CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

The determination of physical, chemical, structural, mechanical, electrical and optical properties of materials is referred as ‘characterization’. A solid-state physicist, druggist or a device engineer is concerned with the properties of their interest for the evaluation of device performance by experimental or theoretical means. Since we need to characterize and analyze nanostructures, it is imperative that an adequate understanding of the involved experimental techniques should be made in the fitness of things. The observations incorporated in the thesis during the present investigation have been recorded by employing different experimental techniques like X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), UV-vis spectroscopy, inductively coupled plasma atomic absorption spectroscopy (ICP-AES), optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive analysis of X-rays (EDAX), vibrating sample magnetometer (VSM), etc. This chapter concerns with the relevant description of these experimental techniques and the apparatus used to characterize the nanostructures.

2.2 EXPERIMENTAL TECHNIQUES

2.2.1 X-RAY POWDER DIFFRACTION (XRD)

X-ray diffraction is an important technique that has long been used to address all issues related to the structure of the solids and their thin films, including lattice constants and geometry, identification of unknown materials, orientation of polycrystals, defects and stresses etc.

In the present study, Bruker’s D8 Advanced X-ray powder diffractometer consisting of a Cu target and X-ray tube of 2 kW was utilized for obtaining diffractograms. The diffracted radiation is detected by dynamic scintillation detector,
which moves through an adjustable range of reflections. The instrument used has an accuracy of ± 0.01 degree. The pattern is recorded at room temperature using monochromatic radiation of CuK\(_\alpha\) (\(\lambda=0.15406\) nm). Compared with photographic methods, the diffractometry, in most cases, offers essential advantages due to its higher sensitivity, higher resolving power, accuracy of the intensity measurements and the elimination of elaborate work in dark room. Above all, the diffractometric records can be obtained in a much shorter time and more conveniently than with photographic methods.

![Figure 2.1 Bruker D8 Advance powder X-ray diffractometer](image)

A diffractometer measures the intensity of X-rays reflected from one stack of planes at a time, so it is of interest to examine what kind of spatial arrangements are best suited for such measurements. The intensity of a diffracted beam is measured by an electronic counter. This circuit counts the number of current pulses/sec and this number is directly proportional to the intensity of X-ray beam entering the counter or detector. A diffractometer is designed somewhat like a Debye Scherrer camera, except that a movable counter replaces the strip of film. In both the instruments, essentially monochromatic radiation is used and the X-ray detector (film or counter) is placed on the circumference of a circuit centered on the powder specimen.

For obtaining the diffractogram of a polycrystalline or powdered sample using the above setup, the counter is set near \(2\theta = 0^\circ\) and then connected to a counting-rate meter. The output of this circuit is fed to a strip-chart recorder. The counter is then driven at a constant angular velocity through increasing values of \(2\theta\) until the whole angular range is scanned. At the same time, the paper chart on the recorder moves at a constant speed so that the distances along the length of the chart are proportional to \(2\theta\).
This results in a diffractogram showing a record of counts per second (proportional to diffracted intensity) versus diffraction angle $2\theta$.

The quadratic form of the Bragg equation for a FCC inverse spinel system $(AB_2O_4)$ is given as

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{h^2 + k^2 + l^2}{a^2}$$  \hspace{1cm} (1)

Here $d$ is the inter planer placing, $h, k, l$ are reflection planes and $a, b, c$ are the lattice parameters. For FCC system $\alpha = \beta = \gamma = 90^\circ$ and $a = b = c$. Lattice parameter of nanoparticles has been computed from the highest intense reflection by using the above formula.

The average crystallite size is obtained from the classical Scherrer’s formula

$$D = \frac{0.9n\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

Here $\beta$ and $\theta$ are the full width half maximum (FWHM) and position of the reflection, $D$ is the crystallite size, $\lambda$ is the wavelength of radiation and $n$ is the order of diffraction. It has been assumed that, the shape of the nanoparticles is spherical and hence, 0.9 is inserted into the Scherrer’s formula as the geometrical factor.

