CHAPTER – I

1. Introduction to Crystal Growth

1.1 Introduction

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications [1,2]. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals [3]. The reason for growing single crystals is, many physical
properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research.

Nonlinear optical (NLO) crystals are very important for laser frequency conversion [4]. Potassium Dihydrogen Phosphate (KDP) is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also KDP has a high laser damage threshold. Potassium Titanyl Phosphate (KTP) is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of Nd:YAG laser. It has high optical nonlinearity, large temperature and angular allowance and it is non hygroscopic and mechanically hard. The method of growing crystals varies widely; it is mainly dictated by the characteristics of the material and its size [5,6]. In recent years there has been considerable progress in the development of coherent UV sources based on non-linear optical processes.
The demand for NLO crystals with superior properties is increasing due to quantum jump in the design of NLO devices with higher performance. With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace [7-10]. To enable a material to be potentially useful for NLO applications, the material should be available in bulk single crystal form [11]. And so, crystal growths of new NLO materials and investigation into their properties have become most indispensable and efficacious disciplines in the field of materials science and engineering.

The rapid development of optical communication system has led to a demand for NLO materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel semi organic systems of considerable potential and high performance. There are three major stages involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices. In this section, various methods of crystal growth with emphasis on low temperature solution growth technique are described.
The solvent to be chosen to grow good quality crystals from solution, the effect of super saturation and pH value of the solution is also discussed.

1.2 Methods of Crystal Growth

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, vapour growth, melt growth and solution growth [12].

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 [13]. The above methods have been discussed in detail by several authors [1, 14, 15]. The different
techniques of each category are found in reviews and books by vapour growth [16], melt [17], gel growth [18], solution growth [5] and high temperature solution growth [19].

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 the above mentioned categories liquid growth includes both melt and solution growth. A survey of the methods of growth suggests that almost 80% of the single crystals are grown from the melt compared with roughly 5% from vapour, 5% from low temperature solution, 5% from high temperature solution, and 3% from the solid and only 2% by hydrothermal methods.

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.

This basic understanding of the deposition of atoms onto a suitable substrate surface – crystal growth – 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 as art. As a result, crystal growth has long had 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’ [20]. 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 and the field from an art to science, technique and to technology.

1.3 Growth from Solution

Materials, which have high solubility and have variation in solubility with temperature, can be grown easily by solution method. There are two methods in solution growth depending on the solvents and the solubility of the solute. They are
1. High temperature solution growth

2. Low temperature solution growth

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

1. Growth from single component system.

2. Growth from multi component system.

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.

1.3.2 Hydrothermal Growth

Hydrothermal implies conditions of high pressure as well as high temperature. Substances like calcite, quartz is 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 and there are 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.

1.4 Gel Growth

It is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. 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.

1.5 Growth from Melt

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 in to the cold zone. The rates of movement for such processes range from about 1 – 30 mm/hr. Crystallization begins at the tip and continues usually by 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 III-V compound semiconductors.

In Kyropoulos technique, the crystal is grown in a 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 the 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 the 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.

1.5.1 Electro Crystallisation

Electrolysis of fused salts is normally used for the commercial production of metals such as aluminium and has great technological importance. The process of crystal growth from fused salts is analogous in many respects, except for the requirement of electron transfer in deposition of the metal. Fused salt electrolysis has been used to grow crystals of oxides in reduced valence states.

1.6 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. To obtain single crystals of high melting point materials this method is used. 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 to 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 e.g. 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.

1.7 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 [12] and also which undergo phase transformations below melting point [21]. 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.

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 thermo dynamical parameters of the process; temperature, pressure and solvent concentration [15]. 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, super saturation 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 can be grown by variations of growth conditions or of solvent [21]. 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 [17].

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. In the low temperature solution growth, crystals can be grown from solution if the solution is supersaturated i.e., it contains more solute than it can be in equilibrium with
the solid. Three principal methods are used to produce the required super saturation:

i. Slow cooling of the solution

ii. Slow evaporation of the solvent

iii. The temperature gradient method.

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. It also permits the preparation of different morphologies of the same materials by varying the growth conditions.

1.7.1 Slow Cooling Technique

It is the best way to grow single crystals by solution technique. The Main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required.

The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which such
crystallization can begin is usually within the range 45 - 75°C and the lower limit of cooling is the room temperature.

1.7.2 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.

1.7.3 Temperature Gradient Method

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are that

(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), KDP and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method.
References


