Chapter 2

EXPERIMENTAL TECHNIQUES USED FOR THE PRESENT STUDY

The characteristics of the materials are analysed by number of experimental techniques. The knowledge of the instruments and the conclusions drawn from the results are helpful to select the type of instrument required in the field of Solid State Research. In this chapter, the principles and techniques of various analytical instruments used for the present study are outlined. They can be subdivided into three categories as shown in Figure 2.1.

2.1 Spectroscopy

Spectroscopy is a branch of optics which deals with measurements and interpretation of absorbed or emitted electromagnetic radiation, when the molecules or atoms or ions of a sample vibrates from one energy state to another. It is a powerful tool in the field of atomic and molecular structural studies and also helpful to understand the nature of chemical bonding. Nowadays, various types of spectroscopic techniques are available. Among these, Ultraviolet-visible (UV-VIS) spectroscopy and Fourier transform infra-red (FTIR) spectroscopy are used for the present study.
Figure 2.1 The block diagram of the experimental techniques
2.1.1 **UV-VIS Spectroscopy**

UV-VIS spectroscopy is a most common technique used by chemist and physicist 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. The ultraviolet spectral region ranges from 190 to 400 nm whereas the visible region is from 400 to 800 nm. 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 [60].

### 2.1.1.1 Basic concepts

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

\[ A = s c b \]  

(2.1)

where A is absorbance (no units)

- e is the molar absorbtivity (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,

\[
\text{Transmittance, } \quad T = \frac{I}{I_0} \quad \quad (2.2)
\]
\[
\text{Absorbance, } \quad A = \log \left( \frac{1}{T} \right) = \log \left( \frac{I_0}{I} \right) \quad \quad (2.3)
\]

where \( I_0 \) is the intensity of the incident radiation and \( I \) is the intensity of the transmitted radiation. Thus, the absorbance can be calculated from transmittance data. If all the light passes through a substance without any absorption, then absorbance is zero and the percent of transmittance is 100%. If all the light is absorbed, then the percent of transmittance is zero and absorption is infinite [61].

### 2.1.1.2 Working principle

The block diagram of UV spectrophotometer shown in Figure 2.2 gives the working principle. 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 lay out of the system is shown in Figure 2.3.
Figure 2.2 The block diagram of UV-VIS Spectrophotometer
Figure 2.3  The optical pathway of UV spectrophotometer
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 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.

2.1.2 IR spectroscopy

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. Usually, the vibration will be in the form of stretching and bending. It is a valuable and formidable 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 jxm [62]. 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 jum</td>
</tr>
<tr>
<td>Mid IR</td>
<td>4,000 - 200 cm(^{-1})</td>
<td>2.5 – 50 jum</td>
</tr>
<tr>
<td>Far IR</td>
<td>200 - 10 cm(^{-1})</td>
<td>50 - 1000 jum</td>
</tr>
</tbody>
</table>
Among these three regions, the mid IR region is used for the present work.

2.1.2.1 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. For a given bond, there are several specific frequencies at which it can vibrate. The absorption of IR radiation increases the frequency of molecular vibration which in turn excite the bond. For any given transition between two states, the light energy absorbed must be equal to the difference in the energy between the two states [63].

\[
\text{Difference in energy states} = \text{Energy of light absorbed} \\
E_i - E_0 = h \epsilon A, \quad (2.4)
\]

where \( h \) - Planck’s constant
\( c \) - velocity of light and
\( \lambda \) - wavelength of light.

The IR absorption is generally measured as transmittance (T). It is the ratio of radiant power transmitted by the sample (\( I_t \)) to the radiant power incident on the sample (\( I_i \)). The absorbance (A) can be expressed as the logarithm of the reciprocal of the transmittance (T) [64].

\[
T = \frac{I_t}{I_i} \quad (2.5) \\
A = \log(I_i/I_t) = \log \left( \frac{I_i}{I_t} \right) \quad (2.6)
\]
2.1.2.2 Working principle

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 analyse 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 Mj 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 Mj and half
Figure 2.4 The block diagram of FTIR spectrophotometer
Figure 2.5 The interferometer unit of FTIR spectrophotometer
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 Mi and B to M2. If path lengths are identical or differ by an integral number of wavelengths, constructive interferences 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 Vi and v2, then the interference pattern of vj 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 resultant 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 [65].

