Experimental and Characterization Techniques

This chapter describes synthesis of nanoparticles and fundamental theory of various characterization techniques to study the structural, electrical and magnetic properties of the synthesized ferrite materials. The structural studies were carried out by using the x-ray diffraction (XRD) method. The electrical properties were studied at room temperature using dielectric and impedance spectroscopy. The magnetic properties at room temperature were investigated by using the vibrating sample magnetometer.
2.1 Preparation Methods of Ferrites

Research and technology present a basic understanding of phenomenon of materials at the nanoscale to generate and utilize structures, devices and systems that have novel properties and functions because of their small and/or intermediate size. Several methods of synthesizing metal, semiconductor and metal oxide nanostructures have been discussed, including physical and chemical routes. The majority of these methods does not yield a single phase materials with momentous quantity of particles with narrow size distribution. As a result, there is all the time a desire to utilize a simple and economic method to fabricate the single phase and high quality materials. Various techniques such as sol–gel process [1], the solid-state method [2], the salt melting method [3], ball milling [4], self-propagating high temperature synthesis [5], chemical co-precipitation method [6-8], hydrothermal [9], sono-chemical method [10-11], oxidation [12] and reverse micelle technique have been used in recent years for the synthesis of nano-ferrite material [13,14]. Ferrites are usually formed by conventional ceramic process involving high temperature over 1000 ºC by mixing the oxide raw materials or carbonates. But the high temperature processing yield rather large or non-uniform particles in size required for reducing the core losses. These non-uniform particles, on compacting, result in the arrangement of voids or low density. Shape-controlled synthesis of nanocrystals is an ever experimental challenge. Successes in shape control of nanocrystals have been reported in the synthesis of metals and semiconductors. Clearly, it is desirable to develop strategies for shape controlled synthesis of complex metal oxides possessing rich properties, especially the electric and magnetic characteristics. The synthesis of nanomaterials have been classified into two main approaches as top-down and bottom-up methodologies (Fig.2.1). Current advances in synthesis and processing of functional materials for high technology emphasize the bottom-up approach to assemble atoms, molecules and particles from the atomic or molecular scale to the macroscopic scale. Increasing interests have been found in chemical synthesis and processing of nanostructured materials [15-19]. The methods of preparation play an important role for enhancing structural, electrical and magnetic properties of spinel ferrites for various applications such as high density magnetic storage, bubble devices, electronic communication devices, sensors, magnetically guided drug delivery. As there are a number of
methods accessible for the production of nano ferrites such as sol-gel, citrate-gel (modified sol-gel) method. They are described in detail as:

2.2 Synthesis of Nanomaterials

2.2.1 Sol-gel Method

Sol-gel method in general, refers to the hydrolysis and condensation of metal alkoxides or alkoxides precursors. This process is a wet chemical process for the fabrication of ceramic and glass materials. This technique involves the conversion of a system from a colloidal liquid, named sol, into a semi-solid gel phase [21, 22, 23].

![Fig. 2.1: Schematic representation of the building up of Nanostructures [20].](image)

The introductory material (or precursor) used to create the "sol" generally contains inorganic metal salts or metal organic components, such as metal alkoxides. These precursors are submitted to a sequence of hydrolysis and polymerisation reactions to generate a colloidal suspension (or "sol"). The SOL is completed by solid particles of a diameter of few hundred of nm suspended in a liquid phase. Then the particles compact in a new phase (GEL) in which a solid macromolecule is occupied in a liquid phase (solvent). Drying the GEL by means of low temperature treatments (25-100°C), it is probable to get porous solid matrices (XEROGELs). The basics of this procedure are to generate ceramic material at a temperature close to room temperature. Therefore, such a procedure opened the possibility of incorporating in
glasses soft dopants, such as fluorescent dye molecules and organic cromophores. Sol-gel process involves the following distinct steps:

**Step 1:** This step involves the formation of stable solution of the alkoxide or solvated metal precursor that is known as sol.

\[
M-OR + H_2O \rightarrow M-OH + ROH \quad (2-1)
\]

**Step 2:** In this step, gelation resulting from the formation of an oxide- or alcohol-bridged network (the gel) by a polycondensation or polyesterification reaction that results in an affected raise in the viscosity of the solution. This gel may be shed into a mold during this step.

\[
M-OR + M-OH \rightarrow [M-O-M]_n + ROH \quad (2-2)
\]

\[
M-OH + M-OH \rightarrow [M-(OH)_2-M] \quad (2-3)
\]

**Step 3:** Aging of the gel (syneresis), through which the polycondensation reactions carry on until the gel converts into a solid mass, accompanied by reduction of the gel network and ejection of solvent from the gel pores. Ostwald ripening and phase transformations may occur concurrently with syneresis. The aging course of gels takes place several days and is serious to the avoidance of cracks in gels that have been cast.

