Chapter V

Synthesis, Growth and Optical Studies on L-arginine Salts
5.1 Introduction

There have been intense research and development on blue-green laser light sources, which provide high density recording capacity for compact disks and other optical data storage systems. Semiconductor laser diodes are now considered as prime candidates because of their potential advantages of compactness and low cost. However, beyond harmonic generation, SHG devices have the advantages of power emission, choice of wavelengths and reliability, which make them desirable for practical applications [1-3]. Inorganic NLO materials have a very high thermal and mechanical stabilities but possess modest optical nonlinearity due to the lack of extended π-electron system between donor and acceptor groups. For example potassium niobate (KNbO₃) has the nonlinear coefficient $d_{31} = 15.8 \text{pm/V}$ and it is suitable for frequency doubling of diode lasers (e.g. GaAs, $\lambda = 808 \text{ nm}$) [4].
Presently, organic materials are attracting great attention due to their fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility and high optical damage threshold. It was proposed that the presence of electron donating and electron accepting groups on benzene and stilbene systems would result in strong second harmonic generation \[5,6\]. In the development of organic SHG devices, some organic nonlinear optical materials have been reported such as 3-methoxy-4-methoxyl–4-nitrostilbene (MMONS) and 4-amino benzophenone (ABP) \[3,7\]. The ABP crystal has large nonlinear coefficients and the powder SHG efficiency is 360 times of ammonium dihydrogen phosphate (ADP). Among the organic NLO materials, amino acid (L-arginine, L-histidine and L-alanine) derivatives have been extensively investigated due to their molecular chirality, wide transparency and donor-acceptor molecules with large hyperpolarizabilities \[8-11\]. For example L-arginine phosphate has SHG efficiency 1.56 times of KDP with optical transparency in the range 250 –1500 nm \[12\].

5.2 Review of Earlier Work

Monaco et al. \[8\] have reported the synthesis and the nonlinear optical properties of L-arginine derivatives viz., L-arginine phosphate, L-arginine fluoride, L-arginine bromide, L-arginine tetrafluoroborate and
L-arginine acetate. L-arginine acetate (LAA) crystallizes in monoclinic system with the space group \( \text{P2}_1 \) and \( Z=2 \) [13]. The unit cell parameters are \( a = 9.229(2) \, \text{Å} \), \( b = 5.178(3) \, \text{Å} \), \( c = 13.271(4) \, \text{Å} \), \( \beta = 114.4(1)^\circ \). Muralidharan et al. [14] have reported the synthesis, X-ray diffraction and thermal properties of LAA. Further the crystal growth, knoop hardness and optical studies of LAA were reported in the literature [15,16]. Xu et al [17] have reported the new organic NLO material L-arginine trifluoroacetate (LATF). It belongs to monoclinic system [Space group \( \text{P2}_1 \), with \( a = 10.581(2)\text{Å} \), \( b = 5.710(10)\text{Å} \), \( c = 10.861(2)\text{Å} \), \( \beta = 106.81(3)^\circ \), \( Z = 2 \), and \( V = 628.2(2)\text{Å}^3 \)]. It exhibits powder SHG efficiency 2.5 times of KDP.

### 5.3 Present Investigations

In the present investigations, efforts were made to synthesize and grow organic NLO materials LAA and LATF. The grown crystals were characterized by single crystal X-ray diffraction, FT-IR, FT-NMR and thermal (TG/DT and DSC) analyses. The linear (UV-Vis) and nonlinear optical (SHG efficiency) properties of these materials were studied. The laser damage threshold of the grown crystals was determined using an Nd:YAG laser (1064 nm).
5.4 Synthesis, Solubility and Crystal Growth

LAA was synthesized from L-arginine and acetic acid according to the following reaction:

\[
\begin{align*}
(NH_2)NHCNH (CH_2)_3 CH(NH_2)COOH + CH_3COOH \\
\downarrow \\
(NH_2)_2^+ CNH (CH_2)_3 CH(NH_3^+ COO^- \cdot CH_3COO^- \quad (5.1)
\end{align*}
\]

The equimolar ratio of L-arginine and acetic acid were thoroughly dissolved in double distilled water and stirred well using a magnetic stirrer. The resulting mixture was evaporated to dryness by heating at 55°C in a temperature controlled water bath to avoid any possible decomposition. The synthesized material was purified by repeated recrystallization in double distilled water. The purity of the material was checked by measuring the melting point as 221 ± 1°C using a Tempo melting point apparatus.

