CHAPTER 1

REVIEW ON CRYSTAL GROWTH, FERROELECTRICS
AND NON-LINEAR OPTICS

1.1 INTRODUCTION

Crystal growth is an important field of materials science, which involves controlled phase transformation. A single crystal consists of atomic arrays that are periodic in three dimensions with equal repeated distances in a given direction. Generally, matter exists in three states, namely, solids, liquids and gases. The solid state materials can be further classified as single crystals, poly crystals and amorphous materials depending upon the arrangement of constituent molecules, atoms or ions. An ideal crystal is one in which the surroundings of any atom would be exactly the same as the surroundings of every similar atom. Real crystals are finite and contain defects. However, single crystals are solids in the most uniform condition that can be attained and this is the basis for most of the uses of crystals. The uniformity of single crystals can allow the transmission without scattering of electromagnetic waves. Since, for the past three decades, one could see that there are lot of developments in science and technology—especially, in the fields of electronics, fibre-optic communication and lasers. The vacuum tubes in electronic equipment have become obsolete and have already been replaced by transistors, integrated circuits and microprocessors. We could achieve this development due to the availability of single crystals like silicon, germanium and gallium arsenide. Also, with the invention of non-linear optical properties in some single crystals, we can have tunable lasers. Since there is a vast market for solid state devices in the fields of computers, telecommunication etc., effort has been made in recent years on producing larger size single crystals (Brice 1986; Laudise 1970).
Crystal growth is a controlled phase transformation to solid phase, either from solid or liquid or gaseous phase. The growth units, namely the atoms or molecules, diffuse to the growth site from the mother phase, when given sufficient time to get orderly arranged on the lattice.

Crystals are the unacknowledged pillars of modern technology, which is very much dependent upon materials/crystals such as semiconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optic, piezoelectric, acoustooptic, photosensitive materials and crystalline films for microelectronics and computer industries. All this involves research in crystal growth.

Days are not far off for the telephone companies to tear out their cables replacing with optical fibers. Regarding the optical communication, most of tomorrow's interesting technologies such as being somewhere, being somebody, and being at someone's time will work by manipulating light and not electricity. It is worth switching to photon, because it travels much faster than electron, has no mass and can be made to pass through each other unperturbed. The above mentioned technological feats are possible only because of the constant and tireless efforts of crystal growers who continue their search for newer and better materials.

The consistency of the characteristics of devices fabricated from a crystal depend on the homogeneity and defect contents of the crystal. Hence, the process of producing single crystals which offer homogeneous media in the atomic level with directional properties, attract more attention than any other process involved. The procedure of growing crystals varies very widely: it is mainly dictated by the characteristics of the material and its size (Buckley 1951; J.W.Mullin 1976) for example, the fabrication of many electronic devices need bulk single crystals which can be either pulled or frozen from the melt.
The growth of large single crystals from aqueous solution is of interest for essentially two reasons. First, there is a growing body of applications in the area of high-power laser technology where such solution grown crystals are required. To date, depending on the material, desired crystals have been either entirely unavailable or else available only at very high cost. Second, research into this area of crystal growth and the corresponding in-depth examination of several key systems provides fundamental case studies generating theory and technology, applicable to all of solution crystal growth, including new aqueous growth systems and high temperature solution growth as well (Bordui 1987).

Since, an understanding of the various crystal growth methods is very much essential for the growth of non-linear optical and ferroelectrics single crystals, the materials of choice for this investigation, the author discusses in the following sections the fundamentals of the various methods of growing single crystals.

1.2 CLASSIFICATION OF CRYSTAL GROWTH

The growth methods for obtaining single crystals may be classified according to their phase transformation,

Growth from solid \( \rightarrow \) solid - solid phase transformation
Growth from liquid \( \rightarrow \) liquid - solid phase transformation
Growth from vapour \( \rightarrow \) vapour - solid phase transformation

Accordingly the crystal growth methods are classified. One can consider the conversion of a polycrystalline piece of a material into a single crystal by causing the grain boundaries to be swept through and pushed out of the crystal in the solid - solid growth of crystals (Mullin 1972). Crystal growth from liquid falls into four categories namely melt growth, flux growth,
hydrothermal and low temperature solution growth. There are number of growth methods in each category. A brief outline on various important techniques of crystal growth has been presented below.

1.3 GROWTH FROM THE MELT

This is the most important method of crystal growth. 80% of the global requirement of crystals is grown by this method. Melt growth is the process of crystallization by fusion and resolidification of the pure material. In this technique, apart from possible contamination from crucible material and surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than the other methods (Gnanam et al 1982). In principle, all materials can be grown into a single crystal from the melt, provided they melt congruently, they do not decompose before melting and they do not undergo a phase transition between the melting point and room temperature. The melt growth can be classified as follows.

