CHAPTER 2

INSTRUMENTATION AND CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

This chapter discusses about the various instrumentation and characterization techniques that are mostly used in nanomaterials and nanostructures. Commonly structural and morphological analysis was done through X-ray powder diffraction (XRD) and scanning electron microscope (SEM). The optical spectroscopy has been broadly used for the characterization of nanomaterials and the techniques can be generally categorized into two groups: absorption or emission spectroscopy and vibrational spectroscopy. The electronic structures of atoms, ions, molecules or crystals through exiting electrons from the ground to excited states (absorption) were found through UV-vis absorbance spectra. Fourier transform infrared spectroscopy (FTIR) can be used to identify the functional groups and vibrational modes of the materials.

All the electrical characterizations like impedance, ac conductivity, dielectric constant, dielectric loss were done by Hioki-3532-50 LCR Hitester. The high pressure electrical resistivity was measured by using Bridgman opposed anvil devices employing four probe method with a maximum pressure limit of 8 GPa.
2.2 STRUCTURAL AND MORPHOLOGICAL STUDIES

2.2.1 X-ray Powder Diffraction

X-rays are electromagnetic radiation of exactly the same nature as light but of very much shorter wavelength about 1 Å. Max Von Laue in 1912, discovered that the crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray powder diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases.

2.2.1.1 Principle

X-ray powder diffraction is based on the constructive interference of monochromatic X-rays and a crystalline material. These X-rays are generated when electrons moving at high speed are directed to a metal target; a small percentage of their kinetic energy is converted into X-rays. The X-rays emitted by the target consist of a continuous range of wavelength and is called white radiation the minimum wavelength in continuous spectrum is inversely proportional to the applied voltage, which accelerates the electron towards the target. If the applied voltage is sufficiently high in addition to the white radiation, the target also emits a characteristic radiation of specific wavelength and high intensity. The radiation emitted by a target includes both types of radiation. In spectroscopic notation, the characteristics radiations are named as $K_\alpha, K_\beta, K_\gamma$, etc. $K_\alpha$ radiation has high intensity and is commonly used for diffraction studies. The wavelength of this radiation for a typical copper metal target is 1.54056 Å. A beam of X-rays directed at a crystal interacts with the electron of the atom that constitutes the crystal.
The diffraction effect produced by the three dimensional grating provided by the crystal obeys Bragg’s law. X-rays penetrate into the solid non-destructively and provides the information about the internal structure of solids. Crystal acts as a natural diffraction grating for the diffraction of X-ray beam incident upon it in all directions. The X-rays are diffracted in accordance with the Bragg’s law \( n\lambda=2d\sin\theta \). Where ‘\( n \)’ is an integer referring to the order of reflection, ‘\( \lambda \)’ is the wavelength, ‘\( d \)’ is the spacing between the crystal lattice planes responsible for particular diffracted beam and ‘\( \theta \)’ is the angle that incident beam makes with lattice planes.

The path difference between the incident beam and the reflected beam in the consecutive lattice planes is shown in Figure 2.1. The width of the Bragg’s reflection in a standard X-ray powder diffraction pattern can provide the information of the average grain size. The peak breadth increases as the grain size decreases, because of the reduction in the coherently diffracting domain size, which can be assumed to be equal to the average crystallite size. The average particle size can be estimated by using Scherrer’s relation (2.1) (Cullity 1956, Guozhong Cao 2004).

\[
D = \frac{K\lambda}{\beta \cos \theta} \tag{2.1}
\]

Where ‘\( \lambda \)’ is the X-ray wavelength, ‘\( \beta \)’ is the full width at half maximum of diffraction peak, ‘\( \theta \)’ is the diffraction angle and ‘\( K \)’ is the Scherrer’s constant of the order of unity for usual crystal.
In this dissertation work, the structure and the average particle size of all samples were identified by using X-ray powder diffraction (XRD) at room temperature on a PANalytical X’pert PRO X-ray diffractometer using CuKα₁ radiation (λ = 1.54056 Å) as the X-ray source.

2.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared (IR) refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Of greatest practical use to the organic chemist is the limited portion between 4000 and 400 cm⁻¹. There has been some interest in the near-IR (14,290-4000 cm⁻¹) and the far-IR regions, 700-200 cm⁻¹. FTIR is conceivably the most powerful tool for identifying the functional groups or the types of chemical bonds (Nakamoto 1986, Richard Brundle et al 1992).

2.2.2.1 Principle

A beam of infrared light (wavelength ~ 0.7-500 μm) is focused on the sample using all-reflective optics. Depending on the sample composition, differing amounts of light are absorbed at different wavelengths. This pattern
of light absorption is unique for almost every organic compound (except optical isomers) and many inorganics. From the pattern of light absorbed, identification of the composition (qualitative analysis) can be made. With additional control over the sample thickness or sampling depth, the intensity of the individual absorbing components can be used to perform quantitative analysis (amount of each compound present). User-provided reference samples aid in positive substance identification and compositional verification. Figure 2.2 shows the schematic diagram of the arrangement of FTIR.

![Schematic representation of FTIR spectrometer](image)

**Figure 2.2** Schematic representation of FTIR spectrometer

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared of the electromagnetic spectrum.

Difference in Energy States = Energy of Light Absorbed

\[ E_1 - E_0 = \frac{hc}{\lambda} \]  \hspace{1cm} (2.2)

Where, 

- \( h \) = Planck’s constant
- \( c \) = Speed of light
- \( \lambda \) = the wavelength of light.
FTIR analysis was done in all the prepared samples with the instrument of FTIR spectrometer (Thermo Scientific Nicolet IS-10).

2.2.3 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is one of the most widely used techniques used in characterization of nanomaterials and nanostructures. The signals that derive from electron-sample interactions reveal information about the sample including surface morphology (texture), chemical composition of the sample. In most applications, data are collected over a selected area of the sample surface and a two dimensional image is generated that displays spatial variations in these properties. The resolution of the SEM approaches a few nanometers, and the instruments can operate at magnifications that are easily adjusted from 10 to over 3,00,000. Not only does the SEM produce topographical information as optical microscopes do, it also provides the chemical composition information near the surface (Guozhong Cao 2004). As well as, it is capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions.

