PART - I

CHAPTER – 1

CRYSTAL GROWTH

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The word "Crystal" as used in every day life may have different meanings for a layman and for a scientist. One thinks of the glistening grains in certain kinds of rocks, sculptured figures in museums, sugar, diamonds, rubies and sapphires or even of simple 'Crystals and cat's whisker' type of radio receiver. Studies of various physical and chemical properties of crystals carried out by earlier scientists have brought them into the scientific field.

In almost all branches of physics, idealization of the actual system under study have been used either in the form of an approximation in a theory or as a means of providing basis for developing a new theory. These idealizations consist mainly of directly or indirectly imparting orderliness to the system. With the discovery of existence of crystalline state of solids in nature by Rene Just Hauy (1743 – 1822), the concept of orderliness in particular or symmetry in general, was justified as being a valid and fundamental attribute of the natural world. As we know today, the theories based on a single crystalline solid have helped us a lot in understanding properties of materials, both crystalline and non-crystalline. Apart from this, the crystalline state of a substance itself has proved to be of enormous use in its application in various fields of technology which is, by large, responsible for the present state of civilization.

With increasing applicability and usage, the need of producing artificial crystals has increased. Single crystals are of great interest in solid state physics which, apart from basic physical properties, also deals with piezo and ferroelectricity, luminescence, photoelectricity and semiconducting properties, etc., for development of devices like transistor, diode, piezoelectric transducers, capacitors, etc. Such fast expanding field of crystal physics is not limited to electronic and mechanical technology and chemical processes but also in metallurgical sciences, geophysics and biosciences. To grow a good crystal is an art as well as a science(1).

During 1936 to 1949, Stockbarger grew about 1500 fluorite crystals for military applications in high-quality optical lenses and Nacken successfully synthesized quartz crystals during the Second World War. It was beginning of the systematic growth of synthetic quartz crystals. The vast field of applications of synthetic crystals is illustrated in Table – 1.

For the growth of synthetic crystals, there are many techniques developed. However, the success of the technique in obtaining good, pure and large crystals depends on various factors:

(a) Nature of material itself

(b) Its purity

(c) Thermal environment

(d) The rate of growth

(e) Pressure

(f) Diffusion coefficients of the materials

(g) Impurity concentration and

(h) Homogeneity.

Crystals of a particular material can be grown by one or more of various techniques and the choice of a particular technique for growing crystals depends on the material properties and the purpose of application. Hence a systematic classification of growth techniques to simplify this problem has been given by Laudise(2). There are three basic categories of the crystal growth process:

(1) Solid growth : S → S Processes involving solid-solid phase transitions.

(2) Vapour growth : V → S Processes involving gas-solid phase transitions.

(3) Melt growth : L → S Processes involving liquid-solid phase transitions

Table– 1

APPLICATION OF SINGLE CRYSTAL IN VARIOUS TECHNOLOGIES

1. Cutting and Abrasives: Sapphire, Diamond, SiC
2. Electroluminescent devices: GaP, GaAs, Ga(AsP)
3. Electromechanical transducers: Quartz, Rochelle salt, ADP, CdS, GaAs
4. Filters and Oscillators: Quartz
5. Infra – red detectors: $Cd_x Hg_{1-x} Te$, InSb
6. Industrial bearings: Sapphire, Ruby
7. Lasers: $CaWO_4$, CaF_2, Yttrium-Aluminum Garnet, Ruby
8. Laser modulators, Harmonic generators and parametric devices: K.D.P., $LiNbO_3$, $LiTaO_3$, Barium Sodium Niobate
9. Microwave limiters and tunable filters: Yttrium- Iron Garnet
10. Optical uses: CaF_2, Quartz, LiF, Calcite
11. Optoelectronic devices: GaAs
12. Radiation detectors : Anthracene, KCL, Si,GaAs, NaI doped with Tl,Ge doped with Li, Triglycine Sulphate, BaF_2, CsF, Csl, BGO
13. Rectifiers: Si and Ge as the base materials
14. Strain gauges: Si, Ga(AsP)
15. Thermoelectric devices and Electronic cooling system: $(Sb_x Bi_{1-x})_2 Te_3$
16. Transistors: Si, Ge, GaAs as the base materials
17. Tunnel diodes, parametric diodes and single diodes: GaAs
18. Ultrasonic amplifiers: CdS

CRYSTAL GROWTH FROM SOLID-STATE :

The method is rarely used and good quality crystals of large size can not be obtained by this method. However, whenever the crystal structure changes due to change in temperature, this method may become useful provided the melting point of the crystal to be grown is sufficiently high.

