CHAPTER I

CRYSTAL GROWTH AND NONLINEAR OPTICAL PHENOMENON – AN OVER VIEW

1.1 INTRODUCTION

Walking around in nature, looking at the sea, feeling the wind or climbing on solid rocks, there is hardly any reason to believe that all matter is constituted of small atoms, moving around in an everlasting motion. In fact, despite the early speculation by the ancient Greek Demokritos, it was not before the beginning of the 20th century that the atomic nature of matter was accepted beyond reasonable doubt. Our direct knowledge of the behaviour of matter is almost exclusively derived from the observation of samples that are very large compared to atomic dimensions. With advancement in instrumentation technology, the attention of crystal growers focused on the quality of the grown crystals and understanding their formation. Also, tailoring of crystal shape or morphology, size and properties play a key role in crystal growth science. Crystal growth is highly interdisciplinary subject that demands the collaboration of physicists, chemists, biologists, engineers, crystallographers, process engineers, material scientists and material engineers. The significance of the beauty of rarity of crystals is now well knitted with their symmetry, molecular structure, purity and physicochemical environment of their formation. These characteristics endow crystals with unique physical

and chemical properties, which have transformed electronic industries for the benefit of human society. Due to this the growth and characterization of single crystals towards device fabrication have gained momentum.

In this chapter, the fundamentals of the various methods to grow good quality single crystals and in particular the solution growth methods along with Sankaranarayanan – Ramasamy (SR) method are discussed. The theoretical aspects of nonlinear optics, the role of NLO materials in science and technology and the various applications of NLO materials are also explained.

1.2 CRYSTAL GROWTH METHODS

1.2.1 Slow evaporation solution growth method

Slow evaporation method is one in which a portion of the solvent is allowed to evaporate from the prepared solution. Among the various methods of solution growth process, this method is the most versatile and suitable method. The main advantage of this method is that the growth of the crystals can be carried out at a fixed temperature. This method can be effectively used for materials having very low temperature coefficient of solubility.

If the solvent is non-toxic like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve a temperature stabilization of about $0.05^{o}C$ and rate of evaporation of a few mm^3/h. But inadequacies of the temperature control system still have a major effect on the growth rate. In order to control the temperature of the system,

constant temperature bath can be used. The saturated solution kept at a particular temperature is allowed to evaporate, to form seed crystals. These seed crystals are used to grow bulk single crystals.

1.2.2 Sankaranarayanan – Ramasamy (SR) method

The SR growth system consists of a growth ampoule made out of borosilicate glass with seed mounting pad (Sethuraman et al 2006). The rings are positioned on the top and bottom of the ampoule. The heaters are connected to a dual channel temperature controller which maintains constant temperature. The entire set up is placed in a dust-free hood. The crystal with specific orientation can be grown from solution by SR method (Sankaranarayanan et al 2006). The SR method is suitable method to effectively control the orientation of molecules during the bulk crystal growth from solution at room temperature with 100% solute–crystal conversion efficiency. The schematic diagram of SR method apparatus is shown in Figure1.1.

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.
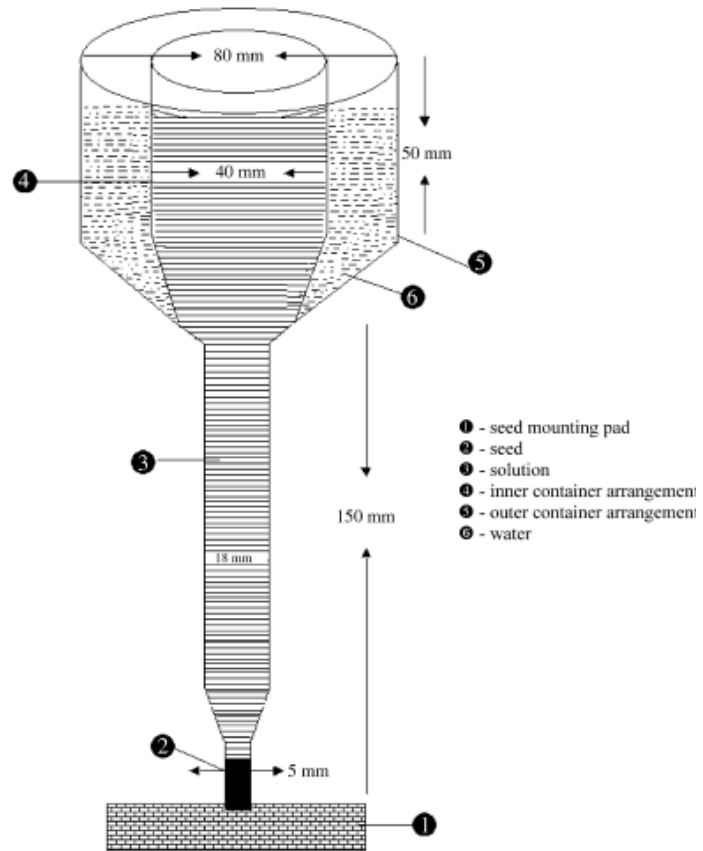
Fig 1.1 The schematic diagram of SR method apparatus

