CHAPTER-II

EARLY WORK, METHODS AND INSTRUMENTATION

2.1 Introduction

This chapter deals with the early work, techniques and instrumentation adopted to carry out the research work. Initially, the salts of β-alanine complexes and DL-alanine complexes were synthesized. The growth of crystals of synthesized salts of this work was carried out by solution method with slow evaporation technique. The characterization of the grown crystals was performed by using various sophisticated instruments available in universities and research institutions and the details are given in this chapter.

2.2 Early work

Amino acids and their complexes are the organic or semi-organic materials that have attracted great attention due to their ability in ease of processing in the assembly of optical devices. The complete understanding of the properties of amino acid crystals, as well as other organic crystals, still requires more attention [63-67]. 3-Aminopropionic acid is commonly known as β-alanine with molecular formula C₃H₇NO₂ and in which the amino group is at the β-position from the carboxylate group. Supplementation with β-alanine has been shown to increase the concentration of carosine in muscles, decrease fatigue from athletes and increase total muscular work done. β-alanine is purely a synthetic amino acid and it is a positional isomer of L-alanine [68-71]. β-alanine is the only naturally occurring amino acid and is a constituent of the dipeptides carnosine and anserine. It also forms crystalline complexes with organic and inorganic acids but unfortunately only a few crystal structures have been published such as β-alanine [72], β-alanine phosphoric acid [73],
β-alanine phosphorous acid [74], β-alanine nitric acid [75], β-alanine maleic acid [76] and β-alanine perchloric acid [77]. Few papers are devoted to infrared properties of β-alanine crystals [68, 78]. Unfortunately there are no reports on phase transitions for crystals of β-alanine complexes. It crystallizes in the orthorhombic system with eight formula units per unit cell [79,80]. It can be used for optoelectronic devices [81]. Also it combines with inorganic compounds and forms organic-inorganic hybrid complex materials [65,79, 82-86].

2,4,6 –Trinitrophenol is commonly known as picric acid with molecular formula C₆H₃N₃O₇ and it is one of the acidic phenols. It is used in dyeing industry and it crystallizes in a non-centrosymmetric space group PCa₂₁. Picric acid forms stable picrates with various organic molecules through H-bonding or ionic bonding [78]. Researchers have been attracted to carry out the investigations on many amino acid picrates recently [87].

DL-Alanine is one among the rare amino acid racemates crystallizing in a non-centrosymmetric space group. The structure of DL-Alanine was elucidated by Subha Nandini et al [65]. The crystal structure is stabilized by a network of characteristic head-to-tail hydrogen bond sequences. The structure contains three types of such sequences: straight sequence along the c-axis with O2 of the carboxylate as acceptor, zigzag sequence along the 21 screw axis with O1 of the same carboxylate group as acceptor and zigzag DL-sequence among the glide-related molecules with O2 of the carboxylate group as acceptor. The carboxyl group is present as a carboxylate ion and amino group as ammonium ion [88]. From the literature survey, it is noticed that a limited number of papers are available on beta-alanine and DL-alanine complexes.
2.3 Low temperature solution growth method

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solution is extremely popular in the production of many technologically important crystals. The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. The mechanism of crystallization from solution 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 process of solution growth now yields good quality crystals for a variety of applications. Crystals intended for practical and technical applications should have a well developed morphology and contain a low density of defects. These requirements may be predicted from a consideration of thermodynamic and kinetic parameters which characterize the overall growth conditions. Thermodynamic parameters determine the growth mechanism, while kinetic parameters determine the growth kinetics and the generation of defects [16,47].

Solution and solubility

A solution is a homogeneous mixture of a solute in a solvent. Solute is the component which is present in a smaller quantity and that one which gets dissolved in the solution. For a given solute there may be different solvents. The solvent must have the factors such as good solubility for the given solute, good temperature coefficient of solute solubility, less viscosity, less volatility, less corrosion and non-toxicity, small vapour pressure and cost advantages.

Solubility of the material in a solvent decides the amount of the material which is available for growth and hence defines the total size limit. Solvents commonly used
are water, ethanol, methanol, acetone, carbontetrachloride, hexane, xylene etc. Almost 90% of the crystals are grown by using water as a solvent. For crystal growth highly purified water is needed. If the solubility is too high, it is difficult to grow bulk single crystals and if too low, it restricts the size and growth rate of the crystals. Solubility gradient is another important parameter which dictates the growth procedure. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain super saturation in the solution.

**Saturation, supersaturation and metastable**

A solution that is in equilibrium with the solid phase is said to be saturated with respect to that solid. However it is relatively easy to prepare a solution containing more dissolved solid than that represented by saturation condition and such a solution is said to be supersaturated. On reaching saturation the concentration of the solute and the solvent are equal. If the solution is attained saturation condition, the solute will not dissolve. But crystals usually grow in the supersaturated solutions. In this case concentration of the solution is more than the equilibrium concentration.

Mier carried out extensive researches on the relationship between supersaturation and spontaneous crystallization. The results can be represented as shown in figure 2.1. The lower continuous line is the normal solubility curve for the salt concerned. Temperature and concentration at which spontaneous crystallization occurs is represented by the upper broken curve, generally referred to as the super solubility curve.
The diagram is divided into three zones.

(i) The stable (unsaturated) zone where crystallization is impossible.

(ii) The metastable (supersaturated) zone between the solubility and supersolubility curves where spontaneous crystallization is improbable. The metastable zone width is a measure of stability of a solution in its supersaturated region. If metastable width is larger, the stability is larger and a number of factors such as stirring rate, cooling rate of the solution, presence of additional crystals or impurities affect its value.

