CHAPTER V

GROWTH AND CHARACTERIZATION OF LTA SINGLE CRYSTAL

5.1 INTRODUCTION

Organic crystals show high damage threshold, wide transparency region and non-linear optical character which make them suitable for device fabrication (Madhavan et al 2006, Senthil et al 2009, Senthil et al 2012). In experimental solid state physics, SR method is a novel technique and used for the growth of unidirectional LTA single crystal (Sankaranarayanan et al 2006). It is also a convenient method used significantly to control the orientation of the growth of single crystals. L-Threonine acetate single crystals were reported as promising nonlinear optical material (Ramesh Kumar et al 2005). In the present study, large size unidirectional single crystal of LTA was grown successfully by the SR method for the first time. The techniques like powder XRD, UV-Vis-NIR, FT-IR, FT-Raman and micro hardness were employed to characterize the grown crystal.

5.2 EXPERIMENTAL PROCEDURE

The experimental setup is as described in Chapter III. The temperature around the growth ampoule was selected based on the solvent used and it is monitored with a temperature controller (40ºC for top and 34ºC for bottom). The seed crystal from the conventional slow solvent evaporation technique was used for the current study. <110> plane of the seed crystal of LTA was chosen

and it was transferred to the saturated solution of LTA. The chemical reaction involved for the grown L-Threonine acetate is given below:

$$C_4H_9NO_3 + CH_3COOH \rightarrow C_4H_{10}NO_3^{+}\ CH_3COO^{-}$$

Growth of highly transparent single crystal of LTA of 10 mm diameter and 40 mm length was harvested in a period of 30 days and reported for the first time. The crystal along with reported crystal (Ramesh Kumar et al 2005) grown by temperature lowering method is shown in Fig.5.1. The average growth rate was found to be nearly 1.5 mm per day. From this, it is depicted that the average growth rate of crystal by SR method was higher than the conventional method under prevailing conditions.

5.3 RESULTS AND DISCUSSION

5.3.1 Powder XRD studies

The grown LTA sample was crushed as fine powder for X-ray diffraction studies. The recorded X-ray diffraction pattern for powdered LTA sample is shown in Fig 5.2. The recorded spectrum of the sample was taken at room temperature in a 2θ range of 10 to 70° using CuKα radiation of wavelength 1.5418 Å. From the diffraction pattern, the d-spacing and hkl values for each diffraction peak in the corresponding spectrum of sample were identified. Using the orthorhombic crystallographic equation, the lattice parameter values of LTA were calculated and compared with the reported values (Ramesh Kumar et al 2005). It is confirmed that LTA belongs to orthorhombic crystal system and the lattice parameter values are shown in Table 5.1.

