CHAPTER 1

CRYSTAL GROWTH AND NON-LINEAR OPTICS

1.1 INTRODUCTION

Crystal growth has been a subject of absorbing interest for many years and the recent development of technology has stimulated the commercial importance of the subject. A crystal is an array of atoms arranged in a three-dimensional structure which extends over distances which are very much larger than the size of an atom. A single crystal is an isolated piece of one crystal of a crystalline solid and the perfect ordering in the crystal gives rise to many of the physical properties of crystals such as ferromagnetism, birefringence, piezo-electricity etc. A polycrystal is an aggregate of crystals which might or might not be of different kinds, generally irregularly shaped and interlocked together at the boundaries of contact.

Single crystals has ushered in a new era in the efficient utilization of available materials on earth. Symmetry, purity and structural simplicity of single crystals has caused major transformation of the electronic industry and the systems based on it. Modern technology is based largely on materials such as semiconductors, ferrites, magnetic garnets, solid state lasers, piezo-electric, ultra-violet and infra red sensitive crystals and crystalline films for microelectronics and computer industries.

The importance of crystals extends daily for things such as frequency controlled oscillators made up of quartz, polarizers by calcite and sodium nitrate, quartz, Rochelle salt and ADP as transducers, diamond for
grinding, potassium chloride and anthracene as radiation detectors. On emerging into the field of opto-electronics, germanium and silicon play a vital role in the transistors, Gallium Arsenide and Indium Phosphide as tunnel-diodes and also magnetic devices (garnets), strain gauges (silicon) ultrasonic amplifiers (CdS), masers and lasers (ruby, GaAs, calcium tungstate), lenses (fluorite). Over one million pounds of synthetic quartz are produced annually for a variety of applications ranging from optical components due to its high transparency to precise time and frequency oscillators based on its piezoelectric properties (Brice, 1973a).

Inorganic crystals like KDP, ADP, KTP and β-BaB₂O₄ are the best nonlinear optical materials increasingly being used for the second harmonic generation, frequency doubling of Nd-YAG laser and also in electro-optical applications. The superionic crystals like silicates, germanates, phosphates and tungstates built of octahedra and tetrahedra form a major group of fast ionic conductors after the discovery of a 3-dimensional ionic conductor, NASICON (Halfpenny, et al., 1994).

Organic crystals show a complex range of phase behavior, photo and thermal stability, solubility and morphology. The rapid development of optical communication systems has led to a demand for non-linear optical materials of high structural and optical quality. The most widely encountered crystals for this type of application are urea, MNA, POM etc (Chemla, et al., 1987). The perfect organic crystal should have high efficiency, low absorption edge cut-off and high damage threshold.

The advantages of organic nonlinear materials are:

1. High second-order nonlinear optical efficiency.
2. High damage threshold.
3. Birefringence used for phase matching.
4. Possible to chemically engineer molecular properties.
There are a number of properties, particularly relevant to crystal growth, which are common to many organic materials. Firstly, the intermolecular forces are comparatively weak, being predominantly Van der Waals forces or permanent dipole-dipole interactions. Due to the technological importance of these nonlinear crystals, the need for high quality organic crystals has grown dramatically in the last decade (Zyss, et al., 1985).

Enormous studies have been devoted to inorganic crystals in comparison to the organic crystals, where problems arise due to the polar nature of the nonlinear optical material. The growth of organic crystals is problematic due to the solvent and solute interaction. A comparison of general crystal growth characteristics of organic and inorganic crystals is shown in table 1.1.

There are various methods available for the growth of organic single crystals but thermal instability is also common in these materials which undergo decomposition at or below the melting point. These organic materials have been grown by solution growth methods like slow cooling and solvent evaporation techniques which are listed below.

1.2 CRYSTAL GROWTH TECHNIQUES

Classification of methods of growth is possible, based on the nature of the starting material. When the starting material is in a solution form, the controlled evaporation of the saturated solution will give rise to single crystals only. When the actual vapour pressure of the crystal is maintained at that temperature, then it is possible to grow crystals even if the material is in the vapour form, where the vapour is supersaturated. The production of bulk crystal results from the melt growth. Melt growth is widely employed for the preparation of congruently melting materials because of the high growth rates which can be used coupled with the high crystalline
Table 1.1

Characteristics of organic and inorganic single crystals

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Organic Crystals</th>
<th>Inorganic Crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical nature</td>
<td>Covalently bonded molecules</td>
<td>Salts, composed of charged inorganic ions.</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in a wide variety of organic solvents</td>
<td>Soluble in water</td>
</tr>
<tr>
<td>Sensitivity to pH and ionic strength</td>
<td>none</td>
<td>sensitive</td>
</tr>
<tr>
<td>Thermal properties</td>
<td>stable up to melting point between 50°-150°C</td>
<td>highly thermally stable</td>
</tr>
<tr>
<td>Size of the crystal</td>
<td>0.1 - 100mm³, from common crystal growth methods</td>
<td>no size limit for many inorganic compounds</td>
</tr>
<tr>
<td>X-ray diffraction quality</td>
<td>good-moderate, excellent</td>
<td>excellent</td>
</tr>
<tr>
<td>Mechanical strength</td>
<td>fair-good</td>
<td>extremely good</td>
</tr>
</tbody>
</table>
perfection attainable. Growing crystals from the melt is more widely used than the solution and the vapour techniques. Growth by chemical reaction of gases or growth from another solid phase is possible by a polymorphic phase change. In the case of compound single crystals the stoichiometry needs must be considered and it is possible as epitaxial layers of thickness anywhere from submicron to hundreds of microns.

