CHAPTER-2

SYNTHESIS AND CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

This chapter includes discussion of synthesis route and various experimental techniques used for the characterization of the nanoferrite samples. The details of various experimental techniques used for the study of structural properties are presented. The structural and magnetic properties were studied by using X-Ray Diffraction, Transmission Electron Microscopy, Fourier Transform Infrared Spectroscopy, Vibrating Sample Magnetometer etc. at room temperature. A detailed description of Vibrating Sample Magnetometer used in the present work has been presented along with method of analysis.

2.1 SYNTHESIS TECHNIQUE:

Ferrite nanoparticles have been synthesized by several techniques including co-precipitation, chemical auto-combustion route, conventional ceramic process, RF–sputtering, reverse micelle method, citrate precursor techniques, sol-gel and hydrothermal synthesis. Among these established synthesis methods, it is still critical to find simple, cost effective, nontoxic and environmental friendly routes to synthesize nanocrystalline ferrites. In this present work, we report for the first time the synthesis of nanoferrites by a modified sol-gel method using high purity nitrates and aloe vera plant extracted solution. This biosynthetic methods employing either biological microorganisms or plant extracts have emerged as a simple and viable alternative to chemical synthetic procedures and physical methods. There are many reports on the synthesis of metal and semiconductor nanoparticles using fungi, actinomycetes and plant extracts. Chandral et.al. have demonstrated synthesis of gold nanotriangles and silver nanoparticles using aloe vera plant extracts as a reducing agent. In their work, the sizes of nanotriangle gold are about 50-350 nm and spherical nanosilvers are about 5-15 nm [1].

This method has emerged as an important technique for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites alloys, intermetallics and nanomaterials. Today modified sol-gel method using high
purity nitrates and aloevera plant extracted solution has become a very popular approach for the preparation of ferrite nanomaterials especially magnetic nano-particles. This biosynthetic method is a versatile, simple and rapid process, which allows effective synthesis of a variety of nanosize materials.

Aloevera is a native plant in Haryana and several other countries. There is 98.5% water content in the aloevera leaves. The rest is solid materials containing over 75 different ingredients including vitamins, minerals, enzymes, sugar, phenolic compounds, polysaccharides and sterols. It also contains amino acids, lipids and salicylic acid. Aloevera gel is widely used in the cosmetics industry as a hydrating ingredient in liquids, creams, sun lotions, lip balms, healing ointments etc. The gel is further used in pharmacology for wound healing, anti-inflammatory and burn treatment. The advantages of this modified sol-gel method using high purity nitrates and aloevera plant extracted solution include (i) use of cheap, non-toxic and environmentally benign precursors and (ii) simpler procedure without time consuming polymerization and problem with the treatment of highly viscous polymeric resin. The current simple synthetic method using cheap precursors of aloevera plant extract provide high yield nanosized material with well crystalline structure and good magnetic properties.

2.2 CHARACTERIZATION TECHNIQUES

2.2.1 X-Ray Diffraction

X-Ray Diffraction is a very important tool for the characterization of the materials. X-Ray Diffraction analysis was used to study the crystalline behavior of powder samples. About 95% of all solid materials can be described as crystalline. When X-rays interact with crystalline substance (phase), one gets a diffraction pattern. In 1919 A.W. Hull gave a paper titled, “A New Method of Chemical Analysis”. Here he pointed out that “Every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others.” The X-Ray Diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. This method is not used only for phase identification of the lattice structure but also for the modeling of the basic unit cell [2]. The variation of the peak positions with the
sample orientation can be utilized to deduce the information regarding the internal strain of the sample.

Analysis of the crystal structure by X-Ray Diffraction (XRD) is a high tech, non destructive, versatile and one of the oldest technique that reveals detailed information about the chemical composition and crystallographic structure of a crystalline material. The main use of the powder diffraction is to identify components in a sample by a search/match procedure. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. Today about 25,000 organic and 50,000 inorganic single components, crystalline phases and diffraction patterns have been collected and stored on magnetic or optical media as standards. Furthermore, the areas under the peak are related to the amount of each phase present in the sample [3].

