CHAPTER 2

CRYSTAL GROWTH AND ITS TECHNIQUES

2.1 Introduction

The regular surface geometry and the shiny and often colorful appearance have made crystals from the mineral kingdom fascinating objects for everybody. Natural crystals have often been formed at relatively low temperatures by crystallization from solutions, sometimes in the course of hundreds and thousands of years. Now a day, crystals are produced artificially to satisfy the needs of science, technology and jewellery. The ability to grow high quality crystals has become an essential for the competitiveness of nations. Crystal growth specialists have been moved from the periphery to the center of the materials-based technology. An interdisciplinary crystal growth science has developed with scientific journals, conventions and societies,
internal networks of crystal growth laboratories and material science centers have been formed. Crystal laboratories operate in large numbers to satisfy the needs of research and technology for high-quality, tailor-made crystals of all kinds [1]. Parallel with the development of other sciences, the curiosity of mankind grown to understand more quantitatively the properties of crystals. The utility of crystals has been extended from the bounds of ornaments to several useful applications in optical, electrical and opto-electronics devices, super-conducting devices, Optical data storage for developing technologies in telecommunications and signal processing [2,6]. The technology development is mainly due to the development of crystal growth technology. New developments in detectors and increase in computer power and graphics capabilities have contributed to the broad success of crystallography in the recent past.

2.2 Crystal and Crystallography

The word crystal comes from the Greek word “Krustallos” used to describe transparent crystals of quartz which was equivalent meaning ice or frozen water. The name was probably given because it was mistakenly thought that these unusual “stones” were formed from water due to intense “cold”. The father of crystal fabrication technology is ‘A. Verneuil’ with his flame fusion growth method described by him in 1902.

What is Crystal?
A crystal can be defined as homogenous solid with definite chemical composition bounded by naturally formed plane faces having definite geometrical shape [7, 8] in which atoms or molecules are arranged in orderly repetitive array.

To study of the structures and properties of crystals, you now know that X-ray diffraction is one of most important ways of discovering the arrangements of atoms within crystals or molecules. One of the reasons why so much research has been done in crystallography is that chemists, biologists and physicists have as intrinsic interest in discovering the secrets of nature. Another reason is that it is a part of science that has great economic importance. By understanding the way atoms pack together in a crystal we can design alloys and other materials to have specific properties.

2.3 Classification of crystal

1) Single crystals (Crystalline )

2) Poly crystals (Semi crystalline)

2.3.1 Single crystals

A piece of pure materials in which the orderly arrangement of atoms extends throughout is called a single crystal. A single crystal also called mono crystal, is a crystalline solid in which the crystal lattice of the edges of continuous and unbroken to the edges of sample, with no grain boundaries. The opposite of a single crystal sample is an amorphous structure where the atomic position is limited to short range order only. In between the two extremes there
exist polycrystalline & Para crystalline phases materials, which are made-up of a number of smaller crystals known as crystallites.

Because of a variety of entropic effects on the microstructure of solid, including the distorting effects of impurities and the mobility of crystallographic defects and dislocations, single crystals of suitable size are rare in nature. Grain boundaries can have significant effects on the physical and electrical properties of a material; single crystals are of interest to industry and have important industrial application. The most notable of these is the use of single crystal silicon in the fabrication of semiconductors. On the quantum scale that microprocessors operate on the presence of grain boundaries would have a significant impact on the functionality of field effect transistors.

Materials in crystalline form have special optical and electrical properties. A typical feature of a single crystal is its anisotropy i.e. the difference in its physical properties in different directions. Single crystal possesses long range periodicity. It has higher density due to closed packing of atoms. It presents sharp diffraction pattern. It exhibits pin-pointed melting point. It has well-defined crystal structure and geometry. Single crystal quartz is employed in generating ultrasonic waves.

2.3.2 Poly crystals

A material consisting of many crystalline grown together in the form of an interlocking mass, oriented randomly and separated by well
defined boundaries is said to be a polycrystalline material. A great majority of materials occurring in nature such as rock, sand metals salts etc. are of polycrystalline structure. However they can be grown as a single crystal, under suitable conditions. Due to random distribution of crystallites, a polycrystalline material is isotropic i.e. its properties are same on an average in all directions. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains which are inevitably present in polycrystalline materials.

