CHAPTER 1

INTRODUCTION TO CRYSTAL GROWTH TECHNIQUES
AND NONLINEAR OPTICS

1.1 INTRODUCTION

Crystal growth is an important field of materials science, which involves controlled phase transformation. In the past few decades, there has been a growing interest in the crystal growth process, particularly in view of the increasing demand for materials for technological applications. The field of crystal growth is interdisciplinary, as it needs expertise in fields such as chemistry, physics, mathematics, crystallography, electrical engineering and optics (Munn et al., 1997). Though it has been studied extensively for more than 100 years, crystal growth still plays an important role in both theoretical and experimental research fields, as well as on application (Zhang 1999). The study of crystalline materials has contributed much to the understanding of solids and has lead to many advances in science and technology (Cahn 2001).

Single crystals play a vital role in the advancing modern technology. It is quite impossible to think of a world without crystals. Crystals have become the pillars of the modern technology and have occupied a key place in the ever growing field of technology. Crystals have printed its foot into almost all fields like lasers, optical devices based applications like nonlinear optics, piezoelectric and optical communication and semiconductor based devices like transducers, infrared detectors and ultrasonic amplifiers (Brice 1986). Good quality crystals are the need of the hour to get the full advantage of the applications for which the crystals are used. In view
of the increasing demand for good quality crystals it is very much important to concentrate more on growing good transparent, defect free crystals. In this regard enormous efforts have been put forward by the crystal growers all around the world. The methods of crystal growth are wide and it mainly depends upon the materials characteristic and the application for which it is to be used and the size required.

This chapter gives a brief introduction on the crystal growth techniques that has been used for growing the materials that are dealt in this thesis. This chapter also explains the fundamentals involved in the growth of single crystals and the characterization techniques that are employed for studying the properties of the grown crystals and moves on to the application point of view in giving a small introduction to the nonlinear optics (NLO), nonlinear optical crystals and finally ends up explaining the scope of the thesis.

1.2 CRYSTAL GROWTH TECHNIQUES

Crystal growth is a heterogeneous or homogeneous chemical process involving solid or liquid or gas to form a homogeneous solid substance having three-dimensional atomic arrangement. Crystals are solids which can be obtained from solid, liquid or vapour phase. The growth of single crystals can be classified according to the phase transformation taking place during the growth process (Mullin 1972).

- Solid – solid phase transformation
- Liquid – solid phase transformation
- Vapour – solid phase transformation
The method by which a particular material can be grown into good, transparent and defect free crystal of processable size depend upon the physical and chemical properties of that particular material. So in order to grow a crystal of a particular material it is very important to have a thorough knowledge about the properties of the material such as its melting point, solubility, thermal stability, etc.

The growth of crystals from liquid can be further categorized into four types.

- Melt growth
- Flux growth
- Hydrothermal growth
- Low temperature solution growth

As the present, thesis focuses on the low temperature solution grown materials, we shall see in detail the fundamentals, types and the mechanisms involved in the low temperature solution growth.

1.3 LOW TEMPERATURE SOLUTION GROWTH

Solution growth is one of the oldest and most widely used methods for growing crystals. This method involves the liquid to solid phase transformation. Those materials that can be dissolved in some solvents at low temperatures ranging from room temperature to 70 °C can be grown by this method. The main advantage of solution growth is the simplicity of the equipment used, control of viscosity and temperature. The crystal growth from liquid and gaseous solutions can only occur if some degree of supersaturation has been achieved. Thus the attainment of
supersaturation is the primary factor that controls the growth process. The crystallisation process occurs by three basics steps.

1. Achievement of supersaturation or supercooling
2. Formation of crystal nuclei (nucleation)
3. Growth of the nuclei into single crystal

In order to understand these basics concepts involved in the process of crystal growth let us see some of the basic terms and also the fundamentals behind those processes.