1.3 MELT GROWTH

Techniques can be classified as either conservative or non-conservative processes. In the conservative process, a volume of melt is progressively solidified until it is consumed, whereas in the non-conservative process, new source material is continuously added to the melt to replace, that removed by crystallization.

In conservative processes, where there is unidirectional solidification, the distribution is given by the normal freeze equation.

\[ C_s^m = k_0 \cdot C_0^m \cdot (1-g)^{k_0-1} \]  

Where \( C_s^m \) is the concentration of the impurity (solute) in the crystal, \( k_0 \) its distribution coefficient and \( C_0^m \) its initial concentration in the charge and \( g \) is the fraction of the melt solidified. The practical choice of a particular melt growth configuration is possible by Czochralski (or crystal pulling in which the growing crystal can be continuously observed and is unconstrained mechanically as it cools).

In contrast, in the non-conservative processes, the motion of a molten zone along a charge of initially uniform concentration \( C_0^m \) leads to a distribution of the form:

\[ C_s^m = C_0^m \cdot (1-(1-k_0) \exp (-k_0x/L)) \]  

where \( L \) is the zone length parallel to the direction of zone motion (x-axis).
Repeated zone passage produces a progressively pure crystal in the leading end of the ingot. The distribution along the ingot after the passage of one zone is

\[
C_s^m = k_0 C_0^m \exp (-k_0 x/L) \quad (1.3)
\]

\[-k_0 C_0^m \text{ for all } x \text{ for which } (k_0 x/L) << 1\]

To produce a near uniform distribution of the solute, zone melting techniques included under the generic name Bridgman - Stockbarger are used. Several other techniques like Verneuil growth, the Kyropoulos technique, float-zone melting are also considered.

1.3.1 Czochralski growth

The charge material is contained in a crucible which is heated to above the melting point of the charge. A pull rod with a chuck containing a seed crystal at its lower end is positioned above the crucible. The seed crystal is dipped into the melt and the melt temperature is adjusted until a meniscus can be supported by the seed crystal. The pull rod is then slowly rotated and lifted and by carefully adjusting the power supplied to the melt a crystal of the desired diameter can be grown. The whole assembly is maintained in an envelope which permits control of the ambient gas and enables the crystal to be observed visually. The technique has been applied to an extremely wide range of materials from elemental metals and semiconductors to complex refractory high melting point oxides. Crystal pullers have revolutionized in the semiconductor industry with the development of the liquid encapsulation techniques. The important semiconducting compounds like GaAs, InP, and GaP are grown by this method (Brice, et al., 1973b).
1.3.2 Bridgman - Stockbarger and Related Technique

The essential feature is the steady motion of a freezing solid-liquid interface along an ingot which is mounted either horizontally or vertically as shown in fig. 1.1. Either the whole charge is melted initially called normal freezing or a molten zone is established namely zone melting. The motion of the interface can be achieved in several ways. Thus one can traverse a muffle furnace over the charge or the charge through the furnace. In the normal freeze configurations, the lowering of a charge and crucible vertically through a furnace is commonly known as the Bridgman-Stockbarger technique. This method is more suitable for growing single crystals like GaAs, silver halides, etc. (Hurle, et al., 1967).

In zone melting, removal of impurities, uniform doping of desired impurity and controlled discontinuities of impurity in a single crystal can be done. A part of the solid material is melted and the molten zone is made to move from one end to the other. So this method is best suited for purification of semiconductors.

1.3.3 Kyropoulus Technique

This method is similar to Czochralski technique but growth onto a rotating seed is achieved by slowly lowering the melt temperature instead of withdrawing the seed. Shallow, large diameter crucibles are required but little control of crystal shape is possible. The quality of the crystal is strongly dependent upon the control of the cooling. The technique has been used mainly to grow halide and oxide crystals.

1.3.4 Float-zone melting

This is an important technique for the production of oxygen-free silicon single crystals and also for refractory metals (Elwell, et al., 1975).
Figure 1.1. Schematic representation of Bridgman apparatus.
This method is the same as zone melting instead vertical configuration without a container. Maintenance of the stable zone is due to surface tension force and it is suitable for materials with high surface tension and low density. Gravitational forces set an upper limit to the zone length and therefore indirectly to the crystal diameter.

1.3.5 Verneuil Technique

In this technique, powdered charge material is fed at a controlled rate down a tube using a tapper. Hydrogen and oxygen are fed down outer, annular tubes and burnt. The flame melts the powder which drops to the molten zone on the top of the seed crystal. As the crystal grows it is lowered down into a heater furnace at a rate commensurate with the feed rate. It achieved commercial importance as a cheap and reliable method for the production of many crystals for the manufacture of jewel bearings for watches and synthetic gems (Laudise, et al., 1970). The disadvantages of the technique include poor control of the thermal environment and limited freedom in the choice of the gas ambient.

1.4 VAPOUR GROWTH

Single crystals of high purity can be grown from the vapour by sublimation and chemical vapour deposition. In these processes, the source material which is a solid or one or two components of the phase to be crystallized is provided from the vapour phase. The ampoule represented in fig.1.2 must be translated through the temperature gradient at a rate equal to the linear growth rate of the crystal. This ensures that the supercooling conditions remain constant so that spurious nucleation does not occur. The most widely known sublimation method is the so-called Piper-Polich technique for the preparation of cadmium sulphide. Small size crystals of better quality can be grown like CdS, Al₂O₃ and HgI₂ (Vengatesan, B.1989).
Figure 1.2. Piper - Polich method
1.5 EPITAXIAL GROWTH

Different methods like Molecular Beam epitaxy, in which device structures of III-V, IV-VI and II-VI compounds have been obtained and VPE, LPE, MBE, CBE, ALE and Electroepitaxy of current interest.

