Synthesis and Characterization Techniques

3.1 Introduction

Synthesis and characterization technique vary from material to material. Synthesis of single phase material is of great importance for the meaningful scientific measurement. To achieve the single phase formation of a material many synthesis parameters have to be carefully controlled. The parameters of prime importance are purity of the material, annealing temperature and atmosphere, rate of heating and rate of cooling, pH, fuel, etc. All these synthesis parameters play a vital role in controlling the physical properties of the material. After the successful preparation of a single phase material, characterization becomes essential. Characterization is necessary to understand the procedures adopted for the preparation of material. Various characterization techniques were employed to study the morphological, structural and physical properties of material.

3.2 Synthesis methods

The synthesis of nanomaterial is the most important step in developing new materials with varying properties. There are numerous methods available for the synthesis of various nanostructure materials like ceramic method, sol-gel auto combustion method, chemical coprecipitation method, hydrothermal method, and spray pyrolysis method etc. Here some of the methods of preparation of nano-materials are briefly discussed.

3.2.1 Ceramic method

Synthesis of single phase material is very important for most practical applications. Ceramic method is the most popular and conventional method of preparation among
other methods. In this method raw materials like oxide and carbonates are taken stoichiometric proportion [1-3]. These oxides are mixed thoroughly and uniformly. The solid state chemical reaction takes place at much elevated temperature. Pre-sintering is the lowest sintering temperature and can start from (900 °C). Similarly the final sintering temperatures can reach up to (1200°C). The pre sintering and final sintering temperature can vary with the constituents of the mixture as well as the parameters of the desired product i.e. particle size, density, porosity etc [4]. Conventional ceramic method involves following steps:

1. Calcination of constituents of oxides/carbonates.
2. Weighing and mixing of oxides/carbonates.
3. Grinding of the mixture for 3-4 h.
4. Pre-sintering at the temperature below the temperature of solid state chemical reaction.
5. Powdering of the samples.
6. Final sintering at the elevated temperature.
7. Slow cooling and high temperature is necessary.

Conventional ceramic processing cannot yield particles of high surface area. Nanocrystalline materials cannot be prepared by ceramic method. During the grinding process there is a possibility of addition of impurities in the sample. The method requires high temperature for the synthesis of the sample. The mixture in ceramic method is less homogeneous as compared to wet-chemical methods. The method requires more time and somewhat tedious.

### 3.2.2 Sol–gel auto combustion method

Among different methods of synthesis of metal oxide (ZnO) nanoparticles, sol-gel auto-combustion technique is quite simple and cost effective which involves both chemical
and physical processes. It produces high purity and uniform nano-particles at comparatively low temperature [5]. Moreover, there is no reaction of precursor materials with the containers and the materials are easily available. Brief outline of the synthesis procedure is given below.

Sol–gel auto-combustion synthesis technique is also called as low-temperature self-combustion method, auto-ignition as well as gel-thermal decomposition method [6-8]. In this technique the chemical sol–gel and combustion process together forms zinc oxide nano-materials. Recently, this method is used as an option to synthesize advanced nano material like one-dimensional and two-dimensional nano-structure materials [9-13]. The products of sol-gel auto-combustion technique are usable for electronic and biological applications, high density magnetic and radar absorbing materials, magneto-electric composites etc. [5, 14-17].

**Advantages of sol–gel auto combustion method**

Sol–gel auto combustion method has acquired great importance during the last years. The sol-gel auto combustion method offers many advantages, such as homogeneous mixing at molecular level, good stoichiometric control and low processing temperature, use of an aqueous-based processing system, and the production of active powders. The advantages of this technique are described below [10, 18-21].

- The intimate mixing of the elements in gel form results in reaching the ingredients in a short period of time.
- It does not require grinding procedure to achieve homogeneous single phase ceramics, which avoids contamination.
- The precise size control of the particles is also a strength of sol-gel processing.
- The possibility of controlling the porosity is highly attractive.
- Sol-gel auto-combustion method is a cost effective method.
3.2.3 Hydrothermal method

Hydrothermal synthesis involves one or more chemical reactions forming the designed ceramic phase in aqueous or non aqueous phase at combination of temperature and pressure. Typically the hydrothermal temperature $(374 ^\circ C)$ of water and pressure up to 15 Mpa. By controlling various processing parameters, a number of crystalline ceramic powders of refined particles characteristics and improved chemical stoichiometry have been successfully prepared. The hydrothermal synthesis technique is used to prepare the nanostructures material one, two and three dimensional.

