

## 1. CRYSTAL GROWTH

Crystal growth is an important field of material technology. Growth of crystal ranges from a small inexpensive technique to a complex expensive technique. Crystallization time ranges from minutes, hours, days and to months. Nucleation is an important phenomenon in crystal growth. The growth of synthetic crystals are very much useful in the field of solid state physics, electronics, photonics, high efficiency photovoltaic cells, etc.

### METHODS OF CRYSTAL GROWTH

Crystal growth techniques are classified into three categories namely,

**Solid growth:** Solid to solid phase transformation.

**Liquid growth :** Liquid to solid phase transformation.

**Solution growth:**

- Low temperature solution growth.
- High temperature solution growth.

**Melt growth:**

1. Bridgman technique    2. Verneuil technique
3. Czochralski technique 4. Zone melting technique.
5. Heat exchanger method

**Vapour growth:** Vapor to solid phase transformation.

1. Physical Vapour Deposition (PVD)
2. Chemical Vapour Deposition (CVD)

### SOLUTION GROWTH

In this method, crystals are grown from aqueous solution. This method is widely used for producing bulk crystals. There are two methods in solution growth depending upon the solvents and the solubility of solute.

- Low temperature solution growth

Example: Growth from aqueous solution, gel growth

➤ High temperature solution growth

Example: Flux growth, hydrothermal growth.

## LOW TEMPERATURE SOLUTION GROWTH

In the low temperature solution growth, single crystals can be grown solution if the solution is supersaturated. The useful techniques used

- ❖ Slow cooling of the solution
- ❖ Slow evaporation of the solvent.
- ❖ Temperature gradient method

## SLOW COOLING OF THE SOLUTION

A saturated solution above the room temperature is filled in a crystallizer and it is thermally sealed. A seed crystal is suspended in the solution. The crystallizer is kept in a water thermostat and allowed to cool slowly. As the temperature decreases solubility decreases and single crystals start growing.

**Advantages:** Easy, works best for soluble substances. Crystallization begins usually from room temperature to 75<sup>0</sup>C.

**Disadvantages:**

- ❖ Needs lot of material,
- ❖ Range of temperatures
- ❖ Disordered or twinned crystals start growing

## SLOW EVAPORATION OF THE SOLVENT

This method is similar to the slow cooling method. Super saturated solution of the compound is prepared in a suitable solvent. The prepared solution is transferred into a clean container. The temperature is fixed constant and provision is made for evaporation. The container is set aside and the solvent is allowed to evaporate over for few days. The super saturated solution is slowly evaporated and small crystals grow. The crystals get bigger as the solution becomes more concentrated.

**Advantages:**

Easy and the crystals grow at a fixed temperature.

**Disadvantages:**

- Needs a lot of material, too much nucleation leading to simultaneous growth of many crystals.
- It requires temperature stabilization of about  $\pm 0.005^\circ\text{C}$  and rates of evaporation of a few ml/hr.

**Application of low temperature solution growth**

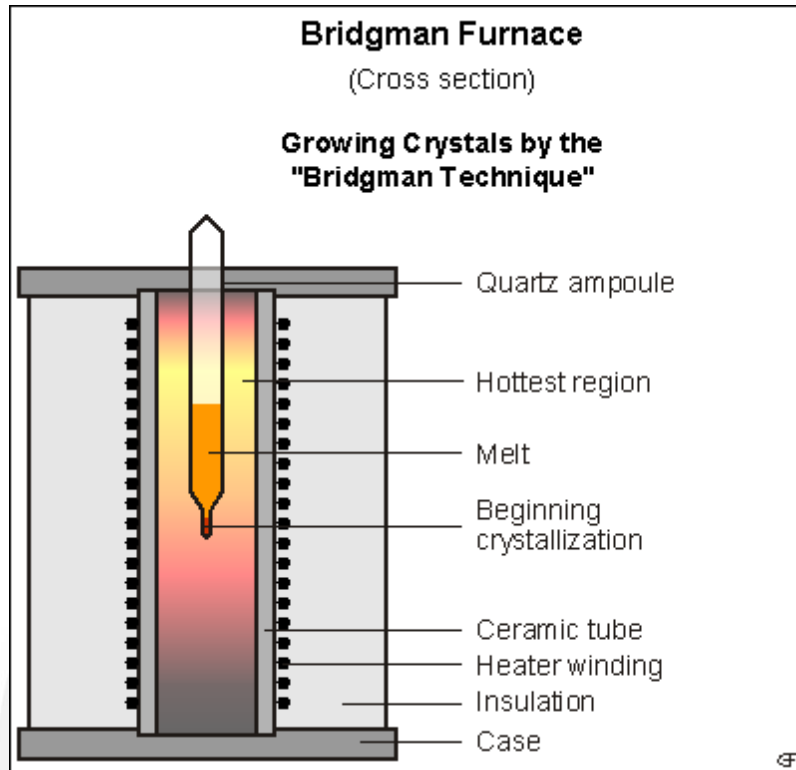
- Excellent quality crystals of ferroelectric and piezoelectric materials ADP, KDP and TGS are grown.

