CHAPTER II

EXPERIMENTAL DETAILS FOR DIFFERENT GROWTH METHODS AND CHARACTERIZATION TECHNIQUES

2.1 METHODS OF CRYSTAL GROWTH

An efficient process is the one, which produces crystals adequate for their use at minimum cost. Better choice of the growth method is essential because it suggests the possible impurity and other defect concentrations. Choosing the best method to grow a given material depends on material characteristics.

In contrast to the historical work, it seems that the essential task for the crystal growers at present is to gain basic knowledge about the correlation of crystal properties and the growth conditions defined to be special parameters. The basic understanding of the deposition of atoms onto a suitable substrate surface – crystal growth – and the generation of faults in the atomic structure during growth and subsequent cooling to room temperature – crystal defect structure, are the input for the design of crystal growth systems and control of growth parameters.

Though the fundamentals are relatively simple, the complexities of the interactions involved and the individualities of different materials, system and growth process have ensured that experimentally verifiable predictions from scientific principles have met with limited success – good crystal growth remains an art. As a result, crystal growth had been the image of alchemy. This is clearly expressed by the title of one of the first text books on crystal growth ‘The Art (!) and Science of Growing crystal’ (Gilman 1963).
The recent advances which include reduction of growth temperature, the reduction or elimination of reactant transport variables and the use of better controlled energy sources to promote specific reactions, coupled with increased development and application of in-situ diagnostic techniques to monitor and perhaps the ultimate control lead to simplified growth systems and the crystal growth process has transferred the field from an art to science, technique and to technology.

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

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

Based on the phase transformation process, crystal growth techniques are classified as solid growth, melt growth, solution growth and vapour growth (Pamplin 1979).

The above methods have been discussed in detail by several authors (Brice 1986; Pamplin 1980; Chernov 1984). The different techniques of each category are found in reviews and books by Faktor and Garret (1974) on vapour growth, Brice (1973) on melt, Henisch (1988) on gel growth, Buckley (1951) on solution growth and Elwell and Scheel (1975) on high temperature solution growth.
2.1.1 Solid Growth Method

The conversion of a polycrystalline piece of material into single crystal by causing the grain boundaries to be swept through and pushed out of the crystal takes place in the solid growth of crystals (Mullin 1972). This is very slow at ordinary temperatures and is only rarely used.

2.1.2 Liquid Growth Method

The crystal growth from liquid can be classified into six categories.

(i) Melt growth
(ii) Hydrothermal growth
(iii) Gel growth
(iv) Electrocrystallization
(v) High Temperature solution growth
(vi) Low temperature solution growth

2.1.2.1 Melt Growth

All materials can be grown in single crystal form from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature. Depending on the thermal characteristics, the following techniques are employed.

1. Bridgman technique
2. Czochralski technique
3. Kyropoulos technique
4. Zone melting technique
5. Verneuil technique
In Bridgman technique the material is melted in a vertical cylindrical container, tapered conically with a point bottom. The container is lowered slowly from the hot zone of the furnace into the cold zone. The rates of movement for such processes range from about 1 – 30 mm/hr. Crystallization begins at the tip and continues its growth from the first formed nucleus. This technique cannot be used for materials, which decompose before melting. This technique is best suited for materials with low melting point.

In Czochralski method, the material to be grown is melted by induction or resistance heating under a controlled atmosphere in a suitable non-reacting container. By controlling the furnace temperature, the material is melted. A seed crystal is lowered to touch the molten charge. When the temperature of the seed is maintained very low compared to the temperature of the melt, by suitable water cooling arrangement, the molten charge in contact with the seed will solidify on the seed. Then the seed is pulled with simultaneous rotation of the seed rod and the crucible in order to grow perfect single crystals. Liquid Encapsulated Czochralski abbreviated as LEC technique makes it possible to grow single crystals of materials, which consists of components that produce high vapour pressure at the melting point. This refined method of Czochralski technique is widely adopted to grow group III-V compound semiconductors.

