The ultimate goal of research in heterogeneous catalysis is to correlate the structure and composition of a catalyst with its performance. Catalyst performance is judged in terms of its activity, product selectivity and life. Catalyst characterization is one of the crucial aspects of catalyst design since it gives information about crystallinity, surface structure, nature of active sites, particle size and morphology, acidity, and other characteristic features. The surface properties are also helpful to correlate the gas sensing performance of the catalysts.

The planned systems were prepared by sol-gel technique. Stochiometric amount of each metal nitrate was dissolved in doubly distilled water. The molar ratio of metal nitrate to citric acid was taken as 1:2. The metal nitrate was dissolved in a minimum amount of double distilled water to get a clear solution. The metal nitrate solution was mixed with citric acid solution to form metal-citrate complex. The above mixed citrate-metal complex solutions were then slowly added to iron (III) citrate solution with a constant stirring. The mixed solution was kept heated to 100°C on a hot plate with continuous stirring. During evaporation, the solution became viscous and finally formed a very viscous gel. With further heating the viscous gel began frothing. After few minutes, the gel automatically ignited and burnt with glowing flints. The auto-ignition was completed within a minute, yielding the black-colored ash termed as a precursor. The as-prepared powders of the samples were sintered separately at 700°C for 8 hr. to get the final product. The sintered samples were characterized by adopting various physico-chemical methods such as X-ray diffraction analysis, infrared spectroscopy, SEM, TG-DTA, FT-IR, electrical transport properties, magnetic behavior, dielectric and complex impedance measurement.

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 (XRD):

Powder X-ray diffraction is used as for basic characterization of different materials. This technique has emerged as powerful tool for determining the crystal structure [1, 2] chemical analysis, stress measurements, phase equilibria and particle size. The XRD pattern is the fingerprint of a crystalline material [1, 4] as this technique gives information on 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].

When the diffraction pattern is recorded, it shows concentric peaks of constructive interference that 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. Because 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 deep 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 [5].
X-rays primarily interact with electrons in atoms. When x-ray photons collide with electrons, some photons from the incident beam will be 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 factors.

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

The above equation is called Bragg equation, where \( n \) denotes the order of diffraction, \( \lambda \) represents the wavelength, \( d \) is the interplanar spacing and \( \theta \) signifies 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.
Chapter II: Theoretical Background

Figure 2.1 Interference between x-ray beams scattering rows of atoms in a crystal.

Choice of target Material:

The choice of radiation (target) required in X-ray analysis depends upon several factors. From technological point of view, it should be good conductor of heat so that it can be easily cooled. It should have reasonably high melting point. From the crystallographers point of view, it should emit X-ray of convenient wavelength (0.5-2.0 Å), which limits the choice of the first and second row of transition metals.

The characteristic wavelength used should not be shorter than the K-absorption edge of the specimen otherwise fluorescent radiation produced will give rise to high level of background noise. The low value of characteristic wavelength will increase the total number of diffraction lines, while high value of wavelength will have reverse effect. The target materials usually employed in X-ray diffraction technique are as follows:
<table>
<thead>
<tr>
<th>Target</th>
<th>Filter</th>
<th>Filter thickness µm</th>
<th>Wavelength (Å°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo Kα</td>
<td>Zr</td>
<td>81</td>
<td>0.711</td>
</tr>
<tr>
<td>Cu Kα</td>
<td>Ni</td>
<td>15</td>
<td>1.542</td>
</tr>
<tr>
<td>Co Kα</td>
<td>Fe</td>
<td>12</td>
<td>1.790</td>
</tr>
<tr>
<td>Fe Kα</td>
<td>Mn</td>
<td>11</td>
<td>1.937</td>
</tr>
<tr>
<td>Cr Kα</td>
<td>V, V₂O₅</td>
<td>11</td>
<td>2.291</td>
</tr>
</tbody>
</table>

In each case appropriate filter is used to suppress the Kβ component of the radiation.

