Chapter 3
SYNTHESIS METHODS AND CHARACTERIZATION TECHNIQUES

3.1 INTRODUCTION

The structural, electrical and magnetic properties of the magnetic material are related to purity, size and morphology of precursor powder. By modifying the microstructure and controlling the chemical composition, size and morphology its properties can be improved [1, 2]. Therefore, the preparation of nano size precursor powder having high purity, ultrafine size, good dispersion and excellent magnetism has been the focus of recent research.

The potential technological applications of ferrites are due to their desired electrical and magnetic properties. It is necessary to create these properties with the relevant structural and chemical aspects of the
material. The structural, electrical and magnetic properties depend on the method of preparation [31], site preference [41], and valance distribution [51].

The presence of Fe$^{3+}$, Fe$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Mn$^{2+}$ ions provide the unpaired electron spins and therefore part of magnetic moment in a spinel. Other divalent ion such as Mg$^{2+}$ or Zn$^{2+}$ are not paramagnetic but are used to disproportionate the Fe$^{3+}$ ion on the crystal lattice to provide or increase the magnetic moment. In spite of the several developments in the technology of ferrite materials, the scientist still pursuer to investigate the structural electrical and magnetic properties of these materials in a systematic manner to obtain correlation between them and to tailor new materials with desired properties.

It is well known that, the ferrites can be prepared by different methods and the method of preparation influences the structural, electrical and magnetic properties. The usual ceramic method of preparation of ferrites proceeds through a high temperature ($\approx 1100^\circ$C) reaction between finally mixed oxides powder followed by shaping, successive pressing and sintering. Materials of the same composition but with varying properties can be prepared by chemical method at lower temperature. These methods include thermal decomposition, spray drying, sol-gel, citrate precursor and wet chemical co-precipitation method.

The advantage of chemical route is that, it requires lower annealing temperature necessary in the crystallization process. Therefore varying the heat treatment in order to prepare nanocrystalline hexaferrite particles with narrow switching field distribution can control the crystal growth easier. With the advent of lower annealing temperature, in the present investigation sol-gel auto combustion method have been employed for the preparation of substituted strontium hexaferrite samples.
3.2 SYNTHESIS METHODS

The synthesis method plays an important role in controlling the structural, electrical and magnetic properties of hexaferrite materials. Various synthesis techniques have been developed to synthesize strontium hexaferrite such as solid state \cite{6}, ball milling \cite{7}, co-precipitation \cite{8}, hydrothermal \cite{9}, spray pyrolysis \cite{10}, micro-emulsion processing \cite{11}, citrate precursor method \cite{12}, and sol-gel method \cite{13}.

3.2.1 Solid state reaction method

This method benefits from the simplicity in forming relatively large quantities of material and does not require expensive laboratory equipment. Among the various processing method solid state synthesis is widely used. Solid state synthesis is the traditional method of forming strontium hexaferrite. In this method oxides or carbonates of precursor materials are mixed together and then heated to form the final compound.

In this method, very pure and fine grains constituents in oxide form are taken. Then they are uniformly mixed. This mixture is sintered for prolonged time at specific temperature so as to facilitate solid state chemical reaction among the oxides and the formation of chemical compound.

The solid state method have several drawbacks as

i) Poor compositional control
ii) Chemical inhomogeneity
iii) During grinding there is probability of contamination of impurities
iv) Large particle size
v) It requires high temperature (>1100\textdegree C).
3.2.2 High Energy Ball Milling (HEBM) Method

The ball mill is a key equipment for grinding. It is widely used for the cement, the silicate product, new type building material, fire-proof material, chemical fertilizer, black and non-ferrous metal, glass, ceramics etc. Ball mill is a good tool for grinding many materials into fine powder. The Ball mill is used to grind many kinds of mine and other materials. There are two type of grinding: the dry process and the wet process. It can be divided into tabular type and flowing type according to different forms of discharging material. After the grinding the state of the solid is changed: the size and shape of grain etc.

Ball mill is horizontal type and tubular running device has two warehouses. This machine is grid type and its outside runs along gear. The material enters spirally and evenly the first warehouse of the milling machine along the input material hollowaxis by input material device. In this warehouse, there is a ladder scale board or ripple scale board, and different specification steel balls are installed on the scale board, when the barrel body rotates and then produces centrifugal force, at this time, the steel ball is carried to some height and falls to make the material grinding and striking. After grinded coarsely in the first warehouse, the material then enters into the second warehouse for regrinding with the steel ball and scale board. In the end, the powder is discharged by output material board and the end products are completed.

3.2.3 Chemical Co-precipitation Method

In this method, separate solutions containing strontium and ferrite ions are precipitated from the solution (usually a nitrate or citrate) and the
solid then dried out. This forms a fine powder which is then mixed and heated to react together in a similar way to the solid state synthesis method \cite{14-15}. This method has been driven by the need for smaller particle sizes within the final strontium hexaferrite compound. This result in a more effective material for perpendicular recording media because higher storage densities can be achieved. Variations of the method produce a range of grain sizes in the final product from 0.1 \( \mu \text{m} \) to 0.5 \( \mu \text{m} \) \cite{16}. These procedures have been further refined such that material produced currently has grain sizes of 80-120 nm \cite{17}. Another benefit of co-precipitation is reduction in intermediate phases present in final product.