### Characterization techniques

In order to investigate different properties of transition metal doped zinc oxide nanoparticles, some specific techniques have been used. Each technique gives different information, some about chemical and physical properties, and others about structure, morphology and geometry.

In the present study, the prepared samples have been characterized by thermal analysis (TGA/DTA), X–ray diffraction technique (XRD), Fourier transform infra-red spectroscopy (FT-IR), UV-Vis spectroscopy techniques, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX), transmission electron microscopy (TEM). The DC electrical resistivity as a function of temperature was studied by two probe technique and the dielectric properties as a function of frequency were studied by LCR-Q meter. The magnetic properties were systematically investigated by vibrating sample magnetometer (VSM) technique.

#### 3.3.1 Thermal analysis (TGA/DTA)

**Principle of thermal analysis**

The thermal analysis is the first step in characterizing the material under investigation. It provides useful information about the decomposition temperature of the various
impurities present in the sample using this method. In thermal measurement, the sample is allowed to heat rapidly to some elevated temperature in a particular atmosphere (Air, Oxygen, Nitrogen, Argon etc.), followed by measurement of change in weight (thermo-gravimetric analysis, TGA) and heat flow with time (Differential Thermal analysis, DTA). The results of such measurements are thermal analysis curves and the changes in these curves correspond to the thermal events like water vaporization, removal of organic ingredients etc. in the sample [22]. The TGA studies determine the weight change of a sample whereas the DTA studies measures the change in temperature between a sample and the reference as a function of temperature and/or time. NETZSCH Geratebau GmbH TG/DTA (Perkin Elmer) has been used for the recording the thermo-grams of the dried precursors of samples. The temperature range is normally from room temperature to 1273 K.

**Construction and working of thermal analyzer**

A thermo-balance consists of an electronic microbalance, furnace and a temperature programmer. The thermo-balance is placed in an enclosed system to control the atmosphere. As temperature of the sample increases, mass of the sample changes. The measurements of mass changes as a function of temperature are carried out with the help of such thermo-balance. The maximum load for thermo-balance is 1 gm and a sensitivity of 1 gm. The sample should be in the form of powder and should be spread in a thin and uniform layer in the sample container. Thermo-balance is normally placed in a glass or metal systems to control the pressure and the atmosphere inside the container. A regular gaseous flow may be maintained in order to remove the evolved gases from the thermo-balance with the care that these the flow of gases do not disturb the balance [23]. The temperature of the samples can be measured using platinum resistance thermometers or thermocouples. The temperature controller attached to the instrument offer heating rate
from a fraction of a degree per minute to nearly 100 °C min⁻¹ with additional characteristic of isothermal heating. The beam is displaced by change in weight loss with temperature on sample side. This displacement is detected optically and the drive coil current is changed to return the displacement to zero. The detected drive coil current change is proportional to the amount of weight change in sample and is output as the TGA signal.

![Diagram](image)

**Fig. 3.1** A schematic thermo-balance

The DTA detects the temperature difference between the sample holder and the reference holder using electromotive force of thermocouples, attached to the holders. The differential is output as the DTA signal. The experimental set-up used for the (thermo-gravimetric analysis, TGA) and heat flow with time (Differential Thermal analysis, DTA) analysis in the present study is shown in Fig. 3.2.

![Image](image)

**Fig. 3.2** Experimental set-up of TGA/DTA analyzer.
Applications of thermal analyzer

- TGA gives us information about the thermal events which are accompanied by changes in mass.
- The mass losses define the stages and the conditions of temperature and atmosphere necessary for the preparation of the material and the stability.
- For desorption, decomposition and oxidation processes, useful information can be collected from TG analysis.

