



Growth, Structural and Dielectric Behaviour of L-Cysteine Hydrochloride Monohydrate Single Crystals

M. LOGANAYAKI^{1,2} and P. MURUGAKOOTHAN^{2,*}

¹Department of Physics, SRM University, Ramapuram, Chennai-600 089, India

²Postgraduate & Research Department of Physics, Pachaiyappa's College, Chennai-600 030, India

*Corresponding author: E-mail: murugakoothan03@yahoo.co.in

(Received: 7 February 2011;

Accepted: 27 July 2011)

AJC-10216

In this present study, L-cysteine hydrochloride monohydrate single crystals have been grown by slow evaporation solution technique. The grown crystals have been subjected to various characterization studies such as single crystal XRD, CHNS and NMR. The microstructural imperfections of L-cysteine hydrochloride monohydrate crystals have been studied by etching. The dielectric behaviour of L-cysteine hydrochloride monohydrate has been measured at various temperatures and the activation energy of electrical processes is also determined at various frequencies. P-E hysteresis loop has been investigated at 50 Hz.

Key Words: Growth from solutions, X-ray diffraction, NMR, Dielectric properties, Etching.

INTRODUCTION

In recent years, dielectric materials play an important role in microelectronics and have been utilized in wide range of technological applications. Materials with high dielectric constant are currently an important challenge for new applications in electronics¹. Materials with high dielectric constant values are good candidates for heating devices². Requirements of these dielectric materials for the development of capacitors must be the combined dielectric properties of a high dielectric constant (ϵ_r) and low dielectric loss. Recently, some results concerning huge dielectric constant in systems have been reported³⁻⁶. The large dielectric constant observed in these materials must ultimately be due to either intrinsic effects that arise from the properties of the material such as lattice vibrations, or extrinsic effects, such as defects⁷ or contact problems⁸. Due to the poor chemical, thermal and mechanical stability, the organic crystals are currently limited in their industrial applications. To overcome these problems, the research of combination of organic and inorganic hybrid compounds leads to find a new class of materials for electronic industries, called semiorganic materials. These semiorganic materials have the advantages of large nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness. In the present work, semiorganic single crystal of L-cysteine hydrochloride monohydrate (L-CHCM) has been grown by slow evaporation solution technique. L-cysteine hydrochloride monohydrate crystallizes with noncentrosymmetric space

group P2₁2₁2₁⁹⁻¹¹. The grown crystals have been characterized by single crystal XRD, CHNS and C-NMR studies. The etching behaviour of L-cysteine hydrochloride monohydrate has been studied. The dielectric constant has been studied as a function of frequency and temperature and the corresponding activation energy (E_a) has been calculated for the grown crystal. In addition, ferroelectric property of the grown crystal has been confirmed by hysteresis loop studies.

EXPERIMENTAL

Crystal growth: Growth of L-cysteine hydrochloride monohydrate was performed by dissolving commercially available high purity L-cysteine hydrochloride monohydrate in millipore (18.2 M Ω /cm⁻¹) water using slow evaporation solution technique. The prepared solution was stirred well for 3 h using a magnetic stirrer at 37 °C (pH was 3.5). A saturated solution of 100 mL was taken and filtered using a Whatmann filter paper. The filtered solution was taken in a beaker, which was closed with a thick filter paper so that the rate of evaporation could be minimized. After 25 days the L-cysteine hydrochloride monohydrate material crystallized at the bottom of the container. The material was three times recrystallized for purification and used for crystal growth. Good-quality L-cysteine hydrochloride monohydrate single crystal of size 23 mm × 14 mm × 7 mm has been obtained and is shown in Fig. 1. The ORTEP diagram of L-cysteine hydrochloride monohydrate crystal is shown in Fig. 2.

