CHAPTER-II

GROWTH METHODS AND CHARACTERIZATION TECHNIQUES

2.1 Introduction

Single crystals are important in the device fabrications and in the applied scientific research [35]. This chapter deals with details of various growth techniques and instrumentation that are adopted for crystallization of single crystals.

2.2 Crystal growth methods

Crystal growth is a controlled phase transformation to ordered solid phase, either from solid or liquid or gaseous phase. The control of the crystal growth environment and consideration of growth kinetics both at the macroscopic and sub-microscopic levels are of vital importance to the success of a crystal growth experiment. According to the phase transition, the methods of growing single crystals are classified as [36]: (i) Solid state growth, (ii) Vapour phase growth, (iii) Melt Growth and (iv) Solution growth.

(i) Solid growth technique

Solid state growth requires atomic diffusion. At normal temperatures, such diffusion is usually very slow. The solid state growth technique for the production of single crystals is very small; however annealing, heat treatment, sintering and quenching are metallurgical process of great importance in explaining the properties of materials [37].

(ii) Melt growth technique

Melt growth is the best method for growing large single crystals of high perfection relatively rapidly. It has been used to grow many metals, semiconductors, ionic crystals and a few organic compounds. These techniques have been developed largely in the electronic, optics and synthetic gemstone industries [38]. Melt growth

normally requires that the material does not decompose below or near its melting point and has a certain vapor pressure at its melting point. Melt growth is divided into four main groups of techniques.

(i)   Normal freezing: ingot gradually frozen from one end.

(ii)   Crystal pulling: Crystal grows on a seed drawn from the melt.

(iii)   Zone melting: a molten zone is passed through an ingot.

(iv)   Flame fusion or pedestal growth: crystal grows below a melt, which is fed from above.

Melt growth is the process of crystallization by fusion and re-solidification of the pure material [39]. In this technique, apart from possible contamination from crucible materials and surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than that possible by other methods [40, 41]. Mainly for the latter reason, melt growth is commercially the most important method of crystal growth. There are several classifications in the melt-growth technique and they are Bridgman-Stockbarger Technique [42, 43], Czochralski Technique, Verneuil Technique [44], Zone-Melting Technique, Kyropolus Technique etc. Since these methods are not used in this work, explanations are given briefly here.

The Bridgman method is based on the invention of Tammann in Gottingen early in the twentieth century. He used the gradient-freeze method as it is called now, in which crystals can be grown by directional solidification in the temperature gradient region of a furnace whose average temperature is reduced gradually. Bridgman has added mechanical movement of the crucible to this Tammann method. Others, such as Stockbarger, have made important contributions to the Bridgman-method. The Bridgman-method is cheap

and simple, although hampered by the problem of crucible interference with the crystallization process. The usual configuration is vertical with the melt in an ampoule being lowered slowly from the hot zone to the cooler zone, which is below the melting point. Large metal single crystals as well as optical quality alkali halide crystals for prisms, and lenses were grown by this technique.

Growth of single crystal from the melt using the crystal pulling process is named after its inventor J.Czochralski. In the Czochralski-method [45] the crystal is pulled out of the melt by crystallization of the upper region of a melt meniscus. The growing crystal is visible and the growth process can be analyzed. The control mechanism, which is required for proper shaping of the meniscus, makes the method rather expensive. The seed crystal is dipped slightly in the molten charge, which has been maintained at its melting point. When the seed temperature is decreased with the use of water-cooling arrangement, the molten charge, which has been in contact, will solidify on the seed. The seed is simultaneously rotated and slowly pulled from the melt to occur the perfect single crystals. The advanced version of this technique is Liquid – Encapsulated Czochralski Technique.

Verneuil introduced this technique in 1902 and gave a full description. In this technique, an oxihydrogen flame is produced and it is used to heat the source material. The powder to be crystallized is allowed to fall on this flame through sleeves, using the vibrator at low amplitude. The powder melts in flame and if the conditions have been set correctly, a film of melt crystallizes on the surface of the seed. Further deposition of melt film leads to growth. During growth, the seed is lowered. The volume growth rate depends on the rate of lowering. By appropriate adjustment, the crystal diameter can be

changed. To maintain thermal symmetry, the seed is rotated. When the seed-lowering rate is less the crystal will grow bigger, and for high, crystal will be smaller.

In the zone melting technique, melting small amount of material in relatively large or long solid charge creates a liquid zone. In this technique, it is noted that the rate of zone migration depends upon the orientation of the solid bouble and the thickness and temperature of the liquid zone. The advantage of this technique is its suitability for growing single crystals as well as it is found to be one of the most useful methods available for purification of a wide variety of materials.

Kyropolus technique is used in many applications for making prisms, windows, lenses and other optical components, which requires larger diameter crystals. This method is just like the Czochralski technique, the seed is brought into contact with the melt and is not raised much during the growth, that is, the part of the seed is allowed to melt and a short narrow neck is grown. The major use of this method is for alkali halides to make optical component. This is the easiest and the most effective way for growing a variety of crystals at room temperature. The saturated solution of the material prepared in a suitable solvent is either cooled or evaporated slowly resulting in the growth of crystals. Several industrially and technologically important materials are grown by this method.

(i) Vapour growth

This method has been used for the production of high quality bulk crystals of materials like CdS and HgS_2. Here all elements present are volatile. It has also led to vacuum evaporation and the crystals were grown by sublimation [46]. Piper and Polish and others have used sublimation method for CdS. It suffers a disadvantage of being a closed tube method. It has two variants, either periodic oscillation of the source temperature or periodic oscillation of the crystal temperature. The periodic temperature oscillations are designed ideally to keep a single nucleation. Vapour growth methods are

classified into two types viz. Physical Vapor Deposition (PVD) method and Chemical Vapour Deposition (CVD) method. PVD method is also called as impure vapuor growth. Usually sublimation and halogen transport are done in closed tubes and CVD in open tubes. The closed tubes are very useful in research but too costly for production of gas phase reactions and hence open tube methods are preferred.

(ii) Solution growth method

Solution growth method is widely used to grow the crystals which have high solubility and have variation in solubility with temperature. Depending upon the solvents and the solubility of its solute, there are two methods under this category. They are (i) high temperature solution growth and (ii) low temperature solution growth.

In high temperature solution growth, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturation may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter region to a cooler region. There are number of ways of high temperature solution growth. The following are the two methods under high temperature solution growth. They are (i) flux growth and (ii) hydrothermal growth.

In flux growth, the solvent is a molten salt or oxide or a mixture. The preliminary need for crystal growth is the achievement of supersaturation. This super saturation is created by temperature change. The solubility of most materials declines with reducing temperature so that cooling is often used to create supersaturation. In some cases, the supersaturation is created by (i) evaporation of solvent or (ii) changing the solvent composition or (iii) chemical reaction. The selection of the method to create supersaturation depends strongly on the facilities available and the required quality, size,

purity and homogeneity of the crystals. In hydrothermal growth, the condition of high pressure as well as high temperature is applied. It is usually defined as the use of an aqueous solvent at elevated temperature and pressure to dissolve a solute which would ordinarily be virtually insoluble at ambient conditions. In this method, the finely divided particles of the material to be grown are taken in the bottom of the vessel and suitably oriented single crystal seed plates are suspended in the upper growth region. The vessel is placed in a furnace that has been designed to heat the lower dissolving section isothermally hotter than the upper growth region, which is also maintained isothermal. As the temperature is raised, the liquid level rises, the pressure increases, and finally, at some temperature below the critical temperature of water, the vessel fills completely with the liquid phase. The temperature, temperature gradient and the initial degree of fill of the vessel fix the pressure. Now the crystallization can be achieved. The requirements of high pressure lead to practical difficulties and there are only a few crystals of good quality and large size grown by this technique.

