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Growth and Characterization of Zinc Acetate dihydrate Formic Acid Single Crystals.

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ABSTRACT

Zinc Acetate dihydrate Formic acid (ZAFA) has been synthesized and good quality single crystals were grown by slow evaporation method at room temperature. Single crystal XRD confirms that the grown crystal belongs to the monoclinic system with the centrosymmetric space group of $P2_1/c$. FTIR spectral analysis confirms the functional group in the synthesized compound. Thermo gravimetric and differential thermal analyses reveal the thermal stability of the crystal. The UV-Visible absorption study assessed the optical behavior of the crystal. The dielectric nature of the grown crystal also reported.

Keywords: Single crystals X-ray diffraction, FT-IR, TG/DTA, UV-visible.

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INTRODUCTION

Organic materials are gaining more attention due to their fast response in electro-optic effect, high non-linear coefficient and more stability in physical and chemical properties. Organic materials have found to be superior due to their high electronic susceptibility (χ) through molecular hyperpolarizability (β) relatively over the conventional inorganic substances [1]. Organic materials have another advantage over inorganic materials, in that the properties of organic materials can be optimized by modifying the molecular structure using molecular engineering and chemical synthesis [2]. Zinc acetate dihydrate a chemical compound with wide applications in many industries, it is one of the important fertilizers for plants and well known in chemical industries, has been used as a raw material for manufacturing various chemicals. Zinc acetate dihydrate crystallizes in monoclinic system with the space group C2/c. The lattice parameter values of zinc acetate dihydrate are a=14.50 Å, b=5.32 Å and c=11.02 Å and β=100.00^{o} and cell volume V=850.0828 Å^{3} [3]. In formic acid combines a large number of divalent metals (Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd) forms isostructural monoclinic crystals with the space group $P2_1/c$ [4]. The metal ions occupy two sets of non-equivalent centres of symmetry, which for simplicity we shall refer to as Me1 and Me2, the same as the metal ions occupying them. Thus, Me1 has a six-fold coordination through six oxygen atoms from formate ions (hexaformate-coordinated Me1 site), while Me2 is surrounded by four oxygen atoms of water molecules and two oxygen atoms belonging to the formate groups (mixed-coordinated Me2 site). Both the water molecules and the formate ions fall into two non equivalents crystallographic Positions (C1 site symmetry). Each water molecule forms two hydrogen bonds with the oxygen atoms of the formate ions [5]. Zinc acetate dihydrate occurs as white crystalline powder. Zinc acetate dihydrate and formic acid are freely soluble in water. The single crystal of Zinc acetate formic acid (ZAFA) single crystal forms monoclinic crystal structure with the space group of $P2_1/_C$. In this paper, we report the growth and characterization of highly transparent single crystals of ZAFA. The structural, thermal, optical and dielectric properties of the grown samples are investigated.

EXPERIMENTAL PROCEDURE

Material Synthesis

In the present study, slow evaporation tenchnique was employed to grow Zinc Acetate Formic acid (ZAFA) single crystals. Highly pure zinc acetate dihydrate (Merck 98%) and formic acid (Sigma Aldrich 99.5%) were taken in equimolar ratio and dissolved in deionised water. The solution was stirred up to saturation state. The solution was filtered by using whatman filter paper and covered with dust free polyethylene sheet then placed at room temperature. After a period of 20 to 25 days good transparent ZAFA seed crystals were grown. A good quality seed crystal was allowed to grow bulk. The crystal of size 9 x 8 x 4 mm^{3} was harvested. The photograph of the as grown single crystal is shown in Fig.1.

