Chapter 6
Growth and Characterization of Semi-organic Nonlinear Optical Crystal: L-Alanine Cadmium Chloride (LACC)

6.1. Introduction
Nowadays amino acids are noticeable materials due to their competent nonlinear optical efficiency. The study of amino acid crystallizes with other organic and inorganic molecules, which presents a high nonlinear optical coefficient, has gained much attention in the last few years because of the possibility of using them in technological devices [12]. L-alanine (LA) is an efficient organic NLO compound under the amino acid category. Several new complexes incorporating the amino acid L-alanine have investigated [37, 67, 134-136]. In the case of metal–organic coordination complexes, the organic ligand is usually more dominant in the NLO effect. As for the metallic part, focus is on the group (IIB) metals, (Zn, Cd and Hg) as these compounds usually have a high transparency in the UV region because of their closed d\textsuperscript{10} shell. Hence, in the present study, the effect of metal complexation with L-alanine has been studied by the synthesis and characterization of a semi-organic NLO compound, L-alanine cadmium chloride (LACC). We have grown the good quality semi-organic nonlinear optical single crystals of LACC by slow evaporation solution growth technique at room temperature. The crystalinity of grown crystal was confirmed by XRD studies. The FTIR spectrum was recorded to analyze the presence of functional groups. The UV–visible transmittance spectrum was recorded using UV-visible analysis. The dielectric measurements were carried out and the nature of variation of dielectric constant and dielectric loss in the different frequency was studied and discussed. The grown single crystals were subjected to various characterization studies such as thermal analyses and microhardnees studies. The SHG conversion efficiency was also confirmed using Kurtz Perry method.

6.2. Crystal Growth

6.2.1 Synthesis of LACC
The single crystal of LACC was synthesized from L-alanine (99.9 % purity) and cadmium chloride monohydrate (CdCl. H\textsubscript{2}O) (99.0 % purity) taken in the equi-molar ratio according to the chemical reaction:

\[
\text{CH}_3\text{CHNH}_2\text{COOH} + \text{CdCl}_2 \rightarrow \text{CH}_3\text{CHNH}_2\text{COOH} \cdot \text{CdCl}_2
\]
The mechanism of this reaction is given below:

\[
\text{CdCl}_2 + \text{CH}_3\text{CHNH}_2\text{COOH} \rightarrow \quad \text{Cd}^{2+}
\]

The calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 2 hours using a magnetic stirrer to obtain a homogeneous mixture. Then the mixture was subjected for heating below an optimum temperature of 60°C in temperature controlled water bath to dry the sample. The colourless crystalline sample of LACC was obtained after the evaporation of the solvent and used for the growth of single crystals of LACC.

6.2.2 Determination of Solubility

The solubility of LACC in double distilled water was determined by adding L-alanine and cadmium chloride taken in the equimolar ratio in 100 ml of the solvent. Using the magnetic stirrer, super saturation was attained with the recrystallized salt as the charge material. After saturation, the homogeneous solution was kept in the container for an hour without any disturbance. A 10 ml saturated solution was pipetted out, dried and weighed. The solubility experiments were carried out for several times in a temperature range between 30 – 50°C in steps of 5°C and the result were plotted as the solubility diagram and is shown in Figure 6.1.

![Figure 6.1: The solubility diagram of LACC crystal](image-url)
From this figure, it is found that the solubility of LACC increases with the increase of temperature. Hence, the solubility of LACC in pure double distilled water is sufficient to allow the growth of good quality single crystals of reasonable size.

6.2.3 Single Crystal Growth

The synthesized powder of LACC were dissolved in double distilled water and stirred well for about 2 hours using a magnetic stirrer at 30°C to form a saturated solution. The solution was then filtered twice to remove the suspended impurities and allowed to crystallize by slow evaporation of solvent at room temperature. The transparent good quality crystals of size around 2.8 cm × 2.7 cm were obtained in a period of about four weeks and are shown in Figure 6.2.

![Figure 6.2: The photograph of the as-grown LACC crystal](image)

6.3. Characterization

6.3.1 Single Crystal X-Ray Diffraction

The single crystal X-ray diffraction analysis has been carried out to identify the structure and to estimate the lattice parameters of the grown crystal. It was found that the title compound crystallizes in the monoclinic system with the space group C2 which is recognized as non-centro-symmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals. The obtained lattice parameters are a = 16.415 (3) Å, b = 7.279 (1) Å, c = 7.989 (1) Å; α = γ = 90.00(0)°, β = 116.53(2)°. These values are in good agreement with the reported values [137].
6.3.2 Powder X-Ray Diffraction

The powder X-ray diffraction analysis has been carried out to confirm the crystallinity of the sample. The XRD pattern of LACC crystal was recorded and is shown in Figure 6.3. This pattern confirms the crystallinity of the sample.

