CHAPTER - II

CRYSTAL GROWTH TECHNIQUES AND INSTRUMENTATION

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2.1 CRYSTAL GROWTH TECHNIQUES

The process of crystal growth is a controlled change of one phase to another phase. This transition may occur from the solid, liquid or vapour[1] The method chosen for the growth of single crystals depends on the characteristics of the material like melting point, solubility and physico-chemical properties [2] Depending on the phase transition in the system, crystallization techniques can be generally classified into four main categories [3,4,5,6].

1. Solid growth : solid - solid
2. Vapour growth : vapour - solid
3. Melt growth : liquid - solid
4. Solution growth : liquid - solid

The figure 2.1 shows how these four main categories break down into sub-families of related growth techniques.

Figure 2.1 : Main categories with sub-family of crystals growth techniques
2.1.1 Solid growth

In solid growth the transformation of a polycrystalline material into a single crystal [7]. Large crystals of several materials like metals have been grown by this technique.

2.1.2 Vapour growth

This technique can be used to grow materials which lack suitable solvents and sublime before melting at normal pressure. Vapour growth is the slow process which involves the growth on a substrate [8].

Growth of crystals from vapour phase may be classified as

1. Physical vapour transport
2. Chemical vapour transport

2.1.3 Physical vapour transport

In this technique crystal is grown from its own vapour and there is no compound formation or reaction. Sublimation and sputtering are the two general techniques employed. Growth is achieved by the sublimation of the charge at a high temperature end of the furnace, followed by the condensation at the colder end. Sputtering techniques are preferred to prepare thin films of substances having low vapour pressure. The physical vapour transport techniques are mainly used to grow a variety of crystals and also to grow epitaxial films [9,10].

2.1.4 Chemical vapour transport

This method involves a chemical reaction between the source material to be crystallized and a transporting agent [11]. The material to be crystallized is first converted into one or more gaseous products which is allowed to diffuse into the
colder region or allowed to be transported by means of a transporting (carrier) gas. At the colder region the reaction is reversed so that the gaseous product decomposes to deposit the parent material liberating the transporting agent which further diffuses to the hotter region and again reacts with the charge. A very thin layer of crystallites of the source material could be grown by this technique [12].

2.2 MELT GROWTH TECHNIQUE

This technique is used for the growth of large single crystals such as metals, semiconductors and laser host materials. The crystallization is initiated by fusion and resolidification of the pure material. The material to be grown is melted and after that it may progressively cooled to yield the crystalline matter. Single crystals with high degree of perfection and purity can be obtained by this method.

Melt growth methods are classified as

1. Normal freezing method
   (a) Bridgman method
   (b) Czochralski method

2. Zone growth method
   (a) Zone melting method
   (b) Floating zone method

Horizontal Bridgman method (Chalmer’s technique) and vertical Bridgman method (Stockbarger technique) are the two versions of Bridgman method. In these techniques direct solidification is obtained by slowly withdrawing a boat containing molten material through a temperature gradient. This technique is mostly used for the growth of metals, semiconductors and alkaline earth halides [13].
Czochralski method is a crystal pulling system in which large single crystals can be grown. Czochralski method is widely used in growing single crystals of semiconductors like silicon and other materials [14,15]. Zone melting is a purification technique, which is used for the growth of single crystals. In this method, a part or zone of the solid material is melted and the molten region travels together with the heating system. Doped crystals with uniform distribution of the dopant can be grown by this method [16]. This method is used to grow high purity silicon and germanium [17].

2.3 LOW TEMPERATURE SOLUTION GROWTH

Solution growth at low temperature plays a vital role because of its simplicity and versatility [18]. The major advantage of this method is crystals can be grown near to equilibrium condition and hence crystals with high perfection can be grown. Low temperature solution growth near ambient temperature offers the best technique of producing crystals under near equilibrium condition and free from strain and dislocation [19]. Single crystals, whose materials are unstable in the melt and undergo decomposition upon melting [5] can be grown by this technique.

The preparation of prismatic morphology is possible using this technique. In general, this method involves seeded growth from a saturated solution. The super saturation is achieved either by slow cooling or by slow solvent evaporation. This technique is widely used to grow bigger crystals, which have high solubility and temperature dependence of solubility [20]. As the crystals are grown at room temperature, the structural imperfections in the grown crystals are low [19].
2.3.1 Crystallization techniques under low temperature

Low temperature solution growth can be sub divided into:

i) Slow cooling method

ii) Slow evaporation method

iii) Temperature gradient method

2.3.1.1 Slow cooling method

Slow cooling is one of the best methods to grow bulk crystals. A narrow range of temperature is needed. Super saturation of the solution can be obtained by lowering the temperature of the solution and that will result a seed crystal to grow. If the solution is cooled very slowly, then the growing crystal takes up the solute from the solution. In this technique much of the solute remains in the solution when the growth period is over. To compensate this and to grow bigger crystals large volume of solution is required.

2.3.1.2 Slow evaporation method

Slow evaporation method is the simplest method. Super saturation can be achieved from a saturated solution by the evaporation of the solvent isothermally. If the solvent is non-toxic, the evaporation may be permitted into the atmosphere. Typical growth condition is to maintain a temperature stabilization of about 0.05°C and the rate of evaporation of the solvent by mm³/h.

2.3.1.3 Temperature gradient method

In this technique, there is a transport of materials from a hot region containing the solute to a cooler region, where the solution is supersaturated and the crystal grows.
2.4 ADVANTAGES OF LOW TEMPERATURE SOLUTION GROWTH OVER OTHER METHODS

Crystal Growth at low temperature using solution has the following advantages.