Polycrystalline solids contain numerous crystallites. Crystals of useful size can be obtained by straining and subsequent annealing at high temperature where stored energy of deformation serves as the driving force of recrystallization by way of the process known as grain growth. The crystalline grains in favorable orientation and relatively larger than the surrounding grains grow at the expense of others.

CRYSTAL GROWTH FROM VAPOUR PHASE :

The method is useful when the size of the crystal is not important. Crystals with good perfection can be obtained from its vapour phase. The method has its own theoretical importance and is used also for production of thin films and also small good quality crystals(3). The technique has been reviewed by several workers(4-8). This method is further divided into three categories:

(1) **Sublimation:** The source material is subjected to a temperature gradient with sublimation made possible by using a suitable high

temperature as the source temperature. The sublimated material condenses into a crystalline solid if proper control over temperature and pressure conditions is maintained.

(2) **Vapour transport :** The transport of the source material takes place as a volatile species by a suitable carrier gas to the crystallization region.

(3) **Gas phase reaction :** The growth of the crystals takes place as a product, from the vapour phase, as a direct result of chemical reaction between the reactant vapour species.

This method of crystal growth has been in use chiefly due to its theoretical importance. It is rarely possible to grow large crystals by this method due to the problem of multinucleation, although exceptions such as CdS, ZnSe, GaP, GaAs and Cd_4GeS_6 are known. The commercial importance of this method is in the production of thin films. The theoretical and practical aspects of crystal growth from vapour have been reviewed by various authors(1-5)

CRYSTAL GROWTH FROM AQUEOUS SOLUTION :

This is the simplest and oldest method of growing crystals in which the material to be crystallized is dissolved in water to the desired degree for supersaturation. The solution is then slowly cooled or evaporated. Using a seed crystal and precise control over temperature, humidity and rate of evaporation, excellent quality large crystals can be grown. Well-known examples are ferroelectric and piezoelectric materials such as ADP, KDP and TGS. Requirement of high solubility in water and chemical stability of solution are limitations of this method to be applicable to many other materials.

CRYSTAL GROWTH BY GEL METHOD :

The growth of crystals from gel was recorded as early as 1913 by Leisegang, Gradford and Holmes. Substances having low solubility in water can be grown by gel method, in which the constituent ions of the material slowly migrate through an inorganic or organic gel, react and form the compound. Hence the crystals grown by gel method are free from strain which is often present in the crystals prepared from melt or from vapour. The crystal is nucleated when the concentration of the compound exceeds its solubility limit. However, for a certain class of substances which have very slight solubility in water and which cannot be satisfactorily grown from melt or vapour, it offers reasonable prospects of success. The crystals like TGS, DGS, $KClO_4$ have been grown successfully in this laboratory by this method. Obviously the method is more useful for organic and semiorganic compounds. The method has been discussed in details by Henisch(9).

HYDROTHERMAL GROWTH :

Metals and metal oxides and other compounds which are insoluble in water show appreciable solubility at high temperature and high pressure in suitable solvents. Oxides are generally grown from alkaline solution and metals from acidic solutions. The requirement of the high pressure is a practical difficulty in this method. The size and quality of the crystals obtained by this method are poor. The industrial production of commercial piezoelectric quartz crystals is an exception. The method has been discussed in detail by Ballman et al(10) and James et al(11).