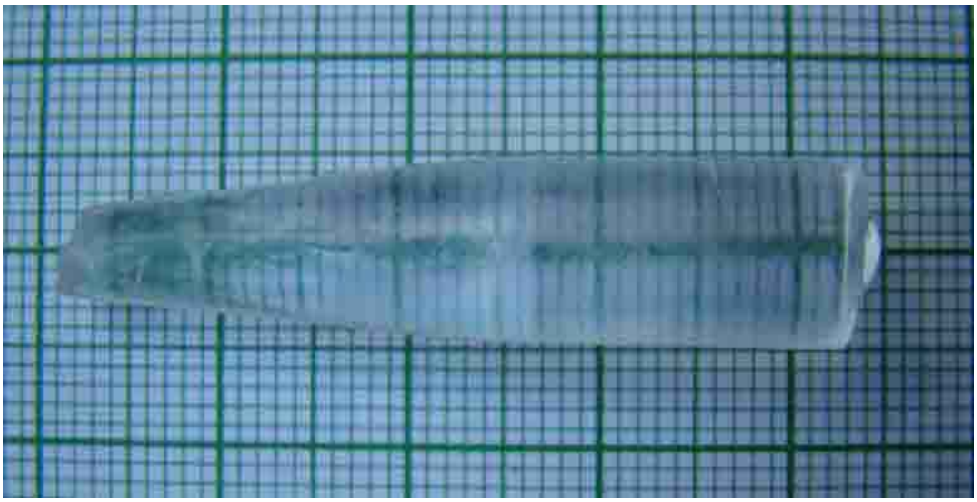

Fig 5.1 LTA crystal grown by SR method

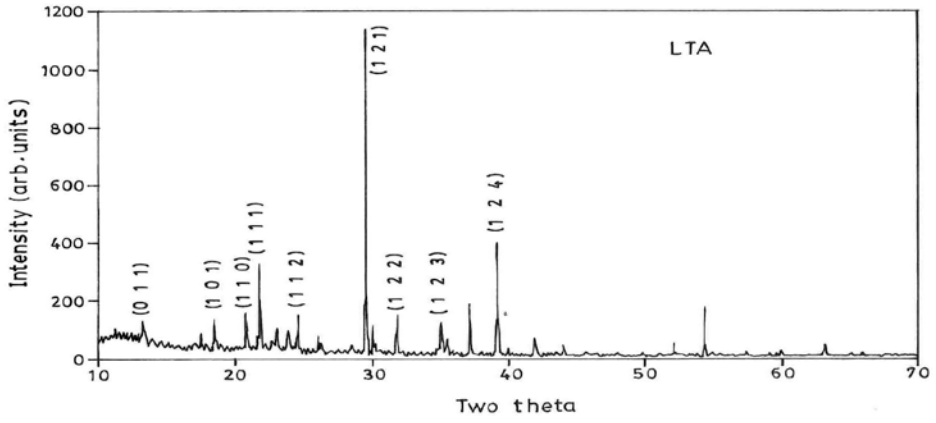

Fig.5.2 Powder X-ray diffraction pattern of LTA crystal

Table 5.1 Crystal data of LTA crystal

Empirical formula	$C_4H_{10}NO_3^+CH3COO^-$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a	5.136 Å
b	7.727 Å
c	13.943 Å
α	90^o
β	90^o
γ	90^o
V	553.34 $Å^3$

5.3.2 CHN analysis

For identifying the synthesized material, the CHN analysis was employed along with powder X-ray diffraction (XRD) analyses. The elemental analysis of LTA was performed using Elementar Vario EL 111 Elemental analyzer. The theoretical and experimental atomic weight percentages are summarized in Table.5.2. Thus the chemical composition of LTA is established.

5.3.3. Vibrational Spectrocopy

The FT-IR spectrum was recorded in the range 450 cm^{-1} – 4000 cm^{-1} employing BRUKER IFS 66V FT-IR spectrometer (Fig 5.3). In order to qualitatively analyze the presence of functional groups in LTA, Fourier Transform Raman (FT-Raman) spectrum was recorded in the range 130 – 3700 cm^{-1}. The recorded FT-Raman spectrum of LTA is shown in Fig 5.4.

N-H Vibrations

The N-H stretching vibrations generally give rise to bands at 3500-3300 cm^{-1} (Bellamy L.J et al 1975 and Spire A et al 2000). In our present study the NH scissoring mode occurred at 3168 cm^{-1}. In the FT-Raman spectrum the weak absorption at 3100 cm^{-1} is due to the NH stretching of amino group. NH_2 deformation is recorded at 1450 cm^{-1}.

Carboxly vibrations (COOH)

These stretching and bending vibrations of acid group are generally expected in the region 1400-1200 cm^{-1} (Roeges N.G.P et al 1994).

Table 5.2 Results of elemental analysis of LTA crystal

Molecular Weight: 179.17 g/mol		
Elements	Weight % composition	
	Theoretical	Experimental
C	40.22	40.11
H	7.31	7.42
N	7.82	7.91

The presence of strong absorption bands at 1626 and 1319 cm^{-1} was confirmed the presence of COOH and COO^- groups in L-Threonine Acetate crystals. The peak at 1626 cm^{-1} is due to C-O stretch of COOH and the aliphatic CH bend appears at 1319 cm^{-1}. The in-plane O-H deformation vibration usually appears as strong band in the region 1440-1260 cm^{-1} (Chandraa S et al 2011). In the FT-Raman spectrum the peak at 1337.9 cm^{-1} is due to C=O stretching.

