n\lambda = 2d \sin\theta \quad (2.1)$$

where n is an integer referring to the order of reflection, λ is the wavelength, d is the spacing between the crystal lattice planes responsible for particular diffracted beam and ' θ ' is the angle that incident beam makes with lattice planes. The path difference ($2x$) between the incident beam and the reflected beam in the consecutive lattice planes is shown in figure 2.1.

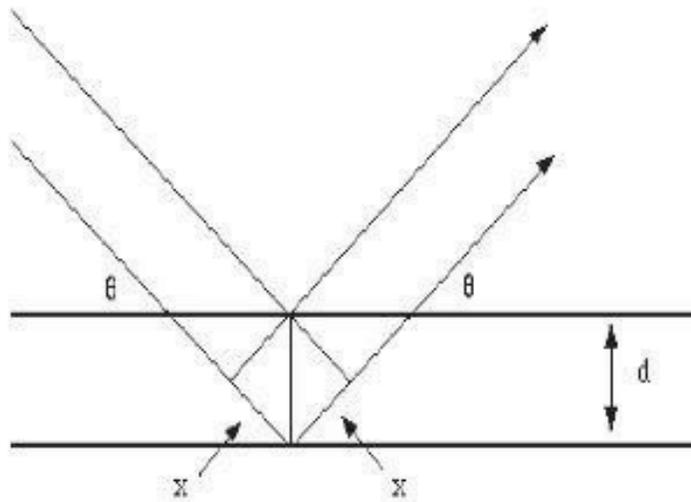


Figure 2.1 Schematic of Bragg's reflection

The width of the Bragg's reflection in a standard X-ray powder diffraction pattern can provide the information of the average grain size. The peak widens as the grain size decreases, because of the reduction in the coherently diffracting domain size, which can be assumed to be equal to the average crystallite size.

Figure 2.2 shows a schematic diagram of powder X-ray diffractometer. The filtered X-rays are collimated and directed onto the sample. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2θ . The diffracted beam may be detected by using a movable detector such as a Geiger counter, which is connected to a recorder. The counter is set to scan over a range of 2θ values at a constant

angular velocity. A detector records and processes this X-ray signal and converts the signal to a count rate which is then fed to a device such as a printer or computer monitor. The sample must be ground to fine powder before loading it in the glass sample holder. Sample should completely occupy the square glass well.

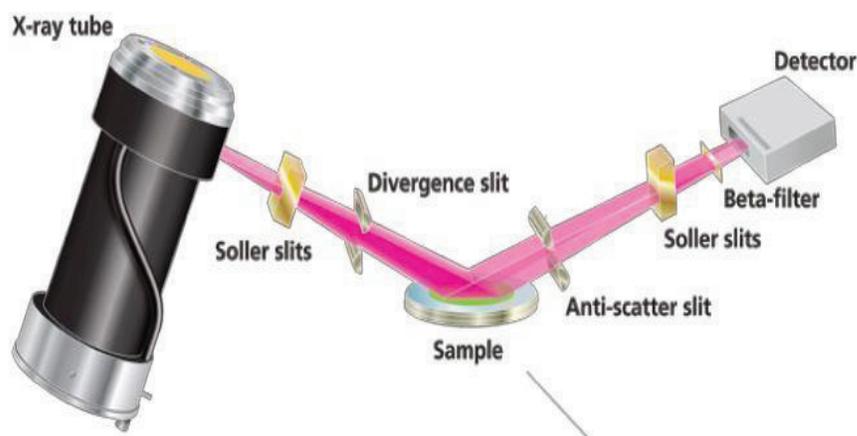


Figure 2.2 Schematic picture of powder X-ray diffractometer

In the present work, the structure and the average particle size of all the samples were identified by using powder X-ray diffraction (PXRD) at room temperature on PANalytical X'pert PRO X-ray diffractometer using CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) at $0.02^\circ/\text{sec}$ step interval.

