Investigation on thermal and mechanical behavior of 8-Hydroxyquinolinium Hydrogen Fumarate Single Crystal

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Abstract. The titled compound 8-hydroxyquinolinium hydrogen fumarate (8HQF) was grown from mixed solvent of ethanol and water using slow evaporation technique. The single XRD analysis confirmed that the grown crystal bear to the crystal system of triclinic with the centrosymmetric space group P ī. The thermal properties of grown crystal were checked out using TG-DTA techniques and the 8-HQF crystal is thermally stable up to 172^{o}C. The mechanical firmness of the grown crystal was measured using Vicker's microhardness testing and it was found that 8-HQF belongs to soft material category.

INTRODUCTION

The origin of nonlinear properties is well understood phenomenon and the progress of optical research depends on the development of new materials technology compatible with various devices which exhibits an ample range of applications in tele-communication, optical information processing and integrated optics [1-2]. Organic molecules come out as propitious candidates since they have numerous advantages like low dielectric constant with electronic polarizability, refractive index, etc., over inorganic nonlinear optical crystals. Organic 8-Hydroxyquinoline is a versatile donor formed variety of charge transfer complexes and their complexes are well identified for their anti microbial and antifungal activities. Franklin et al. has reported the crystal structure of 8-hydroxyquinolinium hydrogen fumarate (8-HQF) using the compound 8-hydroxyquinoline and fumaric acid as precursors [3]. In this present research paper we report the growth, thermal and mechanical firmness of organic 8-hydroxyquinolinium hydrogen fumarate single crystals for the first time

MATERIAL SYNTHESIS

The title compound of 8-hydroxyquinolinium hydrogen fumarate single crystal was synthesized by using high purity grade products of 8-hydroxyqunoline and fumaric acid in the ratio of 1:1. A yellow precipitate was acquired which was further recrystallized and allowed for slow evaporation at room temperature. A crystal of dimension 5x5x3 mm^3 was harvested within 20 days. The grown crystal is portrayed in Fig.1 (a).

RESULT AND DISCUSSION

Single Crystal X-Ray Diffraction and Fundamental Parameters

The single crystal X-ray diffraction (XRD) for the grown 8-HQF crystal was undertaken using the instrument Bruker AXS Kappa Apex II CCD diffractometer containing radiation of Mo-Kα (λ=0.71073 ^{o}: graphite monochromator).It is observed that the crystal belong to system of triclinic with the centrosymmetric space group P ī .The calculated unit cell parameters are found to be a=7.36 Å, b=7.48 Å, c=11.64 Å, α=79.39˚, β=74.85˚, γ=89.32˚ and volume V= 608 Å^3. These values are in good agreement with the literature [3].

The molecular weight of 8-HQF is M=261.23 and entire number of valance electron Z=136. The density of the crystal was found to be ρ=1.532 g.cm^{-3} and with that the dielectric constant at 1 MHz is ε_α =87.6. The plasma energy of valence electron $\hbar$ is depicted below:

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \tag{1}$$

where Z is the total number of valence electrons, ρ depicts the density and M is known to the molecular weight.

Fermi energy depicting in term of Plasma energy [3] is given as:

$$E_P = \left(\frac{\hbar\omega_P}{(\varepsilon_\alpha - 1)^{1/2}}\right) \tag{2}$$

and

$$E_F = 0.2948(\hbar\omega_P)^{4/3} \tag{3}$$

Polarizability, α is estimated using the relation [4]

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_o}{(\hbar\omega_P)^2 S_o + 3E_P{}^2}\right] + \frac{M}{\rho} \times 0.396 \times 10^{-24}\, cm^{-3} \tag{4}$$

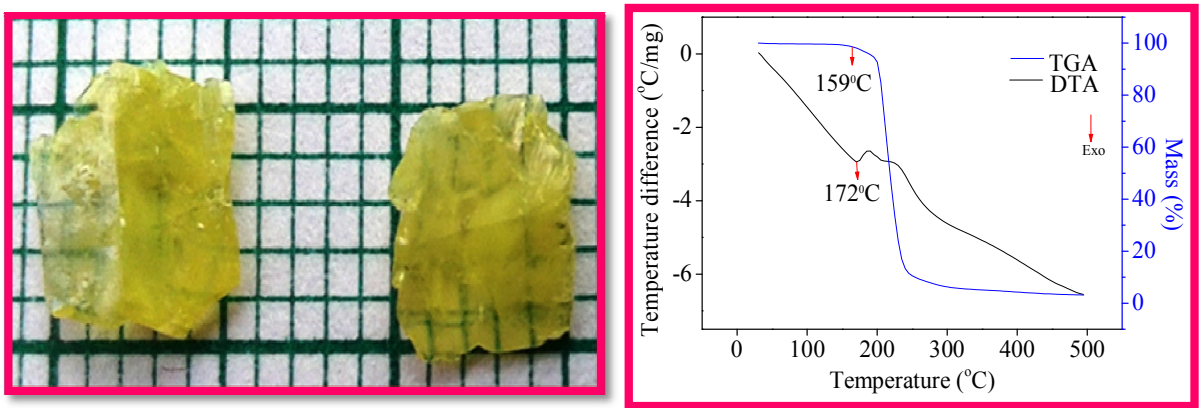
Where S_0 is a constant for distinct material, and is given by:

$$S_0 = 1 - \left[\frac{E_p}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \tag{5}$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation, which is given by :

$$\alpha = \frac{3M}{4\pi N_a \rho}\frac{\varepsilon_\alpha - 1}{\varepsilon_\alpha + 2} cm^{-3} \tag{6}$$

where the symbols have their usual significance. *N*a is Avogadro number and the calculated fundamental parameters of the grown crystal of 8-HQF are listed and compared with KDP [4] in Table1.



