Chapter 2
Crystal growth, synthesis of nanostructures and experimental techniques
2.1. Single crystal growth methods to prepare Bi$_2$S$_3$ and Sb$_2$S$_3$ single crystals.

2.1.1. Introduction

The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research.

2.1.2. Crystal growth method

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapour phase. On the basis of this, crystal growth may be classified into three categories as follows,

- Solid Growth - Solid-to-Solid phase transformation
- Liquid Growth - Liquid to Solid phase transformation
- Vapour Growth - Vapour to Solid phase transformation
Chapter 2

Based on the phase transformation process, crystal growth techniques are classified as solid growth, vapour growth, melt growth and solution growth as shown in Fig. 2.1. The well-known methods over the years for the growth of binary V-VI compounds include Bridgman, direct vapour transport (DVT) and chemical vapour transport (CVT) techniques. Here we have discussed vapour growth technique only in detail which we have used for the growth of single crystals of Bi₂S₃ and Sb₂S₃ compounds.

Fig. 2.1. The flow chart of crystal growth methods.

2.1.3. Vapour growth

The growth of single crystal material from the vapour phase is probably the most versatile of all crystal growth processes. Crystals of high purity can be grown from vapour phase by sublimation,
Chapter 2

condensation and sputtering of elemental materials. Crystal Growth from melt by the classical methods of Kyropoulos and Bridgman becomes exceedingly difficult if applied to materials having high melting points. To obtain single crystals of high melting point materials this method is used. The most frequently used method for the growth of bulk crystals utilizes chemical transport reaction in which a reversible reaction is used to transport the source material as a volatile species to the crystallization region. It is rarely possible to grow large crystals because of multi-nucleation.

The fundamental aspects of vapour phase crystal growth might be divided into four major areas:

1. Thermodynamics, which controls the driving force for the chemical reaction occurring at the vapour solid interface.
2. Mass transport, by which the reactants reach the growing surface and products are removed.
3. Surface kinetics including adsorption of reactants onto the surface, surface diffusion step generation, surface chemical reactions between adsorbed reactants at steps, and adsorption of products.
4. Structural aspects of growth, especially epitaxial growth such as defect generation and surface morphology of homoepitaxial and heteroepitaxial layers.

2.1.4. Crystal Growth by vapour transport method

Vapour transport method is generally preferred due to its relative simplicity and wide applicability. The growth of crystals by vapour transport method can be achieved by two different ways.

(a) Direct Vapour Transport (DVT)
(b) Chemical Vapour Transport (CVT)
(a) **Direct vapour transport technique (DVT)**

Although chemical vapour transport technique gives very large size crystals, it has been observed that crystals grown by the CVT method usually incorporate small amount of the transporting agent, which may remain as an active impurity and affect the measured properties. So for purity, we can use direct vapour transport technique if the reactions are possible without transporting agent.

(b) **Chemical vapour transport technique (CVT)**

Chemical vapour transport reactions are those in which a solid or liquid substance 'A' reacts with a gaseous transporting agent 'B' at a temperature \( T_1 \) to from exclusively vapour phase reaction products \((AB)\), which in turn, undergo the reverse reaction at a different place in the system at a temperature \( T_2 \), resulting in the reformation of crystalline substance 'A'.

\[
iA_{(s,l)} + jB_{(g)} \rightarrow kAB_{(g)}
\]

The process appears to be one of sublimation or distillation. Substance A, however, does not possess an appreciable vapour pressure at the applied temperature. The substance is transported chemically. In addition to a reversible heterogeneous reaction, a concentration gradient must be established. The latter can be the result of temperature gradients, changes in relative pressures, or the difference in the free energy of formation of two substances. The transport of substances by means of heterogeneous reactions has been known for a long time.

➢ **Fundamentals of chemical vapour transport**

First, the principle of chemical vapour transport reactions in a cylindrically closed tube in a temperature gradient is discussed with the aid of the following equations. (Fig. 2.2.)
Fig. 2.2. Chemical Vapour transport in a Cylindrical Closed Tube.

\[ A(s) + B(g) \rightarrow AB(g) \]

\[ n_{AB} = \frac{Dq t}{RT} (P_{AB(1)} - P_{AB(2)}) \]

where \( n_{AB} \) is the number of moles of \( AB \) transported, \( D \) is the diffusion coefficient, \( q \) is the tube cross section, \( l \) is the length of the diffusion path, \( t \) is the duration of the experiment, \( R \) is the gas constant, \( T \) is the absolute temperature of the diffusion path and \( P_{AB(1)} \) and \( P_{AB(2)} \) are the partial pressure of \( AB \) at temperature \( T_1 \) and \( T_2 \) respectively.

In the expression for \( n_{AB} \), the first term on the right hand side represents gas movement and the apparatus constants and the second term represents heterogeneous reaction. Furthermore, all transport equations are written so that the solid reactant is on the left hand side of the equation.

If the solid material \( A \) reacts with a gas \( B \) with the formation of a gaseous material \( AB \) and if the reaction is reversible, then a chemical vapour transport may take place at the suitable temperatures. If the observed reaction is endothermic, then the solid material \( A \) will be consumed at a higher temperature \( T_1 \), with the formation of gaseous product \( AB \) while after the migration of \( AB \) to the location with a lower temperature \( T_2 \), the reverse reaction takes place, and \( A \) is deposited from the gas phase with the release of \( B \). For exothermic reaction transport of the solid phase takes place from low temperature to high temperature.

Normally, for the transport reaction the diffusion in the gas phase is rate-determining. This means that the important concentration
gradient for the diffusion is determined by the existing heterogeneous equilibrium at the temperatures $T_1$ and $T_2$.

**Experimental Procedure**

**Dual zone horizontal furnace**

The furnace is the most important part of present research work to grow the crystals. Two-zone horizontal furnace provides an appropriate temperature gradient over the entire ampoule. Normally the temperatures employed are fairly high. The temperature gradient within the furnace is required over a length of about 25 cm. Stability of the temperature plays an important role, therefore, for this purpose electronic temperature controllers are used.

The furnace was constructed in our University Science and Instrumentation Center (USIC) by using a special sillimanite threaded tube (grade KR 80 GA HG) closed at one end, 450 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm, imported from Koppers Fabriken Feuerfester, Germany. Super Kanthal A1 wire of 17 SWG was wound directly on the muffle tube into two different zones or regions. The tube is enclosed in the hot face insulating brick slabs constructed locally and the brick shell was fully enclosed in thick asbestos sheets, and the entire assembly was supported in a steel framework. This arrangement is shown in **Fig. 2.3**. The power supplied to the furnace windings was regulated by the control circuit shown in **Fig. 2.4**. The two regions of windings are provided with independent power supplies and temperature controllers. Transformers with 70, 80 and 100V taps with 20A current capacity in secondary windings are used to supply sufficient power in order to achieve the required high temperature.