3.2.4 Hydrothermal Method

As one of the wet chemical methods, the powder prepared via the hydrothermal method is homogeneous, fine and of high-purity \cite{18, 19}. Moreover, it can synthesize hexagonal ferrites without subsequent sintering at high temperatures \cite{20}. In recent years, this method has been advanced by the use of super critical water within the autoclave to achieve greater control over particle size and thus electro-magnetic properties of the resulting compound.

Strontium hexaferrite is formed by reacting aqueous solutions of ferric nitrate and strontium nitrate at different temperatures for different lengths of time. Starting solutions using chlorides instead of nitrates have also been used, resulting in nano-sized particles of strontium hexaferrite (average size 12 nm) at lower temperatures of 140-180 \( ^\circ \text{C} \) \cite{21}. Hydrothermal experiments are performed within an autoclave, where reactants can be subjected to temperatures and pressures higher than normal conditions. At a temperature of 300 \( ^\circ \text{C} \), particles of less than 0.1 \( \mu \text{m} \) can be formed \cite{22}. 
3.2.5 Spray Pyrolysis Method
In spray pyrolysis, a thin film is formed by spraying a solution onto a heated surface. The reaction to form the compound occurs on the surface where a suitable temperature is chosen \[^{231}\]. This process is used in conjunction with other methods such as citrate precursors allowing greater control over particle size from 100nm to 50-80 nm \[^{241}\], or focusing on forming strontium hexaferrite at lower temperatures (700 °C) while still producing grain sizes in the nm range \[^{251}\]. When used in conjunction with co-precipitation, strontium hexaferrite powder with particle size of 30-60 nm can be formed at a temperature of 550 °C \[^{261}\].

3.2.6 Micro Emulsion Method
The micro emulsion method has been shown to be a very promising laboratory technique for the preparation of a small quantity of nanoparticles, providing an excellent control over the particle size and shape, as well as the homogeneity and the chemical composition. The co-precipitation occurs in reverse micelles, tiny droplets of aqueous phase that are embedded with a surfactant in an oil phase. The water pools of the reverse micelles act as nano reactors for the synthesis of the particles. The particle size of the product depends primarily on the size of the pools and on the concentration of the reactants dissolved in the aqueous phase. The volume of the reverse micelles is thermodynamically determined, by the water to surfactant molar ratio and the temperature. Thus, the size of the nanoparticles can be controlled by varying the micro emulsion composition, the concentration of reactants, or the temperature.

3.2.7 Citrate Precursor Technique
In the citrate precursor technique, the individual cations in the
stoichiometric ratio are reacted with the poly functional organic acid; citric acid under controlled pH conditions to obtain a precursor at an atomic level bending of the constituent elements in the required stoichiometric ratio is achieved during the reaction in the solution state to form the citrate complex.

This precursor on proper thermal decomposition at right temperatures indicated by thermal analysis data loses the entire organic moiety to give rise to the final ternary oxide. It is important to note that the diffusion controlled solid state reaction between constituent compounds involved in ceramic method and co-precipitation method is not present in the precursor method. The final reaction is the decomposition process and it depends on the decomposition temperature of the precursor. The citrate precursors decompose at temperature less than 700 °C and hence it has been possible to prepare strontium hexaferrite and series of rare earth garnet at these relatively low temperatures [27].

Therefore in principle, if one can prepare precursor complexes using organic materials other than citrates, which decompose at lower temperatures than citrate, it may be possible to further reduce the preparation temperature. The reducing preparation temperature will be extremely useful for producing nanoparticles of the hexaferrite system.

3.2.8 Sol-gel method

In the recent years, sol–gel method has acquired great importance due to their potential for producing very pure and homogeneous nanoparticles, with relatively large quantities of final product and low cost as compared to other chemical processes [28]. Sol-gel is the most effective method for
the synthesis of homogeneous nanoparticles which can be prepared at relatively low temperatures. It consists of hydrolysis and condensation reactions of metal precursors leading to the formation of three-dimensional inorganic networks \(^{29}\). Hydroxyl groups (M–OH) are formed during hydrolysis. These groups subsequently condense into strong and rigid metal-Oxo-metal bridges (M–O–M). These bridges are polymerized during heat treatment whereas they form a gel which is converted into dense particles.

In the preparation of ferrites, the synthesis by combustion reaction technique have a great potential. This process is quite simple and involves an exothermic and self-sustaining chemical reaction between the metal salts and a suitable organic fuel, usually urea \(^{30}\), glycine \(^{31}\), hydrazides \(^{32}\), dl-alanine \(^{33}\), tartaric acid \(^{34}\) and citric acid \(^{35-37}\).

