CHAPTER TWO

EXPERIMENTAL METHODS

2.1. INTRODUCTION:

In the present study, mechano-chemical method as well as wet chemical method has been used for the synthesis of the ferrite materials. Identification and structural determination is necessary once the product has been obtained since it gives insight into the nature and the quality of the product obtained. Secondly, one can visualize the applications of such compounds only after assessing the various properties exhibited by the materials. The products obtained from the synthesis have been characterized by using chemical methods as well as instrumental techniques. The magnetic and the electrical properties of the ferrite materials have been investigated by using common instrumental methods [1-4].

A brief account of the principles and the instrumentation of the different analytical tools used in the investigation has been given in this chapter. The Instrumentations used are Ball-Mill Technique, Atomic Absorption Spectroscopy (AAS), Infrared Spectroscopy (IR), X-Ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), among others.
2.2. BALL-MILL TECHNIQUE IN MECHANO-CHEMICAL SYNTHESIS:

Oxides of manganese, zinc and iron were taken in calculated quantities and ball-milled to obtain a homogeneous mixture. The ball-mill has an electromagnetic rotor which moves stainless steel balls in the container at high speed resulting in thorough mixing of the oxides taken in the container. High speed rotation of the stainless steel balls also reduces the particle size of the oxide powders.

An indigenous Ball mill Aemas Technocracy (Model Acm-8203) with a speed of 80 rpm was used in which oxides of the manganese; zinc and iron were ball milled for 10 hours, with balls to material ratio of 10 to obtain a powdered mixture.

2.3. INSTRUMENTAL TECHNIQUES USED FOR CHARACTERIZATION:

A few techniques have been used in the present study to characterize the ferrite material. These methods are selectively used for the specific information required to confirm the formation of the desired product.

2.3.1. ATOMIC ABSORPTION SPECTROSCOPY (AAS):

Atomic absorption spectroscopy is a well known method for elemental analysis, since it is the most powerful instrumental technique for
the quantitative determination of metals in trace quantity. The analysis is done by drawing the metal in solution state (ionic) and is independent of the molecular form of the metal in the sample. The method is accurate and can detect the presence of small quantity of a metal, even in presence of other metals and amount detected can be lower than one ppm. It is simple as it does not require a sample preparation. It has become an important technique for quantitative analysis of metal because of its high sensitivity and comparative ease with which the results are obtained [3, 5].

Experimentally, a solution containing metallic species is introduced into a flame which produces vapors of those metals. When a light of the required wavelength is allowed to pass through a flame having atoms of the metal, part of that light will be absorbed and the absorption will be proportional to the density of the atoms in the flame. Thus by using atomic absorption spectroscopy, it is possible to determine the amount of light absorbed. By knowing the value of this absorption, the concentration of the metallic element is known, as the absorption is directly proportional to the density of the atoms in the flame.

The total amount of the light absorbed is given by an equation:

\[
\text{At } v \text{ (frequency), the total amount of light absorbed } = \frac{\pi e^2}{mc} N f \quad \text{2.1.}
\]

where 'e' is the charge on the electron of mass 'm', 'c' the speed of the light, 'N' the total number of atoms that can absorb at frequency 'v' in the light path and 'f' the oscillator strength or ability for each atom to absorb
at frequency, \( \nu \). As \( \pi, e, m \) and \( c \) are constants, the equation (2.1.) can be simplified to the following expression:

\[
\text{Total amount of high absorbed} = (\text{constant}) \, N \nu
\]

From expression (2.2.), it follows that:

(a) Firstly, there is no term involving the wavelength (or frequency) of absorption other than the indication of the actual absorption wavelength;

(b) Secondly, there is no term involving the temperature.

From the above, it follows that absorption by atom is independent of the wavelength of absorption and the temperature of the atoms. These two features provide AAS distinct advantage over flame emission spectroscopy.

It should be pointed out, however, that although the temperature does not affect the process of absorption by atoms, it does affect the efficiency with which atoms are produced from a sample and therefore indirectly affects the signal quite significantly. Furthermore, some atoms, particularly those of the alkali metals, easily ionize at high temperatures. Ions do not absorb at atomic absorption wavelengths. Atoms that become ionized are effectively removed from the absorbing population, resulting in a loss of signal, hence efficiency.