(i) Bridgman - Stockbarger technique  
(ii) Czochralski technique  
(iii) Kyropoulos technique  
(iv) Zone melting technique  
and (v) Verneuil technique

The important feature of Bridgman technique is the steady motion of a freezing solid - liquid interface along an ingot which is mounted either vertically or horizontally. The material is melted in a vertical cylindrical container. The container is lowered slowly from the hot zone of the furnace into the cold zone (Bridgman 1925). Crystallization begins at the tip of the container by forming a nucleus and continues to grow from that nucleus. One of the constraints of this technique is the choice of the crucible. The crucible should not contaminate the melt. The crystal should not adhere to the crucible
as this also can introduce excessive strains during cooling. This technique cannot be used for materials which decompose before melting. This technique is best suited for low melting point materials. Germanium, gallium arsenide and such other materials expand on solidification and hence this method is not useful to grow such crystals. By this technique, we can grow AgBr, AgCl, CaF₂, PbS etc..

In Czochralski method, the material is taken in a crucible and is kept in a furnace. By controlling the furnace temperature, the material is melted (Zulchner 1983). A seed crystal is lowered to touch the molten charge which has been maintained at its melting point. 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. Liquid Encapsulated Czochralski abbreviated as LEC technique makes it possible to grow single crystals of materials which consist of components that produce high vapour pressure at the melting point. This refined method of Czochralski technique is widely adopted to grow the III-V compound semiconductors.

In Kyropoulos technique, the crystal is grown in a larger diameter. From the larger diameter crystal, we can make windows, prisms, lenses and other optical components. As in the Czochralski method, here also the seed is brought into contact with the melt and is not raised much during the growth, i.e., 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 into the melt. The major use of this method is for alkali halides to make optical components.

In the zone melting technique, a liquid zone is created by melting a small amount of material in a relatively large or long solid charge or ingot. It is then made to traverse through a part or the whole of the charge. It is a
more advantageous method than the other methods due to the removal or addition of impurities from or to the crystal as the crystal is growing. In this method, the rate of zone movement depends on the orientation of the two solids binding the liquid zone as well as the thickness and temperature of the zone (Keller et al 1981).

In the Verneuil technique, fine dry powder of the material to be grown is showered through a 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, maintained on a pedestal at the bottom of the flame (Hopper et al 1980). 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 for use in jewelled bearing and lasers. This technique is widely used for the growth of synthetic gems.

1.4 GROWTH FROM VAPOUR

Crystals of high purity can be grown from vapour phase by sublimation, condensation and sputtering of elemental materials. Molecular beam techniques have also been applied recently to crystal growth problems. The most frequently used method for the growth of bulk crystals from vapour phase 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 multinucleation. This growth is mainly sub-divided into (i) Physical Vapour Transport (PVT) (ii) Chemical Vapour Transport (CVT). In PVT, no carrier gas is used, but, in CVT, carrier i.e., transporting gas is used to carry the material from source zone to the growth zone (Schafer 1964). The crystals of
Al₂O₃, CdS, ZnSe, GaP and GaAs are grown from vapour phase. The commercial importance of vapour growth is in the production of thin layers by Chemical Vapour Deposition (CVD).

1.5 GROWTH FROM SOLUTION

This method is widely used to grow the crystals which have high solubility and have variation in solubility with temperature (Chernov 1984). There are two methods in solution growth depending upon the solvents and the solubility of the solute. They are

(i) High temperature solution growth (flux growth, hydrothermal growth)
and (ii) Low temperature solution growth.

1.5.1 High temperature solution growth

Flux growth

In this method, a solid is used as the solvent instead of liquid and the growth process takes place well below the melting temperature (Hubner 1969) of the solute. The flux growth is preferably used for the following reasons;

(i) the material melts incongruently
(ii) the melting point of the material is too high
(iii) the material is non-stoichiometric at its melting point due to a high vapour pressure of one or more constituents
(iv) better quality crystals can be grown by this method
and (v) a destructive phase transition is present closer to the melting point.
Hydrothermal growth

A number of metals, metal oxides and other compounds, practically insoluble in water upto its boiling point, show an appreciable solubility when the temperature and pressure are increased well above 100°C and 1 atmosphere respectively. Growth is usually carried out in steel autoclaves with gold or silver linings. The liquids from which the process starts are usually alkaline aqueous solutions. Pressure is typically in the range of hundreds or thousands of atmosphere. The requirements of high pressure presents practical difficulties and there are only few crystals of good quality and large size grown by this technique (Ballman et al 1963). Quartz is the crystal grown industrially by this technique.

