CHAPTER 3
THEORETICAL CONCEPTS

3.1 GENERAL
The theory background of the various equipment used for characterizing the samples are explained in this chapter.

3.2 X-RAY DIFFRACTION
XRD is the most powerful technique when applied to crystalline materials. XRD revealed that crystals are composed of atoms or groups of atoms arranged in a regular and repeated pattern. If a crystal is rotated about an imaginary line through its centre and it gives exactly the same appearance more than once, then that line is called the axis of symmetry. The symmetry axis is twofold, threefold, fourfold or six folds depending on whether the crystal is brought into a similar position every 180, 120, 90 or 60 degrees during rotation.

Bragg's law, given below, is the fundamental of XRD technique

\[ 2d \sin \theta = n \lambda \]  
Eqn (3.1)

where 'n' is an integer denoting order of reflection, ' \lambda ' is the wavelength of X-rays, 'd' is the inter planar spacing between the successive atomic planes in the crystal and ' \theta ' is the angle between the atomic plane and both the incident and reflected beams (Cullity (1972)).

3.2.1 Intensity of Diffracted X-Ray Beam
The intensity of diffracted X-ray beam is influenced by a number of factors. The factors, which influence the relative intensity of the diffracted lines of a powder diffractogram are structure factor, polarisation factor, multiplicity factor, Lorentz factor, absorption factor and temperature factor (XRD reference manual (1999)).

3.2.2 Structure Factor
An atom consists of a nucleus and a number of electrons located around the nucleus in discrete orbits. When the angle between the incident radiation and the direction of observation is zero, there will be no phase difference between the incident wave and the wave in the direction of observation. The resulting wave will have the maximum possibility intensity. As the angle increases, the waves of the outer electrons will gradually go out-of-phase. Their contribution then start to partially cancel the waves in the direction of observation and the
intensity of the resulting wave decreases. So the scattering power of an atom is dependent on its atomic number and the direction of observation. It is also dependent on the wavelength of the incident beam because the difference in path length is also important. In general, the scattering factor will decrease if $\sin\theta/\lambda$ increases. That is why, at higher angles diffraction intensities are lower. The total amplitude of the diffracted wave is simply a summation of all diffracted waves of each unit cell of the crystal lattice. The resulting wave from one elementary cell is made up of all scattered waves from all individual atoms and their respective phase differences. This is the total scattering power of the elementary cell or the structure factor.

3.2.3 Polariation Factor

The incident beam coming from the X-ray tube is unpolarised, but the scattered or diffracted radiation is polarised. The amount of polarization depends on the angle through which the incident beam is scattered or diffracted. The total energy after scattering is proportional to $\left(1 + \cos^2 2\theta\right)$.

3.2.4 Multiplicity Factor

The multiplicity factor in powder diffraction depends on the symmetry of the crystal lattice. From Bragg’s law ($2d \sin\theta = n\lambda$) it is obvious that with monochromatic radiation all planes with identical ‘d’ spacing will reflect at the same angle ‘$\theta$’, which means that they will contribute to the same diffraction intensity.

3.2.5 Lorentz Factor

The reflection intensity of a crystal plane depends on the motion and velocity of that plane while in reflection orientation, depends on the experimental setup. In powder diffractometry (Laue method) this factor is proportional to $1/\sin^2 \theta$. The Lorentz factor is the reflection time factor.

3.2.6 Absorption Factor

The absorption factor, Comprises of the absorption of the incident beam and the diffracted beam in the sample. The absorption factors in the transmission and the reflection method are different. In transmission method, both the incident and diffracted beams are absorbed in a highly absorbing sample resulting in reduction of intensity, whereas, in the reflection method
the diffracted beam from the part closer to the surface are not absorbed, so the intensities are relatively high.

### 3.2.7 Temperature Factor

The motions of the atoms and molecules in a crystal depend on the temperature of the crystals, which is called Brown movement (brownian movement). The amplitude of these motions increases with increasing temperature. A small displacement caused by the motions causes a small phase difference, which weakens the intensity, so the higher the temperature the weaker the diffraction intensities. When the temperature reaches the melting point of the material under investigation the crystal lattice disappears and the intensity of the reflection will merge with the background.

### 3.3 JCPDS DATA

An unknown substance cannot be identified unless its pattern was available in the library records. A joint committee of ASTM and the American society for X-ray and Electron diffraction undertook the task of standardizing the procedure and publishing a card file of the pattern data. This file was updated over the years and it is called Powder Diffraction File (PDF) containing over 21500 numeric patterns of crystalline materials. Afterwards a Joint Committee on Powder Diffraction Standards (JCPDS) was set up as an international organization in 1969 (J.C.P.D.C-I.C.D.D (2003)). As the file increased in size, and more complex compound were added, it was desirable to use longer X-ray wavelengths, such as copper, iron, cobalt and chromium radiations in order to spread out the pattern as much as possible. Now CuKα is the predominant radiation used in preparing patterns for PDF.