Microprocessor based temperature programmers purchased from M/s. Indotherm Instruments Pvt. Ltd., Mumbai, are used to control the temperatures in the two zones of the furnace. The fluctuations in the
local electrical supply are controlled by AC voltage stabilizer with 180-260 V input and 230 ± 1% output volts of capacity 3 kVA. The output of stabilizer is fed to the primary windings of the transformer, which heated the furnace windings and helped to maintain the stability of growth conditions. With the help of temperature programmers, a required temperature gradient could be established across the length of the working tube in the required temperature range. Thermocouples used are Pt (13%), Rh. Pt. and temperature programmers are calibrated for the above thermocouples. It is found that the thermocouples are stable over the prolonged period of time and are kept within the furnace tube itself showing the furnace tube temperature. The entire length of the furnace is calibrated using Cr-Al thermocouple externally.

Fig. 2.3. The dual zone horizontal furnace with co-axially loaded ampoule.
Fig. 2.4. Control circuit for regulating the power.

⇒ Ampoule
High quality fused quartz tubes of various diameters, having a melting point of about 1500 °C is used for growth experiments. Tubes having internal diameter 22 mm and length 220 mm are found to be more suitable. One end of the ampoule is sealed and the other end was drawn into a neck and joined to another 10 mm inner diameter quartz tube to connect it to the vacuum system for evacuation after introducing the source materials.

⇒ Cleaning of ampoule
This is absolutely necessary to provide growth sites for preferential nucleation. For this purpose, first the ampoule is washed with boiling water along with a suitable detergent, after that it was washed with a hot mixture of concentrated HNO₃ and HF (49 %) taken in equal proportions. Then the washing is carried out by double distilled water. A further washing is done with a mixture of concentrated HNO₃ and H₂SO₄ taken in equal volumes, followed by a final washing for about nine to ten times with double distilled water. The clean ampoule is then transferred into a
Chapter 2

contant temperature oven at 100 °C and left overnight to make it moisture free.

⇒ Charge/ Compound preparation

For charge preparation of elements having the following purities (%) W 99.999 are used. This charge (nearly 10 gm) is then introduced into a thoroughly cleaned quartz ampoule in stoichiometric proportions. The ampoule containing the source material was evacuated to a pressure of $10^{-5}$ torr and sealed and then stirred well to ensure the proper mixing of the powdered elements. The homogeneous mixture is then placed into the two-zone furnace having linear temperature gradient. The temperature of the furnace is increased slowly to avoid any explosion, which might occur due to strongly exothermic reaction between the elements. The ampoule is then maintained at a temperature which is depending upon melting point of sample. After heating period of 3 days, the furnace power is switched off and furnace is allowed to cool down to room temperature. At this stage, the compound formed is a polycrystalline mass.

⇒ Crystal growth

For crystal growth, the specially prepared polycrystalline powder (charge) in the manner described above is placed in another quartz ampoule and is connected to the vacuum system for creating pressure lower than $10^{-5}$ torr so that the vapour pressure developed at high temperature within the ampoule does not lead to its blasting. When the desired pressure inside the ampoule is achieved, it is sealed off and then inserted into the two-zone horizontal temperature gradient furnace. The temperature inside the furnace is increased slowly till it attained the required temperature and kept nearly for 10 days after which the furnace is allowed to cool down slowly to room temperature. After breaking the ampoule growth of large number of single crystals are obtained at the cooler end of the ampoule.
Chapter 2

2.2. Synthesis methods to prepare Bi$_2$S$_3$ and Sb$_2$S$_3$ nanostructures.

2.2.1. Introduction

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the ‘bottom up’ or the ‘top down’ approaches to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms as shown in Fig. 2.5.

Fig. 2.5. Schematic illustration of the preparative methods of nanoparticles.

2.2.2. Synthesis methods of nanomaterials

The most common methods used for the preparation of nanomaterials are given in flow chart Fig. 2.6.
Fig. 2.6. The flow chart of synthesis methods of nanomaterials.

In the last decade, the field of nanocrystalline semiconducting materials has become more and more attractive research area and there are many different ways of creating semiconductor nanostructures. But the chemical synthesis method is extremely useful in current laboratory practice as per the literature survey for synthesis of metal chalcogenides semiconductor material because it is a rapid, simple and inexpensive.

Existing literature on preparation of Bi₂S₃ and Sb₂S₃ nanostructures following methods were reported:

- The ultralong Bi₂S₃ nanoribbons via a solothermal process¹
Chapter 2

➢ Sb$_2$S$_3$ nanoribbons and Bi$_2$S$_3$ nanowires via a hydrothermal process$^2$, $^3$
➢ Bi$_2$S$_3$ nanotubes via a solution based method$^4$
➢ Nanoflowers via a vapour deposition process$^5$
➢ Rod like dendrites of Sb$_2$S$_3$ via a hydrothermal process$^6$
➢ Sb$_2$S$_2$ sub microwires via a hydrothermal process$^7$
➢ Sb$_2$S$_3$ nanowires via solvothermal route$^8$

In this study, we have used simple chemical reaction method and solvothermal method to prepare Bi$_2$S$_3$ and Sb$_2$S$_3$ nanostructures respectively.
2.3. Experimental techniques used for characterization.

2.3.1. Introduction

A large number of experimental techniques are available today. An appropriate characterization of any material plays a very crucial role in determining its various properties.

In the present work to determine the purity, stoichoimetric composition, structural determination, microscopy to get particle size and shape, optical studies, thermal studies, electrical and thermal properties we used the following techniques listed below.

For Bi$_2$S$_3$ and Sb$_2$S$_3$ single crystals following techniques were used:

1) EDAX (Energy dispersive analysis of X-rays)
2) XRD (X-ray diffractometer)
3) SEM (Scanning electron microscope)
4) UV-VIS-NIR Spectrophotometer
5) TGA (Thermogravimetric analysis)
6) Raman Spectroscopy
7) Resistivity
8) Thermoelectric power
9) Thermal conductivity
10) Hall effect

For Bi$_2$S$_3$ nanorods and Sb$_2$S$_3$ microspheres following techniques were used:

1) EDAX (Energy dispersive analysis of X-rays)
2) XRD (X-ray diffractometer)
3) XPS (X-ray Photoelectron Spectroscopy)
The basic principle and experimental set up of above mentioned techniques are discussed below.

2.3.2. Characterization methods

2.3.2.1. Energy dispersive analysis of X-rays (EDAX)

(a) Basic Principle

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an X-ray technique used to identify the elemental composition of materials. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. A high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-rays. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer or by Wavelength Dispersive Spectroscopy (WDS). As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.
Fig. 2.7. Production of the characteristic radiation.

The excess energy of the electron that migrates to an inner shell to fill the newly created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. This ejected species is called an Auger electron as shown in Fig. 2.7, and the method for its analysis is known as Auger electron spectroscopy (AES). X-ray photoelectron spectroscopy (XPS) is another technique closely related to EDS, utilizing ejected electrons in a manner similar to that of AES.

