CHAPTER-4

EXPERIMENTAL DETAILS AND CHARACTERIZATION

4.1 INTRODUCTION

Electronic and material engineers are pushing the limits of the material properties in the search for better product with lowest energy consumption and optimum performance. So, the microwave synthesis of ferrites used here is expected to consume less power and it also ensures optimum performance compared to conventional synthesis methods. Structural characterization and electromagnetic parameterization techniques which are followed here are discussed along with the instrumentation used.

4.2 INTRODUCTION TO MICROWAVE SYNTHESIS

Modern trend in materials science and related fields is the fabrication, characterization and applications of materials at nano scale [138]. In recent years, several kind of metal oxide nanoparticles are finding applications in vast fields. Iron oxides are class of ferrite materials with wide applications that improves the technology of ferrite materials [115]. New synthetic routes for the preparation of ultrafine and nano-sized metal oxides to obtain required properties are under constant investigation and some of them include sol-gel, metal oxide chemical vapour deposition, co-precipitation, micro emulsion, by hydrolysis in polyol medium, etc. These methods are employed producing precursor powder with an intimate mixture of initial constituents so as to achieve lower calcination temperature. These methods suffer from evaporation of solvents due to inhomogeneity and
formation of segregated phases. Many of these methods are tedious; some of them are time consuming with many reaction steps and often in many cases a small quantity of material could be synthesized with the formation of agglomerates cannot be ruled out [14].

Synthesis of ferrite materials at nano-dimension routes the synthetic nanotechnology. Microwave synthesis of ferrites has gained great importance in the recent years because of easy scale up [45][122]. Further microwave method is very clean and nonpolluting. In order to use the microwave route, it is desirable that at least one of the reactant should be overcome by the use of a secondary suseptedor, which is chemically inert with respect to the reactants of interest. Several microwave reactions are now known to occur at lower temperature than the conventional methods [14][49].

The homogeneous nature of microwave heating eliminates local overheating at the reaction walls, which can lead to side products. Therefore, microwave-irradiated reactions are not only faster, but proceed with higher purity and, consequently, higher yields. In an industry where time is money, the dramatic rate acceleration and increased purity and yields of microwave assisted reactions make them attractive for high-produced materials [77].

Present work reports, the synthesis of ferrites and nano-sized ferrites using metal oxalate precursors employing microwave route. Urea is used as a fuel for combustion reaction and has shown promising result in the conversion of metal oxalate precursors to its respective metal oxides both in bulk and nano-sized ferrites. As prepared ferrite materials are characterized for its structure, morphology and bonding.

4.3 FERRITE SYNTHESIS

Synthesis of bulk and nano ferrites is carried out by microwave irradiation using urea as a fuel. Details of the experimental procedure for ferrites synthesis is given below.
4.3.1 Synthesis of Nickel ferrite

4.3.1.1 Materials and Methods

Nickel Chloride, ferrous ammonium sulphate, oxalic acid and urea used were AR grade. Microwave method is used for the synthesis of NiFe$_2$O$_4$ materials. Urea is used as a fuel for the combustion reaction.

4.3.1.2 Preparation of Nickel oxalate and iron oxalate precursors

These precursors were prepared by dissolving equimolar quantities of nickel chloride and ferrous ammonium sulphate with oxalic acid. The mixture was stirred well in separate beakers. The precipitates of nickel and iron oxalate obtained was filtered through sintered glass crucible and was washed with oxygen-free distilled water till free from chloride ions and oxalic acid, finally with dry acetone and was then dried under vacuum.

4.3.1.3 Synthesis of NiFe$_2$O$_4$

The nickel oxalate, iron oxalate and urea were mixed in weight ratio 1:1:5 and ground well in a pestle and mortar. Resultant solid was placed in a crucible and ignited in microwave oven having frequency 2.45 GHz. The reaction was found to be completed in about 10 minutes at high (90%) power level yields brown crystalline NiFe$_2$O$_4$ material. On cooling to room temperature, no trace of carbon impurities was observed in the final residue of NiFe$_2$O$_4$. The synthesis scheme is shown in Fig 4.1.
Fig 4.1 Synthesis Scheme of Nickel Ferrite

Synthesis of NiFe$_2$O$_4$

Nickel Chloride (Dissolved in Minimum amount Of water)

Oxalic acid (Dissolved in Minimum amount Of water)

Ferrous ammonium Sulphate (Dissolved in minimum amount Of water)

Mixing both the solutions and stirred

Nickel Oxalate

Mixing both the solutions and stirred

Ferrous Oxalate

Grinding both metal oxalates with urea (Fuel) and ignited in microwave oven.