2.2.2 **THERMOGRAVIMETRIC ANALYSIS (TGA)**

TGA provides analysis with a quantitative measurement of any weight changes associated with a transition at the varying temperature. It can directly record the mass loss, if any, with temperature due to dehydration or decomposition. The sample under experiment is packed uniformly in the molybdenum boat and is placed in the furnace of the TG Analyzer, and the boat is attached to an automatic recording balance. The change in weight is simultaneously recorded with time when the temperature increases at a known uniform rate. This would permit recording the loss in weight as a function of both time and temperature. Thermograms obtained are characteristic of the unique sequence of physico-chemical changes, which occur over definite temperature ranges and at rates that are the function of the molecular structure. Changes in weight
are results of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products.

![Mettler Toledo TGA/SDTA 851e thermal analyzer](image)

**Figure 2.2** Mettler Toledo TGA/SDTA 851e thermal analyzer

The Mettler Toledo TGA/SDTA 851e is used for the TGA measurements. The measurements are carried out in the temperature range of 30-800 °C at a heating rate of 10 °C/min in nitrogen environment. This instrument can measure weight losses from 0.05 to 50 mg/inch.

### 2.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is one of the most powerful analytical techniques, which offer the possibility of chemical identification. One of the most important advantages of infrared spectroscopy over the other usual methods of structural analysis is that it provides useful information about the structure of molecules quickly, without tiresome evaluation methods. The IR methods have been employed in a variety of physiochemical investigations like hydrogen bonding, solute-solvent interactions, charge transfer phenomena, internal rotation, matrix isolation of reactive species, adsorption, reaction kinetics, etc.

The technique utilizes simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations, the molecules of a chemical substance vibrate at many rates, giving rise to close – packed absorption bands, called an IR absorption spectrum, which may extend over a wide
wavelength range. Various bands are present in the spectrum, which correspond to the characteristic functional groups and bonds present in the chemical substance. The infrared absorption spectra of molecules result from transitions between vibrational and rotational energy levels. Thus, an IR spectrum of a substance is a fingerprint for its identification.

![Figure 2.3 Perkin Elmer spectrum GX FTIR spectrophotometer](image)

In the present investigation, the infrared absorption spectrum is obtained on spectrum GX ‘Perkin Elmer’ single beam spectrophotometer. The sample pellet is prepared by mixing of sample with analytical grade dry potassium bromide. The sample is placed in line of IR beam and the relative intensity of the light energy transmitted versus wavelength or wavenumber is measured. ‘Nernst Glower’ is the common light source for IR radiation, consisting of a molded rod containing a mixture of oxides of zirconium, yttrium and erbium, when heated electrically to around 1000 – 1800 °C. For obtaining approximately monochromatic light, either optical prisms or gratings are used. Grating spectrophotometers give higher resolution. For optical prisms and cell containers, glass or quartz cannot be used because they strongly absorb throughout the IR region, while metallic halides (like sodium chlorides or potassium bromide) are commonly used for these purposes. The spectrum is scanned in the range of 4000 – 400 cm\(^{-1}\).

2.2.4 \textit{UV – VIS SPECTROSCOPY}\textsuperscript{4,6}

For the chemical analysis of liquids, gases and solids, a laboratory instrument, Elico’s biospectrophotometer (model no. BL198) is used. The instrument provides a means for analyzing substances with radiant energy in the ultraviolet to near infrared regions of the electromagnetic spectrum. Analytical information can be revealed in terms of transmittance, absorbance or reflectance of energy in the wavelength range between 190 to 1100 nm. Light sources used are Deuterium lamp & Tungsten lamp.
Photodiode is used as a detector. The instrument utilizes a single beam of energy, which is chopped into alternate reference, and sample beams to provide a double beam system with the sample compartment. Both sample and reference beams have common detection and amplification components. To eliminate inaccuracy due to effects such as source fluctuations, changes in amplifier gain, sensitivity of spectral response of the detector and presence of common absorbing gases in the sample and reference path, ratio recording (comparison of sample beam energy with reference beam energy) is used.

