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# Vibrational Spectroscopic Studies and Mechanical Properties of Unidirectional L-alanine Acetate Single crystal

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## ABSTRACT

*Unidirectional <100> L-alanine acetate (LAlA) single crystal was grown for the first time and reported. The grown crystal was characterized by single crystal X-ray diffraction (XRD) studies to confirm the crystal structure. Investigation has been carried out to assign the vibrational frequencies of the grown crystals by Fourier Transform infrared (FT-IR) and Fourier Transform Raman (FT-Raman) spectroscopy technique. The mechanical properties of the grown crystals have been studied using Vickers microhardness tester. The Second Harmonic Generation (SHG) in the sample was confirmed and estimated by Nd: YAG laser employing the Kurtz and Perry powder technique. The laser damage threshold of the grown crystal was also found. Thermal stability of the grown crystal was determined by Thermogravimetic (TG) and Differential theromogravimetric (DTG) analysis. Dielectric and photoconductivity studies were also carried out for the grown LAlA crystals.*

**Key words:** NLO; Unidirectional growth; LA*l*A; FT-Raman; Thermal studies.

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## INTRODUCTION

In the recent past, molecular non linear optical (NLO) materials have been appropriately investigated due to their high performance with respect to electro-optic effect as compared to inorganic NLO materials. Organic NLO material serves an important role in second harmonic generation (SHG), frequency shuffling, under water treatment and in medical applications. In recent trend, amino acid crystals have been grown and their NLO significances are subjected to extensive investigation by several researchers for various applications [1, 2]. Though various techniques to grow bulk single crystals are available, the Sankaranarayanan Ramasamy (SR) method is the best solution growth technique which gives unidirectional crystals with appreciable quality as well as the maximum efficiency [3]. In the present work, bulk single crystal of LA*l*A, a promising NLO crystal was grown by SR method. The grown crystal was characterized by Single Crystal XRD, UV-Vis-NIR, FT-IR, FT-Raman, Vickers micro hardness, thermal and dielectric studies.

## MATERIALS AND METHODS

The SR method consists of heating coils, seed-mounting pad, growth portion and top portion. Heating coil is placed at the top of an ampoule and it was connected to a temperature controller [3]. Growth rate of this method depends on the temperature of SR coil. Water has been used as a solvent for the growth of LA*l*A single crystal. The reaction that takes place between L-alanine and acetic acid in water medium is as follows:

$$C_3H_7NO_2 + CH_3COOH \longrightarrow C_3NO_2H_8^{+}CH_3COO^{-}.$$

Highly transparent single crystal of LA*l*A single crystal of 10mm diameter and 44 mm length was grown in a period of 23 days (Figure.1) and reported for the first time. <100> plane of the seed crystal was selected for unidirectional crystal growth. <100> face of the seed has been mounted at the bottom of the ampoule and this face has been exposed to the solution of LA*l*A. The saturated solution of LA*l*A has been fed in to the inner region of the ampoule. The temperature difference between the top and the bottom region of SR method ampoule has been carefully maintained (40ºC for top and 33ºC for bottom). It was observed that under controlled super saturation, the uniform growth rate of crystal was achieved.

## RESULTS AND DISCUSSION

### 3.1 Single Crystal XRD

Single crystal X-ray diffraction analysis was carried out to confirm the crystalline quality and also to identify the universal lattice parameters using ENRAF NONIUS CAD F4 diffractometer. It is observed that the LA*l*A single crystal belongs to orthorhombic crystal system with a space group $P2_12_12_1$ and unit cell dimensions a=6.262Å, b=19.5330Å, c=5.1588Å.The volume of the system is V=631.002Å$^3$. From these values, it is observed that the unit cell parameters were in very good agreement with the reported values [4].

