EXPERIMENTAL TECHNIQUES USED FOR THE PRESENT STUDY

The properties of the materials can be analyzed by a number of experimental techniques. The knowledge of the instrumental techniques is required to analyze the materials in the field of Solid State Research. In this chapter, the instrumental techniques used for the present study are discussed. They can be subdivided into five categories 1. Elemental analysis, 2. Spectroscopy, 3. X-ray analysis, 4. Thermal analysis and 5. Low temperature (LT) studies as shown in block diagram Figure 2.1.

2.1 Elemental analysis

The chemical composition of the crystal has been analyzed by CHNS analysis and Atomic Absorption Spectroscopy.

2.2. Spectroscopy

Optics is a branch of Physics which deals with the behavior of light. It is clear from the relation $E=hc/A$, that light is a form of energy. Spectroscopy is a branch of optics which deals with the study of interaction of electromagnetic waves with matter. It is concerned with change in internal energy when a molecule absorbs or emits electromagnetic radiation in discrete counts or quanta. On absorption or emission of electromagnetic radiation, the molecules or atoms or ions of a sample vibrates from one
Figure 2.1 Block diagram of the experimental techniques
energy state to another. This absorption and emission of electromagnetic radiation helps to understand the nature of a molecules, chemical bonding and structure. Nowadays, various types of spectroscopic techniques are available. Among these, Ultraviolet-visible (UV-VIS), Fourier transform infra-red (FTIR), Photoluminescence (PL) and Electron paramagnetic resonance (EPR) spectroscopic analysis are used for the present study.

2.2.1 UV-VIS

Sun is the natural source of UV radiation. In laboratories, an electric arc of carbon, iron or other materials, mercury vapour lamps, tungsten-halogen lamp and discharge of electricity through hydrogen contained in quartz tubes are used as sources of UV light [55]. The ultraviolet spectral region ranges from 190 to 400 nm whereas the visible region is from 400 to 800 nm. UV-Visible spectroscopy is a most common technique used by chemists and physicists for material studies. It is the absorption or transmission measurement of different frequencies in the UV-VIS region by a sample. This technique is mainly used for structural elucidation, compound identification and energy gap determination.

2.2.1.1 Basic concepts

The absorption of electromagnetic radiation by the substances in the UV-VIS regions, changes the electronic structure of ions and molecules. Absorbance is directly proportional to the path length (b) and the concentration (c) of the absorbing substance. Beer’s law states that

$$A = ecb$$  

(2.1)
where $A$ is absorbance (no units), $\varepsilon$ is the molar absorptivity (1 mol$^{-1}$cm$^{-1}$), $b$ is the path length of the sample (cm) and $c$ is the concentration of the absorbing substance (mol l$^{-1}$). It is well known that the different compounds absorb radiation of different wavelengths. The amount of radiation absorbed can be measured in a number of ways that is in terms of

$$\text{Transmittance, } T = I/I_0 \quad (2.2)$$

$$\text{Absorbance, } A = \log (I/T) \quad (2.3)$$

where $I_0$ is the intensity of the incident radiation and $I$ is the intensity of the transmitted radiation. [56].

### 2.2.1.2 Working principle

The block diagram of UV-Visible spectrophotometer is shown in Figure 2.2. The electromagnetic radiation emitted from a source passes through a wavelength limiting device and impinges upon the sample in a cell. The unabsorbed or transmitted electromagnetic radiation passes through the cell, then strikes a detector and gets recorded. Commonly, two types of instruments are used. They are single beam and double beam spectrophotometers. For the present study, the double beam spectrophotometer (Perkin Elmer Lambda-35 Model) is used. The optical layout of the system is shown in Figure 2.3. A beam of light from a visible or UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic beam is split into two equal intensity beams by a half-mirror device. One beam passes through the sample and the other beam is the reference beam. The intensities of these light beams are then measured by electronic detectors and compared. This instrument has a wavelength range of 190 nm to 1100 nm and measures the
Figure 2.2  Block diagram of UV-Vis spectrophotometer
Figure 2.3  The optical pathway of UV spectrophotometer
wavelength in the entire range with ± 0.1 nm accuracy. The lamp change occurs automatically at 326 nm. Nowadays, UV-VIS spectroscopy finds applications in physical sciences, chemical sciences, biochemistry, biology and pharmaceutical research.