2.3.2 High Resolution Transmission Electron Microscope

The HRTEM is a vital characterization tool for direct imaging of nanomaterials to obtain quantitative measures of the grain size, size distribution and morphology of the particle. The TEM is capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail even as small as a single column of atoms, which is

thousands of times smaller than the smallest resolvable object in a light microscope. TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to one million times with resolution better than 10 Å. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences and especially materials science.

Selected Area Electron Diffraction

The SAED is a crystallographic experimental technique that can be performed inside TEM. As a diffraction technique, SAED can be used to identify crystal structures and examine crystal defects. It is similar to X-ray powder diffraction, but unique in that area as small as several hundred nanometres in size can be examined, whereas in X-ray diffraction typically sample area extends several centimetres in size. SAED pattern of nanoparticles or nanocrystals gives ring patterns analogous to those from X-ray powder diffraction and can be used to identify texture and discriminate nanocrystalline from amorphous phases. The electron diffraction pattern yield information about the orientation, atomic arrangement and structure of narrow regions of interest in the nanomaterial (Rao et al. 2009).

Figure 2.3 shows the schematic layout of optical components in a basic TEM. The TEM consists of an emission source, which may be a tungsten filament or a lanthanum hexaboride (LaB_6) source. For tungsten, this will be of the form of either a hairpin-style filament, or a small spike shaped filament. LaB_6 sources utilize small single crystals. By connecting this gun to a high voltage source (typically ~100–300 kilo volt) the gun provided with sufficient current, begin to emit electrons either by thermionic or field electron emission into the vacuum. This extraction is usually aided by the use of a Wehnelt

cylinder. Once extracted, the upper lenses of the TEM allow for the formation of the electron probe to the desired size and location for later interaction with the sample (Hamza Abudayyeh 2012).

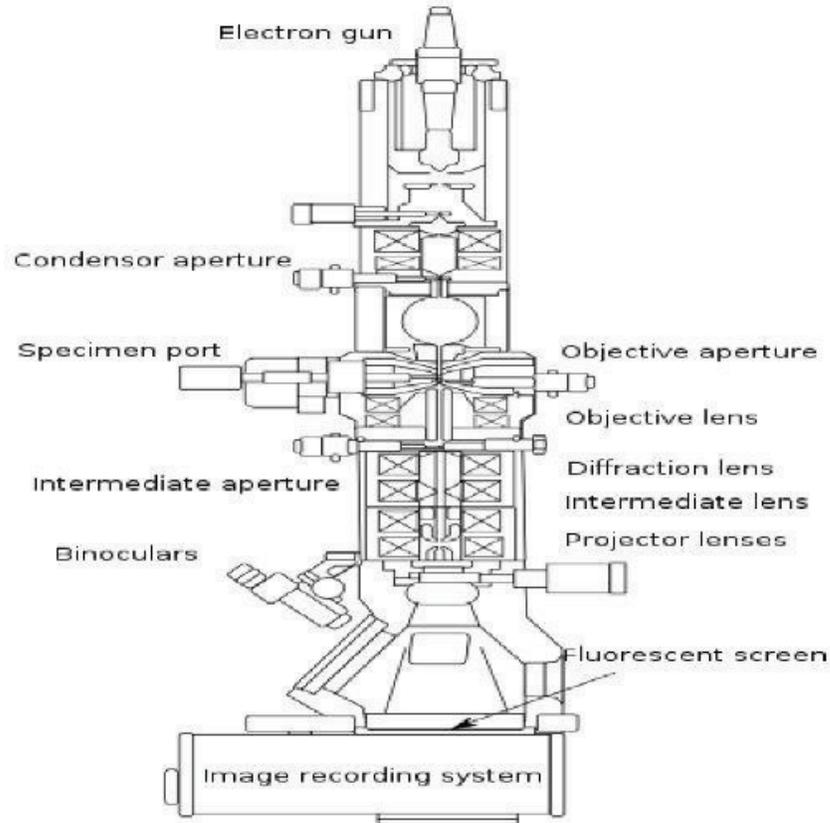


Figure 2.3 Schematic layout of a basic TEM

The use of magnetic fields allows for the formation of a magnetic lens of variable focusing power, the lens shape originating due to the distribution of magnetic flux. Additionally, electrostatic fields can cause the electrons to be deflected through a constant angle. The optical configuration of a TEM can be rapidly changed, unlike that for an optical microscope.