2.2.3.1 Principle of SEM

Figure 2.3 illustrates the typical SEM instrumentation and photograph of Hitachi S-3400N. Electrons are generated in the electron gun. The tungsten-hairpin gun is commonly used, in which a tungsten filament serves as the source of electrons. By applying a current through the filament the tungsten wire will heat up and emission of electrons can be achieved. Generated electrons will be focused in front of an anode. To move the electrons down the column, a voltage difference between the tungsten filament and the anode is applied. This voltage differences is called the accelerating voltage can be varied between 0.2 and 40 keV determining the
energy and wavelength of the electrons within the beam. The beam of electrons to be condensed and focused as a fine spot on the specimen by 2 to 3 electromagnetic lenses located in the microscope column.

The main functions of first to lenses like condenser lens 1 (C1) and condenser lens 2 (C2) are to control the beam current (number of electrons striking the specimen) and the final size of the area illuminated on the specimen (spot size). The third condenser lens (C3) or also called the final lens, is used primarily to focus the beam of electrons on the surface of the specimen. The final lens usually contains deflecting coils and stigmator coils (Richard Brundle et al 1992). Accelerated electrons in a SEM carry significant amount of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples.

![Figure 2.3 Schematic diagram and photograph of Hitachi S-3400N scanning electron microscope](image-url)
2.2.3.2 Limitations

Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually on the order of 10 cm, vertical dimensions are generally much more limited and rarely exceed 40 mm. For most instruments samples must be stable in a vacuum on the order of $10^{-5} - 10^{-6}$ torr. EDS detectors on SEM's cannot detect very light elements (H, He, and Li), and many instruments cannot detect elements with atomic numbers less than 11 (Na). Most SEMs use a solid state x-ray detector (EDS), and while these detectors are very fast and easy to utilize, they have relatively poor energy resolution and sensitivity to elements present in low abundances when compared to wavelength dispersive x-ray detectors (WDS) on most electron probe micro analyzers (EPMA). An electrically conductive coating must be applied to electrically insulating samples for study in conventional SEM's, unless the instrument is capable of operation in a low vacuum mode. However, gold can serve as a conducting layer on the sample and coated on top of the sample. The morphology of the prepared samples was observed using scanning electron microscopy (Hitachi S-3400).

2.3 OPTICAL ABSORPTION ANALYSIS

Absorption of electromagnetic radiation is the way by which the energy of a photon is taken up by matter, typically the electrons of an atom. Thus, the electromagnetic energy is transformed to other forms of energy for example, to heat. The absorption of light during wave propagation is often called attenuation. Usually, the absorption of waves does not depend on their intensity (linear absorption), although in certain conditions, the medium changes its transparency dependently on the intensity of waves going through, and the saturable absorption (or nonlinear absorption) occurs. UV-visible spectroscopy is used when involving the absorption of these high energy lights by atoms or molecules, which causes electronic excitation. This
phenomenon only occurs if conjugated pi-electron systems are present. Molecule absorbs light energy when exposed to light and excites electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Result is usually presented by a graph of absorbance versus wavelength ($\lambda$).

Figure 2.4  Schematic diagram and photograph of UV-vis absorption spectrometer

Figure 2.4 shows the schematic diagram and photograph of UV-vis absorption spectrometer. The UV-Visible spectrophotometer uses two light sources, a deuterium ($D_2$) lamp for ultraviolet light and a tungsten (W) lamp for visible light. After bouncing off a mirror (mirror 1), the light beam passes through a slit and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. At any specific orientation of the grating, only monochromatic (single wavelength) successfully passes through a slit. A filter is used to remove unwanted higher orders of diffraction. The light beam hits a second mirror before it gets split by a half mirror (half of the light is reflected, the other half passes through). One of the beams is allowed to pass through a reference cuvette (which contains the
solvent only), the other passes through the sample cuvette. The intensities of the light beams are then measured at the end.

### 2.3.1 UV-vis Diffuse Reflectance Spectra

In this research work, the optical absorption spectra of the prepared samples were recorded using UV-vis diffuse reflectance spectrophotometer (UV-2102 PCS spectrophotometer). Since light cannot penetrate through opaque (solid) samples, it is reflected on the surface of the samples. As shown in Figure 2.5, the incident light reflected symmetrically with respect to the normal line is called “specular reflection”, while incident light scattered in different directions is called “diffuse reflection” (Kumar et al 1999).

![Figure 2.5 General reflection mechanisms](image)

Figure 2.5 General reflection mechanisms

With integrating spheres, measurement is performed by placing the sample in front of the incident light window and concentrating the light reflected from the sample on the detector using a sphere with barium sulfate-coated inside. The obtained value becomes the reflectance (relative reflectance) with respect to the reflectance of the reference standard. Figure 2.6 shows the schematic arrangement of a UV-vis diffuse reflectance spectrophotometer.
2.4 ELECTRICAL STUDIES

2.4.1 Impedance Analysis

Electrical impedance, or simply impedance, describes a measure of opposition to alternating current (AC). Electrical impedance extends the concept of resistance to AC circuits, describing not only the relative amplitudes of the voltage and current, but also the relative phases. When the circuit is driven with direct current (DC) there is no distinction between impedance and resistance; the latter can be thought of as impedance with zero phase angle. The symbol for impedance is usually Z and it may be represented by writing its magnitude and phase in the form |Z|\theta. However, complex number representation is more powerful for circuit analysis purposes. Impedance is defined as the frequency domain ratio of the voltage to the current. In other words, it is the voltage–current ratio for a single complex exponential at a particular frequency \omega. In general, impedance will be a complex number, with the same units as resistance, for which the SI unit is the ohm. For a sinusoidal current or voltage input, the polar form of the
complex impedance relates the amplitude and phase of the voltage and current. The magnitude of the complex impedance is the ratio of the voltage amplitude to the current amplitude. The phase of the complex impedance is the phase shift by which the current is ahead of the voltage (Barsoukov and Macdonald 2005).

Impedance Spectroscopy is becoming a popular analytical tool in materials research and development because it involves a relatively simple electrical measurement that can readily be automated and whose results may often be correlated with many complex materials variables: from mass transport, rates of chemical reactions, corrosion, and dielectric properties, to defects, microstructure, and compositional influences on the conductance of solids. IS can predict aspects of the performance of chemical sensors and fuel cells, and it has been used extensively to investigate membrane behavior in living cells. It is useful as an empirical quality control procedure, yet it can contribute to the interpretation of fundamental electrochemical and electronic processes (Barsoukov and Macdonald 2005).