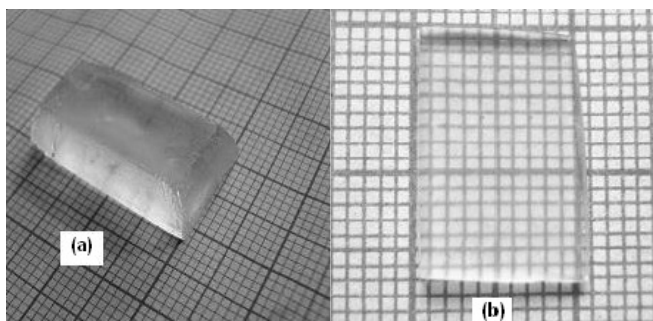


Fig. 1. (a) As grown crystal and (b) Polished crystal of L-cysteine hydrochloride monohydrate

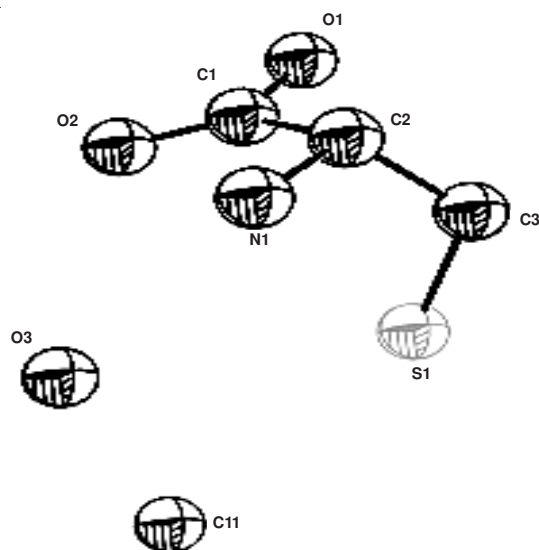


Fig. 2. ORTEP diagram of L-cysteine hydrochloride monohydrate crystal

RESULTS AND DISCUSSION

X-ray diffraction studies: Single crystal X-ray diffraction study was carried out to calculate the lattice parameters of the grown crystal. The single crystal XRD data of the grown L-cysteine hydrochloride monohydrate crystal was obtained using ENRAF NONIUS FR 590 single crystal X-ray diffractometer. The L-cysteine hydrochloride monohydrate crystal crystallizes in orthorhombic system, space group $P2_12_12_1$ with lattice parameters $a = 19.425 \text{ \AA}$, $b = 7.115 \text{ \AA}$, $c = 5.289 \text{ \AA}$, $v = 764.186 \text{ \AA}^3$, which agrees well with the reported values^{9,10}. According to the chemical bonding theory of single crystal growth, the growth morphology is thermodynamically related to corresponding crystallographic structure¹². The different faces of a crystal are known to grow with different growth rates. The grown crystal has well developed faces as shown in Fig. 3. The morphology reveals that the growth rate along the 'a' direction is higher than other directions.

Carbon, hydrogen, nitrogen and sulphur analysis: The chemical composition of the synthesized material L-cysteine hydrochloride monohydrate has been determined by carbon, hydrogen, nitrogen and sulphur (CHNS) analysis using Elemental Vario EL III-Germany analyzer. The weight percentages of carbon, hydrogen and nitrogen present in L-cysteine hydrochloride monohydrate sample have been determined. The calculated (%) values are C = 20.51, H = 5.73, N = 7.97, S = 18.25 and observed values (%) are C = 20.73, H = 5.78,

N = 8.073, S = 17.96. The calculated values agree well with the experimental values. Chemical analysis confirms that the L-cysteine hydrochloride monohydrate crystal contains water molecule and the synthesized L-cysteine hydrochloride monohydrate material has been quantitatively confirmed.

