Growth, Spectral and Thermal Characterization of Zinc hydrogen maleate dihydrate (ZHMD) Single Crystal

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Abstract - Zinc hydrogen maleate dihydrate single crystal has been grown successfully by slow evaporation solution technique at room temperature using water as solvent. Crystals of size 1cm X 1cm X 0.4 cm were obtained in 6 days. The crystalline nature of the grown crystal is confirmed by powder X-ray diffraction analysis. The grown crystals were subjected to single crystal X-ray diffraction analysis which revealed that the sample has crystallized in triclinic system with noncentrosymmetric space group P1. The modes of vibration of different molecular groups present in the sample were identified by the FTIR analysis. The UV-Vis- NIR absorbance study assessed the optical behavior of the crystal. The second harmonic generation test of zinc maleate dihydrate confirmed the nonlinear nature of the crystal. To understand the thermal stability of the synthesized compound, the thermo gravimetric analyses were done. The mechanical strength of the grown crystal was found using Vickers microhardness test. Dielectric constant and dielectric loss of the crystals were studied as a function of frequency at different temperatures.

Key words: Zinc acetate, maleic acid, X-ray diffraction, FTIR, UV and TGA

I. INTRODUCTION

Nonlinear optical (NLO) materials play a major role in the field of opto-electronics and in particular they have a great impact on laser technology and industrial applications[1-6]. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. Recently, the approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganic has been found to be overwhelmingly effective . In the case of metal–organic coordination complexes [7-12], the organic ligand is usually more dominant in the NLO effect, since metal compounds (such as Zn, Cd, and Hg) have high transparency in the UV region. The metal-organic coordination complexes can also provide the following advantages: i) enhancement on the physico-chemical stability. ii) The breaking up of the centro-symmetry of the ligand in the crystal and iii) an increase in NLO intensity, via metal-ligand bridging interactions.

An attempt is made here to find a new useful material by taking maleic acid and Zinc acetate dihydrate in 1:1 ratio. In the present work, single crystal growth of Zinc maleate dihydrate from solution has been reported. Also characterization studies such as single crystal XRD, Powder XRD, FT IR, UV-Vis-NIR, Hardness, TGA, Dielectric and SHG test have been carried out.

II. EXPERIMENTAL

Zinc hydrogen maleate dihydrate crystal was synthesized by dissolving analar grade maleic and zinc acetate dihydrate in the stoichiometric ratio in double distilled water according to the reaction.

$$Zn(CH_3COO)_2 .2H_2O + C_4H_4O_4 \longrightarrow C_4H_3O_4\,Zn.\ 2H_2O + 2CH_3COOH$$

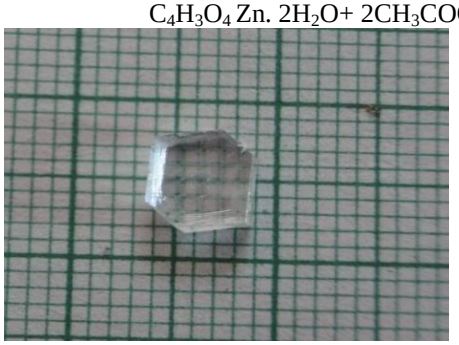

Fig.1. Photograph of the as grown ZHMD

In the present study a solution of Zinc acetate dihydrate and maleic acid of equimolar ratio was prepared. The solution was stirred for 6 hours and then filtered. It was porously sealed and placed in a dust free atmosphere for slow evaporation. Optically transparent crystals of size 0.5x0.5 x0.2 **c**m were harvested in 6 days. The crystal of Zinc hydrogen maleate dihydrate (ZHMD) as grown is shown in Fig.1.

III. RESULTS AND DISCUSSION

a. Single crystal X-Ray diffraction analysis

The unit cell parameters of grown crystal were carried out using Enraf Nonius-CAD4 diffractometer with Mo K alpha radiation at room temperature. The structure was solved by direct method and refined by full matrix lean squares technique using SHELXL-97 program. The

title material Zinc hydrogen maleate dihydrate crystallizes in triclinic system with space group P1. The lattice parameter values are a = 5.25Å, b=7.34Å, c=9.24Å, α= 108.75°, β= 104.65°, γ = 93.24°, V= 323 Å^3. The obtained crystallographic data are in good agreement with reported values [13].

b. Powder XRD analysis

The powder X-ray diffraction pattern recorded for grown crystals with CuK_α (α = 1.5408 Å) radiation is shown in Fig.2. The sharp peaks of XRD pattern indicate high degree of crystalline structure of grown crystals.

