1. INTRODUCTION

1.1 INTRODUCTION OF CRYSTAL GROWTH

Crystal growth is one of the most important fields of material science, which involves controlled phase transformation. Fundamental experimental aspects of crystal growth were derived from early crystallization in the Eighteenth and Nineteenth Century. The phenomena of under cooling, supersaturation and the heat of crystallization were recognized in the Eighteenth Century [1]. Theoretical understanding started with the development of thermodynamics in late Nineteenth Century and with the development of nucleation and crystal growth theories. The critical one to achieve higher quality crystal and the role of transport phenomena was a unique feature of the Twentieth Century. In the past, there was a growing interest in crystal growth process, particularly in view of the increasing demand for materials for technological applications [2-4]. Therefore, researchers worldwide have always been in search of new materials through their single crystal growth. The methods of growing crystals are very wide and mainly dictated by the characteristics of the material and its size [5, 6]. The single crystal technology is the mother of all the recent technologies and modern science. In the modern world, the large-scale uses of crystals are brought about mainly by the demands of solid state materials for research and developments in physics. Varieties of crystals are needed to meet some very important gaps in conventional production in engineering. The several kinds of single crystals and its applications are found in the development of technologies such as; laser, semiconductor, high and low energy particles in physics, nuclear fusion, medical diagnostics, display, and thermal imaging [7]. The contribution of crystals in electrical industry, photonic industry, optical fiber communications, which depends on materials/crystals, such as; semiconductors, superconductors, transducers, polarizer’s, ultrasonic amplifiers, radiation detectors, ferrites, magnetic garnets, solid state lasers, photosensitive, nonlinear optics, piezo-electric, acoustic-optic, electro-optic, refractory of different grades, crystalline films for microelectronics and computer industries. The crystal growth is an interdisciplinary subject which
covers physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past, there had been a growing interest in crystal growth processes, particularly in view of the increasing demand of materials for technological applications. [4,8].

The new solid state and the single crystals explosion lead to the invention of the transistor in 1948. Many new crystals are grown and fabricated in order to assess the device properties. The application of semiconductor based on electronics created an enormous demand for high quality of semiconductor, ferroelectric, piezoelectric, oxide single crystal [9]. The crystal growth plays an important role in the area of immense technological excellence which is useful for many crystals in important areas of service to the humanity, medicine, engineering, technology and also strategic areas of defense and space science. In addition, many crystals are useful as elements in acoustic-optic, piezoelectric, photo-refractive, photo-elastic applications and also as radiation detectors, laser hosts, transducers, parametric amplifiers, Bragg cells, harmonic generators etc., [10-12].

1.2 GENERAL CRYSTAL GROWTH METHODS

The mode of selecting a particular method of crystal growth techniques depends on the properties of the materials, such as melting point, vapour pressure, decomposition, solubility in solvents etc. The growth methods depend on growth kinetics, crystal size, shape and nature of the application of the crystals. The method should also be economically feasible and the crystal formed should be free from defects.

The consistency and the characteristics of devices fabricated from the crystals depend on the homogeneity and defect contents. The process of producing single crystals, which offers homogeneous media on the atomic level with directional properties, attracts more attention than any other process. The methods of growing crystals are wide and mainly dictated by the characteristics of the material and its size [5].

The methods of growing single crystals may be classified according to their phase transformation as given below [13].
Based on the phase transformation processes, crystal growth technique are classified as solid growth, vapour growth, melt growth and solution growth.

1.2.1 High-temperature solution growth

Hydrothermal and flux growths from the category of high temperature solution growth. They are studied at a large scale in this method, a solid molten salt / flux is used as the solvent instead of liquid. The growth takes place below the melting point of the solute [14]. This technique could be applied to incongruently melting materials. Mixed crystals of solid solution could also be grown by the choice of optimum growth parameters. The same techniques could be used for the crystallization of oxide compounds, which generally have the high melting point as well as for materials which undergo phase transitions below the melting point. The crystals were grown from these methods usually have the lower concentration of equilibrium defects and lower dislocation density.

