

Introduction to Nonlinear Optics and Crystal Growth Techniques Process

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Abstract:

Nonlinear optical property is an important phenomenon in optoelectronics. The frequency conversion of the non linear optical (NLO) material has a significant impact on laser technology, optical communication and optical storage technology. Therefore scientists were very much interested in to discover new NLO crystals. The search of new frequency conversion material was concentrated over the organic materials. But they have often-inadequate transparency, poor optical quality, lack of robustness and low laser damage threshold. Hence recent search concentrates on semi organic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness

Introduction:

1.4. Crystal Growth

In recent years, the growth of the single crystals has assumed enormous importance for both academic and applied research and communication. Single crystals are required mainly for the construction of solid state devices. Numbers of devices have been identified effectively for optical and electronic phenomena. These include frequency controlled oscillators by quartz crystal, polarisers by calcite crystals, transducers by ammonium dihydrogen phosphate crystals and radiation detectors by alkali halide crystals etc. In most of these applications, the major role is played by bulk single crystals. In order to fabricate devices with high efficiencies we need to have a thorough understanding of the basic properties of crystals and understand how exactly the materials can be grown. The three general types of solids are amorphous, polycrystalline and single crystals which are classified by the size of the ordered regions within the materials depending upon the arrangement of constituent molecules, atoms, or ions. Among these, a crystal may

be defined as a solid composed of atoms or other microscopic particles arranged in an orderly repetitive array. Single crystals have long range order. The infinite lattices of atoms or molecules which are arranged in patterns are repeated in all the three dimensions in the ordered form. Nevertheless, real crystals do contain defects and are with finite repletion. Hence, it is obvious that the preparation of polycrystalline material is much easier than growing a single crystal, because care is needed to grow a single crystal due to its outstanding merits. Also the existence of grain boundaries and non-uniform composition in the case of polycrystalline material explains the fact that it is easier to prepare them.

1.4.1. Methods of crystal growth

The formation of bonds between the growth units (atoms, ions and molecules) is considered as crystal growth. To obtain single crystals the following methods have been classified according to the phase transition presented in Table 1.1. 7

Table 1.1 Methods of crystal growth and their phase transition

S.NO. Growth Methods

Phase transitions

1 Solid Growth Solid to Solid phase transition

2 Melt Growth Liquid to Solid phase transition

3 Vapour Growth

Vapour to Solid phase transition

4 Solution Growth Liquid to Solid phase transition

The various techniques used for crystal growth for the above classification are melt growth, solid growth, and vapour growth. Crystals can be grown by melting the substances

followed by cooling, by precipitating from solutions or by condensation of vapour. The basic

common principle in all these methods is that a nucleus is first formed and it grows into a single

crystal when ions or molecules get deposited on it. The general approach is to see that this deposition is slow and control of multiple nucleation. Out of these methods, the mode of

selection of a particular method depends on the various properties of the materials such as

melting point, vapour pressure, decomposition, solubility in solvents etc. It also depends on the growth kinetics involved, the required size of the crystal, crystal purity and the nature of the

application of the crystal. The ultimate aim of the crystal grower is to find an economically feasible method which yield

defect free crystals. Substances which have a congruent melting point can be grown in the form of a single crystal by melting followed by careful cooling. If the cooling is carried out under proper conditions the solidification occur which results in single crystal growth. The above principle is

adopted in melt growth. It is the best method for growing large single crystals of high

perfection. Further, this method is appropriate for substances which have a low melting point and low vapour pressure and does not undergo polymorphic phase transition from its melting point to room temperature. However, it is not suitable for materials which undergo polymorphic phase changes. 8 There are several techniques for crystal growth from melt. The commonly employed techniques

are,

- Czochralski technique
- Bridgmann-Stockbarger technique
- Zone melting technique and
- Vernuil technique

1.4.2. Czochralski technique

This method is widely used to grow semiconductors, organic and inorganic materials in the form

of single crystals. It mainly involves the relative motion of the seed and melt.

There is no container problem for growing crystals.

To orient seed crystals suitably, the orientation of seed crystals can be preselected.

When compared to other techniques, the growth time is much less.

High quality crystals can be grown

Temperature and growth can be controlled.

The schematic diagram of Czochralski technique is shown in Fig.1.4. In this method, the

seed holder that is platinum/iridium tube is used to place the seed crystal of desired orientation

and is wired to the bottom of the seed holder. The water or air circulates around the seed holder for cooling. The seed holder is slowly lowered into the crucible which contains melt and is allowed to touch the melt. At this point, the temperature of the seed is much lower than the melt, because

the seed holder in which seed was placed is cooled by either air or water. Thus the crystal growth takes place since melt solidifies at the tip of the seed. The sole benefit of this method is the grown crystal is not in contact with the crucible. The major advantage of this method is that the shape of the crystal is not limited by the shape of the crucible. The temperature at the solid-liquid interface must be lowest otherwise there is a possibility of occurrence of spontaneous nucleation at the sites. The melt which is placed in the crucible should be free from impurities. The first insulator grown by this method was CaWO₄. Some of other crystals grown by this method are, TiO₂, NiMoO₄, CaTiO₃, Si and Ge.