1.5.2 Growth of crystals from low temperature solution

Among the various methods of growing single crystals, solution growth at low temperature occupies a prominent place owing to its versatility and simplicity. Materials which decompose on heating or which exhibit any structural transformation while cooling from the melting point can be grown by solution growth if suitable solvents are available. This method is more widely used to grow bulk crystals (James et al 1975). After undergoing so 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 the melt growth though the rate of crystallization is very slow. Since growth is carried out at room temperature, the concentration of structural imperfections in solution grown crystals is relatively low (Brice 1972).
Solution and solubility

Solution is a homogeneous mixture of a solute in a solvent. Solute is the component which is present in a smaller quantity. For a given solute, there may be different solvents. The solvent must be chosen taking into account the following factors to grow crystals from solution. A solvent of choice is the one with

(i) a good solubility for the given solute
(ii) a good solubility gradient
(iii) less viscosity
(iv) less volatility
and (v) less corrosion

If the solubility is too high, it is difficult to grow bulk single crystals and too small a solubility restricts the size and growth rate of the crystals. Solubility gradient is another parameter which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution; while the level of supersaturation could not be varied by reducing the temperature in the former, even a small fluctuation in the temperature will affect the supersaturation to a large extent in the latter disabling the growth of good quality bulk crystals in both cases. 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.

Growth of crystals from solution is mainly a diffusion controlled process; the medium must be less viscous to enable faster transference of the growth units from the bulk solution by diffusion. Hence a solvent with less viscosity is preferable (Ohara et al 1973). Supersaturation is an important parameter for the solution growth process. Crystal grows by the accretion of the solute in the solution as a degree of supersaturation is maintained. 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 may 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 may be determined gravimetrically. A sample of the clear supernatant liquid is withdrawn by means of a warmed pipette and a weighed quantity of the sample is analysed. The solubility curve can then be plotted in this way by repeating the above for different temperatures.

**Expression of supersaturation**

The supersaturation of a system may be expressed in a number of ways. The basic units of concentration as well as temperature must be specified. The concentration driving force ($\Delta C$) the supersaturation ratio ($S$) and relative supersaturation ($\sigma$) are related to each other as follows:

\[
\Delta C = C - C^* 
\]

where $C$ is the actual concentration of the solution and $C^*$ is the equilibrium concentration at a given temperature.

Supersaturation ratio \[ S = \frac{C}{C^*} \]
Relative supersaturation \[ \sigma = \frac{C - C^*}{C^*} \]
\[ \sigma = S - 1 \]

If the concentration of a solution can be measured at a given temperature and the corresponding equilibrium saturation concentration is known, then, it is easier to calculate the supersaturation.
Meir carried out extensive research into the relationship between supersaturation and spontaneous crystallization (Meir et al 1987) and the results can be represented as shown diagramatically in figure 1.1. The lower continuous line is the normal solubility curve for the salt concerned. Temperature and concentration at which spontaneous crystallization occurs are represented by the upper broken curve, generally referred to as the supersolubility curve. This curve is not well defined as the solubility curve and its position in the diagram depends on the degree of agitation of the solution.

The diagram is divided into three zones.

(i) the stable (undersaturated) zone, where crystallization is not possible
(ii) the second region is a metastable zone, between the solubility and supersolubility curves, where spontaneous crystallization is improbable. However, if a crystal seed were placed in such a metastable solution, growth would occur on it
and (iii) third region is the unstable or labile (supersaturation) zone, where spontaneous crystallization is more probable.

If the solution whose concentration and temperature are represented by point A in figure 1.1 is cooled without loss of solvent (line ABC), spontaneous crystallization cannot occur until conditions represented by point C are reached. At this point, crystallization may be spontaneous or it may be induced by seeding, agitation or mechanical shock. Further cooling to some point D may be necessary before crystallization can be induced, especially with very soluble substances such as sodium thiosulphate.

The evaporation of solvent from the solution may also result in supersaturation. Line AB'C' represents an operation carried out at constant temperature. Penetration beyond the supersolubility curve into the labile zone rarely happens, as the surface from which evaporation takes place is usually
Figure 1.1 Meir's solubility diagram
supersaturated to a greater degree than the bulk of the solution. Crystals which appear on this surface eventually fall into the solution and seed it. In practice, a combination of cooling and evaporation as represented by the line AB'C' in figure 1.1 is also adopted.

**Low temperature solution growth can be subdivided into the following methods,**

(i) Slow cooling method  
(ii) Slow evaporation method  
and (iii) Temperature gradient method

(i) **Slow cooling method**

It is the best way to grow crystals by solution technique. Its main disadvantage 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.

(ii) **Slow evaporation method**

This method is similar to the slow cooling method in view of the apparatus requirements. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.005°C and rates of evaporation of a few mm³/hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. But inadequacies of the
temperature control system still have a major effect on the growth rate. This method is the only one which can be used with materials which have very small temperature coefficient of solubility.

(iii) 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 fixed temperature
(b) this method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change
and (c) economy of solvent and solute.

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

Crystals grown from solution

Ferroelectric, non-linear optical materials attract wide attention due to the increasing applications in telecommunications, optical information storage and computing.

