CHAPTER 1

AN INTRODUCTION TO SOLUTION GROWTH TECHNIQUE AND NONLINEAR OPTICAL PHENOMENON

1.1 GENERAL

The beauty, symmetry, structure, crystallinity and rarity of crystals have fascinated man and the large scale applications of crystals are highlighted mainly by the demands of solid state physicists for materials research and devices. Crystal growth, as a field is in its intellectual vitality with major surprises occurring often resulting in significant advances in the synthesis of materials with controlled structures and micro structures to tailor their physical properties. Rapid progress in the self designing of materials have underlined the ever increasing scope of crystal growing, offering enormous breakthrough in both fundamental and applied research.

Innovation, with an eye for application, has been the key to successful crystal harvesting. It is realized that crystalline material is intrinsically applied and basic research in this area needs to be directed and motivated by specific applications in technology. The developments of high image amplification, frequency multipliers, frequency mixer, fibre optics communication, optical switches, and laser window materials are all veritable activities of nonlinear materials research, well within our reach. Achievement of many of them is to strive towards a research and development driven by passion rather than fashion.

The rapid development of solid state devices necessitates single ideal crystals of near perfection. Electronic industry and fibre optic communication would suffer great backslide but for novel optical crystalline materials. New materials are unceasingly investigated and the applications of crystals are on
the tidal rise [Laudise1995, Brice 1986, Nalwa and Miyata 1996]. Of the infinite realm of significant and vital properties of crystals, nonlinear optical property is of utmost importance attracting the attention of material designers towards the advancement of scientific technology. NLO materials facilitate the amplification of the frequency of laser light and are of considerable interest for the high speed processing of data, which outlines the functioning of digital world. Hence, the growth of single crystals and their characterization have become inevitable for any further development in material science research.

There are two principle reasons for the deliberate growth of single crystals.

(i) Many properties of solids are obscured or complicated by the effects of grain boundaries.

(ii) The full range of tensor relationships between applied physical cause and observed effect can be obtained only if the full internal symmetry of the crystal structure is maintained throughout the specimen.

1.2 METHODS OF CRYSTAL GROWTH

The methods of crystal growth may be classified into three categories:

(i) Growth from melt
(ii) Growth from solution
(iii) Growth from vapour

The basic common principle outlining the formation of a nucleus followed by growth into a single crystal by organizing and assembling of ions or molecules with specific interactions and bonding, the process being slow with multiple nucleations minimized. Crystal growth process and the size of the crystal differ widely and are determined by the characteristics of the material.
Each category of crystal growth is governed by a number of growth methods. The mode of selection of a particular method of crystal growth is dependent on the characteristic physical properties of the materials such as melting point, vapour pressure, decomposition, solubility in solvents, etc. The growth methods are heavily dependent as the growths involve crystal size requirement, shape of the crystal parity and nature of application of the crystal. The ultimate aim of crystal growth is to find an economically viable method which yields defect free crystals.

In general the growth methods are broadly divided on the basis of phase transitions as follows:

(i) Solid growth - solid to solid phase transition
(ii) Melt growth - liquid to solid phase transition
(iii) Solution growth - liquid to solid phase transition
(iv) Vapour growth - vapour to solid phase transition

The various methods of crystal growth have been extensively discussed in detail by several authors [Brice 1986, Pamplin 1979, Chernov 1984]. The different techniques of each category are highlighted in reviews and books by Faktor and Garnet [1974] on vapour growth, Brice [1973] on melt growth, Henisch [1988] on gel growth, Buckley [1951] on low temperature solution growth and Elwell and Scheel [1975] on high temperature solution growth. An efficient process is the one, which yields adequate crystals for their use at minimum cost. In the present study, low temperature solution growth technique is discussed in detail and the other techniques are briefly enumerated in this chapter.

1.3 CRYSTAL GROWTH FROM MELT

The material to be grown is melted and allowed to cool carefully, resulting in the solidification in the direction of cooling or in the direction of relatively at low temperature. Melt growth is the best method for growing
large single crystals of high perfection. Materials which melt congruently relatively low temperatures having low vapour pressure and those which do not undergo phase transition from their melting point to room temperature are defined for melt growth. This method is hence not recommended for the materials subjected to polymorphic phase changes, development of high vapour pressure at the melting point and for the materials in which thermal strains are produced. High melting point of materials also restricts the applicability of these methods making growth impractical. The growth of single crystals from melt may further be subdivided into

(i) Czochralski technique
(ii) Bridgmann - Stockbarger technique
(iii) Zone melting technique
(iv) Verneuil technique

1.3.1 Czochralski technique

This technique involves relative motion between seed and melt. This method is mainly suggested for semiconductors, inorganic and organic materials. This method is advantageous compared to other methods for the growth of single crystals due to the following reasons:

(i) The growth of crystals is free from container in contact
(ii) The orientation of the growing crystals can be pre-selected by using suitably oriented seed crystals
(iii) Growth time is much less, when compared to other crystal growth techniques
(iv) High quality crystals can be produced by this method

Czochralski technique involves the wiring of a seed crystal of desired orientation to the bottom of the sealed seed holder. The seed holder containing the melt is either water cooled or air chilled and is allowed to touch the melt.
The cooling of the seed holder causes the temperature of the seed to be much lower than that of the melt resulting in the solidification of the melt on the tip of the seed and thus promoting crystal growth. TiO₂, NiMnO₄, CaTiO₃, Si and Ge are some of the crystals which can be grown by this method.

