The systems planned for the present study were prepared by coprecipitation technique. Stiochiometric amount of each metal sulphate were dissolved in doubly distilled water. The molar ratio of ferrous sulphate to substituted metal sulphates was taken as 1:2. The metal sulphates were dissolved in a minimum amount of double distilled water to get a clear solution separately. The metal sulphate solutions were mixed with each other. In the above mixed solution, 20% NaOH solution was then slowly added to obtain metal hydroxide precipitate with a constant stirring by maintaining pH 9.0 to 9.5. The precipitate was digested on water bath at 80°C for 4 hours and then oxidized by adding calculated amount of 30% H₂O₂ drop wise with constant stirring. After completion of the reaction, resultant precipitate was filtered and washed with distilled water to remove excess alkali and sulfate ions. The precipitate was dried at 100°C and then sintered at 900°C for 8 hours to get the final product. The sintered samples were characterized by adopting various physico-chemical methods such as X-ray diffraction analysis(XRD), Infrared spectroscopy(IR), Scanning electron microscopy(SEM), Thermogravimetric-differencial thermal analysis(TG-DTA), electrical transport properties, magnetic behavior.

The present chapter gives a brief account of the theory and principle of various characterization techniques used for the current study.

2.1 X-ray diffraction Analysis:

Powder X-ray diffraction (XRD) is used for basic characterization of different materials. The study of crystal structure by X-ray diffraction was invented in the year 1912 by Bragg. This technique has emerged as powerful tool for determining the crystal structure [1-3], chemical analysis, stress measurements, phase equilibria, lattice parameter and particle size[4-9].

The XRD pattern is the finger print of a crystalline material, as this technique gives information about the structure, phase and purity of a material. X-ray diffraction has been the single most important technique for determining the structure of materials [1]. The X-rays are electromagnetic radiations and
wavelength of X-rays used in diffractions lies approximately in the short wavelength region. X-ray diffraction is one of the most useful tool for obtaining structural information of material.

When the diffraction pattern is recorded, it shows concentric peaks of constructive interference which occurs in the scattered rays to the various interplanar spacing in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure of the material. X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength X-rays in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. Since the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deeply into the materials and provide information about the bulk structure. X-rays are produced generally by either X-ray tubes or synchrotron radiation. In a X-ray tube, which is the primary X-ray source used in laboratory X-ray instruments.

X-rays are generated when a focused electron beam accelerated across a high voltage field bombards a stationary or rotating solid target. As electrons
collide with atoms in the target and slow down, a continuous spectrum of X-rays are emitted, which are termed Bremsstrahlung radiation. The high-energy electrons also eject the core electrons in atoms through the ionization process. When an electron from higher energy orbital fills the shell, a X-ray photon with energy characteristic of the target material is emitted. Common targets used in X-ray tubes include Cu and Mo, which emit 8 keV and 14 keV X-rays with corresponding wavelengths of 1.54 Å and 0.8 Å, respectively [10]. X-rays primarily interact with electrons in atoms. When X-ray photons collide with electrons, some photons from the incident beam are deflected away from the direction where they originally travel. If the wavelength of these scattered X-rays does not change, the process is called elastic scattering in that only momentum has been transferred in the scattering process. These are the X-rays that are measured in diffraction experiments, as the scattered X-rays carry information about the electron distribution in materials. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material. When certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. When X-ray radiation strikes a powder sample, the layers of crystals of the sample act like weak mirrors that “reflect” the X-ray beams. The angle of “reflectance” equals to the angle of incidence for each row of atoms (Fig. 2.1.). In 1912, W. L. Bragg recognized the following relationship among several factor:

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

where \( n \) is the order of diffraction, \( \lambda \) represents the wavelength, \( d \) is the interplanar spacing and \( \theta \) is the scattering angle. The distance between similar atomic planes in a crystal is called the d spacing and measured in angstroms. The angle of diffraction is called as the theta angle and measured in degrees.
2.2. Infra-red Spectroscopy

The Electromagnetic radiation having wavelength in the range of 1micron to 1mm is termed as infrared (IR) radiations. It has a wavelength little larger than that of the visible light (400 – 800 nm). Studies of relations between structure and the electromagnetic response of ferromagnetic semiconductors are useful in understanding their properties. The infrared radiations are associated with the changes in the vibrations of molecules, and the distinction between them is a simple matter of instrumentation. In particular the vibrations in electronic and magnetic dipole spectra can give information about the position and valence of the ions in the crystal lattice. In mixed–metal oxides infrared spectrum are used to detect the completion of the solid state reaction, to study metal ion distribution, deformation of the spinel structure and to calculate force constant of A and B sites etc.