![Figure 6.3: Powder XRD pattern of LACC crystal](image)

6.3.3 FTIR Spectral Measurement

The infrared spectral analysis provides useful information regarding the molecular structure and functional groups of the compound. The infrared spectrum of LACC crystals was recorded and is shown in Figure 6.4. The NH$_2$ group of L-alanine is protonated by the COOH group. The presence of NH$_3^+$ is easily identified in the FT-IR spectrum by the broad intense band with the absorption at 3581.93 cm$^{-1}$ corresponding to asymmetric stretching mode of NH$_3^+$. The NH$_3^+$ symmetric stretching frequencies are overlapping with the vibrations of CH$_3$ group. The strong absorption at 1462.09 cm$^{-1}$ and 1599.04 cm$^{-1}$ indicate the bending degenerate frequency of the carbonyl group and NH$_3^+$ group. The strong absorption at 1344.43 cm$^{-1}$ indicates the bending symmetric frequency of the CH$_3$ group. The NH$_3^+$ and CH$_3$ rocking frequencies occur at the 1112.96 cm$^{-1}$ and 1004.95 cm$^{-1}$. The absorption at 1199.76 cm$^{-1}$ and 842.92 cm$^{-1}$ corresponds to asymmetric and symmetric stretching mode of CCN. The COO$^-$ rocking and bending frequencies occur at the 1413.87 cm$^{-1}$ and 765.77 cm$^{-1}$. The absorption peaks at 922.00 cm$^{-1}$ and 842.92 cm$^{-1}$ are assigned to C–C–N symmetric stretching vibrations.
6.3.4 UV-Visible Spectral Measurement

The transmittance spectrum is very important for any NLO material since a nonlinear optical material can be of practical use only if it has wide transparency window. In order to determine the optical transmittance range and hence to know the suitability of LACC single crystals for optical applications, the UV–visible transmittance spectrum was recorded and is shown in Figure 6.5. As observed in the spectrum, there is no significant absorption in the wavelength range of 224–800 nm. This is an advantage of the use of amino acids where the absence of strongly conjugated bonds leads to wider transparency ranges in the visible and UV spectral regions [138]. The lower cut-off at 224 nm combined with the very good transparency, attests the usefulness of this material for different applications like optoelectronics, the generation of the second and third harmonics of the Nd:YAG laser fundamental and for the generation of the higher harmonics of the GaAlAs diode lasers emitting fundamental in the vicinity of 800 nm for the achievement of blue lasers.
The optical energy gap of the grown crystal was determined from the transmittance spectrum using the equation (3.1). From the transmittance spectrum, a graph was drawn between $h\nu$ and $(\alpha h\nu)^2$ and is shown in Figure 6.6. The band gap energy of the grown crystal was evaluated by extrapolating a straight line in the linear region of the graph at $(\alpha h\nu)^2 = 0$ and was found to be 5.3 eV. The higher band gap energy shows that the defect concentration in the grown crystals is very low [136].

![Figure 6.5: UV-visible spectrum of LACC crystal](image)

![Figure 6.6: $(\alpha h\nu)^2$ vs photon energy $h\nu$ plot of LACC crystal](image)
6.3.5 Scanning Electron Microscopy (SEM) Measurement

The morphology of the growth surface of LACC crystal was observed by a scanning electron microscopy (SEM) and is shown in Figure 6.7. From this Figure, it can be seen some darker and brighter areas. This may be due to solvent inclusions, which are most commonly observed in solution grown crystals [101]. It can be also observed that the growth surface shows some craters and formation of pores and cracks.