O-H Vibrations

The O-H group vibrations are likely to be the most sensitive to the environment and are generally (Sajan. D et al 2006) observed in the region around 3500 $cm^{-1.}$ In the case of the un-substituted phenols, it is shown that the frequency of O-H stretching vibration in the gas phase is 3657 cm^{-1} (Michalska. D et al 1996). The O-H in-plane bending vibration lies in the region 1150-1250 cm^{-1} and is not much affected due to hydrogen bonding unlike to stretching and out – of – plane bending frequencies (Michalska. D et al 1996). For the associated molecule the O-H out-of-plane bending mode lies in the region 517-710 cm^{-1} in both inter molecular and intra molecular associations, the frequency is at a higher value in free O-H (Varsanyi. G et al, 1974). In the FT-Raman spectrum the OH stretching gives a peak at 2988.9 cm^{-1}.

5.3.4 NLO studies

An input pulse of 6.2 mJ was used to illuminate the freshly powdered sample of particle size (above 150 μm). The NLO property of the grown LTA single crystal was analyzed by Kurtz technique (Kurtz et al 1968). This study confirmed the green emission of a crystal carried out by SHG test.

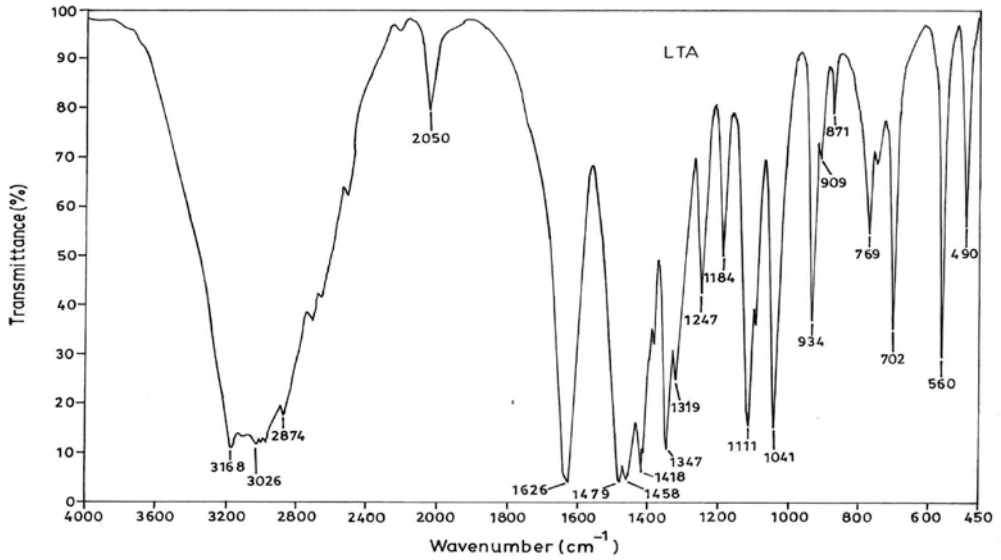

Fig 5.3. FT-IR spectrum of LTA

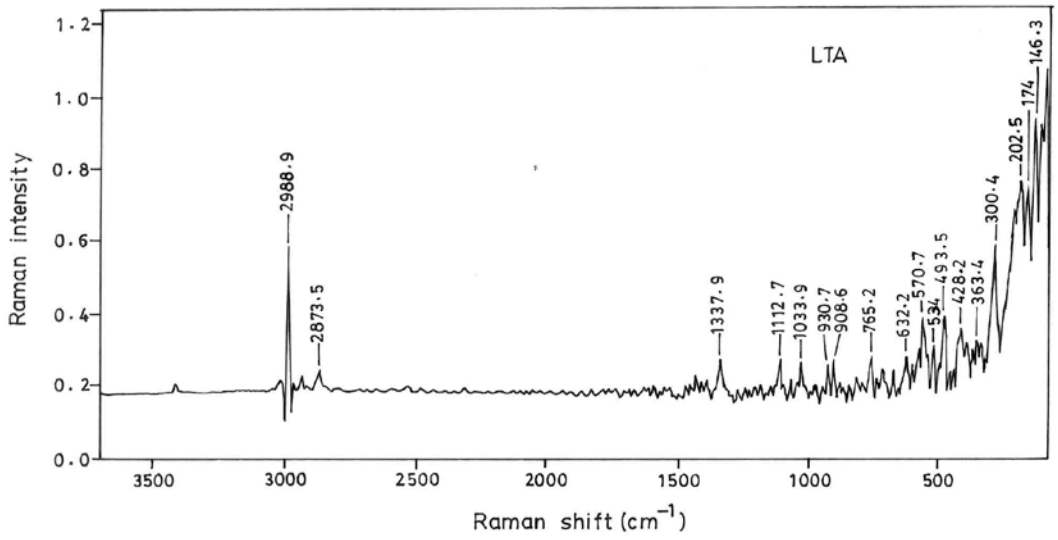

Fig.5.4 FT- Raman spectrum of LTA