In recent years, the use of IR spectroscopy in the diffuse reflectance mode has grown strongly since this technique does not need particular efforts in the sample preparation (the powder is simply deposited on a sample holder). Infrared spectroscopy is the method of choice of qualitative analysis of organic material and it has wide application to inorganic substances as well. The
infrared spectra of a material are scanned in the range of 400-1000 cm$^{-1}$ are known as fingerprint region. It gives the unique property of that material and of its physical state. The spectrum is unique because it reflects the vibration between atoms within the molecule, and even slight changes in geometry or bond strength between atoms cause noticeable shift in the infrared absorption pattern.

When a molecule interacts with the radiation of the proper frequency, it absorbs energy and molecule is set into vibration. By measuring the transmitted energy as a function of radiation frequency, we can determine which frequency has been absorbed by the sample. The resulting plot of energy versus frequency is the infrared spectrum of the sample. Niasari [11], White and De Angelis [12] Santi Maensiri [13] assigned the high frequency band at about 650 cm$^{-1}$ ($\nu_1$) to symmetrical stretching vibrations of tetrahedral groups and lower frequency band at about 400 cm$^{-1}$ ($\nu_2$) due to vibrations of the octahedral M-O groups. Tarate and Preudhomme [14] have observed that in normal ferrites, both the absorption bands depend on the nature of octahedral cations and do not significantly depend upon the nature of tetrahedral ions. The difference in the band positions is due to the difference in the Fe$^{3+}$– O distances for octahedral and tetrahedral complexes.

### 2.3 Scanning electron microscopy

The scanning electron microscopy (SEM) is first developed by Van Avdenne [15] and used to analyze microstructure of ferrites. The primary use of SEM is to study the surface topography and morphology of solids. Any conducting solid material may be studied by this technique. Scanning electron microscope, an instrument that is used to observe the morphology of the sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope. Basically, SEM is used for topographical and compositional observations of surfaces, elemental analysis of specimen, internal structure, internal characteristics, crystalline structure and magnetic domain observations.
The SEM has its own importance in the determinations of material properties based on porosity, grain size and imperfections. The grain boundary acts as a secondary source of resistance. Since porosity decreases with the grain growth insulating property decreases. For the better performance parameters and properties, uniform microstructure is an essential condition. It means all the grains should be of same size and minimum porosity. Microstructural aspects of ferrites have always some special interest, such as to attain proper saturation, to minimize anisotropy, to minimize magnetostriction and to avoid foreign ions that can strain the lattice [16]. There are several conditions mentioned to get proper microstructure for better properties, some of them are synthetical method, variation of sintering conditions, additives etc [17]. Sample thickness and sample preparation is not problem in reflection instruments.

In SEM analysis electron interaction with elements has been extensively used for the characterization of material. Scattering the electron from the electron of the atom results into secondary and backscattered electrons. These scattered electrons give information about the microstructure of the sample in the form of image. These images are classified as

Secondary electron image
Backscattered electron image

*Secondary electron image:* This is most generally used to study surface topography. In this case, detector is sensitive to electrons that emerge from the specimen with energy less than 50 eV. Usually the scintillator is used as a detector which is held at a positive potential of several kV and the secondary electrons are accelerated to give visible light which is then detected by photomultiplier [18]. In SEM, since electrons being charged particles require vacuum environment to avoid change in their density, an electron beam is directed towards the sample in a vacuum of $10^{-4}$ to $10^{-10}$ Torr using electromagnets. The results and depth of field of the image are determined by beam current and the spot size. The spot size and beam current are adjusted by objective and condenser lense. The electron emitted by sample surface as backscattered and secondary electron are detected by the detector. The
secondary electron produced due to interaction of beam electrons and weakly bound electron in the conduction band of the sample are mostly used for investigation of surfaced morphology. The electron beam may be amplified and utilized to control the brightness of the spots. The sample preparation is relatively easy. The sample used for scanning should be electrically conductive to avoid charge build up caused by impinging electrons and resulting in jumping of beam. Non conducting sample can be scanned by coating conducting layer of Pt-Au alloys.

