

# **CHAPTER - 1**

## **INTRODUCTION**

### **1.1 Introduction to crystal growth**

Nature has provided many astounding things among them crystal is one of the best things with fascinating colours, smooth surfaces, reflection of light, sharp edges and deep transparency. Crystals are of two types such as poly crystal and single crystal [1]. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. Single crystals play a very important role in present day technology to the extent that it can be said 'single crystals are the pillars of modern technology'. Crystal growth involves the phase transformation of the material of interest from solid, liquid or gaseous phase to a well ordered solid phase resulting in a crystal [2].

A crystal may be defined as a solid that composed of atoms arranged in a pattern periodic in three dimensions. Early man has the knowledge of crystals to use it as ornaments but in recent days crystals are mainly used in electronic industry, photonic industry, fibre optic communications etc. They were used in such industries in the fabrication of materials such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computers [3]. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for

technological applications (Brice 1986, Nalwa and Miyata 1997) [4, 5]. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort to be put in their crystallization is justified because of the outstanding advantages of single crystals (Laudise 1970) [6]. The reason for growing single crystals is that many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in crystalline and polycrystalline materials. In order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have gained/assumed great impetus due to their importance for both academic as well as applied research.

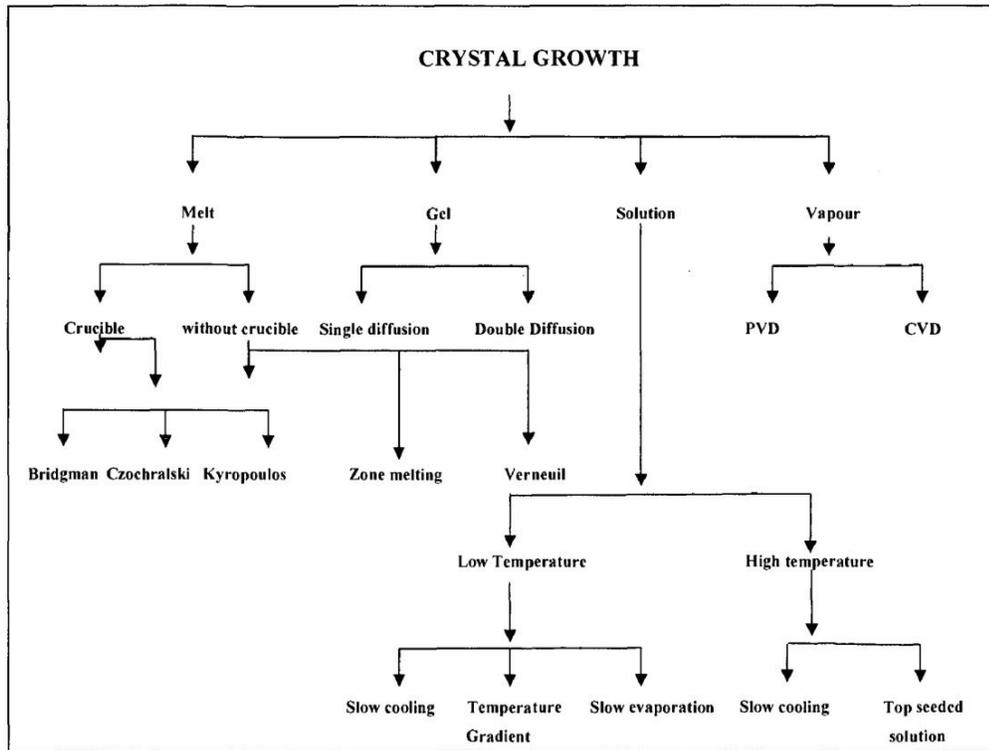
## **1.2 Methods of crystal growth**

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. Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapour phase. On the basis of this, crystal growth may be classified into three categories as follows [7],

- Solid Growth - Solid to Solid phase transformation
- Liquid Growth – Liquid to Solid phase transformation
- Vapour Growth - Vapour to Solid phase transformation

In the above mentioned categories liquid growth includes both melt and solution growth. A survey of the methods of growth suggests that almost 80% of the single crystals are grown from the melt compared with roughly 5% from vapour, 5% from

low temperature solution, 5% from high temperature solution growth, 3% from the solid and only 2% by hydrothermal methods [8].



**Fig. 1.1** Crystal growth methods

### 1.2.1 Growth from solid

The job of the crystal grower is to prepare large specimens of crystalline material such that there is a complete crystallographic continuity across a given specimen in all directions for better achievement. There are two principal reasons for the deliberate growth of single crystals [9].

- i) Many physical properties of solids are obscured or complicated by the effect of grain boundaries.

ii) The full range of tensor relationship causes an observed effect in the full internal symmetry of the crystal structure which should be maintained throughout the specimen.

Solid state growth technique can be considered as the conversion of a polycrystalline material into a single crystal by causing the grain boundaries to be swept through and pushed out of the material due to atomic diffusion. But this is very slow at ordinary temperatures and is only rarely used.

### **1.2.2 Growth from melt**

All materials can be grown in single crystal form from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature [10]. Depending on the thermal characteristics, the following techniques are employed.

- a) Bridgman technique
- b) Czochralski technique
- c) Kyropoulos technique
- d) Zone melting technique
- e) Verneuil technique

#### **1.2.2 (a) Bridgman technique**

In this technique the material is melted in a vertical cylindrical container, tapered conically with a point bottom. The bottom is lowered slowly from the hot zone of the furnace in to the cold zone. The rates of movement for such processes range from about 1- 30 mm/hr. Crystallization begins at the tip and continues usually by growth from the first formed nucleus. This technique cannot be used for materials,

which decompose before melting. This technique is best suited for low melting point materials.

