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Dielectric and photoconductivity properties of semiorganic nonlinear optical LMHCl crystals

M. Kumar, S. Tamilselvan, M. Vimalan[a], P. Saravanan[a], S. Aruna[b], R. Kanagadurai[c]*

Department of Physics, Arignar Anna government Arts College, Cheyyar, Tamilnadu, India.
[a] Department of Physics, Thirumalai Engineering College, Kancheepuram, Tamilnadu, India.
[b]Department of Physics, Government Arts College for Men, Nandanam, Chennai, India.
**[c]Department of Physics, Presidency College, Chennai, Tamilnadu, India.*

ABSTRACT

The potential semiorganic nonlinear optical single crystal of L-Lysine monohydrochloride dihydrate (LMHCl) has been grown by slow evaporation solution growth technique at room temperature. It crystallizes in the monoclinic system with space group of $P2_1$. The dielectric behavior of the crystal is determined at room temperature in the frequency range of 100 Hz to 5 MHz. The dielectric studies prove the low values of dielectric constant and dielectric loss in the sample at high frequency. The negative photoconducting nature of the sample is confirmed by photoconductivity study. The nonlinear optical property of the crystal is tested by Nd:YAG laser source. The ac/dc conductivity studies are carried out and the activation energies are determined.

INTRODUCTION

In the recent past, nonlinear optical (NLO) single crystals has emerged as one of the most attractive fields of research in view of its potential applications in the area of optical switching, optical computing, optical data storage, optical bistability, etc. [1–2]. Recently, complexes of amino acids have been explored. Most of the natural amino acids show nonlinear optical effect. The tetrahedral array of four different groups about α- carbon atom confers optical activity on amino acid. In solid state, amino acid contains a deprotonated carboxyl acid group (COO^-) and protonated amino group (NH_3^+). This zwitter ionic nature favours crystal hardness, thus making them ideal candidates for NLO devices [3]. Complexes of amino acids with inorganic acids and salts are promising materials for optical second harmonic generation (SHG), as they tend to combine the advantages of the organic amino acid with that of the inorganic acid [4]. In recent years, efforts have been made to synthesize amino acid mixed organic inorganic complex crystals, in order to improve the chemical stability, laser damage threshold, linear and nonlinear optical properties [5-6]. L-Lysine monohydrochloride dihyrate (LMHCl) is one such recently developed semiorganic NLO crystals and its growth has been reported [6]. The present investigation deals with the growth of LMHCl single crystal by slow solvent evaporation technique. The grown crystal has been subjected to single crystal XRD, dielectric and photoconductivity studies. The SHG studies of the LMHCl was also studied using Nd:YAG Q-switched laser.

MATERIALS AND METHODS

The LMHCl crystal was synthesized by taking L-Lysine and hydrochloric acid in the appropriate ratio. The calculated amounts of L-Lysine and hydrochloric acid were thoroughly dissolved in double distilled water using a temperature controlled magnetic stirrer. The solution was stirred well and slightly warmed using magnetic stirrer and filtered using filter paper and transferred to Petri dish. The prepared solution was allowed to evaporate at room temperature, which yield the salt of LMHCl. The purity of the synthesized salt was further increased by successive recrystallization process. The supersaturated solution of LMHCl was prepared in accordance with the solubility data. Single crystals of LMHCl were grown by slow evaporation technique at room temperature (30°C). Crystals obtained by spontaneous nucleation were used as seed crystals. Good quality of crystals has been harvested in a span of 25 days.