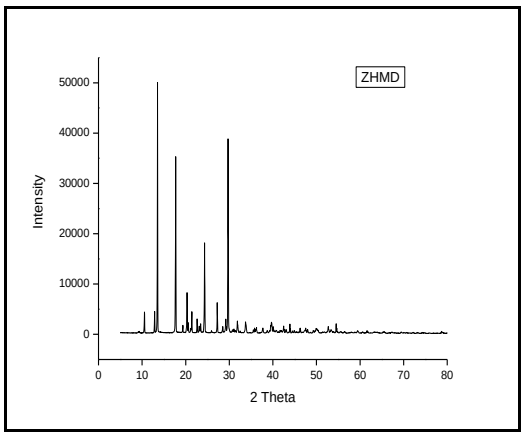

Fig.2. Powder XRD pattern of ZHMD

c. Functional group analysis

The FTIR and FT-Raman spectrum recorded at Sophisticated Analytical Instrumentation Facility (SAIF), Indian Institute of Technology (IIT), Chennai, India, is shown in Fig .3 and 4 respectively.

The presence or absence of absorption bands in FTIR spectrum helps in predicting the presence of certain functional groups in the compound [14]. To analyze the FTIR spectrum, accurate information about structure of maleic acid and zinc acetate dihydrate is much essential. The low frequency spectrum which extends upto ~ 50 cm^{-1} has been divided into three parts:

(i) External oscillations, low frequency hydrogen bond oscillations and vibrational frequencies of the octahedral arrangements of oxygen and water molecules around the metal ion.

(ii) The internal frequencies are made up of acetate, maleate ion frequencies and water bands. The stretching vibration of water molecule in Zinc acetate dihydrate is expected in the region 3000-3600cm^{-1}. Bands due to asymmetric and symmetric H-O-H stretching vibrations are observed in the region 3550-3200cm^{-1}and bands due to H-O-H bending vibration in the region 1630-1600cm^{-1}. Vibrational modes of coordinated water molecules such as wagging, twisting and rocking may become infrared active and the resulting bands occurring in the region 880-650 cm^{-1}. In FTIR spectrum of ZMDH the spectral line at 3773cm^{-1} and in FT-RAMAN spectrum, the peak at 3245cm^{-1} is assigned to be O-H band of the water molecules. Also in the FT-Raman spectrum the peaks at 714cm^{-1}and moderate intensity peak at 303cm^{-1} are assigned to the vibrational mode of the water molecule. It must be noted that CH_2 stretching vibrations are observed at 3050-3000cm^{-1}whilst their symmetric vibration occurs at 2975cm^{-1}. The deformation vibration of C-H may either be perpendicular to or in the same plane containing the carbon-carbon double bonds. The absorption bands due to the out -of -plane vibrations occur mainly at 1000-800cm^{-1} and have strong to medium intensity [15]. In the spectrum of crystal the broad shoulder ranging from 2462 - 2039cm^{-1} is assigned to the CH_3 stretching mode along with overtones. The peaks at 1193 cm^{-1} and 1227cm^{-1} are assigned to CH_3 rocking and bending vibrations. The functional group CO observed both in Zinc acetate and maleic acid give rise to characteristic peak at 1703 cm^{-1} which is assigned to stretching vibration of CO group. Two principal absorption peaks at 1580 and 1400 cm^{-1} correspond to the asymmetric and symmetric stretching of COO vibrations of the unidentate acetate species as well as the maleic acid. In literature the C=O stretching vibrations of maleic acid give its peak at 1642cm^{-1}. In the spectrum the peak at 1505cm^{-1} should correspond to the stretching vibration of COO group. The 377cm^{-1} line in zinc acetate may be assigned to the totally symmetric C-C mode. The slight decrease from the usual value of 393 cm $^{-1}$ may be due to the orderly arrangement of the crystalline field in the acetate compound. From the tentative assignments, the FTIR and Raman spectrum lead to the conclusion that the major functional groups namely C=O, C=C, COO and CH_3 are definitely present in the grown crystal. The band in the range of 80cm^{-1} observed in the FT-Raman spectrum is a strong confirmation of the presence of Zinc in the grown crystal.