1. A convenient growth vessel.
2. In-situ observation is possible.
3. The crystal defects can be minimized. Since growth takes place at ambient temperature.
4. Crystals of required dimensions can be grown.
5. Doping can be easily done.

2.5 SELECTION OF CRYSTAL GROWTH TECHNIQUE

The selection of crystal growth technique is governed by the following factors [23]

a) The nature of solubility of a given substance.
b) The physio-chemical properties of the solvent and the solute (volatility, chemical stability etc.)
c) The apparatus available in a given laboratory.

Substances can be classified according to their solubility [18].

i) Low solubility (less than 1 g per 100 g of the solvent)
ii) Moderate solubility (from 1 to 5 g per 100 g of the solvent)
iii) High solubility (from 5 to 200 g per 100 g of the solvent)
iv) Very high solubility (more than 200 g per 100 g of the solvent)
The classification in accordance with the temperature coefficients of the solubility is as follows:

a) Small temperature coefficient of solubility: less than 0.001 g/deg. per 100 g of the solvent.

b) Moderate temperature coefficient of solubility: from 0.001 g to 0.5 g/deg. per 100 g of the solvent.

c) Larger temperature coefficient of solubility: more than 0.5 g/deg. per 100 g of the solvent.

Taking into account of the solubility data of the substances, we can use various methods.

If the solubility (C) is less than 1 g/100 g of the solvent (log C > 0), crystals can be grown by the chemical reaction method.

Beginning from solubility of 5 g/100 g of the solvent (log C > 0.7), we can grow crystals by the solvent evaporation and concentration convection methods.

2.6 INSTRUMENTATION

A number of techniques are used for the characterization of the grown crystals and to study its physical physical properties. The instruments used are versatile in performance and give perfect results. This chapter contains a brief description of the principle involved in the measurement and the salient features of the instruments.

2.6.1 Powder X-Ray Diffractometer

Powder diffraction patterns has played a vital role in structural physics, chemistry and material science. Important advances in structural studies of materials
ranging from high temperature superconductors and fullerenes to zeolites have relied on the powder diffraction technique.

For structures with less than 100 atoms in the asymmetric unit, single-crystal techniques are almost successful and final refined structure will almost always be more reliable than its powder diffraction results.

A brief description of the construction and working of the powder X-ray diffractometer is given below.

2.6.1.1 Diffractometer Geometries

Guinier focusing cameras were regularly used for obtaining structures in the early period of *initio* structure determination from powder diffraction data. This was because of their high resolution, the accuracy of measured diffraction angles and the use of monochromatic radiation [21]. The instrument configuration most commonly used with conventional divergent beam X-ray sources is based on Bragg – Brentano parafocussing geometry shown in figure 2.2.

![Figure 2.2 Geometry of Bragg – Brentano diffractometer](image)

Figure 2.2 Geometry of Bragg – Brentano diffractometer
The source, sample and receiving slit lie on the ‘focussing circle’, which has a radius dependent on $\theta$. Coherently scattered X–rays from a flat sample then converge on a receiving slit located in front of the detector. The detector rotates about the goniometer axis through twice the angular rotation of the sample.

2.6.1.2 Monochromatic Radiation

The use of highly monochromatic radiation is desirable in diffraction experiments operating in the angle–dispersive mode. The most widely used radiation in conventional powder diffractometry is the CuK$_\alpha_1, 2$ doublet. Two diffraction patterns are thus recorded simultaneously, which contributes to a further loss in resolution with increasing angle, particularly at moderate to high angles.

Better resolution can be obtained by means of a focussing monochromator [22]. There is some reduction in the intensity of the K$\alpha_1$ line, but this can be partially compensated for by using high–power X–ray tubes. Some residual K$\alpha_2$ component is often observed at the focal point of the monochromator. This can be eliminated by incorporating a knife–edge that leaves the K$\alpha_1$ component unaffected. Typically, powder data up to 150º 20 can be collected with good counting statistics within 48 hours.

2.6.1.3 Data Quality

High quality data are essential for structure solution. Diffractometers must be well–aligned and tested using standard materials. In addition to high instrumental resolution, peak positions must also be precise, for both indexing and Rietveld refinement. The principle errors in peak position are zero–point shift and displacement of the specimen. If they are not eliminated at source or properly modelled, experimental imperfections are introduced in the Rietveld refinement.
Laboratory-based X-ray powder diffractometers are sufficient for structure solution of moderately complex crystal structures. Even if higher resolution proves to be essential, in-house diffractometers still offer an inexpensive preliminary stage is study of more complex structures [23].

2.6.1.4 Applications

i. New mineral identification, crystal solution refinement.

ii. Determination of unit cell, bond-lengths, bond-angles and site-ordering.

iii. Characterization of cation-anion coordination.

iv. Variations in crystal lattice with chemistry.

v. With specialized chambers, structures of high pressure and/or temperature phases can be determined.

vi. Determination of crystal–chemical Vs environmental control on mineral chemistry.

vii. Powder patterns can also be derived from single-crystals by use of specialized cameras [24].

2.6.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier Transform Infrared Spectroscopy is a simple mathematical technique to resolve a complex wave into its frequency components. The conventional IR spectrometers are not much use for the far IR region (20-400cm⁻¹) as the sources are weak and detectors insensitive. FTIR has made the middle IR (400-4000cm⁻¹) also more useful. Though slightly differing techniques are followed for the different regions, the basic components of an IR spectrophotometer are the same [25].
2.6.2.1 Vibration-Rotation Spectra

If a molecule is not rigid but contained atoms capable of vibration under elastic forces about equilibrium positions, radiations would be emitted. The frequency emitted would be essentially that of the atomic vibration. If the molecules were rotating at the same time, the emitted line would have a fine structure having frequencies respectively greater or less than the frequency of the atomic vibration. These are the Vibration-Rotation Spectra. Spectral lines of these Spectra fall in the Infrared region. Photon energies are in the range of 0.2eV to 2eV.