### 3.2 FT- Raman and FT-IR spectra

In order to qualitatively analyze the presence of functional groups in LA*l*A, Fourier Transform Raman (FT-Raman) and Fourier Transform Infra Red (FT-IR) spectra were recorded in the range 500 cm$^{-1}$ – 3500 cm$^{-1}$. The recorded FT-Raman and FT-IR spectra of LA*l*A are shown in Figure.2. The sharp intense peaks in the Raman spectra at 2962 cm$^{-1}$ and 2933 cm$^{-1}$ are probably due to $CH_3$ and $CH_2$ stretching respectively. The peaks at 1305 cm$^{-1}$, 1358 cm$^{-1}$ and 1461 cm$^{-1}$ are for the C=O stretching of carboxylic group. The peak at 1481 cm$^{-1}$ is due to $CH_2$ deformation. The intense peak at 2987 cm$^{-1}$ is due to O-H stretching of carboxylic group. The FT-IR Spectra illustrates the presence of $NH_3^+$ stretching frequencies between 3083 cm$^{-1}$ and 2603 cm$^{-1}$ in the form of a broad strong band with multiple peaks on the low frequency wing. A combination band between 2200 cm$^{-1}$ and 2000 cm$^{-1}$ is assigned to $NH_3^+$ asymmetric deformation and $NH_3^+$ hindered rotation. The FT-IR spectrum show strong absorption at 1620 cm$^{-1}$ indicating the presence of primary amino group. The characteristic absorption at 1519 cm$^{-1}$ was due to symmetric $NH_3$ deformation. The symmetric $CO_2$ stretch shows a strong absorption at 1362 cm$^{-1}$. The absorption at 1306 cm$^{-1}$ was due to CH deformation. The FT-IR and FT-Raman spectra of LA*l*A confirmed the structural aspects of the compound.

### 3.3 UV–Vis–NIR with Energy Band Gap

The absorption of the grown crystal was measured by a Varian Cary 5E spectrophotometer for the wavelength range 200-2000 nm covering the entire UV, visible and high energy part of near IR region (Figure 3) The lower UV-cutoff wavelength is 254 nm, thus ascertain the fact that the crystal can be used for laser applications. In the present work, the absorption coefficient (α) of LA*l*A single crystal was determined from optical absorption measurements, measured at room temperature. Fig 3 also shows the plot of $(\alpha h\nu)^2$ versus hν, the energy gap ($E_g$) is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$ and found to be 5.13 eV.

### 3.4 SHG and Laser Damage Threshold

Freshly powdered sample was illuminated using Q–switched, mode locked Nd: YAG laser with input pulse of 6.2 mJ. The second harmonic (SHG) test by the Kurtz technique confirmed the NLO property of the grown LA*l*A single crystal [5]. For quantitative work, single crystals of LA*l*A were powdered and then graded by the use of standard sieves to desired range of particle sizes. To make relevant comparison with known SHG materials, KDP was also powdered and sieved into the same particle size range. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 91.66 mW and 238.71 mW were obtained through KDP and LA*l*A samples respectively. Thus the SHG efficiency of LA*l*A is 2.5 times higher than KDP. The laser damage threshold of LAlA was carried out using a laser setup in single shot mode and it was found to be 8.5 GW / $cm^2$, which indicates the suitability of this crystal for NLO applications.

### 3.5 Vickers Micro Hardness Study

Microhardness studies have been carried out on the LA*l*A single crystals using HMV SHIMADZU microhardness tester, fitted with diamond Vickers pyramidal indenter. The average value of the diagonal lengths of the indentation mark for each load was used to calculate the hardness. The Vickers's micro hardness number was determined from the relation Hv = 1.8544 $P/d^2$ $Kg/mm^2$ where *P* is the load in gm, *d* the length of the diagonal of the indentation impression in mm and $H_V$ the Vickers hardness in $kg/mm^2$. It was observed that the hardness value decrease as load increase as depicted in Figure 4. The decrease of the microhardness with the increasing load is in agreement with the normal indentation size effect (ISE). By plotting log p verses log d (Figure. 4), the value of the work hardening coefficient n was found to be 1.44. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials [6]. Hence, it is concluded that LA*l*A is a hard material.

**3.6 Thermal analysis** The thermo gravimetric analysis of pure and doped LA*l*A was carried out between 23 and 1200˚C in nitrogen atmosphere at a scanning rate of 10K/min. The TGA and DTG traces are shown in Figure 5. The material is thermally stable up to 300ºC, and the sharp weight loss of the material starts around 300˚C. There is a single stage of weight loss which establishes the quality of the grown crystals. The sharp peak in the DTG trace coincides with decomposition shown in the TGA trace.

### 3.7 Dielectric studies

The dielectric constant and dielectric loss of L-alanine acetate were measured using HIOKI 3532 LCR HI TESTER in the frequency range from 100Hz to 5MHz. The samples were coated with silver paint to ensure good electrical contact between the crystal and the electrodes, and mounted between the two electrodes. The capacitance of the parallel plate capacitor formed by the electrodes, with the sample as a dielectric medium was measured. The variation of capacitance was recorded in the frequency range 100Hz to 5MHz at room temperature. The dielectric constant ($\varepsilon_r$) of the material was calculated for different frequencies from the measured capacitance values.