The essential feature of microanalysis is the localized excitation of a small area at the sample surface by a finely focused electron beam, or probe giving a resolution of about 1 μm. The energy of the beam is typically in the range 10-20 keV. This causes X-ray to be emitted from the point of the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth, and thus EDAX is not a surface science technique. By moving the electron beam across the material an image of each element in the sample can be acquired. In principle, the concentration of an element could be determined by comparison of the
intensity of a particular characteristic line from the sample to that of a known standard, usually the pure element, under identical experimental conditions. Analysis at a point could be carried out, or the specimen could be moved continuously in one direction while the X-ray output was recorded to give the distribution of the element.

(b) **Experimental Set up**

Fig. 2.8. shows the EDX system attached to scanning electron microscope (SEM) instruments where the imaging capability of the microscope identifies the specimen of interest. The EDS system is capable of quickly identifying elements with atomic number \((Z) \geq 11\).

EDAX system comprises four basic components that must be designed to work together to achieve optimum results: the beam source, the X-ray detector, the pulse processor and the analyzer. The EDS X-ray detector measures the relative abundance of emitted X-rays versus their energy. The detector is typically lithium-drifted silicon, solid state device. When an incident X-ray strikes the detector, it creates a charge pulse that is proportional to the energy of X-ray. The charge pulse is converted to a voltage pulse (which remains proportional to the X-ray energy) by a charge-sensitive preamplifier. The signal is then sent to a multichannel analyzer where the pulses are sorted by voltage. The energy, as determined from the voltage measurement, for each incident X-ray is sent to a computer for display and further data evaluation. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume.
Fig. 2.8. Experimental set up of Energy Dispersive analysis of X-rays (EDAX)

Elements of low atomic number are difficult to be detected by EDX. The Si(Li) detector is often protected by a Beryllium window. The absorption of the soft X-rays by the Be precludes the detection of elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) have been detected, but the problems involved get progressively worse as the atomic number is reduced\textsuperscript{10,11}.

2.3.2.2. Scanning electron microscope (SEM)

(a) Basic principle

After understanding that an accelerated electron beam can have a very high resolving power, we then move on to see how one can use this electron beam in imaging technology. There are 3 types of electron
microscopes, namely the transmission electron microscope (TEM), scanning electron microscope (SEM), and scanning tunneling microscope (STM).

The scanning electron microscope (SEM) enables the investigation of specimens with a resolution down to the nanometer scale. Here an electron beam is generated by an electron cathode and the electromagnetic lenses of the column and finally swept across the surface of a sample. The path of the beam describes a raster which is correlated to a raster of gray level pixels on a screen. As a consequence the magnification is simply computed by the ratio of the image width of the output medium divided by the field width of the scanned area.

(b) Experimental set up

![Fig. 2.9. SEM chamber](image)

The scanning electron microscope as shown in Fig. 2.9. (Make: Phillips, Model: XL 30 ESEM) with Energy dispersive analysis of X-Ray (EDAX) facility is a versatile electron microscope that combines high vacuum, low vacuum and environmental modes technology into one instrument. The advantages of ESEM technology are capability of a high
Chapter 2

gas pressure in the chamber, pure secondary electron detection and full compatibility with water vapor, to prevent hydrated sample from drying out.

The advantages of SEM system are its low consumption liquid nitrogen and better resolution for qualitative and quantitative analysis. This instrument is very important for study of surface topography. The scanning electron microscope consists of turbo molecular pump based vacuum system, specimen chamber, detectors, camera, monitor, computer etc. Its accelerating voltage range is 0.2-30 kV, resolution range 5 X to 40 kX. The XL 30 ESEM with EDAX is very useful for R&D work on topography study of semiconductor thin and thick crystals and electronic devices, polymers, alloys, clinical samples, cell structures of animal and plant tissues, microbiology, pathological samples, estimation of particle size and nature of color, starch, grain and crystallite etc. This is also useful for making non-destructive chemical analysis at micro level, chemical studies of various alloys, carbon fibers and semiconductor compounds.

In summary, elements with \( Z \geq 11 \) can be readily identified with energy dispersive analysis equipment, usually in a few minutes or even less. For elements present in trace amounts, longer counting times are necessary but instrument stability limits counting time to 10 or 15 minutes in practice.

- **Specifications**
  - **Electron optical system**
    - Accelerating Voltage : 0.2 to 30 kV
    - Resolution : With LaB6 filament 2 nm at 30 kV
      - With W filament 3.5 nm at 30 kV
  - **Scanning system**
    - Magnification : 10 X to 40,000 X or higher
2.3.2.3. X-ray diffraction (XRD)

(a) Basic principle

X-Ray Diffraction is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials\textsuperscript{12,13,14,15}. It is a rapid analytical technique primarily used for phase identification of crystalline material and can provide information on unit cell dimensions.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d\sin \theta$). These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2\(\theta\) angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is
Chapter 2

achieved by comparison of d-spacings with standard reference patterns i.e JCPDS (Joint committee for powder diffraction Standard) files.

(b) Experimental set up

Fig. 2.10. Schematic diagram of powder X-ray diffractometer.

Specifications
- Source : Cu target X-Ray tube
- Operating power of the tube : 2 kW
- Detector : Xe-filled counter or Proportional detector
- Software : JCPDS database for powder diffractometry
- Operation Modes : Vertical & horizontal
- Accuracy : ±0.0025
- 2θ range : 30° to 210°
- 2θ Measurement range : 0° to 136°
- Diffractometer radius : 130 to 230 mm
Fig. 2.11. X-ray powder diffractometer.

X-ray diffractometer consist of three basic elements: X-ray source, the sample under investigation and detector to pick up the diffracted X-rays as shown in Fig. 2.10. In XRD, X-rays are generated within a sealed tube that is under vacuum. A current is applied that heats a filament within the tube, the higher the current the greater the number of electrons emitted from the filament. A high voltage, typically 15-60 kilovolts, is applied within the tube. This high voltage accelerates the electrons, which then hit a target, commonly made of copper. When these electrons hit the target, X-rays are produced. The wavelength of these X-rays is characteristic of that target. These X-rays are collimated and directed onto the sample, which has been ground to a fine powder. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging
Chapter 2

the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector detects the X-ray signal; the signal is then processed either by a microprocessor or electronically, converting the signal to a count rate.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle $\theta$ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of $2\theta$. The instrument used to maintain the angle and rotate the sample is termed a goniometer. The complete experimental set up shown in Fig. 2.11.

The intensity of diffracted X-rays is continuously recorded as the sample and detector rotate through their respective angles. A peak in intensity occurs when the mineral contains lattice planes with d-spacings appropriate to diffract X-rays at that value of $\theta$. Although each peak consists of two separate reflections ($K\alpha_1$ and $K\alpha_2$), at small values of $2\theta$ the peak locations overlap. Greater separation occurs at higher values of $\theta$. Typically these combined peaks are treated as one. The $2\lambda$ position of the diffraction peak is typically measured as the center of the peak at 80% peak height.