3.3.2 X-ray diffraction (XRD)

It is the powerful and unique analysis technique for the phase identification and phase analysis of the solids, which can probe the structural arrangement of atoms and molecules within the crystallographic lattice. XRD is a versatile, non-destructive method that reveals the detail information about the chemical composition, microstructure and crystallographic structure of the materials. This characterization technique is used in the field of material research, building materials, metals, minerals, plastics, pharmaceuticals, and semi-conductor materials. This analysis technique is employed for the phase identification of the material, phase quantification, single and multi-phase analysis, atomic position determination (Rietveld analysis), strain evaluation, crystallite size etc. The XRD of the samples were carried out at “Tata Institute of Fundamental Research, Mumbai.” and photographs of the X-ray diffractometer is shown in the Fig. 3.3. The X-ray diffractometer (PAN alytical, Model - X’Pert PRO MPD) is specified with anode k-alpha in the wavelength range of 1.5405 Å. X-rays are the electromagnetic waves with a very short wavelength ranges from (λ ≈ 0.1 Å) which is comparable to the atomic size. This makes us to calculate the variety of crystalline parameters like lattice parameter (a), inter-planner spacing (d), phase purity, X-ray density (d_X), bulk density (d_B) cation distribution, percentage porosity (P %), and crystalline sizes (t) etc.
Fig. 3.3. X-ray Diffractometer(PANalytical, Model - X’Pert PRO MPD)

**Bragg’s law:**

When monochromatic beam of X-ray is incident on powder sample, it is reflected, this reflected beam interferes and the interference takes place. The interference is constructive if the path difference between the interfacing rays is in integral multiple of the wavelength of incident X-ray beam. Fig. 3.4 shows the interference of X-ray beam in crystal lattice. The condition of constructive interference is given by Bragg’s law [24].

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

(4.1)

where, \(d\) is the inter-planner spacing, \(sin\theta\) is a glancing angle, \(\lambda\) is wavelength of incident radiation and \(n\) is an integer.

[61]
Applications of X-ray powder diffraction (XRD)

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).

Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

- The applications of X-ray powder diffraction include:
  - Phase identification
  - Internal structure of material i.e inter atomic distance between two atoms
  - Identification of material whether amorphous or crystalline
  - Identification of fine-grained minerals such as clays and mixed layer
  - Determination volume of unit cell.
  - Measurement of sample purity
- With specialized techniques, XRD can be used to:
  - Determine crystal structures using Rietveld refinement
  - Determine of modal amounts of minerals (quantitative analysis)
- Characterize thin films samples by:
• determining lattice mismatch between film and substrate and to inferring stress and strain
• determining dislocation density and quality of the film by rocking curve measurements
• measuring super lattices in multilayered epitaxial structures
• determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements.
• Make textural measurements, such as the orientation of grains, in a polycrystalline sample.

3. 3. 3 UV-Vis absorption spectroscopy technique

In the electromagnetic spectrum, ultraviolet (UV) and visible radiation comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic, and X-Rays.

Fig. 3.5 Mechanism in UV-Vis spectrometer

A UV-Vis spectrophotometer measures the amount of light absorbed at each wavelength of the UV and visible regions of the electromagnetic spectrum. A UV or visible
spectrophotometer has the same basic design as an infrared spectrophotometer. Fig. 3.5 shows the mechanism of UV-vis spectrometer. In a standard UV-Vis spectrophotometer, a beam of light is split; one half of the beam (the sample beam) is directed through a transparent cell containing a solution of the compound being analyzed, and one half (the reference beam) is directed through an identical cell that does not contain the compound but contains the solvent. Solvents are chosen to be transparent in the region of the spectrum being used for analysis. Absorption of UV or visible light results in electronic transitions; electrons are promoted from low-energy ground state or orbitals to higher-energy excited-state orbitals. UV-Vis spectrometry is absorption spectrometry in the Ultra Violet and Visible region that quantitatively determines solution of transition metal ions and organic compounds. UV-Vis spectrometers compares the intensities of light before and when it passes the sample. Application include analysis of bio chemicals, chemicals forensics environmental analysis, food or beverages etc. There are three main components typical UV-Vis spectrometer, plus a mechanism for holding a sample in a place the light source is either diffraction grating or a monochrometers. The detector can be either a photo diode or CCD. The third component, the radiation source, was traditionally a tungsten filament which evolved into a more advanced deuterium arc lamp, LED arc lamp, and Xenon arc lamp [25, 26].

3. 3.4 Photoluminscence spectroscopy

Photoluminscence spectroscopy is a contactless, non-destructive method of probing the electronic structure of material. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-ecitation. This excess energy can be dissipated by the sample in the form of light which is nothing but luminescence. In the case of photoexcitation, this luminescence is called photoluminescence [27]. Photo-excitation causes electrons within a material to movie
into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a non-radiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition. The quantity of the emitted light is related to the relative contribution of the radiative process.