2.2.2 FT-IR

Infrared (IR) spectroscopy deals with the absorption of electromagnetic radiation in the IR region which results in changes in the vibrational energy of the molecules. It is a valuable tool to identify compounds, to analyse the chemical bonds and to determine functional groups. The IR radiation spans a section of the electromagnetic spectrum of wavenumbers from 13,000 to 10 cm\(^{-1}\) or wavelengths from 0.78 to 1000 µm [57]. This IR region is commonly divided into three subregions namely near IR, mid IR and far IR whose range of wavenumbers and wavelengths are given below

<table>
<thead>
<tr>
<th>Regions</th>
<th>Wavenumber</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near IR</td>
<td>13,000 – 4,000 cm(^{-1})</td>
<td>0.78 – 2.5 µm</td>
</tr>
<tr>
<td>Mid IR</td>
<td>4,000 – 200 cm(^{-1})</td>
<td>2.5 – 50 µm</td>
</tr>
<tr>
<td>Far IR</td>
<td>200 – 10 cm(^{-1})</td>
<td>50 – 1000 µm</td>
</tr>
</tbody>
</table>

Among these three regions, the mid IR region is used for the present work.

2.2.2.1 Basic concepts

Different functional groups absorb IR radiation of specific wavelengths. This leads to molecular vibration at various frequencies depending upon the elements and the type of bonds present.
The IR absorption is generally measured as transmittance (T). It is the ratio of radiant power transmitted by the sample (I₀) to the radiant power incident on the sample (Iᵢ). The absorbance (A) can be expressed as the logarithm of the reciprocal of the transmittance (T) [58].

\[
T = \frac{I₀}{Iᵢ} \quad \text{(2.4)}
\]

\[
A = \log \left( \frac{1}{T} \right) = \log \left( \frac{Iᵢ}{I₀} \right) \quad \text{(2.5)}
\]

2.2.2.2 Working principle

There are two types of spectrophotometers are available. They have
1. IR spectrophotometer and 2. Fourier transform infrared (FTIR) spectrophotometer. The IR spectrophotometer is a double beam spectrophotometer in which the light is dispersed by the monochromator. But this type of IR measurement is outdated due to high speed, high sensitivity, good resolution and accuracy of Fourier transform infrared (FTIR) spectrophotometer. In dispersive IR spectrophotometer, each component frequency is examined sequentially but in FTIR spectrophotometer all frequencies are examined simultaneously. Therefore, FTIR spectrophotometer has been applied to many areas that are difficult or nearly impossible to analyze by dispersive instruments.

For the present work, the FTIR spectra have been collected from Perkin Elmer 1600 series spectrophotometer. There are three basic components in an FTIR system namely radiation source, interferometer and detector. The undispersed light from the IR source is passed through the sample and the absorbances at all wavelengths are received at the detector simultaneously. A computerized mathematical manipulation known as
Fourier transform is performed on this data, to obtain absorption data for each and every wavelength. The block diagram of FTIR spectrophotometer is shown in Figure 2.4.

The interferometer unit of FTIR spectrophotometer is shown in Figure 2.5. A parallel beam of radiation is directed from the source to the interferometer consisting of a beam splitter (B) and two mirrors M₁ and M₂. The beam splitter is a plate of suitably, transparent materials to IR, such as KBr or CsI coated with germanium, so as to reflect just 50% of the radiation falling on it. Thus half the radiation goes to M₁ and half to M₂, returns from both these mirrors along the same path and is then recombined to a single beam at the beam splitter.

The recombined beam leaving (B) shows the constructive or destructive interference depending on the relative path lengths of B to M₁ and B to M₂. If path lengths are identical or differ by an integral number of wavelengths, constructive interference gives bright beam. If the difference is a half integral number of wavelengths, the beam cancels at B and destructive interference gives low intensity radiation.

