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Studies on Dielectric and Ferroelectric Behaviour of L-Alanine Single Crystal

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Single crystals of L-alanine have been grown by slow evaporation solution technique. Single crystal XRD analysis confirms the orthorhombic structure of the grown crystals. The FTIR spectral analysis has been carried out by KBr pellet technique in order to identify the functional groups present in grown crystals. The dielectric measurements on these crystals are carried out with a fully automated impedance analyzer. The dielectric constants and dielectric loss at different temperatures and frequencies of the applied field are measured and their behaviour has been analyzed. P-E hysteresis loop has been investigated at 50 Hz.

Key Words: Growth from solutions, X-ray diffraction, FTIR, Dielectric materials, Ferroelectric materials.

INTRODUCTION

The ferroelectric materials, which exhibit diffuse phase transition with strong dielectric diffusion, are usually named as RFEs. Dielectric dispersion generally explains the shifting of T_c towards higher temperatures with increasing frequency. A normal ferroelectric generally possess a square hysteresis loop with large coercive field (E_c), spontaneous (P_s) and remanent (P_r) polarization whereas a relaxor possess a slim loop. The relaxor behaviour in normal ferroelectric materials results from compositionally induced disorder or frustration. Amino acids are interesting materials for NLO applications[1]. Among the amino acids, L-alanine (CH_3 CH NH_2COOH) is the smallest and simplest molecule having SHG efficiency of about one third of that of the well known KDP. It is considered as the fundamental building block of more complex amino acids. The L-alanine crystal crystallizes in orthorhombic structure with lattice parameters a = 6.032 Å, b = 12.343 Å, c = 5.784 Å, V = 430 Å^3, $\alpha = \beta = \gamma = 90°$ and space group is $P2_12_12_1$[2]. Nucleation thermodynamical studies on nonlinear optical l-alanine single crystals have also been reported[3]. We present in this paper based on measurements of the dependence of dielectric constant and loss tangent on applied frequency and temperature over a wide range since it has not been reported yet. The overall purpose of this study is to investigate the dielectric properties and the ferroelectric behaviour of L-alanine single crystals.

EXPERIMENTAL

Crystal growth: The commercially available L-alanine is further purified by repeated recrystallization process in double distilled water and the recrystallized material is used for growth. A saturated solution of 100 mL is taken and the solution is filtered using a Whatmann filter paper. The filtered solution is taken in a beaker, which is optimally closed with a thick filter paper so that the rate of evaporation could be minimized. Good transparent single crystals (45 mm × 9 mm × 5 mm) are obtained after 2 weeks as shown in Fig. 1.

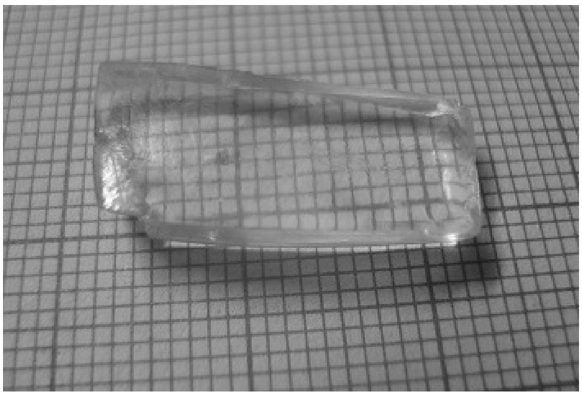

Fig. 1. Photograph of the as grown crystal

RESULTS AND DISCUSSION

Single crystal X-ray diffraction studies: Single crystal X-ray diffraction study has been carried out using ENRAF NONIUS FR 590 single crystal diffractometer. The L-alanine crystal crystallizes in orthorhombic structure with lattice parameters a = 6.03 Å, b = 12.34 Å, c = 5.78 Å, V = 430 Å^3,

$\alpha = \beta = \gamma = 90°$ and space group is $P2_12_12_1$. The unit cell parameters derived are in good agreement with the corresponding reported values[2].