3. Characterization

The single crystal XRD was collected using an automated diffractometer (Messrs Enraf Nonius, The Netherlands). The structure was solved by the direct method and refined by the full matrix least square technique using the SHELXL program. The NLO efficiency of LMHCl crystal was evaluated by Kurtz and Perry powder technique using a Q-switched, mode locked Nd : YAG laser emitting 1.06 µm, 8 ns laser pulses with spot radius of 1 mm. The input laser beam was passed through an IR reflector and then directed on the powdered sample. The light emitted by the sample was measured by the photodiode detector and oscilloscope assembly. The *ac* conductivity, dielectric constant and dielectric loss of the sample were measured at different temperatures using HIOKI 3532-50 LCR HITESTER in the frequency range from 50 Hz – 5 MHz. LMHCl sample of uniform cross sectional area 2 x 2 mm^2 and thickness 1 mm was coated with silver paint to provide good ohmic contact. The dielectric constant and dielectric loss were measured by varying the frequency, for a fixed applied voltage. The measurement of *dc* electrical conductivity was done using the conventional two-probe technique for temperatures ranging from 308 to 368 K. The photo current and dark current of the crystal was measured using Keithley 485 picoammeter. The experiment was performed at room temperature.

3.1 Single crystal XRD study

The structure of LMHCl was solved by the direct method and refined by the full matrix least–square fit technique employing the SHELXL program. It is observed that LMHCl crystallizes in monoclinic structure with space group of $P2_1$. The lattice parameter values a = 5.94 Å, b = 13.4 Å and c = 7.49 Å are in good agreement with the reported values [6].

3.2 NLO test

Second harmonic generation (SHG) efficiency was measured to get an idea how much efficient the material is in transferring energy from fundamental laser beam to second harmonic beam. Powder technique [7] of SHG efficiency measurement is also an extremely valuable tool for screening of materials for second harmonic generation. Second harmonic efficiently test was performed by the Kurtz and Perry powder technique (Kurtz and Perry 1968) using Q-switched, mode locked Nd:YAG laser operating at the fundamental wavelength 1064 nm. For the SHG efficiency measurements microcrystalline material of KDP was used for comparison. When a laser input of 3.2 mJ was passed through LMHCl, second harmonic signal of 97 mV is produced with reference to KDP (55 mV) and the experimental data confirm a second harmonic efficiency of nearly 2 times that of KDP.

3.3 Dielectric studies

Figures 1 and 2 show the variations of dielectric constant and dielectric loss as a function of frequency with varying temperature. The dielectric constant is higher at low frequencies and then decreases with the increasing frequencies and saturates, and dielectric loss decreases with increasing frequency (Figures 1 and 2). The large value of dielectric constant at low frequency is due to the presence of space charge polarization [8]. When the electric charge carriers cannot follow the alteration of the a.c. electric field applied beyond a certain critical frequency [8] the dielectric constant decreases with increase in frequency and remains constant.

Figures 3 and 4 show the variations of dielectric constant and dielectric loss as a function temperature. The dielectric constant increases with the increasing temperature. The hopping (exchange) of the charge carriers in the lattice sites (which is responsible for electrical conduction) is thermally activated by increasing temperature. As a result, dielectric polarization increases causing an increase in dielectric constant and dielectric loss. In addition, both the dielectric constant and dielectric loss increase with temperature (Figures 3-4). The very high value of dielectric constant at lower frequencies may be due to the space charge polarization. It is evident from Figure 4 that the crystal has a very low dielectric loss in the high frequency region, which indicates the lesser number of defects in the crystal.