If the source emits two separate monochromatic frequencies v₁ and v₂, then the interference pattern of v₁ and v₂ would overlay the interference caused by M₁ and M₂. The detector would see a more complicated intensity fluctuation as M₂ is moved, but computing the fourier transform of the signal is a rapid way of obtaining the original frequencies versus intensities emitted by the source. Taking the process further, even white beam from such a source is directed through a sample, before reaching the detector, sample absorptions will show gaps in the frequency distribution which after transformation yields a normal absorption spectrum [59].

Nowadays, FTIR can be used to identify chemicals and structural
Figure 2.4  Block diagram of FTIR spectrophotometer
Figure 2.5 The interferometer unit of FTIR spectrophotometer
analysis of natural products, polymers, coatings, paints, drugs and contaminants.

2.2.2.3 Sampling technique

In the present work, IR spectra have been collected for solid samples by KBr pellet technique. In this method, the solid sample is ground with pure KBr in the ratio of 1:10 and the mixture is pressed into a disc by using hydraulic press [60]. The use of KBr pellet method gives better spectra.

2.2.3 Photoluminescence (PL)
2.2.3.1 Basic concepts

Luminescence is a phenomenon of emission of light from a substance when it is not strongly heated. It is reflected by the term “cold light”. Whenever a material is absorbing some energy, it becomes a source of light by two processes. 1. The absorbed energy is converted into low quantum energy heat which diffuses through the material and emits thermal radiation. 2. The absorbed energy is localized as high quantum energy of atoms, which emits radiation called luminescence radiation. The quantity and quality of luminescence radiation are strongly dependent on the nature of the emitting material. Therefore, the study of luminescence helps to characterize material bodies. The process of luminescence is started by exciting the material with UV radiation, X-ray electrons, alpha particles, electric fields or energy that is liberated in chemical reactions. For the present study, it has been limited to the study of photoluminescence of solids.

The investigations of a luminescence of materials begin with the measurement of the optical absorption. When electromagnetic radiation
interacts with solids, the electrons may absorb the photon and go to an excited state. This process is known as optical absorption. Due to this optical absorption, transition occurs through the interaction of the electric vector of the electromagnetic radiation and the oscillating electrons of the molecules. After the absorption transition the electrons in the atom or molecule in an excited state relaxes to the lowest vibrational level of the excited state by dissipating the difference in energy as heat. The system is then in the relaxed excited state for a short duration. The electrons can return to the ground state accompanied by the emission of energy in the form of photons or heat. If photons are emitted, then the process is called fluorescence. The emission transition is usually at a lower energy than the absorption transition and the phenomenon is known as the Stokes shift. The Stokes shift is a direct consequence of the relaxation process that occurs after the optical absorption. Only the zero vibrational transition is expected to occur at the same energy in the absorption and emission spectra. The radiative part of the relaxation following the excitation is the essence of luminescence spectroscopy.

2.2.3.2 Working Principle

The functional block diagram and the optical path of the fluorescence spectrophotometer are shown in Figures 2.6 and 2.7. For luminescence measurements, VARLAN CARRY ECLIPSE employing 150 Watts Xe arc discharge lamp as the excitation source capable of operating in the region 200 nm to 900 nm is used with a red sensitive photomultiplier tube. The light beam from the xenon light source is condensed and let onto the excitation monochromator. A beam splitter splits the light beam and directs a fraction of it to a monitor detector, which serves to correct for intensity variation arising out of lamp fluctuations. In the excitation monochromator, the other
Figure 2.6 Functional block diagram of the Fluorescence spectrophotometer
Figure 2.7 Electrical and optical connections of the Fluorescence spectrophotometer
beam from the beam splitter is condensed by a lens and is used for exciting the sample. The fluorescence emission from the sample is dispersed at the emission monochromator. The same is detected by a photomultiplier tube and the output signal from the same is processed by an amplifier and is fed to the numerator side of the divider in which it is divided by the monitor electrical signal received earlier. The monitor signal obtained in this way is thus used for compensating variation in the intensity of the light beam from the lamp due to lamp fluctuations. The difference between the output signal from the emission monochromator photo-multiplier tube and the monitor electrical signal is amplified. The excitation and emission monochromators can scan over their ranges synchronously to the selected points in their ranges. The slit width may be varied to give resolutions between 2.5 nm to 15 nm for the excitation monochromator and between 2.5 nm to 20 nm for the emission monochromator in increments of 0.1 nm. For each data collection cycle, spectral data are detainted from the photomultipliers. The data signals undergo integration, conversion, averaging, digital filtering and ratioing before the computer receives the data.