1.3.2 Bridgmann-Stockbarger technique

The melt along with the crucible is slowly cooled to yield a single crystal. This method is recommended to grow crystals which will withstand considerable thermal stress. An important criterion is that the crucible should be unaffected either by melt or vapour. The thermal expansion coefficient of both the material and the ampoule should nearly be identical so that thermal stresses in the crystal will be eliminated. The important feature of this method is that the solid-liquid interface is completely enclosed within the crucible and hence the latent heat of solidification is removed only by thermal conduction through the solid and the crucible. This technique is eradicated for materials, which decompose before melting point and is best suited for materials of low melting point.

1.3.3 Zone melting technique

Originally this technique was used only in the purification of the materials. However, this can also be used to grow single crystals. A small liquid zone is created by melting small amount of the material in a long solid ingot which is moved up or down. Germanium and silicon are few examples of the crystals grown by this technique. The absence of a crucible and simultaneous purification of the material during the growth process are the merits of zone melting technique.

1.3.4 Verneuil technique

Materials with high melting points are favorable for the growth by this method. The material experiences a steep temperature gradient posing a
serious problem of development of strain in the crystals. An oxygen hydrogen flame is used to heat the seed crystal and the powder from the hopper is shaken through the sieve by a vibrator at low amplitude resulting in the melting of the powder during its transit through the flame. Though the volume of growth rate depends on the powder feed, the linear growth rate is approximately proportional to the rate of lowering of the seed. This technique is widely used for the growth of synthetic gems.

1.4 CRYSTAL GROWTH FROM SOLUTION

Of all the methods of crystal growth, low temperature solution growth is practiced next to melt growth. The main advantage of the solution growth is that the crystals are grown at a temperature well below the melting point. Hence, a profound and distinct knowledge about certain parameters of the material like melting point, melting behavior, stability in the reduced pressure and atmosphere are not necessary. Solution growth can be considered as a superior method because of good optical transparency of crystal and uniform mixing of dopant in the lattice is achieved with ease. However, the disadvantages of the slow growth rate and container problem are the most often encountered demerits associated with the method of growth.

Growing good quality large single crystals by solution growth method, demands the materials to have high solubility and there should be a variation of solubility with temperature having low vapour pressure at the growth temperature. The viscosity of the solvent solute system should be low. Another aspect to be notified while employing solution growth method is that the container and stirrer should be non reactive with the material. The materials must be inflammable and less toxic. Easy separation of grown crystal by chemical or physical means and low melting point are cited as additional supporting points of low temperature solution growth.
Solution growth techniques can be broadly classified as

(i) Low temperature solution growth
(ii) High temperature solution growth
(iii) Hydro thermal growth
(iv) Gel growth

1.4.1 Low temperature solution growth

Low temperature solution growth is an extensively employed method for the growth of single crystals, when the starting materials are unstable at high temperatures [Pamplin 1979]. This method demands that the materials must crystallize from solution with prismatic morphology. In general, this method involves seeded growth from a saturated solution. Supersaturation is achieved either by lowering the solution temperature or by solvent evaporation. This method is widely used to grow bulk crystals, which have high solubility and have variation in solubility with temperature [James and Kell 1975; Chernov 1984]. After many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low [Brice 1972].

Low temperature solution growth can be subdivided into the following methods:

(i) Slow cooling technique
(ii) Slow evaporation technique
(iii) Temperature gradient technique
1.4.2 Slow cooling technique

This method is recognized as the most suitable method among various methods of solution growth. However, the main disadvantage of slow cooling method is the need to use a range of temperature. The possible range of temperature is usually narrow and hence much of the solute remains in the solution at the end of the growth run. To compensate this effect, a large volume of solution is required. The use of wide range of temperature may not be desirable because the properties of the grown crystals may vary with temperature. Temperature stability may be increased by keeping the solution in large water bath or by using a vacuum jacket. Achieving the desired rate of cooling is a major technical difficulty. This technique needs only a vessel for the solution in which the crystals grow. The height, radius and volume of the vessel are so chosen so as to attain the required thermal stability. Even though this method has technical difficulty of requiring a programmable temperature controller, it is widely used with great success.