![RF-5301PC Spectrofluorometer](image)

**Fig. 3.6** Shimadzu – RF 5301 PC spectrofluorometer

The photoluminescence spectra were recorded on Shimadzu RF-5301 PC spectrofluorometer. Its diagram is shown in Fig. 3.6. The spectrophotometer consists of two monochromators (one on the excitation and other on the emission side), a light source, two detectors (one for measurement and other for the monitoring), a sample holder, a data processor and graphic plotter.

**Specification:**

**Light Source:**

150W xenon lamp. Ozone resolving type lamp housing.

- **Excitation and emission monochromators:** Blazed holographic concave diffraction grating (F/2.5 for both excitation and emission sides)

- **Number of grating ruled lines:** 1300 grooves/mm.
- **Measuring wavelength range**: 220 to 750 nm and zero order light on both excitation and emission side.
- **Slit width**: 1.5/3/5/10/15/20 nm.
- **Wavelength accuracy**: ±1.5 nm.
- **Wavelength scanning**: 7-stape selection of survey (about 5500 nm/min). Super (about 3000 nm/min) Very Fast, Medium, Slow and Very Slow.
- **Wavelength slewing speed**: About 20000 nm/min.
- **Sensitivity**: The S/N ratio is 150 or higher for the Raman line of distilled water (350 nm excitation wavelength, 5 nm spectral bandwidth, and 2-sec responsibility for 98% of the full scale).
- **Light Source compensation**: Dynode feedback system with monochromatic light monitoring.
- **Detector**: Photomultiplier tube for both photometry and monitor sides. Photometry: R3788-02, Monitor: R212-14.
- **Sensitivity selection**: 2 steps of HIGH and LOW. (The sensitivity at HIGH is about 50 times that of LOW)
- **Response**: 8-Step selection of 0.02, 0.03, 0.1, 0.25, 0.5, 2, 4 and 8 sec for 98% of the full scale.
- **Sample compartment**: Single non-constant temperature cell holder
- **Operational temperature range**: 15-35°C.

### 3.3.5 Fourier transform infrared spectroscopy (FTIR)

FT-IR spectroscopy has been widely used for structural and compositional analysis of organic, inorganic and polymeric materials and played an important role in quality control of raw materials. IR spectroscopy deals with changes in Vibrational motion (stretching and bending) of atoms in a molecule which leads to net change in dipole
moment and results in absorption of IR radiation. These motions are greatly influenced by masses of atoms, their geometrical arrangement and the strength of their chemical bonds. In accordance with both applications and instrumentation involved, the IR spectral region (13,000–100 cm⁻¹) is conveniently divided into near-infrared region (13000 to 4000 cm⁻¹), mid-infrared region (4000 to 400 cm⁻¹) and far-infrared region (400 to 100 cm⁻¹) [28, 29]. The main significance of this division is that most fundamental molecular vibrations occur in mid-IR making this region richest in chemical information while overtones and combination of fundamental vibrations especially those involving hydrogen atoms appear in near-IR. On the other hand, far-IR region contains vibrations involving heavy atoms, lattice modes of solids and some rotational absorption of small molecules. Infrared radiation spans a section of the electromagnetic spectrum having wave numbers from roughly 13,000 to 100 cm⁻¹ or wavelengths from 0.78 to 1000 μm. It is bound by the red end of the visible region at higher frequencies and the microwave region at lower frequencies.

**Instrumentation**

A typical spectrometer mainly comprises of components like radiation source, optical path and monochromator, radiation detector and sample as shown in Fig. 3.7. These components are briefly described below.

**Source**

The source is always some form of filament which is maintained at red-or white-heat by an electric current. Two common sources are the Nernst filament, consisting of spindle of rare earth oxides (ZrO₂ + Y₂O₃) about 1 inch long and 0.1 inch in diameter, and the Globar (SiC) filament a rod of carborundum, somewhat thicker and longer than the Nernst. The Nernst requires to be pre-heated before it will conduct electricity, but once red-heat is reached the temperature is maintained by the current.
**Optical path and monochromator:** The beam is guided and focused by mirrors aluminized or silvered on their surfaces. Normally a focus is produced at the point where the sample is to be placed. Ordinary lenses and mirrors are not suitable as glass absorbs strongly over most of the frequencies used. Normally, highly polished IR transparent mineral salt windows such as, NaCl (transparent above 650 cm$^{-1}$) and KBr (transparent above 400 cm$^{-1}$) are used to contain a sample, or protect to the detector. For aqueous samples, AgCl and CaF$_2$ sample cell can be used. These are infra–red transparent above 400 and 1200 cm$^{-1}$ respectively. A rotatable grating is usually used to disperse the radiation, having largely superseded rotatable prisms, which have poorer resolving power. Where the latter are still in use, the prism is usually made of NaCl or KBr.