1.2.2 Hydrothermal growth

The hydrothermal crystal growth may be defined as the use of an aqueous solvent at high-temperature and pressure to crystalline the sparingly soluble materials at low-temperatures. The substances like calcite, quartz etc., are considered insoluble in water, but high-temperature and pressure these substances are soluble. This method of crystal growth at high-temperature and pressure is known as hydrothermal method. Temperature typically in the range of 400 °C to 600 °C and the pressure involves is about hundreds of atmosphere. Growth is carried out in steel autoclaves with silver or gold 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. In this technique, very few crystals are grown the good quality and large dimensions. Quartz is an outstanding example of industrial hydrothermal crystallization.

1.2.3 Gel growth

Gel growth is a very convenient laboratory process [15]. It gave an excellent survey of this process. Only small crystals can be grown by this technique. Gels are two-phase systems comprising a porous solid with liquid filled pores. The pore dimensions depend on the concentration of the gel material. The most frequently used gels are based on silica. But gels based on gelatin, various soft soaps and pectin are also used. Seed crystals should be used to reduce flaws at the center of the crystals. It is very important to provide constant ambient temperature.

1.3 LOW-TEMPERATURE SOLUTION GROWTH

The growth of crystals from aqueous solution is one of the classical methods of crystal growth. The low-temperature solution growth is one of the popular methods to produce technologically important crystals. This method demands that the materials must crystallize from solution with prismatic morphology. In general, this method involves seeded growth from a saturated solution. The driving force i.e., the supersaturation is achieved either by temperature lowering or by solvent evaporation. This method is widely used to grow bulk crystals, which have high solubility and have variation in solubility with temperature [16]. After many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. The growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. 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 pressure, temperature, and solvent concentration [17].
Low-temperature solution growth could be sub-divided into the following methods:

(i) Slow cooling method  
(ii) Slow evaporation method  
(iii) Temperature gradient method

1.3.1 Slow cooling method

The slow cooling method is the best way to grow crystals by solution growth technique. The main disadvantage of slow cooling is the need to use a particular range of temperature. The possible range of temperature is usually narrow and hence, much of the solute remains in the solutions at the end of the growth run. To compensate this effect, large volumes of the solution is needed. A wide range of temperature may not be described because the properties of the grown crystal may vary with temperature. Even though the method has the technical difficulty of requiring a programmable temperature control, it is widely used with great success. In the recent time, many crystals grew from a slow cooling technique.

1.3.2 Slow evaporation method

The slow evaporation method is similar to slow cooling method in terms of the apparatus concerned. In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. If the solvent is non-toxic like water, it is permissible to evaporate into the open atmosphere. The typical growth conditions involve a temperature stabilization of about 0.05°C and rate of evaporation of a few mm$^{3}$/hour. The evaporation technique has an 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 can effectively be used for materials having very low-temperature coefficient of solubility. But the crystals tend to be less pure than the crystals produced by slow cooling technique, as the size of the crystal increases more impurities find the place in the crystal faces. This
method can effectively be used for materials having a very low-temperature coefficient of solubility.

1.3.3 Temperature gradient method

The temperature gradient method involves the transport of materials from a hot region containing a source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The advantage of this method is

(i) Economy of solvent
(ii) The crystal grows at fixed temperature

1.4 FUNDAMENTAL OF SOLUTION GROWTH

1.4.1 Nucleation

Nucleation is an important phenomenon in crystal growth and is the precursor of the overall crystallization process. It is the process which generates a metastable mother phase, the initial fragments of a new and more stable phase capable of developing spontaneously into gross fragments of the stable phase. It is consequently a study of the initial stages of the kinetics of such transformations [18].

Nucleation might occur spontaneously or it might be induced artificially. These two cases are referred to as homogeneous and heterogeneous nucleation respectively. Both these nucleation’s are called primary nucleation and occur in systems that do not contain crystalline matter. On the other hand, nuclei are often generated in the vicinity of crystals present in the supersaturated system. This phenomenon is referred to as secondary nucleation [6]. The growth of crystals from solutions could occur a certain degree of supersaturation or super cooling has first been achieved in this system. There are three steps involved in the crystallization process.

- Achievement of supersaturation or super cooling
- Formation of crystal nuclei
Successive growth of crystals to get distinct faces

1.4.2 Ostwald's contributions

While the concept of a definite super solubility is contained in the earliest writings on the crystal growth subject, Ostwald appears to be the first to explain the relationship between supersaturation and spontaneous crystallization. The relationship between the concentration and temperature is schematically shown in Figure 1.1 [19].

