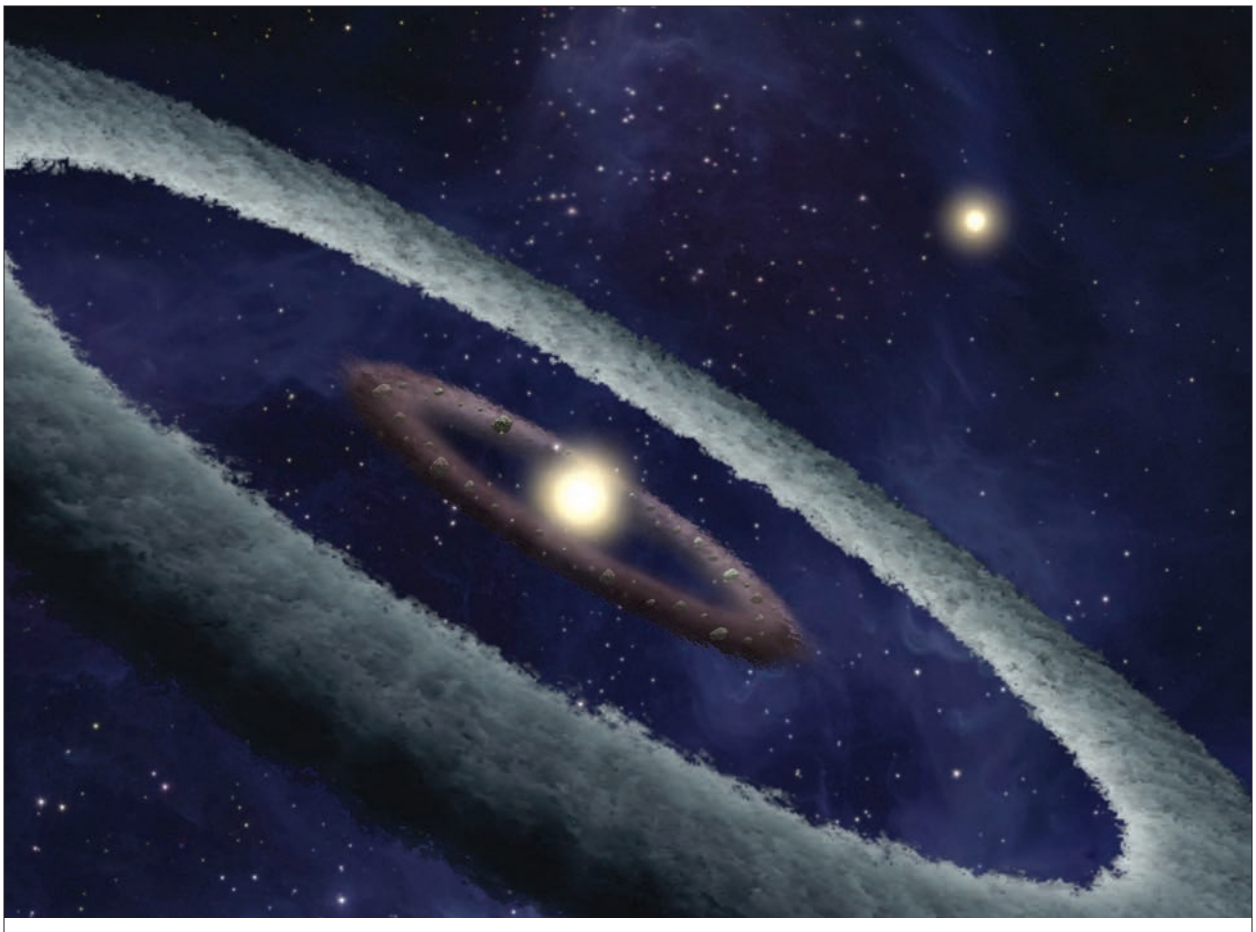

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A Study on Growth, Structural, Optical and Electrical Characterization of L-alanine Single Crystal for Optoelectronic Devices

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ABSTRACT

In this study, an attempt has been made to grow large size optically transparent LA single crystals by slow evaporation solution growth technique at room temperature. The chemical composition of the grown crystals was determined by Energy Dispersive X-ray (EDX) and Fourier Transform Infrared (FTIR) Spectroscopy. The structure of pure LA crystal has been examined by powder X-ray Diffraction (XRD) study. Optical properties of the grown crystal were studied using UV-Visible spectroscopy at room temperature. DC electrical conductivity was measured at different temperatures ranging from 35-140°C by conventional two probe method. Powder XRD analysis confirms the orthorhombic structure of the grown crystals. The transmission in the visible region and DC electrical conductivity of the crystal was found to increase with temperature and doping concentration. Optically transparent, large size and electrically conducting LA crystal were grown successfully in a laboratory for useful application in optoelectronic devices.

