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Archives of Physics Research, 2010, 1 (2):94-102
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0976-0970

Investigations on the optical, electric, dielectric and mechanical properties of nonlinear optical LAM crystal

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Abstract

Single Crystal of L-alaninium maleate (LAM), an organic nonlinear (NLO) material has been successfully grown upto a size of 14 x 5 x 4 mm^3. The lattice parameters of the grown crystals are determined by single crystal XRD. The UV-Vis-NIR spectrum of LAM shows less optical absorption in the entire visible region. Nonlinear optical study reveals that the SHG efficiency of LAM is equal that of KDP. The laser damage density is found to be 8.43 GW/cm^2. The mocrohardness study of the crystal confirms anisotropy in the work hardening co-efficient for different orientations. The dielectric response of the sample has been investigated in the frequency region of 50 Hz to 5 MHz. AC and DC conductivity and photoconductivity experiments are also carried out and reported for the first time.

Key words: Solution growth, Nonlinear optics, Dielectric constant, ac and dc conductivity

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INTRODUCTION

In the last decade, organic non-linear optical (NLO) crystals with aromatic rings have attracted much attention because of their high non-linearity, fast response and tailor-made flexibility [1]. Coherent blue and green light is important for many applications such as display, high resolution printing, and signal processing [2]. These applications depend on the various properties of the materials, such as birefringence, refractive index, dielectric constant and mechanical, photochemical and chemical stability [3]. Considerable efforts have been made to combine amino-acids with interesting organic and inorganic matrices to produce outstanding materials to challenge the established inorganic materials [3]. Further investigations on organic NLO materials have subsequently produced very good materials with highly desirable characteristics [3]. The organic compounds with electron rich (donor) and deficient (acceptor) substituents, provide the asymmetric charge distribution in the π electron system and show large nonlinear optical responses. NLO crystals should meet several requirements, such as large phase – matchable nonlinear optical co-efficient, a wide optical and chemical stability and a high damage threshold [4]. Among the various amino acids, L-alanine is the simplest molecule having SHG efficiency of about one - third of the standard KDP material. The importance is due to the fact that amino acids contain chiral carbon atom and crystallize in the noncentrosymmetric space groups, therefore, they are potential candidates for optical second harmonic generation. This article deals with L-alaninium maleate (LAM), an analog of L-alanine. The structure of L-alaninium maleate (LAM) was solved by Alagar et al [5]. LAM exhibit promising structural background in view of its chirality and structural stabilization with hydrogen bonding, both these factors account for the delocalization and corresponding enhancement in second order NLO activity. LAM is stable up to 164 ºC and transparent from 300 to 1200 nm, thus enabling the use of this material for SHG applications [4]. The Growth, thermal, spectroscopic and optical studies of LAM were carried out by Natarajan et al (2006). The present investigation deals with the growth of LAM single crystal by slow solvent evaporation technique. Physical properties such as damage threshold, microhardness dielectric, ac/ dc conductivity and photoconductivity are investigated for the sample and reported for the first time.

MATERIALS AND METHODS

Experimental

2.1. Synthesis and crystal growth

L-alanine and maleic acid taken in equimolar ratio were dissolved in double distilled water to prepare the aqueous solution of LAM. The solution was filtered and transferred to crystal growth vessel, and crystallization was allowed to take place by slow evaporation at room temperature. Within a week, tiny crystals with good transparency were formed due to spontaneous nucleation, among them the defect free crystals were selected as seeds for growing bulk crystals. In the present work, single crystal of size 14 x 5 x 4 mm^3 was grown in a period of 25 days. Fig. 1 shows the photograph of as grown crystals of LAM.