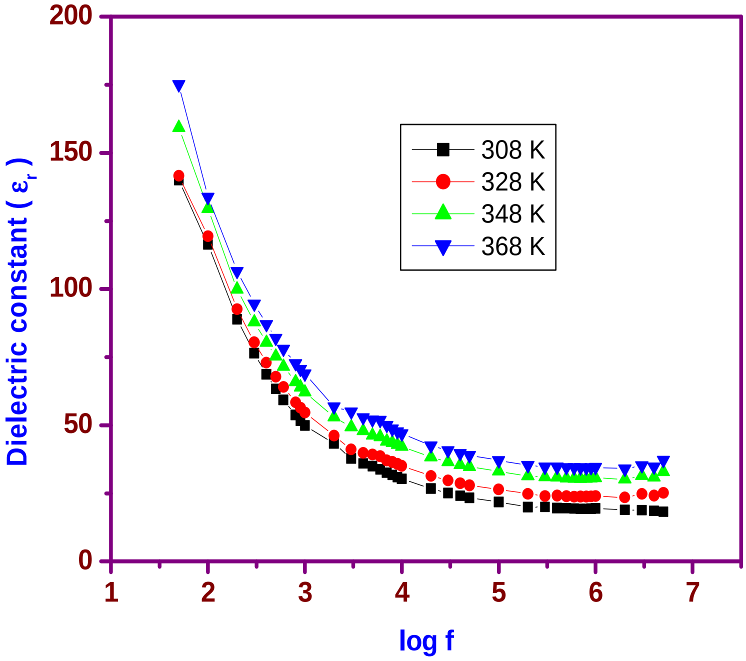

Figure 1. Variation of dielectric constant with log frequency at different temperatures for LMHCl single crystal

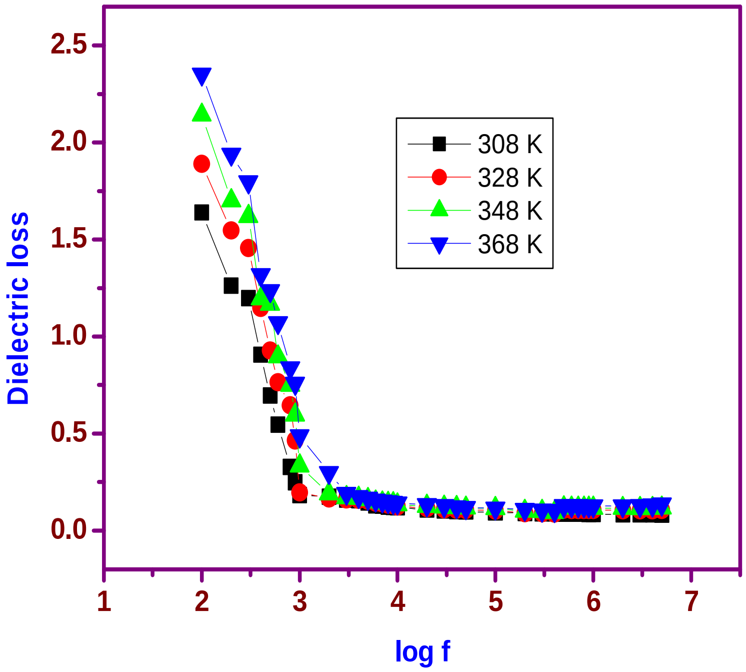

Figure 2. Variation of dielectric loss with log frequency at different temperatures for LMHCl single crystal

