

An Investigation of the Techniques and Advantages of Crystal Growth

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Abstract: An ideal crystal is built with regular and unlimited recurring of crystal unit in the space. Crystal growth is defined as the phase shift control. Regarding the diverse crystals and the need to produce crystals of high optical quality, several many methods have been proposed for crystal growth. Crystal growth of any specific matter requires careful and proper selection of growth method. Based on material properties, the considered quality and size of crystal, its growth methods can be classified as follows: solid phase crystal growth process, liquid phase crystal growth process which involves two major sub-groups: growth from the melt and growth from solution, as well as vapour phase crystal growth process.

Methods of growth from solution are very important. Thus, most materials grow using these methods. Methods of crystal growth from melt are those of Czochralski (tensile), the Kyropoulos, Bridgman-Stockbarger, and zone melting. In growth of oxide crystals with good laser quality, Czochralski method is still predominant and it is widely used in the production of most solid-phase laser materials.

Keywords: Crystal growth; Czochralski method; Kyropoulos method; Bridgman-Stockbarger method.

1 Introduction

An ideal crystal is built with regular and unlimited recurring of crystal unit in the space. Crystal growth is defined as the phase shift control. Regarding the diverse crystals and the need to produce crystals of high optical quality (to be used in optical and electronic structures), various methods have been proposed for crystal growth. Single-crystal silicon growth was first conducted in early and mid-1950s, it is still used in building optical circuits. Electronic and solid state optic industries are widely based on single-crystal materials [1] and their advance investigating optimal growth process. However, because of the complex nature of growth process and the wide extent of controlling growth conditions, a far distance exists between theory and practice of crystal growth. Crystals, with different sizes and impurities, are grown for different usages in industrial fields. The present paper addresses, different methods of crystal growth and their advantages as well as disadvantages.

A special method is used for each group of elements depending on their usage and importance of their impurity, or consideration of form, impurity and size of crystal.

1.1 Crystal Growth

Impurity in crystal growth changes and improves the physical and mechanical properties of crystals. For example, studies on alkali halides crystals, such as KCl, LiI, and NaCl, show that impurities, such as iridium, increase crystal hardness. Crystal growth of every special matter requires careful and proper selection of growth method. Based on the matter properties, the quality and size of crystal are defined. These methods can be classified as the follows:

- 1) Solid phase crystal growth (solid to solid transition)
- 2) Liquid phase crystal growth (liquid to solid transition) which is divided into two major subgroups:
 - A. Growth from melt
 - B. Growth from solution
- 3) Vapor phase crystal growth (gas to solid transition)

If all the three single-crystal methods can be used for a special material, it is better to select the method based on growth rate, size, form, purity, and economic benefit.

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2 Methods

2.1 Solid Phase Crystal Growth

Solid phase crystal growth is only used for some metals on which tension based annealing is effective and in the cases where a crystal network change occurs between the melting temperature and the room temperature.

2.2 Liquid Phase Crystal Growth

Liquid phase crystal growth, which is diverse and important, involves two subgroups: crystal growth from melt and crystal growth from solution.

2.3 Crystal Growth from Solution

The elements with a high melting point and break down in their melting point or go through several structure phases from their melting point to normal temperature can be grown using this method. It comprises two types: crystal growth from solution at low temperature and crystal growth from solution at high temperature. Crystal growth from solution can be done through gradual cooling of the solution and gradual steaming off the solvent. In the first method, temperature of a supersaturated solution raises to a higher temperature than that of crystal growth then, solution temperature gradually decreases. In the second method, crystal grows by steaming off the solvent.

2.4 Crystal Growth from Melt

This method includes crystallization by penetration and refreezing of pure components and has various advantages. Growth speed in this method is much higher than the speed resulted from other methods. Accordingly, it is the best method in terms of economic aspects. For perceptible growth rates, this mechanism requires a finite driving force in order to adequately reduce the nucleation barrier for nucleation to occur by means of thermal fluctuations. [1] In the theory of crystal growth from the melt, Burton and Cabrera have distinguished between two major mechanisms: [2, 3] Non-uniform lateral growth and Uniform normal growth.