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared techniques have gained remarkable importance in the field of heterogeneous catalysis and in the field of surface chemistry and catalysis over metal oxides. A variety of IR techniques have been used in order to get information on the surface chemistry of different solids. With respect to the characterization of metal oxide catalysts two techniques largely predominate, namely, the transmission/absorption and the diffuse reflection techniques.

In recent years, the use of IR spectroscopy in the diffuse reflectance mode is grown strongly since this technique does not need particular efforts in the sample preparation (the powder is simply deposited on a sample holder), especially useful in the case of highly scattering samples employed in heterogeneous catalysis. The theory of diffuse reflectance spectra was developed by Kubelka and Munk [6] and extended by Kortun et al [7]. According to this theory,

\[ f(R_\alpha) = \frac{(1-R_\alpha)^2/2R_\alpha}{K/S} \]

where Ra is the diffuse reflectance from an ‘infinitely’ thick sample, K is the extinction coefficient and S is a scattering coefficient. It is known that structure plays an important role in the catalytic activity of many heterogeneous systems.
In many cases, the positions of the infrared bands are sensitive to the changes in the ratio of metal cations in the catalyst composition. Since in spinels, metal ions are distributed in two different environments, the spinel phase formation can be very well assigned by the appearance of two broad IR bands.

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 spectrum of a material is scanned in the range of 400-1000 cm\(^{-1}\) 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 plots of energy versus frequency are the infrared spectrum of the sample.

Waldron [8], White and De Angelis [9] assigned the high frequency band at 650 cm\(^{-1}\) (\(\nu_1\)) to symmetrical stretching vibrations of tetrahedral groups and lower frequency band at 400 cm\(^{-1}\) (\(\nu_2\)) due to vibrations of the octahedral M-O groups. Tarate and Preudhomme [10] 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 (SEM)

The primary use of SEM is to study the surface topography and morphology of solids. Any solid material may be studied by this technique. Scanning electron microscope (SEM) is 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 [11]. 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 determination of material properties based on porosity, grain size and imperfection. The dependence of properties of mixed-metal oxides on microstructure implies that the properties of their composites also depend on microstructure. The grain boundary acts as a secondary source of resistance. Since porosity decreases with the grain insulating property also decreases.

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

1. Secondary electron image
2. Backscattered electron image

1. *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 > 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 into it to give visible light which is then detected by photomultiplier [12].

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 electrons are detected by the detector. The secondary electrons produced due to interaction of beam electrons and weakly bound electrons 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. Nonconducting sample can be scanned by coating conducting layer of Pt-Au alloys.

2.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is focussed onto a specimen causing an enlarged version to appear on a fluorescent screen or a layer of photographic film, or to be detected by a CCD camera. TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Virtually, TEM is useful for determining size, shape and arrangement of the particles which make up the specimen. Transmission electron microscopy (TEM) is typically used for high resolution imaging of thin films of a solid sample for nanostructural and compositional analysis. The technique involves: (i) irradiation of a very thin sample by a high energy electron beam, which is diffracted by the lattices of crystalline or semicrystalline material and propagates along different directions, (ii) imaging and angular distribution analysis of the forward-scattered electrons (unlike SEM where back scattered electrons are detected), and (iii) energy analysis of the emitted X-rays. The topographic information obtained by TEM in the vicinity of atomic resolution can be utilized for structural characterization and identification of various phases of mesoporous materials, viz., hexagonal, cubic or lamellar [13]. TEM also provides real space image on the atomic distribution in the bulk and surface of a nanocrystal [14].

Transmission Electron Microscopy (TEM) operates on principles similar to that of the optical microscope [15, 16]. The sample illumination source in a TEM is a beam of electrons. This beam of electrons travels through a column under vacuum and is then focused into a very narrow beam with electromagnetic lenses. Some electrons will scatter and those that do not scatter
strike a fluorescent screen giving rise to a contrast image based on sample density. Since the limit of resolution is in the order of a few angstroms, it is a very useful and powerful tool for nanoparticle characterization. Low resolution TEM can generally provide information regarding the size and overall shape of the sample and is routinely used to elucidate such information.