1.5.1 Electroepitaxy

Liquid phase electroepitaxy (LPEE), the crystallization method in which the growth is forced by the flow of DC electric current through the solid-liquid interface at constant temperature, has been used to grow epitaxial layers of AlGaAs on GaAs substrate. In this method, layers grown by LPEE are much thicker and more compositionally uniform than those grown from the same amount of solution by linear cooling LPE.

1.5.2 Liquid Phase Epitaxy

A LPE technique consists of providing mechanisms for 1) Supersaturation of the melt, 2) introduction of the seed crystal upon which the precipitation will occur, 3) controlling the morphology, uniformity and the substrate from the melt. Layers of different composition and/or doping are grown sequentially on the same substrate. This technique actually is used for LPE growth of III-V semiconductors, superconductors and II-VI components.

1.5.3 Vapour Phase Epitaxy

VPE process involves the transport of chemical species from the gas phase onto the substrate sample. The atoms are transported to the growing solid-vapour interface through the vapour phase. There are two types, viz., metal chloride in which HCl, is used to react with hot Ga or In to form volatile chlorides and the other anion chloride technique which uses AsCl₃.
or PCl₃ which can be used to transport both the group III and group V elements.

1.5.4 Molecular Beam Epitaxy

The sources are materials that are heated to high temperature in an effusion cell to provide flux semiconductor. The beam flux, which is controlled by the cell temperature, is directed at the heated sample. The advantage of this method is its low deposition temperature.

1.5.5 Atomic Layer Epitaxy

In this technique, the chemical species that are used for the process of growing semiconductors are deposited and incorporated individually on the surface of the crystal under near equilibrium conditions. Because of its simplicity and uniformity, ALE is currently being studied at numerous laboratories.

1.6 GROWTH FROM FLUX AND SOLUTION

Flux growth is the term used to describe the growth of crystals from molten salts at high temperatures. The growth proceeds at a temperature well below the melting point of the solute phase. There are various techniques classified as

a. Growth by slow cooling
b. Top seeded solution growth

1.6.1 Growth by slow cooling

A saturated solution is prepared by keeping the crucible containing flux and the crystal constituents at a temperature slightly above the
saturation temperature long enough to ensure complete dissolution of the solute. Then the crucible is cooled at a rate of 0.5°C/hr to 5°C/hr, through a temperature range, where the desired crystal is known to precipitate, the crucible is cooled rapidly to room temperature. Single crystals like YAG, BaTiO$_3$, KTP and KTN are grown by this method.

1.6.2 Top seeded solution growth

For fluxes of low volatility allowing the use of open crucibles, crystals can be grown at the surface of the melt when the temperature at the surface is lower than the temperature at the bottom. A seeding rod or a seed crystal can be introduced from above at the saturation temperature. The temperature gradient should be small and the growth temperature has to be continuously lowered by slow cooling of the melt. Crystals grown from this method are BaTiO$_3$, KNbO$_3$, Bi$_{12}$Ti$_2$O$_{20}$, SrTiO$_3$ and La$_{2-x}$Ba$_x$CuO$_4$ and KTP.

1.7 HYDROTHERMAL GROWTH

In this method, an aqueous solvent crystallizes on ordinarily difficult soluble material at high temperature and high pressure. Materials like quartz, calcite, alumina, antimony sulfo-iodide crystals are crystallized. A charge material is dissolved in the lower part of an autoclave which is heated. A hot saturated solution is directed towards the colder part, where it cools and becomes supersaturated. In the colder region, the growth of seeds occur and this process continues until the whole charge is recrystallized. Large amounts of a substance are recrystallized and large crystals of low solubility materials can be obtained.
1.8 LOW TEMPERATURE SOLUTION GROWTH

In this method, solutions are prepared by dissolving a compound in solvents which are in liquid state at ordinary temperature. Crystals for practical and technological applications should have a well developed morphology and contain low density of defects like predicted by thermodynamic and kinetic parameters which determine the growth mechanism and the growth kinetics and the generation of defects respectively.

1.8.1 Criteria for growth

In solution growth, for any material to be grown, the equilibrium concentration of the solution at different temperature must be known. Growth of crystals from solution mainly depends on the supersaturation. High supersaturation of the solution leads to spontaneous nucleation. In order to grow good crystals of perfect morphology, seeded growth is selected. The concentration of the solution must be slightly greater than its equilibrium concentration.

The influence of solvent on crystal growth can be understood by crystal-medium interface. In solution, the solute molecules will be dissolved. The solution can be maintained in the metastable region by maintaining the accurate temperature. A seed crystal is introduced in the solution, for the growth to proceed. On attachment of the molecule to the crystal surface, partial desolvation occurs. Solvation and desolvation of solute molecules are therefore integral parts of the growth process and will to some extent, influence the kinetics and thermodynamics of crystal growth.
1.8.2 Solubility and supersaturation

Solution is a homogenous 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.

(1) An ideal solvent should

a. yield prismatic crystals,
b. have significant, but no successive solubility.
c. have low volatility
d. have low viscosity
e. have a good solubility gradient
f. have no corrosion of growth apparatus
g. have low vapour pressure at the growth temperature
h. be in pure state
i. have reversible solubility of the material.

(2) If the solubility is too high, as in the case of urea dissolving in starch and in water, it is very difficult to grow bulk single crystals. Since solution growth is related greatly to the solubility of the material, the choice of solvent is important.