2.4 Thermal Measurements

2.4.1 Thermo Gravimetric Analysis

Thermogravimetry analysis (TGA) provides quantitative measurements of any change in weight associated with a transition [19]. For TGA, the sample is continuously weighed as it is heated to elevated temperatures. Crucible or shallow dish is used to place the sample for analysis and the automatic null balance to record the loss in weight of the sample. Inside the furnace the analysis samples are mounted in quartz or Pyrex container. By applying the constant heating rate the temperature is monitored by thermocouple and the change in weight loss is plotted. Generally heating rate applied is 5 – 10°C / min. The major components of the balance are shown in Fig. 2.3.

The resulting weight loss verses temperature curve provides information concerning the thermal stability and composition of the residue, if any. In
general, the TGA curve is plotted with the mass change expressed as a percentage against temperature. The thermal event is characteristic of two temperatures $T_i$ and $T_f$ which are reflected to as the procedural decomposition temperature and the final temperature respectively. Simply, $T_i$ stands for the lowest temperature at which the onset of a mass change can be detected under the given experimental conditions. Similarly $T_f$ represents the lowest temperature by which the thermal process responsible for mass change is completed. In a thermogram signal, the characteristic temperature, $T_i$ and $T_f$ depends on the instrumental and sample parameters like furnace heating rate, recording speed, ambient atmosphere, amount of the sample, particle size etc. These effects have been discussed at length in several books [20]. The major applications of this technique include materials characterization through its characteristic decomposition pattern, study of degradation mechanism and kinetics, prediction of lifetime (stability) at desirable time and temperature for a particular environment e.g., screening of additives (stabilizers, flame retardants and plasticizers, etc.).

2.4.2 Differential Thermal Analysis

The versatile differential thermal analysis (DTA) method was introduced by Lechatelier and modified by Robert Astin. Since differential thermocouples are used, the technique is named as differential analysis. DTA is a technique in which the temperature difference ($\Delta T$) between the sample and a thermally inert reference material are continuously recorded as a function of furnace temperature ($T_f$), or time (t), sample temperature ($T_s$) and reference temperature ($T_r$). In DTA, heat effect is associated with chemical and physical changes of a substance are recorded when it is heated at linear rate. Generally sharp endothermic peaks indicate changes in crystallinity or fusion process whereas broad endotherms signify dehydration reactions. In most of the cases, physical changes give rise to endothermic curves while chemical reactions result in exothermic peaks. Thus the endo and exothermal peaks appearing on the thermogram give information regarding the enthalpic changes [21].
Chapter II : Theoretical Background

The nature of the DTA curve and the magnitude of the peak depend on a large number of instrumental factors and also on sample characteristics. The instrumental factors that influence the DTA signal are the geometry and material of the sample holder, nature of the thermocouple and its location, the heating rate and the atmosphere around the sample. The sample characteristics like the particle size, amount of sample used, its heat capacity and thermal conductivity and packing density also play an important role in affecting the DTA curve. The extent to which these parameters influence the shape of the DTA curve can be found in several references [22-28]. Delineation of phase boundary using DTA is done by measuring evolution or absorption of heat accompanying phase changes, when sample is heated and cooled at constant rate. The phase changes correspond to the melting and freezing of pure compounds or eutectics.

The schematic diagram of a typical DTA curve and differential thermal analyzer is shown in Figs.2.4 and 2.5 respectively.

**Fig 2.4 Schematic diagram of DTA curve.**

The DTA instrument requires calibration for both temperature and enthalpy. Several standard materials like pure materials and well characterized compounds have been recommended for these purposes. The melting point of
metals like In, Zn, Sn, Sb, Ag and Au and phase transitions in Li$_2$SO$_4$, BaCO$_3$, etc. can be used for temperature calibration. Enthalpy calibration can be done using the heats of solid–solid transitions or fusion of the above materials or organic compounds of high purity.

