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Dielectric Characterization of L-Arginine Perchlorate Single Crystals

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ABSTRACT

A semi organic non linear optical material, L-arginine Perchlorate (LAPCL) single crystals have been formed by slow evaporation method. Dielectric constant and dielectric loss have been obtained as a function of frequency between 1 KHz and 5 MHz and temperature range between 313 K and 373 K. The dependence of tan δ, ε″ and σ_{ac} on temperature and frequency of the applied field (50 Hz–5 MHz) is established D.C. conductivity has been deduced from the a.c. conductivity data and activation energy is calculated. Impedance plot has also been drawn at four different temperature and results are discussed in the paper.

Keywords: *NLO, dielectric loss, dielectric constant, Impedance*

1. INTRODUCTION

The organic non linear optical materials play an important role in second harmonic generation, frequency mixing, electro-optic modulation, optical parametric oscillation and optical bi-stability [15] . Crystalline salts of L-arginine have attracted considerable interest among researchers. Amino acids are interesting materials for NLO applications. The importance of amino acids in NLO applications are due to the fact that all the amino acids have chiral symmetry and crystallize in non-Centro symmetric space groups. LAPCL is one among them which is considered to be a potential NLO material .Several reports are available and they are well documented in[1-7]

From the structural point of view LAPCL crystallize in the orthorhombic system with space group P2121P2 and Z=4. The unit cell parameters are a= 13.854A°, b=16.573 A° , C= 5.083A° , α=β=γ=90°.[2] Recently, Petrosyan [4] has reported on the FT-IR ATR and Raman spectra of LAPCL crystals. The crystal structure of LAPCL was determined by Srinivasan et al [1]

2. EXPERIMENTAL PROCEDURE

AR grade samples of L-arginine and Perchloric acid are taken in appropriate stoichiometric ratio and dissolved in double distilled water and stirred well for about six hours. Then it was filtered and allowed to crystallize by slow evaporation method. Within 15 days, crystals with good transparency were produced. Figure 1 shows the photograph of the LAPCL single crystal. The reaction that takes place in this process is as follows:

$NH_2CNHNH(CH_2)CHNH_2COOH + HClO_4 =$
$NH_2CNH_2^+NH(CH_2)_3CHNH_3^+COO^-.ClO_4^-$ [3]

3. DIELECTRIC MEASUREMENT

Dielectric properties are correlated with electro-optic property of the crystals: particularly when they are non conducting materials. [13]. Microelectronics industry needs low dielectric constant (ε_r) materials as an interlayer dielectric [14] Suitably cut and polished section (001) of LAPCL crystal was subjected to dielectric studies using a HIOKI model 3532-50 LCR HITESTER with a conventional two terminal sample holder. The sample was electroded on either side with air-dying silver paste so that it behaves like parallel capacitor. The studies were carried from 313 K -373 K for frequency varying from 50 Hz to 5 MHz.

Figure 1: photograph of LAPCL

4. RESULTS AND DISCUSSION

Figure 2 shows the variations of dielectric constant with log frequency. The dielectric constant is calculated using the formula

$\varepsilon' = C\, t\, /\, \varepsilon_o\, A$

Where C is capacitance (F), t is the thickness (m), A the area (9m^2), ε_o is the absolute permittivity in the free space having a value of 8.854 * 10^{-12} Fm^{-1}.
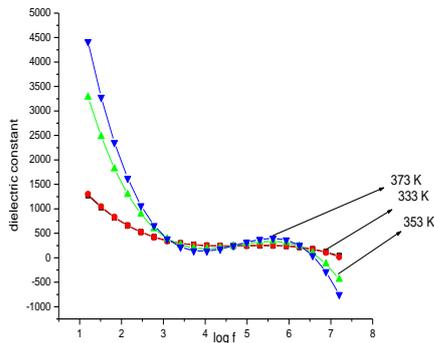
Figure 2 variation of Dielectric constant with Log frequency