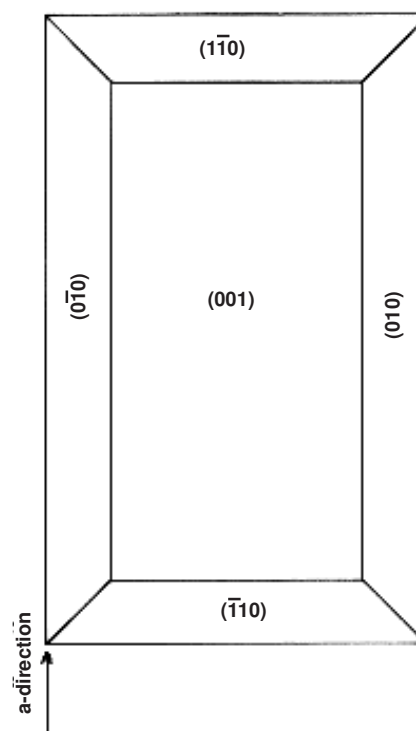


Fig. 3. Morphology of L-cysteine hydrochloride monohydrate crystal

NMR analysis: The NMR spectrum is used to confirm the presence of functional groups in the grown L-cysteine hydrochloride monohydrate crystal. The NMR spectrum was recorded using a JEOL AMX instrument at 30 °C. The chemical shifts are shown in Fig. 4. The peak at 23.87 ppm is attributed to CH_2 group. The peak at 54.35 ppm is attributed to CH group. The peak at 170 ppm is attributed to COO^- group. Thus the presence of all the expected functional groups in L-cysteine hydrochloride monohydrate has been identified.

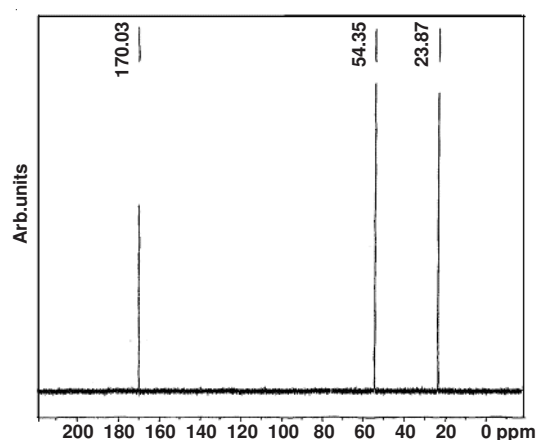


Fig. 4. NMR spectrum of L-cysteine hydrochloride monohydrate crystal

Etching studies: The study of the microstructures on the faces of crystals offers important light on the history of growth

of the crystal and hence it has been of great interest. In the present study, etching study has been made to understand the growth history and growth mechanism of solution grown L-cysteine hydrochloride monohydrate single crystals and water was used as an etchant. The crystals were dipped in water for a few seconds at room temperature and then wiped them with dry filter paper. Etch patterns were observed and photographed under optical Leitz-Wetzlar Metallax II microscope. The etching on {001} face of the as grown crystal produces irregular layered structure for 20 s as shown in Fig. 5. Etching study reveals that the growth occurred by two dimensional layer growth mechanism.