2.4.2 AC Conductivity

Electrical conductivity or specific conductance is a measure of a material's ability to conduct an electric current. When an electrical potential difference is placed across a conductor, its movable charges flow, giving rise to an electric current. The conductivity ‘σ’ is defined as the ratio of the current density ‘J’ to the magnitude of the electric field strength ‘E’. Conductivity is the reciprocal (inverse) of electrical resistivity ‘ρ’ and has the SI units of Siemens per meter (S·m⁻¹) and CGSE units of inverse second (S⁻¹). However, the materials can be classified according to their nature of electrical conductivity such as metals, semiconductors, insulators. Metal is a very good conductor, it has high conductivity and a low resistivity. The conductivity of a semiconductor is generally intermediate, but varies widely under different
conditions, such as exposure of the material to electric fields or specific frequencies of light, most importantly with temperature and composition of the semiconductor material. Electrical conductivity is a very useful property since values are affected by such things as a substance's chemical composition and the stress state of crystalline structures. Therefore, electrical conductivity information can be used for measuring the purity of water, sorting materials, checking for proper heat treatment of metals, and inspecting for heat damage in some materials. Electrical resistivity is strongly dependent on temperature. In metals, electrical conductivity of the material decreases with increasing the temperature. In semiconductors, electrical conductivity of the material increases with increasing the temperature. Thereafter, the electrical conductivity of the material can be approximated as being directly proportional to the temperature (Callister 2007).

2.4.3 Dielectric Constant

The dielectric constant ($\varepsilon_r$) is the ratio of the permittivity of a substance to the permittivity of free space. It is an expression of the extent to which a material concentrates electric flux, and is the electrical equivalent of relative magnetic permeability. As the dielectric constant increases, the electric flux density increases, if all other factors remain unchanged. This enables objects of a given size, such as sets of metal plates, to hold their electric charge for long periods of time and/or to hold large quantities of charge. Materials with high dielectric constants are useful in the manufacture of high-value capacitors.

The dielectric constant of the materials can be calculated as,

$$\varepsilon_r = \frac{Ct}{\varepsilon_0A} \quad (2.3)$$

Where,

$C$- is the capacitance of the material
t- Thickness of the material

\( \varepsilon_0 \)- Permittivity of the free space; \( 8.854187 \times 10^{-12} \) F/m

A- Area of the material

A high dielectric constant, in and of it, is not necessarily desirable. Generally, substances with high dielectric constants break down more easily when subjected to intense electric fields, than do materials with low dielectric constants. For example, dry air has a low dielectric constant, but it makes an excellent dielectric material for capacitors used in high-power radio-frequency (RF) transmitters. Even if air does undergo dielectric breakdown (a condition in which the dielectric suddenly begins to conduct current), the breakdown is not permanent. When the excessive electric field is removed, air returns to its normal dielectric state. Solid dielectric substances such as polyethylene or glass, however, can sustain permanent damage.

2.4.4 Dielectric Loss

Dielectric loss is the loss of energy that goes into heating a dielectric material in a varying electric field. For example, a capacitor incorporated in an alternating-current circuit is alternately charged and discharged each half cycle. During the alternation of polarity of the plates, the charges must be displaced through the dielectric first in one direction and then in the other, and overcoming the opposition that they encounter leads to a production of heat through dielectric loss, a characteristic that must be considered when applying capacitors to electric circuits, such as those in radio and television receivers. Dielectric losses depend on frequency and the dielectric material. Heating through dielectric loss is widely employed industrially for heating thermosetting glues, for drying lumber and other fibrous materials, for preheating plastics before molding, and for fast jelling and drying of foam rubber.
2.4.4.1 Experimental setup

In this work, the impedance of the nanocrystalline samples were carried out with a computer controlled impedance analyzer (Hioki LCR Hi-Tester 3532-50, Japan) over the frequency range of 50 Hz to 5 MHz as shown in Figure 2.7. Using this instrument also measured the ac conductivity, dielectric constant and dielectric loss of the samples when the various frequencies. With variable frequency measurements, the highly acclaimed 3532-50 LCR Hi-Tester has been improved with the power for maximum high speed measurements of 5 ms (4 times that of current models). This means that line tact times can be further shortened, increased line efficiency. Test conditions can now come closer to a component's operating conditions. The high basic accuracy of ±0.08%, combined with ease of use and low price give these impedance meters outstanding cost-performance characteristics. These will find a wide range of applications, whether for laboratory use for evaluation of operating characteristics, or for production line use, exploiting the full-function interface and comparator functions and rapid response.

![Figure 2.7 Photograph of Hioki 3532-50 LCR Hi-Tester setup](image)

2.5 HIGH PRESSURE STUDIES

The high pressure studies were carried out through four probe arrangement with up to a pressure range of ~8 GPa. The high pressure electrical resistivity studies were importantly evidenced for any structural disorder or phase transformation while with applying pressure.
2.5.1 High Pressure – A General View

Pressure, like temperature is a basic thermodynamic variable, which can be used to induce physical and chemical changes, and to transport matter from one state to another. Pressure serves as a versatile tool in materials research. In spite of the superficial similarity between temperature and pressure, these two variables are fundamentally different in the ways they affect a material's internal energy. In many respects pressure and temperature vary with each other. As a general rule, increase in temperature will increase the rate of the reaction in a chemical system and causes the entropy of the systems to increase whereas increasing pressure in a condensed system will generally decrease the rate of the reaction and entropy of the system. The change in temperature reflects on the kinetic energy and thus in the entropy of vibrating atoms. On the other hand, pressure alters the electron interaction, energy of atomic bonds by forcing atoms closer together in a smaller volume. Pressure seems to be a more effective agent in creating new polymorphic forms of substances than temperature. Pressure thus serves as a powerful probe of atomic interactions and chemical bonding. Further pressure is an important tool for synthesizing dense structures, super hard materials, novel solidified gases and liquids and mineral like phases suspected to occur deep within the Earth and other planets. The study of behaviour of materials at high pressures has been useful in observing the new features of physico-chemical properties. Various properties like mechanical, optical, electrical and magnetic gives interesting results at high pressure (Horovits and Johnson 1959, Schmidt et al 1993). For measuring pressure there are numerous units. The S.I unit of pressure is Pascal and it is denoted as Pa. One Pascal is defined as 1 Newton/m\(^2\). Various units of pressure and its conversions are shown in the Table 2.1.
Pressure greater than 1000 atmospheric pressure is termed as high pressure. High pressure provides scientists with a powerful tool of tuning in a controllable and reversible manner the volume of a sample and consequent properties of that sample. There are three important applications of the high pressure techniques in basic and materials science: (1) to synthesize novel materials not accessible by other techniques, (2) to transform a given material from one phase to another, and (3) to uncover underlying systematic and critically test theoretical concepts. Also high pressure can produce structural, electronic and other phase transition polymerization of organic substances and much more. The modern development of the high-pressure field is the widespread application of high methods in many branches of physics, chemistry, biology and geo sciences.