1.3.1 Supersaturation

The driving force for crystallization is the achievement of supersaturation. The supersaturation of a system can be expressed in a number of ways. It can be expressed in terms of concentration driving force, supersaturation ratio (S) and relative supersaturation (σ).

\[
\Delta C = C - C^* \quad (1.1)
\]

\[
S = \frac{C}{C^*} \quad (1.2)
\]

\[
\sigma = \frac{C - C^*}{C^*} \quad \text{i.e., } \sigma = S - 1 \quad (1.3)
\]

where C is the actual concentration of the solution and C* is the equilibrium concentration at a given temperature. If the concentration of a given solution is known for a given temperature and the corresponding equilibrium saturation concentration is known, then the supersaturation ratio can be estimated.
The required supersaturation that is needed to initiate the nucleation can be achieved by cooling, by evaporation or by the addition of a precipitant. Meir and Isaac carried out extensive research into the relationship between supersaturation and spontaneous crystallization and they gave a solubility diagram called the Meir’s solubility diagram (shown in Figure 1.1). The lower continuous line is the normal solubility curve for a particular solute.

The temperature and concentration, at which spontaneous crystallization occurs, are represented by the upper broken curve, which is referred to as the supersolubility curve. The position of this curve depends of degree of agitation and also on the type of the material concerned (Meirs and Isaac 1987). The solubility diagram is divided into three zones.

1. The stable zone (I) : This region corresponds to the unsaturated region where crystallization is not possible.

2. The metastable zone (II) : In this region spontaneous nucleation is not possible but however growth may take place in presence of a seed crystal.

3. The unstable or labile zone (III) : This is the supersaturation region where spontaneous nucleation is possible.

Thus Meir’s solubility diagram gives us a clear picture of the regions of supersaturation.
Figure 1.1 Meir's solubility diagram
1.3.2 Nucleation

The formation of a new crystalline entity from a solution starts through the nucleation process. The condition of supersaturation alone is not sufficient to initiate the crystallization process. For the growth process to take place there must be a number of minute solid bodies called the centers of crystallization, seed or nuclei. The nucleation can be spontaneous or it may be induced artificially. Nucleation can thus be broadly classified into two types.

Primary nucleation includes all types of nucleation that takes place in the absence of crystalline matter whereas secondary nucleation are those which take place in presence of crystalline matter.

Once the supersaturation is achieved, the fluctuation within the supersaturated solution will give rise to the formation of small cluster of molecules known as “embryos” (growth centres). These growth centres become stable only if they achieve a critical size by the addition of molecules.

\[ A_{n-1} + A \rightarrow A_n \text{ (Critical cluster)} \]  \hspace{1cm} (1.4)

Once the critical size is achieved, the subsequent addition of the molecule will result in nucleation followed by growth of the nuclei. Many nuclei fail to achieve maturity and simply dissolve.

The nucleation process can be better understood in terms of Gibbs free energy (ΔG). The change in Gibb’s free energy between the crystalline phase and the surrounding solution results in a driving force, which stimulates crystallization.
NUCLEATION

PRIMARY

- Homogeneous (Spontaneous)

SECONDARY (induced by crystals)

- Heterogeneous (induced by foreign particles)
The probability of an embryo to grow to form a stable nucleus depends on the change in free energy associated with its formation. If the free energy change per unit volume between the solid and liquid is $\Delta G_v$, the free energy of the system decreases by the amount for each unit volume of the solid created, but increase by an amount equal to the interfacial energy for each unit area of the solid-liquid interface formed. Thus the Gibbs free energy associated with the formation of a spherical embryo is given by

$$\Delta G = 4\pi r^2\gamma + \frac{4}{3}\pi r^3 \Delta G_v$$  \hspace{1cm} (1.5)$$

where $r$ is the radius of nucleus, $\gamma$ is the interfacial tension and $\Delta G_v$ is the free energy change per unit volume. A graphical representation of this equation showing the contribution of both the surface and volume free energy changes is shown in the Figure 1.2.

It can be seen that the surface energy term increases with $r^2$ and the volume energy term decreases with $r^3$. The net free energy change increases with the increase in size, attains a maximum and decreases for the further increase in the size of the nucleus. The size of the nucleus corresponding to the maximum free energy change is known as the ‘critical nucleus’. It is the smallest sized embryo which can further grow. If the size of the nucleus is below the critical dimension no further growth is possible and will dissolve into the mother system.

The minimum size of a stable nucleus is obtained by the maximization of the equation for $r$ (1.5), the radius of the critical nucleus is expressed as

$$r^* = \frac{-2\gamma}{\Delta G_v}$$  \hspace{1cm} (1.6)$$
Figure 1.2 Free energy change of a nucleus as a function of radius
The critical free energy barrier is given by

\[ \Delta G^* = \frac{16\pi y^3}{3(\Delta G_p)^2} \]  

(1.7)

The number of molecules in the critical nucleus is given by

\[ n^* = \frac{-32\pi y^3}{3(\Delta G_p)^3} \]  

(1.8)

The important parameter to calculate these critical radius and critical free energy barrier is the interfacial tension between the growing crystal and the surrounding mother solution (Mullin 1972).

