CHAPTER 2
CHARACTERIZATION TECHNIQUES

After preparation of nanoparticles, it is essential to characterize them in terms of size, composition, phase, microstrain etc. For the characterization of nanoparticles some laboratory techniques are required. Following techniques have been used in the work presented in the thesis.

- X-ray Diffraction (XRD) using Synchrotron Radiation Source (SRS);
- X-ray Absorption Near Edge Structure (XANES) using SRS;
- Total X-ray Reflection Fluorescence (TXRF) using SRS;
- Differential Scanning Calorimetry (DSC);
- Ultra Violet Visible (UV-VIS) Spectroscopy;
- Transmission Electron Microscopy (TEM);
- Vibrating Sample Magnetometer (VSM);

In this chapter, we have explained all the above mentioned techniques.

2.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is an analytical technique commonly used for identification of crystalline materials and analysis of the unit cell dimensions. Each material produces a unique signature of X-ray. The X-ray pattern shows the X-ray intensity versus scattering angle that is characteristic of its crystalline atomic structure. Qualitative analysis is possible by comparing the XRD pattern of an unknown material to a library of known patterns. For both qualitative and quantitative analysis of crystalline compounds, therefore, XRD is one of the most powerful techniques. The technique informs about the types and nature of phase present, structural make-up of phases, degree of crystallinity, and amount of amorphous content, micro strain, size and orientation of crystallites.
X-rays incident upon a crystal is scattered in different ways. When the wavelength of the radiation (\( \lambda \)) is comparable to the atomic spacing in a crystal, the scattering which is termed as diffraction, gives rise to a set of well defined beams arranged with a characteristic geometry, thus forming a diffraction pattern. Schematic of X-ray diffraction setup is shown in figure 2.1. X-ray diffraction data collection is the result of relative intensity (I) for each reflection with a set of planes in the crystal, designated by Miller indices (h k l), along with the corresponding scattering angle (2\( \theta \)) for that reflection. The positions and intensities of the diffracted beams are a function of the arrangements of the atoms in space and some other atomic properties. Thus, if the positions and the intensities of the diffracted beams (frequently referred to as reflections, spots or lines) are recorded, it is possible to deduce the arrangement of the atoms in the crystal and their chemical nature. A beam of radiation will only be diffracted when it imposed upon a set of planes in a crystal if the geometry of the situation fulfils quite specific law defined by Bragg’s known as Bragg’s law (shown in figure 2.2)

\[
n\lambda = 2d_{hk\ell}\sin\theta \tag{2.1}
\]

The above equation is known as the Bragg equation, where \( n \) denotes the order of diffraction, \( \lambda \) represents the wavelength, \( d \) is the interplanar spacing of hkl planes in crystal lattice and \( \theta \) signifies the Bragg angle [1].
Fig. 2.2 Schematic drawing of Bragg’s law

A typical diffraction pattern shows the intensity Vs 2θ plot. Each peak corresponds to a specific (h k l) plane of the sample. The broadening of the diffraction peaks is due to two factors:

1) Due to size of crystallite
2) Due to microstrain of crystallite

2.1.1 Broadening due to finite size of the crystallites

Scherrer (1918) first observed that small crystallite size could give rise to line broadening. He derived a well known equation for relating the crystallite size to the broadening, which is called “Scherrer Formula” [2]. Using this formula crystalline size can be calculated

\[ \beta_{\text{size}} = \frac{K \lambda}{L \cos \theta} \]

L = Average Crystallite Size
K = Scherer Constant, in the range 0.87 – 1.0, usually assumed as 0.9.
\( \lambda \) = The wavelength of the radiation
\( \beta \) = The integral breadth of a reflection (in radians 2θ) located at 2θ
2.1.2 Broadening due to crystallite micro distortions (strain)

According to Wilson [3] the broadening due to lattice strain may be expressed as follows

\[ \beta_{\text{strain}} = 4 \varepsilon \tan \theta \]

Where \( \varepsilon \) is the relative deformation of the interreticular distance: \( \varepsilon = \Delta d_{hkl} / d_{hkl} \)

2.1.3 Williamson-Hall Technique

As discussed above broadening of a diffraction peak is due to both lattice strain and crystallite size contribution. It is not easy to separate this contribution. Williamson and Hall in 1953 proposed a method [4-5] for deconvoluting size and strain broadening by looking at the peak width as a function of \( 2\theta \). Williamson – Hall assumed that both size and strain broadened profiles are Gaussian. Based on this assumption, a mathematical relation was established between the integral breadth (\( \beta \)), size (L) and the microstrain (\( \varepsilon \)).

