3.1 INTRODUCTION

Ferrites are among the most widely used electromagnetic materials for a broad category of applications over a wide frequency range due to their low cost and high performance [1]. Recently, ferrite research has been shifted towards developing these materials in nano-metric scales as the performance in their conventional bulk preparation routes is reaching their limits due to their higher electrical conductivity and domain wall resonance [2, 3]. However, the technological advances in electronics industry demand even more compact cores for work at higher frequencies [4]. One way to solve this problem is by synthesizing the ferrite particles in nano scales before compacting them for sintering. When the size of the magnetic particle is smaller than the critical size for multi-domain formation, the particle exists in a single domain state and domain wall resonance is avoided; thus the material can work at higher frequencies.

This chapter gives the information about the theoretical concepts and relevant background for the characterization techniques employed to characterize the prepared material. This chapter contains the detail information about X-ray diffraction, scanning electron microscopy, energy dispersive analysis
technique, transmission electron microscopy technique, DC resistivity, magnetization, AC susceptibility, dielectric properties.

3.1.1: X-ray diffraction technique

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

\[ \text{Figure 3.1: Schematic diagram of X-ray diffractometer.} \]

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law \( (n\lambda=2d \sin \theta) \). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and
counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this. X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays.
needed for diffraction. Kα1 and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with Cu-Kα radiation = 1.5418 Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from ~05° to 80°.

**Applications**

X-ray powder diffraction is most widely used technique for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.
Other applications include:

- characterization of crystalline materials
- identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- determination of unit cell dimensions
- measurement of sample purity
- With specialized techniques, XRD can be used to: determine crystal structures using Rietveld refinement
- determine of modal amounts of minerals (quantitative analysis)
- characterize thin films samples by: determining lattice mismatch between film and substrate and to inferring stress and strain
- determining dislocation density and quality of the film by rocking curve measurements
- measuring super-lattices in multilayered epitaxial structures
- determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements
- make textural measurements, such as the orientation of grains, in a polycrystalline sample

3.1.2: Energy Dispersive X-Ray Analysis Technique

EDAX Analysis stands for Energy Dispersive X-ray Analysis. It is sometimes referred to also as EDS or EDAX analysis. It is a technique used for identifying the elemental
composition of the specimen, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter. During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atom’s own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

The output of an EDX analysis is an EDX spectrum. The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks are unique to an atom, and therefore corresponds to a single element. The
higher a peak in a spectrum, the more concentrated the element is in the specimen.

An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a Ka peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a Kb peak.

3.1.3: Scanning Electron Microscopy:

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample’s surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by the SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathode), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard
detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Figure 3.2: Schematic diagram of Scanning electron microscope

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the
characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

![Diagram of electron specimen interaction]

**Figure 3.3: Electron specimen interaction**

The electron beam comes from a filament, made of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten which functions as the cathode. A voltage is applied to the loop, causing it to heat up.
The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. Some accelerate right by the anode and on down the column, to the sample. Other examples of filaments are Lanthanum hexaboride filaments and field emission guns.

The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.

3.1.5: Fourier Transform- Infrared Spectroscopy

FT-IR stands for Fourier Transform Infra Red, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.
• It can identify unknown materials
• It can determine the quality or consistency of a sample
• It can determine the amount of components in a mixture

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. 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. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

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**Figure 3.3: Schematic diagram for Infrared spectroscopy**

The original infrared instruments were of the dispersive type. These instruments separated the individual frequencies of energy emitted from the infrared source. This was accomplished
by the use of a prism or grating. An infrared prism works exactly the same as a visible prism which separates visible light into its colors (frequencies). A grating is a more modern dispersive element which better separates the frequencies of infrared energy. The detector measures the amount of energy at each frequency which has passed through the sample. This results in a spectrum which is a plot of intensity vs. frequency.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer.

![Schematic of Fourier transform –infrared spectrometer](image)

**Figure 3.7: Schematic of Fourier transform –infrared spectrometer**

The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal
can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. A means of “decoding” the individual frequencies is required. This
can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

The normal instrumental process is as follows:

1. **The Source:** Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

2. **The Interferometer:** The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3. **The Sample:** The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

4. **The Detector:** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

5. **The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation. Because there needs to be a relative scale for the absorption intensity, a
background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the “percent transmittance.” This technique results in a spectrum which has all of the instrumental characteristics removed.

Thus, all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself.

3.1.6: Magnetic Measurements

![Experimental Set-up of Pulse field hysteresis loop technique.](image)

Magnetic measurements were carried out on the instrument provided by Magneta Company, Thane (M.S.) India as shown Fig. 3.8. Magnetic field is generated in a solenoid by
passing a pulse current of sinusoidal shape. A pickup coil system is kept in the solenoid to detect field and magnetization signal of a sample placed in the pickup coil. The signals produced are then processed by an electronic system. These transitory signals are digitized by a microcontroller and then sent to computer for plotting a hysteresis loop, which is observed on the monitor with calculated values of hysteresis parameters.