1.3.3 Growth Methods

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

1. Slow cooling method
2. Slow evaporation method
3. Temperature gradient method

1.3.3.1 Slow cooling method

Slow cooling is one of the widely used methods for growing good quality crystals from solutions. It is known for its simplicity of the equipment required for this method. The supersaturation that is required for initiating the crystallization process is achieved by a change in temperature (decreasing the temperature) throughout the crystallizer. The equipment required for this method is a temperature controller with an accuracy of \( \pm 0.01^\circ \text{C} \) so that the temperature can be most accurately controlled. The temperature range of operation is mostly from room
temperature to 70 °C. Lower temperatures can also be reached with the help of a cryostat.

1.3.3.2 Solvent evaporation method

This method is the oldest and very simple and also a widely used method for growing crystals from solution. In this method supersaturation is achieved by evaporation of the solvent. Here the temperature is kept constant and the solvent is allowed to evaporate. The minimum requirement of this method is a temperature controller with an accuracy of ± 0.01 °C. The main advantage of the method is that the crystals are grown at a constant temperature.

1.3.3.3 Temperature gradient method

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

1. Crystal grows at a fixed temperature,
2. Insensitive to changes in temperature provides both the source and growing crystals undergo the same change.
3. Economy of solvent and solute.

On the other hand, a small temperature difference between the source and the crystal zones has a large effect on the growth rate.
1.3.4 Factors Influencing Solution Growth

In order to grow good quality, transparent single crystal it is very important to consider the following factors which highly influence the growth process.

1. Solvent selection and solubility
2. pH of the solution and the growth temperature
3. Purity of the starting materials.

1.3.4.1 Solvent selection and solubility

A solution is a homogeneous mixture of a solute in a solvent. The most important part of solution growth is the selection of the solvent. Depending on the material different types of solvent can be used. Solvents can be polar or non polar. In general polar materials get dissolved in polar solvents and non polar solvent dissolves in non polar materials. Hence the selection of solvents can be made taking into account of the following factors.

- Moderate solubility for the given solute
- The solvent selected should not react with the solute
- Low viscosity
- Less corrosive

Solubility of a material in a particular solvent is an important factor which influences the quality, morphology and the rate of the growth process. If the solubility is too high, it is very difficult to grow bulk crystals because of the presence of large number of growth centers leads to multinucleation. If the solubility
is very low it would restricts the size of the crystals grown. Hence it is very important to do the solubility studies with different solvents and also at different temperature before starting the growth of bulk single crystal. Solution growth is mainly a diffusion controlled process involving the diffusion of solute molecules from the solution onto the growth centers thus the medium should be less viscous to facilitate faster transport. Also the solvent must be less corrosive in nature for ease of handling.

1.3.4.2 pH and temperature of the growth solution

In solution growth, pH value of the solution greatly influences the solubility, stability of the growth solution and the habit of the crystals. Mainly considering the inorganic complexes, the pH plays an important role. Hence once the solvent is chosen, pH value can be optimized to improve the solubility, quality and morphology of the crystals. The stability of the growth solution can also be improved by adjusting the pH of the solution. Many reports in the literature have explained the influence of pH on the morphology of the grown crystals and also reports the improvement in the transparency of the grown crystal by varying the pH value (Rajasekaran et al., 2003; Rajendran et al., 2003; Ushasree and Jayavel 2002; Wang et al., 2004 a). Depending on the material, the temperature has to be optimised at which the solubility, the stability of the solution and the quality of the crystal obtained is good. The purity of the starting material is an important factor which affects the quality and the property of the crystals obtained. So in order to get good quality crystal with high efficiencies it is very important to start with highly pure starting materials.
1.4 NONLINEAR OPTICS