### 3.4 INFRARED SPECTROSCOPY

#### 3.4.1 Basic Principles and Theory

Spectroscopy is a method used to analyze the interaction of electromagnetic radiation and matter. It depends on the absorption of energy by a collection of molecules, since the energy being in different regions of the electromagnetic spectrum. Infrared is used to gather information about the structure of a compound.

The IR region is divided into three regions: the near, mid and far IR. The mid IR region is of greatest practical use. This region extends from 4000cm⁻¹ to 400cm⁻¹. The regions on either
side of the infrared are known as near infrared (12820cm⁻¹ to 4000cm⁻¹) and far infrared (400cm⁻¹ to 33cm⁻¹) regions. Band intensities can be expressed either as transmittance (T) or absorbance (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm, to the base 10, of the reciprocal of the transmittance: A=\log_{10}(1/T).

The definitions of various wave parameters, equation (E=h\nu) can alternatively be expressed as

\[ E=h\nu=\frac{hc}{\lambda}=h\nu \]  

Eqn (3.2)

A molecule contains electronic, vibration and rotational energy levels. Each electronic level, within a molecule, is associated with a number of vibrational levels with less energy separations and each vibration level in turn is associated with a set of rotational levels with even less energy separations. When a molecule absorbs radiation, its energy increases in proportion to the energy of the photon. The increase in energy may be electronic, vibrational or rotational energy of the molecule. Changes in the electronic energy involve larger quanta, changes in vibrational energy involve smaller quanta and changes in the rotational energy require quanta even smaller than those of vibrational energy (Silverstein and Webster(2004), Mohan(2003) and Mohan(2004)).

Due to relatively smaller amounts of energy associated with the infrared radiation, they are incapable of electronic excitations but induce transitions between vibrational and rotational energy levels of a molecule. Thus, the infrared spectrum of a molecule results from transitions between vibrational and rotational energy levels and is also called vibrational-rotational spectrum of the molecule.

3.4.2. Molecular Vibrations

Molecule Vibrates when it is struck by a photon. The type of molecular vibrations and the relative position of atoms in molecule is not fixed but it fluctuate steadily due to vibrations of different nature. For diatomic or triatomic molecules, nature of vibrations can be described and connect it to energies of absorption; but for polyatomic molecule such vibrations cannot be easily predicted, due to interaction of many centers of vibrations.

There are two types of molecular vibrations. They are stretching and bending vibrations.
A stretching vibration is a rhythmic movement along the bond axis such that the interatomic distance is either increasing or decreasing. Therefore, the distance between the two atoms increases or decreases but the atoms remain in the same bond axis. There are two types of stretching vibrations. They are, symmetric stretching and asymmetric stretching. If the movement of the atoms with respect to a particular atom in a molecule is in the same direction then it is symmetric stretching. If one atom approaches the central atom while the other departs from it then this type of stretching is called asymmetric stretching.

A bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remaining of the molecule without movement of the atoms in the group with respect to one another. For example, scissoring, rocking, wagging and twisting vibrations involve a change in bond angles with reference to a set of coordinates arbitrarily set up within the molecule. In this type of vibrations, the positions of the atoms change with respect to the original bond axis. Bending vibrations are of four types.

They are scissoring, rocking, wagging and twisting. If the two atoms connected to a central

(1) O ⇌ O

stretching vibration 3400 cm$^{-1}$

(2) H ⇌ H

bending vibration 1600 cm$^{-1}$

(3) O ⇌ O

bending vibration 900-1000 cm$^{-1}$

(4) Me$_2$ ⇌ O ± Me$_0$

stretching vibration 600-550 cm$^{-1}$

(5) Me$_0$ ⇌ O

stretching vibration 450-385 cm$^{-1}$

(6) Me$_2$ ⇌ Me$_0$

stretching vibration 330-330 cm$^{-1}$

atom moves toward and away from each other with deformation of valence angle then it is called scissoring. In rocking, the structural unit swings back and forth out of the plane of the molecule. In wagging, the structural unit swings back and forth in the plane of the molecule. In twisting, the structural unit rotates about the bond, which joins it to the rest of the molecule. In the IR spectra of hydrated oxides the following vibrations, with a corresponding (approximate) wavenumber are (Eduards Auzans (1999))
where O is oxygen, H - hydrogen, MeO is metal in the octahedric site and Mt - in the tetrahedric site.

