CHAPTER 2

GROWTH AND CHARACTERIZATION OF LARGEST
L-LYSINE MONO HYDROCHLORIDE DIHYDRATE
CRYSTAL BY SR METHOD

2.1 INTRODUCTION

The fast growing development of optical fiber communication systems has stimulated the search for highly nonlinear materials capable of fast and efficient processing of optical signals. Nonlinear crystals have proven to be interesting candidates for number of applications like second harmonic generation, frequency mixing, electro optic modulation, optical parametric oscillation etc (Chemla and Zyss 1987). The growth of good quality, large size SHG crystals with orientation control is needed for applications. The recently discovered Sankaranarayanan-Ramasamy (SR) method (Sankaranarayanan and Ramasamy 2005) is suitable to control the orientation during bulk crystal growth from solution. Semi-organic crystals have been proposed as new approach for materials with interesting nonlinear optical properties (Debrusa et al 2002). A series of semi organic compounds such as L-arginine tetrafluoroborate (Owens et al 2001), L-arginine dihydrate (Tapati Mallik and Tanusree Kar 2005) and L-tyrosine hydrobromide (Narayana Moolya and Dharmaprakash 2006) crystals have been reported with good NLO, mechanical and chemical stability. The semi organic L-lysine monohydrochloride dihydrate (L-LMHCl dihydrate) crystal is a good candidate for nonlinear optical applications. The L-LMHCl dihydrate ($\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2\text{HCl.2H}_2\text{O}$) crystallizes in monoclinic crystal system with P21 space group. L-LMHCl dihydrate crystals were grown by slow evaporation
In this chapter, the metastable zone width for L-LMHCl dihydrate has been investigated. The growth rate of L-LMHCl dihydrate crystal along <0 -11>, <0 1-1>, <011> and <100> orientations is investigated for SR method. 70 mm length and 80 mm diameter crystal was grown using the SR method under optimized growth condition. The gravity driven concentration gradient effect in the SR method was analyzed. The grown L-LMHCl dihydrate has been subjected to transmission, dielectric, birefringence and piezoelectric studies. The dielectric measurements were performed in the frequency range of 20 Hz to 1 MHz.

2.2 DETERMINATION OF METASTABLE ZONE WIDTH

The solubility of L-LMHCl dihydrate has been determined for five different temperatures, i.e., 27, 30, 35, 40 and 45 °C. The solubility was determined by dissolving the three times recrystallized solute in Millipore water (18.2 mΩ cm) in an air tight container maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility curve was thus obtained. Saturated solution of L-LMHCl dihydrate has been prepared in accordance with the presently determined solubility curve for the nucleation experiments. The studies were carried out in a constant temperature bath controlled to an accuracy of ± 0.01 °C, provided with a cryostat for cooling below room temperature. Metastable zone width of L-LMHCl dihydrate was measured using the polythermal method (Nvylt et al
The obtained solubility and nucleation curve for L-LMHCl dihydrate is shown in Figure 2.1.

![Figure 2.1 Metastable zone width of L-LMHCl dihydrate](image)

In general, the metastable zone width decreases with increasing temperature. In the case of L-LMHCl dihydrate the metastable zone width first decreases and then increases with increasing temperature. Due to high solubility the L-LMHCl dihydrate solution is more viscous at higher temperature. For higher viscous solution, there is an increase in zone width, since the viscosity of the solution greatly reduces the motion of solute molecules in the solution thus providing barrier for nucleation. The viscosity measurements were carried out at different temperatures using Ostwald’s viscometer. Figure 2.2 shows the saturated concentration versus viscosity at different temperatures of the L-LMHCl dihydrate solution. Repeated trials were carried out to ascertain the correctness of the observed results.
2.3 MODIFIED SR METHOD EXPERIMENTAL SETUP

The experimental setup of SR method (Sankaranarayanan and Ramasamy 2005) has been modified in some aspects and L-LMHCl dihydrate crystals were grown (Figure 2.3). The L-LMHCl dihydrate crystal was found to be more sensitive for small variation in temperature. It affects the growth and quality of L-LMHCl dihydrate crystal. To avoid the minute temperature fluctuation at the growth region, care was taken in the modified assembly. In the modified assembly, the bottom portion of the ampoule was surrounded by another ring heater controlled by temperature controller arrangement. It was used to maintain the constant temperature at solution - crystal interface. The ring heaters and ampoule were covered by a glass shield which further avoided minute thermal fluctuations at the interface.