In Kyropoulos technique, the crystal grown is of larger diameter. As in the Czochralski method, here also the seed is brought into contact with the melt and is not raised much during the growth, i.e. part of the seed is allowed to melt and a short narrow neck is grown. After this, the vertical motion of the seed is stopped and growth proceeds by decreasing the power into the melt. The major use of this method is growth of alkali halides to make optical components.
In zone melting technique, the feed material is taken in the form of sintered rod and the seed is attached to one end. A small molten zone is maintained by surface tension between the seed and the feed. The zone is slowly moved towards the feed. Single crystal is obtained over the seed. This method is applied to materials having large surface tension. The main reasons for the impact of zone refining process to modern electronic industry are the simplicity of the process, the capability to produce a variety of organic and inorganic materials of extreme high purity, and to produce dislocation free crystal with a low defect density. In the case of vertical normal freezing, the solid-melt interface is moved upwards from the cold bottom to the hot top so as to get better quality crystals. The method is more applicable in growing single crystals of materials with volatile constituents like GaAs.

In Verneuil technique, a fine dry powder of size 1-20 microns of the material to be grown is shaken through the wire mesh and allowed to fall through the oxy-hydrogen flame. The powder melts and a film of liquid is formed on the top of the seed crystal. This freezes progressively as the seed crystal is slowly lowered. The art of the method is to balance the rate of charge feed and the rate of lowering of the seed to maintain a constant growth rate and diameter. By this method ruby crystals are grown up to 90 mm in diameter for use in jeweled bearings and lasers. This technique is widely used for the growth of synthetic gems and variety of high melting oxides.

2.1.2.2 Hydrothermal Growth

Hydrothermal growth implies conditions of high pressure as well as high temperature. Substances like calcite, quartz are considered to be insoluble in water but at high temperature and pressure, these substances are soluble. This method of crystal growth at high temperature and pressure is known as hydrothermal method.
Temperatures are typically in the range of 400 °C to 600 °C and the pressure involved is large (hundreds or thousands of atmospheres).

Growth is usually carried out in steel autoclaves with gold or silver linings. Depending on the pressure the autoclaves are grouped into low, medium and high-pressure autoclaves. The concentration gradient required to produce growth is provided by a temperature difference between the nutrient and growth areas. The requirement of high pressure presents practical difficulties. Only a few crystals of good quality and large dimensions are grown by this technique. Quartz is the outstanding example of industrial hydrothermal crystallization. One serious disadvantage of this technique is the frequent incorporation of OH ions into the crystal, which makes them unsuitable for many applications.

2.1.2.3 Gel Growth

It is an alternative technique for growing single crystals of substances having poor solubility and unstable thermal behavior. Gel is a two-component system of a semisolid, rich in liquid and inert in nature. The material, which decomposes before melting, can be grown in this medium by counter diffusing two suitable reactants. Crystals with dimensions of several mm can be grown in a period of 3 to 4 weeks. The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place at room temperature.

2.1.2.4 Electrocrystallization

Electrocrystallization is the basis for important fields such as corrosion, energy storage and generation, electrodeposition, electronics material development, electrorefining and electrowinning etc. Crystallization without chemical
transformation or charge transfer is the simplest case. In certain instances, the
crystallization is determined by a chemical transformation occurring prior to or
simultaneously with the crystallization process. The role played by the chemical
reaction is to supply the material, which crystallizes. Electrocrystallization is the
process, which leads to the formation of a new phase at the electrode/electrolyte
interface (Santhana Raghavan and Ramasamy 2000).

2.1.2.5 High Temperature Solution Growth

In high-temperature solutions, 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 to a cooler region. This method is widely used
for the growth of oxide crystals. The procedure is to heat the container having flux
and the solute to a temperature so that all the solute materials dissolve. This
temperature is maintained for a ‘soak’ period of several hours and then the
temperature is lowered very slowly.

The high temperature crystal growth can be divided into two major categories:

1. Growth from single component system.
2. Growth from multi component system.

2.1.2.6 Low Temperature Solution Growth

Growth of crystals from aqueous solution is one of the ancient methods of
crystal growth. The method of crystal growth from low temperature aqueous solutions
is extremely popular in the production of many technologically important crystals. It
is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures (Pamplin 1979) and undergo phase transformations below melting point (Hooper et al 1980). The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. A power failure or a contaminated batch of raw material can destroy months of work.