**Step 4:** Ventilation of the gel, while water and other volatile liquids are detached from the gel network. This procedure is difficult due to fundamental alteration in the structure of the gel. The ventilation progression has itself been broken into four distinct steps [24]: (i) the stable rate time, (ii) the critical point, (iii) the first declining rate period and (iv) the second falling rate period. If isolated by thermal evaporation, the resultant monolith is termed a xerogel. If the solvent is extracted in supercritical or near supercritical circumstances the manufactured material is an aerogel.

**Step 5:** Dehydration, through which surface confined M-OH groups are detached thus stabilizing the gel against rehydration. This is usually attained by calcinate the monolith at temperatures up to 800°C.

**Step 6:** Densification and decomposition of the gels at high temperatures (T > 800°C). The pores of the gel network are indistinct and remaining organic species are
volatilized. This step in general reserved for the research of dense ceramics or glasses. All these steps are graphically represented in Fig. 2.2.

The Sol-Gel process allows synthesizing materials of high purity and homogeneity by means of training that are different from the traditional process of fusion of oxides. This procedure offers numerous reward over other methods such as, controlled stoichiometry, high-purity, phase-pure powders at a lower temperature and flexibility of forming dense monoliths, thin films or nanoparticles. Sol-gel technology is very well-organized in producing various functional materials in which particle size, porosity, thin layer thickness, separation of particles with different compositions and structures could be managed and successful applications can be obtained. They may be summarized in a scheme (Fig. 2.3) after following the analysis of Sakka [25] where examples of materials applied in various technologies are given. The history of sol-gel and the development of materials by using them are far from ending. The possibility of varying both parameters and precursors is endless.

Fig. 2.2: Reaction and processing steps in the sol-gel process.

2.2.2 Citrate-gel (modified sol-gel) Method

A process associated with the sol-gel route is the Pechini, or liquid mix, process. This method was investigated in 1967 as a system of depositing dielectric films of titanates and niobates of lead and alkaline-earth elements in the production of capacitors.
Later, the process was customised for the in-lab synthesis of multi component finely dispersed oxide materials. This method is based on a rigorous blending of positive ions in a solution, controlled transformation of the solution into a polymer gel, removal of the polymer matrix and development of an oxide precursor with a high degree of homogeneity. In this method an aqueous solution of suitable oxides or salts are mixed with an alpha-hydroxycarboxylic acid such as citric acid. Chelation, or the arrangement of complex ring-shaped compounds around the metal cations, takes place in the solution. A polyhydroxy alcohol is then added, and the liquid is heated to 150–250 °C (300–480 °F) to allow the chelates to polymerize, or form large, cross-linked networks. Surplus water is removed by heating, a solid polymeric resin results. Initially, Pechini used citric acid in this method because citric acid is a weak acid and has three carboxylic and one hydroxyl group for coordinating metal ions and therefore enhances the homogeneous mixing. Citric acid helps for the homogenous distribution and segregation of the metal ions. During water dehydration, it suppresses the precipitation of metal nitrates because it has electronegative oxygen atoms interacting with electropositive metal ions. Therefore, at a relative low temperature the precursors can form a homogenous single phase.

**Fig. 2.3:** Applications of sol-gel method according to S. Sakka [25].
2.3 Characterization Techniques

2.3.1 X-ray Diffraction

The Nobel Prize for the discovery of X-ray diffraction (XRD) was achieved by a German Physicist, Max von Laue. He invented that crystalline substances task as three-dimensional diffraction gratings for X-ray wavelengths according to the spacing of planes in a crystal lattice. This technique is useful for all forms of samples, i.e. powder and bulk as well as thin film. At the earliest, this technique was used only for the resolution of crystal structure but today this is applied, not only to structure determination, but to such diverse problems as chemical analysis and stress measurement, to the study of phase equilibria and the measurement of particle size, to the determination of the orientation of one crystal or the ensemble of orientations in a polycrystalline aggregate. This technique is based on the constructive interference of monochromatic X-rays and a crystalline sample. The fundamental of XRD is best explained by the Bragg’s equation which gives a relationship between the diffraction angles (Bragg angle), X-ray wavelength, and interplanar spacing of the crystal plane and takes place the condition for the constructive interference for the scattered X-ray from the successive atomic planes formed by the crystal lattice of the material (Fig.2.4).

![Geometrical illustrations of crystal planes and Bragg’s law.](image)

Fig. 2.4: Geometrical illustrations of crystal planes and Bragg’s law.
Fig. 2.5: Laboratory setup of Rigaku Miniflex II X-ray diffractometer.

The Bragg’s condition is given by;

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

where \( d \) is the spacing between diffraction planes, \( \theta \) is the scattering angle and \( n \) is an integer—the order of diffraction and \( \lambda \) is the wavelength of the beam.

