Chapter - 3

Characterization Techniques and Instrumentation
SrFe$_{12}$O$_{19}$ hexaferrite samples synthesized by three different routes are characterised by using different experimental techniques namely; Fourier Transform Infrared (FTIR) spectroscopy, Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Vibrating Sample Magnetometer (VSM) and Dielectric measurements. Details of these characterization techniques are discussed in present chapter. The effect of Swift Heavy Ion (SHI) irradiation on SrFe$_{12}$O$_{19}$ hexaferrites is studied. The details of SHI irradiation is discussed in this chapter.

3.1 Fourier Transform Infrared (FTIR) Spectroscopy

3.1.1 Working Principle

Infrared spectroscopy is non-destructive technique for materials analysis and used in the laboratory for over seventy years. Infrared absorption spectroscopy is the study of interaction of infrared radiation with matter as a function of photon frequency. Fourier Transform Infrared Spectroscopy (FTIR) provides specific information about the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. 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.

The IR region is commonly divided into three smaller areas: near - IR (400 - 10 cm$^{-1}$), mid - IR (4000 - 400 cm$^{-1}$), and far - IR (14000 – 4000 cm$^{-1}$). Infrared photons have enough energy to cause groups of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiation only at certain wavelengths and frequencies. Chemical bonds vibrate at characteristic frequencies,
and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum that can be used to identify functional groups and compounds. Some impurities produce their own characteristic bands in infrared region. Spectral measurements of these bands are used to determine concentration of the impurities and their bonding with the host materials. In order to make identification, the measured interferogram signal can not 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.

3.1.2 Sample Analysis Process

(i) Instrumentation

There are three basic spectrometer components in an FTIR system: a radiation source, an interferometer, and a detector.

![Michelson interferometer](image)

Figure 3.1 Michelson interferometer

Interferometer divides radiant beams, generates an optical path difference between the beams, and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector. As its name implies, the interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample. The most commonly used interferometer is a Michelson interferometer. It consists of three
active components: a moving mirror, a fixed mirror, and a beam splitter (Figure 3.1). The two mirrors are perpendicular to each other. The beam splitter is a semi-reflecting device and is often made by depositing a thin film of germanium onto a flat KBr substrate. Radiation from the broadband IR source is collimated and directed into the interferometer, and impinges on the beam splitter.

(ii) Sample preparation

IR spectra can be measured using liquid, solid, or gaseous samples that are placed in the beam of infrared light. A drop of a liquid can be placed as a thin film between two salt plates made of NaCl or KBr, which are transparent to infrared light at most important frequencies. A solid can be ground with KBr and pressed into a disk that is placed in the light beam. Alternatively, a solid sample can be ground into a pasty mull with paraffin oil. As with a liquid, the mull is placed between two salt plates. Solids can also be dissolved in common solvents such as CH₂Cl₂, CCl₄, or CS₂ that do not have absorptions in the areas of interest. Gases are placed in a longer cell with polished salt windows. These gas cells often contain mirrors that reflect the beam through the cell several times for stronger absorption.

(iii) Working of an FTIR spectrometer

The basic instrument design is quite simple. Figure 3.2 (a) illustrates the schematic diagram and (b) a typical FTIR spectrometer.

The normal instrumental process is as follows:

a. 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).

b. The Interferometer: The beam enters the interferometer where the ‘spectral encoding’ takes place. The resulting interferogram signal then exits the interferometer.

c. 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.

![FTIR Instrument Diagram](image)

**Figure 3.2** (a) Schematic diagram of FTIR and (b) FTIR instrument

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

e. 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.

### 3.1.3 Analytical information of FTIR

FTIR can be analysed by two techniques namely: Qualitative and Quantitative.

**(i) Qualitative analysis**

The combination of the fundamental vibrations or rotations of various functional groups and the subtle interactions of these functional groups with other atoms of the molecule results in the unique, generally complex IR spectrum for each
individual compound. IR spectroscopy is mainly used in two ways: structural elucidation and compound identification.

**a. Structural Elucidation**

Because of complex interactions of atoms within the molecule, IR absorption of the functional groups may vary over a wide range. However, it has been found that many functional groups give characteristic IR absorption at specific, narrow frequency ranges regardless of their relationship with the rest of the molecule. Generalized tables of the positions and relative intensities of absorption bands (Table 3.1) have been established and used to determine the functional groups present or absent in a molecule. Correlation charts are available in many data books [1, 2].

**b. Compound Identification**

Since the IR spectrum of every molecule is unique, one of the most positive identification methods of an organic compound is to find a reference IR spectrum that matches that of the unknown compound.

Transmittance ($T$) is the ratio of radiant power ($I$) transmitted by the sample to the radiant power ($I_0$) incident on the sample. Absorbance ($A$) is the logarithm to the base 10 of the reciprocal of the transmittance.

$$ A = \log_{10} \left( \frac{1}{T} \right) = - \log_{10} T = - \log_{10} \left( \frac{I}{I_0} \right) $$

(3.1)

The transmittance spectra provide better contrast between intensities of strong and weak bands because transmittance ranges from 0 to 100% $T$ whereas absorbance ranges from infinity to zero.