In general, the crystals produced by this technique are miniature in size [Brice 1986] and the shapes of the crystals are unpredictable. A single crystal of cadmium mercury thiocyanate (CdHg(SCN)4) is grown by using two different solvent mixtures of water-NaCl, water-KCl employing temperature lowering method [Duorong Yuan et al 1998]. Hierle [1984] reported the growth of bulk single crystals of (POM) 3-methyl-4-nitropyridine-1-oxide, a promising NLO material by slow cooling method. Hiroaki Yuan et al [1999] have grown organic nonlinear optical 4-dimethylamino-4-methyl-4-stilbazolium tosylate (DAST) crystals by slow cooling method. L-pyroglutamic acid showed different morphological characteristics and growth rate in different solvents with different crystallographic orientations [Wanga et al 1999]. Rajasekaran et al [2001] have reported the growth of bulk zinc thiourea chloride single crystals from aqueous solution and the influence of pH of the solution on the growth rate of the crystal along (001) and (010) directions. KDP crystals were grown
by Rajesh et al [2002] from aqueous solutions with organic additives by the slow cooling method to enhance nonlinear property. The effect of deuterium on morphology and crystal properties of deuterated potassium acid phthalate (DKAP) grown from aqueous solution by slow cooling method, has been studied by Mohan Kumar et al [2002]. Doped TGS single crystals with 10 wt% of L-asparagine exhibited prominent morphological changes in the (101) and (001) planes [Kalainathan et al 2002]. Haja Hameed and Lan [2004] have determined the solubility, metastable zone width and nucleation parameters of L-tartaric acid-nicotinamide (LTN) crystal grown by slow cooling method. Single crystals of 4-nitro-4-methoxy benzylidene Aniline (NMOBA) [Nixon et al, 2004] and single crystals of L-alanine acetate (L-AlAc) [Mohan Kumar et al, 2005] have been grown by the slow cooling method with optimized growth conditions.

1.4.3 Slow evaporation technique

Slow cooling and slow evaporation methods are analogous to each other with respect to the experimental set up. In slow evaporation method, the saturated solution is kept at a particular temperature and provision is made for evaporation. If the solvent is non-toxic like water, it is permissible to allow evaporation into the open atmosphere. Typical growth conditions involve a temperature stabilization of about 0.05°C and rate of evaporation of a few mm³/h. The evaporation technique has an advantage of growing the crystals at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method can effectively be used for materials having very low temperature coefficient of solubility. The crystals harvested by slow evaporation method tend to be less pure than the crystals produced by slow cooling technique, as the size of the crystal increases more impurities in the crystal faces. Evaporation of solvent from the surface of the solution produces high local supersaturation and unwanted nuclei are formed. Small crystals are also formed on the walls of the vessel near the surface of the
liquid, from the material left after evaporation. These fall into the solution
hindering the growth of the crystal. Another disadvantage involves controlling
the rate of evaporation. A variable rate of evaporation may affect the quality of
the crystal. Inspite of all these disadvantages, slow evaporation technique
proves to be the most simple and convenient technique of growing single
crystals of large size. Crystals of HgCl₂:2KCl:H₂O [Sastry et al 1988] and
ammonium pentaborate [Shahabuddin Khan et al 1992] are grown from
aqueous solutions by the slow evaporation technique.

The single crystals of organic nonlinear optical material Benzoyl
Glycine were grown by the solvent evaporation technique using N, N-dimethyl
formamide (DMF) as solvent [Nagaraja et al 1998]. The experiments
conducted by Sharada Prabhu and Mohan Rao [2000] on the growth of single
crystals of acetoacetanilide suggests that the slow evaporation method is more
convenient for the growth. The habits of NMBA (4-nitro-4-methyl benzylidene
analine) crystals grown with 10 different organic solvents were studied by
Srinivasan et al. Mixed crystals of two nonlinear optical materials, L-arginine
hydrochloride monohydrate (LAHCl) and L-arginine hydrobromide
monohydrate (LAHBr) [Tanusri Pal et al, 2002], L-histidine tetrafluoroborate
(L-HFB) single crystals [Rajendran et al, 2003] L-histidinium bromide
(L-HBr) and L-histidinium diphosphate (LHDP) [Reena Ittyachan, 2003] were
grown with ease by temperature lowering and slow evaporation techniques.

Jayaraman Ramajothi et al [2003] have reported the growth of
L-histidine tetrafluoroborate (L-HFB) from its aqueous solution kept at 26 °C
by employing slow evaporation technique. L-pyrrolidone-2-carboxylic acid
(L-PCA) single crystal was grown by slow evaporation of the solvent at
ambient temperature [Boomadevi and Dhanasekaran 2004b]. L-PCA has been
found to possess laser damage threshold value of 17 GW/cm². Vincent Crasta
et al [2004] have reported 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propen-
1-one crystal grown by slow evaporation technique using acetone / DMF as solvents.

Single crystals of 2-amino-5-chlorobenzophenone (2A-5CB) were grown by employing slow evaporation technique using acetone as solvent [Ramesh Babu et al 2004]. Crystals of 2(L-Arg.HNO₃).H₂O and L-Arg.2HNO₃ have been grown by slow evaporation of aqueous solutions [Terzyan et al, 2004]. Packiam Julius et al [2004a, 2004b] have grown L-arginine hydrofluoride (LAHF) and L-argininium formate (LAF) single crystals by slow evaporation of aqueous solution at 30 °C and the SHG of the samples have been confirmed.