Fourier transform infrared analysis: FTIR spectrum at room temperature in the range 4000-400 cm^{-1} has been recorded using Bruker IFS-66 FTIR spectrometer. The FTIR spectral analysis of L-alanine is carried out by KBr pellet technique in order to identify the functional groups present in L-alanine crystals. The resulting spectrum is shown in Fig. 2. In the higher energy region, there is a broad intense band due to the N-H stretch of NH_3^+. There is a fine structure in the lower energy region of the band due to hydrogen bonding of NH_3^+ with COO^- in the crystal lattice. The bands due to CH stretching modes appear just below 3000 cm^{-1}. The sharp intense peak at 2113 cm^{-1} is due to the combination of NH_3^+ asymmetrical stretching (1620 cm^{-1}) and its torsional oscillation. The symmetrical NH_3^+ stretch is observed to give a less intense peak at 1520 cm^{-1}. The CH_2 bends appear as well-resolved sharp peaks at 1362 and 1455 cm^{-1}. The C-COO^- vibrations produce peaks at 1307, 1237, 1152 and 1114 cm^{-1}. Thus the presence of all the functional groups occurring in L-alanine is identified.

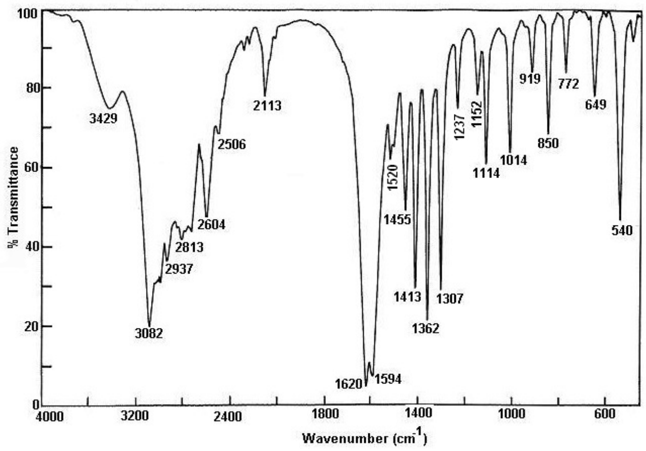

Fig. 2. FTIR spectrum of L-alanine crystal

Dielectric studies: The solution grown single crystals of L-alanine of thickness of about 1.1 mm and 65 mm^2 area is used for dielectric studies. The dielectric constant and loss tangent of L-alanine single crystals are measured with the help of impedance analyzer and further automated by using a computer for data recording, storage and analysis. The instrument directly provides the values of capacitance C and loss tangent tan δ. The dielectric constant is calculated using the formula $\varepsilon' = Ct/\varepsilon_0 A$, where C is the capacitance (F), t the thickness (m), A the cross-sectional area (m^2) of the sample and ε_0 is the absolute permittivity of the free space having a value of 8.854×10^{-12} Fm^{-1}.

A dielectric characteristic study of the solution grown L-alanine indicates its response to an applied electric field. Variations in the dielectric constant (ε') and loss tangent (tan δ) may be attributed to different types of polarizations, which may come into play at different stages of its responses to varying temperature and frequency of the applied alternating field. The dependence of the loss tangent (tan δ) and dielectric constant (ε') on temperature and frequency of the applied ac field is studied in the temperature range of 323-523 K and frequency range of 10^3-10^6 Hz. The variation of dielectric constant (ε') *versus* frequency at different temperatures for L-alanine is shown in Fig. 3. The dielectric constant has high values in the lower frequency region and then it decreases with increase of applied frequency. The variation of dielectric loss *versus* frequency at different temperatures for L-alanine is shown in Fig. 4. From this figure it can be noticed that as the frequency increases the dielectric loss decreases. This behaviour is similar to that of the dielectric constant. At low frequencies the dipoles can easily switch alignment with the changing field. As the frequency increases the dipoles are able to rotate less and maintain phase with the field; thus they reduce their contribution to the polarization field and hence the observed reduction in dielectric constant and dielectric loss. The characteristic of low dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application[4].

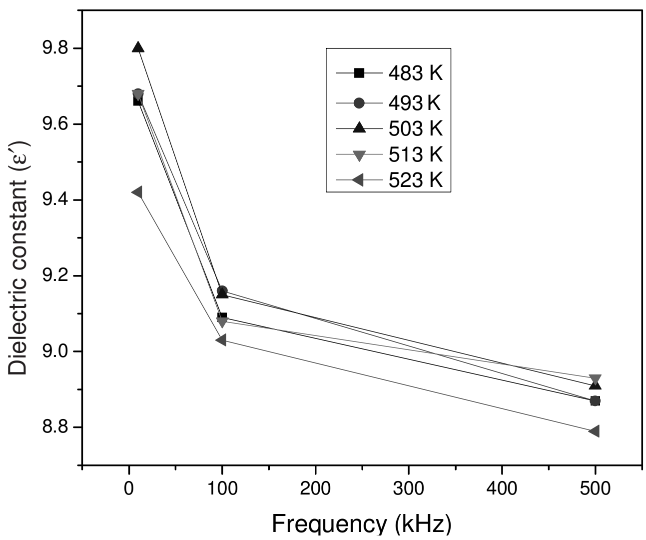

Fig. 3. Variation of dielectric constant (ε') with frequency of the applied ac field