AAS was used to determine the amount of Mn, Zn and Fe in the ultrafine mixed metals oxides prepared by two methods in the present study using atomic absorption spectrophotometer GBC Model 932AA.
2.3.2. INFRARED (IR) SPECTROSCOPY:

Infrared Spectroscopy is one of the most powerful analytical techniques which can be used for chemical and structural identification. This technique, combined with intensity measurements, is also useful for quantitative measurements. The important advantage of infrared spectroscopy over the other methods of structural analysis (XRD, ESR, etc) is that it instantaneously provides useful information about the structure of molecule without the use of much difficult evaluation techniques. IR spectroscopy, therefore, has become a versatile tool for both qualitative and quantitative analysis of molecular species [6].

The technique is based upon a simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations, the molecules (bonds) of chemical compounds vibrate with different modes of vibration giving rise to close-packed absorption bands called as IR absorption spectrum which may extend over a wide wavelength range. Various bands will occur in IR spectrum which will correspond to the characteristic functional groups and bonds present in the chemical substance. Band intensities in IR spectrum may be expressed either as transmittance (T) or absorbance (A).

IR spectroscopy can be applied at all levels of expertise from simple matching of spectra on one hand, to the theoretical calculations at the other. The instruments are simple, relatively inexpensive and easy to operate.
IR includes a broad region from red end of visible spectrum (12500 cm\(^{-1}\)) to the microwave (10 cm\(^{-1}\)) in the electromagnetic spectrum and based upon application and instrumentation involved it is conveniently divided into Near-IR (12500 to 4000 cm\(^{-1}\)), Mid-IR (4000 to 200 cm\(^{-1}\)) and Far-IR (200 to 10 cm\(^{-1}\)). The most fundamental region of interest for the analytical purpose is from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) as it provides the information about the different vibrations of molecules, and therefore about the structure of molecules [7].

When IR radiation is passed through a sample, certain frequencies are absorbed by the molecule of the sample and so it gives rise to vibrational changes in the molecule. For such vibrational changes to occur there must be a mode of interaction between the incident radiation and the vibrational energy levels. This mode of interaction is an oscillating electric dipole induced by the vibration, which interacts with the oscillating electric field of the electromagnetic radiation. IR absorption occurs for each vibrational degree of freedom of the molecule provided that a change in the dipole moment of the molecule takes place during the vibration. In many of the normal modes of vibration of a molecule the main participants in the vibrations will be the two atoms held together by a chemical bond. These vibrations have frequencies which depend primarily on the masses of the two vibrating atoms and the force constant of the bond between them. Also, these frequencies are slightly affected by other atoms attached to the two atoms concerned. These vibrational modes are characteristic of the groups in the molecule and are useful in the identification of a
compound. For a large molecule with many vibrational degrees of freedom there may be many IR bands observed. Since each molecule has individual sets of energy levels, the absorption spectrum is characteristic of the fundamental groups that are in the molecule.

For example, a carbon-carbon triple bond (-C≡C-) absorbs in the region 2250-2100 cm⁻¹, whereas a carbon double bond (-C=C-) is weaker and absorbs at lower frequency, 1670-1620 cm⁻¹.

The hydrogen-oxygen bond of O-H group gives a characteristic absorption band in the infrared region. The frequencies of peak maxima depend on O-H bond strength. This provides information like, the location of O-H group, whether it belongs to water molecule and whether hydrogen bonding is present or not. Peaks associated with vibrational modes of covalently bonded groups such as oxanions usually occur at high frequency. At lower frequency in the far region, lattice vibrations give rise to absorption peaks. At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. Each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinate axes (x, y and z). A polyatomic molecule of 'n' atoms has 3n total degrees of freedom. However, 3 degrees of freedom are required to describe the translation that is the motion of the entire molecule through space. In addition, 3 degrees of freedom correspond to rotation of the entire molecule, therefore the remaining (3n – 6) degrees of freedom are true, fundamental vibrations for the nonlinear molecules.
Linear molecules possess \((3n - 5)\) fundamental vibrational modes because only two degrees of freedom are sufficient to describe the rotation. Among the \((3n - 6)\) or \((3n - 5)\) fundamental vibrations or normal modes of vibrations, those that produce a net change in the dipole moment may result in an IR activity and those that give polarizability changes may give rise to Raman activity. Therefore, some vibrations can be both IR and Raman-active.

The total numbers of observed absorption bands are different from the total number of fundamental vibrations. It is less because some modes are not IR active and a single frequency can cause more than one mode of motion to occur. Conversely, additional bands are generated by the appearance of overtones (integral multiples of the fundamental absorption frequencies), combinations of fundamental frequencies, differences of fundamental frequencies, coupling interactions of two fundamental absorption frequencies, and coupling interactions between fundamental vibrations and overtones or combination bands (Fermi resonance). The intensities of overtone, combination, and difference bands are less than those of the fundamental bands. The combination and blending of all the factors thus create a unique IR spectrum for each compound. The major types of molecular vibrations are stretching and bending, the absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not the discrete lines, commonly observed in the mid IR region.
The transmittance spectra provide better contrast between intensities of strong and weak bands because transmittance ranges from zero to hundred percent, whereas absorbance ranges from infinity to zero.

