Growth, structural, mechanical, etching and dielectric properties of L-methionine L-methioninium hydrogen maleate single crystal

P. VASUDEVAN[a,b], S. SANKAR[a,*], S. GOKULRAJ[c]
[a] *Department of Physics, MIT Campus Anna University, Chennai 600044, India*
[b] *Department of Physics, SKR Engineering College, Chennai 600123, India*
[c] *Department of Physics, Vel-Tech Dr.RR & Dr.SR Technical University, Chennai 600062, India*

L-methionine L-methioninium hydrogen maleate single crystal was grown by using slow evaporation method from aqueous solution at room temperature. Crystal structure and lattice parameters of the grown crystal were determined by single crystal X-ray diffraction analysis. Molecular structure of the crystal was discussed by ^{1}H NMR and ^{13}C NMR studies. Mechanical strength of the grown crystal was studied using Vicker's microhardness tester. Etching studies have been carried out to understand the growth mechanism and density of defects in the grown crystal. Dielectric studies of the sample were carried out at different temperatures in the frequency range from 5 Hz to 5 MHz. Second harmonic generation efficiency was confirmed by Kurtz and Perry technique.

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Keywords: Solution growth, Nuclear magnetic resonance, Microhardness, Etching studies and Dielectric properties

1. Introduction

Nowadays, microelectronic industries make use of low dielectric constant crystals at high frequency region in multilevel interconnected circuits. When low dielectric materials are used as interlayer dielectrics (ILD), they reduce the cross-talk between nearby interconnected circuits and also reduce the power consumption with RC delay [1]. Usually, silica has been used as interlayer dielectric material which has low dielectric constant. To replace silica, several inventive attempts were made for getting low dielectric constant materials. Thus, there is still need for new low dielectric constant value materials. The single crystals used in electronic industries should have properties such as high mechanical strength, better thermal stability, low dielectric constant and minimum density of defects. These crystals can be effectively used in electrical interconnectors with water-proof condition [2]. Literature survey reveals that semi-organic crystals possess low dielectric constant and dielectric loss [3, 4]. Organic materials are attracting great deal of attention due to their potentially nonlinearity and faster response in the electro-optic effect than inorganic materials. Mostly, the semi-organic crystals were prepared using the amino acids along with any kind of organic or inorganic acid to get single crystals [5, 6]. In solid state, amino acids contain donor and acceptor groups which provide the ground state charge of the molecules. Due to dipolar nature of amino acids, they possess good mechanical and physical properties which make them ideal materials for device fabrications in microelectronic industries. Hence, we have chosen L-methionine from the amino acid family, which is one of the sulfur containing proteinogenic amino acids, the other one being cysteine. Maleic acid plays as an acceptor to form various π-stacking complexes with other aromatic molecules and also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions. Some maleic acid derivative crystals have been reported recently [7, 8]. In this direction, L-methionine L-methioninium hydrogen maleate [LMLMHM] single crystals were successfully grown and the structural, optical and thermal properties of LMLMHM crystal were carried out and reported earlier [9, 10]. The other characterization studies are seldom available in the literature. Hence, in the present investigation, we report the relevant NMR, hardness, etching and dielectric studies of the grown crystal LMLMHM for the first time to discuss the molecular structure, mechanical strength, density of defects and dielectric behaviour of the grown crystal. The dielectric behaviour of the crystal was analysed with respect to the application in microelectronic interconnected circuits. NLO test was also performed to confirm the second harmonic generation of the crystal.

2. Experimental details

2.1 Synthesis and growth

Analytical grade of L-methionine and maleic acid along with doubled distilled water were used for the preparation of LMLMHM crystal. Initially, L-methionine and maleic acid were dissolved in water with 2:1 molar ratio and the solution was stirred well for four hours. The

solution was then allowed for slow evaporation. After a period of 7 days, well transparent and colourless crystals of LMLMHM were formed. With repeated crystallization process, we are able to harvest the crystal finally with improved size and transparency. The photograph of the as-grown crystal is shown in Fig. 1. LMLMHM crystal was synthesized from the aqueous solution by the following reaction:

$$C_5H_{11}NO_2S.\ C_5H_{11}NO_2S + C_4H_4O_4 \rightarrow C_{14}H_{26}N_2O_8S_2 \quad (1)$$

Fig. 1. Photograph of as-grown crystal of LMLMHM .

