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An Investigation of Sem, Thermal And Mechanical Properties of Pure and Sodium Acetate Trihydrate Doped Thiourea Single Crystals

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Abstract : Single crystals of sodium acetatetrihydrate doped thiourea (abbreviated as STATH) $NaC_3H_{13}N_2SO_5$ and pure thiourea (abbreviated as TU) CH_4N_2S were successfully grown by slow evaporation method at room temperature from their aqueous solutions. The harvested crystals were of average dimensions 19×18×5 mm^3 (TU) and 38×21×23 mm^3 (STATH).Surface morphology of TU and STATH was studied by scanning electron microscope (SEM). The thermo gravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) analysis were employed to understand the thermal decomposition and mass loss of the synthesized compounds.The micro hardness test reveals that both the crystals possess good mechanical strength.
Keywords : Crystal growth, SEM, TG/DTA and Hardness.

1. Introduction

In order to develop inorganic, organic and semi organic NLO crystals, extensive efforts have been taken in the recent past [1–4].Usually the organic ligand is more dominant in the NLO effect of metal organic coordination complexes. Regarding the organic ligands, small electron systems such as thiourea [$CS(NH_2)_2$], thiocynate (SCN) and urea have been used with remarkable success[5].Now a days more attention is given onsemi organic materials due to their large nonlinearity, high laser damage threshold, good mechanical and thermal stability [6, 7].Thiourea has the proficiency to form a considerable complex of hydrogen bonds and it is a centro symmetric molecule. Most of the thiourea networks are metalorganic coordination complexes [8]. Thiourea crystals also manifest pyroelectric effect, which is exploited in infrared (IR), ultraviolet (UV), scanning electron microscopy (SEM) detection and infrared imaging [9].Thiourea is distinctly contemplated as a model organic material which acquires large dipole moment and has the ability to form metal ligand bond through strong and wide H bonding network [10]. On the other hand the inorganic metals comfortably correlate with thiourea and gain the accentric symmetrical orientation, which is the major requirement to acquire high optical transparency and adequately large nonlinear response from the crystal system [11]. Thiourea has been used widely as a supplement to enhance coating quality and to retard corrosion [12, 13]. It has also been used as an effective reactant to synthesize heterocycles and to separate costly metals [14, 15]. In the present work we

compare the SEM image, thermal and Mechanical properties of pure and sodium acetate trihydrate doped thiourea single crystals.

2. Experimental

2.1. Synthesis and crystals growth

Pure thiourea is dissolved in doubly distilled water and then stirred continuously for 6 hours for homogenization. Sodium acetate trihydrate was mixed with thiourea in a stoichiometric ratio of 1:1 in doubly distilled water and then stirred continuously for 6 hours for homogenization. The chemical reaction is as follows

$CH_4N_2S + C_2H_9NaO_5 \rightarrow NaC_3H_{13}N_2SO_5$

The purity of both the crystals was obtained by the process of repeated recrystallization. The thoroughly dissolved solutions were filtered using micro filter paper and taken in two different beakers. They were optimally closed using a perforated polythene paper and kept in undisturbed conditions and the solutions were allowed to evaporate slowly at room temperature. After a growth period of 28 daysoptically transparent TU single crystals of dimension 19×18×5 mm^3were harvested while optically transparent and well developed STATH single crystals of dimension 38×21×23 mm^3 were harvested after 36 days. The photographs of the grown single crystals are presented in **Fig-1 (a) & (b)**.