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 presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response and high damage threshold.

1.3.1   Nonlinear optical phenomena

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 ie., 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 photons 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 et al 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 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.

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 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.

$$P = \varepsilon_o \chi \, E \qquad\qquad\qquad (1.1)$$

Where χ is the linear susceptibility of the material, $\vec{E}$ is the electric field vector and ε_o 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.

$$P = \varepsilon_o \chi^{(1)} E + \chi^{(2)} E.\,E + \chi^{(3)} E.\,E.\,E + ... \qquad (1.2)$$

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:

$$P\,(-\omega_o) = \varepsilon_o \chi^{(1)}(-\omega_o;\,\omega_1).E(\omega_o) + \chi^{(2)}(-\omega_o;\,\omega_1,\,\omega_2).E\omega_1.E\omega_2 +$$

$$\chi^{(3)}(-\omega_o;\,\omega_1,\,\omega_2,\,\omega_3).E\omega_1.\,E\omega_2.\,E\omega_3 + ... \qquad (1.3)$$

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. 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 ω_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.

$$\Delta k = \frac{2\pi}{\lambda(n2-n1)} = 0 \qquad (1.4)$$

where (n2-n1) 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 η is given by

$$\eta = PL^2 \left(\frac{d_{eff} \sin \Delta kL}{\Delta k.L} \right)^2 \qquad (1.5)$$

Where d_{eff} is the effective nonlinear coefficient, L is the crystal length, P is the input power density and Δk 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   A REVIEW OF AMINOACID NLO CRYSTALS

1.4.1 Analogs of L-histidine

Histidine is the only standard amino acid having an imidazole side chain with pH near neutrality. The function and role of histidine and its residues in living matter is characterized by the imidazole group. The functional amino acid, histidine serves as a proton donor, proton acceptor and as a nucleophilic reagent. Histidine frequently occurs at the active sites of enzymes and also coordinates ions in larger protein structures (Mostad et al 1995). Histidine itself exists in orthorhombic and monoclinic forms (Madden et al 1972). Neutron and X-ray diffractions on histidine hydrochloride were reported (Fuess and Bartunik 1977; Donohue and Caron, 1964). X-ray studies on the following crystalline complexes have also been reported: DL- and L-histidine with succinic acid (Prasad and Vijayan, 1993), L-histidine with glutaric acid (Saraswathi et al 2001), L-histidine with L-aspartic acid (Bhat and

Vijayan 1978), L-histidine with formic acid (Suresh and Vijayan 1995), L- and DL-histidine with glycolic acid (Suresh and Vijayan 1996).

L-histidine salts can display high NLO properties due to the presence of imidazole group in addition to amino-carboxylate. Among the L-histidine analogs, the low temperature solution grown L-histidine tetrafluoroborate (LHFB) $\{[(C_3N_2H_4)CH_2CH(NH_3)(CO_2)]^+BF_4:HFB\}$ is a promising NLO material and has superior NLO properties than L-Arginine Phosphate (LAP). The SHG intensity of L-HFB crystal is five times that of the KDP. The power threshold figure-of-merit compares favourably with BBO and LBO single crystals (Marcy et al 1995). Reena Ittyachan and Sagayaraj (2003a) have reported the growth of L-histidine bromide (LHB), a semiorganic NLO material with molecular formula $C_6H_{12}N_3O_3Br$ by slow evaporation technique and suggested the possibility of LHB being used for fabrication of photonic devices.