GROWTH BY HIGH TEMPERATURE SOLUTION METHOD :

This method is basically a solution method with the main difference of high melting point solvents being used. The melting point of the solvent is usually above 600 ^{0}C. Though this basically involves practical difficulties of proper choice of solvent, chemical and phase stability of the solute and solvent, high melting point, obtaining high temperatures, contamination etc., many important materials are being grown by this method. The perfection of crystals that can be achieved in this method is quite higher than obtained in any other method. On the other hand, the crystals obtained by this method have higher concentration of impurities than in other methods. Also the optimum growth rate in this method is quite small compared particularly to melt growth. Elwell and Scheel$^{(12)}$ have given an excellent account of the principles and techniques involved in this method.

CRYSTAL GROWTH FROM MELT :

This is probably the most useful and most widely used method mainly due to the high growth rates obtainable and because it is easily susceptible to modification. Crystals of metals, metallic alloys, semiconductors, superconductors, ionic solids and alkali halides can be grown from melt. Apart from this, crystal growth from melt carries maximum theoretical important since it is directly the process of phase change from liquid to solid involving systematic aggregation of atoms or molecules into crystalline order from their random distribution in liquid state of the same substance.

The principles of the crystal growth from melt are based on cooling of a liquid (i.e., melt) to solidification in a controlled manner. The solidification process should be so controlled as to promote extension of a single nucleus without producing new nuclei and with minimum of chemical and structural disorder in the growing crystal. Formation of a new nucleus and instability of the growing surface can be eliminated by avoiding extensive zone of supercooling in the melt. This can be done by governing the phenomenon of heat transport in the solidification process. The latent heat continuously evolving at the freezing solid-liquid interface must be removed by conduction along the solid charge, for which a temperature gradient should be present along the solid. More frequently, there exists a temperature gradient in the liquid with the temperature increasing away from the interface, in which case there is a net flow of heat through the freezing interface from the melt, which also must be conducted down the solid. The heat transfer can be described by the equation

$$K_S G_S - K_L G_L = LV$$

where ,

K_S = thermal conductivity of solid

K_L = thermal conductivity of liquid

G_S = temperature gradient in solid

G_L = temperature gradient in liquid

L = latent heat of fusion per unit volume

V = growth velocity

The melt is allowed to solidify in a controlled manner. Many parameters affect the growth process, such as the temperature gradient, the growth velocity and the composition of molten charge. In the case of alloys, if a gradient in composition is established in the liquid during growth there results non-uniform composition of constituents in the alloy crystals and also the constitutional supercooling. The composition of frozen material in such a case is always different from that of the liquid or the molten charge. The instability of interface occurs and cellular structure results. Tiller et al(13) and Delves(14) have shown that the constitutional supercooling can be reduced to minimum

(1) by having slow growth rate

(2) by stirring the melt to minimize solute concentration gradient and

(3) by having a steep temperature gradient.

During crystal growth in such cases, solute segregation occurs at the solid-liquid interface due to unequal equilibrium solute concentrations in the liquid and solid states of the solvent. The segregation is characterized by a segregation coefficient k, which is the ratio of equilibrium solute concentration in solid to that in liquid. Usually, in most of the alloy systems, $k < 1$. For such cases, during crystallization, the solute concentration in the liquid near the interface will increase. The solute rejected at the interface can diffuse into the bulk of the liquid and distribute itself uniformly for sufficiently slow growth rates. In practice, however this condition is not achieved and a concentration gradient is established in the liquid. The solute segregation may cause

(1) Crystal with non-uniform solute distribution along the length of the crystal

(2) Constitutional supercooling.

Rutter et al(15) had introduced the concept of constitutional supercooling. Constitutional super-cooling results in the instability of the interface giving cellular structure, dendritic structure, stray nucleation, waviness of interface, etc., spoiling the quality of the crystal obtained. Further, Delves(14) has defined a parameter "S" known as constitutional supercooling parameter which is given by

$$S = \frac{mG_{LS}}{G_L}$$

where, G_{LS} = solute concentration gradient in liquid

$= -V(C_L - C_S) / D$

V = growth speed

D = diffusivity of solute in liquid

C_L = concentration in liquid

C_S = required concentration in solid

m = slope of the liquidus line at the given composition of alloy

G_L = temperature gradient in liquid

It has been shown that if $S > 1$, constitutional supercooling will occur.