(ii) Quantitative analysis

The basis for quantitative analysis of absorption spectrometry is the Bouguer–Beer–Lambert law, commonly called Beer’s law [3]. For a single compound in a homogeneous medium, the absorbance at any frequency is expressed as,

$$ A = abc $$

(3.2)

Where $A$ is the measured sample absorbance at the given frequency, $a$ is the molecular absorptivity at the frequency, $b$ is the path length of source beam in the
sample, and \( c \) is the concentration of the sample. This law basically states that the intensities of absorption bands are linearly proportional to the concentration of each component in a homogeneous mixture or solution.

### 3.1.4 Interpretation of Infrared Spectra

The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for types of bonds. Table 3.1 shows some characteristic examples of an absorption band in the spectrum.

#### Table 3.1 Characteristic infrared absorption frequencies

<table>
<thead>
<tr>
<th>No.</th>
<th>Bond</th>
<th>Compound Type</th>
<th>Frequency range (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C-H</td>
<td>Alkanes</td>
<td>2960-2850 (s) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1470-1350 ((\nu)) scissoring and bending</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH(_3) Umbrella Deformation</td>
<td>1380 (m(\nu)-w(\nu)) - Doublet-isopropyl, t-butyl</td>
</tr>
<tr>
<td>2</td>
<td>C-H</td>
<td>Alkenes</td>
<td>3080-3020 (m) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000-675 (s) bend</td>
</tr>
<tr>
<td>3</td>
<td>C-H</td>
<td>Aromatic Rings</td>
<td>3100-3000 (m) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenyl Ring Substitution Bands</td>
<td>870-675 (s) bend</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenyl Ring Substitution Overtones</td>
<td>2000-1600 (w) - fingerprint region</td>
</tr>
<tr>
<td>4</td>
<td>C-H</td>
<td>Alkynes</td>
<td>3333-3267 (s) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>700-610 (b(\Delta)) bend</td>
</tr>
<tr>
<td>5</td>
<td>C=C</td>
<td>Alkenes</td>
<td>1680-1640 (m, w) stretch</td>
</tr>
<tr>
<td>6</td>
<td>C≡C</td>
<td>Alkenes</td>
<td>2260-2100 (w) stretch</td>
</tr>
<tr>
<td>7</td>
<td>C=C</td>
<td>Aromatic Rings</td>
<td>1600, 1500 (w) stretch</td>
</tr>
<tr>
<td>8</td>
<td>C-O</td>
<td>Alcohols, Ethers, Carboxylic acids, Esters</td>
<td>1260-1000 (s) stretch</td>
</tr>
<tr>
<td>9</td>
<td>C=O</td>
<td>Aldehydes, Ketones, Carboxylic acids, Esters</td>
<td>1760-1670 (s) stretch</td>
</tr>
<tr>
<td>10</td>
<td>O-H</td>
<td>Monomeric - Alcohols, Phenols</td>
<td>3640-3160 (s, b) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrogen-bonded -Alcohols, Phenols</td>
<td>3600-3200 (b) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carboxylic acids</td>
<td>3000-2500 (b) stretch</td>
</tr>
<tr>
<td>11</td>
<td>N-H</td>
<td>Amines</td>
<td>3500-3300 (m) stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1650-1580 (m) bend</td>
</tr>
<tr>
<td>12</td>
<td>C-N</td>
<td>Amines</td>
<td>1340-1020 (m) stretch</td>
</tr>
<tr>
<td>13</td>
<td>C≡N</td>
<td>Nitriles</td>
<td>2260-2220 (v) stretch</td>
</tr>
<tr>
<td>14</td>
<td>NO(_2)</td>
<td>Nitro Compounds</td>
<td>1660-1500 (s) asymmetrical stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1390-1260 (s) symmetrical stretch</td>
</tr>
</tbody>
</table>

\( s \) - strong, \( v \) - variable, \( m \) - medium, \( w \) – weak, and \( b \) – broad.
3.1.5 Advantages and Limitations of FTIR spectrometer

(i) Advantages

The FT-IR spectrometer has several major advantages over the dispersive instrument. Its sensitivity is better because it measures all frequencies simultaneously rather than scanning through the individual frequencies. Less energy is needed from the source and less time (typically 1 to 2 seconds) is needed for a scan. Several scans can be completed in a few seconds and averaged to improve the signal. Resolution and accuracy are also improved because a laser beam is used alongside the IR beam to control the speed of the moving mirror and to time the collection of data points. The light beam is a precise frequency reference that keeps the spectrometer accurately calibrated.

(ii) Limitations

Few limitations of FTIR spectrometer are listed below:

1) Minimal elemental information is given for most samples.

2) Background solvent or solid matrix must be relatively transparent in the spectral region of interest.

3) Molecule must be active in the IR region; i.e. when exposed to IR radiation, a minimum of one vibrational motion must alter the net dipole moment of the molecule in order for absorption to be observed.

3.2 Differential Thermal Analysis (DTA)

Differential thermal analysis (DTA) is a thermo analytic technique. The method has been used predominantly for the determination of inorganic systems.