For a vibration to be Infrared active, there must be change in the dipole moment during the vibration. If the molecule possesses some degree of symmetry, the direction of the dipole moment change may coincide with one or more of the principal axes of the molecule. If the dipole moment change occurs, parallel to the symmetry axis, then the vibration is known as parallel vibration. On the other hand, if the dipole moment change occurs, perpendicular to the symmetry axis, then the vibration is known as perpendicular vibration.

2.6.2.2 Principle

The conventional spectroscopy, called the frequency domain spectroscopy, records the radiant power \( G (\omega) \) as a function of frequency\( \omega \). In the time domain spectroscopy, the changes in radiant power \( f (t) \) are recorded as a function of time \( t \). In a Fourier Transform spectrometer, a time domain plot is converted into a frequency domain spectrum. In mathematics, the Fourier transform of the function \( f (t) \) is defined by

\[
G (\omega) = \frac{1}{\sqrt{2\pi}} \int f (t) e^{i\omega t} dt \quad \ldots \ldots (1)
\]
Then the inverse relation is 

\[ f(x) = \frac{1}{\sqrt{2\pi}} \int G(\omega) e^{i\omega x} d\omega \] …… (2)

Equations (1) and (2) are said to form a Fourier transform pair.

To illustrate the use of Fourier transform, consider the superposition of two sine waves, figures 2.3a and 2.3b of the same amplitude but of slightly different frequencies. Figure 2.3c represents the superposed wave. The Fourier transform of the individual sine waves and the superposed wave train gives the frequencies in the frequency domain and are represented in figures 2.3d, 2.3e and 2.3f [25].

![Diagram of time and frequency domains with sine waves and their spectra](image)

**Figure 2.3**  
(a) sine wave,  
(b) sine wave of slightly differing frequency,  
(c) sum of the sine waves in a and b,  
(d) – (f) the frequency domain spectra of the waves

The various essential components used in the construction of Fourier Transform Infrared spectrometer are described below:
2.6.2.2.a) **Source of radiation**

Ideal source is a black body radiator. As it is difficult to have a perfect black body radiator, a source which is approximate to it is used. The most commonly used sources are the globar filament and the Nernst glower. The Nernst glower consists of a spindle of rare earth oxide (thorium, cesium or zirconium) of about 2.5 cm long and 0.25 cm diameter with a black body peak around 1.4 μ (7100 cm⁻¹) at 1600-1700°C. It has very good emissivity in the shorter wavelengths. The globar is a low resistance rod of silicon at 1200°C. It is more useful in the longer wavelengths. The Nernst filament requires preheating to make it conductive.

2.6.2.2.b) **Monochromator**

It is important part of the spectrometer as it splits the polychromatic radiation into its component wavelengths. This is achieved by using prisms or gratings or both. Gratings give better resolving power. The prism or grating is rotatable mechanically. The resolution also depends on the slit width and quality of mirrors. Rock salt prism is usually used as monochromator in the region 650 – 4000 cm⁻¹, though the dispersion decreases considerably above 2000 cm⁻¹.

2.6.2.2 c) **Detectors**

Infrared detectors measure the radiant energy by its heating effect. Thermopiles, bolometers, and Golay cells are used as detectors. In the Golay cell, the radiation falls onto a very small cell containing air and the temperature changes are measured in terms of pressure changes within the cell. Another very effective method is based on photoconductivity. The radiation is allowed to fall on photoconducting material and the conductivity of the material is measured continuously by a bridge network. The detector does not show any signal when the energy transmitted by
reference and sample cells are equal. If the sample absorbs radiation there will be inequality in the two beams and a signal is produced. Then signal is fed to a high gain amplifier amplifies the low intensity signal up to a usable level with minimum thermal and electrical noise [25].

2.6.3 Interferometer Arrangement

The basic components of a Fourier transform spectrometer are given in figure 2.4. The source is the usual glower operated at very high temperatures. The Michelson interferometer consists of a source S, a beam splitter B and two plane mirrors M₁ and M₂ (figure 2.5). Mirror M₁ is fixed and M₂ is capable of to and fro movements. The beam splitter allows 50% of the radiation to mirror M₁ and the other 50% to mirror M₂. The two beams are reflected back to B where they recombine with 50% going to the source and the other 50% going to the sample. For monochromatic source, if the path lengths BM₁B and BM₂B differ by an integral number including zero of wavelengths, one gets constructive interference of the two beams at B (bright beam). Destructive interference results when the difference in path lengths is half odd integral number of wavelengths. Thus if mirror M₂ is moved towards or away from B, the sample and detector will see an alternation in intensity. If two different monochromatic frequencies υ₁ and υ₂ are used instead of one, a more complicated interference pattern would follow when M₂ is moved. A Fourier transform of the resultant signal would give the two originals with the appropriate intensities. Extending this, a white light produces an extremely complicated interference pattern which can be transformed back to the original frequency distribution. If the recombined beam is directed through a sample, the sample absorption will show up as gaps in the frequency distribution which on transformation gives a normal absorption
spectrum. In the experiment, the detector signal is collected into a multichannel computer while mirror $M_2$ is moved. The computer then plots the Fourier transform of the data [25].