Materials having moderate to high solubility in temperature range, ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method (James and Kell 1975). 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 (Chernov 1984). The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straightforward equipment design which gives a good degree of control of accuracy of ±0.01 °C. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique. The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance under different growth conditions (Hooper et al 1979). The proximity to
ambient temperature reduces the possibility of major thermal shock to the crystal both
during growth and removal from the apparatus.

The main disadvantages of the low temperature solution growth are the slow
growth rate in many cases and the ease of solvent inclusion into the growing crystal.
Under the controlled conditions of growth, the solvent inclusion can be minimized
and the high quality of the grown crystal can compensate the disadvantage of much
longer growth periods. After many modifications and refinements, the process of
solution growth now yields good quality crystals for a variety of applications. Growth
of crystals from solution at room temperature has many advantages over other growth
methods though the rate of crystallization is slow. Since growth is carried out at room
temperature, the structural imperfections in solution grown crystals are relatively low
(Brice 1973). Low temperature solution growth is a well-established technique due to
its versatility and simplicity. It is possible to grow large crystals of high perfections as
the growth occurs close to equilibrium conditions (McArdle and Sherwood 1987).

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. Three principal methods used to produce the required supersaturation
are

(i) Slow Cooling Technique

(ii) Slow Evaporation Method

(iii) Temperature Gradient Method

(i) Slow Cooling Method

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. The temperature at which such crystallization can begin is usually within the range 45 °C - 75 °C and the lower limit of cooling is the room temperature.

(ii) Slow Evaporation Method

This method is similar to the slow cooling method in view of the apparatus requirements. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.005°C and rates of evaporation of a few ml/hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. 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.

(iii) 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. The main advantages of this method are

(a) Crystal grows at a fixed temperature
(b) This method is insensitive to changes in temperature provided, both the source and the growing crystal undergo the same change.

(c) Economy of solvent and solute.

On the other hand, 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), Potassium dihydrogen phosphate (KDP) and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method. The advantages of low temperature solution growth techniques are as follows:

(i) Eliminates the problem of thermal decomposition
(ii) Selection of growth temperature avoids polymorphic phase transitions
(iii) Morphology could be changed by changing the solvent
(iv) Simple growth apparatus
(v) Growth of strain and dislocation free crystals

In the present study slow evaporation method one of the low temperature solution growth methods is used for the growth of single crystals.

2.1.3 Growth from Vapour

The growth of single crystal material from the vapour phase is probably the most versatile of all crystal growth processes. Crystals of high purity can be grown from vapour phase by sublimation, condensation and sputtering of elemental materials. This method is used to obtain single crystals of high melting point materials. Molecular beam techniques have also been applied recently to crystal
growth problems. The most frequently used method for the growth of bulk crystals utilizes chemical transport reaction in which a reversible reaction is used to transport the source material as a volatile species into the crystallization region. Finding a suitable transporting agent is a formidable problem in this technique. It is rarely possible to grow large crystals because of multi-nucleation.

The commercial importance of vapour growth is the production of thin layers by chemical vapour deposition (CVD), where usually irreversible reactions like decomposition of silicon halides or of organic compounds are used to deposit materials epitaxially on a substrate. Doping can be achieved by introducing volatile compounds of dopant elements into the reaction region. The thickness of the doped layer can be controlled.

2.2 SOLVENT SELECTION

Solution is a homogeneous mixer of a solute in a solvent. Solute is the component present in smaller quantity. For a given solute, there may be different solvents. Apart from high purity starting materials, solution growth requires a good solvent.

The solvent must be chosen taking into account the following factors

(i) Moderate solubility for the given solute
(ii) Must not react with the solute
(iii) Good solubility gradient
(iv) Low viscosity
(v) Low volatility
(vi) Low corrosion and
(vii) Cost effective
If the solubility is too high, it is difficult to grow bulk single crystals and too small solubility restricts the size and growth rate of the crystals. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting growth process. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution. Growth of crystal from solution is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transport of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable (Ohara and Reid 1973).

