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Introduction to Crystal Growth Techniques

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Abstract:

Man had admired crystals for long, as he had appreciated their beauty. The gems and crystals delivered by mother earth have always attracted our mankind, and the belief in the virtues of gems and some minerals dates back to at least two thousand years. The use of gems for ornamental purposes appears to be in practice since the birth of humankind. Today, crystals are the pillars of modern technology. Without crystals, there would be no electronics industry, no photonics industry, no fibre-optic communications, very little modern optical equipment and some very important gaps in conventional production engineering. In the past few decades, there has been a growing interest in crystal growth process, particularly in view of the increasing demand of materials for technological applications (Laudise 1975; Brice1986; Nalwa and Miyata 1996).

The significance of crystal growth to electrical engineering, chemistry and physics is illustrated in Figure 1.1. Modern technology requires physicists, chemists, electrical engineers, metallurgists and crystal growers to assist each other at many levels. Crystal growth is a vital and fundamental part of materials science and engineering, since crystals of suitable size and perfection are required for fundamental data acquisition and for practical devices such as detectors, integrated circuits and for other applications.

Keywords **— crystals, L-histidine, nonlinear optics, second harmonic generation, Barium nitrate.**

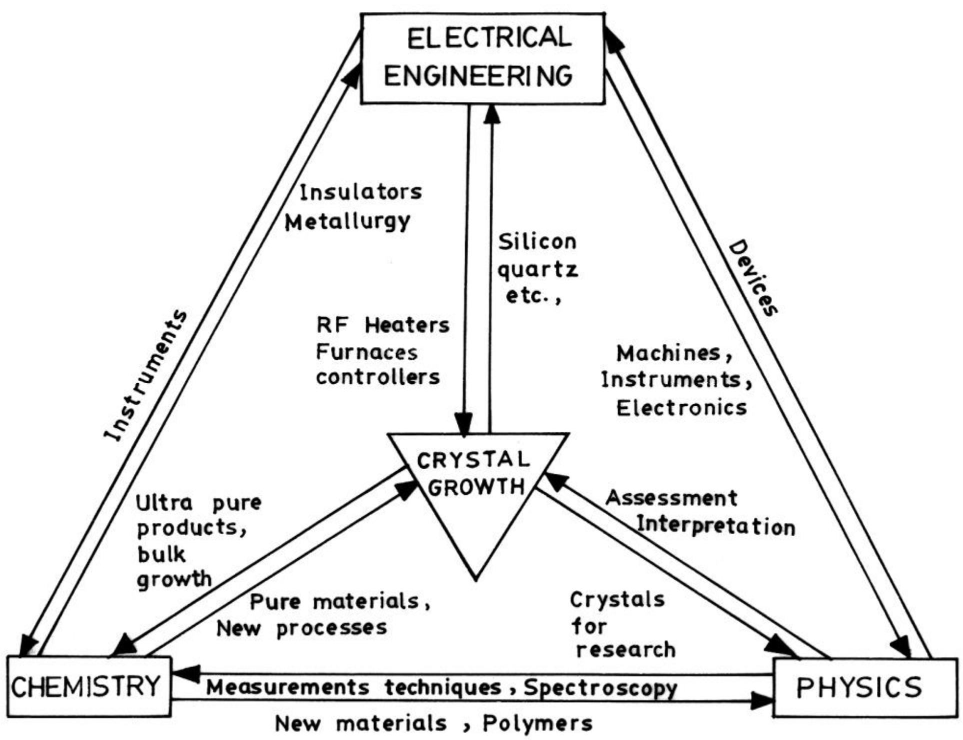

Figure 1.1 Significance of crystal growth to electrical engineering, chemistry and physics

Progress in crystal growth is highly demanded in view of its recent advancements in the fields of semiconductors, polarizer's, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optic, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer industries. The utility of crystals has been extended from the bounds of ornaments to several useful applications in optical, electrical and optoelectronic devices. The fantasy of their external beauty was understood more thoroughly through the natural laws of mathematics, physics and chemistry. The contents of the crystals and their insides were explored, analyzed and understood by modern methods of diffraction as well as with the help of spectroscopic techniques. The external shapes, planes and colours were correlated with the internal atomic content and their arrangements in unequivocal terms. Thus grew a science, the study of "crystal growth and characterization".

Introduction:

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. The starting points are the historical works of the inventors of several important crystal growth techniques and their original aim. The methods of growing crystals are very wide and mainly dictated by the characteristics of the material and its size (Buckley 1951; Mullin 1976).

The methods of growing single crystals may be classified according to their phase transformation as given below.

Growth from solid → Solid solid phase transformation

Growth from liquid → Liquid solid phase transformation

Growth from vapor → Vapor solid phase transformation

The above methods have been discussed in detail by several authors (Brice 1986; Pamplin 1980; Chernov 1984). The different techniques of each category are found in reviews and books by Factor and Garret (1974) on vapour growth, Brice (1973) on melt, Henisch (1988) on gel growth, Buckley (1951) on solution growth and Elwell and Scheel (1975) on high temperature solution growth.

The basic common principle in all these methods is that a nucleus is first formed, and it grows into a single crystal by organizing and assembling ions or molecules with specific interactions and bonding, so that the process is slow and multiple nucleations is minimized. Crystal growth process and size of the grown crystal differ widely and are determined by the characteristics of the material. An efficient process is the one, which produces crystals adequate for their use at minimum cost. 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.