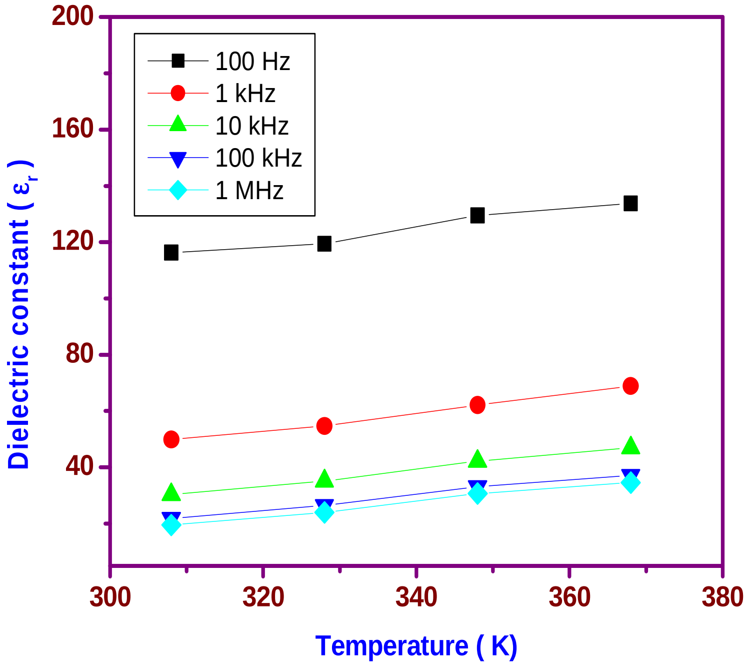

Figure 3. Temperature dependence of dielectric constant for LMHCl single crystal

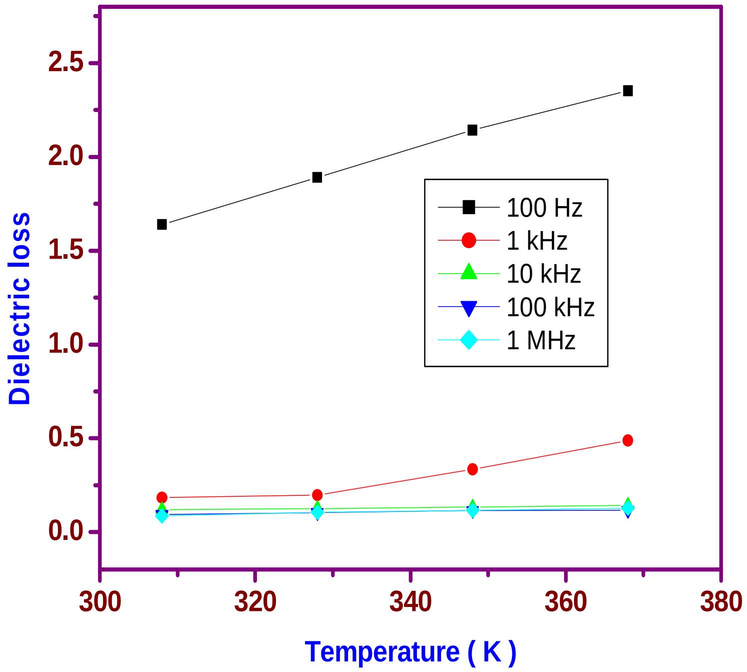

Figure 4. Temperature dependence of dielectric loss for LMHCl single crystal

3.4 *ac* and *dc* Conductivity studies

Figure 5 shows the frequency dependence of the *ac* conductivity in the frequency range of 100 Hz-5 MHz for the temperature interval of 308-368 K for the three samples. It is observed that the *ac* conductivity increases with increasing frequency. The *ac* conductivity plot indicates a typical behavior of most of the solid samples. i.e., a power-law increases at frequencies between 10^5 and 10^6 Hz. Such frequency dependence of the *ac* conductivity is explained in terms of the power law. The power-law dependence of the frequency is of universal nature and corresponds to the short ranges that are separated by energy barriers of varied heights. This regime is attributed to hopping conduction [9-10] which sets in frequency above 10^4 Hz and the regime is clearly visible for the sample under study. As temperature rises, more and more defects are created, and as a result, the conductivity increases, which is predominantly due to moment of defects produced by thermal activation. Plots between ln (σ_{ac}) and 1000/T are found to be very nearly linear (Figure 6). Activation energies are estimated using the slopes of these plots; [E=-(slope) k ×1000]. The variations of activation energies with frequencies are shown in Figure 7. The activation energy is found to increase with increasing frequency.