Results are commonly presented as peak positions at $2\theta$ and X-ray counts (intensity) in the form of a table. Intensity is either reported as peak height intensity, that intensity above background, or as integrated intensity, the area under the peak. The relative intensity is recorded as the ratio of the peak intensity to that of the most intense peak $^{16,17,18}$.

2.3.2.4. X-ray photoelectron spectroscopy (XPS)

(a) Basic principle

X-ray photoelectron spectroscopy (XPS) (XPS, also called electron spectroscopy for chemical analysis, ESCA) is a quantitative
spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions.

XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its "as received" state, or after some treatment, for example: fracturing, cutting or scraping in air or UHV to expose the bulk chemistry, ion beam etching to clean off some of the surface contamination, exposure to heat to study the changes due to heating, exposure to reactive gases or solutions, exposure to ion beam implant, exposure to ultraviolet light.

- XPS is also known as ESCA, an abbreviation for electron spectroscopy for chemical analysis introduced by Kai Siegbahn and his research group.
- XPS detects all elements with an atomic number (Z) of 3 (lithium) and above. It cannot detect hydrogen (Z = 1) or helium (Z = 2) because the diameter of these orbitals is so small, reducing the catch probability to almost zero.
- Detection limits for most of the elements are in the parts per thousand range. Detection limits of parts per million (ppm) are possible, but require special conditions: concentration at top surface or very long collection time (overnight).
- XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, papers, inks, woods, plant parts, make-up, teeth, bones,
medical implants, bio-materials, viscous oils, glues, ion modified materials and many others.

**XPS is used to measure**

- Elemental composition of the surface (top 1–10 nm usually)
- Empirical formula of pure materials
- Elements that contaminate a surface
- Chemical or electronic state of each element in the surface
- Uniformity of elemental composition across the top surface (or line profiling or mapping)
- Uniformity of elemental composition as a function of ion beam etching (or depth profiling)

**(b) Experimental setup**

![XPS Image](image)

**Fig. 2.12. X-ray Photo-electron spectroscopy image.**
A typical XPS spectrum is a plot of the number of electrons detected (sometimes per unit time) (Y-axis, ordinate) versus the binding energy of the electrons detected (X-axis, abscissa). Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc as shown in Fig. 2.12. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated. To generate atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF) and normalized over all of the elements detected.

Fig. 2.13. Experimental set up for XPS.
Chapter 2

⇒ Vacuum system

To count the number of electrons at each kinetic energy value, with the minimum of error, XPS must be performed under ultra-high vacuum (UHV) conditions because electron counting detectors in XPS instruments are typically one meter away from the material irradiated with X-rays.

It is important to note that XPS detects only those electrons that have actually escaped into the vacuum of the instrument. The photo-emitted electrons that have escaped into the vacuum of the instrument are those that originated from within the top 10 to 12 nm of the material. All of the deeper photo-emitted electrons, which were generated as the X-rays penetrated 1–5 micrometers of the material, are either recaptured or trapped in various excited states within the material. For most applications, it is, in effect, a non-destructive technique that measures the surface chemistry of any material.

⇒ X-ray source

XPS can be performed using either a commercially built XPS system, a privately built XPS system or a synchrotron-based light source combined with a custom designed electron analyzer. Commercial XPS instruments in the year 2005 used either a highly focused 20 to 200 micrometer beam of monochromatic aluminium Ka X-rays or a broad 10–30 mm beam of non-monochromatic (polychromatic) magnesium X-rays. A specially designed XPS instruments displayed in Fig. 2.13. can analyze volatile liquids or gases, materials at low or high temperatures, or materials at roughly 1 torr vacuum, but there are relatively few of these types of XPS systems.

Because the energy of an X-ray with particular wavelength is known, the electron binding energy of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):
Chapter 2

\[ E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \]

where \( E_{\text{binding}} \) is the binding energy (BE) of the electron, \( E_{\text{photon}} \) is the energy of the X-ray photons being used, \( E_{\text{kinetic}} \) is the kinetic energy of the electron as measured by the instrument and \( \phi \) is the work function of the spectrometer (not the material).

2.3.2.5. Transmission electron microscopy (TEM)

(a) Basic principle

TEM works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen.

TEMs work the same way except that they shine a beam of electrons (like the light in a slide projector) through the specimen (like the slide). However, in TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density, composition, etc. For example, porous material will allow more electrons to pass through while dense material will allow less. As a result, a specimen with a non-uniform density can be examined by this technique. Whatever part is transmitted is projected onto a phosphor screen for the user to see.
(b) **Experimental set up**

**Fig. 2.14.** A schematic diagram of the transmission electron microscope.

⇒ **Electron source**

The electron source consists of a cathode and an anode. The cathode is a tungsten filament which emits electrons when being heated. A negative cap confines the electrons into a loosely focused beam shown in **Fig. 2.14**. The beam is then accelerated towards the specimen by the positive anode. Electrons at the rim of the beam will fall onto the anode while the others at the center will pass through the small hole of the anode. The electron source works like a cathode ray tube.

⇒ **Electromagnetic lens system**

After leaving the electron source, the electron beam is tightly focused using electromagnetic lens and metal apertures. The system only
Chapter 2

allows electrons within a small energy range to pass through, so the electrons in the electron beam will have a well-defined energy.

1. Magnetic Lens

Circular electro-magnets capable of generating a precise circular magnetic field. The field acts like an optical lens to focus the electrons.

2. Aperture

A thin disk with a small (2-100 micrometers) circular through-hole. It is used to restrict the electron beam and filter out unwanted electrons before hitting the specimen.

⇒ **Sample holder**

The sample holder is a platform equipped with a mechanical arm for holding the specimen and controlling its position.

⇒ **Imaging system**

The imaging system consists of another electromagnetic lens system and a screen. The electromagnetic lens system contains two lens systems, one for refocusing the electrons after they pass through the specimen, and the other for enlarging the image and projecting it onto the screen. The screen has a phosphorescent plate which glows when being hit by electrons. Image forms in a way similar to photography.

In TEM Electrons are thermionically emitted from the electron gun which are accelerated to 100 keV or higher 1MeV in some microscopes. Typically a TEM consists of three stages of lensing. The stages are the condensor lenses, the objective lenses and the projector lenses. The condensor lenses are responsible for primary beam formation, whilst the objective lenses focus the beam down onto the sample itself. The objective lens produces the first image of the object and is, therefore, required to be most perfect of the lenses. The projector lenses are used to expand the beam onto the fluorescent screen, on a layer of photographic film or to be detected by a sensor such as a CCD camera.
Depending on how the beams reaching the back focal plane of the objective lens are subsequently processed distinguishes the operational modes. Basically, either magnified image are formed or diffraction patterns are obtained as shown in Fig. 2.15. Images can be formed in a number of ways.