(3) Changes in supersaturation, solvent etc. may lead to dramatic modifications in the crystal morphology. The solubility of a solute may be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. The solubility data at various temperatures are essential to determine the level of supersaturation. As the 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.
The degree of supersaturation of a solution can be defined in two ways. The concept of absolute supersaturation

\[ \Delta C = C - C_o \]  \hspace{1cm} (1.4)

where \( C \) is the concentration of the dissolved substance at a given moment and \( C_o \) is its solubility limit. The relative supersaturation ‘\( \beta \)' (Hartman, et al., 1973) is defined as

\[ \beta = \frac{C - C_o}{C_o} = \frac{\Delta C}{C_o} \]  \hspace{1cm} (1.5)

The crystal grows by the accretion of the solute in the solution as a degree of supersaturation is maintained.

1.8.3 Metastability limit

The phenomenon of maximum supersaturation is related to the stability of supersaturated solutions, which is governed by the metastability limit. The metastability limit represents the maximum concentrations, obtained at various temperatures, at which spontaneous crystallization begins. The metastability limit separates the region of supersaturated solutions into two parts. The solutions with concentrations above the limit crystallize instantaneously. The supersaturated solutions whose concentrations are below the limit can be stored without inducing crystallization for sometime. The first-mentioned region is known as the labile or unstable zone; the second region as the metastable zone.

The diagram of various states of a solution can be shown schematically as in fig.1.3. The part of the diagram which lies above the x-x' line known as the supersolubility curve represents the labile state of a solution. The region below z-z' represents the stable zone of unsaturated
Figure 1.3. Solubility diagram.
solutions, and the region between the curves x-x' and z-z' is the metastable zone. The x-x' curve is the metastability limit and z-z' the solubility limit or solubility curve. Miers, *et al.* (1987) have defined the metastability limit as that maximum concentration at which the large scale crystallization of a solution begins. The width of the metastable zone is governed not only by the relationship between the solubility and the size of particles, but also by mechanical treatments, impurities, stirring etc. The position of the metastability limit varies not only with the concentration and temperature but also with the mass of solution.

There is a definite quantitative relationship between the metastable zone concept and the higher solubility of fine particles. The following equation for the width of the metastable zone is

$$\frac{C_{r_{\text{max}}}}{C_0} - C_0 = \exp \left(\frac{a}{r_{\text{max}}} - \frac{b}{r_{\text{max}}^4}\right)$$  \hspace{1cm} (1.6)

where $r_{\text{max}}$ is the radius of the particles exhibiting the maximum solubility; $C_{r_{\text{max}}}$ is the maximum solubility. The values of $a$ and $b$ are given by the expressions

$$a = \frac{2\sigma M}{rT\mu} \quad \text{and} \quad b = \frac{e^2M}{8\pi r^2T\mu}$$ \hspace{1cm} (1.7)

where $e$ is the electric charge on the surface of a crystal, $\mu$ is the permittivity, $\sigma$ is the specific surface energy, $r$ is the radius of a particle, $M$ is the molecular weight and $\rho$ is the density. According to eqn. (1.6), the greater the molecular weight of the solute, the wider is the metastable zone. In order to grow single crystals, the solution must be supersaturated and it is a requisite to maintain the solution in the metastable zone where spontaneous nucleation cannot occur and a seed crystal is essential to facilitate growth. As the growth of the crystals is a complex phenomenon
controlled by too many parameters, it is not readily possible to predict the required cooling or evaporation rate for the expected rate of growth.

1.8.4 Attainment of supersaturation

Concentration of the solution can be determined directly by analysis, or indirectly by measuring some property of the system that is a sensitive function of concentration. Properties like density, viscosity, refractive index and electrical conductivity can be measured with high precision, if the actual measurement of the supersaturation is made under carefully controlled conditions. The supersaturation of a solution may be determined from its boiling point elevation by applying the principles of Duhring's rule defining the boiling point of a solution as a linear function of the boiling point of the pure solvent at the same pressure. Crystal growth requires the production of a supersaturated solution at the growing face. The methods commonly used to achieve are described in the following sections.

i. Slow cooling method

ii. Slow evaporation method

iii. Temperature gradient method.

Slow cooling method

In solution growth, this method is widely used to grow all inorganic and organic crystals. The range of temperature for growth \( \frac{\partial T}{\partial t} \) is different for different crystals. The principle of crystal growth by changing temperature for positive and negative temperature coefficient is illustrated in fig.1.4a and fig.1.4b respectively. Temperature \( T_1 \) of undersaturated solution indicated by point A changes to a value \( T_2 \) in supersaturated solution (point C), passing through a temperature of the saturated solution \( T_0 \) at point B. This change of temperature from \( T_2 \) to \( T_3 \) ensures a
Figure 1.4. (a) Solubility curve for positive temperature coefficient.

(b) Solubility curve for negative temperature coefficient.
supersaturated solution necessary for the development of a crystal seed introduced into the solution. This method can be applied to compounds with $\partial C/\partial T$ which is large and has no phase change.

**Solvent evaporation method**

With solvent evaporation technique, the evaporation rate is difficult to control and the resulting fluctuations in supersaturation leads to poor quality crystals. The growth equipment for evaporation methods is similar to those of slow cooling except that a fixed temperature is used and a provision for evaporation. In this case, constant temperature is maintained and the growth occurs at a temperature $T_2$ corresponding to supersaturated solution. The possible range of temperature $\partial C/\partial T$ is very large and the phase changes occur for the compounds grown by this method.

