CHAPTER VI

GROWTH AND CHARACTERIZATION OF LAA SINGLE CRYSTAL

6.1 INTRODUCTION

Crystal growth has become an important area of research in physical sciences and material science. During the last three decades, much progress has been made in the development of new and better nonlinear optical (NLO) materials having large nonlinear optical coefficients. NLO materials are of much importance because of its extended applications, especially to develop new laser sources. In recent years, researchers have identified aminoacid based nonlinear optical crystals with better linear and nonlinear optical properties (Madhavan et al 2006, Madhavan et al 2007). Amino acids are strong candidates for optical Second Harmonic Generation (SHG) because they contain chiral carbon atom and crystallize in noncentro symmetric space groups. Amino acid crystal L-arginine acetate (LAA) has been reported as a promising NLO material by Muralidharan et al 2003. In the present work, attempts have been made to grow unidirectional LAA by SR method. The grown crystal was characterized by powder XRD, FT-IR and FT-Raman studies.

6.2 EXPERIMENTAL PROCEDURE

Aqueous solution of LAA was prepared by dissolving stoichometric L-arginine (AR grade) and acetic acid in double deionized water. The reaction

that takes place between L-arginine and acetic acid in water medium is as follows:

$$C_6H_{14}N_4O_2 + CH_3COOH \longrightarrow C_6N_4O_2H_{15}^{+}CH_3COO^{-}$$

The synthesized salt was purified by repeated crystallization. The seed crystal grown by the conventional slow solvent evaporation technique was used for the current study. <110> plane of the seed crystal of LAA was chosen and it was transferred to the saturated solution of LAA in the ampoule.

The experimental setup is as described in Chapter III. The temperature around the growth ampoule was selected based on the solvent used and it was monitored with a temperature controller (45 ºC for top and 35 ºC for bottom).

Growth of highly transparent single crystal of LAA of 10 mm diameter and 52 mm length was grown (Fig. 6.1) in a period of 30 days and reported for the first time. The average growth rate was found to be nearly 1.7 mm per day. Thus it is found that the average growth rate of crystal by SR method was higher than the conventional method under prevailing conditions.

6.3 RESULTS AND DISCUSSION

6.3.1 Powder XRD studies

The structural property of the grown crystal was studied by X-ray powder diffraction technique. Powder X-ray diffraction studies of LAA crystals were carried out, using Siemens D500 X-ray diffractometer with CuK_α ($\lambda = 1.5418$Å) radiation.

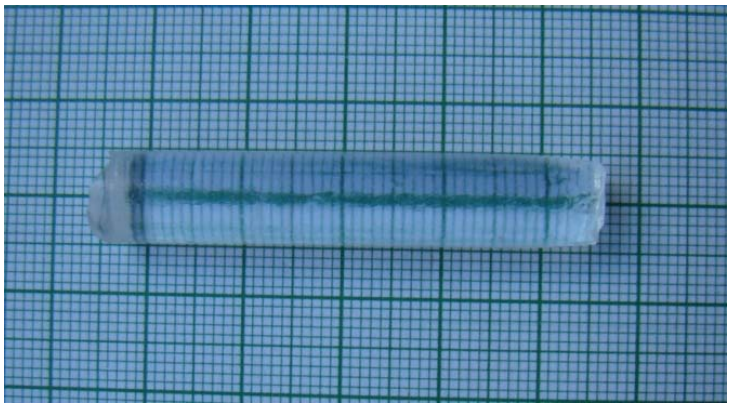

Fig. 6.1. LAA crystal grown by SR method

The samples were scanned for 2θ values from 10° to 50° at a rate of 2° /min. Fig 6.2 shows the powder XRD pattern of LAA crystal. The diffraction patterns of LAA crystal was indexed by least square fit method. The lattice parameter values of LAA crystal were calculated and are well matched with the reported literature. It is seen that the grown crystal crystallizes in monoclinic $P2_1$ space group and the lattice parameters are shown in Table 6.1.

6.3.2 CHN analysis

The elemental analysis of LAA was performed using Elementar Vario EL 111 Elemental analyzer. The theoretical and experimental atomic weight percentages are summarized in Table.6.2. Thus the chemical composition of LAA was estimated.