1.4.1 Introduction

A keen survey of the past few decades clearly reveals the evolution of optics into the application areas previously dominated by electronics (Blau 1987). The fast growing field of nonlinear optics ensures its applications in optical information processing, telecommunications sensors, optical phase conjugation, image processing, optical switching, optical data processing and frequency generation (Long 1995). Because of its extensive applications in various fields, nonlinear optics (NLO) have emerged as an active field of research among the young researchers around the world (Nalwa 1991). It all started off with the invention of laser by Maiman in the late 1960’s followed by the demonstration of second harmonic eneration (SHG) in quartz by Franken et al., (Franken et al., 1961). Following Franken’s demonstration, Bloembergen and his group at the Harvard University put forth the theoretical foundations of nonlinear optics, which provided a clear link between the nonlinear and linear phenomena. The nonlinear optics can thus be defined as a phenomenon that results from a field induced modification in the optical properties of a material (Joseph 1995). As the thesis deal with the nonlinear optical crystals this session gives a brief introduction on the fundamentals of nonlinear optics and types of nonlinear optical crystals.

1.4.2 Fundamental of Nonlinear Optics

Nonlinear optics is concerned with the interaction of light with materials. Light can be considered as an electromagnetic wave. When this wave interact with a molecule, a polarisation $P'$ is induced in that molecule by the electric field
component E of the electromagnetic wave. In linear optics there is an instantaneous
displacement or polarisation of the electron density of an atom by the electric field E
of the light wave. This displacement of the electron density away from the nucleus
results in an induced polarisation \( P' \).

With weak electromagnetic field, the induced polarization is directly
proportional to the strength of the applied electric field.

\[
P' = \varepsilon_0 \chi E \tag{1.9}
\]

where \( \chi \) is the linear susceptibility of the material, \( E \) is the electric field
vector; \( \varepsilon_0 \) the permittivity of free space.

When very high electromagnetic waves like laser interacts with the
molecule, the molecule’s polarizability can change and be driven beyond the linear
regime. The nonlinear molecular polarisation can be expressed as

\[
P' = \varepsilon_0 [\chi^{(1)} E + \chi^{(2)} E.E + \chi^{(3)} E.E.E + \cdots] \tag{1.10}
\]

where \( \chi^{(2)} \) and \( \chi^{(3)} \) are the second order and third order nonlinear
susceptibilities. \( \chi^{(1)} \) is the linear term responsible for materials linear optical
properties like refractive index, absorption, and dispersion. \( \chi^{(2)} \) gives rise to second
harmonic generation in the molecule and \( \chi^{(3)} \) gives rise to third harmonic
generation, stimulated Raman scattering and phase conjugation. Thus the induced
polarization is capable of multiplying the fundamental frequency to second, third
and even higher harmonics (Sheik-bahae et al., 2001). In nonlinear terms, product of
two or more oscillating fields gives oscillation at combination of frequencies and therefore the above equation can be expressed in terms of frequency as:

\[
P'(\omega_0) = E_0 \left\{ \chi^{(1)}(-\omega_0; \omega_1)E(\omega_0) + \chi^{(2)}(-\omega_0; \omega_1, \omega_2)E\omega_1\omega_2 + \chi^{(3)}(-\omega_0; \omega_1, \omega_2, \omega_3)E\omega_1\omega_2\omega_3 + \cdots \right\} \tag{1.11}
\]

It is to be noted that the molecules should be non centrosymmetric for the second order nonlinear susceptibility \( \chi^{(2)} \) to be non zero. If the molecule is centrosymmetric then \( \chi^{(2)} = 0 \). Conversely \( \chi^{(3)} \) is the first non zero nonlinear term in centrosymmetric molecules. The orientations of the molecules in a crystal lattice are important factors since \( \chi^{(n)} \) are tensor quantities. Thus the molecules which are non centrosymmetric can exhibit second harmonic generation. Contrary to \( \chi^{(2)} \), there is no symmetry restriction for \( \chi^{(3)} \), which broaden the scope of the third order nonlinear studies over a wide range of materials (Long 1995).

The Figure 1.3 explains the process involved and the energy level diagram describing the second harmonic generation. The incident radiation at frequency \( \omega \) is converted to a radiation of frequency \( 2\omega \).