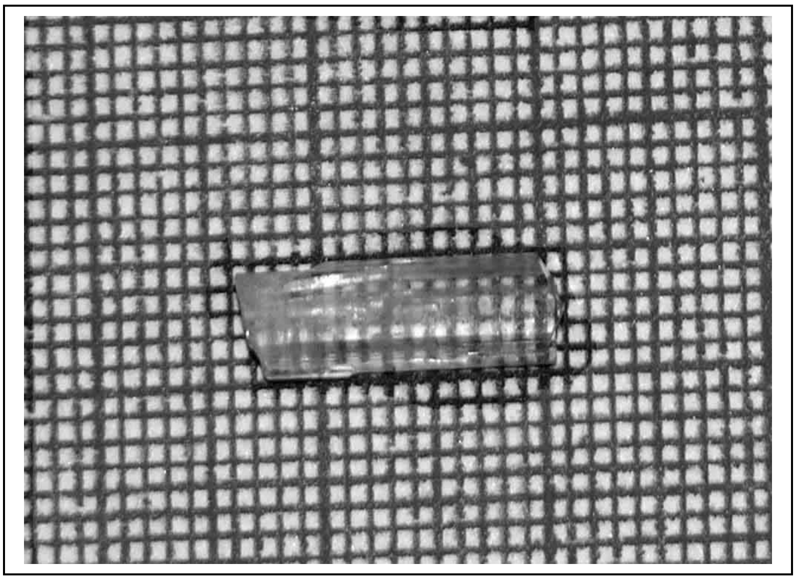

Fig. 1: Grown crystals of LAM

Characterization

The grown crystal was subjected to single-crystal XRD using Enraf Nonius CAD4-F diffractometer with MoK_{α} (λ=0.71073 Å) radiation. The optical absorption spectrum was recorded in the wavelength range 200–2000 nm using VARIAN CARY 5E spectrometer. The

Vickers hardness number was measured using a Leitz Wetzlar Vickers microhardness tester fitted with a diamond pyramidal indenter attached to an incident light microscope. Static indentation tests were made on the (0 1 1), (0 2 0) and (1 2 0) planes of the crystal at room temperature [3, 4]. Measurements were taken by varying the applied load from 10 to 50 g. In order to estimate the a.c conductivity and dielectric behaviour of the crystal, HIOKI 3532-50 LCR Hitester was used. The dc conductivity measurement was done using the conventional two-probe technique. The photo current and dark current were recorded using a picoammeter (Keithley 480).

3.1 XRD analysis of LAM Single Crystal

The single crystal XRD data of LAM crystal confirms the orthorhombic system with lattice parameters, a = 5:5805 Å, b = 7:3778 Å, c = 23:7753 Å and cell volume, V = 978.8722 ($Å^3$). The single crystal XRD results are in good agreement with the reported values and thus confirm the grown crystal [5].

3.2 Optical absorption spectrum

The absorption spectrum of LAM is shown in Fig 2. The crystal has a low UV-cut-off wavelength of 280 nm. In the entire visible region, the absorbance is less then 1 unit. This transparent nature in the visible region is a desirous property for NLO applications. Minimum absorbance is revealed in the near infrared region.