A relevant comparison was made on KDP with LTA. The reference material was also powdered and used for further studies. The experimental samples reported an input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 89.02 mW for KDP and 268.50 mW for LTA. It is thus elucidated that the SHG efficiency of LTA is 3.0 times higher than that of KDP.

5.3.5 Laser Induced Damage Threshold study

The suitability of LTA crystal for NLO applications was investigated from laser damage threshold and the value was reported as 8.2 GW/cm^2 using a laser setup in single shot mode.

5.3.6 UV-Vis-NIR spectrum

The absorption spectra of the directional SR was studied by a Varian Cary 5E spectrophotometer. A crystal of 1mm thickness was used to perform UV–Vis-NIR absorption study (Fig 5.5). It was found that the lower UV-cutoff wavelength was 248 nm; hence the crystal can be used for laser applications.

5.3.7 Microhardness test

Vickers micro hardness indentations were made on the LTA crystal at room temperature using a Leitz-Wetzler hardness tester. The micro hardness number, Hv was determined from the relation, Hv = [1.8544 P/d^2] Kg / mm^2, where *P* is the load in gm, d the diagonal length of the diagonal of the indentation impression in mm and Hv the Vickers hardness in kg/mm^2. A plot is drawn between hardness number and applied load. It is observed that the hardness value is turn to decrease as load increase (Fig 5.6) which is in agreement with the normal indentation size effect (ISE) (Madhavan et al 2006).