1.4.3. Bridgmann-Stockbarger technique

The basic principle of this method is that the melt along with the crucible is slowly cooled to yield a single crystal. Crystal grown by this technique is able to withstand considerable thermal stress. One of the important aspects of this method is that either the melt or the vapour should not attack the crucible. Thermal stresses in the crystal could be avoided by having the same thermal expansion coefficient for both the material and the ampoule. The ampoule has a tapered end. The experimental setup of Bridgmann Stockbarger technique is shown in Fig.1.5. The steady motion to the solid-liquid interface is the main concept of this technique. This can be achieved in many ways. The usual and simple method is to let down the molten material vertically through the furnace. A cylindrical container with a tapered end at the bottom holds the substance to be lowered into an electrically heated double-walled furnace. There are two zones within a furnace called as upper and lower zones. The temperature of these zones is controlled independently.

The temperature of the lower zone is kept slightly lower than the melting point and upper zone is maintained at a higher temperature than the melting point of the material. Therefore the substance melts when it passes through the hotter region. And then it is gradually let down into the cooler region so that it solidifies as nucleation takes place at the bottom of the extremity of the ampoule which acts as the seed for further growth. The growth of the seed occurs when the ampoule is still lowered. Since the solid-liquid interface is completely enclosed within the crucible, the thermal conduction through the solid and the crucible removes the latent heat of the solidification. This method is not suitable for material which decomposes before melting. For the material of low melting this method is best suited.

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1.4.4. Zone melting Process

In this technique small amount of substance is melted in a long solid ingot thus creating a liquid zone where it is moved up and down. Germanium and silicon are few examples of the crystals grown by this technique. The directional solidification of monocrystal superalloys by electron beam floating zone melting have been studied by Zhang Jun et al (1999). Simultaneous purification of the substance during growth process and the needless of using crucible are considered to be the advantages of this method.

1.4.5 Verneuil Technique

This method is suitable for materials with high melting point. Since it does not require a crucible, there is no problem of selecting suitable crucible material. However, there is a steep temperature gradient experienced by the material which is a serious problem because this

produces strains in the crystal. Fig.1.6 shows a schematic diagram of Verenuil technique. The seed crystal is heated by the oxy-hydrogen flame using vibrator. At low amplitude powder from the hopper is shaken through the sieve. The powder melts during its passage through the flame. The growth rate depends on two factors such as the powder feed and the rate of lowering of seed. Synthetic gems are grown by this technique. Materials such as quartz, calcite, sapphire and antimony sulfide can be grown by this technique.

1.4.5. Growth from solution

Among all the methods, solution growth is the easiest, simplest and least expensive method to obtain high quality defect free single crystals. Low temperature solution growth is most widely practiced next to melt growth. The principle of this method is based on the concepts of solubility and super saturation. When a saturated solution is cooled down to lower temperature, number of solute molecules will be present for the formation of crystal nuclei. The same thing happens if some of the solvent is allowed to evaporate. The solution is now in a supersaturated state. If a 'seed' crystal is introduced into the supersaturated solution the substance precipitating from the solution will grow around the seed crystal forming a larger single crystal.

This method is advantageous because the crystals are grown at a temperature well below the melting point and the detailed knowledge about certain parameters such as melting point, melting behavior, stability in reduced pressure and atmosphere are not necessary. This technique

is superior to other methods due to good optical transparency of crystals and also uniform mixing

of dopant in the lattice is easily attainable. Slow growth rate and container problem are the main

disadvantages of this method. The following are of the few pre-requisites for growing good

quality large single crystals by solution growth method.

Materials should have high solubility and there should be variation in solubility with temperature.

The vapour pressure at the growth temperature should be small.

Viscosity of the solvent-solute system should be low.

The container and stirrer should be non-reactive with the material.

Materials must be inflammable and less toxic.

Solution growth techniques are further classified as

Low temperature solution growth

High temperature solution growth

Hydrothermal growth and

Gel growth

1.4.6. Low temperature solution growth

Dislocation free crystals can be grown by this method at a relatively low temperature.

