Original Research Article

J. Funct. Mater. Biomol. 2(1)-2018 pp 35-39

SACRED HEART RESEARCH PUBLICATIONS

Journal of Functional Materials and Biomolecules

Journal homepage: www.shcpub.edu.in

ISSN: 2456-9429

Thermal, Mechanical and Dielectric studies of Urea Phthalic acid (UPA) single crystals

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Received on 15 May 2018, Accepted on 15 June 2018

Abstract

Thermal, Mechanical and dielectrical characterizations of slow evaporation grown single crystals of Urea-Phthalic acid (UPA) are analyzed in this article. Thermal study is carried out by analysing TGA – DSC spectrum of grown samples and the thermal stability is found to be 192.57^{0}C. Mechanical properties such as Vicker's microhardness number, work hardening index, Yield strength, stiffness constant, brittleness index, standard hardness and fracture toughness values are determined using Vicker's microhardness tester. The dielectric study is carried out and analysed by plotting variation of dielectric constant, dielectric loss and ac conductivity with frequency and temperature.

Keywords: Crystal Growth, Thermal Analysis, Micro hardness, Dielectric studies

1 Introduction

The study of growth, XRD, UV-Vis transmittance, FT-IR, microhardness, Photoconductivity and dielectrical characterizations of Urea Phthalic acid single crystals were reported[1]. In this article, Thermal, Mechanical and dielectrical studies of slow evaporation technically grown Urea Phthalic acid(UPA) crystal have been conducted and analyzed. The melting point, thermal stability, decomposition and phase transition properties can be studied from the TGA and DSC spectral analysis. So the UPA crystal was underwent to such thermal studies. The hardness of a crystal is generally defined as its resistance to structural breakdown under applied force or stress. Mechanical properties such as Vicker's microhardness number, work hardening index, Yield strength, stiffness constant, brittleness index, standard hardness value and fracture toughness values give information on its physical strength and about its deformation [2]. The chemical forces resist the motion of dislocations inside the crystal due to the displacements of atoms. This hardness is the intrinsic hardness of a crystal. Generally, the hardness properties was carried out to understand about the plasticity of the crystal[3]. Several papers were reported about this microhardness studies on various crystals using Vicker's indentor [4-5]. So, in present work, the various hardness parameters were determined for UPA crystal using Vicker's microhardness tester. The measurements of electrical properties provide information to projected applications such as in manufacturing processes[6]. The values of dielectric constant and dielectric loss of a material provides the measure of efficiency of the material to store the charges and various types of polarizations in the dielectric material[7]. So the dielectric studies on the UPA crystal have been analyzed and reported in this article.

2 Experimental

2.1Crystal Growth

Slow evaporation solution growth technique was used to grow UPA crystals. AR grade Urea and Phthalic acid were mixed in the stoichiometric ratio of 1:1 and was stirred well using doubly distilled water for about 5 hours using a magnetic stirrer. After that, the supersaturated solution was filtered and kept at constant temperature bath for slow evaporation. After 3 weeks, seed crystals were obtained from the mother solution and were harvested crystals to get optically transparent defect free crystals.

3 Results and Discussion

3.1Thermal Analysis

The thermal properties of UPA crystal was studied from 30 ^{0}C to 800 ^{0}C at a heating rate of 10 K/minute in the nitrogen atmosphere using NETZSCH TG - DSC. Figure 1 shows TGA and DSC curves for the grown sample. The initial mass of the sample material used to analyse was 8.506 mg and the final mass was only 0.9975% of the initial mass. The TGA curve gives the melting point of UPA is 192.57 ^{0}C. DSC curve also confirms this with the evidence of no phase transition before 200 ^{0}C. The major mass loss of 34.47% of initial mass is between 200 ^{0}C and 225.28 ^{0}C. This is due to the decomposition of ammonia molecule of Urea[8]. There is a sharp exothermic peak in DSC curve at 217.52 ^{0}C which is corresponding to the first

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stage of mass loss in TGA. The another major mass loss of 60.06% of initial mass is from 229.56 ^{0}C to 234.67 ^{0}C. This is mainly due to the decomposition of carbon monoxide molecule. A sharp exothermic peak at 229 ^{0}C in the DSC curve is matching to the second stage of major mass loss. The total mass loss is 99.01% of initial mass of the sample at 787.38 ^{0}C. The remaining 0.9975% material is left as residue. Before 200 ^{0}C, there is no phase transition or decomposition takes place which indicates UPA crystal is stable upto 200 ^{0}C. This property confirms one can grow UPA crystals by melt growth technique [9]. The sharp exothermic peaks indicate that good crystalline nature of UPA material[10].