2.4 Significance of single crystal

Single crystals are being used for the fabrication of many solid state devices. This meant that many new crystals have to be grown and fabricated in order to access their device properties. The ever increasing application of semi conductors based electronics creates an enormous demand for high quality semi conducting, ferroelectric, piezoelectric, oxide single crystals.

The photonic device evolution we see today is due to the advent of compounds of semiconductors crystals like III-V (GaAs, InP, InSb, GaSb etc.) II-VI (ZnSe, CdTe, Zn: CdTe, HgCdTe etc) compounds. The major use of GaAs at present is in the area of microwave device, high speed digital integrated circuits and the substrate for epitaxial layer growth to fabricate photonic and electronic devices. With the recent advancement of mobile communication and
digital telephony there has been increasing demand of semi-conducting GaAs. Apart from the semiconductor crystals and oxide crystals, there are several other materials, which are technologically and strategically important [9-16].

**Mono crystals of silicon & other semiconductors are important for manufacture of Integrated circuits.**

In device arena the technology of fabrication was $10^3$ transistors per chip during 1970 (desk calculator) and has matured to $10^8$ transistors per chip during 1998. The ever-increasing demand for single crystals arising from electronic industry depicts the task for science and technology of crystal growth [17].

Crystals are used in solid-state lasers, flat screen computer displays, and a wide variety of other devices [7].

Monocrystal of metals especially super alloys are used for their special mechanical properties, Turbine blades of same gas turbines are made of single crystal cast super alloy.

The ability to develop new advanced materials systems is greatly aided by access to “custom “single crystals. In response to this need the bulk crystal growth facility will permit growth of single crystals of wide range of materials such as refractory metals, intermetallics & ceramics from the melt at temperatures greater than 3000 degrees Celsius. Research areas use the facility including, high temperature structural sensors and detector resistant materials.
Mono crystals of Nd: YAG, Nd: YVO₄, Nd: KGW, Sapphire and other materials are used for Laser & nonlinear optics

Although Nd: YAG was invented in 1960 in last century, it has been and is still the most commonly used solid state crystal material. Nd: YAG crystals are widely used in all types of solid-state lasers systems such as frequency-doubled continuous wave, high-energy Q-switched, and so forth. Nd: KGW Neodymium doped Potassium-Gadolinium Tung-state crystals are low-threshold high effective laser medium exceptionally suitable for laser rangefinders. KGW single crystals can also be used for the fabrication of high-efficiency lasers with output energy. The single crystals exhibit a high optical quality and it has great value of the bulk strength for laser radiation.

The growth of oxide crystals for use in the electronic industry has progressed significantly since the early 1960s. Today, parts fabricated from oxide single crystals are used as the active component in laser systems (Nd: YAG, Ti: Al₂O₃, Cr: Al₂O₃ etc.) substrates for GaN, Silicon epitaxy (Al₂O₃), optical components (LiNbO₃, LiTaO₃) and substrates for magnetic bubble devices Gd₃Ga₅O₁₂)

Lasers have wide applications in science and technology. The extension of laser utility to many scientific applications had been made easy by nonlinear optics- a new branch of optical sciences by which the intensified electromagnetic radiations with wide spectrum of frequencies are generated. It
seems today, that nearly all electro optical technologies of practical importance rely on at least one nonlinear optical effect.

The very first materials to be used and exploited for their nonlinear optical and electro optical properties were Potassium Dihydrogen Phosphate (KDP) and Ammonium Dihydrogen phosphate (ADP). They are still used widely in nonlinear optical devices and continue to popular as electro-optic materials, together with their isomorphs.

Modern technology is based on single crystal of nonlinear optical, semiconductors, dielectric, ferroelectric, superconductors, acousto-optic and optoelectronics materials, hence much attention is paid on the growth of single crystals which is a vital and fundamental part of material science and engineering, as single crystals of suitable size and perfection are required for lasers, optical communication, detectors, integrated circuits and data storage technology [18-19]. The uniformity of single crystal allows transmission of electro magnetic waves without scattering, hence in the past few decades there is lot of development in science and technology especially in the field of electronics, fiber optics and lasers. As there is a vast market for solid state devices in the field of computers, telecommunication and optical storage, frequency doubling, frequency mixing electro-optic modulation and optical communication and ferro-electric, efforts have been made in recent years on producing larger single crystals [20-25].
The Nonlinear optical crystals are very important for laser frequency conversion. The KDP is a suitable crystal for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also the KDP crystal has a high laser damage threshold. The KTP crystal is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of Nd: YAG laser.