3.2.1 Working Principle

In DTA, the material under study and an inert reference (which does not go through phase transition in the temperature range of interest) are heated (or cooled) under identical conditions, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or
against temperature (DTA curve or thermo gram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation [4]. Differential temperatures can arise between two inert samples when their response to the applied heat-treatment may not identical. So DTA can also be used to study thermal properties and phase changes which do not lead to a change in enthalpy.

3.2.2 Instrumentation

(i) Apparatus

The DTA cell consists of mainly four parts:

1. Sample holder comprising thermocouples, sample containers and a ceramic or metallic block
2. Furnace
3. Temperature programmer
4. Recording system

The essential requirements of the furnace are that it should provide a stable and sufficiently large hot-zone and must be able to respond rapidly to commands from the temperature programmer. A temperature programmer is essential in order to obtain constant heating rates. The recording system must have a low inertia to faithfully reproduce variations in the experimental set up. Figure 3.3 shows the experimental set up of a DTA cell.

The sample holder assembly consists of a thermocouple each for the sample and reference, surrounded by a block to ensure an even heat distribution. The sample is contained in a small crucible designed with an indentation on the base to ensure a snug fit over the thermocouple bead. The crucible may be made of materials such as Pyrex, silica, nickel or platinum, depending on the temperature and nature of the tests involved. The thermocouples should not be placed in direct contact with the sample to avoid contamination and degradation, although sensitivity may be compromised.
Metallic blocks are less prone to base-line drift when compared with ceramics which contain porosity. On the other hand, their high thermal conductivity leads to smaller DTA peaks. The sample assembly is isolated against electrical interference from the furnace wiring with an earthed sheath, often made of platinum-coated ceramic material. The sheath can also be used to contain the sample region within a controlled atmosphere or a vacuum. During experiments at temperatures in the range 200 to 500°C, problems are encountered in transferring heat uniformly away from the specimen. These may be mitigated by using thermocouples in the form of flat discs to ensure optimum thermal contact with the now flat-bottomed sample container, made of aluminium or platinum foil. To ensure reproducibility, it is then necessary to ensure that the thermocouple and container are consistently located with respect to each other.

The effects of specimen environment, composition, size and surface-to-volume ratio all affect powder decomposition reactions, whereas these particular variables may not affect solid-state phase changes. Experiments are frequently performed on powders so the resulting data may not be representative of bulk samples, where transformations may be controlled by the build up of strain energy. The packing state of any powder sample becomes important in decomposition.

Figure 3.3 (a) Concept sketch of a DTA cell and (b) DTA instrument
reactions and can lead to large variations between apparently identical samples. In some circumstances, the rate of heat evolution may be high enough to saturate the response capability of the measuring system; it is better than to dilute the test sample with inert material. For the measurement of phase transformation temperatures, it is advisable to ensure that the peak temperature does not vary with sample size. The shape of a DTA peak does depend on sample weight and the heating rate used. Lowering the heating rate is roughly equivalent to reducing the sample weight; both lead to sharper peaks with improved resolution, although this is only useful if the signal to noise ratio is not compromised. The influence of heating rate on the peak shape and disposition can be used to advantage in the study of decomposition reactions, but for kinetic analysis it is important to minimize thermal gradients by reducing specimen size or heating rate.

(ii) Interpretation and Presentation of Data

A simple DTA curve may consist of linear portions displaced from the abscissa because the heat capacities and thermal conductivities of the test and reference samples are not identical, and of peaks corresponding to the evolution or absorption of heat following physical or chemical changes in the test sample. The test results are a graph of the DTA signal (micro-volts) on the Y-axis plotted versus the sample temperature in °C on the X-axis. The sample graph of enhanced output for Ceramics-Structe Clay is shown in Figure 3.4.
3.3 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric Analysis (TGA) continuously monitors the weight of a sample during isothermal or dynamic temperature scans over the range from 30° C to 1000° C in an air, nitrogen, oxygen, or specialty atmosphere. Its principal uses include measurement of a material's thermal stability and composition. Thermo gravimetric analysis instruments are routinely used in all phases of research, quality control and production operations.

3.3.1 Working Principle

Thermo Gravimetric analysis (TGA) technique uses heat to force reactions and physical changes in materials. TGA provides quantitative measurement of mass change in materials associated with transition and thermal degradation. TGA records change in mass from dehydration, decomposition, and oxidation of a sample with time and temperature. Characteristic thermo-gravimetric curves are given for specific materials and chemical compounds due to unique sequence from physicochemical reactions occurring over specific temperature ranges and heating rates. These unique characteristics are related to the molecular structure of the sample [5]. When used in combination with FTIR, TGA/FTIR is capable of detailed FTIR analysis of evolved gases produced from the TGA.

3.3.2 Instrumentation

TGA analyzer consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument. Figure 3.5 shows the instrument for TGA and a typical characteristic output.
3.3.3 Analysis of TGA curve

TG Analysis can be carried out by raising the temperature gradually and plotting weight (percentage) against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data are obtained, curve smoothing and other operations may be done such as to find the exact points of inflection. Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation). Hi-resolution TGA technique is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified.
As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

3.4 X-Ray Diffraction (XRD)

In a crystalline solid, the constituent particles (atoms, ions or molecules) are arranged in a regular order. An interaction of a particular crystalline solid with X-rays helps in investigating its actual structure. Crystals are found to act as diffraction gratings for X-rays and this indicates that the constituent particles in the crystals are arranged in planes at close distances in repeating patterns. The phenomenon of diffraction of X-rays by crystals was studied by W. L. Bragg and his father W. H. Bragg in 1913. They used crystals of zinc sulphide (ZnS) for this purpose.