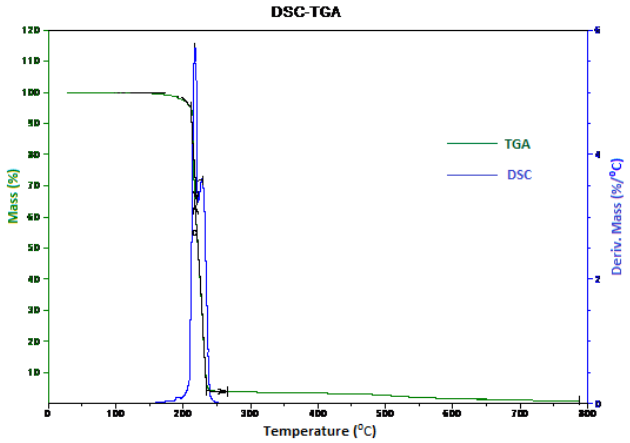

Figure 1 TGA – DSc spectrum of UPA

3.2 Mechanical Studies

Mechanical properties are essential factors for the device fabrication. Microhardness Studies were conducted using Lietz Wetzler microhardness tester with Vicker's diamond pyramidal indentor on UPA crystal specimen grown by slow evaporation method. The indentations for various loads such as 25g, 50g and 100g was made with a constant indentation time interval of 25 seconds.

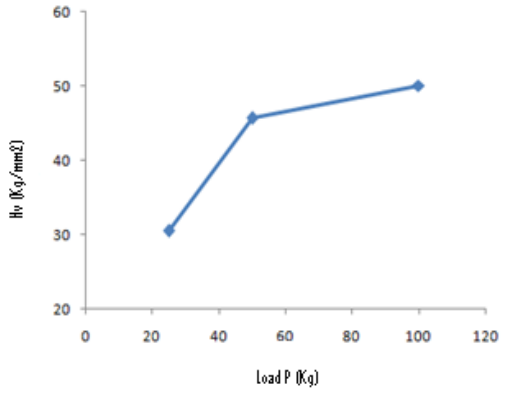

Figure 2 Plot between load P and Hv

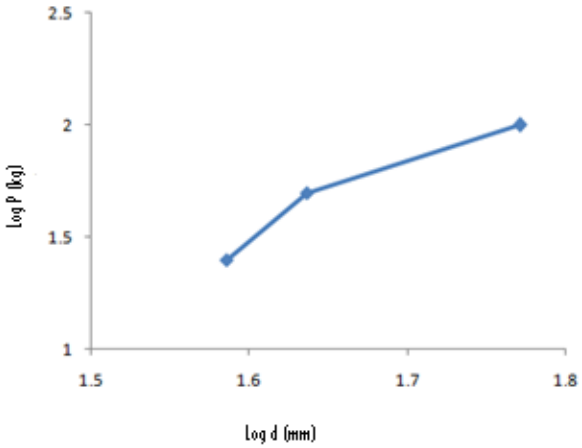

Figure 3 Plot between log d and log P

The values of Vicker's hardness number (H_v) was calculated for different loads using the relation,

$$H_v = \frac{1.8544P}{d^2} \quad kg/mm^2$$

Where P and d respectively being the applied load (in kg) and mean diagonal length of the indentor impression (in mm). The plot of Vicker's hardness number H_v with the applied load P shown in the figure 2 indicates that the hardness number increases with the increase in load which is termed as reverse indentation size effect, thus makes the material more suitable for device fabrication[11].

According to Mayer's hardness analysis, the relation between load P and indentation length d is given by[12],

$$P = k_1 d^n$$

Or $$\log P = \log k_1 + \log d^n$$

$$\log P = \log k_1 + n \log d$$

Where n is the work hardening coefficient. Mayer's microhardening index n was determined from the slope of the curve drawn between log d and log P (Figure 3). The standard hardness k_1 was determined from the intercept of log k_1.The value of work hardening coefficient(n) of UPA crystal was found to be 2.8, which shows that the material is a soft material [13].