A typical IR spectrophotometer consists of components like radiation source, optical path, monochromator, radiation detector and the sample holder.

Fourier Transform Infrared spectrophotometer (FTIR) is superior to the IR spectrophotometer. The FTIR instrument is based upon Michelson interferometer. The absorbing material is placed in one of the beams and the resulting interferogram carries the spectrum characteristics of the sample in the beam. The information from the interferogram is converted into infrared spectrum through computer processing. It is easier to study small samples with weak absorption, which is an added advantage in FTIR.

IR spectra of Mn-Zn ferrite samples obtained by both the methods of preparation, were recorded in the range 4000-400 cm\(^{-1}\) by using FTIR Shimadzu Model IR prestige 21 series spectrophotometer.

2.3.3. SIMULTANEOUS THERMAL ANALYSER (TGA-DTA):

When a substance is heated, it undergoes certain physical and/or chemical change. This change is characteristic of the given sample. By
knowing the temperature at which such reaction occurs, the heat involved in the reaction and the loss in weight, if any, during the change, it is possible to characterize the given material.

Over the last few decades, the methods in thermal analysis have been widely used in characterization of materials as one of the most important analytical techniques. The thermal analysis is a group of technique in which physical and/or chemical changes occurring in a substance is measured as a function of temperature (heating or cooling). The different techniques commonly used include Thermogravimetry (TGA), Derivative Thermo Gravimetry (DTG), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Thermometric Titrimetry, Dynamic Reflectance Spectroscopy (DRS), Evolved Gas Analysis (EGA), Thermo Mechanical analysis (TMA) etc. In many cases the use of a single thermal analysis technique may not provide complete information, hence the use of additional thermal technique independent or simultaneous, becomes necessary.

In the present study, simultaneous TGA and DTA is used as an analytical tool for the study of the precursor. TGA is a technique in which the weight of a substance, during heating or cooling at a controlled rate, is recorded as a function of time or temperature. In this technique, the sample is heated in an environment of which temperature is changing in a predetermined manner at a linear rate. A sensitive thermobalance records the weight during the linear increase or decrease of temperature. Results
from the programmed operation of the thermobalance are represented by a graph of weight change versus temperature. This graph is referred to as the thermogram or TG curve. From the TG curve one can draw useful information regarding the thermal stability, weight loss, composition and decomposition reaction at temperature indicated therein. This tool can also be used to confirm the composition assigned to a compound.

Differential thermal analysis (DTA) often used along with TGA, is considered to be an adjunct to TGA. Together they constitute the method that yields a data of fundamental nature. The DTA technique is simple as it records the difference in temperature between the sample and the reference material against time or temperature, as the two substances are subjected to an identical temperature regime, in an environment, while heating or cooling at a controlled rate. Thus differential temperature detector records a differential thermogram, which consists of difference in temperature of the sample and the reference (differential temperature \( \Delta T \)), plotted as a function of time or reference temperature or furnace temperature. The origin of difference in temperature (\( \Delta T \)) in the sample lies in the energy difference between reactant and product or between two phases of a substance, which is manifested as enthalpic changes—either endothermic or exothermic. DTA allows detection of each and every physical or chemical change whether or not accompanied by a change in weight [2-4].

TGA-DTA analysis of a few representative samples of precursors, obtained by both the methods of preparation, was carried out to ascertain
the decomposition temperature on TGA-DTA instrument Model Netzsch DSC-TG STA 409PC.

2.3.4. X-RAY DIFFRACTION SPECTROSCOPY (XRD):

A crystal lattice is considered to be made up of regular layers or planes of atoms equal distance apart. Since the wavelength of X-rays is comparable to the interatomic distances of $10^{-8}$ cm, Laue (1912) suggested that crystal can act as grating to X-rays. Thus when a beam of X-rays is allowed to fall on a crystal, a large number of images of different intensities is formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots is produced on a photographic plate placed in their path. On the other hand, if the diffracted waves are out of phase, dark spots are caused on the photographic plate. From the overall diffraction patterns produced by a crystal, we can arrive at the detailed information regarding the position of particles in the crystal [8].

