CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

The main objective of this chapter is to throw light on the theoretical background of the instruments and formulae used to analyze and explain the structural, optical, electrical and magnetic properties of nanocomposite materials. The interpretation of the results based on the various possible mechanisms and models. The electromagnetic properties of ferrites depend upon the method of preparation, chemical composition and metal ion distribution on the tetrahedral and octahedral sites. The properties of the magnetic nanomaterials can be modified by suitably doping metal cations such as Co\(^{2+}\), Mn\(^{2+}\), Zn\(^{2+}\) ions etc. and preparation techniques. Properties of the material are also affected by the raw material, method of preparation, presintering-sintering temperature. Cobalt substituted lithium ferrite \((\text{Li}_{0.5}\text{Co}_{x}\text{Fe}_{2.5-x}\text{O}_4, x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6)\) has been prepared by citrate precursor method. Hexa-ferrites are the class of magnetic nanoparticles which are becoming an area of research because of their extraordinary electrical and magnetic properties. Among various hard magnetic materials barium hexa ferrites are attractive magnetic materials attributed to their superior electro resistive magnetic semi conductive properties and have application in the formation of protective layer for radar absorbing materials, magnetic recording media, electronic equipment’s due to low eddy current losses, satellite communication etc., because of their large electrical resistivity and lower induction current and can be optimized by substitution of divalent or trivalent cations. Effect of sintering has been studied on \(\text{BaZn}_{1.5}\text{Co}_{0.5}\text{Fe}_{16}\text{O}_{27}\). The W type hexagonal ferrite have got much attention because of their highly magneto crystalline anisotropy. The ferrites with planer structure are the potential microwave absorbing materials due to their higher efficiency and lower cost as compared to other type of hexagonal ferrite material. The barium based W-type ferrites, such as Co\(_2\)W, absorbs more microwave energy through a lossy interaction of the magnetic field of the wave with higher magnetization. W-type hexagonal ferrites are good magnetic semiconductors with low electrical conductivity as well as reduced eddy currents and can play a
dominant role in a variety of technological applications such as in microwave absorbers. In the present work the W-type barium hexagonal ferrite with chemical formula BaMn$_x$Co$_2$Fe$_{16}$O$_{27}$ was prepared by citrate precursor method.

### 3.2 Method of Preparation for cobalt substituted lithium ferrite

The several research works reported on the preparation of lithium ferrite with different synthesis approaches such as conventional ceramic method, double sintering method, wet chemical methods such as self-propagating exothermic reaction method, combustion method, co-precipitation method, hydrothermal method, citrate precursor method, microwave induced combustion synthesis. Kavanloui et al., (2011) prepared Li$_{0.30}$Zn$_{0.40}$Fe$_{2.30}$O$_4$ with B$_2$O$_3$ as densification agent by solid-state reaction method and with the addition of higher amount of B$_2$O$_3$ secondary phase were obtained and sintering behavior decreased. Akhter et al., (2010) prepared Li$_{0.5-x/2}$Cd$_x$Bi$_{0.02}$Fe$_{2.48-x/2}$O$_4$ by conventional ceramic technique, the pre-sintering temperature was done at 850 °C and the sintering was done at 950 °C and 1000 °C for 4 hours in order to neglect the loss of lithium. As lithium oxide with various metal oxides in the presence of oxygen is volatile, so low sintering temperature wet chemical techniques are preferred over high sintering temperature ceramic methods to obtain final product in stoichiometric and homogeneous proportions. Thus in the present investigation, citrate precursor method is used for the preparation of cobalt substituted lithium ferrite because of its cost effectiveness, homogeneous formation of cubic ferrites, less time consuming technique and uniform particle size. The objective of the present work is to synthesize and characterize, high density cobalt substituted lithium ferrite at lower sintering temperature without using sintering aid.

#### 3.2.1 Materials used and methodology for cobalt substituted lithium ferrite

The cobalt substituted lithium ferrite (Li$_{0.5}$Co$_x$Fe$_{2.5-x}$O$_4$, with x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) were prepared by a citrate precursor method in which citric acid was used as chelating as well as reducing agent. The high purity analytical grade of Li(NO$_3$)$_3$, Fe(NO$_3$)$_3$·9H$_2$O, Co(NO$_3$)$_2$·6H$_2$O Merck, India were used as raw materials for the synthesis. These chemicals were weighed in the required stoichiometric ratio. The metal nitrates were dissolved in de-ionized water until clear solution was obtained at 40 °C by ensuring no loss of material. The process was carried out until a
brownish residue of ferrite metal oxide was obtained. The obtained metal citrate complex was then heated and stirred until brownish residue was obtained, so that all the cations are homogeneously mixed at atomic level. Pre-sintering and sintering of residue was done at 700 °C and 900 °C respectively. The phase was identified on a Panalytical X-Pert Pro Diffractometer with CuKα (λ = 1.54 Å) radiations. Further, the phase confirmation was done on Perkin Elmer Fourier Transform Spectrophotometer by using KBr pellet method. Raman studies were carried on Reinshaw in Via Raman Microscope. The morphological and Topographical studies were carried out by FESEM (Field Transmission Scanning Electron Microscope) and TEM (Transmission Electron Microscope). The powder was molded into torroids and pellets using 2% PVA as a binder for electrical as well as electromagnetic studies. DC resistivity was done on Marine India set up with computer interface. Electromagnetic studies were done on Keysight LCR meter. Magnetic parameters were measured with Mössbauer spectroscopy using WinNormos program.