Good quality NLO single crystals of meta-NitroAniline (mNA) [Valluvan et al 2005], single crystal of γ-glycine (GG) [Narayana Moolya et al, 2005] have been grown by slow evaporation solution growth technique. Bulk single crystals of Chalcone derivates [Indira et al, 2002], L-arginine acetate [Muralidharan et al, 2003], Cadmium thiourea acetate [Rajesh et al, 2004], benzamidazol [Vijayan et al, 2003] and L-alanine [Razzetti et al, 2002] were also grown by slow evaporation solution growth technique.

Sodium paranitrophenolate dihydrate (NPNa) and deuterated sodium paranitrophenolate (DNPNa) having an effective nonlinear coefficient of 5 pm/V and 5.5 pm/V respectively are grown by solvent evaporation technique using methanol as solvent [Hisashi Minemoto et al 1994]. Anhydrous and hydrated forms of NPNa (NPNa.2H₂O, NPNa.4H₂O) crystal and their thermal properties and possible solvents which can be used to grow NLO active NPNa crystal by using solvent evaporation technique are reported by Brahadeeswaran et al [1999]. Normally water grown NPNa crystal changes to its hydrated form (NPNa.4H₂O) resulting in a transformation from transparent to opaque nature.
The advantages of solution growth techniques are listed as follows:

(i) Simple growth apparatus
(ii) Growth of strain and dislocation free crystals
(iii) The growth of prismatic crystals by varying the growth conditions
(iv) It is the only method, which can be used for substances that undergo decomposition before melting

The conditional limitations of solution growth techniques are

(i) the growth substance should not react with solvent and
(ii) this method is applicable for substance fairly soluble in a solvent.

The disadvantages of solution growth techniques are given as follows:

(i) The interstitial incorporation of solvent ions into the crystal lattice causes the formation of cloudiness
(ii) Impurities may be absorbed on the growth face of the crystal thereby changing the crystal habit
(iii) The slow growth rate can be improved only to a certain extent. It is beyond our control
(iv) Non-uniform doping

The above disadvantages can be rectified by selecting a proper solvent of high purity, by regulating the growth by the control of temperature and by the circulation of the solution by efficient stirring.

1.5 CRITERIA FOR OPTIMIZING GROWTH PARAMETERS

The growth of good quality single crystals by slow evaporation and slow cooling techniques dictates the optimized conditions, which may be achieved with the help of the following criteria:
(i) Material purification
(ii) Solvent selection
(iii) Solubility
(iv) Solution preparation
(v) Seed preparation
(vi) Agitation
(vii) Crystal habit
(viii) Cooling rate

1.5.1 Material purification

An essential prerequisite for success in crystal growth is the availability of material of the highest purity. Solute and solvents of high purity are required since impurity may be incorporated into the crystal lattice resulting in the formation of flaws and defects. Sometimes, impurities may hinder and slow down the crystallization process by being adsorbed on the growing face of the crystal, which can change the crystal habit [Buckley 1951]. Meticulous, repetitive use of standard purification methods of recrystallization followed by filtration of the solution should tactically be performed to enhance the percentage of purity.

1.5.2 Solvent selection

Selection of a suitable solvent plays a vital role in solution growth technique. Solution constitutes a homogenous mixture of a solute in small quantities in a solvent. For a given solute, there may be different solvents and it must be chosen taking into account the following factors,

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

Solubility is an important parameter, which dictates the growth procedure. Highly soluble materials pose much difficulty in yielding bulk single crystals and low solubility restricts the size and growth rate of the crystals. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution.

Low temperature solution growth is effectively a diffusion controlled process, the medium must be less viscous to enable faster transfer of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supersaturation is an important parameter for the solution growth process. The solubility data at various temperatures are essential to determine the level of supersaturation. Thus the determination of the solubility of the solute in the chosen solvent must be determined before starting the growth process [Christian 1990].

The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined gravimetrically. A known quantity of the clear sample is analyzed. The solubility curve can then be plotted between the amount of solute dissolved and temperature by repeating the measurements for different temperatures.

1.5.4 Solution preparation and crystal growth

For solution preparation it is essential to have the solubility data of the material at different temperatures. Sintered glass filters of different pore sizes are used for solution filtration. The clear saturated solution, kept at the desired temperature is taken in a growth vessel and is sealed to prevent the solvent
evaporation. Solvent preparation at constant temperature can be achieved by providing a controlled vapour leak. A small crystal suspended in the solution serves to test the saturation. By varying the temperature, a situation where neither the occurrence of growth nor dissolution is established. The test seed is replaced with a good quality seed. All unwanted nuclei and the surface damage on the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after saturation. Solvent evaporation can also be helpful in initiating the growth.

The quality of the grown crystal depends on the

(i) Nature of seed
(ii) Cooling rate employed and
(iii) Agitation of the solution

1.5.5 Seed preparation

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

1.5.6 Agitation

Regular and even growth is achieved by maintaining the level of supersaturation equally around the surface of the growing crystal. An uneven growth leads to localized stresses at the surface generating imperfection in the bulk crystals. Moreover, the concentration gradients that exist in the growth vessels at different faces of the crystal cause fluctuations in supersaturation, seriously affecting the growth rate of individual faces. The gradient at the bottom of the growth vessel exceeds the metastable zone width, resulting in
spurious nucleation. The degree of formation of concentration gradients around the crystal depends on the efficiency of agitation of the solution. This is achieved by agitating the saturated solution in either direction at an optimized speed using a stirrer motor.