![Figure 2.4 Fourier Transform spectrometer](image)

![Figure 2.5 Interferometer arrangement of Fourier Transform spectrometer](image)
2.6.4 Sample Preparation

The sampling of a solid, taken in the form of powder, for plotting the IR spectrum is carried out using the pressed pellet technique.

KBr disks are prepared by grinding the sample (0.1 – 2.0 per cent by weight) with KBr and compressing the whole into a transparent wafer or disk. The KBr must be dry, and it is an advantage to carry out the grinding under an IR lamp to avoid condensation of atmospheric moisture, which gives rise to broad absorption at 3500 cm$^{-1}$. This can be alleviated by having a blank disk in the reference beam, but the best remedy is prevention. The grinding is usually done with an agate mortar and pestle, although commercial ball mills are available; considerable work is needed to achieve good dispersion, and poorly ground mixtures lead to disks that scatter more light than they transmit. The particle size that must be achieved to avoid scattering is less than the wavelength of the IR radiation – that is, less than 2µm.

Compression to a cohesive disk requires high pressure, the commonest technique beign to use a special die from which air can be evacuated before hydraulic compression to about 10 tonnes load. Disks produced in this way are fairly easy to handle and measure commonly 13mm in diameter and 0.3mm in thickness. Less expensive equipment can consists of the special die, used with a simple screw – jack; even a large steel nut with 2 bolts screwed in from opposite ends with the KBr between them can give satisfactory disks [26].

FTIR techniques have made significant impact with regard to (i) rapid scanning, ii) signal to noise (S/N) ratio, (iii) high sensitivity, (iv) high resolution and (v) data processing. The simultaneous data collection helps one to investigate the spectrum of transient species such as unstable molecules or intermediaries in a
chemical reaction and for the analysis of environmental samples etc. The rapid scanning property of FTIR spectrometers is having its greatest impact in the field of gas chromatography – FTIR.

An S/N ratio of 3 to 4 is necessary for an unambiguous recognition of a signal in conventional spectrophotometers. The incorporation of powerful computers enables one to do computer averaging techniques. In this technique, the spectrum is recorded stepwise into the computer and stored in separate locations in the memory.

The high sensitivity helps one to investigate species absorbed on metal oxide and supported metal catalysts, pharmaceuticals, proteins etc. Its potential for the detection of photoacoustic signal and for biochemical research is enormous. The possibility for high resolution in the infra-red permits a more detailed knowledge of molecular vibrations and energetics. High resolution FTIR has enabled one to measure the presence of components in the atmosphere to the level of a few parts per billion.

The incorporation of a computer in the instrument allows rapid spectral searches as high as 10,000 in about 6 to 7 seconds at the end of a run. The subtraction of the spectrum of a reference sample from the spectrum of a mixture, the determination of the number of components in a mixture, curve fitting routines etc., are some of the popular operations possible with a FTIR spectrometer [25].

Applications of infrared spectroscopy are of varied types. The advent of FTIR created renewed interest in the field of IR spectroscopy. It is one of the most widely used analytical tools available today. The rapidly increasing demand for routine analysis of a wide range of compounds and the data handling capabilities has
generated this interest. They are used for identification of molecular constituents by assigning the experimentally observed bands to possible functional groups and stretching and bending vibrations of bonds, in elucidation of molecular structure only if Raman results are also taken into consideration since both are complementary to each other and in the area of ceramics, infrared spectroscopy is mainly used for characterization purposes and used in applications of biological and biomedical significance [25].

2.6.5 Advantages of FTIR instrument

i. Speed and sensitivity of the instrument is very high. A single scan of the moving mirror results the entire frequency scan.

ii. The signal to noise ratio of the instrument is very low when compared to ordinary dispersive type instruments.

iii. FTIR instrument eliminate stray light and sample emissions.

iv. Since data storage is in a computer, we can perform Fourier transformation, spectral subtraction, base line correction, smoothing, integration etc.

v. Amount of sample required is very less [27].

2.7 SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscopy (SEM) is the most widely used form of electron microscope in the field of material sciences. The SEM is popular because it uniquely combines some of the simplicity and ease of specimen preparation of the optical microscope with much of the performance capability and flexibility of the more expensive and complex Tunneling Electron Microscope (TEM) [26].
2.7.1. Principles of the SEM

The schematic diagram showing basic principles of SEM is shown in figure 2.6 and 2.7. Two electron beams are used simultaneously. One strikes the specimen to be examined, the other strikes a cathode ray tube (CRT) viewed by the operator. As a result of the impact of the incident beam on the specimen a variety of electron and photon emissions are produced. The chosen signal is collected, detected, amplified and used to modulate the brightness of the second electron beam so that a big collected signal produces a bright spot on the CRT while a small signal produces a dimmer spot. The two beams are scanned synchronously so that for every point scanned on the specimen there is a corresponding point on the CRT. Typically the beams scan square patterns on both the specimen and the CRT. They start at the top left hand corner of the area, scan a line of points parallel to the top edge and then, when they reach the end of the line, they fly back to the starting edge and scan a second line and so on until the whole square area has been rastered. Each complete image is conventionally called a frame. If the display area of the CRT tube is $A \times A$ in size and the area scanned on the specimen is $B \times B$ in size, then variations in the signal from the specimen will be mapped on to the CRT as variations in brightness with a linear magnification of $A/B$. Thus a magnified map or image of the specimen is produced without the need for any imaging lenses.
Figure 2.6 Schematic diagram showing basic principles of Scanning Electron Microscope (SEM)

Figure 2.7 The SEM scan raster arrangement
This method of imaging offers several important advantages:

- Magnification is achieved in a purely geometric manner and can be varied by simply changing the dimensions of the area scanned on the specimen. It is therefore easy to change from a low (×20) to a high (×100000) magnification or to any intermediate value since it is not necessary to change any lenses or even to refocus the image.