**Temperature gradient techniques**

Temperature gradient methods rely on the transport of materials from a hot region containing a source of material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The advantages of the technique include:

i. economy of solvent

ii. the crystals grow at fixed temperature

iii. the method is insensitive to changes in temperature provided both the source and the growing crystal surface have the same change.

Changes in the small temperature difference between the source and the crystal have a large effect on the growth rate. Two regions of different temperatures $T_1$ and $T_2$ with $T_1 > T_2$ is used as shown in fig.1.5. A crystallizer is the one in which a single chamber is used with a bottom
Figure 1.5. Valenton's modified two tank crystallizer

(1) Porous vessel with nutrient
(2) Growing crystal
(3) Motor with stirrer
(4) Pipes connecting the two tanks and
(5) Heaters.
heater, nutrient is placed on the bottom of the bath and the slightly hotter solution is pumped from there up the support and then allowed to flow downward over the crystals.

Limitation

i) Good temperature control is needed.

1.9  GEL GROWTH

When growth of monocrystals poses problems by conventional techniques due to decomposition before melting or non-availability of suitable flux, gel growth serves as an excellent alternative method. Applicability is mainly for sparingly soluble substances and which decompose below their melting point. The general features are due to low temperature and low defect density. This method suppresses actual, forced and free convection flows. The types of gels are physical gel and chemical gels. In physical gels, organic gels like agar-agar and gelatine are used whereas in chemical gels silica and polyacrylamide gels are prepared. Good crystals can be grown in gels in a variety of ways like U-tube and test-tubes method as shown in fig.1.6. Tartrate, ADP, KDP and Biological crystals are grown from this method (Sangwal, 1994).

1.10  NONLINEAR OPTICS

Nonlinear optical devices, such as harmonic generators and parametric oscillators, provide a means of extending the frequency range of available laser sources. Franken et al. (1961) detected ultraviolet light at twice the frequency of a ruby laser beam when this beam was propagated through a quartz crystal. This experiment marked the beginning of an intense investigation into the realm of the nonlinear optical properties of matter.
Figure 1.6. (a) Single diffusion - two layer gel method
(b) Single diffusion - three layer gel method
(c) Double diffusion gel method.
(1) and (2) solutions of reactants
(3) gel (4) crystal
Nonlinear optical effects are analyzed 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 the temporal distribution of electrical charges as the electrons and atoms react to the electromagnetic fields of the wave. The main effect of the forces exerted by the fields on the charged particles is a displacement of the valence electrons from their normal orbits. This perturbation creates electric dipoles whose macroscopic manifestation is the polarization. For small field strengths, this polarization is proportional to the electric field. In the nonlinear case, the re-radiation comes from dipoles whose amplitudes do not faithfully reproduce the sinusoidal electric field that generates them. As a result, the distorted reradiated wave contains different frequencies from that of the original wave.

In a given material, the magnitude of the induced polarization per unit volume $P$ will depend on the magnitude of the applied electric field $E$. The polarization $P$ is expanded in series of powers of $E$

$$ P_\omega = \chi^{(1)}_{lm} E_m (\omega) + \ldots + \chi^{(3)}_{lmn} E_m (\omega_r) E_n (\omega_s) E_p (\omega_t) + \ldots + \chi^{(6)}_{lmnp} (-i\omega) E_m (\omega_r) E_n (\omega_s) B_p (\omega_t) + \ldots $$

(1.8)

where $P$ and $E$ are vectors linked by tensor of second ($\chi^{(1)}$), third ($\chi^{(3)}$, $\chi^{(6)}$), and fourth ($\chi^{(4)}$) rank. The values of the tensor coefficients are functions of frequency and temperature.

For small field strengths, the polarization is proportional to the electric field $E$ and is accounted for by the polarizability tensor $\chi^{(1)}_{lm}$. Linear optics encompass all the interaction of light and dielectrics, where the first term of the equation (1.8) is a valid approximation. In linear optics the index of refraction is given by
\[ n = (1 + 4\pi \chi^{(1)} \delta) = \varepsilon^{\frac{1}{2}} \]  

(1.9)

where \( \varepsilon \) is the dielectric constant of the material.

The \( \chi^{(3)} \) term is responsible for SHG, optical mixing and the Pockels effect. The nonlinear polarization tensor \( \chi^{(3)} \) vanishes in crystals that have a centre of symmetry. In these crystals SHG is not possible. The third rank tensor \( \chi^{(3)} \) in general has 27 components. As a result of crystal symmetry, mainly the components of \( \chi^{(3)} \) will be zero or equal to other components of the tensor. Furthermore, for those crystals of main interest, there is usually one predominant coefficient associated with a single light propagation direction which yields maximum harmonic power. If \( \omega_r = \omega_s \) we obtain the relationship of SHG

\[ P_1(2\omega) = \chi^{(3)}_{lmn} E_m(\omega) E_n(\omega) \]  

(1.10)

The generation of harmonics is a special case of optical mixing in nonlinear materials. The simultaneous application of two fields with frequencies \( \omega_r \) and \( \omega_s \) produces a polarization at the sum and difference frequencies. The polarizations produced all of the form

\[ P_1 \begin{pmatrix} \omega_r + \omega_s \\ \omega_r - \omega_r \end{pmatrix} = \chi^{(3)}_{lmn} E_m(\omega_r) E_n(\omega_s) \]  

(1.11)

In general, if 3 waves \( \omega_r, \omega_s \) and \( \omega_i = \omega_r + \omega_s \) are superimposed in a nonlinear medium, each wave is coupled to the other two through polarization waves. This is called the parametric interaction of three waves.