NiFe$_2$O$_4$
(Crystalline Product)
4.3.2 Synthesis of Cobalt ferrite

Cobalt ferrite (CoFe$_2$O$_4$) possesses excellent chemical stability, good mechanical hardness and a large positive first order crystalline anisotropy constant, which makes this ferrite a promising candidate for magneto-optical recording media[139].

Cobalt ferrite is an important ferromagnetic material. Above Curie temperature; a ferromagnetic material behaves as a paramagnetic material. This ferrite forms a face-center cubic lattice containing eight tetrahedral holes and four octahedral holes per molecule.

Cobalt ferrite is an important material not only for its magnetic properties but also for its catalytic properties which depends on the textural and morphological characteristics. This kind of ferrite is a spinel but it exhibits a large coercivity differently from the rest of the spinel ferrites [63].

4.3.2.1 Materials and methods

Chemicals like cobalt nitrate, ferrous ammonium sulphate, benzoic acid and urea used were AR grade. Double distilled water is used as a solvent. Microwave method is adopted for the synthesis of cobalt ferrite particles through microwave ignition with fuel (Urea)

4.3.2.2 Preparation of metal benzoates

These precursors were prepared by dissolving equimolar quantities of cobalt nitrate and ferrous ammonium sulphate with benzoic acid. Cobalt nitrate and ferrous ammonium sulphate were dissolved in benzoic acid in separate beakers to get cobalt benzoate and ferrous benzoate. Obtained precipitate is filtered, washed and dried.
4.3.2.3 Synthesis of Cobalt ferrite

Microwave method is adopted for synthesis of cobalt ferrite. Known quantities of ferrous benzoate and cobalt benzoate are mixed with urea in the ratio 1:4 and ground well in a pestle and mortar. Resultant solid was placed in a crucible and ignited in microwave oven having frequency 2.45 GHz. The reaction was found to be completed in about ten minutes at high (90%) power level yields and burns with golden yellow colored light. After 10 minutes it gives brown cobalt ferrite particles. The synthesis scheme is given in Fig4.2
4.4 NANO-SIZED FERRITES

Synthesis of nano-sized magnesium ferrite and barium ferrite are discussed in detail.
4.4.1 Synthesis of Nano-sized Magnesium ferrite

The ferrite MgFe$_2$O$_4$ is a well-known spinel (space group $Fd-3m$) with a cation distribution that can be represented as $\text{Mg}_{1-t}\text{Fe}_t\text{O}_4$, Where $t$ depends on the thermal treatment and it has a ferromagnetic structure with curie temperature depending on the cation distribution[101]. Among different ferrites, magnesium ferrite (MgFe$_2$O$_4$) enjoys a special attention because of its vast applications in high density recording media, heterogeneous catalysis, adsorption, sensors and magnetic technologies. Mg ferrite may be used also in lower requirement television yokes and fly-back transformers because of the lower cost of Mg and because of its higher resistivity that eliminates the need for taped insulation between yoke and winding [130].

4.4.1.1 Materials and Methods

Magnesium Chloride, ferrous ammonium sulphate, oxalic acid and urea used were AR grade. Microwave method is used for the synthesis of MgFe$_2$O$_4$ materials. Urea is used as a fuel for the combustion reaction.

4.4.1.2 Preparation of Magnesium oxalate and iron oxalate precursors

These precursors were prepared by dissolving equimolar quantities of magnesium chloride and ferrous ammonium sulphate with oxalic acid. This mixture was stirred well in separate beakers. The precipitates of magnesium and iron oxalate obtained was filtered through sintered glass crucible and was washed with oxygen-free distilled water till free from sulphate ions and oxalic acid, finally with dry acetone and was then dried under vacuum.

4.4.1.3 Synthesis of nano-sized MgFe$_2$O$_4$

The magnesium oxalate, iron oxalate and urea were mixed in weight ratio 1:1:5 and ground well in a pestle and mortar. Resultant solid was placed in a crucible and ignited in microwave oven having frequency 2.45 GHz. The reaction was found to be completed in about 10 minutes at high (90%) power level and a brown crystalline MgFe$_2$O$_4$ material is formed. On cooling to room
temperature no trace of carbon impurities was observed in the final residue of MgFe$_2$O$_4$. Synthesis scheme is shown in Fig 4.4

**Fig 4.3 Synthesis scheme of nano-sized Magnesium Ferrite**
4.4.2 Synthesis of Nano-sized Barium ferrite

Ferrites have continued to attract attention over the years. As magnetic materials, ferrites cannot be replaced by any other magnetic material because they are relatively inexpensive, stable and have a wide range of technological applications in transformer core, high quality filters, high and very high frequency circuits and operating devices. The physical properties of ferrites are controlled by the preparation conditions, chemical composition, sintering temperature and time, type and amount of substitutions [92].