![Figure 1.3 Second harmonic generation](image-url)
During this process, a polarization wave at the second harmonic frequency $2\omega$ is produced. The refractive index ($n_1$) is defined by the phase velocity and wavelength of the medium. The phase velocity and wavelength of the electromagnetic wave are determined by the refractive index of the doubled frequency ($n_2$). To obtain high conversion efficiency, the phase vectors of input beams and generated beams are to be matched.

where $\Delta K$ represents the phase-mismatch. Higher conversion efficiency is the important criterion for selecting a crystal for nonlinear applications. The conversion efficiency ($\eta$), is given by

$$\eta = P L^2 \left[ d_{eff} \sin \frac{\Delta K L}{\Delta K L} \right]^2$$

(1.12)

where $d_{eff}$ is the effective nonlinear coefficient, $L$ is the crystal length, $p$ is the input power density and $\Delta K$ is the phase mismatching. In general, higher power density, longer crystal, large nonlinear coefficients and smaller phase mismatching will result in higher conversion efficiency. Also, the input 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.

1.5 NONLINEAR OPTICAL CRYSTALS

The nonlinear optics started off with inorganic quartz crystal, with which Franken et al., demonstrated the first frequency doubling experiment with the ruby laser termed as the second harmonic generation. Following this an extensive work on inorganic materials were done leading to the development of many NLO
Table 1.1 Optical effects of nonlinear optical materials

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Effects</th>
<th>Application</th>
<th>Structural requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second order nonlinear susceptibility $\chi^{(2)}$</td>
<td>SHG</td>
<td>Frequency doubling</td>
<td>Non centrosymmetric</td>
</tr>
<tr>
<td></td>
<td>Frequency mixing</td>
<td>Optical parametric oscillations</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pockel’s effect</td>
<td>Electro-optical modulators</td>
<td></td>
</tr>
<tr>
<td>Third order nonlinear susceptibility $\chi^{(3)}$</td>
<td>4 wave mixing</td>
<td>Raman coherent spectroscopy</td>
<td>No symmetry constrain</td>
</tr>
<tr>
<td>(Sheik-bahae, M. and Hasselbeck 2001)</td>
<td>Gratings</td>
<td>Real time holography</td>
<td></td>
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<tr>
<td></td>
<td>Kerr effect</td>
<td>Ultra high speed optical gates</td>
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<td></td>
<td>Optical Amplitude</td>
<td>Amplifiers</td>
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<tr>
<td></td>
<td>Self Focusing</td>
<td>Optical limiting</td>
<td></td>
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<tr>
<td></td>
<td>Two photon absorption</td>
<td>Optical data storage</td>
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</table>
materials like lithium niobate, potassium titanyl phosphate, gallium arsenide and the list goes on. The fast growing field of the nonlinear optics have led to the urge for new materials with better performance. In early 1970s the attention of the researcher moved towards the organic materials because of their large NLO responses, high laser damage threshold, fast optical response, architectural flexibility and ease of fabrication (Long 1995). Following the organic materials, the semi organic materials, which combine the advantages of the inorganic and the organic materials, came into the picture. Thus the nonlinear optical materials can be broadly classified into three types.

- Inorganic materials
- Organic materials
- Semi organic materials

1.5.1 Inorganic and Organic Materials

A very large number of inorganic materials have been investigated in connection with nonlinear optics. A few typical examples are LiNbO$_3$, KTiOPO$_4$, NH$_4$H$_2$PO$_2$ (ADP), KH$_2$PO$_4$ (KDP), HIO$_3$, LiB$_2$O$_5$, CdSe, quartz, etc. Although many highly efficient inorganic NLO materials exist, there were some drawbacks such as low laser damage threshold and poor optical quality of the inorganic materials which turned the focus toward the organic materials with better properties. Some of the advantages of the organic over inorganic materials are listed below.

- Large nonlinear figure of merit
- High optical damage threshold
- Fast response time
- Architectural flexibility.
The strong NLO efficiency of the organic compound is due to electron-donor and electron acceptor groups attached to an aromatic ring, which are involved in conjugated bonds, which in turn contribute to the large polarisation. Also the optical nonlinearity can be increased by the addition of strong electron donating and withdrawing entities. Some of the most popular highly efficient organic materials are 4 dimethyl amino- N-methyl-4-stilbazolium tosylate (DAST), 2-methyl-4-nitroaniline (MNA), 4-methoxy-3-methyl-4-nitrostilbene (MMONS), N-(4-nitrophenyl)-(S)-prolinol (NPP), trans-4-dimethyl amino-methyl stilbazolium-methyl sulfate (DSMS), etc. In spite of all these advantage, organic materials have not got a dominate position in the market for practical application due to some of the draw backs like

- Moderate environmental stability
- Low mechanical strength
- Limited temperature range of operation.

