CHAPTER 1

CRYSTAL GROWTH METHODS & NON LINEAR OPTICS

1.1 INTRODUCTION

Crystal growth represents a controlled change of state or phase change, to the solid (condensed) state. This transition may occur from the vapor, liquid or even the solid state itself. The objective of crystal growth is usually to obtain a single crystal defined as the macroscopic extension of regular repeated geometric network of atoms, consisting of one or more elements, from a microscopic scale to a unit ingot. To start the growth process, the nutrient is often 'seeded' with a small piece of crystal to be grown, and one can speak of 'reaping the harvest' after certain span of time. It is obvious that crystal production and fabrication became a major commercial activity after transistor, solar cells and transducers were invented.

The method of growing crystals varies widely and it is mainly dictated by the characteristics of the material and its size (Buckley 1951; Mullin 1976). In recent years there has been considerable progress in the development of coherent UV sources based on non-linear optical processes. The demand for nonlinear optical crystals with superior properties is increasing due to quantum jump in the design of nonlinear optical devices with higher performance. With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace (Chemla and Zyss 1987). To enable a material to be potentially useful for NLO applications, the material should be available in bulk single crystal form. And so, crystal growth of new nonlinear optical materials and investigation into their properties has become most indispensable and efficacious disciplines in the field of materials science and engineering.
**1.2 CRYSTAL GROWTH METHODS**

A material can be transformed into the form of a single crystal by slow and gradual transformation from melt, solution or vapor phase. Good quality crystals are always required for various applications. The requirement for better, cheaper and larger single crystals has driven extensive research and development in crystal growth. This has brought the field of crystal growth into the lime light.

**1.2.1 Crystal Growth Techniques**

Crystal growth technique ranges from a simple inexpensive process to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. Crystal growth methods can generally be classified into three basic categories:

- **Solid Growth**: solid to solid phase transitions.
- **Melt Growth**: liquid to solid phase transitions.
- **Vapor Growth**: vapor to solid phase transitions.

**1.2.2 Methods for growing crystals**

A number of methods are available for growing crystals and the method chosen depends on the chemical property of the compound of interest. All the crystals presented in this thesis were grown by slow evaporation method and this method is described below:

**1.2.3 Slow evaporation Method**

This is the simplest method of growing crystals and is most suitable for compounds which are not sensitive to air or moisture in the laboratory. A saturated or nearly saturated solution of the compound in a suitable solvent is prepared. It is then transferred to a clean crystal growing dish and covered with an aluminum foil provided with some holes. The solution is allowed to evaporate slowly and gradually. This method is very convenient, when it is possible to dissolve a large amount of compound in a small volume of the solvent.

**1.3 NONLINEAR OPTICS**

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular, they have a great impact on information technology and industrial applications.
In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The aim is to develop materials with large nonlinearities and satisfying all the technological requirements for applications such as wide transparency range, fast response and high damage threshold.

1.3.1 Nonlinear Optical Phenomenon

Nonlinear optics is completely, a new effect in which light of one wavelength is transformed to light of another wavelength. The creation of light of new wavelength can be best understood, as we think about the electrons in nonlinear crystal. Electrons in a nonlinear crystal are bound in potential well, which acts like a spring, holding the electrons to lattice point in the crystal. If an external force pulls an electron away from its equilibrium position the spring pulls it back with a force proportional to the displacement. The spring’s restoring force increases linearly with the electron displacement from its equilibrium position. The electric field in a light wave passing through the crystal exerts a force on the electrons and pulls them away from their equilibrium position. In an ordinary optical material i.e., linear optical material the electrons oscillate about their equilibrium position at the frequency of this electronic field.

The nonlinear material is different from the linear material in several aspects. We can think of a nonlinear material as the one whose electrons are bound by very short springs. If the light passing through the material is intense enough, its electric field can pull the electrons so far that they reach the end of their springs. The restoring force is no longer proportional to the displacement and then it becomes nonlinear. The electrons are jerked back roughly rather than pulled back smoothly and they oscillate at frequencies other than the driving frequency of the light wave. These electrons radiate at the new frequencies, generating the new wavelength of light. The exact values of the new wavelengths are determined by conservation of energy. The energy of the new photons generated by the nonlinear interaction must be equal to integral multiple of the energy of the photon used.
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, third order and even higher harmonics. The irradiation 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.

1.3.2 Theoretical explanation of nonlinear optics

The explanation of nonlinear effect lies in the way in which a beam of light propagates through a solid. The nuclei and the associated electrons of the atoms in the solid combine to form electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate, which by the classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation.