According to W- H method the individual contribution to the broadening of diffraction peaks can be expressed by following equation [4]

\[ (\beta_{\text{measured}})^2 = (\beta_{\text{instrumental}})^2 + (\beta_{\text{strain}})^2 + (\beta_{\text{size}})^2 \]

Defining:

\[ (\beta)^2 = (\beta_{\text{measured}})^2 - (\beta_{\text{instrumental}})^2 \]

\[ \beta^2 = 4 \varepsilon \tan \theta + \left( \frac{0.9 \lambda}{L \cos \theta} \right)^2 \]

\[ \beta^2 \cos^2 \theta = 4 \varepsilon^2 \sin^2 \theta + \left( \frac{0.9 \lambda}{L} \right)^2 \]

Where \( \beta \) is the FWHM of the Bragg peaks (in radians), \( \theta \) is the Bragg angle and \( \lambda \) is the wavelength of the X-ray, \( L \) is particle size in nm and \( \varepsilon \) is micro strain. Obtained data are used to construct a linear plot of \( \beta^2 \cos^2 \theta \) as a function of \( 4 \sin^2 \theta \) \{see Eq. (2.1.3)\}. The intercept on y- axis and the slope of the best fit straight line...
through data points gives \((0.9 \frac{\lambda}{L})^2\) and \(4\varepsilon^2\) respectively. This gives the particle size and the micro strain.

2.1.4 Applications of X-ray Diffraction

1. It can identify unknown phase of the crystal.
2. Determination of lattice constant.
3. Determination of phase purity.
4. Determination and refinement of lattice parameters.
5. Investigation of phase changes.
7. Determination of crystallite size.

2.2 X-ray Absorption near Edge Structure (XANES)

X-ray Absorption Near Edge Structure (XANES) is a type of absorption spectroscopy and is also called as near edge X-ray absorption fine structure (NEXAFS). XANES is a region of x-ray absorption spectrum within ~50eV of the absorption edge. X-rays have sufficient energy to excite a core electron of an atom in an excited state which is below the ionization threshold state, or to the continuum which is above the ionization threshold thus creates a core hole. Core holes are very unstable in nature as they are extremely energetic (electronegative). The average life span of a core hole is around 1 femtosecond. A core holes are created when either a core electron absorbs an X-ray photon (X-ray absorption) or absorbs part of the X-ray photon's kinetic energy (X-ray Raman scattering). The core hole decays by emitting a fluorescence photon or auger electron [6].

- Absorption edge

When X-ray radiation falls on the sample, X-ray photon is absorbed by a specific type of core electrons (e.g. 1s electrons of Cu) and sudden increase of absorption appears. This gives rise to a so-called absorption edge in the XAS spectrum due to its vertical appearance. The name of the absorption edges is given as per the principle quantum number, n, of the excited electrons (table 2.1).
Table: 2.1 Absorption edges [6]

<table>
<thead>
<tr>
<th></th>
<th>K edge</th>
<th>L Edge</th>
<th>M Edge</th>
<th>N Edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>2s</td>
<td>3s</td>
<td>4s</td>
<td></td>
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<td>2p</td>
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<td>3d</td>
<td>4d</td>
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<td></td>
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</table>

The identity of the element is revealed by the amount of energy absorbed in X-ray absorption spectra. The important factor in this spectrometry is that the photoelectrons act as very sensitive probes which sense the charge distribution and the arrangement of the neighboring atoms around the absorbing atom [7]. The photo effect can take place if the photon energy is large enough. These results in the step like shape of the absorption spectrum: the increased photo absorption cross-section due to the knocking-out of an electron is called absorption edge (Fig. 2.3).

![Image of K-shell absorption edge of cobalt](image)

**Fig 2.3** K-shell absorption edge of cobalt [7]

The photoelectrons go to either unoccupied bound states or low-lying continuum states if the photon energy $h\nu$ is low. This part of the spectrum (Fig. 2.3)
2.3) is called the XANES region; the acronym stands for X-ray Absorption Near-Edge Structure. On its high-energy end, XANES extends up to Extended X-ray Absorption Fine Structure [7-8], EXAFS in short, where the photoelectron kinetic energy is high. Transition from XANES to EXAFS is smooth; as $h\nu$ is increased, the transition starts happening gradually. The thumb rule is near-edge structure ends approximately where the electron wavelength equals the distance from the absorbing atom to its nearest neighbors, which is about 40–50 eV above the edge. As electron’s Kinetic energy is small in case of XANES, scattering is strong on the neighboring atoms, while the effect of scattering is small in high energy region as in the case of EXAFS [7].

### 2.2.1 Sensitivity of XANES to Oxidation State

The energy of an absorption edge is measured at half-height or, more commonly, as the maximum in the first derivative with respect to energy. However, as shown in fig 2.4 edge spectra frequently has unresolved transitions superimposed on the rising edge.

![Fig 2.4 Expansion of the XANES region [9]](image)

These will affect any attempt to define unique edge energy. Despite this ambiguity, edge energies have proven extremely useful in determining the
oxidation state of the absorber. It is known that as the oxidation state of the absorber increases the energy of an edge increases. The reason is atoms with a higher oxidation state should have a higher charge, thus requiring more energetic X-ray to eject a core electron. This is called as electrostatic model. However, an alternative interpretation of edge energies treats the edge features as continuum resonances. In continuum resonance, core electron excites into a high-energy state (above the continuum) that has a finite lifetime. An example is the potential well created by the absorbing and scattering (nearest neighbor) atoms. As the distance between the absorber–scatterer becomes smaller, the energy of the continuous state increases. Both models predict an increase in edge energy with increasing oxidation state as higher oxidation-state metals have shorter bond lengths. For both the methods (electrostatic model & continuum resonance) it is very clear that the correlation between edge energy and the oxidation states are well established, and is widely used in coordination chemistry [9].