1.5.7 Crystal habit

The growth of a crystal at approximately equivalent rates along all the directions is a prerequisite for its accurate characterization. This will result in a large bulk crystal from which samples of any desired orientation can be sliced. Further, such large crystals should also be devoid of dislocation and other defects. These imperfections become isolated into defective regions surrounded by large volumes of high perfection, when the crystal grows with a bulk habit. In the crystals, which grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect [Pamplin 1979]. Needle like crystals have very limited applications and plate like crystals need to be favorably oriented.

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

(i) Changing the temperature of growth
(ii) Changing the pH of the solution
(iii) Adding a habit modifying agent and
(iv) Changing the solvent

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

Supersaturation, the driving force that governs the growth of a crystal, is achieved by lowering the temperature of the solution and has to be precisely controlled for desirable results. The growth rate is maintained linear in order to grow large crystals. This requires an increase in the supersaturation level and linear cooling will not provide this. Hence, after the initial growth, the rate of temperature lowering is increased. Operation within the metastable limit occurs without any spurious nucleation in the solution. A large cooling rate changes the solubility beyond the metastable limit. Further, fluctuations in supersaturation may encourage solution inclusion flaw in growing crystals [Wilcox 1983]. Hence, a balance between the temperature lowering rate and the growth rate has to be maintained.

1.5.9 Crystal perfection

The perfection of the final crystal is based on the

(i) Purity of the starting materials
(ii) Quality of the seed crystal
(iii) Cooling rate employed and
(iv) Efficiency of agitation

An efficiently stirred homogeneous solution yields seed crystals promoting the growth of perfect single crystals.

1.6 HIGH TEMPERATURE SOLUTION GROWTH (Flux growth)

Flux and hydrothermal growths form the category of high temperature solution growth. In this method, a solid (molten salt/flux) is used as the solvent instead of liquid and the growth takes place well below the melting point [Hubner 1969] of the solute. This technique can be applied to incongruently
melting materials. Mixed crystals of solid solution can also be grown by the choice of optimum growth parameters.

This technique can be used for the crystallization of oxide compounds, which generally have phase transitions below the melting point [Ramachandra Raja 1993]. The crystals grown from melt will have lower concentration of equilibrium defects and lower dislocation density. The present status of flux growth is reviewed by many authors [Gornert 1990, Tolksdorf 1985]. Single crystals of Barium Cuprate (BaCuO$_2$) are obtained by slow cooling of melt solution of the system BaO-CuO$_2$BaCl$_2$-K$_2$CO$_3$ homogenized at 800 °C [Yakulovich et al 1990]. Nitch et al [1993] have reported the growth of crystals of K$_3$PbCl$_4$, Rb$_2$PbCl$_4$ and Cs$_4$PbC$_6$ from high temperature solution by slow cooling.

1.7 HYDROTHERMAL GROWTH

A number of metals, metal oxides and other compounds, practically insoluble in water up to their boiling point, show an appreciable solubility when the temperature and pressure are increased well below 100° C and 1 atmosphere respectively. It is an excellent method for the growth of refractory materials and nanocrystals. Rapid rate of growth is an advantage of this technique. For example, growth in quartz crystal is observed to be as fast as 3 cm/day on the basal plane.

1.8 GEL GROWTH

This is a very convenient laboratory process resulting in the formation of small crystals. Henisch [1988] highlights an excellent survey of the process. Gels are two-phase systems comprising a porous solid with liquid filled pores. The pore dimensions depend on the concentration of the gel material. The most frequently used gels are based on silica. But gels based on gelatines, various soft soaps and pectin are also used. Seed crystals should be used to
Table 1.1 Parameters for selecting a NLO crystal

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Laser parameters</th>
<th>Crystal parameters</th>
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<tbody>
<tr>
<td>1.</td>
<td>NLO process</td>
<td>A type of phase-matching, $d_{\text{eff}}$</td>
</tr>
<tr>
<td>2.</td>
<td>Power, repetition rate</td>
<td>Damage threshold</td>
</tr>
<tr>
<td>3.</td>
<td>Divergence</td>
<td>Acceptance angle</td>
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<td>4.</td>
<td>Bandwidth</td>
<td>Spectral acceptance</td>
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<td>5.</td>
<td>Beam size</td>
<td>Crystal size, walk-off angle</td>
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<td>6.</td>
<td>Pulse width</td>
<td>Group velocity mismatching</td>
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<tr>
<td>7.</td>
<td>Environment</td>
<td>Moisture, temperature acceptance</td>
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first induces a nonlinear response in the medium. Then the medium in reaction modifies the optical field in a nonlinear way. This process is governed by Maxwell's equations [Shen 1984; Butcher and Cotte 1990]

NLO materials have a nonlinear response to the electric field associated with the light of a laser beam. The study of this complex interaction is the subject of nonlinear optics, a field that started in the sixties soon after the discovery of the laser. Nonlinear interaction of light with matter can lead to a variety of optical phenomena such as the generation of new light frequencies or the alteration of the material's optical properties that can be used for the manipulation of optically encoded information. NLO materials are usually divided into different classes based on the nonlinear susceptibilities $\chi^{(n)}$ where $n$ refers to the order of nonlinear susceptibility. $\chi^{(n)}$ describes the response of the materials and its polarization to the electric field associated with the light radiation. NLO materials are usually divided into two main classes.