### 2.3.2 Instrumentation

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. A detector precedes 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 detector movement is coupled with the X-ray source in such a means that it constantly makes an angle \( 2\theta \) with the incident direction of the X-ray beam. The resulting spectrum is a plot between the intensity recorded by the detector versus \( 2\theta \). These spectra contain several components, among them the most common are \( K\alpha \) and \( K\beta \). \( K\alpha \) has two parts as \( K\alpha_1 \), and \( K\alpha_2 \). \( K\alpha_1 \) has a little shorter wavelength and double the intensity as \( K\alpha_2 \). The specific wavelengths are the features of the target material (Cu, Fe, Mo, and Cr). Filtering, by crystal monochromaters, is essential to produce monochromatic X-rays desired for diffraction. \( K\alpha_1 \), and \( K\alpha_2 \) are suitably close in wavelength such that a weighted average of the two is used. Copper is the familiar target material for single-crystal with Cu K\( \alpha \) radiation = 1.5406 Å.
These X-rays are collimated and going to the sample. When 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. In the present work, the XRD pattern of our all synthesized nanoparticles was recorded by using Rigaku Miniflex diffractometer, shown in Fig. 2.5. In all the cases the radiation source was Cu-Kα (λ = 1.5406 Å). The crystallite size was calculated from the most intense peak (311) of XRD data using Debye Scherrer formalism:

$$t = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2-4)

where $\beta = (\beta_M^2 - \beta_i^2)^{1/2}$, $\lambda$ is x-ray wavelength (1.5406 Å for Cu Kα), $\beta_M$ and $\beta_i$ are the measured and instrumental broadening in radians, respectively and $\theta$ is the Bragg’s angle in degrees, $t$ is the average crystallite size, $\lambda$ the X-ray wavelength, $K$ is the Scherrer constant which equals to 0.9 for spherical particles. The Scherrer formula is acceptable for small grains (large broadening) in the absence of the major microstrain. A microstrain explains the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence of the strain it is reasonable to assume that there is a radial strain gradient, but from X-ray diffraction only a homogeneous, volume-averaged value is obtained.

2.3.3 Field Emission Transmission Electron Microscopy (FETEM)

The first transmission electron microscope (TEM) was invented by Dr. Ernst Ruska at the University of Berlin in 1931. For that, and other related work, he was awarded the Nobel Prize in physics in 1986. The TEM is a multifarious viewing system organized by a set of electromagnetic lenses used to control the imaging electrons in order to generate the extremely fine structural information that are normally recorded on photographic film. Since the illuminating electrons pass through the specimens, the information is said to be a transmitted image. The image is formed as a shadow of the specimen on a phosphorescent screen. In this technique electrons are used as “light source” and their much lower wavelength make it promising to find out a resolution a thousand times better than with a light microscope. Modern TEMs use a field emission (FE) source for their electrons. It can get magnifications of one million times with resolutions of 0.1 nm. At this time this technique has turned into a
multitalented and crucial instrument in exploration of nanomaterials. The schematic diagram of the FE-TEM instrument used is presented in Fig. 2.6. In this, electron beam emitted from the electron gun is accelerated by accelerating voltage of 200KV. The focused beam is incident on the specimen surface and interacts with the specimen. The transmitted electrons form an image and the final enlarged image is projected on a fluorescent screen.

2.3.4 Field Emission Scanning Electron Microscopy (FESEM)

The field emission scanning electron microscopy (FESEM) is an electron microscope that images the sample surface by scanning it by a high-energy beam of electrons in a raster scan pattern. It is used for the analysis of shapes and spatial differences in properties such as chemical composition, crystalline phase distributions, and examination of orientations of individual crystals within a polycrystalline sample. In addition to logical and imaging capabilities, the FESEM is also capable of electron beam lithography, which is an imperative technique in numerous fields including engineering and physics in addition to geological sciences. Field emission microscopes differ from conventional SEMs in several significant ways. The superior FESEM as shown in Fig. 2.7 probe allows one to obtain images of significantly higher resolution as compared with conventional SEMs. Researchers in biology, chemistry and physics employ this instrument to study structures that may be as small as few nanometers. The energy dispersive X-ray detector (EDX) can sort the X-ray signal by energy and produce elemental images, so the spatial distribution of particular elements can be detected by SEM. SEM usually has resolution of 1 nm for 1 KV, even resolution of 0.6 nm is possible for 5 KV. Working of this technique takes place such as an electron beam is thermionically liberated from an electron gun that is fitted with a tungsten filament cathode. Within the high vacuum column these so-called primary electrons that are focused and deflected by electronic lenses to create a narrow scan beam that bombards the object. As a consequence the "electron hail" secondary electrons are dislocated from each spot on the object. The smaller the angle of incidence of the electron beam is with respect to the sample surface and the higher a certain point is in the sample, the more secondary electrons are able to reach the detector and the lighter this appear in the final image following electronic signal amplification and digitalization. Also, the composition of the sample has an effect on
the number of deflected electrons too and thus on the 'gray value' of the corresponding pixel in the final image.