2.5 Energy Dispersive X-ray Spectroscopy:

It is an analytical technique used for the elemental analysis or chemical characterization of a sample. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. The technique utilizes X-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analyzed volume. Features or phases as small as about 1 µm can be analyzed using Energy Dispersive X-ray Spectroscopy (EDAX) [14]. When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms comprising the samples surface. A resulting electron vacancy is filled by an electron from a higher shell and an X-ray is emitted to balance the energy difference between the two electrons.

In EDAX, X-ray detector measures the number of emitted X-rays versus their energy. The energy of the X-ray is characteristic of the element from which the X-ray was emitted. A spectrum of the energy versus relative counts
of the detected X-rays is obtained and evaluated for qualitative and quantitative
determinations of the elements present in the sampled volume. In this thesis we
have used EDAX measurements in order to determine the chemical
composition of various nanoparticles synthesized using chemical method.

Accuracy of EDAX spectrum can be affected by many variants. EDAX
detectors cannot detect presence of elements with atomic number less than 5,
meaning that EDAX cannot detect H, He, Li, or Be. Differing the over-voltage
of the EDAX will result in different peak sizes - Raising over-voltage on the
SEM will shift the spectrum to the larger energies making higher-energy peaks
larger while making lower energy peaks smaller. Also many elements will have
overlapping peaks (ex. Ti K$\beta$ and V K$\alpha$, Mn K$\beta$ and Fe K$\alpha$.). The accuracy of
the spectrum can also be affected by the nature of the sample.

2.6 Transport Properties

The study of semiconductor properties has stimulated intensive research
efforts in its utilization in radios, solar batteries etc. The localized and
collective electron models have played a vital role in explaining the various
electrical and magnetic phenomenon in solids.

When the overlap of orbitals is small, the electrons will necessarily be
localized at the ionic sites and will experience only a minor perturbation of
their energy due to the surrounding ionic fields, which gives rise to the crystal
field splitting of the degenerate orbitals. The various parameters such as the
charge on the cations, the transition series to which the cations belong, the
distance of the cations from the neighboring anions and the extent of covalent
character in the chemical bond influence the energy difference between the
resultant sub-orbitals.

In the localized atomic orbitals the arrangement of the electrons is
governed by the Hund’s rule and the Pauli’s exclusion principle, the electrons
have a net non-zero magnetic moment with a value determined by the orbital
moment which is either totally or partially quenched and the spin moment
alone contributes to the atomic moment. These atomic moments may interact
with those of the neighboring atoms/ions and give rise to a spontaneous magnetic ordering in such materials.

The direct exchange mechanism proposed by Heisenberg in which only the spins of the nearest neighbors interact with each other and the interaction energy is given by

$$U_e = -2J (\vec{S}_i \cdot \vec{S}_j) \quad \text{---------- 2.10}$$

Here $\vec{S}_i$ and $\vec{S}_j$ are the spins on the atoms/ions i and j and J is the exchange integral. The value of J depends upon the overlap of the atomic orbitals under consideration. If J is positive, the parallel spin state is more stable, whereas, if J is negative, the anti parallel spin state is more stable. However, the interactions between the more distant spin pairs are neglected. In the case of compounds containing cations with localized magnetic moments, the exchange interactions are possible through the empty orbitals of the intervening anions and the strength of these interactions depends upon the nature of the bond and angle between the cations and anions.

In the collective electron model, it is assumed that in a solid, the outer electrons of the constituent atoms move throughout the crystals as if they are free and the interelectronic correlations are neglected. The positive ions in the crystals give rise to a periodic potential, the effect of which can be treated as a minor perturbation. As a result of this perturbation the electron wave functions take the form, introduced by the potential and has the same periodicity as that of the lattice.

$$\Psi_{k} = e^{ik\cdot\vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{----------- 2.11}$$

Where

$e^{ik\cdot\vec{r}}$ is the free electron wave function and $u_{\vec{k}}(\vec{r})$ is the periodic term

The Schrödinger wave function equation shows that there are forbidden energy gaps in the energy spectrum of the otherwise free electrons of the energies corresponding to the propagation vectors (k) lying on the Brillouin zone
boundaries. The width of these forbidden energy gaps depends upon the extent to which the electron orbitals of the neighboring atoms overlap.