3.2.2 Chemical reaction for cobalt substituted lithium ferrite

\[
0.5\text{LiNO}_3 + 2.5\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} + n \text{C}_6 \text{H}_6 \text{O}_7 \\
\rightarrow \text{Li}_{0.5} \text{Fe}_{2.5} \text{O}_4 + 4\text{N}_2 + 6n\text{CO}_2 + (10 - 4.5n)\text{O}_2
\]

\[
0.5\text{LiNO}_3 + x\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} + (2.5 - x)\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} + n \text{C}_6 \text{H}_6 \text{O}_7 \\
\rightarrow \text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x} \text{O}_4 + (8 - x)\text{N}_2 + 6n\text{CO}_2 + (10 - 4.5n)\text{O}_2
\]

3.3 Method of preparation for BaZn\textsubscript{1.5}Co\textsubscript{0.5}Fe\textsubscript{16}O\textsubscript{27}

W-type barium ferrite (BaZn\textsubscript{1.5}In\textsubscript{x}Co\textsubscript{0.5-x}Fe\textsubscript{16}O\textsubscript{27}) was prepared by co-precipitation technique and effect of sintering temperature on the structural and electrical properties of the BaZn\textsubscript{1.5}Co\textsubscript{0.5}Fe\textsubscript{16}O\textsubscript{27} was studied.

3.3.1 Materials used and methodology for BaZn\textsubscript{1.5}Co\textsubscript{0.5}Fe\textsubscript{16}O\textsubscript{27}

W-type BaZn\textsubscript{1.5}Co\textsubscript{0.5}Fe\textsubscript{16}O\textsubscript{27} with nominal composition (x ≤ 0.6, step = 0.1) has been prepared by co-precipitation method. Analytical grade of raw chemicals Ba(NO\textsubscript{3})\textsubscript{2} (Merck India), Fe(NO\textsubscript{3})\textsubscript{3} · 9H\textsubscript{2}O (Merck India), Co(NO\textsubscript{3})\textsubscript{2} · 6H\textsubscript{2}O (Merck India). NaOH was used as an alkaline medium for precipitation to occur. Stoichiometric ratios of chemicals were mixed in a triple distilled water to obtain
clear solution. 0.2 M solution of NaOH was prepared and pH ≈ 11.5 was adjusted, so that optimum precipitation could be occur. Clear solution of the metal nitrates was added slowly to the NaOH solution under constant stirring and heating (90 °C ≈ 95 °C). Heating and stirring was carried for another 30 minutes to remove segregation and formation of large aggregates. The precipitates were washed to wash out impurities until pH ≈ 7 obtained. Precipitates obtained were centrifuged in a centrifugal machine under ≈ 5000 rpm to get the slurry. Slurry was dried in a hot air oven for overnight to get dry residue. Residue was grinded in a mortar and pestle until fine powder formed. The powder was presintered at 900 °C, during presintering there is a removal of impurities. Then presintered powder was molded into pellets and torroids for dielectric studies. Structural studies were carried on a Panalytical X-Pert Pro Diffractometer with CuKα (λ = 1.54 Å) target, the phase confirmation was done with FTIR spectroscopy studies were done on Perkin Elmer. Electrical studies were done on Marine India set up with computer interface.

3.4 Method of preparation for manganese substituted Co₃W barium ferrite

Citrate precursor method was followed for the preparation of manganese doped Co₃W barium ferrite.

3.4.1 Material and methodology for manganese substituted Co₃W barium ferrite

\[ \text{BaMn}_x\text{Co}_{2-x}\text{Fe}_{16}\text{O}_{27} \] (x = 0.0, 0.2, 0.4, 0.6) was prepared by citrate precursor method. The chemicals were used for the preparation of Barium Nitrate (97%, Merck, India), Iron (III) Nitrate (>98% Merck, Germany), and Citric acid (99.5%, Merck, India), Manganese Nitrate,(97%, Merck India) Cobalt Nitrate.(97%, Merck, India). These chemicals were weighed to the required stoichiometry proportion. 3g of citric acid dissolved in 30 ml of distilled water and in another beaker all the nitrates were dissolved in 70 ml of distilled water until clear solution obtained. Then both the solutions were mixed with uniform stirring at constant temperature of 90 °C till the brownish residue obtained. Powder was molded into pellets using hydraulic press. Pre-sintering and sintering was done at 900 °C and 1300°C for 3 hours. XRD studies were done on Panalytical Xpert Pro Diffractometer using CuKα radiation. Spectroscopic studies were done on UV and FTIR. DC resistivity studies were done on two probe set up with computer interface software Marine India.
3.5 Flowchart for citrate precursor route

**CITRATE PRECURSOR ROUTE**

Metal nitrates of Li\(^+\), Fe\(^{3+}\) and Co\(^{2+}\) taken in stoichiometric ratio

Citric acid act as a chelating as well as reducing agent

Metal nitrates dissolved in de-ionized water until clear solution obtained at 40 °C

Citric acid dissolved in another beaker in de-ionized water

Clear solution of metal nitrates added to solution of citric acid so as to obtain metal citrate complex

Metal citrate complex continuously stirred under constant heating at 40 °C until brownish residue obtained

Presintering was done at 700 °C so as to remove impurities and formation of ferrite phase

Powder was molded into pellets and torroids followed by sintering at 900 °C.

