# Growth and characterization of thiourea single crystal from sulphuric acid solutions

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Thiourea single crystals were grown from sulphuric acid solution by solvent evaporation technique. The structure of the crystals is identified as orthorhombic by single crystal X-ray diffraction technique. The molecular structure with functional group and band absorption spectrum are observed by using FTIR and UV-Vis spectrometer respectively. The mechanical hardness is performed on the grown crystals by Vicker's microhardness study and the results reveal that the crystals are mechanically hard.

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*Keywords*: Solution growth, Single crystal XRD, FTIR, UV-Vis, Microhardness, Vicker's hardness test

## 1. Introduction

Crystals of organic materials for use in Non-Linear Optical (NLO) devices are of great interest due to their high nonlinearity, high flexibility in terms of molecular structure, high optical damage threshold and low cost [1]. Single crystals of thiourea are used extensively and have vast demand in the electronic industry as polarization filter, electronic light shutter, electronic modulator, optical voltmeter and as elements of electro-optic and electro-acoustic devices. The origin of nonlinearity in NLO materials arises due to the presence of delocalized π–electrons system. Donor and acceptor groups connection are responsible for enhancing their asymmetric polarizability [2]. Thiourea crystals also exhibit pyroelectric effect, which is utilized in infrared (IR), ultraviolet (UV), scanning electron microscopy (SEM) detection and infrared imaging [3].

Pure and thiourea added potassium dihydrogen phosphate (KDP) single crystals were grown by the sol-gel method and their lattice vibration and thermal properties were studied by Priya et al [4]. Spectroscopic and microscopic studies of thiourea single crystals were performed byPatel et al [5]. Growth of bis (thiourea) cadmium chloride (BTCC) single crystals and growth and characterization of zinc thiourea chloride (ZTC) have been investigated byUshasree et al [6] and Rajasekaran et al [7]. In view of finding good quality thiourea crystal, in the present investigation, an attempt has been made to grow an optical quality thiourea single crystal by low temperature solutions growth technique. In addition, FT-IR, XRD and optical studies, mechanical hardness, and etching studies, etc. have been performed in details.

## 2. Experimental

### 2.1 Crystallization of thiourea crystal

The growth of thiourea single crystal was carried out from concentrated sulphuric acid solution by Solvent evaporation technique. 50 ml saturated solution was prepared at room temperature and then filtered to remove any insoluble impurities. The spontaneous nucleation was prevented during the filtration process. Seed crystals were prepared by isothermal condition. The saturated solutions were kept in the Petri dish and the outer face was covered by perforated transparent polythene paper or filter paper. The petri dishes were kept at the room temperature until small transparent well-shaped crystals obtained within first week and at the second week, the seed crystals and single crystals were grown in the petri dishes. The growth period of single crystal takes within 2 weeks. The grown crystals possess well defined morphology with reasonable size of about $1 \times 1 \times 0.5$ cm$^3$ and $1.1 \times 1 \times 0.4$ cm$^3$ along all the three crystallographic directions as shown in Fig. 1.

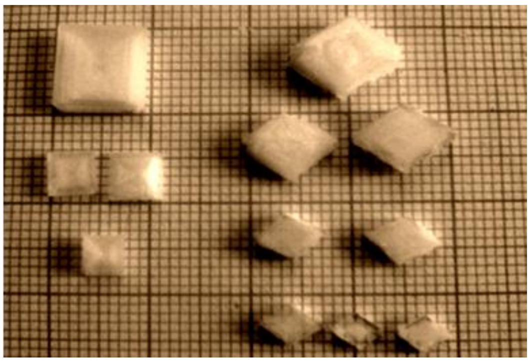

*Fig. 1.Photograph of single crystals of thiourea.*

## 3. Results and discussion

### 3.1. X-ray Diffraction

X-ray diffraction pattern for the single crystal of grown crystal was carried out using Bruker-Nanius CAD-4 diffractometer (Mo$K_{\alpha}$) radiation. The lattice parameters were determined as: a = 5.493(1) Å, b = 7.655(3) Å and c = 8.561(3) Å, α = β = γ = 90° and cell volume equals to 360.0(9) $Å^3$ for the crystal. The crystals exhibit orthorhombic crystal in nature.

### 3.2. FT-IR studies

The Fourier transform infrared (FT-IR) spectrum is recorded by using KBr pellet technique to identify the functional groups in determining the molecular structure of the grown crystals. The FT-IR spectrum is recorded by using Perkin Elmer Spectrum RXI spectrophotometer in the region 400-4000 cm-1 and is as shown in Fig. 2. The symmetric and asymmetric C = S stretching vibrations of crystal are observed at 728 $cm^{-1}$. The $CH_3$ asymmetrical deformation, or $CH_2$ bending vibration or N-C-N asymmetric stretching mode is assigned at 1464 $cm^{-1}$. The combination band occurs at 1400 $cm^{-1}$. The absorption band occurs at 1616 $cm^{-1}$, it is due to $NH_2$ in-group deformation. The symmetric $NH_2$ stretching is assigned to the band at 3387 $cm^{-1}$.

