CHAPTER 1
INTRODUCTION TO CRYSTAL GROWTH METHODS AND CHARACTERIZATION: AN OVERVIEW

1.1 INTRODUCTION

Crystallization from solutions is a process that has great technological importance, as it is used to separate and purify industrially significant substances such as pharmaceuticals, electro-optical and nonlinear optical materials. Crystals are ordered arrangements of atoms (or molecules). Materials in crystalline form have special optical and electrical properties, in many cases improved properties over randomly arranged materials (also said to be amorphous or glassy) (Tilly 2006).

Crystal-growth technology and epitaxial technology had developed along with the technological development in the 20th century. Orientation control during bulk crystal growth is one of the important development targets for crystal growers. Effective control of growth direction (orientation control) has attracted a great deal of attention. It is obvious that new functions can be created through the orientation control of molecules in the fields such as semiconductors, light-emitting devices, dosimetry (Tiwari et al 2010), nonlinear optical (NLO) materials, and photonic crystals. The rapid advances in microelectronics, communication technologies, medical instrumentation, energy and space technology were only possible after the remarkable progress in fabrication of large, rather perfect crystals and of large-diameter epitaxial layers (Muller et al 2004).
Due to the fact that many of today's technological systems in the fields of information, communication, energy, transportation, medical and safety technologies depend critically on the availability of suitable crystals with tailored properties, their fabrication - crystal growth - has become an important technology. The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, etc., all with applications and examples of materials in electronics and optoelectronics. The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure-property relationships have always been fundamentally and intrinsically important to materials science and engineering (Capper 2005).

The growth of high quality single crystals remains a challenging endeavour of materials science. Crystals of suitable size (from fibre crystals with diameters of tens of micrometers up to crystalline ingots of blocks with volume up to 1 m³) and perfection (free from precipitates, inclusions, and twins with good uniformity and low concentration of dislocations) are required for fundamental research and practical implementation on microelectronic circuits, electro-optic switches and modulators, solid-state lasers, light emitting diodes, sensors, and many other devices (Fornari and Roth 2009).

The production of most single crystals is a difficult process requiring significant technical skills in the synthesis of materials, growth, processing and characterization (Byrappa and Ohachi 2003). It acts as a link
between science and technology for the practical device applications of single
crystals as can be seen from achievements in the modern microelectronics
industry.

1.2 CRYSTAL GROWTH METHODS

Crystal Growth needs the careful control of a phase change. Thus we may define three main categories of crystal growth methods.

Growth from solid → Processes involving solid-solid phase transitions
Growth from liquid → Processes involving liquid-solid phase transitions
Growth from vapour → Processes involving vapour-solid phase transitions

1.2.1 Growth from Solid

The solids are in general polycrystalline materials with very large number of crystallites. They can be recrystallized by straining the material and subsequently annealing or by sintering. If a metal rod of fine-grained structure is subjected to strain at an elevated temperature, some grains grow considerably at the expense of others which is called strain annealing. If a polycrystalline rod or compressed powder of some materials is held at an elevated temperature below its melting point for many hours some grains grow at the expense of other and it is called sintering or annealing. The recrystallization is possible only in those materials, which are stable at high temperature where appreciable diffusion can occur. This method is not suitable for growing large crystals.
1.2.2 Growth from Vapour

In vapour growth the vapour obtained from a solid phase at an appropriate temperature is subjected to condense at lower temperature by utilizing the concept of chemical vapour transport reaction. Vapour growth processes may be subdivided into three main types. They are sublimation, vapour transport and gas phase reaction. In sublimation the solid is passed down a temperature gradient and crystals grow from the vapour phase at the cold end of the tube. In vapour transport the solid material is passed down the tube by a carrier gas. In gas phase reaction the crystals grow as a product precipitated from the vapour phase as the direct result of chemical reaction between vapour species (Pamplin 1979).