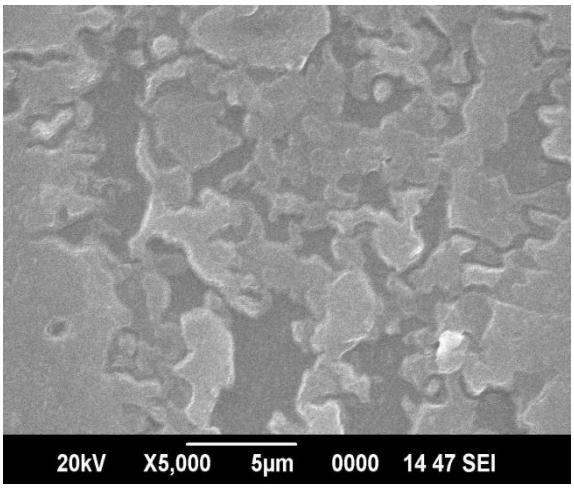

Fig-1(a): Photograph of TU

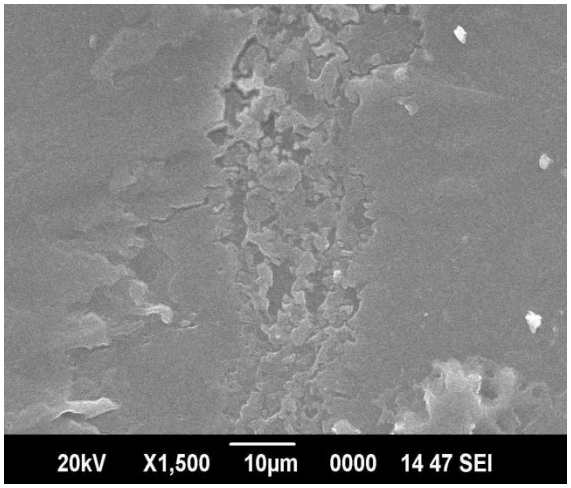

Fig-1(b): Photograph of STATH

2.2 Characterization Studies

In order to study the surface morphology of TU and STATH crystals, SEM images were taken in different magnitudes by using FEI Quanta 200 SEM scanning electron microscope (SEM). The thermo gravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) analysis were employed to understand the thermal decomposition and mass loss of the synthesized compounds by using the instrument Perkin Elmer STA 6000Simultaneous Thermal Analyzer. The mechanical property of both the crystals was studied by Vickers's micro hardness test.

3. Result and discussion

3.1 SEM Analysis

Scanning electron microscopy (SEM) can produce magnified images and in situ chemical information from virtually any type of specimen. In order to obtain high resolution surface image of a sample, Scanning Electron Microscopy (SEM) is used. This instrument generally operates in a high vacuum and a very dry environment in order to produce the high energy beam of electrons needed for imaging and analysis. The

formation of the image depends on collecting the different signals that are scattered as a consequence of the high energy beam interacting with the sample. Backscattered electrons and secondary electrons are generated within the primary beam-sample interactive volume and are the two principal signals used to form images. In order to analyze the nature and surface morphology of the grown crystals, SEM analysis was employed. Scanning Electron Microscope studies for TU and STATH single crystals were carried out using FEI Quanta 200 SEM**.** Since the organic materials are non-conducting in nature, carbon coating should be done for 10 s to both the samples before subjecting their surface to electron beam. The SEM images of TU and STATH crystals were taken into different magnifications and are shown in **Fig-2(a) & (b)**respectively and they depict the surfaces of as grown crystals. From the image it is observed that the surface of both the samples appears as smooth.