The Pockels effect is obtained if one of the electric fields is taken to be a dc field applied across a suitable crystal. For \( \omega_s = 0 \) and \( E_n = E_{dc} \) one obtains \( \omega_i = \omega_r \) and the index of refraction becomes a function of \( E_{dc} \), i.e.

\[ P_1(\omega_i) = [\chi_{lmn} E_{dc}] E_m(\omega_i) \]
The $\chi^{(4)}$ term couples the polarization to three electric field vectors generating third harmonic which leads to nonlinear processes, such as the Kerr effect and electrostriction.

With the application of a dc magnetic field ($\omega_s = 0$) the $\chi^{(6)}$ term describes the Faraday effect.

The second order term can be represented (Franken, et al., 1961) as a $3 \times 6$ matrix which operates on the $E^2$ column to yield $P$ according to:

$$
\begin{bmatrix}
  P_x \\
  P_y \\
  P_z 
\end{bmatrix}
= \begin{bmatrix}
  d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\
  d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\
  d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36}
\end{bmatrix}
\begin{bmatrix}
  E_x^2 \\
  E_y^2 \\
  E_z^2 \\
  2E_xE_y \\
  2E_yE_z \\
  2E_zE_x
\end{bmatrix}
$$

(1.12)

Depending upon the point symmetry of the crystal some of the elements of the tensor will be identically zero and others will have equal or equal and opposite magnitude. The piezoelectric symmetry class for urea (tetragonal, point Group P42m) is as shown below:

$$
\begin{bmatrix}
  0 & 0 & 0 & d_{14} & 0 & 0 \\
  0 & 0 & 0 & d_{25} & 0 \\
  0 & 0 & 0 & 0 & d_{36}
\end{bmatrix}
$$
Therefore, for the urea case the nonlinear polarization can be represented by:

\[ P_x = 2d_{14} E_x E_y \]
\[ P_y = 2d_{25} E_y E_z \]
\[ P_z = 2d_{36} E_z E_x \]  

(1.13)

The Kleinman symmetry condition postulates that "all times \( d_{ijk} \) which result from a rearrangement of subscripts \( i, j, k \) are equal". For the urea case, Kleinman symmetry requires that

\[ d_{14} = d_{25} = d_{36} \]

so that urea has two independent constants for SHG. The units of \( d_{ij} \) are usually expressed in pm/V and is used to predict the utility of a material.

1.11 SECOND HARMONIC GENERATION

The process of harmonic generation represented by fig.1.7 shows an incident wave of frequency \( \omega_1 \) which must be viewed as two-step process: first, a polarization wave at the second harmonic \( 2\omega_1 \) is produced which has a phase velocity and wavelength in the medium which are determined by \( n_1 \), the index of refraction for the fundamental wave that is \( \lambda_1 = c/2\nu_1 \) where \( c \) is the velocity of light and \( \nu \) is the frequency. The second step is the transfer of energy from the polarization wave to an electromagnetic wave at frequency \( 2\omega_1 \). The phase velocity and the wavelength of this electromagnetic wave are determined by \( n_2 \), the index of refraction for the doubled frequency. \( \lambda_2 = c/2\nu_2 \). For efficient energy transfer it is necessary that the two waves remain in phase, which implies that \( n_1 = n_2 \). Since almost all materials have normal dispersion in the optical region, the radiation will generally lag behind the polarization wave.
Figure 1.7. Schematic representation of second harmonic generation by Urea crystal.
The phase mismatch between the polarization and the electromagnetic wave for collinear beams is usually expressed as the difference in wave number

\[ \Delta k = \frac{4\pi}{\lambda_1} (n_1 - n_2) \]  

(1.14)

1.11.1 Phase Matching

An effective method of providing equal phase velocities for the fundamental and second-harmonic waves in the nonlinear medium utilizes the fact that dispersion can be offset by using the natural birefringence of uniaxial or biaxial crystals. These crystals have two refraction indices for a given direction of propagation, corresponding to the two allowed orthogonally polarized modes, by an appropriate choice of polarization and direction of propagation it is often possible to obtain \( \Delta k = 0 \). This is termed phase matching or index matching.

The distance required for the two waves to get completely out of phase is called the coherence length, \( l_c \). The coherence length is typically only a few microns and it is given by the expression:

\[ l_c = \frac{\lambda_o}{4 (n_1 - n_2)} \]  

(1.15)

where \( \lambda_o \) is the vacuum wavelength at the fundamental frequency. If the crystal thickness is made equal to the coherence length or any even multiple of it, the harmonic radiation disappears completely.

Certain asymmetric crystals are birefringent (doubly refracting) because through them, light can travel at two different velocities, described as ordinary (o) and extra-ordinary (e). These velocities actually vary with propagation direction and polarization as well as with wavelength. In a certain direction the ordinary fundamental light travels at exactly the same
velocity as extraordinary harmonic light. When this happens the SHG is greatly enhanced and the system is said to be phase matched. The direction in which this happens is called the phase-matching direction. Phase-matching greatly increases the SHG efficiency and also it enables extension of the range of laser wavelengths into the blue and ultraviolet parts of the spectrum which are not rich in naturally occurring laser lines.