Growing by this technique, the crystals that are produced are free from thermal strains and have

well-defined facets. Attaining supersaturation, formation of crystal nuclei and growth of crystals

are the three basic steps in this process of crystallization. The prime fact of crystallization

process is the attainment of supersaturation. The solution attains a supersaturated state, when the

saturated solution prepared at a certain temperature is allowed to cool at a lower temperature.

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The deciding factor in controlling the growth of the crystal is the extent of supersaturation from

the equilibrium saturated solution. Cooling, evaporation, the addition of precipitant, doping,

chemical reaction between two homogeneous phases is some of the means to attain supersaturation. There are a number of nuclei present in the solution for a crystal to grow. The seed crystals can be chosen from the nucleated small crystals which are inserted into this solution so that the substance precipitating from the top will grow around the seed forming a single crystal. Depending upon the material, the rate of growth of single crystals varies from 10⁻⁴ to 10⁻⁶ cm per day. This method may further sub-divided into,

- Slow cooling
- Slow evaporation and
- Temperature gradient method

1.4.7. Slow cooling technique

A solution that is in equilibrium with the solid phase is said to be saturated with respect to that solid. For this technique, a slightly under saturated solution is taken in a small beaker and is kept inside a large water bath. This solution when cooled slowly without disturbance in a dust free atmosphere can readily be made to show appreciable degrees of supersaturation. This technique adopts the above principle. Since growth is carried out at low temperature, purity of crystals obtained is high but at the same time the rate of growth is small compared to other techniques.

1.4.8. Slow evaporation technique

In this process the temperature of the solution is not changed, but the solution is

allowed to evaporate slowly. Since the solvent evaporates, the concentration of solute increases,

supersaturation is achieved. For example 40 gm of solute in 100 ml solvent is considered as a saturated solution at 50°C. Now the solution is allowed to evaporate at the same temperature, 100 ml of the solution is reduced to some lower level say 70 ml, then 40 g in 70 ml at 50°C is a supersaturated solution.

1.4.9. Temperature gradient technique

The basic principle of this method is when a saturated solution kept at a higher temperature (T+dT) than the region containing seed crystal at a room temperature T, the seed crystals will grow into a larger crystal. The main advantages of this method are the possibility of growing big crystals and the defects are minimized since growth is being carried at a fixed temperature.

1.4.10. High temperature solution growth

This method is also named as flux method. The solvent of this technique is the molten salt and the growth process takes place will below the melting point. The main disadvantage of this method is that the grown crystals contain a higher concentration of impurities than those grown from melt. This technique is suitable for,

- Highly refracting materials with container problem (MgO)
- Substances that decompose before they melt (CaCO₃)
- Materials with very high vapour pressure at the melting point (AlF₃, ZnO) and
- Incongruently melting materials

The crystals grown by this technique are not exposed to rapid temperature gradient and due to this reason stain free crystals can be obtained. This method is preferred next to melt growth for growing crystals at high

temperatures. Growth and characterisation and $RM_3(BO_3)_4$ single crystals where $R=Y, La, Lu, B, I, In$ and $M=Al, Sc, Fe, Ga, Cr$ (Leonyuk and Leonyuk 1996) and flux growth of YBCO super conductors with the increase in content of BaF_2 (Chen Changkang et al 1996) have been realized in the literature. From the Cu_2O flux, single crystal of $Y_2Cu_2O_5$

is grown by slow cooling method (Imanaka et al 1994). The solution growth of Silicon from

SiO_2 substrates is discussed in detail by Zhengrong Shi (1994). Growth of $NiWO_4$ crystals from

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NaW_2O_7 flux is reported by Shuji Oishi et al (1996). The growth of single crystals of $KTiOPO_4$

doped with Mg^{4+} ions by Nikolov et al (1990) is a novel report in High temperature solution growth.

1.4.11. Hydrothermal Growth

The quartz crystals of high quality are grown primarily by this technique. The following are

the few conditions to be fulfilled for the growth of the crystal under this technique.

- To permit reasonable super-saturation, a combination of solvent pressure and temperature

must be studied and the substance should have sufficient solubility.

- The temperature co-efficient of solution density should be sufficiently large.

- The vessel must be without corrosion so as to be suitable to contain the pressure temperature condition of the experiment.

1.4.12. Gel Growth

Gel growth technique is used to grow only small crystal and it can be carried out in ordinary

laboratory. The principle underlying this method is that the solutions of suitable compounds say

AX and BY are diffused a Gel medium which give rise to insoluble substance. The equation is,



The advantages of the solution growth method are as follows:

- Since growth takes place near ambient temperature, the crystals would be less concentration of equilibrium defects.

- In the low temperature solution growth and Gel growth the crystals can be observed in

the transparent medium.

- In all this methods, the grown crystals are preserved without much damage to the crystal surface.

- It yields a good quality crystal and the growth procedure is simple and economical.