**Steps in sol-gel synthesis**

The six important steps in sol-gel synthesis are given below

i) **Hydrolysis:** The processes of hydrolysis may start with a mixture of a metal alkoxide and water in solvent at the ambient or a slightly elevated temperature. Acid or base catalysts are added to speed up the reaction.

ii) **Polymerization:** This step involves condensation of adjacent molecule wherein H\(_2\)O and alcohol are eliminated and metal oxide linkages are formed. Polymeric networks grow to colloidal dimension in the liquid state.

iii) **Gelation:** In this step, the polymeric networks link up to form a three dimensional network throughout the liquid. The system becomes somewhat rigid, characteristic of a sol-gel, on removing
the solvent from a sol-gel, on removing the solvent from the sol. Solvent as well as water and alcohol molecules however, remain inside the powder of the gel.

iv) **Drying:** Here, water and alcohol are removed at moderate temperature, leaving a hydroxylated metal oxide with residual organic content. If the objective is to prepare a rough surface area aero gel powder of low bulk density, the solvent is removed super critically.

v) **Dehydration:** This step is carried out between 670K and 1070 K to drive off the organic residue and chemically bound water, yielding a glassy metal oxide with up to 20-30 % microporosity,

vi) **Densification:** Temperatures in excess of 1270 K are used to form the dense oxide product.

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**Fig.3.1 General Flow chart of sol-gel auto-combustion method**

Figure 3.1 represents the flowchart of Sol gel auto combustion method. Sol gel auto combustion also called as low temperature self-combustion, self-propagation, auto-ignition, gel-thermal decomposition. The advantage of
sol-gel auto combustion method is good chemical homogeneity (mixing of cations of desired composition at molecular level), high product purity and crystallinity, fine particle size and narrow particle size distribution, it is easy to control the stoichiometry, dopants can be easily introduced into the final product, simple equipment and preparation process, low processing time, low external energy consumption (process initiates at low temperatures) and multiple steps are not involved [38-40].

With the advent of low annealing temperature sol-gel auto combustion method have been used in the present investigation. Analytical reagent (AR) grade Strontium nitrate Sr(NO$_3$)$_2$, Ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O), Zirconium nitrate (ZrO(NO$_3$)$_2$.H$_2$O), Nickel nitrate (Ni(NO$_3$)$_2$.6H$_2$O), Zinc nitrate (Zn(NO$_3$)$_3$.9H$_2$O) and citric acid (C$_6$H$_8$O$_7$.H$_2$O) as fuel were used as a starting materials to prepare SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ and SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) hexaferrites by sol-gel auto-combustion technique.

The desired proportion of precursor nitrates have been separately dissolved in minimum amount of distilled water and stirred on a magnetic stirrer for ten minutes. Then all the solutions have been mixed together and stirred on a magnetic stirrer until the nitrates were completely dissolved. The metal nitrate to citric acid ratio was 1:3. The solutions were made with continuous stirring on magnetic stirrer and drop by drop ammonia solution is added to adjust the pH value to 7, then it was heated on hot plate at 80 °C to 90 °C with constant stirring. The precursor solution was heated continuously, due to the removal of water vapor it gets converted into the gel. Persisted heating provides a pure phase raw powder through a single step combustion reaction with evolution of voluminous gases. The resulting precursor powder was calcined at 950 °C for 9 hrs to obtain pure SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ and SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ hexaferrite powder.
3.3 CHARACTERIZATION TECHNIQUES

Various experimental techniques have been developed to characterize the nanoparticles of strontium hexaferrite. In the present study, the as prepared samples have been characterized by Thermal analysis (TGA/DTA), X-ray diffraction technique (XRD), Fourier Transform Infra-red spectroscopy (FT-IR), Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS). The electrical properties were studied by D.C. electrical resistivity and dielectric measurement. The magnetic properties were systematically investigated by Vibrating sample magnetometer (VSM) technique and Curie temperature was determined by A.C. susceptibility technique as shown in Fig. 3.2.

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Fig. 3.2 Pictorial representation of the characterizations studied
3.3.1 THERMAL ANALYSIS

Thermogravimetric analysis (TGA) is a technique that involves continuously measuring the mass of a sample as a function of temperature. Thermal analysis were carried out to evaluate the mechanism for the formation of hexaferrite phase and to observe the effect of heating on structural changes of the synthesized sample.

The thermogravimetric curves provide information concerning the thermal stability and the composition of the initial sample, any intermediate compounds formed and the residue. It can be used to qualitatively determine the stabilities of compounds, the rate of reaction and the composition of sample [41]. The shape of TGA curves and the temperatures at which mass changes occur are of interest. The magnitude of mass changes is directly related to the specific stoichiometries of the occurring reactions. Shimadzu Model DTG-60 (Fig. 3.3) has been used for recording the thermograms of the dried precursors of the as-prepared samples.

Fig. 3.3 Shimadzu Model DTG-60
**Principle of Thermal Analysis**

The TGA determines the weight change of a sample whereas the DTA measures the change in temperature between a sample and the reference as a function of temperature and/or time. The sample is allowed to heat rapidly to some elevated temperature, followed by measurement of change in weight i.e. thermogravimetric analysis (TGA) and heat flow with time i.e. differential thermal analysis (DTA). The results of such measurements are thermal analysis curves and the changes in these curves correspond to the thermal events in the sample [42].

**Construction and Working of Thermal Analyzer**

The thermo balance is placed in an enclosed system to control the atmosphere. A thermo balance is a combination of an electronic microbalance, furnace and a temperature programmer. The maximum load for thermo balance is 1g and a sensitivity of 1 μg. The measurements of mass changes with temperature are carried out with the help of such thermo balance. Thermo balance is normally housed in a glass or metal systems to control the pressure and the atmosphere inside it.