2.2 Characterization techniques

Single crystal XRD studies were carried out using Bruker Kappa APE XII single crystal X-ray diffractometer to determine the crystal structure and lattice parameters of the grown LMLMHM crystal. The ^{1}H NMR and ^{13}C NMR spectral experiments were performed for LMLMHM crystal and the spectral data were recorded in the magnetic field of 11.75 Tesla using Bruker AV III Fourier Transformed NMR spectrometer (For^1 H NMR data ν_0 = 500 MHz and ^{13}C NMR data ν_0 =125 MHz). Microhardness measurements of the grown crystal were carried out using REICHERT MD 4000E ULTRA microharness tester with diamond pyramid indenter attached to an optical microscope. Etching studies were analysed using RICHERT POLYVAR 2 MET photomicroscope with magnification 80 x and water was used as solvent. Dielectric parameters were calculated with an accuracy of ± 2 % using an HIOKI LCR Hitester varying the temperatures in the frequency range from 5 Hz to 5 MHz. Non-linear optical property of LMLMHM crystal was confirmed by Kurtz and Perry powder technique using Q-switched high energy Nd:YAG laser (QUANTA RAY model LAB-170-10).

3. Results and discussion

3.1 Single crystal XRD analysis

X-ray data of the grown crystal LMLMHM were collected at 293º C using Bruker Kappa APE XII single crystal X-ray diffractometer with MoKα (λ=0.71069 Å) radiation. A selected transparent grown crystal was used to measure the intensity data and θ values were varied from 2.55º to 25º. The structure of the crystal was solved by direct method procedure using the SIR-92(WINGX) computer program. The structure was refined by the full matrix least square using SHELXL-97(WINGX) program. During the course of data collection, one standard reflection was monitored for every 100 reflections without significant variation. The crystallographic informations are summarized as follows:

The grown crystal LMLMHM crystallized with monoclinic structure and non-centrosymmetirc space group $P2_1$. The cell parameters were found to be a = 12.78 Å, b = 5.35 Å, c= 15.13 Å; α = γ = 90º, β= 114.07º with unit cell volume 955.5 Å^3. The obtained crystallographic data are found to be in good agreement with the reported literature values: a = 12.981 Å, b = 5.326 Å, c= 15.124 Å; α = γ = 90º, β= 114.09º with unit cell volume 954.6 Å^3 [9].

3.2 NMR studies

Molecular structure of LMLMHM crystal was analysed by NMR studies. The ^{1}H NMR and ^{13}C NMR spectra of the grown LMLMHM crystal have been recorded by dissolving in D_2O and the obtained spectra are shown in Figs. 2 and 3 respectively. The chemical shifts for ^{1}H NMR and ^{13}C NMR spectra are represented in δ ppm. In the ^{1}H NMR spectrum, the triplet peaks at δ = 2.533 ppm, δ = 2.568 ppm and δ = 2.583 ppm are due to the presence of COOH in L-methionine. An intense singlet peak at δ = 4.713 ppm is due to presence of undeuterated water in D_2O. The triplet peaks at δ = 3.893 ppm, δ = 3.904 ppm and δ = 3.916 ppm are attributed to the influence of adjacent C-H groups over each other. The presence of two protons of CH_2 group is assigned against the intense peak at δ = 3.916 ppm. ^{1}H NMR results reveal the presence of amino acid and carboxylic groups. The dipolar nature of the material is thus confirmed for second harmonic generation when powerful radiation is incident on the material. It is concluded from ^{1}H NMR studies that the various signals confirm the molecular structure of the grown LMLMHM crystal.

The characteristics peaks of ^{13}C NMR spectrum of LMLMHM are discussed in this section. In the spectrum, carbon atoms are identified from different peaks located at various chemical environments. The signals at δ = 170.517 ppm and δ = 173.249 ppm are attributed to the presence of carboxylic groups in the compound. The presence of the signal at δ = 133.67 ppm is attributed to the carbons of two aromatic groups. The signal at δ = 53.077 ppm is due to carbon atom connected to amino group in L-methionine. The resonance peaks at δ = 28.708 ppm and δ = 29.352 ppm indicate the presence of two CH (isopropyl) in L-methionine. Methyl group CH_3 in LMLMHM is confirmed corresponding to the peak at δ = 13.896 ppm. Thus, the functional groups are interpreted from the peaks of ^{13}C NMR spectrum to confirm the amino acid group. Since there are no other peaks observed, the purity of the compound is confirmed.