**Table 2.1 Comparison between different pressure units**

<table>
<thead>
<tr>
<th>Units</th>
<th>N/m²</th>
<th>Dyne/cm²</th>
<th>Lb/in²</th>
<th>Kg/cm²</th>
<th>Atm</th>
<th>Bar</th>
<th>Mm Hg (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/m²</td>
<td>1</td>
<td>10</td>
<td>1.4504 x 10⁻⁴</td>
<td>1.0197 x 10⁻⁶</td>
<td>9.8692 x 10⁻⁶</td>
<td>1.0000 x 10⁻⁵</td>
<td>7.5506 x 10⁻³</td>
</tr>
<tr>
<td>Dyne/cm²</td>
<td>0.10000</td>
<td>1</td>
<td>1.4504 x 10⁻⁵</td>
<td>1.0197 x 10⁻⁶</td>
<td>9.8692 x 10⁻⁶</td>
<td>1.0000 x 10⁻⁶</td>
<td>7.5506 x 10⁻⁴</td>
</tr>
<tr>
<td>Lb/in²</td>
<td>6.8947 x 10⁻³</td>
<td>6.8947 x 10⁻⁴</td>
<td>1</td>
<td>0.0703</td>
<td>0.0680</td>
<td>0.0689</td>
<td>51.7150</td>
</tr>
<tr>
<td>Kg/cm²</td>
<td>0.98067 x 10⁻⁵</td>
<td>0.98067 x 10⁻⁶</td>
<td>14.2230</td>
<td>1</td>
<td>0.9679</td>
<td>0.9807</td>
<td>735.56</td>
</tr>
<tr>
<td>Atm</td>
<td>1.0133 x 10⁻⁵</td>
<td>1.0133 x 10⁻⁶</td>
<td>14.6960</td>
<td>1.0332</td>
<td>1</td>
<td>1.0133</td>
<td>760.00</td>
</tr>
<tr>
<td>Bar</td>
<td>1.0000 x 10⁻⁵</td>
<td>1.0000 x 10⁻⁶</td>
<td>14.5040</td>
<td>1.0197</td>
<td>0.9869</td>
<td>1</td>
<td>750.10</td>
</tr>
<tr>
<td>Mm Hg (Torr)</td>
<td>1.3332 x 10⁻²</td>
<td>1.3332 x 10⁻³</td>
<td>1.9337 x 10⁻²</td>
<td>1.3595 x 10⁻³</td>
<td>1.3158 x 10⁻³</td>
<td>1.3332 x 10⁻³</td>
<td>1</td>
</tr>
</tbody>
</table>
Percy W. Bridgman, “The Father of High Pressure” was honored by Nobel Prize for Physics for his valuable works in the field of high pressure (Bridgman 1946, 1952). He documented the effects of pressure on electric conductivity, thermal conductivity, viscosity, melting, reaction kinetics and other material properties. Pressure, induce both continuous and discontinuous changes in matter. According to Bridgman, the electrical conductivity or volume versus pressure varies smoothly with pressure for most of the materials. However, some substances displayed sharp, reproducible discontinuous in these properties at specific pressures. The reproducible discontinuity properties results in phase transitions. Under sufficient high pressures, every material is expected to undergo structural transformation to denser and more closely packed atomic arrangements. The transformations produced in solids by the effect of pressure may be differentiated as “permanent” or “reversible”. The formation of diamond from graphite by the combined action of pressure and temperature can be classed as permanent or irreversible change. A reversible change takes place in bismuth. As bismuth is compressed, it transforms to new polymorphic modifications at 25, 27 and 75 kbar. As pressure reduces, the bismuth reversibly transforms through the lower pressure phases until it returns to the normal condition. This reversible transformation is also sluggish in some cases like a transformation from a fcc to bcc in ytterbium (Hall 1962).

Transformations in solids are further classified as follows:

i. Solid-Solid

ii. Liquid-Solid

iii. Isostructural transformation (Same crystal structure to same crystal structure of higher density)

iv. Electronic transformation
v. Close-packed to non-close packed
vi. Non-metal to metal
vii. Metal to non-metal
viii. Magnetic transitions.
ix. Growth of large crystals

High Pressure X-ray crystallographic studies of atomic structures reveal three principal compressions in solids: (i) bond compression, (ii) bond angle, and (iii) bending and intermolecular compression. The compression of matter is normally reduced under pressure (i.e.) Gruneisen parameter is always positive. At extremely high pressures, the innermost atomic states broaden into bands and the number of valence electrons increases until the atomic shell structure is completely destroyed and Thomas-Fermi gas of conduction electrons are left behind (Schilling 1998).

During the last two decades following the introduction of the diamond anvil cell, not only the pressure and temperature capabilities of the laboratory experimental techniques are extended. The ways are opened for new experimental methods like high pressure laser Raman Spectroscopy, Mossbauer spectroscopy, X-ray absorption spectroscopy and so on (Jayaraman 1983)

In condensed matter science, these techniques have evolved with time as versatile experimental tools and have played key roles in various aspects. New phenomena like pressure induced metal-insulator transitions, (Minomura 1992), valence transitions (Benedict 1993) and crystalline amorphous transitions (Chen et al 1994) have been observed. Super hard materials like diamonds (Minoru Akaishi et al 1993) and cubic boron nitride (Demazeau et al 1994, Solezenko et al 1994) have been synthesized under
high pressure. A lot of high Tc superconductors have been discovered at high pressures (Antipov et al 1993, Hirori et al 1993). Indeed, the attempt to apply sufficient pressure to transform insulating solid hydrogen into a metal has long been an important goal in high pressure research (Jorge Kohenoff et al 1997).