It is seen from the figure 2, that the dielectric constant decreases with increasing frequency at almost all temperatures and appears to attain saturation at high frequency range of 50 KHz and above. The decrease in the dielectric constant of LAPCL crystal at low frequencies may be attributed to the contribution of the electronic, ionic, orientation and space charge polarization which depend on the frequencies [11, 12]. At low frequencies all the four polarizations are active. It is also seen that dielectric constant increases with increasing temperature. The high value of dielectric constant is attributed to high ionic conductivity[19]. Most of the solid electrolytes have higher dielectric constant. [16] Higher values of dielectric constant at higher temperature may be due to the thermal excitation of atoms about their lattice points and these would have happened due to disorder at the lattice. Space charge contribution to polarization may be attributed to the purity of the crystal. Dielectric constant at low frequencies can be compared to optical frequencies[17]. This leads to minimization of the phase mismatch between optical and electrical pulses in high speed traveling wave devices. However, the low values of dielectric loss suggest that the grown crystals possess good optical quality which is the essential parameter for the non linear optical material for their applications. [10,20]. Hopping of charge carriers would have happened in the lattice sites and this has happened because of thermal excitations of atoms about their lattice points.
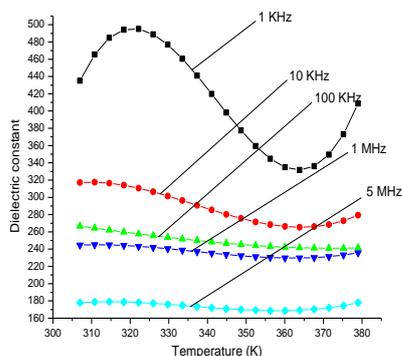
From the figure 3 it can be seen that at 1 KHz the contribution from interfacial polarization becomes maximum and this happens at lower temperature and this decreases with increase in frequency. The interfacial or surface polarization can be explained using a Maxwell-Wagner mechanism[16]. This is concerned with polarization due to ionic motion in the presence of an electric field. At low frequencies the mobile charges, usually impurity ions, diffuse under the influence of the applied electric field up to the interface and build up the surface charge until the applied field reverses with the alternating frequency of the alternating field and this cannot follow the field variations at very high frequencies [18]
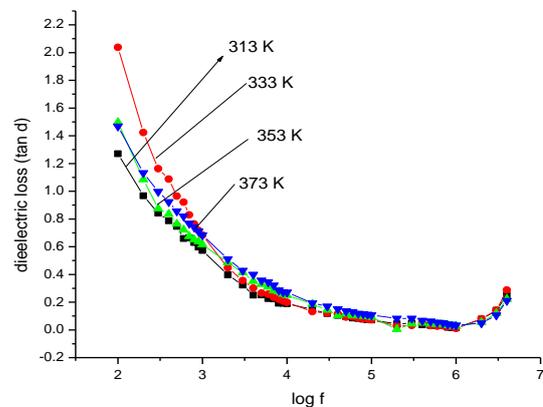

Fig 4. Dielectric loss as a function of frequency at four different temperatures

The variation of dielectric loss as a function of frequency at different temperatures is depicted in fig4. And it is found that the same trend is followed as that of dielectric constant. It is also observed that the higher dielectric loss occurs at higher temperatures and at lower frequencies. This is understandable from the fact that at lower frequencies the trend is due to space charge polarization and at higher temperatures the trend may be due to macroscopic distortion in the charges [18]
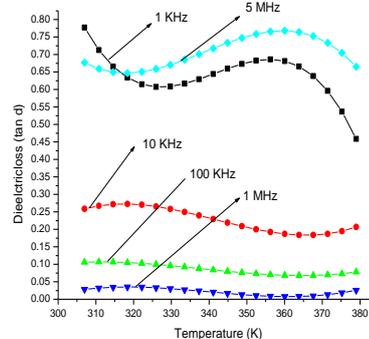

Figure 3 Variation of dielectric constant with temperature at 5 selected frequencies

Figure 5 Temperature dependence of dielectric constant (ε_r) at various frequencies

From the figure 5 it is seen that there is a maximum at lowest and highest frequencies and that too this happens at higher temperature.[18] No frequency dispersion of the dielectric permittivity occurs and this suggests that the sample has no relaxation behavior[19].. It is also seen that tan δ remains almost constant at certain frequency ranges over a certain range of temperature and this happens in our case at 10 KHz, 100 KHz and 1 MHz. In the case of 1 KHz and 5 MHz there is sine wave like variation as temperature is increased. Barring the value at 5 MHz the general trend can be assumed as the value of tan delta is found to increase with increasing temperature and decreasing frequency. The variation of dielectric loss with respect to temperature and frequency may be due to space charge polarization[19]. Further the space charge polarization can be explained through Shockley-Read mechanism[17]. For low and middle order frequencies and at high temperature the impurity ions in the bulk crystal matrices capture the surface electron, causing the space charge polarization at the surface. The electron capture process increases with increase in temperature. This type of surface polarization can be accounted by statistical method and that is the reason for explaining the above results through Shockley- Read mechanism[17]. By this mechanism it is given that at low and middle order frequencies and at higher temperatures the impurity ions in the bulk crystal matrices capture the surface electron, causing the space charge polarization at the surface. The electron capture process increases with increase in temperature. By this mechanism one can presume that the loss tangent increases with increasing temperature and at low frequencies [15]

The imaginary dielectric constant $(\varepsilon^{"})$ of the material is calculated using the relation

$$\varepsilon" = \varepsilon' \tan\delta$$ Where tan δ is the dielectric loss[21].
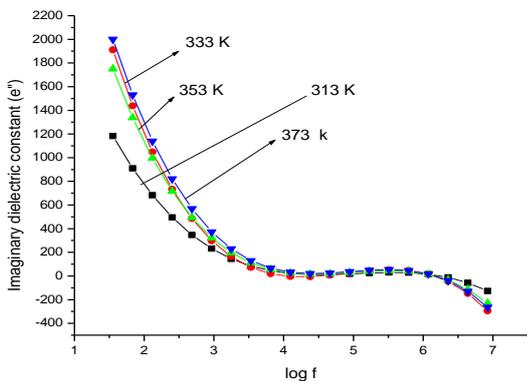

Figure 6: Variation of imaginary dielectric constant ($\varepsilon"$) with frequency

Figure 6 shows the variation of imaginary dielectric constant ($\varepsilon"$) with frequency at different temperatures (313K -373K).