1.2.3 Growth from Liquid

The crystal growth from liquid falls into four categories namely,

(i) Melt growth
(ii) Flux growth
(iii) Hydrothermal growth and
(iv) Low temperature solution growth.

There are a number of growth methods in each category. Among the various methods of growing single crystals, solution growth at low temperature occupies a prominent place owing to its versatility and simplicity. Growth from solution occurs close to equilibrium conditions and hence crystals can be grown with high perfection. The present thesis deals with the growth of crystals by low temperature solution growth. A brief outline of this important technique of crystal growth is described below.
1.3 LOW TEMPERATURE SOLUTION GROWTH

The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. The principal advantages of crystal growth from low temperature solution are the proximity to ambient temperature and, consequently, the degree of control which can be exercised over the growth conditions. Though the technology of growth of crystals from the solution has been well perfected, it involves meticulous work, much patience. 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 solution growth method (Santhanaraghavan and Ramasamy 2000).

This method is well suited to those materials which suffer from decomposition in the melt or in the solid at higher temperatures and which undergo structural transformations while cooling from melting point and as a matter of fact numerous organic materials which fall in this category can be crystallized using this technique. Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications.

1.3.1 Materials Purification

High purity of material is an essential prerequisite for crystal growth. Therefore the first step in crystal growth is the purification of material in appropriate solvents. Impurities as low as possible at the scale of 10 - 100 ppm are required. Purification needs repetition of the crystallization process in an appropriate solvent. Although the chromatographic techniques
like high performance liquid chromatography or gas chromatography can be used for purification, they yield very small quantity of purified product per cycle. Recrystallization is the most common technique of purifying materials.

### 1.3.2 Solvent Selection

In solution growth, it is very important to choose the correct solvent to grow the crystals. A good solvent ideally displays the following characteristics.

(i) Good solubility for the given solute  
(ii) Good temperature coefficient of solute solubility  
(iii) Non corrosiveness  
(iv) Non toxicity  
(v) Non volatility  
(vi) Non flammability  
(vii) Less viscosity  
(viii) Maximum stability  
(ix) Small vapour pressure  
(x) Cost advantage

Almost 90% of the crystals produced from low temperature solutions are grown by using water as a solvent. Probably no other solvent is as generally useful for growing crystal as is water. Because of its higher boiling point than most of the organic solvents commonly used for growth, it provides a reasonably wide range for the selection of growth temperature. Moreover, it is chemically inert to a variety of glasses, plastics and metals used in crystal growth equipment (Buckley 1951, Santhanaraghavan and Ramasamy 2000).
1.3.3 Seed Preparation

The quality of the grown crystal very much depends on the quality of the seed crystals used. Small seed crystals can be obtained by spontaneous nucleation in the labile region of the supersaturated solution. A seed used to grow large uniform crystal must be a single crystal without inclusions, cracks, block boundaries, sharp cleaved edges, twinning and any other obvious defects. It should be of minimum size, compatible with other requirements. When larger crystals of the same material are already 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 seed crystal must be cut in such a way that is has larger cross-section in the fast growing direction.

Growth of crystals from solution is mainly a diffusion controlled process, the medium must be less viscous to enable faster transference of the growth units from the bulk solution by diffusion. Hence a solvent with less viscosity is preferable.

Low temperature solution growth method can be subdivided into the following categories:

(i) Slow evaporation method

(ii) Slow cooling method

(iii) Temperature gradient method

1.3.4 Slow Evaporation Method

This method is also called solvent evaporation method. The temperature is fixed constant and provision is made for the evaporation of solvent. With non toxic solvents like water, it is permissible to allow
evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.01 °C. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. In this method the solution loses particles, which are weekly bound to other components, and therefore the volume of the solution decreases. In almost all cases, 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 super saturated (Petrov 1969). This method can effectively be used for the materials having moderate solubility coefficient.