Low temperature solution growth occupies a prominent place owing to its versatility and simplicity. This method is widely used to grow bulk crystals [47]. Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low temperature solution method. The mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process; temperature, pressure and solvent concentration.

The growth from solution takes place in two stages: (1) nucleation [48-50] and (ii) growth. A suitable solvent is required to dissolve the solute to an appreciable extent. This

may be possible either under normal conditions or high pressures/temperatures. The solvent may be water or melt of a metal. Nucleation can be carried out from highly supersaturated solutions. The growth can then occur over the few 'seed' nuclei already grown. The supersaturation decreases when the growth proceeds. To get a reasonable growth rate, the super saturation must be kept constant. This can be achieved by (i) isothermal evaporation of the solvent (ii) lowering the temperature. (iii) Addition of solute or (iv) Adding another solvent.

Theory for Nucleation

Nucleation is explained by many authors in literature. The solid crystals were grown from a "nutrient" phase (solid or liquid or gas). To start growing the nutrient must be "seeded" with a small crystal to be grown after a definite time. The basic principle of the growth process is that a nucleus is formed first and then it grows into a single crystal by assembling ions or molecules with specific interaction and bonding. So the process is slow and multiple nucleations are decreased. The growth process and size of crystals vary widely and are determined by the characteristics of the material used.

Supersaturation alone is not sufficient for crystallization, but also there exist a number of minute solid bodies known as centers of crystallization, seeds, embryos or nuclei [51]. The formation of stable nuclei happens only by addition of a number of molecules (A_1) until a critical state is formed. In general,

$$A_{(n-1)} + A_1 \longrightarrow A_n \text{ (critical)}$$
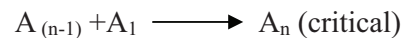
Further addition of molecules to the nucleus will result in nucleation that gives rise to crystal growth. Once the nuclei grow beyond a critical size, it becomes stable. The creation of a new phase in the homogeneous solution releases a quantity of energies. The overall excess free energy ($\triangle G$) between an embryo and solute in a supersaturated solution in the process of homogeneous nucleation can be written as

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$$\triangle G = \triangle G_s + \triangle G_v \tag{i}$$

Where $\triangle G_s$ is the surface excess free energy and $\triangle G_v$ is the volume excess free energy. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly [52, 53] and a bright sparkling particle is seen. The time of observation of the sparkling particle in the undisturbed solution from the time at which the solution reaches experimental temperatures is called the induction period (τ). For a given volume of solution, the frequency of formation of nuclei is inversely proportional to the induction period. The expression for the induction period in terms of Gibbs' free energy is given by

$$\ln \tau = -B + \triangle G / kT \tag{ii}$$

Where B is a constant, k is the Boltzmann's constant, T is the absolute temperature. Usually nucleus formed in supersaturated solution is assumed to be spherical in shape.

According to Gibbs' theory in terms of surface thermodynamics, the overall excess free energy between a spherical nucleus and solute can be written as

$$\triangle G = 4\pi r^2 \sigma + (4/3) \pi r^3 \triangle G_v \tag{iii}$$

Where $\triangle G_v$ is the free energy change per unit volume, r is the radius of the nucleus and σ is the interfacial tension or surface energy per unit area. This energy will be high for certain value of r, which is known as critical radius. Nuclei formed with radius greater than this r are stable and decrease their free energy by growing. According to Thomson-Gibbs equation, the volume excess free energy is given by

$$\triangle G_v = (kT/v) \ln S \tag{iv}$$

Where S is the supersaturation ratio and v is volume of one molecule. S is given by $S = C/C_0$ where C is the supersaturated concentration and C_0 is the equilibrium

concentration. The net free energy change ($\triangle$G) increased with the increase in size of nucleus, attains maximum and decreases with further increase in the size of nucleus. The size corresponding to the maximum free energy change is called critical nucleus. The radius of the critical nucleus can be obtained by setting the condition.

$$d\,(\triangle G)\,/\,dr = 0$$

Differentiating equation (iii) we get,

$$d\,(\triangle G)\,/\,dr = 8\pi r\,\sigma + 4\pi r^2\,\triangle G_v' = 0$$

The size of critical nucleus is obtained as

$$r^* = 2\,\sigma\,/\triangle G_v' \qquad\qquad\qquad\qquad \text{(v)}$$

Substituting eqn. (iv) in the eqn. (v), we get

$$r^* = 2\,\sigma v\,/\,kT\,\ln S$$

Since N k = R,

$$r^* = 2\,\sigma v\,N\,/\,RT\,\ln S \qquad\qquad\qquad \text{(vi)}$$

Where R is the universal gas constant and N is the Avagadro's number.

Substituting eqn. (vi) in the equation (iii), we get Gibbs free energy change for the critical nucleus

$$\triangle G^* = (16\pi\sigma^3\,V^2\,N^2\,/\,[3R^2\,T^2\,(\ln S)^2]) \qquad\qquad \text{(vii)}$$

Therefore, equation (ii) can be written for critical nucleus as

$$\ln \tau \;=\; -B + \;(16\,\pi\sigma^3\,V^2\,N^3\,/\,[3R^3\,T^3\,(\ln S)^2]) \qquad\qquad \text{(viii)}$$

A plot of $1\,/\,(\ln S)^2$ against $\ln \tau$ from equation (viii) is straight line and the slope is

$$m = (16\,\pi\sigma^3\,V^2\,N^3\,/\,[3R^3\,T^3]) \qquad\qquad\qquad \text{(ix)}$$

Therefore, $\qquad\qquad\qquad \triangle G^* = mRT\,/\,[N\,(\ln S)^2] \qquad$ or

$$\triangle G^* = \; mkT\,/\,(\ln S)^2 \qquad\qquad\qquad\qquad \text{(x)}$$

From equation (ix) we have,

$$\sigma = (RT/N) \, [3m/ \, (16\pi v^2) \,]^{1/3} \tag{xi}$$

The number of molecules in a critical nucleus is found using the following equation

$$n = (4/3) \, (\pi/v) \, r^{*3} \tag{xii}$$

Nucleation and crystal growth kinetics in connection with the amount of material available for crystal growth determine the number and volume of crystals produced. The number of crystals produced in the supersaturated solution is expressed as nucleation rate i.e. the number of crystals produced per unit volume per unit time. The nucleation rate J were calculated using the equation

$$J = A \exp [-\Delta G^* / \, (kT)] \tag{xiii}$$

Where A is the pre-exponential factor (approximately A= 1 x 10^{30} for solution), ΔG^* is the critical free energy of the nucleus, k is the Boltzmann's constant and T is the constant temperature of the solution [54-56]. The nucleation parameters such as (1) radius of the critical nucleus, (2) Gibbs' free energy, (3) interfacial tension, (4) the number of molecules in the critical nucleus and (5) nucleation rate can be determined using the equation (vi), (x), (xi), (xii) and (xiii).