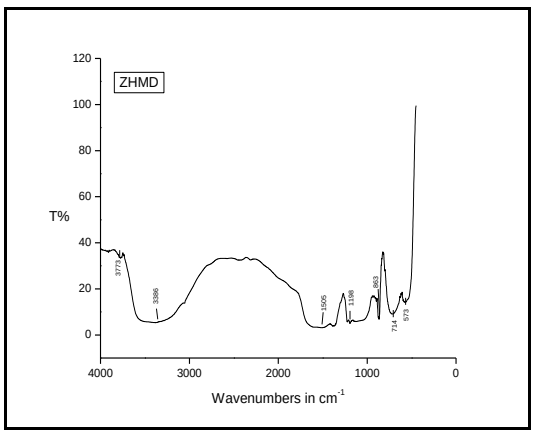

Fig.3. FTIR Spectrum of ZHMD crystal

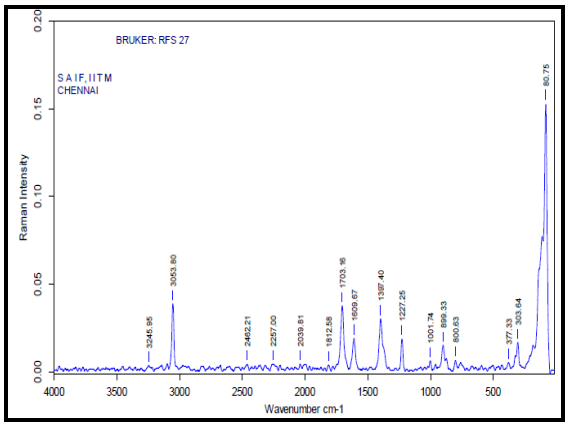

Fig.4. FT-RAMAN Spectrum of ZHMD crystal

d. UV-Vis-NIR spectral analysis

To understand the optical transparency of the Zinc hydrogen maleate dihydrate crystal in the UV-Visible region of the electromagnetic spectrum, an optical absorption spectrum of Zinc maleate crystal (Fig.5) is recorded. The spectrum is recorded by employing Perkin Elmer Model-Lambda 35 spectrometer at room temperature in the range 200-1100 nm. The lower cut-off wavelength was found to be 300 nm. In the entire visible region the optical absorption spectrum is flat and constant. This transparent nature in the visible region is a desirable and useful property for NLO applications.

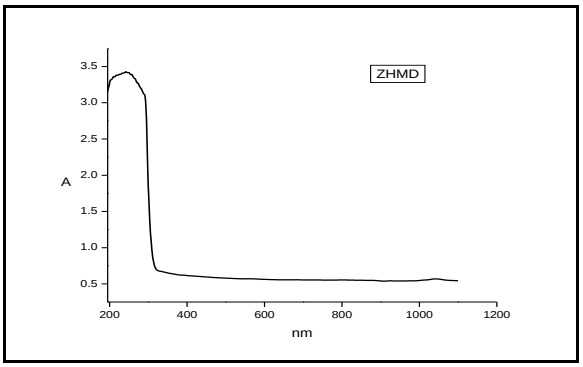

Fig.5. UV absorption spectrum of ZHMD Crystal

e. Microhardness

Hardness of the material is a measure of the resistance it offers to local deformation [16]. Zinc hydrogen maleate dihydrate was taken, free from visible inclusion and crack. Vickers micro hardness indentations were made on the as-grown surface of the Zinc hydrogen maleate dihydrate crystals at room temperature with the loads varying from 10 to 50g. The Vickers hardness number (H_v) of the crystals was calculated using the relation $H_v = 1.8544P/d^2$ kg/mm2, where P is the applied load in kg and d is the average diagonal length of impression in mm. The plot of Vickers hardness (H_v) versus load (P) is shown in Fig.6. It is seen that the hardness increases with the increase of load.

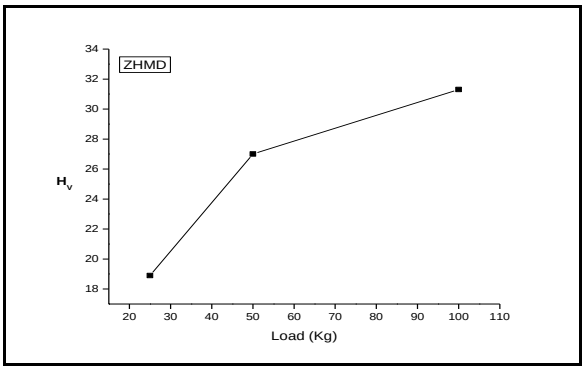

Fig.6. Microhardness of ZHMD Crystal

f. SHG test

The SHG efficiency of ZHMD was measured by the powder technique of Kurtz and Perry. The second harmonic output was generated by irradiating powder samples by a pulsed laser beam of Nd:YAG laser with a pulse width of 8 ns. The second harmonic signal generated in the crystal was confirmed by the emission of green radiation.

g. Dielectric studies

The dielectric constant and dielectric loss of ZHMD crystals was determined using Multi-frequency LCR meter (LCR-800 SERIES). A rectangular sample of ZHMD crystal with dimensions of 3.90x2.86x2.31mm was subjected to dielectric measurements. The sample was coated with silver paint and placed between the copper electrodes of the sample holder. The crystal faces are coated with silver paint in order to ensure good electrical contact between the crystal and the electrodes. The capacitance of the parallel plate capacitor formed by the copper electrodes having the sample as a dielectric medium was measured by varying the frequency in the range 50Hz to 5MHz. The dielectric constant can be calculated using the relation,

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$

where ε_r is known as relative permittivity, ε_0 absolute permittivity in the free space having a value of 8.854×10^{-12} Fm^{-1}, C is capacitance (F), A is the area of the sample and d is the thickness of the sample. The variation of dielectric constant and dielectric loss of the ZHMD crystals are characterized. Repeated trials were performed to ascertain the correctness of the observed results.