6.3.3. Vibrational Spectrocopy

The FT-IR Spectrum of LAA crystal was recorded in the range 450 cm^{-1} to 4000 cm^{-1}, using KBr pellet on BRUKKER IFS FT-IR Spectrometer. The FT-IR Spectrum of LAA crystal is shown in Fig. 6.3. In order to analyze the presence of functional groups in LAA, the polarized FT-Raman spectrum was recorded in the range 50 cm^{-1} – 3500 cm^{-1}. The recorded spectrum is shown in Fig. 6.4.

C-H Vibrations

The characteristic region for C-H stretching is 2700-3000 cm^{-1}. The CH in plane bending vibrations is generally observed in the region 1300-1000 cm^{-1}. For LAA molecule prominent number of CH in plane bending vibrations are observed at frequencies 1400, 1334, 1194 and 1131 cm^{-1} respectively.

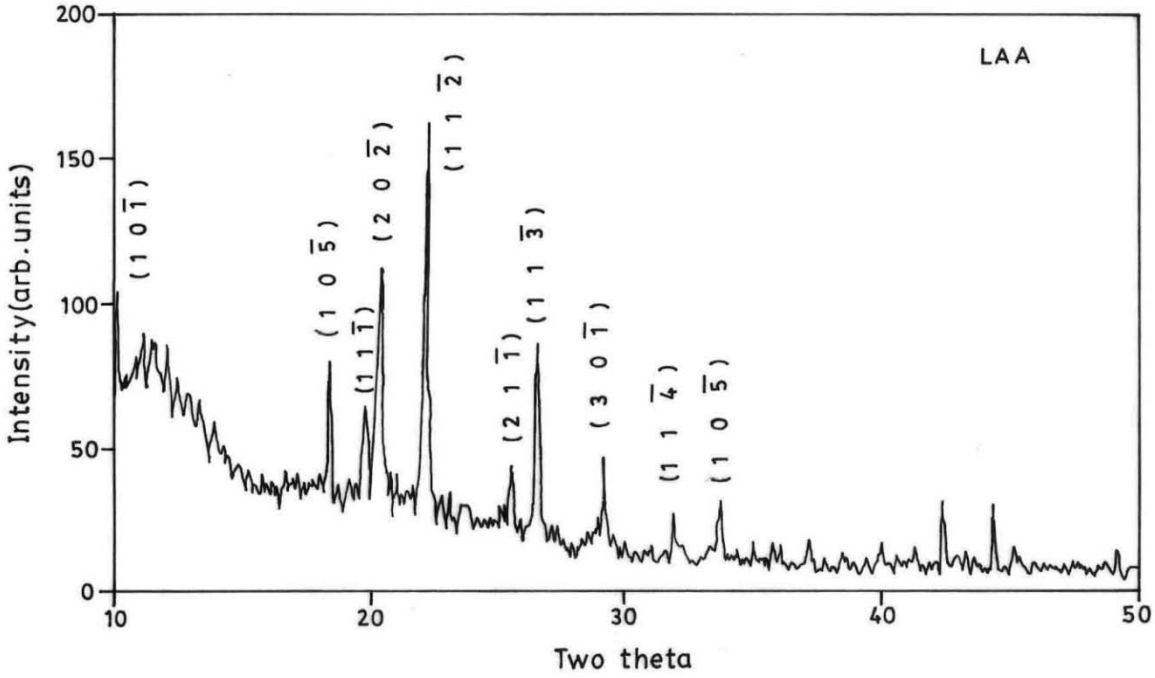

Fig. 6.2. Powder XRD pattern of LAA crystal

Table. 6.1 Crystal data of LAA crystal

Empirical formula	**$C_6N_4O_2H_{15}{}^{+}CH_3COO^{-}$**
Crystal system	Monoclinic
Space group	$P2_1$
a(Å)	9.212
b(Å)	5.191
c(Å)	13.10
α°	90
β°	109.61
γ°	90
Volume $Å^3$	590.10

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Table 6.2 Results of elemental analysis of LAA crystal

Molecular Weight: 234.26 g/mol		
Elements	Weight % composition	
	Theoretical	Experimental
C	41.02	41.13
H	7.75	7.80
N	23.92	23.99

In the FT-Raman spectrum, the bands are slightly affected by the nature of the substituents. The CH in plane bending vibrations is generally observed in the region 1300-1000 cm^{-1}. For LAA prominent number of CH in plane bending vibrations are observed at frequencies 1415, 1330, 1202 and 1118 cm^{-1} respectively. Aliphatic CH_3 and CH_2 vibrations are observed at 2965 and 2930 cm^{-1}. CH_3 symmetric deformation is observed at 1330cm^{-1}.