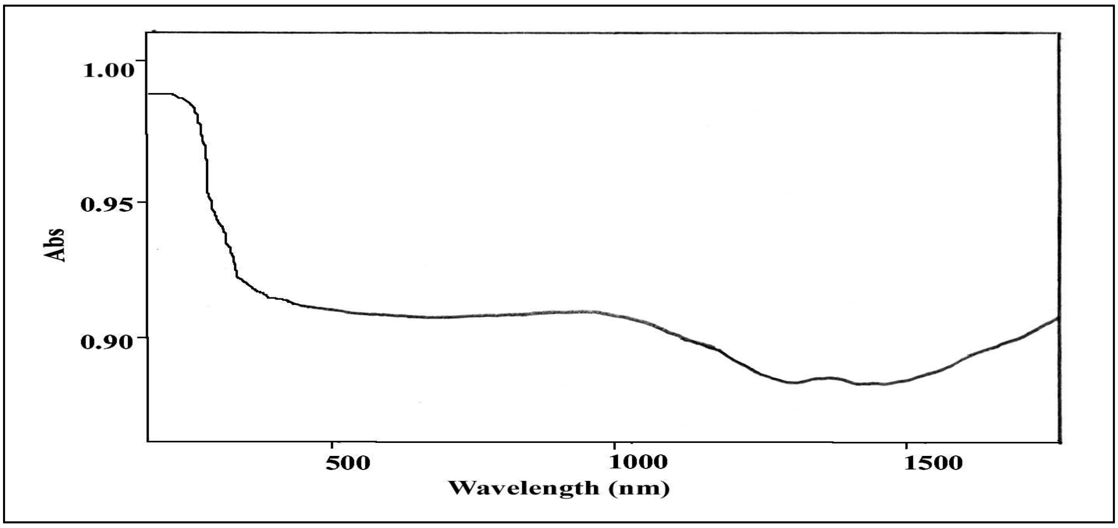

Fig. 2: Absorption spectrum of LAM

3.3 NLO Test

The second harmonic generation efficiency of the powdered material was tested using Kurtz and Perry method. For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison. When a laser input of 6.2 mJ was passed through LAM, second harmonic signal of 532 nm is produced. The second harmonic signal of 130 mV was obtained for LAM with reference to KDP (124 mV). Thus the SHG efficiency of LAM sample is comparable to that of KDP.

3.4 Laser Damage threshold

The laser damage threshold study was made on L-alaninium maleate single crystals using a Q-switched Nd:YAG laser (λ=1064 nm) with a pulse duration of 10 ns. The sample was mounted on the goniometer, which was used to position the different sites in the beam. During laser radiation, the power meter record the energy density of the input laser beam for which the crystal gets damaged. The energy density was calculated using the formula:

$$\text{energy density} = E/A \ (GW/cm^2)$$

where E is the input energy in millijoules and A is the area of the circular spot. The laser damage density of LAM was found to be 8.43 GW/cm^2. The observed damage threshold value is grater than that of standard KDP and other known organic single crystals. The observed damage threshold value is greater than that of few well-known NLO crystals are given in Table 1 for comparison [6]. Hence these materials are advantageous for NLO and photonic devices.

Table. 1: Laser damage threshold values of some NLO materials

Compound	Laser damage threshold (GW/cm^2)
Potassium dihydrogen phosphate (KDP)	0.2 [6]
Urea	1.5 [6]
Benzimidazole	2.9 [6]
L-alaninium maleate*	8.43

* Present work

3.5 Microhardness test

Microhardness behaviour of the LAM single crystal was studied by employing Vickers microhardness tester. LAM single crystal was subjected to Vickers microhardness test with the applied load varying from 10 to 50 g for a constant indentation time of 10 seconds. Indentation was done on the well-defined faces such as (0 1 1), (1 2 0) and (0 2 0) of the crystal.

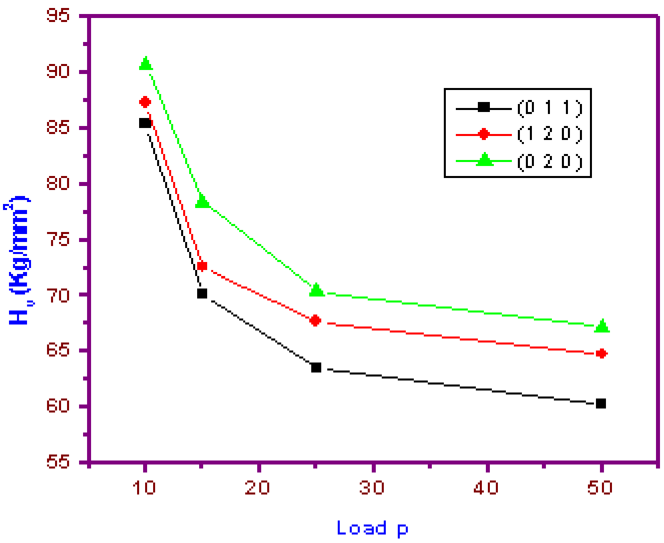

Fig. 3. Variation of microhardness with applied load on(0 1 1), (1 2 0) and (0 2 0) faces of LAM single crystal