Crystal growth from melt other growth methods because a higher purity results and lower deficits occur. The grown crystal is more perfect and can be built in larger sizes [1].

Methods of crystal growth from melt involve:

- A. Czochralski method (tensile)
- B. Kyropoulos
- C. Bridgman-Stockbarger
- D. Zone melting

In growth of oxide crystals with good laser quality, Czochralski method is still predominant [4]. It is also widely used in the production of most solid phase laser materials.

Other advantages of crystal growth from melt, compared to vapor and solution phase growth methods, are defined as follows:

1. The crystal always grows purely in crystal growth from melt method because solvent and soluble materials (used in gas phase crystal growth method) are not used.
2. Using this method, more perfect crystals with larger sizes (up to 6 inches) can be grown.
3. If solid solution crystals do not break down in melting temperature and if the solid solution does not return to several structural phases as a result of cooling, solid solution crystals can be grown using this method.
4. According to gradual and controlled cooling of the melting matter, crystal growth speed in this method is higher than other methods. Hence, through controlling the temperature, the speed of crystal growth from melt can be also controlled.

2.5 Czochralski Method

The process is named after the Polish scientist Jan Czochralski [4] who discovered the method in 1915 while investigating the crystallization rates of metals. [5] He accidentally made this discovery when he dipped his pen in molten tin, and drew a tin filament, which later proved to be a single crystal [6], instead of dipping it into his inkwell. Currently, it is a dominant method for producing oxide and semi-conductor crystals in industry [7]. It involves heating the investigated material in an appropriate crucible to be melted. Then, the system is formed only from a solid zone (starting point) through controlling the environment temperature.

- If this starting point is raised upward in appropriate rotation speed and adequate tension rate (not more than crystal growth rate), a wide cylinder, such as ingot results. The diameter of crystal can be controlled through controlling the temperature of the melting matter.
- In the following section, the material of crucible and the type of heating resource are reviewed. The crucible is selected based on its suitability for the melting matter, melting point, mechanical properties, chemical sustainability, and the type of heat. On the other hand, the size of the crucible is defined based on the size of the needed crystal and heat. Czochralski device consist of the following parts:
 - Furnace: Asbestos isolates it from the external environment.
 - Crucible: It is selected according to the form and size fitting to the considered matter.
 - Holder, starting point, lifter, and rotator

Figure 1 presents a schematic image of Czochralski crystal growth device.

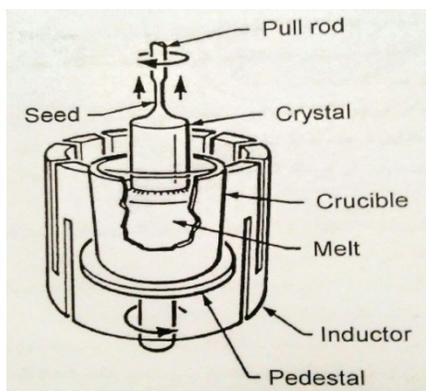


Fig. 1: A schematic image of Czochralski crystal growth device.

Czochralski crystal growth is appropriate for the cases where the ratio of the crystals length to its diameter is more than 1.

2.6 Advantages of Czochralski Method

The main advantage of this method is that crystals grow freely. Single crystals can easily grow because inappropriate germination creating polycrystalline does not occur. It is a kind of purification process. The most important advantage of this technique is its changeability, i.e. the growth conditions can easily change at the time of tension. In addition the interface of the melting matter and the growing crystal can be observed and crystals of any form and within any section can grow using this method. Due to easy access to the melting matter level, pollutants or other impurities can be added to that in each stage of growth [8].

2.7 Crystal Growth by Kyropoulos Method

However, Kyropoulos system is similar to function to that of Czochralski. However, the lifter device in the first system does not have any role. The crystals used for optical valves of prisms, lens, and other optical structures, have almost larger diameters than length. Accordingly, Kyropoulos method is better than Czochralski method.