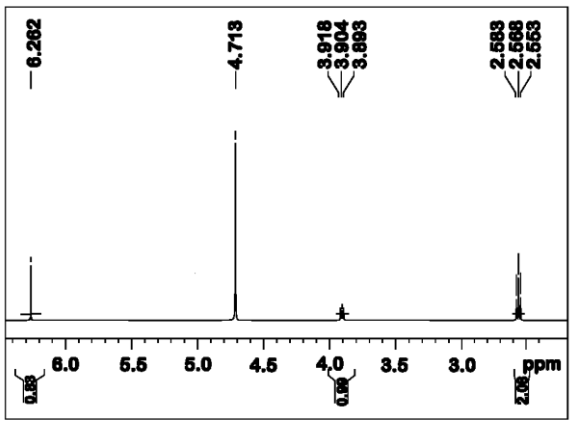

Fig. 2. [1]H NMR spectrum of LMLMHM crystal.

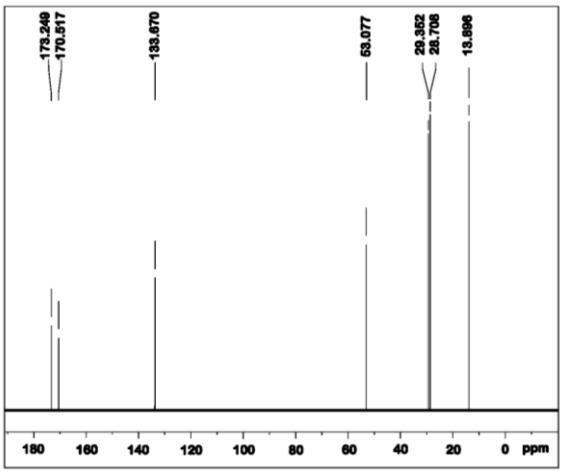

Fig. 3. [13]C NMR spectrum of LMLMHM crystal.

3.3 Vicker's microhardness

Hardness is an important mechanical property required for the fabrication of electronic and optical devices. Microhardness studies have been carried out on a selected well transparent single crystal using microhardness tester, fitted with a Vicker's diamond pyramidal indenter [11]. To get accurate results of hardness of the grown crystal, several indentations were made on the sample for different applied loads from 5g to 50g and mean diagonal length was measured. The hardness was calculated using the relation,

$$H_v = 1.8544\ P/d^2\ \ kg/mm^2 \qquad (2)$$

where P is the applied load and d is the mean diagonal length of the indenter impression. Fig. 4 shows the variation of hardness behaviour as a function of applied load. It is observed from the figure that the hardness of LMLMHM increases with increasing load up to 35g. Above 35g the hardness of the sample starts decreasing up to 50g. After that cracks occur. This may be due to the release of internal stress generated locally by indentation. The increasing trend of microhardness with the load up to 35g is well understood from Mayer law and onitisch condition. According to Mayer law, the relationship between the load (P) and the size (d) of the indentation is given as

$$P = k\ d^n \qquad (3)$$

where n is called Mayer index or work hardening index. Hence the slope of the plot of log P versus log d (Fig. 5) will give the work hardening index (n) which is found to be 4.21. According to onitisch if n is greater than 2, the microhardness will increase with the increase of load. Hence, the material shows increasing trend for the hardness of the material upto a particular load of 35g. The material LMLMHM is confirmed with large amount of mechanical strength which is better for device fabrications.

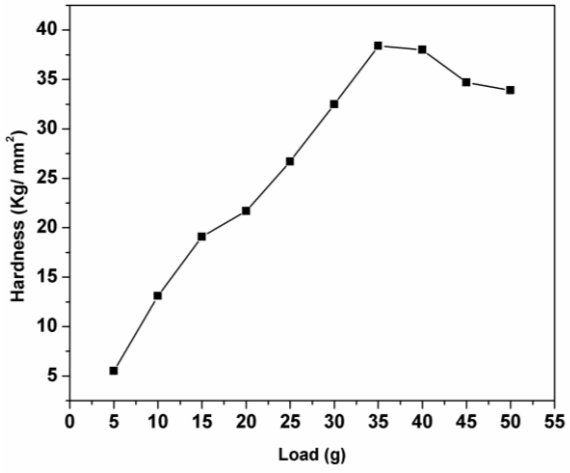

Fig. 4. Vicker's microhardness of LMLMHM crystal.