2.2.4 EPR

2.2.4.1 Basic concepts

Electron Paramagnetic Resonance (EPR), also known as Electron Spin Resonance (ESR) or Electron Magnetic Resonance (EMR), was invented by the Russian physicist Zavoisky [61] in 1945. EPR phenomenon may be understood with a simple EPR sensing probe system such as spin $^6\text{Li}$ radical. The EPR of a free radical or coordination complex with one unpaired electron is the simplest of all forms of spectroscopy. It is a non destructive
technique for deducting and characterizing the paramagnetic defects/impurities in any material. When such material is placed in a magnetic field, the ground electronic state of centre splits and the splitting is called Zeeman splitting [62, 63]. The EPR spectroscopy deals with the study of absorption of electromagnetic addition between these levels. This is a resonance phenomenon and the absorption frequency is given by the relation

\[ g = \frac{hv}{\beta H} \]  

(2.6)

where \( g \) is the spectroscopic splitting factor, \( \beta \) is the Bohr magnetron, \( h \) is the Planks constant, \( H \) is the external magnetic field and \( v \) is the resonance frequency. In general case, the selection rule for EPR transition is detected by \( \Delta M_z = \pm 1 \). This method enables the determination of concentration and nature of paramagnetic centers including the valancy states, surrounding symmetry and interactions taking place with neighbors [64]. Very low level impurities corresponding to about \( 10^{11} \) spins/cm\(^3\) can be deducted under favorable conditions.

2.2.4.2 Experimental Setup

A typical EPR spectrometer consists of an electromagnet to generate a variable magnetic field and a generator of microwaves. It mainly required three essential components; a source of electromagnetic radiation, a sample and a detector. For a fixed microwave frequency magnetic field is varied to get the EPR absorption spectrum. The block diagram of EPR is shown in Figure 2.8. The electromagnetic radiation source and the detector are in a box called microwave bridge. The sample is in a microwave cavity, which is a metal box that helps to amplify weak signals from the sample. There is a magnet to tune the electronic energy levels. In addition, it has a console, which contains signal processing and control electronic circuits and a
Figure 2.8 The block diagram of EPR spectrometer
The basic requirements of an EPR spectrometer are, 1. A magnetic field to split the Zeeman levels apart, 2. Microwave source for EPR magnetic dipole transition, 3. A microwave detector in order to detect the absorption of power in the sample, 4. Means to sweep the magnetic field and record microwave absorption at same time, i.e., a data system and 5. a suitable sample.

To detect the EPR effect, one has to bring a paramagnetic sample into a magnetic field and measure its absorption as a function of frequency. Unfortunately, this can be only done with the necessary sensitivity for a very narrow frequency band. This problem is overcome by leaving the frequency fixed and sweeping the magnetic field in and out of resonance. The Figure 2.9 shows the general lay out of EPR spectrometer. The region labeled source contains those components that produce the excitation of electromagnetic waves and control the frequencies. The modulation and deduction system monitor, amplify and record the signal. The magnet system provides a stable homogeneous and linearity variable magnetic field within the desired range. Microwave generator takes microwave power from the wave guide ahead of the circulator and restores it, with adjusted power level and phase, behind the circulator (and resonator). With suitable settings, this arm not only allows for appropriate biasing of the power of the level at the detector, but also allows phase control and thus the choice of whether the absorption or dispersion signal from the spin system is detected.