Static indentation tests were made on the (0 1 1), (0 2 0) and (1 2 0) planes of the crystal at room temperature [4]. The Vickers microhardness number as a function of the applied test load is depicted in Fig. 3. It is observed that the Vickers hardness number of the crystal decreases with increasing load. The work hardening coefficients were found to be 1.651, 1.687 and 1.604 for (0 1 1), (1 2 0) and (0 2 0) planes respectively. Fig. 4 shows the Meyer's plot for the planes (0 1 1), (1

2 0) and (0 2 0) of LAM crystal. According to Onitsch [7], if n > 2, the microhardness number H_V increases with increasing load and if n < 2, H_V decreases with increasing load. It increases the possibilities of this crystal towards SHG device applications.

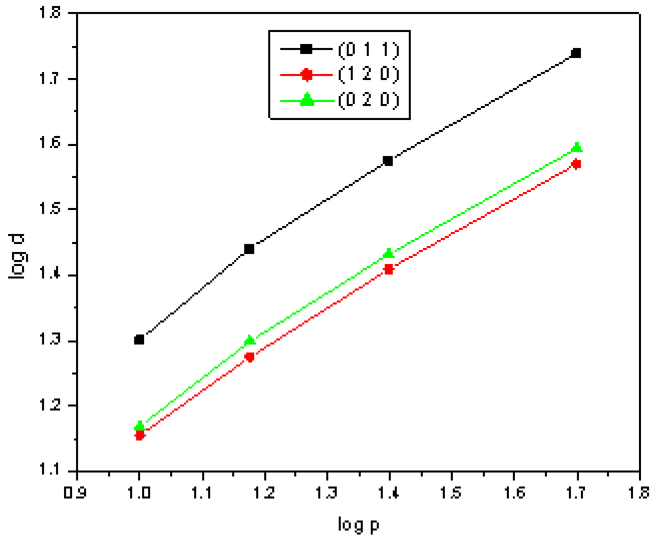

Fig. 4. Plot of log p Vs log d for LAM single crystal along (0 1 1), (1 2 0) and (0 2 0) planes

3.6 Dielectric studies

Fig. 5 shows the variation of dielectric constant and dielectric loss of LAM crystal along (100) orientation at different temperatures (308 to 408 K) and frequencies range (50 Hz to 5 MHz). At low frequencies, the dielectric constant is found to have high values and then it decreases with frequency. The dielectric constant is found to depend on temperature (Fig. 6).