In recent years there has been considerable progress in the development of coherent UV sources based on nonlinear optical process in borate crystals. The success of these crystals can be attributed to the unique structural characteristics of boron-oxygen groups that confer these compounds with enhanced UV transparency, good nonlinearity and high resistance to laser damage. β-Barium Borate, Lithium Borate, Potassium beryllium boro-fluoride, Strontium beryllium borate, Cesium borate and Cesium lithium borate are promising for UV generation because of its wide band gap and adequate optical nonlinearity. YCa₄O (BO₃)₃ (YCOB) and GdₓY₁₋ₓCa₄O (BO₃)₃ crystals are suitable for second and third harmonic generation of Nd: YAG laser radiation [17]. Various kinds of the NLO crystals have been developed because of possibility of extreme high optical nonlinearity [26-29]. The demand for the nonlinear optical crystals with superior perfection and higher second harmonic generation (SHG) efficiency is rising day by day due to the quantum jump in the design of nonlinear optical devices with higher performance. Therefore,
Crystal growth of the nonlinear optical materials has become indispensable and efficacious disciplines in the field of material science and engineering. In recent years there has been a growing interest in the organic materials for the nonlinear optical (NLO) applications because of their high potential, used in a device such as second harmonic generators, electro-optic modulators etc. [30-31].

The NLO materials play an important role in the field of fiber optic communications and optical signal processing. Applications such as laser based imaging, communication; remote sensing and counter measure system require improved nonlinear optical materials to accomplish such conversions. A strong need continues to exist for lower cost, more efficient, higher average power materials for optical parametric amplifier operation and second harmonic generation (SHG) through out the blue near UV spectral regions. Another area of growing need is materials for birefringent, phase matched optical parametric oscillators (OPO) for the generation of broadly tunable microwave and long wave infrared radiation. In the literature it is found that the large nonlinear optical effects make the crystals attractive for applications in frequency conversions. Optoelectronics and nonlinear optics play a major role in photonics, which is emerging as a multidisciplinary new frontier area of science and technology [33-39].
2.5 Reason for Growing Single Crystal

There are two principle reasons for growth of single crystal,

1) Many physical properties of solid are obscured or complicated by the effects of grain boundaries.

2) The full range of tensor relations between applied physical cause and observed effect can be obtained only the full internal symmetry of the crystal structure is throughout the specimen

2.6 Crystal growth

Crystal growth is a first -order phase transition. It is always associated with liberation of latent heat. The transfer of this heat from the solid-fluid interface region to the bulk of the solution is major concern during growth. Additionally the process of mass transfer and the convection modes adopted to achieve the desired mass transport rates present a difficult optimization problem during growth. These transport processes significantly affect the rate of the growing crystal, compositional homogeneity and the surface microstructure over the growing crystal faces. As a result the science of crystal growth is governed by the principles of physico-chemical hydrodynamics during fluid to solid phase transition, where as the technology of crystal growth involves designing and developing necessary apparatus and
instrumentation for achieving the controlled phase transition to enable growth of single crystalline solids [40].

2.7 Crystal growth phenomena

Crystallization is the natural or artificial process of formation of solid crystals from a uniform solution. It is the process of arranging atoms or molecules that are in a fluid or solution state into an ordered solid state. The crystallization process consists of two major's events "Nucleation & Crystal growth "
The crystal start growing process is called Nucleation.

