Growth and Characterization of Sodium Hydrogen Maleate Trihydrate (SHMT) Single Crystals

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Abstract — Sodium hydrogen maleate trihydrate single crystal is synthesized from an aqueous solution of sodium acetate and maleic acid by slow evaporation technique at room temperature. The crystal structure is confirmed to be triclinic by single crystal XRD. The functional groups present in the crystal are identified by recording the FTIR spectrum. The optical property of the grown crystal is established from the UV-Vis-NIR spectrum. The mechanical strength is identified by Vicker's micro hardness. Thermal analysis and dielectric measurements have been performed on the grown crystal. The NLO property of the single crystal is verified by the SHG test.

Key Words - Sodium acetate, FTIR, Maleic acid, TGA, SHG test

I. INTRODUCTION

Non linear optics has emerged as one of the most attractive fields of current research in view of its vital applications in areas such as optical modulation, optical switching, optical logic, frequency shifting, and optical data storage for the developing technologies in telecommunications and signal processing [1,2]. Researchers follow various strategies to bring out suitable materials such as formation of metal complex and salts or introduction of steric effects and hydrogen-bonding interactions [3-5]. Optical nonlinearity of the crystals with O-H bond has been extensively studied [6,7]. Metal organic complexes offer high environmental stability combined with greater diversity of tunable electronic properties by virtue of their coordinated metal center [8,9]. So in the present investigation, the growth of sodium maleate trihydrate crystal has been attempted by slow evaporation technique at room temperature. Also characterization studies such as single crystal XRD, FT IR, UV-Vis-NIR, Hardness, TGA, Dielectric and SHG test have been carried out.

II. EXPERIMENTAL

Sodium hydrogen maleate trihydrate was synthesized from the starting materials, namely sodium acetate trihydrate and maleic acid. The expected chemical reaction is as follows.

$$(CH_3COO)_2Na\ .3H_2O + C_4H_4O_4 \longrightarrow$$
$$C_4H_3O_4Na\ .\ 3H_2O + 2CH_3COOH$$

Sodium acetate and maleic acid were dissolved in double distilled water in stoichiometric ratio of 1:1. The prepared mixture was stirred well for 12 hrs and a clear solution was obtained. After 7 days, optically transparent good quality crystals were harvested with a maximum size of 1x0.6x1cm as shown in Fig.1.

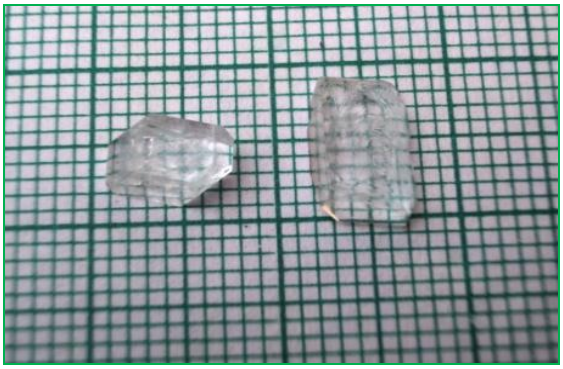

Fig.1. Photograph of the SHMT crystal

III. CHARACTERIZATION STUDIES

A. Flame Photometry

Photoelectric flame photometry, a branch of atomic spectroscopy is used for inorganic chemical analysis for determining the concentration of certain metal ions such as sodium, potassium, lithium, calcium, cesium, etc. The concentration of sodium is found to be 11.18% thus confirming its presence in the grown crystal.

B. Single Crystal X-Ray Diffraction

The unit cell parameters of grown crystal were carried out using Enraf Nonius-CAD4 diffractometer with Mo Kα radiation at room temperature. The title material sodium hydrogen maleate trihydrate crystallizes in triclinic system with space group P1. The lattice

parameter values are: a = 5.96Å, b=6.39Å, c= 11.21Å, α= 104.18°, β= 91.67°,

γ = 100.15°, V= 406 Å^3 . The obtained crystallographic data are in good agreement with reported values [10, 11].