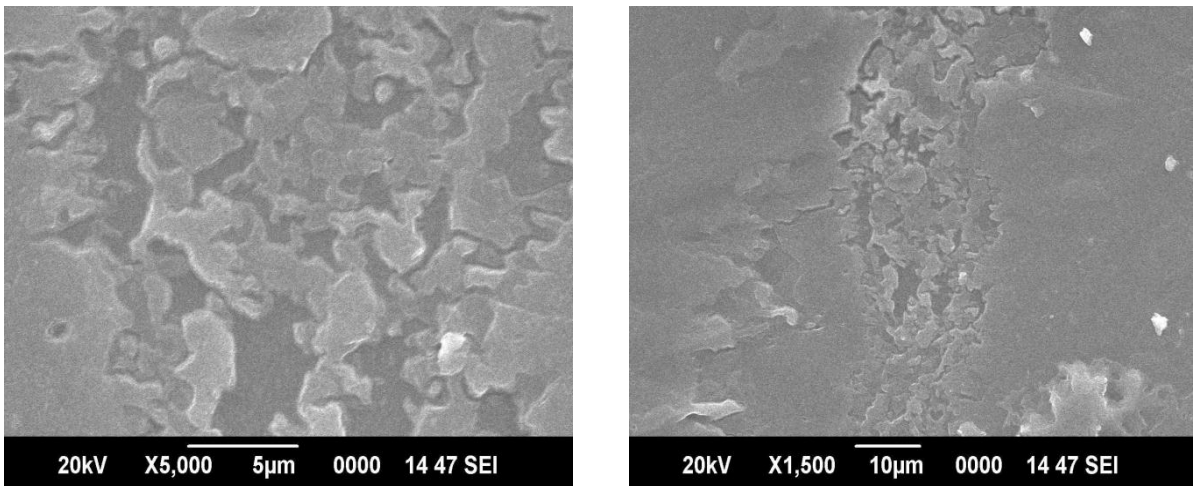

Fig-2(a): SEM images of TU

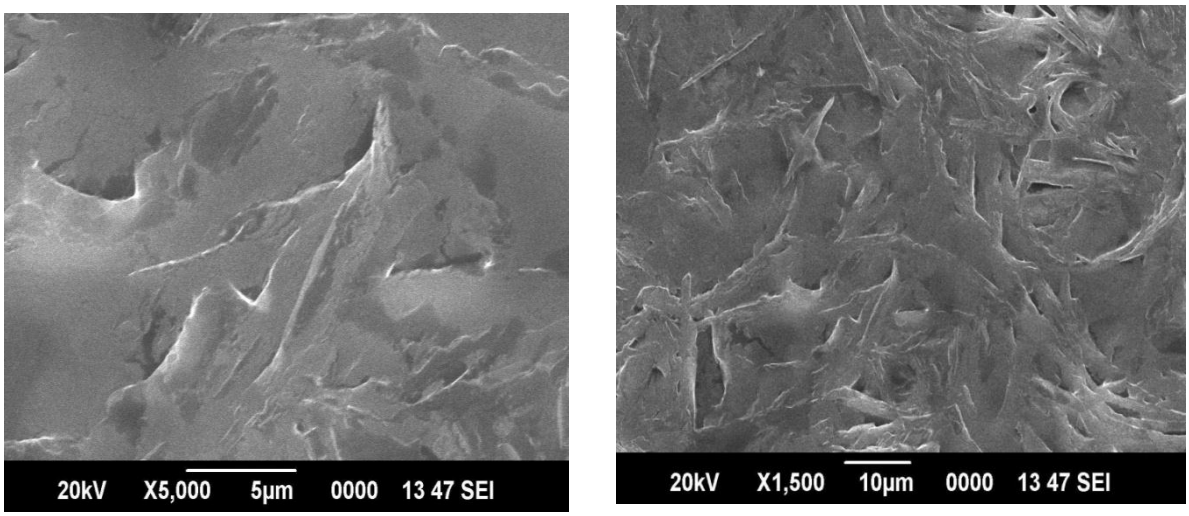

Fig-2(b): SEM images of STATH

3.2 Thermal Analysis

Thermo gravimetric analysis (TG) is used to measure the mass change but thermal analysis (TA) is used to measure the thermal change accompanying a structural metamorphosis. Endothermic process is a solid state reaction in which heat is absorbed while in exothermic process heat is released. Phase transition and different stages of decomposition of a crystal system were given by Thermo gravimetric analysis (TG) and Differential Scanning Calorimetry analysis (DSC)**.** In order to obtain the thermal characteristics of TU and STATH single crystals, Differential Scanning Calorimetry analysis (DSC) and thermo gravimetric analysis (TG) were carried out simultaneously by using the instrument Perkin Elmer STA 6000Simultaneous Thermal Analyzer. Initially8.345 mg of TU and7.501 mg of STATH were taken and they were heated from 40°C to

740°C at a rate of 20°C/min in protected nitrogen gas flow. The TG and DSC curves of TU are shown in **Fig-3(a)** and that of STATH are shown in **Fig-3(b)**. The TG curve of TU reveals that there is a conspicuous weight loss between 181.69 and 246.34°C due to the liberation of volatile substance of decomposed TU**.** But there is no weight loss below 181.69°C and this illustrates the absence of physically absorbed or lattice water in TU crystal. Hence it is evident that the sample is stable up to181.69°C and thereafter, melting and dehydration processes commence. At 246.34°C an endothermic peak is obtained in the DSC curve where the weight loss is about 77.5% of the initial mass taken and the mass is reduced to 1.873 mg. The final residue obtained at 648.9^{o} C is 0.267 mg and it is 3.19% of the initial amount of the sample.