Thus by using slow growth rate, good stirring of the melt to minimize G_{LS} and using steep temperature gradient, chances of constitutional supercooling can be greatly reduced. However, very small growth rate would require extreme care in maintaining stable thermal environment and very much steep gradient would produce curved interface.

The crystal growth from melt can be pictured as an atom- to – atom addition to lattice similar to the growth from vapour and the experimental evidences rule out the necessity of a screw dislocation to promote the growth of metal crystals from melt. This has been concluded from a number of observations. Firstly Dash(16) has successfully grown large areas of single crystals of silicon free from dislocations. A few other metal crystals have also been grown without observable dislocation. Secondly, if the dislocations are necessary to promote growth, the high symmetry of the dendritic growth cannot be accounted. Hence the conclusion of nucleation at the re-entrant edge of a screw dislocation is not so important for the growth of metal crystal from melt. Chalmers et al(17) have proposed a step like interface which provides permanent re-entrant steps which are not propagated by dislocation and evidences for the existence of such steps have been obtained.

Study of crystal growth from melt mainly involves

1. Study of morphology of the interface and the effect of various growth parameters on it.
2. Study of the growth features observed on the crystal grown from melt

3. Study of imperfections, their formation and distribution in the crystal and

4. Study of preferred orientation and the influence of various parameters responsible for this property of crystals.

Many crystals have been grown from melt by various workers and many reviews have been published(18 – 23).

There are three basic techniques for crystal growth from melt:

(1) Bridgman method

(2) Czochralski method and

(3) Zone melting method.

A short account of these methods is given below.

1. BRIDGMAN METHOD :

This method was first developed by Bridgman(24) in 1925 to grow single crystals. In this technique, the melt in a suitable container is moved relative through a fixed temperature gradient so that the solidification starts from one end and proceeds gradually to the other. The tip of the container, which enters the freezing temperature region first is usually kept conical so that initially only a small volume of the melt is supercooled. As a result, only one nucleus is formed or if at all more than one nuclei are formed, only one nucleus with favorable orientation is given the chance to grow by the tapering end. To this method, a modification was introduced successfully by Stockbarger who used two furnaces at different temperatures and separated by a baffle, instead of using a single furnace. This method is called Bridgman – Stockbarger method and provides for desired variation of the temperature gradient. The limitation of Bridgman method is that, it can be used only for the low melting point metals, which is overcome by the horizontal moving furnace technique given by Chalmers(25). The Bridgman method has been most frequently applied for three types of material:

1. Metals-(26 – 27)
2. Semiconductors(28-29)
3. Alkali and Alkaline Earth halides(30 – 31)

As per the specific requirements posed by the nature of materials, the technique has been developed into a sophisticated one. Kumagawa et al(32) have grown ternary mixed crystals on InSb and GaSb seed crystals successfully by the Bridgman method with high-speed rotation of about 80 to 120 rpm. The growth of $(Sb_xBi_{1-x})_2Te_3$ single crystals with programmable temperature control by vertical Bridgman method has been reported by Fang-Lang Hsu(33). Yokota et al(34) have grown Cadmium telluride crystals by horizontal two-zone Bridgman furnace in quartz ampoules evacuated to as low a pressure as 3×10^{-7} Torr. Voda et al(35) have grown pure and doped CdF_2 single crystals by Bridgman method wherein unwanted vapour reaction were avoided by using an argon atmosphere and glassy carbon crucibles. Cabric et al(36) developed a method for crystallization of several substances at different rates in a chamber furnace. Siddiqui(37) has grown eutectic intermetallic compound alloy crystals by the Bridgman-Stockbarger method. One of the important present day semiconductors namely CdTe crystals are also usually grown by the Bridgman method(38).