C. FTIR Studies

Infrared spectroscopy is effectively used to identify the functional groups in the synthesized compound. The FTIR spectrum of the crystal shown in Fig.2 is recorded using BRUKER IFS 66V spectrometer by KBr pellet method in the wave number range of 4000-400cm^{-1}. Bands due to symmetric and asymmetric H-O-H stretching vibration are observed in the region 3550-3200cm^{-1} and bands due to H-O-H bending vibration occur in the region 1630- 1600cm^{-1}. So, in the FTIR spectrum, the peak at 3375cm^{-1} is assigned to H-O-H stretching. The hydrogen maleate ion forms a close to planar ring structure containing a short intramolecular hydrogen bond which is normally found also in other acid maleates. The five membered hetero atomic compounds have a broad absorption at 2800-2600 cm^{-1} due to the C-H bond and the twisting vibration near 730 cm^{-1}. Hence, the peak of medium intensity at 2195 cm^{-1} is assigned to C-H stretching and the peak at 762 cm^{-1} to its twisting vibration. The peak at 1495 cm^{-1} is assigned to C-C stretching, 1084 and 892 cm^{-1} to in-plane and out of plane vibration of C-H respectively [12,13]. The seven membered ring of the hydrogen maleate ion is close to planar [14]. In order to form this plane structure some strain must be imposed on the bonds. A medium-to-strong band at 1320-1210 cm^{-1} is observed in compounds containing the carboxylic C=O group and also a band of medium-to-strong intensity in the region 955-915 cm^{-1} due to the out-of-plane deformation of the carboxylic acid OH----O group.

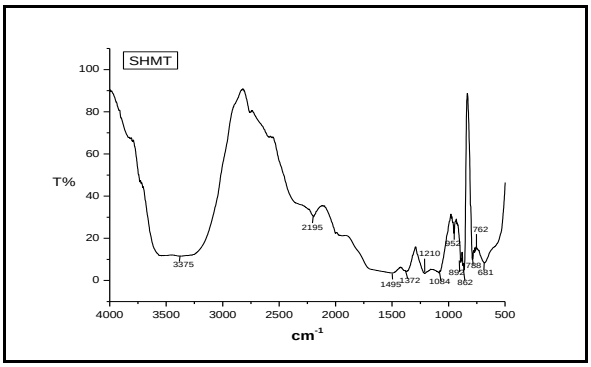

Fig.2. FTIR spectrum of SHMT Crystal

Three strong bands not usually well resolved in the region 675-570 cm^{-1} are due to the in-plane vibration of the O-CO group. So, based on the above, the peak at 1372 cm^{-1} is assigned to C=O stretching, the peak at 952 cm^{-1} to out-of-plane vibration of OH----O group of COOH and the peak at 681cm^{-1} to in plane vibration of O-CO group. The band at 1210 cm^{-1} and 788 cm^{-1} is because of C-O-H in plane bending and carbonyl anion deformations respectively. All these assignments are in good agreement with that made in literature. The detailed FTIR vibrational band assignment is presented in Table 1.

Table.1. FTIR Frequencies of SHMT crystal and its vibrational band assignments

Wave number (cm^{-1})	Band Assignment
3375	H-O-H stretching
2195	C-H Stretching
1495	C-C stretching
1372	C=O stretching
1210	In plane bending of C-O-H
1084	In plane vibrations of C-H
952	Out of plane vibrations of OH----O of COOH group
892	Out of plane vibrations of C-H
788	Carbonyl anion deformation
762	C-H twisting vibration
681	In plane vibrations of O-CO group

D. UV Studies

The UV-VIS-NIR spectrum of the crystal in Fig.3 is recorded in the region 190 to 1200 nm using Perkin Elmer Model-Lambda 35 spectrometer. Sodium hydrogen maleate crystals are found to have less absorbance in the entire spectral range and also have a lower cut-off wavelength of 250nm. Since the absorbance is minimal it is suggested that the grown crystal could be a good candidate for electro-optic applications and also SHG efficient.

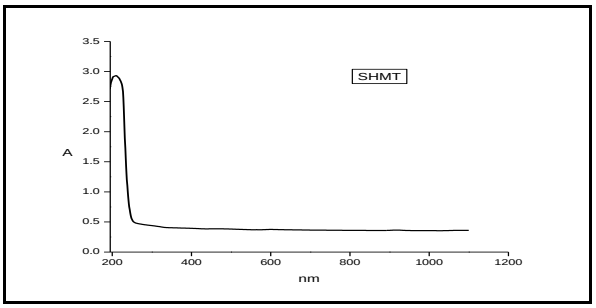

Fig.3. UV absorbance spectrum of SHMT Crystal

E. Microhardness Measurement

The structure and composition of the crystalline solids are related to the mechanical hardness. Hardness of a material is a measure of resistance it offers to local deformation [15]. The crystal is subjected to Vickers microhardness testing. The plot of Vickers hardness (H_v) versus load (P) for the grown crystals is shown in Fig 4. The hardness number is found to increase with the load.