The following solution grown crystals were chosen for this piece of work, considering their potential applications in the fields of non-linear optics and ferroelectrics.
(i) **Potassium dihydrogen phosphate (KDP) and its family**

This crystal is a non-linear, ferroelectric crystal exhibiting tetragonal structure at room temperature having point group of 42m and it is being potentially used for the following applications:

(a) this is an electro-optic crystal which is widely used in laser communication systems, computer memory devices and non-linear optics

(b) this can be used for polarization filter, electronic light shutter, electronic light modulator, optical voltmeter, piezo optic resonator and optical rectifier

(c) the piezoelectric property of KDP makes it useful for the construction of crystal filters and frequency stabilizers in electronic circuits

and (d) this can also be used for frequency reforming in a neodymium laser.

(ii) **L-arginine phosphate (LAP) and its family**

Organic non-linear materials gain importance over ionic materials because of their large polarizability and wide transmission window. This is one of the new semi-organic non-linear crystals with relatively better non-linear properties than KDP. It crystallizes in a monoclinic structure with space group P2₁. Because of its superior properties, LAP is expected to replace KDP, especially in the laser fusion experiments.

(iii) **Triglycine sulphate (TGS) and its family**

Triglycine sulphate is a ferroelectric crystal exhibiting monoclinic structure having the space group of P2₁. This crystal has outstanding pyroelectric properties at room temperature and has been identified as ideal
material for pyroelectric detectors. Elements of these crystals are used as detectors in FT-IR spectrometers. Some of the amino mixed TGS crystals show reduction in dielectric permittivity and loss as compared with pure TGS. The presence of one of the amino acids, L-alanine, contributes to effective internal bias in these crystals, which inhibits ferroelectric switching that results in considerably improved device characteristics. Normally, operating close to the Curie temperature, as in TGS, introduces additional problems such as depoling, Barkhausen noise and excessive element capacitance. A series of amino mixed crystals have been grown from aqueous solution and their electrical properties have been evaluated using standard techniques to identify the better additive so as to improve the performance of TGS crystals as a pyroelectric detector.

1.6 FERROELECTRICS

One of the most general classes of materials is dielectrics. A dielectric is a material whose electrical and often optical properties are influenced by electric fields. Ferroelectrics are materials belonging to a special class of dielectrics which have the following special features.

(i) Ferroelectric materials exhibit a dielectric hysteresis loop between polarization (P) and applied field (E) below a certain critical temperature; this temperature is called ferroelectric transition temperature ($T_c$).

(ii) They possess a high dielectric constant along the polar axis, which is a function of temperature and reaches a peak value at the Curie temperature.

(iii) They have a ferroelectric domain structure which may be visible in polarized light.

(iv) They possess a pseudo-symmetric structure and in the ferroelectric phase the structure belongs to the polar class.
(v) they have a transition at the Curie temperature to form a structure of higher symmetry
(vi) all ferroelectric materials show pyroelectric and piezoelectric properties below Curie temperature
(vii) there is sudden appearance of surface charge at the transition
and (viii) the transition at the Curie temperature is associated with either specific heat anomaly or the latent heat phenomenon.

Ferroelectricity usually disappears above a certain temperature called the transition temperature ($T_c$), at which the crystal switches over from the polar state to the non-polar state. The phase transition at $T_c$ can be of the first order or of the higher (usually second) order. In the first kind transition, spontaneous polarization ($P_s$) abruptly drops to zero at the Curie point. In the second transition, $P_s$ smoothly goes to zero at the Curie point. In the diffused phase transition, $P_s$ gradually decreases and in the temperature region, known as the Curie region, the ferroelectric and paraelectric phases coexist. The phase transition can be explained by other way. In the first order transition, volume, entropy and polarization of the crystal change discontinuously at the transition point. In the second order transition, specific heat changes discontinuously whereas volume, entropy and polarization change continuously at the transition point. In the first order transition, the energy appears as latent heat in an infinitely narrow temperature range, while in second order transition, there is no release of latent heat but the thermal expansion coefficient shows anomalous behaviour over a finite range of temperature.

1.6.1 Spontaneous Polarization

The intensity of polarization ($P$) is equivalent to the electric dipole moment per unit volume of the dielectric material. Spontaneous polarization is due to the ordering of dipoles that occur under the influence of internal process in a dielectric, without the effect of external factors. A ferroelectric
material generally consists of domains or regions of homogeneous polarization, which differ only in the direction of spontaneous polarization \( P_s \) so that the total polarization of the specimen is equal to zero. The polarization (\( P \)) of ferroelectrics varies in a non-linear fashion with field strength \( E \). This relation takes the form of a closed curve, called the hysteresis loop (figure 1.2). When \( E=0 \), the spontaneous polarization \( P_s \) in a single domain specimen is either positive or negative in sign. As the field strength grows in the direction of vector \( P_s \), the polarization (\( P \)) increases due to induced polarization, such as electronic, ionic and dipolar types. However, if the applied electric field is of opposite sign, then at a certain field strength \( E_c \), polarization reversal will take place. This field strength \( E_c \) is referred to as coercive field. Saturation polarization is the maximum polarization obtained from the hysteresis loop as shown in figure 1.2. The intercept on polarization axis at \( E=0 \) gives remanent polarization (\( \pm P_r \)) and the intercept on the field axis when the polarization becomes zero and gets reverted on increase of the field in opposite direction gives the coercive field \( E_c \).