Figure 2.2 Solution concentration versus viscosity of L-LMHCl dihydrate
2.4 STUDIES OF GRAVITY DRIVEN CONCENTRATION GRADIENT

Mullin and Leci (1969) observed that concentration gradients developed in long columns of supersaturated solution. Similar observations were reported by Allen et al (1972) for sucrose solutions and by Lo (1989) for glycine solution. Gravity driven concentration gradients have been used for ‘embryo’ formation studies. The gravity driven concentration gradient effect was investigated in the SR crystallizer (Figure 2.4). The good quality cut and well polished 40 mm diameter ingot of L-LMCl dihydrate crystals were used as seeds. The 30, 60 and 90 cm ampoules were used for this study. The identical seed crystals were placed in the bottom of these ampoules. The three SR method setups were arranged in identical condition. The identical concentration L-LMCl dihydrate saturated solution prepared at 36 ºC was used for this purpose. The L-LMCl dihydrate crystal was growing initially
at the rate of 1.5, 2.5 and 3 mm/day respectively for 30, 60 and 90 cm ampoules.

Figure 2.4 SR method experimental setup for investigation of effect of gravity driven concentration
This is due to gravity driven concentration increase at the bottom of the ampoule, the longer column resulting in higher concentration. However, the motion of the solution (which is again due to gravitational forces) stems from the difference between the densities resulting from the concentration in the solution.

Belyustin has used this motion of solution to grow crystals using seeds mounted in the middle portion of the ampoule (Petrov 1969). In SR method however only one face is growing whereas in Belyustin’s method several faces are growing.

2.5 GROWTH RATE STUDIES

The different faces of a crystal are known to grow with different growth rates. The present SR method offers an elegant way to evaluate the growth rate of different faces of a crystal by choosing the appropriate seed face for conducting growth. The L-LMHCl dihydrate single crystal was grown by slow evaporation solution growth technique (SEST) as well as by SR method. Many crystals with good morphology have been collected from the slow evaporation method (Figure 2.5). The collected crystals have the dimension of 25 mm × 12 mm × 6 mm.

The <0-11>, <01-1>, <011> and <100> directional faces (Figure 2.6) have been chosen to study the growth rate at different faces. To investigate the growth rate at different orientation of L-LMHCl dihydrate crystal, the experiment was carried out at four identical ampoules having uniform diameter of 20 mm. These seeds were facing the saturated L-LMHCl dihydrate solution. The growth rates along <0-11>, <01-1>, <011> and <100> orientation of the L-LMHCl dihydrate crystals were analyzed at identical conditions. The L-LMHCl dihydrate crystals were growing at the rate of 1 mm/day in the orientations <0-11>, <01-1> and <011>. The <100> orientation crystal was growing at the rate of 2 mm/day.
Figure 2.5  SEST grown L-LMHCl dihydrate crystals

Figure 2.6  Morphology of L-LMHCl dihydrate crystal
Three to four runs were made for every one face. Under identical condition the experiments were highly reproducible. According to the Periodic bond chain (PBC) theory, the growth rate of crystal at particular orientation is directly proportional to attachment energy. The faces which have higher attachment energy grow faster (Wang Yan et al 2005). The <100> orientation face has more attachment energy than the other orientations.

2.6 CRYSTAL GROWTH

Our growth trials with 20, 30, 40 and 50 mm diameter ampoules lead us to the conclusion that scaling up is less complicated than all the methods thus far employed in crystal growth (Figure 2.7). The fast growth orientation <100> was used for growth of large size L-LMHCl dihydrate crystals. A volume of 1500 ml of L-LMHCl dihydrate saturated solution was prepared at 38.5 ºC using Millipore water as a solvent. We carefully ensured that the prepared solution was well within the metastable zone width region. The SR method grown 50 mm × 10 mm ingot of L-LMHCl dihydrate crystal was used as a seed. The seed crystal was carefully placed at the bottom of 1 foot length and 80 mm diameter ampoule.