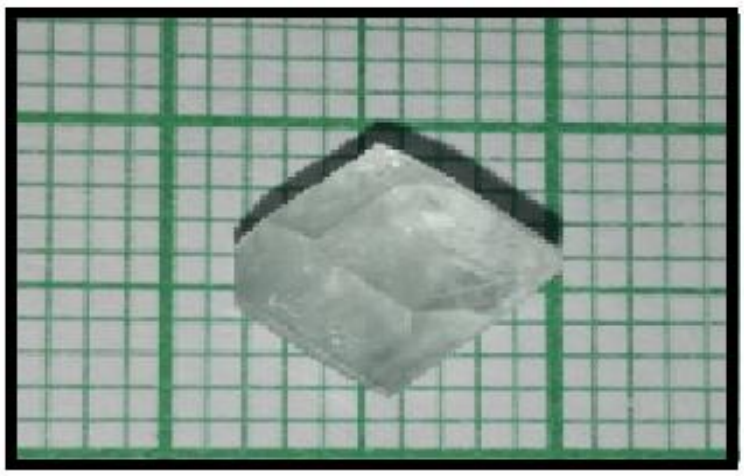

Fig.1. Photograph of as grown single crystal of Zinc Acetate Formic Acid

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RESULTS AND DISCUSSION

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 acetate formic acid crystallizes in monoclinic system with space group $P2_1/c$. The lattice parameter values are a=8.71 Å, b=7.17 Å, c=9.34 Å, α=90°, β=90.53°, γ=90° and cell volume V= 578 $Å^3$.

Fourier Transform Infrared (FTIR) Spectroscopic Studies

The FTIR spectrum recorded at Sophisticated Analytical Instrumentation Facility (SAIF), Indian Institute of Technology (IIT), Chennai, India, is shown in Fig .2.respectively

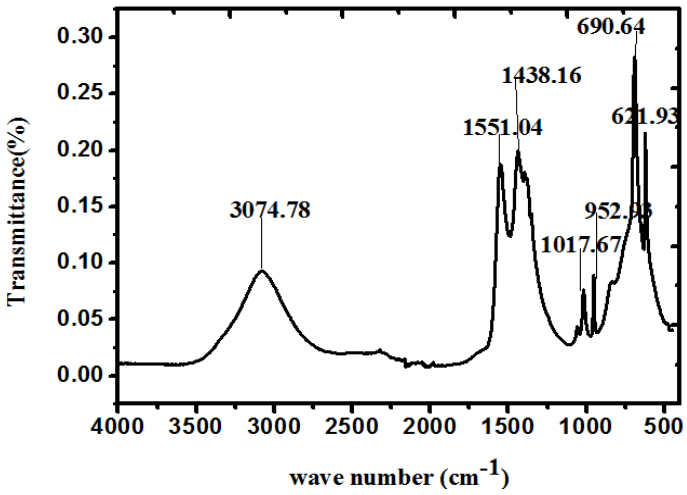

Fig.2. FT-IR spectrum of grown ZAFA crystal.

The identification of functional groups was performed by infrared spectroscopy. FTIR spectrum of a compound provides more information than normally available electronic spectra. The presence or absence of absorption bands helps in predicting the presence of certain functional groups in the compound. The FTIR spectra of the ZAFA crystals recorded by Perkin Elmer spectrometer in the frequency region of 400-4000 cm^{-1} using KBr pellet technique are shown in Fig.2. In Zinc acetate dihydrate, zinc ion coordinated with two oxygen atom of COO. In FTIR spectrum, functional groups of CH_3, C=O and H_2O of zinc acetate dihydrate are expected. The functional group CO observed both in Zinc acetate and formic acid give rise to characteristic peak at 1551 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 formic acid. In literature the C=O stretching vibrations of formic acid give its peak at 1437 cm^{-1}. The peak observed at 1017 cm^{-1} is assigned for C-N stretching. The other peaks at 690cm^{-1} and 952 cm^{-1} are due to the out of plane bending of C-H and OH group vibrations [7].

Thermal Analysis

Thermo gravimetric (TG) and differential thermal analysis (DTA) experiments were carried out using SEIKO model TG/DTA 6200 instrument with a heating rate of 10°C/min starting from 30 to 700 ^{0}C. The results of TG/DTA traces of ZAFA material are illustrated in Fig. 5. The grown crystals are thermally stable up to 96.9◦C and decomposition starts at 96.9 ^{0}C. A major weight loss up to 80% was obtained between 96.9◦C and 130◦C. The DTA curve exhibits an endothermic peak at 96.9°C. The sharpness of the endothermic peak shows a good degree of crystalline nature and purity of the grown crystal [8]. From the TGA curve one finds that a gradual weight loss occurs with increasing temperature before attaining the melting point of the sample (Fig. 3.)