In order to overcome the drawbacks of the organic and inorganic materials a new class of material, the semi organic materials combining the advantages of organic and inorganic materials emerged out and are studied extensively by many research groups all around the world.

1.5.2 Semi Organic Materials

Semi organic crystals are the class of materials which contain an organic and inorganic part in it. These crystals combine the high nonlinearity and chemical flexibility of organics with high mechanical strength and excellent transmittance of inorganic materials. The semi organic materials are further classified into three types.
• Organic-inorganic salts
• Organometallic materials
• Metal organic materials

1.5.2.1 Organic-Inorganic salts

The organic part and the inorganic part combine together to form a salt. The well known amino acid based crystals comes under this category. Some of the well known crystals of this type are glycine phosphate, Larginine phosphate monohydrate, tri glycine sulphate, L-alanine hydrochloride, etc.

1.5.2.2 Organometallic materials

These are complex materials in which a metal acts as the inorganic part and combines with the organic ligands. In organometallic complexes the metal atom is directly bonded with the carbon atom of the organic ligand. Metallocenes like ferrocene derivatives in which Fe is coordinated with the carbon atom of the benzene ring, metal carbonyl and metal carbonyls pyridine complexes are some of the well known organometallic complex exhibiting good SHG efficiency.

1.5.2.3 Metal-organic materials

These are a class of materials in which the metal is coordinated to organic ligands through donor atoms like sulphur, nitrogen that is present in the ligand and not through the carbon atom. The only difference between the organometallic and the metal organics is the donor to which the metal gets coordinated. Some of the well known metal-organic complexes are the thiourea, thiocyanate, thiosemicarbazide and amino acid based metal complexes. These metal organic
Coordination complexes are characterised by various polyhedrals with the central metal ion surrounded by a number of organic ligands. The main advantages of these metal organic complexes are

- They possess two types of charge transfer transitions; metal to ligand or ligand to metal charge transfer, this transfer of electron density between metal ions and ligands increases the polarisation which in turn increases the NLO efficiency of the materials.

- The ligands can influence the property of the material. More electron withdrawing ligands coordinate to the metal increasing the electronegativity of the metal atom. On the other way round, the electron donating ligands decrease the electronegativity of the metal atom. Larger the difference in the electronegativity of the metal-ligand bond, larger the polarities which in turn increasing the NLO efficiency of the material as a whole.

- A ligand involving conjugated systems (alternating single and double bond) would effectively overlap with the metal ion π–orbital leading to greater intramolecular interactions.

- A wide variety of central metal atoms, differing in size, nature and oxidation state are available. Also the size and the nature the organic ligand can be varied. Thus providing structural flexibility to tailor the structure according to the need of the application.

The metal organic complexes can be classified according the structure of the materials.
1. **Island type**: These are structures in which the individual polyhedral held together by weak intermolecular interactions such as vander walls forces, hydrogen bonding, and long distance coulomb interactions. The well known thiourea complexes bis thiourea chloride, ally thiourea complexes of metals like zinc, cadmium and mercury come under this category.

2. **Chain type**: These are structures in which the polyhedral connected by chemical bonds, corner by corner or edge by edge, forming one dimensional polymer. Some examples of this type of structure are thiosemicarbazide cadmium chloride monohydrate, thiosemicarbazide cadmium bromide monohydrate, bis (4- nitropyridine-N-Oxide) cadmium chloride, bis (4-nitropyridine-N-oxide) cadmium chloride in which the metal organic complexes crystallize in the chain type structures.

3. **Network type**: These are structures in which the polyhedras are chemically bonded to form two or three dimensional structures. The bimetallic thiocyanates of the type AB(SCN)4 (where A and B are metals like Cd, Zn, Hg, Mn..) like zinc cadmium thiocyanate, manganese mercury thiocyanate, zinc mercury thiocyanate, etc. and their Lewis base adduct falls under this category (Jiang and Fang 1999).

1.6 MATERIALS FOCUSED IN THE PRESENT INVESTIGATION

In the present work, metal organic complexes of transition metals are investigated. The transition metal complex belonging to the II B group cadmium and
mercury and zinc which are having closed d10 shell are chosen. These metals with filled d orbitals are usually responsible for the high transparency in the UV region. Considering the organic ligands, small π electron systems like thiocyanate and thiourea are focused a lot. These ligands combined with the above said metal atom give rise to complexes with good physical and thermal properties that are required for NLO application. In general these metal organic complexes are said to possess the following advantages which is required for a material to be practically applicable for device fabrication.