Meirs solubility diagram consists of three zones, which are termed as region I, II and III respectively. Region I correspond to the under saturated zone, where crystallization is not possible. This region is thermodynamically stable. The region II between the super solubility curve and solubility curve is called as metastable zone, where spontaneous crystallization is not possible, but seeded growth could be initiated in this region. In the region III, spontaneous nucleation is more probable, called as unstable or labile zone.

![Solubility diagram showing different levels of saturation.](image)

1.4.3 Supersaturation

The solution in which the concentration of the solute exceeds that of the equilibrium condition at a given temperature is known as supersaturated
solution. The supersaturated solution is thermodynamically unstable. The supersaturation required for crystallization process could be achieved by (i) slow evaporation (ii) slow cooling and (iii) by adding any external impurity. The supersaturation achieved by slow cooling is the best method to grow bulk size crystals by solution technique. In this case, crystallization takes place by lowering the temperature of the solution under a controlled cooling rate. The supersaturation can be achieved by slow evaporation of the solvent for materials, which are having a very small temperature coefficient of solubility. Here crystallization could take place at a constant temperature. The supersaturation could also be achieved by the addition of some impurities. The growth proceeds by the reduction of solubility of the solute due to the presence of impurity. The selection of suitable growth methods depend mainly on the shape of the solubility curve.

The degree of supersaturation (S) of a solution could be expressed by the ratio:

\[ S = \frac{C}{C^*} \]  \hspace{1cm} (1.1)

where, \( C \) is the actual concentration of the solution and \( C^* \) is the equilibrium saturation concentration of the solution at a given temperature. Thus, for a saturated solution, \( S = 1 \), \( S < 1 \) denotes under saturation and \( S > 1 \) indicates supersaturation.

The concentration driving force \( \Delta C \) is given by

\[ \Delta C = C - C^* \]  \hspace{1cm} (1.2)

The relative supersaturation is defined as,

\[ \delta = \frac{C - C^*}{C^*} \]  \hspace{1cm} (1.3)

\[ \delta = \frac{C}{C^*} - 1 \]  \hspace{1cm} (1.4)

\[ \delta = S - 1 \]  \hspace{1cm} (1.5)
The crystallization process is initiated by the formation of embryos or nuclei with number of micro size solid particles present in the solution, termed as centers of crystallization. The mechanism of formation of such embryos is the simple collision process of a single molecule $A_1$ with a cluster $A_{i-1}$ consisting of $(i-1)$ molecules and thus giving rise to a cluster $A_i$, i.e.,

$$A_{i-1} + A_1 \rightarrow A_i$$  \hspace{1cm} (1.6)

The total Gibb’s free energy change, $\Delta G$ of the embryo between the two phases associated with this process is given as

$$\Delta G = \Delta G_s + \Delta G_v$$  \hspace{1cm} (1.7)

where $\Delta G_s$ is the surface free energy and $\Delta G_v$ is the volume free energy.

For the spherical nucleus of radius, $r$

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v$$  \hspace{1cm} (1.8)

where $\gamma$ is the interfacial tension and $\Delta G_v$ is the free energy change per unit volume and is a negative quantity. The quantities $\Delta G$, $\Delta G_s$, and $\Delta G_v$ are represented in Figure 1.2. Since the surface free energy increases with $r^2$ and volume free energy decreases with $r^3$, the total net free energy change increases with increase in size and attains a critical size after which it decreases.

At critical condition, the free energy of formation obeys the condition,

$$\frac{d\Delta G}{dr} = 0$$  \hspace{1cm} (1.9)

Hence, the radius of the critical nucleus is expressed as

$$r^* = \frac{-2\gamma}{\Delta G_v}$$  \hspace{1cm} (1.10)
\[ \Delta G_v = -\frac{kT \ln S}{V} \]  \hspace{1cm} (1.11)

\[ V = \text{molar volume of the crystal} \]

\[ k = \text{Boltzmann constant} \]

\[ T = \text{Temperature of the solution in K} \]

Hence, the critical free energy barrier

\[ \Delta G = \frac{16\pi \gamma^3 V^3}{3\mu^2} \]  \hspace{1cm} (1.12)

\[ \text{Figure 1.2: Change in free energy due to the formation of the nucleus.} \]

The number of molecules in the critical nucleus is expressed as

\[ i^* = \frac{4\pi (\gamma^*)^3}{3V} \]  \hspace{1cm} (1.13)

The crucial parameter between a growing crystal and the surrounding mother solution is the interfacial tension (\( \gamma \)). This complex parameter could be determined by conducting the nucleation experiments [3].
1.5 OPTIMIZING SOLUTION GROWTH METHOD

1.5.1 Solvent selection

The solution is a homogeneous mixture of a solute in a solvent. The solute is the component present in a smaller quantity. For a given solute, there may be different solvents. Apart from high purity starting materials, solution growth requires good solvents. The solvent must be chosen taking into considering the following factors.