L-histidine diphosphate (LHDP) with molecular formula $C_6H_{15}N_3O_{10}P_2$ is a new semiorganic NLO crystal, which possesses good transparency, dipolar strength and is regarded as a promising material for NLO applications (Reena Ittyachan and Sagayaraj 2003b). Single crystal of L-histidinium perchlorate (LHPC), a semiorganic NLO crystal has been grown by slow solvent evaporation method at room temperature (Reena Ittyachan et al 2005).

A new organic nonlinear optical (NLO) material, L-histidinium tetrafluorophthalate (L-HFP), has been synthesized and crystals were grown from its solution by slow evaporation technique at a growth rate of

0.21 mm/day. The optical transmittance spectrum shows that UV cut-off wavelength is 230 nm. A laser damage threshold of 56.58 MW/cm^2 has been measured by irradiating the (1 0 0) crystal face using a Q-switched Nd:YAG laser (1064 nm) (Ramajothi and Dhanuskodi 2006). L-histidine hydrofluoride dihydrate (LHHF) is a semiorganic nonlinear optical crystal grown by Madhavan et al (2006). It is seen from the absorption spectrum that the absorption is minimum in the entire UV-Vis-NIR region. Its SHG efficiency is 6 times that of KDP. Single crystals of L-histidinium dihydrogen orthophosphate orthophosphoric acid (LHP) were grown and the physicochemical properties were investigated by Madhavan et al (2007). Kannan et al (2006) have grown single crystals of L-histidine monohydrochloride (LHMHCl) and L-histidine dihydrochloride (LHDHCl) and confirmed that LHMHCl crystal is thermally more stable and has higher melting point than LHDHCl crystal. Laser damage threshold study shows that LHDHCl is more resistant to laser damage than LHMHCl. Crystals of LHDHCl in monoclinic form give strong second-harmonic generation (SHG) signals, while orthorhombic forms do not. Bulk single crystals of L-histidine acetate dihydrate (LHA) upto a dimension of 21 x 13 x 9 mm^3 were successfully grown using slow evaporation technique by Madhavan et al (2007a). Madhavan et al (2007b) have grown single crystals of L-histidine hydrochloride monohydrate (LHC) by slow evaporation technique at room temperature and its thermal, mechanical and dielectric properties were studied. Single crystals of L-histidinium perchlorate (LHPCl), were grown upto a size

of 6 x 5 x 2.5 mm^3 by Aruna et al (2007a) and found to have a fairly high thermal stability up to 272°C. Single crystals of L-histidinium dinitrate (LHDN) with needle morphology were grown with an optimized pH of 2 by solvent evaporation method. The crystalline perfection of LHDN was investigated by high-resolution X-ray diffractometry (HRXRD) (Aruna et al 2007b). Ramajothi and Dhanuskodi (2007) have grown L-histidine bromide (LHB) single crystal and evaluated the SHG efficiency and laser damage threshold. The optical birefringence was also measured in the visible region as a function of temperature in the range 30°C –150°C by interference technique. A large single crystal of L-histidinium dihydrogen phosphate (LHDP) with dimension of 4 x 1.5 x 1 cm^3 has been grown in an aqueous solution at 35°C by Rajendran et al (2007). Anisotropy in hardness behaviour has been observed while measuring for individual planes. L-histidinium acetate dihydrate (LHAc) was grown from aqueous solution and its spectroscopic and thermal properties were analysed. Its SHG efficiency was found to be d_{eff} = 2.2 d_{eff} (KDP) (Mathivanan et al 2007). Crystal structure and vibrational analysis of novel nonlinear optical L-histidinium tetrafluoroborate (L-HFB) single crystals have been explained by Gokul Raj et al (2007). The infrared (IR) and Raman spectroscopic measurements fully confirmed the X-ray crystal structure of L-HFB. Bulk single crystal, L-histidine nitrate (LHN), was obtained by the temperature-lowering method. The LHN crystal was characterized by single-crystal X-ray diffraction, FT-IR spectral analysis, thermal analysis, UV–Vis-NIR spectral studies, microhardness and optical studies. The transmission