Along with nanostructure of the material, it is highly useful for determination of the lattice planes and the detection of atomic-scale defects in areas of few nanometers in diameter with the help of selected area electron diffraction (SAED) technique [17, 18]. The $d$ spacing between lattice planes of crystalline materials can be calculated from a SAED pattern using the relationship

$$dr = \frac{\lambda L}{2}$$

where $L$ is the distance between the specimen and the photographic plate, $\lambda$ is known as the camera constant and $r$ is the radius of diffracted rings. It is easy to measure $r$ directly from the photographic plate, and $\lambda L$ can be established from the instrument by calibrating it with a standard material (usually Ag), and hence one can easily get $d$ values. Since each $d$ value corresponds to a specific lattice plane for a specific crystal structure, a minimum description of the crystal structure of a crystalline specimen can be obtained from a SAED pattern. In some cases SAED pattern is more helpful as compared to XRD, due to the detection limit of XRD instruments.

2.5 Thermal analysis:

Thermal analysis is used for the measurement of physical or chemical changes in the materials as a function of temperature, usually heating or cooling at a uniform rate. (i) Thermogravimetric analysis measures weight loss or gain during programmed heating of sample (ii) Differential thermal analysis measures temperature difference ($\Delta T$) between a sample and reference material during heating (iii) Differential scanning calorimetry (DSC), measures the differential heat flow between a sample and reference material during heating.
**Thermogravimetric Analysis (TG)**

Thermogravimetric analysis is a technique that permits the continuous monitoring of weight of a sample as a function of temperature when it is heated at a desired heating rate [19, 20]. 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 $5 - 10^\circ$C / min. The major components of the balance are shown in Fig. 2.2.

![Fig 2.2 Major components of the thermobalance](image)

The major applications of this technique include materials characterization through their characteristic decomposition patterns, study of degradation mechanisms 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.).
Differential Thermal Analysis

DTA can be used to detect the physical or chemical changes in a material that accompany by absorption or desorption of heat [19, 20]. DSC provides similar information but, unlike DTA, can quantify the thermal events. Many of the physical or chemical changes are associated with heat absorption (endothermic) or release of heat (exothermic).

DTA measures the differential temperature between an inert reference and the sample upon heating or cooling at a particular rate or under isothermal conditions. Applications of DTA and DSC include evaluation of phase transformations (glass transition, melting, solidification, etc.), decomposition, thermal and mechanical histories.

In DTA, changes in heat content as a function of the difference in temperature between the sample and an inert reference compound, is measured. The schematic diagram of a differential thermal analyzer and typical DTA curve are shown in Figs. 2.3 and 2.4 respectively. The curve is described by the characteristic temperatures. The initiation temperature (Ti) the peak temperature (Tp) and the termination temperature (Tf) are the three temperatures used to characterize the main features of the DTA curve. The initiation temperature represents the temperature where the DTA signal begins to deviate from a steady base line. The extrapolated onset temperature (Te) corresponding to the point of intersection of the base line with the tangent drawn to the rising part of the DTA curve at the point of maximum slope is often preferred to the initiation temperature. The peak temperature indicates either the end of the reaction or transformation or the temperature at which the rate of transformation is maximum and finally Tf denotes the temperature at which the signal returns to the base line. The temperature changes in the sample can be due to enthalpy changes caused by phase transitions, fusion decomposition reaction, oxidation or reduction reactions etc. 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 [21-27] Delineation of phase boundary using DTA is done by measuring evolution or absorption of heat accompanying phase changes, when the sample is heated or cooled at constant rate. The phase changes correspond to the melting and freezing of pure compounds or eutectics.

