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, FTIR, 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.

$\text{(CH}_3\text{COO)}_2\text{Na \cdot 3H}_2\text{O + C}_4\text{H}_4\text{O}_4 \rightarrow C_7\text{H}_8\text{O}_4\text{Na \cdot 3H}_2\text{O + 2CH}_3\text{COOH}}$

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 parameters are a = 8.048(2) Å, b = 8.305(2) Å, c = 10.500(3) Å, α = 89.24(1)°, β = 88.02(1)°, γ = 90.00°.
parameter values are: a = 5.96Å, b=6.39Å, c= 11.21Å, α= 104.18°, β= 91.67°, γ = 100.15°, V= 406 Ǻ³. The obtained crystallographic data are in good agreement with reported values [8,11].

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 3375 cm⁻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.

![FTIR spectrum of SHMT Crystal](image)

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 681 cm⁻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>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3375</td>
<td>H-O-H stretching</td>
</tr>
<tr>
<td>2195</td>
<td>C-H Stretching</td>
</tr>
<tr>
<td>1495</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>1372</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1210</td>
<td>In plane bending of C-O-H</td>
</tr>
<tr>
<td>1084</td>
<td>In plane vibrations of C-H</td>
</tr>
<tr>
<td>952</td>
<td>Out of plane vibrations of OH---O of COOH group</td>
</tr>
<tr>
<td>892</td>
<td>Out of plane vibrations of C-H</td>
</tr>
<tr>
<td>788</td>
<td>Carbonyl anion deformation</td>
</tr>
<tr>
<td>762</td>
<td>C-H twisting vibration</td>
</tr>
<tr>
<td>681</td>
<td>In plane vibrations of O-CO group</td>
</tr>
</tbody>
</table>

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.

![UV absorbance spectrum of SHMT Crystal](image)

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 (Hv) versus load (P) for the grown crystals is shown in Fig 4. The hardness number is found to increase with the load.

![Microhardness measurement graph](image)
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ascertain the correctness of the observed results. The

crystals is reported. Repeated trials were

Multiphase LCR meter shown in Fig.

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 t

pulsed 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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