(iii) The unstable or labile (supersaturated) zone where spontaneous crystallization is possible.

**Expression for supersaturation**

In order to grow crystals the solution must be supersaturated concentration.

Supersaturation is the driving force which governs the rate of crystal growth.

The concentration driving force \( = C - C^* \)

Supersaturation ratios \( = \frac{C}{C^*} \)
Relative supersaturation \[= \frac{(C/C^*)-1}{S-1}\]

Where \(C\) is the solution concentration, \(C^*\) is the equilibrium saturation at the given temperature. If the concentration of a solution can be measured at a given temperature and the corresponding equilibrium saturation known, then the supersaturation can be calculated.

**Nucleation**

Growth of crystals starts from nucleation process. Nucleation plays an important role in a wide variety of engineering processes wherever condensation, boiling, crystallization, sublimation and catalytic processes occur. In a supersaturated or super cooled system, when a few atoms or molecules join together, a change in energy and phase takes place in the process of formation of the cluster. The cluster consisting of such atoms or molecules is called nuclei. The kinetics of phase change takes place in four different stages. In the first stage, a supersaturated state is developed. It may arise due to chemical, photo-chemical reaction or the consequence of a change in temperature, pressure, tension or other chemical or physical conditions. The second stage is the generation of minute specks or nuclei. The third stage is the growth of nuclei to form particles of macroscopic dimensions or domains of a new phase. The final stage is called the relaxation process such as agglomeration by which the texture of the new phases changes.

Nucleation may occur spontaneously or it may be induced artificially and they are usually referred to as homogeneous and heterogeneous nucleation respectively. If the nuclei form homogeneously in the interior of the parent phase, it is called homogeneous nucleation. In other words, in the absence of foreign particles, the occurrence of phase transition is termed as homogeneous nucleation. In homogeneous
nucleation, the probability of nucleation occurring at any given site is identical to that at any other site within the assembly.

If the nuclei form heterogeneously around ions, impurity molecules or on dust particles, on surfaces or at structural singularities such as dislocations or other imperfection, it is known as heterogeneous nucleation. In the heterogeneous nucleation, the probability of nucleation occurring at certain preferred sites in the assembly is much greater than that at other sites. The heterogeneous nucleation is common for all systems namely vapour-liquid, vapour-solid and liquid-solid transformation. The criterion for a heterogeneous nucleation from thermodynamic point of view is that the interfacial energy of the crystal-substrate interface should be lower than that for the sum of the liquid-substrate interface and the liquid-crystal interface. The greater the difference in the interface energies, the more effective will be the substrate.

The nucleation can also be classified as primary and secondary nucleation. The term primary nucleation is used for both homogeneous and heterogeneous nucleation in systems that do not contain crystalline matter. In the secondary nucleation process, the nuclei are generated in the vicinity of crystals present in the supersaturated systems. This process involves the displacement of nuclei from the parent crystal at the supersaturation which prevents primary homogeneous nucleation to occur [37].

**Stirring and growth temperature**

For the successful and relatively fast growth of a substance from solution containing a reasonably high solute concentration and having a high viscosity, effective stirring is an important operation. Stirring enhances growth rates and decreases the generation of defects, but very high stirring rates cause turbulence in
the solution, which leads to high inclusion content. Thus to ensure good crystal
growth it is useful to have a sufficiently high value of the surface entropy factor of the
system, medium supersaturation, elevated temperatures and non turbulent stirring.
The rate of stirring is to sweep off the depleted solution at the crystal surface,
providing it with fresh supersaturated solution which would otherwise have been
supplied by diffusion. Stirring may be achieved by various types of stirrers but the
rate of their rotation should not exceed an optimum value. The rotation of stirrers, at
a rate greater than the optimum, induces turbulence at a point in the system, which
favours trapping of inclusions on the crystal surface.

The simplest method of stirring is unidirectional rotation of the crystal fixed at
the holder of a stirrer. This type of stirring leads to the formation of cavities in the
central regions of a crystal face because of malnutrition of the solute there is
comparison with edges and corners which receive more solute supply. Consequently,
edges and corners serve as sources of growth steps by two-dimensional nucleation.
This non-uniform solute supply favours the formation of thick layers which
subsequently lead to the trapping of inclusions and to the generation of dislocations.
Periodic rotation of the crystal in opposite directions suppressed eddy formation but
does not eliminate the formation of the central cavity. Consequently, eccentric
reverse rotation is often used.

In order to grow a substance in a given phase and / or composition at a
reasonable rate, the choice of an optimum temperature interval is important. As in
the case of other processes, growth at elevated temperatures takes place faster.
However, at elevated temperatures, smooth growth necessitates better temperature
control, while increased vapour pressure creates problems of control of super
saturation and spurious nucleation. These difficulties may be overcome during crystal growth from boiling solutions[3,10].

**Impurities/Additives**

Growth aids which modify the properties of a growth system may be taken as impurities. Small amounts of the ion additives like metal ions, oxy-ions and dye ions are known either to produce improvements in crystal growth or to change the growth habit. In general highly polarizable metal ions and oxy-ions are the most effective impurities, and the habit of crystals is readily modified in the presence of these impurities.

**Seed preparation**

The quality of the crystal grown very much depends on the quality of the seed crystal used. Seed crystals can be obtained by spontaneous nucleation in the labile region of the saturated solution. A seed used to grow a large uniform crystal must be a single crystal free of inclusions, cracks, block, boundaries, sharp cleared edges and other obvious defects. When large crystals of the same materials are readily available they can be cut in the required orientation to fabricate the seed crystal. Since the growth rate of the crystal depends on the crystallographic orientation the crystal must be cut in such a way that it has larger cross section in the fast growing direction.