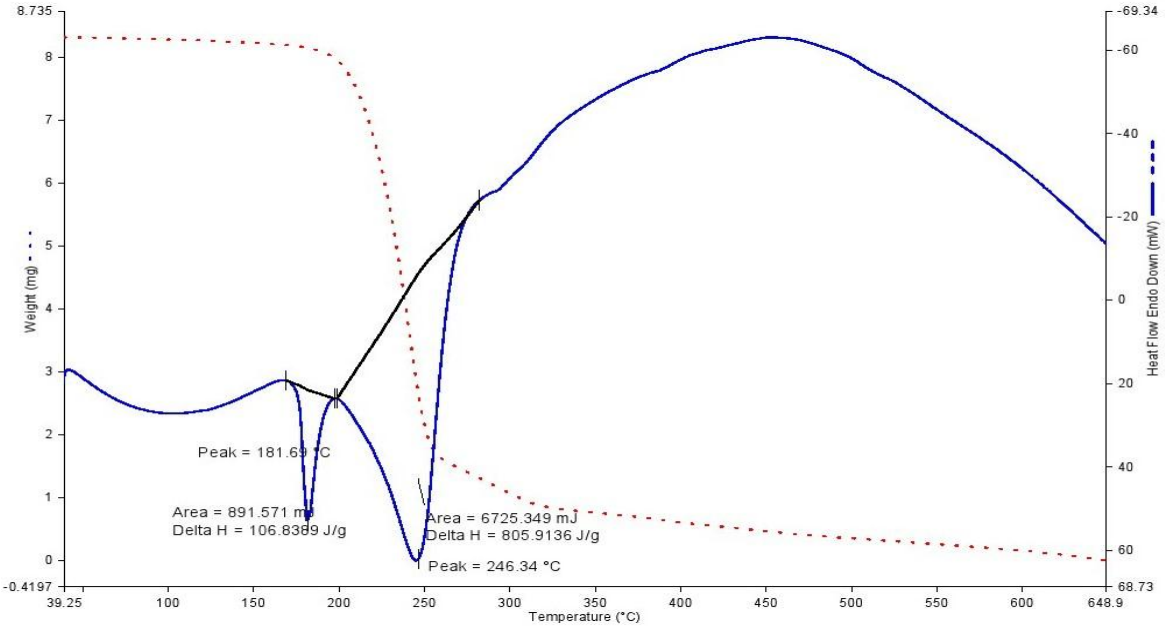

Fig-3(a) TG and DSC curves of TU

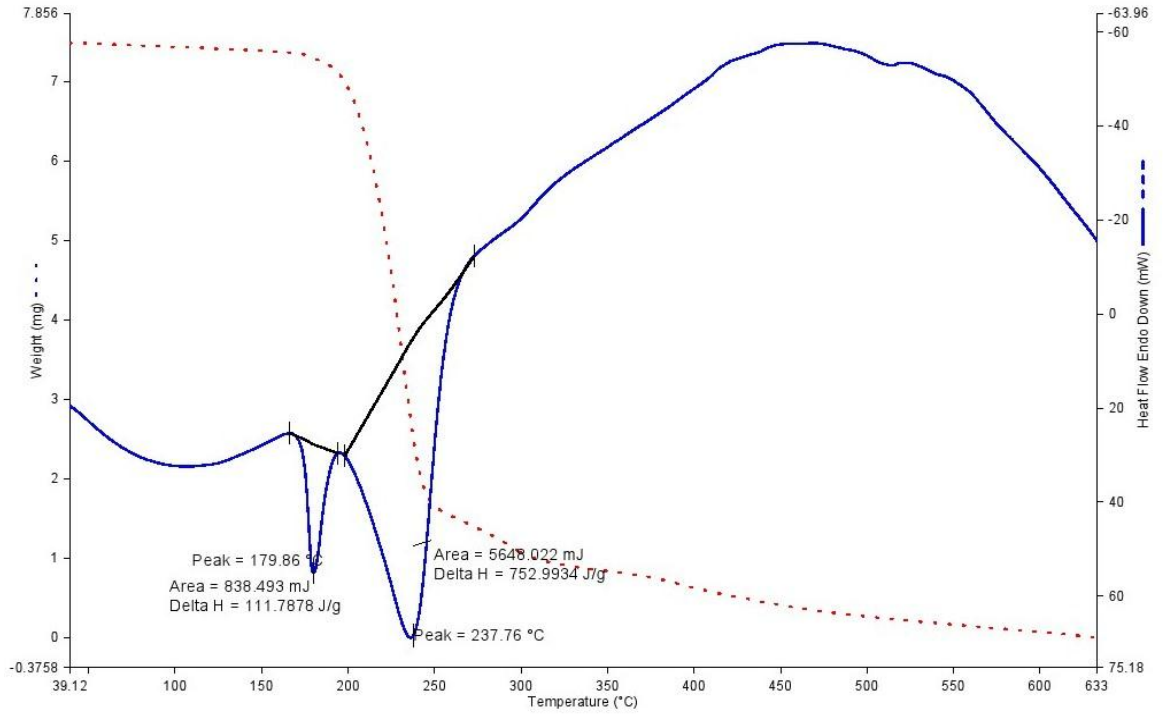

Fig-3(b) TG and DSC curves of STATH

The TG curve of STATH reveals that there is a conspicuous weight loss between 179.86 and 237.76°C due to the liberation of volatile substances, probably water molecule of decomposed STATH**.** But no loss in weight was obtained below 179.86°C and this illustrates the absence of physically absorbed or lattice water in STATH crystal. Hence it is evident that the sample is stable up to179.86°C and thereafter, melting and dehydration processes commence. In the DSC curve of STATH, an endothermic peak is obtained at 237.76°C where the mass is reduced to 1.238 mg and the corresponding weight loss is about 83.4% of the initial mass taken. The final residue obtained at 633^{o} C is 0.198 mg and it is 2.63% of the initial amount of the sample. From the Fig-3(a) & (b), it is concluded that the thermal stability of TU decreases slightly by the addition of sodium acetate trihydrate.

3.3 Micro hardness Measurement