X-ray powder diffraction (XRD), is an instrumental technique that is used to identify materials. XRD provides the researcher with a fast and reliable tool for routine material identification. XRD in particular can be used for identifying fine-grained minerals and mixtures or intergrowths of minerals that may not lend themselves to analysis by other techniques. Crystal structure cannot be visualized by visible light of wavelength approximately $5000\text{A}^{0}$ as arrangement of atoms or placement of atoms in
the material is too close for resolution. The interatomic spacing in crystal is of the order of $10^{-8}$ cm. Therefore, a wave with wavelength of similar order will give rise to diffraction phenomena. Diffraction provides information about arrangement of atoms in the crystals [9].

For crystal diffraction, X-rays are more suitable as the energy of X-ray quanta is

$$E = \frac{hc}{\lambda}$$

where $\lambda$ is of order $10^{-8}$ cm.

When X-ray radiation passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the atoms are organized in planes (i.e. the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interferences occur. These diffracted X-rays are emitted at characteristic angles based on the spacings between the atoms organized in crystal planes. Each atom can belong to many sets of crystal planes. Each set of planes has a specific interplanar distance and will give rise to a characteristic angle of diffracted X-rays. In 1913, W. L. Bragg and W. H. Bragg worked out a mathematical relation to determine interatomic distances from X-ray diffraction patterns. This relation is called the Bragg equation. They showed that: (1) The X-ray diffracted from atoms in crystal planes obey the laws of reflection. (2) The two rays reflected by successive planes will be in phase if the extra distance travelled by the second ray is an integral number of wavelengths.
If the illuminating wavelength is known and the angle can be measured then the interplanar distance can be calculated.

From the Bragg equation, a set of d-spaces obtained from a single compound will represent the set of planes that can be passed through the atoms and can be used for comparison with sets of d-spaces obtained from standard compounds. Diffraction of monochromatic X-rays by crystal takes place according to Bragg's law

\[ n\lambda = 2dsin\theta \]  

\( \lambda \) = wavelength of X-rays, \( n \) = order of diffraction, \( d \) = interplanar separations, \( \theta \) = Bragg angle.

This condition helps in finding the size, shape and orientation of crystallite unit cell. From Bragg's law, it is seen that intensities are stronger only at certain values of \( \theta \) for specific \( \lambda \) and \( d \). This intensity depends on the atomic scattering factor of each atom and position of each atom in the unit cell. The most widespread use of X-ray powder diffraction is for the identification of crystalline compounds by their diffraction pattern. One can also determine crystallite size from analysis of peak broadening.
The primary components of a powder diffractometer are the sources of X-ray, usually called X-ray tube, the sample chamber, a goniometer- for measuring angles, and a X-ray detector for measuring the intensity of diffracted X-ray beam. Apart from these there are several slits to reduce the divergence of the incident and diffracted beam and monochromator are also used.

X-ray powder diffraction pattern of Mn Zn ferrite samples obtained by both the methods of preparation, was recorded on a Rigaku, X-ray advance Power diffractometer using Cu Kα radiation (λ = 1.54183 Å). The step size employed was 0.02°, in the range of 20°–80°.

2.3.4.1. LINE BROADENING ANALYSIS FOR CRYSTALLITE DIMENSION:

As the particle size decreases the peaks get broadened due to incomplete destructive interference. The broadening caused by fine crystallites relates to the size of the grains by Scherer formula [8].

\[ T = 0.9 \frac{\lambda}{D_p \cos \theta} \]

where ‘T’ = crystallite size, ‘\( \lambda \)' = wavelength, ‘\( D_p \)' = FWHM (full width half measure), ‘\( \theta \)'=Bragg angle

The X-Ray data was used to calculate XRD density of the solid samples by method reported elsewhere (3.5.10) The XRD density values and the experimentally determined mass density values were subsequently
employed to calculate the porosity of the ferrite samples as described in Chapter Three.

2.3.5. SCANNING ELECTRON MICROSCOPY (SEM):

Scanning Electron Microscopy (SEM) technique is a widely used form of electron microscopy in the field of materials science. SEM is an instrument, which is used to observe the morphology of a sample at higher magnification, higher resolution and depth of focus compared to an optical microscope. In SEM an accelerated beam of mono-energetic electrons is focused on to the surface of the sample and a small area is scanned by it. Several signals are generated and appropriate ones are collected depending on the mode of its operation. The signal is amplified and made to form a synchronous image on the cathode ray tube, the contrast resulting from the morphological changes and the variation of atomic number over the area probed [10-12].