**Different techniques in low temperature solution method**

The quality of the crystal grown depends upon the quality of the seed crystal used. Small seed crystals can be obtained by spontaneous nucleation. The seed crystal is used to grow large uniform crystal and it must be a single crystal free of inclusions, cracks, block boundaries, twinning and any other obvious imperfections. A defect-free crystal must be used for various studies.
Low temperature solution growth method can be sub-divided into the following techniques: Slow cooling technique, Slow evaporation technique and Temperature gradient technique.

Slow cooling method is the best method to grow bulk single crystals from solution. In this method, supersaturation is created by a change in temperature usually throughout the whole crystallizer. The crystallization process is carried out in such a way that the point on the temperature dependence of the concentration moves into the metastable region in the direction of lower solubility. Since the volume of the crystallizer is finite and the amount of substance placed in it is limited, the supersaturation requires systematic cooling. It is achieved by using a thermo-stated crystallizer. Volume of the crystallizer is selected based on the desired size of the crystals and the temperature dependence of the solubility of the substance.

In slow evaporation technique, the solution loses particles which are weakly bound to other components and, therefore, the volume of the solution decreases. An excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and the solute. Normally, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and therefore, the solvent evaporates more rapidly and the solution becomes supersaturated. It is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. This method of crystal growth is the oldest and technically it is very simple. For non-toxic solvents such as water, evaporation is permissible into the atmosphere but for toxic and inflammable solvents precautions are taken to avoid the leakage of solvent vapour in the atmosphere. The simplest apparatus for growth by this method is a beaker covered with a few holes in the lid to allow solvent evaporation. The rate of crystallization depends on the rate of
solvent evaporation which may be governed by changing the total area of the holes. In sophisticated crystallizers, evaporation is controlled by passing air or an inert gas at a controlled rate over the solution. Good control of evaporation rate can also be obtained by using some sort of condenser to allow the removal of condensed solvent at a controlled rate [36, 89]. In temperature gradient technique, the materials are transported 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 (i) crystal grows at fixed temperature, (ii) It is insensitive to change in temperature, provided both the source and the growing crystal undergo the same change and (iii) Economical use of solvent and solute etc. [16]. Some details of another low temperature growth method viz. gel growth method is given in the chapter-I

**Advantages / Disadvantages of low temperature solution method**

The low temperature solution growth technique has the following merits.

i) Simple growth apparatus

ii) Growth of strain and dislocation-free crystals

iii) Crystals can be grown in large size

iv) Morphology of crystals can be controlled

v) Permits to grow crystals of substances that undergo decomposition before melting and

vi) Organic, inorganic and semi-organic crystals in the suitable solvents can be grown.

The low temperature solution growth technique has the following demerits

i) This technique is applicable for substances that are fairly soluble in a solvent
ii) The growth material should not react with the solvent and

iii) The growth period is long unlike melt method [3,10,16].

2.4 Techniques and Instrumentation

2.4.1 X-Ray Diffractometers

X-rays are electromagnetic waves whose wavelengths range from 0.1 to 10 Å. They are produced when rapidly moving electrons strike a solid target and their kinetic energy is converted into radiation. X-ray Diffraction (XRD) is an efficient analytical technique used to identify and characterize unknown crystalline materials. X-ray diffraction technique is the most definitive one available for the determination of crystal and molecular structures and the results obtained are usually unambiguous and generally quite accurate [90-93]. Since the scattering of X-rays is done by electrons, the observed geometrical parameters usually reflect the locations of the inner core electrons of the atoms in a complex with the valence electrons contributing relatively little to the overall scattering. Thus, from a crystallographic point of view, the distribution of bonding electrons in a molecular complex is a relatively minor perturbation except with regard to how it affects the relative locations of the inner shell electrons of the different atoms in the complex. Despite certain limitations, the geometrical parameters obtained from single crystal diffraction studies such as molecular geometry and accurate bond distances and bond angles offer considerable insight into the bonding and electronic structures.

Out of the various possible X-ray diffraction methods, the powder method is of special importance. This is so because the powder method is the only technique which is readily applicable to all crystalline materials. Also, it is the most convenient method by which diffraction data can be obtained from the crystalline material. These data
which depend on the lattice parameter are unique for a particular substance and thus can be employed for its identification.

In this technique, a monochromatic X-ray beam be incident at Bragg angle \( \theta \) on the set of lattice planes with interplanar spacing \( d \) in a particular crystallite, so that the Bragg diffraction condition \( 2d \sin \theta = \lambda \) for the above lattice planes is satisfied. For the diffracted beam from a large number of crystallites which are randomly oriented, and consider the diffraction from the planes with the same interplanar spacing as the first one, the locus of the diffracted team would lie on a cone with half apex angle \( 2\theta \), since the angle between the incident beam and the diffracted beam is \( 2\theta \). In a similar way, the diffracted became from other sets of lattices planes with different interplanar spacings \( d_1, d_2 \) etc. would lie along different cones with different half-apex angles \( 2\theta_1, 2\theta_2 \) etc. These cones could be co-axial since the incident beam direction remain the same for all these lattice planes. It is usually necessary to rotate the cylindrical specimen about its own axis during exposure. This ensures that sufficient number of crystallites are present so that the diffracted became forms continuous cones.