If the amplitude of vibration is small, the dipoles emit radiation of the same frequency as the incident radiation. As the intensity of the incident radiation increases, the relationship between irradiance and amplitude of vibration becomes nonlinear resulting in the generation of harmonics in the frequency of radiation emitted by the oscillating dipoles. Thus frequency doubling or second harmonic generation (SHG) and higher order frequency effects occur as the incident intensity is increased.

In a nonlinear medium the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal.

At very low fields, the induced polarization is directly proportional to the electric field.

\[ P = \varepsilon_0 \chi \ E \]  

(1.1)
Where $\chi$ is the linear susceptibility of the material, $\vec{E}$ is the electric field vector and $\varepsilon_0$ is the permittivity of free space.

At high fields, polarization becomes independent of the field and the susceptibility becomes field dependent. Therefore, this nonlinear response is expressed by writing the induced polarization as a power series in the field.

$$P = \varepsilon_0 \chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \ldots \quad (1.2)$$

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:

$$P (-\omega_0) = \varepsilon_0 \chi^{(1)} (-\omega_0; \omega_1) E(\omega_0) + \chi^{(2)} (-\omega_0; \omega_1, \omega_2) E \omega_1 E \omega_2 +$$
$$\chi^{(3)} (-\omega_0; \omega_1, \omega_2, \omega_3) E \omega_1 E \omega_2 E \omega_3 + \ldots \quad (1.3)$$

Where $\chi^{(2)}$, $\chi^{(3)}$, ..., are the nonlinear susceptibilities of the medium. $\chi^{(1)}$ is the linear term responsible for material's linear optical properties like refractive index, dispersion, birefringence and absorption. $\chi^{(2)}$ is the quadratic term which describes second harmonic generation in noncentrosymmetric materials. $\chi^{(3)}$ is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical instability. Hence the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. If the molecule or crystal is centrosymmetric then $\chi^{(2)} = 0$. If a field $+E$ is applied to the molecule (or medium), equation 1.3 predicts that the polarization induced by the first nonlinear term is predicted to be $+E^2$, yet if the medium is centrosymmetric the polarization should be $-E^2$. This contradiction can only be resolved if $\chi^{(2)} = 0$ in centrosymmetric media.

If the same argument is used for the next higher order term, $+E$ produces polarization $+E^3$ and $-E$ produces $-E^3$, so that $\chi^{(3)}$ is the first non-zero nonlinear term in centrosymmetric media. In second harmonic generation, the two input wavelengths are the same $2\omega_1 = \omega_2$ or $(\lambda_1 = 2 \lambda_2)$.

During this process, a polarized wave at the second harmonic frequency $2\omega_1$ is produced. The refractive index, $n_1$ is defined by the phase velocity and wavelength of the medium. The energy of the polarized wave is transferred to the electromagnetic wave at a
frequency $\omega_2$. 
The phase velocity and wavelength of this electromagnetic wave are determined by 
$n_2$, the refractive index of the doubled frequency. To obtain high conversion efficiency, the 
phase vectors of input beams and generated beams are to be matched.

$$\Delta k = \frac{2\pi}{\lambda(n_2 - n_1)} = 0$$  \hspace{1cm} (1.4)

Where $\Delta k$ represents the phase–mismatch. The phase–matching can be obtained 
by angle tilting, temperature tuning or other methods. Hence, to select a nonlinear optical 
crystal, for a frequency conversion process, the necessary criterion is to obtain high 
conversion efficiency.

The conversion efficiency $\eta$ is given by

$$\eta = P L^2 \left( \frac{d_{\text{eff}} \sin \Delta k L}{\Delta k L} \right)^2$$  \hspace{1cm} (1.5)

Where $d_{\text{eff}}$ 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.