Fig 2.3 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.

2.6 Energy dispersive X-ray Spectroscopy (EDAX)

Elemental analysis and chemical composition of the material were estimated by EDAX. 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 EDAX [10]. When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms comprising the...
sample’s 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 biological methods.

2.7 Electrical conductivity:

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 carriers. The electrical conductivity is given by the relation

\[ \sigma = n \cdot e \cdot \mu \]  

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,

\[ \sigma = n_e \cdot e \cdot \mu_e + n_h \cdot e \cdot \mu_h \]  

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 \((10^{23} \text{ per cc})\) 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, vary with temperatures because of the phonon scattering of the electrons and it is given by

\[ \mu(T) \propto \frac{1}{T} \]

Thus \[ \sigma = n \cdot e \cdot \mu = \frac{A}{T} \] \[ \rho = C T \]

where \( \rho \) is the electrical resistivity and \( A \) 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

\[ n(T) = n_o e^{-\frac{E_a}{2kT}} \]

whereas the mobility, an algebraic function of temperature is given by

\[ \mu(T) = B T^{-3/2} \]

Thus, \[ \sigma = \sigma_o(T) e^{-\frac{E_a}{2kT}} \]

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
\[ \mu (T) = e^{-\frac{E_a}{kT}} \]  

Thus,
\[ \sigma = \sigma_0 (T) e^{-\frac{E_a}{kT}} \]

It can be seen from equations 2.8 and 2.9 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 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.

The localized electron model

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

$$\Delta E = - 2J \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$  \hspace{1cm} (2.10)

Here $\mathbf{S}_i$ and $\mathbf{S}_j$ 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 antiparallel 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.

**The collective Electron model**

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,

$$\Psi_{\mathbf{k}} = e^{i \mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$  \hspace{1cm} (2.11)

where, $e^{i \mathbf{k} \cdot \mathbf{r}}$ is the free electron wave function and $u_{\mathbf{k}}(\mathbf{r})$ is the periodic
term introduced by the potential and has the same periodicity as that of the lattice.

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 Brillion 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. The various criteria for the localized electron model and collective electron model are summarized in Table 2.1.
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 $\mu$V/k</td>
<td>&lt; 20 $\mu$V/k</td>
</tr>
<tr>
<td>4</td>
<td>Mobility</td>
<td>0.1 cm$^2$/v-sec</td>
<td>&gt; 1 cm$^2$/v/sec</td>
</tr>
<tr>
<td>5</td>
<td>Fermi surface</td>
<td>Dose 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 law</td>
<td>Pauli paramagnetic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\mu_{\text{eff}}$ = Spin only values</td>
<td></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>

**Thermoelectric effect:**

The thermoelectric effects include the Seebeck, the Peltier and the Thomson effects. Some of these phenomena have found wide applications in practice; therefore a look at them is not only of educational, but also practical interest. We have discussed the Seebeck effect in detail.

In 1821, Seebeck discovered that an electromotive force $V_T$ is established in a circuit consisting of two conductors 1 and 2 made of different materials, if the junctions of these conductors A and B, are kept at different temperature $T_1$ and $T_2$ (Fig 2.5 a). This emf is termed thermal emf. The emf difference depends upon the nature of the solids under consideration, the temperature difference between the two ends and the ambient temperature at which the solid is maintained. Experiments show that in a narrow temperature interval, it is proportional to the difference in the temperatures of the junctions A and B and is called differential or specific thermoelectric power.

$$V_T = \alpha (T_2 - T_1)$$

----------------------------- 2.12
The proportionality factor
\[ \alpha = \frac{dV_T}{dT} \]  

--- 2.13

The sign of \( \alpha \) depends upon the nature of the majority carriers; \( \alpha \) is positive for holes and negative for electrons.