Ferroelectric materials are distinguishable from the other classes of dielectrics in the hysteresis measurements. The area of the hysteresis loop represents energy that is dissipated within the sample as heat. For this reason, the hysteresis behaviour is mainly carried out at low frequency i.e., 60 Hz. The hysteresis arises from the energy needed to reverse the metastable dipoles during each excursion of the field (Landolt-Bornstein 1969).

The rectangularity of the hysteresis loop is the main requirement imposed on the materials used for memory cells. In the absence of an electric field, a polarized ferroelectric is found to be in two stable states, positive and negative, with polarization \( + P_s \) and \( - P_s \). In one of these states, the memory cell of a digital computer system is assigned to store 'one' and in the other 'zero' changing the polarity of the record voltage that switches the ferroelectric from one state to the other (Lines et al 1977).
Figure 1.2. A hysteresis loop illustrating the coercive field $E_c$, the spontaneous polarization $P_s$ and the remanent polarization $P_r$. 
1.6.2 Ferroelectric domains

When ferroelectric crystal is cooled below the Curie temperature, in the absence of external electric field and mechanical stress, it breaks up into domains of different orientations. These domains are nothing but the regions of homogeneous polarization. In a ferroelectric crystal, all these spontaneously polarized unit cells are oriented identically with in a domain. As a result, each domain has macroscopic spontaneous polarization. A line of separation between two neighbouring domains is called a domain wall. Accordingly, the dipoles in the neighbouring domains are oriented in such a way that, at a wall, the projection of the polarization vector of one domain is equal in magnitude and opposite in direction to the projection of the polarization vector of the neighbouring domain. A single crystal cannot contain more than one crystallite and has domain walls but no grain boundaries. A polycrystalline material may contain a number of domains in each crystallite. A domain wall does not interrupt the crystal lattice (Jona et al 1962).

1.6.3 Pyroelectric materials

The pyroelectric effect is the change in electrical polarization ($P_8$) caused by a change in temperature. Pyroelectric materials are characterized by the fact that they have a unique polar axis. For a pyroelectric effect to exist, reversibility of polarization is not necessary.

Pyroelectric effect

Pyroelectric effect is a vectorial phenomenon. Mathematically, it is a relation between a scalar (temperature) and a vector (polarization). Physically, it is the change of positive and negative polarization charges on the polar crystals with temperature. When pyroelectric material is heated, spontaneous polarization ($P_8$) changes giving rise to free unlike charges on the opposite sides of the crystal surface, the sign of the charge depending on the sense of
the domain orientation. The flow of these charges registered by the electrometer makes for pyroelectric polarization, which is a function of temperature \( T \).

The pyroelectric properties of substances are quantitatively described by pyroelectric coefficient 'p' which relates a change in polarization to the temperature change inducing the said variations in polarization

\[
p = \frac{dP}{dT}
\]

Because polarization 'P' is a function of temperature 'T' and strain 'x', which in turn depends on T

\[
p = \frac{dP}{dT} = \frac{dP}{dT} + (\frac{dP}{dx}).(\frac{dx}{dT}) = p_1 + p_2
\]

where \( p_1 = \frac{dP}{dT} \) defines the true or primary pyroelectric effect (i.e., a change in spontaneous polarization with temperature) and \( p_2 \) defines the secondary effect.

If the sample is constrained and is incapable of vibration with temperature changes, the secondary effect is non-existent. All pyroelectric materials also exhibit an inverse electrocaloric effect, which is a change in the temperature of crystals under polarization.

1.6.4 Piezoelectricity

In the year 1880, Jacques and Pierre Curie discovered the phenomenon of piezoelectricity. Piezoelectricity is the phenomenon in which a crystal, under the action of mechanical stress, becomes electrically charged with opposite charges appearing at the two ends of the crystal. This effect occurs only with some special classes of crystals which have polar axes. The phenomenon may be explained as follows. Matter is electrical in nature and
a crystal is made up of a large number of positive and negative ions which ordinarily neutralize each other resulting in no dipole moment. But, the stressed crystal undergoes a slight geometrical deformation, thereby disturbing and deforming the charge distribution; this causes a net resultant dipole moment, which can be detected by an electrometer or some other suitable electrical devices. This phenomenon is different from pyroelectricity (Burfoot 1967).