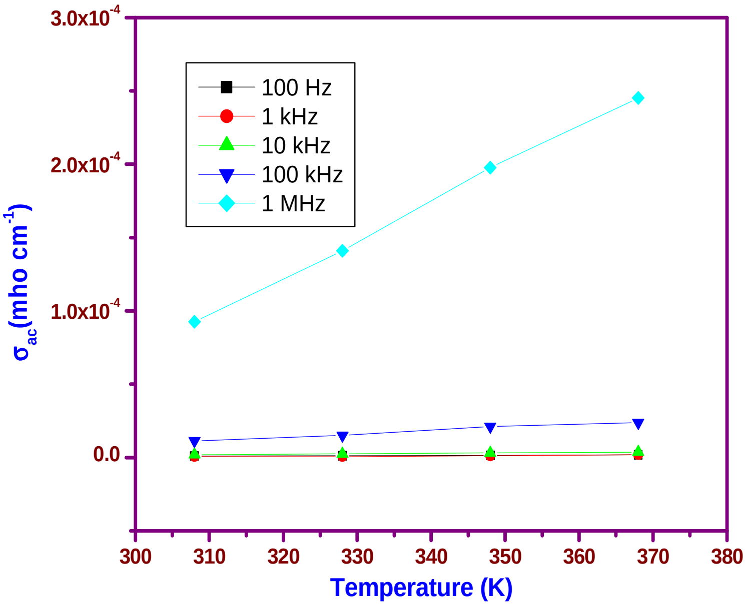

Figure 5. The *ac* electrical conductivities for LMHCl crystal

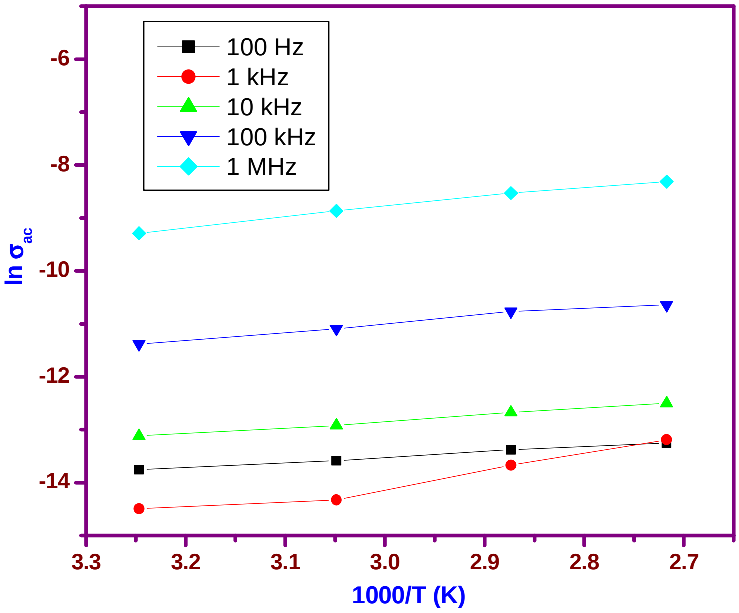

Figure 6. Plot of ln(σ_{ac}) versus 1000/T for LMHCl single crystal

The *dc* electrical conductivity measurement was carried out for the LMHCl crystals using the conventional two-probe technique in the temperature range 308-368 K. The study of *dc* electrical conductivity sheds light on the behaviour of charge carriers under a DC field, their mobility and mechanism of conduction. At any particular temperature, the Gibb's free energy of a crystal is minimum when a certain fraction of ions leave the normal lattice.

As the temperature rises, more and more defects are produced which in turn, increases the conductivity (Figure 8). The *dc* conductivity of the crystal in the higher temperature region is determined by intrinsic defects caused by thermal fluctuations in the LMHCl crystal. The activation energy (E_{dc}) is calculated from the slope of the graph between *ln* (σ_{dc}) *vs* 1000/T (Figure 9) and it is found to be 0.073 eV for LMHCl respectively.