In the present study, the crystallite size and shape has been determined using micrographs obtained from JEOL/JEM 2100 model HRTEM.

2.3.3 Scanning Electron Microscope

Scanning electron microscope (SEM) is one of the most widely used techniques in characterization of nanomaterials and nanostructures. The signals that are derived from electron-sample interactions reveal information about the sample including surface morphology (texture) and chemical composition of the sample. In most applications, data are collected over a selected area of the sample surface and a two dimensional image is generated that displays spatial variations in these properties. The resolution of the SEM approaches a few nanometres and the instrument can operate at magnifications that are easily adjusted from 10 to over 3,00,000. Not only does the SEM produce topographical information as optical microscopes do, it also provides qualitative information of the chemical composition near the surface.

Figure 2.4 illustrates the typical SEM instrumentation. Electrons are generated in the electron gun. The tungsten-hairpin gun is commonly used, in which a tungsten filament serves as the source of electrons. By applying a current through the filament the tungsten wire will heat up and emission of electrons can be achieved. Generated electrons will be focused in front of an anode. To move the electrons down the column, a voltage difference between the tungsten filament and the anode is applied. This voltage difference is called the accelerating voltage which determines the energy and wavelength of the electrons within the beam. The beam of electrons to be condensed and focused as a fine spot on the specimen by 2 to 3 electromagnetic lenses located in the microscope column. The main functions of first two lenses namely condenser lenses are to control the beam current and the final size of the area illuminated on the specimen. The third condenser lens also called the final lens is used primarily to focus the beam of electrons on the surface of the

specimen. The final lens usually contains deflecting coils and stigmator coils (Richard Brundle et al. 1992).