The saturated solution of L-LMHCl dihydrate was carefully filtered and poured into the ampoule. The top ring heater temperature was set as 38.5 ºC. The bottom ring heater temperature was set as 35 ºC. The entire arrangement was kept in glass shield inside the water bath. Due to the transparent nature of the solution and the experimental set-up, real-time close-up observation revealed solution - crystal interface, which was found to be flat. Under optimized condition highly transparent crystal growth was achieved. The shape of solution - crystal interface was monitored during growth process.
Figure 2.7  SR method grown 80 mm length and 35 mm diameter L-LMHCl dihydrate crystals
Bulk size cylindrical shape 70 mm length 80 mm diameter good quality L-LMHCl dihydrate crystal was grown after 30 days with an average growth rate of 2.5 mm/day. The cut and polished ingot of 80 mm diameter grown crystals of L-LMHCl dihydrate are shown in Figure 2.8. The attainment of L-LMHCl dihydrate crystal with the shape resembling the shape of the ampoule, leads to the conclusion that choosing a particular shape to the container and also taking a multicontainer assembly it is also possible to grow the bulk crystal of any desired shape.

Figure 2.8 The largest L-LMHCl dihydrate crystals grown by SR method
2.7 **MULTICRYSTAL X-RAY DIFFRACTOMETER**

A multicrystal X-ray diffractometer designed and developed at National Physical Laboratory (Krishan Lal et al 1989) has been used to study the crystalline perfection of the single crystal(s). Figure 2.9 shows the schematic diagram of the multicrystal X-ray diffractometer. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm × 8 mm; 2kW Mo) is first reduced by a long collimator fitted with a pair of fine slit assemblies. This collimated beam is diffracted twice by two Bonse-Hart (Bonse and Hart 1965) type of monochromator crystals and the thus diffracted beam contains well resolved MoK$_{\alpha_1}$ and MoK$_{\alpha_2}$ components. The MoK$_{\alpha_1}$ beam is isolated with the help of fine slit arrangement and allowed to further diffract from a third (111) Si monochromator crystal set in dispersive geometry (+, -, -).

![Schematic diagram of multicrystal X-ray diffractometer](image)

*Figure 2.9 Schematic diagram of multicrystal X-ray diffractometer*
Due to dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the dispersion broadening in the diffraction curve of the specimen does not arise. Such an arrangement disperses the divergent part of the MoK$_\alpha_1$ beam away from the Bragg diffraction peak and thereby gives a good collimated and monochromatic MoK$_\alpha_1$ beam at the Bragg diffraction angle, which is used as incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+, -, -) and non-dispersive (+, -, +) configurations (Bhagavannarayana 1994). This arrangement improves the spectral purity ($\Delta \lambda / \lambda \ll 10^{-5}$) of the MoK$_\alpha_1$ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be $\ll 3$ arc sec. The specimen occupies the fourth crystal stage in symmetrical Bragg geometry for diffraction in (+, -, -, +) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.5 arc sec. The diffracted intensity is measured by using a scintillation counter. The detector (scintillation counter) is mounted with its axis along a radial arm of the turntable. The rocking or diffraction curves for all the specimens were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position $\theta_\text{B}$ starting from a suitable arbitrary glancing angle (denoted as zero). The detector was kept at the same angular position $2\theta_\text{B}$ with wide opening for its slit, the so-called $\omega$ scan.

Before going to record the diffraction curve, the specimen surface was prepared by lapping and polishing and then chemically etched by a non-preferential chemical etchant mixed with water and acetone in 1:2 ratio. This process removes non-crystallized solute atoms on the surface and also the surface layers, which may sometimes form for e.g. a complexating epilayer
could be formed on the surface of the crystal due to organic additives (Bhagavannarayana et al 2006).

2.7.1 High Resolution X-Ray Diffraction (HRXRD) Studies of L-LMHCl dihydrate

To reveal the crystalline perfection of the grown crystals, a multicrystal X-ray diffractometer (MCD) developed at NPL has been used to record high-resolution diffraction curves (DCs). The DC of SR grown specimen (Figure 2.10) contains a single peak and shows that this specimen is free from structural grain boundaries. However, the FWHM of this curve is 36 arc s. It is interesting to see the asymmetry of the DC with respect to the peak position. As seen in the case of conventional method grown L-LMHCl dihydrate crystal the DC is with satellite peaks (Ramesh Babu 2006b) which are due to internal structural grain boundaries that exist in the sample. In SR grown crystal for a particular angular deviation ($\Delta \theta$) of glancing angle with respect to the peak position, the scattered intensity is much more in the negative direction in comparison to that of the positive direction.