2.7.1 Nucleation

Nucleation is the onset of a phase transition in small region. The phase transition can be the formation of a crystal from liquid. Nucleation is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale, that becomes stable under the current operating conditions. These stable clusters constitute the nuclei. However when the clusters are not stable they re-dissolve. Therefore the clusters need to reach a critical size in order to become stable nuclei such critical size is dictated by operating conditions (i.e. temperature & super saturation). It is stage of nucleation that the atoms arrange in a defined & periodic manner that defines the crystal structure. (i.e. term -refers to the relative arrangements of the atoms.)
Nucleation is an important phenomenon in the crystal growth. The nucleation is the precursor of crystal growth in this solution growth technique. The nucleation may occur spontaneously or it may be induced artificially. These two cases for nucleation are called as homogeneous and heterogeneous nucleation. When the nucleation is generated in the vicinity of crystal present in the supersaturated system, it is referred to as secondary nucleation. The achievement of supersaturation is an essential criterion for crystal growth. Nucleation may occur at a seed crystal, but in the absence of seed crystals usually occurs at some particle of dust or at some imperfection in the surrounding vessel.

Crystal grows by the ordered deposition of material from the fluid or solution state to a surface of the crystal. The probability of nucleation increases with increasing supersaturation.

Growth of crystal can be considered to comprise three basic steps.

i) Achievement of super saturation or super cooling

ii) Formation of crystal nuclei of microscope size

iii) Successive growth of crystals to yield distinct faces.

All above steps may occur simultaneously at different regions of the crystallization unit. However an ideal crystallization process consists of a strictly controlled stepwise program. Meirs and Issac (1987) conducted a
detailed investigation on the relationship between super saturation and spontaneous nucleation [41].

The driving force for crystallization comes from the lowering of the Potential energy of atoms or molecules when they form bonds to each other. Supersaturation is the driving force of the crystallization. Hence rate of nucleation and growth is driven by the existing supersaturation in the solution.

Supersaturations means the solution has to contain more solute entities (molecules or ions dissolved that it would contain under the equilibrium (saturated solution) Producing good quality crystals of a suitable size is first and most important step in determining any crystal structure. The shapes of crystals depend on both the internal symmetry of the material and on the relative growth rate of the faces.

In general the faces of the crystal that grow most rapidly are those to which the crystallizing particles are bound most securely. These rapidly growing faces are usually the smaller, less well developed faces. Thus the larger faces are usually associated with directions in the crystal where there are only weak inter molecular interactions.

There are numerous ways to grow crystals. The choice of methods depends greatly upon the physical and chemical properties of the sample. For solution methods of crystallization, the solubility of the sample in various
systems must be explored. If heating methods are selected for growing crystals; thermal stability and melting point of the sample should be determined.

The techniques of crystal growth chosen will largely depend on the chemical properties of the compound of interest whether the compound is air sensitive, moisture sensitive (hygroscopic).

2.8 Crystal growth techniques

Crystal growing is an art and there are as many variations to the basic crystal growing recipes as there are crystallographers. Crystal growth represents a controlled change of state or phase change, to the solid (condensed) state. This transition may occur from the vapor, liquid, or even the solid state itself. The objective of crystal growth is usually to obtain a single crystal defined as the macroscopic extension of regular repeated geometric network of atoms consisting of one or more elements, from a microscopic scale to a unit bulk single crystal.

Single crystals are grown by many techniques.

Single crystal may be grown by the transport of crystal constituents in the solid, liquid or vapor phase. On this basis, the crystal growth may be classified into three different categories as follows.

Solid Growth ---- solid to solid phase transition

Liquid Growth ---- liquid to solid phase transition

Vapor Growth ---- Gas to solid phase transition
2.8.1 Solid Growth

In this method of crystal growth the single crystals are grown by solid to solid phase transition. The solid state growth requires atomic diffusion in the given material. If a polycrystalline material is held at an elevated temperature, below the melting point for many hours, some grains may grow at the expense of their neighbors. To improve this method, strain annealing and zone heating techniques are used [42]. This method of crystal growth is limited only for those materials which are stable at the high temperature where appreciable diffusion can occur. The metal crystals are particularly grown by this method. However it is unlikely that any process which is carried out in the solid state can reproducibly result in crystals with the necessary high quality required for any applications.