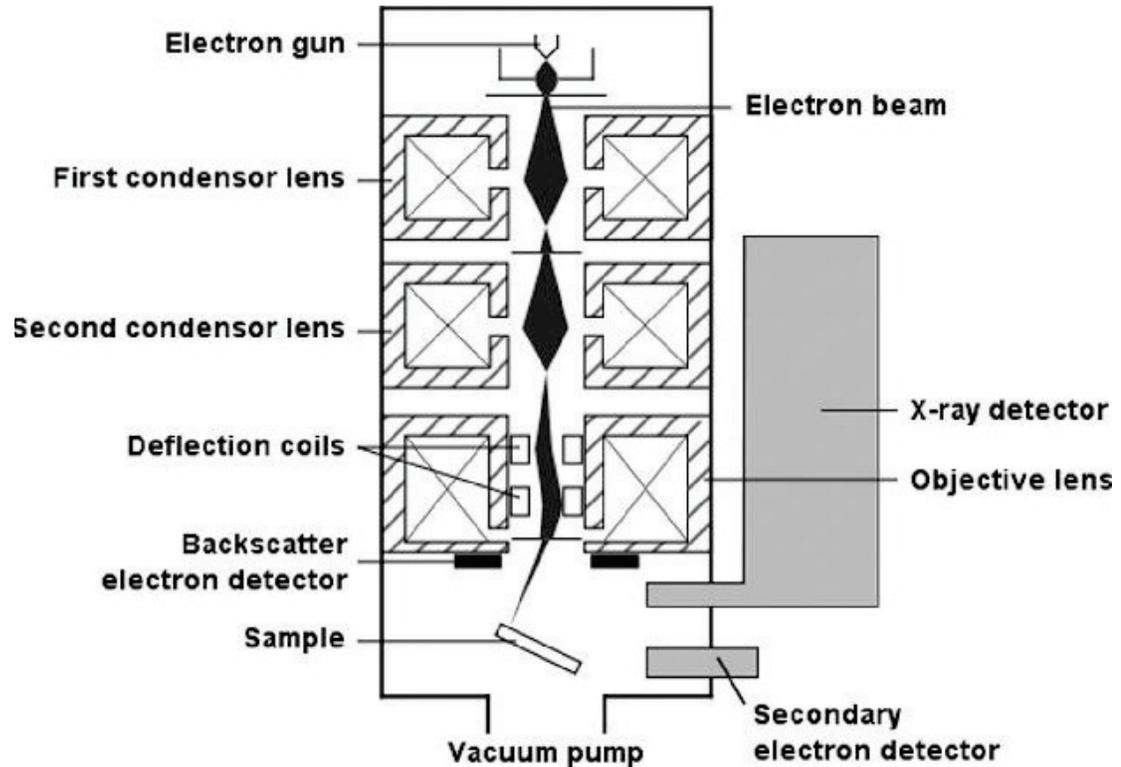


Figure 2.4 Schematic diagram of scanning electron microscope

Accelerated electrons in a SEM carry significant amount of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (that are used to determine crystal structures and orientations of minerals). Secondary electrons are most valuable for showing morphology and topography of samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples.

Energy-Dispersive X-ray spectroscope

Energy-dispersive X-ray analysis (EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample which is taken with SEM. It relies on the investigation of the interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured (Rao et al. 2009).

In the present work morphology and elemental composition were analysed using images obtained from JEOL/JSM 6390 model SEM.

2.3.4 Fourier Transform Infrared spectroscope

Infrared (IR) refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Of greatest practical use to the organic chemist is the

limited portion between 400 cm^{-1} and 4000 cm^{-1} . FTIR is conceivably the most powerful tool for identifying the functional groups or the types of chemical bonds.

FTIR spectrum is often called as the finger print of the sample and is the characteristic of each material. The spectrum represents the molecular absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Like a finger print no two unique molecular structures produce the same infrared spectrum because each different material is a unique combination of atoms. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. Infrared spectroscopy gives information on the vibrational and rotational modes of motion of a molecule and hence an important technique for identification and characterization of a substance. The peaks exhibited in the FTIR spectrum are analyzed and correlated to their respective rotational and vibrational modes of molecules. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. Organic compounds have very rich, detailed spectra but inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown material can be identified by comparison to a library of known compounds (Nakamoto 1986; Richard Brundle et al. 1992).

A beam of infrared light is focused on the samples using all-reflective optics. Depending on the sample composition, differing amounts of light are absorbed at different wavelengths. This pattern of light absorption is unique for almost every organic compound (except optical isomers) and many inorganics. User-provided reference samples aid in positive substance identification and compositional verification. Figure 2.5 shows the schematic diagram of the arrangement of FTIR (Theophanides Theophile 2012).

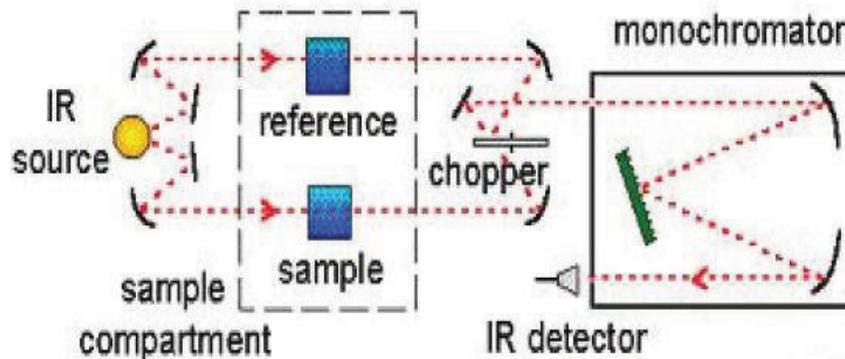


Figure 2.5 Schematic representation of FTIR spectrometer

In the present work FTIR analysis was done for all the prepared samples with the instrument Perkin Elmer model spectrophotometer by KBr pellet method in the range of $400 - 4000 \text{ cm}^{-1}$.