This feature clearly indicates that the crystal contains predominantly vacancy type of defects rather than that of interstitial defects. This can be well understood by the fact that due to vacancy defects or voids in the crystalline matrix, the lattice around these defects undergo tensile stress and the lattice parameter d (interplanar spacing) increases and leads to give more scattered (also known as diffuse X-ray scattering) intensity at slightly lower Bragg angles ($\theta_B$) as d and $\sin \theta_B$ are inversely proportional to each other in the Bragg equation ($2d \sin \theta_B = n\lambda$; n and $\lambda$ being the order of reflection and wavelength respectively which are fixed). Fast growth rates of the crystals some times lead to this type of vacancy defects. However, these point defects with much lesser density as in the present case (if the
concentration is high, the FWHM would be much higher and often lead to structural grain boundaries) hardly affect the performance of the devices based on such crystals.

Figure 2.10 Diffraction curve recorded for L-LMHCl dihydrate (SR) single crystal for (100) diffracting planes by employing the multicrystal X-ray diffractometer with MoK$_{\alpha_1}$ radiation

2.8 TRANSMISSION SPECTRA

The optical transmittance plays an important role in identifying the potential of an NLO material because a given material can be of utility only if it has a wide transparency window without absorption at the fundamental and second harmonic wavelength and lower cutoff below 400 nm. In these crystals, the UV-Vis transmittance range from 200 to 400 nm is very important for the realization of SHG output using diode lasers. The transmission spectra of L-LMHCl dihydrate crystal grown from Millipore water was recorded using PerkinElmer (Lambda 35) UV-Visible
spectrometer. The UV-Vis analysis was made between 200 nm and 1100 nm. For this study, the cut and polished 3.5 mm thickness wafer has been used. At 225 nm a sharp fall of transmittance was observed (Figure 2.11) indicating a single transition in near UV region of L-LMHCl dihydrate. It has a good transparency (>80 %).

![Transmittance spectra of L-LMHCl dihydrate crystal](image)

**Figure 2.11** Transmittance spectra of L-LMHCl dihydrate crystal

## 2.9 DIELECTRIC STUDIES

The dielectric property of L-LMHCl dihydrate crystal was carried out on <100>orientation. Typical sample dimensions were $3 \times 3 \text{ mm}^2$ in surface area and 1.5 mm in thickness. Dielectric measurement was carried out using a precision LCR meter (Model4284A) in the frequency range 20Hz - 1MHz. The measurements were carried out in the temperature range 40 - 65 ºC, the plots are given for only three temperatures. From the figure (Figure 2.12) it is found that the value of dielectric constant decreases with increase of frequency. This behaviour is due to the fact that at low frequency
the dipoles are able to follow the applied field, whereas at higher frequency they are not (Chao-Yu Chung et al 2005). The contributions of all the four polarizations such as electronic, ionic, dipolar and space charge are predominant in low-frequency region (Rao and Smakula 1965, Rao and Smakula 1966). It is also observed that as the temperature increases, the value of dielectric constant also increases to a considerable value. The decreasing trend of dielectric constant variation with increasing frequency is similar to any polar (non centro symmetric) dielectric and obeys Debye equation. At lower frequencies, space charge polarization is more predominant and hence the dielectric constant increases abnormally.

![Graph showing dielectric constant versus frequency for L-LMHCl dihydrate crystal at different temperatures.](image)

**Figure 2.12  Dielectric constant versus frequency of L-LMHCl dihydrate crystal**

The L-LMHCl dihydrate structure contains bound water molecules. Their contributions weaken as frequency is increased. It is possible that the bound water molecules may get activated with its contribution to dielectric constant as temperature is increased. Since water has high dielectric constant, the activation of bound water at higher temperature may be responsible for
increase in the dielectric constant. The characteristics of low dielectric constant and dielectric loss (Figure 2.13) with high frequency for a given sample indicate lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications (Balarew and Duhlew 1984).