The sample should be powdered where possible and should be spread in a thin and uniform layer in the sample container. A regular gaseous flow may be maintained in order to remove the evolved gases from the thermo-balance with the care that these flow gases don not disturb the balance [43].

Temperature sensors are either platinum resistance thermometers or thermocouples. The temperature controller attached to the instrument offer heating rates from a fraction of a degree per minute to nearly 100°C min⁻¹ with additional characteristic of isothermal heating.
The beam is displaced by change in weight loss with temperature on sample side. This displacement is detected optically and the drive coil current is changed to return the displacement to zero. The detected drive coil current change is proportional to the amount of weight change in sample and is output as the TGA signal.

The DTA detects the temperature difference between the sample holder and the reference holder using electromotive force of thermocouples, attached to the holders. The differential is output as the DTA signal.

**Applications of Thermal Analyzer**

- TG gives us information about the thermal events which are accompanied by changes in mass.
- The mass losses define the stages and the conditions of temperature and atmosphere necessary for the preparation of the spinel phase and the stability.
- For desorption, decomposition and oxidation processes, useful information can be collected from TG analysis.
- It gives accurate information about drying and the decomposition of metal hydroxides into oxides in ferrite processing.
- TG curves for complex ternary metal hydroxides may not give the exact reaction occurring even then it can be used for ‘finger print’ purpose \(^1\text{431}\).
- Further it can be utilized for engine oil volatility measurements, filler content, flammability studies, heat of transition, oxidative stabilities, thermal stabilities, transition temperatures and catalyst and coking studies.
3.3.2 STRUCTURAL PROPERTIES

[A] X-ray diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. There are several methods of getting the X–ray diffraction using a crystal specimen, such as Laue method, rotating crystal diffractometer method, powder diffractometer method etc.

The powder diffractometer in particular is relevant to the present study. In this method the crystal to be investigated is in the form of fine powder. Each particle of this powder is a tiny crystal oriented totally at random with respect to the incident X–ray beam. The method is of immense importance since it can take polycrystalline specimen and thus it is not necessary to have a single crystal, which is not always possible to grow. This method has widened the horizons of the utilization of X–ray diffraction tool in great number of cases where single crystals were not available.

Fundamental Principles of X-ray Powder Diffraction (XRD)

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

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

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this. Fig. 3.4 shows the photograph of the X-ray diffractometer (Rigaku Miniflux-II) used in the present investigation.

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**Fig. 3.4 X-ray diffractometer (Rigaku Miniflux-II)**
Working of X-ray Powder Diffraction (XRD)

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. Characteristic X-ray spectra are produced, when electrons have sufficient energy to dislodge inner shell electrons of the target material.

These spectra consist of several components, the most common being $K_a$ and $K_{\beta}$. $K_a$ consists of $K_{a1}$ and $K_{a2}$. $K_{a1}$ 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 CuK$_a$ radiation (wavelength $\lambda = 1.5418$ Å). The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering by foils or crystal monochrometers is required to produce monochromatic X-rays needed for diffraction. 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.
X-ray diffractometer consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector as shown in Fig. 3.5.

**Fig. 3.5 Schematic diagram of X-ray diffractometer**

**X-ray tube:** The X-ray tube is a high vacuum, sealed off unit, usually with a copper, iron or molybdenum target. During the process of X-ray generation, the target is cooled by the water circulation. The generated X-rays beam is passed through thin beryllium window.

**Detector:** In addition to photographic film, the Geiger counter, the proportional counter, the scintillation counter and sometimes semiconductors are used in X-ray detection. The Scintillation counter is widely used. They have shortest dead time of around 0.25 μsec and have nearly uniform and high quantum efficiency throughout the important wavelength region.

**Goniometer:** It comprises of two circular tracks. On outer track the X-ray tube is usually made fixed. Detector is mounted on the arm moving on outer track. The sample holder is fixed on the inner track. The inner track
rotates at half the angular distance than the outer arm. The movement of both the inner track and outer arm is controlled by mechanical motors. Since the mass of powder is equivalent to a single crystal rotated not only about the one axis but in fact, about all possible axes, it has simplified to get signature of all the planes in one shot.

The specimen for this method is a flat thin layer of powdered sample on a glass or a silicon single crystal holder. The randomness in the orientations of small crystals (or crystallites in the case of polycrystalline material) with respect to each other is such that there is a presence of all possible orientations of crystals.

In other words, there is a presence of a set of all permissible (hkl) planes with different d values and oriented parallel to flat surface of the specimen. Assume that the size of each crystal is such that it possesses enough number of planes necessary for perfect constructive and destructive interference. Now for any incident X-rays beam at angle $\theta$, the detector is set at angle $2\theta$ with respect to the incident beam. At a particular value of $2\theta$, the d spacing of any of the (hkl) planes fulfilling the Bragg’s condition will give constructive interference and all other (hkl) planes will give perfect destructive interference.