**Detector:** Two main types are in common use, one sensing the heating effect of the radiation and the other depending on photoconductivity. In both greater the effect (temperature or conductivity rise) at a given frequency, greater is the transmittance (and the less the absorbance) of the sample at that frequency.

An example of the temperature method is to be found in Golay cell, thermocouples or bolometers. Pyroelectric detectors such as, deuterated triglycine sulphate (DTGS) which are specialized thermal detectors are in common use in FT spectrometers. Liquid
nitrogen cooled Mercury cadmium telluride (MCT), Indium antimonide (InSb) etc. are some examples of photoconductive detectors used in IR spectroscopy. These have a faster response time and sensitivity, compared even with the deuterated triglycine sulphate (DTGS).

**Sample:** Sample is held between plates of polished mineral salt such as NaCl, KBr or AgCl. The following procedure is normally employed for gas, liquid and solid sample preparation.

**Gas:** Glass cells either 5 or 10 cm long fitted with rock salt windows are used for gaseous samples at pressures of up to 1 atmosphere or greater. Special long-path cell, in which the radiation is repeatedly reflected up and down the cell, may be used for gases at low pressure.

**Liquid:** Pure liquids are studied in thickness of about 0.01 mm, while solutions are usually 0.1-10 mm thick, depending on the dilution. Carbon tetrachloride, carbon disulfide, chloroform etc are used as solvents.

**Solid:** Two methods are generally followed: (a) Mull Method and (b) KBr pellet method. In former method a solid sample is thoroughly grounded along with a weakly absorbing, non-volatile liquid normally Nujol to form a thick paste, called a mull which can then be held between salt plates in the same way as a pure liquid or solvent. It is very important that the sample be ground to a very fine particle size to reduce light scattering and salt plate scratching. Nujol is transparent in the infrared except for narrow bands at 2900, 1450, 1375 cm\(^{-1}\). An alternative mulling liquid, which does not absorb in these regions, is a perfluorokerosene, such as Fluorolubs. In KBr pellet method, the solid is finely ground with pure, dry KBr, the mixture is pressed in a hydraulic press to form a transparent pellet, and the spectrum of pellet is measured. It is important that the solid be extremely finely divided and well mixed. The pellet is usually pressed in a special die
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that can be evacuated in order to avoid entrapped air, which causes cloudiness in the pellet. A major advantage of this method is that, KBr has no absorptions in the IR above 250 cm$^{-1}$, so that an unimpeded spectrum of the compounds is obtained.

3.3.6 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) is a microscope that uses electrons instead of light to form an image. Since their development in the early 1950's, scanning electron microscopes have developed new areas of study in the medical and physical science.

The scanning electron microscope has many advantages over traditional microscopes. Schematic diagram of Scanning Electron Microscopy has been shown in Fig 3.8. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope as one of the most useful and powerful instruments in research today.

![Schematic diagram of scanning electron microscopy (SEM)](image)

Fig. 3.8 Schematic diagram of scanning electron microscopy (SEM)
The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample (Fig. 3.9).

Fig. 3.9 Interaction of incident beam on matter

Fig. 3.8 shows interaction of incident beam on the matter which produces X-rays, Auger electrons, primary backscattered electrons, secondary electrons. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image [30, 31].

**Sample preparation for SEM**

The SEM utilizes vacuum conditions and uses electrons to form an image and therefore, special preparations must be done to the sample. All water must be removed from the samples because the water would vaporize in the vacuum. Generally, all metals are conductive and require no preparation before being used, whereas, non-metals need to be made conductive by covering the sample with a thin layer of conductive material. This is
done by using a device called a "sputter coater." The sputter coater uses an electric field and argon gas. The sample is placed in a small chamber that is at a vacuum. Argon gas and an electric field cause an electron to be removed from the argon, making the atoms positively charged. The argon ions then become attracted to a negatively charged gold foil. The argon ions knock gold atoms from the surface of the gold foil. These gold atoms fall and settle onto the surface of the sample producing a thin gold coating [31].