![Figure 2.13 Dielectric loss versus frequency of L-LMHCl dihydrate crystal](image)

### 2.10 PIEZOELECTRIC STUDIES

Advanced crystal materials with exceptional piezoelectric properties play an ever increasing role in modern electric applications. In piezoelectric crystals, those having non centre of symmetry, displacement due to stress distorts the original charge distribution in such a way that it is no longer symmetrical. A net polarization results in such crystals and we observe piezoelectric effect. If the crystal has a centre of symmetry and is electrically neutral, a mechanical deformation alone does not bring about electric dipoles.
In such crystals, though, on applying stress, charges are displaced but distribution of charges still maintains its symmetry and they exhibit no net polarization. Hence no piezoelectric effect is observed. Therefore, that the piezoelectricity is related to crystal symmetry. The symmetry element involved is essentially the center of inversion. A crystal can exhibit piezoelectricity only if its unit cell lacks a center of inversion.

The piezoelectric constant $d_{33}$ was measured in the $<100>$ orientation of the L-LMHCl dihydrate crystal. The L-LMHCl dihydrate crystal was cut into rectangular shape and was well polished to achieve flat and parallel surface. Typical sample dimensions were 3 mm × 3 mm in surface area and 1.5 mm in thickness. The sample was placed between piezoelectric sensors (PZT). The force 0.25 N was applied on the L-LMHCl dihydrate sample at frequency 110 Hz. Piezoelectric coefficient $d_{33}$ value 4 pC/N, capacitance 1.9 pF and tan delta 1.1221 values were measured from the Piezo test at constant frequency.

2.11 BIREFRINGENCE STUDIES

Birefringence is defined as the anisotropy in a material’s refractive index with respect to the polarization state of light propagating through it. The birefringent materials are used in many optical devices such as circulator, glan polarizer, beam splitter, etc. (Fischer et al 1995, Zhang et al 2003). The SR and conventional method grown L-LMHCl dihydrate crystals of thickness 0.55 mm and 0.50 mm respectively were cut and polished to get the plates.

The polished plate was placed in a birefringence interferometer for measuring the birefringence of the crystal along the thickness of the sample which is along $<100>$ crystallographic direction. The principle and optical schematic of birefringence interferometry (Figure 2.14) is given by Verma and Shlichta (2008) and its usage for measuring birefringence along any
specific crystallographic direction and also to make qualitative assessment of the quality of the grown crystal is reported by Kar et al (2008).

![Figure 2.14 The schematic diagram of birefringence interferometry](image)

The birefringence interferogram obtained for SR grown L-LMHCl dihydrate crystal plate is shown in Figure 2.15. The birefringence calculated along the <100> axis of SR grown crystal is \( \Delta n = n_e - n_o = 0.0057527 \). The uniformity of fringes signify that the grown crystal has good refractive index homogeneity and hence good optical quality. The uniformity of the interference fringes also points towards uniform dislocation density inside the crystal.

The birefringence interferogram obtained for conventional grown L-LMHCl dihydrate crystal plate is shown in Figure 2.16. The birefringence calculated along the <100> axis of the SEST crystal is \( \Delta n = n_e - n_o = 0.0050624 \).

Due to non-uniform thickness of sample the fringes are circular in shape. The irregular fringe pattern as compared to the SR grown crystal shows that the crystal quality is inferior. Minor difference in the birefringence values of SR grown and conventional grown L-LMHCl dihydrate crystal could be attributed to the irregularity in the sample thickness and the local variations in dislocation density resulting in strain in the sample.
Figure 2.15 Birefringence interferogram of SR grown L-LMHCl dihydrate crystal

Figure 2.16 Birefringence interferogram of Conventional grown L-LMHCl dihydrate crystal
2.12 CONCLUSION

A novel unidirectional crystal growth method at room temperature has been employed for the growth of semi organic largest diameter L-LMHCl dihydrate crystal. The width of metastable zone was determined which was helpful for growth of largest diameter L-LMHCl dihydrate single crystal. The gravity driven concentration gradient effect in the SR method was analyzed at different heights. The growth rate of L-LMHCl dihydrate crystal along <0 -11>, <0 1-1>, <011> and <100> orientations was investigated by SR method. The faces which have higher attachment energy grow faster. The HRXRD rocking curve measurements substantiate the good quality of the crystals. The dielectric constant and dielectric loss studies establish the normal behaviour. Piezoelectric coefficient $d_{33}$ value 4 pC/N, capacitance 1.9 pF and tan delta 1.1221 values were measured from the Piezo test at constant frequency. The value of birefringence and quality were ascertained by birefringence interferometer. The results from various characterization studies demonstrate the suitability of this method to obtain nonlinear element right during crystal growth thus decreasing material consumption when making products for non-linear optical applications.