2.3.5 UV- Visible spectroscope

UV-Visible spectroscopy refers to absorption spectroscopy in the ultra-violet and visible spectral region. In this region of the electromagnetic spectrum, molecules undergo electronic transition. When sample molecules are exposed to light having an energy ($E = h\nu$, where E is energy, h is Planck's constant and ν is frequency), that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance versus wavelength. Figure 2.6 shows the schematic of UV-Vis spectrophotometer.

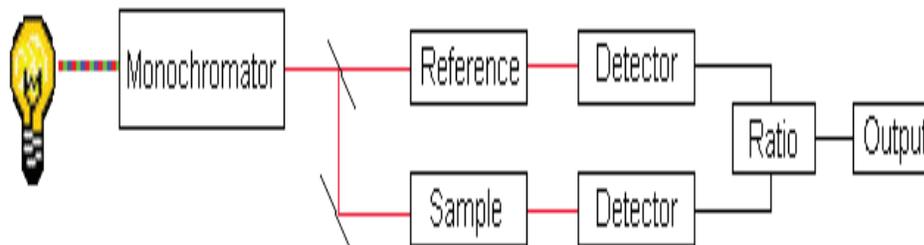


Figure 2.6 Schematic block diagram of UV-Vis spectrophotometer

The main components are a light source, double beams (reference and sample beam), a monochromator, a detector and a recording device. The source is usually a tungsten filament lamp for visible and deuterium discharge lamp for UV measurements. The light coming out of the source is split into two beams. The sample and reference cells are rectangular quartz/glass containers; they contain the solution (to be tested) and pure solvent, respectively. The spectrometer records the ratio between the reference and sample beam intensities. The recorder plots the absorbance against the wavelength. The sample is prepared into a paste and then dissolved into the solvent to make a dilute sample solution. This sample solution is filled up to mark line of the sample cell.

In the present work, UV-Visible absorption analyses were performed by Perkin Elmer Lambda 35 model UV-Vis spectrophotometer using ethanol as a dispersing medium.

2.3.6 Vibrating Sample Magnetometer

The vibrating sample magnetometer was invented by Simon Foner, 1956. This experimental technique has now become a widely used instrument for determining magnetic properties of a large variety of materials. By using this technique, the magnetic moment of a sample can be calculated with high accuracy. A schematic representation of VSM is shown in figure 2.7 (Constantinescu et al. 2010).