**Fig. 2.6:** Schematic diagram of Field Emission Transmission Electron Microscope.

**Fig. 2.7:** Schematic diagram of Field Emission Scanning Electron Microscope.
2.3.5 Fourier Transform Infrared (FTIR) Spectroscopy

The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly new growth in the way in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more responsive than the older dispersive instruments. FTIR is most helpful for identifying chemicals that are either organic or inorganic on the basis of its response to infra-red radiation. It can be utilized to quantitative some components of an unfamiliar combination. It can be functionalized to the analysis of solids, liquids, and gasses. It can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. It is the most powerful tool for identifying types of chemical bonds (functional groups). In this technique a sample is put in the pathway of an IR radiation source and its absorption of different IR frequencies is measured [26, 27]. Infrared (IR) spectroscopy measures the infrared intensity versus wavelength (wave number) of light. Based upon the wave number, infrared light can be categorized as far infrared (4 ~ 400 cm\(^{-1}\)), mid infrared (400 ~ 4,000 cm\(^{-1}\)) and near infrared (4,000 ~ 14,000 cm\(^{-1}\)). Infrared spectroscopy utilizes the information so as molecules contain specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. Using the knowledge of these energy levels, a spectrum can then be produced for evaluation of compound identification or sample composition. The covalent bonds that caught molecules in concert are neither stiff nor rigid, but rather they vibrate at specific frequencies corresponding to their vibrational energy levels. The vibrational frequencies succumb on numerous factors together with bond strength and the atomic mass. Samples can be ready in more than a few ways for an IR measurement. For powders, a small amount of the sample is added to potassium bromide (KBr), after which this mixture is ground into a fine powder and then compressed into a small, thin, quasi-transparent disc (Fig. 2.8). For liquids, a drop of sample may be sandwiched between two salt plates, such as NaCl, KBr and NaCl are chosen as neither of these compound shows an IR active stretch in the region typically observed for organic and some inorganic molecules. Also, we milled our samples with spectroscopic grade KBr and ground for few minutes. As Potassium bromide (KBr) does not influence the IR spectrum in the wave number range 4000-400 cm\(^{-1}\). The powder material was then pressed into disk shaped thin pellet, which was then analyzed for different functional groups. Moreover, in the case of samples
prepared by the chemical routes especially those involving the organic precursors like ethanol, citrate etc. it is essential to confirm the presence/absence of any of these groups for further processing.

Fig. 2.8: Various processes take place in IR spectroscopy.

Principle of operation

A common FTIR spectrometer consists a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer. Fig. 2.9 shows a block diagram of an FTIR spectrometer.

Fig. 2.9: Schematic illustration of FTIR spectrometer.
All IR instruments have a source of IR radiation. The infrared source generates a broad band of different wavelength of infrared radiation. This radiation passes the sample through the interferometer and reaches the detector. Then the signal is amplified and changed to a digital signal by the amplifier and analog-to-digital converter, respectively. Finally, the signal is transferred to a computer in which Fourier transform is passed out. The absorption versus frequency characteristic of light transmitted through a specimen irradiated with a beam of infrared radiation gives a fingerprint of molecular structure. Infrared radiation is absorbed when a dipole vibrates logically at the same frequency in the absorber. The pattern of vibrations is exclusive for a given molecule and the intensity of absorption is linked with the quantity of absorber. Molecular bonds vibrate at different frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate.

2.3.6 Vibrating Sample Magnetometer (VSM)

The vibrating sample magnetometer was invented in 1956 by Simon Foner, a scientist of the MIT. This experimental technique has now become a widely used instrument for determining magnetic properties of a large variety of materials: diamagnetics, paramagnetics, ferromagnetics, ferrimagnetics and antiferromagnetics. By using this technique, the magnetic moment of a sample can be calculated with high accuracy. A schematic representation of VSM is shown in Fig. 2.10. A vibrating sample magnetometer (VSM) based on Faraday's law of induction, which tells us that a changing magnetic field produces an electric field. This electric field can be calculated and can give us information about the change in magnetic field. When a material is subjected to a uniform magnetic field, a dipole moment gets induced in the sample that is proportional to the product of the sample susceptibility and the applied field. If the sample is completed to experience sinusoidal movement, the resultant magnetic flux alters near the sample that induces an electrical signal in suitable positioned motionless coils. The signal is proportional to the movement, amplitude, and frequency of vibration. The samples in powder form have been filled in a cylindrical tubes (1mm diameter and 2mm long) carefully. One end of the tube is previously closed and the other end was closed by cotton after filling the sample. The
weight of unfilled tube and weight of the tube with sample were calculated so as to get the weight of the sample taken for the experiment.

Fig. 2.10: Schematic representation of vibrating sample magnetometer (VSM).

These tubes were loaded in between the electromagnet using a long sample holder. The sample holder rests centered in a pair of pickup coils between the poles of an electromagnet. The sample holder is mounted on electromechanical transducer that passes through the center of a driving coil. The transducer is ambitious by a power amplifier that itself is driven by an oscillator. The sample under investigation is restraint 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 lock in amplifier comes from the sine wave oscillator used to drive the sample holder.
The output of the lock in amplifier as well as the strength of the applied field measured by gauss meter whose probe is located at the center of electromagnet given to data acquisition system. The specifications of the instruments and the parameters set at the time of experiment are as above.