Key words: L-alanine, nonlinear optical material, Fourier transform infrared, bang gap energy, DC electrical conductivity

INTRODUCTION

Technologically developed world is looking for Nonlinear Optical (NLO) materials for developing optical fiber communication system and optoelectronic devices. Amino acid L-alanine (LA) (CH_3CHNH_2COOH) crystal has NLO property which has been reported by Misoguti *et al.* (1996). Bernal (1931), Simpson and Marsh (1966), Destro *et al.* (1988), Vijayan *et al.* (2006) and Guzman *et al.* (2003) grew large size transparent pure LA crystals by solution evaporation technique and characterized different properties. From their investigations it is expected that pure LA would be a good candidate for laser and optical Second Harmonic Generation (SHG) and also for frequency conversion application. Amino acids such as LA, L-histidine and L-threonine have special features such as (1) molecular chirality which forces the molecule to crystallize in a non centrosymmetric space group, the essential criterion for SHG material (2) wide transparency ranges in the visible and UV spectral regions (3) zwitterionic nature of the molecule ($^+NH_3$-C_2H_4-COO^-) which favors the way for possessing high electro-optic parameters and good mechanical and thermal stability of the crystals (Kumar *et al.*, 2006).

It was reported that addition of bimetallic impurities influence the growth kinetics of potassium dihydrogen phosphate (KDP) from aqueous solutions by Begum and Podder (2009) and

Claude *et al.* (2006a). The properties of ADP crystal were modified by the addition of novel Ni and Mg were reported by Claude *et al.* (2006b). It was also reported that the addition of L-alanine as dopant enhances the optical, thermal and electrical properties of semi organic material, KAP by Akhtar and Podder (2011). The key factor that affect the transmission characteristics of the 90° bent photonic crystal waveguides was explained by Dekkiche and Naoum (2008) and Nasipuri *et al.* (2011) and they elucidate the reason for enhancement of crystal size by Microbes. The effects of L-alanine dehydrogenase in the living things have been investigated by Al-Onazi *et al.* (2011). The amino acid is also used as additives to animal feed. Higher amount of amino acid added food increases the body weight of the broiler which is investigated by Nasr and Kheiri (2011). Hassan *et al.* (2011) studied the presence of plasma free amino acid is more in the male than the female in Sudan.

This study has reported the bulk growth by slow evaporation process at room temperature and characterization studies of as grown single crystal.

MATERIALS AND METHODS

Solubility study: The solubility of pure LA crystals in double distilled water was determined in the temperature range 30-45°C in steps of 5°C using a constant temperature bath of accuracy±0.01°C. The variation of solubility (g/100 mL H_2O) with temperature is shown in Fig. 1. The results indicate that there is a positive slope of solubility of LA crystal.

Crystal growth: The pure LA (AR grade chemical from SIGMA) was grown using a good quality seed crystal at room temperature (30°C) by solvent evaporation method. For the preparation of seed crystals, saturated solution of LA was prepared first and then kept in a petri dish covered with a perforated polyethylene and allowed to grow seed crystals within 4-5 days. The pH of the solution was found 6.73. The purity of the crystals was improved by successive recrystallization process. The growth period takes 25-30 days for bigger size. The grown crystals were found color-less and transparent. The as grown crystal of LA is shown in Fig. 2.

Characterization: The as grown pure LA crystals were subjected to various characterizations. Quantitative measurements were performed with an Energy Dispersive X-ray (EDX). In order to confirm the presence of functional groups in the crystal, FTIR spectrum was recorded by KBr pellet technique using a Shimadzu FTIR-8900 spectrophotometer in the wave number range