1.3.5 Slow Cooling Method

This method is suitable to grow bulk single crystals in short duration. In this technique, supersaturation is achieved by changing temperature usually throughout the period of crystal growth. The crystallization process is carried out in such a way that the point on the temperature dependence on the concentration moves into the metastable region along the saturation curve in the direction of lower stability. The main disadvantage 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 these effects large volume of solution is required. This method is widely used with great success.

1.3.6 Temperature Gradient Method

This method involves the transport of materials from the hot region containing source materials 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) The method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change and

(iii) Economy of solvent and solute

On the other hand, changes in the small temperature difference between the source and the crystal zones have a larger effect on the growth rate.

1.4 CRYSTALLIZATION FROM SOLUTION

The mission of crystal grower is to adopt suitable technique for a particular material to produce a large size single crystal. There are many methods available to grow crystals by solution. Some of the methods named after the scientists are given below

- Wulff rotating cylinder method - 1901
- Kruger-Finke U-tube method - 1910
- Johnsen rotating crystal method - 1915
- Nacken method - 1916
- Moore’s method - 1919
- Walker-Kohman method - 1948
- Holden’s method - 1949
- Mason-jar method - 1960
1.5 SANKARANARAYANAN-RAMASAMY METHOD

It is one of the methods to grow the crystals from solution. Unidirectional Benzophenone crystal was reported to Journal of Crystal Growth by Sankaranarayanan and Ramasamy (2005). In this method, there are 65 papers published in Refereed International Journals so far.

1.5.1 Importance of Unidirectional Crystals

Unidirectional crystals are very important for the preparation of functional crystals. For example, as the conversion efficiency of second harmonic generation is always highest along the phase-match direction for nonlinear optical crystals, the unidirectional crystal growth method is most suitable for the crystal growth along that direction. In addition, the unidirectional solution crystallization usually occurs at around room temperature; much lower thermal stress is expected in these crystals over those grown at high temperatures. This is particularly helpful for growth of mixed crystals because thermal stresses can cause these crystals to crack easily.

Crystals with all the facets and different morphology are grown by conventional solution growth technique but from application point of view, orientation controlled good quality, large size SHG crystals are needed. In all the methods of growth by solution, planar habit faces contain separate regions common to each facet having their own sharply defined growth direction known as growth sectors. The boundaries between these growth sectors are more strained than the extended growth sectors due to mismatch of lattices on either side of the boundary as a result of preferential incorporation of impurities into the lateral section (Gallagher et al 2003). The wastage of chemicals is also high.
1.5.2 Salient Features of SR Method

The salient features of SR method are listed below:

(i) Single crystal with desired orientation is possible at room temperature

(ii) With a thin plate as seed, growth of large size crystal is possible.

(iii) It is easy to adjust the growth rate as per our need.

(iv) Scaling up is relatively very simple.

(v) The achievement of solute-crystal conversion efficiency of 100% reduces the preparation and maintenance of growth solution to a large extent because in conventional solution growth method, to grow such a large size crystal, a large quantity of solution in a large container is normally used and only a small fraction of the solute is converted into a bulk single crystal. But, in the present method, the size of the growth ampoule is the size of the crystal.

(vi) It is not necessary to prepare all the solution in a time. After mounting the seed crystal with a small amount of solution the rest can be prepared and transferred separately into the growth ampoule.

(vii) Simple experimental set-up offers the feeding of the growth solution at a definite interval which depends on the growth rate of the crystal, thereby minimizing the exposure of the growth solution to the environment.
(viii) In the case of amino acid-based solution, this provides the possibility for avoidance of microbial growth.

(ix) The results obtained from the characterization techniques such as XRD, phase-matching study and laser damage threshold measurement demonstrate the suitability of this method to obtain nonlinear elements right during crystal growth thus decreasing material consumption when making products for nonlinear optical applications.

(x) In the case of thread hanging technique, inclusion appears and the quality of the crystal is poor if a suspension thread is used. This situation is avoided in this method.