3.3.7 Energy dispersive X-ray analysis (EDAX)

Energy dispersive X-ray spectrometry (EDAX) 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. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an elements atomic structure to be identified uniquely from each other. Most modern EDAX systems can detect X-rays from all the elements in the periodic table above beryllium, \( Z = 4 \), if present in sufficient quantity. X-rays are produced as a result of the ionization of an atom by high-energy radiation wherein an inner shell electron is removed [32]. To return the ionized atom to its ground state, an electron from a higher energy outer shell fills the vacant inner shell and in the process, releases an amount of energy equal to the potential energy difference between the two shells. This excess energy, which is unique for every atomic transition, will be emitted by the atom as an X-ray photon.

For example, if the K shell is ionized and the ejected K-shell electron is replaced by an electron from the L shell, the emitted X-ray is labelled a characteristic Ka1 X-ray Fig. 3.10. The hole that exists in the L shell will be filled by an electron from a higher shell,
say the M shell, if one exists. This M – L transition may result in the emission of another X-ray, labeled in turn according to the one of the many M–L transitions possible. The cascade of transitions will continue until the last shell is reached.

**Fig. 3.10** Elements in an EDAX spectrum are identified based on the energy content of the X-rays emitted by their electrons

**Design of the spectrometer:**

The different components of the Energy Dispersive spectrometer are as shown in the Fig. 3.11. It consists of i) The X–ray tube  ii) Specimen iii) Si (Li) counter and a FET preamplifier, both cooled by liquid Nitrogen and iv) Multichannel Analyzer (MCA).

**Fig. 3.11** A schematic diagram of energy dispersive spectrometer
If the element is bombarded with the X-ray of high enough energy, it will emit its ‘characteristic lines’. In most cases they are the Kα and Kβ lines. They are called the characteristic lines to emphasize that the wavelength of them are fixed and characteristic to the emitting element. The phenomena are called the fluorescence. It provides a basis for a method of chemical analysis. If the different elements in the sample are bombarded with X-ray they will emit their characteristic lines of different wavelengths thus providing identification of the elements.

The X-ray spectrometer is used in two different modes for this purpose.

1. **Wavelength dispersive**: In this mode the wavelength of the emitted radiation from sample are analyzed by diffracting the radiations through a single crystal of known d value and obtaining the wavelength distribution.

2. **Energy dispersive**: In this mode diffraction of the radiation is not involved in the process of analyzing on the basis of their energies rather than their wavelengths.

**Working of energy dispersive spectrometer**

The sample specimen is bombarded with X–rays of enough high energy generated from the X–ray tube. The fluorescence radiation, emitted by the sample comprising of various wavelengths according to the various elements present in the sample is analyzed and various wavelengths are separated on the basis of their energies by means of a Si (Li) counter and a multi-channel analyzer (MCA).

The counter produces the pulses proportional in height to the energies in the incident beam and MCA sorts out the various pulse heights. The excellent energy resolution of the Si (Li) counter with FET preamplifier and the ability of the MCA to perform rapid pulse height analysis make the spectrometer to measure the intensities of all the spectral lines from the sample in about a minute, unless there are elements in very low concentration are to be determined.
Chemical analysis

The energy dispersive spectrometer is used to make a rapid chemical analysis qualitatively. It can also be used for a semi quantitative, if not quantitative, analysis. The energy dispersive spectrum one gets from this spectrometer is the intensity (in counts) v/s energy spectrum. The energies in keV cover all the K and L lines emitted by the samples.

The analysis is done with the help of the computer software. There is a table or chart of the energies of all K and L lines arranged in consequent manner of all the elements. The information from it is retrieved by the computer for assigning any energy peak in the diagram with the respective element. Thus, from the peak energy the elements present in the sample can be detected.

The semi quantitative analysis can be done with calculating the total number of counts recorded for a particular energy. This examination is difficult to do manually since all the energy peaks may not be well separated and may be diffused with each other. Since the analysis needs the total area under the curve and not the height of the peak, it is difficult to separate the contributions of each peak. But computer software simulates the peaks with different areas under the curve and it checks their resultant effect when merged. It can separate out the contribution from each peak in this manner. The relative concentrations of the elements can be known from this analysis, if not the absolute.