#### **1.2.2 (b) Czochralski technique**

In this method, the material to be grown is melted by induction or resistance heating under a controlled atmosphere in a suitable non-reacting container. By controlling the furnace temperature, the material is melted. A seed crystal is lowered to touch the molten charge. When the temperature of the seed is maintained very low compared to the temperature of the melt, by suitable water cooling arrangement, the molten charge in contact with the seed will solidify on the seed. Then the seed is pulled with simultaneous rotation of the seed rod and the crucible in order to grow perfect single crystals.

#### **1.2.2 (c) Kyropoulos technique**

In this technique, the crystal is grown in a larger diameter. As in the Czochralski method, here also the seed is brought into contact with the melt and is not raised much during the growth (part of the seed is allowed to melt and a short narrow neck is grown). After this, the vertical motion of the seed is stopped and growth proceeds by decreasing the power supplied to the melt. The major use of this method is for alkali halides to make optical components.

#### **1.2.2 (d) Zone melting technique**

In this technique, the feed material is taken in the form of sintered rod and the seed is attached to one end. A small molten zone is maintained by surface tension between the seed and the feed. The zone is slowly moved towards the feed. Single crystal is obtained over the seed. This method is applied to materials having large surface tension. The main reasons for the impact of zone refining process to modern

electronic industry are the simplicity of the process, the capability to produce a variety of organic and inorganic materials of extreme high purity, and to produce dislocation free crystal with a low defect density.

### **1.2.2 (e) Verneuil technique**

In this technique, fine dry powders of size 1-20 microns of the material to be grown is shaken through the wire mesh and allowed to fall through the oxy-hydrogen flame. The powder melts and a film of liquid is formed on the top of the seed crystal. This freezes progressively as the seed crystal is slowly lowered. The art of the method is to balance the rate of charge feed and the rate of lowering of the seed to maintain a constant growth rate and diameter. By this method ruby crystals are grown up to 90 mm in diameter for use in jewellery bearings and lasers. This technique is widely used for the growth of synthetic gems and variety of oxides.

### **1.2.3 Growth from vapour**

The growth of single crystal material from the vapour phase is probably the most versatile of all crystal growth processes. Crystals of high purity can be grown from vapour phase by sublimation, condensation and sputtering of elemental materials [11]. To obtain single crystals of high melting point materials this method is used. Molecular beam techniques have also been applied recently to crystal growth problems. The most frequently used method for the growth of bulk crystals utilizes chemical transport reaction in which a reversible reaction is used to transport the source material as a volatile species to the crystallization region. Finding a suitable transporting agent is a formidable, problem in this technique. It is rarely possible to grow large crystals because of multi-nucleation.

The commercial importance of vapour growth is the production of thin layers by chemical vapour deposition (CVD), where usually irreversible reactions e.g. decomposition of silicon halides or of organic compounds are used to deposit materials epitaxially on a substrate. Doping can be achieved by introducing volatile compounds of dopant elements into the reaction region. The thickness of the doped layer can be controlled.

#### **1.2.4 Growth from solution**

Crystals of all materials cannot be made from their melts especially those which do not melt congruently or decomposes before melting or having very high melting point. For such materials solution growth technique is adapted. For efficiently growing crystal from solution growth the material should be moderately soluble in the given solvent and the system should be less viscous and non-volatile. Solution growth is one of the oldest crystal growing techniques whose basics lie in preparing supersaturated solution using material to be crystallized and suitable solvent to give rise to nucleation followed by growth. This is achieved either by slow evaporation of solvent or slow cooling of solution [12]. Materials having high solubility and variation in solubility with temperature can be grown easily by solution method. Depending on the solvents and the solubility of the solute the solution growth has the following methods to prepare good crystals

1. Hydrothermal growth
2. Gel Growth
3. High temperature solution growth
4. Low temperature solution growth

#### **1.2.4.1 Hydrothermal growth**

Hydrothermal implies conditions of high pressure as well as high temperature. Substances like calcite, quartz is considered to be insoluble in water but at high temperature and pressure, these substances are soluble. This method of crystal growth at high temperature and pressure is known as hydrothermal method. Temperatures are typically in the range of 400° C to 600° C and the pressure involved is large (hundreds or thousands of atmospheres). Good quality and large dimension of crystals are grown by this technique.

Growth is usually carried out in steel autoclaves with gold or silver linings. Depending on the pressure the autoclaves are grouped into low, medium and high-pressure autoclaves. The concentration gradient required to produce growth is provided by a temperature difference between the nutrient and growth areas. The requirement of high pressure presents practical difficulties limit the growth of many single crystals. Quartz is the outstanding example of industrial hydrothermal crystallization. One serious disadvantage of this technique is the frequent incorporation of OH<sup>-</sup> ions into the crystal, which makes them unsuitable for many applications.

#### **1.2.4.2 Gel growth**

It is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. Gel is a two component system of a semisolid rich in liquid and inert in nature. The material, which decomposes before melting, can be grown in this medium by counter diffusing two suitable reactants. Crystals with dimensions of several mm can be grown in a period of 3 to 4 weeks.

The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place by slow diffusion and also grown at room temperature.

