CHAPTER 2

GROWTH AND CHARACTERIZATION STUDIES OF L-ALANINE (LA) SINGLE CRYSTALS FOR NLO APPLICATIONS

2.1 INTRODUCTION

Epochal advances have been accounted recently in the field of nonlinear optics in the area of materials engineering and the associated optoelectronic device technologies (Zyss 1994, Ledoux et al 1990) which experiences a revival of both practical and conceptual nature. The second order NLO properties necessitate high molecular hyperpolarizability and an optimal arrangement of those molecules in a crystal, which is the macroscopic equivalent (Wong et al 1995). The challenge confronted by researchers in this emerging field is the identification of new types of functional materials by intellectual construction of molecular assemblies exhibiting nonlinear optical effects. An added difficulty of this task is fulfillment of subalternate requirements such as thermal, mechanical and chemical stabilities in addition to the allay of growth in the case of single crystals (Chen et al 1999).

The vantage of organic amino acid materials over their inorganic counterparts is that they have high electronic polarisability ($\chi^{(2)}$) through high molecular hyperpolarisability ($\beta$), facile modification through standard synthetic methods and relative ease of device processing. Among organic crystals for nonlinear optical (NLO) applications, aminoacids display specific features of interest, such as (i) molecular chirality, which secures acentric
crystallographic structures; (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (iii) zwitterionic nature of the molecule, which favours crystal hardness. Further to that, aminoacids can be used (iv) as chiral auxiliaries for nitroaromatics and other donor-acceptor molecules with large hyperpolarizabilities (Delfino 1979) and (v) as a basis for synthesizing organic-inorganic compounds like L-arginine phosphate and derivatives (Eimerl et al 1990). L-alanine (LA) is the smallest, naturally occurring chiral amino acid with a non-reactive hydrophobic methyl group (CH₃) as a side chain.

A non essential amino acid that occurs in high levels in its free state is produced from pyruvate by transamination. It is involved in sugar and acid metabolism, increases immunity, and provides energy for muscle tissue, brain, and the central nervous system. LA has the zwitterionic form \((+\text{NH}_3^-\text{C}_2\text{H}_4\text{COO}^-)\) both in crystal and in aqueous solution over a large range of pH. L-alanine can be considered as the fundamental building block of more complex amino acids (Misoguti et al 1996).

The growth of large single crystals of amino acids has been little investigated so far, even as regards the simplest acentric member of the family, L-alanine (CH₃CHNH₂COOH). L-alanine was first crystallized by Simpson et al (1966) who refined the structure with lattice parameters \(a=6.032\text{Å}, b = 12.343 \text{ Å}, c = 5.784 \text{ Å}; \alpha = \beta = \gamma = 90^\circ\) and the space group \(\text{P}2_1\text{2}1\text{2}_1\). It belongs to the orthorhombic crystal system with a molecular weight of 89.09 and has a melting point of 297°C. In above cases, very small crystals were grown, unsuitable for optical investigations.

Figure 2.1 represents the molecular structure of L-Alanine. The crystal structure of L-alanine shows that alanine molecule belongs to the noncentrosymmetric space group (Vijayan et al 2006a). Figure 2.2 shows the
structure of L-alanine projected on the (020) plane. The following are the indication of different atoms, black circles: C; shaded circles: N; open circles: O; small open circles: H. Microscopic and optical observations point to rank the growth faces of L-alanine crystals, as far as the magnitude of their surface area is concerned, following the sequence \{120\} > \{011\} > \{020\}, but just the reverse as to structural perfection, clearness and optical applicability. As however the (020) faces can hardly be of use, because of their very small size (Razzetti et al 2002).

Figure 2.1 Molecular structure of LA

Figure 2.2 The structure of L-alanine projected on the (020) plane
The SHG efficiency of L-alanine is about one third of that of KDP (Vijayan et al 2006b). The donor/acceptor benzene derivatives are sure to produce such high molecular nonlinearity. Also as it is a parent material to synthesis the compounds L-alanine alaninium nitrate (LAAN) and L-alaninium tartrate (LAT). In this investigation, the bulk growth and characterization like Structural, Vibrational, Optical and Factor group analysis of L-alanine (LA) single crystals are presented.