2.2.2 Multiple Scattering and XANES

Multiple scattering is particularly important in the XANES region. In principle, it is possible to determine the three-dimensional structure of the absorbing atom from analysis of the XANES features. The XANES region is quite sensitive to small variations in structure. This sensitivity is due to the fact that geometrical differences between sites alter the multiple scattering pathways and thus the detailed structure in the immediate vicinity of the absorption edge [9-10].

2.2.3 Bound State Transitions in XANES

From bound state transitions weakest pre-edge transitions (Figure 2.4) arise. In case of first row transition metal, transition to K edge arises from 1s→3d and is observed for every metal that has an open 3d shell. As such the 1s→3d transition is forbidden by dipole selection rules, it is however, observed due to direct quadrupole coupling and 3d + 4p mixing [9].
The sensitivity to 3d+4p mixing signifies that the intensity of the 1s→3d transition can be used as a probe of geometry. With the progressive increase in intensity the site is progressively distorted from a centrosymmetric environment (i.e., octahedral < square–pyramidal < tetrahedral) or it helps to distinguish between square–planar (i.e., centrosymmetric) and tetrahedral sites. Thus, the analysis of the 1s→3d transitions in detail can be used to investigate the electronic structure of the absorbing atom. The similar 1s→4d transition for second transition series metals is generally not visualized. These edges occur at higher energy, where monochromator resolution is worse and core-hole lifetimes, which determine the intrinsic line width of a transition, are much shorter [11].

This gives rise to broader edges and hence the weak 1s→4d transitions are undetectable. It is still possible for second row transition metals, to obtain information about the empty bound states by measuring data at the L3 and L2 edges, which have 2p→4d transitions [12]. These transitions are relatively sharp as the energy of the edges is low and the 2p→4d transition is allowed, thus making these transitions intense. Similar spectroscopic advantages (narrow lines, allowed transitions) are found in L edge studies of the first transition series metals [13]. In addition to excitations into the 3d (or 4d) shells, XANES can also be used to probe higher lying excited states. A complete series of “Rydberg” transitions can be seen for atomic spectra. The allowed 1s→4p transition is sometimes observed for first transition series metals [9].

2.2.4 Applications of XANES spectroscopy

From the XANES region chemical information like formal valence (very difficult to experimentally determine in a nondestructive way); coordination environment (e.g., octahedral, tetrahedral coordination) and subtle geometrical distortions of it can be extracted. Transitions can be seen of bound vacant states just above the Fermi level. This XANES spectrum can be used as a probe of the unoccupied band structure of a material.
2.3 Synchrotron Radiation

Synchrotron radiation (SR) has emerged as a powerful tool for basic and applied research in physics, chemistry, biology and industry because of its unique characteristics, namely as a broad spectrum, small beam size, small divergence, high brightness, short pulse duration and high degree of polarization.

Whenever a charge particle is accelerated or decelerated, it emits electromagnetic radiation. The acceleration can result in a change in speed or a change in the direction of motion. When a beam of charged particle is forced to move in a curved path under the action of the magnetic field which then experiencing centripetal acceleration and hence emits radiations. These radiations are known as synchrotron radiation. SR is emitted when a charge particle moving at relativistic speeds follows a curved trajectory shown in fig 2.5. The wavelength and the intensity of the emitted radiation depend upon the strength of the magnetic field, mass, charge and energy of the charged particles.

![Synchrotron Radiation Generation](image)

**Fig. 2.5** Synchrotron radiation generation

The total radiation spectrum that can be obtained from the synchrotron source is given in fig 2.6 shows the critical energy which is equal to \( E_c \) (KeV) = 0.665 BE^2.
The photon production is of extreme interest for spectroscopy, because SR has a number of outstanding properties:

- Continuum radiation from infrared to gamma ray region.
- High intensities, several orders of magnitude higher than rotating anode laboratory source (typically 10 orders of magnitude) as compared to a typical rotating anode source.
- High degree of collimation (~1mrad to 0.1mrad).
- Well-defined state of polarization; completely linear in the plane of electron orbit and elliptically polarized above and below the plane of the orbit.
- High brilliance of the source, because of the small cross section of the electron beam and high degree of collimation of the radiation.
- Time structure as short as 50ps.

![Synchrotron spectrum](image)

**Fig. 2.6** Synchrotron spectrum

- Quantitatively known characteristics which makes it a standard radiation source.
- Clean, ultra high vacuum environment ($10^{-9}$ to $10^{-10}$ Torr) and high stability of the electron beam. Thus synchrotron radiation spans the large gap...
between the far UV and X-ray range as well as being a unique X-ray source, and the unique combination of the above characteristics offers far-reaching possibilities for many fields of science and technology [14-15].