2.8.2 Vapour Growth

In vapour growth, the vapour obtained from solid phase at an appropriate temperature is subjected to condense at a lower temperature by utilizing the concept of vapour transport reaction. In this method the suitable transporting agent is required which is a formidable problem in this technique. This method is commercially important due to the production of thin layers by chemical vapour deposition (CVD), where usually irreversible reactions are used to deposit materials epitaxially on a substrate.
2.8.3 Liquid Growth

The liquid growth involves the liquid to solid phase transitions. Many techniques of crystal growth come under the category of liquid growth method, particularly Melt growth, Gel growth and solution growth. The process of crystal growth essentially involves a change of phase where the molecules of the material undergoing the change of phase are gradually, uniformly and continuously losing their random character achieve the long range order. A number of techniques for the preparation of crystalline materials have been developed essentially to suit the requirements of different perfection for their intended applications. Crystal growth techniques have been divided into two categories Direct and Indirect techniques [43].

The direct techniques are those that do not contain any components other than those of the desired crystal product. The phase, from which the crystal is growing, whether it is vapor, liquid, or solid, has the same overall major constituency (excluding trace impurities, whether added for doping purposes or inadvertently present) as the growing crystal.

An indirect technique involves the use of either additional foreign components or excesses of constituent components that act as mineralizes, fluxes, solvents, or carries of the constituents. These indirect techniques include the growth of crystals that decompose on melting to form a
liquid and another solid of different compositions; these are referred to as incongruently melting compounds

### 2.9 Classification of crystal growth techniques:

#### Table 2.1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Source</th>
<th>Growth technique</th>
<th>Source</th>
<th>Growth technique</th>
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<tbody>
<tr>
<td>Liquid</td>
<td>Melt</td>
<td>Directional solidification</td>
<td>Flux-solution</td>
<td>Slow cooling</td>
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<td>Bridgman - Stockbarger</td>
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<td>Temperature gradient tech.</td>
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<td>Kyropoulos technique</td>
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<td>Solvent evaporation</td>
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<td>Czochralski technique</td>
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<td>Top seeded(Isothermal)</td>
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<td>Verneuil technique</td>
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<td>Hydrothermal, Gel</td>
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<td></td>
<td></td>
<td>Zone melting technique</td>
<td></td>
<td>Any solvent aqueous, molten, etc.</td>
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<td></td>
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<td>Heat Exchanger method</td>
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<td></td>
<td></td>
<td>Skull melting</td>
<td>Reaction</td>
<td>Chemical</td>
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<td></td>
<td></td>
<td>Shaped crystal growth</td>
<td></td>
<td>Electrochemical</td>
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<tr>
<td>Vapour</td>
<td>Constituent gas</td>
<td>Sublimation-condensation</td>
<td>Compound gas</td>
<td>Reaction condensation</td>
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<td></td>
<td>(Epitaxy)</td>
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<tr>
<td>Solid</td>
<td>Solid</td>
<td>Recrystallization</td>
<td>Solid solution</td>
<td>Exsolution Spinodal</td>
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<td></td>
<td></td>
<td>Strain</td>
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<td>decomposition</td>
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<td></td>
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<td>Polycrystal</td>
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PVD-Physical vapor deposition; MBE-Molecular epitaxy; ALE-Atomic layer epitaxy; CVD-Chemical vapor deposition; MOCVD-Metal-organic chemical vapor deposition.

2.9.1 Utility factor for various techniques:-

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 vapor, 5 % from low temperature solution, 5 % from high temperature solution, 3 % from the solid and only 2 % by hydrothermal methods [44-45]

2.10 Crystal growth from the melt:-

Melt growth is the process of crystallization by fusion and re-solidification of the pure material, crystallization from a melt on cooling the liquid below its freezing point. 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 important techniques available have summarized in Table 2.1.

The major practical factors to be considered during growth of crystals from the melt are

a. Volatility or dissociability

b. Chemical Reactivity

c. Melting point

The materials which exhibit volatility of one or more of their components require special melt growth technique to prevent evaporation loss during growth. The chemical reactivity of material determines many practical
matters in the growth process. Many oxides and ceramics particularly high melting point materials require one of the noble metals as a crucible material. High melting point inevitably cause problems with high temperature gradients and these can bring severe convection problems. High temperature gradients can be responsible for thermal shock and stress in the materials, which can be severe problems in oxide materials [46-48].

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. Crystallization begins in 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 low melting point materials.

In the Kyropoulos technique the seed crystal makes contact with the melt. The seed is kept cool by circulating water; it thus acts as heat sink for the melt. A small quantity of the melt solidifies around the seed, which is slowly lifted up by enabling more and more of the melt to solidify as a single crystal.