NH Vibrations

The N-H stretching vibrations generally give rise to bands at 3500-3300 cm^{-1}. In the present study NH stretching vibrations are observed at 3373 cm^{-1}. In the FT-Raman spectrum the NH stretching frequencies are found between 3100 cm^{-1} and 2600 cm^{-1} in the form of a broad strong band with multiple peaks. The characteristic band at1579 cm^{-1} is due to the symmetric NH deformation. The weak absorption band observed at 3065cm^{-1} shows the NH stretching of amino group.

Carboxyl vibrations (COOH)

Carboxyl group vibrations give rise to intense characteristic bands due to conjugation or formation of hydrogen bonds. These stretching and bending vibrations of acid group are generally expected in the region 1400-1200 cm^{-1}. The COOH vibrations are observed at 1334 cm^{-1} and 1323 cm^{-1}. In the FT-Raman spectrum it is inferred from the spectrum that the peaks at 1415 cm^{-1} and 1579 cm^{-1} are due to C=O stretching of carboxylic group. C=C stretching vibration is observed at 2125cm^{-1}.

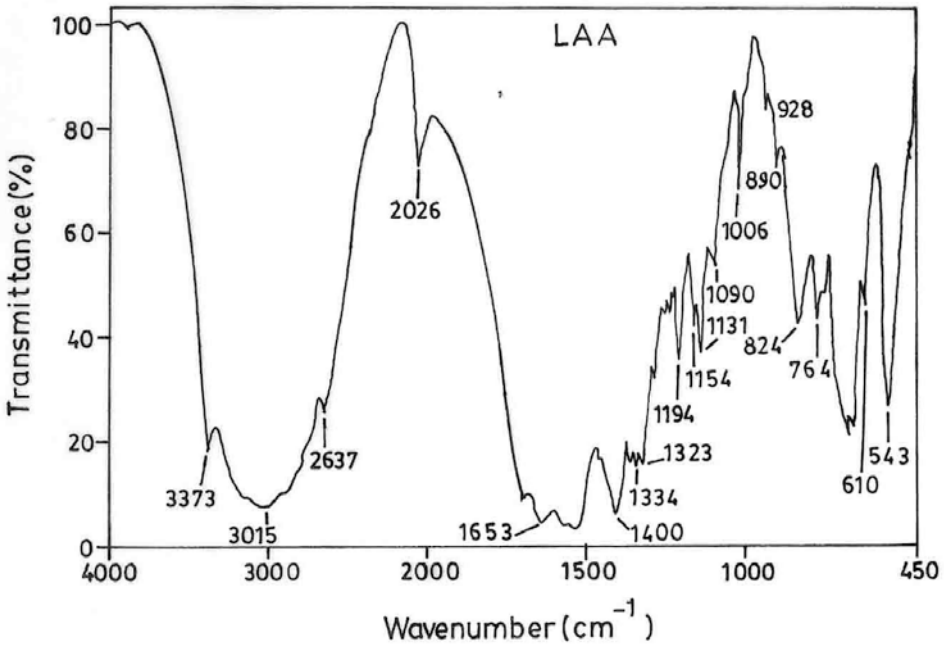

Fig. 6.3. FT-IR spectrum of LAA

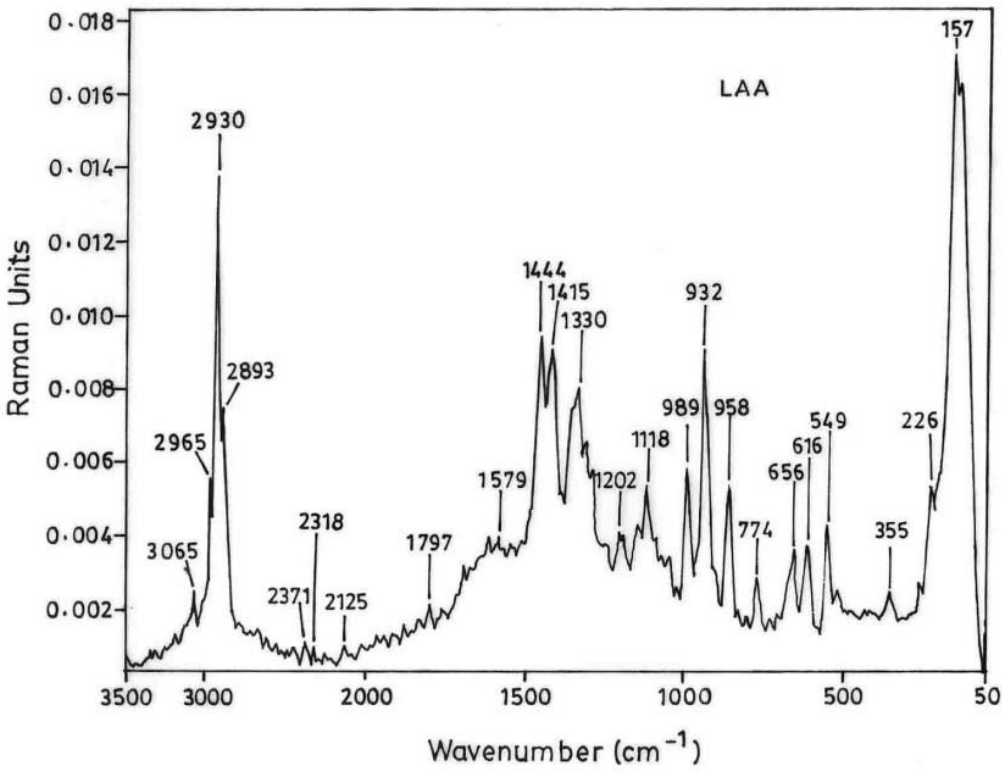

Fig. 6.4 FT-Raman spectrum of LAA

6.3.4 NLO studies

Kurtz SHG tests were carried out on the powdered sample of LAA samples using Nd:YAG Q-switched laser beam as a source (Kurtz et al 1968). For a laser input of 6.2mJ, the second harmonic signal (532nm) of 91.66 mW and 322.14 mW were obtained for KDP and LAA respectively. Thus, the SHG efficiency of LAA is 3.5 times higher than that of KDP.

6.3.5 Laser Induced Damage Threshold study

Inorganic crystals are usually known to have high resistance to laser damage. In this section the results of laser induced damage threshold studies performed on LAA are presented. The laser damage threshold of LAA was carried out using laser setup in a single shot mode and it was found to be about 7.5 GW / cm^2, which indicates the suitability of this crystal for NLO applications.

6.3.6 UV-Vis-NIR spectrum

Optical absorption data were taken on these polished crystal samples of about 4 to 6 mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200–1200 nm. The spectrum (Figure 6.5) indicate that the LAA crystal have minimum absorption in the entire visible region. The required properties for NLO activity are minimum absorption and low cut-off wavelength. LAA possess a good transparency for the wavelengths of sources which are used for photonic devices.