In recent years, nanostructured materials have drawn outstanding attention due to the unique mechanical, electrical, optical, and magnetic properties. The unique properties of nanostructured materials are due to their changed electronic structure, close to that of an isolated atom or molecule. Among the nanoscale inorganic materials, the magnetic metal oxides and their composites are of particular interest due to their exciting applications in the areas of quantum computing, information storage media, magnetic resonance imaging, sensors, refrigeration, electromagnetic wave absorption and modulation [94].

Recent studies have shown that, physical properties of nano particles are influenced significantly by the processing techniques. Since crystalline size, distribution of particle sizes and inter particle spacing have the greatest impact on magnetic particles, the ideal synthesis techniques must provide superior control over these parameters. A variety of techniques have been employed for the synthesis of nano particles with definite shapes and sizes [31].

Barium ferrite, which is a well-known ferric-magnetic material with superior chemical stability and anti-erosion properties, attracted extensive attention in recently. Owing to its high anisotropy property; this material has been widely used in the fabrication of magnetic and magneto-optic devices.
are also found in microwave devices mainly because of its high resistivity and permittivity at high frequency [137].

Nanocrystalline barium ferrites are very interesting because of its chemical properties and thermal studies [125]. These materials are technologically important and have been used in many applications such as magnetic recording media [87]. Recently, nanocrystalline magnetic materials have been receiving more and more attention due to their novel material properties, which are significantly different from those of their bulk counterparts [3].

4.4.2.1 Materials and Methods

Barium chloride, ferrous ammonium sulphate, oxalic acid and urea used were AR grade. Microwave method is used for the synthesis of barium ferrite materials using urea as a fuel for the combustion reaction.

4.4.2.2 Preparation of barium oxalate and iron oxalate precursors

Barium oxalate and iron oxalate precursors was prepared by dissolving equimolar quantities of barium chloride and ferrous ammonium sulphate with oxalic acid and was stirred well in a separate beakers. The precipitates of barium and iron oxalate obtained was filtered through sintered glass crucible and was washed with distilled water till free from chloride ions and oxalic acid, finally with dry acetone and was then dried under vacuum.

4.4.2.3 Synthesis of nano-sized BaFe$_2$O$_4$

The barium oxalate, iron oxalate and urea were mixed in weight ratio 1:1:5 and ground well in a pestle and mortar. Resultant solid was placed in a crucible and ignited in microwave oven having frequency 2.45 GHz. The reaction was found to be completed in about 10 minutes at high (90%) power level yields and forms a brown crystalline BaFe$_2$O$_4$ material. On cooling to room temperature no trace of carbon impurities was observed in the final residue of nano-sized barium ferrite. The synthesis scheme is given in Fig 4.5.
Fig 4.4 Synthesis scheme of nano-sized Barium ferrite

1. **Synthesis of BaFe$_2$O$_4$**

2. **Barium Chloride** (Dissolved in Minimum amount of water)

3. **Oxalic Acid** (Dissolved in Minimum amount of water)

4. **Ferrous Ammonium sulphate** (Dissolved in Minimum amount of water)

5. **Oxalic Acid** (Dissolved in Minimum amount of water)

6. **Mixing both the solution and stirred**

7. **Barium Oxalate**

8. **Ferrous Oxalate**

9. **Grinding both metal oxalates with urea (fuel) and ignited in microwave oven**

10. **BaFe$_2$O$_4$**

    **Crystalline Product**
4.4.3 Synthesis of nano-sized Gamma ferrite

Gamma iron oxide ($\gamma$-Fe$_2$O$_3$) is a ferromagnetic material that is already widely used as magnetic storage media in audio and video recording, magneto-optical devices, magnetic refrigeration, bioprocess, gas sensor and controlled drug delivery [142].

In most cases, Magnetite (Fe$_3$O$_4$) and Maghemite ($\gamma$-Fe$_2$O$_3$) have been employed for magnetic nanoparticles. These iron oxide particles can be formed at low temperatures under mild conditions, and display strong super paramagnetic behaviour (thus having a reduced ability to aggregate due to mutual magnetic attraction, since they do not retain magnetization when not exposed to an external magnetic field)[141].