For taking the powder diffraction pattern, the characteristic X-ray radiation CuK\(_\alpha\) is used, so that the wave length \( \lambda \) is known. Thus from the Bragg's equation \( 2d \sin \theta = \lambda \), the interplanar spacing \( d \) can be calculated if \( \theta \) can be measured.

The experimental arrangement of powder crystal method is shown in figure 2.2. A is a source of X-rays which can be made monochromatic by a filter. This allows the X-ray beam to fall on the powdered specimen P through the slits S\(_1\) and S\(_2\). The function of these slits is to get a narrow pencil of X-rays. Fine powder, P, struck on a hair by means of gum is suspended vertically in the axis of a cylindrical camera. This enables sharp lines to be obtained on the photographic film which is surrounding
the powder crystal in the form of a circular arc. The X-rays after falling on the powder passes out of the camera through a cut in the film so as to minimize the flogging produced by the scattering of the direct beam.

![Diagram of X-ray diffraction setup](image)

**Figure 2.2: The experimental arrangement of powder X-ray diffraction technique**

This method is most useful for cubic crystals and used for determining the complex structures of metals and alloys. However, their structures could not be revealed by the earlier studies.

Powder X-ray diffraction provides less information than single-crystal diffraction, however, it is much simpler and faster. Powder X-ray diffraction is useful for confirming the identity of a solid material and determining crystallinity and phase purity. Many books give details of principles and methods involved in the determination of crystal and molecular structures of inorganic and organic substances [94-99]. Both the methods of XRD can be carried out for the grown crystals to check the correctness of the results of the crystalline data. In the present work, single crystal XRD data for the grown crystals were collected using a single X-ray diffractometer (Bruker-Nonius MACH3/CAD4) at School of Physics, Madurai Kamaraj University,
Madurai. Powder XRD patterns of the powder form of the grown crystals were recorded at Regional Research Laboratory (RRL), Tiruvananthapuram using a powder X-ray diffractometer (PANalytical XPERT – PRO MPD).

2.4.2 Fourier Transform Infrared (FTIR) spectrometer

FTIR technique is most useful for identifying functional groups of organic and inorganic compounds. It can be utilized to quantify some components of an unknown mixture. It can be applied to the analysis of solids, liquids and gases. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum [100]. Today’s FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments.

Infrared spectroscopy deals with the study of vibrational spectra of molecules. An infrared absorption spectrum originates from molecular vibrations (vibrations of bonds) which cause a change in the dipole moment of the molecule. The vibrational frequencies, their relative intensities and shapes of the infrared bands recorded in a double beam spectrometer are used for the qualitative characterization of a sample.

Fourier transform infrared (FTIR) technique is based on the blending of a Michaelson Interferometer with a sensitive infrared detector and a digital minicomputer. FTIR spectrometers provide higher resolution, total wavelength coverage, higher accuracy in frequency and intensity measurements. The instruments also possess greater ease and speed of operation. The three basic components in an FTIR spectrometer are the radiation source, interferometer and detector. Two common IR sources are the Nernst filament, consisting of a spindle of rare earth oxides, and the globar filament, a rod of carborundum. These IR sources are heated to very high temperature in the range of 1000 to 1800°C. The most commonly used
interferometer is the Michelson’s interferometer. It consists of three active components: a moving mirror, a fixed mirror and a beam splitter. The two mirrors are perpendicular to each other. Radiations from the broad band IR source is collimated and directed into the interferometer. Due to changes in the relative position of the moving mirror to the fixed mirror, an interference pattern is generated. Fourier transformation converts this interferogram from the time domain to the frequency domain. The resulting beam then passes through the sample and is focused on the detector.

The two most important detectors used in FTIR instruments are deuterated triglycine sulphate (DTGS) and mercury cadmium telluride (MCT). The DTGS detector is a pyroelectric detector that delivers rapid responses with respect to temperature changes. The MCT detector is a photon detector which is faster than the DTGS detector.

Infrared spectra of both gases and liquids may be obtained by direct study of the undiluted specimen. Solids can be examined in crystalline form by dilution in a mull, an alkali halide disc or by spreading pure solid on cell plate. 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 [101-105]. 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).

![FTIR spectrometer](image)

**Fig.2.3: FTIR spectrometer**

By interpreting the infrared absorption spectrum, the functional groups of a compound and chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular fingerprint. While organic compounds have very detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds.

### 2.4.3 Microhardness Tester

Microhardness studies find wide applications in the study of material properties of solids. Hardness testing has been widely used to study the strength and deformation in materials. Hardness test methods are used to determine the stress needed to produce plastic flow in the brittle material. It measures the mean contact pressure when a spherical, a conical or a pyramidal indentor is pressed on to the
surface of a flat specimen, thus providing a simple and non-destructive means of assessing the resistance of the material to plastic deformation. Hardness is defined as the ratio of the load applied to the surface area of the indentation [106,107].

The definition of hardness depends entirely on the method of measurement which will determine the scale of hardness obtained. The best general definition that can be given is that hardness is a measure of the resistance to permanent deformation or damage. The method of measuring hardness is not dependent on a single physical property but may involve both the elastic and plastic deformation characteristic of the material so that the elastic limit, elastic modulus, yield point, tensile strength, brittleness etc., all play a part in the result obtained. An important use of microhardness studies is the possibility of making an indirect estimate of other mechanical characteristics of materials having a specific correlation with their hardness.

Microhardness tests have been applied to fine components of clock and instruments mechanism, thin metal strips, foils, wires, metallic fibers, their galvanic coatings, artificial oxide films as well as the then surface layers of metals which change their properties as a result of mechanical treatment, cooling, friction and other effects. The microhardness method is widely used for studying the individual structured constituent elements. The microhardness of materials is determined by different techniques. They are: Static indentation test, Dynamic indentation test, scratch test, rebound test, pendulum recoil test, Vickers hardness test etc.