If the specimen and detector are now moved in such a way that the specimen rotates half the angular distance than the detector in the same angular direction, the incident angle $\theta$ can be changed and each time the presence of Bragg peak can be detected. Thus, whole spectra of diffracted intensities by various planes at different angles will be traced. The X-ray diffractograms contains the information regarding the peak positions and the intensity counts of respective peaks along with the plot and other instrumental information.
Applications of X-ray Powder Diffraction (XRD)

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

The applications of X-ray powder diffraction include:

- Characterization of crystalline materials
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- Determination of unit cell dimensions
- Measurement of sample purity

With specialized techniques, XRD can be used to:

- Determine crystal structures using Rietveld refinement
- Determine of modal amounts of minerals (quantitative analysis)
- Characterize thin films samples by:
  - determining lattice mismatch between film and substrate and to inferring stress and strain
  - determining dislocation density and quality of the film by rocking curve measurements
  - measuring super lattices in multilayered epitaxial structures
  - determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements
- Make textural measurements, such as the orientation of grains, in a polycrystalline sample
B] FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FT-IR spectroscopy has been widely used for structural and compositional analysis of organic, inorganic and polymeric materials and played an important role in quality control of raw materials. IR spectroscopy deals with changes in Vibrational motion (stretching and bending) of atoms in a molecule which leads to net change in dipole moment and results in absorption of IR radiation. These motions are greatly influenced by masses of atoms, their geometrical arrangement and the strength of their chemical bonds.

In accordance with both applications and instrumentation involved, the IR spectral region (12,500 – 10 cm⁻¹) is conveniently divided into near-IR (12,500 to 4000 cm⁻¹), mid-IR (4000 to 400 cm⁻¹) and far-IR (400 to 10 cm⁻¹). The main significance of this division is that most fundamental molecular vibrations occur in mid-IR making this region richest in chemical information while overtones and combination of fundamental vibrations especially those involving hydrogen atoms appear in near-IR. On the other hand, far-IR region contains vibrations involving heavy atoms, lattice modes of solids and some rotational absorption of small molecules.

Infrared radiation spans a section of the electromagnetic spectrum having wave numbers from roughly 12,500 to 10 cm⁻¹ or wavelengths from 0.78 to 1000 μm. It is bound by the red end of the visible region at higher frequencies and the microwave region at lower frequencies.

Instrumentation

A typical spectrometer mainly comprises of components like radiation source, optical path and monochromator, radiation detector and sample as shown in Fig. 3.6. These components are briefly described below
**Source:** The source is always some form of filament which is maintained at red-or white-heat by an electric current. Two common sources are the Nernst filament, consisting of spindle of rare earth oxides (ZrO₂ + Y₂O₃) about 1 inch long and 0.1 inch in diameter, and the Globar (SiC) filament a rod of carborundum, somewhat thicker and longer than the Nernst. The Nernst requires to be pre-heated before it will conduct electricity, but once red-heat is reached the temperature is maintained by the current.

**Optical path and monochromator:** The beam is guided and focused by mirrors aluminized or silvered on their surfaces. Normally a focus is produced at the point where the sample is to be placed. Ordinary lenses and mirrors are not suitable as glass absorbs strongly over most of the frequencies used. Normally, highly polished IR transparent mineral salt windows such as, NaCl (transparent above 650 cm⁻¹) and KBr (transparent above 400 cm⁻¹) are used to contain a sample, or protect to the detector.
For aqueous samples, AgCl and CaF₂ sample cell can be used. These are infra-red transparent above 400 and 1200 cm⁻¹ respectively. A rotatable grating is usually used to disperse the radiation, having largely superseded rotatable prisms, which have poorer resolving power. Where the latter are still in use, the prism is usually made of NaCl or KBr.

**Detector:** Two main types are in common use, one sensing the heating effect of the radiation and the other depending on photoconductivity. In both greater the effect (temperature or conductivity rise) at a given frequency, greater is the transmittance (and the less the absorbance) of the sample at that frequency.

An example of the temperature method is to be found in Golay cell, thermocouples or bolometers. Pyroelectric detectors such as, deuterated triglycine sulphate (DTGS) which are specialized thermal detectors are in common use in FT spectrometers.

Liquid nitrogen cooled Mercury cadmium telluride (MCT), Indium antimonide (InSb) etc. are some examples of photoconductive detectors used in IR spectroscopy. These have a faster response time and sensitivity, compared even with the deuterated triglycine sulphate (DTGS).

**Sample:** Sample is held between plates of polished mineral salt such as NaCl, KBr or AgCl. The following procedure is normally employed for gas, liquid and solid sample preparation.

- **Gas:** Glass cells either 5 or 10 cm long fitted with rock salt windows are used for gaseous samples at pressures of up to 1 atmosphere or greater. Special long-path cell, in which the radiation is repeatedly reflected up and down the cell, may be used for gases at low pressure.
**Liquid:** Pure liquids are studied in thickness of about 0.01 mm, while solutions are usually 0.1-10 mm thick, depending on the dilution. Carbon tetrachloride, carbon disulfide, chloroform etc are used as solvents.

**Solid:** Two methods are generally followed: (a) Mull Method and (b) KBr pellet method. In former method a solid sample is thoroughly grounded along with a weakly absorbing, non-volatile liquid normally Nujol to form a thick paste, called a mull which can then be held between salt plates in the same way as a pure liquid or solvent. It is very important that the sample be ground to a very fine particle size to reduce light scattering and salt plate scratching.