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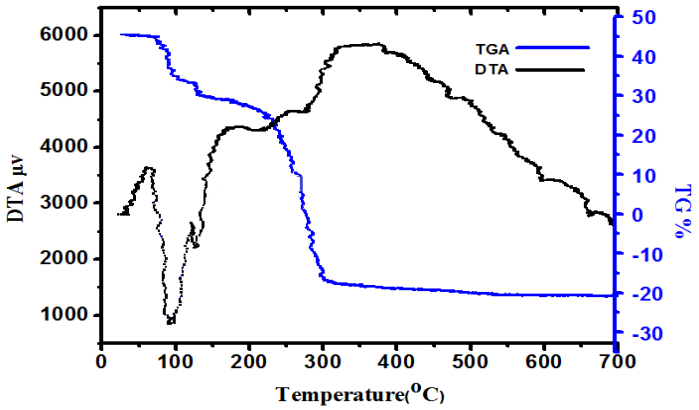

Fig. 3. TG/DTA Curve for ZAFA crystal

Optical Absorption Studies

The optical behaviour of the material basically includes the interaction of light radiation over the range of the electromagnetic spectrum. The ultra violet light absorbed by the sample gives information about the transparency window which is very essential in many optoelectronic applications [9]. The optical absorption spectrum of the grown crystals was recorded in the wavelength range 200 to 1200 nm using a Perkin Elmer lambda 35 UV-Vis spectrometer. The optical absorption spectrum for Zinc Acetated Formic Acid is shown in the Fig.4. The lower cut off wave length is around 230 nm. It is observed the grown crystals show good transparency in the entire visible region. The band gap energy of the material is found to be 4.92 eV by using tauc's plot relation were shown in the Fig. 5. This represents that Zinc acetate Formic acid crystals have higher band gap, which is Suitable for optoelectronics applications [10].

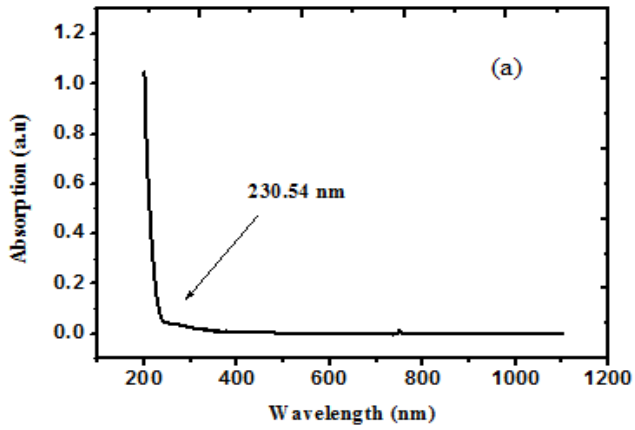

Fig.4. UV-Vis spectrum for absorbance

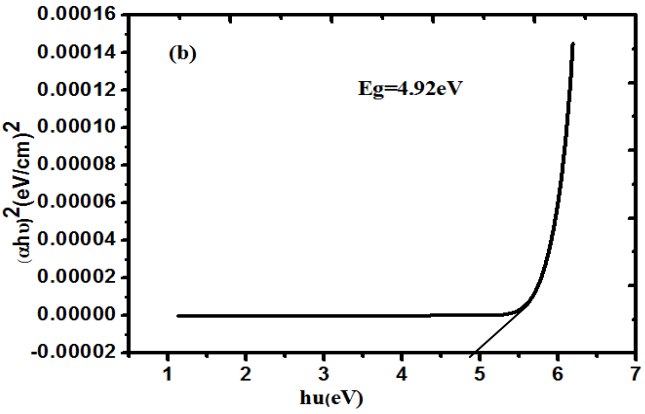

Fig.5. Tauc's plot for optical band gap.