**Structural, Morphological, Optical, Electrical and Magnetic Studies done**
3.6 Flowchart for co-precipitation route

1. **CO - PRECIPITATION ROUTE**
2. Metal nitrates taken in stoichiometric ratio
3. Sodium Hydroxide (NaOH) act as alkaline medium for precipitation
4. Metal nitrates dissolved in de-ionized water until clear solution obtained
5. 0.2 M NaOH solution with pH ≈ 11.5 at temperature 90 °C ≈ 95 °C taken
6. Clear solution of metal nitrates added to NaOH solution so that precipitation occurs
7. Precipitates left under constant heating and stirring so as to remove agglomeration
8. Precipitates washed until 7 pH obtained, then centrifuged under ≈ 5000 rpm
9. Residue obtained dried in oven at 80 °C and grind in mortar and pestle to obtain fine powder
10. Presintering was done at low temperature so as to remove impurities and formation of ferrite phase
11. Powder was molded into pellets and torroids followed by sintering at higher temperature.
12. **Structural, Morphological, Optical, Electrical and Magnetic Studies done**
3.7 Details of techniques used for characterization

3.7.1 X-ray Diffraction

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material on unit cell dimensions based on their diffraction pattern. It depends on the dual nature of X-rays to obtain information about the structure of crystalline material. In 1895 Wilhelm Roentgen discovered the X-ray radiations for which he got Nobel Prize in 1901. Wavelength of X-rays varies from 0.01-10 nm.

3.7.1.1 Principle of X-ray Diffraction

A crystal is built up of a periodic three dimensional arrangement of atoms, ions, or group of atoms (molecules). X-ray diffraction is a common technique for the study of crystal structures and atomic spacing. It is based on the principle of constructive interference of monochromatic X-rays and a crystalline sample. The dominant effect that occurs when an incident beam of monochromatic X-rays interact with a target material is scattering of those X-rays from atoms within the target material. In a crystalline material the diffracted X-rays undergo constructive and destructive interference. The diffraction of X-rays is described by Bragg’s Law (Cullity, 1957).

3.7.1.2 Bragg’s law

Figure 3.1 shows the schematic diagram for Bragg’s Law. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. When a crystal is bombarded with X-rays of a wavelength approximately equivalent to the atomic spacing of the crystal lattice planes and at certain incident angles, intense reflected X-rays are produced when the wavelengths of the scattered X-rays interfere constructively. In order for the waves to interfere constructively, the differences in the travel path must be equal to integer multiples of the wavelength. When this constructive interference occurs, a diffracted beam of X-rays will leave the crystal at an angle equal to that of the incident beam.

Consider a crystal lattice with (d) interplanar spacing of incidence and spacing, where n (an integer) is the “order” of reflection, λ is the wavelength of the
incident X-rays, \(d\) is the interplanar spacing of the crystal with hkl miller indices and \(\theta\) is the angle of incidence. Then, mathematically, the general relationship between the wavelength of the incident X-rays angle of incidence and spacing between the crystal lattice planes of atoms is given by:

\[
n\lambda = 2d_{hkl} \sin \theta \tag{3.1}
\]

The direction of the possible diffraction depends on the size and shape of the unit cell of the crystal.

### 3.7.1.3 Working of X-ray Diffractometer

X-ray Diffractometer consists of three basic elements:

1) X-ray tube,
2) Sample holder, and
3) 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 as shown in Figure 3.2. 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 $K_a$ and $K_b$. $K_a$ consists, in part, of $K_{a1}$ and $K_{a2}$. $K_{a1}$ has a slightly shorter wavelength and twice the intensity as $K_{a2}$. $K_{a1}$ has a slightly shorter wavelength and twice the intensity as $K_{a2}$. $K_{a1}$ and $K_{a2}$ 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$K_a$ radiation = 1.5418Å. 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 $\theta$ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of $2\theta$. The instrument used to maintain the angle and rotate the sample is termed as goniometer. For typical powder patterns, data is collected at $2\theta$ from 5° to 70°, angles that are preset in the X-ray Scan.