Solubility curve

The solubility curve or temperature concentration (T-C) diagram is essential to study any solution growth experiment [57]. The typical solubility curve is shown in figure 2.1. The solubility curve in solid line divides the region into two and they are under saturated solutions below the curve and supersaturated above the curve. The supersaturated region is divided into metastable region and labile region. The metastable region is formed because of energy release on the formation of critical nucleus. Labile region is unstable and are strongly supersaturation solutions. The solubility curve gives

the solubility data at different temperatures and these data could be used to prepare saturated and supersatureated solutions and also used for carrying out the nucleation kinetic experiments. The solubility can be determined by gravimetrical method.
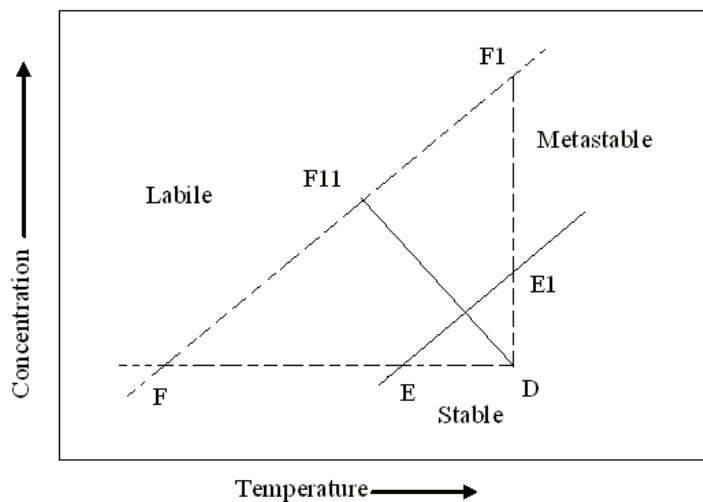

Fig. 2.1: A typical solubility diagram

Solvent and purification

A good solvent must have the characteristics such as solubility of the given solute must be good, positive temperature co-efficient of solubility, small vapor pressure, should not be corrosive, non-toxic, low cost, less viscosity and volatile. Solvents having all these characteristics do not exist practically and solvents used in practical are water (H_2O) and heavy water (D_2O), ethylalcohol, acetone, carbontetrachloride, hexane, xylene, etc.

High purity of materials is required for crystal growth. First step in the growth of crystal is the material purification in solvent. Purification can be done by repeated crystallization of the materials by chromatographic techniques such as high performance liquid chromatography (HPLC) or gas chromatography (GC) can be used and they yield small amount of purified product. Zone refining sublimation and distillation methods can

be used for ultra-purification and yield large quantities of materials. In re-crystallization method, the materials are dissolved in a hot solvent and then gradually cooled down to crystallize. Re-crystallization is the most commonly used technique of purifying materials. Zone refining method is used to produce ultra pure material and sublimation is used for thermally unstable solid materials.

Preparation of solutions

Preparation of solution to grow the crystal is an important role in crystal growth. The solution is saturated as per the solubility diagram. The saturated solution is then filtered using the Wattmann filter paper. The filtered solution is transferred to the growth vessel and placed in a vibration free platform or constant temperature bath for crystallization. The pH of the solution can be noted using a digital pH meter. Care should be taken to avoid under saturation which results in dissolution of seed crystal and high super saturation must also be avoided in order to prevent the formation of spurious nucleation. The growth vessel is sealed by a perforated cover to avoid evaporation of the solute. The solution is tested for saturation by suspending a small test seed crystal into the solution. If the system is not in equilibrium condition the seed crystal will dissolve or the solute will crystallize on the seed. By adjusting the temperature, the required equilibrium condition is reached and the test seed crystal is removed and a fresh seed crystal is suspended for crystal growth.

Low temperature solution growth techniques

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. In the low temperature solution

growth, crystals can be grown from solution if the solution is supersaturated i.e. it contains more solute than it can be in equilibrium with the solid. There are mainly five techniques viz.

a) Slow cooling technique

b) Slow evaporation technique

c) Temperature gradient technique

d) Gel technique

Slow cooling technique

It is the best way to grow single crystals by solution technique. The main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success.

Slow evaporation technique

This method is similar to the slow cooling method [58] in view of the apparatus requirements. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials, which have very small temperature coefficient of stability. The advantages/disadvantages of slow evaporation method are given below.

Advantages

i)   The slow evaporation method is much simpler and cheaper.

ii)   The growth of crystals nearly at room temperature.

iii)   Growth of strain dislocation free crystal

iv)   Supersaturation can be very accurately controlled.

v)   This method is well suited to those materials which suffer from decomposition before melting.

vi)   It permits the growth of prismatic crystals by varying the growth condition.

Disadvantages

i)   The main disadvantage of this method is the slow growth rate.

ii)   Substitutional or interstitial incorporation of solvent into the crystal is possible. There can be microscopic or macroscopic inclusion of solvent or impurities.

Temperature gradient method

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are that crystal grows at a fixed temperature this method is insensitive to changes in temperature provided both the sources and the growing crystal undergo the same change and economy of solvent and solute. The changes in the small temperature differences between the source and the crystal zones have a large effect on the growth rate. Excellent quality crystals of ferroelectric and piezo-electric materials such as ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP) are commercially grown for use in devices by the low temperature solution growth method.

Gel technique

Gel is a loosely linked polymer of a two component system formed by the establishment of a three dimensional system of cross linkages between molecules of one of the components. The system as a whole is permeated in the other component as a continuous phase giving a semi-solid, generally rich in liquid. Gel growth belongs to low

temperature solution growth [59]. Only small crystals can be grown through this technique. In this method, solutions of suitable compounds say AX and BY are allowed to diffuse through a gel medium to give rise to insoluble substance AB (crystal) and the waste material XY. This reaction is given as follows:

$$AX + BY \qquad \rightarrow \qquad AB + XY$$

Several crystals are grown well in certain gels. Most oxalate crystals are insoluble in water and they decompose before melting [60]. Therefore either slow solvent evaporation or melt technique cannot be used to grow single crystals of these materials. But they can suitably be grown by gel method. The gel medium prevents turbulence and remains chemically inert, thus provides a three-dimensional structure which permits the reagents to diffuse at a desirable controlled rate. Further, its softness and the uniform nature of constraining forces that it exerts upon the growing crystal encourage orderly growth. The growth of single crystals in a gel is a self-purifying process and free from thermal strains, which are common in crystals grown from the melt.

Amongst the wide variety of techniques used today for the growth of single crystals, the gel technique gained considerable importance due to its simplicity and feasibility. Gel growth is an alternative technique to solution growth with controlled diffusion [61] and the growth process is free from convection. For materials, which are insoluble in water and for materials, which decompose before melting, gel growth is found to be a versatile technique. It has the added advantage that the crystals can be grown at room temperature and therefore the grown crystals will be free from the defects arising from the growth at elevated temperature. The different methods of growing crystals in gels fall under the following classes: chemical reaction method, solubility reduction method, complex dilution method and gel-solution method.

The chemical reaction method is suitable for crystals, which are mostly insoluble or sparingly soluble in water. In this method, two soluble reactants are allowed to diffuse through the gel where they react and form an insoluble or sparingly soluble crystalline product. The basic requirements of this method are: (a) The gel must remain stable in the presence of reacting solutions; and (b) It must not react either with the solutions or with the product crystal. Solubility reduction method is particularly suitable for growing single crystals of highly water soluble substances. In this method the substance to be crystallized is first dissolved in water and incorporated within the gel solution before gelation. When the gel sets in, a solution which reduces the solubility of the substance is added over the gel. This, on diffusion into the gel induces crystallization. In the complex dilution method, the material to be crystallized is first complexed in some reagent which enhances its solubility. It is then allowed to diffuse into a gel, which is free from active reagents [62-66]. As the complex solution diffuses through the gel, its concentration gets reduced. This results in a high supersaturation of the material to be crystallized and hence nucleation begins [67-69].

The methods described above may not be useful to grow crystals of organic compounds which are insoluble in water at near ambient temperature. In gel-solution method, the substance to be crystallized is first dissolved in a suitable organic solvent and taken over the gel. The solvent or the solute molecules, as per the convenience, diffuse into the gel inducing the crystallization of the solute. If the solute molecules diffuse into the gel, the crystals will be observed within the gel. If the solvent molecules diffuse into the gel, the crystals will be observed over the gel.

2.3 Characterization techniques

It is important to study the various properties of grown crystals. In the present study attempts have been made to confirm the structure, functional groups, surface

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features, mechanical strength, optical activity and nonlinear activity etc by various characterization methods such as X-ray diffraction, FTIR, SEM, TG/DTA, Vickers microhardness, UV-Visible spectroscopy, dielectric measurements and SHG.