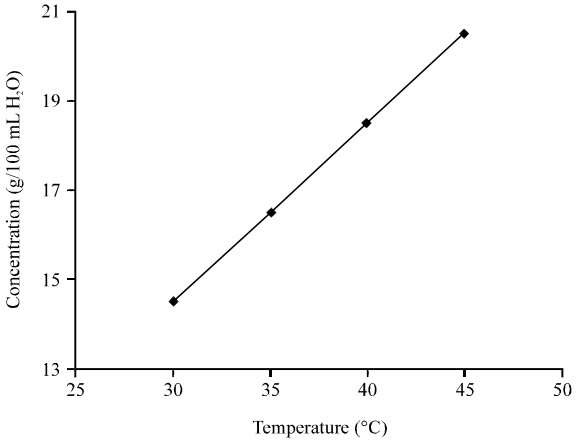

Fig. 1: Solubility curve of pure L-alanine

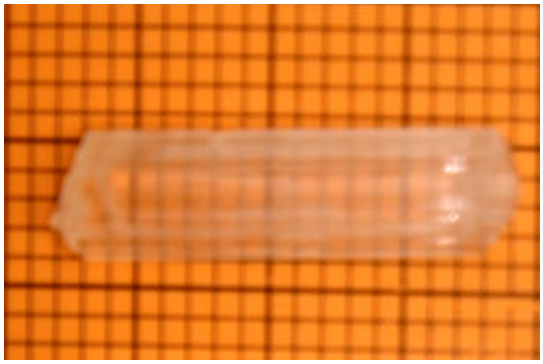

Fig. 2: L-alanine crystal

400-4000 cm^{-1}. In order to identify the structure of the pure LA crystal, XRD study was carried out using a Philips PW-3040 X' pert PRO X-ray diffractometer with CuKα (λ = 1.5418 Å) radiation in the 2θ ranges from 10-70° operated at 40 kV and 30 mA. The optical transmission spectrum was recorded in the wavelength range of 200-1100 nm using a Shimadzu UV-1601 visible spectrometer. Crystals with high transparency and defect-free with the dimensions of 8×6×2 mm were cut into a rectangular size and surfaces were coated with silver paint to give good electrical contact between the electrodes for the electrical conductivity measurements. The DC electrical conductivity measurements were carried out along the unique axis (c-) using the conventional two-probe technique using an ohmmeter at various temperatures ranging from 35-140°C. The field is applied to perpendicular to c-axis. The conductivity, σ of the crystal was calculated using the relation σ = d/(RA), where R is the measured resistance, d is the thickness of the sample crystal and A is the area of the face of the crystal in contact with the electrode.

RESULTS AND DISCUSSION

Compositional analysis: The compositional analysis of the pure LA crystal was performed using EDX. The EDX spectrum of the LA crystal is shown in Fig. 3. The EDX spectrum corresponding to C, O and N confirmed that the grown crystal is pure LA. The average atomic percentage of C, O and N was found to be 48.77, 37.82 and 13.42, respectively.

FTIR analysis: Fourier Transform Infrared (FTIR) spectrum of pure LA crystal is shown in the Fig. 4. The broad envelope between 2400 and 3400 cm^{-1} is due to overlapping of peaks by N-H of NH_3 and C-H stretching modes. The peak at 2111.9 cm^{-1} is due to the contribution of the asymmetrical bending vibration of NH_3^+. The C = O bond is also expected with its peak in the same region of asymmetrical NH_3^+ bending vibration. The presence of torsional oscillation at 538.1 cm^{-1} of NH^+_3 is evident from the Fig. 4. The bending modes of CH_3 are positioned at 1355.9 and 1450.4 cm^{-1}, respectively. The peak at 1112.9 cm^{-1} is due to C-O (with a vertical double bond of oxygen on C) stretch. The peaks at 1502.4 and 1413.7 cm^{-1} could be assigned to asymmetric and symmetric modes of carboxylate anion. Wave number assignment for pure LA crystal through FTIR studies are presented in Table 2.

XRD analysis: The well grinded powder of as grown LA crystal was used to identify the crystal phase and structure. The XRD pattern is shown in Fig. 5. Well defined Bragg peaks are obtained

Table 1: Powder XRD data of pure LA crystal

		References	
Crystal parameters (Å)	Calculated values	Vijayan *et al.* (2006)	Suresh *et al.* (2010)
a	6.028	6.032	6.041
b	12.317	12.343	12.356
c	5.804	5.784	5.778
V (Å)^3	430.929	430.636	431.284
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic

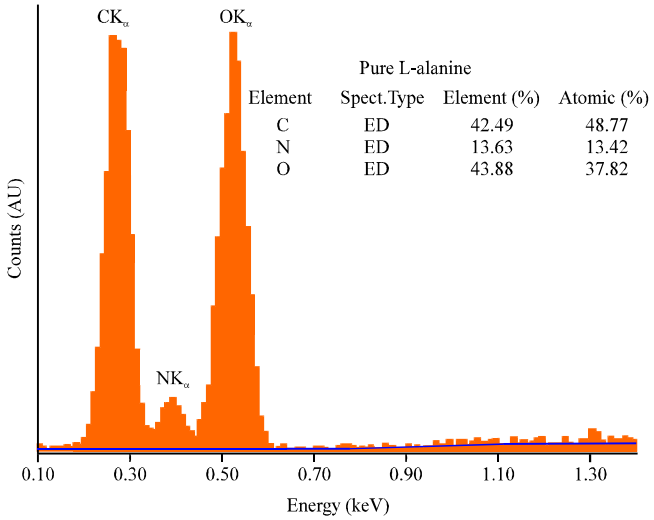

Fig. 3: EDX spectrum of pure LA

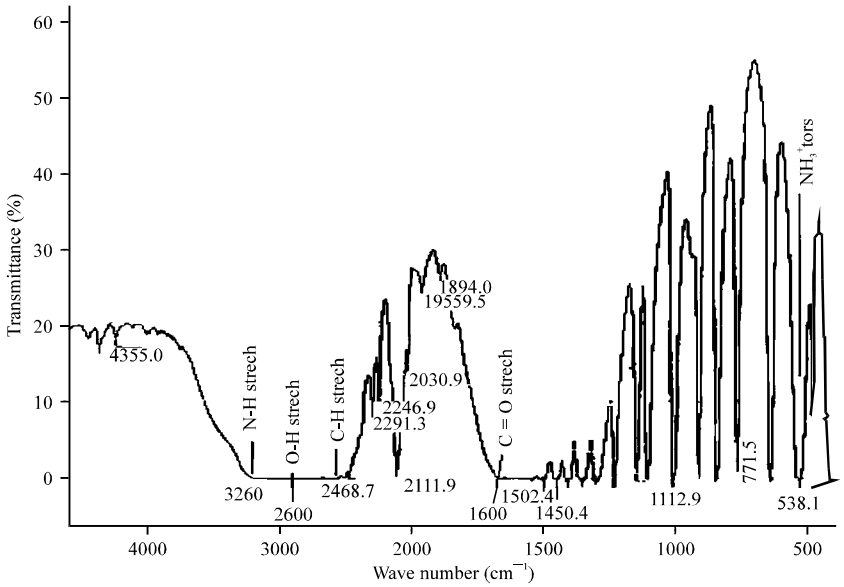

Fig. 4: FTIR spectrum of LA crystal

at specific 2θ angles, narrow and strongest peak along the plane (120) confirm the crystalline nature of the grown crystal. The 'd' spacing and hkl values for prominent peaks in the spectrum

Table 2: Wave number assignment for pure LA crystal through FTIR studies

Wave number (cm^{-1})	Assignments
3260	N-H stretching
2600	O-H stretching
2469	C-H stretching
2112	Degenerative deformation of NH_3^+ and torsional vibration of NH_3^+
1600	Asymmetric stretching of CO_2^-
1502	Symmetric bending of NH_3^+
1450	Degenerative deformation of CH_3
1414	Symmetric stretching of CO_2
1356	C-H deformation in CH_3
1113	C-O stretching, NH_3 rocking
850	O-H out-of-plane deformation
771	CH_2 rocking
648	O-C = O in plane deformation
538	Torsional vibration of NH_3^+

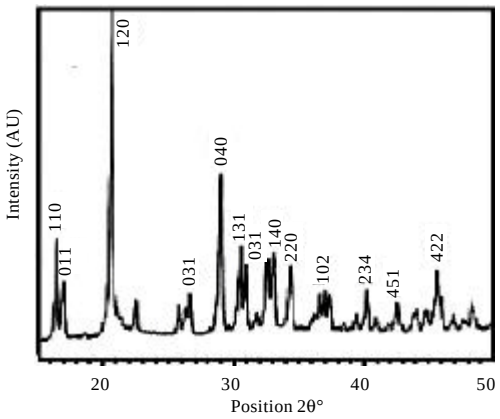

Fig. 5: X-ray diffraction pattern of LA

were identified and compared with ICDD (International Centre for Diffraction Data). Using orthorhombic crystallographic equation, lattice parameters are calculated. It was confirmed that the crystal belongs to the orthorhombic crystal system with the lattice parameters, a = 6.008 Å, b = 12.317 Å, c = 5.804 Å and volume of the unit cell, V = 429.53 $(Å)^3$ (Table 1). The obtained lattice parameter values are in good agreement with the reported literature values (Ravi *et al.*, 1999).