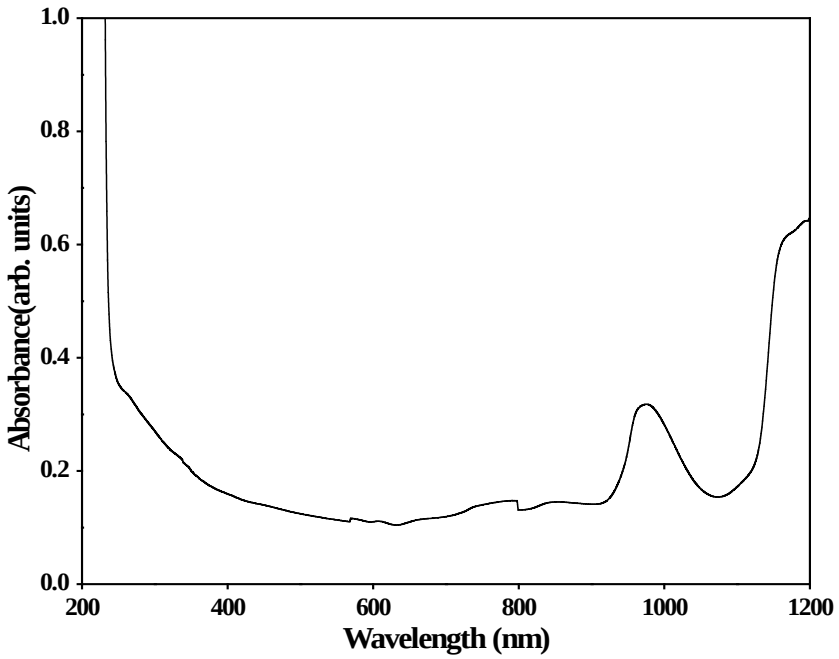

Fig. 6.5 UV–Vis–NIR absorption spectrum of LAA crystal

6.3.7 Microhardness test

Microhardness measurement was done on transparent crystal free from cracks. The indentations were made on the grown surface with the load ranging from 5 to 25 g using Vickers microhardness tester.

Fig 6.6 shows the variation of hardness with applied load for the plane (100). From the plot, it is found that the hardness of the crystal decreases with increasing load. The work hardening coefficient 'n' for the (100) plane was found to be 1.54 for LAA. Hence, it is concluded that LAA crystals are hard materials.

6.3.8 Thermal studies

The thermo gravimetric analyses of LAA crystal was carried out between 23 and 1200 °C using STA 409C instrument, in the nitrogen atmosphere at a heating rate of 10 K/min. Fig 6.7 shows the resulting TGA and DTG traces of LAA crystal. The sharp weight loss of the material starts around 200˚C. The crystal is completely free of any water of crystallization or any physically adsorbed water on the surface. The absence of significant band in the region 3500 cm^{-1} to 3400 cm^{-1} in the FT-IR spectrum also confirms the absence of any water molecule (Kanagadurai et al 2006). The DTA trace of LAA shows that, there is a sharp endotherm matching with the decomposition of LAA. Heating the material above 200°C, results in the formation of volatile substances, probably carbon dioxide and ammonia.

6.3.9 Dielectric studies

Single crystal of LAA was cut in the appropriate orientation and subjected to dielectric measurements. The dielectric study of LAA single crystal was carried out using the instrument, HIOKI 3532-50 LCR HITESTER.