Nujol is transparent in the infrared except for narrow bands at 2900, 1450, 1375 cm\(^{-1}\). An alternative mulling liquid, which does not absorb in these regions, is a perfluorokerosene, such as Fluorolubs. In KBr pellet method, the solid is finely ground with pure, dry KBr, the mixture is pressed in a hydraulic press to form a transparent pellet, and the spectrum of pellet is measured. It is important that the solid be extremely finely divided and well mixed.

The pellet is usually pressed in a special die that can be evacuated in order to avoid entrapped air, which causes cloudiness in the pellet. A major advantage of this method is that, KBr has no absorptions in the IR above 250 cm\(^{-1}\), so that an unimpeded spectrum of the compounds is obtained.
**C | Scanning Electron Microscopy (SEM)**

Since their development in the early 1950's, scanning electron microscopes have developed new areas of study in the medical and physical science communities. The SEM has allowed researchers to examine a much bigger variety of specimens. The scanning electron microscope has many advantages over traditional microscopes. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the degree of magnification.

All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in the research today.

**Working of Scanning Electron Microscope (SEM)**

The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image.
Scanning electron microscopy (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. Not only the topographical information is produced in the SEM, but also information concerning the composition near surface regions of the material is provided as well [44].

In SEM, a source of electrons is focused (in vacuum) into a fine probe that is rastered over the surface of the specimen Fig. 3.7.
As the electrons penetrate the surface, a number of interactions occur that can result in the emission of electrons or photons from the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors, and the output can be used to modulate the brightness of a cathode ray tube (CRT) whose x- and y-inputs are driven in synchronism with the x– y voltages rastering the electron beam. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen.

**Fig. 3.8 Electron specimen interaction**

The principal images produced in SEM are of three types: secondary electron images, back scattered electron images, and elemental X–ray maps. Secondary and back scattered electrons are conventionally separated according to their energies. They are produced by different mechanisms. Secondary electrons result from the inelastic scattering of electrons from the beam (primary electrons) with atomic electrons. During this process some energy is transferred to atomic electrons which allow the
last to exit the solid. When the energy of the emitted electron is less than 50eV, by convention it is referred to as a secondary electron. Higher energy electrons are primary electrons that have been scattered without loss of kinetic energy by the nucleus of an atom.

An additional electron interaction of major importance in the SEM occurs when the electron from the beam (primary electron) collides with and ejects a core electron from an atom in the solid. The excited atom will decay to its ground state by emitting a characteristic X–ray photon. The X–ray emission signal can be sorted by energy in energy dispersive X–ray detector.

Fig.3.9 shows schematic photograph of the scanning electron microscope used in the present investigation.

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**Fig. 3.9 Scanning Electron Microscope (Model LEO 1430)**
**D| Energy Dispersive X-Ray Spectrometry (EDAX)**

Energy dispersive X-ray spectrometry (EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from each other. Most modern EDS systems can detect X-rays from all the elements in the periodic table above beryllium, Z = 4, if present in sufficient quantity.

X-rays are produced as a result of the ionization of an atom by high-energy radiation wherein an inner shell electron is removed [44]. To return the ionized atom to its ground state, an electron from a higher energy outer shell fills the vacant inner shell and in the process, releases an amount of energy equal to the potential energy difference between the two shells. This excess energy, which is unique for every atomic transition, will be emitted by the atom as an X-ray photon.

For example, if the K shell is ionized and the ejected K-shell electron is replaced by an electron from the L shell, the emitted X-ray is labeled a characteristic Ka, X-ray Fig. 3.10. The hole that exists in the L shell will be filled by an electron from a higher shell, say the M shell, if one exists. This M – L transition may result in the emission of another X-ray, labeled in turn according to the one of the many M–L transitions possible. The cascade of transitions will continue until the last shell is reached.
Fig. 3.10 Elements in an EDAX spectrum are identified based on the energy content of the X-rays emitted by their electrons

Design of the Spectrometer:
The different components of the Energy Dispersive spectrometer are as shown in the Fig. 3.11. It consists of i) The X–ray tube, ii) Specimen, iii) Si (Li) counter and a FET preamplifier, both cooled by liquid Nitrogen and iv) Multichannel Analyzer (MCA).

Fig. 3.11 Energy Dispersive Spectrometer
If the element is bombarded with the X-ray of high enough energy, it will emit its ‘characteristic lines’. In most cases they are the Kα and Kβ lines. They are called the characteristic lines to emphasize that the wavelength of them are fixed and characteristic to the emitting element. The phenomena are called the fluorescence. It provides a basis for a method of chemical analysis. If the different elements in the sample are bombarded with X-ray they will emit their characteristic lines of different wavelengths thus providing identification of the elements.

The X-ray spectrometer is used in two different modes for this purpose.

1. **Wavelength dispersive**: In this mode the wavelength of the emitted radiation from sample are analyzed by diffracting the radiations through a single crystal of known d value and obtaining the wavelength distribution.

2. **Energy dispersive**: In this mode diffraction of the radiation is not involved in the process of analyzing on the basis of their energies rather than their wavelengths.

**Working of Energy Dispersive Spectrometer**

The sample specimen is bombarded with X–rays of enough high energy generated from the X–ray tube. The fluorescence radiation, emitted by the sample comprising of various wavelengths according to the various elements present in the sample is analyzed and various wavelengths are separated on the basis of their energies by means of a Si (Li) counter and a multi-channel analyzer (MCA).