Iron is the fourth most abundant element of the earth’s crust (5.1 mass %). Iron oxides (including oxyhydroxides) should be a kind of natural minerals and geocatalysts. The iron oxides are found in soils and rocks, lakes and rivers, on the seafloor, in air and organisms. Major iron oxides include goethite ($\alpha$-FeOOH), hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), lepidocrocite ($\gamma$-FeOOH) and magnetite (Fe$_3$O$_4$). In natural conditions, hematite usually exists together with maghemite[28].

4.4.3.1 Materials and methods

Microwave synthesis of cubic phase $\gamma$-Fe$_2$O$_3$ was carried out using iron benzoate precursor employing microwave route. PVA is used as a fuel for complete conversion of iron benzoate into Gamma iron oxide particles. Ferrous ammonium sulphate, benzoic acid and poly vinyl alcohol (PVA) used were AR grade.
4.4.3.2 Preparation of ferrous benzoate

The hydrated iron benzoate precursor was prepared by dissolving equimolar proportions of the ferrous ammonium sulphate in minimum volume of water and benzoic acid in ethyl alcohol followed by water. Both solutions are stirred for about 15 minutes on a magnetic stirrer. Further, the precipitates of ferrous benzoate were washed with cold distilled water till it becomes free from sulphate and excess benzoic acid. Finally, the precipitate was washed repeatedly with dry acetone and dried under vacuum.

4.4.3.3 Synthesis of $\gamma$-Fe$_2$O$_3$

The prepared ferrous benzoate was mixed with PVA in the weight ratio of 1:5 and ground well using pestle and mortar. Then the mixture was transferred in to a crucible and ignited in an electrical oven. The dispersed phase is ignited with the emission of gases. Here, PVA reacts with the precursor and only a partially decomposed product was obtained after the complete emission of gases. The temperature of the whole process does not exceed 300°C at any time. This partially decomposed product was placed in a domestic microwave oven having a frequency of 2.45GHz for about 15 minutes at 90% power level. The solid burns by producing yellow colour light due to the presence of iron content in the benzoate precursor leaving behind gamma iron oxide particles. The synthesis scheme is given in Fig 4.3
Fig 4.5 Synthesis scheme of nano-sized Gamma ferrite

- **Synthesis of Gamma Fe$_2$O$_3$**

  - **Ferrous Ammonium Sulphate** (Dissolved in Minimum amount of water)
  - **Benzoic Acid** (Dissolved in Ethyl Alcohol)

  - Mixed both the solution and stirred

  - Ferrous Benzoate

  - Grinding Ferrous Benzoate with PVA (fuel) and ignited in microwave oven

  - Crystalline γ-Fe$_2$O$_3$
4.5 CHARACTERIZATION TECHNIQUES OF FERRITES

4.5.1. Introduction
The characterization is very much essential for synthesized sample to know whether the desired stoichiometry and phase were obtained and to correlate the observed physical properties with structure and stoichiometry. Impurities either inherent or as additions and / or dopants in starting materials also play an important role in modifying the properties of synthesized materials. In order to study the various characteristics of the synthesized samples, we have undertaken different characterization studies by means of standard techniques as shown below to know their structural properties, electrical, dielectric and magnetic behavior.

4.5.2 X-Ray diffraction (XRD) studies
XRD gives the detailed information about the chemical composition and crystallographic structure of materials. It is a non-destructive technique which is used widely to obtain a wealth of physical, chemical and structural information about the material under investigation.

An X-ray diffraction pattern is obtained for a powder sample, either in transmission mode (the diffracted beam is recorded at the back side of the sample) or in a reflection mode (recorded at the side of the incident beam). The result is a “powder pattern” containing the X-ray reflections as a function of the diffraction angle $\theta$.

The main applications of the powder method are:

1. Determination of the unit cell size.
2. Determination of the crystal structure
3. Crystalline structure
4. Orientation of the crystalline in the sample [42].
In polycrystalline materials, the crystallites are oriented in all possible random directions satisfying Bragg’s relation,

\[ 2dsin\theta = n\lambda \]  \hspace{1cm} (4.1)

Where \( d \) = interplanar distance,

\( \theta \) = angle of diffraction,

\( n \) = integral number termed as order of diffraction,

\( \lambda \) = wavelength of monochromatic X-ray.