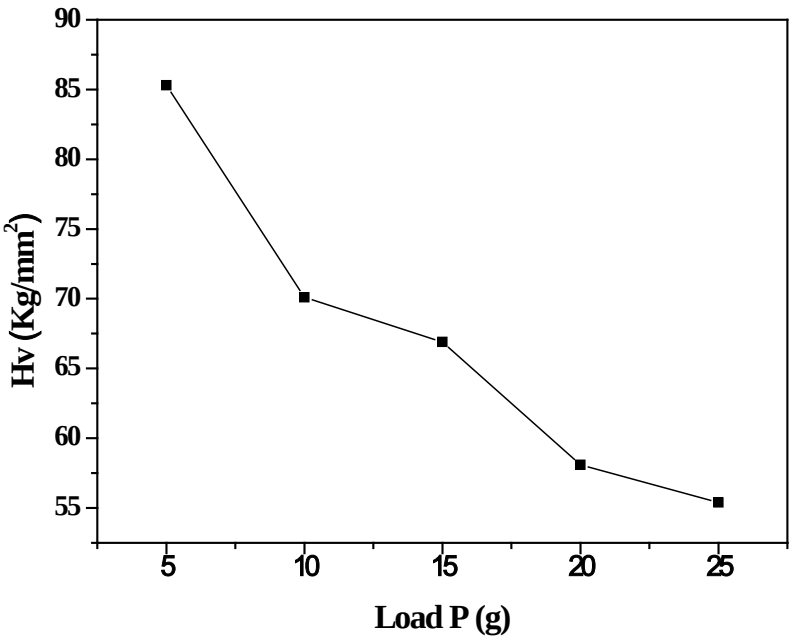

Fig. 6.6 Vickers hardness profile of LAA

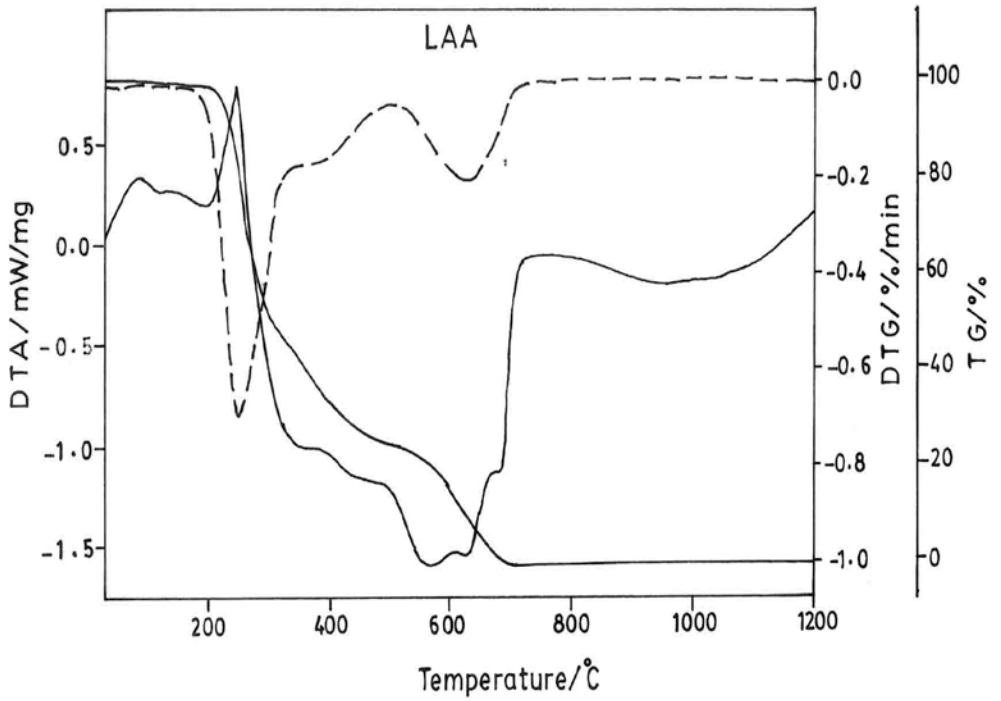

Fig. 6.7 TGA and DTG thermogram of LAA crystal

The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 5 MHz at room temperature. Fig.6.8 shows the plot of dielectric constant (ε_r) versus applied frequency for LAA. The applied frequency has been represented by logarithmic values in the plot. The dielectric constant is high at low frequencies and decreases with the applied frequency. The dielectric constant of LAA is mainly due to the contribution of space charge polarization at low frequencies (below 10 KHz). The magnitude of dielectric constant is a measure of the electrostatic binding strength between ions. The larger values of dielectric constant can be attributed to the lower electrostatic binding strength.

Fig 6.9 shows the variation of dielectric loss with frequency. The measurements show that there is no abrupt change but only a smooth variation in dielectric loss over the entire frequency for the crystal studied. The low values of dielectric loss suggest that the grown crystals are of moderately good quality. In the lower frequency region, dielectric loss shows larger values due to the associated ionic mobility (Shinichi et al 1990).

6.3.10 Photoconductivity studies

Photoconductivity studies were carried out at room temperature for LAA crystals, using Keithley 485 picoammeter. Darkcurrent and photocurrent are measured for various values of applied electric field the plot of photocurrent and darkcurrent as a function of the applied field for LAA crystal is shown in Fig 6.10. It is observed from the plots that the photocurrent is always higher than the darkcurrent, hence it is concluded that LAA exhibit positive photoconductivity.