3.4.1 Basic Theory

Bragg gave a mathematical equation to establish a relationship between wavelength of the incident X-ray, the distance between the layers and the angle of diffraction.

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

(3.3)

Here, \(\lambda\) = wavelength of X-ray used

\(\theta\) = Angle between incident X-rays and plane of the crystal. The diffracted beam makes an angle 2\(\theta\).

\(d\) = Distance between planes of the constituent particles in a crystal.

\(n\) = An integer (1, 2, 3, 4, …etc) which represents the serial order of diffracted beams.

Bragg's equation can be used to calculate the distances between repeating planes of the particles in a crystal. Similarly, if interplanar distances are given, the corresponding wavelengths of the incident beam of X-ray can be calculated.
In case of fine particles, with reduction in the size of the particles, the XRD lines get broadened, which indicates clearly that particle size has been reduced. Information of the particle size is obtained from the full width at half maximum (FWHMs) of the diffraction peaks.

The FWHMs ($\beta$) can be expressed as a linear combination of the contributions from the strain ($\varepsilon$) and particle size ($L$) through the following relation:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{L} + \frac{\varepsilon \sin \theta}{\lambda}$$

(3.4)

3.4.2 XRD instrumentation

A typical powder XRD instrument consist of four main components such as X-ray source, specimen stage, receiving optics and X-ray detector as shown in Figure 3.6. The source and detector with its associated optics lie on the circumference of focusing circle and the sample stage at the centre of the circle. The angle between the plane of the specimen and the X-ray source is $\theta$ (Bragg’s angle) and the angle between the projection of X-ray and the detector is $2\theta$. For the XRD analysis, fine powder samples can be mounted on the sample holder and the powder was assumed to consist of randomly oriented crystallites. When a beam of X-ray is incident on the sample, X-rays are scattered by each atom in the sample. If the scattered beams are in phase, these interfere constructively and one gets the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as ‘reflecting planes’.

![Figure 3.6 Schematic of the X-ray diffraction by a crystal.](image)

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3.4.3 XRD data analysis

After recording the X-ray diffraction pattern, first step involves the indexing of XRD peaks. The indexing means assigning the correct Miller indices to each peak of the diffraction pattern.

There are three main methods for indexing of X-ray diffraction pattern:

(i) Comparing the measured XRD pattern with the standard data base (JCPDS-cards)

(ii) Analytical methods

(iii) Graphical methods.

X-ray diffraction (XRD) is used to check the monophasic nature of the samples. XRD is the most essential technique to investigate the structural aspects of the material. It helps to identify the presence of different phases, including the impurities and unreacted components in a given material. Such information provides a very useful guideline towards modification of synthesis procedures. Analysis of XRD data gives the unit cell parameters of the system. In the present study, X-ray diffraction was extensively used to investigate the course of the reaction during the synthesis of the samples and to change the heat treatment procedures accordingly.
Important Parameters from XRD Data

Analysis of XRD data provides some very useful information about the important parameters of the sample. Some of them are discussed below.

a. Unit cell volume

X-ray diffraction provides us the lattice cell parameters of crystal unit cell and therefore its volume.

Volume of a cubic unit cell,

\[ V = a^3, \ (\text{where} \ a = b = c) \]  \hspace{1cm} (3.5)

Volume of a tetragonal unit cell,

\[ V = a^2c, \ (\text{where} \ a = b) \]  \hspace{1cm} (3.6)

and Volume of a hexagonal unit cell,

\[ V = \frac{\sqrt{3}}{2} a^2 c \]  \hspace{1cm} (3.7)

Where a, b, and c are the unit cell dimensions called unit cell or lattice parameters.
b. **X-ray density**

\[
X \text{- ray density} = \frac{\text{Weight of the atoms in unit cell}}{\text{Volume of unit cell}}
\]  
(3.8)

\[
\rho = \frac{\sum A_i/N}{V} \equiv \frac{1.66042}{V_0} \text{ Å}^3
\]  
(3.9)

Where, \(\rho\) = density (gm cm\(^{-3}\))

\(A\) = atomic weight of all atoms in the unit cell

\(N\) = Avogadro number

\(V\) = Vol. of unit cell (cm\(^3\))

\(V_0\) = Vol. of unit cell (Å\(^3\))

c. **Porosity**

By comparing X-ray density to that of macroscopic density of a pressed and sintered pellet one can calculate the percent porosity in the compact. Porosity can be evaluated by using equation [6],

\[
P = \left(1 - \frac{d}{\rho}\right) \times 100 \%
\]  
(3.10)

Where, \(d\) is the bulk density of the material can be calculated by mass/volume of the samples in pellet form or by Archimedes principle.

d. **Particle size**

When the particle size of the individual crystal is less than 100 Å\(^3\), the term particle size is used. Crystals of this size range cause broadening of the Bragg peak, the extent of the broadening is given by

\[
B = \frac{0.89 \lambda}{\beta \cos \theta}
\]  
(3.11)

Where, \(B\) = broadening of the diffraction line (Bragg peak) measured at full width at half of its maximum intensity (FWHM) (in radian)

\(\lambda\) = wavelength of target

\(\beta\) = diameter of the crystal particle
3.5 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three dimensional appearance and are useful for observing the surface structure of the sample. The microstructures of hexaferrites were examined using a scanning electron microscope, SEM.