Nowadays, FTIR can be used to identify chemicals and structural analysis of natural products, polymers, coatings, paints, drugs and contaminants.

2.1.2.3 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 [66]. The use of KBr pellet method gives better spectra.

2.2 Crystallography

Crystallography is a branch of science which deals with geometric structure of crystal lattices by looking at the image of the crystal under an x-ray beam. Modern crystallography is based on the x-ray diffraction of crystals. The x-ray diffraction which plays an important role in the field of material science, is based on Bragg’s law,

\[ 2d \sin \theta = nk \]  

where \( n \) is the order of diffraction pattern, \( X \) 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 [67]. 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 2.6. In angle dispersive x-ray powder diffraction (ADXRPD), the sample is fixed and
Figure 2.6 The difference between angle dispersive diffraction and energy dispersive diffraction

ANGLE DISPERSIVE DIFFRACTION

\[ \lambda = \text{constant} \quad \theta = \text{variable} \]

ENERGY DISPERSIVE DIFFRACTION

\[ \theta = \text{constant} \quad \lambda = \text{variable} \]
the detector is moving (i.e. 20 is varying). The incident beam is of monochromatic radiation. The ADXRPD pattern gives the variation of intensity as a function of 20. 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 [68].

2.2.1 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 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 Rich Seifert x-ray powder diffractometer. The principle of ADXRPD is shown in Figure 2.7. 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 20. 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.
Figure 2-7 The schematic diagram of the angle dispersive x-ray powder diffractometer set up
2.2.2 Computational method of simulating ADXRPD

Computational material science has emerged as a new discipline in science and technology. The theory allows us to interpret experimental data and also serves as an aid, in the search for novel materials and their characterisation. The structures of these crystals are also confirmed by the theoretical calculation of x-ray intensities using Lazy-Pulverix programme [69]. The comparison of powder patterns is a standard procedure in the characterization of solid state materials. It is a crystallographic problem which contains pitfalls for the people with a limited knowledge of crystallography. It was therefore desirable to search for a computer program that does not jely upon this knowledge and which nevertheless gives reliable results. Lazy-Pulverix is a computer program which helps to calculate the powder patterns from the known information necessary to correctly describe a crystal structure. The information includes the lattice parameter, the debye-waller factor, the space group symbol, the atomic coordinates and chemical symbols of atoms contained in one asymmetric unit. All other parameters required for powder pattern calculations include general equivalent point positions, the multiplicities of atoms in special positions, the laue symmetry, the scattering factors with proper corrections for anomalous dispersion and so on. These parameters require a certain minimum crystallographic knowledge and are more burdensome to retrieve. The main advantage of the Lazy-Pulverix programme is that it derives them automatically from the space group and element symbols. The program also allows a graphical representation of the powder pattern to be printed to any desired resolution.
Lazy Pulverix is written in fortran language and it consists of two programs which are run one after the other. The first routine Lazy reads the data cards and prepares the input for the second routine Pulverix, which is the main routine for calculating the powder patterns. Lazy derives the equipoints, the conditions for systematic absent reflections, the atomic form factors and the coefficients for anomalous dispersion. Scattering factors are approximated by the analytical function.

\[ f(\sin \theta/\lambda) = \sum_{i=1}^{4} a_i \exp (-b_i \sin^2 \theta/\lambda^2) + C \]  

(2.8)

The coefficient \(a_i\), \(b_i\) and \(C\) are called up by the program through the element symbols. The values for the dispersion correction, the coherent neutron scattering lengths and the most frequently used wavelengths are also accessible to the program.

Provisions are available to get the output for a variety of experimental techniques such as diffractometers, Debye-Scherrer and different Guinier cameras.