LATF \((C_7H_{14}N_4O_2\cdot CF_3COOH)\) was synthesized by taking L-arginine and trifluoroacetic acid as per the reaction scheme given below:

\[
\begin{align*}
(NH_2)NHCNH (CH_2)_3 CH(NH_2)COOH + CF_3COOH \\
\downarrow \\
(NH_2)_2^+ CNH (CH_2)_3 CH(NH_3^+ COO^- \cdot CF_3COO^- \quad (5.2)
\end{align*}
\]

The equimolar ratio of L-arginine and trifluoroacetic acid was thoroughly dissolved in double distilled water and adopting the previous procedure, the synthesized crystalline material of LATF was obtained
and purified by repeated recrystallization process in double distilled water. The melting point of the compound was found to be 215 ±1°C.

The solubility test was carried out for LAA and LATF in water and ethanol in the temperature range 30° - 50°C. The LAA solution was prepared in water at 30°C with continuous stirring using a magnetic stirrer to ensure homogeneity of temperature and concentration over the entire volume of the solution. On reaching saturation, the content of the solution was analyzed gravimetrically and this process was repeated for every 5°C for water and ethanol. The solubility curves of LAA and LATF are shown in Figs.5.1 and 5.2 respectively. It is observed that LAA and LATF have a positive temperature gradient and the solubility of these materials is high in water and hence water was used as the solvent for crystal growth.

![Solubility curves of LAA.](image)

Fig. 5.1 Solubility curves of LAA.
The synthesized salt of LAA was thoroughly dissolved in double distilled water using a magnetic stirrer. The solution was saturated at 30°C with pH 4.0. The solution was filtered twice to remove the suspended impurities and allowed for slow evaporation at the same temperature. The single crystals of the size 15 × 7 × 5 mm³ were grown within 30 days with an approximate growth rate of 0.51 mm/day (Fig.5.3). The LATF solution was prepared with pH 3.7 and allowed for slow evaporation at 30°C. A single crystal of the size 12 × 7 × 4 mm³ was grown within 30 days (Fig.5.4).
Fig. 5.3 As grown single crystals of LAA.

Fig. 5.4 As grown single crystal of LATF.
5.5 Characterization

5.5.1 Single Crystal X-ray Diffraction Analysis

The grown crystals (LAA and LATF) were subjected to single crystal X-ray diffraction using an Enraf Nonious CAD4 X-ray diffractometer with MoKα radiation (λ = 0.7107 Å) to find out the unit cell dimensions (Table 5.1). Both LAA and LATF belong to monoclinic system with space group P2₁ [14,17]. The noncentrosymmetric space group thus satisfies the basic and essential material requirement for the SHG activity of the crystal.

<table>
<thead>
<tr>
<th>Cell dimensions</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L-Arginine acetate</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.221(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.179(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.274(4)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>114</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>586</td>
</tr>
</tbody>
</table>
5.5.2 FT-IR Spectral Analysis

The FT-IR spectrum of LAA and LATF was recorded using a JASCO 460 Plus FT-IR spectrometer by KBr pellet technique in the range 400 - 4000 cm\(^{-1}\) to confirm the molecular structure of the synthesized compounds (Figs.5.5 and 5.6).

The N-H stretching of guanidyl group \((+\text{(H}_2\text{N})_2\text{CNH})\) in L-arginine appears at 3289 cm\(^{-1}\) whereas in LAA and LATF it is shifted to 3350 cm\(^{-1}\) and 3380 cm\(^{-1}\) respectively, due to the protonation of nitrogen in the guanidyl group. Similarly, in L-arginine the C=O stretching appears at 1661 cm\(^{-1}\), but it is shifted to 1650 cm\(^{-1}\) and 1640 cm\(^{-1}\) in LAA and LATF respectively, due to the deprotonation of carboxylic group [18,19]. The strong band at 1195 cm\(^{-1}\) is assigned to C-F stretching frequency of LATF. The vibrational bands at 3170 cm\(^{-1}\) and 3171 cm\(^{-1}\) are assigned to C-H stretching in LAA and LATF respectively. The CH\(_2\) bending appears at 1340 cm\(^{-1}\) in LAA whereas in LATF it is at 1365 cm\(^{-1}\). The other characteristic vibrational frequencies are compared with L-arginine and presented in table 5.2. From the spectral analyses, it is confirmed that the guanidyl and amino (NH\(_3\)) groups are protonated and thus balance with the negative charge of the carboxylate (COO\(^-\)) functionality [20, 21].