3.5.1 Principle of SEM

Scanning electron microscope (SEM) consists of an electron gun and electromagnetic lens system to study the surface structure and morphology of solids. A well defined electron beam impinges on the specimen and leads to generation of secondary electrons, back scattered electrons, absorbed electrons, characteristic X-rays etc. These electrons can be detected by suitable detectors and give information about the surface structure and morphology of the specimens. The characteristic X-rays generated are used for the identification and estimation of different elements present in the specimen by energy dispersive spectrometer (EDS) and wavelength dispersive spectrometer (WDS). The depth of focus is much larger than the optical microscope image even at lowest magnifications is one of the major advantages of SEM.

3.5.2 Working of an SEM instrument

Electrons from a thermionic or field-emission cathode are accelerated by a voltage of 1-50 kV between cathode and anode. The smallest beam cross section at the gun (the crossover) with a diameter of the order of 10-50 µm for thermionic and 100-100nm for field-emission guns, is demagnified by two or three stage electromagnetic lens system, so that an electron probe of diameter 1-10 nm carrying current of $10^{-10}$ to $10^{-12}$ A is formed at the specimen surface.

A deflection coil system in front of the last lens scans the electron probe in a raster across the specimen and in synchronism with the electron beam of a separate cathode ray tube (CRT). The intensity of the CRT is modulated by one of the signals
recorded to form an image. The magnification can be increased simply by decreasing the scan-coil current and keeping image size on CRT constant.

An advantage of SEM is the wide variety of electron - specimen interactions that can be used to form an image to give qualitative and quantitative information. The large depth of focus, excellent contrast and the straightforward preparation of solid specimen are advantages of SEM.

Here an electron beam scans the object (the specimen) and because of synchronized scans of electron beam and the CRT screen (nowadays, monitor), there is one-to-one correspondence between the spot on the specimen and the spot on the screen. Unlike Optical microscopy, SEM requires the vacuum environment and specimen surface to be electrically conductive. Figure 3.9 (a) shows the general schematic diagram of SEM.

![Figure 3.9 (a) Schematic diagram of Scanning Electron Microscope (SEM) BSE=back scattered electrons, SE=secondary electrons, SC=specimen current, EBIC=electron-beam-induced current, X=x-rays, CRT=cathode-ray tube and (b) Typical SEM instrument](image)

The electron beam is produced by hair-pin shaped tungsten (W) filament by thermionic emission. The acceleration voltage of 5 to 50 kV can be applied between anode and cathode and hence we get the electron beam of such energy. This diverged
electron beam passes through a pair of electro-magnetic lenses (coils) and finely passes through probe forming lens, which makes the beam in a form of a fine probe (~10 nm diameter). This fine electron probe scans on the specimen area (marked as lines in Figure 3.9 (a)) in a linear manner. Another electron beam is in synchronization with this beam which scans on the CRT (or monitor) with the help of same scan generator. In SEM, the formation of image takes place because of electron beam-specimen interaction [7].

### 3.5.3 Sample preparation

Specimen preparation is crucial for specimens to be examined under SEM as the specimen have to be occupied within the system vacuum and the incident beam is high voltage electron beam (of the order of thousands of Volts). The specimen (or its surface) must be electrically conductive and vacuum compatible.

For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metallic samples and alloys can be examined as it is but for organic materials, insulators and non conducting materials (like poly carbonates, rubber, plastics, concrete, ceramics, biological specimens such as bacteria and other biological specimens), objects tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultra-thin (about 100-1000 Å) layer of electrically-conducting material, like carbon, aluminium, gold, or Au-Pd alloy. These coatings/depositions are applied to the specimen by high temperature evaporation or by plasma discharge techniques. Normally carbon coating and Au-Pd coating by magnetron sputtering plasma discharge is used. Two reasons for coating, one is to prevent charging of the specimen, and other is to increase signal and surface resolution, especially with samples of low atomic number (Z). Gold coating is most widely used because gold has a high atomic number and sputter coating with gold produces high topographic contrast and resolution [8]. The improvement in resolution arises because backscattering and secondary electron emission near the surface are enhanced and thus an image of the surface is formed. Elastic and inelastic scattering are the
elementary atomic interaction processes takes place when electron beam interacts with the specimen. The incident electrons interact with specimen atoms and are significantly scattered by them.

### 3.5.4 Electron-specimen interaction

Electron beam -specimen interaction gives various signals which can be used to form images and also can be used for other important information.