2.3 CHARACTERIZATION TECHNIQUES

In order to study the properties of the grown crystals, it is necessary to involve the crystals for various characterizations. The usage of crystals depends on the properties and so the characterization is an important part in crystal growth. The instrumentation details and operating procedure of important characterization techniques used in the present work are given in the following sections.

2.3.1 X-ray Diffraction Analysis

X-rays are electromagnetic waves whose wavelengths range from 0.1 Å 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. 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. Both Single crystal XRD and Powder XRD methods are used to identify and characterize unknown crystalline materials. Powders of crystalline materials diffract X-rays. The powdered sample of the grown crystal is ground using an agate mortar and it is spread in a sample holder. It is allowed to rotate with respect to the impinging X-ray beam. The diffracted X-ray photons are recorded by a scintillation counter, which is connected to an electronic counting system and it is synchronized with a strip chart recorder, a rate meter, a timer, a goniometer and a pulse height analyzer. These are often connected to a digital printer to get the printed diffraction pattern. Powder X-ray diffraction provides less information than single crystal X-ray 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. Both the methods of XRD can be carried out for the grown crystals to check the correctness of the results of the crystalline data (Stout and Jensen 1968; Woolfson 1970).
In powder XRD 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’s diffraction condition $2d \sin \theta = n\lambda$ for the lattice planes is satisfied. For the diffracted beam from a large number of crystallites which are randomly oriented and considering the diffraction from the planes with the same interplanar spacing as the first one, the locus of the diffracted beam 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 beam from other sets of lattice 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 remains 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 beam forms continuous cones.

The experimental arrangement of powder XRD method is shown in Figure 2.1. The source of X-rays (A) is 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, mixed with 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 powdered specimen 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.
Figure 2.1: The experimental arrangement of powder X-ray diffractometer

The single crystal X-ray diffractometers (typical diffractometer is in Figure 2.2) are used for measuring X-ray diffraction data like unit cell parameters, space groups and molecular structure of crystalline solids. The facility can also be utilized for Miller indexing of different faces of crystals. Unit cell parameters are dimensions of the basic molecular brick with which the crystal is built. Space group tells us the symmetry with which molecules are arranged within the unit cell. Coordinates of individual atoms of the molecules which can be obtained from diffraction studies constitutes the structure. All the geometrical features of molecules (bond distances, bond angles, torsion angles about bonds, dihedral angle between planes etc.) may be obtained from coordinates (Buerger 1958; Chan 1961).
In most cases, the properties of a single crystal are not only a function of the type and the quality of the crystals, but strongly dependent on its orientation. The determination of single crystal orientation thus represents an essential step towards the successful use of single crystals in technological applications.

In the present work, single crystal XRD data for the grown crystals were collected using Bruker-Nonius MACH3/CAD4 diffractometer with MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å) at School of Physics, Madurai Kamaraj University, Madurai. Powder XRD patterns of the grown crystals were recorded at Regional Research Laboratory(RRL), Tiruvananthapuram using a powder X-ray diffractometer (Copper target, Nickel filter, 1.54056 Å, 35 KV, 10 mA, Model: PANalytical XPERT – PRO).

2.3.2 Fourier Transform Infrared (FTIR) Spectroscopic Analysis

Infrared spectroscopy is the study of the interaction of infrared light with matter. The fundamental measurement obtained in infrared spectroscopy is an infrared
spectrum, which is a plot of measured intensity versus wavelength (or wave number) of light. An instrument used to obtain an infrared spectrum is called an infrared spectrometer.

There are several kinds of spectrometers in the world used to obtain infrared spectra. The most relevant type of spectrometer is called a Fourier Transform Infrared Spectrometer (FTIR). FTIR technique is most useful for identifying functional groups of organic and inorganic compounds. It can be applied for the analysis of solids, liquids and gases. The term Fourier Transform Infrared (FTIR) spectroscopy refers to fairly recent development in which the data is collected and converted from an interference pattern to a spectrum. 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 causes 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.