In our study, the measurement of the field dependence of the magnetization for materials, was performed with the VSM Lake Shore (Model 7405, Fig. 2.11), having an electromagnet capable of deliver fields up to 1.5 Tesla. The magnetometer is able to detecting magnetic moments down to $10^{-6}$ emu. Room temperature, high temperature (up to 1273K) and low temperature (up to 10K) measurements can be performed with the help of a high temperature oven and cryostat assembly. For obtaining precise results with VSM a great care should be taken during measurements and calibration of the vibrating sample magnetometer is must. The magnetic moment

**Fig. 2.11:** Vibrating sample magnetometer Model 7405 Lakeshore.
calibrations were performed using a standard commercial Nickel sample with a known saturation magnetization of 6.92 emu in the presence of an external magnetic field of 5000 Oe. After calibration, the measurements were being performed.

2.3.7 Dielectric & Impedance Spectroscopy

2.3.7.1 Dielectric Constant

A dielectric material is an electrically insulating (nonmetallic) material that exhibits an electric dipole structure; that is, there is a separation of positive and negative electrically charged entities on a molecular or atomic level. As a result of dipole interactions with electric fields, dielectric materials are utilized in capacitors.

Dielectric constant is usually used to get the capability of an insulator to store electrical energy. Various polarization mechanisms in solids such as atomic polarization of the lattice, orientational polarization of dipoles, space charge polarization etc. can be explicit readily by recitation the dielectric properties as a function of frequency and temperature. In general, the dielectric constant is the ratio of the capacitance induced by two metallic plates with an insulator between them to the capacitance of the same plates with air or a vacuum between them. It scales the inefficacy of an insulating material [28]. If the material is to be used for firmly insulating reason, it would be better to have a lower dielectric constant. The dielectric constant of solids can greatly vary in magnitude with variations in their structural properties. Any mechanism of polarization can proceed in solid bodies.

A vacuum capacitor with an electric field $E$ between its metallic plates has an interfacial charge $Q_0 = \varepsilon_0 E$,

where $\varepsilon_0 = \frac{10^7}{4\pi C^2} = 8.854 \times 10^{-12}$ F/m is the dielectric permittivity of free space. If the field $E$ varies with temperature, the charge $Q_0$ follows accurately, there is no "inertia" in the vacuum response. If the capacitor is filled with a material medium-gaseous, or solid, the charge induced is increased by the polarization $P$ of the medium, so

$$Q = Q_0 + P = \varepsilon_0 (1+\chi) = \varepsilon E$$

(2-5)

where $\varepsilon$ is the permittivity and $\chi$ is the susceptibility of the dielectric medium. The dielectric constant, $\varepsilon'$ of the sample was computed using the formula.

$$\varepsilon' = \frac{C}{C_0},$$

(2-6)
where $C$ is the measured capacitance and $C_0 = \varepsilon_0 \frac{A}{t}$, where, $\varepsilon_0$ is the permittivity of free space, $A$ is area of the electrode and $t$ is thickness of the sample. The loss tangent is the dissipation factor itself.

Carrier polarization covers a very wide range of mechanisms and materials, the one common feature being that the charge carriers involved move by discontinuous hopping jumps between localized sites, they may be electrons, polarons or ions. Electrons or polarons normally jump between sites randomly distributed in space and in energy but it is almost impossible to differentiate between them experimentally. The d.c. conductivity is strong-minded by hops in percolation paths between the two electrodes, whereas the a.c. conductivity is thought to arise from more limited displacements. In contrast, ions move typically over much smaller nearest-neighbour distances and it is particularly interesting to note, therefore, that neither the magnitude of the a.c. conductivity and its activation energy nor its frequency dependence can be taken as reliable guides to the nature of the dominant carrier responsible for polarization.

### 2.3.7.2 Dissipation Factor/$\tan\delta$

Dissipation factor is the reciprocal of the ratio between the insulating materials capacitive reactance to its resistance at a specified frequency [29]. The dielectric loss in an insulating material that can be described by the power dissipated per unit volume, called the specific loss, often, in evaluating the degree to which a dielectric can dissipate the energy of the field; use is made of the angle dielectric loss and also the tangent of this angle.

The dielectric loss angle $\delta$ is the complement of the dielectric phase angle $\phi$ to $90^\circ$. The angle $\phi$ is the angular difference in phase between the voltage and current in the capacitive circuit, in the ideal case, the current phase or in such a circuit will lead the voltage phase or by $90^\circ$, and the loss angle $\phi$ will be zero. As the thermal dissipation of the electrical energy rises, the phase angle $\phi$ decreases, but the dielectric loss angle grows and so does its function $\tan\delta$. 

2.3.7.3 ac Conductivity

Ac conductivity is the physical property that characterizes the conducting ability of a material. The study of electrical conduction is one of the important characteristics of dielectric materials required not only for practical application but also for the interpretation of various physical phenomena. This is an elegant experimental tool to investigate the structural defects and internal purity of material. The profound changes that take place in physical and chemical nature of a material basically provide information through its conductivity data. Practical information regarding the mobility and generation as well as the movement of lattice defects in hydrogen bonded molecules can also be achieved by studying the electrical conductivity of the material.