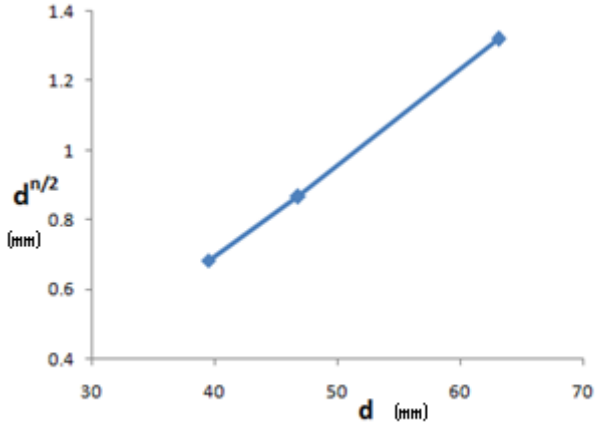

Figure 4 Plot between d and $d^{n/2}$

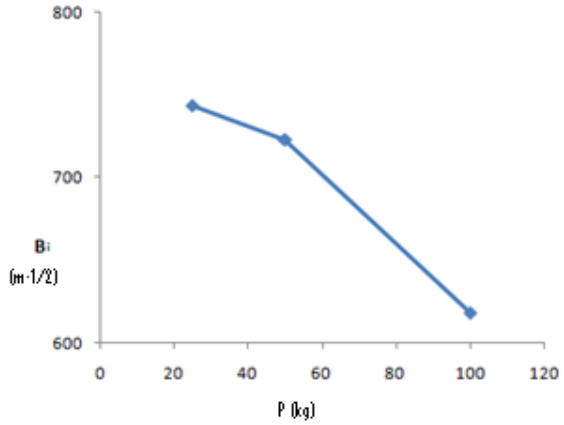

Figure 5 Plot between load P and B_i

Once the load was removed , the material takes some interval of time to revert to the elastic mode. So a correction of x is included to the observed value d. The Kick's law is given by

$$P = k_2(d+x)^2$$

Substituting value of P, we get $k_1 d^n = k_2(d+x)^2$

$$d^n = \left(\frac{k_2}{k_1}\right)(d+x)^2$$

$$d^{n/2} = \left(\frac{k_2}{k_1}\right)^{1/2}(d+x)$$

Or $$d^{n/2} = \left(\frac{k_2}{k_1}\right)^{1/2} d + \left(\frac{k_2}{k_1}\right)^{1/2} x$$

The above equation is the equation of a straight line. Figure 4 shows the curve drawn between d and $d^{n/2}$. The slope $\left(\frac{k_2}{k_1}\right)^{1/2}$ and the intercept $\left\{\left(\frac{k_2}{k_1}\right)^{1/2} x\right\}$ were calculated from the graph. The value of k_2 can be determined by substituting the value of k_1. From the intercept, the correction value x has been calculated.

The fracture toughness (K_c) is given the relation[14],

$$K_c = \frac{P}{\beta C^{3/2}}$$

Where C is the cracklength, which can be measured from the centre of the indentation mark to the crack tip, P the applied load and β is the geometrical constant which depends upon the indentation geometry. For Vicker's indentor, $\beta = 7$. The fracture toughness (K_c) of UPA crystal was obtained from the above formula.

The Brittleness index (B_i) of UPA crystal was calculated for various loads by the following relation,

$$B_i = \frac{H_v}{K_c}$$

Figure 5 is the plot drawn between load P and Brittleness index B_i , which shows the decrease in Brittleness index (B_i) with the increase in load P.

The microhardness value correlates with other mechanical properties such as Yield strength (σ_v) and elastic stiffness constant (C_{11}). The Yield strength of the grown crystal was calculated using the relation,

$$\sigma_v = \frac{H_v}{2.9}\left\{[1-(2-n)]\left[12.5(2-n)/(1-(2-n))\right]^{2-n}\right\}$$