**Fig. 2.15. Shows two different modes of TEM.**

The bright field image is obtained by intentionally excluding all diffracted beams and only allowing the central beam this is done by placing suitably sized apertures in the back focal plane of the objective lens. Intermediate and projection lenses then magnify this central beam. Dark field image are formed by magnifying a single beam; this time one of the diffracted beams is chosen by means of an aperture that blocks the central beam and the other diffracted beams.
Chapter 2

Bright Field is particularly sensitive to extended crystal lattice defects in an otherwise ordered crystal, such as dislocations.

The microstructure, e.g. the grain size and lattice defects are studied by use of the image mode while the crystalline structure is studied by the diffraction mode\textsuperscript{19,20,21,22,23}.

2.3.2.6. UV-VIS NIR spectrophotometer

(a) Basic Principle

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state\textsuperscript{24}. Instrument design necessitates that the wavelength of radiation to be studied must be a narrow 'window'. Accordingly, the predetermined electromagnetic radiation wavelengths for ultra-violet (UV), visible (VIS) and near infra-red (NIR) radiation are defined as follows:

- **UV radiation** 200 to 400 nm
- **VIS radiation** 400 to 765 nm
- **NIR radiation** 765 to 3200 nm

If radiation of a particular and discrete wavelength is used to illuminate a sample, then there may be absorption of that radiation. At
other wavelengths, such absorption will not occur. It is this absorption phenomenon which is used to characterize materials.

Light is quantized into tiny packets called photons, the energy of which can be transferred to an electron upon collision. However, transfer occurs only when the energy level of the photon equals the energy required for the electron to get promoted onto the next energy state, for example from the ground state to the first excitation state. This process is the basis for absorption spectroscopy. Generally, light of a certain wavelength and energy is illuminated on the sample, which absorbs a certain amount of energy from the incident light. The energy of the light transmitted from the sample afterwards is measured using a photodetector, which registers the absorbance of the sample. A spectrum is a graphical representation of the amount of light absorbed or transmitted by matter as a function of wavelength.

Bouguer-Beer law as shown in Fig. 2.16. is a basic principle of quantitative analysis, is also called the Lambert-Beer rule. The following relationship is established when light with intensity $I_0$ is directed at a material and light with intensity $I$ is transmitted.

\[ I = I_0 \times 10^{-k \cdot c \cdot l} \]

**Fig. 2.16. Shows Bouguer-Beer Rule**
Chapter 2

In this instance the value $I/I_0$ is called transmittance ($T$) and the value $I/I_0 \times 100$ is called transmission rate ($T\%$). The value $\log (1/T) = \log (I_0/I)$ is called absorbance (Abs).

$$T = I/I_0 = 10^{-kcl}$$
$$Abs = \log(1/T) = \log(I_0/I) = -kcl$$

Here $k$ is proportionality constant, $c$ concentration of the material and $\ell$ is the length of light path through the cuvette in cm.

As can be seen from the above formulas, transmittance is not proportional to sample concentration. However, absorbance is proportional to sample concentration (Beer's law) along with optical path (Bouguer's law). In addition, when the optical path is 1cm and the concentration of the target component is 1mol/l, the proportionality constant is called the molar absorption coefficient and expressed using the symbol $\varepsilon$. The molar absorption coefficient is a characteristic value of a material under certain, specific conditions. Finally, stray light, generated light, scattered light, and reflected light must not be present in order for the Bouguer-Beer rule to apply.

(b) Experimental set-up

The basic part of a spectrophotometer are a light source, a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light and a detector. The radiation source is often a tungsten filament, a deuterium arc lamp which is continuous over the ultraviolet region, and more recently light emitting diodes (LED) and xenon arc lamps for the visible wavelengths. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. A schematic diagram of UV-VIS spectrometer is shown in Fig. 2.17.
In a double beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. One beam, the sample beam, passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference, passes through an identical cuvette containing only the solvent. The containers for the sample and reference solution must be transparent to the radiation which will pass through them. Quartz or fused silica cuvettes are required for spectroscopy in the UV-VIS region. Some double beam instruments have two detectors, and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam, the information display on an LCD screen.

The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$. The intensity of the sample beam is defined as $I$. Over a short period of time, the Spectrometer automatically scans all the component wavelengths in the manner...
Chapter 2

described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. Therefore, this method is excellent to both determine the concentration and identify the molecular structure or the structural changes. Spectrophotometer is also useful to study the changes in the vibration and conformation energy levels after and before an interaction with a substrate, or another molecule. **Fig. 2.18.** shows UV-VIS-NIR Spectrophotometer25.

![UV-VIS-NIR Spectrophotometer](image)

**Fig. 2.18. Shows UV-VIS-NIR Spectrophotometer**

2.3.2.7. Spectrofluorometer – PL (Photoluminescence)

(a) **Basic principle**

When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually, these excitations relax and the electrons return to the ground state. If radiative relaxation occurs, the emitted light is called photoluminescence (PL). This light can be collected and analyzed to yield a wealth of information
Chapter 2

about the photo excited material. The PL spectrum provides the transition energies, which can be used to determine electronic energy levels. The PL intensity gives a measure of the relative rates of radiative and non radiative recombination. Variation of the PL intensity with external parameters like temperature and applied voltage can be used to characterize further the underlying electronic states and bands.

(b) Experimental set up

Fig. 2.19. shows the experimental set up of spectrofluorometer, which having the following apparatus.

Fig. 2.19. Experimental set up of FluoroMax - Compact Spectrofluorometer

Pallavi N. Sakariya /Ph.D. Thesis/Department of Physics/Sardar Patel University/2014
Chapter 2

⇒ The Source

Starting with a Xenon source that supplies prime UV performance, we mount the bulb vertically, since horizontal mounting leads to sagging of the arc that increases instability and decreases the useful life. The Xenon source is focused onto the entrance slit of the excitation monochromator with an elliptical mirror. Besides ensuring efficient collection, the reflective surface keeps all wavelengths focused on the slit, unlike lenses with chromatic aberrations that make them totally efficient only at one wavelength.

⇒ The Slits

The slits themselves are bilaterally, continuously adjustable from the computer in units of band pass or millimeters. This preserves maximum resolution and instant reproducibility.

⇒ The Excitation Monochromator

The excitation monochromator is an aspheric design which ensures that the image of the light diffracted by the grating fits through the slit. The gratings themselves are plane, blazed gratings that avoid the two major disadvantages of the more common concave holographic gratings: poor polarization performance and inadequate imaging during scans that throws away light. The unique wavelength drive scans the grating at speeds as high as 80nm/s. The grating grooves are blazed to provide maximum light in the UV and visible region.