The physical interpretation of the origin of the forbidden energy gap can be obtained in terms of standing waves formed by the wave functions for the values of the propagation vector \( k \) corresponding to Brillion zone boundaries. Here, two sets of standing wave patterns are formed, one corresponding to the electron charge concentrated between two ionic sites and the other corresponding to the electronic charge concentrated at the ionic sites. The difference in the energies of these two states manifests itself as the forbidden gap.

The localized electron model is applicable in case of the f electrons, which have an orbital spread smaller compared to the interatomic distances. The collective electron model gives an adequate picture of the outer s and p electrons which have a large orbital spread as compared to the interatomic distances. However, the d electron orbital spreads are of the order of the interatomic distances. Thus both the localized and collective electron approaches are required for the proper understanding of the d electron behavior.

**Table 2.1 Criteria for localized and collective behavior of the electrons in a solid**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Criterion</th>
<th>Localized</th>
<th>Collective</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Theory</td>
<td>Crystal field</td>
<td>Band</td>
</tr>
<tr>
<td>2</td>
<td>Charge Transport</td>
<td>Hopping</td>
<td>Band conduction</td>
</tr>
<tr>
<td>3</td>
<td>Seebeck coefficient</td>
<td>( &gt; 100 \mu \text{v/k} )</td>
<td>( &lt; 20 \mu \text{v/k} )</td>
</tr>
<tr>
<td>4</td>
<td>Mobility</td>
<td>( 0.1 \text{ cm}^2 / \text{v-sec} )</td>
<td>( &gt; 1 \text{ cm}^2 \text{v/sec} )</td>
</tr>
<tr>
<td>5</td>
<td>Fermi surface</td>
<td>Does not exist</td>
<td>Exists</td>
</tr>
<tr>
<td>6</td>
<td>Super conductivity</td>
<td>Not possible</td>
<td>Possible</td>
</tr>
<tr>
<td>7</td>
<td>Magnetic Susceptibility</td>
<td>( C = W \text{law} ) ( \mu_{\text{eff}} = \text{Spin only values} )</td>
<td>Pauli paramagnetic</td>
</tr>
<tr>
<td>8</td>
<td>Magnetic Ordering</td>
<td>Spontaneous long range ordering below ( T_c/T_n )</td>
<td>No ordering</td>
</tr>
</tbody>
</table>
2.7 Electrical Conductivity

The mixed-metal oxides possess metallic, semiconducting and insulating behavior, however most of the mixed metal oxides under investigation are semiconductors. In ferrites, the cations are surrounded by close-packed oxygen anions and as first approximation, can well be treated as isolated from each other. The amount of charge carriers through a unit block of a material under the influence of unit electron field per unit volume is known as the electrical conductivity of solid and is dependent upon the concentration and mobility of charge carrier [29-30].

The electrical conductivity, is given by the relation

$$\sigma = n \cdot e \cdot \mu$$  \hspace{1cm} 2.4

where, $n$ = number of charge carriers per unit volume,
$e$ = electrical charge of each charge carrier and
$\mu$ = mobility of the charge carriers.

When both electrons and holes contribute to the electrical conductivity, then,

$$\sigma = n_e \cdot e \mu_e + n_h \cdot e \mu_h$$ \hspace{1cm} 2.5

where the subscript $e$ refers to the electron and $h$ refers to the hole. The dependence of the electrical conductivity on temperature is determined from the values of $n$ and $\mu$

The band type description of materials can be classified into two categories.

a) In case of partially filled bands, since the electrons are free to move in the crystal, the value of $n$ is very large ($10^{23}$ per cc) compared to its possible variations due to the addition of temperature activated electrons. Thus $n$ can be assumed to remain constant with temperature. The mobility of charge carriers, however, very with temperatures because of the phonon scattering of the electrons and it is given by

$$\mu (T) \propto 1/T$$

Thus

$$\sigma = n \cdot e \cdot \mu = A/T$$ \hspace{1cm} 2.6

i.e. $\rho = CT$
where $\rho$ is the electrical resistivity, $A$ and $C$ are the constants that depend upon the nature of the bands in the solids and Debye temperature. Thus the resistivity of a material having partially filled bands varies linearly with temperature. At absolute zero in the absence of any impurity scattering the resistivity of these materials is very small.