- Moderate solubility for the given solute
- Must not react with the solute
- Good solubility gradient
- Low viscosity
- Low correction

If the solubility is too high it is difficult to grow bulk single crystal and if the solubility is too small, it 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 the growth process [5]. 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. The 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 [20].

1.5.2 Preparation of solutions

Preparation of the solution to grow the desired crystal is an important stage in solution growth. The saturated solution is filtered using the filter paper. The filtered solution is transferred into the beaker. Extreme care is to be taken to avoid under saturation, which results in the dissolution of the seed crystal. Similarly, high supersaturation is also to be avoided in order to
prevent the formation of spurious nucleation. The growth vessel is hermetically sealed in order to avoid the evaporation of the solvent. The solution is tested for saturation by suspending small test seed crystal in the solution. By adjusting the temperature, the necessary equilibrium condition is achieved and the test seed crystal is removed and a fresh seed crystal is introduced for crystal growth.

1.5.3 Seed preparation

The quality of the grown crystal very much depends on the quality of the seed crystal used. Small seed crystals could be obtained by spontaneous nucleation in the labile region of the supersaturated solution. The seed used to grow a large uniform crystal must be a single crystal free of 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 could 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 it has larger cross-section in the fast growing direction.

1.5.4 Agitation

In order to get a regular and even growth, the level of supersaturation is to be maintained equally on the surface of the growing crystal. An uneven growth leads to localized stress at the surface, generating imperfection in the bulk crystals. Moreover, the concentration gradients that exist in the growth vessel cause fluctuations in supersaturation at different faces of the crystal, which seriously affect the growth rate of individual faces. The degree of formation of concentration gradients around the crystal depends on the efficiency of agitation of the solution. This is achieved by agitating the saturated solution in either direction at an optimized speed using a stirrer motor.
1.5.5 Crystal habit

The growths of a crystal in equivalent rates along the crystallographic directions are the prerequisite for its accurate morphology with developed faces. This will result in a large bulk crystal from which samples of any desired orientation could be cut. Further, such large crystals should also be devoid of dislocation and other defects. These imperfections become isolated from defective regions surrounded by large volumes of high perfection when the crystal grows with a bulk habit. In the crystals, which grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect. The needles like crystals are very limited applications and plate-like crystals need to be favorably oriented. Changes of habit in such crystals, which naturally grow as needles or plates could be achieved by any one of the following ways:

- Changing the temperature of growth
- Changing the pH of the solution
- Adding a habit modifying agent and
- Changing the solvent

The achievement in this area is of great industrial importance where such morphological changes are induced by crystallization to yield crystal with better perfection and packing characteristics.

1.5.6 Factors that influence the perfection of crystal

In order to grow large size, well-faceted optically clear crystals there are five basic factors need to be optimized:

- The purity of the starting material
- The precision of the seed
- Cooling or evaporation rate
- pH of the growth solution
The efficiency of agitation of the seed and the solution

Hence, good quality single crystals could be grown from quality seed in an efficiency stirred the solution.

1.6 SCOPE OF THE THESIS

In the field of single crystal growth, several important contributions have been made to grow crystals due to their potential applications in optoelectronics, Infrared detector (IR) and nonlinear optical (NLO) applications.