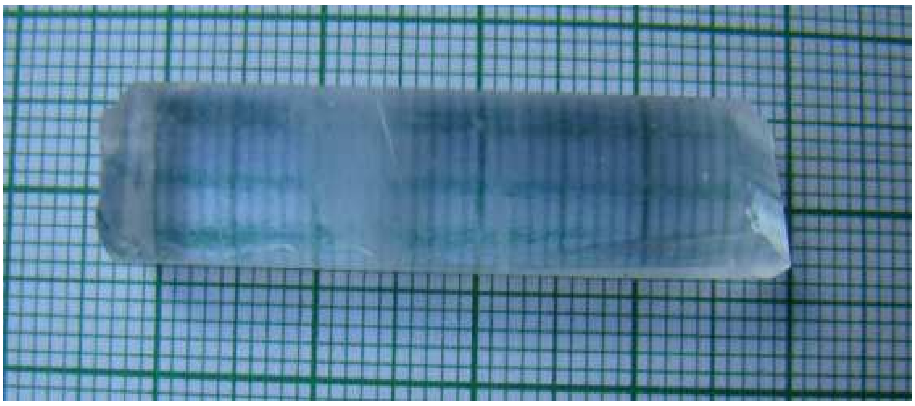

**Fig.1. LA*l*A crystal grown by SR method**

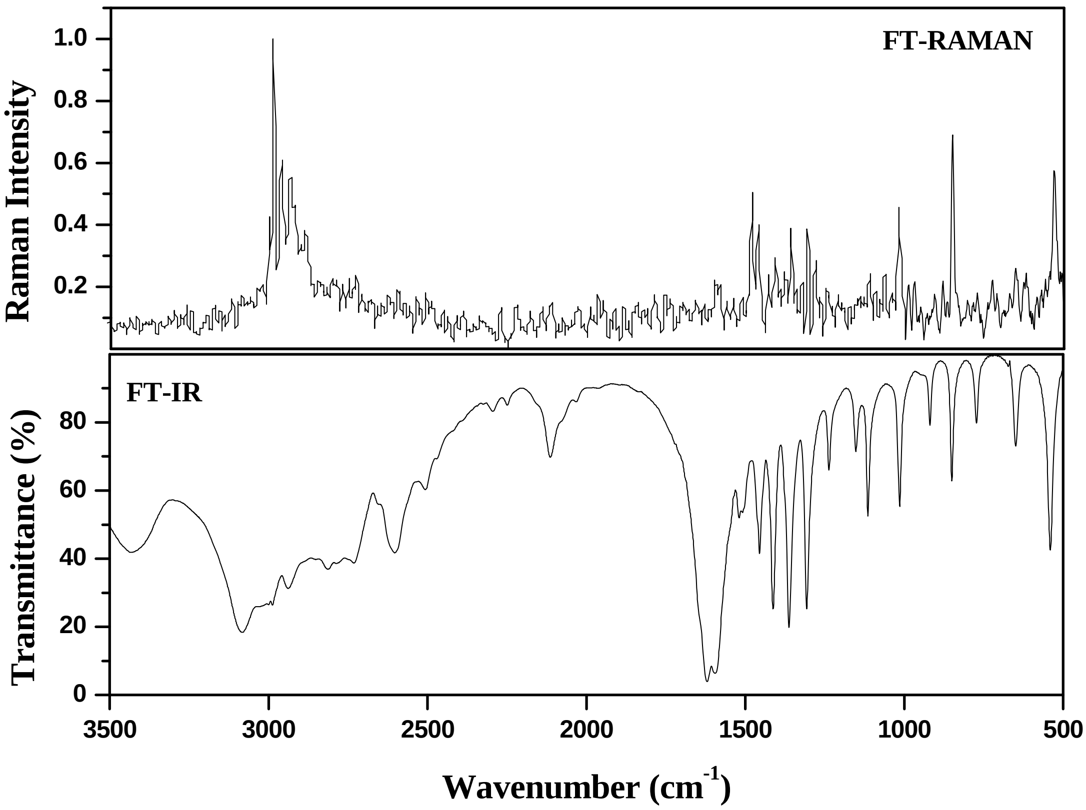


**Fig.2. FT- Raman and FT-IR spectra of LA*l*A single crystal**

The plot of dielectric constant verse applied frequency was shown in the Figure 6. It was observed that dielectric constant has high valued in the low frequency region and thereafter decrease with the applied frequency. The high value of $\varepsilon_r$ at low frequencies may be due to the presence of all the four polarizations namely space charge, orientational, electronic and ionic polarization and the low values at higher frequencies may be due to the loss of significance of these polarization gradually. The variations of dielectric loss with frequencies were shown in the Figure 7. For the given sample if there is low dielectric loss with high frequency, it suggests that the sample possess good optical quality with lesser defects.