- Lower cut off wavelength
- Good transparency over the entire range of visible region
- Good thermal and environmental stability
- Good mechanical stability
- High laser damage threshold

1.6.1 Coordination Complexes

Since the two chapters of the present work is based on the metal organic coordination complexes let us have a brief introduction on the basics terms involved in coordination chemistry. Coordination complexes consist of central metal ions which are coordinated with the Lewis bases or ligands. The neutral molecules or ions which are attached to the central metal ions are ligands. The ligands are classified based on the number of donor atoms present in them.

- Monodentate
- Bidentate, tridentate and poly dentate
The term coordination number denotes the number of ligands that are coordinated to the central metal ion. The central metal ion and the ligands that are directly linked are enclosed inside a square bracket which is called the coordination sphere. The ions that are not involved in coordination are placed outside the sphere.

1.6.2 Thiourea Complexes

Among the metal organic complexes the thiourea complexes play a vital role because of their high non-linear efficiency, lower cut off wavelength, transparency over the entire UV-visible region, good thermal and mechanical stability (Caroline and Vasudevan 2009). Thiourea as a ligand possesses large dipole moment and has the ability to form extensive hydrogen bonding. It is a bidentate ligand with sulphur and nitrogen as the donor atom but in most of the complexes it acts as an ambidentate ligand, coordinating only through the one of the donor atom. Several metal organic complexes of thiourea have been reported. Some of them are zinc thiourea sulphate (ZTS), zinc thiourea chloride (ZTC), bis thiourea cadmium chloride (BTCC) and bis thiourea lead acetate (BTLA). These complexes were reported to show good SHG efficiency compared to the standard material like KDP and urea. BTCC is 110 times more nonlinear than quartz (Venkataramanan et al., 1997). Second order nonlinear coefficient of ZTS is nearly 1.2 times more nonlinear than KDP (Marcy et al., 1992 and Ushasree et al., 1999). UV-Visible cut-off wavelength of ZTS is 260 nm compared to 340 nm of KDP. BTLA (Chidambaram et al., 2011) has been reported to be 5 times more efficient than that of KDP crystal.
1.6.3 Bimetallic Thiocyanate complexes

The bimetallic thiocyanate complexes are a class of materials known for their good NLO efficiency. These coordination complexes are formed by the combination of two metal atoms with the thiocyanate ligand. The coordination of these complexes can be explained based on hard and soft acid base theory popularly known as the HSAB concept. According to this principle, a hard acid will prefer to combine with a hard base and a soft acid will prefer to combine with the soft base.

- **Soft and hard bases:** Soft Lewis bases are those in which the donor atoms are easily polarised and have low electronegativity. Hard Lewis bases are those in which the donor atoms have low polarizability and high electronegativity.

- **Soft and hard acids:** A hard acid is difficult to polarise. Soft acids are those which can be readily polarised.

Classifying the metals and the ligands that are considered in the present work, according to the above concept gives us a clear idea about the mechanism involved in the formation of these complexes. The Table 1.2 classifies some of the transition metals and the donor atom of the ligands according to the HSAB concept.

The thiocyanate ligand (SCN) in the bimetallic thiocyanate complexes acts as a bridging bidentate ligand with two donor atoms sulphur and nitrogen. It coordinates with the two metal ions according the HSAB concept forming two slightly flattened tetrahedral $\text{AN}_4$ and $\text{BS}_4$. The most attracting feature in these complexes are the thiocyanate bridge $-\text{A-N-C-S-B}$ which connect the flattened tetrahedra forming a three dimensional network like structure.
Table 1.2 Classification of some metals and donor atoms according to the HSAB concept