The converse piezoelectric phenomenon is also possible— that is, under the action of an electric field, elastic strain is developed in a crystal. Both the direct and converse piezoelectric effects are exhibited by the same classes of crystals. The nature of charges developed on the opposite faces of a piezoelectric crystal depends upon the nature of the applied stress. Thus, if a compressional stress on a crystal produces a positive dipole moment, then a tensile stress on the same crystal produces in it a negative dipole moment. Similar cause exists for converse piezoelectric effect also. Electrostriction is a phenomenon in which the physical or geometrical strain produced in a crystal is proportional to the square of the applied electric field and consequently independent of the field direction. On the other hand, owing to piezoelectricity, the strain is linearly proportional to the applied electric field and hence the nature of strain changes its sign with the reversal of the electric field. Electrostriction is a universal phenomenon in the sense that it is exhibited by crystals of all classes i.e., both centrosymmetric and non centrosymmetric.

1.6.5 Classification of Ferroelectrics

The classification of ferroelectric materials has become very difficult, because this includes variety of parameters. However, classification of ferroelectric materials has been proposed according to different criteria as follows.
(i) **Crystal chemical classification**

According to this classification, this can be divided into two groups:

(a) Hydrogen bonded (soft ferroelectrics) which can be easily prepared by solution method. Eg., Potassium dihydrogen phosphate (KH$_2$PO$_4$), Rochelle salt (NaKC$_4$H$_6$O$_6.4$H$_2$O), Triglycine sulphate ((NH$_2$CH$_2$COOH)$_3$H$_2$SO$_4$)

and (b) Ferroelectric oxides (hard ferroelectrics) which can be prepared at high temperature either in single crystals or ceramics forms. Eg. KNbO$_3$, BaTiO$_3$, PbNb$_2$O$_3$ etc..

(ii) **Classification according to the existence of lack of centre of symmetry in the point group of their non polar phase**

This kind of classification also divides ferroelectrics into two groups. The first group consists of those ferroelectrics that are piezoelectric in the unpolarized phase. eg., KH$_2$PO$_4$(KDP), Rochelle salt. The second group includes those ferroelectrics which are not piezoelectric in unpolarized phase, such as BaTiO$_3$, ((NH$_2$CH$_2$COOH)$_3$H$_2$SO$_4$) (TGS), PbNb$_2$O$_7$ etc. This classification is useful for the thermodynamic treatment of the ferroelectric transitions.

(iii) **Classification according to the nature of the phase change at the Curie point**

According to this classification, the ferroelectrics are divided into two groups. Order-disorder group and displacive group. Hydrogen bonds are responsible for order-disorder phase transition eg. KDP, TGS etc. In oxygen bonded crystal, a small change in atomic position will cause the displacive phase transition, eg., BaTiO$_3$ and other oxide ferroelectrics.
(iv) **Classification according to the number of directions of spontaneous polarization**

According to this classification, there are two groups. The first group comprises those ferroelectrics that can polarize along only one axis, such as TGS, KDP, Rochelle salt, Colemanite etc. The second group includes those ferroelectrics that can polarize along several axes that are equivalent in non-polar phase, eg., BaTiO$_3$, PbNb$_2$O$_6$ etc.

### 1.6.6 Applications of ferroelectrics

The study of ferroelectricity has been closely linked with device applications. The pyroelectric properties of ferroelectrics make them very suitable for thermal detection. This can be used to detect any radiation which results in a temperature change of the crystal. They also have useful features at room temperature operation. Eg., TGS has been the most extensively studied material for thermal detector applications. Pyroelectric detectors can be used to record infrared images(pyroelectric vidicon tubes).

The presence of hysteresis loop makes them possible to use ferroelectrics as memory elements in computers. The ferroelectric materials can be used as a thermoautostatic non-linear dielectric element (TANDEL). They can be used to measure pressure and can also be used as frequency multiplier.

Applications based on piezoelectric, dielectric and semiconducting effects of the ferroelectrics have already lead to industrial products. Transducer uses the piezoelectric effect to convert small motions into electric charges, as in ultrasonic detectors, strain-gauges, microphones, etc. Since piezoelectric materials have a natural resonance frequency, they are commonly used to control oscillator frequencies and in narrow-band wave filters in the field of telecommunications. The high permittivity values near
the transition temperature lead to the use of ferroelectric materials in miniature capacitors. Ferroelectric condensers have values which can be changed electrically. Thus ferroelectric condensers have been used for tuning in superhets and frequency modulators. It can be used as dielectric amplifier and low frequency power amplifier in remote controls.

1.7 NON-LINEAR OPTICS

NLO effects are analysed by considering the response of the dielectric material at the atomic level to the electric fields of an intense light beam. The propagation of a wave through a material produces changes in the spatial and temporal distribution of electrical charges as the electrons and atoms interact with the electromagnetic fields of the wave. The main effect of the forces exerted by the field on the charged particles is displacement of the valence electrons from their normal orbits. This perturbation creates electric dipoles whose macroscopic manifestation is the polarization (Narasimhamurty 1981).

In linear materials, the response is always proportional to the stimulus. The induced polarization is proportional to the field and the susceptibility is independent of the field. In practice, this is always the case at low fields. However at high fields, the polarization stops being proportional to the field and hence the susceptibility starts depending on the field.