⇒ The Reference Detector

Before the excitation light reaches the sample, a photodiode reference detector monitors the intensity as a function of time and wavelength. The photodiode detector has a wider wavelength response than the older, traditional rhodamine-B quantum counter, and requires no maintenance.
Chapter 2

⇒ The Sample Chamber

A spacious sample chamber is provided to allow the use of a long list of accessories for special samples, and encourages the user to utilize a variety of sample schemes.

⇒ The Emission Monochromator

All the outstanding features of the excitation monochromator are also incorporated into the emission monochromator. Gratings are blazed to provide maximum throughput in the visible region.

⇒ The Emission Detector

Emission detector electronics employ photon-counting for the ultimate in low light level detection. Photon-counting concentrates on signals that originate from fluorescence emission, ignoring smaller signals originating in the detector tube (PMT). The more common method of analog detection (used by lower performance fluorometers) simply adds noise and signal together, masking weak emissions. The emission detector housing also contains an integral high-voltage supply which is factory set to provide the signal-to-noise ratio.

⇒ Computer Control

The entire control of the FluoroMax-4 originates in your PC with our revolutionary new Fluor Essenc software and is transmitted through a serial link. On start-up, the system automatically calibrates and presents itself for new experiments or stored routines instantly called from memory.

2.3.2.8. Thermogravimetric Analysis (TGA)

(a) Basic principle

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition,
oxidation, or loss of volatiles (such as moisture). Common applications of TGA are

(1) materials characterization through analysis of characteristic decomposition patterns,
(2) studies of degradation mechanisms and reaction kinetics,
(3) determination of organic content in a sample, and
(4) determination of inorganic (e.g. ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis.

Thermogravimetric analysis (TGA) is the most widely used thermal method. It is based on the measurement of mass loss of material as a function of temperature. In thermogravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. A plot of mass change versus temperature (T) is referred to as the thermogravimetric curve (TG curve). For the TG curve, we generally plot mass (m) decreasing downwards on the y axis (ordinate), and temperature (T) increasing to the right on the x axis. Sometime we may plot time (t) in place of T. TG curve helps in revealing the extent of purity of analytical samples and in determining the mode of their transformations within specified range of temperature.

In thermogravimetry, the term 'decomposition temperature' is a complete misnomer. In a TG curve of a single stage decomposition, there are two characteristic temperatures; the initial Ti and the final temperature Tf. Ti is defined as the lowest temperature at which the onset of a mass change can be detected by thermo balance operating under particular conditions and Tf as the final temperature at which the particular decomposition appear to be complete. Although Ti has no fundamental significance, it can still be a useful characteristic of a TG curve and the term procedural decomposition temperature has been
Chapter 2

suggested. The difference $T_f - T_i$ is termed as reaction interval. In a dynamic thermogravimetry a sample is subjected to continuous increase in temperature usually linear with time whereas in isothermal or static thermogravimetry the sample is maintained at a constant temperature for a period of time during which any change in mass is noted. Now we will take up the instrumentation commonly used to obtain TG Curve.

(b) Experimental set up

The instrument used in thermogravimetry (TG) is called a thermobalance. It consists of several basic components in order to provide the flexibility necessary for the production of useful analytical data in the form of TGA Curve.

Fig. 2.20. Experimental set-up of Thermogravimetric analysis
Chapter 2

Basic components of a typical thermobalance are listed below and its experimental set up is shown in Fig. 2.20.

i) Balance

ii) Furnace: heating device

iii) Unit for temperature measurement and control (Programmer)

iv) Recorder: automatic recording unit for the mass and temperature changes

⇒ Balance

The basic requirement of an automatic recording balance includes accuracy, sensitivity, reproducibility, and capacity. Recording balances are of two types, null point and deflection type. The null type balance, which is more widely used, incorporates a sensing element which detects a deviation of the balance beam from its null position. A sensor detects the deviation and triggers the restoring force to bring the balance beam back to the null position. The restoring force is directly proportional to the mass change. Deflection balance of the beam type involve the conversion of the balance beam deflection about the fulcrum into a suitable mass-change trace by (a) photographic recording i.e change in path of a reflected beam of light available of photographic recording, (b) recording electrical signals generated by an appropriate displacement measurement transducer, and (c) using an electro-chemical device. The different balances used in TG instruments are having measuring range from 0.0001 mg to 1 g depending on sample containers used.

⇒ Furnace

The furnace and control system must be designed to produce linear heating at over the whole working temperature range of the furnace and provision must be made to maintain any fixed temperature. A wide temperature range generally -150°C to 2000°C of furnaces is used in different instruments manufacturers depending on the models. The
Chapter 2

range of furnace basically depends on the types of heating elements are used.

⇒ Temperature Measurement and Control

Temperature measurement are commonly done using thermocouples, chromel-alumel thermocouple are often used for temperature upto 1100°C whereas Thermogravimetric analysis Pt/(Pt-10% Rh) is employed for temperature upto 1750°C. Temperature may be controlled or varied using a program controller with two thermocouple arrangement, the signal from one actuates the control system whilst the second thermocouple is used to record the temperature.

⇒ Recorder

Graphic recorders are preferred to meter type recorders. X-Y recorders are commonly used as they plot weight directly against temperature. The present instrument facilitate microprocessor controlled operation and digital data acquisition and processing using personal computer with different types recorder and plotter for better presentation of data26,27,28,29.

2.3.2.9. Raman spectroscopy

(a) Basic principles

The principle of the Raman spectroscopy is relatively simple. It consists in sending a monochromatic light (only one color and not a mixture) on the sample to study and analyze the scattered light. The scattering process is the following: the incidental photons are destroyed and their energy is used for creating scattered photons and creating (Stokes process) or destroying (anti-Stokes process) vibrations in the studied sample.
The scale used in $X$-coordinate is an energy scale which zero has been moved to match the energy of the incoming photons and reversed so that energies corresponding to Stokes processes is positive. Indeed, the Stokes diffusion is more intense than the anti-Stokes diffusion (except in the event of strong resonant processes) and thus, it is much used.

At the molecular level photons can interact with matter by absorption or scattering processes. Scattering may occur either elastically or inelastically. The elastic process is termed Rayleigh scattering, while the inelastic process is termed Raman scattering. The electric field component of the scattering photon perturbs the electron cloud of the molecule and may be regarded as exciting the system to a ‘virtual’ state. Raman scattering occurs when the system exchanges energy with the photon, and the system subsequently decays to vibrational energy levels above or below that of the initial state. The frequency shift corresponding to the energy difference between the incident and scattered photon is termed the Raman shift. Depending on whether the system has lost or gained vibrational energy, the Raman shift occurs either as an up- or down-shift of the scattered photon.

**Fig. 2.21. Vibrational level of sample material.**
frequency relative to that of the incident photon. The down-shifted and up-shifted components are called respectively the Stokes and anti-Stokes lines. Stokes radiation occurs at lower energy (longer wavelength) than the Rayleigh radiation, and anti-stokes radiation has greater energy. Fig. 2.21. shows the energy of the vibrational level of the sample material.