2.3.1   X-ray Diffraction (XRD) technique

The powder X-ray diffraction (XRD) was invented in 1916 by Peter Joseph William Debye, and P.Scherer in Germany [70] and in 1917 by A.W. Hull in United States [71]. The powder XRD technique was widely used for the characterization of crystalline materials. This method has been used for phase identification, quantitative analysis and the determination of structure imperfections of crystalline materials. In the pharmaceutical industries the powder XRD is used popular for identification of drug molecule and its polymorphs. The physical states of the materials can be loose powders, thin films, poly-crystalline and bulk materials. By properly using this technique one can get structural information about the material. For most applications, the amount of information depends on the nature of the sample microstructure (crystalline, structure imperfections, crystalline size and texture) the complexity of the crystal structure (number of atoms in the asymmetric unit cell and unit cell volume), and the quality of the experimental data (instrument performances and counting statistics) [72]. The most important uses of the powder method were in the identification of an unknown material. If a set of standard diagrams of known substances or their tabular representations of them are available, then it is possible to identify a pure substance with the help of a set of rules for finding an unknown material. The JCPDS data files are available for large number of substances. Identification of phases can be done by powder technique without solving crystals structure or assigning indices to the reflections. This method involves diffraction of monochromatic X-ray by a powdered specimen.

In X-ray powder diffractometry, 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. This generation of electrons is analogous to the production of electrons in a television picture tube. 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. A detector detects the X-ray signal, the signal is then processed either by a microprocessor or electronically, converting the signal to count rate. Changing the angle between the X-ray source, the sample, and the detector at a controlled rate between preset limits is an X-ray scan. The characteristic set of d-spacings generated in typical X-ray scan provides a unique fingerprint of the crystal sample. When properly interpreted by comparison with standard reference patterns and measurements, this fingerprint allows for identification of the material. XRD has a wide range of applications in geology, material science, environmental science, chemistry and the pharmaceutical industry.

Single crystal X-ray diffractometer collects intensity data required for structure determination. ENRAF NONIUS CAD4 diffractometer is used for this purpose and this single crystal X-ray diffractometer is a fully automated four circle instrument controlled by a computer (Fig.2.2). It consists of a goniometer, CAD4 interface and a micro VAX3100 equipped with a printer and plotter. The detector is a scintillation counter. A single crystal is mounted on a thin glass fiber fixed on the goniometer head. The unit cell dimensions and orientation matrix are determined using reflections and then the intensity data of a given set of reflections are collected automatically by the computer. An IBM

compatible PC/AT 486 is attached to micro VAX facilitating the data transfer on to a DOS floppy of 5.25" or 3.5". Mo and Cu targets are available. Maximum X-rays power is 140 mA × 50 kV. Polaroid camera is available. UPS backed power supply takes care of the instrument during power failure for short periods. The ideal dimensions of the single crystal required are approximately $0.3 \times 0.3 \times 0.3$ mm^3. However, these dimensions may vary based on the habit of crystal growth and the diffracted beam intensity.   Single crystal X-ray diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure.

Fig. 2.2: ENRAF NONIUS CAD4 single crystal X-ray diffractometer

2.3.2 Fourier Transform Infrared Spectrometer (FTIR)

Infrared spectroscopy has been a work horse technique for materials, analysis in the laboratory for over seventy years. An infrared spectrum represents absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms. Because each different material is a unique combination of atoms, no two compounds

produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kinds of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared spectrometer is an excellent tool for quantitative analysis [73].

FTIR spectrometer consists of (i) a moving mirror source, (ii) a fixed mirror and (iii) a beam splitter (Fig.2.3). Radiation from the infrared source is collimated by a mirror and the resultant beam is divided at the beam splitter; half the beam passes to fixed mirror and half is reflected to the moving mirror. After reflection, the two beams recombine at the beam splitter and for any particular wavelength, constructively or destructively interfere, depending on the difference in optical paths between the two arms of the interferometer. With a constant mirror velocity, the intensity of the emerging radiation at any particular wavelength modulates in a regular sinusoidal manner. In the case of broadband source the emerging beam is a complex mixture of modulation frequencies that, after passing through the sample compartment, is focused on to the detector. The detector signal is sampled at precise intervals during the mirror scan. Both the sampling rate and the mirror velocity are controlled by a reference signal incident upon a detector, which is produced by modulation of the beam from helium-neon laser.

Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror to move a very short distance away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror

moves, the signal which exits the interferometer is the result of these two beams. The resulting signal is called an interferogram which has the unique property which makes up the signal having information about every infrared frequency which comes from the source.

The spectrum of a solid sample is often best determined as an alkali halide pellet. The KBr pellet technique depends on the fact that dry, powdered potassium bromide can be compacted under pressure to form transparent disks. The sample of about 0.5 - 1.0 mg is intimately mixed with approximately 100 mg of dry, powdered KBr. Mixing can be effected by thorough grinding in a smooth agate mortar, or more efficiently with a small vibrating ball mill. The mixture is pressed with special dies under a pressure of 10,000-15,000 psi into a transparent disk. As KBr does not absorb infrared radiation in the region 400-650 cm^{-1}, a complete spectrum of the solid is obtained. In the present work, the Fourier Transform Infrared (FTIR) spectra of the grown crystals were obtained using an FTIR spectrometer (Model: SHIMADZU FTIR 8400S) by KBr pellet technique in the region 4000-400 cm^{-1}.
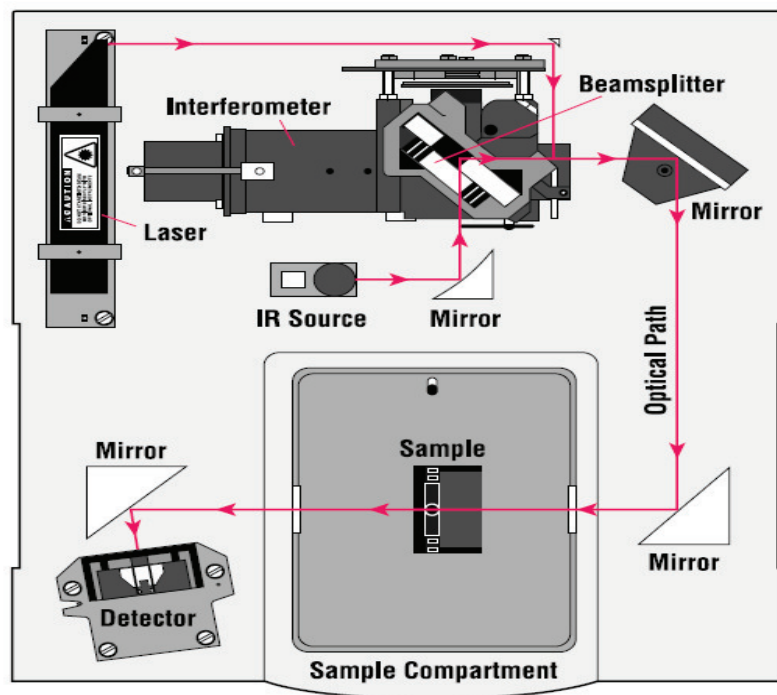
Fig. 2.3: A simple FTIR spectrometer layout

2.3.3 Scanning Electron Microscopy (SEM)

Electron microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield information about the topography (surface features of an object), morphology (shape and size of the particles making up the object) and composition. Electron microscopes were developed due to the limitations of light microscopes which are limited by the light to ×500 or ×1000 magnification and a resolution 0.2 micrometer.

The first scanning electron microscope (SEM) was developed in 1942 and the first commercial instruments were available around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample. Electronic microscopes function exactly as their optical counterparts except that they use a focused beam of electrons instead of light to 'image' the specimen and gain information as to its structure and composition. The basic steps involved are the following. A stream of

electronics formed in high vacuum (by electron guns). This stream is accelerated towards the specimen (with a passive electric potential) while it is confined and focused using metal apertures and magnetic lenses into a thin, focused, monochromatic beam. The sample is irradiated by the beam and interactions occur inside the irradiated sample, affecting the electron beam. These interactions and effects are detected and transformed into an image.