<table>
<thead>
<tr>
<th>Acids</th>
<th>Hard</th>
<th>Borderline</th>
<th>Soft</th>
<th>Bases (donor atoms)</th>
<th>Hard</th>
<th>Soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$</td>
<td>Zn$^{2+}$,Co$^{2+}$,Fe$^{2+}$</td>
<td>Hg$^{2+}$,Cd$^{2+}$</td>
<td>Cl$^-$,N$^-$,O,S$^-$</td>
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These structural features will lead to large macroscopic nonlinearities and very good physicochemical stability. The well known highly efficient thiocyanate nonlinear complexes are zinc cadmium tetra thiocyanate (ZCTC), cadmium mercury tetra thiocyanate (CMTC), manganese mercury tetra thiocyanate (MMTC) and zinc mercury tetra thiocyanate (ZMTC). These complexes are much interesting because of their unique properties like high SHG efficiency at shorter wavelengths, good thermal, mechanical and environmental stability. CMTC crystals were reported to generate blue – violet light when GaAlAs laser diodes are used (Wang et al., 2003 a; Wang et al., 2001 a). Wang et al., reported that the insertion of CMTC into the Nd:YAG laser cavity lead to blue light at 473 and 471 nm with a output power of 1.6 mW (Wang et al., 1999). The output of UV laser light of 380 nm through frequency doubling of a diode laser of wavelength 760 nm was realized by the use of ZCTC crystal (Feng et al., 2011). ZMTC has been reported to be 10 times more efficient than that of urea, but since ZMTC is almost insoluble in all organic and inorganic solvents like water, no report on crystal growth of this complex has been made till now. However the growth of ZMTC in gel have been reported (Ambujam et al., 2007). MMTC is reported to show a 532 nm second harmonic efficiency of 50 times as that of urea. The optical transparency of the complex was also found to be good (Wang et al., 2002 a).

Although all these bimetallic thiocyanates are reported to have good SHG efficiency the only drawback of these complexes is the growth of single crystals of processable size. Hence attempts have been made to combine these bimetallic thiocyanate complexes with some Lewis bases like dimethyl sulphoxide, N, N-dimethyl acetamide, N-methyl-2-pyrolidone,glycol monomethyl ether and thiourea
to form new complex with good NLO efficiency and that can be easily grown. These adducts were found to exhibit good SHG efficiency comparable to that of the parent complexes and also can be comparatively easily grown. Some of the adducts that are reported are tetra thiourea mercury tetrathiocyanate zincate (TMTZ) (Rajarajan et al., 2006), tetra thiourea mercury tetrathiocyanato manganate (TMTM) (Rajarajan et al., 2007), bis dimethyl sulfoxide cadmium mercury thiocyanate (CMTD) (Rajarajan et al., 2006), cadmium mercury thiocyanate glycol monomethyl ether (CMTG) (Potheher et al., 2013), Diaquatetrakis (thiocyanato) cobalt (II) mercury (II) N-methyl-2-pyrolidone (CMTWMP) (Potheher et al., 2008), bis (dimethyl sulfoxide) manganese mercury thiocyanate (MMTD) (Wang et al., 2001 b), bis (dimethylsulphoxide) Cadmium mercury thiocyanate (CMTD) (Guo et al., 2001), Diaqua (thiocyanato) manganese mercury-N,N-dimethylacetamide (MMTWD) (Raghavan et al., 2009), manganese mercury tetrathiocyanate glycol monomethyl ether (MMTG) (Bhaskaran et al., 2010), tetrathiourea mercury tetrathiocyanato zincate TMTZ (Wang et al., 2004 b) and many new materials were designed from the parent complex with comparable SHG efficiencies.

1.7 SCOPE OF THE PRESENT WORK

The present work deals with the growth and characterization of semi-organic non-linear optical crystals and some metal organic complexes combining metals like Cd, Hg with some organic ligands like thiocyanate, N-methyl formamide and dimethyl sulfoxide. It is very much important to grow single crystals of good quality of processable size in order to ensure its use in the application field. In order to grow quality crystals the growth parameters and the growth conditions have to be
optimized. Thus the present thesis mainly focuses on the synthesis, systematic optimization of the growth parameters like solvent, pH and temperature and the growth of single crystals using slow solvent evaporation methods. The grown crystals are characterized to study their structural, optical, thermal, mechanical and surface properties and are discussed in detail.

The present thesis reports the synthesis, single crystal growth and characterization of the following semi-organic, metal organic complexes.

1. Tetra thiourea potassium iodide (TTPI)
2. Tetra thiourea potassium bromide (TTPB)
3. Cadmium mercury thiocyanate bis (N-methyl formamide) (CMTN)
4. Bis (dimethyl sulphoxide) Cadmium mercury thiocyanate (CMTD)