2.5.2 Generation of High Pressure

The technique presently available for generation of high pressures in the laboratory can be separated into two broad classifications: “Static” techniques where the pressure is maintained for an arbitrary length of time and “dynamic” techniques where only very brief time period in the microsecond range are available for the experiment. Table 2.2 shows the comparison between static and dynamic pressure loading techniques. Further, in either technique the types of high pressure classified into three types depending upon the pressure-transmitting medium as (1) hydrostatic, (2) uniaxial and (3) quasi-hydrostatic.

Hydrostatic pressure directed everywhere normal to the sample surface, as far as the sample is in a fluid transmitting medium. Fluid transmitting medium (liquid or gas) results in hydrostatic pressure. As far as uniaxial pressure is concerned, the pressure directed in a particular direction causing the sample to compress in one direction but expands in the other direction. In quasi-hydrostatic, stress applied to the sample has both hydrostatic and uniaxial components (Spain and Paauwe 1977). Solid pressure transmitting medium builds up quasi-hydrostatic pressure as shown in Table 2.3.
Table 2.2  Comparison between static and dynamic pressure loading techniques

<table>
<thead>
<tr>
<th>Salient Features</th>
<th>Dynamic</th>
<th>Static</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of Experiment</td>
<td>~2µs</td>
<td>As desired</td>
</tr>
<tr>
<td>Strain rate</td>
<td>~$10^8$ s$^{-1}$</td>
<td>~5 s$^{-1}$</td>
</tr>
<tr>
<td>Shear</td>
<td>Always present</td>
<td>No / may be</td>
</tr>
<tr>
<td>Temperature</td>
<td>Increases</td>
<td>Isotherm</td>
</tr>
<tr>
<td>Defect</td>
<td>Generated</td>
<td>No / may be</td>
</tr>
<tr>
<td>Heterogeneous heating</td>
<td>Possible</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 2.3  Classification of high pressure devices based on the pressure medium employed

<table>
<thead>
<tr>
<th>Hydrostatic (Pressure medium- Liquid, Gas)</th>
<th>Quasi-Hydrostatic (Pressure medium- Solid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure vessels</td>
<td>Opposed Anvils</td>
</tr>
<tr>
<td>Monoblock</td>
<td>Diamond Anvil Cells</td>
</tr>
<tr>
<td>Multilayer Cylinders</td>
<td>Multianvils</td>
</tr>
<tr>
<td>Pressure Plates</td>
<td>Mass</td>
</tr>
<tr>
<td>Autofrettaged Pressure Vessels</td>
<td>Belt, Girdle</td>
</tr>
</tbody>
</table>

2.5.2.1  Static pressure

All the static high pressure generating devices can simply be divided into two main categories namely, (1) piston-cylinder device and (2) opposed anvil devices. These devices are the basic types of apparatus being
now used at various laboratory introduced by Bridgman. The excellent reviews of these apparatus can be found in the literature (Crossland and Spain 1983, Sherman and Stadmuller 1987). An overview of these devices with their pressure capabilities listed in the Figure 2.8.

![Figure 2.8 Schematic representation of principal methods of high pressure generation and pressure capabilities](image)

### 2.5.2.2 Dynamic pressure

In the dynamic techniques, one or more multiple shock waves are sent through the sample either by detonating an explosive charge or allowing a hyper velocity projectile to slam into a plate on which the sample is mounted. The magnitude of pressure generated may be extremely high of the order of 500 Mbars for nuclear explosives but the duration time is very short in the order of microseconds. The high-pressure zone within the shock wave passes quickly through the sample. The temperature rise in the shock zone is appreciable, reaching to many thousands degreed Kelvin. A lesser
temperature increase is observed if the multiple shock technique is used or if the sample is compressed isoentropically using magnetic flux compression techniques.

The trajectory of a given material in P-T space is called its Hugoniot. From the Hugoniot, it is possible to calculate the isothermal equation of state of the material at any temperature for comparison with experiments employing static pressure techniques. Multiple shock wave reverberate through the sample generating pressures and temperatures in the range 90-180 GPa and 2200-4400 K respectively.

Compared to most static pressure techniques, dynamic pressure techniques require a relatively large commitment of space, equipment, time and financial resources. Experiments utilizing dynamic pressure techniques are however, invaluable since they remain as the only way to reach pressures significantly above 500 GPa or to attain simultaneous very high pressure and high temperature conditions.

2.5.3 Static Pressure Devices

2.5.3.1 Piston-Cylinder Devices

The simple way of producing the hydrostatic pressure is to compress the sample. The piston–cylinder apparatus consist of a piston compressing the sample in a single walled cylinder. The schematic diagram of piston-cylinder device is shown in Figure 2.9.

Pistons are constructed generally of cemented carbide. This helps one to reach higher pressure but tungsten carbide is much fragile and brittle. To avoid crack and rapture of the piston one must provide support to the piston. To generate pressure the piston is driven usually by means of hydraulic press into the cylinder thereby compressing the pressure-
transmitting medium, which in turn compress the sample. Pressure capability of this device can be increased by providing external support to piston and cylinder. The cylinders usually used are of multi ring design. By using a suitable pressure, transmitting medium like silicon oil, methanol-ethanol mixtures etc, hydrostatic pressures up to 8 GPa approximately can be generated. With the concept of multi staging pressure range can be enhanced to 10 GPa. Piston- cylinder devices are widely used for several number of high pressure experiments like electrical resistivity, thermo electric power, optical studies and compressibility of fluids.

Figure 2.9  Schematic diagram of piston-cylinder device

2.5.3.2  Opposed Anvil Devices

In 1950, P.W. Bridgman reported about the construction of an anvil apparatus using two important principles: (1) the principle of massive support and (2) the principle of motion by means of a compressible gasket. The Bridgman Opposed anvil technique is very widely used in high-pressure solid-state studies and thus plays an important role in the high pressure since, it is simple in construction. The opposed anvil device works on the principle namely “Principle of Massive support” (Bridgman 1941). The principle uses the fact that the yield stress of a flat semi-infinite plate subjected to an
indenter is several times higher than the compressive yield stress of the plate material. The typical arrangement of photograph of the opposed anvil high pressure device is shown in Figure 2.10.