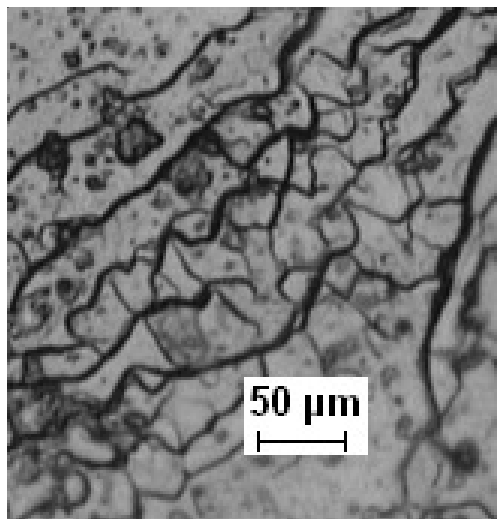


Fig. 5. Etch pattern of L-cysteine hydrochloride monohydrate

Dielectric studies: The dielectric constant was measured at various temperatures using HIOKI 3532 LCR HITESTER in the frequency range 3 kHz to 1 MHz. A sample dimension of 6.65 mm × 4.20 mm × 2.18 mm having silver coating on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed. The dielectric constant is calculated using the formula $\epsilon' = Ct/\epsilon_0 A$, where C is the capacitance (F), t the thickness (m), A the cross-sectional area (m²) of the sample and ϵ_0 is the absolute permittivity of the free space having a value of $8.854 \times 10^{-12} \text{ Fm}^{-1}$. The imaginary dielectric constant (ϵ'') of the capacitor is calculated using the relation $\epsilon'' = \epsilon' \tan \delta$ where $\tan \delta$ is the loss tangent. The alternating current conductivity is calculated using the relation $\sigma_{ac} = 2\pi f \epsilon_0 \epsilon' \tan \delta$, where f is the frequency of the applied ac field (Hz). The activation energy of the crystal is calculated from an Arrhenius plot of $\ln \sigma_{ac}$ using the relation $\sigma_{ac} = \sigma_0 \exp(-E_a/kT)^{13}$, where σ_{ac} is the conductivity at temperature T, E_a the activation energy for the electrical process and k is the Boltzmann constant.

The variation of dielectric constant of L-cysteine hydrochloride monohydrate with temperature is shown in Fig. 6. From the figure, it is found that the value of dielectric constant decreases with increase of frequency. This behaviour is due to the fact that at lower frequency the dipoles are able to follow the applied field, whereas at higher frequency they are not¹⁴. The contributions of all the four polarizations such as electronic, ionic, dipolar and space charge are predominant in low-frequency region^{15,16} and hence the dielectric constant

increases abnormally. And, the L-cysteine hydrochloride monohydrate structure contains water molecule. Its contribution weakens as frequency is increased. As the temperature reaches phase transition temperature ($T_c=368 \text{ K}$), the dielectric constant reaches a maximum ($\sim 33,000$ at 3 kHz) and then decreases. Thus, L-cysteine hydrochloride monohydrate crystal having high dielectric constant may be useful for applications in high-performance capacitors and miniaturized electronics.

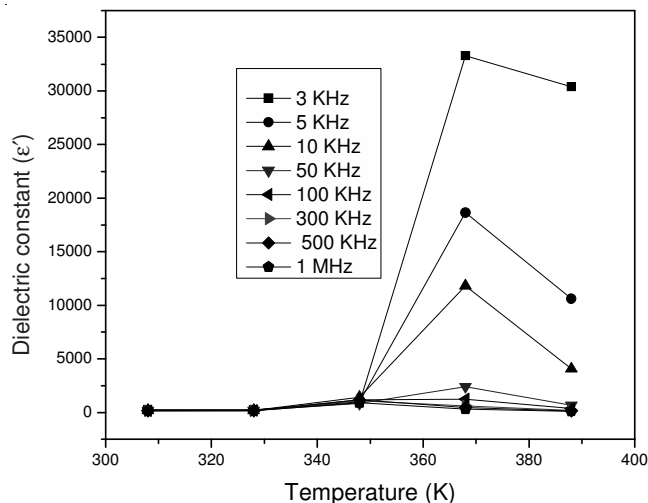


Fig. 6. Variation of ϵ' with temperature

The behaviour of conductivity with temperature ranging from 308 to 388 K at various frequencies is shown in Fig. 7. The value of conductivity $\ln \sigma_{ac}$ is found to increase with the increase in frequency. The activation energy at various frequencies is calculated from the slope of the graph between $\ln \sigma_{ac}$ versus $1/T$. The variation of activation energy with frequency is shown in Fig. 8. The trend shows that the activation energy decreases with the increase in frequency and its value falls more rapidly at higher frequencies.