### 3.7.2 Scanning Electron Microscopy

Electron beam technology was developed in 1960s. A Scanning Electron Microscopy is a technique which scans a focused electron beam over a surface to create an image (Argast, 2004). Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. It is the most important electron-optical instrument for the investigation of Bulk specimen. In this microscope electrons are used instead of light to form an image.
3.7.2.1 Principle of Scanning Electron Microscopy

Accelerated electrons in SEM carry significant amount of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the sample. Figure 3.3 shows the mechanism for SEM. These signals include secondary electrons that produce SEM images, backscattered electrons, diffracted backscattered electrons that are used to determine crystal structures, photons that are characteristic X-rays used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL) and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples that is for rapid phase discrimination (Beane, 2004). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield x-rays that are of a fixed wavelength that is related to the difference in energy levels of electrons in different shells for a given element. Thus, characteristic X-rays are produced for each element in a mineral that is “excited” by the electron beam. SEM analysis is considered to be “non-destructive”; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. The SEM is also widely used to identify phases on qualitative chemical analysis and crystalline structure. Precise measurement of very small features and objects down to 50nm in size is also accomplished using the SEM. Backscattered electron images (BSE) can be used for rapid discrimination of phases in multi phase samples. SEMs equipped with diffracted backscattered electron detectors (ESBD) can be used to examine microfabric and crystallographic orientation in many materials. SEM always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically on dependent on which detectors it accommodates.
3.7.2.2 Working of Scanning Electron Microscope

A Scanning Electron Microscope uses electrons from a filament consisting of a typically heated tungsten wire accelerated down a column through a voltage potential. The electron beam is rastered over the surface of a sample. Electrons from the sample surface either secondary electrons or backscattered incident electrons are detected and an image is rendered. The accelerated electrons forming the beam may have sufficient energy to displace inner shell electrons in the target material. This leads to the production of characteristic X-rays that can be used to produce a quantitative chemical analysis. In energy dispersive X-ray spectroscopy, the energy not to be confused with the intensity of each individual X-ray arrival is determined and counted toward the development of an energy distribution histogram. With sufficient counts the histogram becomes an EDX spectrum consisting of background and characteristic X-rays peaks which can be processed to yield a quantitative analysis of an area as small as about 4 μm².

3.7.3 Transmission Electron Microscopy

A transmission electron microscopy is a technique used to view images of extremely small objects or areas of objects by passing a beam of electrons through a very thin slice of the area of interest. Transmission Electron Microscope (TEM) is a large piece of scientific equipment that forms detailed images called micrographs.
3.7.3.1 Principle of Transmission Electron Microscope

The transmission electron microscope operates on the same basic principles as the light microscope but uses electrons instead of light. The transmission electron microscope is a very powerful tool for materials science. A high energy beam of electrons is shone through a very thin sample, and the interactions between the electrons and the atoms can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries. Chemical analysis can also be performed. TEM can be used to study the growth of layers, their composition and defects in semiconductors. High resolution can be used to analyze the quality, shape, size and density of quantum wells, wires and dots.

3.7.3.2 Working of Transmission Electron Microscope

Magnetic lenses guide the electrons. A “light source” at the top of the microscope emits the electrons that travel through vacuum in the column of the microscope. Instead of glass a lens focusing the light in the light microscope the TEM uses electromagnetic lenses to focus the electrons the electrons into a very thin beam. The electron beam then travels through the specimen you want to study. Depending the density of the material present, some of the electrons are scattered and disappear from the beam. At the bottom of the microscope the unscattered electrons hit a fluorescent photographed with a camera. Figure 3.4 shows schematic representation for TEM. Transmission electron microscope type of electron microscope that has three essential systems:

1. An electron Gun, which produces the electron beam and the condenser system, which focuses the beam onto the object.
2. The image-producing system, consisting of the objective lens, movable specimen stage and intermediate and projector lenses, which focus the electrons passing through the specimen to form a real, highly magnified image, and
3. The image-recording system, which converts the electron image into some form perceptible to the human eye. The image-recording system usually consists of a fluorescent screen for viewing and focusing the image and a digital camera for permanent records. In addition, a vacuum system, consisting
of pumps and their associated gauges and valves, and power supplies are required.

![Figure 3.4 Schematic representation for TEM](image)

3.7.4 Fourier Transform Infrared Spectroscopy

IR absorption spectroscopy is an important non-destructive tool, which provides qualitative information regarding structural details of crystalline materials. It is based on the interaction of electromagnetic radiation with a molecular system, in most cases in the form of absorption of energy from the incident beam. The absorption of IR light induces transitions between the vibrational energy levels, is a quantized for Fourier Transform Infra-red Spectroscopy (FTIR) is a sensitive technique for the identification of functional group and structure of a compound under investigation. The technique provides a spectrum consists of a collection of absorption bands to identify a pure compound or to detect the presence of specific impurities. Absorption of Infra-red radiations causes the various bands in a molecule to stretch and bend with respect to one another. The ordinary Infra-red region extends from 4000 cm$^{-1}$ to 667 cm$^{-1}$. The region from 12500 cm$^{-1}$ to 4000 cm$^{-1}$ is called Near Infra-red region and region between 667 cm$^{-1}$ to 50 cm$^{-1}$ called Far Infra-red region. The important region for ferrites is 400 cm$^{-1}$ – 600 cm$^{-1}$. The absorption of Infra-red radiations can be expressed either in terms of wavelength ($\lambda$) or in wave number ($\tilde{\nu}$).
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The graph is plotted between transmittance (%) and wave number (\(\tilde{\nu}\)). There is inverse relation between wavelength and wavenumber expressed as:

\[
\text{Wave number (}\lambda\text{)} = \frac{1}{\text{Wavelength (}\tilde{\nu}\text{)}}
\]  