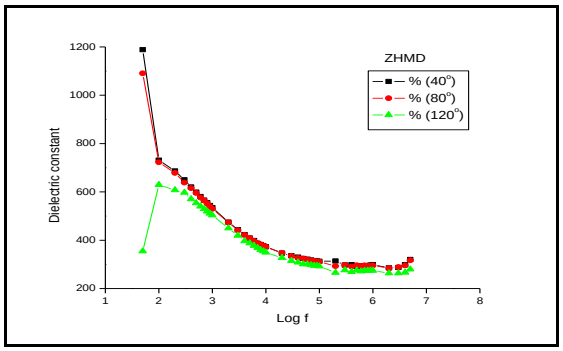

Fig.7. The plot of the dielectric constant versus the log frequency

Fig.7 shows the variation of dielectric constant with different frequencies for the grown crystals. The magnitude of dielectric constant depends on the degree of polarization in the crystals [17-19]. It is seen that the dielectric constant has high value in the lower frequency region and then it decreases with the increasing frequency. According to Miller rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient.

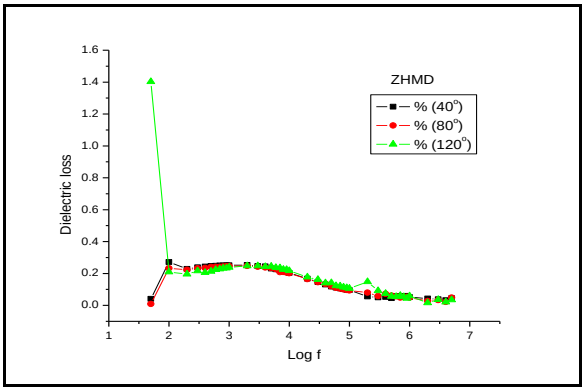

Fig.8. The plot of the dielectric loss versus the log frequency

From Fig.8, it is noticed that as the frequency increases the dielectric loss decreases. This behavior 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 can 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 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.

h. Thermal Studies

For TGA studies, the crystals were taken in an alumina crucible and were heated from 50˚C to 800˚C at a scanning rate 20˚C/min (in nitrogen atmosphere).The TGA trace for the ZHMD crystals is presented in Figure .9. From TGA it is seen that the crystal is thermally stable up to 150 °C. The melting point of zinc acetate in literature is 230 ^{0}C which has decreased probably due to the addition of maleic acid. The TGA curve show that the weight loss occurs in three steps. The first weight loss is 49.8% due to the decomposition of maleic acid and the second weight loss of 7.48 % occurs due to decomposition of zinc acetate and the third weight loss of 11.74% due to the residue.

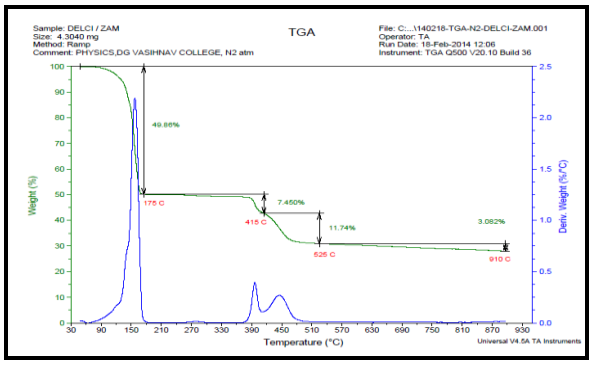

Figure.9. TGA trace of the ZHMD crystal

IV. CONCLUSION

Singe crystals of zinc maleate dihydrate has been synthesized by slow evaporation solution growth technique. The structure of grown crystals has been identified using X-ray diffraction studies. Vibrational frequencies were assigned from FT-IR and FT-Raman spectral analysis. The results obtained from the characterization techniques of optical transmission study and dielectric confirm the quality and perfection of the crystal. The microhardness study was performed on Zinc maleate crystal, which shows an increase in hardness value with increase in 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.

V. REFERENCES

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