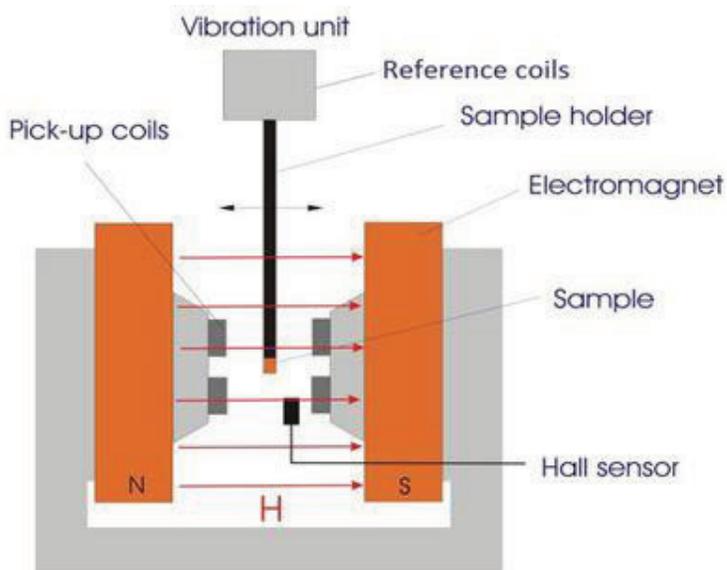


Figure 2.7 Schematic representation of vibrating sample magnetometer

A vibrating sample magnetometer is based on Faraday's law of induction, which tells us that a changing magnetic field produces an electric field. This electric field can be calculated and can give us information about the change in magnetic field. When a material is subjected to a uniform magnetic field, a dipole moment gets induced in the sample that is proportional to the product of the sample susceptibility and the applied field. If the sample is completed to experience sinusoidal movement, the resultant magnetic flux alters near the sample that induces an electrical signal in suitable positioned motionless coils. The signal is proportional to the movement, amplitude, and frequency of vibration. The samples in powder form have been filled in a cylindrical tube carefully. One end of the tube is previously closed and the other end was closed by cotton after filling the sample. The weight of unfilled tube and weight of the tube with sample were calculated so as to get the weight of the sample taken for the experiment.

These tubes were loaded in between the electromagnet using a long sample holder. The sample holder rests centred in a pair of pickup coils between the poles of an

electromagnet. The sample holder is mounted on electromechanical transducer that passes through the centre of a driving coil. The transducer is actuated by a power amplifier that itself is driven by an oscillator. The sample under investigation is restrained to vibrate only along the vertical axis. When the sample vibrates vertically, it induces a signal in the pickup coil. The pair of stationary coils picks up the induced AC signal. The output of the sample coil is fed to the differential input of a lock in amplifier. The reference input of the lock in amplifier comes from the sine wave oscillator used to drive the sample holder. The output of the lock in amplifier as well as the strength of the applied field measured by gauss meter whose probe is located at the centre of electromagnet given to data acquisition system.

In the present study, the measurement of the field dependence of the magnetization for materials was performed with the VSM Lakeshore (Model 7410). The magnetic measurements were made in the field range of ± 15000 G. For obtaining precise results with VSM a great care should be taken during measurements and calibration of the vibrating sample magnetometer is must.

2.3.7 Dielectric measurement

The dielectric analysis is an important studies carried out to investigate the conducting behaviour of a material.

Dielectric constant

The dielectric constant is the ratio of the capacitance induced by two metallic plates with an insulator between them to the capacitance of the same plates with air or a vacuum between them. It scales the inefficacy of an insulating material. The dielectric constant of solids can greatly vary in magnitude with variations in their structural properties. When an alternating field is applied to a dielectric material a phase lag between

the applied field and displacement is produced. Hence dielectric constant is a complex quantity. Thus $\epsilon = \epsilon' + j \epsilon''$ where ϵ' is the real part and ϵ'' is the imaginary part of dielectric constant (Von Hippel, 1954).

Dielectric loss

Dielectric loss or dissipation factor is the reciprocal of the ratio between the capacitive reactance of the material to its resistance at AC conductivity. The AC conductivity is a physical property that characterizes the conducting ability of a material. This is an elegant experimental tool to investigate the structural defects and internal purity of material. When a capacitor is charged under an AC voltage will have some loss in current due to ohmic resistance or impedance by heat absorption. It gives the dielectric loss of the sample.

In the dielectric analysis, fine powder of the test materials were pressed into pellets under high pressure. The pellets were coated with silver on both the sides for good ohmic contact with the electrodes. The pellet is placed between the electrodes and an alternating electric field is applied so that the meter directly measures the capacitance of the pellet and dielectric loss. Figure 2.8 shows the instrument used for dielectric measurement.



Figure 2.8 Instrument for dielectric measurement

In the present work the dielectric studies was carried out using PS11735 impedance analysing LCR meter in the frequency ranging from 1Hz to 10 MHz for various temperatures (383 K, 403 K, 423 K, 443 K and 463 K). From the measured values of capacitance and dielectric loss, the dielectric constant and AC conductivity is calculated and their frequency response is studied.