![Figure 2.10 Photograph of the opposed anvil high-pressure arrangement](image)

**Figure 2.10 Photograph of the opposed anvil high-pressure arrangement**

Using the Bridgman Opposed anvil electrical resistivity of the material can be studied (Bridgman 1952). For high temperature studies this anvil can be used surrounded by any heating element, it is possible to reach upto 1000 °C, and the highest attainable pressure is 20,000 atmospheres. The OHPAD devices can be used to determine the elastic modulli of crystals by Brillouin scattering at high pressure (Whitfield et al 1976), Hall Effect measurements (Pitt 1977), Mossbauer spectroscopy, positron lifetime measurements and materials synthesis are carried out using Opposed anvil devices.

### 2.5.4 Diamond Anvil Cell

The versality of the diamond anvil cell is attributed to its extreme strength and transparency to almost the entire electromagnetic radiation including gamma rays, X-rays, visible light and infrared and ultraviolet
region. Thus, the diamond anvil cell has provided the first opportunity for high-pressure research to observe visually the effects of pressure and it allows convenient access for variety of techniques. Pressures as high as greater than 500 GPa has been reported using DAC (Ruoff et al 1992).

In 1950, the evolution of diamond anvil cell is started. Jamieson et al (1959), Weir et al (1959, 1965) are pioneers who worked for the development of DAC. The utility of the diamond anvil cell is greatly enhanced when Valkenburg (1965) introduced the metal gasket between the two diamond anvil faces. Barnett et al (1973) developed the ruby pressure calibration using DAC. Figure 2.11 shows a schematic representation of DAC loaded with sample.

![Schematic representation of DAC loaded with sample](image)

**Figure 2.11** Schematic representation of DAC loaded with sample

Mao and Bell (1978) developed a very significant pressure-cell design. They introduced the detachable piston and cylinder assembly and employed cylindrical rockers instead of hemispherical ones, which were used in NBS cell. By using this device, it is possible to generate a pressure upto 100 GPa. Introduction of bevelles on DAC made a turning point and raised the pressure limit to 500 GPa (Moss and Goettel 1987). The phenomenal advances achieved by innovative modifications in the mechanical design have
turned diamond anvil cell into a unique and reliable static pressure apparatus for carrying out detailed study of condensed matter under extreme pressure.

During the last two decades, DACs play a vital role in advancing knowledge and understanding the behaviour of matter under extreme conditions of pressure, and under conditions of both elevated temperatures and pressures. DAC enable direct measurements of changes in volume and density, as function of changes in a material’s crystal structure and of melting under high-pressure. The obvious choice for selecting diamond as a anvil material in static high pressure experiments is due to the following properties. Diamond is a hardest and strongest material ever known. It have high yielding strength, high thermal conductivity and also transparency to radiation over a wide range of wavelengths which affords the feasibility of studying materials using X-rays. Berman (1965) and Field (1979) review the physical properties of the diamond. It is difficult to determine the yield strength accurately because it is complicated by orientation dependence, size of the specimen and the presence of impurities. Many groups (Panda and Ruoff 1979, Ruoff 1979, Bersenev and Efros 1986) discussed the yeild strength of the anvils at high pressure.

The stability of diamond at megabar pressures is studies by means of ab initio simulations by Scandalo et al (1996). According to ab initio simulations the mechanical failure of diamond only occurs at exceptionally high pressure of 300 Mbar under hydrostatic compression.

2.5.5 Gaskets and Pressure Transmitting Media

2.5.5.1 Gasket

In high-pressure experiment gaskets plays an important role in holding the sample under investigation. They also provide support to the edge of the anvils and critically determine the pressure distribution on the anvils.
The use of a compressible gasket to obtain motion of anvils, conical pistons or other components in high-pressure apparatus has become well established since P.W. Bridgman anvil work. His work helps to systematically determine the important variables that enable the gasket to perform its required function. The gasket performs three important and fruitful functions in the area of experimentation.

The first function performed by the gasket is “yielding” to the thrust placed on it by moving an anvil or similarly functioning apparatus component. Yielding can occur through simple compression of the gasket material, by flow or by a combination of compression and flow. The amount of yielding should be relatively large in order that the anvils might move a sufficient amount to compress the contents of the high-pressure chamber. The second function of the gasket is that of “confining” (not yielding to the thrust of) the material being compressed by the advancing anvil. The tasks of yielding and confining are contradictory to each other.

The third and more important function of the gasket is “support”. Inside the inner edge of the gasket, the surfaces of the high-pressure apparatus components was subjected to the full pressure generated within the chamber. At the outer edge of the gasket, the apparatus components are subjected to only one atmosphere pressure. Ideally, the pressure exerted by the gasket against the components of the apparatus should gradually decrease from the full chamber pressure at the inner edge to one atmosphere pressure at the outer edge. If this is the case then a sharp line of demarcation between the chamber pressure and atmospheric pressure is avoided and consequently there will be no line of high stress concentration. When the gasket width and pressure gradient are judiciously chosen, the apparatus components will support each other and make it possible for the highly stressed portions of the components to withstand more load than would otherwise be possible.
Pressure gradients patterns can be varied by the choice of gasket materials and by changing the cross sectional profile of the gasket from the inner to the outer edge.

The gasket functions of yielding, confining and supporting enumerated above, must in any given design be accomplished without having the gasket absorb an inordinate fraction of the ram thrust available for operating the device. In the belt and tetrahedral devices the thrust absorbed by the gaskets and by the internal friction of the solid pressure transmitting medium is low compared with the other devices.

Selection of materials to meet these opposing requirements must be made from materials of intermediate compressibility and internal friction. Universal, optimum values of compressibility and internal friction probably do not exist. In order to provide information about the potential usefulness in gasket design, internal frictions of several substances have been measured by use of Bridgman’s shear apparatus (Bridgman 1935). Most of the ultrahigh-pressure gaskets in use today have coefficients of friction in the range of 0.25 to 0.50.