3.3.8 Transmission electron microscopy (TEM)

It is microscopy technique whereby a beam of electron is transmitted through an ultra thin specimen, interacting with the specimien as it passes through. An image is formed from the interaction of the electrons transmitted through the specimien; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEMs are
capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument’s user to examine fine detail even as small as a single column of atoms, which is tens of thousands time smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological science. TEMs find application in cancer research, virology, materials science as well as pollution and semiconductor research. Fig. 3.12 shows the transmission electron microscope image. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnification complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and simple induced electron phase shift as well as the regular absorption based imaging. The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

**Working principle of transmission electron microscopy**

- The electron gun, producing a stream of monochromatic electrons.
- This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens (usually controlled by the “spot size knob” largely determines the “spot size; the general size range of the final spot that strikes the sample. The second lens (usually controlled by the “intensity or brightness knob” actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.
The beam is restricted by the condenser aperture (usually user selectable), knocking out high angle electrons (those far from the topic axis, the dotted line down the center).

Fig. 3.12. The transmission electron microscopy.

The beam strikes the specimen and parts of it are transmitted.

This transmitted portion is focused by the objectives lens into an image.

Optical objectives and selected area metal aperture can restrict the beam, the objectives aperture enhancing contrast by blocking out high angle diffracted electrons, the selected area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the samples.

The image is passed down the column through the intermediate and projector lenses, being enlarged all the way. The image strikes the phosphor image screen and light is generated, allowing the user to see the image. The darker areas of the image.
represent those areas of the sample to see the image. The darker area of the image represent those areas of the sample that fewer electrons were transmitted through (they are thicker or less denser). The lighter areas of the image represent those areas of the sample that more electrons were transmitted through (they are thicker or less dense).

**Electrical properties**

**3. 3.9 DC electrical resistivity measurement**

The temperature dependence of DC electrical resistivity of all the samples was studied by two-probe method. For good electrical ohmic contact the pellets were polished and silver pasted on both the surfaces. A typical sample holder as shown in Fig.3.13, is specially designed which consist of two brass electrodes, one of which is fixed to ceramic beads by means of screw. Another electrode at other side is attached to ceramic beads and is spring loaded to keep the pellet interact in between the electrodes.

![Fig. 3.13 Schematic diagram of two probe method.](image)

[78]
The samples in the form of disc type pellet were held in a sample holder whole assembly was held in an electrical furnace. The temperature of the furnace was controlled by digital controller and maintained through a variac. The temperature of the sample was measured with the help of calibrated chromel-alumel thermocouple attached to the controller and the temperature was read directly from the digital display in steady state. The resistance of each pellet is measured for rising and falling temperature at the steps of 10 °C. During each measurement, sufficient time was allowed for the sample to attain the equilibrium temperature.

The two-point probe method was used for the measurement of resistivity of undoped and transition metal doped ZnO nanomaterials in the temperature range of 300 K to 490 K. As the resistivity of the pure ZnO is very high and it was not possible to use the four-point probe method because it is used for the samples having low resistance [33]. The use of four-point probe method is also not suitable at high temperature due to unstability of silver paste used for connections. While the two point probe method is suitable for the samples having high resistivity and at high temperature.

![Fig. 3.14 DC electrical resistivity measurement experimental set-up](image-url)
The schematic diagram of the DC resistivity apparatus is shown in Fig. 3.14. The samples were used in the form of pellets of 10 mm diameter and of 3 mm thickness. The pellets were prepared using hydraulic press by compressing at 6 tons. Zero polish paper is used to make the uniform surface of the pellet after making the uniform surface the silver paste is applied on it for good ohmic contact. This silver pasted pellet is placed in between electrodes of sample holders. The most commonly used methods to determine the electrical resistivity are as follows:

(a) **Four probe method**

(b) **Van der Pauw method**

(c) **Two probe method**

a) **Four probe method:**

Four probe method includes four equally spaced probes in contact with a material of unknown resistance. The outer two probes are used for sourcing the current and the two inner probes are used for measuring the resulting voltage drop across the surface of the sample. Four-probe method is more accurate and is used to measure the low resistivity.

b) **Van der Pauw method:**

The van der Pauw Method is a technique commonly used to measure the resistivity and the Hall coefficient of a sample.

c) **Two probe method:** Two probe method involves bringing two probes in contact with a material of unknown resistance. The resistivity of the semiconducting material is often measured using a two probe technique. The shape of the sample in two probe method may be disc shaped, cylindrical, cube, or parallelepiped. Electrodes are located symmetrically with respect to each other on opposite sides of the sample. In this method, the amount of current that flows through a sample with the variation of temperature is measured between the two electrodes of the sample holder.
3.3.10 Dielectric measurements

**Principle of dielectric measurements**

LCR-Q meter is used to measure the resistance, capacitance, inductance, impedance, loss factor etc. of the materials. In an automatic LCR meter bridge method, the bridge circuit employs a fixed standard resistor beside the unknown impedance, and a multiplying digital-to-analog convertor (MDAC) that works as a resistive potentiometer.