(xi) Usually in solution growth it is difficult to control the shape and in this method by changing the ampoule shape it is possible to change the shape of the crystal.

(xii) The crystal quality is always higher compared to the conventional method grown crystals.

1.5.3 Gravity Driven Concentration Gradient

The main concept of the method is gravity driven concentration gradient. The solutions at the bottom of the ampoule have more concentration compared to top solutions. The concentration gradient is directly proportional to time. The typical diagram explaining the concentration gradient is given in the Figure 1.1.
Figure 1.1 Typical diagram of gravity driven concentration gradient

1.5.4 Experimental Arrangements

In SR method a glass ampoule was made up of an ordinary hollow borosilicate-glass with a tapered V-shaped or flat bottom portion to mount the seed crystal and a U-shaped top portion to fill a good amount of saturated solution to grow a good size crystal. The middle portion was cylindrical in shape with lesser diameter than that of the U-shaped portion, wherein one can get a cylindrical shaped crystal. Some of the ampoules are shown in the Figure 1.2.
Figure 1.2 Ampoules used to grow unidirectional crystals by SR method

The schematic diagram of experimental setup of SR method is shown in the Figure 1.3. It consists of temperature controllers, ammeters, transformers, ring heaters at top and bottom portions, sensors, glass ampoule and water bath. Ring heater was directly connected to the temperature controller to maintain the heater voltage and it provides the necessary temperature for solvent evaporation and for growing crystals. The growth ampoule was placed inside the water bath for avoiding temperature fluctuations in the growth portion. Growth condition of this method depends on the temperatures of the heating coils. The entire experimental setup is porously sealed and placed in a dust free hood. Alcohol thermometers show the temperatures near the heating coils.
In SR method the following main points have to be considered i.e. concentration of the solution, size of the ampoule, selection of seed, seed orientation and mounting, temperature at top and bottom portion, evaporation rate and growth rate. According to the solubility data, saturated solution was prepared and transferred to crystallizer for collecting the seed crystal by slow evaporation solution technique (SEST). A suitable seed crystal having a reasonable size was selected for SR method of crystal growth with specific orientation. The saturation solution was fed into the SR glass ampoule. In the freshly prepared solution, the solute concentration was deliberately kept slightly undersaturated in order to avoid any possible physical instability at the growth interface. For controlled evaporation, the top portion was closed
with some opening at the middle using thick plastic cover. Due to the transparent nature of the solution and the experimental setup, real-time close-up observation revealed the solid-liquid interface which was found to be flat. In contrast to the SEST method, in the SR method the crystal was restricted to grow with a specific direction inside a growth ampoule. The experimental setup of SR method is shown in the Figure 1.4.

Figure 1.4 Experimental setup of SR method

1.6 EFFECT OF IMPURITIES ON CRYSTAL GROWTH KINETICS

Impurities play an important role in modifying the properties of the crystals. For example, trace amounts of impurities present in crystalline solids have a profound influence on their mechanical, thermal, electrical and optical
properties. Consequently, the performance of different types of devices based on these solids depends on the nature and concentration of impurities present in them. Trace amount of impurities present in the growth medium also have a strong influence on the process of nucleation of crystallizing phases of the same substance and subsequent growth of the nucleated phase. Typical examples of such processes are:

(i) beneficial mineralization such as the formation of bone and tooth, and pathological mineralization such as the formation of human kidney stones

(ii) scale formation in domestic appliances and

(iii) crystallization of saturated fatty acid methyl ester components of biodiesel during cold seasons, clogging fuel lines and filters of engines (Sangwal 2007).