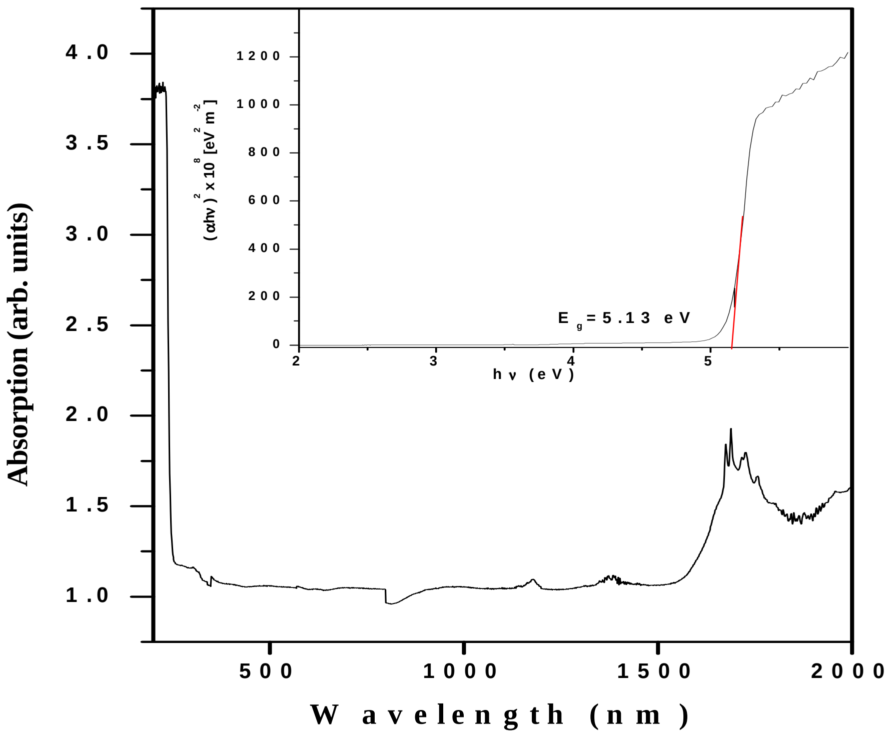


**Fig.3. UV–Vis–NIR absorption spectra**

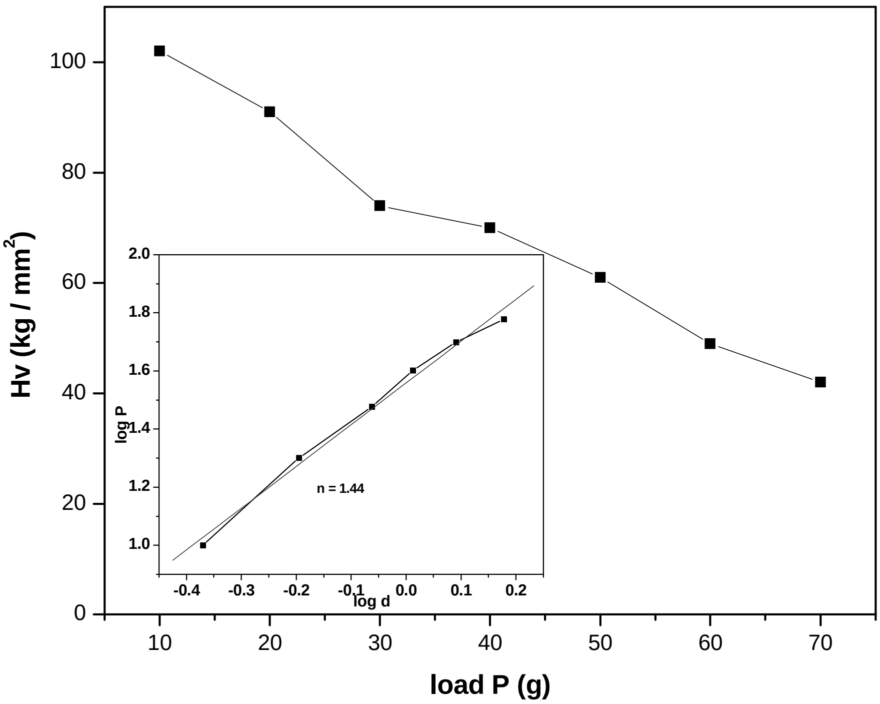


**Fig.4. Vickers hardness profile**

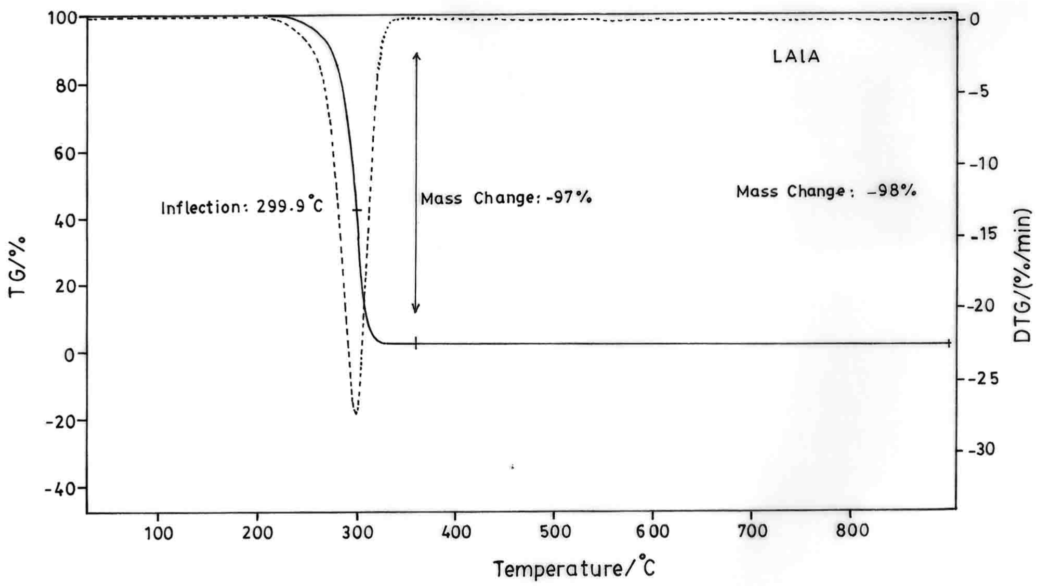


**Fig 5 TGA and DTG thermogram of LAlA crystal**

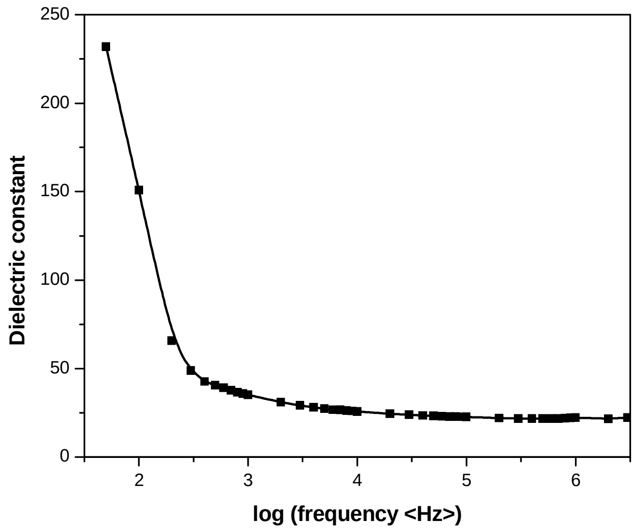


**Fig 6 Plot of dielectric constant versus log frequency**

### 3.8 Photoconductivity studies

Photoconductivity of the crystal was studied using Keithley 485 Picoammeter at room temperature. By connecting the sample in series to a Dc power supply and a picoammeter, the dark conductivity of the sample was studied. Electrical contacts were made at a spacing of about 0.9mm on the samples using silver paint. Increasing the DC input 0 to 200 volts in steps of 20, the corresponding values of dark current was noted from the electrometer. In order to measure the photo current, the sample was illuminated with a halogen lamp (100W) by focusing a spot of light on the sample with the help of a convex lens. The DC input was increased in the same range as done in the previous case and the corresponding photocurrents were measured. The variations of photocurrent ($I_p$) and dark current ($I_d$) with applied field of the samples were shown in the Figure 8. It was observed that both the photo and dark currents L-alanine acetate crystals increase linearly with the applied electric field, with the photo current more than the dark current which was termed as positive photoconductivity.