- Any emission which can be stimulated from the specimen under the impact of the incident electron beam - e.g., electrons, X-rays, visible photons, heat or sound - can be collected, detected and used to form an image. The SEM is therefore not restricted to imaging with radiations which can be focused by lenses and can give many different views of the same specimen.

Several different types of image can be produced and displayed simultaneously from the same area of the sample so enabling different types of information to be correlated. It is only necessary to provide a suitable detector, amplifier and display screen for each signal of interest. Furthermore these signals can be mixed with each other to generate still more types of imaging information.

Because the picture on the screen is formed from an electrical signal which varies with the position of the beam and hence with time the image can be electronically processed to control or enhance contrast, reduce noise, identify features etc.

A consequence of this arrangement is that a fundamental limit to the imaging performance is set by the display CRT screen. The smallest feature that can be discerned on the CRT is equal to the size of the electron spot on the display screen. Conventionally it is assumed that 1000 scan lines, each containing 1000 picture elements or pixels, make up each image frame scanned. Each picture is
therefore composed of $1000 \times 1000$ i.e., $10^6$ pixels. When the SEM is operating at a magnification of $M$ then the resolution in the image i.e. the smallest detail on the specimen that can be observed, is equal to the pixel size divided by the magnification. Since the size of the spot on the CRT is typically 100 to 200 micrometers then for magnifications of a few hundred times the resolution is limited to a micrometer or so. Only at high magnifications is the resolution limited by more fundamental electron-optical considerations.

### 2.7.2 Components of the Scanning Electron Microscope

The main components of an SEM are contained in two units, the *electron column* which contains the electron beam scanning the specimen, and the *display console* which contains the second electron beam which impinge on the CRT. The high energy electron beam incident on the specimen is generated by an electron gun, two basic types of which are in current use. The first (figure 2.8a) is the thermionic gun in which electrons are obtained by heating a tungsten lanthanum hexaboride cathode of filament to between 1500 to 3000k. The cathode is held negative at the required accelerating voltage $E_0$ with respect to the grounded anode of the gun so that the negatively charged electrons are accelerated from the cathode and leave the anode with an energy $E_0$ kilo-electron volts (KeV). Thermionic guns are in very wide use because they may safely be run in vacuums of $10^{-5}$ Pa (i.e., $10^{-7}$ torr) or worse. The alternative source (figure 2.8b) is the field emission gun in which a sharply pointed wire of tungsten is held close to an extraction anode to which is applied a potential of several 1000 volts. Electrons tunnel out of the tungsten wire, which need not be heated and can be at room temperature, into the vacuum and are
then accelerated as in the thermionic gun towards the anode. Field emission guns depend on atomically clean emitter surface, thus they must be operated under ultra-high vacuum conditions, typically in a vacuum of $10^{-7}$ Pa (i.e., $10^{-9}$ torr) or better. For either emitter the entire length of the electron column travelled by the electron beam from the gun to the specimen chamber must also be pumped to an adequate vacuum using oil-diffusion, turbo-molecular or ion pumps individually or in combination.

![Schematic diagram of (a) thermionic electron gun and (b) field emission electron gun.](image)

**Figure 2.8** Schematic diagram of (a) thermionic electron gun

(b) Field emission electron gun
2.7.3. Sample Preparation

Because the SEM chamber can readily accommodate big samples, and therefore the beam can focus samples which are rough and irregularly shaped, the preparation of specimens for SEM examination is relatively straightforward. In an ideal world no prior preparation at all would be necessary, but in practice it is always desirable to ensure that the surface(s) to be examined are free from oil or grease, such as that carried by the fingers, which can cause contamination. Samples in which water plays a substantial role, such as animal or plant tissue, cannot be examined directly because the evaporation of the water into the vacuum system of the microscope will lead to extensive shrinkage of the sample and even to total structural collapse. Instead the water must be removed by substituting it with alcohol and the structure then stabilized chemically. Alternatively the water can be cryo-fixed by rapid freezing to, and subsequent maintenance at, liquid nitrogen temperatures.

If the specimen is not a good electrical conductor then it is often desirable to provide some conductivity by evaporating a thin metal layer (typically 3 to 10 nm of gold) on to the surface of interest and electrically grounding this. The sample can then be stably examines at any desired beam energy.

The SEM is one of the most versatile forms of microscope available. Its combination of high spatial resolution, high depth of field, and its analytical power make it the ideal tool with which to examine and interpret the microstructure of materials [28].

2.8. DIFFERENTIAL SCANNING CALORIMETER

2.8.1. The Instrument

There are two types of DSC instruments. The initial type, from which the technique derives its name, is called the "power compensating" version and was developed by Perkin-Elmer Co [29, 30].
A schematic representation of this instrument is shown in figure 2.9. The inventive concept keeps the value of \( \Delta T \) equal to zero by placing the temperature sensors, Platinum resistance thermometers, into a bridge circuit. Any imbalance is used to drive a heater in the appropriate sample or reference portion of the cell. The power needed to keep the bridge circuit in balance is proportional to the change in heat capacity or enthalpy occurring. The integral of the power over the time of the event gives the energy difference between the sample and the reference.