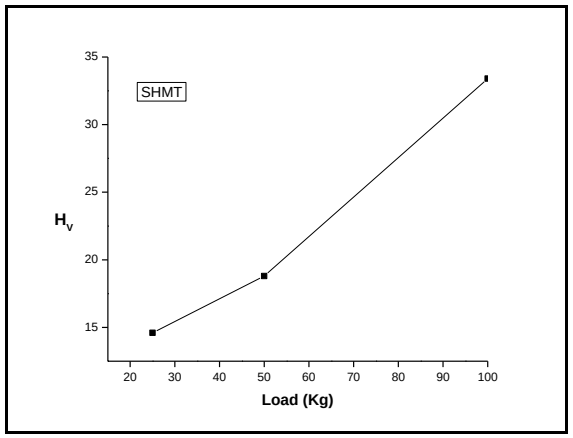

Fig.4. Microhardness of SHMT Crystal

F. Dielectric Studies

The dielectric constant and dielectric loss of sodium hydrogen maleate trihydrate crystals is determined using Multi-frequency LCR meter shown in Fig.5.

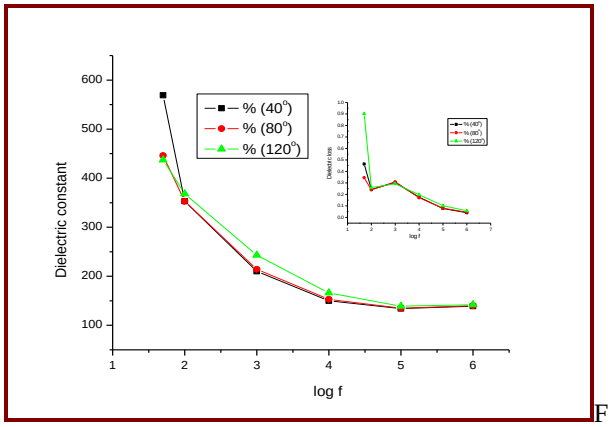

Fig.5.Dielectric constant & loss Vs log frequency

The variation of dielectric constant and dielectric loss with frequency of the sodium hydrogen maleate crystals is reported. Repeated trials were performed to ascertain the correctness of the observed results. The magnitude of dielectric constant depends on the degree of polarization in the crystal. It is seen that the dielectric constant has high value in the lower frequency region and then it decreases with increasing frequency. According to Miller rule [16], the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient. It is noted that as the frequency increases the dielectric loss decreases. At low frequencies the dipoles can easily switch alignment with the changing field but as the frequency increases the dipoles rotate less and hence lag phase with the applied field [17,18]. So they reduce their contribution to the polarization field. The 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.

G. Thermal Studies

The TGA traces for the sodium hydrogen maleate crystals are presented in Fig.6. From TGA it is seen that the crystal is thermally stable upto 150 °C. The TGA curve shows that the weight loss occurs in four steps. Based on the melting point of maleic acid and sodium acetate the first weight loss of 28.11% is due to the decomposition of maleic acid, the second weight loss of 28.81% occurs due to decomposition of sodium acetate, the third and fourth weight loss of 8.19% and 19.69% is due to the residue.

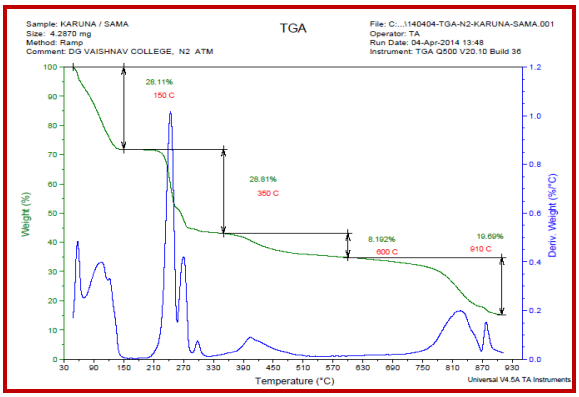

Fig.6. TGA graph of SHMT Crystal

H. NLO Studies

The NLO property of the crystal is confirmed by Kurtz powder technique. The crystals are ground to powder and packed between two transparent glass slides. The first harmonic output of 1064 nm from an Nd:YAG laser was made to fall normally on the prepared sample with a pulse width of 8ns. The second harmonic signal generated in the crystal is confirmed by the emission of green radiation.

IV. CONCLUSION

Good quality single crystals of sodium hydrogen maleate trihydrate were grown by solution growth technique. Flame photometry confirms the presence of sodium in the crystal. The lattice parameters of the grown crystals were determined by single crystal X-ray diffraction studies. From the FTIR spectrum a detailed vibrational band assignment of the grown crystal has been carried out. Optical absorption studies show that the sample has minimum absorption in the entire visible region. The microhardness studies reveal that the hardness value increases with applied load. The lower value of dielectric constant at high frequency suggests that the crystal has enhanced NLO property. The crystal is found to be thermally stable upto 150°C evident from TGA. The NLO nature of the crystal was proved by SHG test. Thus it is realized that the crystal is a potential candidate for the fabrication of NLO devices.

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