**Working of LCR-Q meter**

Two independent quasi-balances are maintained in the bridge by varying the potentiometer settings and the unknown value of the standard resistance. In automatic LCR-Q meter bridge, a fixed standard resistor despite a variable standard resistor is used. In order to determine the values of dielectric constant for the materials, an ideal capacitor C pin parallel with a resistor R is taken as the equivalent circuit of a capacitor with dielectric having certain conductivity. The resistor R can be considered as built up from two parallel resistors, one representing the finite ohmic resistance of the dielectric sample and the other representing an equivalent resistance of such a value that the energy dissipated in it is equal to the dielectric losses in the dielectric.

The dielectric measurements were carried out with the help of two probe sample holder. The two flat surfaces of pellets were polished with the help of zero polish paper. The silver paste is applied on the two flat surfaces of pellets for good ohmic contact. The variation of dielectric parameters such as dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent (tan $\delta$) were studied using LCR-Q meter [Model 4192, HP make] as a function of logarithm of frequency. The dielectric constant is the ratio of permittivity of substance to the permittivity of free space. It is an expression of the extent to which a material concentrates electric flux, and is the electrical equivalent of relative magnetic
permeability. As the dielectric constant increases, the electric flux density increases, if all other factor remains unchanged.

The dielectric constant decreases with increasing frequency and at higher frequency it remains constant, this behavior is normal ferrimagnetic behavior. The variation of dielectric constant with frequency reveals the dispersion due to Maxwell-Wanger type interfacial polarization in agreement with the Koop’s phenomenological theory[34-36]. According to these models the dielectric structure is supposed to be composed of the fairly well conducting grains, separated by a second thin layer of grain boundaries of poorly conducting substances. These grain boundaries could be formed during the sintering process due to the superficial reduction or oxidation of crystallites in the porous materials as a result of their direct contact with the firing atmosphere.

Dielectric loss in samples is considered to originate from two mechanisms: electron hopping and charged defect dipoles. The former contributes to the dielectric loss mainly in the low frequency range. In the high frequency range, the dielectric loss mainly results from the response of defect dipoles to the field. The relaxation of dipoles under an electric field is decreased with increasing frequency ultimately resulting in a decrease in the dielectric loss in the high frequency range. Dielectric properties like dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan\delta$) were studied using LCR-Q meter as a function of logarithm of frequency. The capacitance of all the samples was measured in the frequency range of 50Hz to 5MHz.

**Magnetic properties**

**3. 3.11 Vibrating sample magnetometer measurement (VSM)**

Magnetization measurements at room temperature were performed using vibrating sample magnetometer (VSM). Using M-H plots, the saturation magnetization (Ms), coercivity (Hc), remanence magnetization (Mr) remanence ratio (Mr/Ms) were
calculated. A vibrating sample magnetometer (VSM) operates on Faraday’s law of induction, which tells us that a change in magnetic field will produce an electric field. This electric field can be measured and gives information about the changing the magnetic field. When a material is placed in a uniform magnetic field, a dipole moment gets induced in the sample proportional to the product of the sample susceptibility and the applied field. If the sample is made to undergo sinusoidal motion, the resulting magnetic flux changes near the sample will induce electrical signal suitable placed stationary coils, the signal is proportional to the moment, amplitude and frequency of vibration. The sample in the powder form is required for vibrating sample magnetometer technique. The powder form sample was field in a one end closed cylindrical tube having 2-3 mm diameter and 3-4 mm long. Then the weight of the empty tube and weight of the tube with sample were measured and the difference between them gives the weight of the sample for experiment. This sample filled tube is loaded in between electromagnet using a long sample holder. The sample rests centered in pair of pickup coils between the poles of an electromagnets. The sample holder is mounted on electromechanical transducer, which possess through the center of driving coil. The transducer is driven by an oscillator. The sample under study is constraint to vibrate only along the vertical axis. When the sample vibrates vertically, it induces a signal in the pickup coil. The pail of stationary coils picks up the induced ac signal. The output of the sample coil is fed to the differential input of a lock in amplifier. The reference input of the lockin amplifier comes from the sine wave oscillator used to drive the sample holder. The output of the lockin amplifier as well as the strength of the applied field measured by gauss meter whose probe is placed at the center of electromagnet given to data acquisition system.
References