b) When some bands are completely filled and other are completely empty, the material acts as insulator at absolute zero temp. However at finite temperatures, some of the electrons are promoted to the conduction band due to thermal activation. This process creates some holes in the otherwise filled valence band, thus enabling both the electrons and holes to contribute to the charge transport. In this case the number of electrons in the conduction band is given by

$$n(T) = n_o e^{(-E_a/2kT)} \tag{2.7}$$

where as the mobility, an algebraic function of temperature is given by

$$\mu(T) = BT^{-3/2}$$

Thus,

$$\sigma = \sigma_o(T) e^{(-E_a/2kT)} \tag{2.8}$$

Where, $\sigma_o(T)$ can be assumed to be constant because the exponential is a much faster varying function than the algebraic function.

Thus, in the case of band type semiconductors the conductivity is expected to increase exponentially with the increasing temperature.

The presence of impurities and non-stoichiometry result in the formation of shallow impurity levels in the forbidden energy gap which gives rise to the impurity type (extrinsic) semiconduction at low temperatures. In the case of localized electron model, the electron transfer from one ion to the neighboring ion leads to unstable final states of the two ions. These one are essentially insulators However, the presence of impurities, point defects and non-stoichiometry creates mixed valencies among the constituent atoms. Such materials conduct the electrical charge by a process known as ‘hopping’. The number of charge carriers in such materials is temperature variant, and depends upon the amount of the mixed valencies. However, the mobility is an exponential function of temperature as given by
\[ \mu (T) = e^{-\frac{E_a}{kT}} \quad \text{------} \quad 2.9 \]

Thus,

\[ \sigma = \sigma_o (T) e^{-\frac{E_a}{kT}} \quad \text{------} \quad 2.10 \]

It can be seen from equations 2.9 and 2.10 that both the band type and hopping type semiconductors exhibit identical temperature dependence. Thus, it is not possible to distinguish between the two models using the conductivity data alone. However, the study of the Seebeck coefficient allows for the distinction between the two types of charge transport.

2.8 Magnetic Properties

Magnetic properties of mixed-metal oxides are interpreted on the basis of magnetic parameters, such as saturation magnetization, magnetic moment, coercivity etc. The choice of mixed metal oxides for an application is based on its magnetic properties. Mixed-metal oxides possess large spontaneous magnetization due to their antiparallel alignment of spin magnetic moments having unequal magnitudes. The oxygen ions present between the metal ions in mixed-metal oxides drastically change all the properties of mixed-metal oxides to make them most versatile materials for device applications. The indirect exchange interaction between the magnetic moment of neighboring atom is responsible for the magnetization in mixed-metal oxides. The interaction is said to be positive when the moments are parallel and negative when the moments are antiparallel. The intrinsic magnetization can be attributed to the antiparallel arrangement of spins of sublattice, assuming inverse spinel type of distribution. Magnetic properties of spinel ferrite depends on particle size of the material [31]. Partical size depends upon various parameters such as preparation method, sintering temperature , etc[32].

Spinel represents a classical example of a crystal allowing a special type of magnetic order called ferrimagnetism. This property results from the antiferromagnetism coupling between magnetic moment of the ions on the tetrahedral and octahedral sublattice, which are crystallographically non
equivalent. Consequently, the net magnetization of the spinel oxides at a
temperature \((T)\) below Curie temperature \((T_c)\) is given by the relation,
\[
M(T) = MB(T) - MA(T)
\]
where \(MB(T)\) and \(MA(T)\) are the magnetization of octahedral and
tetrahedral sublattice.

The interaction arises from an indirect exchange mechanism in which
magnetic ions are coupled through electron transfer with intermediate anions.
This concept of indirect exchange has been put forth by Kramers [33] and then
developed by Anderson [34] in the form of super exchange interaction. The
idea of superexchange interaction is used to account for the magnetization in
normal and inverse spinel mixed-metal oxides.