When an electron beam interacts with the atoms in a sample, individual incident electrons undergo two types of scattering like elastic and inelastic. In the elastic scattering only the trajectory changes and the kinetic energy and velocity remain constant. In the case of inelastic scattering, some incident electrons will actually collide with and displace electrons from their orbits (shells) around nuclei of atoms comprising the sample. The interaction places the atoms in an excited (unstable) state. Specimen interaction is what makes electron microscopy possible. The interactions (inelastic) noted on the top side of the diagram are utilized when examining they are thick or bulk specimens (Scanning Electron Microscopy, SEM) while on the bottom side are those examined in thin or foil specimens (Transmission Electron Microscopy, TEM).

As the electrons penetrate the surface, a number of interactions occur that can result in the emission of electrons or photons from or through the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors, and the output can be used to modulate the brightness of a cathode ray tube (CRT) whose X-and Y-inputs are driven in synchronism with the X-Y voltage rastering the electron beam. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen. SEM works on a voltage between 2 to 50 kV and its beam diameter that scans the specimen is 5 nm-2 μm.

The principal images produced in SEM are of three types: secondary electron images back scattered electron images and elementary X-ray maps. Secondary and back scattered electrons are conventionally separated according to their energies. When the energy of the emitted electron is less than about 50 eV, it is referred as a secondary electron and backscattered electrons are considered to be the electrons that exit the specimen with energy greater than 50 eV [74]. Detectors of each type of electrons are placed in the microscope in proper positions to collect them (Figure.2.4) [75].

Electrons in scanning electron microscopy penetrate into the sample within a small depth, so that it is suitable for surface topology, for every kind of samples (metals, ceramics, glass, dust, hair, teeth, bones, minerals, wood, paper, plastics, polymers, etc). It can also be used for chemical composition of the samples surface since the brightness of the image formed by back scattered electrons is increasing with the atomic number of the elements. This means that regions of the sample consisting of light elements (low atomic numbers) appear dark on the screen and heavy elements appear bright. Back scattered are used to form diffraction images, that describe the crystallographic structure of the sample. In SEM, X-rays are collected to contribute in Energy Dispersive X-ray analysis (EDX or EDS), which is used to the topography of the chemical composition of the sample. SEM is only used for surface images and both resolution and crystallographic information are limited. Other constraints are firstly that the samples must be conductive, so non-conductive materials are carbon-coated and secondly, that materials with atomic number smaller than the carbon are not detected with SEM.
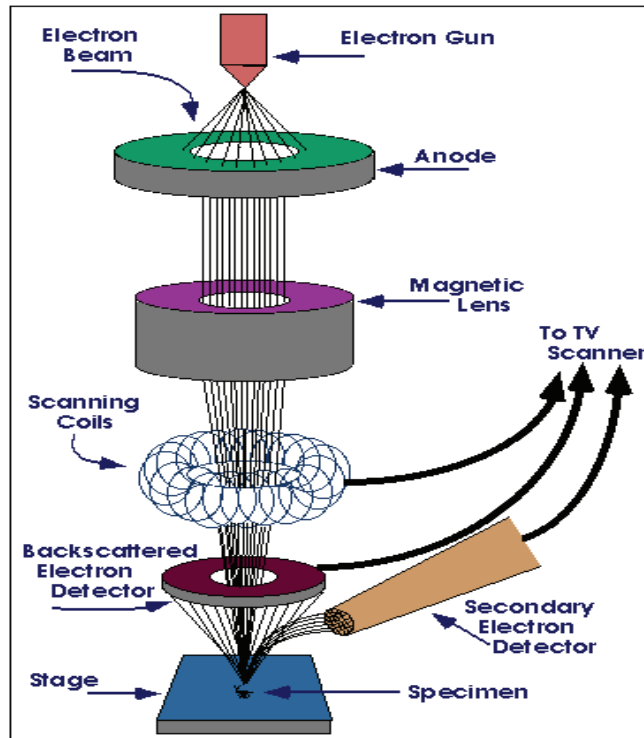
Fig.2.4: The typical geometry of SEM

2.3.4 TG/DTA Analysers

Thermogravimetry (TG)

Thermogravimetry is a technique measuring the variation in mass of a sample when it undergoes temperature scanning in a controlled atmosphere. This variation in mass can be either a less of mass (vapour emission) or a gain of mass (gas fixation). It measures the mass of sample as a function of temperature and determines sample purity, decomposition behaviour, and chemical kinetics. The main parts of TGA are high sensitive thermo balance, microfurnace, furnace–temperature program or controller and recorder or computer with plotter.

The thermobalance is used to measure the accurate weight and microfurnace is used to change the temperature in a controlled manner at a specific rate. The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with

35

the sample. That pan resides in a furnace and is heated or cooled during the experiment. A different process using a quartz crystal microbalance has been deviced for measuring smaller samples on the order of a microgram, (versus milligram with conventional TGA) [76]. The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to percent oxidation or undesired reactions. A computer is used to control the instrument. Analysis is carried out by raising the temperature of the sample gradually and plotting weight (percentage) against temperature. The temperature in many testing methods usually reaches $1000^{o}C$ or more. After the data are obtained, curve smoothing and other operations may be done to find the exact points of inflection. In this method, temperature increase slows as weight loss increases. This is to more accurately identify the exact temperature where a peak occurs. Thermogravimeter analysis is the act of heating a mixture to a high enough temperature so that one of the components decomposes into a gas, which dissociates into the air. It is a process that utilizes heat and stoichiometry ratios to determine the percent by mass ratio of a solute. If the compounds in the mixture that remain are known, then the percentage by mass can be determined by taking the weight of what is left in the mixture and dividing it by the initial mass. Knowing the mass of the original mixture and the total mass of impurities liberating upon heating, the stoichiometric ratio can be used to calculate the percentage mass of the substance in a sample. TG is commonly used in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Differential thermal analysis (DTA)

Differential thermal analysis is a technique to measure the difference in temperature between a sample and reference as a function of the time or the temperature, when they under go temperature, when they under goes temperature scanning in a controlled atmosphere. Any transition which the sample under go will result in the liberation or absorption of the energy by the sample with corresponding variation of its temperature with respect to reference [77]. The information obtained allows differentiation between endothermic and exothermic events with no associated loss (e.g melting and crystallization) and those that involve a weight loss (e.g. degradation).

TG/DTA analyses are often run simultaneously on a single sample. The TG/DTA studies were carried out using a SDT Q600 V8.3 Build 101 thermal analyzer in the temperature range from ambient temperature to 1000 ºC at the heating rate of 20 ºC/min in nitrogen atmosphere and the TG/DTA thermal analyzer is shown in figure 2.5.

Fig. 2.5: The TG/DTA thermal analyser

2.3.5 Dielectric measurement

Dielectric constant and loss tangent

A material is classified as dielectric if it has the ability to store energy when and external electric field is applied. If a DC voltage source is placed across a parallel plate capacitor, more charge is stored when a dielectric material is between the plates than if no material (a vacuum) is between the plates. The dielectric material increases the storage capacity of the capacitor by neutralizing charges at the electrodes, which ordinarily would contribute to the external field. From the point of view of electromagnetic theory, the definition of electric displacement (electricflux density) is $D = \varepsilon E$ where $\varepsilon = \varepsilon_o \, \varepsilon_r$ is the absolute permittivity, ε_r is the relative permittivity or dielectric constant and ε_o is the free space permittivity and E is the electric field.

Permittivity describes the interaction of a material with an electrified E and is a complex quantity and it is given by $K = \dfrac{\varepsilon}{\varepsilon_o} = \varepsilon_r = \varepsilon_r{}' - j \, \varepsilon_r{}''$. The real part of permittivity ($\varepsilon_r{}'$) is a measure of how much energy from an external field is stored in a material. The imaginary part of permittivity $\varepsilon_r{}''$ is called the loss factor and is a measure of low dissipative or loss tangent. The imaginary part of permittiving is always greater than zero and the loss factor includes the effects of both dielectric loss and conductivity. When complex permittivity is drawn as a simple vector diagram (figure 2.6), the real and imaginary components are 90° out of phase. The vector sum forms an angle δ with the real axis ($\varepsilon_r{}''$).