It is called Non-linear Optics (NLO) because, at high intensity, the graph representing the dependence of optical polarization on the light field amplitude has curvature and deviates from straight line. When a string is bowed with much force or a wind instrument is blown hard, many overtones may be generated; similar thing happens to the electrons in matter when they are violently excited by high intensity light; overtones of light are created. This has the dramatic effect that a red light beam may be changed to a UV beam with twice or thrice the frequency or one half or one third of the wavelength.
Coherent radiation at a few discrete frequencies can be produced by laser devices as in solid-state lasers or with narrow range of tunability as in dye lasers. Many applications require frequencies that are not readily available from such laser sources. The most effective way for converting a fundamental laser frequency to other frequencies, either to higher or to lower frequencies, is harmonic generation or parametric oscillation in a noncentrosymmetric crystalline medium (Bhawalkar et al 1965). Now, after 30 years of research with NLO materials, it is possible to cover almost continuously the range from 170nm to 18μm. As a result, further extension of applications to the ultraviolet (UV) and far-infrared regions will be possible. However, materials limitations are significantly slowing the development of required optical devices.

One of the obvious requirements for a non-linear crystal is that it should have excellent optical quality. This means that for new materials, for which single crystal specimens are not available, it is necessary to grow single crystal specimens of optical quality. Thus in many cases the search for new and better non-linear optical materials is very largely a crystal growing effort. It is realized that the requirements on optical quality for a useful non-linear optical material are more stringent than even the most exacting requirements on optical quality for materials used in linear optics. For a device to succeed, it is vital that it meets a number of other criteria and these other criteria should receive greater emphasis. The relevant issues include reliable crystal growth techniques for availability, optical non-linearity, birefringence, moderate to high transparency and optical homogeneity for high conversion efficiency, mechanical strength, chemical stability, polishing and coating technology for ease of fabrication, low absorption, temperature phase matching bandwidth, fracture toughness, thermo-mechanical properties for high average power, damage threshold, non-linear absorption and brittleness index for lifetime and system capability.
KDP is an efficient angle-tuned dielectric medium for optical harmonic generation in and near the visible region (Sliker et al 1963). This material offers high transmission throughout the visible spectrum and meets the requirements for an optical birefringence large enough to bracket its refractive index for even the extreme wavelength over which it is transparent. An additional advantage of KDP is its ability to withstand repeated exposure to high power density laser radiation without inducing strains and subsequent inhomogeneities in the refractive index (Endert et al 1982). These characteristics make KDP a desirable material for frequency doubling and mixing experiments with many solid state and dye lasers with fundamental wavelengths between 1060 and 525nm.

KD$_2$PO$_4$ (DKDP) provides the same excellent conversion efficiency and resistance to optical damage as KDP, but has the advantage of higher transmittance at 1060 nm. This characteristic is useful when harmonic generation is attempted with high repetition rate, high average power lasers operating in the 1000nm region.

The non-linear effect observed in some crystals provides a means of obtaining additional wavelengths from single frequency lasers. To generate an optical harmonic, two conditions must be fulfilled. First, a non-linear material must be selected such that the necessary interaction between the incident electromagnetic wave and the material occurs. Second, the crystal material must be oriented so that the laws of conservation of energy and momentum are preserved. This condition can be achieved by matching the velocities of the fundamental and second-harmonic waves propagating through the crystal. The direction of propagation must be at an appropriate angle $\theta$, with respect to the crystal optic axis (angle tuning). Each combination of fundamental and second harmonic requires a different polar angle to provide the necessary indices of refraction. Alternatively changing the crystal temperature (temperature tuning) can, in some materials, achieve the same effect (Koechner 1992).
1.7.1 Electro-optic modulator

Crystals which belong to twenty symmetry classes, which lack a center of symmetry, can show a linear electro-optic effect; that is, a change in refractive indices being directly proportional to an applied voltage. The symmetry conditions for the occurrence of this effect, are exactly the same as for the occurrence of the piezoelectric effect. The linear change in refractive index obtained at room temperature with practical electric fields (upto 20 kV/cm) is only of the order of $10^{-4}$. Although this is too little to change refraction angles for most practical purposes, it is sufficient to produce retardations of the order of one wavelength and hence lead to interference phenomenon, which is used to modulate light phase or intensity (Jones 1964). A one-half wavelength relative retardation can change the transmission of polarized light from 0 to 100 percent. An ac voltage producing a peak retardation of one fourth wavelength can give 100 percent modulation of the carrier (Chen 1970).