In static indentation test, a steady lead is applied to an indenter which may be a ball, diamond cone or diamond pyramid and the hardness is calculated from the area or depth of indentation produced.
In dynamic indentation test, a ball, cone or a number of small spheres is allowed to fall from a definite height and the hardness number is obtained from the dimension of the indentation and the energy of impact.

The scratch test is made with a diamond or steel indenter traversing the surface at a steady rate and under a definite load. The hardness number is expressed in terms of the width or depth of the groove formed.

In the Rebound test, the hardness is given by the height of rebound of a diamond tipped weight falling on the surface from a fired height.

In pendulum recoil test, a steel ball is attached to a pendulum which is made to swing and the amplitude of the first swing or the time of oscillation of a number of swings is taken as a measure of hardness.

In the Vickers hardness test, an indenter with a square based pyramid is used for which the angle between opposite faces is ideally 136°. From the general definition of hardness, for a given diagonal \( d \) mm of the square impression formed on the sample and for the load \( P \),

\[
V_{\text{ickers}} \text{ hardness number, } H_v = \frac{2P \sin(\alpha/2)}{d^2}
\]

Since \( \alpha = 136° \), \( H_v = \frac{1.8544P}{d^2} \text{ kg/mm}^2 \)

Vickers microhardness test is found to be the most suitable (among various types of hardness measurements available) for the measurement of microhardness of crystals. Hardness measurement is to performed on a limited area with small damage to the area being measured and must yield extremely reliable results. A hardness tester fitted with a diamond pyramidal indenter attached to an incident light microscope is used for this study. The diamond indenter is in the form of a square pyramid, opposite faces of which make an angle 136° with one another. The indenter can be pressed on
the sample under a load (P) of 5, 10, 15, 20 etc grams. The duration of the indentation time was kept constant (10 seconds). Hardness is computed form the size of the impression left on the sample surface after indentation and hence includes the effects involved in the material response to the indentation pressure during loading and relaxation during unloading. For each load several indentations were made and the average value of the diagonal length of the indentation mark was considered to calculate the microhardness. The impression of a square pyramid has a superficial area of \( d^2 / 2 \sin 68^\circ \) where \( d \) is the diagonal length of the indentation. The area of impression is related to hardness as Vicker's Hardness numbers \( H_v \),

\[
H_v = \frac{\text{load}}{\text{area of impression}} = \frac{(2 \sin 68^\circ)}{d^2}
\]

\[
= \frac{1.8544 \text{ P}}{d^2} \text{ kg/mm}^2
\]

Here \( P \) is the load in kilograms and \( d \) is diagonal length of indentation in millimeters [108-111].

2.4.4 UV-Visible spectrophotometer

The wavelengths of visible light range from 400 nm to 700 nm. The visible region however, is a very small part of the entire electromagnetic spectrum. Wavelengths slightly shorter than those of the visible region fall into the ultraviolet region.

Ultra Violet (UV) radiation has sufficient energy to excite valence electrons in many atoms or molecules. Consequently, UV is involved with electronic excitation. Ultraviolet absorption spectra arise from transition of electron or electrons within a molecule or an ion from a lower to a higher electronic energy level and the ultraviolet emission spectra arise from the reverse type of transition.
When a molecule absorbs ultra violet radiation of frequency $\nu \text{ sec}^{-1}$, the electron in that molecule undergoes transition from a lower to a higher energy level or molecular orbital. The energy difference is given by

$$E_1 - E_0 = h\nu$$

where $E_1$ is the energy level of excited state of the electron and $E_0$ is the ground state energy level. The total energy of a molecule is equal to the sum of electronic, vibrational and rotational energy. The magnitude of these energies decreases in the following order, $E_{\text{elec}}, E_{\text{vib}}$ and $E_{\text{rot}}$.

As ultraviolet energy is quantized, the absorption spectrum arising from a single electronic transition must consist of a single discrete line. But a discrete line is not obtained because electronic absorption is superimposed upon rotational and vibrational sub levels. In case of complex molecules having more than two atoms, discrete bands coalesce to produce absorption bands or band envelopes.

Energy absorbed in the ultraviolet region produces charges in the electronic energy of the molecule resulting from transitions of valence electrons in molecules. In organic molecules, $\sigma$ -electrons, $\pi$-electrons and $n$-electrons are involved in UV spectrum. As n electron can be excited by UV radiation, any compound that contains atoms like nitrogen, oxygen, sulphur, halogen compounds or unsaturated hydrocarbons may absorb UV radiation. From the absorption level for the wavelength of UV radiation, the structure could be determined [112-114].

The essential features of a simple UV spectrophotometer are:

(i) Light source

(ii) Filter to select the appropriate wavelength of light

(iii) A container for the solution

(iv) A photocell to receive the transmitted light
(v) A metre for measuring the response of the photocell

The make up of a single beam spectrophotometer is shown in figure 2.4.

![Figure 2.4: A typical spectrophotometer](image)

An image of the light source A is focused by the condensing mirror B and the diagonal mirror C on the entrance slit at D. The entrance slit is lower of the two slits placed vertically, one above the other light falling on the collimating mirror E is rendered parallel and reflected to the quartz prism F. The back surface of the prism is alumnised, so that light refracted at the first surface is reflected back through the prism, undergoing further refraction as it emerges from the prism. The collimating mirror focuses the spectrum in the plane of the slits D, and light of the wavelength for which the prism is set passes out of the monochromator or through the exit (upper) slit, through the absorption cell G to the photo cell H. The photocell response is amplified and is registered on the meter M.