**MELT GROWTH**

Crystal growth from melt is the most widely used for growing single crystals. The materials which don't decompose at the melting point and don't undergo any phase transformation between the melting point and room temperature can be grown from melt growth technique.

**BRIDGMAN TECHNIQUE**

In Bridgman technique, the temperature gradient of the furnace plays an important role in growing single crystal.



- It consists of a vertical cylindrical container made by platinum or quartz, tapered conically with a point bottom.
- The crystal to be grown is kept inside the container.
- The container is surrounded by two furnaces namely upper furnace and lower furnace.
- The container is slowly lowered from hot zone of the furnace into the cold zone by using an electric motor.
- The temperature of the lower furnace is maintained below the melting temperature of the melt inside the container.
- The rates of movement slowly range from about 1-30 mm/hr.

- Crystallisation begins at the tip and continues usually growth from the first formed nucleus.

**Advantages:**

- Simpler technology
- Relatively cheaper
- Control of shape and size of growing crystals.
- Easy control and maintenance
  - No radial temperature gradients are needed to control the crystal shape.

**Disadvantages :**

- This technique can't be used for materials, which decompose before melting. This is the best suited for materials with low melting point.
- Dislocation crystals can be grown.
- Growth rate is low.
- difficult to observe seeding and growing processes

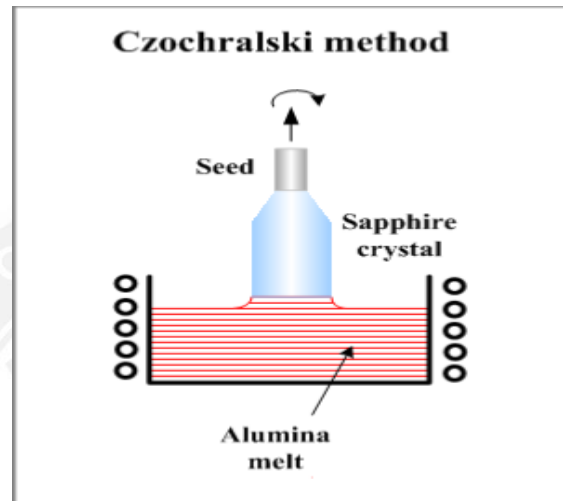
**Applications :**

- It is popular method of producing single crystal semiconductors such as GaAs, ZnSe, CdS, CdTe and ZnS.

**CZOCHRALSKI METHOD**

Czochralski's crystal pulling method is the most common technique of crystal growth from melt. A refractory container contains the pure material heated by magnetic induction, under a controlled atmosphere. By controlling the furnace temperature, the material is melted. A seed crystal is attached to a rod in the desired orientation. The seed is slightly lowered into the surface of the molten material. When the temperature of the seed is maintained very low compared to the temperature of the melt by suitable cooling effect. The molten charge in contact

with the seed will solidification on the seed. By activating a pulling mechanism, the seed is withdrawn from the melt. If the rod is pulled up slowly, the diameter increases because, crystal grows on the sides and on the end of the crystal.



### Advantages

- Growth rate is high
- Growth of large oriented single crystals. High crystalline perfection can be achieved

### Disadvantages

- Possible contamination of the melt by the crucible.
- Problems in temperature maintenance.
- cannot grow materials with high vapor pressure

### Applications:

- Used in industry to grow semiconductor materials. [Si, GaAs, InP]
- Silicon grown by this method is for the production of IC's used in TV, Computers, Cellphones, Laptops, etc.