Growth from Solution

The crystal growth from liquid can be classified into six categories namely,

(i) Melt growth
(ii) High temperature solution growth (Flux growth)
(iii) Hydrothermal growth
(iv) Gel growth
(v) Electrocrystallization and
(vi) Low temperature solution growth

There are number of growth methods

in each category. Among various methods of growing single crystals, solution growth at low temperature occupies a prominent place owing to its versatility and simplicity. Growth from solution occurs close to equilibrium conditions and hence crystals of perfection can be grown. Study of anisotropy of the properties of crystals requires specimens cut in different orientations from the same single crystal. This can be easily done from crystals of large size.

Growth from melt

Melt Growth is the process of crystallization by fusion and resolidification of the pure material. In this technique apart from possible contamination from crucible materials and surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than that possible by other methods. Mainly for the latter reason, melt growth is commercially the most important method of crystal growth. The preferential role of the electrochemical process responsible for the change in composition of the crystals when they grow in melt in an applied field has been studied (Balasanyan et al1990). The growth from melt can further be sub-grouped into various techniques.

The main techniques are:

Bridgman Technique
Czochralski Technique
Zone melting Technique
Verneuil Technique
Heat exchanger Method
Skull melting and
Shaped crystal growth

The major practical factors to be considered during growth of crystals from melt are, (a) volatility, (b) the chemical reactivity and (c) the melting point.

High temperature growth (Flux growth)

Flux and hydrothermal growths form the category of high temperature solution growth. In the growth of crystals from 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 supersaturation 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: first one is growth from single component systems and the second one is that from multi-components. In this method, a solid (molten salt/flux) is used as the solvent instead of liquid and the growth takes place well below the melting point (Hubner 1969) of the solute. The success of crystal growth from high temperature solution largely depends on the selection of the solvent system.

This technique can be used for the crystallization of oxide compounds which generally have high melting points as well as for materials which have phase transitions below the melting point (Ramachandra Raja et al 1993). The crystals grown from melt have lower concentration of equilibrium defects and lower dislocation density. One major disadvantage of this method is the corrosive nature of the fluxes used, which attack the common furnace materials.

Hydrothermal growth

The term hydrothermal means, literally, “hotwater”. But in the jargon of the crystal grower, hydrothermal also implies conditions of high pressure as well as high temperature. Closely related to growth from aqueous solution at ambient or near-ambient conditions is growth from hydrothermal solution. Hydrothermal growth is usually defined as the use of an aqueous solvent at elevated temperature and pressure to dissolve a solute which would ordinarily be virtually insoluble at ambient conditions. The disadvantages of the hydrothermal techniques are mainly associated with high pressure and inability to observe growth during the process. Quartz is the crystal grown industrially by this technique.

Gel growth

The growth of variety of crystals having immense importance for their practical consideration and theoretical interest has been achieved by gel technique (Henisch 1988). The importance of the gel growth is attributed to its simplicity in technique, effectiveness in growing single crystals of compounds that cannot easily be grown by other methods. Though the origin of the method dates back to 1899 – the famous work of Liesegang who discovered the periodic crystallization in gels, interest in gel technique received attention only after the work of Henisch and his co-workers (Henisch 1970; Henisch 1988; Henisch and Garcia-Ruiz 1986). Crystal growth in gels is a promising technique for growing single crystals of substances which are slightly soluble in water and which cannot be grown conveniently from melt or vapour. The gel method has also been applied to study the crystal formation in urinary calculi and rheumatic diseases.

Electrocrystallization

Electrocrystallization is the basis for important fields such as corrosion, energy storage and generation, electrodeposition, electronics material development, electrorefining and electrotwinning etc. Crystallization without chemical transformation or charge transfer is the simplest case. In certain instances, the crystallization is determined by a chemical transformation occurring prior to or simultaneously with the crystallization process. The part played by the chemical reaction is to supply the material, which crystallizes. Electrocrystallization is the process, which leads to the formation of a new face at the electrode/electrolyte interface, which in turn plays a major role.

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. The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Much attention has been paid to understand the growth mechanism of the process.

Materials having moderate to high solubility in temperature range, ambient to 100 ^{O}C at atmospheric pressure can be grown by low temperature solution growth method. This method is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperature (Pamplin 1979). This method is widely used to grow bulk crystals, which have high solubility and have variation in solubility with temperature (James and Kell 1975; Chernov 1984). 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 (Brice 1972). The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance, which can be grown by variations of growth conditions or of solvent. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and on 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 undergoing so many modification and refinements, the process of solution growth now yields good quality

crystals for a variety of applications.
Low temperature slution growth can be subdivided into the following methods:
(i) Slow cooling method
(ii) Slow evaporation method and
(iii) Temperature gradient method

Conclusion:

Solution preparation and crystal growth

For solution preparation, it is essential to have the solubility data of the material at different temperatures. Sintered glass filters of different pore size are used for solution filtration. The clear solution, saturated at the desired temperature is taken in a growth vessel. For growth by slow cooling, the vessel is sealed to prevent the solvent evaporation. Solvent evaporation at constant temperature can be achieved by providing a controlled vapour leak. A small crystal suspended in the solution is used to test the saturation. By varying the temperature, a situation where neither the occurrence of growth nor dissolution is established.

The test seed is replaced with a good quality seed. All unwanted nuclei and the surface damage on the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after saturation. Solvent evaporation can also be helpful in initiating the growth. The quality of the grown crystal depends on the (a) nature of seed, (b) cooling rate employed and (c) agitation of the solution.

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