2.2 GROWTH OF L-ALANINE (LA) SINGLE CRYSTALS

2.2.1 Solubility Measurement

The size of a crystal depends on the amount of material available in the solution, which in turn is decided by the solubility of the material in that solvent. Hence, the solubility of L-alanine in deionized water was determined. The solubility of L-alanine in the water solvent was determined by adding a known quantity of solute in the solvent which was maintained at a constant temperature until it was completely dissolved. Using this technique, the magnitude of the solubility of L-alanine for various temperatures viz. 36, 40, 45 and 50°C was evaluated. The temperature dependence of solubility of L-alanine is shown in Figure 2.3. From the graph, it is found that the solubility of L-alanine increases with an increase of temperature. Hence, it is attempted to grow bulk crystals of L-alanine using deionized water as a solvent.
2.2.2 Growth

The commercially available L-alanine (Thomas and Baker make) was further purified by repeated recrystallization process before growth to improve the purity of the material. The solution of recrystallized L-alanine was prepared at 40°C using water as a solvent. The beaker containing the solution was covered at the top to prevent the evaporation of the solvent. The solution was housed in a constant temperature bath (CTB) (accuracy ± 0.1°C) (Figure 2.4) and continuously stirred using Teflon coated magnetic stirrer. The saturated solution was preheated to 2°C above the saturation temperature for homogenization. Initially the prepared solution was subjected to the cooling rate of 0.5°C/day and after observing formation of the speck (nucleation) by direct vision method the solution was cooled at the rate of 0.15°C/day. The single crystals of L-alanine (1 cm × 0.5 cm × 0.4 cm) were harvested after 15 days and the as grown crystals are shown in Figure 2.5.

Figure 2.3 Solubility curve of L-alanine
Figure 2.4 Constant temperature bath (CTB) used for the growth of L-alanine

Figure 2.5 As grown single crystals of L-alanine
2.3 SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

The single crystal X-ray diffraction data of the grown L-alanine crystals were obtained using a single crystal X-ray diffractometer (Model: ENRAF NONIUS CAD4) and the data are given in Table 2.1. It is confirmed that L-alanine crystallizes in the orthorhombic crystal system with space group of $P2_12_12_1$.

Table 2.1 Crystallographic data of L-alanine single crystal

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>$a$ Å</th>
<th>$b$ Å</th>
<th>$c$ Å</th>
<th>$\alpha = \beta = \gamma$ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>6.032</td>
<td>12.343</td>
<td>5.784</td>
<td>90</td>
</tr>
<tr>
<td>2$^b$</td>
<td>6.012</td>
<td>12.140</td>
<td>5.241</td>
<td>89.02</td>
</tr>
</tbody>
</table>

$^a$ – (Simpson and Marsh 1966)

$^b$ – present work

2.4 HIGH RESOLUTION X-RAY DIFFRACTION ANALYSIS

2.4.1 Introduction

Crystalline perfection can be estimated by recording high resolution X-ray diffraction curves. In perfect crystals, the full width at half maximum (FWHM) and the area under the diffraction curve known as integrated intensity are close to the theoretically calculated values using plane wave dynamical theory of X-ray diffraction. By comparing the theoretical and experimental values one can get good idea about the crystalline perfection in perfect crystals, which are free from boundaries or dislocations.
The misorientation angle (tilt angle) \( \alpha \) made by the subgrain boundaries (\( \alpha \geq 1 \) arc degree), low angle boundaries (\( \alpha \geq 1 \) arc min.) and very low angle boundaries (\( \alpha \leq 1 \) arc sec.) with the crystallographic lattice planes can be determined quantitatively by the angular separation between the diffraction peak positions of the respective boundaries.