spectra of LHN crystal show lower UV cutoff wavelength and lies at 320 nm. SHG intensity of LHN crystal is 1.5 times greater than that of KDP (Yun Zhang et al 2008). Structural, vibrational and theoretical studies of L-histidine bromide were reported by Ben Ahmed et al (2008). Single crystals of pure, Cu^{2+} and Mg^{2+} doped L-histidine acetate were grown by slow evaporation technique (Praveen kumar et al 2008).

Experimental and computational studies of the macrocyclic effect of an auxiliary ligand on electron and proton transfers within ternary copper(II)–histidine complexes were investigated by Tao Song et al 2009. Nearly perfect single crystal of L-Histidine bromide (LHB) was grown and its structural, optical and electrical characterizations were reported by Vijayan et al 2009. Growth and characterization of a nonlinear optical crystal L-histidine trifluoroacetate was investigated by Sun G.H et al 2009. L-Histidine sulfates were studied by Petrosyan H.A et al 2010. Single crystals of L-histidine hydrochloride monohydrate (LHC) were grown by unidirectional growth technique and spectral, optical, mechanical studies were carried out by Robert. R et al 2010. Single crystal EPR and optical absorption study of Cr^{3+} doped L-histidine hydrochloride monohydrate were reported by Ram Kripal et al 2011. Nucleation kinetics, micro-crystallization and etching studies of L-histidine trifluoroacetate crystal were carried out by Sun G.H et al 2011. Semiorganic single crystals of L-Histidine family were grown and the characterization of L-Histidine family for NLO applications was reported by Pandurangan Anandan et al 2011. Natural bond orbital analysis, electronic

structure, non-linear properties and vibrational spectral analysis of L-histidinium bromide monohydrate: Density functional theories are reported by Sajan D et al 2011. A nonlinear optical material L-histidine was grown and crystalline perfection, optical and dielectric studies were reported by Riscob B et al 2011. Growth and characterization of L-histidine cadmium chloride monohydrate semiorganic nonlinear optical crystals were investigated by Chandrasekaran J et al 2012. Crystal growth and characterization of L-histidine hydrochloride monohydrate semiorganic nonlinear optical single crystals were also reported by Anandan P et al 2012. Crystal structure, optical and thermal studies of a new organic nonlinear optical material: L-Histidinium maleate 1.5-hydrate was reported by Alosious Gonsago.C et al 2012. Growth and characterization of L-histidinium 2-nitrobenzoate single crystals: A new NLO material was studied by Moovendaran K et al 2012. Spectral, optical, thermal and mechanical studies on L-Histidine oxalate crystals are reported by Sahaya Jude Dhas. S et al (article in press).

1.4.2 Analogs of L-alanine

Growth, spectroscopic, dielectric and nonlinear optical study of semi organic nonlinear optical crystal – L-Alanine lithium chloride was studied. (Redrothu Hanumantharao et al 2012). Experimental values of density (ρ) and speed of sound (u) of aqueous solutions of the amino acid L-alanine at different temperatures i.e. T = (275.15, 279.15, and 283.15) K were reported (Sudhakar S. Dhondge et al 2012). Effect on crystalline perfection, second harmonic generation efficiency, laser damage threshold and optical transparency due