In Czochralski technique, the material is taken in a crucible and is kept in a furnace. 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 consist of components that produce high vapor pressure at the melting point. This refined method of Czochralski technique is widely adopted to grow the III-V compound semi conductors.

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 in 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.

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 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 for use in jeweled bearings and Lasers. This technique was widely used for the growth of synthetic gems.

2.11 Crystal growth from solution:-

A solid crystal (essentially, the solute) can be retrieved from a liquid solution by either cooling slowly or thus changing the solubility relations or by evaporating a solvents that is volatile under the conditions of crystal growth. The solvent can range in composition of the desired crystal (an excess of one of its constituents) to a totally foreign material that dissolves the desired compound under certain conditions such as heating but allows it to solidify intact on cooling. For Important techniques of crystal growth from solution see Table 1. The solution growth, both from aqueous medium and the molten salt solutions, as well as the hydrothermal growth technique are suitable for special cases.
2.11.1 Hydrothermal growth Technique:-

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

Growth is usually carried out in steel auto claves with gold or silver linings. 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, grown by this technique. Quartz is the outstanding example of industrial hydrothermal crystallization. One serious disadvantage of this technique is the frequent incorporation of \( \text{OH}^- \) ions into the crystals which makes them unsuitable for many applications. Quartz is the outstanding example of industrial hydrothermal crystallization.

2.11.2 Gel Growth

Gel is the two component system of semi-solid 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 dimension of several millimeters can be grown in a period of three to four
weeks. In this method crystals are grown at room temperature hence have fewer defects.

**2.11.3 Growth by Electro-Crystallization**

The process of crystal growth from fused salt is analogous in many respects, except for requirements of electron transfer in deposition of metal. Fused salt electrolysis has been used to grow the crystals of oxides in reduced valence states. An important application of the electro-crystallization technique has been in the area of crystalline, low-dimensional molecular solids based on redox active molecular components. The electro-crystallization process typically involves the electrochemical conversion of neutral, planar, conjugated pai-donor or acceptor molecules into ionic species which precipitate at the working electrode upon association with a counter charged ion provided by the electrolyte. This is the method of choice for growing crystals of numerous charge transfer salts, especially molecular conductors and superconductors (Williams et al 1992)

**2.11.4 Solution growth technique**

Out of all methods discussed above for growth of crystal, the solution growth method is widely used to grow the crystals. The principle of this method is based on the concept of solubility and supersaturation. At a given temperature a limited amount of substance dissolved in a particular solvent. This amount defines the solubility at that temperature. The solubility
is function of the temperature of the solvent. In most cases, the solubility increases with temperature. If a saturated solution is prepared at a certain temperature and then cooled to a lower temperature it contains more salt than permitted by solubility at the lower temperature. The same thing happens if some of the solvent is allowed to evaporate. The solution is now in a supersaturated state. This is a metastable state and with the slightest induction, the extra salt precipitates. If a seed crystal is introduced into the solution, the substance precipitating from the solution will grow around the seed crystal forming a larger single crystal. In the absence of the seed even dust particle provide a nucleus for crystal growth.

The mechanism of crystallizations from solution is governed in addition to other factor by the interaction of the ions or molecules of the solute and solvents, which is based on the solubility of substances on the thermodynamical parameters of the process, temperature, pressure and solvent concentration. **Solution growth is advantageous because due to the low temperatures involved, costly and complex growth apparatuses are usually avoided.**

2.11.4.1 Solution, Solubility and Supersolubility

Solution is a homogeneous mixture of a solute in a solvent. Solute is the component which is present in a smaller quantity. Solubility of the material in a solvent decides the amount of the material which is available for
the growth and hence defines the total size limit. Solubility gradient is another important parameter, which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution: while the level of supersaturation could not be varied by reducing the temperature in the former, even a small fluctuation in the temperature will affect the supersaturation to a large extent in the latter resulting in disabling the growth of good quality bulk crystals in both cases. If the solubility gradients are very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution.

![Diagram showing the states of a solution (Temperature Vs. Concentrations).](image)

Figure 2.1 Diagram showing the states of a solution (Temperature Vs. Concentrations).
The crystal growth from solution hinges on achieving supersaturation in the system. The crystal grows by the accession of the solute in the solution as a degree of supersaturation maintained. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of solute in the chosen solvent must be determined before starting the growth process. The compositions of a solution can be expressed in number of ways like,

i) The weight of solute present in a given volume of solution.

ii) The weight of solute present in a given weight of solution.