The OH stretching vibration

(1) causes a strong absorption band at about 3400 cm\(^{-1}\). The bending vibration
(2) at about 1600 cm\(^{-1}\), typical of the H\(_2\)O molecule, is less intensive. The third absorption band
(3) is due to the OH deformation vibration. For strong hydrogen bridges, its maximum lies at about 900-1000 cm\(^{-1}\). These first three bands indicate the presence of free and crystalline water. The metal-oxygen absorption bands
(4) and (5) are characteristic pronounced for all spinel structures in particular or ferrites.

(6) is less intense than bands (4) and (5), sometimes it merges with the band (5) and gives one wide band at 420-330 cm\(^{-1}\).

3.5 INDUCTIVELY COUPLED PLASMA- ATOMIC EMISSION SPECTROMETRY (ICP-AES)

Inductively coupled plasma (ICP) emission spectrometry was developed by, Fassel. in United States and Greenfield in United Kingdom in 1970’s. The ICP offered the best features of all those analytical techniques that were in use during those days such as atomic absorption (AA), spark emission. The detection limits were intermediate between those of flame and furnace of ‘AA’. In addition ICP afforded simultaneous multi-element capability similar to spark technique. The inductively coupled plasma (ICP) is also known as the radio frequency (RF) plasma. This is operated at high power levels, 0.5 to 3.0 kW and a frequency of 15-50 MHz. Temperature over 10000 K are reached in the plasma.

3.5.1 Principle of Atomic Emission

A given atom has a large number of possible energy levels. An emission spectrum is produced by an electronic transition from a high energy level ‘E\(_n\)’ to a lower energy level ‘E\(_m\)’. The acceptable transitions are given by the quantum mechanics selection rules. A quantity of energy Q is transferred to an atom by collision with another particle, resulting in excitation of the atom. An electron from an outer layer of the atom is excited to a higher energy level. Following this electron excitation, the electron returns, in one or several stages, to its original
energy level. The atomic emission technique measures the energy lost by an atom passing from an excited state to a lower energy state. The energy is released in the form of light rays with a wavelength ‘\( \lambda \)’, or more specifically, in the form of a photon with a frequency ‘\( \nu \)’ carrying energy ‘\( h \nu \)’.

The atomic emission spectrum is composed of discrete spectral lines. The number of photons emitted is proportional to the number of atoms of the element present. To get excited, the sample must be atomized, i.e., dissociated into free ions or atoms. For a liquid sample, the atomization process can be used.

Depending on the species excited, the lines have different names. They are line I, Line II and Line III. Line I is the emission from an atom, line II is the emission from an ion once ionized, line III is the emission from an ion twice ionized. In the plasma lines I and II are frequently observed while lines III are rarely observed and lines of a higher degree are not observed (User Manual I.C.P. Spectrometers (2001), Ewing (1960)).

3.5.2 Plasma

The gas used is argon. The emission phenomenon takes place in plasma. The plasma is a more or less ionized gas, which is electrically neutral.

3.5.3 Plasma Creation

Argon is allowed to flow through a crystal tube, which is kept inside a solenoid. The lines of force generated by the magnetic fields are directed along the axis of the solenoid, which is kept inside the tube. This takes the form of an ellipse on the outside of the circle. An electrical discharge is created to arc the plasma by partially ionizing the gas in the torch.

The electrons, which are produced, are subjected to the magnetic field induced and circulated along the axis of the crystal tube describing annular circuits, which produce induced or eddy currents. The electron path is stopped by collision, resulting in heating and ionization of other gas atoms.

3.5.4 Gas Used

Argon is generally used. Like all rare gases it is monatomic, chemically inert and has a high ionization energy (15.6 eV). The advantages are provided by argon are

(i) Emission of a relatively simple spectrum producing little spectral interference in emission spectrometry,
(ii) Capacity to atomise, ionise and excite most of the elements of the periodic table,

(iii) Absence of formation of stable composites between argon and elements,

(iv) Lower cost than that of other rare gases as it is the most widely available (1 % in air)

Its only limitation is its low thermal conductivity compared to that of molecular gases such as nitrogen or oxygen. During heating, the argon ions transfers energy to the atoms present in the sample solutions.