Optical properties: The optical transmission spectrum of LA single crystal was recorded in the wavelength region from 200-1100 nm (Fig. 6). The good transmission of the crystal in the visible region suggests its suitability for second harmonic generation devices (Venkataramanan *et al.*, 1997). The UV absorption edge for the grown crystal was observed to be around 260 nm. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons. The optical absorption coefficient, α was calculated from the transmittance using the following relation:

$$\alpha = \frac{1}{d}\log(1/T)$$

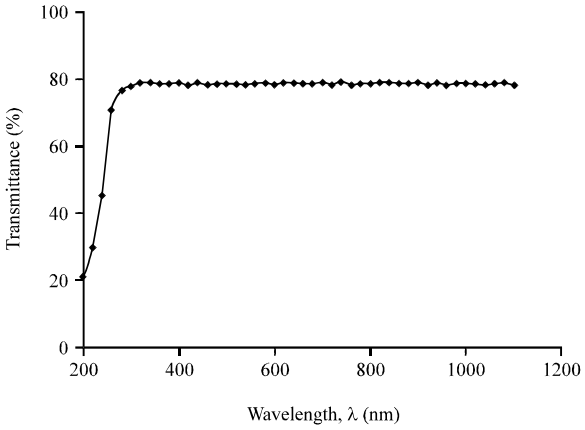

Fig. 6: Optical transmission spectrum of LA

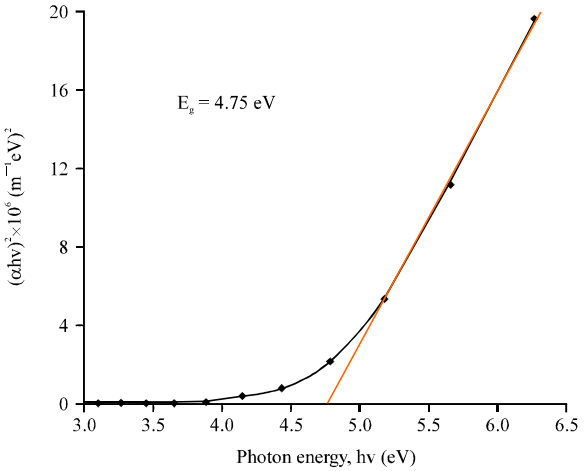

Fig. 7: Photon energy vs. $(\alpha h\nu)^2$ for LA

where, T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal has an absorption coefficient, α obeying the following relation for high photon energies $h\nu$:

$$\alpha = \frac{A(h\nu - E_g)^{\frac{1}{2}}}{h\nu}$$

where, E_g is optical band gap of the crystal and A is a constant. The variation of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 7. E_g was evaluated by the extrapolation of the linear part (Rajan Babu *et al.*, 2002). The calculated band gap is 4.75 eV. The wide band gap usually happens due to the large transmittance in the visible region (Suresh *et al.*, 2010).

Extinction coefficient and refractive index: The extinction coefficient, k and the refractive index, n provide the optical properties of the pure LA crystal. The value of k was obtained by the equation:

$$K=\frac{\alpha\lambda}{4\pi}$$

where, λ is the wavelength of light. Fig. 8 shows the variation in k as a function of wavelength. From Fig. 8 it is clear that k decreases rapidly with increasing wavelength from 200-1100 nm. The decreasing value of k is directly related to the absorption of light.

The refractive index has been calculated using the relation:

$$n=\left(\frac{1+R}{1-R}\right)+\sqrt{\left(\frac{4R}{1-R^2}-K^2\right)}$$

where, R is the optical reflectance. The variation of n with wavelength is shown in Fig. 9. From the Fig. 9 it is clear that the maximum refractive index is recorded at wavelength 1040 nm and the minimum refractive index is recorded in the visible range (400 nm<λ<700 nm) which is occurred due to successive internal reflections.

DC electrical conductivity: The variation of DC electrical conductivity with temperature is shown in Fig. 10. It is found that conductivity increases with temperature. At low temperature region, conductivity is expected due to the presence of weakly attached impurities and vacancies in the crystal lattice. The conductivity mainly caused for intrinsic defects. The experimental data and especially the character of the temperature dependence of conductivity allow us to state that the conductivity of LA crystal is determined by thermally generated defects. It is also assumed that the conductivity of LA crystal is determined by the simultaneous presence of positive and negative ions and orientational defects-vacant hydrogen bonds and doubly occupied hydrogen bonds.