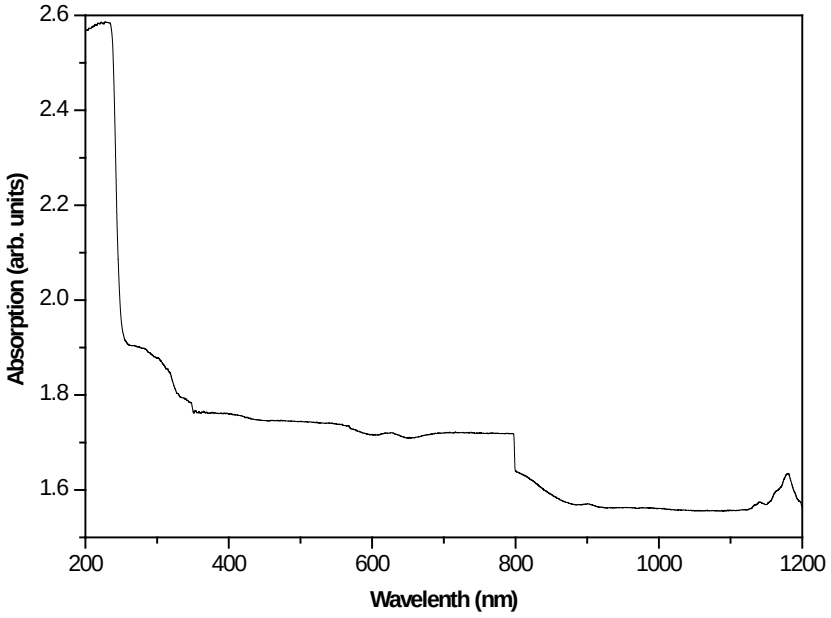

Fig.5.5. UV - Vis – NIR Absorption Spectrum of LTA Crystal

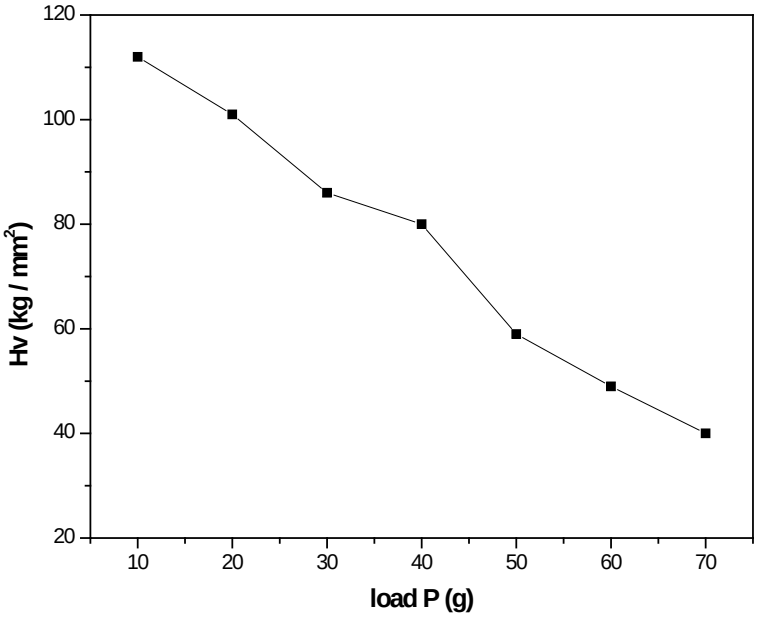

Fig.5.6 Vickers micro hardness Profile of LTA

5.3.8 Thermal studies

LTA crystals were subjected to thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) simultaneously using STA 409C instrument, in the nitrogen atmosphere at a heating rate of 10 K/min. Fig 5.7 shows the resulting TGA and DTA traces of the crystal. The decomposition of the material starts at 260ºC. The material was found to be thermally stable up to 260ºC, and the sharp weight loss of the material starts around 260ºC. The DTA trace of LTA shows that, there is a sharp endotherm matching with the decomposition of LTA.

5.3.9 Dielectric studies

The dielectric study of LTA single crystals were carried out using the instrument, HIOKI 3532-50 LCR HITESTER. The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 5 MHz at room temperature. The plot of dielectric constant (ε_r) versus log frequency is shown in Fig 5.8. The dielectric constant is high at low frequencies and decreases with the applied frequency for LTA crystals. The low value of ε_r at higher frequencies is due to the loss of significance of the polarizations gradually.

The variation of dielectric loss with frequency is shown in Fig 5.9. The low dielectric loss with high frequency of the crystal proves that this material possess enhanced optical quality with lesser defects. This characteristic is an important parameter which is of vital importance for nonlinear optical materials in their applications.