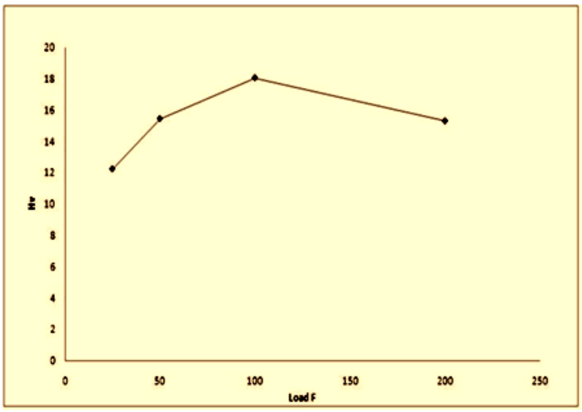


*Fig. 2. FT-IR spectrum for sulphuric acid grown thiourea.*

### 3.3. UV-VIS studies

An optical transmission spectrum is taken at room temperature using LAMBDA 35 spectrometer (UV-VIS-NIR). The UV-Vis transmission spectrum is as shown in Fig. 3 Optical transmission spectrum gives valuable information about the structure of the molecule because the absorption of UV and visible light involves promotion of electron in σ and π orbital from the ground state to higher energy state. From device point of view, the transmission spectrum is important, since the grown crystal can be used only in the highly transparent region. The transmission is uniformly high for light in the visible region of the electromagnetic spectrum, which is useful for device application. It is evident that the crystal has low optical absorption and high transmittance and UV cut off wavelength is about 222 nm, which is sufficiently low for second harmonic generation.

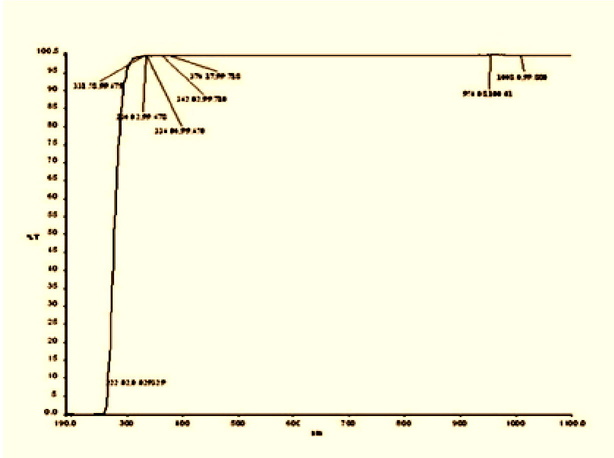

*Fig. 3. UV-Vis spectrum for sulphuric acid grown thiourea.*

### 3.4. Micro-Hardness test

The hardness of a material is influenced by various parameters such as lattice energy, Debye temperature, internal heat of formation and interatomic spacing. Micro-hardness measurement is a general microprobe technique for assessing the bond strength. Micro hardness studies were carried out on the crystal at room temperature using a Micro hardness tester, fitted with a diamond pyramidal indentor attached to an incident light microscope. For a static indentation test, load varying from 25 to 200 gm and the time of indentation is kept constant at 10 seconds for all trials. The diagonal lengths of indented impressions obtained at various loads are measured by using a micrometer eyepiece. The Vicker's Hardness Numbers (Hv) are calculated by using the following relation [8]

$$Hv = 1.8544\ (F/d^2)$$

where F is the applied load in Kg and d is the average diagonal length of the indentation mark in mm.

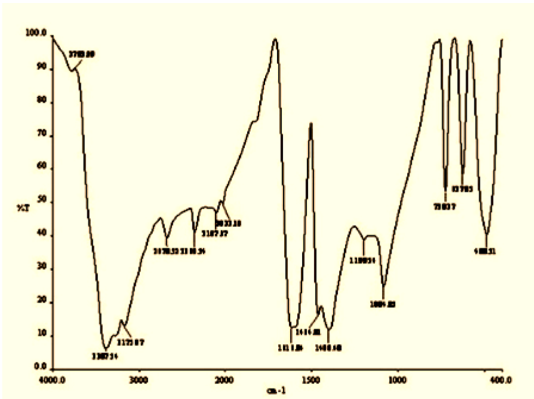

*Fig. 4. Variation of Hv with load.*

The variations of Hv with loads is shown in Fig. 4. When indenter just touches the surface, micro hardness increases from 25 to 100 gm, then dislocations are generated from 100 gm onwards in the indenter region, and hence micro hardness decreases. The increase in the hardness with load due to work hardening of the surface layers. The plot of log (d) against log (F) is shown in Fig. 5. The slope (n) is found to be less than two for above 100 gm of load crystals. It is in good agreement with Onistch concept. It reveals that the Vicker's hardness increases, indicating their hardening nature.

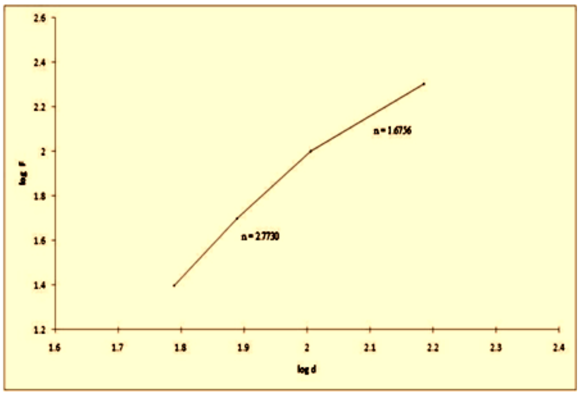


*Fig. 5. Variation of log F with log d.*

## 4. Conclusions

Single crystals of thiourea were grown by solvent evaporation method. Their structural, optical and mechanical properties are studied. The crystals exhibit orthorhombic structure with lattice parameters: a = 5.493(1) Å, b = 7.655(3) Å and c = 8.561(3) Å. The hardness of the crystal is good and they are suitable for NLO applications, and it is also good agreement with Onistch concept. The low absorption in the IR- Vis region and high absorption wavelength cut off around 222 nm are very good expected characteristics for NLO materials.

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