There are three sources of the thermal emf

1) the directional current of the carriers in the conductors, due to the presence of a temperature gradient (the volumetric component \( V_v \)),

2) the change in the position of Fermi level (the junction component \( V_j \)) and

3) the drag of the electrons by the phonons (phonons drag effect).

Suppose a temperature difference \( (T_2 - T_1) \) is maintained at the terminals of an uniform conductor AB (Fig.2.5b), so that there is a temperature gradient \( dT/dX \) in the direction from B to A. the current carriers in the hot end have greater kinetic energy than the carriers at the cold end. Therefore, a current will flow in the conductor from the hot end to the cold end, this current will charge the conductor. In cases where the current is carried by electrons, the cold end will accumulate a negative charge and the hot end a positive charge, and a potential difference \( V_v \) will be established between them. This is the volumetric component of thermal emf. The differential thermoelectric power corresponding to this component is expressed as

\[ \alpha_v = \frac{dV_v}{dT} \]  

--- 2.14

As a rule, in n type conductor \( \alpha_v \) is directed from the hot end to the cold end.

The change in temperature causes a change in the position of the Fermi level. In n-type conductors the Fermi level sinks on the energy diagram as the temperature is raised (Fig.2.5c). By force of this, it should be higher on the cold end of the n-type conductor than on its hot end. The difference in the Fermi level positions is equivalent to a potential difference;

\[ dV_j = - \left( \frac{1}{q} \right) \left( \frac{\delta \mu}{\delta T} \right) dT \]  

--- 2.15
The above is the junction component of the thermal emf. The differential thermoelectric power corresponding to this component is

\[ \alpha_j = - \frac{1}{q} \frac{d\mu}{dT} \] \quad \text{2.16}

Then the resultant differential thermoelectric power will be,

\[ \alpha = \left( \frac{1}{q_n} \frac{dp}{dT} \right) - \left( \frac{1}{q} \frac{d\mu}{dT} \right) \] \quad \text{2.17}

In the case of band type semiconductors, it is observed that Seebeck coefficient is independent of temperature in the impurity region, whereas in the intrinsic regions it varies linearly with the inverse temperature. The activation energy of the charge carriers in the intrinsic conductivity region can be calculated from the seebeck coefficient data using the equation 2.18.

\[ E_a = \frac{1}{2.303k/e} \times s \] \quad \text{2.18}

where \( e \) is the electronic charge, \( k \) is the Boltzmann constant and \( s \) is the slope of \( \alpha - T \) curve.

In the case of localized model the seebeck coefficient is given as

\[ \alpha (T) = \frac{k}{e} \left[ \frac{\hbar}{k} - \frac{\ln(c / (1-c))}{k} \right] \] \quad \text{2.19}

where, \( \frac{\hbar}{k} \) is the effective lattice/spin entropy transported by the charge carriers, \( c \) is the velocity of the charge carriers and \( (1-c) \) is the density of unoccupied states.
Chapter II: Theoretical Background

2.9 Magnetic behavior

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,

\[
M(T) = M_B(T) - M_A(T)
\]

where \(M_B(T)\) and \(M_A(T)\) are the magnetization of octahedral and tetrahedral sublattice. Magnetic properties of mixed-metal oxides can be discussed 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.

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 [28] and then developed by Anderson [29] 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, magetoelastic coupling, magnetic hardness or softness of material, magnetic ordering etc. Ferrites exhibit almost all the properties of ferromagnetic materials, when the magnetization may vary from zero to saturation value. This behavior has been explained by Weiss [30] by introducing the idea of existence of domains.