#### **1.2.4.3 High temperature solution growth**

In 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 [13]. The supersaturated 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:

1. Growth from single component system.
2. Growth from multi component system.

This method is widely used for the growth of oxide crystals. The procedure is to heat the container having flux and the solute to a temperature so that all the solute materials dissolve. This temperature is maintained for a ‘soak’ period of several hours and then the temperature is lowered very slowly

#### **1.2.4.4 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 popular in the production of many technologically important crystals. It is a used method for the growth of single crystals, when the starting materials are unstable at high temperatures (Pamplin 1979) [14] and also which undergo phase transformations below melting point (Hooper et al 1980) [15]. Though the

technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. A power failure or a contaminated batch of raw material can destroy months of work.

Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low-temperature solution method (James and Kell 1975) [16]. The mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process; temperature, pressure and solvent concentration (Chernov 1984) [17]. The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straight forward equipment design which gives a good degree of control of accuracy of  $\pm 0.01$  °C. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique. The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent (Hooper et al 1979) [18]. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and 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 many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. 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 1973) [19].

In the solution growth, crystals can be grown from solution if the solution is supersaturated i.e., it contains more solute than it can be in equilibrium with the solid. Three principal methods are used to produce the required supersaturation:

- a) Slow evaporation of the solvent
- b) Slow cooling of the solution
- c) The temperature gradient method

#### **1.2.4.5 Slow evaporation method**

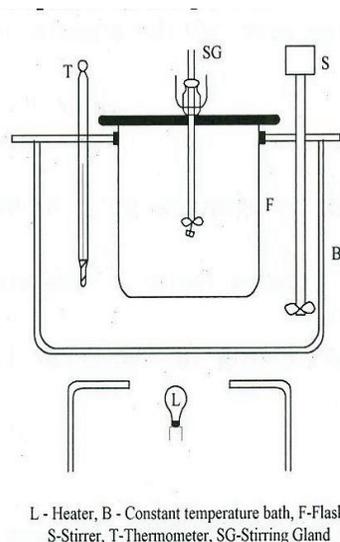
It is the best way to grow single crystals by solution technique. As far as the apparatus is concerned, slow cooling and slow evaporation methods are similar to each other. In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. If the solvent is non-toxic like water, it is permissible to allow evaporation into the atmosphere. The solution loses particles which are weakly bound to other components and, therefore, the volume of the

solution decreases [20]. An excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and the solute. Normally, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and, therefore, the solvent evaporates more rapidly and the solution becomes supersaturated. It is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. This method of crystal growth is the oldest and technically it is very simple. For nontoxic solvents such as water evaporation is permissible into the atmosphere but for toxic and inflammable solvents precautions are taken to avoid the leakage of solvent vapour in the atmosphere. Typical growth conditions involve a temperature stabilization of about 0.05 °C with rate of evaporation of a few mm<sup>3</sup>/h. The evaporation technique has an advantage due to the crystals that grow at a certain temperature. But inadequacies of the temperature control system still have a major consequence on the growth rate.

This method can be effectively used for materials having very low temperature coefficient of solubility. Evaporation of solvent from the surface of the solution produces high local supersaturation and unwanted nuclei are formed. Small crystals also form on the walls of the vessel near the surface of the liquid from the material left after evaporation. These fall into the solution and hinder the growth of the crystal. Another disadvantage lies in controlling the rate of evaporation. A variable rate of evaporation may affect the quality of the crystal. In spite of all these disadvantages, this is a simple and convenient method for growing single crystals of large size [21].

### 1.3 Crystallization apparatus

The basic apparatus used for the solution growth technique is shown in **Fig 1.2**. The apparatus is the constant temperature bath, which consist of a control system, thick walled glass chamber filled with water, heating element, temperature sensor, control relay, temperature indicator, stirrer and illumination lamp. Special care has to be taken to make the control system more reliable because the process of crystal growth requires long duration and non-interruption of temperature control. The apparatus make use of an optical heating system which is free from fluctuations in temperature generally found in ordinary water heaters. For initial heating an immersion heater of 500W capacity is fixed with bottom of the chamber. The system uses a contact thermometer for temperature control. The desired temperature is set in the jumo contact thermometer coupled to an on-off controller, which has a controlling accuracy of  $\pm 0.01^{\circ}\text{C}$ . The temperature of the constant temperature bath is converted into a signal by a suitable sensor. The controller is contacted with an on-off switch. It gets activated when the process variable (bath temperature) crosses the set point. There are only two stable states in an on-off controller. “On” state is enabled when the temperature is below the set point. As the desired set point is arrived, the controller goes to the “off” state. To get change in the state, the temperature must cross the set point. Set point variations, which occur due to electrical noise interference and process disturbances, seriously affect the practical applications of the controller. Contrary to this, a proportional controller continuously manipulates the process variable so that the heat input is in balance with the heat demand. The controller consists of a power supply, processor, booster and proportional controllers.



**Fig. 1.2** Apparatus for solution growth

### 1.3.1 Solution preparation

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 to the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after saturation. Solvent evaporation also can be helpful in initiating the growth.

### **1.3.2 Seed preparation**

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

### **1.3.3 Fundamentals of crystal growth**

The growth of good quality single crystals by slow evaporation requires optimized conditions. The same may be achieved with the help of the following criteria; (i) Material purification, (ii) Choice of Solvent , (iii) Solubility, (iv) Nucleation (v)Time vi) Supersaturation, and vii) Crystal habit.