2.3 - X-ray analysis

2.3.1 Basic concepts

X-rays were discovered by Roentgen in 1895. They are electromagnetic waves of short wavelength in the range of 10Å to 0.5 Å. The longer
Figure 2.9 The block diagram of a simple EPR spectrophotometer showing the essential components
wavelength x-rays are called soft x-rays and shorter wavelength are known as hard x-rays. These x-rays undergo diffraction phenomena by the crystal planes and therefore they are used for crystal structure analysis. The condition for the diffraction to occur is Bragg's law,

\[ 2d\sin\theta = n\lambda \]  

(2.7)

where \( n \) is the order of diffraction pattern, \( \lambda \) is the wavelength of the incident beam, \( d \) is the distance between the planes in the crystal and the \( \theta \) is the angle of diffraction. The instrument used for the structural analysis is x-ray diffractometer [65]. This diffractometer is of two types (i) Single crystal x-ray diffractometer and (ii) X-ray powder diffractometer (XRPD). Among these, x-ray powder diffractometer is used for the present study. And, it can be further classified into two types

(i) Angle dispersive x-ray powder diffractometer

(ii) Energy dispersive x-ray powder diffractometer

The difference between them is clearly shown in Figure 2.10. In angle dispersive x-ray powder diffraction (ADXRPD), the sample is fixed and the detector is moving (i.e. \( 2\theta \) is varying). The incident beam is of monochromatic radiation. The ADXRPD pattern gives the variation of intensity as a function of \( 2\theta \). In energy dispersive x-ray powder diffraction (EDXRPD), the sample is fixed and the detector is also fixed. The incident beam is of white radiation. The EDXRPD pattern gives the variation of intensity as a function of energy [66]. Among these, ADXRPD is used for the present work

2.3.2 Angle dispersive x-ray powder diffraction (ADXRPD)

The angle dispersive x-ray powder diffraction is a scientific technique for structural analysis of materials. As the name indicates, the sample is of
Figure 2.10 Difference between angle dispersive diffraction and energy dispersive diffraction
powder form consisting of fine grains of single crystalline material to be studied. The ADXRPD study of the samples has been carried out by using the RichSeifert x-ray powder diffractometer. The principle of ADXRPD is shown in Figure 2.11. The proportional counter is used as a detector. In order to get monochromatic radiation suitable foil filter is placed at the detector window. The sample is prepared by grinding the material to fine powder, then mixing it with quickfix and pressing between two glass plates. The flat sample thus prepared is exposed to radiation produced by the x-ray generator and the XRD pattern is recorded which gives the details of variation of intensity with \(2\theta\). The performance of the system is checked by using high purity of samples at ambient condition. The lattice parameters obtained are in good agreement with reported values. The advantage of this method is that it shortens the time of data collection considerably compared to film method.

2.4 Thermal analysis

Thermal analysis is an analysis in which a physical property of a substance is measured as a function of temperature under controlled temperature programme. There are different types of techniques such as TGA, DTA and DSC.

2.4.1 Thermogravimetric Analysis (TGA)

2.4.1.1 Principle

Thermogravimetry (TGA) is a technique which measures the change in weight of the sample when it is heated, cooled or held at constant temperature. It’s main use is to characterize materials with respect to their
Figure 2.11 The schematic diagram of the angle dispersive X-ray powder diffractometer set up
compositions. In TGA curve of single stage decomposition, there are two characteristic temperatures. 1. Initial temperature $T_i$ and 2. Final temperature $T_f$. Initial temperature $T_i$ is defined as the lowest temperature at which the onset of a mass change can be detected by thermobalance operating under particular conditions and $T_f$ as the final temperature at which the particular decomposition appear to be complete.

2.4.1.2 Instrumentation

The instrument for thermogravimetric (TG) analysis is called thermobalance. It consists of several basic components 1. Balance, 2. Furnace, 3. Temperature controller and 4. Recorder. The block diagram is shown in Figure 2.12

**Balance:** The thermobalance is of two types 1. null point and 2. deflection type. The null type balance is widely used. It incorporates a sensing element which detects a deviation of the balance beam from its null position. The restoring force is directly proportional to the mass change. Deflection balance of beam type involve the conversion of the balance beam deflection about the fulcrum into suitable mass change traced by photographic recording, electrical signals recording and recording by electrochemical device.