The system consists of 1) pulsed power supply 2) solenoid and pick up coil assembly 3) signal processor 4) data acquisition system.

1) **Pulsed power supply**

Pulsed power supply consists of logic circuits to operated solid state relay, which sends a repetitive signal cycle sine wave current through a solenoid. This current produces a pulse magnetic field in the solenoid by taking 230 V ac signal as input giving an output sinusoidal waveform of 20 milli seconds period.

2) **Solenoid and pick up coil assembly**

Solenoid is wound on high quality Bakelite former with an enameled copper wire. A pickup coil system is wound with a fine copper wire on a former concentric with the solenoid. It consists of a two main windings whose resultant voltage is very accurately balanced network consisting of a magnitude and phase balance. An additional winding is used for perfect balance. The output of this winding is connected to a balancing network
consisting of a magnitude and phase balance. The assembly containing the solenoid and pickup coil is kept in an acrylic box.

3) **Signal processor**

The signals produced in the pickup coil are proportional to the rate of change of magnetization of the sample as well as to the applied field. These are processed using integrating, amplifying and phase correcting circuits to produce single representative of magnetization of the sample and the applied field.

4) **Data acquisition system**

The data acquisition system consists of a microcontroller with fast digitizing and high resolution circuit. The digitized data is sent to PC through a RS 232 Port. With help of specially ordered software the hysteresis loop is plotted.

3.1.7: **A.C. Susceptibility Measurements:**

The experimental setup for the thermal variation of a.c. susceptibility is as shown in Fig. 3.3. The Curie temperature of each sample was determined from the low field a.c. susceptibility data. The measurements of a.c. susceptibility were carried out in the temperature range 300–800 K. From the plots of $\chi_T/\chi_{RT}$ versus temperature, Curie temperature of the sample is obtained. The Curie temperature setup comprises of

1) A.C. susceptibility unit,

2) Solenoid and pickup coil assembly,

3) Platinum furnace,
4) Furnace power supply,
5) Thermocouple and temperature indicator.

**Figure 3.9:** Experimental Set-up of a.c. susceptibility measurement.

1. **A.C. susceptibility unit**

   Model ACS 2A the schematic diagram of the a.c. susceptibility unit is given in Fig. 3.4. It consists of function generator, balancing circuit and signal Processing circuit based on lock-in amplifier principle.

2. **Solenoid and pickup-coil assembly**

   The pickup coil is wound in two sections comprising three windings. The main two windings are identical and wound in opposition direction. The sample under test is placed in the vicinity of one of the windings producing a differential voltage proportional to the magnetization of the sample.

3. **Platinum furnace**

   The sketch of the furnace is shown in Fig. 3.5. The platinum wire is wound on a quartz tube of diameter 18 mm and
wrapped with a fiber glass ribbon and pushed tightly in another quartz tube. The furnace is introduced in a double wall jacket which can take water for cooling the outer region of the furnace. This whole assembly is put into the solenoid and then held in plastic container.

4. **Furnace power supply**

   It is a regulated d.c. power supply whose voltage and current can be varied continuously in the range 0-30 volts, 0-5 amperes respectively.

5. **Thermocouple and temperature indicator**

   The thermocouple used to measure the temperature of the furnace was platinum-platinum-rhodium (13%) junction, which is terminated into a linear temperature indicator and also into one channel of Data Acquisition System (DAS). When the thermocouple is in good contact with the samples, the temperature indicator directly reads the temperature of the sample.

3.1.8: **Electrical Properties Measurement**  

**DC resistivity:**

   Electrical properties of ferrites have been the subject of many researchers since the artificial production of spinels by Snoek [5]. The amount of charge transported through a unit block material on the application of a unit electric field per unit volume is known as the electrical conductivity of the solids. Magnetic oxides, which are commonly known as ferrites,
attracted the attention of physicist and technologists because they are magnetic semiconductors as well as electric insulator.

Hence ferrites, which are ferrimagnetic semiconductor, opened a new area in the physics of material and the need for high resistivity ferrite led to the synthesis of the various ferrites. The increasing demand for low loss-ferrites resulted in detailed investigations on the various aspects of the conductivity and on the influence of the various substitutions on the electrical conductivity, thermo- electric power, hall mobility etc. It is an experimental fact that, electrical conductivity of ferrite depends much upon the amount of iron present in the lattice in the ferrous state. A high concentration of ferrous ions leads to high electrical conductivity.