In inelastic scattering, the trajectory of the incident electron is only slightly perturbed, but energy is lost through interactions with the orbital electrons of the atoms in the specimen. ‘Loss’ of kinetic energy (of the primary electron) is mainly caused by the interaction with the electrons of atoms of the specimen.

### 3.5.5 Magnification, brightness and contrast of the SEM images

Electron images are obtained by rastering the electron beam across the specimen surface using the deflection coils inside the objective lens and synchronously rastering the output signal of the detector on a cathode-ray tube (CRT). The ratio of the area rastered on the specimen to that of the CRT gives the magnification. For example, a rastered area of 200 μm² (200 x 10⁻⁶ m²) displayed on CRT with an area of 20 cm (200,000 x 10⁻⁶ m²) yields a magnification of 1000x. This is a very different process than the production of an image by an optical microscope. Electronic images are sequentially "constructed" during the rastering of the beam, whereas in optical systems all parts of the sample are imaged simultaneously. Brightness can be increased /decreased by amplifying /decreasing the signal from the sample and it can be affected by topography, composition, electrical conductivity, and other properties of the sample. Contrast reflects the variation in the signal from point to point. Contrast can also be enhanced by electronically increasing the difference between small and large signals. Working distance (WD), probe current and probe diameter, incorrect electron gun alignment, astigmatism, diffused scattering of electrons from the edges (edge effect), electrostatic charging of the sample, external disturbances(magnetic fields, flooring, improper grounding) are factors affecting the quality of the image. The SEM image looks three dimensional Because of SEM's ability to focus up to certain depth and hence the images can be easily interpreted.
3.5.6 Detectors

There are number of detectors around the specimen in the specimen chamber which collects different signals for the required information. The most common imaging mode collects low-energy (≤ 50 eV) secondary electrons that are ejected from the k-orbitals of the specimen atoms by inelastic scattering interactions with beam electrons. Due to their low energy, these electrons originate within a few nanometers from the sample surface [9]. The electrons are detected by a type of scintillator-photomultiplier system known as an Everhart-Thornley detector [10]. The secondary electrons are first collected by attracting them towards an electrically-biased grid at about + 400 V, then further accelerated towards a phosphor or scintillator positively biased to about + 2,000 V. The accelerated secondary electrons are now sufficiently energetic to cause the scintillator to emit flashes of light (cathode-luminescence) which are conducted to a photomultiplier outside the SEM column via a light pipe and a window in the wall of the specimen chamber. The amplified electrical signal output by the photomultiplier is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital conversion and displayed and saved as a digital image. This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons ‘escape’ from within the sample. As the angle of incidence increases, the ‘escape’ distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Image resolution less than 0.5 nm is possible using SEM technique.

3.6 Vibrating Sample Magnetometer (VSM)

3.6.1 Basic Theory

Ferrite exhibits ferrimagnetisms. This means there is a net magnetic moment in molecular level as a result of super exchange interaction between Metal and oxygen
ions. In a bulk ferrite, there exist domains called “Wiess Domains” in which all these molecular magnets are aligned in one direction. Domain walls separate different domains aligned in random directions and in the presence of an external magnetic field these moments can be forced to align in one direction as shown in Figure 3.10. Some energy has to be spent for this process and the magnetization always lags behind the magnetizing field and results in a magnetization loop called as B-H Loop.

![Figure 3.10 Alignment of domains with an applied magnetic field](image)

In the absence of an applied magnetic field, the infinitesimal magnetic dipoles in most materials are randomly oriented, giving a net macroscopic magnetization of zero Figure 3.10 (A). When an external magnetic field is applied, the magnetic dipoles have a tendency to align themselves with the applied magnetic field (Figure 3.10 (B) and (C)). Material is said to be magnetically saturated when all the magnetic dipoles present are aligned in one direction (Figure 3.10 (D)).

![Figure 3.11 (a) Theoretical M-H curve (b) Variation of the coercivity (Hc) of magnetic nanoparticles with size](image)
Figure 3.11 (a) shows a theoretical magnetization, \( M \) versus magnetic field, \( H \) curve for superparamagnetic (SPM) and ferromagnetic nanoparticles (FM); where the coercive field \( H_c \), the saturation magnetization \( M_S \) and the remanent magnetization \( M_R \) parameters are indicated. Figure 3.11 (b) indicates the relation between particle size and coercivity.

3.6.2 Principle

A magnetic sample in oscillatory motion creates a time varying magnetic field in its surrounding due to its magnetization, and a voltage will be induced in a coil placed close to the sample. This principle is used in a vibrating sample magnetometer (VSM), also called Foner magnetometer [11] after its inventor Simon Foner.

3.6.3 Working of an VSM instrument

The mechanism of the VSM is to measure the induced magnetization of the samples by mechanically vibrating them in a uniform magnetic field. The magnetic moment of the sample is measured by generating a signal voltage in pick up coils due to the time varying flux emanating from the vibrating sample. The output measurement displays the magnetic moment \( M \) as a function of the field \( H \). A schematic diagram of the VSM instrument is shown in Figure 3.12 (a) and Figure 3.12 (b) shows a photograph of an instrument.
The magnetic (dipole) moment is measured in the unit \([\text{Am}^2]\). If the sample weight is known then one can calculate the magnetic moment per unit weight in \([\text{Am}^2/\text{kg}]\). If also the density or the volume of the sample is known, it is possible to calculate the magnetic moment per unit volume which corresponds to the magnetization in \([\text{A/m}]\).