![SEM micrograph of LACC crystal](image)

Figure 6.7: SEM micrograph of LACC crystal

6.3.6 Dielectric Measurement

The surfaces of the grown crystal were polished and coated with silver paste to ensure good electrical contacts during dielectric measurement. The capacitance and dissipation factor of the crystal was measured at different temperatures (30, 50, 70, 90°C). The dielectric constant $\varepsilon_r$ was calculated using the equation (2.1). Figure 6.8 shows the variation of dielectric constant with applied frequency at different temperatures. It can be seen that the values of dielectric constant increase with the increase in temperature and decreases with the increase of frequency. The high value of dielectric constant at lower frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization as discussed earlier. The low value at higher frequencies may be due to the loss of significance of these polarizations gradually. When the frequency increases to an optimum value, the space charge cannot sustain and comply with the external field and hence the polarization decreases. Also it was observed that the dielectric constant increases with the increase of temperature. In accordance with Miller rule, the lower
value of dielectric constant at high frequency for a given sample is a suitable parameter for the enhancement of SHG coefficient [128].

The variation of dielectric loss $\tan \delta$ as a function of frequency at different temperatures is shown in Figure 6.9 From the Figure, it can be seen that the dielectric loss was found to increase with increase in temperature and decrease with increase in frequency. The characteristic low dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects, and this parameter is of vital importance for the fabrication of nonlinear optical devices [129].

The ac conductivity ($\sigma_{ac}$) is calculated by substituting the value of dielectric constant $\varepsilon_r$ and dielectric loss $\tan \delta$ in the relation (2.2). Figure 6.10 shows the response of ac conductivity with frequency in the range from 20 Hz to 5 MHz at different temperatures. The ac conductivity increases with increase in frequency and temperatures. It is inferred from Figure 6.10 that the electrical conductivity of LACC is low at low temperature owing to trapping of some carriers at defect sites. As the temperature increases, more and more defects are created and as a result, the conductivity increases, which is predominantly due to the movement of defects produced by thermal activation [7, 39].

![Figure 6.8: The variation of dielectric constant with Log frequency at different temperatures of LACC crystal](image-url)
6.3.7 DC Conductivity Measurement

The dc conductivity $\sigma_{dc}$ of the grown crystal was calculated using the relation (5.3). The conductivity measurements were carried out at different temperatures ranging from 27 to 100°C. The I-V characteristic curves of LACC crystal at different temperatures are shown in Figure 6.11 and from which the conductance values were
calculated. The dc conductivity values of LACC crystals at different temperatures are given in Table 6.1.

![I-V graph of LACC crystal at different temperatures](image)

**Figure 6.11:** I-V graph of LACC crystal at different temperatures

**Table 6.1:** DC conductivity values of LACC crystals at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conductivity (Ω.m)^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>4.92 × 10^{-10}</td>
</tr>
<tr>
<td>40</td>
<td>6.11 × 10^{-10}</td>
</tr>
<tr>
<td>50</td>
<td>1.93 × 10^{-9}</td>
</tr>
<tr>
<td>60</td>
<td>4.01 × 10^{-9}</td>
</tr>
<tr>
<td>70</td>
<td>4.91 × 10^{-9}</td>
</tr>
<tr>
<td>80</td>
<td>5.16 × 10^{-9}</td>
</tr>
<tr>
<td>90</td>
<td>6.10 × 10^{-9}</td>
</tr>
<tr>
<td>100</td>
<td>7.98 × 10^{-9}</td>
</tr>
</tbody>
</table>

**Figure 6.12** shows the plot of dc conductivity with temperature for LACC crystal. From **Table 6.1** and **Figure 6.12**, it can be seen that the dc conductivity was found to increase with increase in temperature. The conductivity graph exhibits the intrinsic and extrinsic regions. The conductivity at high temperature is intrinsic, which is due to the thermally created vacancies and defects created in crystalline lattice. The extrinsic region at low temperatures is a structure-sensitive region i.e., electrical conductivity is controlled by impurities. As the temperature rises, more and more defects are produced which in turn, increases the conductivity [39, 80, 84].
Figure 6.12: Variation of dc conductivity versus temperature for LACC crystal

Figure 6.13 shows the plot between Lnσ\text{dc} and 10^{3}/T of LACC crystal. The activation energy for the grown crystal was calculated using the equation (5.2), The DC activation energy was estimated and it was found to be 0.37 eV.

Figure 6.13: Plot of Lnσ\text{dc} versus \frac{1000}{T} (K^{-1}) for LACC crystal
6.3.8 Refractive Index (RI) Measurement

Brewster's angle method was used to study the refractive index of LACC crystals by using a red He-Ne laser of 633 nm wavelength. The refractive index values of pure and doped crystals were calculated using the relation (5.4). The polarizing angle \( \theta_p \) for LACC crystal was found to be 55.56 degree and refractive index of the crystal was found to be 1.46. The relatively lower refractive index of LACC in comparison to inorganic materials makes it a better material for NLO applications.