Most modern general-purpose ultraviolet/visible spectrophotometers are double beam instruments which cover the range between 200 and 800 nm by a continuous automatic scanning process producing the spectrum as a pen trace calibrated chart paper.
In these instruments, the monochromated beam of radiation, from tungsten and deuterium lamp sources, is divided into two identical beams, one of which passes through the reference cell and the other through the sample cell. The signal for the absorption of the contents of the reference cell is automatically subtracted from that from the sample cell giving a net signal corresponding to the absorption for the components in the sample solution.

The microprocessor which is used to operate such an instrument will automatically correct the dark current of its photocell, i.e., the small current which passes even when the cell is not exposed to radiation.

Diffraction gratings can give raise the spectra of different orders, some of which may overlap the main or first order beam, and the effect of these can be overcome by suitable filters correctly cited within the instrument. Although the interior of the monochromator is blackened, some stray light arising from reflection with the monochromator may pass through the exit slit, and when the photo detector is small, the stray light, which can contain wave length which are not absorbed by the solution under test, may well account for a significant proportion of the reading. When this happens, a calibration plot departs from the expected straight line, and with increasing absorbance of the solution, becomes curved towards the concentration axis. This complicates quantitative determinations and every effort is therefore made to reduce the amount of stray light. By the inclusion of an additional monochromator, this could be achieved. The source of radiation in UV-Visible spectrophotometer is a tungsten, hydrogen or deuterium lamp. A source of radiation must be provided with each spectral region having its own requirements. All spectrophotometers include some way to discriminable between different radiation frequencies either through use of filters, prisms, or gratings. The polychromatic radiation is separated into its
component wavelength using monochromators which consist of a prism and a plane grating. The sample absorbs a portion of the incident radiation and the remainder is transmitted on to a detector where it is changed into an electrical signal and displayed, usually after amplification, on a meter, chart recorder, or some type of readout device.

Automatic instruments gradually and continuously change the frequency or wavelength. The spectrum of a compound represents a group of either wavelength or frequency, continuously changing over a small portion of the electromagnetic spectrum versus either percent transmission (％T) or absorbance (A).

UV-Visible transmittance spectra of the grown crystals were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range 200-1100 nm covering the near, visible, near infrared region to find the transmission range to know the suitability for optical applications.

2.4.5 Experimental method for Dielectric Measurements

Dielectric materials find extensive use in the electrical industries for insulation purposes and as capacitors. The most commonly measured small signal electrical property is the dielectric permittivity \( \varepsilon_r \), also often referred as the dielectric constant. The dielectric constant in polar materials is rarely a constant, but varies with the applied field, stress, temperature and other parameters. When a dielectric material is subjected to an electric field, the net polarization loss may be obtained from the measurements are particularly straightforward with impedance bridge, which separates the conductance of the crystals. Unpoled crystals have been used for the measurement and this is mainly used for the identification of phase transition and the recording of transition temperature. Any strain or inhomogenetics in the crystal tend
to broaden the phase transition so that there is no apparent discontinuity in dielectric permittivity.

When an insulating solid (a dielectric) is placed in an external electric field, electrons of the ions are displaced slightly with respect to the nuclei and thereby induced dipole moments result and it causes the electronic polarization. When atoms of different types form molecules, they will normally not share their electrons symmetrically and the electron clouds will be displaced eccentrically towards the stronger binding ions. Thus the ions acquire charges of opposite polarity and an external field acting on these net charges will tend to change the equilibrium positions of the ions themselves. By this displacement of charged ions or groups of ions with respect to each other, a second type of polarization viz. ionic polarization of the dielectric is created. The asymmetric charge distribution between the unlike partners of molecule gives rise, in addition, to permanent dipole moments which exists even in the absence of an external electric field. Such moments experience a torque in an applied field that tends to orient them in the direction of the field. Consequently, an orientational (dipolar) polarization can arise. These three mechanisms of polarization are due to charges locally bound in atoms, molecules or in the structure of solids [115-116]. Additionally to all these, there usually exist charge carriers that can migrate for some distance through the dielectric. When such carriers are impeded in their motion, space charges and macroscopic field distribution result. Such a distortion appears as an increase in the capacitance of the sample. Thus a fourth type of polarization called the space charge polarization comes into play. The total polarization is a sum of four polarizations if they act in a dielectric independently.

When a dielectric is placed in an alternating field, the four types of polarizations set up in the material and the dielectric constant is a consequence of
them. There will be a temporal phase shift found to occur between the driving field and the resulting polarization and loss current component appears. It gives the dielectric loss of the sample. The amount of power losses in a dielectric material under the action of the voltage applied to it is commonly known as dielectric losses, which usually mean the losses precisely under an alternating voltage. The dielectric loss angle (loss factor) is an important parameter both for the dielectric material and an insulated portion. A phase lag between the applied field and the displacement is produced when an alternating field is applied to a dielectric. So, the dielectric constant is described as a complex quantity,

\[ \varepsilon = \varepsilon' - i\varepsilon'' \]

and \( \varepsilon'' / \varepsilon' = \tan \delta \)

where \( \tan \delta \) is called the dielectric loss factor.