If power is supplied to the sample, the process is endothermic. If it is supplied to the reference side, then the process is exothermic. Power applied to the sample has a positive sign so that the integral yields a positive value of \( \Delta H \) consistent with the endothermic process. Positive power correlates with a negative value of \( \Delta T \) so that an endothermic peak points upward in DSC.

The second type of DSC referred to as operating in a "heat flux" mode. It is similar in operation to a conventional Differential Thermal Analysis (DTA) except that the quantitative compensation for the problem areas, such as temperature dependence of thermal transport and sensor sensitivity, are carefully built into the associated hardware and software. Both instruments are capable of giving satisfactory data. Some instruments have a built in switch to operate in either the DTA or heat flux DSC modes. Table 2.1 lists many of the processes that are commonly investigated by DSC. The nature of the effect i.e., whether endothermic, exothermic, or shift in base line is also indicated. Metastable to stable, most decompositions, and polymerization reactions are not reversible. Hence, comparing the heating curve with the cooling curve or a one taken during a reheat is often informative as to the nature of the phenomena observed.
Table 2.1 Events detected by DSC and their effects during heating.

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Observation</th>
<th>Reaction</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order</td>
<td>Endothermic</td>
<td>Decomposition</td>
<td>Either</td>
</tr>
<tr>
<td>Higher order</td>
<td>Step in base</td>
<td>Liquid – solid</td>
<td>Either</td>
</tr>
<tr>
<td>Vaporization</td>
<td>Endothermic</td>
<td>Solid – solid</td>
<td>Either</td>
</tr>
<tr>
<td>Fusion</td>
<td>Endothermic</td>
<td>Polymerization</td>
<td>Exothermic</td>
</tr>
<tr>
<td>Metastable to Stable</td>
<td>Exothermic</td>
<td>Chemisorptions and catalysis</td>
<td>Exothermic</td>
</tr>
</tbody>
</table>

Figure 2.9 A schematic representation of a power Compensating DSC instrument
DSC can also be used to determine the heat capacity, $C_p$, of a substance by comparison with a known standard, usually sapphire (single crystal $\text{Al}_2\text{O}_3$). The method is summarized in figure 2.10a. The basis is comparison of the differences in the power level for the empty pan, the pan and the sample, and the pan with the reference material. The comparative aspect negates the need to determine the instrumental constant. The relative displacements in figure 2.10(b) are proportional to the products of the mass and $C_p$ for the sample and the reference.

Figure 2.10(c) indicates the effect a change in heat capacity, $C_p$, accompanying some reactions can have on the base line. There are many other factors which can affect the nature of the base line.

It is important to have well-defined points for comparisons of curves and association with the cause of the event. Construction of a proper baseline is essential to determine the area of the peak accurately.

Some of these points are considered in figure below. The beginning of the event is associated with the initial departure of the curve from the baseline. This is highly subjective evaluation and easily influenced by the degree of amplification. The extrapolated onset, point A in figure 2.11, is generally used to alleviate this variability. The other curves illustrate ways in which the baseline has been determined.
Some instruments have the ability to adjust the baseline through adjustments in hardware. All computerized instruments have the opportunity to subtract a stored baseline determined under nearly identical circumstances to the actual experiment.
2.8.2 Factors which influence the nature of the DSC patterns

The factors which influence the nature of the DSC patterns were represented in the following table. These effects are highly interactive. For example, variations of the parameters described in the first three lines of the table will determine how changes in the heating rate, the last line of the table 2.2, influence the results.
Table 2.2 Classes of variables in DSC

<table>
<thead>
<tr>
<th>Construction – thermal linkages – sensor response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere – reactions – thermal conductivity</td>
</tr>
<tr>
<td>Sample size – packing – particle size</td>
</tr>
<tr>
<td>Heating rate – hysteresis</td>
</tr>
</tbody>
</table>

The critical thermal transport between the sample, reference and furnace is affected by (1) the physical arrangement between them; (2) the choice of sensor, its size, and position; and the materials of construction are all crucial factors in determining these important thermal linkages. Along with the sensor sensitivity, these factors determine the shape and size of the peak corresponding to the thermal event. The stronger the thermal coupling between the sample and reference the smaller the observed $\Delta T$ but the faster the return to the baseline with a concomitant improvement in resolution of events.

The pattern and rate of the flow around and over the sample plays a major role in controlling the processes. The thermal conductivity of the atmosphere is an important link in the thermal connection between the source of heat, the sample, and the reference[31,32]. The thermal properties of vacuum or low molecular weight gases such as hydrogen and helium are much different from the normal gases at atmospheric pressures. Similarly, work at high pressures substantially alters the characteristics of the system.

The relative humidity of the gas stream is important in determining the decomposition temperatures of hydrates and hydroxides as well as the oxidizing power of an otherwise inert gas such as nitrogen.
Not only does the flow pattern influence the ability of the gas phase to react with the sample, but also the sample packing determines how well the two phases can interact. The sample packing also affects the thermal conductivity and, hence, the critical thermal linkages. Dilution of the sample with an inert material has been used to control the size of the effect and aid in achieving a linear baseline, particularly if the diluent corresponds closely to the reference material.

As in the TG, the faster the heating rate the greater the opportunity for a lag in temperature between the sample and the sensor. There is, however, another aspect to be considered when performing DSC. The amplitude of the ΔT signal is increased with increasing heating rate because the thermal event takes place in a shorter period of time. Consequently, the rate of change in the process and hence the signal is greater.