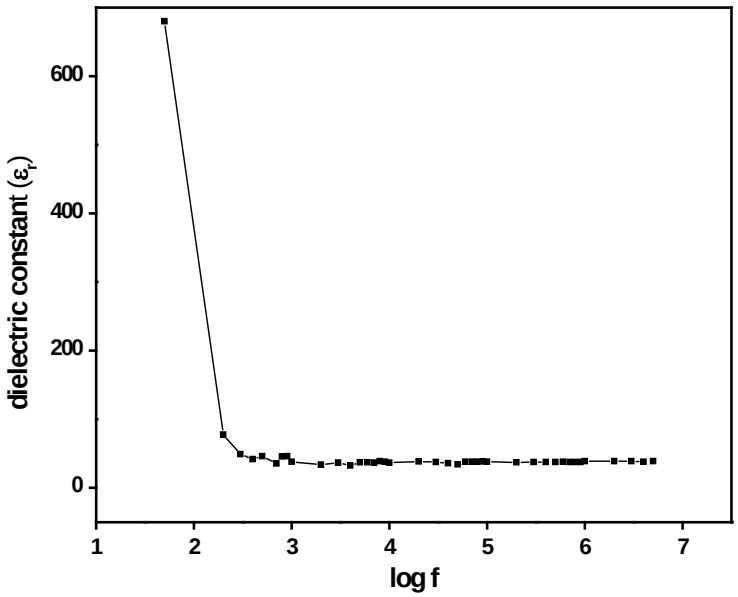

Fig. 6.8 Plot of dielectric constant versus log frequency

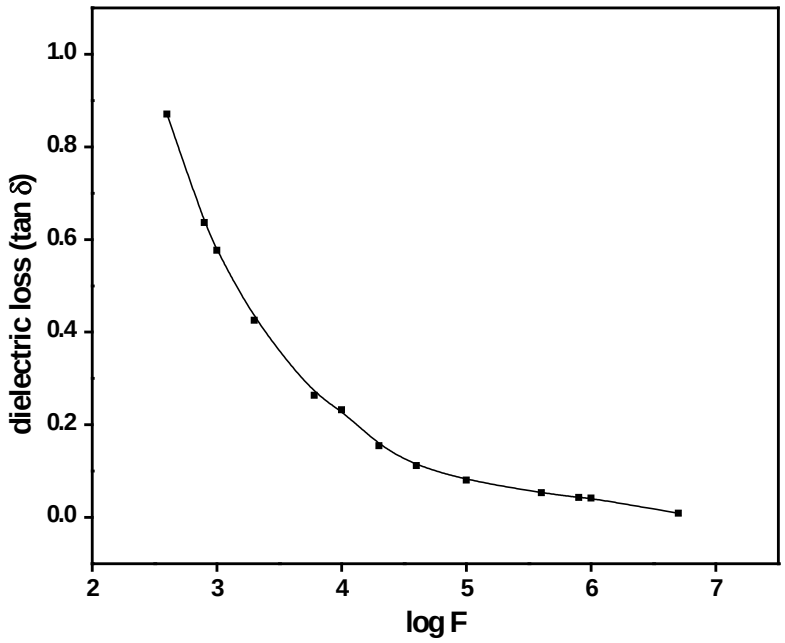

Fig. 6.9 Plot of dielectric loss versus log frequency

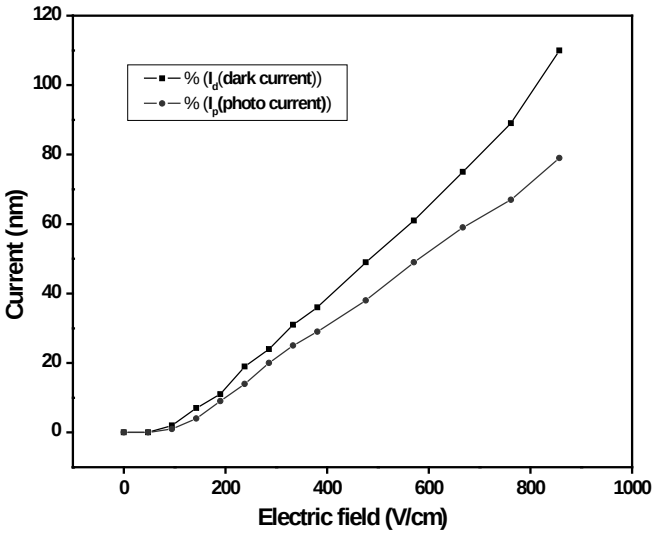

Fig. 6.10 Field dependent conductivity of LAA single crystal

6.4 CONCLUSION

Good quality unidirectional bulk crystal L-Arginine Acetate (LAA) was grown successfully by SR method. Powder X-ray diffraction study was carried out and the lattice parameters were calculated. NLO studies proved that LAA have second harmonic generation efficiency that is 3.5 times that of KDP. The FT-IR and FT-Raman spectral studies confirmed the presence of the functional groups and their different mode of vibrations. It is also understood from the present work that the SR technique is found suitable to grow high quality and large- size single crystal of L-arginine acetate.