**Furnace:** The furnace and control system must be designed to produce nonlinear heating over the whole working temperature range of the furnace. And the temperature is maintained by temperature controller.

**Temperature measurement and Control:** Temperatures are commonly measured by using thermocouples. Chromel-alumel thermocouples are used for temperature upto 1100°C, whereas Pt/ (Pt-10% Rh) is employed for temperature upto 1750°C.
Figure 2.12 The block diagram of Thermobalance
Recorder: The digital data acquisition has been made and processed by using personal computer.

2.4.2 Differential Thermal Analysis (DTA)

Eventhough TGA has many applications, they are limited to the reactions, in which mass change has occurred. Therefore, researchers go for other two similar thermal techniques, differential thermal analysis and differential scanning calorimetry. Both these techniques have much wider applications than TGA technique. In DTA, the heat change within a material is monitored by measuring the difference in temperature (AT) between sample and the inert reference. This differential temperature is then plotted against temperature or time to get DTA curve.

2.4.2.1 Principle

DTA is a technique in which the temperature of the sample under investigation is compared with the temperature of the thermally inert material such as a-alumina. It is recorded with furnace temperature, as the substance is heated or cooled at a predetermined uniform rate. The range of temperature measurable in the course of DTA is much larger than TGA determination. Thus during TGA, pure fusion reaction, crystalline transition, glass transition, crystallization and solid state reaction with no volatile product would not be indicated because they provide no change in mass of the specimen. However, these changes are indicated during DTA by endothermal or exothermal departure from the baseline. Since DTA is dynamical method, it is essential that all aspects of the technique has been standardized in order to obtain reproducible results. Generally, phase transition, dehydration,
reduction and some decomposition reactions produces endothermic effects whereas crystallization, oxidation and some decomposition reaction produces exothermic effects.

2.4.22 Instrumentation

The Figure 2.13 has shown a block diagram of a differential thermal analyzer. It consists of the following basic components, 1. Furnace assembly, 2. Sample and reference holder, 3. Temperature programmer, 4. Amplifier and recorder and 5. Atmosphere control equipment for furnace and sample holder as shown in Figure 2.14.

Source of uniform heating: Nichrome furnace can be used upto 1300°C, Platinum and its alloys upto 2000°C. A special type of higher frequency induction heating may be used for higher temperature.

Temperature regulating system: The uniform rate of heating of furnace is ensured through electronic temperature regulators.

Specimen holder: It is designed to accommodate even small quantity of material and to give maximum thermal effect. It can be of Pt, Ni, stainless steel, Ag and alloys, such as Pt-Rh. Certain ceramic materials such as sintered alumina, silica, fire clay, heat resistant glass and even graphite have been recommended as material specimen holder for the sample under investigation and reference material like a-alumina.

Measurement of temperature: Rare metal alloy such as Pt- (Pt-10-13%Rh) are commonly used as thermocouple for measuring the temperature. For higher temperature upto 2000 °C, W-Mo thermocouple may also be used. Very thin thermocouple is inserted in the sample and reference holder.

Temperature recording system: Nowadays automatic pen and ink electronic recorder have been found to be more convenient.
Figure 2.13 The simple block diagram of DTA
Figure 2.14 The Schematic diagram of a differential thermal analyzer
(a) complete layout (b) furnace part sharing continuous heating of sample and standard
Direct recording of the heating curve: When a sample is heated at a constant rate, the temperature function $T$, is linear up to the moment when the sample undergoes change, its slopes represent the rate of heating which remains constant. At the moment, when an exothermic or endothermic changes takes place, the shape of the curve changes as shown in Figure 2.15.