Fig.2.2.(a). Scanning Electron Microscope JEOL Model 840(SEM).
A camera is used to photograph the image which may be digitized and processed on a computer. The characteristic X-rays emitted may be analyzed for their energy and intensity energy absorption X-rays (EAX), the energy being the signature of the element emitting them and the intensity as to how much of it is present.

A well-focused mono-energetic (~25KeV) beam is incident on a solid surface giving various signals such as scattering electrons, secondary electrons, Auger electrons and X-rays. Therefore the SEM renders imaging with radiations, which can be focused by lenses, and in addition, it can give many different views of the same specimen. Back-scattered electrons and secondary electrons are particularly pertinent for SEM applications, their intensity being dependent on the atomic number of the host atoms.
Each may be collected, amplified and utilized to control the brightness of the spot on a cathode ray tube (CRT). To obtain signals from an area, the electron beam is scanned over the specimen surface by two pairs of electro-magnetic deflection coils and so is the CRT beam in synchronization with this. The signals are transferred from point to point and the signal map of the scanned area is displayed on a long persistent phosphor CRT screen.

Changes in brightness represent changes of a particular property within the scanned area of the specimen. Some of these signals carry information about the sample which provides clues to its compositions. The performance of the SEM depends on a number of related factors; perhaps the most important is the output of the electron source.

SEM micrographs were obtained for a few samples to evaluate change in morphology of the samples after sintering them at various temperatures as well as for determining the particle size of ferrite samples prepared in the present study using Scanning Electron Microscope Model JEOL 5800LV.

2.3.6. ENERGY DISPERSIVE X-RAY ANALYSIS (EDS):

Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid substances. The signals that derive from electron sample interaction reveal
information about the sample including external morphology (texture), chemical composition, EDS identifies the elemental composition of materials imaged in a SEM for all elements with an atomic number greater than boron. Most elements are detected at concentrations on the order of 0.1%. crystalline structure and orientation of materials. Thus, it provides elemental analysis data of the sample.

The fundamental principle of Scanning Electron Microscopy (SEM) is that the accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron sample interaction, when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons, diffracted backscattered electrons (that are used to determine crystal structures and orientations of materials), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathode-luminescence), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: of these, the secondary electrons are most valuable for showing morphology and topography on samples and the backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).

Two of the most commonly used signals for investigating the composition of samples are X-rays and backscattered electrons. X-ray
signals are commonly used to provide elemental analysis by the attachment of an Energy Dispersive Spectrometer to the SEM system. X-ray emission results from inelastic scattering between the beam of incident electrons and the electrons in discrete orbitals (shells) of the atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a sample that is excited by the electron beam. As the electron beam of the SEM is scanned across the sample surface, it generates X-ray fluorescence from the atoms in its path. The energy of each X-ray photon is characteristic of the element, which produces it. The EDS microanalysis system collects the X-rays, and analyses, sorts and plots them by their energy. Thereby, it automatically identifies and labels the elements responsible for the peaks in this energy distribution.

The EDS data obtained is compared with either known or computer-generated standards to produce a full quantitative analysis showing the sample composition. The data output is either this element analysis, the original spectrum showing the number of X-rays collected at each energy, or maps of distributions of elements over areas of interest. SEM analysis is considered to be non-destructive; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.
EDS spectra giving percentage compositions of Mn, Zn, Fe and O are obtained and reported for the few samples using Scanning Electron Microscope JEOL Model 840 (SEM).

2.3.7. TRANSMISSION ELECTRON MICROSCOPY (TEM):

The Transmission Electron Microscope (TEM) has been used in all areas of biological and biomedical investigations because of its ability to view the finest cell structures. It is also used as a diagnostic tool in hospital pathology labs. The transmission electron microscope uses a high energy electron beam. For a crystallographer or a metallurgist or a semiconductor research scientist, current high voltage/high resolution TEMs, utilizing 200 keV to 1 MeV, have permitted the routine imaging of atoms, allowing materials researchers to monitor and design materials with custom-tailored properties. With the addition of energy dispersive X-ray analysis (EDAX) or energy loss spectrometry (EELS), the TEM can also be used as an elemental analysis tool, capable of identifying the elements in areas less than 0.5μm in diameter. Transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light (with 200kV, the electrons have a wavelength of 0.025Å).
However, the resolution of the optical microscope is limited by the wavelength of light, while that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 1-2 Å. Because even for very thin samples one is looking through many atoms, one does not usually see individual atoms. Rather, the high resolution imaging mode of the microscope images the crystal lattice of a material as an interference pattern between the transmitted and diffracted beams. This allows one to observe planar and line defects, grain boundaries, interfaces, etc. with atomic scale resolution. The brightfield/darkfield imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable in giving information about the morphology, crystal phases, and defects in a material. Finally, the microscope is equipped with a special imaging lens allowing for the observation of micromagnetic domain structures in a field-free environment [12].