After the completion of melting the matter and keeping the furnace temperature constant (20 centigrade degrees above the melting temperature), the starting agent enters into the melting matter by rotation and after the start of process; the vertical movement of the starting agent stops and the melting temperature simultaneously decreases.

Furthermore, the growing speed is less than that of Czochralski method and it reaches at most some millimeters per hour. Moreover, rotating the crucible is not required the speed of crystal rotation is much lower. The schematic form of Kyropoulos crystal growth device is presented in figure 2.

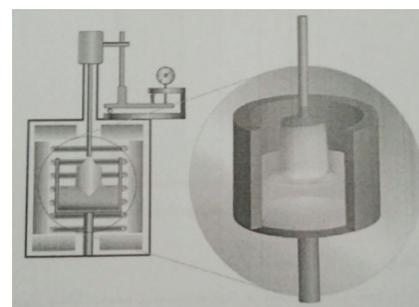


Fig. 2: Kyropoulos crystal growth device.

2.8 Bridgman Crystal Growth Method

In this method, a tube, similar to furnaces, is placed in vertical or horizontal position. The furnace has a specific temperature difference which ranges from 1 to 5 C°/mm. In this way, after melting the considered matters in the crucible, their form resembles the crucible. Then, they are taken down of the furnace with a speed which can be set [9]. It also involves crystal growth starts with horizontal movement of the crucible towards lower temperature. Meanwhile, instead of moving the crucible, we can move the furnace. In horizontal Bridgman method, another state called zone melting. In vertical state, crucible is not needed melting matter is kept by surface tension force. Consequently, it is also called “floating zone” method. The schematic form of Bridgman growth device is presented in figure 3.

2.9 Vapor Phase Crystal Growth

In this state, crystal growth is done by high purity. This method is suitable for growth of thin layers and volumetric crystal. It also has a low growth speed. Some of the volumetric crystals, such as (Cds) which are built with a low quality in other methods, are well produced in this method. Thin layers have been built in semi-conductor compounds, such as (Si) and (VI, II, V, III) metal and inorganic compounds with high quality have resulted. When we need a small crystal, we use this method if all conditions are observed, a perfect crystal will be obtained. For example, in optical modulators which are only needed in millimeter crystal, this method is used. For growing crystals with multiple compounds, we can use this method through selecting the appropriate element and controlling the gas amount of each element. Moreover, we can add the considered impurity to gas and grow a crystal containing impurity. Using this method, more elements are grown with sublimation phase.

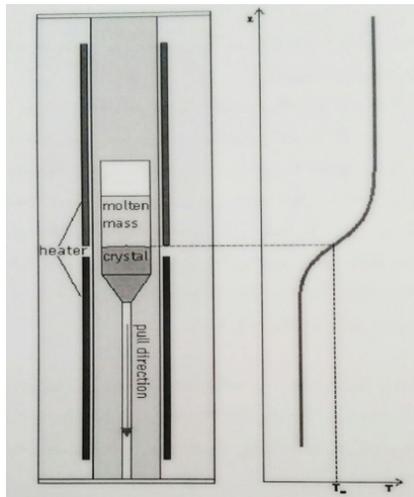


Fig. 3: Bridgman growth device.

3 Conclusion

An ideal crystal is built with regular and unlimited recurring of crystal unit in the space. Crystal growth is defined as the phase shift control. Crystal growth of any specific matter requires careful and proper selection of growth method. Based on material properties, the quality and size of the crystal are defined. Crystal growth methods are classified as follows: solid phase crystal growth process, and liquid phase crystal growth process which comprises two major sub-groups: growth from melt and growth from solution, as well as vapor phase crystal growth. Crystal growth from melt methods comprises those of Czochralski (tensile), Kyropoulos, Bridgman-Stockbarger, and Zone melting. In growth of oxide crystals with good laser quality, Czochralski method is still dominant, and it is widely used in the production of most solid phase laser materials.

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