#### **(i) 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, because impurity may get 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.

#### **(ii) Choice of solvent**

The solution is a homogeneous mixture of a solute in a solvent. The solute is a component present in 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 [22].

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

### **(iii) 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, besides 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 supersaturation in the solution.

Supersaturation is an important parameter for the growth process of solutions. 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 which is 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 the clear sample is analyzed. The solubility curve can then be plotted from the amount of dissolved solute and temperature by repeating the measurements for different temperatures.

#### **(iv) Nucleation**

Nucleation is an important phenomenon in crystal growth and is the precursor of the overall crystallization process. Nucleation is the process of generating within a metastable mother-phase, the initial fragments of a new and more stable phase capable of developing spontaneously into gross fragments of the stable phase. Nucleation is consequently a study of the initial stages of the kinetics of such transformations (Santhanaraghavan and Ramasamy 2000) [23].

Nucleation may occur spontaneously or it may be induced artificially. There are cases are referred to as homogeneous and heterogeneous nucleations respectively. Both these nucleations are called primary nucleation and occur in systems that do not contain crystalline matter. On the other hand, nuclei are often generated in the vicinity of crystals present in the supersaturated system. This phenomenon is referred to as secondary nucleation (Mullin 1972) [24]. Growth of crystals from solutions can occur if some degree of supersaturation or supercooling has been achieved first in the system. There are three steps involved in the crystallization process.

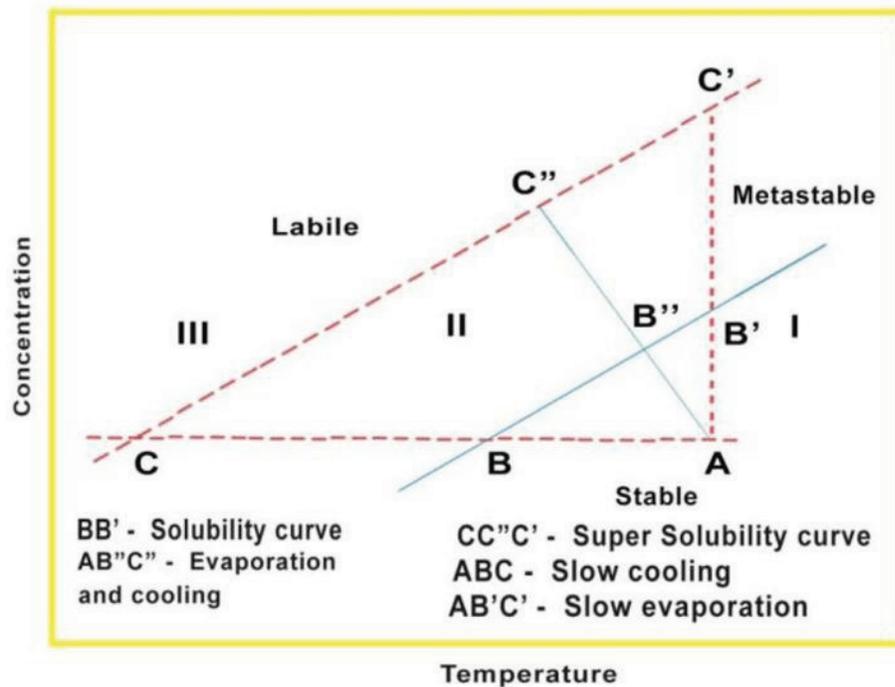
- i) Achievement of supersaturation or supercooling
- ii) Formation of crystal nuclei
- iii) Successive growth of crystals to get distinct faces

All the above steps may occur simultaneously at different regions of a crystallization unit. However an ideal crystallization process consists of a strictly controlled stepwise program.

#### **(v) Ostwald's contributions**

While the concept of a definite super solubility is contained in the earliest writings on the crystal growth subject, Ostwald appears to be the first to explain the

relationship between supersaturation and spontaneous crystallization. Meir's solubility diagram is shown in **Fig. 1.3**. Meir's solubility diagram consists of three zones, which are termed as region I, II and III respectively. Region I corresponds to the under saturated zone, where crystallization is not possible. This region is thermodynamically stable. The region II between the super solubility curve and solubility curve is called as metastable zone, where spontaneous crystallization is not possible, but seeded growth could be initiated in this region. In the region III, spontaneous nucleation is more probable, called as unstable or labile zone.



**Fig. 1.3** Solubility diagram showing different levels of saturation

**(vi) Time**

This is related to the mechanics and the solubility of the solute in a given solvent.

### **(vii) Supersaturation**

A solution in which the concentration of the solute exceeds that of the equilibrium at a given temperature is known as supersaturated solution. A supersaturated solution is thermodynamically unstable. Supersaturation required for crystallization process can be achieved by (i) slow evaporation (ii) slow cooling and (iii) by adding any external impurity. In this case, crystallization takes place by lowering the temperature of the solution under a controlled cooling rate. Supersaturation can be achieved by slow evaporation of the solvent for materials, which are having very small temperature coefficient of solubility. Here crystallization takes place at a constant temperature. Supersaturation can also be achieved by the addition of some impurities. The growth proceeds by the reduction of solubility of the solute due to the presence of an impurity. The selection of suitable growth method depends mainly on the shape of the solubility curve.