The Figure 2.12 summarizes the important results on the gasket behavior under pressure. From the Figure 2.12 it is clear that all gaskets with an initial thickness $h_i > h_c$ are reduced to $h_c$. The critical thickness is denoted as $h_c$, whereas the gaskets with $h_i < h_c$ remain undistorted. The gasket amplification, M defined as the ratio of pressure at the centre of the gasket to the average pressure, increases steeply as $h_i \to h_c$ and reaches a maximum at $h_c$. The function of the gasket is to reduce the magnitude of pressure gradients, confine the sample, and to provide additional support for the anvils and prevent the failure of the anvils by using greater gasket thickness due to
concentration of stresses at high pressures. Bandyopadhyay et al (1981) have discussed the gasket thickness optimization in the Bridgman anvil system.

Figure 2.12 Gasket behaviour under pressure (Govindarajan et al 1981)

The commonly used gasket material in Diamond anvil cell is T 301 stainless steel. Depending upon the experimental requirements, materials like Inconel X750, Waspalloy, Re, Mo, W are used in the DACs as gasket materials. The theory of gasket and usage of a gasket with a pre-indentation in the diamond anvil cells have been discussed by many authors (Chan et al 1982, Dunstan 1989).

2.5.5.2 Pressure transmitting media

Another important aspect of high-pressure experiments is the pressure-transmitting medium. Higher pressures are usually generated by the applications of a one-dimensional thrust into a confined pressure-transmitting medium. The function of the pressure–transmitting medium is to transform the pressure generating thrust into an adequately uniform pressure upon the
sample. The hydrostatic pressure should be maintained by including a fluid around the sample to be compressed. Solid, liquids and gases are used as pressure transmitting medium. At pressures to 35,000 atmospheres and temperatures to 1500°C, liquids and gases have been used to transmit pressure to a sample contained in a sample cell. At pressures greater than 35,000 atmospheres (at room temperature) all liquids that were liquids at 1 atmosphere and room temperature become solids. All other liquids freeze at lower pressures except n-pentane and iso-pentane which remains liquid upto 35,000 atmospheres. Gases like hydrogen and helium would undoubtedly be liquids in the 1,00,000 atmosphere range of pressure but, at present not been used as pressure media because of difficulties engendered in confining these elements at very high pressures. In order to overcome all the difficulties faced by liquid and gas pressure medium solid transmitting medium become important and works has been reported (Yangali Cho 1958). The use of solids to transmit pressure has simplified high pressures, high temperatures apparatus design and opened up new design possibilities. It is natural that there is considerable frictional ‘hold up’ in a solid material and therefore poor transmission. Frictional hold–up in some designs utilizing solid media have been as low as 3 percent In any event, frictional hold up is reproducible and determinable. In Table 2.4, some of the pressure–transmitting media and their maximum pressure ranges are listed.

2.5.5.3 Characteristics of pressure transmitting medium

An effective way to subject a substance to high-temperature and high pressure simultaneously is to enclose the substance in a thin walled electrically heated capsule to which pressure is transmitted through a medium. The pressure transmitting medium can be liquid or solid. Ideally, the pressure transmitting medium must meet the requirements enumerated below.
(i) It should have zero shear strength (fluid or soft solid)

(ii) The volume change of the transmitter with pressure should not be too large (low compressibility)

(iii) It should be an electrical insulator (if electrical instruments are contemplated)

(iv) Easy to handle (non toxic, non-flammable)

(v) Be Chemically inert

(vi) Easy to fabricate in a desired shape

(vii) Cheap and readily available

(viii) Easy to seal within the high pressure chamber

(ix) Very low thermal conductivity.

(x) Be thermally stable

(xi) Should have very high melting point and the melting point should increase with increasing pressure.

These requirements must be met at both ordinary and high temperatures. In some instances, additional special requirements must be met, as would be the case where x-ray transparency is necessary for diffraction work at high pressure and high temperature. Of course it is impossible to choose a material, which could fulfill all these criteria and requirements fully, and hence choice is made for each experiment in terms of an adequate performance and more specific requirement of the particular experiment.
Table 2.4  Some pressure-transmitting media and their useful pressure ranges (Jayaraman  1983)

<table>
<thead>
<tr>
<th>S.No</th>
<th>Medium</th>
<th>Freezing pressure at RT (GPa)</th>
<th>Pressure range of nearly hydrostatic behavior (GPa)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol : Ethanol (4:1)</td>
<td>10.4</td>
<td>-20</td>
<td>Easy filling</td>
</tr>
<tr>
<td>2</td>
<td>Methanol : Ethanol : Water</td>
<td>14.5</td>
<td>-20</td>
<td>Easy filling</td>
</tr>
<tr>
<td>3</td>
<td>He</td>
<td>11.8</td>
<td>&gt;60</td>
<td>Cryogenic or high-pressure filling needed</td>
</tr>
<tr>
<td>4</td>
<td>Ne</td>
<td>4.7</td>
<td>16</td>
<td>Cryogenic or high-pressure filling needed</td>
</tr>
<tr>
<td>5</td>
<td>Ar</td>
<td>1.2</td>
<td>16</td>
<td>Cryogenic or high-pressure filling needed</td>
</tr>
<tr>
<td>6</td>
<td>H₂</td>
<td>5.7</td>
<td>&gt;60</td>
<td>Cryogenic or high-pressure filling needed</td>
</tr>
<tr>
<td>7</td>
<td>D₂</td>
<td>5.3 ± 2</td>
<td></td>
<td>Cryogenic or high-pressure filling needed</td>
</tr>
<tr>
<td>8</td>
<td>N₂</td>
<td>2.4</td>
<td>13</td>
<td>Cryogenic filling</td>
</tr>
<tr>
<td>9</td>
<td>O₂</td>
<td>5.9</td>
<td></td>
<td>Cryogenic filling</td>
</tr>
</tbody>
</table>
2.5.6 Measurement of Pressure

To make good use of high-pressure data, one must see to measure the pressure very accurately. In general measurements of pressure is divided into two categories, namely

(1) Primary methods and

(2) Secondary methods.

A primary pressure gauge is one, which measures the pressures in terms of fundamental equation, which obtained by connecting pressure with force exerted on the area. Thus, by using a primary gauge one can measures directly the force exerted by pressure on a particular area. In contrary, for secondary gauges the systematic variation of any physical property of a material forms the basis for measurement of pressure. Accordingly, the secondary methods further classification are made into three basic types based on the change in the physical property of the material with pressure such as mechanical, electrical, optical and fixed points.