The solubility of pure LA determined by the solution method agrees well with that reported in the literature (Vijayan *et al.*, 2006). Large size, transparent, pure LA crystal was grown by slow evaporation technique within a period of 30 days. EDX spectroscopy confirmed the presence of all elements of pure LA crystal which is agreed with calculated values. Functional groups and

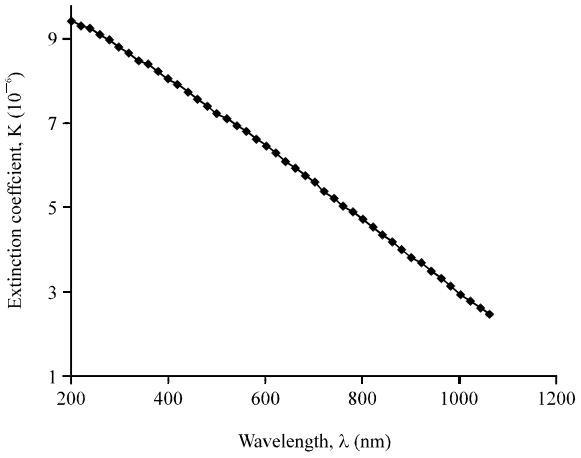

Fig. 8: Wavelength vs. extinction coefficient (K)

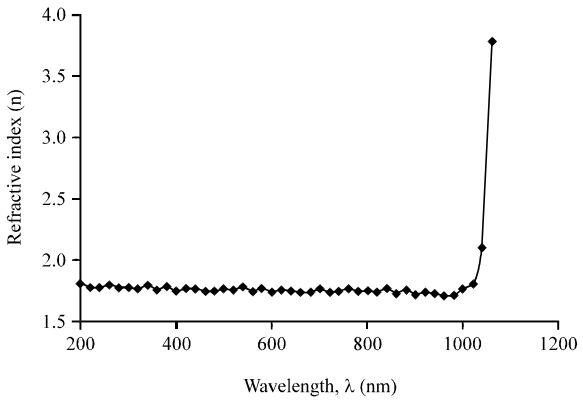

Fig. 9: Wavelength vs. refractive index

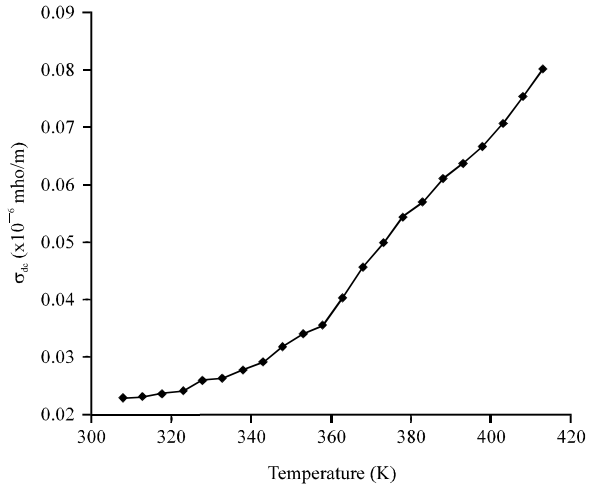

Fig. 10: DC electrical conductivity vs. temperature (K)

orthorhombic structure of the grown crystal agrees well with that reported in the literature (Kumar *et al.*, 2008; Vijayan *et al.*, 2006). The optical transmission in the visible region and less absorption in the UV region is reported. Increasing of DC electrical conductivity with temperature also is reported in this paper.

CONCLUSIONS

An organic optical material, LA crystals were successfully grown using the solvent evaporation technique at room temperature for second order NLO applications. The grown crystals have been subjected to structural, optical and electrical characterization. The X-ray diffraction analysis confirmed the orthorhombic structure of the crystal. Various functional groups have been identified by the FTIR spectral analysis. It is evident that the hydrogen bonding due to NH^{+}_{3} and COO^{-} is the additional major force in the crystal lattice. In the optical transmission spectra recorded on the grown crystal, the lower cut off wavelength near 260 nm in the UV region and the transmittance of about 80% exhibit the good optical quality of the materials. The obtained direct band gap, 4.75 eV of the material shows its suitability for the fabrication of various optoelectronic devices.

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