### 3.7 Measurement of Dielectric properties

The measurement of complex dielectric properties of materials at radio frequency has gained increasing importance especially in the research fields, such as material science, microwave circuit design, absorber development, biological research, etc. Dielectric measurement is important because it can provide the electrical or magnetic characteristics of the materials, which proved useful in many research and development fields [12, 13]. Many techniques have been developed to measure these complex properties such as techniques in time domain or frequency domain with one port or two ports, etc. Every technique is limited to specific frequencies, materials and applications by its own constraint.

#### 3.7.1 Dielectric measurement techniques

Measurement of dielectric properties involves measurements of the complex relative permittivity \((\varepsilon_r)\) and complex relative permeability \((\mu_r)\) of the materials. A complex dielectric permittivity consists of a real part and an imaginary part. The real part of the complex permittivity, also known as dielectric constant \((\varepsilon'')\) is a measure of the amount of energy from an external electrical field stored in the material. The imaginary part is zero for lossless materials and is also known as loss factor \((\tan \delta)\). It is a measure of the amount of energy loss from the material due to an external electric field. The loss factor (or loss tangent/ dissipation factor, \(\tan \delta\)) represents the ratio of the imaginary part to the real part of the complex permittivity.

#### 3.7.2 Sample preparation

The disc shaped specimens are used for Dielectric measurements. The flat faces of disc are lapped, a record of the thickness and the diameter is done and then
the parallel faces are painted with silver paste. Silver paste is applied to both the surfaces (front and back) to provide electrical contact.

The sample is first inserted in the cell and the electrodes closed with the micrometer until they just touch the sample. The electrodes should not be forced against the sample. The micrometer is turned with a light finger touch and the electrometer setting recorded. Experimental set-up is shown schematically in Figure 3.14. The capacitance and the dielectric loss tangent values of the ceramics can be determined simultaneously. The dielectric constants of samples can be determined using various equations.

Figure 3.13 Schematic representation of the set-up for dielectric property investigations

Figure 3.14 Precision LCR meter with sample holder and sample pallets

Many materials have unique sets of electrical characteristics which are dependent on its dielectric properties. Precision measurements of these properties can provide valuable information in the manufacture or use of these materials.
The real dielectric constant ($\varepsilon'$) from the measured capacitance ($C$) and the geometry of the sample can be calculated by equation,

$$C = \frac{\varepsilon_0 \varepsilon' A}{t}$$  \hspace{1cm} (3.12)$$

Where, $\varepsilon_0 = \text{dielectric permittivity of space} = 8.854 \times 10^{-14} \text{Farad/cm}$

$A = \text{metalized area of one circular face, cm}^2$

$t = \text{thickness of the ceramic, cm.}$

### 3.8 Swift Heavy Ion (SHI) Irradiation

Research on the influence of irradiation on the magnetic properties of ferrites has been a subject of great interest with the application of these as memory storage units in equipment operating under irradiation. SHI irradiation has been carried out on few hexaferrite samples at Inter University Accelerator Centre (IUAC), New Delhi, India.

#### 3.8.1 Pelletron

The main building at IUAC houses the Pelletron tower, beam hall and the laboratory complex. The 15UD Pelletron [14], a versatile heavy ion tandem electrostatic accelerator is installed in a vertical configuration in an insulating tank of 26.5 meter height and 5.5 meter diameter. The accelerator tank is filled with an insulating, gas sulphur hexafluoride (SF$_6$) maintained at a pressure of 6-7 atmosphere. A schematic diagram of 15UD Pelletron is shown in Figure 3.15. In this machine the negative ions are produced and preaccelerated to ~ 300 keV by Cesium sputter ion source known as SNICS (Source of Negative Ions by Cesium Sputtering). Now it has been replaced by name MCSNICS (Multi Cathode SNICS).

The ions are mass analyzed by dipole magnet called injector magnet and are turned vertically downward direction. The ions then enter the strong electric field inside the accelerator. A terminal shell is located at the centre of the tank which can be charged to a high voltage (~ 15 MV) by a pellet charging system. The negative ions on traversing through the accelerating tubes from the column top of the tank to the positive terminal get accelerated. On reaching the terminal they pass through a
stripper (foil or gas) that removes some electrons from the negative ions thus transforming the negative ions into the positive ions. For very heavy ions (i.e. atomic number A >50), the lifetimes of the carbon foils used in stripper are limited to a few hours due to radiation damage. Therefore a gas filled canal or a combination of the gas stripper followed by a foil stripper is used for heavy ions. The transformed positive ions are then repelled away from the positively charged terminal and are accelerated to ground potential to the tank.

\[ E_t = E_{decpot} + (1 + q_t) V \]  \hspace{1cm} (3.13)

*Figure 3.15 The Pelletron Accelerator at IUAC*

In this way, same terminal potential is used twice to accelerate the ions. Therefore this accelerator is called tandem Pelletron accelerator. The final energy of the emerging ions from the accelerator is given by
Where, $E_i$ is the energy of the ion having a charge state $q_i$ after stripping; $V$ is the terminal potential in MV and $E_{\text{decpot}}$ is the deck potential of the SNICS source. On exiting from the tank, the ions are bent into horizontal plane by analyzing magnet.