Generally, all the physical properties tend to change on application of pressure. It is more important to find and identify those properties, which change in a manner, which could form the basis for a useful pressure guage. On this aspect, we have three gauges such as Bourdon guage, Strain guage and X-ray pressure guage. Among three the X-ray pressure guage is widely used for calibration. In this gauge, the pressure is calibrated with the help of an equation of State (EOS). If the equation of state \( V= V(P, T) \) of some substance is obtained, then pressure can be determined since the volume can be measured accurately with the aid of a neutron or x-ray techniques. Therefore some semi empirical EOSs such as Birch Equation and more simple, Murnaghan Equation are also measured to pressure. The equation of state of materials such as NaCl, KCl, CsCl and a number of other substances
like Cu, Ag, Au, and Pt are proposed for the pressure scales. (Mao et al 1978, Sherman and Stadmuller 1987, Vohra and Ruoff 1990). A recent review by Holzapfel (1998) on the equation of state of solids under strong compression gives the historical and theoretical background for the different mathematical forms commonly used to represent the equation of state and their physical significance.

A new universal EOS was proposed by Vinet et al (1986) which is able to describe the data for all classes of solids accurately. (Schlosser and Ferrante 1991) and is given below,

\[ P = 3 B_0 (1-X) \exp \left[ \frac{3}{2} \left( B_0' - 1 \right) \right] / X^2 \text{Gpa} \]  (2.4)

Where,

\[ X = (V/V_0)^{1/3} \]

\[ P \] - pressure at the samples site

\[ V_0 \] - original volume

\[ V \] - reduced volume

\[ B_0 \] - isothermal bulk modulus

\[ B_0' \] - first order pressure derivative of the bulk modulus at zero pressure.

The drawbacks in using the Vinet equation have been discussed in detail by Zheng-Hua-Fuang (1998). This equation has a restriction on applying to low pressure boundary condition and hence the two parameter Birch equation of state developed by Birch (1938) is being effectively used. It is given as,
\[ P = \frac{3}{2} B_0 \left\{ \left[ \left( \frac{V_0}{V} \right)^{2/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left[ 1 + \frac{3}{4} (B_0' - 4) \left( \frac{V_0}{V} \right)^{2/3} - 1 \right) \right\} \]

(2.5)

Where,

- \( P \) - pressure at the sample site
- \( V_0 \) - original volume
- \( V \) - reduced volume
- \( B_0 \) - isothermal bulk modulus
- \( B_0' \) - first order pressure derivative of the bulk modulus at zero pressure

**Table 2.5  The equation of state data for a few materials used as pressure scale**

<table>
<thead>
<tr>
<th>Calibration</th>
<th>Pressure Range (GPa)</th>
<th>EOS</th>
<th>Method (Static/Shock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>100</td>
<td>Birch – Murnaghan</td>
<td>Static</td>
</tr>
<tr>
<td>Au</td>
<td>70</td>
<td>Birch – Murnaghan</td>
<td>Static</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>Birch – Murnaghan</td>
<td>Static</td>
</tr>
<tr>
<td>Fe</td>
<td>300</td>
<td>Birch – Murnaghan</td>
<td>Static</td>
</tr>
<tr>
<td>Mo</td>
<td>100</td>
<td>Birch – Murnaghan</td>
<td>Static</td>
</tr>
<tr>
<td>Pb</td>
<td>200</td>
<td>Vinet</td>
<td>Static</td>
</tr>
<tr>
<td>Pd</td>
<td>100</td>
<td>Birch – Murnaghan</td>
<td>Static</td>
</tr>
<tr>
<td>Pt</td>
<td>550</td>
<td>Vinet</td>
<td>Shock</td>
</tr>
</tbody>
</table>

The fixed point pressure scales are used to calibrate the large volume apparatus. The transition observed between phases is known as fixed point in a substance. Almost all the fixed points of interest in the field of high
pressure is described as first order, where discontinuities occur in volume, entropy or enthalpy. The following points have to be borne in mind the criteria for choosing a fixed point.

1. The transition should be relatively detectable.
2. Hysteresis for the transition should be small
3. The effect of temperature on transition should be small
4. The effect of variable such as purity, grain size, and shear strain etc., on transition should be well known.

2.6 MEASUREMENT OF ELECTRICAL RESISTIVITY

Electrical resistivity is an efficient tool to study the properties of materials. The nature of variation resistivity with temperature, pressure, magnetic field or any other variable yields the direct information of the processes. High pressure resistivity measurements provide useful information about superconductivity, electronic transition, phase transformation (Jamieson 1963), structural changes in metals, semiconducting glasses and insulators (Minomura et al 1992, 1992 a).

Resistivity data is normally acquired by two methods. It can be measured either by two probe or four-probe method. The four-probe method gives the accurate resistance measurements and is suitable especially for conductors whose resistance is low. The two probe method is more suitable for the measurement of materials whose resistance is high. Electrical resistivity (ρ) is defined by the relation

$$E = \rho J$$  \hspace{1cm} (2.6)
Where $E$ is the electric field applied, $J$ is current density and $\rho$ is a second rank tensor which is symmetric. In the linear four probe method the resistivity is determined using the relation.

$$\rho = \frac{VA}{IL} \quad (2.7)$$

Where,  

- $A$ – Area of cross section of the sample  
- $L$ – Distance between the two points between which voltage $V$ is measured  
- $I$ – Current passed through the sample.

The linear four-probe method is employed in the high pressure resistivity measurements and the two probe method is used for measuring the low temperature resistivity in the closed cycle refrigerator experiments. The two probe method has been brought to high state of perfection and is very valuable in working with semiconductors and oxides (Rugan 1975). Two probe method is easy to set up than its four-probe counterpart but it offers less accuracy in resistivity information. This technique permits only the measurements of the sample of uniform flat thickness with arbitrary shape provided the following conditions are met.

i. The contacts should be at the periphery of sample  
ii. The sample should be uniform in thickness  
iii. The sample should be homogeneous.

Figure 2.13 shows the overall arrangement of high pressure electrical resistivity setup.
Figure 2.13 Photograph of arrangement for high pressure electrical resistivity setup