In the solubility diagram the line joining the points corresponding to the equilibrium concentration at different temperature is called the solubility curve. A typical solubility diagram, as shown in Figure 2.1.

The whole concentration temperature field is separated by the saturated-solution line (solubility curve) into two regions: unsaturated and supersaturated solutions. Saturated solutions are those mixtures which can retain their equilibrium indefinitely in contact with the solid phase with respect to which they are saturated. The solubility of most substances increases with temperature (the temperature coefficient of the solubility is +ve). Crystals can be grown only from supersaturated solutions which contain an excess of the solute above the equilibrium value. The region of supersaturation solutions can be divided into to sub-regions; metastable (stable) and labile (unstable)
zones. The region where spontaneous crystallization is impossible is called stable or under saturated region.

Nucleation will occur spontaneously in the labile zone. Measurable zone refers to the level of supersaturation where spontaneous nucleation cannot occur and a seed crystal is essential to facilitate growth. The solution containing more dissolved solid that represented by equilibrium saturation are said to be supersaturated. It is most important factor for growth of the crystal by solution growth technique, it depend on the temperature of solution. The quality of crystal is depending on supersaturation. There may be different solvents for a given solute.

The solvent must be chosen by taking into consideration the following properties.

(I) High solubility for given solute

(II) High positive temperature coefficient of solubility

(III) Low viscosity

(IV) Low volatility

(V) Less corrosion and non-toxicity

(VI) Low cost

(VII) Maximum stability

The total size of the grown crystal depends on the solubility of the material in the given solvent. The solubility coefficient dictates the growth procedure.
2.11.5 Formation of Supersaturation Solution

The concentration driving force ($\Delta C$) the super saturation ratio ($S$) and relative super saturation ($\sigma$) are related to each other as follows;

The concentration for driving force

$$\Delta C = C - C^*$$

Where $C$ is actual concentration of solution, $C^*$ is equilibrium concentration at given temperature.

Super saturation ratio $\quad S = C/C^*$

Relative Super saturation $\quad \sigma = (C-C^*)/C^*,$

$$\sigma = S - 1$$

If the concentration of the solution can be measured at a given temperature and the corresponding equilibrium saturation concentration is known, then it is easier to calculate the supersaturation.

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

1) Low temperature solution growth

2) High temperature solution growth
2.11.5.1 High Temperature Solution Growth

In the high temperature solution growth a solid is used as the solvent instead of liquid and the growth process takes place well below the melting temperature and is known as flux method. 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 period of several hours and then the temperature is lowered very slowly.

2.11.5.2 Low Temperature Solution Growth

Growth of crystal from aqueous solution is one of the ancient methods of crystal growth. The material which decomposed on heating or exhibits any structural transformation while cooling from melting point can be grown by solution growth technique if suitable solvent is used [49]. Low temperature solution growth is perhaps the most widely practiced method. The formation of crystalline products in scores of industrial processes employs this technique. In this method water is widely used as solvent, which is cheap, low viscosity, high solvent action, high stability, non toxic and easily available. The principal advantage of this method is that temperature ranges near to 100°C which result in simple and straight forward equipment design which gives good degree of control to an accuracy of ±0.01°C, due this precise temperature control, the supersaturation can be very accurately controlled, also
the efficient stirring of solution reduces fluctuations to a greater extent. This method is relatively simple, cheap and widely used to grow the bulk crystal [50-67]. Due to the low temperature, there is small thermal stress on the grown crystal. The crystals grown by this method usually have well developed faces. One of the basic factors in the growth of crystal from the solution and study of kinetics of crystallization is the stability with which the super saturation is maintained and the determination of the change in super saturation can be accurately controlled. This is only method for growth of substances that undergo decomposition before melting.

Solution growth is carried out by placing one or more crystallographically oriented seeds in a saturated solution, then supersaturating the seed region in such a way as to control the growth process. At any temperature, there is a range of small super saturations (metstable region) within which nucleation can be kept under control. Beyond this range, at greater supersaturations (labile region), the growth process becomes uncontrollable because of spontaneous nucleation.