FTIR spectroscopic technique is based on the principle of Michelson 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. 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 fingerprint. While organic compounds have detailed spectra, inorganic
compounds are usually much simpler. Samples of FTIR can be prepared in a number of ways. For liquid samples, the easier way is to place one drop of sample between two plates of sodium chloride (salt), which is transparent to infrared light. The drop forms a thin film between the plates.

Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively solid samples can be dissolved in a solvent such as methylene chloride and the solution is placed on a single plate. The solvent is then evaporated off leaving a thin film of the original material on the plate. This is called a cast film and is frequently used for polymer identification (Griffiths and De Hoseth 1986; Socrates 1980; Albert et al 1973; Nagamoto 1978; Aruldhas 2000).

In the present work, the FTIR spectra of all samples were recorded in KBr matrix using Perkin Elmer Fourier Transform Infrared spectrometer (Model: Spectrum RXI shown in Figure 2.3) at ACIC, St. Joseph’s College (Autonomous), Trichy. The FTIR spectra of the grown crystals were recorded in the wave number range 4500 cm\(^{-1}\) to 400 cm\(^{-1}\).

![Figure 2.3: Perkin Elmer Fourier Transform Infrared spectrometer](image)
2.3.3 UV-Visible Transmission Spectral Analysis

The wavelength of visible light ranges from 400 nm - 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. An UV-Visible spectrophotometer, for example, allows light of a given frequency to pass through a sample and detects the amount of transmitted light. The instrument compares the intensity of the transmitted light with that of the incident light. 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 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 consists 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 percentage of transmission (%T) or absorbance (%A) (Jag Mohan 2001; Jaffe and Orchin 1962; Rao 1961). UV-Visible transmittance spectra of the grown crystals were recorded using a Perkin Elmer Lamda 35 spectrometer (Figure 2.4) in the range 190 nm - 1100 nm covering the near UV, visible, near infrared region to find the transmission range for optical applications.
2.3.4 Density Measurements

The floatation method was employed for the precise determination of density and this method is sensitive to point defects and insensitive to dislocations of crystals. Bromoform (density: 2.89 g/cc) and xylene (density: 0.99 g/cc) were used for the experiment. After mixing the liquids bromoform and xylene in suitable proportion in a specific gravity bottle, small piece of crystal was immersed in the mixture of liquids. When the sample attains a state of mechanical equilibrium, the density of the crystal would be equal to the density of mixture of liquids. The density was calculated using the relation

\[ \rho = \frac{(W_3 - W_1)}{(W_2 - W_1)} \]

Where \( W_1 \) is the weight of the empty specific gravity bottle, \( W_2 \) is the weight of the specific gravity bottle with full of water and \( W_3 \) is the weight of specific gravity bottle with full of mixture of bromoform and xylene (Krishnan et al 2008b).

The density is also confirmed from the crystallographic data using the relation

\[ \rho = \frac{(M \cdot Z)}{(N \cdot V)} \]

where \( M \) is the molecular weight of the material used, \( Z \) is the
number of molecules per unit cell, $N$ is Avagadro's number and $V$ is the volume of the unit cell (John et al 2007; Ramachandran et al 2004; Ramachandran et al 2005).

2.3.5 Second Harmonic Generation (SHG) Test

Kurtz-Perry technique remains an extremely valuable tool for initial screening of NLO materials. A quantitative measurement of the conversion efficiency of the sample can be determined by the modified version of powder technique developed by Kurtz and Perry (Kurtz and Perry 1968). The experimental set up is shown in Figure 2.5. The crystal is ground into powder and it is packed densely between two transparent glass slides. An Nd:YAG (DCR 11) laser is used as the light source. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse in depth with 10 Hz pulse rate is made to fall normally on the sample cell. The power of the incident beam is measured using a power meter and it is 0.68 J/pulse. The transmitted fundamental wave is passed over a monochromator (Czerny tuney monochromator), which separates 532 nm (SHG signal) from 1064 nm and absorbed by CuSO$_4$ solution.