The German Physicist, Von Lue in 1912 was the first who took up the problem of X-Ray Diffraction (XRD) with the reason that, “if crystals were composed of regularly spaced atoms which might act as scattering centers for X-rays, and if X-rays were electromagnetic waves of wavelength about equal to the interatomic distances in crystals, then it should be possible to diffract X-rays by means of crystals” [4]. Today X-Ray Diffraction is a routine technique for the characterization of the materials [5]. This is an appropriate technique for all forms of samples, i.e. powder and bulk as well as thin film. Using this technique, one can get the information regarding the crystalline nature of a material, nature of the phase present, lattice parameter and grain size [6]. From the position and shape of the lines, one can obtain information regarding the unit cell parameters and microstructural parameters (grain size, microstrain etc.) respectively.

Bragg’s Condition for XRD

The condition for constructive interference between the scattered X-ray is given by the Bragg’s condition. Constructive interference of the X-ray from successive planes occurs when the path difference is an integral multiple of the wavelength so that

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

………………..(2.1)
Here \( d_{hk1} \) is the interplaner spacing, \( \theta \) is the angle of incidence also known as the Bragg’s angle. For the XRD taken in the \( \theta - 2\theta \) scan mode, a monochromatic beam of X-ray is incident on the material at an angle \( \theta \) and the detector motion is coupled with the X-ray source in such a way that it always makes an angle \( 2\theta \) with the incident direction of the X-ray beam. The resultant spectrum can be plotted between the intensity and \( 2\theta \). \( \lambda \) is the wavelength of the X-rays and \( n \) is the order of diffraction maximum. The resulting diffraction pattern comprising both the position and intensities of the diffraction effects is a fundamental physical property of the substance. Analysis of the positions of the diffraction effects leads immediately to a knowledge of the size, shape and orientation of the unit cell.

The interaction of X-ray radiation with crystalline sample is governed by Bragg’s law, which depicts a relationship between the diffraction angles (Bragg angle), X-ray wavelength, and interplanar spacing of the crystals plane. According to the Bragg, the X-Ray Diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in Figure 2.1

![Figure 2.1 Schematic representation of X-ray diffractometer](image)

In an X-ray diffractometer, X-rays are generated within evacuated tube and exits through a window composed of a light element, usually beryllium. Inside the
tube, a current is passed through the filament (usually tungsten) to generate electrons. These electrons are then accelerated through a potential difference towards a metal target, such as a copper. The high speed electron have sufficient energy to ionize some of the Cu 1s electron. The vacancies of Cu 1s orbital are then immediately occupied by electrons dropping down from higher energy level orbitals (2p-3p), and at the same time; energy released as X-ray radiation. Schematic diagram of Bragg’s diffraction is shown in Figure 2.2.

For powder diffraction, a monochromatic X-ray source with its wavelength comparable or slightly smaller than the atomic or ionic distance of the solid samples, and with its intensity as high as possible is desired. Kα X-rays meet these requirements and are used as source for powder the X-Ray Diffraction measurement. The Kβ X-ray in the initial X-ray can be filtered by a Ni foil. The energy required to ionize a 1s electron of Ni corresponds to an electromagnetic wavelength of 1.488 Å [7]. The electrons in the material start vibrating due to interaction with X-ray. Each
electrons that can be treated as a secondary point source of X-ray waves of electrons-rays. The secondary X-ray waves of the electron of the same atom are much smaller than the wavelength of the X-ray. The basic principle involved in the diffraction of X-ray beam from assembly of lattice–atoms is shown in Figure 2.3.

Figure 2.3 Basic principle involved in the diffraction of X-ray beam from assembly of lattice–atoms.

The interference among these atomic X-rays source in a solid give rise to constructive and destructive diffracted X-rays intensities, which carry the information of the crystal structure of the solid.