(a) (b)

FIGURE 1. (a) As grown crystal of 8-HQF and (b) TG-DTA of 8-HQF crystal

TABLE 1. Some calculated theoretical data for 8-HQF single crystal

Parameters	Values	KDP[4]
Plasma energy(eV)	25.72	17.33
Penn gap (eV)	4.67	2.39
Fermi gap (eV)	22.38	12.02
Polarizability ($\times 10^{-23} cm^{3)}$		
Penn analysis	6.84	2.142
Clausius-Mossotti Equation	6.15	2.181

Thermal Analysis

The thermogravimetric and differential thermal analysis are of immense importance in order to find out the thermal stability of the material. 8-HQF sample was subjected to TG-DTA using NETZSCH STA449F3 instrument within the temperature range between 0^oC-500^oC at a heating rate of 20 K/min in nitrogen atmosphere. The traces of TG-DTA result are illustrated in Fig.1(b). From the TG curve it is clear that initial weight loss of 8-HQF starts at 159^0C also there is no weight loss observed before 159^oC which indicates the absence of water of crystallization. The first exothermic peak of the grown crystal is found at 172^oC and is assigned to the melting point of 8-HQF. The major disintegration of the material starts immediate after its melting. Based on the TG-DTA results, it is found that 8-HQF crystal is thermally stable up to 172^oC which can be used for solid state type of applications

Microhardness Studies

Hardness of a crystal sample takes over enormous information such as the strength, molecular bindings and elastic constant; hence it plays a major role in device fabrication. Mechanical behavior of single crystal is related mainly to the structure of the molecule and composition of crystalline solids. Mechanical strength of 8-HQF crystal is tested using Vicker's micro harness study. It was carried out on a crack free smooth polished surface of the grown crystal. The indentations were taken for different loads ranging from 10g to 100g with a constant indentation time of 10s at room temperature in all of the each case. The Vickers microhardness (H_v) is calculated by the below equation:

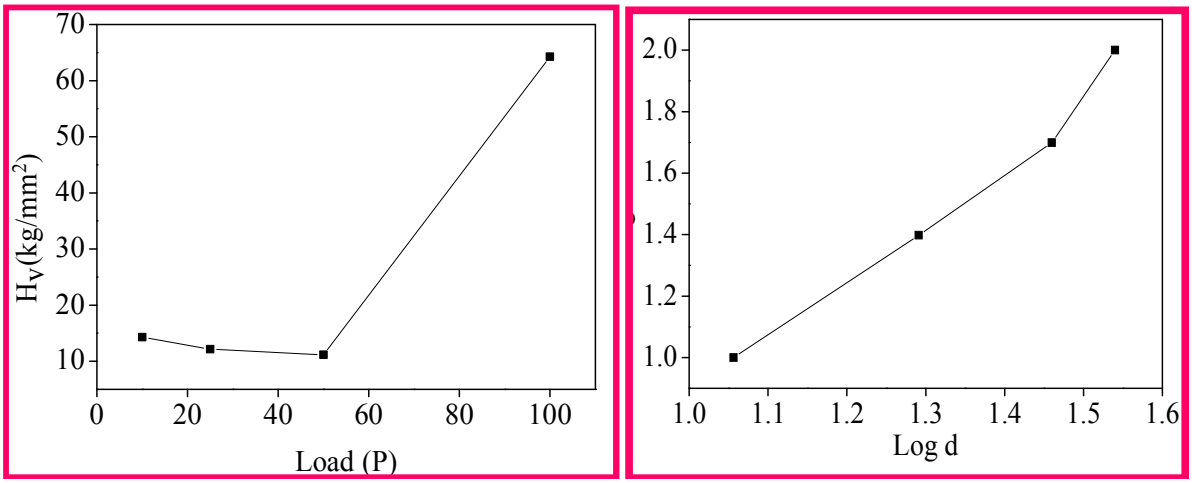
$$H_v = 1.854\left(\frac{P}{d^2}\right) kg/mm^2 \tag{7}$$

The parameters 'Hv' is the Hardness no. in kg/mm, 'P' corresponds to the load applied in gm and'd' is assigned to the mean length of diagonal in mm of indentation impression. It is noticed that hardness number rises on increasing the load applied to the crystal which is represented in Fig.2 (a). This circumstance is known a reverse indentation size effect (RISE) [5]. The measurement performed beyond 100g was resulted in a crack which is due to the stress generated by the indenter.

The relation bridging the load applied (P) and the mean diagonal length (d) of the indenter is given by the Meyer's Law as shown below:

$$P = k_1 d^n \tag{8}$$

Where 'k' is the material constant and 'n' is the Meyer's index. This relation is used to plot the graph between log (d) and log (P) as drawn in Fig. 2(b) for the 8-HQF crystal. The slope of this straight line gives out the value of 'n' for 8-HQF sample and it was calculated to be 1.98. The value of 'n' should lie between 1 and 1.6 for harder materials and more than 1.6 for soft materials [6]. Thus the material belongs to soft material category.



(a) (b)

FIGURE 2. (a) Plot of Vicker's microhardness number vs. load for 8-HQF crystal and (b) Plot between log (p) and log (d) for 8-HQF crystal.

CONCLUSION

Perfect single crystals of 8-HQF was synthesized using slow evaporation solution growth technique and X-ray diffraction studies confirm that the 8-HQF crystal belongs to triclinic crystal system with the space group of P $\bar{1}$ and the unit cell parameters are agreed with the reported values. Fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. The result of TG-DTA reveals that the compound is stable up to 172^0C. Hardness studies using Vicker's microhardness indicate that the 8-HQF crystal belongs to softer material category

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