Pulverix is an extended version to calculate the position of the diffraction lines from Bragg's law and their d-spacings. The diffraction intensity \(I_{hkl}\) is calculated as

\[ I_{hkl} = MLP F_{hkl}^2 \]  

(2.9)

where \(M\) is the multiplicity factor of a powder line, \(L\) is the Lorentz factor and \(P\) is the polarization factor. The structure factor \(F_{hkl}\) is defined by
\[ F_{hkl} = \sum_{j} f_j O_j \exp \left[ 2\pi i (hx_j + ky_j + lz_j) \right] \exp \left( -B_j \sin^2 \theta / \lambda^2 \right) \]  

(2.10)

where \( f_j \) is the atomic or nuclear scattering factor of atom \( j \), \( Q \) represents the unit cell, \( O_j \) is the occupation factor of site \( x_j, y_j, z_j \) for atom \( j \) and \( B_j \) is the Debye-waller factor in \( \AA^2 \) for atom \( j \). The program output gives the tabular listing of \( hkl \), \( d \) spacings, \( 2\theta \) values, structure factors, intensities, \( 1/d^2 \) and \( \sin^2 \theta \) values, along with graphical representation of the powder pattern of any desired resolution in which the reflections are identified by their \( hkl \) values. In complex powder patterns where several reflections may fall within a small interval, the number of the reflections within the resolution interval and the \( hkl \) value of the strongest reflections are given.

2.2.3 Energy dispersive x-ray powder diffraction (EDXRPD)

In the energy dispersive x-ray powder diffractometer, the incident beam consists of white radiation and the angle \( \theta \) is fixed for all planes. The different sets of planes will reflect a set of different wavelengths into a counter which is fixed at an angle \( 2\theta \). If the counter is connected to a multichannel analyzer, the reflected wavelengths can be sorted out on the basis of their energies. This technique was first developed by Giessen, Gorden and Buras et al based on Bragg’s law.

The Bragg’s law can be rewritten in terms of quantum of energy \( E \) as

\[ E = hv = hc/\lambda \]  

(2.11)
We know

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

Substituting (2.7) in (2.11) and \( n = 1 \),

\[ E = \frac{hc}{2d \sin \theta} \]

\[ Ed = \frac{hc}{2 \sin \theta} \quad (2.12) \]

The equation (2.12) shows that the LHS is constant when \( \theta \) is constant. Therefore, the measurement of \( E \) will give the spacing of \( d \) of each set of planes and their corresponding indices (hkl) can be found out. The EDXRPD is much faster when compared to the conventional method of ADXRPD, because the diffraction pattern is acquired simultaneously in EDXRPD rather than serially in ADXRPD. Typically, in case of EDXRPD, the entire pattern can be recorded in 1 to 5 minutes whereas the conventional method requires over an hour.

The experimental arrangement of EDXRPD is shown in Figure 2.8. The incident beam of x-ray white radiation is produced by Rigagu rotating anode x-ray generator. The sample is made thin by using soft emery paper and it is placed on the goniometer base. The Ge detector converts the detected radiation into electrical signal and further amplified by the pulse amplifiers and the spectrum is collected by the multichannel analyzer.
Figure 2.8 The experimental arrangement of EDXRPD

1. SAMPLE
2. GONIOMETER BASE

RIGAGU ROTATING ANODE X-RAY GENERATOR

Ge DETECTOR

PULSE AMPLIFIER

MCA
2.23.1 **Germanium detector**

The germanium detector is a semiconductor detector which produces pulses proportional to the absorbed x-ray energy with better energy resolution than any other counter. A high purity planar Ge detector of active volume of 200 mm$^2$ was used. This photon detector system provides efficient conversion of the detected radiation into a measurable electrical signal which appears as an output voltage pulse with amplitude proportional to the incident photon energy. The heart of the system is a single crystal of Ge that can withstand high reverse voltage at cryogenic temperature. Ge with its highest atomic number and larger photon absorption cross section is more suited to the detection of higher energy photons than the lithium drifted silicon detectors. In order to achieve a good energy resolution, the semiconductor must be cooled to liquid nitrogen temperature 77 K.