When a capacitor is charged under an a.c. voltage will have some loss in current due to ohmic resistance or impedance by heat absorption. If Q is the charge in coulomb due to a potential difference of V volts between two plates of a condenser of area A, and inter plate distance t, then AC conductivity ($\sigma_{AC}$) due to a.c. voltage V ($V_0e^{j\omega t}$) is given by the relation,

$$\sigma_{a.c.} = \frac{J}{E}$$

where $J$ is the current density and $E$ is the electrical field strength vector which is $E = D = \varepsilon$; $D$ being the displacement vector of the dipole charges and $\varepsilon$ is the complex permittivity of the material.

For the a.c. conductivity to be a real quantity, the term containing $j$ must be neglected, hence

$$\sigma_{a.c.} = \omega \varepsilon''$$

In a dielectric material, there will be some power loss due to that some work has been done to overcome the frictional damping forces encountered by the dipoles for the duration of their rotation. If an a.c. field is assumed, then in an ideal case the charging current $I_c$ will be 90° out of phase by the voltage. Other than in the majority of the capacitors due to the absorption of electrical energy some loss current, $I_L$ will also be formed, which will be in phase with the voltage. Charging current $I_c$ and loss current $I_L$, will build angles $\delta$ and $\theta$ correspondingly with the total current I, passing through the capacitor. The loss current is demonstrated by $\sin\delta$ of the total current I.
Usually \( \sin \delta \) is known as the loss factor but when \( d \) is small, the \( \sin \delta = \delta = \tan \delta \). The two components \( \varepsilon' \) and \( \varepsilon'' \) of the complex dielectric constant will be frequency dependent,

\[
\begin{align*}
\varepsilon'(\omega) &= D_o \cos \left( \frac{\delta}{E_o} \right) \\
\varepsilon''(\omega) &= D_o \sin \left( \frac{\delta}{E_o} \right)
\end{align*}
\]

(2-9)

(2-10)

As the displacement vector (Do) is a time varying field will not be in phase with \( E \) and hence, there will be a phase difference \( d \) between them. From equation (2.9) and (2.10), we have

\[
\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}
\]

(2-11)

Substituting the value of \( \varepsilon''(\omega) \) from (2.11) into (2.8), we have

\[
\sigma_{AC} = \omega \varepsilon'(\omega) \tan \delta
\]

(2-12)

where, \( \omega = 2\pi f \) and \( \varepsilon = \varepsilon_0 \varepsilon_r \), (\( \varepsilon_r \) is the relative permittivity of the material and \( \varepsilon_0 \) the permittivity of free space). So

\[
\sigma_{AC} = 2\pi f \tan \delta \varepsilon_0 \varepsilon_r
\]

(2-13)

The equation (2.13) has been used to calculate the a.c. conductivity of the ferrite materials at a given frequency. The principle and the theory underlying the evaluation of \( \sigma_{AC} \) from dielectric measurements are based on a treatment dealt by Goswamy [30].

### 2.3.7.4 Impedance Spectroscopy Analyses

When an alternative electric field is applied to the ferrite material, the polarization of the material is connected to the dielectric constant or relative permittivity and the energy dissipated as the leakage, heat energy through friction and other ways was termed as the loss tangent of power dissipation. At diverse levels, the dielectric constant and loss tangent may have unusual uniqueness at diverse frequency, which could be characterized by the impedance spectroscopy. This is a classical process for studying the frequency response of dielectric materials. This method was put forward 60 years ago by K. S. Cole and R. H. Cole through the famous Cole-Cole diagram. A plethora of models explains the dielectric material and
was urbanized since then, such as the Debye relation model. The origin of the dielectric properties ranges from the atomic level to the macroscopic level, and it is difficult to construct a model to describe the dielectric properties at all levels.

Impedance Spectroscopy (IS) is an ideal and powerful technique for investigating the electrical response of dielectric materials as a function of frequency. It may be used to learn the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic-ionic and even insulators (dielectrics). Impedance behaviour of a material can be analysed based on an idealized circuit model with discrete electrical components.

The experimental data can be analysed in terms of any of the five possible complex formalisms, the permittivity ($\varepsilon^*$), the admittance ($Y^*$), the electric modulus ($M^*$), the impedance ($Z^*$) and the loss tangent ($\tan\delta$). The interrelations between these are given by the formula:

$$\tan\delta = \frac{\varepsilon'}{\varepsilon''} = \frac{M'}{M''} = \frac{Z'}{Z''} = \frac{Y'}{Y''}$$  (2-14)