According to Bragg, diffraction of X-rays by crystal is possible only when their wavelength is comparable with the inter-atomic spacing of the crystal, which is of the order of 2-3\( \text{Å} \), and hence acts as three-dimensional grating, with its periodic array of atoms. Hence, a monochromatic X-ray on incidence gives a diffraction pattern; showing the intense peaks observed from different interplanes (hkl).

The X-ray diffraction patterns were obtained at room temperature, using GEOL JDX-8P X-ray diffractometer at a scanning rate of 2\(^{\circ}\) minute using CuK\(_{\alpha}\) radiation of wavelength (\( \lambda \)) 1.54056\( \text{Å} \). For phase identification and study of preferred orientations a full scan of 2\( \theta \) (from 20-65 degrees) was carried. The XRD patterns were taken on a plotter, which were analyzed to calculate \( d \) (inter atomic spacing) and to index hkl. The relative intensities were taken from XRD pattern, using highest peak as reference. The scanning is made for 2\( \theta \) angles ranging between 10\( ^{\circ} \) and 90\( ^{\circ} \).

All the XRD peaks were indexed and lattice parameters were determined in different cell configurations. The crystallite size of the samples was calculated using the Scherrer’s formula [117],

\[ D = \frac{0.89\lambda}{\beta_{1/2}} \cos \theta_{hkl} \]  \hspace{1cm} (4.2)
Where $\lambda =$ Wavelength of X-rays used and

$\beta_{1/2} =$ Half peak width,

$\theta_{hkl} =$ Bragg’s angle, and

$hkl =$ Miller indices

### 4.5.2.1 Phase identification process

For phase identification a data base is needed. Here, the so-called $d$ –values (in Å) are listed for every known substance together with the corresponding intensities (normalized with 100). The $d$-values are the net plane distances in the crystal structure, which are a property of the material and independent of the X-ray wavelength $\lambda$ used in the experiment. They can be calculated from the diffraction angle $\theta$ of the observed peak positions by using the Bragg equation,

$$d = \frac{n\lambda}{2 \sin \theta} \quad \text{---------------- (4.3)}$$

$n =$ order of reflection

$\theta =$ glancing angle of incidence

The Joint Committee on Powder Diffraction Standards (JCPDS) provides such a data base, the Powder Diffraction File (PDF), which is distributed by the International Center for Diffraction Data (ICDD) and is located near Philadelphia (USA). The PDF also exists in a commercial electronic version on the web. There are various search and match programs associated with this database, which are used to identify unknown substances (and even mixtures) [42].

The PDF (2001 release) consists of 51 sets of data and 136895 patterns (over 87500 experimental and 49000 patterns calculated from the ICSD (ICSD is the
Inorganic Crystal Structure Database) is maintained by Fachs Information Zentrum (FIZ) in Karlsruhe and NIST. The file covers ceramic mineral, metal, alloy, organic and other inorganic crystalline materials. The PDF is subdivided into various sub files, such as inorganic, mineral, organic, metal, alloy, common phases, ICSD, forensic, education, zeolite, explosive, superconductors and cement [42].

4.5.3 Scanning Electron Microscopy studies

The scanning electron microscopy (SEM) technique is used in determining the properties of materials based on size, shape, porosity and microstructure. Leica Cambridge-440, Scanning Electron Microscope was used here to get images. The SEM was operated at 20 kV [84].

4.5.4 Infrared Spectroscopy (IR) studies

Infrared spectroscopy is most widely used for the identification of the functional groups in materials because of the fact that their spectra are generally complex and provide numerous peaks that can be used for comparison purpose. In fact the infrared absorption spectrum of a material is a fingerprint of its functional groups.

Fingerprint of a sample with absorption peaks represents the frequencies of vibrations between the bonds of the atoms of the material under investigation. Note that, each individual material/compound is a unique combination of atoms i.e. two compounds produce two different spectrums. So, IR represents a unique identification of every different kind of material available.

The infrared region has been subdivided into three parts as shown below and the units of measurements are wave numbers and are measured in reciprocal cm\(^{-1}\),

(i) Near infrared region 12800-4000 cm\(^{-1}\) (0.8-2.5 μm);
(ii) Middle infrared region \(4000-667 \text{ cm}^{-1}\) (2.5-15 \(\mu\text{m})\); and 
(iii) Far infrared region \(667-50 \text{ cm}^{-1}\) (50-200 \(\mu\text{m})\).