to Mn^{2+} doping in L-alanine crystals has been investigated (Kushwaha et al 2011). Growth, structural, vibrational, optical, laser and dielectric aspects of L-alanine alaninium nitrate single crystal were investigated. The presence of hydrogen and carbon atoms in the grown sample was confirmed using proton and carbon NMR analyses (Lydia Caroline. M et al 2011). L-alanine hydrogen chloride (LAHC) was synthesized and it density is found as 1.325 g/cc. Grown LAHC crystal has 0.76 times higher NLO efficiency than KDP (Lucia Rose A.S.J. et al 2011). L-alanine is an efficient organic NLO compound under the amino acid category. Jaikumar et al 2010 reported on the growth and characterization of a new organic NLO material Urea - L-alanine acetate single crystals. Influence of metal dopants (Cu and Mg) on the thermal, mechanical and optical properties of L-alanine acetate single crystals was reported by Sankar et al 2010. Bulk single crystals of L-alanine formate of 10 mm diameter and 50 mm length have been grown with an aid of modified Sankaranarayanan–Ramasamy (SR) uniaxial crystal growth method within a period of ten days. The optical properties of the grown crystal were calculated from UV transmission spectral analysis. The second harmonic generation efficiency of the grown crystal was confirmed by Kurtz powder test (Justin Raj et al 2008). L-alanine alaninium nitrate (LAAN) was grown by slow evaporation technique at room temperature from its aqueous solution at pH value of 2.5. As grown single crystals were characterized for its spectral, thermal, and second order nonlinear optical properties (Lydia Caroline et al 2007). Photoacoustic studies and thermal properties of the NLO compound

of L-alaninium maleate were reported by Martin Britto Dhas et al (2007). Vijayan et al (2006) have reported the bulk growth and characterization studies of L-alanine single crystal. A temperature lowering rate of 0.1°C/day was maintained for a period of 15 days to grow large size single crystals of L-alanine acetate (L-AlA) by keeping the mother solution at a pH value of 3 (Mohan Kumar et al 2005). Rajan Babu et al 2002 and 2003 reported the growth of single crystals of L-alanine derivatives such as L-alanine tetrafluoroborate (L-A1FB) and studied their fundamental growth properties. The linear optical properties showed that L-alanine family crystals have lower cut-off wavelength in the UV-region. Among all L-alanine derivatives, L-A1A possesses high transmittance of 80%. The powder SHG test confirms that the nonlinear optical property of the grown crystals of L-alanine derivatives is comparable with other semiorganic crystals. The growths, optical, thermal and dielectric studies of an amino acid organic nonlinear optical material L-Alanine were reported by Lydia Caroline. M et al 2009. Growth and spectroscopic characterization of a new organic nonlinear optical crystal L-Alaninium succinate were investigated by Ramachandra Raja. C et al 2009a. Crystal growth and characterization of new nonlinear optical single crystals of L-alaninium fumarate were studied by Ramachandra Raja. C et al 2009b. Synthesis, growth, thermal, optical and mechanical properties of new organic NLO crystal: L-alanine DL-malic acids were reported by Jaikumar D et al 2009. Crystal growth, structure and characterizations of a new semiorganic nonlinear optical material β-alanine zinc chloride were investigated by

Anbuchezhiyan.M et al 2010. Organometallic L-alanine cadmium chloride single crystals were grown by slow evaporation technique and its characterization studies were reported by Bright K.C et al 2010. The determination of second order nonlinear optical entities for L-alanine single crystals using semi-classical anharmonic oscillator model were investigated by Suria Kumar K et al 2011. The growth, structural, spectral, mechanical and dielectric characterization of RbCl-doped L-alanine hydrogen chloride monohydrate single crystals were reported by Lucia Rose A.S.J et al 2011.

Studies on the effect of 1 mol% L-alanine mixed bisthiourea cadmium chloride (LABTCC) crystals were reported by Senthilkumar. M et al 2012. Solid L-α-alanine: Spectroscopic properties and theoretical calculations were done by Yamilet Rodríguez-Lazcano et al 2012. The Growth and characterization of L-alanine cadmium bromide semiorganic nonlinear optical crystals were investigated by Ilayabarathi.P et al 2012.