Impedance is, by definition, a complex quantity that can be written as sum of the real ($Z'$) and imaginary parts ($Z''$):

$$Z^*(\omega) = Z'(\omega) + iZ''(\omega)$$  (2-15)

where $Z'$ and $Z''$ of the impedance can be written as:

$$Z' = \frac{R_g}{(1+\omega_g C_g R_g)^2} + \frac{R_{gb}}{(1+\omega_{gb} C_{gb} R_{gb})^2}$$  (2-16)

$$Z'' = \frac{-R_g^2 \omega_g C_g}{1+(R_g\omega_g C_g)^2} + \frac{R_{gb}^2 \omega_{gb} C_{gb}}{1+(R_{gb}\omega_{gb} C_{gb})^2}$$  (2-17)

where $R_g$ and $C_g$ denote the resistance and capacittance of the grain and $R_{gb}$ and $C_{gb}$ stand for grain boundary, whereas $\omega_g$ and $\omega_{gb}$ denote the frequency at the peaks of the semicircles for grain and grain boundary likewise. The resistances are intended from the circular arc intercepts on the $Z'$ axis, even as the capacitances are derived from the maximum height of the circular arcs. The maximum height in each semicircle is $Z' = -Z''$, thus by means of this situation and using relations (2.20) and (2.21), we can compute the capacitances for grain and grain boundary as:

$$C_g = \frac{1}{R_g \omega_g}$$  (2-18)

$$C_{gb} = \frac{1}{R_{gb} \omega_{gb}}$$  (2-19)
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By using the above two relations the relaxation times for grain and grain boundary were calculated by relations (2.18) & (2.19):

\[ \tau_g = \frac{1}{\omega_g} = C_g R_g \]  
\[ \tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \]  

(2-20)  
(2-21)

2.4 Magnetization

The magnetization is an influential tool to learn the diverse parameters such as domain wall rotation, anisotropy, magnetic hardness or softness of material, magnetic ordering etc. Ferrites show approximately all the properties parallel to that of ferromagnetic materials. When a magnetic field is applied to the ferromagnetic material, the magnetization possibly will vary from zero to saturation value. This behaviour was articulated by Weiss [31] by starting the existence of domains. According to Weiss, though each domain is spontaneously magnetized in the direction of field, magnetization may vary from one domain to another domain. In general, specimen contains many domains, in domain configuration i.e. a function of applied field. The magnetic moment of sample is a vector addition of magnetic moment of every domain. As a result, the magnetization or average magnetic moment per unit volume may have value between zeros to saturation.

Studies on magnetic hysteresis of ferrite give practical intimation of the magnetic parameter such as saturation magnetization (Ms), coercive force (Hc) and remanence ratio (Mr/Ms). According to the values of these parameters, the ferrites can be divided as soft and hard ferrites. The ferrites having low coercive force are called soft ferrites and ferrites with high Hc are called hard ferrites. Soft ferrites are those materials which do not keep hold of permanent magnetism, which offer easy magnetic path. Hard ferrites retain permanent magnetism and are difficult to magnetize and demagnetize. According to Neel [32] the coercive force (Hc) is linked with saturation magnetization, internal stress, porosity [33] and anisotropy [34]. The hysteresis properties are very responsive to crystal structure, heat treatment, chemical composition, porosity and grain size. A huge pact of information can be educated regarding the magnetic properties of a material by studying its hysteresis loop. A hysteresis loop gives the relationship between the induced magnetic flux density (B)
and the magnetizing force (H). It is often referred to as the B-H loop. An instance hysteresis loop is shown below (Fig. 2.12).

The magnetization curve characterizes the variation in magnetization or magnetic flux of the material with the applied field. When a field is employed to a material with arbitrarily oriented magnetic moments, it will be gradually magnetized owing to the movement of domain boundaries. At first, when no field is applied, the magnetic dipoles are randomly oriented in domains; therefore, the net magnetization is zero. When a field is applied, the domains start to rotate, rising their size in the case of the domains with direction constructive with respect to the field, and decreasing for the domains with unfavorable direction. As the field increases, the domains carry on growing until the material becomes a single domain, which is oriented in the field direction. At this point, the material got saturation [35]. As the magnetic field is increased or decreased constantly, the magnetization of the material increases or decreases but in a discontinuous manner. This phenomenon is called the Barkhausen effect and is attributed to discontinuous domain boundary motion and the discontinuous rotation of the magnetization direction within a domain [36].

**Fig. 2.12:** Schematic diagram of hysteresis loop.
2.4.1 Neel's Theory of Ferrimagnetism

The magnetic properties of ferrites are attributed to the several models like Neel’s model, Yafet Kittel Model, Random canting model, and localized canting model. The Néel theory of ferrimagnetism is based on magnetic ordering in systems which have nonequivalent substructures of magnetic ions. Such as in ferrites, the positive metal ions, which have the magnetic moment, are far away for a direct exchange interaction to be possible, because the level of overlapping of the wave functions decreases exponentially through distance. Therefore, in ferrites the exchange interaction between the metal ions takes place through the oxygen ions by means of an indirect exchange mechanism, known as super exchange. In addition, the exchange energy $J_{EX}$ between the spins of the adjacent metal ions is found to be negative, so that antiparallel alignment provides the lowest energy.