The mechanical characterization of the crystals was studied by Vickers's micro hardness test. Hardness of the material is defined as the resistance offered by it to the motion of dislocations, deformations or damage under an applied stress. In order to measure the hardness, TU and STATH crystals with a thickness of 3 mm were used and loads of different magnitudes were applied. The variation of hardness with different load for TU is shown in **Fig-4(a)** and that of STATH is shown in **Fig-4(b)**. Vickers hardness number (H_v) was calculated for both the samples by using the equation

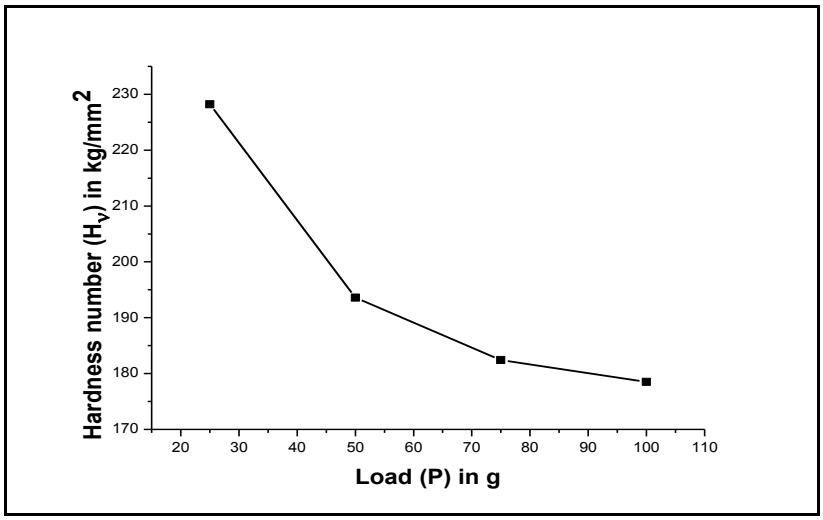

Fig-4(a): Variation of Hardness with Load for TU

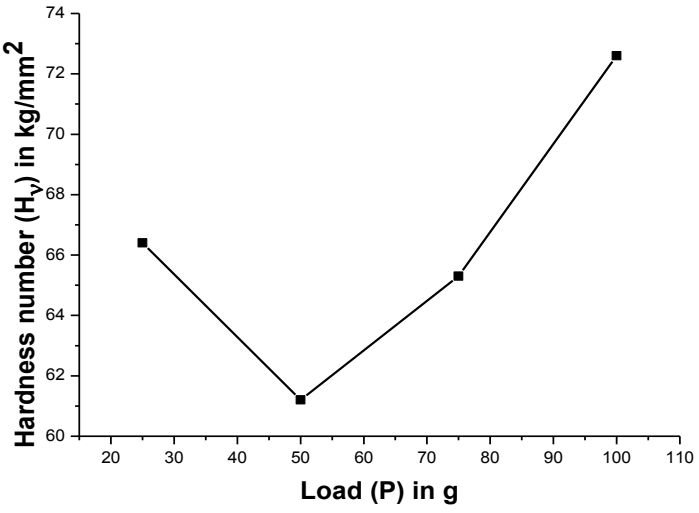

Fig-4(b): Variation of Hardness with Load for STATH

$$H_v \frac{(1.8544 \text{ X P})}{d^2} \ kg/mm^2$$

where P is the applied load in kg and d is the average diagonal length in mm. From Fig-4(a), it is evident that the micro hardness of TU crystal decreases on increasing the load. Fig-4(b) clearly shows that the micro hardness of STATH crystal decreases first and then increases with increase of load. For loads above 100g, cracks were developed on the surface of the crystals due to the release of internal stress generated locally by indentation. From the Fig-4(a) & (b), it is evident that the mechanical strength of TU increases with increase of load by the addition of sodium acetate trihydrate.