The solution growth method at room temperature and at slightly elevated temperatures offers simple equipment to grow good quality single crystals. The present investigation of the thesis is aimed towards the development of nonlinear optical single crystals of organic and inorganic materials by low-temperature solution growth method. To study the various properties of the grown crystals, characterization studies are the assessment technique to study the chemical composition, structure, optical properties, physio-chemical properties etc., The single crystals chosen for the present investigation were characterized by single crystal X-ray diffraction (SXRD) and Powder X-ray diffraction (PXRD) studies in order to confirm the crystalline nature and lattice parameters. The functional groups present in the crystals were analyzed using Fourier transform infrared (FT-IR) spectral analysis. The optical properties were examined by UV-vis-NIR spectral analyzes and the thermal stability of the grown crystals was analyzed using TG-DTA studies. Second harmonic generation (SHG) efficiency of the crystals was confirmed by Kurtz and Perry powder technique. The third order nonlinear optical properties, such as nonlinear refractive index $n_2$, nonlinear absorption coefficient $\beta$, and nonlinear susceptibility $\chi^{(3)}$ were studied using the Z-scan technique. The studies are carried out to determine the sign and magnitude of nonlinearity and to investigate nonlinear refractive index and nonlinear absorption coefficient. The magnitude and response of third order nonlinear susceptibility are important parameters in characterizing and determining the applicability of any materials as a nonlinear optical device.
In the present analysis, the growth and investigation of the third order nonlinear optical properties of pure and potassium doped meta-Nitroaniline, potassium dichromate, L-alanine single crystals are examined.

1.7 OUTLINE OF THE THESIS

This thesis is divided into seven chapters

Chapter I: The Chapter I discusses the brief introduction of crystals growth. The various methods of crystal growth are explained in this chapter. The scope of the thesis is presented in brief manner.

Chapter II: The Chapter II analyzes the theoretical concept of nonlinear optics. The nonlinear optical (NLO) crystals built from inorganic, organic and semi organic materials and third order nonlinear optical crystal are included in this chapter. The literature survey is made in elaborate manner.

Chapter III: The Chapter III illustrates an overview of various principles and instrumentation techniques, which are used to characterize the grown crystals.

Chapter IV: This Chapter deals with growth, thermal, mechanical, linear and nonlinear optical properties of pure and doped meta-Nitroaniline single crystals. The crystals are grown using solution growth technique, using methanol as a solvent. The structure of the grown crystal were confirmed by single crystal and powder X-ray diffraction technique, The EDX spectrum is used to identify the doped material, potassium presentation. The linear and nonlinear optical properties of pure and potassium doped meta-Nitroaniline crystals. The optical transmission studies reveal that the mNA and mNAK crystals have UV cut-off wavelength around 345 nm and 352 nm respectively. The nonlinear optical property (NLO) of the crystal was tested by pulsed Nd: YAG laser as a source. The third order nonlinear optical properties were measured using single beam Z-scan technique using continuous wave Nd: YAG laser.
Chapter V: The Chapter V presents the growth and characterization of pure potassium dichromate (KDC) single crystal. The single crystal of potassium dichromate (KDC) is grown from aqueous solution by slow evaporation technique. The lattice parameters of the grown crystal were determined by single and powder X-ray diffraction analysis. The optical absorption studies reveal that the crystal has UV cut-off wavelength around 240 nm. The thermal stability of the grown crystal analyzed using TG/DTA studies. The mechanical strength of the grown crystal was carried out by Vickers micro hardness test. The crystal perfection was confirmed by etching study. The third order nonlinear optical study was performed using by a single beam Z-scan technique using continuous Nd: YAG laser. The closed aperture Z-scan studies reveal the negative nonlinearity in the crystals and open aperture Z-scan reveals the saturation absorption. Also, various parameters such as nonlinear refractive index $n_2$, absorption co-efficient $\beta$ and nonlinear optical susceptibility $\chi^{(3)}$ were calculated for the grown crystal.

Chapter VI: The Chapter VI studies the effect of potassium dihydrogen phosphate on L-alanine single crystal. The lattice parameters of the grown crystal were determined by X-ray diffraction analysis. The optical transmission study reveals very good transparency of the grown crystal. The thermal stability of the grown crystal is found to be 288.7°C. The nonlinear optical property (NLO) of the crystal was tested by pulsed Nd: YAG laser as a source. The third order nonlinear optical studies were performed using single beam Z-scan technique using continuous Nd: YAG laser. The closed aperture Z-scan studies reveal the negative nonlinearity in the crystals and open aperture Z-scan reveals the saturation absorption. The various parameters such as, nonlinear refractive index $n_2$, absorption co-efficient $\beta$ and nonlinear optical susceptibility $\chi^{(3)}$ were calculated for the grown crystal.

Chapter VII: The Chapter VII illustrates the concluding remarks and presents the prospect of the research work.