6.3.9 Microhardness Measurement

The transparent crystals of LACC free from cracks were selected for microhardness measurements and subjected to static indentation tests at room temperature using Vicker's microhardness tester. The loads ranging from 25 to 200 gm were used for making indentations, keeping time of indentation constant at 10 s. The microhardness value was calculated using the equation (5.5). Figure 6.14 shows the variation of Vicker's hardness number with applied load for the grown crystal. From the Figure, it can be seen that the microhardness was found to decrease linearly as the applied load increases.

![Figure 6.14: Variation of Vicker's hardness number with load of LACC crystal](image)

The Meyer’s index number \( n \) was calculated by using the equation (5.6) and (5.7). To calculate the value of \( n \), a graph Log \( P \) versus Log \( d \) is plotted and is shown in Figure 6.15 which gives a straight line; the slope of this straight line gives the
The calculated value of $n$ of the grown crystal was found to be 1.303. According to Onitsch [133] $n$ should lie between 1 and 1.6 for harder materials. Thus LACC crystal belongs to the hard material category. Low work hardening coefficient shows less dislocation in the grown crystal since work hardening coefficient is caused by the dislocation present in the crystal.

![Figure 6.15: Plot of Log P versus Log d of LACC crystal](image)

6.3.10 Thermal Measurements

The TGA and DTA of the grown crystals were carried out between 30 and 400°C. Figure 6.16 shows the thermograms illustrating simultaneously recorded TGA and DTA. From the DTA curves it is inferred that the decomposition of the material takes place in the vicinity of 147.79°C. The sharpness of this endothermic peak shows the good degree of crystallinity and purity of the sample. The other endothermic peak at 221.55°C and exothermic peak at 229.79°C reveal the decomposition of LACC structure and coincide with the decomposition observed in TGA curve. From the TGA curve, it can be seen that there was gradual weight loss between 141.85–157.35°C and 200.82–246.48°C. It is seen that at different stages, various gases like CO, CO$_2$, NH$_3$, Cl etc., are liberated leading to bulk decomposition of the compound.

The DSC thermogram of the grown LACC crystal was performed in the temperature rang 30 - 200°C. The recorded DSC curve is shown in Figure 6.17. The absence of endothermic or exothermic peak in the temperature range of 30 - 137.47°C
suggests that the LACC is thermally stable up to 137.47°C. Further, it indicates no phase transition before this temperature. The endothermic peak at 137.74°C clearly shows the phase transition from solid to liquid. It is in agreement with the melting point measurement (137.5°C) and it is also coincides with the DTA trace.

**Figure 6.16:** TGA/DTA curves of LACC crystal

**Figure 6.17:** DSC thermogram of LACC crystal
6.3.11 Powder SHG Measurement

A Q-switched Nd:YAG laser beam of wavelength 1064 nm with an input power of 4.2 mJ and pulse of width of 10 ns with a repetition rate of 10 Hz were used. The grown LACC crystal was powdered and then packed in a micro capillary of uniform bore and exposed to laser radiations. The signal amplitude in mV on the oscilloscope indicates the SHG efficiency of the grown crystal. A second harmonic signal of 9.5 mV was obtained from LACC, with reference material KDP (14 mV). So the SHG conversion efficiency of LACC grown crystal was found to be 0.68 times that of KDP.

6.4. Conclusions

The single crystals of LACC were grown by slow evaporation technique at room temperature. The solubility of the sample was tested at various temperatures. The lattice parameter values were confirmed by single crystal XRD and the crystalline nature of the grown crystal was confirmed by powder XRD. The presence of carbonyl and NH$_3^+$ functional groups were identified by FTIR spectral analysis. The UV-visible spectrum reveals that the grown crystal was transparent in the wavelength region 224 to 800 nm. The SEM gives information about surface morphology of the grown crystal. The value of dielectric constant was found to increase with increase in temperature and decrease with increase of frequency. AC conductivity strongly depends on frequency and the conductivity was found to be increase at high frequencies. The present study also reveals that the dc conductivity increases with increase in temperature. The mechanical property was tested by Vicker’s microhardness measurement and confirms that the LACC crystal belongs to the category of hard material. Thermal measurements revealed that there is no phase transition occurs below 131.87°C. The SHG conversion efficiency of LACC grown crystal was found to be 0.68 times that of KDP. Therefore, LACC crystal is a good candidate for NLO applications.