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 connected with sintering process such as porosity, size, shape of ions and shape of crystals. The rotation of domains have been observed by Berkhausen [31] 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**

Studies on magnetic hysteresis of ferrites provide useful information of the magnetic parameters like saturation magnetization, coercive force and remanance ratio. 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 directions of magnetic field. Such a behavior is called of hysteresis. The variation of magnetization over the complete cycle of external field is called hysteresis loop. (Fig 2.6)

At a certain magnetic field, the material attains a saturation value and after reduction of magnetic field, certain magnetization is retained which is termed as residual or remanent magnetization. When direction of applied magnetic field is reversed, the remanent magnetization reduces and finally becomes zero at certain magnetic field called as coercive field. The hysteresis loop provides information about the work done in each cycle of magnetization, coercivity and saturation magnetization. The shape of loop provides the information about the domain state of grains inside the sample. Based on the hysteresis phenomenon, Bean [32] classified the magnetic particles into single domain, multi domain and super multi domain.
2.10 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. The change in resistance of oxidic 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 (O$_2^-$) and atomic (O$^-$, O$_2^-$) species [33, 34].

\[
\begin{align*}
O_2 \text{(gas)} & \leftrightarrow O_2 \text{(ads)} \quad \text{------ 2.20} \\
O_2 \text{(ads)} + e^- & \leftrightarrow O_2^- \text{(ads)} \quad \text{------ 2.21} \\
O_2 \text{(ads)} + e^- & \leftrightarrow 2O^- \text{(ads)} \quad \text{------ 2.22}
\end{align*}
\]

In case of hydrocarbon gas sensor the test gas reacts with O$^-$ (ads) to form RO, and electrons enter the conduction band of the sensing material, leading to an increase in the conductance. In summary, test gas reacts with adsorbed O$^-$ and decomposes into gases CO$_x$ and water vapors [35, 36] with release of electrons.

\[
\begin{align*}
R\text{(ads )} + O^- \text{(ads)} & \quad \leftrightarrow \quad RO + e^- \quad \text{------ 2.23} \\
C_nH_{2n+2} + O^- \text{(ads)} & \quad \rightarrow \quad H_2O + C_nH_{2n}O + e^- \quad \text{------ 2.24}
\end{align*}
\]

Ethanol sensing mechanism also works in same way. The oxygen is adsorbed on the surface of the sensor in air and adsorbed oxygen is transformed into chemisorbed oxygen at a definite temperature. The above part of mechanism is represented in equation 2.25–2.27. The chemisorption of ethanol vapors can be mechanized as [37, 38],

\[
\begin{align*}
C_2H_5OH & \quad \leftrightarrow \quad C_2H_5OH \text{(ads)} \quad \text{----- 2.25} \\
C_2H_5OH \text{(ads)} + O^- \text{(ads)} & \quad \rightarrow \quad C_2H_5O^- \text{(ads)} + H_2O \text{ (g)} \quad \text{----- 2.26} \\
C_2H_5O^- \text{(ads)} & \quad \rightarrow \quad C_2H_5O \text{ (g)} + e^- \quad \text{----- 2.27}
\end{align*}
\]

These reactions induce electrons into the zinc ferrite material leading to an increase in electron concentration and a decrease in resistance of zinc ferrite–based sensor. The desorption of gases into CO$_2$ and H$_2$O by reaction of adsorbed O$^-$ is notable in the reaction mechanism of ethanol.
Criteria for the choice of material

The following are the essential criteria for a material to be used as sensor:

- The material should be of high sensitivity in terms of the variation of resistance or capacitance on contact with a very small quantity of the gas or vapours.
- Some materials (e.g., Pt supported on SnO$_2$) are equally sensitive to main gases. This is not a desirable characteristic. Selectivity is an important criteria;
- The material should sense the gas over a large number of cycles for extended periods and the sensor should not undergo environmental degradation rapidly due to humidity, temperature and other factors.
- As far as possible, the sensor should not employ expensive materials such as a noble metal.
- The operating temperature should be as low as possible.
- It should not consume more power for continuous operation.
- The response time as well as recovery time should be as small as possible.

2.11 Catalysis

There is hardly any fact of life which has not been directly or indirectly touched by catalysis. Fertilizers, motor fuels, plastics, synthetic rubbers, synthetic fibers, pharmaceuticals, perfumes, pollution control, fuel cells, rocket propulsion, all use catalysis at some stage or other of manufacturing or operations.