$\chi^{(2)}$ materials are used for second harmonic generation. For instance, these materials must have an asymmetrical structure. Their refractive indices can also be controlled with an external electric field, a property that is referred to as the electro-optic effect. This property is of paramount importance for many applications and is currently used in electro-optic modulators. It also plays a major role in the photo-refractive effect.

$\chi^{(3)}$ materials are expected to play a key role in all-optical switching devices since their optical properties can be controlled by light. However, due to the higher order of nonlinearity, these materials are usually less efficient and have not reached the maturity of $\chi^{(2)}$ materials for device applications. A number of research efforts are underway to improve their performance and to optimize their efficiency in new device geometry.

Optics is already preferred for many applications owing to its wide bandwidth and autonomy from electromagnetic interference. Nonlinear optical
processes are useful in optical communications and signal processing and integrated optics. Nonlinear optics (NLO) has been an active field of research since the late 1960's with the advent of lasers followed by the demonstration of harmonic generation in quartz by Franken et al [1961]. Nonlinear optics deals with the interaction of intense electromagnetic fields in a suitable medium producing magnified field different from the input field in frequency, phase or amplitude [Zernike and Midwinter 1973; Munn and Ironside 1994]. Nonlinear optics is now established as an alternative field to electronics for the future photonic technologies.

The fast growing development in fibre optic communication systems have stimulated the search for new highly nonlinear materials that are capable of fast and efficient processing of optical signals. In recent years, many significant achievements have been realized in this field because of the development of new nonlinear optical materials of inorganic, semiorganic and organic types. When the electromagnetic field of a laser beam is illuminated on an atom or a molecule, it induces electric polarization, which gives rise to many of the unusual and interesting properties that are optically nonlinear. In a dielectric material the influence of an electric field causes distortion in the spatial distribution between the electrons and the nucleus. These distortions cause electric dipoles, which in turn manifest as polarization [Narasimhamurthy 1981]. At very low fields, the induced polarization is directly proportional to the electric field. However, at intense electric fields, polarization becomes independent of the field and the susceptibility becomes field dependent. The induced polarization is capable of multiplying the fundamental frequency to second order, third order and even higher harmonics. The reradiation from the oscillating dipoles differs in amplitude with respect to the incident sinusoidal electric field. As a consequence, the distorted reradiated waves contain different frequencies from that of the incident wave.
When the electric field associated with the radiation is small, the induced polarization is given by

\[ P = \varepsilon_0 \chi^{(1)} \cdot E \]  \hspace{1cm} (1.1)

where \( P \) is the polarization vector, \( E \) is the electric field vector, \( \chi^{(1)} \) is the linear susceptibility and \( \varepsilon_0 \) is the permittivity of free space.

When the optical electric field strength is very high and comparable to the intra-atomic electric field, the induced polarization is given by

\[ P = \varepsilon_0 \chi^{(1)} \cdot E + \chi^{(2)}\cdot E\cdot E + \chi^{(3)}\cdot E\cdot E\cdot E + \ldots \]  \hspace{1cm} (1.2)

where, \( \chi^{(2)}, \chi^{(3)}, \ldots \) are the nonlinear susceptibilities of the medium.

The nonlinear susceptibilities have decreasing magnitudes as their order increases at \( \chi^{(1)}:\chi^{(2)}:\chi^{(3)} \approx 1:10^{-8}:10^{-16} \). The first order susceptibility which is the linear term \( \chi^{(1)} \), gives rise to refractive index, absorption, dispersion and birefringence of the medium. The second order, \( \chi^{(2)} \), gives rise to second harmonic generation (SHG), frequency mixing and parametric generation, while the third order nonlinear susceptibility, \( \chi^{(3)} \), gives rise to third harmonic generation, stimulated Raman scattering, optical bistability and conjugation. If there are two traveling waves,

\[ E_1 (z,t) = E_1 \cos (\omega_1 t + k_1 z) \]  \hspace{1cm} (1.3)

\[ E_2 (z,t) = E_2 \cos (\omega_2 t + k_2 z) \]  \hspace{1cm} (1.4)

the second order nonlinearity in polarization alone

\[ P = \chi^{(2)} E^2 \]  \hspace{1cm} (1.5)

\[ P = \chi^{(2)} \left[ E_1^2 \cos^2 (\omega_1 t + k_1 z) + E_2^2 \cos^2 (\omega_2 t + k_2 z) \right. \\
+ 2E_1E_2\cos(\omega_1 t + k_1 z)\cos(\omega_2 t + k_2 z) \]  \hspace{1cm} (1.6)