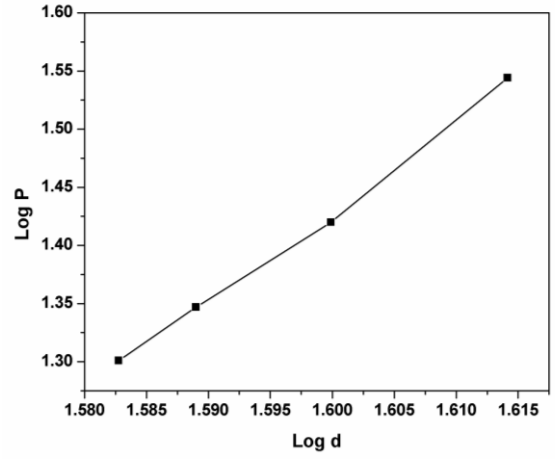

Fig. 5. Plot of log P vs log d.

3.4 Etching studies

The study of micromorphology is very important to analyse the impurities, dislocations and any other defect present in the grown crystal and also to understand the growth mechanism. The grown crystal is highly soluble in water. Therefore water was chosen as etchant. A well transparent crystal was selected for etching the surface by dipping the crystal in distilled water for a few seconds at room temperature and then wiping it with dry filter paper. Etch pattern was photographed using RICHERT POLYVAR 2 MET photomicroscope with 85W halogen reflector bulbs. Microphotograph of crystal before etching is shown in Fig. 6(a). Before etching, the surface is showing scattered striations and minute cracks. After etching for 15 seconds and 30 seconds the etchant is able to develop small rocky ledges as shown in Figs. 6(b) and 6(c). According to Hartman [12], the growing crystal contains F (flat), S (stepped) and K (kinks) faces. As the steps are not visible in the figures, it is understood that the growing crystal surface contains atomic flat faces. The appearance of flat faces is due to the higher coefficient of volume diffusion (10^{-5} cm^2s^{-1}) than the coefficient of surface diffusion (10^{-8} cm^2s^{-1}) in the case of solution growth. Owing to higher coefficient of volume diffusion, the pressure of more flat faces is predicted with uninterrupted chains of strong bonds. Hence, it is established that the morphology of the grown crystal is due to faces endowed with strong periodic bond chains. Consequently, the etch pattern looks like rocky sledges on the flat faces. Hence, the presence of rocky sledges due to the development of more flat faces confirms the two dimensional nucleation theory with less defects [13]. Therefore, by adjusting the initial growth conditions, the density of defects can be minimized. The shape of etch pits may be changed by varying the concentration of the solvent [14, 15]. The factors such as temperature of etching, stirring and adsorption of impurities or reduction products lead to the change in the geometry of each pits [16].

Fig. 6. (a) Before etching.

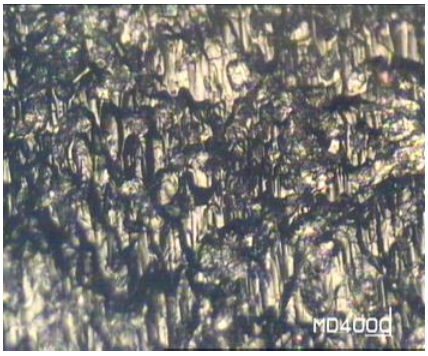

Fig. 6. (b) After etching for 15 secs.

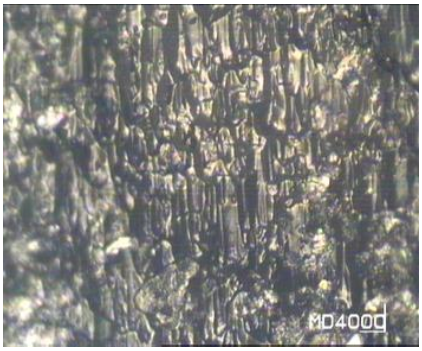

Fig. 6. (c) After etching for 30 secs.