The electrical signals produced by this semiconductor detector are similar in magnitude to those produced by an ionization chamber. The detector is ideal for the energy range of 3 to 1000 keV, delivering clean spectra with high efficiency. Below 3 keV and above 1000 keV, the efficiency drops down rapidly.

2.23.2 **Multichannel pulse height analyzer (MCA)**

All the counters produce pulses having an amplitude proportional to the energy of incident x-rays. Electrical circuits can distinguish between pulses of different amplitude and so in turn distinguish between the x-rays of different energies (wavelengths). One such electric circuit
called multichannel pulse height analyzer is used in EDXRPD. It has a thousand channels. A counter receives incident radiation of many wavelengths. The MCA separates pulses from this counter, by sorting pulses depending upon their size or amplitude. It has three important functions known as digitizing, sorting and storage and display.

Digitizing: An analog to digital converter (ADC) converts the analog information contained in each pulse (amplitude in volts) into digital form, suitable for storage in a memory.

Sorting and storage: These are performed in the memory of the MCA. If the x-ray energy range to be examined extends from 0 to 20 keV and the MCA has 1000 channels, then each channel spans an energy range of 20 eV and stores the corresponding data.

Display: The contents of the MCA memory that is total counts in each channel, may be displayed visually as counts versus channel number (i.e. counts versus x-ray energy) on a TV screen or by an X-Y plotter.

So, the operation of MCA in performing pulse-height analysis may be summarized as follows. A large number of fixed channels covers the energy range and all channels simultaneously receive the count rate information appropriate to each channel [70].
2.2.4 • Applications

This XRPD finds wide range of applications in various fields such as Geology, Material Science, Environmental Science, Chemistry, Forensic Science and Pharmaceutical industry. It is used

- to find the orientation and quality of single crystal
- to determine the crystal structure and structure of polycrystalline aggregates
- to deduce phase diagrams
- to determine order, disorder transformation
- to do chemical analysis and to identify the elements in the sample
- to confirm the formation of compounds [71].

2.3 Electrical resistivity

Electrical resistivity is a powerful tool in the field of materials research. The nature of variation of resistivity with pressure, temperature, magnetic field, concentration or any other variable gives the direct information on the processes being studied. The electrical resistivity (ρ) study can be carried out by three important methods (i) Two probe method (ii) Four probe method and (iii) Vanderpauw method.

The two probe method is shown in Figure 2.9. In this each probe serves as a current and voltage probe. The total resistance $R_T$ between the two probes is given by
Figure 2-9 The two probe method
\[ R_t = \frac{V}{I} = 2R_c + 2R_{sp} + R_s \]  \hspace{1cm} (2.13)

where \( R_c \) is the contact resistance at each metal probe-sample contact, \( R_{sp} \) is the spreading resistance under each probe and \( R_s \) is the sample resistance. The contact resistance arises from the contact of the mechanical metal probe with the sample. The spreading resistance accounts for the resistance encountered by the current when it flows from the small metal probe into the sample. Unless \( R_c \) and \( R_{sp} \) are accurately calculated, \( R_s \) cannot be accurately determined from the measured resistance and therefore, this method is more difficult to interpret. A solution to this problem is the use of the four probe method.

In the four probe method, two probes carry the current and the other two probes sense the voltage as shown in Figure 2.10. This method was originally proposed by Wenner [72], to measure the earth’s resistivity and this method is referred to as Wenner’s method in geophysics. The advantage of the four probe method over the two probe method is that the four probe method neglects the contact resistance and spreading resistance. Although the two current carrying probes still have the contact and the spreading resistance associated with them, it will not affect the two voltage probes. This is because, the voltage is measured either with a potentiometer which draws no current at all or with a high impedance voltmeter which draws very little current. The two parasitic resistances, \( R_c \) and \( R_{sp} \) are negligible in either case because the voltage drops across are negligibly small due to the very small current that flows through them.
\[ V = V_{fg} \]

Figure 2-10 The four probe method
In the four probe method, if ‘A’ be the cross sectional area of the sample which is the product of the breadth ‘b’ and the thickness ‘t’ of the sample and ‘l’ be the distance between the voltage leads (Figure 2.10), the resistivity ‘\( \rho \)’ is calculated by using the formula,

\[
\rho = \frac{RA}{l} \quad (2.14)
\]

\[
= R \frac{b \times t}{l}
\]

\[
\rho = \frac{V}{l} \frac{b \times t}{l} \quad (2.15)
\]

where ‘V’ is the voltage measured between two inner leads and ‘I’ is the constant applied current. Thus, four probe is a powerful monitoring tool for uniform and regular shaped samples.