With its multifaceted capabilities such as nano-beam diffraction and composition analysis, and imaging abilities at angstrom level, TEM has emerged as an instrument for complete characterization of microstructure of the materials. The TEMs are available in several forms, which are referred to by different acronyms such as HRTEM (High resolution TEM), STEM (Scanning TEM) and AEM (Analytical TEM).

TEMs basically comprise of an electron gun, a vacuum system, electromagnetic lenses, a high voltage generator, recording devices and the
associated electronics. TEM also needs a source of electrons to illuminate the specimen. In order to get the best images, the best diffraction effects and the appropriately optimum suitable chemical analysis capabilities, the best available electron source needs to be used. The resolution of the modern TEM is under 0.2 nm (point to point) even with a fair amount of specimen tilt. These microscopes are therefore capable of satisfactorily resolving the structure of different phases in most metals and alloys.

Fig.2.3(a). Transmission Electron Microscope- Philips model CM200.
A modern day TEM has about five to six image forming lenses. The final image is projected on the screen. The diffraction pattern is formed on the back focal plane of the objective lens and the first image is formed on the back plane of the objective lens. If the image forming lenses following the objective lens are excited in such a way that these see the back focal plane of the objective lens as the object then what one sees on the screen is the diffraction pattern. However, if the lenses are excited in such a way that these see the back image plane of the objective lens as an object then what we see on the screen is the image of sample. Therefore, in a modern TEM it is possible to switch from diffraction to imaging and vice-versa by changing the excitation of the lenses following the objective lens. TEM can be used to image the specimen by focusing the final image in the plane of the fluorescent screen or it can be used to image the diffraction pattern from the sample.

Fig. 2.3(b). Sketch of radiation path in TEM.
Electron diffraction can be explained on the basis of concepts of Reciprocal lattice and Ewald sphere. When combined with the reciprocal lattice concept, the Ewald sphere construction provides a very simple way of visualizing electron diffraction. Since the reciprocal of electron wavelength is much larger than the interplanar spacings in the reciprocal space, many reciprocal lattice points are simultaneously intersected by the Ewald sphere giving rise to many diffracted rays, even from a single crystal, in case of electron diffraction. The diffraction patterns can be of various types i.e. Selected Area Electron Diffraction (SAED), Convergent Beam Electron Diffraction (CBED), Reflective High-Energy Electron Diffraction (RHEED) and Low Energy Electron Diffraction (LEED). Diffraction patterns form the basis of all image formation in the TEM.

TEM micrographs were obtained for a few samples to evaluate the particle size of ultrafine ferrite samples prepared in the present study using Transmission Electron Microscope of Philips Model CM200.

2.4. MAGNETIC AND ELECTRICAL PROPERTIES:

Mn-Zn ferrites exhibit magnetic and electrical behaviour. These compounds are of technological importance because of these properties. Many techniques are available to study the magnetic properties such as saturation magnetization, permeability, susceptibility etc. as also electrical properties such as resistivity, thermo-electric power and dielectric
behaviour. A brief description of the instrumental techniques employed in the study of these properties is given below.

2.4.1. MAGNETIC PROPERTIES:

Magnetization is one of the fundamental properties of ferrites. The magnetization is the magnetic moment per unit volume of material which is induced in it when it is placed in external magnetic field. The saturation magnetization, coercivity and remanance are studied with the help of hysteresis. In ferrites, there exist the domains, which possess the magnetic moments or spins of atoms in parallel with each other. This ordering is due to the presence of internal molecular field which is found to be, maximum at 0K. Therefore, the magnetization is found to be maximum at absolute zero. An increase in the temperature of ferromagnetic substances is found to oppose this alignment because with the increase in temperature, magnetization is found to decrease.

The critical temperature at which the ferromagnet behaves as paramagnet is called the Curie temperature. It is an important intrinsic property of the ferrites. A. C. susceptibility helps in determining the existence of multidomain (MD), single domain (SD) and super paramagnetic (SP) particles in the material. From the susceptibility curves, the Curie temperature and domain structure can be studied. The origin of magnetic permeability in ferrites has been a subject of research for the last
several years. Basically two processes are responsible for permeability viz. (i) rotations of domains and (ii) domain wall displacement.