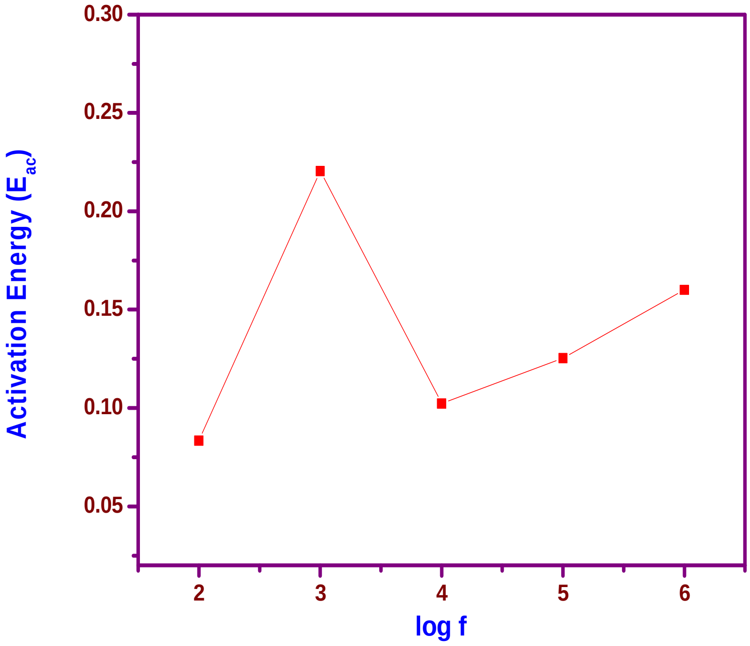

Figure 7. Frequency dependence of *ac* activation energy for LMHCl single crystal

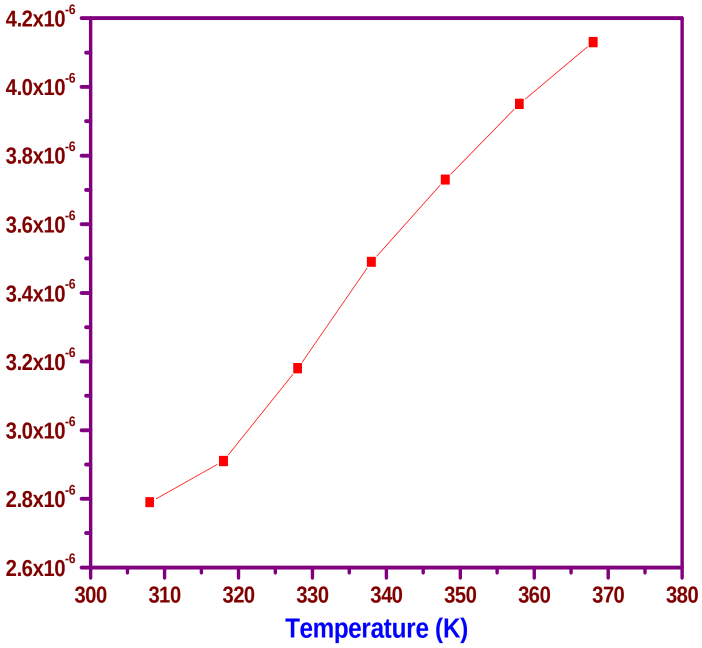

Figure 8. The *dc* electrical conductivities for LMHCl crystal

3.5 Photoconductivity study

Photoconductivity measurements were made using the Keithley 485 picoammeter. The dark current was recorded by keeping the sample unexposed to any radiation. The applied field was varied from 90 to 2550 V/cm. For measuring the photo current, the sample was illuminated with a halogen lamp of 100W power by focusing a spot of light on the sample with the help of a convex lens. The resulting photo current was measured by varying the applied field for the same range. The plots of dark current and photo current versus applied field are drawn on the same graph (Figure 10). It is observed from the plots that the dark current is always higher than the photo current. Thus, LMHCl single crystal is found to exhibit negative photoconductivity.