3.6 VIBRATION SAMPLE MAGNETOMETER (VSM)

The characterization of magnetic materials by the VSM is done through the following process:

A magnetic sample is placed in a uniform magnetic field created by an electromagnet that magnetizes the sample. The sample is then vibrated perpendicular to the magnetic field in a sinusoidal motion through mechanical means. An induced electromagnetic force (e.m.f.) is created by the electromagnet and the sinusoidal motion of the sample on to coils situated next to the sample (V.S.M. System Hardware Reference Manual (2006)). By finding the periodic field changes proportional to the vibrating frequency, magnetic properties of the sample can be found.

The VSM is able to measure the DC magnetic moment as a function of temperature, displacement, magnetic field, angle and time. These data are used to plot hysteresis loops, which are used to identify several characteristics of the magnetic sample. Some of these characteristics include: the coercivity of the material, the time it takes to change the polarity of the material and the saturation point of the material.

The mechanical motion used to vibrate the sample is typically created by a Voice Coil Actuator (VCA) or a linear motor. Such devices are powered by an amplifier and controlled by a generated signal to control the frequency and amplitude of the motion. Displacement of the sample can be measured through a series of sensors located on the shaft that connected the sample holder to the VCA or linear motor.

The spacing, arrangement, and number of coils being used need to be designed such that the signal induced on the coils by the sample is insensitive to external fields. The signal from the coil is sent to a lock-in amplifier and then to an analog-to-digital converter (A/D), which creates a digital signal that will be captured by a computer interface. By using a lock-in amplifier the VSM will filter out noise thus insuring accurate results.
A computer will be the interface between the VSM and the user. The user will be able to control the power supply, which controls the frequency, direction and amplitude of the current being fed to the electromagnet, which determines the intensity and direction of the electric field magnetizing the sample. The interface will also be able to control the signal being sent to the amplifier powering the VCA/linear motor, thus controlling the vibration of the sample. A Gauss meter will be used to accurately measure the magnetic field produced by the electromagnet displaying these results on the interface. The interface will show a detailed hysteresis loop detailing the properties of the magnetic sample.

The Vibrating Sample Magnetometer (VSM) is widely used for determining the magnetic characteristics of magnetic materials. The magnetometer measures the total magnetic moment of the sample, which is vibrating parallel to a uniform applied magnetic field. When the sample is vibrating, an induced electromagnetic force (e.m.f.) is created by the electromagnet and the sinusoidal motion of the sample on to the coils situate next to the samples. By finding the periodic changes in field, changes proportional to the vibrating frequency, magnetic properties of the sample can be measured.

The development of the VSM was accidental. Simon Foner (Simon Foner (1959)), a scientist who was at Lincoln Laboratory working with ferrite microwave components, obtained the basic patent of the VSM. The basic concept of a VSM was found when he was trying to do an AC magnetic induction experiment using a tube of Duco cement, a small replacement of $2.00 loudspeaker, a conical paper cup, and a paper straw. In the first VSM, the sample vibrated perpendicular to the opposing field produced by a normal electromagnet. It was found that as a general principle an even number of coils needed to be used in order to make for the measurements of the sample to be insensitive to position and external fields of higher order.

Simon Foner (1959) published a short note for the first model in 1956. Since the note was published, his design has become the underlying foundation to all subsequent designs. The VSM is now an ASTM standard to measure the strength of magnetic fields. It is also used worldwide in basic measurements dealing with magnetism. After the preliminary findings of Foner (Simon Foner (1959)), many variations have been made. VSM’s currently on the market have Magneto Resistance measurements, sample temperature control and automation rotation vector and torque analysis, thus making them very costly. Several of these options are designed
to measure the sample under severe conditions such as at extremely low and high temperatures or varying the sample size widely.

Once the computer has collected the signals through the Gaussmeter and lock in amplifier, the signals are used to calculate magnetic flux and magnetic field of the sample. These calculations are made, resulting in the correct variables to plot a hysteresis loop (B-H loop) onto the user interface. From the B-H loop, saturation, retentivity, and coercivity can be easily determined. B-H loop is dependent on measuring magnetic flux when the magnetizing force is changed. The vibrating sample in the rod produces this change in magnetizing force, thus performing the basic action for creating a hysteresis loop.

Retentivity is a characteristic used to measure the amount of residual magnetic field when the magnetizing force is removed once saturation is achieved. Residual magnetic flux is the amount of magnetic flux density that remains in the material once the magnetizing force is removed. The coercivity details the amount of reverse magnetic field to be applied to a material so that the remaining magnetic flux within the material returns back to zero. Saturation is the point when a material has absorbed the maximum magnetic field without drastically changing the magnetic flux density, or causing damage to the magnet.