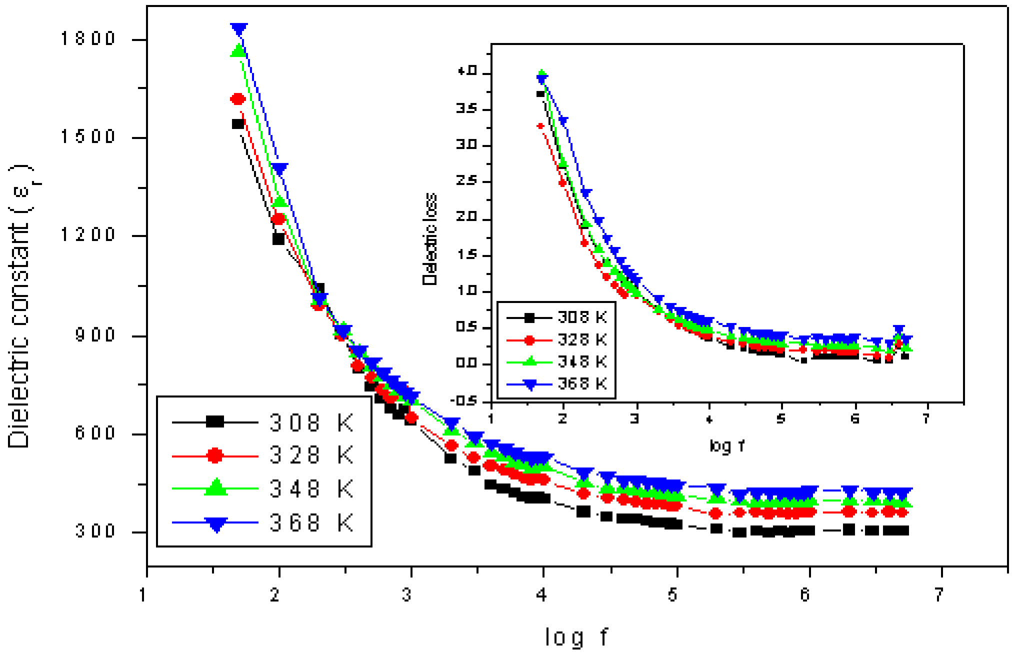

Fig. 5. Variation of dielectric constant and dielectric loss of LAM with frequency at different temperatures

In high frequency region (above 10 kHz for all temperatures), both the dielectric constant and dielectric loss are fairly remaining constant. The high dielectric constant at low frequency is due to the presence of all types of polarizations [8-9] viz., electronic, ionic, orientation, space charge polarization, etc. The space charge polarization will depend on the purity and perfection of the sample. Its influence is large at high temperature and is noticeable in the low frequency region. The variation of dielectric loss with frequency at different temperatures is shown in inset to Fig. 5. It is well observed that the dielectric loss decreases with increasing frequency. The low value of dielectric loss indicates that the grown crystals are of moderately good quality [10]. The low value of dielectric constant at higher frequencies is important for extending the material applications towards photonic, electro-optic and NLO devices.

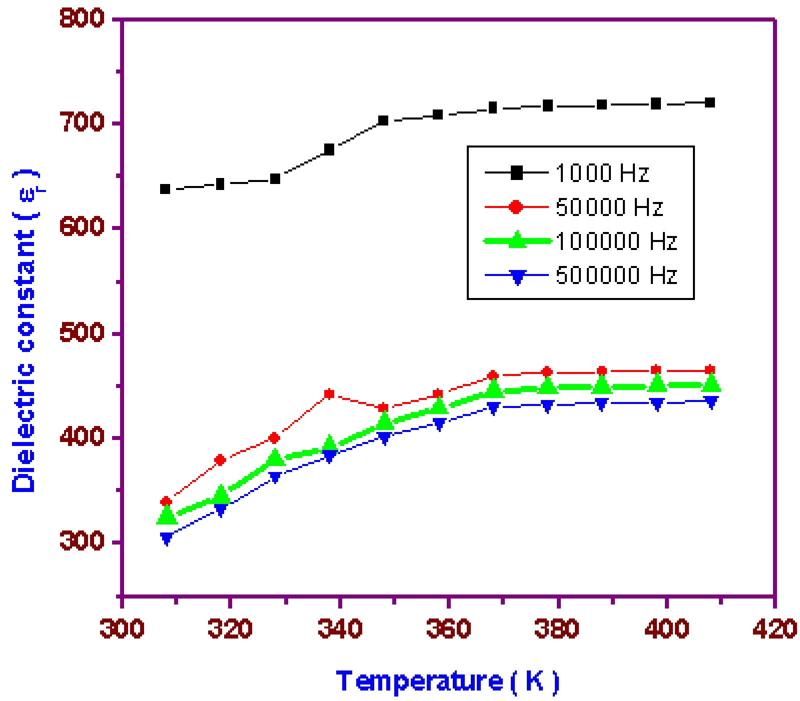

Fig. 6. Temperature dependence of dielectric constant of LAM single crystal

3.7 AC/ DC conductivity studies

The temperature dependence of conductivity of the samples is shown in Fig. 7, as a plot of *log* $\sigma_{ac}T$ versus *1000/T*. It is evident from the graph that the conductivity increases with temperature. From the graph, the value of activation energy for ionic migration was estimated. The line of best fit for the plot of *ln* $\sigma_{ac}T$ versus *1/T* obeys Arrhenius relationship, $\sigma_{ac} = \sigma_o \exp(-E_a/kT)$. Therefore, the sample exhibits Arrhenius type conductivity behaviour in the temperature range of investigation. The calculated activation energy of LAM using the plot is 0.078 eV.