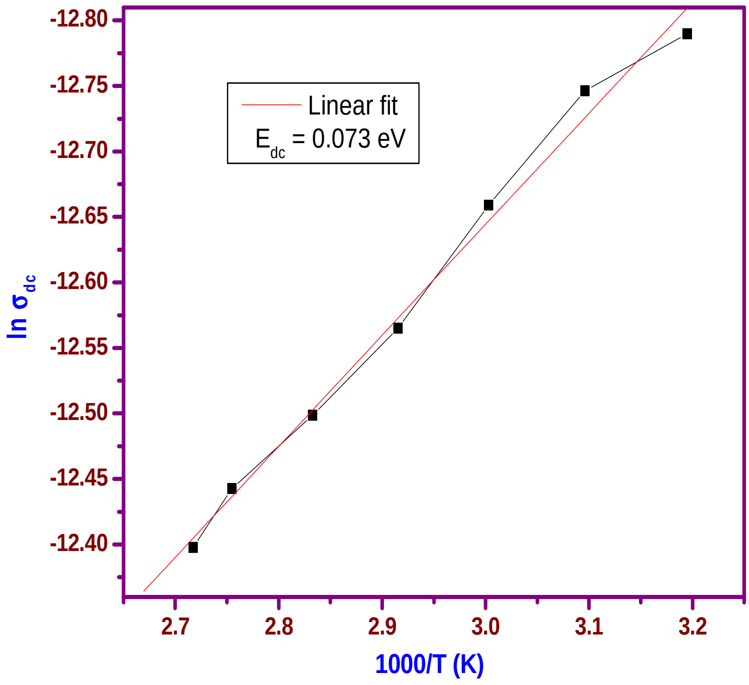

Figure 9. Plot of ln(σ_{dc}) versus 1000/T for LMHCl single crystal

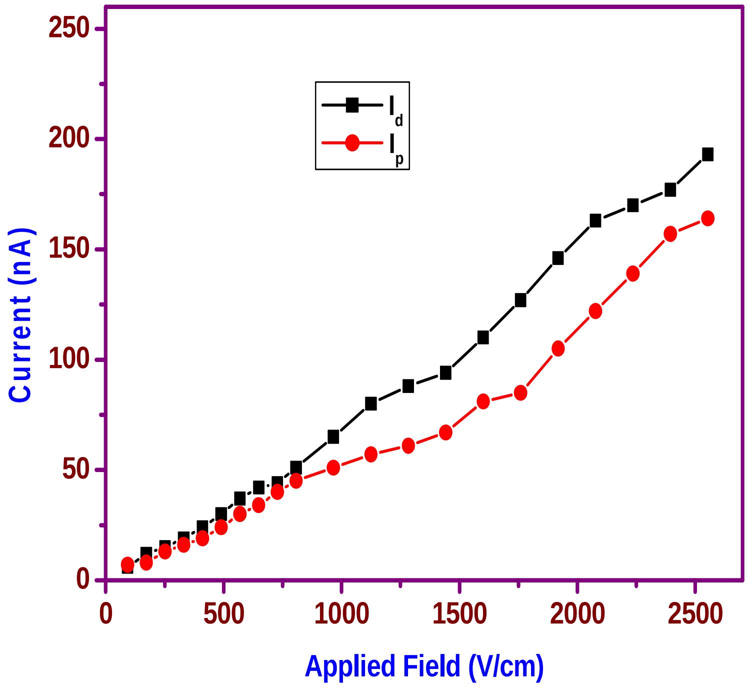

Figure 10. Field dependent photoconductivity of LMHCl single crystal

CONCLUSION

Single crystals of LMHCl of appreciable size with needle morphology were grown by slow evaporation technique at room temperature. Single crystal XRD confirms the grown crystal. The NLO property was confirmed using Nd : YAG laser of wavelength 1064 nm and the efficiency was estimated to be 2 times higher than that of KDP. The microhardness study indicates that the crystal belongs to the class of hard materials. The dielectric studies prove the low values of dielectric constant and dielectric loss in the sample at high frequency. The activation energies are determined from the plots for *ac*/*dc* conductivity. The photoconductivity study ascertains the negative photoconducting nature of the crystal. The promising crystal growth characteristics and properties of LMHCl crystal indicate it as a potential material for photonic, electro-optic and SHG device application.

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