The dielectric constant and dielectric loss are the basic electrical properties of solids and dielectric constant and loss as a function of frequency and temperature is of great interest both from theoretical point of view and from the Applied Physics. Dielectric constant can be measured by determining the change in the capacitance of specially designed condenser when the dielectric material is inserted between the plates of that condenser. Practically, the presence of a dielectric material between the plates of a condenser enhances the capacitance. This enhancement of capacitance provides the basic experimental method for the measurement of dielectric constant. Various polarization mechanisms in solids such as electronic, ionic, orientational and space charge polarizations can be understood very easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids.

The dielectric constant is of great interest and is related to the symmetry and structure of crystals, the co-ordination number and the polarizabilities.
Combined with other quantities like the refractive index and the absorption frequency, it throws light on the bonding in crystals. The dielectric constant provides information about certain defects in the crystal, particularly in the case of doped and mixed crystals.

The capacitance and dielectric loss factor (tan δ) measurements were carried out using the parallel plate capacitor method at various temperatures ranging from 30 to 70 °C using an Agilent 4284A LCR meter at different frequencies ranging from $10^2$ to $10^6$ Hz. The sample cleaved perpendicular to the axis (b-axis) was used. Opposite faces of the sample crystals were coated with good quality silver paste to obtain a good conductive surface layer. The samples were annealed before making observations in the sample holder assembly at 60 °C for about 30 minutes to remove moisture content if present. The dimensions of the crystals were measured using a travelling microscope (LC =0.001 cm). Air capacitance ($C_{\text{air}}$) was also measured. Since the variation of air capacitance with temperature was found to be negligible, air capacitance was measured only at room temperature. The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = \frac{C}{C_0}$$

Where $C$ is the capacitance of the crystal and $C_0$ 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,

$$\varepsilon_r = \left\{ \frac{C_{\text{cryst}} - C_{\text{air}} \left( 1 - A_{\text{cryst}}/A_{\text{air}} \right)}{C_{\text{air}}} \right\} \left( \frac{A_{\text{air}}}{A_{\text{cryst}}} \right)$$
where \( C_{\text{crys}} \) is the capacitance with crystal (including air), \( C_{\text{air}} \) is the capacitance of air, \( A_{\text{crys}} \) is the area of the crystal touching the electrode and \( A_{\text{air}} \) is the area of the electrode [117,118].

The measurement of dielectric constant has its own utility. It provides information about certain defects in the crystal. Particularly in the case of doped (impurity added) and mixed crystals the measurements yield interesting information about relaxation effects. Several methods are in use for the measurement of dielectric constant and loss. The particular method adopted is determined by the nature of the specimen and the frequency within which the measurement is done.

2.4.6 TG/DTA and DSC techniques

Thermal analysis is useful in both quantitative and qualitative analyses. Samples may be identified and characterized by qualitative investigations of their thermal behaviour. Information concerning the detailed structure and composition of different phases of a given sample is obtained from the analysis of thermal data [119,120].

Thermogravimetry (TG) or Thermogravimetric Analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. For example, TG can record directly the loss in weight as a function of temperature or time (when operating under isothermal conditions) for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. TG data are useful in characterizing materials as well as in investigating the thermodynamics and kinetics of the reaction and transitions that result from the application of heat to these materials [121, 122]. The usual temperature range for TG study is from ambient to 1200 °C in either inert or reactive atmospheres.
The instrument provides a quantitative measurement of any weight changes associated with thermally induced transition. This is a technique whereby the weight of a substance on an environment is recorded when the sample is heated or cooled at a controlled rate and the change of weight (loss or gain) is measured as a function of temperature or time. The major parts of TGA are high sensitive balance, micro furnace, furnace temperature programmer or controller and recorder or computer with plotter.

The high sensitive balance is used to measure the weight accurately and the micro furnace is used to change the temperature in a controlled fashion at a specified rate. The balance chamber consists of a servo-controlled balance arm. At one end of the balance arm, a tare weight is suspended and at the other end, sample pans hung down by means of a nichrome wire through a quartz link. This pan extends down to the micro furnace chamber through a metallic anti-static tube. This uses a servo operated balance system in which the electrical signal from an optical null detector is applied directly to control the current in a torque motor. The weight loss as a function of temperature is measured by the principle of null deflection method using alight source and photosensitive diode. Here, the torque enacted by servo motor to restore the balance arm to its null position, is directly proportional to the weight of the sample which has been already calibrated. The model of this instrument is shown in figure 2.5.
Figure 2.5: Instrumentation for Thermo Gravimetric (TG) Analysis

In Differential Thermal Analysis (DTA), the difference in temperature between the sample and a thermally inert reference material is measured as a function of temperature (usually the sample temperature). Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of the differential temperature, $\Delta T$, versus the programmed temperature, $T$, indicates the transition temperature and whether the transition is exothermic or endothermic. DTA and TG analyses are often run simultaneously on a single sample [119, 123].

The difference in temperature between the sample and the reference is continuously measured form the thermocouple connected in series position. It is amplified ($\approx 1000$ times) by a high gain, low noise direct coupled amplifier for microlevel signals and is recorded in the y-axis. The temperature of the furnace is
measured using another thermocouple and is recorded in the X axis. This instrument is used in the temperature range from -190 °C to 1600 °C and the sample size changes from 0.1 to 100 mg.

Differential Scanning Calorimetry instrument uses a constantan (Cu-Ni) disc as the primary means of transferring heat to the sample and the reference position and also one element of a temperature sensing thermo-electric junction. The sample material and the reference material are placed in separate pans that sit on the raised platforms on the disc. The heat transferred to the sample and the reference pan is monitored by the chromel constantan thermocouples formed by the junction of the constantan disc and chromel- wafer covering the underside of each platform. Chromal- Aluminel thermocouple is used to monitor the sample temperature. Constant calorimetric sensitivity is maintained by computer software, which linearizes the cell- calibration co-efficient. This DSC provides maximum calorimetric accuracy from 170 to 750 °C. The sample sizes range from 0.1 mg to 100mg.