Two types of phase matching are possible according to the polarization of the $\omega$ and $2\omega$ beams. The total field at $\omega$ will be

$$E_\omega = E^o_\omega + E^e_\omega$$

The SHG arises as a result of polarization which is variable with $E^2$, i.e.

$$(E^o_\omega)^2 + (E^e_\omega)^2 + 2E^o_\omega E^e_\omega$$

The $2\omega$ wave may also be of ordinary or extraordinary type and phase matching occurs when the refraction index of one of the $2\omega$ waves equals the average refractive index of the $\omega$ fields producing it. Type I phase matching ($n^o_{2\omega} = n^e_{2\omega}$) or vice versa arises from a wave of one type (either ordinary or extraordinary) and type II phase matching [$(1/2) (n^o_{2\omega} + n^e_{2\omega}) = n^o_{2\omega}$ or $n^e_{2\omega}$] arises from a combination of the ordinary and extraordinary waves. If only one type of ($\omega$) wave is present (as when the electric field is polarized along or perpendicular to a dielectric axis) then only type I phase matching can occur.

1.11.2 Maker fringes

Maker fringes is a method of measuring the $d_{ij}$ values of a crystal by demonstrating this interference between the bound and free harmonic waves for a variety of input and output polarizations. In the case of absolute determination, the formula relating SHG to fundamental power is evaluated
very carefully using the experimental data for beam profile, crystal length, and orientation in the phase-matching direction. The laser frequency output is measured to discover the number of oscillating modes and the power distribution, and the second-harmonic power generated is measured as the crystal is turned through phase matching. It is then possible to derive a number for the optical nonlinearity.

According to Jesphagnon and Kurtz (Munn, et al., 1993) the transmitted second-harmonic power can be written:

\[
P_{2\omega} = (512 \pi^3/A)d^2 T_{\omega}^2 T_{2\omega}R(\Theta)P^2(\Theta)
\]

\[
x P_{\omega}^2 [1/(n_1^2 - n_2^2)] \sin^2 \psi
\]

\[
\psi = (\pi L/2)(4/\lambda)(n_\omega \cos \Theta_\omega - n_{2\omega} \cos \Theta_{2\omega})
\]

where

- \(\Theta\) - is the angle of refraction instead of incidence.
- \(P_{\omega}\) - fundamental laser power
- \(A\) - beam area
- \(d\) - NLO coefficient
- \(T_{\omega}, T_{2\omega}\) - transmission factors
  (defined by Jesphagnon and Kurtz)
- \(R(\Theta)\) - multiple reflection correction
  (usually negligible)
- \(L\) - sample thickness
- \(\lambda\) - wavelength of the fundamental beam in air
- \(P(\Theta)\) - projection factor dependent on the nonlinear tensor, \(d\), and on the direction of the nonlinear polarization compared with the plane of incidence.
- \(n_{2\omega}, n_\omega\) - refractive indices at \(2\omega\) and \(\omega\) respectively
The \( \sin^2 \psi \) part of the equation gives rise to the periodicity of intensity and the separation of maxima is closely related to \( n_1 - n_2 \). This difference in refractive indices can be calculated from this spacing using the zeros of the functions. To get the refractive index tensor at \( w \) and \( 2w \), it is only required to measure one and the fringe separation gives the other. The \( d_{ij} \) coefficients were extracted by using computer programs.

Knowing the values of the refractive index at \( w \) and \( 2w \), it is possible to compute the theoretical shape (envelope) of the Maker fringe using a computer program. This becomes necessary since the amplitudes of the maxima can be affected by variation in the laser power and due to non-zero minima values.

### 1.12 PROPERTIES OF ORGANIC NON-LINEAR MATERIALS

Optical communication systems are increasingly displacing electronic methods because of their speed, bandwidth and reliability. However, at present they suffer from the difficulty that all-optical switching and routing are not possible on the microcircuit-sized scale. This problem arises from the rather low values of the electro-optic coefficients of currently favoured materials. For example (Ammon Yariv, et al., 1975) in the case of direct current (DC) (pockels) effect, the efficiency of a material used in an optical modulator can be expressed as the number of degrees of phase shift per applied volt. For \( \text{LiNbO}_3 \) this is \( 0.05^\circ \text{V}^{-1} \) for a unit cube (the reduced half-wave-voltage dimension). To achieve the necessary compactness of device, the electro-optic coefficient must be increased by a factor of at least 100. For several years now, attention has been focused on organic materials as a solution to this problem. The figure of merit associated with DC non-linear effect is the reduced half-wave voltage \( (V_n) \) ie, the voltage required for a cube of the material to produce a phase shift of \( \pi \). Already, organic materials such as DCNP [2-(1-phenyl-4,5-dihydro-1-H-pyrazol-3-yl)] ethene-
1, 1-dicarbonitrile] have been produced with two orders-of-magnitude better performance than LiNbO₃.

The corresponding figure of merit for frequency doubling is the ratio $d^2/n^3$. This arises from the efficiency of frequency doubled light generation in a $\chi^2$ experiment. Again, in this quite different application, organic materials such as NPP [N-(4-nitrophenyl)-L-proline] have also been designed to have a two order-of-magnitude advantage over LiNbO₃ (Zerinke, et al., 1973) Indeed, such a figure of merit is 40 times higher than that of the best inorganic materials, potassium titanyl phosphate and $\beta$-barium borate.

The high-frequency [second-harmonic generation (SHG)] effect depends on factors similar to those governing the DC effect, but is desirable for frequency doubling lasers (eg. from red to blue) to give robust compact blue or UV sources from lower-frequency laser diodes to be used in optical data storage, CD players etc (Eimerl, et al., 1990)

One major difference between inorganic and organic materials in the crystalline state is that organic materials preserve their molecular identity in the crystal, the molecules being held together by the comparatively weak dispersion forces.