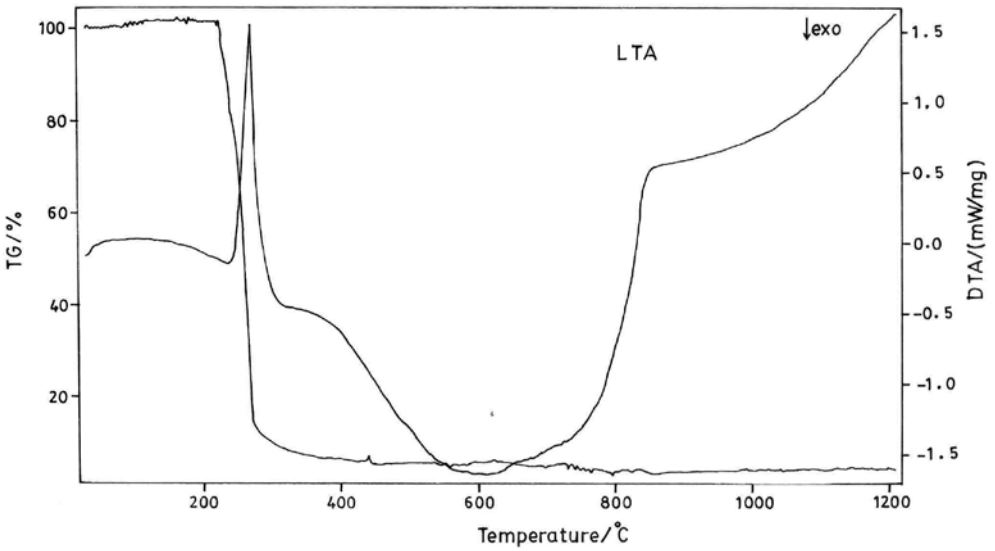

Fig 5.7 TGA and DTG thermogram of LTA crystal

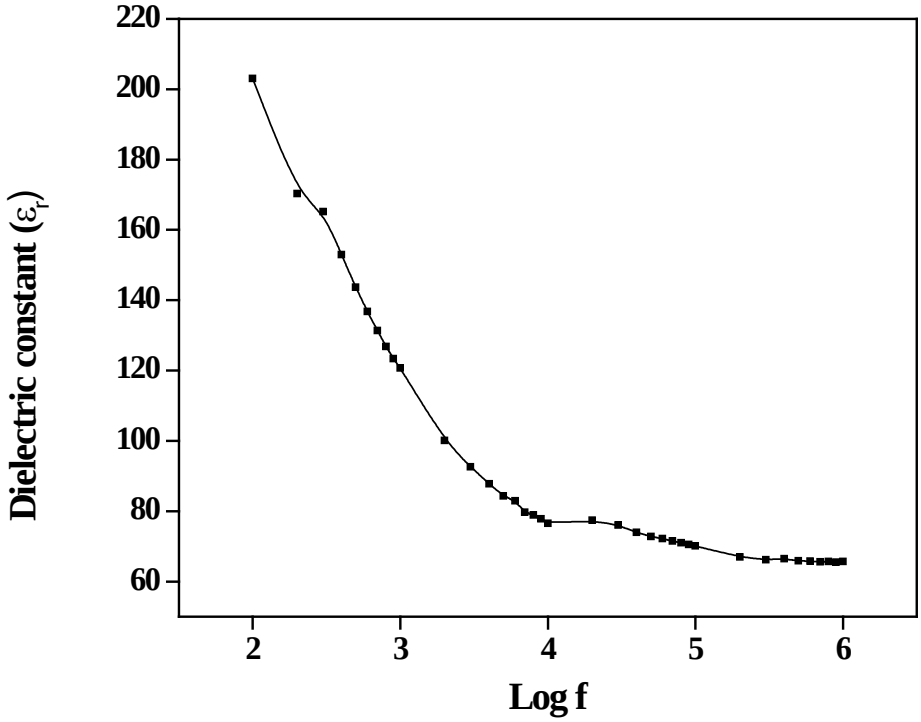

Fig 5.8 Plot of dielectric constant versus log frequency

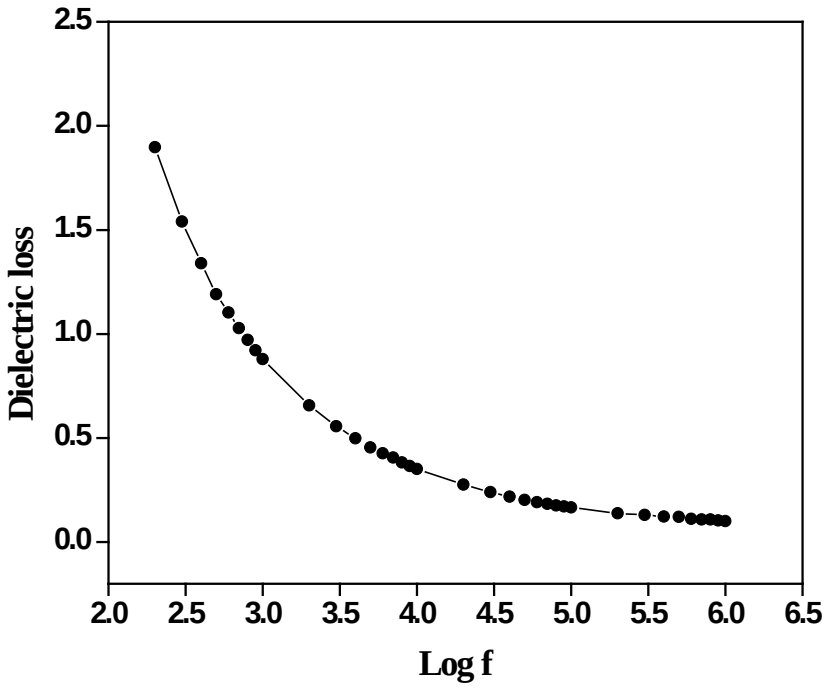

Fig 5.9 Plot of dielectric loss versus log frequency

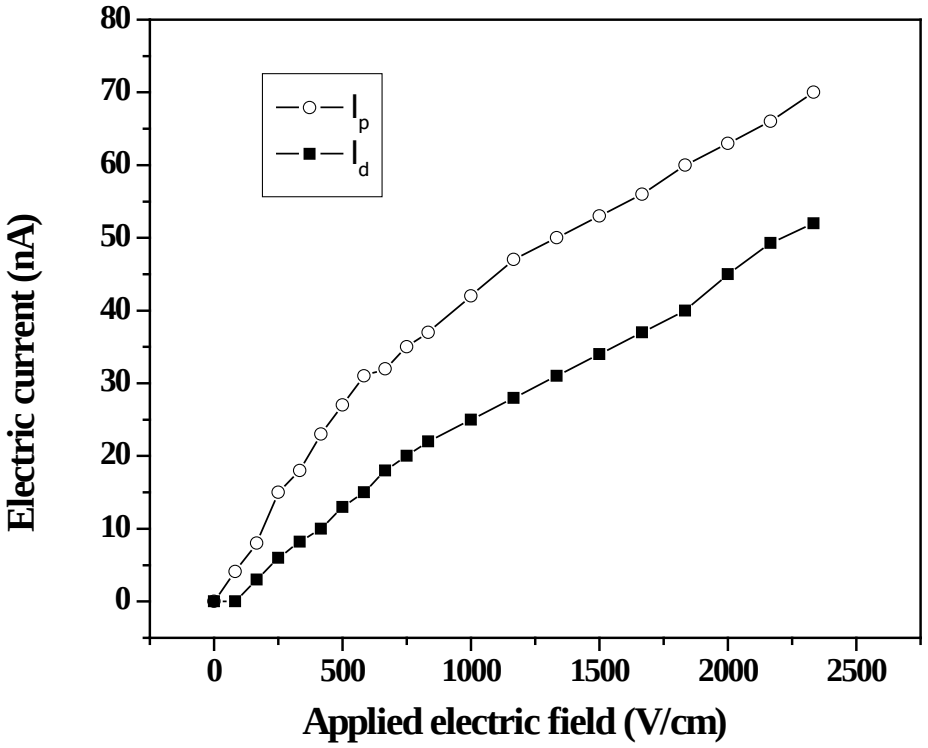

Fig 5.10 Field dependent conductivity of LTA single crystal

5.3.10 Photoconductivity studies

Photoconductivity studies were carried out at room temperature for the LTA crystal using keithley 485 picoammeter. Fig. 5.10 shows the plot of photocurrent and dark current as a function of the applied field for LTA. The dark current was recorded for the samples by keeping them unexposed to any radiation. The light from the halogen lamp (100 W) containing iodine vapour was focused on the respective sample and the photo currents of the samples were measured. The DC inputs were increased in steps and the photo currents were measured for the LTA sample. It is observed from the plot that darkcurrent (I_d) and photocurrent (I_p) of the sample increase linearly with the applied field and the photocurrent is always higher than the dark current, hence it is concluded that LTA shows positive photoconductivity.

5.4 CONCLUSION

Good quality single crystal of L-Threonine acetate was grown successfully by unidirectional solution growth SR method. The lattice parameters were determined from the powder XRD and it is shown that it belongs to the orthorhombic crystal system with a space group of $P2_12_12_1$. The FT-IR and FT-Raman spectral studies confirmed the presence of the functional group and their different mode of vibrations. The UV–Vis-NIR absorption study confirms the wide transparency of the SR grown material. Vickers microhardness was determined to understand the mechanical property of the grown crystal. It is also understood from the present work that the SR technique is found to be a suitable method to grow high quality and large- size single crystal of L-Threonine acetate.