2.3.1 **General layout of synchrotron radiation source**

There are two major components of the synchrotron radiation source. They are storage ring and the beam line. The storage ring is designed to keep charged particles circulating under ultra high vacuum in a closed orbit at relativistic speed.

The major components of storage a ring are:

1. The injection system: It generates the electrons, accelerates them, and injects them in the vacuum chamber.
2. The vacuum chamber: It is made up of metal tube in which the electrons circulate along the closed trajectory under ultra high vacuum, a typically pressure of $10^{-10}$ to $10^{-11}$ Torr.
3. The radio frequency cavity system: It periodically acts on the circulating electrons, restoring the energy they loss because of the emission of synchrotron radiation.
4. The dipole bending magnets: It bends the trajectory of the electrons and forces them to circulate in a closed orbit inside the vacuum chamber of the storage ring.
5. Other magnets: e.g. quadruple magnets and sextuple magnets, which are necessary for the practical operation of the ring.
6. The insertion device: They consist of periodic arrays of magnets, which modify the trajectory of the electrons in a straight section of the ring.
7. The control systems: Including one or more computers, which monitor the status of the ring components and automatically or semi automatically make the changes in the different phases of operation.
8. The radiation shielding system: It prevents dangerous neutron and gamma radiation from reaching the areas accessible by the users and staff of the facility.

In synchrotron radiation ring, electrons are injected into ring and accelerated via oscillating electric field. This oscillation also forms the electrons into groups such that there is standing wave of electrons within the ring. Magnetic fields are used to bend the electrons path in to the shape of the ring. Since a change of direction of velocity is a form of acceleration, photons are emitted at each bend in the ring [16].

2.3.2 Beam line

Synchrotron radiation is very useful because of its wide spectral range, but one cannot use directly the synchrotron radiation from storage ring just like other laboratory sources because of the following reasons:

1. The special nature of the synchrotron radiation.
2. Safety from hazardous radiations.
3. Maintain UHV conditions in the storage ring. Hence there is need of a coupling system that connects the exit port of the storage ring to the experimental station. Such coupling systems are known as beam lines.

The beam line conveys the radiation emitted by dipole magnets and insertion device to the experimental chamber. The major components of the beam line are:

The monochromator: It selects the desired photon energy. More exactly, the monochromator eliminates photons of all energies except those in a narrow band centered on the desired value.

1. The vacuum system: It keeps the pressure in the beam line at levels compatible with its connection to the vacuum chamber of the storage ring.
2. The mirrors: it focuses and refocuses the radiation along the beam line.
The beam line control system: Typically based on a small computer, which operates the monochromator and in many cases, monitors the status of the vacuum system.

The experimental chamber: Each experimental chamber design for a specific line of experiments

Other miscellaneous components such as filters, baffles, collimators, and beam stoppers are necessary for the effective and reliable operation of the beam line.

### 2.3.3 X-ray Diffraction Beam line in Indus Synchrotron Radiation Source

With the advent of synchrotron radiation (SR) source, X-ray characterization techniques have been greatly benefited. SR has several unique properties, which makes it more advantageous over the X-ray from laboratory sources. SR gives about four to eight orders of magnitude higher photon flux, higher brilliance and most importantly, tunability in the X-ray region. We can afford to lose intensity in order to monochromatize X-rays with a narrow energy spread as magnitude of photon flux is very high. This narrow line width of recorded X-ray diffraction pattern contains lots of information. In addition, tunability of the SR enables one to record multi-wavelength anomalous dispersion data quickly and conveniently. XANES can also be easily carried out by the same beamline. These experiments on SR are especially useful in characterization of nanomaterials because of size induced broadening of XRD peaks and small scattering volume.

Indian synchrotron radiation source Indus-2 is a 2.5 GeV third generation source having critical wavelength 1.98 Å for radiation from bending magnets. A high resolution powder X-ray diffraction beamline (BL) has been used. The beamline is designed to operate in the photon energy range of 5-25 KeV [17].

An angle depressive X-ray diffraction (ADXRD) beamline installed on BL-12 bending magnet port of the Indus-2 synchrotron has been used for the present
work. Schematic of beamline is given in fig. (2.7) and photograph of beamline is in fig 2.8.

The size of electron source is approximately equal to 0.5 mm (H) x 0.5 mm (V). The beam acceptance of the beamline is 2 mrad (H) x 0.2 mrad (V). A plane and bendable platinum coated pre-mirror (M1) is used for vertical focusing/collimation of the X-ray beam, which is the first optical element. The Photon beam is monochromatized using a second optical element; Double Crystal Monochromator (DCM) with Si (311) crystals. Second crystal of the DCM is also used for the focusing of the beam. The platinum coated bendable post mirror (M2) used for vertical focusing/collimation of the beam is the third optical element. The beamline can be operated in high flux, moderate energy resolution or moderate flux, high-energy resolution modes and high angular resolution mode depending upon the experiment requirements.