Any foreign particle substance other than the crystallizing compound is considered as an impurity. Thus, a solvent used for growth and any other compound deliberately added to the growth medium or inherently present in it is an impurity. Irrespective of its concentration, a deliberately added impurity is called an additive. An Impurity can accelerate or decelerate the growth process (Sangwal 1998). The impurity that decelerates growth is called a poison or an inhibitor, while one that accelerates growth is said to be growth promoter. Foreign substances present in the aqueous solutions used for the crystallization of substances can be as diverse as simple ions of common bivalent metals and proteinaceous compounds such as aspartic and glutamic acids in the crystallization of different phases of calcium carbonate and calcium phosphate, and the same impurity can modify the crystallization behaviour of highly and sparingly soluble compounds. For example, bivalent
cations of various metals modify the crystallization behaviour of highly soluble compounds such as sodium chloride and potassium dihydrogen phosphate and also sparingly soluble compounds such as calcium carbonate. Additives affect different processes involved during crystallization (Sangwal 2007).

- Some may exert a highly selective effect, acting only on certain crystallographic faces.
- Some are adsorbed onto growing crystal surfaces
- Adsorption of impurities onto the crystal changes the relative surface free energies of the faces
- Some may modify the habit of the crystalline phase

Therefore, the understanding of interactions between additives and crystallizing phase is important in different crystallization process encountered in the laboratory, in nature and in such diverse industries as the pharmaceutical, food and biodiesel industries (Sangwal 2007).

1.7 NONLINEAR OPTICAL MATERIALS

Since the discovery of second harmonic generation by Franken et al (1961), nonlinear optical mixing has been widely recognized as an effective method for the generation of high power coherent radiation in spectral regions where efficient laser sources are unavailable. Devices based on nonlinear optical interaction promise to be efficient, compact, easy to operate, and capable of operating in a wide spectral range (Chemla et al 1975). With a single fixed frequency laser, a combination of harmonic generation and optical parametric oscillation can provide fully tunable radiation, throughout the UV-Vis and the IR. The widespread use of these devices has been limited
by the lack of materials with suitable characteristics. Substantial progress has been made in the development of nonlinear optical materials recently. Novel materials having attractive properties are being discovered at a rapid pace, with advances in crystal growth technology making possible the commercial development of promising materials such as urea, KDP, ADP, lithium niobate, potassium niobate, KTP (Wang et al 2009), YAB (Leonyuk et al 2005) and β-BBO (Sabharwal and Sangeeta 1997)

The applicability of a particular crystal depends on the nonlinear process used, the desired device characteristics and the pump laser. Special material properties that are important in one application may not be important in another. For instance, efficient doubling of very high power lasers having poor beam quality requires a material with large angular bandwidth. A crystal, which has a smaller nonlinearity but allows noncritical phase matching, will perform better than one, which is more nonlinear but is critically phase matched (Boyd 2003).

The NLO crystals are playing an important role in the establishment of nonlinear optics as a major area of laser science and of such techniques as harmonic generation, frequency mixing and parametric oscillation as viable methods for generating coherent radiation in new regions of the optical spectrum. To date, several thousand nonlinear crystals and their closely related isomorphs like Li₆CuB₄O₁₀, Bi₂Cu₅B₄O₁₄ etc., have been developed (Pan et al 2006, Pan et al 2008). However the simultaneous requirement for such characteristics as transparency, phase matchability, high optical quality, nonlinearity and availability in bulk form has restricted the number of potentially useful materials to a few out of this entire selection (Lin et al 2007).
1.7.1 General Requirements of NLO Crystals

The following properties are very important for a noncentrosymmetric crystal for device applications.

(i) High transparency in the entire visible region
(ii) Wide phase matching angle
(iii) Non hygroscopic nature
(iv) High mechanical and thermal stability
(v) High laser damage threshold
(vi) High NLO coefficient
(vii) Moderate birefringence
(viii) Low absorption
(ix) Ease of device fabrication

1.8 CHARACTERIZATION TECHNIQUES

In order to find the quality and study the properties of the grown crystals, it is necessary to involve the crystals for the various characterizations. The usage of the crystals depends on the properties and so the characterization is 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.