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1.5. Criteria for Optimizing Solution Growth

Parameters:

The growth of a good quality single crystal by slow evaporation and slow cooking techniques requires the optimized conditions; the same may be achieved with the help of the following criteria:

i) Material Purification

ii) Solvent Selection

iii) Solubility

iv) Solution Preparation

v) Seed Preparation

vi) Agitation

vii) Crystal habit and

viii) Cooling Rate

1.5.1. Material Purification

An essential prerequisite for success in crystal growth is the availability of

material of the highest purity attainable. Solute and solvents of high purity are required, since impurity may be incorporated into the crystal lattice resulting in the formation of flaws and defects. Sometimes, impurities may slow down the crystallization process by being adsorbed on the growing face of the crystal which changes the crystal habit. A careful repetitive use of standard purification methods of recrystallization followed by filtration of the solution would increase the level of purity.

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1.5.2. Solvent Selection

The solution is a homogeneous mixture of a solute in a solvent. The solute is the component present in a smaller quantity. For a given solute, there may be different solvents.

Apart from high purity starting materials, solution growth requires a good solvent. The solvent

must be chosen taking into account the following factors.

- i) High Solubility for the given solute,
- ii) Good solubility gradient,
- iii) Low viscosity
- iv) Low volatility and
- v) Low corrosion

1.5.3. Solubility

Solubility is an important parameter, which dictates the growth procedure. If the solubility is too high, it is difficult to grow bulk single crystals and too low solubility restricts the

size and growth rate of the crystals. Neither a flat nor a steep solubility curve will enable the

growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation

of the solvent is the other option for crystal growth to maintain the supersaturation in the solution.

Low temperature solution growth is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transfer of the growth units from the bulk solution by diffusion. Hence a solvent with less viscosity is preferable. Supersaturation is an important

parameter for the solution growth process. The solubility data at various temperatures are

essential to determine the level of supersaturation. Hence, the solubility of the solute in the

chosen solvent must be determined before starting the growth process.

The solubility of the solute can be determined by dissolving the solute in the solvent

maintained at a constant temperature with continuous stirring. On reaching saturation, the

equilibrium concentration of the solute can be determined gravimetrically. A known quantity of

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the clear sample is analyzed. The solubility curve can then be plotted from the amount of solute

dissolved and temperature by repeating the measurements for different temperatures.

1.5.4. 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 preparation 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.

1.5.5. Seed Preparation

Seed crystals are prepared by self nucleation under slow evaporation from a saturated solution, the seeds of good visual quality, free from any inclusion and imperfections are chosen for growth. Since strain free refracting of the seed crystals results in low dislocation content, a few layers of the seed crystal are dissolved before initiating the growth.

1.5.6. Agitation

To have a regular and even growth, the level of supersaturation has to be maintained equally around the surface of the growing crystal. An uneven growth leads to localized stresses at the surface generating imperfection in the bulk crystals. Moreover, the concentration gradient

that exists in the growth vessel at different faces of the crystal cause fluctuations in supersaturation, seriously affecting the growth rate of individual faces. The gradient at the bottom of the growth vessel exceeds the metastable zonewidth, resulting in spurious nucleation.

The degree of formation of concentration gradients around the crystal depends on the efficiency

18 of agitation of the solution. This is achieved by agitating the saturated solution in either direction at an optimized speed using a stirrer motor.

Changes of habit in such crystals which naturally grow as needles or plates can be achieved by any one of the following ways:

- i) changing the temperature of growth
- ii) changing the pH of the solution
- iii) adding a habit modifying agent and
- iv) changing the solvent

Achievement in this area is of great industrial importance where such morphological changes are induced during crystallization of yield crystal with better perfection and packing characteristics.

1.5.7. Cooling Rate

Supersaturation, the driving force which governs the growth of a crystal, is achieved by lowering the temperature of a solution, temperature and supersaturation have to be precisely controlled for desirable results. The growth rate is maintained linear in order to grow large crystals. This requires an increase in the supersaturation level and linear cooling will not provide this. Hence after the initial growth, the rate of temperature lowering is increased. Operation

within the metastable limit occurs without any spurious nucleation in the solution. A large cooling rate changes the solubility beyond the metastable limit. Further, fluctuations in supersaturation may encourage solution inclusions flaw in growing crystals (Wiclox1983). Hence a balance between the temperature lowering rate and the growth rate has to be maintained.

1.5.8. Crystal Perfection

The perfection of the final crystal is based on

- i) the purity of the starting materials
- ii) the quality of the seed crystal
- iii) cooling rate employed and
- iv) the efficiency of agitation

Hence, high quality single crystals can be grown from quality seed in an efficiently stirred solution.

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