(3.2)

3.7.4.1 Principle of Fourier Transform Spectrophotometry

Absorption in the infra-red region is due to the changes in the vibrational and rotational levels. The absorption of Infra-red radiations causes an excitation of molecule from a lower to the higher vibrational level. With each vibrational level there are rotational levels associated, therefore Infra-red is called as vibrational-rotational spectra. All the bonds in a molecule are not capable of absorbing Infra-red radiations but only those which accompanied by a change in dipole moment will absorb in the Infra-red region. The vibrational transitions which are accompanied by a change in dipole-moment of the molecule these are Infra-red active, but the vibrational transitions which are not accompanied by a change in dipole-moment are Infra-red inactive. The absorption in Infrared region is quantized (Sharma).

FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The ratio of the sample spectrum to the background is directly related to the sample’s absorption spectrum. The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range. The vibrational energy depends on:

1. Masses of the atoms present in a molecule,
2. Strength of bonds, and
3. The arrangement of atoms within the molecule
3.7.4.2 Working of Fourier Transform Spectrophotometer

The development of Fourier Transform Infrared Spectroscopy in the early 1970s provided a quantum leap in infrared analytical capabilities for monitoring trace pollutants in ambient air. This technique offered a number of advantages over conventional infrared systems, including sensitivity, speed and improved data processing. The basic components of an FTIR are shown in Figure 3.5. The infrared source emits a broad band of different wavelength of infrared radiation. The IR radiation goes through an interferometer that modulates the infrared radiation. The interferometer performs an optical inverse fourier transform on the entering IR radiation. The modulated IR beam passes through the sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally the intensity of the IR beam is detected by a detector. The detected signal is digitized and fourier transformed by computer to get the IR spectrum of the sample:

1. A source generates light across the spectrum of interest
2. A monochromater separates the source radiation into its different wavelengths.
3. A slit selects the collection of wavelengths that shine through the sample at any given time.
4. In double beam operation, a beam splitter separates the incident beam in two half goes to the sample and half to a reference.
5. The sample absorbs light according to its chemical properties.
6. A detector collects the radiation that passes through the sample and in double-beam operation, compares its energy to that going through the reference.
7. The detector puts out an electrical signal, which is normally sent directly to an analog recorder. A link between the monochromater and the recorder allows you to recorder energy as a function of frequency or wavelength, depending on how the recorder is calibrated.

![Figure 3.5 Basic components of FTIR](image-url)
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The unique part of an FTIR spectrometer is the interferometer. A Michelson type plane mirror interferometer. Infrared radiation from the source is collected and collimated that is made parallel before it strikes the beam splitter. The beam splitter ideally transmits one half of the radiation and reflects the other half. Both transmitted and reflected beams strike mirrors, which reflect the two beams back to the beam splitter ideally transmits one half of the radiation and reflects the other half. Thus, one half of the infrared radiation that finally goes to the sample gas has first been reflected from the beam splitter to the moving mirror and then back to the beam splitter. The other half of the infrared radiation going to the sample has first gone through the beam splitter and then reflected from the fixed mirror back to the beam splitter. When these two optical paths reunited, interference occurs at the beam splitter because of the optical path difference caused by the scanning of the moving mirror.

3.7.5 Raman Spectroscopy

Raman spectroscopy is a non-destructive material characterization technique that is complementary to infrared absorption spectroscopy. It is very sensitive to structural disorder and an important tool to probe the surface and structural properties of materials. The Raman Spectra of all samples in the frequency range 200 – 1000 cm\(^{-1}\) at room temperature. Like Infrared absorption Raman scattering is governed by completely different selection rules. Raman band arise from an oscillating induced dipole caused by light waves interacting with the polarizability ellipsoid of a vibrating molecule.

3.7.5.1 Principle of Raman Spectroscopy

Raman spectroscopy is based on inelastic scattering of monochromatic light usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. It provides information about molecular vibrations that can be used for sample identification and quantification. The technique involves shining a monochromatic light source that is laser to fall on a sample and detecting the scattered light is of the same frequency as the excitation source, this is known as Rayleigh or elastic scattering. A very small amount of the scattered light is shifted in energy from the laser frequency due to interaction between the incident electromagnetic waves and the vibrational energy.
levels of molecule in the sample. Photons of the laser light are absorbed by the sample and then re-emitted. Frequency of re-emitted photons is shifted up or down in comparison with original monochromatic frequency, which is called Raman Effect. As a result Raman spectroscopy provides an invaluable analytical tool for molecular finger printing as well as monitoring changes in molecular band structure.