1.8.1 X-Ray Diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of manufactured materials. A crystal lattice is a regular three dimensional distribution of atoms in space. These are arranged
so that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations - each with its own specific d-spacing.

When a monochromatic X-ray beam with wavelength ‘λ’ is projected onto a crystalline material at an angle ‘θ’ diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths. By varying the angle theta, the Bragg's law conditions are satisfied by different d spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. A host of application techniques for various material classes is available, each revealing its own specific details of the sample studied. The most commonly used laboratory X-ray tube uses a Copper anode, but Cobalt, Molybdenum are also popular.

1.8.2 High Resolution XRD

A multicrystal X-ray diffractometer designed and developed at National Physical Laboratory (Lal and Bhagavannarayana 1989) has been used to study the crystalline perfection of the single crystal(s). Figure 1.5 shows the schematic diagram of the multicrystal X-ray diffractometer. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm x 8 mm; 2kWMo) is first reduced by a long collimator fitted with a pair of fine slit assemblies. This collimated beam is diffracted twice by two Bonse-Hart (Bonse and Hart 1965) type of
monochromator crystals and the thus diffracted beam contains well resolved MoKα₁ and MoKα₂ components. The MoKα₁ beam is isolated with the help of fine slit arrangement and allowed to further diffract from a third (111) Si monochromator crystal set in dispersive geometry (+, -, -).

Due to dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the dispersion broadening in the diffraction curve of the specimen does not arise. Such an arrangement disperses the divergent part of the MoKα beam away from the Bragg diffraction peak and thereby gives a good collimated and monochromatic MoKα₁ beam at the Bragg diffraction angle, which is used as incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+,-,-) and non-dispersive (+,-,+) configurations. This arrangement improves the spectral purity (Δλ/λ << 10⁻⁵) of the MoKα₁ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be ≪ 3 arc sec.

The specimen occupies the fourth crystal stage in symmetrical Bragg geometry for diffraction in (+, -, -, +) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.5 arc sec. The diffracted intensity is measured by using a scintillation counter. The detector (scintillation counter) is mounted with its axis along a radial arm of the turntable. The rocking or diffraction curves for all the specimens were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ₃B starting from a suitable arbitrary glancing angle (denoted as zero). The detector was kept at the same angular position 2θ₃B with wide opening for its slit, the so-called ω scan.
Before going to record the diffraction curve, the specimen surface was prepared by lapping and polishing and then chemically etched by a non-preferential chemical etchant mixed with water and acetone in 1:2 ratio. This process also ensures to get rid from non-crystallized solute atoms on the surface and also to remove surface layers, which may sometimes form for e.g. a complexating epilayer could be formed on the surface of the crystal due to organic additives (Bhagavannarayana et al 2006).

1.8.3 UV-Vis-NIR Spectrophotometer

The instrument used in ultraviolet-visible-Near infrared spectroscopy is called a UV-Vis-NIR spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I₀). The ratio I / I₀ is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

\[ A = - \log(%T / 100\%) \quad (1.1) \]
The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm) and Xenon arc lamps for the visible wavelengths. The detector is typically a photodiode or a charge coupled device (CCD). Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collect light of different wavelengths on different pixels. A spectrophotometer can be either single beam or double beam. In a single beam instrument all of the light passes through the sample cell. I₀ must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken.

1.8.4 Thermal Analysis

The basic principle in thermo gravimetric analysis (TGA) is to measure the mass of a sample as a function of temperature. This simple
measurement is an important and powerful tool in solid state chemistry and materials science. The method for example can be used to determine water of crystallization, follow degradation of materials, determine reaction kinetics, study oxidation and reduction, or to teach the principles of stoichiometry, formulae and analysis.

Many thermal changes in materials (e.g. phase transitions) do not involve a change of mass. In differential thermal analysis (DTA), one instead measures the temperature difference between an inert reference and the sample as a function of temperature. When the sample undergoes a physical or chemical change the temperature increase differs between the inert reference and the sample, and a peak or a dip is detected in the DTA signal. The technique is routinely applied in a wide range of studies such as identification of melting point, quantitative composition analysis, phase diagrams, hydration-dehydration, thermal stability, polymerization, purity, and reactivity.