The filter $F_1$ removes the 1064 nm light. $F_2$ is a BG-38 filter, which also removes the residual 1064 nm light. $F_3$ is an interference filter with bandwidth of 4 nm and central wavelength 532 nm. The green light is detected by a photo multiplier tube (Hamatsu RC 109, a visible PMT) and displayed on a storage oscilloscope (TDS 3052 B 500MHz phosphor digital oscilloscope). KDP crystal is powdered to identical size and is used as the reference material for the SHG measurement.
Figure 2.5: Experimental arrangement for SHG measurement

The non-zero measured power 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 can be measured.

2.3.6 Microhardness Measurements

Hardness of a material is the resistance offered to indentation by a much harder body. It may be termed as a measure of the resistance against lattice destruction or the resistance offered to permanent deformation or damage (Stillwell 1938). It is the resistance to penetration to a metallurgist, resistance to wear to a lubrication engineer, resistance to scratching to a mineralogist and resistance to cutting to a machinist. All these are related to the plastic flow stress of the material. The hardness properties are basically related to the crystal structure of the material. Microhardness study of the crystals brings out an understanding of the plasticity of the crystal (Desai and Rai 1983).

Hardness is a technique, in which a crystal is subjected to a relatively high pressure within a localized area. By suitable choice of indenter material and relatively simple equipment construction, hardness tests can be easily carried out on all crystalline materials under various conditions of temperature and pressure.
Deformation is local, so that a number of trials can be made on a single specimen of small dimensions and can be reproduced by maintaining the specimen indenter orientation relationship. Specimen of flat relatively smooth surface is required.

2.3.6.1 Methods of Hardness Test

Hardness measurement can be carried out by various methods. They are classified as follows

- Static indentation test
- Dynamic indentation test
- Scratch test
- Rebound test
- Abrasion test

The most popular and simplest form is the static indentation test wherein the specific geometry is pressed into the surface of a test specimen under known load. The indenter may be ball or diamond cone or diamond pyramid. Upon removal of the indenter, a permanent impression is retained in the specimen. The hardness is calculated from the area or depth of indentation produced. The variables are the type of indenter or load. The indenter is made up of a very hard material to prevent its deformation by the test piece so that it can cover materials over a wide range of hardness. For this reason either a hardened steel sphere or a diamond pyramid or cone is employed. A pyramid also has advantage that geometrically similar impressions are obtained at different loads. So naturally a pyramid indenter is preferred.

In this static indentation test the indenter is pressed perpendicularly on the surface of the sample by means of an applied load. Then by measuring the cross sectional area or the depth of the indentation and knowing the applied load
empirical hardness number may be calculated. This procedure is followed by Brinell, Meyer, Knoop and Rockwell test (Wyatt and Hughes 1974; Tabor 1951; Neil 1967).

In the dynamic indentation test, a ball or a cone (or a number of small spheres) is allowed to fall from a definite height and the hardness number is obtained from the dimensions of the indentation and the energy of impact.

The scratch test can be classified into two types:

- Comparison test is one, in which one material is said to be harder than another if the second material is scratched by the first.

- A scratch test is done with a diamond indenter on the surface at a steady rate and under a definite load. The hardness number is expressed in terms of the width of depth of the groove formed.

In the rebound test an object of standard mass and dimensions is bounced from the test surface and the height of rebound is taken as the measure of hardness. In abrasion test, a specimen is loaded against a rotating disk and the rate of wear is taken as the measure of hardness.

2.3.6.2 Vickers Test

Among the various methods of hardness measurements discussed above, the most common and reliable method is the Vickers hardness test method. In this method, microindentation is made on the surface of a specimen with the help of a diamond indenter (Figure 2.6).
Smith and Sandland (1923) have proposed that a pyramid may be substituted for a ball in order to provide geometrical similitude under different values of load. Vickers pyramid indenter where opposite faces contain an angle \( \alpha = 136^\circ \) is most widely accepted pyramid indenter. A pyramid is suited for hardness tests due to the following two reasons (Balta Calleja et al 1980).

- The contact pressure for a pyramid indenter is independent of indent size.
- Pyramid indenters are less affected by elastic release than other indenters.