Iron K-edge XANES spectra were recorded on the same ADXRD beamline in the transmission mode, using a pair of ionization chambers. The measured energy resolution (E/ΔE) of the beamline at ~ 8 KeV (Cu-K edge) is ~ 7000 and the energy repeatability is ~ 100 meV. The normalization of the XANES spectra was done for comparison among samples annealed at different temperatures.

Fig. 2.7 optical layout of beam line[18]
2.4 Total X-ray Reflection Fluorescence (TXRF)

2.4.1 Basic principle:

Total reflection X-ray fluorescence (TXRF) is a surface elemental analysis technique. It is used for the ultra-trace analysis of particles, residues, and impurities on smooth surfaces. TXRF requires extremely low-angle X-ray excitation of a polished sample surface. For the substrate the incident angle of the X-ray beam (typically 0.05°) is below the critical angle. It results in reflection of almost 100% of the excitation beam photons to the outermost surface layers of the sample. The fluorescence photons emitted from the surface atoms are characteristic of the element present. TXRF is basically an energy dispersive X-ray fluorescence (XRF) technique in a special geometry. Due to its unique configuration, the main advantage of TXRF over conventional XRF is that in it sample scattering is eliminated hence reduced measurement background contributions resulting in increased elemental measurement sensitivity [19]. The schematic of TXRF setup is shown in fig 2.9.
In the present work TXRF measurements have been performed on TXRF Beam Line 16 (BL-16) [20], Indian synchrotron radiation source Indus-2, RRCAT, Indore. The beamline -16 works in the X-ray energy range of 4-20 KeV. Using the micro-focused mode of the beamline, it is possible to examine a specimen for spatial distribution of elements. The μ-probe XRF beamline (BL-16) is at the 5º port of bending magnet. The optics of the BL-16 beamline have a double crystal monochromator (DCM) with Si (111) symmetric and asymmetric crystals (mounted side-by-side), a Kirkpatrick-Baez (KB) focusing optics and the combination of slits.

These slits are used in order to reduce the scattered x-ray background reaching the experimental station which usually radiates from different optical elements of the beamline. These slits also help to give collimated x-ray beam. The DCM is placed ~ 19m from the source and the KB is focusing optics placed ~ 4.7m apart from the DCM. The advantage of side-by-side mounting of the Si (111) symmetric and asymmetric crystals is to use the DCM optics either in the energy resolution mode or high flux mode with a minimal setup time. The KB focusing optics (Xradia, USA) includes a pair of Pt coated (25nm) elliptical bendable mirrors. The measured R.M.S. Slope errors (tangential) for the two elliptical mirrors were found to be better than 1.4 microrad whereas R.M.S. surface roughness were found to be ~ 0.3nm. The experimental stations of BL-16 beamline
consist of a 5-axis sample manipulator for microprobe XRF–scanning applications and a 2-circle goniometer for total reflection x-ray fluorescence and grazing incidence x-ray fluorescence measurements for thin layered materials characterization. Also, an optical microscope was installed for alignment of a sample in the x-ray beam path.

**Fig. 2.10** A schematic layout of the micro focus XRF beamline (BL-16) [22]

**Fig. 2.11** (a) Photograph of the beamline inside optics shielding hutch (b) XRF experimental Station [22]
Various detectors (Ionization chamber, Photodiode, single element SDD detector) are also available on the BL-16 beamline that makes possible to record high quality X-ray fluorescence data. Fig. 2.10 shows a schematic layout of the BL-16 beamline whereas Fig. 2.11 depicts the photographs for the beamline radiation shielding hutch and XRF experimental station.

2.5 Differential Scanning Calorimetry (DSC)

2.5.1 Basic principle:

Differential Scanning Calorimetry (DSC) is a thermal analytical technique which measures the difference in heat flow rate or the change in enthalpy ($\Delta H$) or heat flux between a sample and inert reference as a function of time and temperature when a substance undergoes either a physical or a chemical change [23]. Enthalpy is the amount of heat that is either absorbed or released. $\Delta H$ is a function of the specific heat capacity ($C_p$) of a material and change in temperature ($dT$) as is given by following equation,

$$\Delta H = \int C_p \, dT \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.5.1$$

$C_p$ is the amount of heat energy required to increase the temperature of 1g of a substance by 1°C at a constant pressure [23]. By measuring the displacement of heat flux from the baseline $\Delta H$ is measured. Heat flux ($Q$) is the quantity of heat transferred per unit time and mass ($m$) and is given by following equation.

$$\frac{Q}{m} = \nu, C_p \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.5.2$$

Where, $Q$ is heat flux, $m$ is mass of the sample, and $\nu$ is heating rate.

It is a technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Throughout the experiment both the sample and reference are maintained at nearly the same temperature. The temperature program for a DSC analysis is designed in such a way that the sample holder temperature increases linearly as a function of time. Heat capacity should be well defined over the range of temperatures to be scanned for the reference sample. The basic principle
underlying this technique is that whenever the sample undergoes a physical transformation such as phase transitions, more heat will need to flow to it than the reference to maintain both at the same temperature [24]. The flow of heat to the sample depends on whether the process is endothermic and exothermic.