3.6.1 Theory for Finite Size Samples

Vibrating sample magnetometers (VSM) have traditionally been calibrated by using a small high purity nickel sphere as the sample. The magnetic moment of the sample at saturation is known from the mass of the sphere and the voltage induced in the coils of the VSM is measured. The nickel sample is replaced by the sample to be measured and the calibration constant is used to convert voltage readings to a moment reading. Since the introduction of the VSM (Simon Foner (1959)), various authors (Joseph and Pesch (1983), Krishnan and Banerjee (1999), Xiaonong Xu et al., (1996), Pacyna . and Ruebenbaur (1984), Pacyna(1982) and Bragg and Seehra (1976)) have presented methods for calculating the voltage induced in different VSM coil configurations. These methods have predominantly used a point dipole approximation for the sample.
3.6.2 Voltage Induced in a Coil from a Vibrating Sample

A sample that has a magnetization \( \overrightarrow{M}(x, y, z) \) will produce a field external to the sample (assumed to be free space) \( \overrightarrow{H}(x, y, z) = \alpha_0 \overrightarrow{H}(x, y, z) \) [146]. The ‘H’ field is calculated from,

\[
\nabla \cdot \overrightarrow{H} = \nabla \cdot \overrightarrow{M} \quad \text{Eqn (3.3)}
\]

For a uniformly magnetized sample, \( \nabla \cdot \overrightarrow{M} = 0 \) everywhere except on the surface of the sample. If the sample vibrates in the z direction with \( z(t) \neq A \sin(\omega t) \), the ‘B’ field at the observation point \( x, y, z \) will be \( \overrightarrow{B}(x, y, z(t)) \). If the center of a single turn coil of radius \( (r) \) is located at \( (x_c, y_c, z_c) \) and its normal is in the x-axis direction, the flux through the coils is:

\[
\phi(t) = \int_{t_0}^{t_1} B_x(x_c, y_c, z(t))dydz. \quad \text{Eqn (3.4)}
\]

The voltage induced in the coil will be:

\[
V \frac{d\phi}{dt} = A.\cos(t) \int_{t_0}^{t_1} dB_x(x_c, y_c, z(y))dydz \quad \text{Eqn (3.5)}
\]

The well-known result that the signal induced in the coils of a VSM is proportional to the amplitude of vibration, the frequency of vibration and the gradient of the field from the sample in the direction of vibration. For the particular case of equation, the z integral can be easily solved:

\[
\frac{d\phi}{dt} = A.\cos(t) \int_{y_c^-}^{y_c^+} B_x(x_c, y_c, z(y))dy \quad \text{Eqn (3.6)}
\]

Where for a given value of \( y \), \( \Delta B_x(x_c, y, z(y)) \) is the change in \( B_x \) between the two z-values at the edge of the coil. This allows the calculation of the induced voltage without doing a field derivative.

3.6.3 Hysteresis

In an unmagnetized ferromagnetic or ferrimagnetic material the collections of parallel spins in a domain are randomly oriented throughout the material and therefore collectively self-cancel resulting in a minimal to zero net magnetization (Fig. 3.1 at \( M = 0 \)). When placed in the presence of a sufficiently large external magnetic field, the spins in each domain rotate parallel to the direction of the applied magnetic field until all the dipoles are aligned. The
plateau region of the magnetization curve is the saturation magnetization (Ms) (Fig. 3.1). Ms is a measure of the magnetization (M) and is given by

\[ M_s = \frac{M}{\rho} \quad \text{Eqn(3.7)} \]

Where ‘\( \rho \)’ is density of the material. The smooth curve in Fig. 3.1, depicts the rotation of the vector moment in the domain wall as the magnetic field strength (H) is varied and actually occurs in very small jumps, which is referred as Barkhausen effect.

**Fig. 3.1.** Magnetization (M) versus magnetic field strength (H) where \( M_s \) is the saturation magnetization, \( M_r \) is the remanence magnetization and \( H_c \) is the coercivity.

In the Fig. 3.1 (the magnetization (M) versus magnetic field strength (H)) Ms is the saturation magnetization, \( M_r \) is the remanence magnetization and \( H_c \) is the coercivity. When the applied field is decreased, magnetization decreases. In multi-domain bulk materials, demagnetization occurs primarily by spin rotation through the domain walls. If the demagnetization curve, during the removal of the applied field, does not follow the initial magnetization curve, the material displays hysteresis, which is the lag observed in Fig. 3.1. Remanence magnetization (\( M_r \)) is the magnetization remaining at zero applied field (\( H = 0 \), Fig. 3.1). The magnetic field applied in the negative direction required to return the magnetization to zero is the coercive field (\( H_c \)).