In the present thesis the analyses were carried out using Perkin-Elmer Diamond TG-DTA equipment. It carries out simultaneous TGA and DTA in the temperature range 30 - 1550 °C. For all experiments, a selection of crucibles are available (platinum, gold, aluminum) and the measurements can be done in a flow of different inert gases. The rate of flow is 20 ml/min. The measurement is normally carried out in nitrogen or in an inert atmosphere, such as Helium or Argon. Samples are normally heated from ambient to the required temperature at 10 °C per minute. Slow heating rates are preferred so that the weight change can occur over a narrower time span and temperature. It is working with PYRIS software and it displays the test progress on the monitor, stores the data and enables the user to perform analysis on the data.
1.8.5  Vickers Microhardness

The indenter employed in the Vickers test is a square-based pyramid whose opposite sides meet at the apex at an angle of 136°. The diamond is pressed into the surface of the material at loads ranging up to approximately 120 kilograms-force, and the size of the impression (usually not more than 0.5 mm) is measured with the aid of a calibrated microscope. The indentation hardness was measured as the ratio of applied load to the surface area of the indentation. Indentations were carried out using Vickers indenter for varying loads. For each load \( p \), several indentations were made and the average value of the diagonal length \( d \) was used to calculate the microhardness of the crystals. Vickers microhardness number was determined using the following formula:

\[
H_v = 1.854 \left( \frac{p}{d^2} \right) \text{ kg/mm}^2
\]  

(1.2)

1.8.6  Dielectric Measurements

The term dielectric was first coined by Faraday to suggest that there is something analogous to current flow through a capacitor structure during the charging process when current introduced at one plate (usually a metal) flows through the insulator to charge another plate (usually a metal). The important consequence of imposing a static external field across the capacitor is that the positively and negatively charged species in the dielectric become polarized. Charging occurs only as the field within the insulator is changing. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. The dielectric constant and dielectric loss were measured using Agilent 4284-A LCR meter available at S.T. Hindu College, Tamilnadu. The dimensions of the used samples were 9 x 9 x 2 mm\(^3\). Two opposite surfaces across the breadth of the sample were treated with good quality silver paste in order to obtain good Ohmic contact.
Using the LCR meter, the capacitance of these crystals was measured for the
frequencies 1, 10 kHz and 1 MHz at various temperatures. The dielectric
constant of the crystal was calculated using the relation

$$\varepsilon_r = \frac{C_{\text{crys}}}{C_{\text{air}}} ,$$

(1.3)

where $C_{\text{crys}}$ is the capacitance of the crystal and $C_{\text{air}}$ is the capacitance of same
dimension of air.

### 1.8.7 Laser Damage Threshold

Like other optical materials used in Laser technology, NLO crystals
are susceptible to optically induced catastrophic damage. Optical damage in
non-metals (dielectrics) may severely affect the performance of high power
laser systems as well as the efficiency of optical systems based on nonlinear
process and has therefore been subjected to extensive research for some 30
years. Laser damage threshold testing is a destructive test. When performing
LDT testing the sample is irradiated numerous times using a small beam over
the whole clear aperture of the sample (Boling et al 1973).