2.4.2 Multicrystal X-ray Diffractometer

Figure 2.6 shows a schematic line diagram of the multicrystal X-ray diffractometer designed, developed and fabricated at National Physical Laboratory (NPL) (Lal and Bhagavannarayana 1989) and employed in the present investigations for high resolution XRD. In this system a fine focus (0.4 mm \( \times \) 8 mm; 2 kW MoK\(_\alpha\)) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was used. The well-collimated and monochromated MoK\(_\alpha\) beam obtained from the three monochromator Si crystals set in dispersive (+, -, -) configuration was used as the exploring X-ray beam. This arrangement improves the spectral purity (\( \Delta \lambda/\lambda \ll 10^{-5} \)) of the MoK\(_\alpha\) beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be \(< 3 \) arc sec. The specimen crystal is aligned in the (+, -, -, +) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve of the specimen crystal is insignificant. 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, which is mounted with its axis along a radial arm of the turntable. The rocking curves 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 $\theta_B$ starting from a suitable arbitrary glancing angle
(denoted as zero). The detector was kept at the same angular position $2\theta_B$ with
wide opening for its slit, the so-called $\omega$ scan.

Figure 2.6 Schematic representation of multicrystal X-ray
diffractometer

2.4.3 Multicrystal X-ray diffraction analysis of L-alanine (LA)

Figure 2.7 shows the diffraction curve (DC) recorded for the LA
crystal using (020) diffracting planes having a very sharp and single peak.
This indicates that the LA crystal does not contain any grain boundaries and
its crystalline perfection is very good.
2.5 FACTOR GROUP ANALYSIS OF L-ALANINE

From the X-ray diffraction analysis, it is found that L-alanine crystallizes in the orthorhombic system with the noncentrosymmetric space group $P2_12_12_1$. The primitive unit cell contains 4 molecules which occupies general sites of $D_2^4$ symmetry.

A single molecule of L-alanine possesses 13 atoms which gives rise to $(4 \times 13) = 52$ atoms in a unit cell. Group theoretical analysis of the fundamental modes of L-alanine crystal predicts that there are 156 vibrational optical modes and are seen to decompose into $\Gamma_{156} = 39A + 38B_1 + 38B_2 + 38B_3$ and acoustic modes $(B_1 + B_2 + B_3)$. In orthorhombic crystals like L-alanine, the modes have associated polarizability tensors of the form
Here the polarizability tensors are depicted along the crystallographic X, Y and Z axes. Phonons belong to B are Raman and infrared active.

2.5.1 Vibrational Analysis of L-alanine

Studies on the vibrational spectra of L-alanine by IR and Raman spectroscopy are useful in obtaining information regarding the nature of hydrogen bonding and material confirmation. From the molecular structure of L-alanine, it is observed that the L-alanine consists of NO₂ and OH groups. The vibrations of L-alanine may be due to lattice vibrations and internal vibrations of these groups. The formal classification of fundamental mode predicts 153 internal vibrations which can be distributed as 39A + 38B₁ + 38B₂ + 38B₃ and external modes such as (3A + 2B₁ + 2B₂ + 2B₃) translational and (3A+ 3B₁+3B₂+3B₃) rotational modes. From correlation scheme presented in Table 2.2 using Fateley et al (1972), each internal mode of L-alanine ions should split into two components out of which (A (Z), B (X) and B(Y)) are infrared active and (A (αₓₓ, αᵧᵧ, αzz, αₛₛ), B (αₓz, αᵧz)) are Raman active. Also Table 2.3 gives the summary of factor group analysis of LA.
Table 2.2 Correlation scheme for LA

<table>
<thead>
<tr>
<th>Site Symmetry C₁</th>
<th>Factor Group Symmetry</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Raman</td>
</tr>
<tr>
<td>A₁₅₆</td>
<td>39A</td>
<td>$\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$</td>
</tr>
<tr>
<td></td>
<td>38B₁</td>
<td>$\alpha_{xy}$</td>
</tr>
<tr>
<td></td>
<td>38B₂</td>
<td>$\alpha_{xz}$</td>
</tr>
<tr>
<td></td>
<td>38B₃</td>
<td>$\alpha_{yz}$</td>
</tr>
</tbody>
</table>