In the FT-IR spectrum, the vibrational band at 2000 cm\(^{-1}\) was assigned to C-H stretching in LAA.
Fig. 5.5 FT-IR spectrum of LAA.
Table 5.2 The FT-IR spectral band assignments.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignments</th>
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</thead>
<tbody>
<tr>
<td>L-arginine</td>
<td>LAA</td>
</tr>
<tr>
<td>3289</td>
<td>3350</td>
</tr>
<tr>
<td>3155</td>
<td>3170</td>
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<td>1681</td>
<td>1689</td>
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<td>1661</td>
<td>1650</td>
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<td>1441</td>
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<td>......</td>
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</tr>
<tr>
<td>1136</td>
<td>1132</td>
</tr>
<tr>
<td>667</td>
<td>671</td>
</tr>
</tbody>
</table>

5.5.3 FT-NMR Spectral Analysis

The \(^1\H \) and \(^{13}\C\) NMR spectrum of LAA and LATF were recorded using a JEOL GSX –300 MHz FT-NMR spectrometer with DMSO as the solvent (Figs. 5.7, 5.8, 5.9 and 5.10).

\(^1\H\) NMR spectrum of LAA (Fig.5.7) shows signals at \(\delta = 1.329 \) ppm and \(\delta = 1.341 \) ppm due to the CH₃ group of the acetic acid and the amino acid. The protons of the CH₂ group give a triplet at \(\delta = 3.40 \) ppm
by the influence of adjacent CH₂ group in the amino acid. The triplet at \( \delta = 2.89 \text{ ppm} \) is attributed to the other two CH₂ groups in the amino acid. The area under these two signals is 0.476 and 1.00 indicating the proton population as 1:2 [19]. The \(^{13}\text{C} \text{-NMR} \) spectrum of LAA contains eight signals as shown in Fig.5.8. The signals at \( \delta = 24.966 \text{ ppm} \) and 25.482 ppm are attributed to the carbon associated with the CH₂ group of the amino acid. The signals at \( \delta = 175.848 \text{ ppm} \) and 182.729 ppm confirm the presence of carbon in the COO\(^{-} \) group of both the amino acid and acetic acid [20,21].

In the \(^{1}\text{H-NMR} \) spectrum of LATF, the proton in the CH₂ group gives a signal at \( \delta = 3.44 \text{ ppm} \) due to the influence of adjacent CH₂ group. Another triplet at \( \delta = 2.92 \text{ ppm} \) is attributed to the CH₂ group with the influence of neighbouring methine group. The area under these groups is 1.00 and 2.093 indicating the proton population as 1:2. In \(^{13}\text{C-NMR} \) spectrum, the signals at \( \delta = 116.014 \text{ ppm} \) and 119.883 ppm are due to the presence of carbon in the methyl (CH₃) of acetic acid and C=NH₂ group of L-arginine. The signals at \( \delta = 158.317 \text{ ppm} \) and 175.804 ppm confirm the carbon of carboxylate group in the arginine chain and acetic acid respectively [20,21]. The other chemical shifts in \(^{1}\text{H} \) and \(^{13}\text{C-NMR} \) spectrum of LAA and LATF are presented in table 5.3.
Fig. 5.7 $^1$H – NMR spectrum of LAA.

Fig. 5.8 $^{13}$C – NMR spectrum of LAA.
Fig. 5.9 $^1$H – NMR spectrum of LATF.