A plot of detected number of photons versus Raman shift from the incident laser energy gives a Raman spectrum. Different materials have different vibrational modes, and therefore characteristic Raman spectra. This makes Raman spectroscopy a useful technique for material identification. A molecular polarizability change, or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman effect. The amount of the polarizability change will determine the intensity, whereas the Raman shift is equal to the vibrational level that is involved. Homonuclear diatomic molecules such as H₂, N₂, O₂, etc which do not show infrared spectra since they do not possess a permanent dipole moment do show Raman spectra since their vibration is accompanied by a change in polarisability of the molecule. Thus, Raman spectroscopy permits us to examine the vibrational spectra of compounds that do not lend themselves to IR absorption spectroscopy.

(b) **Experimental setup**
Fig. 2.22. Raman spectrometer.

Laser: STA-01SH
LD: laser driver
POL: polarization rotator
USB SMD: two-axis stepper motor controller 8SMC-USBh-B2-2
M1: motorized flip-mirror - 8MR174-11+ 5MBM22SP-1
M2: mirror @ 5MBM23-05
L1, L2: focusing lenses @ XYZ translate stage
S@H: sample holder @ XYZ translate stage
Condenser
W-meter: Ophir USB power meter
FN: Notch filter (531 nm)
Spectrograph
PC: computer
Chapter 2

CCD(USB): Hamamatsu C7045 with S7035-1007 Sensor and USB-2 controller

The Raman measurements are made using the instrumentation shown in Fig. 2.22. The output light from a laser is focused on the sample cell. The scattered light is collected at right angles to the excitation laser beam and focused onto the polychromator where it is dispersed and detected by a charge coupled device camera.

In recent years, Raman spectroscopy has become even more accurate and easier due to advancements in optics, laser and computer technology. Charge coupled device (CCD) detectors have enormously helped the use of Raman spectroscopy by allowing scientist to take data quicker and with more precision that they were able to with the older photomultiplier tubes. The CCD has an array of detectors that can look at a range of wavelengths at one time greatly reducing the collection time. In older spectrometers with photomultiplier tubes the grating of the spectrometer would physically move in small increments over a period of time to take a scan of the spectrum which is a very time consuming process.

Raman spectroscopy can be used on liquids, solids and gases making it very versatile for studying various materials. Because of the distinct spectra that certain classes of materials give off, due to their structural arrangement, Raman spectroscopy can be used to determine the composition of unknown substances. This also makes Raman spectroscopy ideal for qualitative analysis of materials. In Raman spectroscopy no probe physically touches the material the laser light is the only thing to disturb the sample, this means that the material is not disturbed by the probe physically touching it and in some cases is the only way to accurately study a material.

Surface Enhanced Raman Spectroscopy (SERS) and Resonance Raman Effect (RRE) are different types of Raman spectroscopy. The goal
Chapter 2

of these two processes is to enhance the weak signal of the Raman spectra. Micro Raman spectroscopy (MRS) is another type of Raman spectroscopy and this process reduces the spot size of the light source on the sample, which is helpful if a small area of the sample is to be observed. It is also used to reduce damage or heating of the sample by the laser light\textsuperscript{30,31,32}.

2.3.2.10. Resistivity

(a) Basic principle

The resistivity of a conducting material is determined by measuring the resistance of a sample of known geometry. To determine the electrical resistance of an object, one measures the relationship between two quantities: the current run through the object, and the voltage that arises due to that resistance. There are different methods to determine the resistivity of a sample depending on the size and shape of the sample. All the methods require a sensitive voltmeter with a current source or a micro-ohmmeter because the resistance to be measured is very low.

(b) Experimental set up

1. Four point probe method

The four point probe method is most common way to measure the semiconductor material’s resistivity. Two of the probes are used to source current and the other two are used to measure voltage. Using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and the semiconductor material. This technique involves bringing four equally spaced probes into contact with
the material of unknown resistance. The probe array is usually placed in the centre of the material as shown in Fig. 2.23.

![Fig. 2.23. Four point collinear probe resistivity method.](image)

The current is sourced through the two outer probes and the voltage drop is measured between two inner probes. The surface or sheet resistivity is calculated as

\[
\rho_s = \left( \frac{\pi}{\ln 2} \right) \frac{V}{I}
\]  

(2.1)

where \( \rho_s \) = sheet resistivity

\( V \) = measured voltage

\( I \) = source current

If the thickness of the sample is known, the bulk or volume resistivity can be calculated as

\[
\rho = \left( \frac{\pi}{\ln 2} \right) \frac{V}{I} t
\]  

(2.2)

where \( \rho \) = volume resistivity

\( t \) = thickness

2. **Van der pauw method**

The advantage of vander pauw method for resistivity measurements is that it allows avoiding due to the incorrect knowledge of sample geometry. This method was developed in order to measure the
resistivity of thin and flat samples of semiconductor as shown in Fig. 2.24.

![Van der Pauw Method](image)

**Fig. 2.24. Van der Pauw method for resistivity measurement.**

To make a measurement, current is caused to flow along one edge of the sample (for instance, $I_{12}$) and the voltage across the opposite edge (for instance, $V_{34}$) is measured. Then the resistance can be calculated as

$$R_{12,34} = \frac{V_{34}}{I_{12}} \tag{2.3}$$

Van der Pauw discovered that the sheet resistance of an arbitrarily shaped sample can be determined from such resistances. The actual sheet resistance is related to these resistances by van der Pauw formula,

$$e^{-\frac{\pi R_{12,34}}{R_s}} + e^{-\frac{\pi R_{34,12}}{R_s}} = 1 \tag{2.4}$$
In order to measure the resistivity a high temperature resistivity measurement setup was designed at the Department of Physics, Sardar Patel University. Using this setup a temperature dependent resistivity can be measured from room temperature to 1000K. Schematic image of the sample holder is shown in Fig. 2.25. The sample under test is pressed on the ceramic base containing horizontal electrical leads. Then the sample holder is inserted in a vertical tubular furnace. Source current is applied by a constant current source and voltage is measured.

2.3.2.11. Thermoelectric Power

(a) Basic Principle

The thermopower, or thermoelectric power of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material\(^{33}\).

An applied temperature difference causes charged carriers in the material, whether they are electrons or holes, to diffuse from the hot side to the cold side, similar to a gas that expands when heated.
Mobile charged carriers migrating to the cold side leave behind their oppositely charged and immobile nuclei at the hot side thus giving rise to a thermoelectric voltage (thermoelectric refers to the fact that the voltage is created by a temperature difference). Since a separation of charges also creates an electric field, the buildup of charged carriers onto the cold side eventually ceases at some maximum value since there exists an equal amount of charged carriers drifting back to the hot side as a result of the electric field at equilibrium. Only an increase in the temperature difference can resume a buildup of more charge carriers on the cold side and thus lead to an increase in the thermoelectric voltage. Incidentally, the thermopower also measures the entropy per charge carrier in the material.