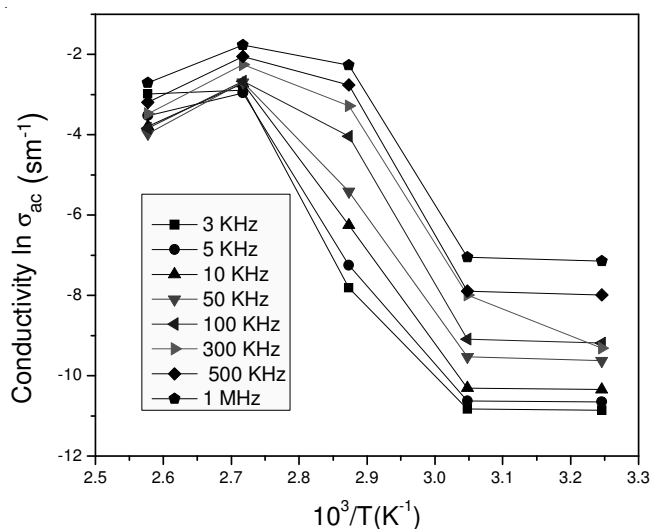


Fig. 7. Graph of $\ln \sigma_{ac}$ vs. T^{-1} corresponding to the frequencies

Ferroelectric studies: Registration of hysteresis loop is a standard technique for the fast characterization of ferroelectric crystals¹⁷. The variation of the polarization signal with respect to the ac field to the ferroelectric specimen is given by

hysteresis loop. The fundamental ferroelectric P-E hysteresis traced using computer interface Sawyer-Tower Circuit¹⁸ for L-cysteine hydrochloride monohydrate crystals at the frequency of 50 Hz at room temperature is shown in Fig. 9. In order to examine the P-E Hysteresis loop, the grown sample was cut from grown crystals by a wet thread saw followed by polishing. The investigated crystal has an electrode area of 46 mm² and a thickness of 1.46 mm. Gold electrodes were deposited on the polished surface. The measured coercive field is 0.6 kV/cm. The positive polarization parameter state saturates at a value of 0.09 $\mu\text{C}/\text{cm}^2$.

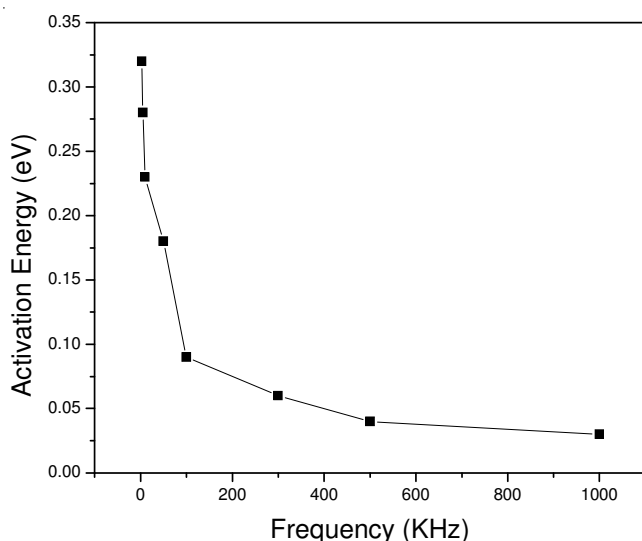


Fig. 8. Variation of activation energy E_a with frequency of L-cysteine hydrochloride monohydrate crystal