Figure 3.16 A schematic diagram represents the principle of acceleration of ions in Pelletron

This magnet works as an energy analyzer and depending on the dipole magnetic field, ions of particular energy travel in the horizontal direction. The switching magnet diverts the high-energy ion beam into desired beam line of the beam hall. The ion beam is kept centred and focused using steering magnets and quadruple triplet magnets. The beam line of the accelerator is in ultra vacuum condition ($\sim 10^{-10}$ mbar). The beam is monitoring by beam profile meter (BPM) and the current is observed by means of Faraday cups. Entire machine is computer controlled and is operated from the control room. The accelerator can accelerate an ion from Proton to Uranium from few MeV to hundreds of MeV (200 MeV) depending on the ion.
3.8.2 Material Science Beam Line

The accelerated beam of desired ions from the Pelletron is brought to the beam hall and switched to any one of the seven beam lines using the switching magnet. The Material Science beam line is at 15° to the right with respect to the zero degree beam line. This beam line houses three chamber-high vacuum chamber, ultra high vacuum chamber and goniometer chamber. The high vacuum chamber is a cylindrical shaped multiport stainless steel chamber.
Most of the irradiation experiments are performed in high vacuum chamber. A typical vacuum of $1 \times 10^{-6}$ mbar is generally maintained during irradiation. The samples to be irradiated are mounted on the four sides of the target ladder (on copper block). The whole body of the ladder is made stainless steel and a perforated square copper block is brazed at the end of the ladder. The target ladder is mounted through a Wilson seal from the top flange of the chamber. This top flange is connected to the chamber through a flexible bellow that can expand up to 11 cm from its minimum position. A stepper motor in conjunction with suitable mechanical assembly is used to control the up and down motion of the ladder. The beam on the ladder can be observed by observing the luminescence of the beam on the quartz crystal mounted on all sides of the ladder.

After the observation of the beam on the quartz, the samples to be irradiated are brought to the same position as that of the quartz by moving the ladder in the desirable position. A CCD camera is attached to one of the ports of the chamber for viewing the sample and the quartz position. The positions can be monitored using close circuit television (CCTV) in the data acquisition room. The magnetic scanner that can sweep the beam (25 mm in y-direction and 10 mm in x-direction) ensures the sample ladder, which is kept at a negative potential of 120 V. This enclosure suppresses the secondary electrons coming out of sample during irradiation. An opening in the suppressor allows the ion beam to fall on the sample. The total number of particles/charges falling on the sample can be estimated by a combination of the current integrator and the pulse counter (Faraday cup) from which the irradiation fluence can be measured.

The second chamber, UHV chamber contains facilities like in-situ scanning tunnelling microscopy (STM) for in-situ surface studies and residual gas analyzer (RGA) for ion beam induced desorption. Third chamber is the goniometer chamber, which incorporates the in-situ X-ray reflectivity (XRR), large area position sensitive detector for Elastic recoil detector analysis (ERDA) and other channelling facilities.

The irradiation experiments were performed in high vacuum chamber, with a typical vacuum maintained at $1 \times 10^{-6}$ mbar. The reason for requiring vacuum is to avoid any collision of the particle (beam) with gas molecules. The samples to be
irradiated were mounted on the four sides of the target ladder (on copper block), which were separated from each other by a distance of about 1 cm.

The counts calculated for the fluence for each sample can be calculated by using the following relation

\[
\text{n (dose)} = \text{I (nA) x t} / 1.6 \times 10^{-19} \times q \quad (3.14)
\]

or

\[
\text{Number of Counts} = \text{dose x q x 1.6 x 10^{-19}} / \text{Pulse height} \quad (3.15)
\]

### 3.8.3 SRIM Calculations

SRIM (Stopping and Range of Ions in Matter) is a group of programs, which calculate the stopping, and range of ions (10 eV - 2 GeV / amu) into matter using a quantum mechanical treatment of ion-atom collisions. During collisions, the ion and atom have a screened Coulomb collision, including exchange and correlation interactions between the overlapping electron shells. The ion also has long-range interactions with target atoms creating electron excitations and plasmons within the target. These are described by including a description of the target’s collective electronic structure and inter-atomic bond structure when the calculation is setup. The charge-state of the ion within the target is described using the concept of effective charge, which includes a velocity dependent charge state and long range screening due to the collective electron sea of the target. A full description of the calculation is found in the tutorial book [15]. This book presents the physics of ion penetration of solids in a sample tutorial manner, and then presents the source code for SRIM programs with a full explanation of its physics. SRIM program creates tables of the stopping and range of ions in matter over a wide band of ion energies. These tables are useful to set up the full Monte Carlo TRIM program, so that the target thickness is adequate to contain all the ions. The target may be a complex compound, but may only contain one layer. The stopping powers are reported as electronic energy loss (to the target electrons) and as nuclear energy loss (to the target nuclei). These are the traditional components of the ion’s energy loss.
References