(b) Experimental setup

The thermoelectric power measurement set up developed in Physics department, Sardar Patel University, was used to measure thermoelectric power (S) of a sample as a function of temperature (T). Schematic image of sample holder shown in Fig. 2.26. The sample under test is pressed between two circular block A and B, then sample holder is inserted in tubular furnace, hence block A and B having same temperature as the temperature of the furnace. To make the temperature difference between block A and B, an additional heater is attached with block A. Thermocouples connected with these block which indicate temperature of the block and voltage between the two surfaces of the sample was measured by electrodes attached with block A and B.
2.3.2.12. Thermal Conductivity

(a) Basic principle

Thermal conductivity (often denoted $k$, $\lambda$, or $\kappa$) is the property of a material to conduct heat. Heat transfer occurs at a higher rate across materials of high thermal conductivity than across materials of low thermal conductivity. Thermal conductivity of materials is temperature dependent. The reciprocal of thermal conductivity is called thermal resistivity, usually expressed in kelvin-meters per watt ($K\cdot m\cdot W^{-1}$).
(b) **Experimental set up**

Consider a sample of cross section A across which a thermal gradient exists. T₂ and T₁ are the temperatures measured over a length ΔL. Let Q be the quantity of heat flowing through A as shown in Fig. 2.27. below.

![Experimental setup for thermal conductivity](image)

**Fig. 2.27. Experimental setup for thermal conductivity.**

Now, thermal conductivity K is given by the ratio of the heat flux Q/A to the thermal gradient ΔT / ΔL.

\[
K = \frac{Q/A}{\Delta T/\Delta L}
\]  

(2.5)

⇒ **Thermal Conductivity and System Configuration**

The length of a sample is influenced by the magnitude of the thermal conductivity. When the thermal conductivity of the sample is high, the amount of heat flowing is high and the heat lost from the
sample's lateral surface is small. As a high temperature gradient is established in this case, it is possible to measure it accurately.

On the other hand, samples with low thermal conductivity (and correspondingly low heat flux) are usually of a smaller thickness, which is sufficient to generate an accurately measurable thermal gradient. Smaller thicknesses also mean less lateral losses. Sometimes, self-guarding is provided for lateral surfaces by the use of additional pieces of the sample material.

For low temperatures, the sample is packed inside insulation to minimize heat losses or heat gains along the radial direction. Installation of a guard, which can be controlled to have a temperature gradient same as that across the sample, is often required at high temperatures.

At such high temperatures, heat losses are difficult to control. Therefore, the ratio of conductance of the sample to the conductance of lateral insulation becomes significant, as does the quality of guarding.

⇒ **Methods for Conductivity Measurement**

Here we discuss a few methods of measuring thermal conductivity of solid materials at temperatures ranging from sub ambient temperatures to 1500°C. These include:

- Axial flow methods
- Absolute axial heat flow method
- Comparative cut bar method
- Guarded/Unguarded Heat Flow Meter Method
- Guarded Hot Plate Method
- Hot Wire Method
- The Probe Method
Chapter 2

2.3.2.13. Hall Effect

(a) Basic principle

Fig. 2.28. Typical set up for Hall measurement.

If a current-carrying conducting strip is placed in a magnetic field $B$ that is perpendicular to the current, a transverse electric potential, called the Hall voltage $V_H$ will appear across the conductor as shown in Fig. 2.28. This potential is related to the current $I$ and to $B$ by

$$R_H = \frac{V_H t}{I B}$$

(2.6)

where $t$ is the dimension of the sample parallel to the magnetic field $B$. The Hall coefficient $R_H$ characterizes the conducting properties of the material. Its sign is determined by the sign of the charge carriers, its magnitude by their density $n$ (carriers/unit volume)

$$R_H = \pm \frac{1}{ne}$$

(2.7)

The mobility $\mu$ of the charge carriers in an electric field $E$, is related to their drift velocity by

$$v = \mu E$$

(2.8)

and can also be extracted from $R_H$ if the resistivity($\rho$) of the material is known because
In the metallic conductors the charge carriers are generally electrons of high mobility and density. In a semiconductor the carriers may be electrons or positive holes and their mobility and density may differ significantly from those metals.

The Hall effect experiment is also used to measure magnetic fields by passing a known current $I$ through a sample whose Hall coefficient is known and then measuring $V_H$. The sensitivity of such probe is defined as $\text{Sensitivity} = \frac{V_H}{IB}$.

(b) Experimental set up

Fig. 2.29. Experimental arrangement for Hall effect.

Specification:

- Hall Effect Set-up Model.
- Electromagnet.
- Constant Current Digital Power Supply.
- Digital Gaussmeter.

Fig. 2.29. shows experimental set-up used for Hall effect studies.
Chapter 2

2.4. References


Chapter 2

10 J. P. Sibilia,  
A Guide to Materials Characterization and Chemical Analysis,  

11 D. Brondon, W.D. Kaplan,  
Microstructural Characterization of Materials,  

12 C. R. Brundle, C. A. Evans, J. S. Wilson,  
Encyclopedia of Materials Characterization,  

13 L. H. Van Vlack,  
Materials Science for Engineers,  

14 B. D. Cullity,  
Elements of X-ray Diffraction,  

15 C. Hammond,  
The Basics of Crystallography and diffraction (2nd Edition)  

16 B. E. Warren,  
X-ray Diffraction,  
Chapter 2

17 C. Suryanarayana, M. G. Norton,  
X-ray Diffraction : A Practical Approach,  

18 P. F. Fewster,  

19 D. B. Williams, C. B. Carter,  
Transmission Electron Microscopy,  

20 B. Fultz, J. M. Howe,  
Transmission Electron Microscopy and Diffractometry of Materials  

21 X. F. Zhang, Z. Zhang  
Progress in Transmission Electron Microscopy,  

22 M. D. Graef,  
Introduction to Conventional Transmission Electron Microscopy,  
Cambridge University Press.

23 D. K. Racker,  
Transmission Electron Microscopy: Methods of Application,  
Thomas (1983).

24 Skoog, et al.  
Principles of Instrumental Analysis.
Chapter 2


25 G. R. Chatwal, S. K. Anand,
   Instrumental methods of chemical analysis,

26 P. Kent,

27 J. D. Menczel, B. Prime,

28 Wendlandt,
   Thermal Methods of Analysis,

29 Keattch, C.J. & Dollimore,
   An Introduction to Thermogravimetry,

30 I. R. Lewis, H. G. M. Edwards,
   Handbook of Raman Spectroscopy,
   Published by CRC Press (2001).

31 E. Smith, G. Dent,
   Modern Raman Spectroscopy,
Chapter 2

32 J. R. Ferraro, K. Nakamoto, C. W. Brown
   Introductory Raman Spectroscopy,

33 K. M. Blundell,
   Concepts in Thermal Physics,