DC electrical resistivity was measured by a two point probe method. The schematic diagram of the two probe method is shown in Fig 3.8. The samples were used in the form of pellets of 10 mm diameter and of 3 mm thickness. The pellets were prepared at room temperature by compressing at 6 tons. Zero polish paper is used to make the uniform surface of the pellet after making the uniform surface the silver paste is applied on it for good ohmic contact. This silver pasted pellet is placed in between the two electrodes of the sample holder. The temperature measurements were carried out with the help of chromel-alumel thermocouple in the range of 300 K - 800 K.
The resistivity of the sample was calculated using the relation

$$\rho_{dc} = \frac{R \pi r^2}{t} \quad 3.2$$

where, R is the ohmic resistance of the sample, r is the radius of the sample in meter and t is the thickness of the pallet in meter. The plots of log \( \rho \) versus 1000/T were plotted and the resultant activation energies for conduction were computed by using relation 3.1.

This resistivity plot obeys the exponential relation given by [6],

$$\rho = \rho_0 \exp \left( \frac{\Delta E}{kT} \right) \quad 3.3$$

![Figure 3.8: Schematic diagram of two probe method](image)

The plot between log \( \rho \) and 1000/T breaks at temperature; which corresponds, closely with the observed ferrimagnetic Curie temperature. The value of \( \Delta E \) which varies between 0.1 eV to 0.5 eV, The high activation energy is associated with the high
resistivity at room temperature [6]. The activation energy increases on changing from ferromagnetic to paramagnetic region, this anomaly strongly support the influence of magnetic ordering pen conductivity process in ferrites. Many reports are available where in the slope of the plot \( \log \rho \) versus \( 1000/T \) varies at Curie temperature [7, 8]. The value of resistivity of various ferrites at room temperature varies on a wide range. For example; the resistivity at room temperature of cobalt ferrite is \( 10^6 \) ohm-cm [9].

**Dielectric measurement:**

Electrical conductivity and dielectric behaviour in ferrite depends on many factors such as preparation method, sintering temperature, amount of dopant and type of the dopant. They have relatively high resistivity at carrier frequency, sufficiently low losses for microwave applications and wide range of other electrical properties. The dielectric measurements were made using the two probe method. Then the silver paste is applied on the flat surface of the pellet. The ac parameter such as dielectric constant (\( \varepsilon' \)) dielectric loss (\( \varepsilon'' \)), dielectric loss tangent (\( \tan \delta \)) depends on the frequency under investigation. The measurement of ac resistance (R) and capacitance (c) were measured with the help of LCR-Q meter (HP 4284A) in the frequency range of 100 Hz to 1 MHz.

The dielectric constant decreases with increasing frequency and at higher frequency it remains constant, this behavior is
normal ferrimagnetic behavior. The variation of the dielectric constant with frequency reveals the dispersion due to Maxwell-Wagner type interfacial polarization in agreement with the Koop’s phenomenological theory [10]. According to these models the dielectric structure is supposed to be composed of the fairly well conducting ferrite grains, separated by a second thin layer of grain boundaries of poorly conducting substances. These grain boundaries could be formed during the sintering process due to the superficial reduction or oxidation of crystallites in the porous materials as a result of their direct contact with the firing atmosphere.

Dielectric constant ($\varepsilon'$) is calculated by the equation [11].

$$\varepsilon' = \frac{C d}{\varepsilon_0 A}$$

where, C is the capacitance of the pellet in Farad, d is the thickness of the pellet in cm. A is the cross-sectional area of the flat surface of the pellet and $\varepsilon_0$ is the permittivity constant of free space.

Dielectric loss in ferrites is considered to originate from two mechanisms: electron hopping and charged defect dipoles. The former contributes to the dielectric loss mainly in the low frequency range. In the high frequency range, the dielectric loss mainly results from the response of defect dipoles to the field. These dipoles in ferrites are formed due to the change of the cation state, such as Fe$^{3+}$/Fe$^{2+}$, during the sintering process. The relaxation of dipoles under an electric field is decreased with
increasing frequency ultimately resulting in a decrease in the
dielectric loss in the high frequency range.

The dielectric loss in ferrite is calculated by using the formula

\[ \varepsilon'' = \varepsilon' \tan \delta \]

3.5

where, \( \varepsilon' \) is the dielectric constant and \( \tan \delta \) is the
dielectric loss tangent.

The dielectric loss tangent is defined as the ratio of loss or
resistive current to the charging current in the sample. The
dielectric loss tangent was calculated using the relation

\[ \tan \delta = \frac{1}{2 \pi f C_p R_p} \]

3.6

where, \( \delta \) is the loss angle, \( f \) is the frequency, \( R_p \) is the
equivalent parallel resistance and \( C_p \) is the equivalent parallel
capacitance.

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