During the programmed heating, power is supplied to both micro furnaces through a control circuit in order to change their mean temperature in accordance with the present heating rate. If there is ideal thermal symmetry, the temperature of both the furnaces is always the same. Whenever asymmetry occurs, for example as a result of reaction in the sample, a temperature difference results between the furnaces and the system adjusts the power supplied to both the furnaces in such a way that the temperature difference maintained is zero. The two control circuits employed are:

(i) Differential temperature control
(ii) Average temperature control

In the differential temperature control circuit signals representing the temperatures of the sample and reference pan are compared and are fed to the
amplifier. The amplifier output adjusts the power input to the two furnaces in such a way that their temperatures are kept identical. In the absence of any reaction taking place in the sample, the differential power input to the sample and reference furnaces is almost zero. When a reaction takes place in the sample, a differential power input is fed to the furnaces. Depending upon whether the reaction is endothermic or exothermic, the differential power input increases the power in one furnace while decreasing it to other furnace. This differential power, usually in mw is plotted as a function of temperature.

In the present work DTA and TG studies on the grown crystals have been carried out using SDTQ 600 V 8.2 (Universal V4.2 ETA) thermal analyzer in the temperature range 35 – 750 °C. Differential scanning calorimetric (DSC) study was performed using NETZSCH DSC 204 in the temperature range 50 - 950 °C at a heating rate of 10 °C/min in the nitrogen atmosphere and 15 mg of sample was placed in the alumina crucible

2.4.7 SHG studies

Nonlinear optical organic materials will be the key elements for future photonic technologies. Photonic technologies are analogous to the field of electronics. It is appropriate to mention that current research activities are aimed for the photonics versus electronics theme. Photonics technologies are based on the fact that photons are capable of processing information with the speed of light. In electronic devices, electrons are the key elements performing multifunction, where as in photonic devices photons will perform the same functions of a much faster speed and in a cleaner and easier way.

Lasers are sources of electromagnetic radiation, which are characteristically different from an ordinary light source. Laser light beam posses coherence,
collimation and a narrow spectral width and can focus at a possible minimum spot size. The combination of these unique features of laser radiation makes lasers highly desirable for a wide range of applications in optics. The importance of lasers was realized long ago with the invention of optical fiber systems widely used in telecommunication. It is now almost three decades since the report of the first nonlinear optical phenomena in a quartz crystal. In the beginning, studies were concentrated mainly on inorganic crystals and semiconductors.

An important development in nonlinear optical material occurred when researchers reported a strong second harmonic generation (SHG) in organic molecules having electron donor and acceptor groups connected with a benzene ring. This discovery led to an entirely new concept of molecular engineering to synthesize new organic materials for the SHG studies.

Powder second harmonic generation test offers the possibility of assessing the nonlinearity of the new materials. Kurtz et al proposed a powder SHG method for comprehensive analysis of the second order nonlinearity [124]. This is a useful method for characterizing the materials before going through the long and tedious process of growing large optical quality crystals. Using this technique, very large number of compounds is studied for SHG.

The experimental setup used for this method is shown in figure 2.6. It consists of a Q-switched laser and the sample is illuminated using UV-visible cut filter. The second harmonic generation is detected by a photomultiplier tube and displayed on an oscilloscope. The system permits the insertion of narrow band pass filters at its second harmonic wavelength between the short filter and photomultiplier to eliminate spurious signals. In order to obtain the efficiency of a second harmonic collection at the detector, a parabolic reflector is placed directly in front of the sample with a small
access hole for the laser beam. Samples were prepared and mounted using several techniques. For qualitative results, a thin layer of ungraded powder was placed on a microscope slide and held with transparent tape. For quantitative work, powder was graded by use of standard sieves for desired range of particle size and loaded into a fused silica cell of known thickness.

This technique enables us to classify materials into three categories.

i) Materials in which the phase matchable component is larger than the other component: noncentro symmetric crystal structure.

ii) Materials in which the non phase matchable component is larger than the other component: non-centrosymmetric crystal structure.

iii) SHG inactive: centrosymmetric crystal structure.

Figure 2.6: Kurtz powder experimental setup
It is easy to classify a material in class (iii) since those materials do not exhibit any SHG in powder form. Furthermore, it is possible to determine whether a material belongs to class (i) or class (ii) by observing the powder SHG intensity as a function of particle size. The SHG intensity of a non-phase matchable material is described by

\[
I(2\omega) \propto d^2 \frac{l_c^2 I(\omega)}{2< r >} \quad (< r > >> l_c, \text{non-phase matchable})
\]

\[
I(2\omega) \propto d^2 / I(\omega) \quad (< r > >> l_c, \text{phase matchable})
\]

![Figure 2.7: Phase and non-phase matchable diagram](image)

The SHG intensity of non-phase matchable material decreases with the increase of average particle size < r > when < r > is larger than coherence length \( l_c \) (figure 2.7). In the case of phase matchable material, the SHG intensity does not decrease when < r > is larger than \( l_c \). Therefore, this difference can evaluate whether the material is phase matchable or not in bulk crystal.

The non-zero measured powder SHG signal is consistent with the SHG activity predicted from the non-centrosymmetric crystal structure. The relative efficiency of the grown crystals with that of KDP has been measured. This work was carried out at Crescent Engineering College, Chennai.