Optimization of a system requires numerous compromises in the operating parameters and the instrumental design. Various adjustments are necessary to achieve the maximum sensitivity, accuracy and resolution. Table (2.3) indicates some of these considerations. A careful approach with ample sample is to use a fast heating rate and large sample for the initial experiment in order to maximize the ability to detect the minor events. Then a second experiment with smaller sample and slower heating rate in order to best resolve the events and determine the associated temperatures more accurately.
Table 2.3 Operational compromises for DSC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum resolution</th>
<th>Maximum Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample size</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Heating rate</td>
<td>Slow</td>
<td>Fast</td>
</tr>
<tr>
<td>Sample reference</td>
<td>Linked</td>
<td>Isolated</td>
</tr>
<tr>
<td>Particle size</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>High conductivity</td>
<td>Low conductivity</td>
</tr>
</tbody>
</table>

DSC has found frequent and wide ranging use from qualitative analysis to quantitative analysis, to many process related applications.

DSC has been run in a simultaneous mode with X-ray diffraction to observe the crystallization melting and fusion in polyethylene [33]. It has been used extensively in the pharmaceutical and organic chemical industries for purity analysis [34]. An example of the use of DSC to provide qualitative essentially fingerprint type information is illustrated in figure 2.12.

7 Thermoanalytical Methods

Figure 2.12 DSC of sample plastic waste
The melting points of each component in the collection of plastic scrap can be used to indicate the materials present [35].

Kosak [36] used the area under the exotherm in a high pressure DSC cell to estimate the extent of hydrogenation reaction. Under a specified set of conditions, the area was used to establish the optimum catalyst support system and as a quality control tool thereafter.

The advent of photo curing has led to the modification of DSC instruments to allow for the exposure of both the sample and reference compartments to a controlled source of radiation. By matching the radiant energy to both cells, it is possible to follow the photo curing process accurately. The wavelength of the light can be scanned to determine the spectral dependence of the photochemistry. Isothermal studies can be used to evaluate the kinetics of the process.

A DSC instrument can be used to sense the onset of an exothermic event with considerable accuracy and sensitivity. This has been exploited to determine reactions of the gas phase with the sample surface. The oxidative degradation of many materials, particularly electrical insulation, has been studied along with the effects of various anti oxidants [37]. Similarly, the onset of catalytic activity can be detected and used efficiently to screen potential catalysts [38]. The poisoning effects of various additives to either the catalyst or the gas stream can also be effectively studied by these techniques [26].
2.9 THERMAL ANALYSIS - THERMOGRAVIMETRIC ANALYSIS (TGA) AND DIFFERENTIAL THERMOGRAVIMETRIC (DTGA) ANALYSIS

In thermo gravimetric analysis, the mass of the sample in a controlled atmosphere is reduced continuously and recorded as a function of temperature or time, as the temperature of the sample is increased. To estimate the decomposition temperature, both thermo gravimetric (TGA) and differential thermal analysis (DTA) are performed on the precursor. The detailed information regarding TGA/DTA instrumentation and its working principles are discussed below.

2.9.1. The Basic Instrument

The schematic diagram for a typical thermo balance is illustrated in figure 2.13. The sample can be linked to the balance in several ways. It can be suspended directly from the balance beam to hang down into a furnace or controlled temperature environment. Since heated air rises, this means of suspension generally requires careful baffling or cooling to prevent the heat from affecting the balance.

Alternatively the sample and furnace arrangement can be placed above the furnace so that the heat is less likely to affect the balance. The greater mass of the counterbalance used in this method of suspension, however must be subtracted from the ultimate capacity of the instrument. A third approach is to fix the sample as a horizontal extension of the beam. This also minimizes the heating effect and frequently appears less influenced by the flow patterns set up within the balance and furnace chambers.

The modern electromagnetic balances are remarkable instruments showing relatively little dependence on vibration, high sensitivity and temperature stability. This class of balances has evolved from the original Cahn electro balance.
The beam position is monitored by a photo detection scheme. Assuming that the sample suspension has been tarred and the balance is in equilibrium, addition of a sample to the left side of the beam will cause the right side of the beam to be displaced upward and sufficient current is supplied to the electric torque motor to restore it to the original beam position. The restoring force, and hence the current, is proportional to the change in weight. A typical sensitivity of 0.1µg is possible. Any portion of the sample’s mass can be tared within the capacity range of the particular balance.

The overall capacity of the system is determined by the strength of the balance beam and the linear range of the torque motor. Alternatively, the effective capacity of the balance can be increased, at the expense of sensitivity, by coupling the sample suspension closes to the fulcrum of the balance. The mass of the sample holders and suspension system will, of course, subtract from the actual range of sample mass that can be utilized. Many manufacturers produce several models having different capacities and sensitivities.
Nearly all of the modern, commercially available TG equipment is based on similar electro balances; however, there are other special purpose mass sensors. The resonance frequency of a piezoelectric crystal, generally quartz (SiO₂), varies with the mass deposited on the crystal surface. As little as 1 pg cm⁻² can be detected in this manner [16]. This sensitivity allows the vaporization or deposition rates of sub-monolayer to be measured. These detectors have a limited range of temperature and require careful compensation for the many factors which lead to a drift of the signal with time and small changes in temperature. This has been partially achieved through the use of a matched crystal for compensation [17].

Thermal methods depend upon uniform precisely controlled heating or cooling of the sample. Several physical arrangements of the balance compartment and furnace are depicted in figure 2.14.

Figure 2.14 Schematic representation of the Cahn Electrobalance
These show the furnace as external to the sample compartment. There are, however, since instruments designed primarily for small samples, which have the furnace inside the sample chamber and hence in the same gaseous environment as the sample.