1.4.3 Analogs of L-threonine

L-threonine is a promising organic NLO crystal among the aminoacid crystals. The crystal structure of L-threonine dehydrogenase (TDH) was reported by Ishikawa Kazuhiko et al (2007). Santana et al (2007) have reported the growth, EPR and optical absorption spectra of L-threonine single crystals doped with Cu^{2+} ions. Effect of pH, thermal, electrical and thermomechanical properties of nonlinear optical L-threonine single crystals were reported by Ramesh Kumar et al (2007a). Crystallization kinetics and high-resolution X-ray diffraction analysis on nonlinear optical L-threonine single crystals were also

reported by Ramesh Kumar et al (2007b). Raman spectroscopic study was carried out on the behavior of NH_3 torsional vibration of L-threonine crystals under high pressure by Freire et al (2007). Deuterated crystals of L-threonine have been grown by slow cooling technique. The grown crystals were subjected to XRD, FT-IR, UV–Vis–NIR and thermal analyses. Isotopic exchange of protons in NH and OH sites of L-threonine has been confirmed from the Fourier transform infrared spectroscopy (FT-IR). The powder SHG efficiency of the deuterated salt was found to be 0.91 times that of KDP. The results have been discussed in detail by Ramesh Kumar et al (2008a). NLO susceptibilities of L-threonine amino acid single crystals were evaluated using anharmonic oscillator model (Ramesh Kumar et al 2008b). L-Threoninium picrate an efficient NLO material was reported by Natarajan et al 2010. Growth, spectroscopy, dielectric and nonlinear optical studies of novel organic NLO crystal: L-Threonine formate was reported by Redrothu Hanumantharao et al 2012.

1.4.4 Analogs of L-arginine

The low-temperature three dimensional structural determination of L-arginine bis(trifluoroacetate) crystal and its vibrational spectral analysis were investigated and hydrogen bonding interactions were analyzed on the basis of its vibrational spectra (Sun Z.H. et al 2011). The preparation and crystal structure of acetatobis (L-arginine zinc (II) acetate trihydrate, X-ray structure of a zinc (II)–arginine complex was reported (Ahmed Alagha et al 2011). 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. K et al 2011). Thermal, mechanical, electrical, linear and nonlinear optical properties of L-arginine dihydrofluoride single crystal were reported by Sankar et al (2010). L-arginine trifluoroacetate (LATF), an organic nonlinear optical material have been 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 can be grown by two dimensional layer growth mechanisms. The SHG efficiency of LAMD was found to be 1.4 times that of KDP crystal (Kalaiselvi et al 2008).

Haja Hameed et al 2007 have obtained pure and additive mixed LAP single crystals by slow cooling technique. The surface second harmonic generation (SHG) analysis was done on (100) face of the grown crystals and the SHG intensity on (100) face of the crystals were measured. A nonlinear optical L-arginine iodate (L-Arg·2HIO$_3$) crystals were successfully grown by the temperature-lowering method with an optimized pH of 6 by Sankar et al 2007 and evaluated its laser induced damage threshold and SHG efficiency. L-arginine trifluoroacetate (LATF) crystals have been grown from aqueous solution using the micro-crystallization method by Liu et al (2007). It has been

reported that the growth properties could be improved by adding appropriate amount of HCl. Bulk single crystal of L-arginine maleate dihydrate (LAMD) of size $48 \times 33 \times 7 \text{ mm}^3$ was grown by slow cooling technique in a period of 3 weeks, whose SHG efficiency was found to be 1.4 times that of KDP crystal and also investigated its physicochemical properties (Sun et al 2007a).

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 L-argininium perchlorate (LARPCL) with improved SHG efficiency were grown by Aruna et al (2007) and studied its physical properties.

Single crystals of L-arginine diiodate (LADI) with good mechanical stability were grown by slow evaporation technique (Preema C. Thomas et al 2006). Single crystals of amino acid (glycine and valine) substituted L-arginine diphosphate (GLADP and VLADP) were grown by slow evaporation technique (Joseph Arul Pragasam et al 2006). It was found that the presence of glycine and valine have improved the optical transmission range, thermal stability and mechanical properties. In the case of GLADP (215 $^{\circ}$C) and VLADP (214 $^{\circ}$C) there is an appreciable increase in the thermal stability when compared to pure LADP (191°C). Pricilla Jeyakumari et al 2006 established the phase matching property of L-arginine tetrafluoroborate (LAFB). Preema C. Thomas et al (2005) have grown single crystals of L-argininium dinitrate (LADN) by the

slow evaporation technique. Bulk single crystals of L-arginine dihydrate (LAD) was grown successfully by slow cooling and slow evaporation techniques (Tapati Mallik and Tanusree Kar 2005a). Single crystals of L-arginine perchlorate (LAPCl) were grown from its aqueous solution (pH=8) by slow evaporation technique (Tapati Mallik and Tanusree Kar 2005b).