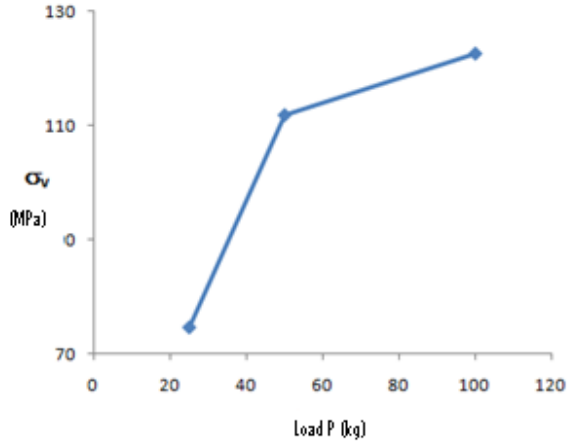

Figure 6 Plot between load P and σ_v

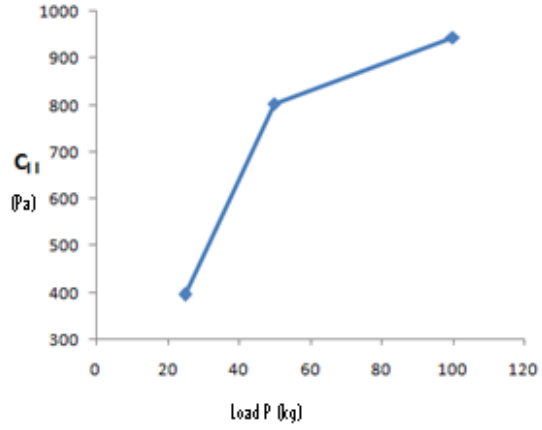

Figure 7 Plot between load P and C_{II}

Figure 6 is the graph plotted between load P and Yield strength (σ_v) ,which shows the variation of σ_v with the varying load P and the Yield strength of UPA crystal is found to be 74.65 MPa.

The stiffness constant (C_{II}) of a material helps to understand the nature of tightness of the bonding between adjacent atoms. The C_{II} for different loads has been determined using Wooster's empirical formula[15],

$$C_{II} = {H_v}^{7/4}$$

Figure 7 is the curve drawn between load P and C_{II}. It shows the increase in stiffness constant with increase in load. High value of C_{II} indicates that the binding forces between the atoms and ions are quite strong [16].

Table 1 Values of microhardness parameters of UPA crystal.

Hardness parameters	Calculated values		
n	2.8		
k_1 in kg/m	14.125×10^{-3}		
k_2 in kg/m	1.007×10^{-3}		
x in m	1.611×10^{-6}		
	P=25g	P=50g	P=100g

K_c in $MNm^{-3/2}$	0.041	0.0632	0.081
B_i in $m^{-1/2}$	743.9	723.1	618.52
σ_v in MPa	74.65	111.84	122.61
C_{II} in Pa	395.85	803.26	943.44

3.3 Dielectric Studies

The dielectric studies gives information about the orientation of the atoms, ions and their bonding in the material. The capacity of storing and transferring electric charges in the material can be understood from the dielectric analysis. From this analysis the various types of polarization mechanisms can also be understood.

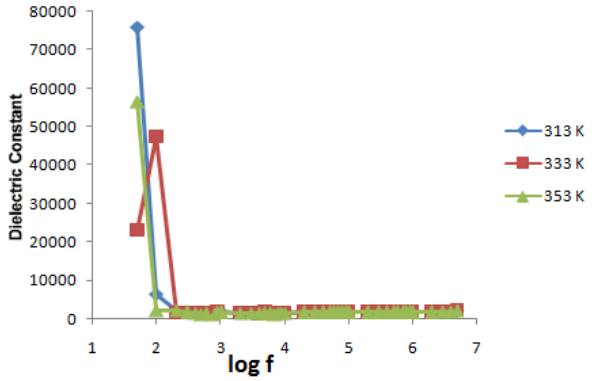

Figure 8 Plot between log f and dielectric constant

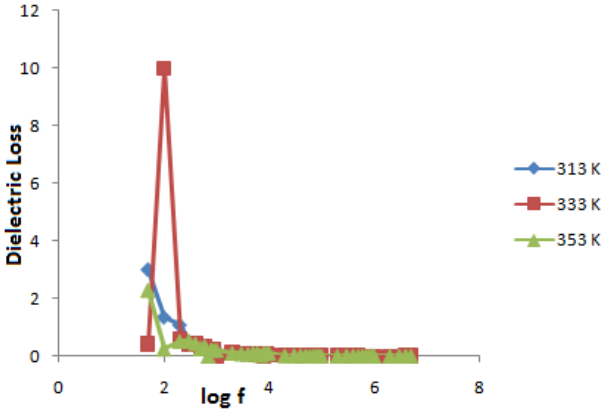

Figure 9 Plot between log f and dielectric loss

The dielectric study of UPA crystal was carried out using LCR meter for different frequencies from 50 Hz to 5 MHz at different temperatures of 313 K , 333 K and 353 K. The dielectric constant (ε_r) or relative permittivity was determined by the relation,

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

Where d is the thickness of the sample, C is the capacitance, A is the area of the crystal and ε_o is the permittivity of free space which is equal to 8.854×10^{-12}. Figure 8 shows the curves drawn between logarithm of frequency $\log f$ and dielectric constant ε_r for different temperatures of 313 K , 333 K and 353 K. The curves show that the value of ε_r is high in the lower frequency region for all temperatures, which may corresponds to space charge polarization due to charged lattice defects[17] in addition to electronic, ionic and orientation polarizations. Also, higher value of ε_r may decrease the electrostatic binding of the material and also leads to change in entropy or free energy of the system[18].