1. **Endothermic**: A transition which absorbs energy.
2. **Exothermic**: A transition which releases energy.

### 2.5.2 DSC Instrumentation

Differential Scanning Calorimetry (DSC) is mainly concerned with the measurement of energy changes in materials. It is therefore applicable for all thermal analysis methods, since every physical or chemical change involves a change in energy. Samples taken are small and flat. They are kept in shallow pans so that there is a good thermal contact between sample, pan and heat flux plate shown in fig (2.12) & fig (2.13).

![Fig 2.12 Traditional Heat Flux DSC](image)

Symmetrical heating of the cell, and therefore S and R, is achieved by constructing the furnace from a metal of high thermal conductivity. Gas flow through the cell is required in order to assist in heat transfer, to sweep away volatiles and to provide the required atmosphere.
**Operation Details**

- DSC works in the range of typically up to 700°C and down to -140°C with a liquid nitrogen cooling system.
- Temperature calibration is carried out by running standard materials, generally very pure metals with accurately known melting points.
- Energy calibration may be carried out by using either known heats of fusion for metals, commonly indium, or known heat capacities. In the present work DSC measurements of the samples were done using TA Instruments MDSC model 2910 at a scan rate of 10°C /min (shown in fig 2.14).

*Fig. 2.13 Traditional Heat Flux DSC: Cell Schematic Diagram [25]*
2.5.3 **Applications of DSC:**

Following parameters can be obtained

- Crystallization time and temperature
- Reaction Kinetics
- Melting and Boiling Points
- Percent Crystallinity
- Specific Heat / Heat Capacity
- Glass Transitions
- Oxidative/Thermal Stability
- Heats of Fusion and Reactions

2.6 **UV -VIS - NIR Spectroscopy**

2.6.1 **Basic principle**

Electromagnetic radiations used in absorption spectroscopy are between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible
(VIS, 400-800 nm) regions. The absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule; hence it is also called as electronic spectroscopy. The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule [27]. Thus the broad absorption peak is obtained which is smooth and never very sharp as the electronic absorption is accompanied with a corresponding change in the vibrational and rotational energies (Fig 2.15).

\[ \Delta E = h\nu = \frac{hc}{\lambda} \]

Fig.2.15 Peak Broadening

The relationship between the energy absorbed (E) in an electronic transition and the frequency (\(\nu\)), wavelength (\(\lambda\)) of the radiation producing the transition is

\[ \Delta E = h\nu = \frac{hc}{\lambda} \]

Where, \(h\) = Planck’s constant
\(c\) = velocity of light, \(\Delta E\) = energy absorbed in an electronic transition in a molecule

Depending upon the energy difference between the ground state level to that of excited state of the absorption maxima of a molecule occurs; larger the difference between the energies, higher is the frequency of absorption and thus smaller will be the wavelength. The absorption band reflects two important characteristic; one is position of the band and other is intensity. The position of the band depends on the energy difference between electronic levels. While intensity
depends on the interaction between the radiation and electronic system as well as on the energy difference between the ground and excited state.

A convenient expression, which gives the relation between absorbance and path length, when the radiation travels within the system and the concentration of the species, can be derived from the **Lambert-Beer law** and is given as, shows the linear relationship between the absorbance and the concentration of a sample [28]. The method is frequently used in a quantitative way to find out the concentrations of an absorbing species.

When the radiation passes through a sample, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the sample and also a function of length of the path of radiation through the sample. Therefore,

\[
\log \frac{I_o}{I} = \varepsilon c l \quad \text{.........................2.6.2}
\]

Where

\( I_o \) = Intensity of the incident light (or the light intensity passing through a reference)

\( I \) = Intensity of light transmitted through the sample

\( c \) = concentration of sample

\( l \) = path length of the sample

\( \varepsilon \) = absorptivity or the molar extinction coefficient of the substance. It is a constant and is a characteristic of a given absorbing species. The ratio \( I / I_o \) is known as transmittance \( T \) and the logarithm of the inverse ratio \( I_o / I \) is known as the absorbance \( A \). Therefore,

\[
- \log \frac{I}{I_o} = - \log T = \varepsilon c l \quad \text{.........................2.6.3}
\]

\[
\log \frac{I_o}{I} = A = \varepsilon c l \quad \text{.................................2.6.4}
\]

\[
or A = \varepsilon c l \quad \text{.................................2.6.5}
\]
2.6.2 Determination of the optical energy gap using Tauc formula \[29\]

\[
\alpha h\nu = B(h\nu - E_g)^n
\]

\(n=1/2\) for direct band gap and \(n=2\) for indirect band gap.

Where, \(\alpha\) is absorption coefficient. With the help of \(\alpha\) band gap is determined.

We plot the photon energy \(h\nu\) vs \((\alpha h\nu)^2\) and \(h\nu\) vs \((\alpha h\nu)^{1/2}\) for direct and indirect band gap respectively. By fitting a straight line to this plot. The constant term of its equation is equal to \(E_g\).