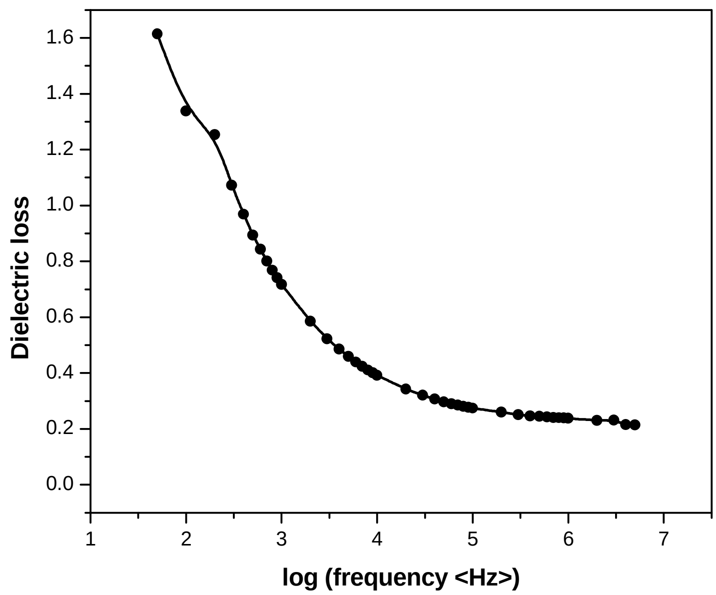


**Fig 7 Plot of dielectric loss versus log frequency**

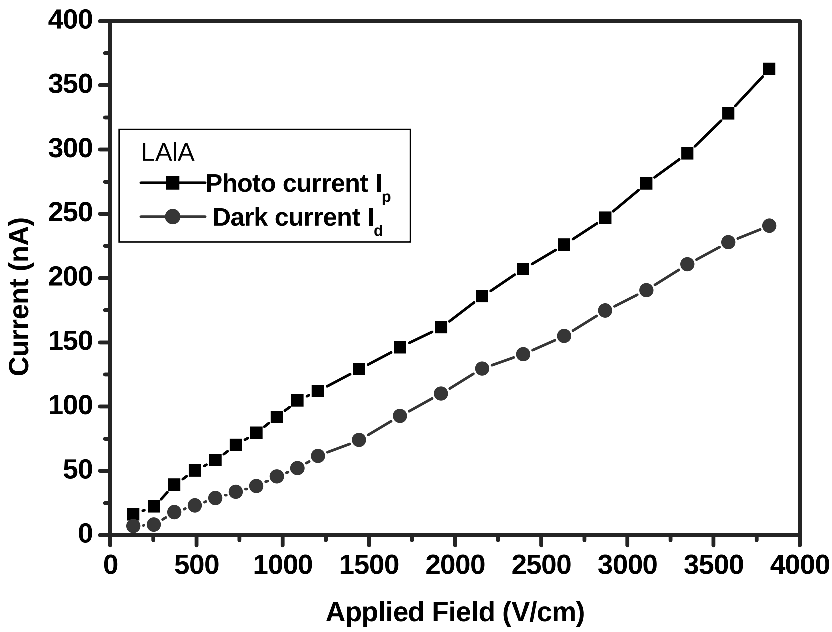


**Fig 8 Photo conductivity of LA*l*A**

## CONCLUSION

Good quality unidirectional single crystal of L-alanine acetate has been grown successfully by SR method by optimizing the growth conditions. The lattice parameters were determined from the single crystal XRD which confirms that the crystal 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 analysis showed that the material was suitable for laser applications. Vickers micro hardness studies were performed to understand the mechanical property of the grown crystal. It was also understood from the present work that the SR technique was found suitable to grow high quality and large- size single crystal of L-alanine acetate.

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