The conductivity measurements were carried out along *c*-axis for the LAM crystal using the conventional two-probe technique at different temperatures ranging from 313 to 423 K. The conductivity LAM sample is the same both for the forward and reverse currents. The dimension of the crystal was measured using a travelling microscope (L.C = 0.001 cm). The data fits the equation $\sigma_{dc} = \sigma_o \exp(-E_d/kT)$. The σ_{dc} values in the temperature region studied are found to increase with increase in temperature for LAM crystal. Electrical conductivity depends on thermal treatment of crystal. The value of conductivity *ln* σ_{dc} is found to increase with temperature. The conduction region considered in the present study seems to be connected to mobility of vacancies. From the plot of *log* $\sigma_{dc}T$ versus *1000/T*, the activation energy (E_d) is calculated (Fig. 8) to be 0.06 eV.

3.8 Photoconductivity study

Field dependence of dark and photo currents of LAM crystal is shown in Fig. 9. It is observed that both dark and photo currents of LAM single crystal increase linearly with the applied voltage. The dark current of the crystal is more than the photo current, which is termed as negative photoconductivity. The negative photoconductivity exhibited by the sample may be due to the reduction in the number of charge carriers in the presence of radiation [11].

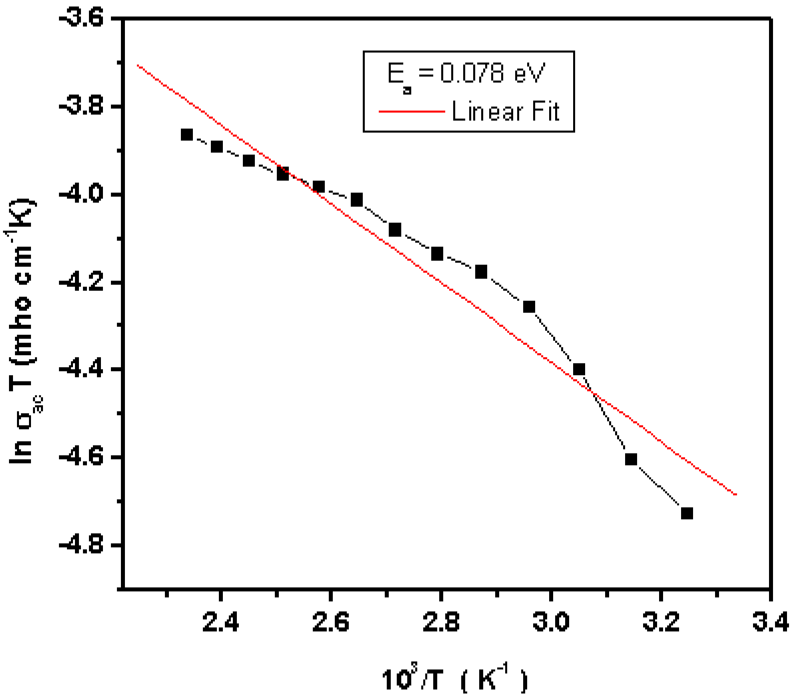