It can be found that the polarization consists of a number of components with different frequencies viz.,
\begin{align*}
P_1\omega_1 &= \chi_0^2 E_1^2 \cos \left[ 2 (\omega_1 t + k_1 z) \right] \\
P_2\omega_2 &= \chi_0^2 E_2^2 \cos \left[ 2 (\omega_2 t + k_2 z) \right] \\
P_1\omega_1 + P_2\omega_2 &= \chi_0^2 E_1 E_2 \cos \left[ (\omega_1 + \omega_2) t + (k_1 + k_2) z \right] \\
P_1\omega_1 - P_2\omega_2 &= \chi_0^2 E_1 E_2 \cos \left[ (\omega_1 - \omega_2) t + (k_1 - k_2) z \right]
\end{align*}

and a steady term,
\[ P_{\text{direct}} = \frac{\chi_0^2}{2} (E_1^2 + E_2^2) \]  

The different components of nonlinear polarization generate electromagnetic waves having frequencies different from those of the incident waves. Fraction of the incident energy used to create nonlinear polarization can be reradiated at one or more number of different frequencies.

By employing proper phase matching conditions it is possible to generate any one of these components of the polarization wave with high efficiency.

\[ k_1 + k_2 = k_3 \]

(or)
\[ \frac{n_1 \omega_1}{c} + \frac{n_2 \omega_2}{c} = \frac{n_3 \omega_3}{c} \]  

Franken et al [1961] observed the frequency doubling for the first time, by irradiating a quartz crystal with a ruby laser beam that operated at 694.3 nm. A very small amount of the light striking the crystal was converted into a light with a wavelength of 347.2 nm. This wavelength lies in the ultraviolet region of the spectrum and is exactly half the wavelength and twice the frequency of the incident laser light.

The conversion efficiency, \( \eta_{\text{SHG}} \) defined as the ratio of the emerging second harmonic power \( P_{2\omega} \) to the incident power \( P_\omega \) is one of the most useful measures of the performance of a nonlinear crystal. It is given by
\[ \eta = \frac{P_{2\omega}}{P_{\omega}} = 2 \left[ \frac{\mu_0}{\varepsilon_0} \right]^{\frac{3}{2}} \omega^2 d^2 l^2 \sin^2 \left[ \frac{\Delta k l}{2} \right] \frac{n^3}{A} \left[ \frac{\Delta k l}{2} \right]^2 \]

where, \( \Delta k = k_{2\omega} - 2k_{\omega} \)

\[ k = \frac{2\pi}{\lambda} \]

\[ \varepsilon_0 = \text{permittivity of free space} \]

\[ \mu_0 = \text{permeability of free space} \]

\[ n = \text{index of refraction} \]

\[ \omega = \text{angular frequency of the incident light} \]

\[ l = \text{length of the crystal and} \]

\[ A = \text{beam area} \]

The factor \( \Delta k \) represents the amount of phase mismatch between the second harmonic wave fronts generated at different points in the crystal. When \( \Delta k \) is zero (proper phase matching) then the interference term,

\[ \sin^2 \left[ \frac{\Delta k l}{2} \right] \frac{n^3}{A} \left[ \frac{\Delta k l}{2} \right]^2 = 1 \]

reaches a maximum value that in turn maximizes the efficiency of the SHG process. The efficiency of second harmonic generation is directly proportional to the intensity \( I(\omega) = \frac{P_{\omega}}{A} \) of the incident fundamental radiation.

In general, higher power density, longer crystal, larger nonlinear coefficients and smaller phase mismatching will result in higher conversion efficiency. In turn, the input and power density has to be lower than the damage threshold of the crystal. Table 1.1 lists the laser and crystal parameters for selecting a NLO crystal for a particular application.
Table 1.1 Parameters for selecting a NLO crystal

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Laser parameters</th>
<th>Crystal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NLO process</td>
<td>A type of phase-matching, $d_{\text{eff}}$</td>
</tr>
<tr>
<td>2.</td>
<td>Power, repetition rate</td>
<td>Damage threshold</td>
</tr>
<tr>
<td>3.</td>
<td>Divergence</td>
<td>Acceptance angle</td>
</tr>
<tr>
<td>4.</td>
<td>Bandwidth</td>
<td>Spectral acceptance</td>
</tr>
<tr>
<td>5.</td>
<td>Beam size</td>
<td>Crystal size, walk-off angle</td>
</tr>
<tr>
<td>6.</td>
<td>Pulse width</td>
<td>Group velocity mismatching</td>
</tr>
<tr>
<td>7.</td>
<td>Environment</td>
<td>Moisture, temperature acceptance</td>
</tr>
</tbody>
</table>
Advancement in the development of NLO materials can be divided into three different areas,

(i) Discovery of NLO materials
(ii) Growth of promising NLO crystals and
(iii) Improving the characteristics of NLO crystals.