In the present investigation, the infrared spectra of all the ferrite samples were recorded on a Perkin-Elmer FTIR spectrophotometer (Model 1000) in different ranges.

4.6 ELECTROMAGNETIC PARAMETERIZATION AND MEASUREMENT TECHNIQUES OF FERRITES

The spinel ferrites are having properties of both magnetic materials and insulators. The study of spinel ferrites is of great interest from both the fundamental and the applied research point of view. They have many applications in high frequency devices and play a useful role in technological and magnetic applications because of their high electrical resistivity and consequently low magnetic losses over a wide range of frequency. Hence, some of these properties are investigated for their possible applications to electronics and communication engineering.

4.6.1 Preparation of pellets for electromagnetic measurements

The powders were crushed and ground finally to reduce it to small crystallites of uniform size. Then the powder was pressed into different shapes for the studies. The mixture was dried and a small amount of PVA binder was added to the powder. The resulting powders were pressed by applying a pressure of 70Mpa in a stainless steel die to make pellets of 1cm diameter and 1cm thickness for dielectric measurements and toroid shaped particles for magnetic measurements. Then some of the pellets were polished to get a uniform parallel surface. These samples were polished to remove any roughness present on the surfaces. Silver paste was coated on their surfaces to enable them to act as good electrical contacts for measuring electrical and dielectric properties. The binder burn off was carried out by a slow heating rate and
soaking time being an hour. Then toroid shaped pellets were used for magnetic measurements with VSM (vibrating sample magnetometer).

4.6.2 DC Conductivity and Resistivity studies

D.C electrical resistivity [R] values of ferrite sample were obtained by using a two probe method with keithley electrometer (Model 2010) in the temperature range from room temperature to 400°C and conductivity was determined. Resistivity[ρ] and dc conductivity [$\sigma_{dc}$] values were calculated by using the following relation [42],

$$\rho = \frac{R \times A}{l} \quad (4.4)$$

Where $R$ is the resistance values of the samples,

$A$ (cm$^2$) the area of the electrodes,

$l$ (cm) the thickness of the sample.

Conductivity was calculated by using the formula

$$\sigma_{dc} = \frac{l}{\rho} \quad (4.5)$$

It is observed that dc characteristics show semiconducting behavior at low temperature and metallic behavior at high temperature as reported earlier by (KD Mandal et al). From literature it is observed that, the general practice in the preparation of high resistivity ferrites is to avoid excess iron in the lattice and to add small quantities of manganese or cobalt. The decrease in the resistivity with temperature shows that, the conduction is due to thermally activated mobility of charge carriers i.e. it follows electron hopping mechanism.

Generally, the total conductivity is the summation of the band and hopping parts as per equation

$$\sigma_{tot} = \sigma_0(T) + \sigma(\omega t) \quad (4.6)$$
The first term is dc conductivity due to the band conduction, it is frequency independent. The second term is the pure ac conductivity due to the hopping processes at the octahedral site. This plot shows that dc conductivity increases from room temperature. The conductivity increases with temperature as expected from the semiconductor behavior of spinel ferrites. So, conductivity peak may be observed. After that it starts decreasing and finally it remained constant. The decrease in the number of iron ions in octahedral site will result in the decrease of Fe\(^{2+}\)\(\leftrightarrow\)Fe\(^{3+}\) pairs contributing to the decrease in conductivity at high temperature. It is observed that, in all samples the conductivity is very low.

**4.6.3 Dielectric and ac conductivity calculations**

Dielectric properties were measured using an impedance analyzer (Model HP-4192 A) in the frequency range 1 KHz to 1MHz and in the temperature range 0\(^{0}\) C to 700\(^{0}\) C. The dielectric constant (\(\varepsilon'\)), dielectric loss factor (\(\varepsilon''\)), loss tangent (\(\tan \delta\)) and conductivity were was calculated,

\[
\varepsilon' = C \frac{d}{\varepsilon_0 A} \quad (4.7)
\]

Where

- \(A\) = Cross sectional area of the sample (cm\(^2\))
- \(d\) = thickness of the sample (cm)
- \(\varepsilon_0\) = permittivity of free space (8.854\(\times\)10\(^{-2}\)pf/cm)
- \(C\) = capacitance of the pellet in farads

The complex dielectric constant (\(\varepsilon''\)) of the samples is given by,

\[
\varepsilon'' = \varepsilon' \tan \delta \quad (4.8)
\]

Similarly, the ac electrical conductivity is obtained using the data of dielectric measurements using the relation,
\[ \sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta \quad \ldots \ldots \ldots \ldots \quad (4.9) \]

Where \( \omega \) = angular frequency

### 4.6.4 AC Conductivity studies

The ac conductivity increases with an increase of frequency. The conduction mechanism in ferrites is explained on the basis of hopping of charge carriers between the two Fe ions at octahedral site. The increase in frequency enhances the hopping frequency of charge carrier, resulting in an increase in the conduction process. The increase in conductivity does not mean increase in charge concentration but increase in mobility of charge carriers [130].