2.2.1 Indexing and Determination of Lattice Constants, Particle Size

In the powder X-Ray Diffraction, the observed pattern comes in the form of the intensity of the diffracted rays as a function of 2θ. The indexing of pattern has been done by using the powder X-ray software developed by Chen Dong [8]. If one has the knowledge of the crystal structure, then different ‘a’ values of lattice constants
are tried so that all the peaks are assigned \((h,k,l)\) values. Secondly, the exact 20 values at which reflections are observed are noted carefully using Gaussian fitting and then with the help of Bragg’s law, is used in the form:

\[
a = \left[\frac{\lambda}{2}\right] \left[ h^2 + k^2 + l^2 \right]^{1/2} / \sin \theta \quad \text{...........(2.2)}
\]

The corresponding ‘a’ values are calculated from the above formula. In order for crystal to diffract at all, in phase the reflection plane must meet the incident X-ray beam at one of the specified angles. It is necessary in order that the X-ray reflected from the different points on these planes reach the detector in phase. This condition is satisfied very accurately, when the diffraction planes are large and hence the diffraction maxima are sharp. However, in case of smaller crystallites, this condition is somewhat relaxed due to smaller number of co-operating planes. Therefore, when the crystallites are so small that they contain only a few planes in phase, diffraction by these planes is no longer valid for producing sharp diffraction minima. In general, the reduction in size affects the broadening of the peaks. If the path difference between rays scattered from the first two planes differs slightly by an integral multiple of wavelength then the planes scattering a ray exactly out of phase with the ray from the first plane will lie deep with in the crystal. As the crystal is too much small that this plane does not exit then complete cancellation of all the scattered rays will not exit. This means that there is a correlation between the amounts of out of phasesness that can be tolerated and the size of the crystal. The crystallite size of nanocrystalline samples was measured from the line broadening analyses using Debey-Scherer’s formula after accounting for instrumental broadening Equation [9-11]

\[
D = 0.89 \frac{\lambda}{\beta \cos \theta} \quad \text{.......... (2.3)}
\]

Where \(\lambda\) is X-ray the wavelength of X-ray (1.5405 Å for Cu- Kα ), \(\theta\) is the diffraction angle, \(\beta\) is the full width at half maximum (FWHM) in radians in the 20 scale, \(D\) is the crystallite size in nm.

In the present work XRD were done on PANalytic Powder Diffractometer (Figure 2.4 ). The wavelength of the source employed is 1.5405 Å (Copper Kα) with photon energy of 8 kev at SAIF (P. U), Chandigarh.
2.2.2 TRANSMISSION ELECTRON MICROSCOPE

Transmission Electron Microscope (TEM) is one of the most widely used techniques in the characterization of nanomaterials and nanostructures. The greatest advantages that TEM offers are the high magnification and its ability to provide both image and diffraction information from single sample. The high magnification or resolution of all TEM is a result of the small effective electron wavelength. The complementary imaging, spatial resolution micro analysis technique in TEM provides the information about morphology, composition, crystal structure electronic/ magnetic structure, size and shape of nanomaterials on a very fine scale. TEM works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus transmitted beam replicate the pattern of the slide, forming an enlarged image of the slide when falling on the screen. Transmission Electron Microscope
(TEM) operates on the same basic principle as the optical (light) microscope but uses electrons instead of light. The shorter the wavelength of electrons (200kV electrons have a wavelength of 0.025 Å) makes it possible to get a resolution (0.2nm) and high magnification (thousand times better than the light microscope). Also, in an optical microscope, the lenses are made up of glass and have fixed focal lengths, where in TEM, the electromagnetic lenses are constructed with ferromagnets and copper coils. The focal length of the electromagnetic lenses could be changed by varying the current through the coil.

TEM works the same way except they shine a beam of electrons (like the light in a slide projector) through the specimen (like the slide). However, in TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density, composition, etc. For example, porous material will allow more electrons to pass through while dense material will allow less. As a results, a specimen with a non-uniform density can examined by this technique. Whatever part is transmitted is projected on to a phosphor screen for the user to see.