For irregular shape samples, the Vanderpauw method [72,73] can be employed for measuring the electrical resistivity. This method permits the measurement of resistivity of an isotropic sample of uniform flat thickness but with arbitrary shape, if it meets the following criteria:

- the contacts are at periphery of the sample
- the contacts are sufficiently small
- the sample is uniform in thickness
- the sample is homogenous and
- the sample is simply connected, that is, it does not contain holes.
Since the samples used for the present study, can be cut into required rectangular shapes, four probe method has been followed for the present study under pressure. An overview of high pressure generating techniques is discussed first in the forthcoming section.

2.3.1 High pressure generating techniques

Recent developments in high pressure technology have transformed pressure as an effective tool for discovering new phenomena and exploring new materials. Pressure is defined as force per unit area. The units of pressure are atmosphere, pascal, kilobar and gigapascal. The high pressure generating techniques can be classified into two categories namely, static pressure and dynamic pressure. The static method is a laboratory method in which the uniaxial load is converted into hydrostatic or nearly hydrostatic pressure, by employing suitable geometry. In this case, the pressure is generated in steps. However, this static pressure is further classified into hydrostatic and quasi hydrostatic based on the pressure transmitting medium used. In the first category of hydrostatic method, liquids and gases are used as pressure transmitting medium. They transmit the pressure hydrostatically due to negligible internal friction. In the second category of quasi hydrostatic method, soft solids are used as pressure transmitting medium. They produce nearly hydrostatic or quasi hydrostatic environments due to their finite shear strength.

For dynamic pressure method, shock wave technique is a good example. In this method, pressure is generated within a very short duration of few micro seconds and this poses difficulties in carrying out
the measurements. Therefore, static pressure methods are preferred in laboratories [74]. Among these, opposed anvil devices are widely adopted in high pressure experiments due to the simple construction, ease of operation and economy. In the present work, opposed anvils made up of EN24 alloy steel are used. Before describing the opposed anvil technique, the important role of gasket and pressure transmitting medium is to be discussed.

2.3.2 Gasket materials

The main function of the gasket is to hold the sample in the sample assembly without squeezing while applying pressure. It should have three independent functions: yielding, confining and support. The first function of the gasket is that of “yielding” at a sufficiently small load to compress the content of the high pressure cell, to generate the pressure. The second function is that of confining the high pressure cell content, thereby sealing the high pressure region. The tasks of yielding and confining are contradictory and somehow have to be reconciled. The third function is that of “support”. The gasket is subjected to a large pressure difference. The inner edge would be at the full pressure generated within the chamber whereas the outer edge would be at atmospheric pressure. Therefore, the pressure exerted by the gasket against the anvil components should be gradually decreased from the full chamber pressure at the inner edge to the atmospheric pressure at the outer edge of the gasket [75].

The last factor to be considered is critical thickness [76]. It is the thickness at which the pressure is transmitted uniformly throughout the
area. It has been shown that the pressure distribution depends critically on the gasket thickness and the critical gasket thickness is given by \( h_c = 0.055 \times \text{(working diameter of the anvil)} \) above which the radial pressure gradient becomes large. So, the gasket thickness should be less than or equal to critical thickness.

Some of the examples of gasket materials are pyrophyllite, talc, boron, lithium hydride and mica sheet. In the present study, pyrophyllite is used as the gasket material. It has been found that, for a 10 mm dia pyrophyllite gasket, \( h_c \) is 0.25 mm.