This allows for miniature furnaces capable of high heating and cooling rates. Such conditions conserve sample and allow for a more rapid turn around time for the instrument. There are some situations, however, that require a large sample size. Examples are when using a relatively heterogeneous sample like a mineral, coal, etc.; when specific sample geometry is required such as foils for corrosion studies, when the highest precision is necessary for very small changes in mass such as for thin films or minute changes in oxygen stoichiometry.

The heating elements of the furnaces are most often based upon resistive heating. Nichrome and Kanthal are alloys commonly used in the range of temperature up to 1000 to 1200°C. Fused quartz tubes and accessories are frequently used to contain the sample and atmosphere. Aluminium is often used as a sample container up to 600°C because of its thermal conductivity, ease of fabrication and low cost.

Molybdenum disilicade or silicon carbide heating elements and platinum or platinum alloys are used in the range up to 1500 to 1700°C. Ceramic refractories such as alumina or mullite are used to contain controlled atmospheres and platinum or alumina to hold the sample. The heating elements are molybdenum, tungsten, or graphite and require protective atmospheres free of oxygen. The other materials of construction and temperature sensors at > 1700°C also are very limited and expensive.
Radiant heating, such as shown in figure 2.15 is capable of even faster controlled heating rates approaching 500 °C min\(^{-1}\) for temperatures up to 1200 °C. Various focal arrangements for the infra-red radiation will heat a point, plane, surface or volume. The walls containing the atmosphere can be essentially transparent to the radiation and therefore remain at much lower temperatures. But any deposition on these walls will drastically alter the thermal characteristics of the system. It is not possible, however, to cool samples at anything approaching those cooling rates while simultaneously following their mass [26].

![Types and Maximum Attainable Temperature of Radiant Heating](image)

**Figure 2.15** The radiant furnaces available for thermal analysis

2.9.2. Factors Affecting Thermo gravimetry

The influences of atmosphere and sample are best considered in conjunction with the sources of error for TG. The major factors affecting thermo gravimetry are shown in the following table 2.4.
Table 2.4 Major factors affecting thermo gravimetry

<table>
<thead>
<tr>
<th>Mass</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buoyancy</td>
<td>Heating rate</td>
</tr>
<tr>
<td>Atmospheric turbulence</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>Condensation and reaction</td>
<td>Enthalpy of the process</td>
</tr>
<tr>
<td>Electrostatic and magnetic forces</td>
<td>Sample, furnace and sensor arrangement</td>
</tr>
<tr>
<td>Electronic drift</td>
<td>Electronic drift</td>
</tr>
</tbody>
</table>

2.10. IMPEDANCE ANALYZER

The Impedance Analyzer is a low frequency instrument for measuring dielectric constant. The determination of dielectric constant is based on the measurement of capacitance of a parallel plate capacitor containing the material under test.

\[ C = (\varepsilon_r \varepsilon_0 A/d) \]

Where A is the area of the capacitor plates

D is the spacing between the plates

\( \varepsilon_r \) is the relative dielectric constant of the medium

\( \varepsilon_0 \) is the dielectric constant for free space \((8.854 \times 10^{-12})\)

2.10.1. Sample Preparation

The material is taken in the form of a powder and made into a pellet by putting the powder into a dial and applying pressure of about 1.5. The pellet is then coated with a silver paste on the opposite sides and conducting copper wires are
attached on either side to mount it on the sample holder. This sample is then dried at 700°C to form a very good capacitor.

Operating in the normal mode and entering the desired frequency, the value of the capacitances displayed on the seven segments LED display from which the dielectric constant is calculated [39].

2.10.2 Applications of TGA

The mass losses define the stages, and the conditions of temperature (and surrounding atmosphere) necessary for preparation of the anhydrous compounds or intermediate hydrates, can be established immediately.

Knowledge of the thermal stability range of material provides information on problems such as the hazards of storing explosives, the shelf-life of drugs and the conditions for drying tobacco and other crops. By using an atmosphere of air or oxygen, the conditions under which oxidation of metals and degradation of polymers become catastrophic can be determined.

2.10.3 Applications (DTA)

1. A DTA curve can be used as a finger point for identification of their thermal properties. DTA is widely used in the pharmaceutical and food industries.

2. DTA may be used in cement chemistry, mineralogical research and in environmental studies.

3. DTA curves may also be used to date bone remains or to study archaeological materials [40].
2.10.4 Vickers micro hardness measurement

The Vickers micro hardness measurement method the test material is indented using a diamond indenter, in the form of a right pyramid with a square base subjected to a load of 1 to 100 kg. The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left on the surface of the material after removal of the load are measured using a powerful microscope and their average diameter is calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is the square mm area of the indentation.

The Vickers hardness number $H_V$ of the crystal was calculated using the formula,

$$H_V = 1.8544 \frac{p}{d^2} \text{ Kg mm}^{-2}$$

where,

- $p$ is the applied load
- $d =$ Average of the two diagonals, $d_1$ and $d_2$ in mm.
The Vickers micro hardness should be reported like $800 \text{ H}_V/10$, which means a Vickers micro hardness of 800, was obtained using a 10 Kg force. The advantages of the Vickers hardness test are that extremely accurate readings can be taken, and one type of indenter is used for all types of materials and surface treatments. The very precise method for testing the softest and hardest of materials, under varying loads, the Vickers machine is a floor standing unit that is more expensive than the Brinell or Rockwell machines [41].
2.11 REFERENCES


[39] Suji.G., A project report on Preparation, Characterisation and properties of Ba(Ni$_{0.33}$ Sb$_{0.67}$)O$_3$ ceramics compound, University of Kerala, 1994.