**Magnetization process**

The magnetization is a powerful tool to study the domain wall motion,
anisotropy, magnetoelastic coupling, magnetic hardness or softness of material,
magnetic ordering etc. Ferrites exhibit almost all the properties of
ferromagnetic materials.

A demagnetized ferromagnetic material exhibits a state of a zero
magnetization. When, sufficiently large magnetic field is applied to a
ferro/ferrimagnetic material, the magnetization changes from zero to saturation
value. This was explained first by Weiss [35] on the basis of domain theory.
These domains are arranged such that the magnetization is zero. Their
existence is a consequence process which minimizes the free energy of the
system. The magnetization is homogeneous inside the domain and its direction
vary with the domain wall.

A ferro/ferrimagnetic substance becomes magnetized due to domain
boundary displacement and domain rotation. Both processes can be irreversible
resulting in hysteresis Loop. Domain rotations are mostly associated with
intrinsic properties viz. the chemical composition of the material. Domain
boundary displacement depends not only on the intrinsic properties but also on
factors concerned with sintering process, such as porosity, size, shape of ions
and shape of crystals. The rotation of domains have been observed by
Berkhausen [36] and has shown that, the discontinuous variation of magnetization at low field takes place, where the field is continuously increasing. These are known as Berkhausen jumps. Magnetization by domain rotation requires large energy.

**Magnetic hysteresis**

Magnetic hysteresis of ferrites give useful information about the magnetic parameter like saturation magnetization, coercive force and remanance ratio[37-38]. When ferromagnetic substance is subjected to an external magnetic field, its magnetization increases as a function of applied field and reaches a saturation value, at a certain critical field at which all the domains rotate in the direction of magnetic field. On decreasing the external field to zero, magnetization lags behind the applied field. Such a behaviour is called the phenomenon of hysteresis. The residual magnetization at zero external fields is called as retentivity (Mr), when the direction of the field is reversed; the retentivity goes on decreasing and becomes zero at a certain value of magnetic field called coercivity (Hc) or coercive field. The variation of magnetization over the complete cycle of external field is called hysteresis loop (Fig.2.3). The loss of energy per unit volume per cycle due to hysteresis is equal to the area of the loop.

The slope of the tangent to the B-H curve at the origin gives the magnitude of initial permeability. The maximum permeability plays an important role in magnetic recording. The distortion factor, the corecivity and retentivity are the important parameters in selecting the materials as permanent magnets.

The shape of the hysteresis loop provides the valuable information about the domain state of grains inside the samples. Bean [39] on the basis of hysteresis phenomenon has classified the magnetic particle as single domain (SD), multidomain (MD) and supermagnetic (SP). Depending on the extent of the degree of orientation, the materials are classified as single domain or multidomain. According to domain theory, domains which are oriented favourably with respect to applied magnetic field may grow at the greater rate
than other domains which are unfavorably oriented. The Bloch wall contains very large volume of small particles with increasing the energy. Such particles, for which sub divisions into domains is energetically unfavorable are called as single domain particles.

The magnetization vector within each domain may rotate in the direction of the field when applied field is large. This process is known as magnetization by domain rotation. There the spins have to be turned from any easy direction to a hard one and work must be done against the anisotropic forces. Magnetisation by rotation requires large energy. Domain rotations are mostly associated with intrinsic properties of the material (chemical composition).

![Fig 2.3 Hysteresis loop of a ferromagnetic material](Image)
2.9 Applicative studies
2.9.1 Gas Sensors

Simply the semiconducting gas sensor can be described as the variation of conductivity of oxide materials according to gas concentration change. This is caused by adsorption/desorption due to gas concentration changes. This reaction changes the electric potential on the sensor and results in the increase/decrease in the resistance under the presence of oxidizing/reducing gases [40].

The change in resistance of gas sensor arises from the change in the electron concentration near to surface by reaction with gases or vapours. A reducing molecule (e.g. CO, H₂) or atom adsorbed on the sensor surface acts as a surface donor injecting electrons into the semiconductor. The adsorption can be associated with decomposition or dissociation of the gas or vapours. The opposite phenomenon occurs during exposure to oxidizing gas like NO. In the case of n-type semiconductor, the resistance of pellet or film decreases when the sensor is in contact with reducing gas; the resistance increases when the sensor is in contact with oxidizing gas in the case of p-type semiconducting sensors.