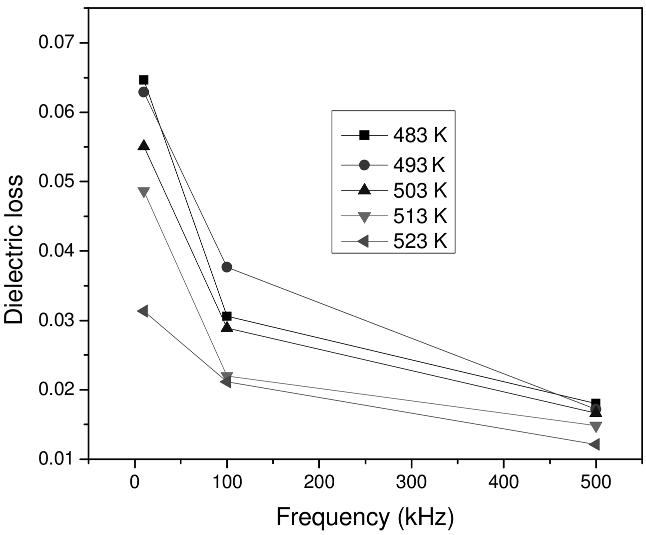

Fig. 4. Dependence of dielectric loss (tan δ) on frequency of the applied ac field

The variation of dielectric constant with temperature at different frequencies of the applied ac field for L-alanine single crystals is shown in Fig. 5. The dielectric constant increases with the rise in temperature upto its maximum value (ε_{max}) at the curie temperature (T_c) and then decreases with further increase in temperature. It is observed that the compound undergo a phase transition from ferroelectric to paraelectric at a particular temperature. Curie temperature T_c shifts towards higher temperature side at higher frequencies. It is observed that material has the maximum value of the dielectric constant at a particular temperature for all the three frequencies (10, 50 and 100 kHz). The dielectric peak is found to be broadened over a certain temperature interval, which indicates the existence of diffuse phase transition and the broadness decreases with the increase of frequency. The temperature dependence of dielectric loss is shown in Fig. 6. So it is called a "relaxor" ferroelectric material because of its dispersive (frequency dependent) dielectric response and diffuse phase transition (over a wide range of temperature, 475-525 K) around the curie point T_c. They are attractive in applications such as medical imaging, telecommunication and ultrasonic devices.

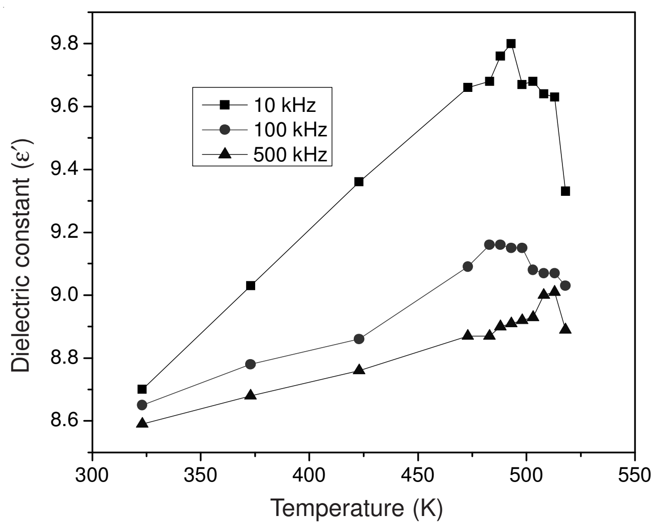

Fig. 5. Plot of dielectric constant ε' against temperature at different frequencies