2. CZOCHRALSKI METHOD :

Czochralski(39) developed a melt growth method in 1918. This method is known as Kyropolous method or a crystal pulling method. In this technique, the material to be grown is melted in a suitable crucible. A seed crystal is then dipped slightly into the melt and slowly pulled away from the melt. The seed is simultaneously rotated also to attain thermal symmetry and to stir the melt. Accurate control of temperature and rates of pulling and rotation are the main requirements for obtaining good crystals. The diameter of the growing crystal depends on the temperature and the pulling rate while it is limited by the diameter of the crucible. Crystals of various materials have been grown by this method(40 - 43). Gilman(1) and Brice(43) have discussed the principles of the method. Practical aspects of the technique have been treated in detail by Draper(44). The excess of heat is removed by conduction and the water circulation through the seed-holder which also helps in maintaining temperature gradient. The essential factors for obtaining good crystals are

a. accurate control of temperature

b. pulling rate

c. rotation rate of seed

The technique has reached hi-tech status due to its applicability for technologically important materials.

Laudise et al(45) have grown doped single crystals of Bi_2Te_3 by Czochralski method in H_2 and in inert atmospheres. Wenzl et al(46) have grown copper crystals by Czocharaski method in a hydrogen atmosphere at a pressure of 1 bar. A modification known as liquid encapsulated Czochralski technique has also been used(47).

3. ZONE - MELTING METHOD :

This is relatively a more efficient method of growth from melt discovered by Pfann(48) in 1952. In this method a small molten zone is created in a large solid ingot of the material to crystallize and is passed from one end of the ingot to the other end. The quality of the crystals depends on the relative zone length, growth velocity and the temperature gradient. The smaller the zone length, the better is the quality of the crystal.

The impurity concentration is generally required to be varied in one of the following ways:

(1) Impurity removal :

This method is capable of purifying a material to utmost sparse level of impurities by giving a large number of passes to the ingot in the same direction, the process being known as zone refining process. Here various impurities are collected at the two ends of the ingot (depending on their segregation coefficients). In this process, the impurities with segregation coefficient $K > 1$, are collected at the end molten and frozen first, whereas the impurities with segregation coefficients $K < 1$, are collected at the other end. The portion between the two ends of the ingot can be obtained purer and purer after each successive zone pass.

(2) Uniform doping of impurity :

An ingot doped with a known impurity can be made uniform in impurity distribution by the process known as zone – leveling. In this process, a molten zone is repeatedly passed through the length of the ingot in alternate directions. After several such repeated runs, effects of segregation of dopant can be virtually eliminated and the ingot can be made homogeneous. Discontinuous bands of impurity such as in a p-n junction are often required in the fabrication of semiconductor devices. This can be efficiently done by the zone-melting technique.

The factors affecting crystal-growth by zone melting such as the ratio of zone length to ingot length, speed of zone travel and the temperature gradient at the solid-liquid interface should be properly adjusted. The theoretical and practical aspects of this method describing various modifications are discussed in detail by Parr(49) and Shah(50). Herington(51) has reviewed the technique with particular reference to organic compounds. This method is widely used to grow crystals and to refine various materials by different workers, e.g. Harman et al, Richards, Delves, Hamaker et al, Brower et al, and Swineheart(52- 57). Balazyuk et al(58) have grown cadmium antimonide and zinc antimonide single crystals by zone-melting method to study the effect of crystal growth condition on the structural perfection and thermal propereties . Lunin et al(59) have studied the distribution of AlSb in varizone layers of $Al_xGa_{1-x}Sb$ growing in a temperature gradient field. Shukla et al(60) have grown $CdBr_2$ single crystals by the zone-melting method. Serra et al(61) have successfully grown large area zinc sheet crystals by using a modified zone-melting method. This is a hybrid of the zone-melting and the horizontal Bridgman techniques. Fan Zhanguo et al(62) have used the zone-melting method for preparing YBaCuO superconductor successfully.

A detailed account of the work on growth of InBi:Sb and InBi:Se single crystals is given in chapter 6.

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