The degree of supersaturation of a solution can be expressed by the ratio  $S = C / C^*$ , where  $C$  is the actual concentration of the solution and  $C^*$  is the equilibrium saturation concentration of the solution at a given temperature. Thus,  $S = 1$  denotes saturated solution,  $S < 1$  denotes under saturation, and  $S > 1$  indicates supersaturation.

### **(viii) Crystal habit**

The growth of a crystal at approximately equivalent rates along all the directions is a prerequisite for its accurate characterization. This will result in a large bulk crystal from which samples of any desired orientation can be cut. Further, such large crystals should also be devoid of dislocation and other defects. When the crystal grows with a bulk habit, these imperfections become isolated into defective regions surrounded by large volumes of high perfection. In the crystals which grow

as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect. Needle like crystals have very limited applications and plate like crystals need to be favourably oriented.

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 to yield crystal with better perfection and packing characteristics.

#### **1.4 Advantages of solution growth technique**

The solution growth technique has the following merits

- Simple growth apparatus
- Growth of strain and dislocation free crystals
- Permits the growth of prismatic crystals by varying the growth conditions
- This is the only method which can be used for substances that undergo decomposition before melting

The technique has the following limitations.

- The growth substance should not react with solvent
- This method is applicable for substances fairly soluble in a solvent

### **1.5 Slow cooling technique**

The Main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which such crystallization can begin is usually within the range 45 - 75 °C and the lower limit of cooling is the room temperature.

### **1.6 Temperature gradient method**

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are that

- (a) Crystal grows at a fixed temperature
- (b) This method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change.
- (c) Economy of solvent and solute.

On the other hand, changes in the small temperature differences between the source and the crystal zones have a large effect on the growth rate.

Excellent quality crystals of ferroelectric and piezo-electric materials such as Ammonium dihydrogen phosphate (ADP), Potassium dihydrogen phosphate (KDP) and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method.

## 1.7 Ferroelectricity

A ferroelectric material has a permanent electric dipole, and is named in analogy to a ferromagnetic material (e.g. Fe) that has a permanent magnetic dipole. A ferroelectric solid can be made up by adding together large numbers of molecules with their dipoles aligned. Ferroelectric materials are the part of group of spontaneously polarized pyroelectrics. However, they have an additional property that the polarization can be reversed by an applied field. This feature cannot be predicted from crystal structure.

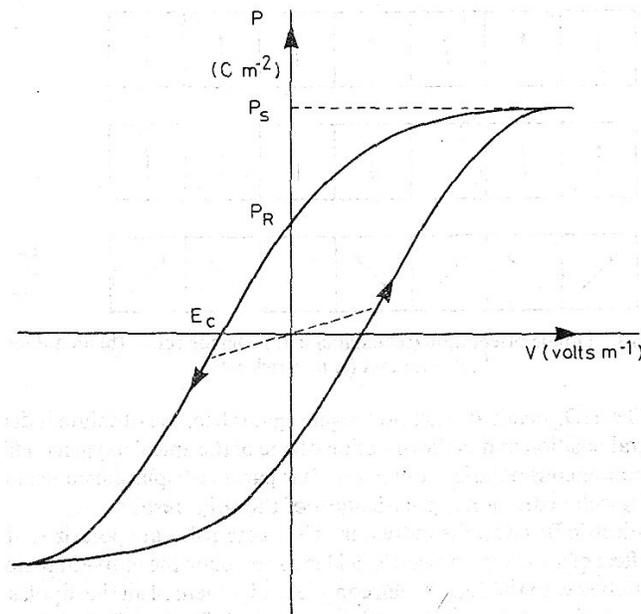
### 1.7.1 Theories of Ferroelectricity

Mason and Mathias (1948) proposed a model theory for BaTiO<sub>3</sub>. In this model they have suggested that stable position for Ti<sup>4+</sup> ion is not at the centre of the oxygen octahedral, but it is at any of the six positions which correspond to slight displacement from the centre towards oxygen ions. When Ti<sup>4+</sup> is in any of these six positions, the unit cell would have dipole moment. However it was not possible to obtain the good agreement of this theory with experimental calculations. Devonshire's Model Theory (1949) [25] considered the atomic dipoles vibrating in the field of its neighbours. The dipole moment is not fixed in magnitude but depend on the displacement from equilibrium positions. Jaynes (1950) [26] proposed a model in which oxygen ions are displaced rather than Ti<sup>4+</sup> ions. Jaynes (1953) [27] has also proposed a theory in which dipole moments are not attributed to atomic displacements. Only electronic states of TiO<sub>6</sub> octahedral are considered. This theory satisfactorily predicts entropy change but its prediction about infrared absorption line at 10 $\mu$  could not be experimentally detected.

In 1950, Slater proposed a similar model. He assumed that in addition to the dipole moment due to displacement, there exists an electronic polarization for each atom. Megaw (1952, 1954) [28] suggested that directional covalent bonding is very important in ferroelectricity of  $\text{PbTiO}_3$  and antiferroelectricity of  $\text{PbZrO}_3$ . According to Megaw  $\text{Zr}^{4+}$  ion has directional covalency which influences behaviour of Pb. However Megaw attributed ferroelectricity to the changes that occur in the character of the bonds at transition temperature which could not be understood properly.