In order to find the increase in strength that accompanies plastic deformation of the grown crystal, work hardening coefficient (n) was calculated using the Meyer's relation $P = ad^n$, where a is the constant for the given material. A graph was drawn for both the samples between logarithmic values of the applied load and average diagonal length of the indentation formed on the crystals as depicted in**Fig- 5 (a) & (b).** From the graph a slope was taken from a straight line for both the crystals and the calculated work hardening coefficient of TU and STATH were 1.8 and 1.76 respectively. The value of work hardening coefficient of TU has good agreement with the reported value [16]. According to Onitsch, if the value of n lies between 1 and 1.6, the grown crystal comes under the category of hard material and the material will be soft if it is more than 1.6 [**17, 18**]. From the calculated value of work hardening coefficient (n), it is evident that both the crystals are soft materials.

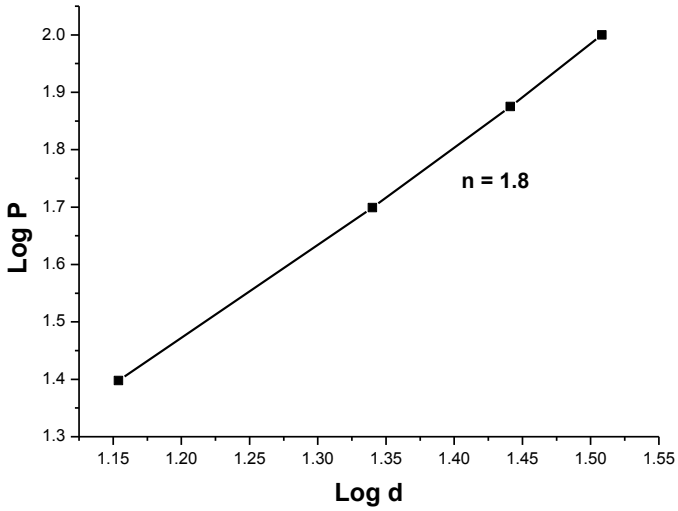

Fig- 5(a) Plot of Log d versus Log P of TU

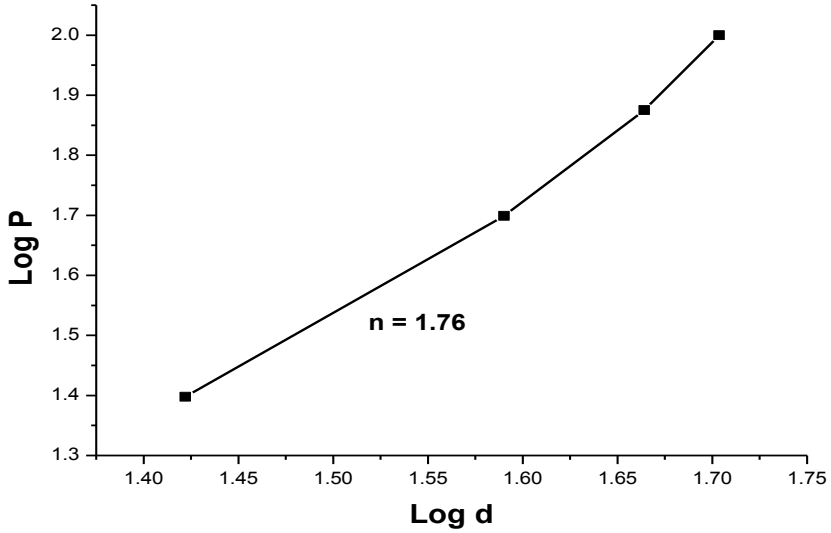

Fig- 5(b) Plot of Log d versus Log P of STATH

4. Conclusion

Single crystals of TU and STATH have been successfully grown by the slow evaporation technique from their aqueous solutions. Surface morphology of TU and STATH was studied by scanning electron microscope (SEM) and the surface of both the samples appears as smooth. From the thermo gravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) the thermal decomposition and mass loss of the synthesized compound were analysed. The thermal stability of pure TU single crystal decreases slightly by the addition of sodium acetate trihydrate. The micro hardness test reveals that the mechanical strength of TU increases with increase in load when it is doped with sodium acetate trihydrate.

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