Low temperature solution growth methods can be sub divided into three methods

i. Slow cooling method

ii. Slow evaporation method

iii. Temperature gradient method
2.11.5.2.1 Slow Cooling method

A saturated solution is slowly cooled in growth vessel in which one or more seeds are located on a seed supporter, which also acts, in the solution bulk, as a rotating stirrer. The growth vessel is usually placed in a thermostatic bath. In this method the supersaturation is achieved by changing the temperature usually throughout the crystallizer. When applying these techniques to the NLO single crystals an appropriate solution circulation (stirring) is needed to minimize super saturation and temperature non uniformities ahead of the growing interface. This will favor compositional and structural homogeneity (i.e. a good optical quality) in the final crystal. The main disadvantage of this method 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 growth period.

2.11.5.2.2 Slow evaporation method

These techniques which are based on a controlled supersaturation increase by means of a programmed solvent evaporation under isothermal conditions. In the slow evaporation method the temperature is fixed and provision is made for evaporation. For the evaporation in the atmosphere the nontoxic solvent like water is used. The main advantage of this method is that the crystal grows at the constant temperature. This method has been widely used for materials having very small temperature coefficient of solubility or
negative temperature coefficient. In the present investigation all crystals are grown by employing the slow evaporation method.

In contrast to the cooling method, in which the total mass of the system remains constant, in the solvent evaporation methods, the solution loses particles which are weakly bound to other components and therefore, the volume above of 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)

2.11.5.2.3 Temperature gradient method

A temperature gradient is applied to a saturated solution in which the solute (i.e. the source material) is present as a solid phase. The higher temperature which is chosen to be the saturation temperature is imposed on the source region, usually the bottom of vertically positioned glass tube. When a seed is located in the colder end of the tube it will start growing, since at any temperature below the saturation one the solution is supersaturated. When growing crystals great care should be taken to work far from the "labile" region. This means using temperature gradients not exceeding 1 to 2 °C per cm. In this method of crystal growth the transport of material takes place from the hot region where the source of material is placed to the cooler region where the super saturation is achieved. The economy of solute and solvent is the main advantage of this method of crystal growth.
2.11.5.2.4 Advantages of Low Temperature Solution Growth

The low temperature solution growth method has following advantages.

- Growth apparatus is simple and very cheap
- Small thermal stress on the grown crystal due the low temperature
- The crystals obtained usually have well-developed faces which enable to investigate crystal growth process including insitu observations and capture impurities
- It is the only method for the growth of substances that undergo decomposition before melting

The low temperature involved, costly and complex growth apparatuses are usually avoided. The low temperature solution growth technique has the following conditional limitations.

i. The growth substance should not react with solvent

ii. This method is applicable for substances fairly soluble in a solvent

2.12 The equipment is required for the growth of crystals

2.12.1 Constant Temperature Bath (CTB):-

CTB is required for the growth of good quality crystal. The temperature affects the driving forces of crystallization very much, highly stable temperature maintenance is essential throughout the growth process. To achieve this, an active thermo stating systems with fine controlling accuracy is necessary. A general design of a thermostat with a control system, also
known as constant temperature bath (CTB). It consists of a thick-walled glass chamber filled with water, heating element, temperature sensor, control relay, temperature indicator, stirrer and illuminating lamp. The long periods necessary to grow crystals and the need to avoid any interruption of the temperature control process mean that special measures must be taken to ensure that the control system is reliable. A CTB designed and fabricated for the present work is shown in Figure (2.2).

It has an ability to hold a crystallizer of 10 liters of maximum capacity. Instead of using general purpose water heaters, which always gives temperature fluctuations in huge amount due to thermal inertial an optical heating system is employed in this CTB. It has three 250 W Philips Infrafil lamps energized through a relay circuit. Power to these lamps is controlled by a Triac based electronic circuit comprising active and passive components. For initial heating, an immersion heater of 500 w is fixed in the bottom of the chamber. The CTB has a provision to set and read the temperature with an accuracy of ±0.01 °C by means of three and half segment digital display. Also it has the capacity of controlling the temperature with an accuracy of ±0.01 °C in the temperature range from ambient to 100 °C.
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