3.7.5.2 Working of Raman Spectrophotometer

A Raman system typically consists of four major components:

1) Excitation source (Laser)
2) Sample illumination system and light collection optics
3) Wavelength selector (Filter or Spectrophotometer)
4) Detector (Photodiode array, CCD or PMT)

A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Since spontaneous Raman scattering is very weak the main difficulty of Raman Spectroscopy is separating it from the intense Rayleigh scattering. More precisely, the major problem here is not the Rayleigh scattering itself, but the fact that the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the useful Raman signal in the close proximity to the laser wavelength. In many cases the problem is resolved by simply cutting off the spectral range close to the laser line where the stray light has the most prominent effect.

3.7.6 Mössbauer Spectroscopy

The Mössbauer Spectroscopy is a versatile technique that provides information about the chemical, structural, electric, magnetic and time-dependent properties of a Mössbauer atom, such as its valence, spin state or magnetic moment. The “Mössbauer Effect” was first observed by Rudolf Ludwig Mössbauer in 1958 for which he received the Nobel Prize in Physics in 1961 for his work. He discovered that when the emitting and absorbing nuclei are bound in a solid matrix and in similar environment, a certain fraction of gamma rays are emitted and absorbed with
negligible energy loss due to recoil. Thus recoil-free nuclear resonance emission and absorption of gamma ray photon is called as Mössbauer Effect (Mössbauer, 1961). Therefore Mössbauer spectroscopy can be used to study a variety of phenomenon producing shift and splitting of nuclear energy levels.

3.7.6.1 Principle of Mössbauer Spectroscopy

When an atom in an excited state makes a transition to the ground state, the resulting radiation may be absorbed by the atoms of the same kind there by raising them into the excited state. This process is known as resonant absorption. But in case of free nucleus resonant absorption and emission does not take place, because of the relatively large momentum associated with gamma ray photon. When a stationary nucleus of excitation energy (E) emits radiation to its ground state, the nucleus recoils so as to conserve linear momentum and energy of emitted gamma ray is less than E by the recoil energy $E_R$ provided by the kinetic energy given as:

$$\Delta E = \frac{1}{2}mv^2 = \frac{1}{2m}p_k^2 = \frac{E_R^2}{2M_c^2}$$

(3.3)

The energy in the nuclear transition is divided in accordance with the law of conservation of momentum, the maximum energy is carried by the emitted gamma ray, and the rest energy is taken away by the emitting nucleus in the form of recoil energy as shown in Figure 3.6.

![Figure 3.6 Recoil of free nuclei in emission or absorption of a gamma ray](image)

The emitted gamma ray has $E_R$ less energy than the nuclear transition but to be resonantly absorbed it must be $E_R$ greater than the transition energy due to the recoil of the absorbing nucleus. The key factor of the Mössbauer Effect is the absorption of recoil momentum by the entire lattice of the solid. As the lattice is much more...
massive than the nucleus, its recoil kinetic is effectively zero. In this case the gamma ray carries away exactly the energy of the transition and the emission and absorption lines overlap, centered about the transition energy. Suppose a nucleus emits a gamma ray without recoil of energy ($E_r$) in making transition from excited state to ground state. The overlap between emission and absorption lines allow another nucleus to absorb that gamma ray in going from ground state to excited state. When the nucleus of an atom radiates electromagnetic energy in the form of a wave packet known as a gamma-ray photon it is also subject to a Doppler shift the frequency change, depends on how fast the nucleus is moving with respect to the observer. When the atoms are within a solid matrix the effective mass of the nucleus is very much greater than its actual mass. The recoiling mass is now effectively the mass of the whole system, making $E_R$ and $E_D$ very small. If the gamma-ray energy is small enough the recoil of the nucleus is too low to be transmitted as a phonon (vibration in the crystal lattice) and so the whole system recoils, making the recoil energy practically zero: a recoil-free event. In this situation, as shown in Figure 3.7. if the emitting and absorbing nuclei are in a solid matrix the emitted and absorbed gamma-ray is the same energy.

![Figure 3.7 Recoil-free emission or absorption of gamma-ray when the nuclei are in a solid matrix such as crystal lattice](image)

As atoms are held tightly in crystalline atomic structure, the gamma radiations emitted by the nuclei are very close to being recoil-free. Nuclei can exist in certain definite energy states. For a gamma ray to be absorbed its energy must be exactly equal to the difference between two of these states. Such an absorption is called resonance absorption. This means that the emitted photon has the same frequency that corresponds to the transition energy between the ground state and excited state. When
this photon having full nuclear transition energy strikes with another similar nucleus which is also tightly bounded in crystalline structure, may absorb the incident photon. If emitting and absorbing nuclei are in identical environments then the transition energies are identical and this produces a spectrum a single absorption line. As the energy levels are well defined in the nucleus, so photon that carries the same energy, may excite the nucleus as shown in Figure 3.8.