### 1.7.2 Hysteresis behaviour of Ferroelectric crystals

A ferroelectric crystal is polarized even in the absence of an external field [29]. In the ferroelectric ordered state, a hysteresis in the plot of polarization (P) versus applied electric field E is observed. It is analogous to that exhibited by ferromagnetic materials and thus could be explained on the basis of domain theory. Inside an individual domain, the atomic dipoles are aligned parallel to one another, but this direction varies from one domain to another. In the absence of the external electric field the dipoles are oriented in the random direction and the net polarization of the specimen is zero. On increasing the strength of the field, the favourably oriented domains grow at the expense of others and at high-enough field strength, the polarization reaches a maximum value, the crystal has become a single domain. The extrapolation of the linear part in **Fig. 1.4** to zero external field gives spontaneous polarization ( $P_S$ ). When the applied field for a crystal is reduced, the polarization of the crystal decreases, but for zero applied field there remains the remanent polarization ( $P_R$ ).



**Fig. 1.4** P-E hysteresis curve

In order to remove remanent polarization, the polarization of approximately half the crystal must be reversed and this occurs only when a field in the opposite direction is applied. The field required to make the polarization zero again is called the coercive field  $E_c$ . If the coercive field is larger than the breakdown field of the crystal, no change in the direction of spontaneous polarization can be achieved, i.e. under those circumstances we cannot speak of the solid as ferroelectric. Further increase in the field strength results in saturation of the polarization in the reverse direction. The ferroelectric properties of a ferroelectric disappear above a critical temperature  $T_C$  called ferroelectric curie temperature. In transition from the ferroelectric to the non-ferroelectric (paraelectric) phase there are anomalies associated in its physical properties. Thus for a first order transition, there will be a latent heat and for a second order transition, the specific heat will show discontinuity.

At curie temperature ( $T_C$ ), the static dielectric constant attains a high value and obeys Curie – Weiss law [30] in the paraelectric range

$$\epsilon_r = \frac{C}{T - T_C} + \epsilon_{r0}$$

Where  $\epsilon_{r0}$  is a constant having a value of the order of 1% greater or less than  $\epsilon_r$ , and is due to the electronic polarizability only. In the vicinity of the transition temperature  $\epsilon_{r0}$  can be neglected and

$$\epsilon_r = \frac{C}{T - T_C} \quad C \text{ is a constant}$$

### 1.7.3 Ferroelectric domains

The electrostatic energy of a crystal is lowered if the crystal has the direction of the spontaneous polarization which is randomly distributed. This is accomplished in the ferroelectric material by its breaking up into domains, which are volume elements possessing polar axis in one direction. Domains with their polar axis in different direction are separated by domain walls or boundaries. In general, the domains are so randomly distributed as to cause the ferroelectric crystal or ceramic to exhibit net zero polarization. When an electric field or mechanical stress is applied, the favourably oriented domains grow at the expense of the less favourably oriented domains through nucleation and growth mechanism [31]. Under the favourable conditions of sufficiently high stress, this process of domain reorientation continues until a single domain configuration is achieved. Reversal of the direction of the applied stress favours another polar axis and appropriate domain reorientation takes place. The hysteresis loop has its origin in domain rearrangements under the influence of applied electric field. The time used for polarization reversal is called

the switching time. It is of the order of microseconds in case of ferroelectric. It is the basis for considering ferroelectrics for switching purposes and as memory cores for computers. The types of the domain wall motion that can occur in ferroelectric crystal depend on symmetry of both non ferroelectric and ferroelectric phases of the crystals. For tetragonal structure domain walls may give rise to either  $180^\circ$  or  $90^\circ$  polarisation orientations. The rhombohedral crystal structure gives rise to  $71^\circ$  or  $109^\circ$  domain walls [32].

#### **1.7.4 Characteristic properties of Ferroelectrics**

When an electric field,  $E$  is applied to an insulator, polarization is induced into it, which forms an important parameter in the theory of insulators and hence when polarization is being investigated, dielectrics are included into this category [33]. Classification of these materials based on their response in a realizable range of an electric field gives two types of dielectrics, linear and nonlinear. From the theory of linear dielectrics, as the nomenclature shows, the electric polarization  $P$  varies linearly with the applied electric field  $E$ , whereas it varies inversely in the case of nonlinear dielectrics and the ferroelectric materials fall into the latter category which can exhibit spontaneous polarization  $P_s$ . A suitably directed external electric field can be used to bring about a transformation from one state to another, which is a characteristic of ferroelectrics. Pyroelectric materials, which are very closely related to ferroelectrics, result from the interaction between thermal and electrical forces and form a suitable source of research, as the re-orientation of domain structure with an applied electric field as in the case of ferroelectrics is not feasible in pyroelectrics. Thus, spontaneous polarization  $P_s$  and its reversibility are the most fundamental properties of the ferroelectric crystals. It is measured in terms of displacement per

unit volume. The usual hysteresis loop is schematically shown in **Fig. 1.4**. In this figure spontaneous polarization  $P_s$  (OE) is given by the extrapolation from saturation region to the zero field. The intercepts made by the hysteresis loop on the P- axis and the E -axis indicate the remnant polarization,  $P_r$  (OD) and coercive field,  $E_c$  (OF) respectively., the intercept OG represents the total polarization of the ferroelectric material in the saturation field,  $P_{sat}$ . Other methods, which are used, commonly for measuring the magnitude of spontaneous polarization,  $P_s$ , are charge integration technique and pyroelectric measurement using calibration for scaling [34]. The spontaneous polarization,  $P_s$ , in ferroelectric materials generally vanishes at a certain temperature termed as transition temperature or Curie temperature ( $T_c$ ). As a rule, the low temperature phase is polar and possesses a lower symmetry as compared to non polar phase above  $T_c$ . Generally all materials are characterized by only one transition temperature above which  $P_s$  is zero. Exception to this general rule is Rochelle salt, which has two transition temperatures, upper = 24°C and lower = -15°C and its polar phase is only stable in the temperature range between 24°C to -15°C. From this example, one may conclude that the experimental limitations could be the main hurdles for finding the lower  $T_c$ , for majority of materials and its existence cannot be ruled out. Almost all the properties of ferroelectric materials such as dielectric, thermo-optical, etc.; exhibit pronounced variation in the neighbourhood of  $T_c$ . The properties exhibited by most of the ferroelectric materials are enlisted below:

1. They exhibit dielectric hysteresis loop between polarization and the applied electric field, below Curie temperature  $T_c$ .

2. They have ferroelectric domain structure, which may be visible polarized light.
3. They have a high relative permittivity along the polar axis, which is a function of temperature. Above the Curie temperature,  $T_c$ , it falls off obeying Curie-Weiss Law.
4. They possess a pseudo-symmetric structure belonging to polar class.
5. They undergo a transition at the Curie temperature to form a structure of higher symmetry.
6. The Curie temperature is generally raised by the application of biasing field or the hydrostatic pressure.
7. They exhibit piezoelectric and pyroelectric properties below  $T_c$ .
8. There is a sudden appearance of surface charges at the transition.

### **1.7.5 Dielectric properties of Ferroelectrics**

Dielectrics have been primarily used in capacitors and as electrical insulators. This section is essentially concerned with the static dielectric constant, the frequency dependence of dielectric constant and dielectric losses. The most often used terminology is the dielectric permittivity or dielectric constant instead of susceptibility, which is defined as the ratio of the capacitance  $C$  of the capacitor filled with a dielectric to the value  $C_0$  of the same capacitor under vacuum [35]. The electric susceptibility and permittivity are non-dimensional real quantities.

$$\epsilon_r = \frac{C}{C_0} \text{ and } \chi = \epsilon_r - 1$$

The polarization effect, which occurs due to displacement of charges within the material through the progressive orientation of permanent or induced dipoles when subjected to electric field, is important in dielectric. Relative permittivity  $\epsilon_r$  which is referred to as a quantitative measure of displacement or charge effect of the material has a characteristic value for each material. The permittivity is a measure of ease with which polarization is produced in a material and is defined as the ratio of the permittivity  $\epsilon$  of the dielectric to the permittivity of empty space [36].

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

The relative permittivity  $\epsilon_r$  of the dielectric material depends on several factors such as temperature, frequency bonding crystal structure phase constitution and defects. All these factors influence the response of the induced or permanent electric dipoles in the dielectric to a static or alternating electric field. The dielectric constant in the ferroelectric phase consists of two components. Firstly, the component in the dielectric constant due to individual domains, which is independent of the frequency of the electric field, generally up to far infrared frequencies. The second component is due to the domain wall motion that is to partial reversal of the spontaneous polarization. The process can give rise to dielectric losses and it depends strongly on the frequency of the electric field strength, the domain structure and temperature. The following are some important points regarding the ferroelectric ceramics based on the thermodynamical model suggested by Yurkevich and Rolov [37].

1. The ferroelectric Curie temperature  $T_c$  or the temperature of ceramic material strongly depends upon the grains in it in the presence of pores and the micro volume in homogeneity.

2. The Curie -Weiss constant has a value higher than that of the single crystal and depends on the dimension and density of pores in ceramics.

Once the electric field is applied, the balances of charges are perturbed by the following four basic polarization mechanisms [38]

- Electronic polarization
- Atomic/Ionic polarization
- Dipolar/ Orientational polarization
- Space charge polarization

The ability of a dielectric material to store electric energy under the influence of an electric field, results from the field-induced separation and alignment of electric charges. Polarization occurs when the electric field causes a separation of the positive and negative charges in the material. The larger the dipole moment of this charge separation in the direction of a field and the larger the number of these dipoles, the higher the material's dielectric permittivity. In the presence of electronic, ionic and dipolar polarization mechanisms, the polarization is

$$P = \chi_e \epsilon_0 E = (\epsilon_r - 1) \epsilon_0 E$$

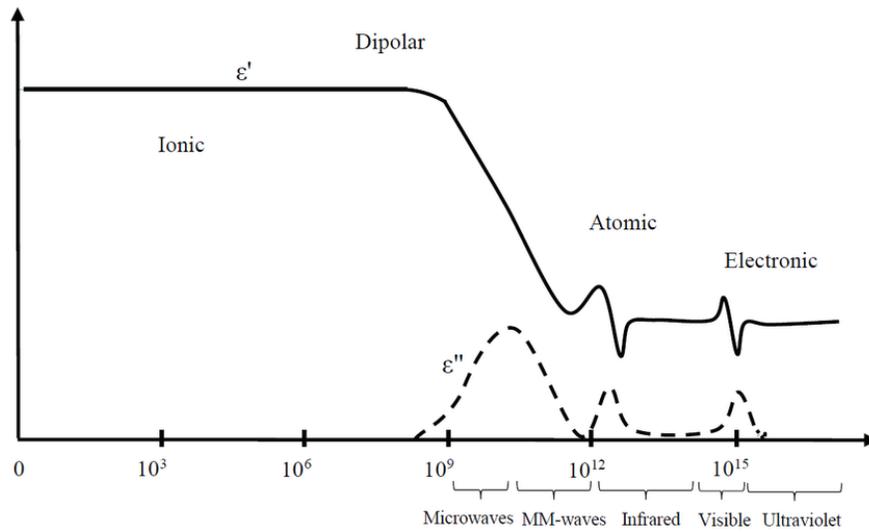
using this Clausius and Mossotti and Debye derived their equations relating dielectric permittivity and polarizability.