Linear electro-optic phenomena were discovered by Roentgen in quartz and thoroughly investigated in several crystals before the turn of the century by Pockels, in whose honour the effect is now generally called the Pockel's effect. The linear electro-optic effect may be regarded as a special case of second-order (non-linear) electric interaction in the crystal. In many linear electro-optic devices, the longitudinal effect is used, that is, the light beam and electric field are parallel. Longitudinal effect devices are particularly useful for light beams of large cross-sectional area. In longitudinal effect devices, the required voltage is independent of the dimensions of the crystal. It can be shown from symmetry considerations that a longitudinal effect free of background birefringence and optical activity is obtained only with crystals of two classes; the class 43m of the cubic system and the class 42m of the tetragonal system. Class 42m is represented by KH$_2$PO$_4$ (KDP) and its isomorphs. Relatively large electro-optic effects and the availability of large
crystals of high perfection have given crystals of this group continuing major importance for both 'longitudinal' and 'transeverse' modulators as well as in frequency doubling and mixing devices (Bornarel et al 1966).

A beam propagating through the crystal in the presence of electric field produces phase shift between the ordinary and extraordinary ray i.e., electric field produces retardation on extraordinary ray. This effect can be used to control the amplitude of the light beam in accordance with the applied field. Thus, this gives us a method for imposing information on a light beam through the electro-optic effect. Such a modulator is of great use in optical communications (Amnon Yariv 1975).

1.7.2 Application of DKDP electro optic modulator in solar fields

Measurements of polarized light from the sky allow astronomers to determine the nature of the physical medium emitting or absorbing that light. In solar astronomy, the sun’s magnetic field could not be measured insitu, but, by using the Zeeman effect, they can relate measurements of polarized light with the magnetic field strength and direction. Since magnetic fields are related to solar activity, the measurement of polarized light is one of the most important tools to the solar astronomer. The basic component of any instrument used to analyze the polarized light emitted by the sun is a polarization modulator. Thus, the development of stable polarization modulators with long life time is important for ground based observations of solar magnetic fields. Rotating wave plates have stable retardation properties but are slow and cannot eliminate atmospheric effects. Also quartz wave plates have a limited wavelength range and produce a spurious modulation in the transmitted beam which is related to the crystal axes. Use of electronic modulators (EM) can eliminate these problems and electronic modulators are used extensively in ground based observations where their fast time response minimizes image variations due to atmospheric effects. Of all the electro-optic crystals, deuterated KDP (DKDP) and liquid crystal devices (LCD) have stable
retardation characteristics and can be interfaced easily to an image system. Each has a unique property that makes them useful to the solar astronomer; the LCD operates at low voltages and has stable modulation characteristics while DKDP modulators can be adjusted to produce any retardation and have a very high contrast ratio. The disadvantages are the following: DKDP require high voltage (5500 volts for half wave retardance) and a limited field of view. Optical modulators are used as the polarization analyzer and as an electronic shutter to the CCD camera system. The design of the relay controller is driven by the DKDP modulator which requires approximately 3000 V dc to drive it to a quarter wave retardance.

Electro-optical crystals such as DKDP provide retardation proportional to the applied voltage. This property provides much more flexibility than a LCD modulator where the thickness of the cell must be adjusted to obtain a known retardance for a given wavelength. The tuning of a DKDP to a quarter wave retardance can be done easily which makes them quite useful in eliminating cross talk between polarization measurements (West 1985).

The electro-optic effect (Pockel’s effect) is related to the position of the deuterium atoms in the DKDP crystalline structure (figure 1.3). An asymmetry in the DKDP structure (tetrahedron) is created when an electric field is applied producing (D-O) dipoles. This shift in the crystalline structure will then produce changes in the optical properties of the crystal (West 1985).

Although the external field changes the energy states of the deuterium atom in the crystal, DKDP does not exhibit the fluid motion properties seen in LCD modulators. However, DKDP modulators have their own set of problems which are related to a limited electrode lifetime and the breakdown of the crystalline structure. The DKDP crystals that are used in the solar vector magnetograph are longitudinal modulators that are 30mm$^2$ in area and
Figure 1.3 The position of the deuterium atom in DKDP (a) para and
(b,c) ferro-electric states
3mm thick. A glass plate with thin transparent coating (usually Indium Tin Oxide (ITO)) is placed on each side of the crystal. In some models, a thin insulating material is placed between the crystal and the conductive coatings.

1.8 SUMMARY AND SCOPE OF THE THESIS

The overview of the different methods of crystal growth have been discussed briefly along with an elaborate discussion on solution growth. The various parameters which control the growth of crystals from solution and different methods of solution growth have been discussed. The grown crystals being ferroelectric and widely used in opto-electronics, the necessary introduction to ferroelectrics and non-linear optics are also presented.

In view of the applications and scientific interest on non-linear and ferroelectric crystals and their increasing demand, the present investigation was aimed at;

(i) growing large size single crystals of KDP, TGS and LAP family from solution
(ii) studying their fundamental characteristics
(iii) studying their physical properties which are relevant to application
and (iv) making devices from the crystals having good characteristics.

The study, as mentioned above, is connected with three families of crystals namely Potassium dihydrogen phosphate (KDP), L-arginine phosphate (LAP) and Triglycine sulphate (TGS).