The mechanism of gas sensing on metal oxide-based gas sensors is much more difficult. The normal operation temperature of metal oxide gas sensors is in general within the range between 200 and 500°C. It comprises of the interaction with atmospheric oxygen which leads to its ionosorption as molecular (O₂) and atomic (O⁻, O²⁻) species [41,42].

\[
\begin{align*}
\text{O}_2(\text{gas}) & \leftrightarrow \text{O}_2(\text{ads}) \quad \text{---------- 2.11} \\
\text{O}_2(\text{ads}) + e^- & \leftrightarrow \text{O}_2^-(\text{ads}) \quad \text{---------- 2.12} \\
\text{O}_2(\text{ads}) + e^- & \leftrightarrow 2\text{O}^- \quad (\text{ads}) \quad \text{---------- 2.13}
\end{align*}
\]
When a reducing gas like CO comes into contact with the surface, the following reactions may take place:

\[
\text{CO}_{\text{gas}} \rightarrow \text{CO}_{\text{ads}} \quad \quad \quad \quad 2.14
\]

\[
\text{CO}_{\text{ads}} + \text{O}^\text{ads} \rightarrow \text{CO}_2 \text{gas} + e^- \quad \quad \quad \quad 2.15
\]

These consume ionosorbed oxygen and in turn change the electrical conductance of metal oxide. The overall effect is a change of the density of ionosorbed oxygen that is detected as an increase of sensor conductance. Direct adsorption is also proposed for the gaseous species like strongly electronegative \(\text{NO}_2\) whose effect is to decrease sensor conductance:

\[
\text{NO}_2 \text{gas} \rightarrow \text{NO}_2 \text{ads} \quad \quad \quad \quad 2.16
\]

\[
e^- + \text{NO}_2 \text{ads} \rightarrow \text{NO}_2^- \text{ads} \quad \quad \quad \quad 2.17
\]

The occupation of surface states, which are much deeper in the band-gap than oxygen’s, increases the surface potential and reduces the overall sensor conductance.

The gas sensing mechanism is based on conductance of the ferrites. The oxygen adsorbed on the surface of the material influences conductance of the magnesium ferrite. The amount of oxygen adsorbed on the surface of the material depends on the particle size, specific area and operating temperature of the sensor [43].

The interaction between the sensing material and gas to be detected determines the gas response. The interaction includes physical and chemical adsorption. The chemical interaction typically involves exchange between adsorbed gas molecule and metal oxide semiconductor, resulting change in the band bonding near interfaces and hence the electric property of the sensing element [44].

### 2.9.2 Photocatalytic activity

Photocatalysts are important materials that provide a relatively simple way for the conversion of light energy for use in oxidation and reduction processes. Photocatalysis is applied in many areas including the elimination of contaminants from water and air, odor control, bacterial inactivation, water
splitting to produce H$_2$, the inactivation of cancer cells, degradation of organic compounds and many others [45-47]. Generally, photocatalytic degradation of organic compounds includes various processes. An electron is excited from the valence band to the conduction band (CB) of metal oxides by absorption of light with energy equal to or greater than the band gap of the semiconductor. The separated photo induced electrons and holes transfer to the semiconductor surface efficiently. At the surface, electrons react with acceptors (usually O$_2$ dissolved in the solution) to produce oxidant species, for example hydroxyl radicals. Meanwhile, holes react with donors (H$_2$O, OH$^-$) to produce oxidant species. Oxidant species produced from electrons and holes have strong oxidizing abilities and can directly oxidize organic compounds into CO$_2$ and H$_2$O [47-51].

In general, the conduction bands of stable oxide semiconductor photocatalysts are composed of empty orbitals (LUMOs) of metal cations with d$^0$ and d$^{10}$ configurations. Although the valence band level depends on crystal structure and bond character between metal and oxygen, the level of the valence band consisting of Oxygen 2p orbitals is usually ca. 3.0 eV. Accordingly, a new valence band or an electron donor level (DL) must be formed with orbitals of elements other than Oxygen 2p to make the band gap (BG) or the energy gap (EG) narrower because the conduction band level should not be lowered.
References


Chapter II : Theoretical Background