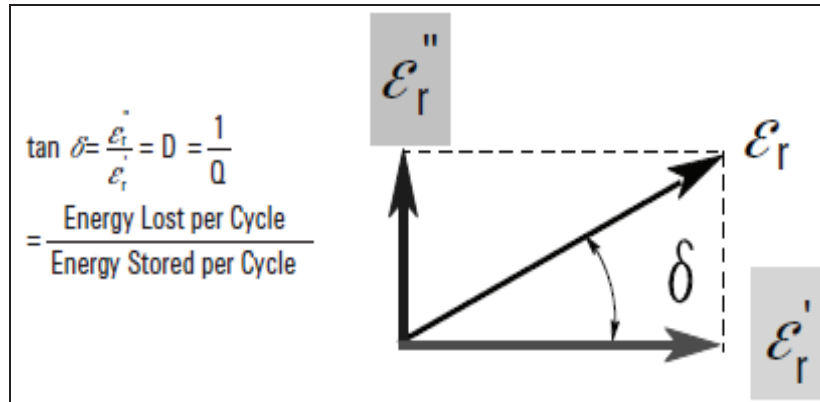**Fig. 2.6: Loss tangent vector diagram**

The loss tangent or tan δ is defined as the ratio of the imaginary part of the dielectric constant to the real part. D denotes dissipation factor and Q is quality factor. The loss tangent tan δ is called dielectric loss or dissipation factor. Sometimes the term quality factor or Q - factor is used with respect to an electronic microwave material, which is the reciprocal of the loss tangent. For very low loss materials, since tan δ = δ, the loss tangent can be expressed in angle units, milliradians or microradians.

Measurement dielectric parameters

LCR meters are used to measure the dielectric parameters like dielectric constant and dielectric loss at various frequencies. Dielectric constant can be measured by determining the change in the capacitance of specially designed condenser when the dielectric is inserted between the plates of the condenser. Various polarization mechanisms in solids such as electronic, atomic polarization of the lattice, orientational polarization of dipoles and space charge polarization [78, 79] can be understood very easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids where it is of great interest both from theoretical point of view and from the applied physics. All the polarization mechanisms are active at low frequencies. The space charge polarization will depend on the purity and perfection of the crystals. Its influence is negligible at low temperatures and is noticeable in the low frequency region.

The dipole orientational effect can sometimes be seen in some materials even upto 10^{10} Hz. The ionic and electronic polarization always exists below 10^{13} Hz [80]. The dielectric constant provides information about certain defects in the crystal. In the present study, the capacitance and dielectric loss factor measurements were carried out using an Agilent 4284A LCR meter at different frequencies ranging from 10^2 to 10^6 Hz. The dielectric measurements were made while cooling the samples. The samples were cut into circular shapes of the desired thickness of 2 to 3 mm and polished. For good electrical contact, opposite faces of the sample crystals were coated with good quality graphite. The dimensions of the crystals were measured using a traveling microscope and a screw gauge. Air capacitance was also measured. The dielectric constant of the crystal was calculated using the relation (as the crystal area was smaller than the plate area of the cell),

$$\varepsilon_r = C/C_o$$

Where C is the capacitance of the crystal and C_o is the capacitance of the air medium of the same dimension as the crystal. As the crystal area was smaller than the plate area of the cell, parallel capacitance of the portion of the cell not filled with the crystal was taken into account and consequently, the above equation becomes,

$$\varepsilon_r = \left\{ \frac{C_{crys} - C_{air}\,(1 - A_{crys}/A_{air})}{C_{air}} \right\} \frac{(A_{air})}{(A_{crys})}$$

Where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode. The apparatus used for measurement of dielectric parameters such as dielectric constant and dielectric loss is shown in figure 2.7.
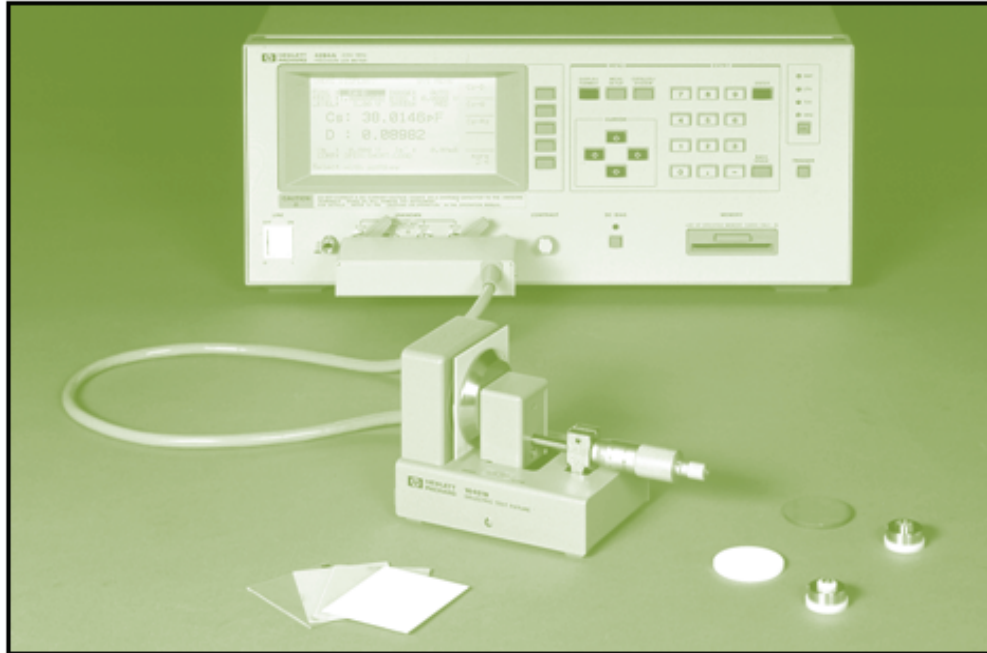
Fig. 2.7: Apparatus for measuring dielectric parameters

Using the data of dielectric constant and dielectric loss, AC electrical conductivity of a crystal was calculated using the formula $\sigma_{ac} = 2\pi\ f\ \varepsilon_0\ \varepsilon_r\ \tan\delta$ where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the sample, $\tan\delta$ is the dielectric loss of the sample and f is the frequency of AC signal. AC activation energy of a substance is the minimum energy required for the atoms or molecules in the compound to activate while an AC voltage is applied. The dependence of AC conductivity on temperature is usually obeying the well known relation $\sigma_{ac} = \sigma\ \exp(-E_{ac}/kT)$ Where k is the Boltzmann's constant, T is the absolute Temperature, σ is the constant depending on the material and E_{ac} is the AC activation energy. The above equation can be written as $\ln\sigma_{ac} = \ln\sigma - E_{ac}/kT$. This is the equation for a straight line. A plot of $\ln\sigma_{ac}$ versus $(1/T)$ gives E_{ac}/kT as the slope and $\ln\sigma_{ac}$ as the Y intercept. It is customary to plot $\ln\sigma_{ac}$ versus $(1000/T)$, from the slope of which the activation energy (E_{ac}) can be calculated.