From figure 6 it is concluded that the value of dielectric constant decreases sharply in the low frequency

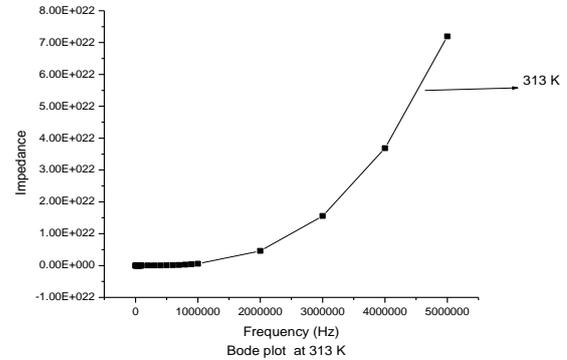range and attains the very low value at all frequencies for all temperatures.

Fig 7 Bode Plot at 313 K

From the fig 7 it is seen that impedance increases with frequency. This is the characteristic feature for the optically active crystal. The purpose of the graph is to get d.c. resistivity. This will be obtained from the intercept where the impedance is independent of frequency. The value from the graph is $2.032*10^7$. Like this the d.c resistivity is obtained at other temperatures and d.c. conductivity versus temperature is plotted and it is shown in Fig 8.
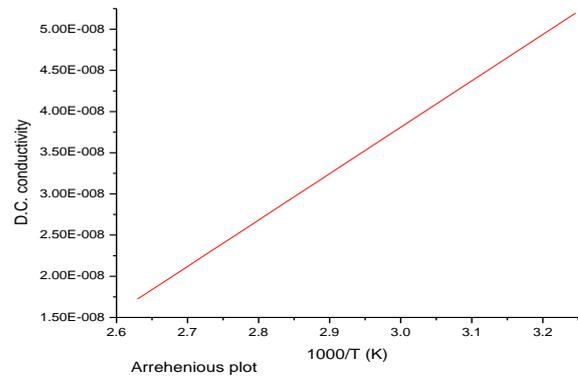

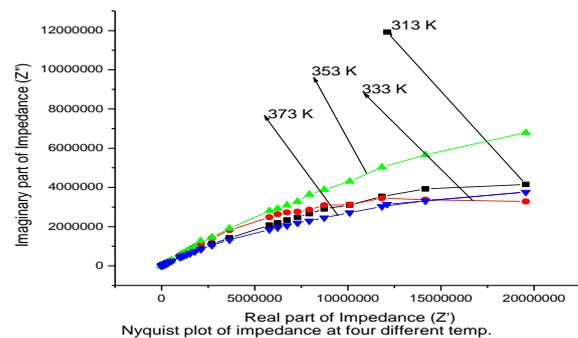Figure 8: From this plot , Energy of activation is calculated and it is found to be 0.0085 eV

Figure 9: Nyquist plot of impedance at four different temperatures

From the figs of 7,8 and it is seen that a.c. conductivity is governed by the presence of a small number of free charges which result in small leakage or conduction currents and by the displacement of bound charges that give rise to polarization or displacement currents in the solid state dielectrics whereas in the d.c. conductivity there is no contribution from localized charges. Further ionic conduction plays a major role at higher temperatures for both a.c and d.c conductivity because at higher temperatures some ions detach from the sites of crystal lattices[8] However, at lower temperatures mostly weekly bound ions, particularly impurity ions, are free to drift as already discussed. At low frequency space charge polarization is dominant mechanism in the transport processes which is absent at high frequencies. The space charge polarization decreases with increase in frequency due to inertia of the ions to follow the variation in field.

5. CONCLUSION

The dielectric constants (ε' and ε'') , dielectric loss (tan δ) and conductivity (σ_{ac}) of LAPCL crystals are strongly dependent on temperature and frequency of the applied ac field, the variation depends on the ranges of temperature and frequency. The dielectric constant and dielectric loss decreases with increasing frequency and higher values of dielectric constant occurs at higher temperature. The rate of variation of imaginary dielectric constant (ε'') with temperature is strongly dependent on temperature and frequency of the applied field. The conductivity increases with temperature and the activation energy is calculated and it is found to be 0.0085 eV. From all those analysis, it can be concluded that L-arginine Perchlorate is not only a potential Non linear Optical material but also a promising low ε_r value dielectric material, expected to be useful in the microelectronics industry. The encouraging dielectric properties of the crystal indicate the suitability of this crystal for photonics device fabrication.

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