Fig. 5.10 $^{13}$C – NMR spectrum of LATF.
Table 5.3 $^1$H and $^{13}$C-NMR spectral assignments of LAA and LATF.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Chemical shifts $\delta$ (ppm)</th>
<th>Assignments [20,21]</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>LAA</td>
<td>LATF</td>
</tr>
<tr>
<td>$^1$H – NMR</td>
<td>1.329</td>
<td>1.372</td>
</tr>
<tr>
<td></td>
<td>1.341</td>
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<td></td>
<td>1.561</td>
<td>1.600</td>
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<tr>
<td></td>
<td>2.890</td>
<td>2.921</td>
</tr>
<tr>
<td></td>
<td>3.402</td>
<td>3.440</td>
</tr>
<tr>
<td>$^{13}$C – NMR</td>
<td>24.966</td>
<td>25.477</td>
</tr>
<tr>
<td></td>
<td>25.482</td>
<td>29.121</td>
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<td></td>
<td>29.144</td>
<td>42.064</td>
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<td></td>
<td>55.823</td>
<td>55.850</td>
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<td></td>
<td>42.058</td>
<td>116.014</td>
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<td></td>
<td>158.848</td>
<td>119.883</td>
</tr>
<tr>
<td></td>
<td>175.848</td>
<td>158.317</td>
</tr>
<tr>
<td></td>
<td>182.729</td>
<td>175.804</td>
</tr>
</tbody>
</table>

5.5.4 Thermal Analyses

5.5.4.1 TGA and DTA

Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) for LAA and LATF were carried out using a Seiko Thermal analyzer to determine the thermal stability of the grown crystals in the temperature range 35°C-700°C (Figs.5.11 and 5.12). A ceramic crucible was used for heating the sample and the analyzes were carried out in nitrogen atmosphere at a heating rate of 20°C/min.
In Fig. 5.11, the DTA curve shows an endothermic peak at 221°C which represents the melting point of the compound. The TGA curve reveals that there is a weight loss of about 45% at 257°C due to the liberation of the volatile substances probably ammonia, carbon monoxide and carbon dioxide in LAA. There is no significant endothermic or exothermic peak beyond 300°C in DTA curve whereas TGA shows a complete weight loss at 700°C and the residue is 15% of the initial mass. This indicates the step-by-step decomposition of the material in the temperature range 257°-700°C. The results indicate that the material is stable upto 221°C and ensure the suitability of the material for possible applications (frequency doubler, optical parametric oscillator etc.).

In Fig. 5.12, the endothermic peak in the DTA curve at 215°C represents the melting point of the LATF compound. The TGA curve shows that there is a weight loss of about 40% in the temperature range 250°- 270°C due to the decomposition of the compound. There is no significant endothermic or exothermic peak above 250°C in the DTA whereas TGA shows a complete weight loss (5%) at 700°C. This is due to the step-by-step decomposition and the release of volatile substances (probably ammonia and carbon dioxide) in this compound.
Fig. 5.11 TGA and DTA curves of LAA.

Fig. 5.12 TGA and DTA curves of LATF.
5.5.4.2 Differential Scanning Calorimetry (DSC) Analysis

The specific heat and DSC analyses were carried out for LAA and LATF in the temperature range 35°C-160°C at a heating rate of 2°C/min in nitrogen atmosphere using a TA instrument (2920 Modulated DSC). The specific heat of LAA is 1.629 J/g°C at 41°C and it increases with the temperature. The DSC curve shows that there is no phase transition in this compound upto 160°C (Fig. 5.13). The above procedure was followed to analyze the thermal properties of LATF in the temperature range 30°C-250°C. The specific heat is 0.860 J/g°C at 50°C (Fig. 5.14) and it increases with temperature. The DSC curve shows that there is no phase transition in LATF in the temperature range 30°C-250°C.

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**Fig. 5.13 DSC and specific heat curves of LAA.**

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Fig. 5.14 DSC and specific heat curves of LATF.

5.5.5 UV-Vis Optical Transmittance

The UV-Vis transmittance spectrum of LAA and LATF was recorded using a Varian Cary 5E- UV-Vis spectrophotometer in the range 200-800 nm (Figs. 5.15 and 5.16).

The figures show that the materials have a wide optical transmittance in the entire visible region (400 – 800 nm) and the lower cutoff wavelength is down to 270 nm and 280 nm respectively due to \( \pi - \pi^* \) transition in the compounds [20]. From the UV-Vis spectral analysis, it is noted that there is no significant absorption in the UV and visible region thereby confirming the advantage of the crystal for optical applications. The large transmission in the entire visible region and the
lower cutoff wavelength enable them to be the potential candidates for second and third harmonic generation of Nd:YAG laser fundamental and for the generation of the higher harmonics of the GaAlAs laser diode emitting the fundamental in the vicinity of 800 nm for the achievement of blue lasers.

Fig. 5.15 UV-Vis transmittance spectrum of LAA.