**The UV-VIS-NIR Spectrometer:**

In single-beam (UV-VIS) absorption spectroscopy, obtaining a spectrum requires manually measuring the transmittance of the sample and reference at each wavelength. The double-beam spectrometer is designed to measure the transmittance of the sample and reference simultaneously.

**2.6.2 UV-VIS Instrumentation**

For the present work, the Lambda 950 versatile spectrometer was used which operates in the ultraviolet, visible (UV/Vis) spectral range as well as in the near infrared region. The spectrometer features a double-beam, double monochromator, and ratio recording optical system.

![Schematic diagram of a double-beam UV-Vis Spectrophotometer](image)
Some important facts:

1. Selection of the source or detector depends on the defined wavelength range.
2. The spectrometer scans from higher toward wavelength to lower wavelengths. The optional depolarizing filter (DP) accessory can be swung into the beam.
3. Lambda 950 consists of internal attenuators, which can be swung individually into the sample beam (SBA) and the reference beam (RBA).
4. This system is equipped with microcomputer electronics, controlled by PC.
5. The detectors are Photomultiplier R6872 for high energy in the whole UV/Vis wavelength range, while Peltier cooled PbS detector for NIR range.
6. Operating wavelength range is 175 nm–3300 nm.

2.8 Transmission electron microscope (TEM)

2.8.1 Basic Principle: Working principle of TEM is analogous to that of an optical microscope. But TEM uses electrons instead of photons as a source. As per the uncertainty principle, there is a fundamental limit on the spatial resolution, while using a beam of particles with de Broglie wavelength. Thus, smaller the wavelength of the source, higher will be the resolution of the system. In TEM electron beam of 100 KeV of wavelength 0.03Å can be used instead of photons (λ>1000 Å) and hence provides much higher resolution. The important condition in TEM analysis is that sample should be thin. The thin sample allows the beam of electron to pass through it without absorption. For 100KeV electron beam, the thickness of metallic sample should be of the order of a 1000Å. During TEM analysis, this thin sample is bathed with a collimated beam of accelerating electrons uniformly over the illuminated area. As electrons are negatively charged, they can be easily deflected in an external electric or magnetic field and can be accelerated using external potential. As the electrons travel through the sample, they are either scattered or are transmitted unaffected through the sample. The probability of scattering is described in terms of the interaction cross-section or the mean free path. The scattering can be elastic or inelastic. This results into a non
uniform distribution of electrons in the beam that comes out of the sample, which contains all the structural information of the sample [31].

![Ray diagram of electron beam for image & diffraction pattern](image)

**Fig. 2.17** Ray diagram of electron beam for image & diffraction pattern from a sample

The scattered (diffracted) electrons beam deflected away from the optical axis of the microscope are blocked using an aperture and thus the transmitted electron beam generates a contrast on the fluorescent screen depending on its varying intensity (shown in fig.2.17). If the objective aperture allows only the transmitted beam and cuts off diffracted beams, the image obtained on the screen is a “**Bright Field Image**” shown in fig 2.18. If the objective aperture allows only one of the diffracted beam to pass through and cuts of transmitted and other diffracted beams, the image obtained in such a case is called “**Dark Field Image**” shown in fig 2.19. The Bright Field (BF) and Dark Field (DF) imaging is very useful in identifying phases in the material.
In the case of nanomaterials the crystalline structures interact with the electron beam mainly by diffraction rather than absorption, though the intensity of the transmitted beam depends largely on the density and thickness of the material through which it passes. The intensity of the diffraction thus depends on the orientation of the planes of atoms in the crystal relative to the electron beam. The angular distribution of electrons due to diffraction can be viewed in the form of scattering patterns, usually called diffraction patterns, and spatial distribution of electrons can be observed as contrast in images of the sample.

**Fig. 2.18** Bright field image

**Fig. 2.19** Dark field image
Figure 2.20 shows the layout of the various components of a transmission electron microscope. The transmitted electron beam strikes the fluorescent screen and generates an image with varying contrast. The darker areas with higher contrast, are those from where fewer electrons have been transmitted due to high density or thickness of the sample while the areas of lower contrast show the areas in the sample, which have less density or thickness, and thus the number of transmitted electrons are present.

2.8.2 TEM Instrumentation

Electron beam transmitted from specimen forms a magnified image on the back focal plane of the image plane of the microscope. The magnified image is further magnified by intermediate lens, it can be viewed on a fluorescent screen, and recorded on a photographic film or a charged coupled detector [31].

Fig. 2.20 Showing the various components of a TEM [32]
For the present work Philips 200 kV TEM model CM200 has been used, which has a point resolution of 2.4 Å. Another advantage offered by electron beam is their ability to produce diffraction pattern. Area of the specimen can be selected from which the diffraction pattern is desired. This feature is known as a Selected Area Diffraction (SAD), which is useful in phase identification of a small area of the specimen.