1.10 NONLINEAR OPTICAL MATERIALS

The discovery of inorganic photo-refractive crystals such as lithium niobate (LiNbO$_3$), barium titanate (BaTiO$_3$), bismuth silicon oxide (Bi$_{12}$SiO$_{20}$) and their optimization during the last thirty years have led to numerous demonstration of principle of a variety of optical applications. Such applications include, for instance, holographic storage, optical correlation, phase conjugated mirrors, real time optical processing, image amplification, etc. One of the obvious requirements for a nonlinear crystal is that it should have excellent optical quality. For a device to succeed, it is vital that it meets a number of other criteria and these criteria should receive greater emphasis. The relevant issues include reliable crystal growth technique for availability, optical nonlinearity, birefringence, moderate to high transparency and optical homogeneity for high conversion efficiency, mechanical strength, chemical stability, thermal stability, polishing and coating technology for ease of fabrication, low absorption, phase matching bandwidth, and fracture toughness for high average power and damage threshold, nonlinear absorption and brittleness index for lifetime and system capability [Ballman et al 1987].

1.10.1 Criteria for selecting useful nonlinear materials

The applicability of a particular crystal depends on the nonlinear process used, the desired device characteristics and the pump laser. Special material properties that are important in one application may not be significant in another. For instance, efficient doubling of very high power lasers having poor beam quality requires a material with large angular bandwidth. A crystal,
which has a smaller nonlinearity but allows no critical phase matching, will perform better than one, which is more nonlinear, but is critically phase matched. On the other hand, for the doubling of femtosecond optical pulses, the preferred material will be one with a large nonlinearity so that a very thin crystal can be used to avoid dispersive broadening of the second harmonic output pulses [Cheng et al 1990].

For a material that has favorable features such as large nonlinearity, high damage threshold, favorable crystal growth, etc., an application can invariably be found that uses the crystal efficiently. From the material point of view, only general criteria can be established to gauge the usefulness of a nonlinear crystal. For specialized applications where device performance requirements are well established, quantitative criteria for the selection of suitable nonlinear crystals can be obtained which are often invaluable in aiding system design. Nonlinear frequency converters are most commonly used with an efficient, non tunable laser source. Obviously, the nonlinear crystal should have good transparency at the pump laser wavelength.

Specific applications of nonlinear crystals of current interest can be divided into the following (i) efficient harmonic generation and up-conversion, (ii) optical parametric oscillation, (iii) frequency conversion of ultra-short pulses, (iv) frequency conversion of high average power sources, (v) frequency conversion of low average power sources and (vi) laser fusion.

1.11 TRENDS IN NLO MATERIAL DEVELOPMENT

The emergence of new materials with superior quality is often responsible for major advances in new technologies. New techniques applied to the fabrication of ultra-pure silica glass that enabled the fabrication of fibres with ultra-low loss provided the main stimulus to fibre optic communication. The recent emergence of Erbium doped glasses and the fabrication of amplifiers, another major milestone in this area, enabled transmission rate of
50 gigabytes per second. Such amplification rates cannot be achieved with standard electronic amplifiers. The high speed, high degree of parallelism of optics will lead to optoelectronic systems where an increasing number of functions will be implemented optically. However, the development of photonic technology relies largely on the progress achieved in fabricating new optical materials with better performance. In that respect materials with a nonlinear optical (NLO) response are expected to play a major role in enabling optoelectronic and photonic technologies.

1.12 SCOPE OF THE THESIS

The search for nonlinear optical (NLO) materials have been of great interest in the recent years because of their numerous potential applications towards device fabrication. The objective of the present research work is to grow efficient nonlinear optical organic and semiorganic crystals based on novel aromatic system. The materials chosen for the present investigation are Benzoyl glycine (BG), Sodium paranitrophenolate dihydrate (NPNa), Sodium parantiphenolate paranitrophenol dihydrate (SPPD) and Barium bis (paranitrophenolate paranitrophenol) tetrahydrate (BBPT) are excellent NLO materials possessing higher SHG efficiency than KDP crystals.

This thesis contains mainly the following three parts:

(i) Growth and characterization of organic nonlinear optical material benzoyl glycine (BG)

(ii) Growth and characterization of semiorganic nonlinear optical materials NPNa, SPPD and BBPT and

(iii) Measurement of second harmonic generation efficiency (SHG) of BG, NPNa, SPPD and BBPT

In the first part of the thesis, the growth aspects of BG and its characterization are discussed extensively. The characterization of the material includes the study of structural determination by single crystal x-ray diffraction
analysis, Fourier transform infrared (FTIR) and UV spectral investigations, thermal, mechanical and electrical properties.

The second part of the thesis presents the material preparation and characterization of semiorganic materials NPNa, SPPD and BBPT. The essential features of structural, optical, thermal, mechanical and electrical properties of the grown materials are elaborated extensively in this section.

The third part of the thesis makes an attempt to study the nonlinear behaviour of the grown organic and semiorganic materials BG, NPNa, SPPD and BBPT by measuring second harmonic generation efficiency (SHG) and a comparative study has been made with KDP in order to comprise the suitability of the grown materials for device fabrication.