![Exchange interactions between ions in an inverse cubic ferrite.](image)

**Fig. 2.13:** Exchange interactions between ions in an inverse cubic ferrite.

The A and B sites are crystallographically dissimilar in ferrimagnetic materials, since an ion present on A site has a different number and arrangement of neighbours than the same ion on B site. Fig. (2.13) illustrates the exchange interactions that would have to be considered in a rigorous treatment of an inverse spinel ferrite $\text{MO.Fe}_2\text{O}_3$. These interactions are shown by arrows and there are 5 in all. To make simpler the problem, Neel [37] have changed the real ferromagnetic
material with a model composed of identical magnetic ions divided unequally between A and B sub lattices. These are A-A, B-B and A-B interactions and the values of these negative interactions depend on the distances between the metal ions and the oxygen ion that links them and also on the angles between the three ions. The interaction is maximum for an angle of 180° and also where the inter-atomic distances are the shortest. In the A-A and B-B cases, the angles are too small or the distances between the metal ions and the oxygen ions are too long. The best combination of angles and distances are found in the A-B interaction and hence it is the strongest. As a result, the magnetic moments on A sites are held anti parallel to those on B sites. In ferrimagnetism the A and B sub lattice magnetizations are not equal and hence this results in a net spontaneous magnetization.

In Neel’s theory, when the A-B antiferromagnetic interaction dominates the A-A and B-B interactions, A and B sub lattice magnetizations will be aligned antiparallel, resulting in ferrimagnetism in ferrites. When A-A or B-B interaction is dominant, according to Neel, the substance remains paramagnetic down to the lowest temperature. But this conclusion was not correct, as in the presence of strong interactions some kind of ordering may occur at low temperature. Yaffet and Kittel resolved this discrepancy by introducing triangular spin configuration due to angle formation of spin moments in any one of the two sub lattices.

2.4.2 Mössbauer Spectroscopy

In 1957, a graduate student Rudolf Mössbauer has done the first experimental examination of the resonant absorption and recoil-free emission of nuclear γ-rays in solids during his work at the Max Planck Institute for Medical Research in Heidelberg, Germany. For his research in resonant absorption of γ-radiation and the discovery of recoil-free emission he got the 1961 Nobel Prize in Physics. The Mössbauer effect is the basis of Mössbauer spectroscopy. This is widely used in mineralogy to observe the valence state of iron, which is found in nature as Fe⁰ (metal), Fe²⁺, and Fe³⁺, as well as the type of coordination polyhedron occupied by iron atoms (trigonal, tetrahedral, octahedral, etc.). Sometimes, it is used to find out redox ratios in glasses and (less successfully) in rocks. Mössbauer spectroscopy is
also used to assist in the identification of Fe oxide phases on the basis of their magnetic properties.

2.4.3 Instrumentation

Mössbauer spectrometer contains the basic elements such as: a source, sample, detector, and a drive to move the source or absorber. Most usually, this is fulfilled by moving the source toward and away from the sample, while velocity linearly varying with time. For instance for $^{57}$Fe, moving the source at a velocity of 1 mm/sec towards the sample increases the energy of the emitted photons by about ten natural line widths. The location of the detector relative to the source and the sample defines the geometry of the experiment (Fig.2.14); most commonly, either transmission or backscatter modes are used. It consists of γ-ray source that oscillates toward and away from the sample by a “Mossbauer drive”, a collimator to filter γ-rays, the sample and a detector.

![Mössbauer geometry of the experimental set up.](image)

**Fig. 2.14**: Mössbauer geometry of the experimental set up.
The primary characteristics observed in Mössbauer spectra are isomer shift (IS), quadrupole splitting (QS) and magnetic splitting (MS or hyperfine splitting). When source and absorber atoms are in unlike local environments, their nuclear energy levels are different (Fig. 2.15). At its simplest (blue), this shows in the transmission spectrum as a shift of the minimum away from zero velocity; this shift is generally called isomer shift (IS). The oxidation state of an absorber nucleus is one feature that can be obtained by the IS of a spectra. The 1/2 and 3/2 labels as shown in Fig. (2.15) represents the nuclear spin, or intrinsic angular moment, quantum numbers, I. Interaction of the nuclear quadrupole moment with the electric field gradient leads to splitting of the nuclear energy levels (red). When a magnetic field is in attendance at the nucleus, Zeeman splitting takes place, yielding a sextet pattern (green). So Mössbauer spectra are described using three parameters: isomer shift ($\delta$), which is due the difference in $s$ electron density between the source and the absorber, quadrupole splitting ($\Delta$ which is a shift in nuclear energy levels that is induced by an electric field gradient caused by nearby electrons, and hyperfine splitting (for magnetic materials only). Graphically, quadrupole splitting is the separation between the two component peaks of a doublet, and isomer shift is the difference between the midpoint of the doublet and zero on the velocity scale (Fig. 2.15). Mössbauer parameters are temperature-sensitive, and this quality is often exploited by using lower temperatures to improve peak resolution and induce interesting magnetic phenomena.

Fig. 2.15: Isomer shift, quadrupole splitting and magnetic hyperfine splitting for the Mössbauer transition.
References