3.4 Dielectric studies

Dielectric properties of the crystal are important to study the lattice dynamics. The dielectric constant and dielectric loss were measured for the frequency range from 5 Hz to 5 MHz at various temperatures for the grown LMLMHM crystal. The cut and polished single crystal of size 6.65 mm × 4.92 mm × 1.45 mm was used for dielectric studies. The surface of the sample was coated with silver paste for electrical contact. Dielectric constant and dielectric loss was calculated using the relations

$$\varepsilon' = \frac{cd}{A\varepsilon_{\circ}} \tag{4}$$

$$\varepsilon'' = \varepsilon_r D \tag{5}$$

where d is the thickness of the grown crystal, A is the area of the crystal and D is the dissipation factor. Figs. 7 and 8 show the plots of the dielectric constant and dielectric loss versus applied frequency respectively. From the plots, the values of dielectric constant and dielectric loss are high in the lower frequency range and decrease with applied higher frequency. The very high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations such as electronic, ionic, orientational and space charge polarizations. The low value of dielectric constant at higher frequencies may be due to the loss of significance of these polarizations

gradually [17]. The low value of dielectric loss at high frequencies reveals the high optical quality of the crystal with less defects, which is desirable property for nonlinear optical applications [18].

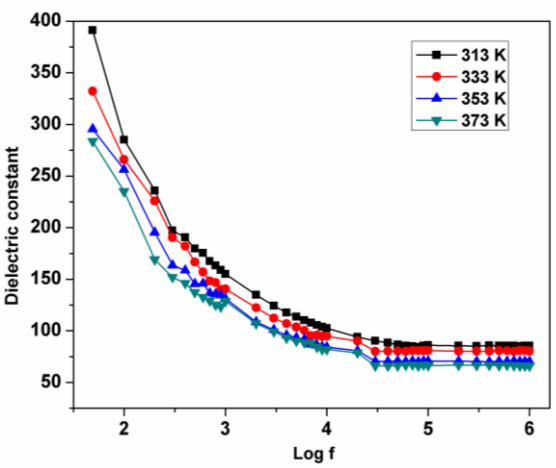

Fig. 7. Plot of dielectric constant of LMLMHM crystal vs frequency.

When low dielectric constant and dielectric loss material is used as an interlayer dielectric in the electronic circuits, the circuits will withstand high frequency power protectiing the circuits from electrical damage. Moreover, these interconnected circuits will reduce cross-talks and power consumption with RC delay [1].

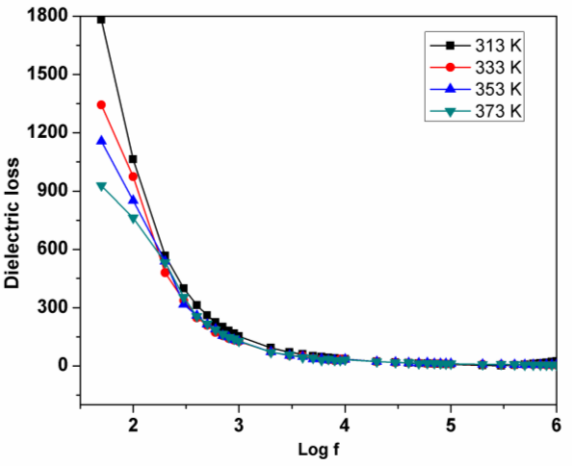

Fig. 8. Plot of dielectric loss of LMLMHM crystal vs frequency.

3.5 NLO test

Second harmonic generation of the grown crystal was estimated using Kurtz and Perry powder technique [19]. A high intense beam of laser wavelength 1024 nm was illuminating the sample with pulse width of 8 ns. The emission of green radiation from the sample confirms the NLO property. To measure the second harmonic generation efficiency (SHG) of the grown crystal, the output radiation was converted into electrical pulses using photomultiplier tube. The output power from LMLMHM sample was measured as 7.5 mJ and then compared with the value of 8.8 mJ obtained for the standard material KDP. Hence, the SHG efficiency of the grown crystal was estimated as 85% of that of KDP which is found to be fairly in good agreement with earlier reported value of 90% [10]. Therefore, the grown crystal is one of the promising NLO materials to find applications in optoelectronic industries.

4. Conclusion

Nonlinear optical crystal of L-methionine L-methioninium hydrogen maleate was grown by solution growth technique at room temperature. The single crystal nature and molecular structure were confirmed by single crystal X-ray diffraction and NMR studies. Vicker's microhardness studies reveal that the grown crystal is having large amount of mechanical strength. Etching studies strongly suggest that the growth mechanism is based on two dimensional nucleation theory with minimum density of defects. Dielectric studies reveal that the dielectric constant and dielectric loss of the crystal are low at high frequency region. The nonlinear optical property of the grown crystal was confirmed by Kurtz and Perry powder technique and its second harmonic generation (SHG) efficiency was found to be 85% of that of standard material KDP. The above studies suggest that the grown material LMLMHM can find useful application in microelectronic industries.

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*Corresponding author: ssankarmit@gmail.com