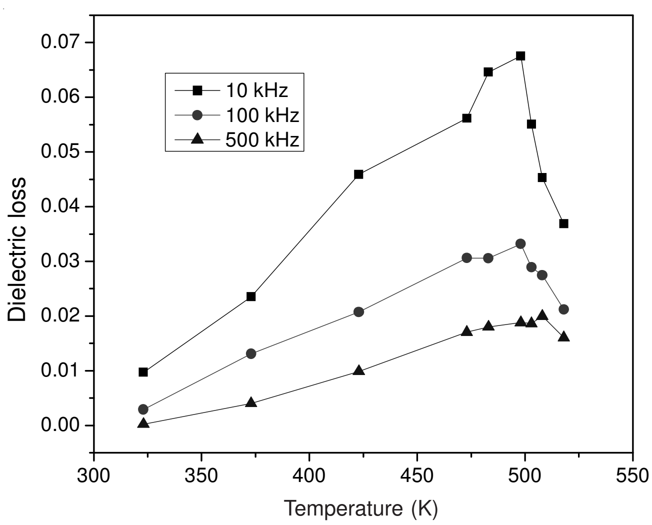

Fig. 6. Plot of dielectric loss (tan δ) *vs* temperature at different frequencies

Ferroelectric studies: Registration of hysteresis loop is a standard technique for the fast characterization of ferroelectric crystals[5]. The fundamental ferroelectric P-E hysteresis traced using computer interface Sawer-Tower Circuit[6] for L-alanine crystals at the frequency of 50 Hz at room temperature is shown in Fig. 7. In order to examine the P-E hysteresis loop, the crystals are investigated having an electrode area of 48 mm^2 and a thickness of 1.38 mm. Gold electrodes are deposited on the polished surface. L-alanine crystal shows slim loop with $P_r = 0.01 \mu C/cm^2$ indicating the existence of a weak ferroelectric phase at room temperature. The positive polarization parameter state saturates at a value of 0.02 $\mu C/cm^2$.

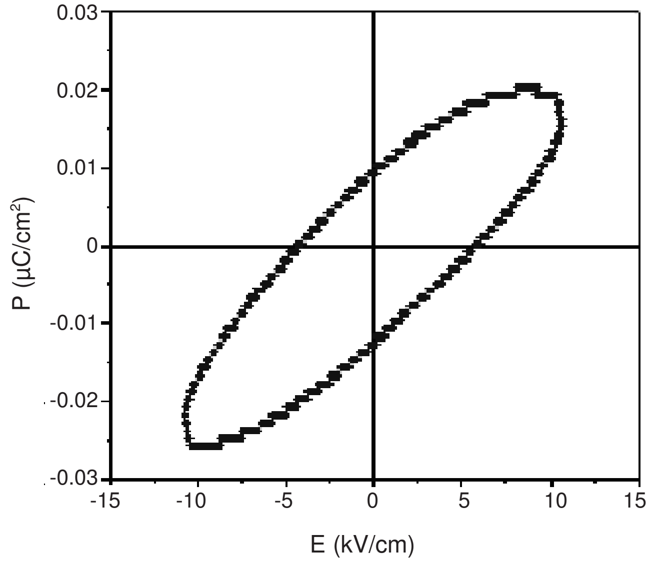

Fig. 7. P-E Hysteresis loop of L-alanine crystal

Conclusion

Good optical quality single crystals of L-alanine have been grown from by slow evaporation technique. The crystallanity of the grown sample has been confirmed by single crystal diffraction analysis. Various functional groups present in the grown crystal have been identified by FTIR spectroscopy. The dielectric response at various frequencies clearly demonstrates the relaxational behaviour in the temperature range 475-525 K, characterized by strongly diffuse dielectric peak and a shift of the temperature of dielectric maximum to a higher temperature side with increasing frequency. These crystals exhibit hysteresis loop and their ferroelectric parameters have been measured. Hence, these crystals can be used for advanced applications such as medical ultrasonic imaging and high-performance underwater communication devices.

REFERENCES

1. C. Razzetti, M. Ardoino, L. Zanotti, M. Zha and C. Paorici, *Cryst. Res. Technol.*, **37**, 456 (2002).
2. L. Misoguti, A.T. Varela, F.D. Nunes, V.S. Bagnato, F.E.A. Melo, J.M. Filho and S.C. Zilio, *Opt. Mater.*, **6**, 147 (1996).
3. T. Raghavalu, G.R. Kumar, S.G. Raj, V. Mathivanan and R. Mohan, *J. Cryst. Growth*, **307**, 112 (2007).
4. C. Balarew and R. Duhlew, *J. Solid State Chem.*, **55**, 1 (1984).
5. R.Z. Rogowski, K. Matyjasek and R. Jakubas, *Cryst. Res. Technol.*, **41**, 557 (2006).
6. C.B. Sawer and T.H. Tower, *Phys. Rev.*, **35**, 269 (1930).