2.3.6 UV-Vis Spectrosphotometer

Ultraviolet-visible (UV-Vis) spectroscopy involves electro-magnetic radiation in the UV-Visible region (200-400 nm UV-region and 400-800 nm visible region). The absorption in the visible region affects the colour of the compound or sample. In this region of the electromagnetic spectrum, molecules undergo transitions and electrons absorb electromagnetic radiation [81] and excited from ground state to the higher energy state. The instrument used in ultraviolet-visible spectroscopy is called a UV-Vis spectrophotometer. It measures the intensity of light passing through a sample (I) and compares it to the intensity of light used before passing through the sample (I_o). The ratio I/I_o is called transmittance and expressed in percentage (%). The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths, detector, signal processor and readout as shown in the figure 2.8.
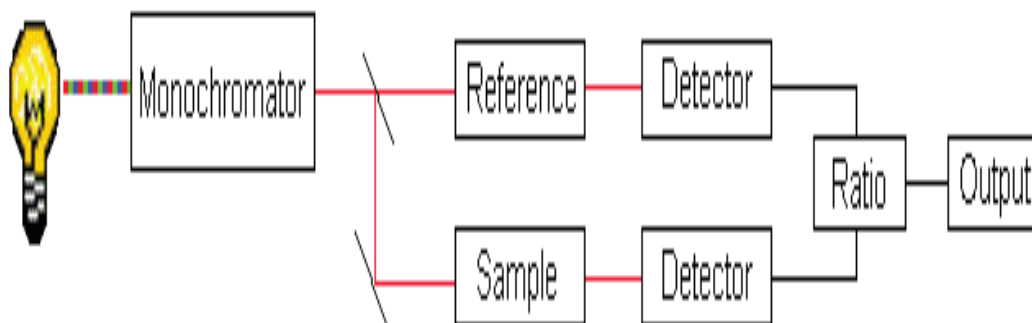

Fig. 2.8: A block diagram of a UV-visible spectrophotometer

The source of UV radiation is a deuterium arc lamp or hydrogen at low pressure produces a continuous UV spectrum. The electrical excitation of deuterium involves the formation of an excited molecular species, which breaks up to give two atomic species and an ultraviolet photon. Both deuterium and hydrogen lamps emit radiation in the range 160-375 nm. Quartz windows must be used in these lamps, and quartz cuvettes must be used, because glass absorbs radiation of wavelengths less than 350 nm. The tungsten

filament lamp is commonly used as a source of visible light. This type of lamp is used in the wavelength range of 350-2500 nm. The energy emitted by a tungsten filament lamp is proportional to the four power of the operating voltage. This means that for the energy output to be stable, the voltage to the lamp must be very stable indeed. Electronic voltage regulators or constant-voltage transformers are used to ensure its stability. Tungsten/halogen lamps contain a small amount of iodine in a quartz envelope which also contains the tungsten filament. The iodine reacts with gaseous tungsten, formed by sublimation, producing the volatile compound WI_2. When molecule of WI_2 hits the filament they decompose, re-depositing tungsten back on the filament. The lifetime of a tungsten / halogen lamps is very efficient, and their output extend well into the ultraviolet. They are used in many modern spectrophotometers. All monochromators contain basic parts such as entrance slit, a collimating lens, a dispersing device (usually a prism or a grating) a focusing lens and an exit slit. Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or Prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit. 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 region. These cells are also transparent in the visible region. Silicate glasses can be used for the manufacture of cuvettes for use between 350 and 2000 nm.
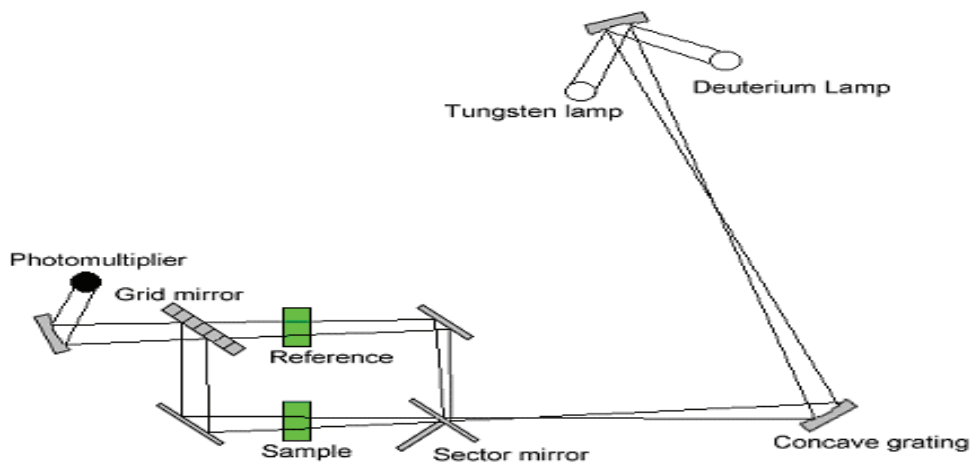
Fig.2.9: Schematic diagram of UV-Vis spectrophotometer

The photon multiplier tube is a commonly used detector in UV-vis spectroscopy. Photo multipliers are very sensitive to UV and visible radiation. They have fast response times. The linear photodiode array is an example of a multichannel photon detector. These detectors are capable of measuring all elements of a beam of dispersed radiation simultaneously. A linear photodiode array comprises small silicon photodiodes formed on a single silicon slip. There can between 64 to 4096 sensor elements on a chip, the most common being 1024 photodiodes. For each diode, there is also a storage capacitor and a switch. The individual diode capacitor circuits can be sequentially scanned. In use, the photodiode array is positioned at the focal plane of the monochromator (after the dispersing element) such that the spectrum falls on the diode array. They are useful for recording UV-visible absorption spectra of samples that are rapidly passing through a sample flow cell, such as in an HPLC detector. The result is recorded in recorder, meter or digital indicator. The schematic diagram of a typical UV-vis spectrophotometer is shown in the figure 2.9. UV-visible transmittance spectra of the grown crystals were recorded using a UV-vis spectrophotometer in the range 190-1100 nm covering the near, visible, near infrared region to find the transmission range to know the suitability for optical applications.

2.3.7 Microhardness test

Hardness is not a fundamental property of a material, but rather a composite one having yield strength, work hardening, true tensile strength, modulus of elasticity, and others [82]. It is the property of a crystal, which gives it the ability to resist against permanently deformed or damaged (bent, broken, or have its shape changed), when a load is applied [83]. Hardness is defined as resistance against lattice destruction [84]. The greater the hardness of the crystal the greater resistance it has to deformation. In mineralogy the property of matter commonly described as the resistance of a substance to being scratched by another substance. In metallurgy hardness is defined as the ability of a material to resist plastic deformation. The plasticity of the crystals [85] can be studied by microhardness study.

Hardness is a technique, in which a crystal is subjected to high pressure within a localized area. Hardness measurement can be defined as macro-, micro- or nano-scale according to the applied forces and displacements obtained. Measurement of the macrohardness of materials is a quick and simple method of obtained mechanical property data for the bulk material from a small sample. It is also widely used for the quality control of surface treatments processes. When the sample is available with coatings and surface properties of importance to friction and wear processes for instance, the macroindentation depth would be too large relative to the surface-scale features. Where materials have a fine microstructure, are multi-phase, non-homogeneous or prone to cracking, macrohardness measurements will be highly variable and will not identify individual surface features. It is here that micro-hardness measurements are preferred. Microhardness is the hardness of a material as determined by forcing an indenter such as a Vickers or Knoop indenter into the surface of the material under 15 to 1000 g load, usually, the indentations are so small that they must be measured with a microscope.

Microintenders work by pressing a tip into a sample and continuously measuring applied load, penetration depth and cycle time. Nanoindentation [86] tests measure hardness by indenting using very small, on the order of 1 nano-newton, indentation forces and measuring the depth of the indentation that was made. By measuring the depth of the indentation, progressive levels of forcing are measurable on the same piece. This allows the tester to determine the maximum indentation load that is possible before the hardness is agreed and the sample is no longer within the testing ranges. This also allows us to determine if the hardness remains constant even after an indentation.