The counter produces the pulses proportional in height to the energies in the incident beam and MCA sorts out the various pulse heights. The excellent energy resolution of the Si (Li) counter with FET preamplifier
and the ability of the MCA to perform rapid pulse height analysis make the
spectrometer to measure the intensities of all the spectral lines from the
sample in about a minute, unless there are elements in very low
concentration are to be determined.

Chemical analysis
The energy dispersive spectrometer is used to make a rapid chemical
analysis qualitatively. It can also be used for a semi quantitative, if not
quantitative, analysis. The energy dispersive spectrum one gets from this
spectrometer is the intensity (in counts) v/s energy spectrum. The energies
in keV cover all the K and L lines emitted by the samples.

The analysis is done with the help of the computer software. There is a
table or chart of the energies of all K and L lines arranged in consequent
manner of all the elements. The information from it is retrieved by the
computer for assigning any energy peak in the diagram with the respective
element. Thus, from the peak energy the elements present in the sample
can be detected.

The semi quantitative analysis can be done with calculating the total
number of counts recorded for a particular energy. This examination is
difficult to do manually since all the energy peaks may not be well
separated and may be diffused with each other. Since the analysis needs
the total area under the curve and not the height of the peak, it is difficult
to separate the contributions of each peak. But computer software
simulates the peaks with different areas under the curve and it checks their
resultant effect when merged. It can separate out the contribution from
each peak in this manner. The relative concentrations of the elements can
be known from this analysis, if not the absolute.
### 3.3.3 ELECTRICAL PROPERTIES

#### A) D.C. Electrical Resistivity Measurements

The temperature dependence of d.c. resistivity of all the samples was studied by two-probe method. For good electrical ohmic contact the pellets were polished and silver pasted on both the surfaces.

A typical sample holder as shown in Fig. 3.12, is specially designed which consist of two brass electrodes, one of which is fixed to ceramic beads by means of screw. Another electrode at other side is attached to ceramic beads and is spring loaded to keep the pellet intact in between the electrodes.

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

**Fig. 3.12 Schematic diagram of two probe method**

The samples in the form of disc type pellet were held in a sample holder whole assembly was held in an electrical furnace. The temperature of the furnace was controlled by digital controller and maintained through a
variac. The temperature of the sample was measured with the help of calibrated chromel-alumel thermocouple attached to the controller and the temperature was read directly from the digital display in steady state. The resistance of each pellet is measured for rising and falling temperature at the steps of 10 °C. During each measurement, sufficient time was allowed for the sample to attain the equilibrium temperature.

The two-point probe method was used for the measurement of resistivity of hexaferrite materials in the temperature range of 300 K to 923 K. As the resistivity of the Sr-hexaferrite is very high and it was not possible to use the four-point probe method because it is used for the samples having low resistance [145]. The use of four-point probe method is also not suitable at high temperature due to unstability of silver paste used for connections. While the two point probe method is suitable for the samples having high resistivity and at high temperature.

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Fig. 3.13 D. C. Resistivity apparatus
The schematic diagram of the D. C. resistivity apparatus is shown in Fig. 3.13. The samples were used in the form of pellets of 10 mm diameter and of 3 mm thickness. The pellets were prepared using hydraulic press by compressing at 6 tons. Zero polish paper is used to make the uniform surface of the pellet after making the uniform surface the silver paste is applied on it for good ohmic contact. This silver pasted pellet is placed in between the two electrodes of the sample holder.

**B) Dielectric Measurements**

**Principle of Dielectric Measurements**

LCR meter is used to measure the resistance, capacitance, inductance, impedance, loss factor etc. of the materials. In an automatic LCR meter bridge method, the bridge circuit employs a fixed standard resistor beside the unknown impedance, and a multiplying digital-to-analog convertor (MDAC) that works as a resistive potentiometer.

**Working of LCR Meter**

Two independent quasi-balances are maintained in the bridge by varying the potentiometer settings and the unknown value of the standard resistance. In automatic LCR meter bridge, a fixed standard resistor despite a variable standard resistor is used. In order to determine the values of dielectric constant for the materials, an ideal capacitor C pin parallel with a resistor R is taken as the equivalent circuit of a capacitor with dielectric having certain conductivity. The resistor R can be considered as built up from two parallel resistors, one representing the finite ohmic resistance of the dielectric (ferrite) and the other representing an equivalent resistance of such a value that the energy dissipated in it is equal to the dielectric losses in the dielectric.
The dielectric measurements were carried out with the help of two probe sample holder. The two flat surfaces of pellets were polished with the help of zero polish paper. The silver paste is applied on the two flat surfaces of pellets for good ohmic contact. The variation of dielectric parameters such as dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent (tan $\delta$) were studied using LCR-Q meter [Model 4192, HP make] as a function of logarithm of frequency.

The dielectric constant is the ratio of permittivity of substance to the permittivity of free space. It is an expression of the extent to which a material concentrates electric flux, and is the electrical equivalent of relative magnetic permeability. As the dielectric constant increases, the electric flux density increases, if all other factor remains unchanged.