![Elico biospectrophotometer (model BL 198)](image)

**Figure 2.4** Elico biospectrophotometer (model BL 198)

### 2.2.5 Inductively Coupled Atomic Emission Spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation, which is a characteristic wavelength of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

In the present work, this technique is used to quantify the concentration of elemental silver in core-shell nanostructures of Fe$_3$O$_4$-Ag. The measurements were carried out on Perkin Elmer Optima 2000 inductively coupled plasma atomic emission spectroscope (ICP-AES).
2.2.6 **OPTICAL MICROSCOPY**

The optical microscope, often referred to as the "light microscope", is a type of microscope, which uses visible light and a system of lenses to magnify images of small samples. There are two basic configurations of the conventional optical microscope in use, the simple (one lens) and compound (many lenses). The actual power or magnification of an optical microscope is the product of the powers of the ocular (eyepiece), usually about 10x, and the objective lens being used. Compound optical microscopes can produce a magnified image of a specimen up to 1000x.

The objective lens is, at its simplest, a very high power magnifying glass *i.e.* a lens with a very short focal length. This is brought very close to the specimen being examined so that the light from the specimen comes to a focus about 160 mm inside the microscope tube. This creates an enlarged image of the subject. This image is inverted. By carefully focusing a brightly lit specimen, a highly enlarged image can be seen. This real image is viewed by the eyepiece lens that provides further enlargement. In most microscopes, the eyepiece is a compound lens, with one component lens near the front and one near the back of the eyepiece tube. This forms an air-separated couplet. In many designs, the virtual image comes to a focus between the two lenses of the eyepiece, the first lens bringing the real image to a focus and the second lens enabling the eye to focus on the virtual image.

At very high magnifications with transmitted light, point objects are seen as fuzzy discs surrounded by diffraction rings. These are called Airy disks. The *resolving power* of a microscope is taken as the ability to distinguish between two closely spaced Airy disks (or, in other words the ability of the microscope to reveal adjacent structural detail as distinct and separate). The magnitude of the diffraction patterns are affected by both

---

**Figure 2.5** Perkin Elmer Optima 2000 inductively coupled plasma atomic emission spectorscope
the wavelength of light ($\lambda$), the refractive materials used to manufacture the objective lens and the numerical aperture (NA) of the objective lens. Therefore, there is a finite limit beyond which, it is impossible to resolve separate points in the objective field, known as the diffraction limit. Usually, a $\lambda$ of 550 nm is assumed, corresponding to green light, with air as medium, the highest practical $NA$ is 0.95, and with oil, up to 1.5, in practice, the highest resolving power obtainable is about 200 nm.

![Figure 2.6 Carl-Zeiss optical microscope](image)

In the current study, optical microscopic images are captured on a Carl-Zeiss microscope equipped with a CCD camera. The magnification used is 100X. For the optical microscopy, dilute suspension of nanostructures are prepared in ethanol. A fine of the suspension is put on a glass slide and ethanol is allowed to evaporate slowly at room temperature. The sample thus prepared is investigated under light microscope to determine fine details of the specimen.

### 2.2.7 Scanning Electron Microscopy

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from
approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD).

![Leo 1430vp scanning electron microscope](image)

**Figure 2.7** Leo 1430vp scanning electron microscope

Accelerated electrons in a SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each
element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

In the present investigation Leo 1430vp scanning electron microscope is used. The sample is coated with gold prior to investigation. The sample is prepared on carbon grid and magnification used is 78 kX.

2.2.8 Transmission Electron Microscopy

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. Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; 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 (spatial resolution of 0.1 nm), 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 times smaller than the smallest resolvable object in a light microscope. 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 magnifications, complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.
In this study transmission electron microscopic images and energy dispersive X-ray spectrums (EDS) were obtained on JEOL (Model GEM 200) transmission electron microscope operated at 200 kV. For this purpose, a fine drop of samples is either dispersed in hexane or ethanol and are placed on carbon coated copper grids. The solvent is allowed to evaporate slowly at room temperature.