A graph drawn between $\log f$ and dielectric loss for different temperatures of 313 K , 333 K and 353 K which is shown in figure 9. The low value of dielectric loss at higher frequency range of UPA crystal shows the sample crystal has lesser number of electrically active defects[19]. The low value of dielectric loss at higher frequencies also indicates that the grown UPA crystals acquire good optical quality. This is one of the important parameters for nonlinear optical materials for their applications[20]. From the graph it can be understood that the dielectric loss is more for low frequencies and remain same at high frequencies at all temperatures for the sample. The values of dielectric constant and dielectric loss are decreasing exponentially to lower values when the frequency increases.

The ac conductivity σ_{ac} of the sample was calculated for different frequencies by the relation,

$$\sigma_{ac} = 2\pi f \varepsilon_r \varepsilon_o \tan\delta \quad (s/m)$$

Where ε_o is the absolute permittivity of free space, ε_r is the dielectric constant, f is the frequency and δ is the dielectric loss which can be directly measured from the instrument.

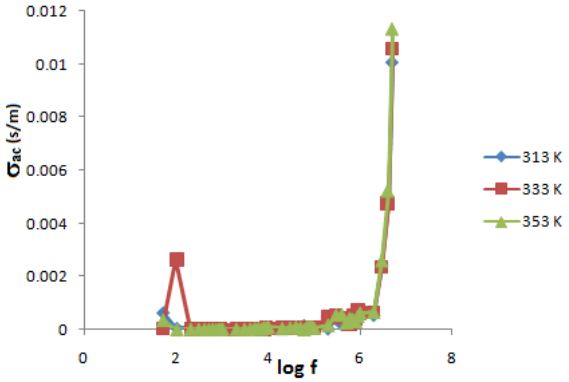

Figure 10 Plot between log f and ac conductivity

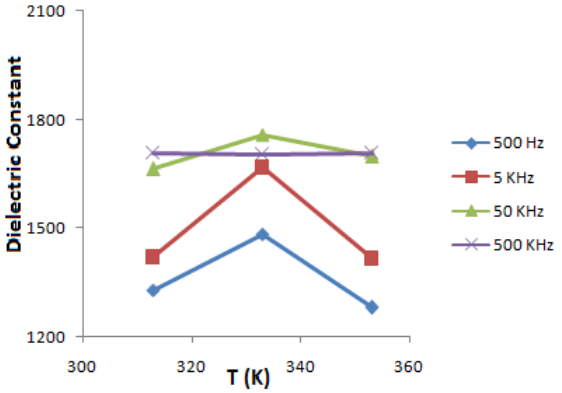

Figure 11 Plot between temperature and dielectric constant

Figure 10 shows the curves drawn between log f and σ_{ac} for the temperatures of 313 K , 333 K and 353 K. The ac conductivity of the sample increases with increase in frequency in the high frequency range. A graph of dielectric constant Vs temperature in the figure 11 shows the variation of dielectric constant with increase in temperature for various frequencies. The dielectric constant initially increases and then decreases with increase in temperature. This indicates that UPA crystal sample undergoes the phase transition from paraelectric to ferroelectric about 333 K which is known as Curie temperature (T_c). This reveals the ferroelectric property of UPA crystal [21].

4 Conclusions

The TGA – DSC thermal analysis gave the melting point of UPA material is 192.57 ^{0}C. The study confirms that the material is thermally stable upto 200^{0}C. So the material can be grown by melt growth method. Mechanical properties such as Vicker's microhardness number, work hardening coefficient, Yield strength, stiffness constant, brittleness index, standard hardness and fracture toughness values were determined using Vicker's microhardness tester. It was observed that the hardness number increases with increase in load, thus termed as reverse ISE. The value of work hardening coefficient(n) showed that the crystal is a softer material. The value of stiffness constant confirms strong binding forces between atoms and ions. The variation of dielectric constant, dielectric loss and ac conductivity as a function of frequency and temperature have been analyzed. The dielectric constant and dielectric loss of the material was found to decreases with increase in frequency. This shows the UPA crystal is suitable in microelectronic industry. Also, the electrical conductivity was found to increase with increase in frequency. The temperature dependent dielectric constant study shows that the UPA crystal may possess ferroelectric properties.

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