It is observed that the AC conductivity increases with increasing frequency and reaches a maximum. This variation remains same for all the samples. As the frequency of the applied field increases, the hopping of carriers also increases; thereby increasing the conductivity. The increase in AC conductivity with frequency could also be explained on the basis of Koops model. According to this model, low frequency conductivity is due to the grain boundaries, while the dispersion at higher frequencies is due to the conducting grains. This behaviour may be attributed to the Maxwell–Wagner model. The dielectric structure of ferrites is given by Koops phenomenological theory and Maxwell–Wagner theory. At lower frequencies, the grain boundaries are more active and hence the hopping of \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions is less at lower frequencies. As the frequency of the applied field increases, the conductive grains become more active thereby promoting the hopping between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions, thereby increasing the hopping conduction. A gradual increase in conductivity was observed with frequency [123].
4.6.5 Dielectric constant (\(\varepsilon\)) studies

Unlike the electrical conductor, which provides the path for charges to move when electric field or voltage is applied, dielectric material will not provide the path for electrical charges when an electric field is applied to its body and this further leads to a phenomenon called polarization inside the body. Due to this polarization, bonded charge particles align themselves with the applied electric field. This alignment of the bonded charge particles will produce additional electric field to compensate the applied electric field. This happens due to the interaction of dielectric material with the applied electric field. Finally, this interaction is characterized by dielectric constant.

In case of ferrites, electron hopping between Fe\(^{2+}\) and Fe\(^{3+}\) ions on the octahedral sites is responsible for the conduction that is thermally activated by increasing temperature. It was expected that the valence Fe\(^{2+}/Fe^{3+}\) ions is the predominant one. The electron hopping causes local displacement of electrons in the direction of the externally applied field, causing dielectric polarization in the ferrite. At the temperature above maximum peak, the decrease in the dielectric constant with temperature is attributed to the increase in chaotic thermal oscillation of the ferrite composite molecules and the diminishing degree of order of the orientation of the dipoles. Also, it may be due to random vibrational motion of ions and electrons as they become less susceptible in the direction of applied field [84].

The variation of dielectric constant as a function of frequency at different temperatures is attributed to the Maxwell and Wagner type of interfacial polarization in agreement to Koop’s theory. As the frequency increases ionic and orientation sources of polarizability decrease and finally disappear due to inertia of the molecules and ions. In practice, there is relaxation time for charge transport and therefore, the dielectric constant depends upon the applied frequency. The high value of dielectric constant may be associated
with space charge polarization and inhomogeneous dielectric structure. These inhomogeneities are impurities, grain structure and pores [84].

4.6.6 Dielectric loss ($\varepsilon''$) studies

All dielectric materials have two types of losses. One is conduction loss, representing the flow of actual charges through the dielectric material. The other dielectric loss is due to the movement or rotation of the atoms in an alternating field [13]. Usually $\varepsilon'$ shows a continuous increase with temperature until reaching a peak. The decrease in $\varepsilon'$ with increasing frequency agrees with Deby’s type relaxation process. In this case a maximum of $\varepsilon'$ is observed when the hopping frequency becomes equal to the external electric field frequency. However, the increase in $\varepsilon'$ with temperature is due to the relaxation of dipole molecules coupled with the resulting drop in relaxation time [32].

4.6.7 Complex impedance spectroscopy studies

Complex impedance spectroscopy is a well-known and powerful technique, used for investigating dielectric materials. Impedance spectroscopy has been widely used for investigating the properties of electric materials and electrochemical synthesis. The aim of the impedance measurements is identification of the physical process and the determination of various electrical properties appropriate for the electrical system under study. The basic information about the dielectric properties of materials can be obtained from the complex impedance analysis. The contribution of various processes such as the electrode effects, and their interfaces can be resolved in the frequency domain [68].