1.4 AN APPRAISAL OF NLO CRYSTALS

The nonlinear material is different from the linear material in several aspects. We 
can think of a nonlinear material as the one whose electrons are bound by very short springs. 
If the light passing through the material is intense enough, its electric field can pull the 
electrons so far that they reach the end of their springs. The restoring force is no longer 
proportional to the displacement and then it becomes non-linear. The electrons are jerked 
back roughly rather than pulled back smoothly and they oscillate at frequencies other 
than the driving frequency of the light wave. These electrons radiate at the new frequencies, 
generating the new wavelength of light. The exact values of the new wavelengths are 
determined by conservation of energy. The energy of the new photons generated by the 
nonlinear interaction must be equal to the energy of the photon used.
Two new polymorphs of Schiff base, (E)-2-((2, 6-dichlorobenzylidene) amino) benzonitrile, were prepared from the condensation of 4-amino-benzonitrile and 2, 6-dichlorobenzaldehyde by Benarous et al. (2016). A new complex, Ni (C$_{2}$H$_{2}$N$_{2}$O$_{10}$S$_{2}$) ·2CH$_{3}$OH, with a sexidentate (N$_{2}$O$_{4}$) symmetric Schiff base ligand (C$_{22}$H$_{26}$N$_{2}$O$_{10}$S$_{2}$ = 1, 2-bis (2-methoxy-6-formylphenoxy) ethane-2-aminoethane-sulfonic acid) has been synthesized and characterized by physico-chemical and spectroscopic methods. Two new copper(II) complexes with polypyridyl ligands, [Cu(phen)$_{2}$ (H$_{2}$O)] (ClO$_{4}$)$_{2}$ (1) and [Cu(bipy)$_{2}$ (NO$_{3}$)]ClO$_{4}$ (2) (phen = 1,10-phenanthroline and bipy = 2,2'-bipyridyl) have been synthesized and characterized by elemental analysis, FAB (fast atomic bombardment), magnetic measurements, electronic absorption, conductivity measurements, cyclic voltammetry (CV) and electronic paramagnetic resonance (EPR) spectroscopy (Ram et al. 2016). A new series of 1-(furan-2ylmethyl)-2,4,5-triphenyl-$IH$-imidazole derivatives are conveniently synthesized and characterized by IR, $^{1}$H NMR and $^{13}$C NMR spectral techniques (Rajaraman et al. 2016).

L proline lithium bromide monohydrate a semi organic nonlinear optical material was grown and characterized by XRD, spectral, thermal, optical, Vicker’s micro hardness, dielectric, SEM-EDAX techniques and for second order nonlinear optical properties (Sathishkumar et al. 2015). Sureka et al. (2014) reported the third order nonlinear optical luminescence and electrical properties of Bis Glycine Hydro Bromide single crystals (BGHB). BGHB crystal has positive nonlinear absorption coefficient. The open and closed aperture Z scan showed negative nonlinear refractive index. Xavier and Periandy (2015) reported the spectral analysis of 1-phenyl 2-nitro propene using the FT-IR, FT-Raman, UV-Vis spectra and NMR with the help of quantum mechanical computations using ab initio and density functional theories. The HOMO-LUMO mappings revealed the different charge transfer possibilities with in the molecules. The study of NLO property in relation with dipole moment and hyperpolarizibility was done. The group vibrations of 3-aminophenylacetic acid were investigated by electronic structure calculations based on DFT and frequency calculations carried out at B3LYP(d-31Gid) and B3LYP/6-311++(d, p) levels of theory (Yasemin Akkaya et al. 2015). Vibrational spectra and NLO analysis of HOMO-LUMO studies of 2-chloro 6-fluoro benzoic acid and 3,4-dichlorobenzoic acid was reported by Senthil Kumar et al. (2015). Mulliken’s charges HOMO-LUMO and MEPs analysis were performed. The first order hyperpolarizability and several thermodynamic properties were performed by the DFT method. The calculated
HOMO-LUMO energies show that charge transfer occurs within the molecules which are responsible for the biological property of the molecules. An experimental and theoretical studies on N,N' diphenylguanidinium dihydrogen phosphate semi-organic NLO material reported by Saravanakumar et al. (2015). The grown crystals showed potential third order nonlinear optical parameters ascertained from Z scan technique. Single crystals of semi-organic nonlinear optical material of L anilinium perchlorate were grown and its third order nonlinear refractive index and nonlinear absorption coefficient of the grown crystal were measured by Z scan studies. Josephine Usha et al. (2014) studied and reported the optical mechanical, electrical properties of Manganese Mercury ThioCyanate (MMTC). A density functional theoretical approach of L-Asparaginum picarate single crystals was reported by Nabil Elleuch et al. (2014). Single crystals of L-Phenylalanine L-Phenylalaninum Perchlorate (LPLPP) were grown by the slow evaporation solution growth technique and repeated recrystallization yielded to good quality crystals by Nabil Elleuch et al. (2014). Vetrivel et al. (2013) has reported the growth and characterization of L – Proline cadmium chloride monohydrate. L- Histidine Oxalate was grown using the submerged seed solution growth and characterized by Sagaya Jude Dhas and Jerome Das (2015). Growth, spectroscopic, dielectric and nonlinear optical studies of semi-organic nonlinear optical crystal - L-Alanine lithium chloride was studied by Redrothu Hanumantharao and Kalainathan (2012). Experimental values of density (ρ) and speed of sound (u) of aqueous solutions of three amino acids L-alanine at different temperatures (275.15, 279.15, and 283.15 K) are reported (Sudhakar S Dhondge et al. 2012). High resolution X-ray diffraction (HRXRD), Raman spectroscopy, photoluminescence, SEM, micro-hardness, thermal and birefringence analyses was studied for L-Arginine acetate (LAA) an organic nonlinear optical single crystal (Renuka et al. 2012). A novel organic NLO crystal L-Threonine formate was grown and its spectroscopy, dielectric and nonlinear optical studies were carried out by Redrothu Hanumantharao and Kalainathan (2012). Single crystals of L-Histidinium Maleate were synthesized and characterized by Aloisious Gonsago et al. (2012). Moovendran et al. (2012) have grown L-Histidinum 2-Nitrobenzoate and analysed the optical and thermal properties. Crystal growth, structural, optical, dielectric and thermal studies of L-Phenylalanine L-phenylalaninum malonate was reported.
L-Arginine monohydrochloride monohydrate (LAHCl) single crystals were grown successfully by conventional and unidirectional solution growth methods. The crystalline perfection of grown crystals was analyzed by high-resolution X-ray diffraction (Sangeetha et al. 2011). Thermal, mechanical, electrical, linear and nonlinear optical properties of L-arginine dihydrofluoride single crystal was reported by Sankar et al. (2010). L-arginine trifluoroacetate (LATF), an organic nonlinear optical material was grown by temperature lowering technique from its aqueous solution. The microhardness study shows that the LATF crystal is a hard material. LATF is thermally stable up to 212 °C (Arjunan et al. 2008). Bulk single crystals of L-arginine maleate dihydrate (LAMD), an organic nonlinear optical material have been grown from aqueous solution by slow cooling technique. Analysis of surface micrographs reveals that LAMD crystal grows by two dimensional layer growth mechanisms. The SHG efficiency of LAMD was found to be 1.4 times that of KDP crystals (Kalaiselvi et al. 2008).