The growth and characterization of L-argininium formate (LAF) single crystals grown with an optimized pH of 2.5 have been carried out by Packiam Julius et al (2004). Arunmozhi and Gomes, 2004 have studied the stability of saturated LAP solution as a function of supercooling rate by observing the metastable zone width at different cooling rates using a polythermal method. Crystal growth kinetics has been investigated as a function of supersaturation. L-arginine acetate (LAAC) single crystals were grown by Muralidharan et al 2003 by employing low temperature solution growth technique. LAAC has its lower UV cut-off wavelength at 240 nm and hence it is suitable for frequency conversion applications.

The growth and characterization of NLO based L-arginine maleate dihydrate single crystals were reported by Baraniraj.T et al 2010. Specific heat measurements in pure and (Cu, Mn, Fe, Ni)-doped single-crystals of L-arginine phosphate monohydrate were reported by Machado F.L.A et al 2010. Effect of rare-earth dopants on the growth and structural, optical, electrical and mechanical properties of L-arginine phosphate single crystals were reported by Arjunan.S et al 2010. A comparative study on pure, L-arginine and glycine doped ammonium dihydrogen orthophosphate single

crystals grown by slow solvent evaporation and temperature-gradient method were reported by Pattanaboonmee .N et al 2011. Unidirectional growth of organic nonlinear optical L-arginine maleate dihydrate single crystal by Sankaranarayanan–Ramasamy (SR) method and its characterization were reported by Urit Charoen-In et al 2011. The characterization studies on the additives mixed L-arginine phosphate monohydrate (LAP) crystals were reported by Haja Hameed A.S et al 2011. Crystal growth, structural and thermal studies of amino acids admixtured L-arginine phosphate monohydrate single crystals were investigated by Anandan.P et al 2011. Synthesis, growth and optical properties of semiorganic nonlinear optical single crystal: L-Arginine acetate was reported by Renuka N et al 2012. Growth, structural, dielectric, laser damage threshold, linear and nonlinear optical properties of methylene blue admixtured l-arginine phosphate single crystal were reported by Peramaiyan.G et al 2012.

1.5   SCOPE OF THE THESIS

In the recent years, organic crystals are under extensive investigation due to their low cost, fast and large nonlinear second order co-efficient, synthetic flexibility, high optical damage threshold and intrinsic tailorability. The search for organic nonlinear optical (NLO) materials with best optical and nonlinear optical parameters is of great interest due to their numerous applications in lasers and photonic devices.

L- histidine acetate (LHA) (Madhavan et al 2007b), L-alanine acetate (LAlA) (Mohan Kumar et al 2005), L-threonine acetate (LTA) (Ramesh Kumar

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et al 2005), L-arginine acetate (LAA) (Muralidharan et al 2003), crystals of aminoacid based acetate family have been reported to be promising NLO materials. Keeping this in view, attempts were made to improve the physicochemical properties of NLO active single crystals LHA, LAlA, LTA and LAA of aminoacid based acetate family by growing bulk crystals by SR method.

The present investigation is aimed at

(i)   Synthesizing the chosen materials for the growth of single crystals

(ii)   Preparing seed crystals and growing bulk size single crystals by SR method.

(iii) Estimating the lattice parameters of the crystals by powder X-ray diffraction analysis

(iv)   Characterizing the grown crystals by FT-IR, FT-Raman and Optical absorption studies

(v)   Determining the SHG efficiency of the crystals by Kurtz powder technique

(vi)   Studying the thermal behaviour of the grown crystals

(vii) Determining the microhardness values of the grown crystals

(viii) Measuring the dielectric constant and dielectric loss of the grown crystals and

(ix)   Determining the photoconductivity of the grown crystals.