The base of the Vickers pyramid is a square and the depth of indentation corresponds to \( 1/7 \)th of the indentation 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 defined as

$$H_v = \frac{2P \sin(\alpha/2)}{d^2} \text{kg/mm}^2 \quad (2.21)$$

Where $\alpha$ is the apex angle of the indenter ($\alpha = 136^\circ$).

The Vickers hardness number is therefore calculated from the relation

$$H_v = 1.8544 \frac{P}{d^2} \text{kg/mm}^2 \quad (2.22)$$

Where $P$ is the applied load in kg and $d$ is the diagonal length of the indentation mark in mm (Mott 1956; www.worldoftest.com/microhardnesstester; Shockley and Read 1950).

Hardness values are measured from the observed size of the impression remaining after a loaded indenter has penetrated and has been removed from the surface. Thus the observed hardness behaviour in the final measurement of the residual impression is the summation of a number of effects involved in the material’s response to the indentation pressure during loading.

The relationship between load($P$) and diagonal length($d$) of indentation is given by $P = ad^n$. This is called Meyer’s law (Meyer 1908). Here $a$ and $n$ are constants for a particular material, $P$ and $d$ are respectively the applied load and average diagonal length of the indentation impression. Plots of $\log(P)$ versus $\log(d)$ are drawn and from the slopes of these plots, the work hardening coefficient ($n$) is determined.
In the present study, the microhardness measurements were made using a Shimadzu microhardness Tester HMV-2 Series (Figure 2.7).

2.3.7 Energy Dispersive Spectrum (EDS) Analysis

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). This technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed.

When the sample is bombarded by the SEM's electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state, and an X-ray is emitted to
balance the energy difference between the two electrons states. The X-ray energy is characteristic of the element from which it was emitted.

The EDS X-ray detector measures the relative abundance of emitted X-rays versus their energy. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sample. Features or phases as small as 1 μm or less can be analyzed.

The sample X-ray energy values from the EDS spectrum are compared with known characteristic X-ray energy values to determine the presence of an element in the sample. Elements with atomic numbers ranging from that of beryllium to uranium can be detected. The minimum detection limits vary from approximately 0.1 to a few atom percent, depending on the element and the sample matrix.

In the present study, EDAX studies were performed using the EDAX detector (model-Thermoelectron Corporation with superdry/II) equipped in Hitachi model S-3000H scanning electron microscope (Figure 2.8).

![Figure 2.8: Scanning Electron Microscope - HITACHI Model S-3000H](image)
2.3.8 Atomic Absorption Spectroscopic Studies

Atomic absorption spectroscopy is the most powerful technique for the quantitative determination of trace metals in liquids. Using this method we can find the total metal content of the sample in the liquid. It can be used to analyze the concentration of different metals in a solution. The absorption of energy by ground state atoms in the gaseous state forms the basis of atomic absorption spectroscopy. Atomic absorption technique is specific because the atoms of a particular element can only absorb radiation of their own characteristic wavelength.

The technique makes use of a flame to atomize the sample, but atomizers such as a graphite furnace are also used. In order to analyze a sample for its atomic constituents, it has to be atomized. The sample should then be illuminated by light. The light transmitted is finally measured by a detector. In order to reduce the effect of emission from the atomizer or the environment, a spectrometer is normally used between the atomizer and the detector.

There are three steps involved to turn a liquid sample into an atomic gas such as (a) dissolvation - the liquid and solid is evaporated and the dry sample remains, (b) Vapourisation – the solid sample vapourises to a gas and (c) Volatilisation – the compounds making up the sample are broken into free samples.

The flame is arranged such that it is laterally 10 cm long and not deep. A beam of light is focussed through this flame at its longest axis onto a detector past the flame. A hollow cathode lamp produces the light that is focused into the flame. Inside the lamp is a cylindrical cathode containing the metal for excitation and an anode. When high voltage is applied across the anode and cathode, the metal atoms in the cathode are excited to produce light with a certain emission spectra. The type of
hollow cathode tube depends on the metal being analyzed. For analyzing the concentration of copper in an ore, a copper cathode tube would be used and likewise for any other metal being analyzed.