Fig. 5.16 UV-Vis transmittance spectrum of LATF.
5.5.6 Measurement of Powder SHG Efficiency

The powder SHG efficiency of LAA and LATF were measured following the Kurtz and Perry technique [22] using an Nd:YAG laser (1064 nm, 8 ns, 10 Hz). The sample was ground and sieved into different particle sizes (<106, 106-125, 125-150, >150 μm). All the powdered samples were tightly packed into the separate microcapillary tube of uniform bore of 1.5 mm diameter. The laser power incident on the capillary tube was 6 mJ. The SHG at 532 nm (green light) was collected by the photomultiplier tube (PMT). The optical signal incident on the PMT was converted into voltage output in the CRO. The result obtained for LAA shows a powder SHG efficiency 0.11 times that of a well-known organic NLO material urea. The SHG efficiency for various particle sizes shows that SHG intensity increases with particle size (Fig.5.17), thus giving a proof for the phase matching property of LAA. The powder SHG measurement of LATF was carried out by adopting the foregoing procedure. It reveals that it has a powder SHG efficiency 0.35 times that of urea and it is phase-matchable (Fig.5.18). The powder SHG efficiency of these materials is compared with related materials in table 5.4.

Ungraded urea sample was used as reference in the powder SHG efficiency measurement for all the materials. The reference sample urea was held in a same sample holder and was not changed physically for every experiments.
Fig. 5.17 Phase matching curve of LAA.

Fig. 5.18 Phase matching curve of LATF.
Table 5.4 Comparison of SHG efficiency with related materials.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Samples</th>
<th>Powder SHG efficiency with respect to urea</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L-arginine acetate</td>
<td>0.11</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>L-arginine trifluoroacetate</td>
<td>0.35</td>
<td>*</td>
</tr>
<tr>
<td>3</td>
<td>L-arginine phosphate monohydrate</td>
<td>0.52</td>
<td>[12]</td>
</tr>
<tr>
<td>4</td>
<td>L-arginine sulphophosphate</td>
<td>0.62</td>
<td>[12]</td>
</tr>
<tr>
<td>5</td>
<td>L-arginine maleate dihydrate</td>
<td>0.50</td>
<td>[23]</td>
</tr>
</tbody>
</table>

* Present work

5.5.7 Laser Damage Threshold

The laser damage threshold of LAA and LATF was measured using a Q-switched Nd:YAG laser (λ = 1064 nm, 10 Hz, 10 ns). The grown crystal of the size 15 x 7 x 5 mm$^3$ was used to measure the laser damage threshold. The damage was observed and the energy of the laser beam was measured by the power meter (Scientech Model No.ACX5004). The laser damage threshold was calculated from the laser energy divided by the focused area as 162.42 MW/cm$^2$ and 177.34 MW/cm$^2$ for LAA and LATF respectively.

Further, comparison is drawn with the reported values of the laser damage threshold of the well-known NLO material LiNbO$_3$ [24] and other related materials (Table 5.5).
Table 5.5  Comparison of laser damage threshold with similar materials.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Samples</th>
<th>Laser damage threshold (MW/cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L-arginine acetate</td>
<td>162.42</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>L-arginine trifluoroacetate</td>
<td>177.34</td>
<td>*</td>
</tr>
<tr>
<td>3</td>
<td>Lithium niobate</td>
<td>100.00</td>
<td>[24]</td>
</tr>
<tr>
<td>4</td>
<td>L-histidine bromide</td>
<td>96.73</td>
<td>#</td>
</tr>
<tr>
<td>5</td>
<td>L-histidine phosphate</td>
<td>113.17</td>
<td>#</td>
</tr>
</tbody>
</table>

* Present work; # Chapter - IV.

5.6 Conclusions

Single crystals of LAA and LATF were grown by the slow evaporation technique. The molecular structure of the synthesized compounds is confirmed by FT-NMR and FT-IR spectroscopic techniques. The unit cell parameters are evaluated by single crystal X-ray diffraction technique and both the crystals belong to monoclinic system with the space group P$2_1$. The TG-DTA and DSC show a good thermal stability of the grown crystals. The UV-Vis transmittance spectrum highlights a good transmittance in the entire visible region and the lower cutoff wavelength is around 275 nm. The powder SHG efficiency is measured which indicates the phase matchability of the materials. The laser damage threshold of LAA and LATF is greater than LiNbO$_3$. 

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[10] P.A. Angeli Marry, S.Dhanuskodi,