**Fig. 2.21** Ray diagram two mode of operation in electron microscope having an objective and two projector lens imaging system (a) imaging mode of operation (b) Diffraction mode of operation [33]
Schematic diagram of a typical TEM imaging is shown in Fig. 2.21. Electrons emitted from the source (thermoionically from the LaB$_6$ crystal) are accelerated to 200 KeV. Normally 2eV is the energy spread of these accelerated electron beams. Thus, to a good approximation, the electron beam could be considered as a monochromatic beam. Number of electro-magnetic lens is used to form the probe and image. In order to control the size and divergence of the beam and minimize lens aberrations apertures are used. Between twin objective lens systems the specimen is located. The function of objective lens is to take the electrons emerging from the exit surface of the specimen and disperses them to create a diffraction pattern (DP) in the back focal plane and recombines them to form an image in the image plane. Fig. 2.21 (a) shows the imaging mode of operation. P1 is the first projector lens and is focused on the first image and forms a second image in the object plane of the second projector lens P2. P2, then forms final image on the viewing screen. In order to view the diffraction pattern, less current is allowed to flow through the lens coil of P1. This increases the focal length of the objective lens which is required, rather than the first image plane. The diffraction patterns are first focused on the object plane of P2 and finally on the viewing screen Fig 2.21 (b).

Electron diffraction (ED), like other diffraction techniques such as X-ray diffraction (XRD), maps the real space periodicity of the specimen on to reciprocal space or angular space, through the famous Bragg’s law $n\lambda=2dsin\theta$, where $n$ is the order of diffraction, $\lambda$ is the wavelength of radiation, $d$ is lattice spacing and $\theta$ is the Bragg angle. Analysis of diffraction pattern gives the lattice spacing of crystals. This enables us to determine the crystalline phase of the nanomaterials. In TEM we always get diffraction spots, which is not in the case for XRD. ED is more suitable for nanomaterials characterization because the desired region of the specimen can be selected. Ability of imaging with diffraction is the strongest feature of a TEM. In the present study, TEM has been used for analyzing the phase and size of the iron oxide, cobalt oxide and nickel oxide nanoparticles synthesized using the ash supported method.
2.9 Vibrating Sample Magnetometer (VSM)

2.9.1 Basic Theory

In external magnetic fields, magnetic materials have distinguished behavior. For ferromagnetic material, the magnetization versus magnetic field (M(H)) dependence is characterized by domain wall movement and magnetization rotation. According to the theory of Weiss a non-saturated ferromagnetism contains a number of small regions called domains. In these domains the local magnetization is homogeneous and reaches the saturation value. The direction of magnetization is not necessarily parallel in different domains. The walls of the domains act as a separator for different domains aligned in random directions [34].

![Diagram](image_url)

**Fig. 2.22** Alignment of domains with an applied magnetic field [35]

When an external magnetic field is applied, these domains can be forced to align in one direction as shown in Figure 2.22. But this process needs some energy and therefore the magnetization always lags behind the magnetizing field and results in a magnetic loop called as a B-H Loop.

The net macroscopic magnetization is zero in the absence of an applied magnetic field as the infinitesimal magnetic dipoles in most materials are randomly oriented (Figure 2.22 (A)). In the presence of an external magnetic field, the magnetic dipoles align themselves with the applied magnetic field (Figure 2.22 (B))
and (C)). When all the magnetic dipoles present is aligned in one direction material is said to be magnetically saturated (Figure 2.22 (D))

![Theoretical M-H curve](image)

**Fig. 2.23** Theoretical M-H curve [36]

### 2.9.2 Principle

Principle of Vibrating Sample Magnetometer (VSM) or Foner magnetometer [37] after its inventor Simon Foner is based on Faraday's law. It states that in a coil whenever there is a change in flux linking the coil an electromagnetic force is generated [38]. When a magnetic sample is kept in oscillatory motion it creates a time varying magnetic field in its surroundings due to its magnetization and a voltage will be induced in a coil placed close to the sample.

### 2.9.3 Working of a VSM instrument

The purpose of the VSM is to measure the induced magnetization of the sample. Sample is mechanically vibrated in a uniform magnetic field. This field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins, with the field if the sample is magnetic in nature. The stronger is the constant field, the larger the magnetization will be. This will create a net
magnetic dipole moment. This dipole moment of the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. As the sample is moved up and down, this magnetic stray field will change as a function of time and can be sensed by a set of pick-up coils.

Fig. 2.24 Schematic diagram of a VSM Instrument [39]

The alternating magnetic field will create an electric field in the pick-up coils according to Faraday’s Law of Electromagnetic Induction. This current is proportional to the magnetization of the sample. The greater the magnetization, the greater is the induced current. The induction current is amplified by a lock-in amplifier. The output measurement displays the magnetic moment \( M \) as a function of the field \( H \). A schematic diagram of the VSM instrument is shown in Figure 2.24 and Figure 2.25 shows a photograph of an instrument.
The unit of magnetic (dipole) moment is \([\text{Am}^2]\). The magnetic moment per unit weight in \([\text{Am}^2/\text{kg}]\) can be calculated if the sample weight is known. If also the density or the volume of the sample is known it is possible to calculate the magnetic moment per unit volume which corresponds to the magnetization in \([\text{A/m}]\).