2.2.9 Dynamic Light Scattering

When a beam of light passes through a colloidal dispersion, the particles or droplets scatter some of the light in all directions. When the particles are very small compared with the wavelength of the light, the intensity of the scattered light is uniform in all directions (Rayleigh scattering); for larger particles (above approximately 250 nm in diameter), the intensity is angle dependent (Mie scattering).

If the light is coherent and monochromatic, as from a laser source for example, it is possible to observe time-dependent fluctuations in the scattered intensity using a suitable detector such as a photomultiplier capable of operating in photon counting mode. These fluctuations arise from the fact that the particles are small enough to undergo random thermal (Brownian) motion and the distance between them is therefore constantly varying. Constructive and destructive interference of light scattered by neighboring particles within the illuminated zone gives rise to the intensity fluctuation at the detector plane, which, as it arises from particle motion, contains information about this motion. Analysis of the time dependence of the intensity fluctuation can therefore yield the diffusion coefficient of the particles from
which, via the Stokes Einstein equation, knowing the viscosity of the medium, the hydrodynamic radius or diameter of the particles can be calculated.

The time dependence of the intensity fluctuation is most commonly analyzed using a digital correlator. Such a device determines the intensity autocorrelation function which can be described as the ensemble average of the product of the signal with a delayed version of itself as a function of the delay time. The "signal" in this case is the number of photons counted in one sampling interval. At short delay times, correlation is high, over time as particles diffuse, correlation diminishes to zero, and the exponential decay of the correlation function is characteristic of the diffusion coefficient of the particles. Data are typically collected over a delay range of 100 ns to several seconds depending upon the particle size and viscosity of the medium.

Analysis of the autocorrelation function in terms of particle size distribution is done by numerically fitting the data with calculations based on assumed distributions. A truly monodisperse sample would give rise to a single exponential decay to which fitting a calculated particle size distribution is relatively straightforward. In practice, polydisperse samples give rise to a series of exponentials and several quite complex schemes have been devised for the fitting process. One of the methods most widely used today is known as Non-Negatively Constrained Least Squares (NNLS).

Particle size distributions can be calculated either assuming some standard form such as log-normal or without any such assumption. In the latter case, it becomes possible, within certain limitations, to characterize multimodal or skewed distributions. The size range for which dynamic light scattering is appropriate is typically submicron with some capability to deal with particles up to a few microns in diameter. The lower limit of particle size depends on the scattering properties of the particles concerned (relative refractive index of particle and medium), incident light intensity (laser power and wavelength) and detector / optics configuration.

Hydrodynamic particle size and its distribution of core and composite nanoparticles were determined on Beckman Coulter’s particle size analyzer (model Delsa Nano C). For the purpose dilute colloidal suspension of nanostructures have been prepared in water, ethanol or hexane. The measurements were carried out either at room temperature of at elevated temperature.
2.2.10 *Vibrating Sample Magnetometer (VSM)*

A vibrating sample magnetometer (VSM) is a scientific instrument that measures magnetic properties. A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated sinusoidal oscillations. The induced voltage in the pickup coil is proportional to the sample’s magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup, a lock-in amplifier measures the induced voltage by taking sinusoidal oscillation frequency as its reference signal. By measuring in the field of an external electromagnet, complete hysteresis curve of a material can be obtained.

![Indigenously built vibrating sample magnetometer along with the live data accusation program](image1)

In the present study, a homemade vibrating sample magnetometer is used to determine the magnetic characteristics of nanostructures. The indigenously built
magnetometer has a sensitivity of $10^{-6}$ emu/g and can make FC-ZFC as well hysteresis loop measurement from 77 – 300 K. A software package developed on Labview environment provides real time measurements. In the present investigation, magnetization measurements are carried out at room temperature (300 K). The magnetometer is calibrated with Ni standards prior to each measurement.

REFERENCES

1. B Cullity (1978) Elements of X-ray diffraction, 2nd Ed. Addison-Wesley publication company, USA
11. B Cullity (1972) Introduction to magnetic materials, Addison-Wesley Publication company, UK