The catalytic reactions can basically be classified into two groups as homogenous catalysis and heterogeneous catalysis. In homogenous Catalysis the catalyst and reactants are in same phase, but in heterogeneous catalysis the catalyst and reactants are in different phases. The efficiency of the process depends mainly on the contact surface as well as contact time. The reactants form a transition state in which the catalyst’s surface takes on active part. This
makes the knowledge of surface composition and energy sites on the surface, extremely important in understanding the phenomenon of heterogeneous catalysis, which can be explained with the help of two models as follows:

1. Band model:

   This model does not take into consideration the microscopic details of the surface atoms, and describes in terms of surface bands and surface states. Surface states are peculiar electronic energy levels at the surface. The model is generally used by surface physicist.

2. Localized model:

   This model describes the surface in terms of surface atoms or a group of surface atoms. According to this model, chemical nature of the surface and oxidation state and electronic configuration of the ions present on the surface is a very important factor to explain the catalytic reactions. This model is being extensively used in explaining the heterogeneous catalytic reactions in recent years, though in late fifties and early sixties, this was not so popular and the band model was extensively used by the chemists.

   Research workers have been trying to correlate the physical properties of the catalysts with their catalytic activity and selectivity. Those using the band model looked for the correlation between electrical conductivity, band gap, type of works functions of charge carriers etc. and the catalytic activity, while those using localized model tried to correlate the surface acidity; oxidation state of the metal ions and point defects on the surface etc. with the catalytic activity. These have been reviewed by Krylov [39]. The band model is not much successful as compared to localized model, due to the uncertainty of the catalyst. In the recent years there seems to be some reaction in the two models [40].

   Wolkenstein [41], who originally proposed the band theory of catalysts, related fermi energy to the catalytic activity, the experimental
parameters being electrical conductivity and work function. However, it has been shown recently that good correlation between electrical conductivity and catalytic activity can be obtained, when the charge carriers in the solid state crystals are inherent, but localized and the conduction proceeds viz. hopping mechanism [42]. While the band model predicts that the catalytic activity changes due to the change in Arrhenius activation energy [40], the change in activity in hopping type semiconductor is due to the change in the frequency factors.

2.11.1 Oxidation of Oximes

Our literature indicates that oxidation of oximes has been studied using pure oxides and homogenous catalysts [43-45]. There are very few reports on the oxidic spinels as catalysts. The oxidation of oximes is an important aspect in the field of organic intermediates. The oxidation of oximes can follow two distinct paths. Both the intermediates have several applications in the synthesis of different organic commercial products. The selectivity towards oxidation of oximes depends upon the nature of the catalysts.

The catalysts of ZnMn$_{1-x}$Cr$_x$FeO$_4$ system was studied for oxidation of oxime at moderate reaction conditions. The catalyst Zn-Cr ferrite shows highest catalytic activity as well as selectivity. These results are correlated with their physico-chemical properties. It is assumed that there is good correlation between catalytic activity and band gap of the material. The surface acidic centers play a significant role in the performance of the catalyst. There is maximum number of acidic centers on the surface of ZnCr ferrite catalyst.

2.12.1 Photocatalysis:

The photocatalytic activity studies of the ferrite photocatalyst was carried by photodegradation rate of different dyes such as methyl red, thymol blue and disperse red dye. The experiment of photocatalytic reaction was conducted in a 100-ml Pyrex glass vessel with magnetic stirring and a UV lamp (20W) with the main wavelength of 253.7nm. The as-prepared ferrite was used
as photocatalyst during the study. It was, from this study, concluded that enhanced photodegradation is directly related to the reduced particle size of the ferrite, which implies that photosensitization is the process primarily involved. The degradation product was analysed by using UV-Visible spectrophotometer.

References