The schematic diagram of TEM is shown in Figure 2.5. With an electron gun, a monochromatic beam is formed, which is accelerated by an electric field formed by a voltage differences of typically 200 kV and this beam is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens defines the “spot size” of the final spot that strikes the sample and the second lens changes the size of the spot on the sample from a wide dispersed spot to a pinpoint beam. The condenser lenses are fitted with apertures, which are usually small platinum disks with holes of various sizes. These apertures protect specimen from too many stray electrons, which contribute to excessive heat and limit the X-ray production further down the column. The most important function of the condenser lens and its aperture is to define the angular aperture of illumination. The maximum angular aperture occurs when the beam as at crossover. In this condition, the beam is round and is at maximum intensity. When the focused electron beam strike on the sample and traversed through it, the objective lens focus it to from an intermediate image.
This intermediate image is in turn magnified by a projector lens to form a magnified final image. A TEM usually operates at $10^{-6}$ Torr in the column and $10^{-9}$ Torr in the electron gun chamber. There are number of drawbacks of the TEM. Many materials require extensive sample preparation to produce a sample thin enough to be electron transparent, which makes TEM analysis relatively time consuming process with low throughput of samples [12]. The structure of the sample may also be changed during the preparation process. Also, the field of view is relatively small.
raising the possibility that the region analyzed may not be characteristic of the whole sample. The sample may also be damaged by the electron beam in some cases.

2.2.2.1 Sample Preparation

Sample preparation in TEM can be a complex procedure. TEM specimens are required to be at most hundreds of nanometers thick. Materials that have dimensions small enough to be electron transparent, such as powder or nanotubes, can be quickly prepared by the deposition of a dilute sample containing the specimen onto support grids or films. Standard TEM grid size is a 3.05 mm. The usual grid materials are copper, molybdenum, gold or platinum. This grid is placed into the sample holder which is paired with specimen stage. TEM at SAIF (P.U), Chandigarh is shown in Fig. 2.6.

Figure 2.6 Transmission Electron Microscope at SAIF (P.U), Chandigarh
2.2.3 **FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY**

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for many years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms, making up the material. Because each different material is a unique combination of atom, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through it (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

The original infrared instruments were of the dispersive type. These instruments separated the individual frequencies of energy emitted from the infrared source. This was accomplished by the use of a prism or grating. An infrared prism works exactly the same as a visible prism which separates visible light into its frequencies. A grating is a more modern dispersive element which better separates the frequencies of infrared energy. The detector measures the amount of energy at each frequency which has passed through the sample. This results in a spectrum which is a plot of intensity vs. frequency. Figure 2.7 shows the schematic diagram of Michelson interferometer, configured for FTIR.
Fourier Transform Infrared Spectroscopy is preferred over dispersive or filter methods of infrared spectral analysis for several reasons:

- It is a non-destructive technique.
- It provides a precise measurement method which requires no external calibration.
- It can increase speed, collecting a scan every second.
- It can increase sensitivity – one second scans can be co-added together to ratio out random noise.
- It has greater optical throughput.
- It is mechanically simple with only one moving part.

Fourier Transform Infrared (FTIR) Spectroscopy was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously rather than individually, was needed.

A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. The main component in the FTIR spectrometer is an interferometer. This device splits and recombines a beam of light such that the combined beam produces a wavelength dependent interference patterns or an interferogram. Michelson interferometer is most commonly used which consist of two mirrors and a beam splitter positioned at an angle of 45° to the mirrors. A KBr beam splitter coated with germanium is typically used for mid infrared region. The incident light strikes the beam splitter so that, half of the light is transmitted through the beam splitter and half is reflected to the mirrors. The two components are then reflected back and recombined at the beam splitter with half of the light passing on towards the sampling area and half traveling back towards the source. The signal at the detector is a cosine wave. In general the function of the interferometer is to disperse the radiation provided by the IR source into its component frequencies. With polychromatic light, the output signal is the sum of all the waves which is the Fourier transform of the spectrum or the interferogram. This signal is the sum of three cosine wave signals from each frequency separately. The interferogram contains the information on frequencies and intensities.
characteristic of a spectrum but in a form that is not directly interpretable. Fourier Transform converts them into more familiar form.

Fourier Transform Infrared (FTIR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

2.2.3.1 Sample Analysis Process

The normal instrumental process is as follows:

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

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

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

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

5. **The Computer**: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.
Figure 2.8 Schematic diagram of whole process of FTIR.