It is generally assumed that the initial permeability is caused by the reversible displacement of the domain walls, the contribution of rotation of spin inside each domain being negligibly small on account of relatively high crystal anisotropy.

2.4.1.1 SATURATION MAGNETIZATION:

The saturation magnetization measurements of all the samples were carried out at room temperature using Pulse Field Magnetic Hysteresis Loop Tracer, supplied by Magneta India Model PFMHT-1.

In this instrument a high magnetic field is generated in a solenoid by passing a pulse current of Sinusoidal shape. A sample is placed in the pickup coil which, in turn, is kept in solenoid to detect field and magnetization signal. The signals produced are then processed by an electronic system. These transitory signals are digitized by a micro-controller and then sent to a computer for plotting a hysteresis loop observed on the monitor with calculated values of hysteresis parameters. These can be printed or stored as files. The system is useful for samples in powder or pellet form [13].
The system consists of pulsed power supply with input of 230 volts AC, generating magnetic field of 5,000 Oersteds. The output gives a pulse current in Sinusoidal Wave form in 20 ms period. Solenoid and pick-up coil assembly detect the field and magnetization signal. Signal processor is used to process signals produced in the pickup coil by integrating, amplifying and phase correcting circuits to produce signals representing magnetization of the sample and the applied magnetic field. The data acquisition system (DAQ) consists of a micro-controller with a fast digitizing and high resolution circuit. The digitized data is sent to the PC through a RS-232 port. The special software is designed to plot the hysteresis loop and display the hysteresis parameters.

2.4.1.2. A. C. SUSCEPTIBILITY:

The Curie temperature of all the Mn-Zn ferrite samples was determined. These samples were subsequently sintered at different predetermined higher temperatures and experiment was repeated for each of these temperatures. The measurements were done by using Dual Channel Data Acquisition System supplied by the Magneta India Model pfm-2.

This system consists of a power supply to run the furnace. It is a regulated digital power supply whose voltage and current are varied automatically by the PID temperature controller output which can be programmed for a set temperature and predetermined heating rate. The
instrument also has Helmholtz coil, two pick-up coils, furnace, sample holder, temperature measuring device, control unit, data acquisition system, and a PC with related software in the instrument to execute the run cycle. The information from two channels (X-T) is automatically acquired at periodic intervals and the data is sent to the PC through a RS – 232 link and thus magnetization ($M_s$) versus temperature ($T$) graph can be obtained [14].

2.4.1.3. MAGNETIC PERMEABILITY:

Magnetic permeability measurements were carried out on the torroids which had a winding of 100 turns of super enameled doubly insulated copper wire of 33 gauge. For this purpose, each powdered sample synthesized by mechano-chemical method was pressed into torroids with inner and outer diameter of 1 cm and 2 cm respectively with a thickness ranging between 3 mm – 4 mm. The torroids were sintered at $1000^\circ C / 1100^\circ C / 1200^\circ C / 1300^\circ C$ in nitrogen atmosphere for 4 hours with a heating and cooling rate of $5^\circ C \, \text{min}^{-1}$. The initial permeability and loss factor as a function of frequency and temperature were measured by recording the inductance values and dissipation factor starting from room temperature to $500^\circ C$ and with frequency variation from 20 Hz to 1 MHz using LCRQ meter of Wayne Kerr Model 6400.

The LCRQ meter is a micro processor based instrument with a suitable software designed to plot the graph of various functions under
study for a given frequencies and temperatures. It is connected to a furnace, which can measure the different functions at various frequencies for a temperature up to 500°C. It can measure major functions [15], such as Impedance Z, Capacitance C, Inductance L, AC Resistance R, Susceptance B, Admittance Y, and minor functions such as Phase Angle A, Dissipation Factor D, Quality Factor Q, Conductance G, Reactance X. Any two functions, one major and one minor, (C, D, L, Q, R, G, B, and X) in combination—both as series or both as parallel—can be measured at a given time for various frequencies from 20 Hz to 10 MHz at room temperature and for various frequencies at varied temperatures, up to 500°C.