![Figure 3.8 Emission and absorption scheme for Mössbauer spectrum](image)

**Figure 3.8 Emission and absorption scheme for Mössbauer spectrum**

3.7.6.2 Mössbauer Source

The most typical Mössbauer Source is $^{57}$Fe is normally obtained from $^{57}$Co which undergoes a spontaneous electron capture transition to give a metastable state of $^{57}$Fe which in turn decays to the ground state with emission of gamma ray which includes the 14.4 keV Mössbauer Gamma ray. The resonant absorption process depends on the factor that the emitting Mössbauer nucleus (Source) and absorbing Mössbauer Nucleus are embedded in a solid matrix. For the Mössbauer experiment a source and absorber with the same isotope of an atom embedded in a rhodium matrix are used. The most commonly used Mössbauer isotope is $^{57}$Fe, with natural linewidth of $5 \times 10^{-9}$ eV. Compared to the Mössbauer gamma-ray energy of 14.4 keV this gives a resolution of $1 \times 10^{12}$. As resonance only occurs when the transition energy of the emitting and absorbing nucleus match exactly the effect is isotope specific. The relative number of recoil-free events (and hence the strength of the signal) is strongly dependent upon the gamma-ray energy and so the Mössbauer effect is only detected in isotopes that can be used successfully for Mössbauer spectroscopy. The most used is $^{57}$Fe, which has both a very low energy gamma-ray and long-lived excited state, matching both requirements well. The emitting $^{57}$Fe results from electron capture in a
Nuclei in atoms undergo a variety of energy level transitions followed by the emission or absorption of a gamma ray. These energy levels are influenced by their surrounding, both electronic and magnetic, which can change or split these energy levels. These changes in the energy levels can provide information about the atom’s local environment which leads to resonance. There are, however, two major obstacles in obtaining this information: the ‘hyperfine’ interactions between the nucleus and environment is extremely small; and the recoil of the nucleus as the gamma-ray is emitted or absorbed prevents resonance. When source and absorber atoms are in different local environments, their nuclear energy levels can be modified by the following hyperfine interactions: Isomer Shift; Quadrupole Splitting; Magnetic Splitting.

3.7.6.3 Isomer Shift

Isomer shift arises from the difference in s-electron density between source and absorber. The isomer shift depends on the Coulomb interaction between the atomic electrons and the nucleus. Coulomb interaction of the nuclear charge distribution over the radius of the nucleus in its ground and excited state and the electron charge density at the nucleus results in a shift of the overall spectrum to higher and lower energies. It depends on the ionization state of the atom, as shielding effects due to valence electrons will influence the s-electron density at the nucleus. Non-zero volume of the nucleus and the electron charge density due to s-electrons results in monopole interaction, which alters the nuclear energy levels. If there is difference in the environment of the s-electron between the source and absorber a chemical shift arises in the resonance energy. For example: the electron configurations for ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) ions are 3d$^6$ and 3d$^5$ respectively. Fe$^{2+}$ has larger positive isomer shifts than Fe$^{3+}$ due to greater screening of the d-electrons. Graphically, isomer shift is a shift of the minimum away from the zero velocity in the transmission spectrum.

3.7.6.4 Quadrupole Splitting

Quadrupole splitting is a shift in nuclear energy levels that is induced by an electric field gradient caused by nearby electrons. Nuclei in states with an angular momentum quantum number $I > \frac{1}{2}$ have a non-spherical charge distribution. The
nuclear quadrupole moment (Q) is a measure of the deviation of the nuclear charge from spherical symmetry. In the presence of an asymmetrical electric field this splits the nuclear energy levels. The charge distribution is characterized by a single quantity called the Electric Field Gradient (EFG). Quadrupole splitting is a consequence from the interaction between the Electric Field gradient at the site of the nucleus and the electric quadrupole moment (eQ) of the nucleus itself. If a nucleus has a quadrupole moment, its energy depends on its orientation with respect to electric field gradient. The energy level with quantum number I and \( m_I \) is shifted from its zero gradient. The energy shift is given by:

\[
\Delta E = eQV_{zz} \frac{3m_I^2 - I(I+1)}{4I(2I-1)}
\]

where \( \Delta E \) is shift in energy level, \( e \) is charge on electron, \( Q \) is electric quadrupole moment, \( V_{zz} \) is electric field gradient given by \( \frac{1}{e} \frac{dE}{dz} \), \( m_I \) is the magnetic quantum number and I is the total isospin. For example: \(^{57}\text{Fe}\) for I nuclear excited state split into a pair of doublets \( I_z = +1/2, -1/2 \) and \( +3/2, -3/2 \) as shown in Figure 3.9.

![Figure 3.9 Schematic diagrams for isomer shift and quadrupole splitting](image)

3.7.6.5 Zeeman Splitting

The nuclear magnetic dipole moment interacts with an applied magnetic field \( B \) to produce this splitting of the energy levels at the nucleus. In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field that is Zeeman splitting. There are many sources of magnetic
fields that can be experienced by the nucleus. The total effective magnetic field at the nucleus $B_{\text{eff}}$ is given by:

$$B_{\text{eff}} = (B_{\text{contact}} + B_{\text{orbital}} + B_{\text{dipolar}}) + B_{\text{applied}} \quad (3.5)$$

The first three terms being due to the atom’s own partially filled electron shells. $B_{\text{contact}}$ is due to the spin on those electrons polarizing the spin density at the nucleus, $B_{\text{orbital}}$ is due to the orbital moment on those electrons, $B_{\text{dipolar}}$ is the dipolar field due to the spin of those electrons. A nucleus can have a characteristic angular momentum, $I$, which is accompanied by dipole moment. When the nucleus is placed in a magnetic field, the energy states are split with energies depending on the orientation of the nuclear moment with respect to field. A state with quantum number ($I$) can split into $2I + 1$ components characterized by the quantum number ($m_I$). The splitting of the energy levels is called nuclear Zeeman effect. The splitting of the line corresponding to the transition between two states. This is shown in Figure 3.10 for $^{57}$Fe. Transitions between the excited state and ground state can only occur where $m_I$ changes by 0 or 1. This gives possible transitions for a $3/2$ to $1/2$ transition, giving a sextet as shown in Figure 3.10 with the line spacing being proportional to $B_{\text{eff}}$.