Table 2.3 Factor group analysis of LA – Summary

<table>
<thead>
<tr>
<th>Factor group Symmetry</th>
<th>Site Symmetry</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Optical</th>
<th>Acoustic</th>
<th>Total</th>
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<tbody>
<tr>
<td></td>
<td>External</td>
<td>Internal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>39</td>
<td>9</td>
<td>21</td>
<td>3</td>
<td>6</td>
<td>39</td>
<td>0</td>
<td>39</td>
</tr>
<tr>
<td>B₁</td>
<td>3T, 3R</td>
<td>38</td>
<td>9</td>
<td>21</td>
<td>3</td>
<td>6</td>
<td>1</td>
<td>38</td>
</tr>
<tr>
<td>B₂</td>
<td>3T, 3R</td>
<td>38</td>
<td>9</td>
<td>21</td>
<td>3</td>
<td>6</td>
<td>1</td>
<td>38</td>
</tr>
<tr>
<td>B₃</td>
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<td>9</td>
<td>21</td>
<td>3</td>
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<td>38</td>
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<td>36</td>
<td>84</td>
<td>12</td>
<td>24</td>
<td>156</td>
<td>3</td>
<td>153</td>
</tr>
</tbody>
</table>
2.6 UV-VIS. SPECTRAL ANALYSIS OF L-ALANINE

For optical device applications, the study of optical transparency in the near IR and visible region is significant in optical telecommunication systems etc., (Krishnakumar and Nagalakshmi 2005). The UV-Vis spectrum gives limited information about the structure of the molecule because the absorption of UV and Visible light involves promotion of the electron in the \( \sigma \) and \( \pi \) orbital from ground state to higher energy state. The UV spectrum of LA was recorded between 300 to 190 nm using Shimadzu UV-1061 UV-Visible spectrophotometer.

The spectrum is shown in Figure 2.8. For LA, when the absorbance was monitored from 300 to 190 nm, the absorption was evident below 240 nm. It is assigned to electronic excitation in the COO group of L-alanine. Also there is no absorption band between 245 nm and 300 nm, hence LA is identified to be transparent to all the visible radiation.

Figure 2.8 UV-Visible spectrum of L-alanine (LA)
2.7 PHOTOLUMINESCENCE STUDIES OF L-ALANINE

Photoluminescence spectroscopy is a contact less, nondestructive method of probing the electronic structure of materials. In the present study, luminescence behavior has been carried out using a 5 mW Ar\textsuperscript{+} ion laser operating at 490 nm with power density of 0.125 W cm\textsuperscript{-2} for excitation in all the measurements. The inclusion free as grown crystals of LA was scanned between 495 to 795 nm.

The recorded emission spectrum of LA is shown in Figure 2.9. For 490 nm excitation wavelength, the observed emission band lies between 495 to 795 nm. The high intense peaks are observed in the region between 515 to 620 nm for LA. In addition to this peak, the medium intense peaks at 650 nm and 680 nm also appear in the middle region of the spectrum. The higher value of the luminescence may be due to N-H \cdots O hydrogen bonds, two to O (2) atoms and one to an O (1) atom in the molecule. One of the N-H\cdots O (2) hydrogen bonds links molecules together lengthwise to form columns along the c-direction. In the mean time, the low intense luminescence peak may be due to the major axes of the oxygen atoms are oriented approximately perpendicular to the plane of the carboxyl group, and the major axis of C(3) is approximately perpendicular to the C(2)-C(3) bond for LA molecule.
2.8 SECOND HARMONIC GENERATION (SHG) MEASUREMENT OF L-ALANINE BY KURTZ AND PERRY POWDER TECHNIQUE