2.4.2. ELECTRICAL PROPERTIES:

Ferrites are semiconductors in nature with resistivity ranging from $10^{-3}$ to $10^{11}$ ohm cm. at room temperature. The resistivity depends on the preparative conditions, especially the temperature at which a desired ferrite is obtained, the atmosphere in which it is prepared and the presence of impurity. The conduction mechanism in ferrites has been attributed to exchange of electrons between Fe$^{2+}$ and Me$^{3+}$ ions. The presence of Fe$^{2+}$ results in n-type behavior and of Me$^{3+}$ in p-type behavior. The conductivity arises due to the mobility of the extra electron (from Fe$^{2+}$) or the positive hole (Me$^{3+}$) through the crystal lattice. The conductivity also depends on (a) the porosity, (b) the grain size, and (c) the chemical inhomogeneity caused during the preparation.
Thermo electric power measurement also helps in understanding the mechanism of transport of charges in the ferrite and to determine whether it shows n-type or p-type semiconductor behaviour.

Ferrites have high dielectric constants at low frequencies which decrease to low values at high frequencies. They are sensitive and depend on the method of preparation, sintering temperature as well as sintering atmosphere.

2.4.2.1. RESISTIVITY:

The resistivity of all the Mn-Zn ferrite samples was determined. These samples were subsequently sintered at different predetermined higher temperatures and experiment was repeated for each of these temperatures. Two probe method was used to measure the resistivity using this instrument supplied by Pushpa Scientific Hyderabad.

The instrument consists of a muffle type furnace, which can give temperature upto $800^\circ$C. It has a stable D. C. source of 10 volts (D. C. voltmeter 0 to 10 volts range), a D. C. microammeter (0 to 500 $\mu$A ranges) and ionic conductivity cell with two brass electrodes. In a typical experiment, the Mn-Zn ferrite powder sample was pressed under 75 KN pressure applied for about 5 minutes to make pellets of 1.0 cm diameter and 2-3 mm thickness. The pellet was silver pasted on either side for establishing good ohmic contacts with the electrodes. It was then placed
between the two brass electrodes of the conductivity cell. At constant voltage, the current at various temperatures was recorded while cooling from 500°C to room temperature. The experiment was repeated for other samples [16].

2.4.2.2. THERMO ELECTRIC POWER (TEP):

The thermo electric power of the Mn-Zn ferrite samples was measured by using differential method. The thermo emf measurements of these samples were carried out from room temperature to 500°C by maintaining a temperature difference between the two ends, hot and cold junctions of electrodes, by 10°C.

The instrument supplied by Pushpa Scientific Hyderabad, consists of muffle type furnace, which can give temperature upto 800°C. D. C. Voltmeter, (0 to 500 mV range) and a TEP cell with two brass electrodes. Each electrode is connected to a temperature controller and a terminal of D.C. voltmeter. The upper electrode acts as a hot junction while lower electrode acts as a cold junction. A difference of 10°C is maintained between the two junctions [16].

The Mn-Zn ferrite powder sample was pressed to make pellet of the size as mentioned in the preceding section. The pellet was silver pasted on either side for establishing good ohmic contacts with the electrodes and placed between the two brass electrodes of the TEP cell. The pellet was
heated from room temperature to 500°C and simultaneously voltage at different temperatures was recorded. The experiment was repeated for other samples.

2.4.2.3. DIELECTRIC CONSTANT:

With rapid developments in solid-state electronics, the study of the A. C. electrical properties of ferrites has acquired great importance. Ferrites show high dielectric constant and also dispersion of dielectric constant in the frequency range from 20Hz to 1GHz. When a dielectric material is subjected to an alternating electric field, the positive and negative charges within the material get displaced with respect to one another and the system acquires an electric dipole moment. The dipole moment per unit volume is called polarization. The dielectric property of ferrites depends on the method of preparation, sintering temperature, chemical composition and grain size. LCRQ meter of Wayne Kerr model 6400 was used to measure the dielectric properties of ferrite in the pellet form. The capacitance and dissipation factor at various frequencies as well as variation of capacitance and dissipation factor with frequencies and at different temperature was also measured [15].

The LCRQ meter is a micro processor based instrument with a suitable software designed to plot the graph of various functions under study for a given frequencies and temperatures. It is connected to a furnace, which can measure the different functions at various frequencies.
for a temperature upto $550^\circ\text{C}$. It can measure major functions such as Impedance $Z$, Capacitance $C$, Inductance $L$, AC Resistance $R$, Susceptance $B$, Admittance $Y$, and minor functions such as Phase Angle $A$, Dissipation Factor $D$, Quality Factor $Q$, Conductance $G$, and Reactance $X$. Any two functions, one major and one minor, ($C$, $D$, $L$, $Q$, $R$, $G$, $B$, and $X$) in combination- both as series or both as parallel- can be measured at a given time for various frequencies from 20 Hz to 10 MHz. at room temperature and for various frequencies at varied temperatures, upto $550^\circ\text{C}$. 
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