The electrons of the atoms in the flame can be promoted to higher orbitals for an instant by absorbing a set of quantity of energy. This amount of energy is specific to a particular electron transition in a particular element. As the quantity of energy put into the flame is known and the quantity remaining at the other side can be measured, it is possible to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured (Michael and Bernhard 1999).

2.3.9 TG/DTA Techniques

Thermal analysis is a branch of materials science where the properties of materials are studied as they change with temperature.

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. The usual temperature range for TG study is
from ambient to 1100 °C in either inert or reactive atmospheres. In TG, the weight of the sample is continuously recorded as the temperature is increased. Samples are placed in a crucible or shallow dish that is positioned in a furnace on a quartz beam attached to an automatic recording balance. Linear heating rates from 5 °C/min. to 10 °C/min. are typical. Computer software allows the computation of weight change which is important in kinetic interpretations of reactions and processes.

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 (Brown 1988; Wendlandt 1974).

In the present work TG and DTA studies on the grown crystals have been carried out using SDT Q600 V 8.3 (Universal V4.7A TA) thermal analyzer (Figure 2.9) in the temperature range 30 °C – 1010 °C.

Figure 2.9: Thermal analyzer Model: SDT Q600 V 8.3 (Universal V4.7A TA)
2.3.10 Dielectric Measurements

Various polarization mechanisms in crystalline solid such as atomic polarization of the lattice, orientational polarization of dipoles, space charge polarization and electronic polarization can be easily understood by studying the dielectric properties as a function of frequency and temperature. The frequency dependence of these properties gives a great insight into the material applications. The dielectric constant determines the share of the electric stress which is absorbed by the material without any dielectric breakdown.

The dielectric loss is a measure of the energy absorbed by a dielectric medium. The capacitance ($C_{\text{cry}}$) and dielectric loss factor ($\tan\delta$) measurements were carried out to an accuracy of $\pm 2\%$ using LCR meter (Agilent 4284A) (shown in Figure 2.10) with four different frequencies, viz. 1 kHz, 10 kHz, 100 kHz, 1MHz at various temperatures ranging from 35 °C – 100 °C in a way similar to that followed by Mahadevan and his co-workers (Goma 2006; Manonmani 2007; Meena 2008). Temperature was controlled to an accuracy of $\pm 1 \degree$C. Air capacitance ($C_{\text{air}}$) was also measured.

![Figure 2.10: LCR meter (Model: Agilent 4284A)](image)
The dielectric constant of the crystal was calculated using the relation

\[ \varepsilon_r = \left[ \frac{C_{\text{crys}}}{C_{\text{air}}} \right] \]

The AC conductivity \( (\sigma_{\text{ac}}) \) was calculated using the relation

\[ \sigma_{\text{ac}} = \varepsilon_0 \varepsilon_r \tan \delta \]

Where \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}) \) and \( \omega \) is the angular frequency.

### 2.3.11 Activation Energy Measurements

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 general relation proposed by Arrhenius for the temperature variation of conductivity is given by

\[ \sigma_{\text{ac}} = \sigma_0 \exp \left( -\frac{E_{\text{ac}}}{kT} \right) \]

Where \( \sigma_0 \) is a constant depending on the material, \( E_{\text{ac}} \) is the activation energy, \( T \) is the absolute temperature and \( k \) is the Boltzmann’s constant. The above equation may be rewritten as

\[ \ln \sigma_{\text{ac}} = \ln \sigma_0 + \frac{E_{\text{ac}}}{kT} \]

A plot of \( \ln(\sigma_{\text{ac}}) \) versus \( 1/T \) gives \( -E_{\text{ac}}/K \) as the slope and \( \ln(\sigma_0) \) as the intercept. It is customary to plot \( \ln(\sigma_{\text{ac}}) \) versus \( 1000/T \), from the slope of which the activation energy \( (E_{\text{ac}}) \) can be calculated. Values of \( \ln(\sigma_{\text{ac}}) \) were plotted against \( 1000/T \) for all the grown samples and the activation energy values were calculated from the slope of the straight line best fitted by least square analysis.