In the present work, the FTIR measurements on nanoparticles were carried out using Perkin Elmer Spectrum RX1, at SAIF (P.U), Chandigarh.
2.2.4 VIBRATING SAMPLE MAGNETOMETER (VSM)

The study of magnetic properties of materials is a basic requirement for understanding electronic behavior in condensed matter. A popular method for determining the magnetic properties of wide variety of magnetic samples is Vibrating Sample Magnetometer (VSM). With this technique, the magnetic moment of a sample can be measured with high accuracy. VSM is used to measure the magnetic behavior of magnetic materials. VSM operates on Faraday’s law of induction; a changing magnetic field will produce an electric field. This electric field can be measured and can give us information about the changing magnetic field. When a sample of some magnetic material is placed in a uniform magnetic field, a dipole moment is induced in the sample and is proportional to the product of the applied field and the susceptibility of the sample. This sample is made to vibrate perpendicular to the uniform magnetic field by a transducer assembly and an electrical signal can be induced in suitably located pick-up coils around the sample [13]. This induced voltage, which is at the vibrating frequency, is proportional to the magnetic moment induced in the sample, amplitude of vibration and the frequency of vibration.
Since the signal at vibrating frequency is proportional not only to the magnitude of the magnetic moment of the sample but also to the vibration amplitude and vibration frequency, therefore to get the magnetic moment of the sample, a comparison voltage is induced in the same set of reference coils by a vibrating capacitor, which is vibrated by the same transducer. A block diagram of Vibrating Sample Magnetometer is shown in Figure 2.10. The VSM consists of a head assembly for the sinusoidal motion of the drive, the sample rod, electromagnet assembly, controller and a computer. The transducer in the head assembly, a loud speaker, converts a sinusoidal a.c. drive signal of frequency normally 84 Hz, into a vertical vibration of the sample rod. The sample is normally placed at the other end of the rod which is placed in between the pole pieces of an electromagnet.

Figure 2.10 Block diagram of a Vibrating Sample Magnetometer

The coils mounted on the pole pieces of the electromagnet pick up the signal resulting from the sample motion. A vibrating capacitor beneath the transducer generates an a.c. control signal proportional to the vibrational amplitude and frequency. This signal is fed back to the oscillator where it is compared with the drive signal and also it is phase-adjusted and routed to the signal demodulator where it functions as the reference drive signal. The signal from the sample is also buffered,
amplified and applied to the demodulator. There it is demodulated with respect to the reference signal from the moving capacitor assembly. The resulting signal gives the sample’s magnetic moment alone. The VSM controller connected to a computer measures the magnetic moment vs. field value of the sample which is obtained after calibration.

The schematic diagram showing the position of the sample, the hall probe for measuring the magnetic field and the pick up coil for measuring the magnetic moment is shown in Figure 2.11.

![Figure 2.11 illustration of Vibrating Sample Magnetometer](image)

A VSM operates by first placing the sample to the studied in a constant magnetic field. If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins, with the field. If the value of the applied constant magnetic field is higher, then,
magnetization will be higher. The magnetic dipole moment of the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. As the sample is moved up and down, this magnetic stray field changes as a function of time and can be sensed by a set of pick-up coils.

The alternating magnetic field will cause an electric field in the pick-up coils according to Faraday’s law of induction. This current will be proportional to the magnetization of the sample. If the sample possesses higher magnetization, induced current will be higher. The induction current is amplified by a lock-in amplifier. The various components are hooked up to a computer interface. Using controlling and monitoring software, the system can give information about the magnetization value of sample and how its magnetization depends on the strength of the constant magnetic field. The working principle of VSM is shown in Figure 2.12.

![Figure 2.12 Working principle of VSM](image)

For the measurements using VSM, the powdered sample were weighted, pressed into a small quartz container and finally mounted at the end of a rigid ceramic rod. The VSM is calibrated out using a Ni standard with known saturation magnetization 55.01 emu/gm at a saturation field of 8 kOe.

The measurements in this thesis were carried out using VSM system. The VSM system installed in National Physical Laboratory, Delhi is shown in Figure 2.13.
Figure 2.13 Vibrating Sample Magnetometer installed at NPL, Delhi
REFERENCES