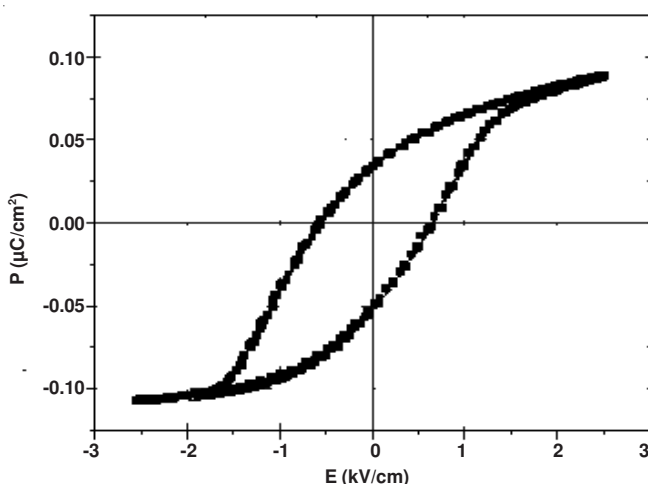


Fig. 9. P-E Hysteresis loop of L-cysteine hydrochloride monohydrate crystal

Conclusion

Single crystals of L-cysteine hydrochloride monohydrate have been grown from aqueous solution by slow evaporation solution technique. The crystallinity of the grown sample was confirmed by single crystal diffraction analysis. Chemical composition of the synthesized material was confirmed by CHNS analysis. The presence of all the functional groups in the grown sample has been identified using NMR analysis. The study of microstructures on L-cysteine hydrochloride monohydrate crystal suggests that the growth occurred by two dimensional layer growth mechanism. The variation of dielectric constant with temperature was studied at different frequencies and the phase transition temperature has been determined by dielectric studies. The ferroelectric property was further confirmed by the hysteresis loop studies. Hence these crystals can be used in multilayer capacitors and sensors because of its superior dielectric properties.

REFERENCES

1. R.J. Cava, *J. Mater. Chem.*, **11**, 54 (2001).
2. J. Bijwe and N. Phougat, *J. Porphyrins Phthalocyan.*, **2**, 223 (1998).
3. P.M. Botta, J. Mira, A. Fondado and J. Rivas, *Mater. Lett.*, **61**, 2990 (2007).
4. J. Wang, X.G. Tang, H.L.W. Chan, C.L. Choy and H. Luo, *Appl. Phys. Lett.*, **86**, 152907 (2005).
5. K.-P. Chen, X.-W. Zhang and H.S. Luo, *J. Phys. Condens. Matter*, **14**, L571 (2002).
6. M. Lenin, N. Balamurugan and P. Ramasamy, *Cryst. Res. Technol.*, **42**, 39 (2007).
7. G.A. Samara and L.A. Boatner, *Phys. Rev. B*, **61**, 3889 (2000).
8. P. Lunkenheimer, V. Bobnar, A.V. Pronin, A.I. Ritus and A.A. Volkov, *Phys. Rev. B*, **66**, 052105 (2002).
9. R.R. Ayyar, *Z. Kristallogr.*, **126**, 227 (1968).
10. R.R. Ayyar and R. Srinivasan, *Curr. Sci.*, **34**, 449 (1965).
11. G. Bhagavannarayana, S. Kumar, M. Shakir, S.K. Kushawaha, K. Maurya, R. Malhotra and K.R. Rao, *J. Appl. Cryst.*, **43**, 710 (2010).
12. D.L. Xu and D.F. Xue, *J. Cryst. Growth*, **286**, 108 (2006).
13. B. Lal, K.K. Bamzai, P.N. Kotru and B.M. Wanklyn, *Mater. Chem. Phys.*, **85**, 353 (2004).
14. C.-Y. Chung, Y.-H. Chang, G.-J. Chen and Y.-L. Chai, *J. Cryst. Growth*, **284**, 100 (2005).
15. K.V. Rao and A. Smakula, *J. Appl. Phys.*, **36**, 2031 (1965).
16. K.V. Rao and A. Smakula, *J. Appl. Phys.*, **37**, 319 (1966).
17. R.Z. Rogowski, K. Matyjasek and R. Jakubas, *Cryst. Res. Technol.*, **41**, 557 (2006).
18. C.B. Sawyer and T.H. Tower, *Phys. Rev.*, **35**, 269 (1930).