Fig. 7. The ac conductivity of LAM crystal

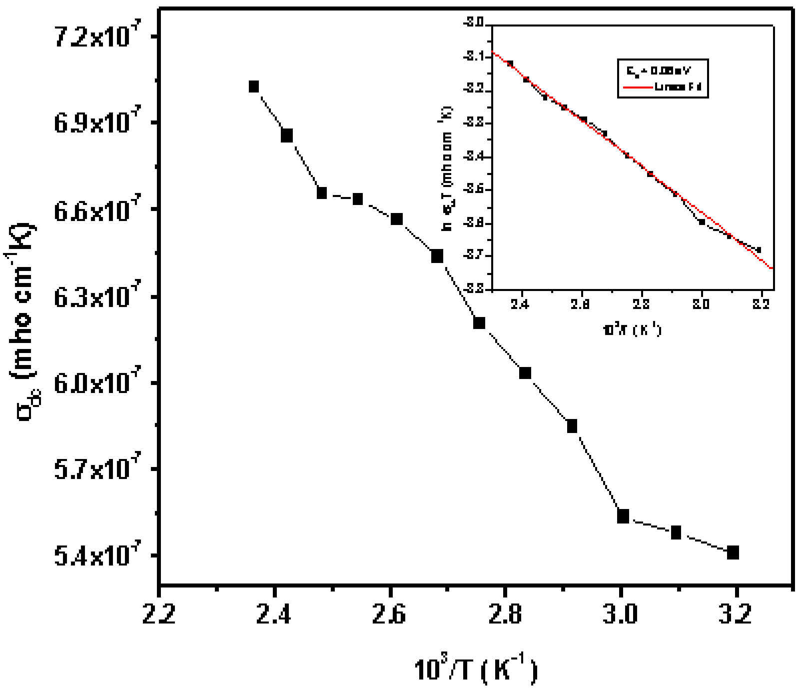

Fig. 8. The dc conductivity of LAM crystal

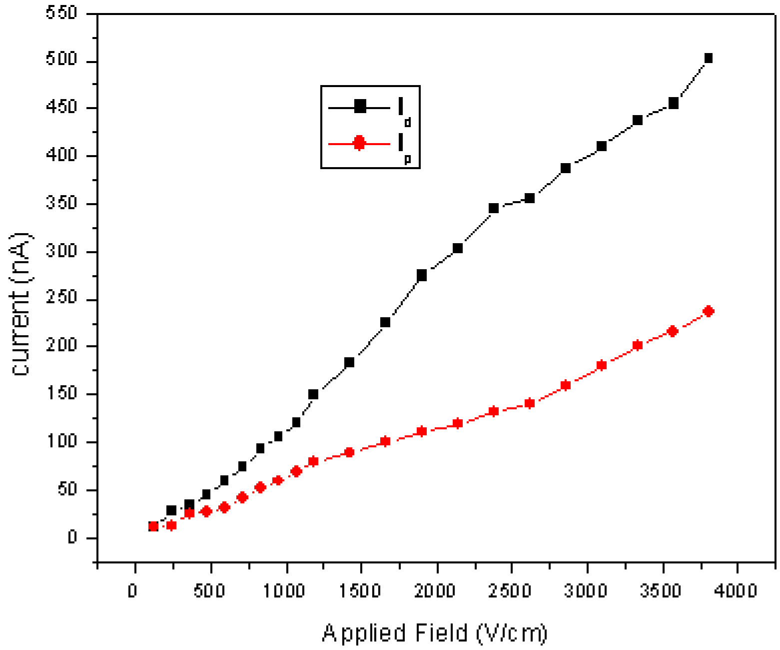

Fig. 9. Field dependent conductivity of LAM single crystals

CONCLUSION

Single crystal of LAM was grown by slow evaporation technique at room temperature. The powder SHG efficiency analysis reveals that the efficiency of this material is about 1.1 times that of KDP, the laser damage threshold of LAM is about 8.43 GW/cm^2 at 1064 nm and that LAM is phase matchable. The microhardness studies of the crystal indicate anisotropy in the work hardening co-efficient and Vickers hardness values of the crystal. The dielectric studies on the crystal reveal that dielectric constant decreases with increasing frequency but attains saturation for frequencies larger than 10 kHz. Electrical conductivity studies reveal that the conduction in these crystals is due to the movement of ions as well as electrons. The activation energy is determined from the plots for ac/dc conductivity. The material has very low absorption in the entire visible region and infrared region, with the lower UV cut off around 280 nm and its mechanical stability makes it an attractive candidate for second and third harmonics generation and device applications. The photoconductivity study confirms the negative photoconducting nature of the crystal.

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