![Figure 3.10 Schematic diagram for magnetic hyperfine splitting](image)
3.7.7 Impedance Analyzer

Dielectric materials play a key role in electronic circuits such as capacitors or insulators. Characterization of these materials in the early stage of development is essential to predict the performance of the final devices. The electrical properties of a dielectric material are characterized by its complex permittivity. The real part of permittivity, also called dielectric constant, represents the material’s ability to store energy when an external electric field is applied. Materials with a higher dielectric constant can store more energy in a small volume, while those with a lower value are preferred for signal transmission where minimum propagation delay is critical. The imaginary part of permittivity represents the loss dissipated in the material. Loss of material can lead to extra power consumption. It is possible to achieve various dielectric constants by controlling the micro structure of ceramics or nano composition of materials. Impedance analyzers can be used with dielectric material test fixtures to provide a precise, repeatable, cost-effective and easy to-operate measurement system over wide frequency range. There are various ways of measuring dielectric constant, however it requires specialized knowledge of electromagnetic field theory. The parallel plate capacitance method is generally used in low-frequency, which measures the capacitance of the material sandwiched between the two electrodes. Its principle is straightforward, but precise measurements are difficult due to the measurement errors, especially for low loss materials. The complex permittivity is not a constant over a wide frequency range and must be evaluated at the frequency where the material is used, however, at higher frequencies, errors due to the measurement system become significant.

3.7.7.1 Principle of LCR meter

When there is a change in the current flowing through a conductor, a corresponding change is induced in the voltage in it and in conductors surrounding it. This property is known as inductance. The ability of a body or a conductor to store electrical charge is known as capacitance. The opposition that a conductor offers to the passage of electric current through it is called resistance. A digital LCR meter is used to measure the impedance flowing through a Device Under Test (DUT). It measures the voltage (V) across it, the current (I) flowing through it, and the phase angle between current and voltage. Subsequently, we can determine all the impedance parameters from these three factors.
3.7.7.2 Working of LCR meter

An LCR meter measures the following parameters related to a circuit: Inductance; Capacitance; Resistance; Dissipation factor; Quality factor; Current; Voltage; Phase angle between the current and voltage; Conductance; Susceptance. Impedance is the opposition that a circuit offers to the flow of direct or alternating current through it. It is a vector quantity composed of 2 scalars: resistance and reactance. Reactance is the name given to the opposition by an electronic component to the flow of alternating current due to capacitance and inductance. The parallel plate method uses two electrodes between which the material under test is sandwiched. The impedance of the material is measured and converted to the complex permittivity using the size of the material and the electrode. AC voltage passes through a DUT (Device Under Test). The LCR meter is used to measure the voltage and the current across the DUT. The magnitude of the impedance can be calculated from the ratio of these two quantities. An LCR meter is used to measure the impedance of a circuit or a device. An LCR meter is used to measure the inductance, capacitance and resistance of a circuit. Hence the name LCR meter.

3.7.8 DC resistivity

It is the method used to determine the resistivity of the material.

3.7.8.1 Principle of DC resistivity

Ohm’s Law: If physical conditions like mechanical stress and temperature remain unchanged, then potential difference across two ends of a conductor is proportional to current flowing through a conductor.

\[ V = IR \]  \hspace{1cm} (3.6)

where, R is the constant of proportionality and is called the ‘R’ resistance of the conductor. At constant temperature, the resistance R of a conductor is: proportional to its length; and inversely proportional to area of cross-section.

\[ R = \rho \frac{L}{A} \]  \hspace{1cm} (3.7)
The constant of proportionality, $\rho$ is called resistivity of the conductor and is the internal property of the material.

### 3.7.8.2 Working of DC resistivity

A long thin wire-like geometry of uniform cross-section or for a long parallelepiped shaped sample of uniform cross-section, the resistivity $\rho$ can be measured by the voltage drop across the sample due to passage of known (constant) current through the sample as shown in Figure 3.11 is the sample whose resistivity is to be measured. C is the source of supplying current (through probe 1 and probe 2). Let the current in specimen be $I$ and measured by the ammeter (A). The potential difference between the two contacts

\[
\rho = \frac{VA}{IL} \quad (3.8)
\]

The DC resistivity is measured by a two-point probe method. As the resistance of the sample is very high of the order of $10^8 \, \Omega$cm, the potential difference applied is also high of the order of 100 V and the samples are in the form of disks. Also the effect of wire and contact resistances seems to be negligible in case of two-point probe method.