Linear and nonlinear optical properties of the organic-inorganic hybrid crystal, L-arginine phosphate monohydrate have been investigated. The results showed both organic and inorganic structural building blocks and also the intermolecular hydrogen bonds contribute to the large nonlinear optical activity of LAP (Kechen Wu et al. 2007). Optically good quality bulk single crystals of Largininium perchlorate (LARPCL) with improved SHG efficiency were grown by Aruna et al. (2007) and studied its physical properties.

1.5 OBJECTIVES AND SCOPE OF THE WORK

The ever increasing demand for highly efficient nonlinear optical (NLO) crystals for visible and ultraviolet regions is extremely important for laser and material processing. In this context, the molecular design and growth of single crystal materials suitable for such requirements, assumes center stage, keeping this in view, attempts are made to grow and study NLO active L - Aspararginium Tartrate (LAsT), L-Prolinium Tartrate (LPT), Thiosemicarbazone 4-Methoxy Benzaldehyde Zinc Chloride (BLZC) and Thiosemicarbazone 2-Chloro Benzaldehyde Cadmium Bromide (BLCB).

Chapter I is an introduction to crystal growth and nonlinear optical phenomena. The fundamentals of Density Functional Theory (DFT) computations to obtain stabilized state
molecular parameters are explained. The theoretical aspects of nonlinear optics with its applications are outlined. It also deals with the various characterization techniques and tools used for characterizing the grown crystals.

**Chapter II** deals with characterization techniques adapted to analyze the materials. Characterization of crystal essentially consists of an evaluation of its chemical composition, structure, defects and the study of its optical, thermal, mechanical and electrical properties. Assessment techniques are essential in order to estimate the quality and character of the grown crystals. These studies help us to trigger rapid progress in the growth process and to improve the quality of the grown crystals. The second chapter itemizes the various techniques, instrumentation and applications of spectroscopy to crystals. Apart from this, the other salient instrumentation discussed are the single crystal X-ray diffraction, powder X-ray diffraction, thermal analysis, dielectric and hardness studies. These techniques have been employed for characterizing the NLO active crystals grown in the present work.

**Chapter III to VI** explains synthesis, growth and characterization of LAST, LPT, BLZC and BLCB single crystals. XRD analysis, Density Functional Theory (DFT) computations such as bond lengths and bond angles were obtained for all the materials. Hyperpolarizability and HOMO-LUMO analysis were performed with B3LYP/6-31(d, p) basis set. Bond lengths and bond angles are compared with XRD parameters. Theoretical and Experimental IR analysis were done to identify various functional groups present in the materials. UV-Vis spectra are obtained for the materials. From the absorption data other linear optical parameters like extinction coefficient, reflectance, refractive index, complex dielectric constant and optical conductivity are calculated and related with incident photon energy. Thermal analysis of the materials revealing the stability was also done. Mechanical strength and SHG efficiency were done for all the materials to understand its suitability in NLO applications. Dielectric studies and photoconductivity studies were carried out to recognize the photo response nature of the crystals.

**Chapter VII** gives a summary of the investigations carried out on these four crystals. The chapter concludes with some of the aspects that are yet to be answered/explored, setting the tune for the future work.