2.3.3 **Pressure transmitting medium**

The main purpose of using a pressure transmitting medium is to transfer the pressure uniformly to the sample under investigation. They can be solids such as pyrophyllite, steatite, NaCl, KC1 and AgCl; liquids such as methanol, ethanol, water, n-pentane, isopentane, butane and propane and gases such as helium, neon and argon. An ideal pressure transmitter should satisfy the following requirements. It should be a soft solid or fluid, electrically insulating, easy to handle, non-toxic, non-flammable, easy to fabricate in the desired shape, cheap, readily available, thermally stable, easy to seal within the high pressure enclosure, low compressibility, low thermal conductivity, low electrical conductivity, chemically inert and optically transparent. It is not possible practically to think of a material satisfying all the requirements [75]. Depending upon the performance and requirements of a particular experiment, the pressure transmitting medium is to be chosen. In the present study, steatite is used as a pressure transmitting medium.
2.3.4 Experimental set up for high pressure electrical resistivity

The opposed anvil high pressure device is used for present electrical resistivity measurement. The opposed anvil is a high pressure device in which the pressure is generated within a thin sample held between the end faces of two pistons. It is sometimes referred to as the “squeezer”. Bridgmann, the father of high pressure research first generated high pressure up to 100kbar, by squeezing a pair of pistons with their truncated cones opposite to each other. By adopting this simple geometry, the truncated cones of small surface can withstand pressure much higher than the compressive strength of the material. In other words, when small pressure applied to large area is transferred to small area, high pressure is generated. The principle is known as the “Principle of massive support” and is shown in Figure 2.11 [77].

The experimental set up used for high pressure electrical resistivity study is schematically shown in Figure 2.12. The anvils are made up of EN24 alloy steel with composition C - 0.4%, Mn - 0.6%, Ni - 1.55%, Mo - 0.3%), Cr - 1.1% and balance % Fe, hardened to RC60. The working face of the anvil is 10 mm dia and the outer diameter is 99 mm. The taper angle is 10° in order to get maximum massive support [78]. The load is applied by using a 100 ton hydraulic press and the sample cell assembly is placed between the two opposed anvils.

Sample cell assembly: The heart of the experiment is the high pressure cell in which the sample and the electrical leads are assembled
Figure 2.11 The pair of truncated cones describing the principle of massive support
Figure 2.12 The experimental setup for electrical resistivity measurements.
as shown in Figure 2.13. The gasket is a pyrophyllite disc which has a 10 mm outer diameter, a 2 mm inner diameter and a thickness of 0.25 mm. Steatite of 2 mm dia which serves as the pressure transmitting medium is placed in the hole at the centre of the pyrophyllite. The sample is placed over the steatite disc. Tungsten or copper wires are used as electrical leads. Another disc of pyrophyllite of the same dimensions is placed on the initial gasket. Quickfix is applied at the circumference of the gaskets so as to form a cell arrangement. Another disc of steatite is placed on the sample cell. The whole sample cell assembly have been made under a microscope. A hollow cylinder insulation cover is tightly held at the circumference of the anvil containing the sample cell. Another anvil is gently placed on the cell, in such a way that, its face rests exactly on the sample cell assembly. The entire setup is kept centrally between the jaws of the hydraulic press. By applying the load from the hydraulic press, the anvils are pressed against each other. The frictional forces acting between the anvil face and the gasket material, prevent the extrusion of the material and the high pressure is transmitted to the sample under investigation. At constant current, the voltage is measured for various pressures. A constant dc current source and a high sensitive digital micro voltmeter have been used for measuring the current and voltage.

23.5 Pressure calibration

The pressure calibration has been done using the bismuth sample. A graph is drawn with pressure in tons along the X-axis and the sample voltage along the Y-axis as shown in Figure 2.14a. The graph shows
Figure 2.13 The high pressure sample cell assembly
Figure 2.14

(a) The variation of the sample voltage of Bismuth with load

(b) The pressure calibration using Bismuth
phase transitions which are already known for bismuth at 25.5 kbar, 27 kbar and 77 kbar. From this, a calibration graph is drawn with oil pressure in tons along the X-axis and the actual pressure along the Y-axis as shown in Figure 2.14b. This graph gives the values of the actual pressure in kbar corresponding to any value of the hydraulic pressure in tons.