2.4.3 Differential Scanning Calorimetry (DSC)

In DTA, thermal reactions are observed by measuring the deviation of the sample temperature from that of the reference material. This deviation affects the DTA curve and decreases the sensitivity. This is another technique called Differential Scanning Calorimetry (DSC) which has the advantages of keeping the sample and reference at the same temperature and heat flow into the sample and reference is measured. This can be achieved by placing separate heating devices in the sample and reference chambers. This is in contrast to the DTA, where both sample and reference are heated by the same source.

2.4.3.1 Principle

In DSC, the heat flow is measured and plotted against temperature of furnace or time to get a thermogram. This is the basis of DSC. The curve obtained in DSC is between $\frac{dH}{dt}$ in mJs$^{-1}$ or meals$^{-1}$ as a function of time or temperature. The deviation observed above the base (zero) line is called exothermic transition and below is called endothermic. The area under peak is directly proportional to the heat evolved or absorbed by the reaction and the height of the curve is directly proportional to the rate of reaction.
Figure 2.15 A representation of a DTA curve showing exotherm, endotherm and baseline changes.
2.43.2 Instrumentation

The block diagram of DSC instrumentation is shown in Figure 2.16. It essentially works on the temperature control of two similar sample holder in which average temperature of the sample and references increases at a linear rate. The differential temperature control circuit monitors the difference in temperature between sample and reference and automatically adjust the power to either the reference or sample chambers to keep temperature equal. In thermogram, the temperature of the sample and difference in power supplied to the two differential heaters is plotted on the x and y-axis respectively. The sample and reference compounds are provided with their own separate heaters, as well as their own separate temperature sensors. They are maintained at identical temperature by electrical controlling at the rate at which heat is transferred to them.

In DSC, sample from 1 to 100mg is placed in a sealed sample container. A wide range of heating rate (0.5 to 80°C/min) can be used. DSC measurements are generally sensitive energy detection of heat evolution or absorption at a rate less than millicalories per second. Electrical signals are amplified and recorded similar to TGA and DTA. During thermal process, reactions either liberate or absorb heat. Thus, when AH is negative, the reference heating device is energized and a negative signal is obtained. The peak area in DSC is proportional to the amount of sample, the heat of reaction and similar to DTA peak area.
Figure 2.16 The block diagram of a DSC instrument
2.5. Low Temperature Studies

2.5.1 Low Temperature Luminescence

The luminescence spectrum also helps to find the change in energy levels with respect to low temperature. The changes of spectra with temperature provide information regarding temperature time-dependent processes such as thermal line broadening and change of line positions. The dependence of the spectral intensity on the concentration of luminescence centers may provide information on the threshold of quenching and up-conversion. The instrumentation involved for the low temperature luminescence has been explained under section 2.2.3.1. The low temperature environment has been maintained by placing the sample in dewar flask in which liquid nitrogen has been poured.

2.5.2 Low Temperature Magnetic susceptibility

Magnetic susceptibility measurements provide a powerful tool for deducing useful informations of materials such as electronic configuration, type of magnetic material etc., [67, 68]. The variation of magnetic susceptibility with respect to temperature helps to study temperature dependent magnetic behavior, the magnetic phase transitions and the nature of the materials. The low temperature magnetic susceptibility has been carried out using 9 Tesla PPMS Physical Property Measurement System-Vibrating sample magnetometer (Quantum design USA). The schematic diagram of the PPMS experimental setup, is shown in Figure 2.17. The system is capable of measuring the electric properties such as dc and ac resistivities as well as current-voltage characteristics (I-V curves), Hall measurements and magnetic moments for any thin film, bulk material and
nano wires over the temperature range 4.2 - 300 K in the presence of applied magnetic fields upto 9 Tesla. For the present work, the sample has been maintained in the magnetic field of 500 Oe and the magnetic susceptibility measurements has been carried out in the temperature range of 4.2K to 300K during both cooling and heating process. In this experimental setup Helium is used for cooling and heaters are provided to warm the gas to particular temperature. The M-H study has also been carried out in the same setup upto the magnetic field of 10,000 Oe.
Figure 2.17 The outer view of Quantum Design PPMS