1.13 OPTICAL PROPERTIES OF UREA

Urea is a particularly useful crystal for generating (Ultra Violet) radiation (Nayar, 1989 & Pugh, et al., 1987) by frequency doubling and mixing, as it is transparent down to 0.2 μm. In addition, it has a large birefringence, high optical damage threshold (3GW cm⁻² at 0.532 μm) with 10ns pulses and little temperature dependence of its refractive indices. The second-harmonic coefficients are not particularly large ($d_{14} = 1.4$ pm V⁻¹)
(Boyd, et al., 1964) but they compared favourably with the more commonly used inorganic materials such as $\beta$-Ba$_2$O$_3$ and KDP.

The large birefringence of urea allows phase-matched frequency doubling with the pump radiation in the 0.476 to 0.750 $\mu$m range (Cassidy, et al., 1979). It is also possible to generate UV radiation in the 0.229 to 0.400$\mu$m (Zyss, et al., 1982a) range by frequency mixing a Nd:YAG laser at 1.064 $\mu$m and a tunable dye laser. More importantly, urea can be used as a tunable optical parametric oscillator over the 0.58 to 1.225 $\mu$m wavelength range when pumped with 0.355 $\mu$m radiation (third harmonic of a Nd: YAG laser). Average powers of up to 50mW have been reported over the 0.55 to 0.9 $\mu$m range. Above 0.96 $\mu$m the material absorption limits the output power (Hobben, 1967).

1.14 REVIEW OF THE LITERATURE

The importance of single crystals of urea has prompted several workers to attempt its crystal growth. However, a literature search had not been helpful in assessing what the difficulties were and what measures had been taken to overcome them.

Growth had been attempted from solution, melt and vapour phase. But there has not been any detailed published data on the melt and the vapour growth. The few reports available were weak by virtue of the lack of data on the conditions of growth, experimental technique, type of seed, and finally the quality of the crystal by visual presentations.

It is known that the optical phenomena study group of Cornell University have been attempting the crystal growth of urea from methanol solutions for many years (Halbout, et al., 1979). Previously, they have reported that crystals of dimensions up to 23 x 20 x 20mm$^3$ have been produced which were transparent over most of the volume. These were
grown by very slow temperature decrease of a saturated methanol solution. The duration of growth is reportedly of the order of one year (or more) to produce the above mentioned sized crystals. They had previously doped the crystals with bromine in an attempt to produce larger, high quality crystals but without success.

Feigelson et al., (1985) have investigated growth of urea crystals from the vapour phase and although the study was interesting, the crystals produced were of small size and poor quality. They report growth rates of > 2.5 mm/day. Whilst the possibility of growth from the vapour phase remains a potentially viable method, an extensive work has to be done for obtaining large size urea crystals.

A NASA experiment (Gerbi, et al., 1986) involved using DMOS (Diffusive Mixing of Organic solutions) to study the growth properties of urea crystals aboard the space shuttle (ie. in a microgravity environment). These were then compared with crystals grown under similar conditions in the gravity. The project was not directed towards obtaining large crystals but more at studying the effects of variation in gravity on crystal quality. The crystals grown in microgravity were reported to be of higher quality than those grown in one-gravity, although the length/breadth ratio apparently increased. The higher quality was attributed to the absence of sedimentation, turbulence and convection in the microgravity environment which prevented extensive aggregation of crystals.

Growth from the melt phase has not been reported due to the decomposition of urea upon melting. Although the decomposition of urea is well known and is mentioned repeatedly in connection with urea, the nature of the reaction and the extent to which it actually takes place during solution growth and at the melting point, has not been investigated.
Hence from the reports available, the crystal size or quality was usually poor. In the instances, where reasonable crystals were obtained the duration of growth was excessive (greater than 12 months) (Donaldson, et al., 1984).

To the author's knowledge, no concise analysis of the crystals has been carried out. Crystal defects and inclusions are known to adversely affect the optical properties of single crystals. Therefore, the determination of the crystal perfection is vital, both from the application point of view. The crystal grower and the device producer's need to know the degree of purity and perfection of crystals to interpret the structure dependent properties. The crystal grower requires to have knowledge of the nature and distribution of the imperfections and impurities for correlation with the growth conditions, thus enabling modifications to assist the production of better crystals.

Since the only serious limitation in the implementation of urea in devices is the non-availability of high quality large crystals, this project aimed to rectify this by making a comprehensive investigation into the crystal growth from the solution phase and by proposing a novel method for its growth from the melt phase.

The project began by assessing some urea and benzophenone crystals for use as second harmonic generation media and involved proceeding with the crystal growth of any useful materials identified.

Tachibana et al., (1993) have grown urea single crystals by solution and melt growth by the Czochralski method. The crystals grown were analyzed for their images by X-ray topography.
1.15 SUMMARY AND SCOPE OF THE THESIS

A brief account of the different crystal growth methods like melt, vapour, gel have been discussed and a wide perspective have been placed on solution growth. An introduction has been given for nonlinear optics. Both these two features are covered in chapter 1.

Chapter 2 discusses the theory which is applicable to growth and the morphology of the crystals. The growth rate for a particular system and the concentration profiles have been plotted for different cooling rate and interface kinetics. The theory which leads to the perfect habit and morphology are covered by the Periodic Bond Chain analysis.

The Chapter 3 elaborates the growth system, growth conditions, crystals with different solvent and habit-modifiers and the problems encountered during the growth of urea single crystals. Similarly, chapter 4 describes the fundamental characteristics, physical, chemical, optical and structural properties. An assessment has been made on the characteristics of urea single crystals.

Investigations were also made to grow urea single crystals from melt and this is included in chapter 5. Different system has been designed and fabricated, the grown crystal has been analyzed.

Chapter 6 describes the growth and characterisation of benzophenone single crystals.