Quantitative measurement of the relative efficiency of LA single crystal was determined by Kurtz and Perry powder technique (Kurtz and Perry 1968). The schematic of the experimental setup is shown in Figure 2.10. The finely powdered sample of LA crystal was densely packed between two transparent glass slides. A fundamental laser beam of 1064 nm wavelength (8 ns pulse width with 10 Hz pulse rate) from an Nd-YAG (DCR11) laser was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter. The transmitted fundamental wave was passed over a monochromator (Czerny turner monochromator) which separates 532 nm (second harmonic signal) from 1064 nm and absorbed by a CuSO$_4$ solution F1 which removes the 1064 nm light. F2 is a BG-38 filter, which also removes the residual 1064 nm light. F3 is an interference filter with bandwidth of 4 nm and central wavelength.
532 nm. The green light was detected by a photomultiplier tube (Hamamatsu R5109, a visible PMT) and displayed on a storage oscilloscope (TDS 3052 B 500MHz, Phosphor digital oscilloscope). KDP and urea crystals were powdered separately to the identical size and were used as reference materials in the SHG measurement. The results are tabulated in the Table 2.4.

**Table 2.4 Comparison of SHG Signal Energy Output**

<table>
<thead>
<tr>
<th>Input power</th>
<th>KDP</th>
<th>Urea</th>
<th>L-alanine</th>
</tr>
</thead>
<tbody>
<tr>
<td>mJ / pulse</td>
<td>mV</td>
<td>V</td>
<td>mV</td>
</tr>
<tr>
<td>5</td>
<td>220</td>
<td>2.1</td>
<td>121</td>
</tr>
</tbody>
</table>

**Figure 2.10 Schematic of Experimental set up of SHG**

M1 and M2 - Monochromators  
F1, F2 and F3 - Filters  
B - Beam splitter  
S - Sample
2.9 MELTING POINT AND DENSITY MEASUREMENT OF L-ALANINE

The powdered material of the LA single crystal was inserted into the capillary tube and placed in the melting point apparatus. The temperature was increased at a rate of 2°C/minute and the melting of material at 297°C was noted. The error in the measurement is ±1°C.

The experimentally (floatation technique) determined density value is in good agreement with the theoretically found value using the formula \( \rho = \frac{(MZ)}{(NV)} \); where M is the molecular weight, Z is the number of molecules per unit cell, N is the Avagadro number and V is the volume of the unit cell. The theoretical value is obtained from the crystallographic data. The density values are given below:

(1) Experimental : 1.35 g/cm\(^3\)
(2) Theoretical : 1.37 g/cm\(^3\)

2.10 CONCLUSION

Single crystals of L-alanine were successfully grown by slow cooling solution growth technique. From single crystal X-ray diffraction studies it is confirmed that L-alanine crystallizes in the orthorhombic crystal system with the lattice parameters \( a = 6.012 \) Å, \( b = 12.140 \) Å, \( c = 5.241 \) Å and space group \( P2_12_12_1 \). The structural perfection of the grown crystal was analysed by high-resolution X-ray diffraction. A very sharp and single peak obtained in the rocking curve confirms that the LA crystal does not contain any grain boundaries and its crystalline perfection is excellent. The theoretical factor group analysis of L-alanine crystal predicts that there are
156 vibrational optical modes that decompose into $\Gamma_{156} = 39A + 38B_1 + 38B_2 + 38B_3$ modes among which three acoustic modes $B_1 + B_2 + B_3$ are included that correspond to the block transitions of the crystal. From powder SHG efficiency studies, it is clearly ascertained that LA relatively ostentates high efficiency with KDP and Urea. From UV-Vis studies of L-alanine, the absorption was confirmed below 240 nm. It may be due to electronic excitation in the COO$^-$ group of L-alanine. The photoluminescence emission spectrum of LA shows the high intensity peaks in the region of 515 to 620 nm. Thus it is found that LA is material for applications in nonlinear optical devices (Aravindan et al 2007b).