There are three types of tests used with accuracy: they are the Brinell hardness test, the Rockwell hardness test and the Vickers hardness test. The Rockwell hardness test is a hardness measurement based on the net increase in depth of impression when a load is applied. Brinell hardness [87] is determined by forcing a hard steel or carbide sphere of certain diameter under a known load into the surface of a material and measuring the diameter of the indentation left after the test. Knoop test [88], a pyramid-shaped diamond indenter with apical angles of $130°$ and $172°$ 30' (called a Knoop indenter) is pressed on a material. Making a rhombohedral impression with one diagonal seven times longer than the other, the hardness of the material is determined by the depth to which the Knoop indenter penetrates. The Knoop hardness (H_k) is obtained from the formula $H_k = 14.229$ P/d^2 where, P is the applied load (measured in N) and d^2 is the area of the indentation (measured in square metre). Among the various methods used, Vickers hardness measurement is the standard method for measuring the hardness of crystals and other type of materials and in this case the surface is subjected to a standard pressure for a standard length of time by means of a pyramidal-shaped diamond indenter [89].

Fig 2.10: Vickers microhardness tester

The diagonal of the resulting indentation is measured under a microscope and the Vickers hardness value is read from a conversion table. Vickers hardness is a measure ment of the hardness of a material, and calculated from the size of an impression produced under load by a pyramidal shaped diamond indenter. For Vickers test, the specimen is placed on anvil that has a screw threaded base. The anvil is turned up by the screw threads until it is close to the point of the indenter. The load is slowly applied to the indenter by activating start lever. The load is released and the anvil with the specimen is lowered. The operation of applying and removing the load is controlled automatically. A microscope is swung over the specimen to measure the square indentation to a plus or minus 1/1000 of a millimetre. Measurements are taken across the diagonals to determine the area (d^2) and are averaged. The base of the Vickers pyramid is a square and the depth of indentation corresponds to $1/7^{th}$ of the indentation diagonal. The longitudinal and transverse diagonals are in the ratio of 7:1 and the depth of the indentation is only about

$1/30^{th}$ of the longitudinal diagonal. Hardness is generally defined as the ratio of the load applied to the surface area of the indentation. The Vickers hardness number (H_v) or Diamond Pyramid Number (DPN) is calculated using the relation

$$H_v = 1.8554 \, P/d^2 \quad kg \, mm^{-2}$$

Where P is the applied load in kg and d is the diagonal length of the indented impression in mm and 1.8544 is a constant of a geometrical factor for the diamond pyramidal indenter. The advantages of the Vickers hardness test are that accurate readings can be taken, and just one indenter is used for all types of samples. Although it is thoroughly adaptable and very precise for testing the softest and hardest of materials, under varying loads, the Vickers machine is an outstanding unit that is more expensive than the Brinell or Rockwell machines.

2.3.8 Second harmonic powder test

The study of second harmonic generation in powder technique was devised by Kurtz and Perry [90, 91]. This technique consists of a Q-switched Nd: YAG laser the output of which was filtered through 1064 nm narrow pass filter. The power of the fundamental beam was monitored by a split beam technique, in one channel of the power meter. The sample was grinded in the form of fine powder of known grain size and pressed between two glass plates. The sample size was kept larger than the beam cross section. The generated harmonic wave is passed through a 532 nm narrow pass filter and fed to other channel of the power meter. The ratio of the fundamental and harmonic intensities determines the efficiency of the sample. The SHG efficiency varies with the grain size of the powdered sample [92]. To eliminate the experimental error, urea or KDP sample of the same size was also tested in the same set up and the efficiency was evaluated as a ratio. Both the reference and test samples had uniform particle size of 125

to 250 microns. Throughout the experiment the laser power was kept constant. In order to improve the efficiency of second harmonic generation at the detector, a parabolic reflector was placed directly in front of the sample, (between the laser and the sample) with a small hole for the laser beam to pass through it. The Nd:YAG Laser was Q-switched by a rotating mirror at a rate of 400 Hz.

Several techniques were used for sample preparation and mounting. For qualitative analysis a thin layer (0.2 mm) of upgraded powder was placed on a microscope slide and held in place with transparent tape. For quantitative analysis, powder was graded by using standard sieved to the desired range of particle sized (125 mm-250 mm) and loaded into a quartz cell of known thickness (0.2mm, 0.1mm, etc) with the vibrator to have uniform packing. If the crystals are in single crystal form, the crystals were powdered by using a ball mill, and then graded using sieves. Similar procedure was also used in the case of polycrystalline or single crystalline material. To determine the essential features of second harmonic generation (SHG) in thin powder layers, experiments were conducted to measure the dependence of second harmonic intensity [93] on the following parameters, (i) angle between detector and direction of incident light beam (Q), (ii) powder layer thickness (L) and (iii) average particle size (r) and laser beam diameter (D) [91]. The photometric intensity I_o of the front and back surface of the powder layer is not equal for powders in air. When the same powder is contained in a liquid of matching refractive index, the uniaxial distribution is observed. The advantage of index matching of the powder is that the second harmonic is not scattered due to reflection and refraction at the particle interfaces and all the harmonic flux is collected in a narrow cone in the forward direction.

The second harmonic signal varies linearly with layer thickness L for fixed particle size and it shows that the second harmonic intensity is proportional to the total

number of particles present. A linear dependence on layer thickness L was also found in the case of immersion of the powder in the refractive index-matching liquid.

The particle size depends on (i) a peak in the intensity when the particle size is close to the average coherence I_c and (ii) approximately linear increase in intensity with increasing of particle size. The nonlinear optical response of powder technique is only a rough estimate. Fundamental laser beam is allowed to pass through the powder sample and the generated second harmonic light is detected by a photomultiplier tube (Fig.2.11).
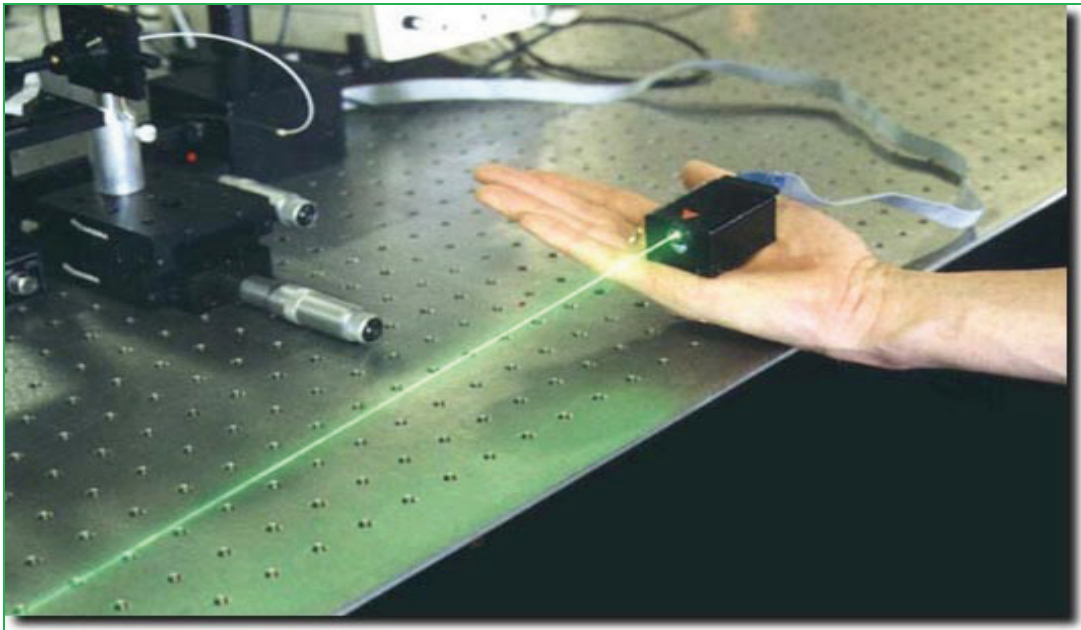

Fig 2.11: Q-switched Nd: YAG laser