The dielectric constant decreases with increasing frequency and at higher frequency it remains constant, this behavior is normal ferrimagnetic behavior. The variation of dielectric constant with frequency revels the dispersion due to Maxwell-Wanger type interfacial polarization in agreement with the Koop’s phenomenological theory [46-48]. According to these models the dielectric structure is supposed to be composed of the fairly well conducting ferrite grains, separated by a second thin layer of grain boundaries of poorly conducting substances. These grain boundaries could be formed during the sintering process due to the superficial reduction or oxidation of crystallites in the porous materials as a result of their direct contact with the firing atmosphere.

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

Dielectric properties like dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent (tan $\delta$) were studied using LCR-Q meter as a function of logarithm of frequency. The capacitance of all the samples was measured in the frequency range of 50Hz to 5MHz.

### 3.3.4 MAGNETIC PROPERTIES

#### [A] A. C. Susceptibility Measurements

The a.c. susceptibility measurements of all the powdered samples were taken using the set up provided by Magneta Company, Thane. The setup is shown in Fig. 3.14.

![A C. Susceptibility set up](image)

**Fig. 3.14 A. C. Susceptibility set up**
The A. C. susceptibility set up consists of Helmholtz coil, pick up coil, furnace, sample holder. The magnetic field is produced by the double coil set up operating at a frequency of 263 Hz with r.m.s. field 7 Oe. The two coils are oppositely wound relative to each other producing uniform magnetic field along the axis perpendicular to coil. For the magnetization measurement a pick-up coil provided at the center of Helmholtz coil. To avoid overheating of coils a glass jacket with water circulation is used. The glass jacket is placed at the center of pick-up coil. The temperature was measured using Platinum-Rhodium thermocouple. The powdered sample was gradually heated and at various temperatures, the signals corresponding to the magnetic moments were taken.

The Curie temperature of each sample was determined from the low field a.c. susceptibility data. The measurements of a.c. susceptibility were carried out in the temperature range 300–800 K. From the plots of $\chi_T / \chi_{RT}$ versus temperature, Curie temperature of the sample is obtained. The measurements were taken from room temperature to Curie temperature.

The Curie temperature setup comprises of

1) A.C. susceptibility unit.
2) Furnace power supply.
3) Thermocouple and temperature indicator.
4) Platinum furnace.
5) Solenoid and pickup coil assembly.

1) A. C. susceptibility unit

The schematic diagram of this unit is given in Fig.3.15. It consists of function generator, balancing circuit and signal processing circuit based on lock-in amplifier principle.
2) Furnace power supply
It is a regulated d.c. power supply whose voltage and current can be varied continuously in the range 0-30 volts, 0-5 amperes respectively.

3) Thermocouple and temperature indicator
The thermocouple is Platinum-Platinum-Rhodium (13%) junction which is terminated into a linear temperature indicator and also into one channel of Data Acquisition Unit. When the thermocouple is in good contact with the samples, the temperature indicator directly reads the temperature of the sample.

4) Platinum furnace
The sketch of the furnace is shown in Fig. 3.16. The platinum wire is wound on a quartz tube of diameter 18 mm and wrapped with a fiber glass ribbon and pushed tightly in another quartz tube. The furnace is introduced in a double wall jacket, which can take water for cooling the
outer region of the furnace. This whole assembly is put into the solenoid and then held in plastic container.

![Diagram](image)

**Fig. 3.16 Schematic diagram furnace assembly.**

5) Solenoid and pickup-coil assembly

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

[B] Vibrating Sample Magnetometer (VSM) Measurements

Magnetization measurements at room temperature were performed using vibrating sample magnetometer (VSM). Using M-H plots, the saturation magnetization (Ms), corecivity (Hc), remanence magnetization (Mr) remanence ratio (Mr/Ms) and magneton number (nB) were calculated.

A vibrating sample magnetometer (VSM) operates on Faraday’s law of induction, which tells us that a change in magnetic field will produce an electric field. This electric field can be measured and gives information
about the changing the magnetic field.

When a material is placed in a uniform magnetic field, a dipole moment gets induced in the sample proportional to the product of the sample susceptibility and the applied field. If the sample is made to undergo sinusoidal motion, the resulting magnetic flux changes near the sample will induce electrical signal suitable placed stationary coils, the signal is proportional to the moment, amplitude and frequency of vibration.

The sample in the powder form is required for vibrating sample magnetometer technique. The powder form sample was field in a one end closed cylindrical tube having 2-3 mm diameter and 3-4 mm long. Then the weight of the empty tube and weight of the tube with sample were measured and the difference between them gives the weight of the sample for experiment. This sample filled tube is loaded in between electromagnet using a long sample holder. The sample rests centered in pair of pickup coils between the poles of an electromagnets. The sample holder is mounted on electromechanical transducer, which possess through the center of driving coil. The transducer is driven by an oscillator.

The sample under study is constraint to vibrate only along the vertical axis. When the sample vibrates vertically, it induces a signal in the pickup coil. The pail of stationary coils picks up the induced ac signal. The output of the sample coil is fed to the differential input of a lock in amplifier. The reference input of the lockin amplifier comes from the sine wave oscillator used to drive the sample holder. The output of the lockin amplifier as well as the strength of the applied field measured by gauss meter whose probe is placed at the center of electromagnet given to data acquisition system.
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