Here, the complex impedance spectroscopy (CIS) technique was used to analyze the electrical response of the sample in a wide range of frequencies (1 KHz to 1MHz) at different temperatures (0–700 $^\circ$C) using HP-4192
Impedance analyzer. The dielectric properties of a material are often represented in terms of complex dielectric permittivity $\varepsilon^*$, complex impedance $Z^*$ and electric modulus $M^*$, which are related to each other by the relation

$$ Z^* = Z' - jZ'' \text{……………………….(4.10)} $$

$$ M^* = 1/\varepsilon^*(\omega) = j(\omega C_0) Z^* = M' + jM'' \text{….. (4.11)} $$

Where $(Z', M')$ and $(Z''; M'')$ are the real and imaginary components of impedance and modulus, respectively, $j = \sqrt{-1}$ the imaginary factor and $\omega$ is the angular frequency, $\omega = 2\pi f$ [92].

However, only two parameters are considered for investigation i.e. the variation of real part and imaginary part of impedance at selected temperatures and frequencies. This plot is suitable for evaluation of the relaxation frequency of the most resistive component. Such plots would allow an in-depth study of the contribution of both grain and grain boundary phase on the conductivity. Here, relaxation processes may be observed in the frequency response. The behaviour of impedance pattern (up to 100 KHz) arises due to the presence of space charge in the material. However, at low frequencies (<10 KHz) and at high temperature, relaxation peaks are observed and is due to the occurrence of space-charge relaxation, which is related to the charge carriers in association with oxygen vacancies [120].

Experimental measurements in the present impedance spectroscopy area usually result in values of impedance as shown below,

$$ Z(\omega) = Z''(\omega) + Z''(\omega) \text{……………… (4.12)} $$

**4.7 MAGNETIC STUDIES**

Here, Q-factor and M-H hysteresis loop parameters are studied.

**4.7.1 Quality factor (Q) studies**

Quality factor, $Q$ is defined as the reciprocal of the loss coefficient,
The Q-factor of the ferrite sample was studied at the temperature range $0^\circ\text{C}$-$700^\circ\text{C}$. The Q-values depend on the ferrites microstructure, e.g., pores, grain size and second phase and all these parameters will influence its Q value. The Q value may be very low due to incomplete densification of the sample [25]. The quality factor (Q) was obtained from the LCR-Q precision meter (Model HP-4192A).

The use of nonmagnetic materials is clearly essential for high frequency operation since NiZn ferrites typically exhibit severe property changes above 200 MHz due to the Snoek limit. The maximum quality factor of multilayer chip inductors made with nonmagnetic materials is above 500 MHz. However, the quality factors at frequencies around 200–300 MHz are much lower than the values at higher frequencies. Therefore, it is desirable to develop a material that has a higher quality factor than nonmagnetic materials at 200–300 MHz and can be used in making multilayer chip inductors. Improved densification of ceramics at lower temperature scan is achieved by optimizing the powder morphology, adding glass flux and optimizing the sintering profile. Of the above methods, lowering the sintering temperature with addition of glass is the most effective and least expensive technique as proposed by [47]. So, a lot of research activities are in progress to improve the magnetic properties or to avoid magnetic losses at frequencies around 200-300 MHz, leading to a significant improvement in Q-factor values.

4.7.2 M-H Hysteresis loop

The hysteresis curves are used to check the difference between the soft magnetic materials and the hard magnetic materials. For a hard magnetic material, the area inside the hysteresis loop should be large because it represents the amount of useful magnetic energy that can be made available to do work. But for a soft magnetic material, it represents undesirable core loss
Ferromagnetic materials, which have tall, narrow hysteresis loops with small loop areas, are referred to as ‘soft’ ferrites. Materials having properties between hard and soft materials are referred to as semi-hard magnetic materials [92].

The hysteresis loop gives the relation between the magnetization M and the applied field H. The parameters extracted from the hysteresis loop that are most often used to characterize the magnetic properties of magnetic media include; the saturation magnetization Ms, the remanence Mr, the coercivity He [92]. Hysteresis loop parameters at room temperature were evaluated for the sample by using a vibrating sample magnetometer (Model DMS 1660 VSM) at a maximum applied field. Now, we will proceed to the next chapter to analyze the results obtained in the present investigation and validate these results with the data already published by different investigators using different synthesis methods.

4.8 CONCLUSIONS
Various microwave synthesis schemes were discussed for the five targeted ferrite samples. Different characterization techniques used to investigate the structural properties were discussed. Various behavioral mechanisms involved in determining different electromagnetic parameters were discussed. Required formulas and calculations used in the present investigation are also given for reference.