A Q-switched Nd:YAG (yttrium aluminum garnet) Innolas laser
(available at Advanced Centre for Research in High Energy Materials,
University of Hyderabad, Hyderabad) of pulse width 7 ns and 10 Hz
repetition rate operating in TEM00 mode is used as the source. The energy
per pulse of 532 nm laser radiation attenuated using appropriate neutral
density filters is measured using an energy ratiometer (Scientech Inc.) which
is externally triggered by the Nd:YAG laser. Since the surface damage is
affected by the energy absorbing defects such as polishing contaminants and
surface scratches, which get incorporated during mechanical polishing, all the
experiments are performed on the highly polished crystals (uniformly
polished with high quality polishing powder) thus minimising the strain and
incorporation of impurities. For both single and multiple shot experiments, the sample is mounted on an X-Y translator which facilitates in bringing different areas of the sample for exposure precisely. For surface damage, the sample is placed at the focus of a plano-convex lens of focal length of 80 mm. The schematic diagram of the laser damage threshold setup is shown in Figure 1.6.

![Schematic diagram of the laser damage threshold setup](image)

**Figure 1.6** Schematic diagram of the laser damage threshold setup

### 1.8.8 Second Harmonic Generation Studies

The powder sample was packed in a triangular cell and was kept in a cell holder. A 1064 nm laser from Nd:YAG irradiates the sample. The monochromator was set at 532 nm. NLO signal was captured by the oscilloscope through the photomultiplier tube. The Nd:YAG laser source produces nanosecond pulses (8 ns) of 1064 nm light and the energy of the laser pulse was around 300 mJ. The beam emerging through the sample was focused onto a Czerny-Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R-928 photomultiplier tube. The signals were captured with an Agilent infinium digital storage oscilloscope interfaced to a computer. After the 4 averages, the signal height
was measured (peak to peak volts). Similarly the signal height for the standard was also measured.

1.9 SCOPE OF THE THESIS

Enhancement of the quality of technologically important single crystals is of great interest for various applications, like electro optic modulators, fiber optic communications and particularly in the production of laser sources with different wavelengths. Among various second order NLO materials, ammonium dihydrogen phosphate has attracted much more attention due to its high NLO and piezoelectric coefficients, stable physico-chemical properties, higher mechanical and thermal stability and good laser stability. Crystal grown along the specific orientation is useful to cut along its phase matching angle. In this case wastage of crystal is minimum. In view of this fact, the present thesis aimed at the growth of high quality large size ADP single crystals by conventional method and SR method and the properties of the grown crystals.

Suitable addition of selected impurities in the mother solution can increase the overall quality of the crystals. In order to enhance the quality, size and properties of the ADP crystals of L-LMHCL was added in the mother solution. The presence of ammonium compounds in the mother solutions of ADP always results in high quality crystals. Keeping this in mind, ammonium malate was used as a dopant and large size crystals were harvested. Similarly DL-Malic acid, L-Asparagine monohydrate and oxalic acid were added separately in the appropriate molar ratio and the crystals were harvested. Different methods were used to grow crystals. In each case, pure ADP crystals were also grown using the same material ingredients. The grown crystals have been subjected to single crystal XRD, powder XRD, FTIR, UV-Vis-NIR, TG-DTA, HRXRD, dielectric, laser damage threshold, piezoelectric and SHG studies to know the various properties of the crystals.
In order to get the crystals with necessary orientation SR method has been used. Good quality $<1 \ 0 \ 0>$ directed pure, $<0 \ 0 \ 1>$ directed DL-Malic acid, L-asparagine monohydrate doped single crystals and $<1 \ 0 \ 0>$, $<0 \ 0 \ 1>$ directed ammonium chloride added ADP single crystals were grown. The grown crystals were subjected to the above said characterizations and the results were compared and reported as against the single crystals grown by conventional method. A growing crystal segregates the unwanted impurities as much as possible. In SR method growth, the growing crystal segregates the unwanted impurities and the segregated impurities are accumulated just above the crystal. In this connection, in order to drive the impurities away from the crystal, slots were made in the ampoule with equal distance above the seed mounting pad. The slots made in the ampoule allow diffusion of impurities from the high concentration to the low concentration medium, that is the impurities present near the crystal diffused to the outer ampoule and several slots were made to continue this process throughout the crystal growth process. The harvested crystal from this modified SR method was subjected to various studies and the results are compared with the regular SR method grown crystal.