$$\alpha = \frac{3}{4} \frac{M}{\pi N_a \rho} \frac{\epsilon_r - 1}{\epsilon_r + 2} \quad \text{Clausius and Mossotti Relation [39]}$$

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0} \quad \text{Debye relation [40]}$$

### 1.7.6 Dielectric loss

The permittivity of a dielectric material has both real and imaginary mathematical representations. The imaginary part of permittivity is represented in mathematical equations as  $\epsilon''$ . This imaginary part of permittivity describes the energy loss from an AC signal as it passes through the dielectric. The real part of permittivity  $\epsilon_r$  is also called the dielectric constant and relative permittivity. The permittivity of a material describes the relationship between an AC signal's transmission speed and the dielectric material's capacitance. When the word "relative" is used in front of permittivity, the implication is that the number is reported relative to the dielectric properties of a vacuum. The imaginary part of the dielectric permittivity which is a measure of how much field is lost as heat during the polarization of a material by an applied alternating electric field is also termed as dielectric loss. The characteristic orientation of the dipoles in an electric field results in a frequency variation of dielectric constant and loss over a broad band of frequencies. The typical behaviour of real and imaginary part of the permittivity as a function of frequency is shown in **Fig. 1.5**.



**Fig. 1.5**  $\epsilon'$  and  $\epsilon''$  as a function of frequency

The relative permittivity of a material is related to a variety of physical phenomena that contribute to the polarization of the dielectric material. In the low frequency range the  $\epsilon''$  is dominated by the influence of ionic conductivity. The dielectric properties of solid dielectrics at microwave and radio frequencies are highly influenced by the ionic positions and changes caused by the lattice vibrations. The dielectric loss is another parameter of great concern in dielectrics which occurs due to lagging with applied as well as electron and ion migration.

A good dielectric material exhibits high relative permittivity and dielectric loss. Two types of dielectric losses are identified in crystalline solids at high frequencies, namely intrinsic losses and extrinsic losses. The low frequency phonons are responsible for the intrinsic dielectric losses in solid dielectrics. The extrinsic losses are occurred due to the interaction between the charged defects and the microwave fields. The dielectric loss can be estimated from the following relations.

$$\varepsilon = \varepsilon_r \varepsilon_0$$

The loss tangent is given as [41]

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

Here  $\varepsilon'$  is known as the real part of the permittivity,  $\varepsilon_r$  is the relative permittivity or dielectric constant and  $\varepsilon_0$  is the permittivity of free space. Here the first and second term in the imaginary part of the complex permittivity represent the dielectric and ohmic losses respectively.

### 1.7.7 Classification of Ferroelectric crystals

Based on the magnitude of Curie constant, ferroelectrics can be classified in to three groups [42]

- perovskite
- Tangsten Bronze
- Layered perovskite

#### 1.7.7.1 Perovskite

The Curie- Weiss constant is about 105 and most of the compounds in this family are mixed metal oxides. Barium Titanate was the first perovskite type compound shown as ferroelectric and is till to date the most thoroughly investigated ferroelectric material.  $\text{TiO}_6$  Octahedra , forms the basic cell of Barium Titanate, which determines its dielectric properties because of its high polarizability. The small  $\text{Ti}^{4+}$  ions, having more space with oxygen octahedra are the cause for this high polarizability.

### **1.7.7.2 Tungsten Bronze**

The second group comprises of materials whose C values are near 103. The bronze form has a meta stable structure at room temperature. The stabilization of 7<sup>th</sup> bronze structure seems to be possible with a certain degree of disorder, as the bronzes usually appear as solid solutions of at least two components. Ordering of rotatable permanent dipoles in this group takes place at 6 the transition temperatures. Such dipoles are associated with hydrogen bonds as in  $\text{KH}_2\text{PO}_4$  or with molecular groups such as  $\text{NO}_2$  in  $\text{NaNO}_2$ . Most water soluble ferroelectrics are in this category. Tungsten bronze type sodium niobate is useful for frequency doubling applications. Meta niobate is still widely used in poled ceramic form as a low Q piezo-electric transducer.

### **1.7.7.3 Layered Perovskite**

The third group possesses C values near one and is termed improper ferroelectrics. The best example in this category is Gadolinium Molybdate. Ceramics capacitors of  $\text{BaTiO}_3$  with dielectric constants in excess of 2000 are made commercially. Layered perovskites which are effective ferroelectric substances with higher Curie temperature and coercive fields, and low dielectric loss are good candidate materials for high frequency applications.

## **1.8 Objectives of the present work**

The present investigation was aimed at

- (i) Synthesizing the chosen materials for the growth of single crystals.
- (ii) Crystal structures are confirmed together with the vibrational analysis and single crystal XRD studies.

- (iii) Confirming the presence of some functional groups using FTIR and Raman studies.
- (iv) Determination of Optical bandgap energy using Tauc plot.
- (v) To find the ferroelectric properties of tetrachloro zincate crystals.