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Dielectric Studies

The dielectric characteristics of the material is important to study about the lattice dynamics, transport phenomena, nature of atoms, ions, bonding and their polarization mechanism [11]. To determine the above mentioned characteristics, quality single crystals were chosen and subjected to dielectric studies at room temperatures respectively. The capacitance of the sample was noted for the applied frequency varying from 50Hz to5MHz and the dielectric constant (ε_r) was calculated using the relation

$$(\varepsilon_r) = Cd/ \varepsilon_0 A$$

where d is the thickness, and A is the area of the crystal. Fig. 6 and Fig. 6a depict the variation of dielectric constant (ε_r) and dielectric loss respectively as a function of frequency at room temperatures of the grown crystal [12]. The dielectric constant and the dielectric loss decreases exponentially with increasing frequency and attain almost a constant value at high frequency region. The dielectric curve suggests that the dielectric constant is found to be increases with increasing temperature and the reverse is true for dielectric loss. The higher values of dielectric constant at low frequencies are due to the low values of dielectric loss at higher frequencies suggests that the sample possesses enhanced optical quality with lesser defects and this is a vital parameter for NLO applications.

Table 1. Functional Group Assignments of ZAFA

Band frequencies wave number(cm^{-1})	Assignment
690	C-H out of plane Bending
952	O-H out of plane Bending
1017	C-N stretching
1438	O-H in plane bending
1551	CH_3 asymmetric stretching.
3078	OH stretching vibration of H_2O

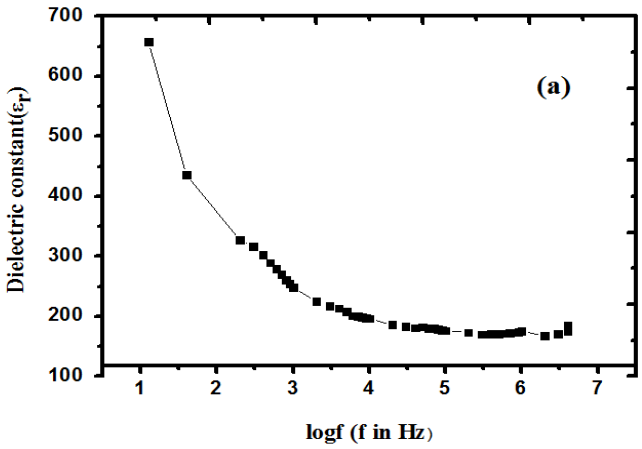

Fig.6.(a). Variation of dielectric constant with frequency

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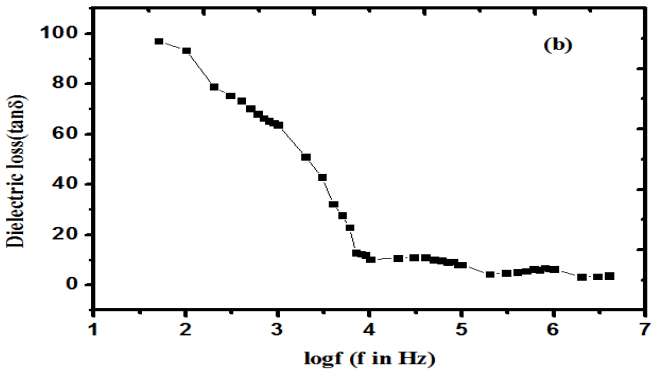

Fig.6. (b) Variation of dielectric loss with frequency

CONCLUSION

Zinc Acetate Formic Acid single crystals have been successfully grown by slow evaporation technique. Single crystal XRD analysis confirms the crystalline nature of the grown crystal. From the FTIR spectroscopy analysis, the various functional groups present in the grown crystals were identified. Thermal stability of 96.9°C has been observed by TG/DTA analysis. From the absorption spectroscopy analysis, the grown crystals are transparent in the visible region and the cut-off wavelength is 230 nm. The dielectric property studied at room temperature indicates that the dielectric constant and dielectric loss decreases with the increase in frequency which is the normal behaviour of nonlinear optical materials. The characteristics of low dielectric loss with high frequency for a given sample suggest that the sample possesses enhanced optical quality with lesser defects and this parameter is vital for various NLO materials and their applications.

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