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RESEARCH ARTICLE

# SYNTHESIS AND CHARACTERIZATION OF A NOVEL UREA THIOUREA SODIUM SULPHATE CRYSTAL

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**ABSTRACT**

A semi organic non-linear optical crystal Urea Thiourea Sodium Sulphate (UTNS) has been grown by slow evaporation method at room temperature. The grown crystal was characterized by the presence of powder XRD technique. The presences of various functional groups of the crystal were identified by FT-IR analysis. Optical transmission property of the material was established by UV-Vis spectrum. Thermal studies (TG/DTA) confirm that the stability of the crystal is around at 230 °C. Surface Morphology of the grown crystal of UTNS was carried out by SEM.



## INTRODUCTION

The development of Non-Linear Optical crystal (NLO), semi organic materials find extensive optoelectronic applications such as optical frequency conversion, optical data storage and optical switches in the initially confined laser fusion systems (Marcy *et al*., 1992; Wangg *et al*., 1999). Materials with second-order optical nonlinearities, short transparency lower cut-off wavelength, and high thermal and mechanical properties are the essentialities for the realization of many of these applications (Ushasree *et al*., 2008). Urea ($(NH_2)_2CO$) is a good organic nonlinear crystal. It is a useful material for high power laser frequency shifting in a wide spectral range, because of its large transparency window, large birefringence, relatively high damage threshold and low temperature dependence of refractive indices. The centro-symmetric thiourea molecule, when combined with inorganic salt, yields excellent non centro-symmetric complexes, which has quiet good non- linear optical properties. Examples are Zinc Tris Thiourea Sulfate (ZTS) (Sastry *et al*., 2004; Ushashree *et al*., 1999; Gopinath *et al*., 2012), zinc thiourea chloride (ZTC) (Ravindiran *et al*., 2011; Begum *et al*., 2009) and Bis Thiourea Cadmium Chloride (BTCC) (Boomadevi *et al*., 2002) etc., Thiourea crystals also exhibit piezoelectric effect, which is utilized in Ultraviolet (UV), Infrared (IR), Scanning Electron Microscopy (SEM) detection and imaging. In this study, an attempt is made to combine urea with thiourea and sodium sulphate for growing a new semi organic non-linear optical material by slow evaporation technique. Also structural, optical, thermal and mechanical properties were established through characterization techniques.

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## MATERIALS AND METHODS

### Crystal Growth

To grow a single crystal of UTNS, slow evaporation method was employed. The solution was prepared by dissolving urea, thiourea and sodium sulphate in a stoichiometric ratio 1:3:2 in double distilled water. The solution was constantly stirred for 6 hours and was filtered and then allowed to evaporate at room temperature. The purity of the synthesized salt was improved by successive recrystallization process. Well developed, good transparent crystals were harvested in a growth period of 25 days and as shown in Fig.1.

## RESULTS AND DISCUSSIONS

### FT-IR Spectral Analysis

The functional groups were identified by Fourier transform infrared studies using Perkin Elmer RX1 FT-IR spectrometer in the range 4000 – 400 $cm^{-1}$ KBr pellet technique was employed for recording the spectra. The FTIR spectrum of UTNS crystal as shown in Fig.2.

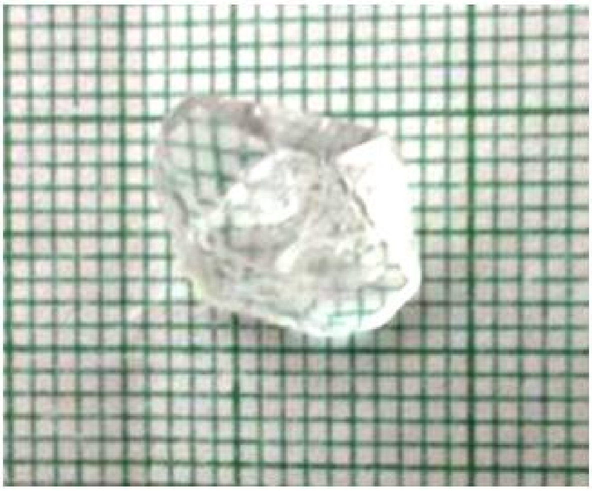


**Fig.1. Photograph of UTNS Crystal**

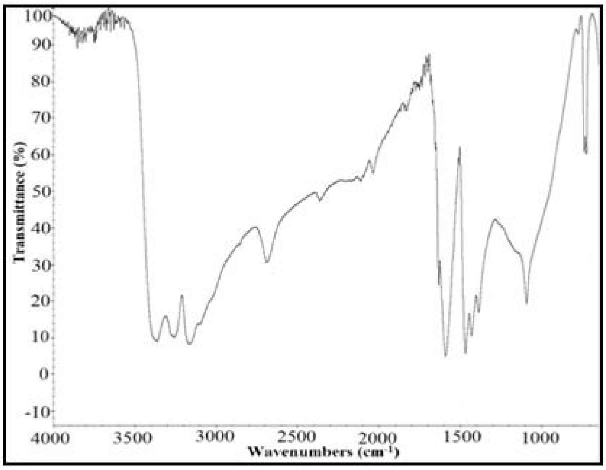



**Fig.2. FTIR spectrum of UTNS Crystal**

The strong absorption bands at frequency region 3400 $cm^{-1}$ to 3100 $cm^{-1}$ corresponds to asymmetric and symmetric stretching vibration of $NH_2$ group of thiourea (Selvasekarapandian *et al*., 1997; Kumararaman *et al*., 2012). Band at 1633 $cm^{-1}$ may be attributed to $NH_2$ bending (scissors) vibration. The band at 1468 $cm^{-1}$ is due to asymmetric stretching vibration and at 1092 $cm^{-1}$ is assigned to symmetric stretching vibration of N-C-N. The C=S asymmetric and symmetric stretching vibration of UTNS crystal were observed band at 1432 and 724 $cm^{-1}$ respectively (Silverstein *et al*., 1998; Andreeti *et al*., 1968).

## Powder X-Ray Diffraction Analysis

The powder X-ray diffraction analysis using diffraction system X-PERT -PRO with Cu K alpha radiation (λ=1.54060Å) was carried out. The grown crystals were grounded using an agate mortar and pestle. The sample was scanned over the range (2θ) of 10 to 80 °. The XRD pattern of the UTNS crystal is shown in Fig.3. The obtained XRD pattern was analyzed using PROSZKI software package. The results suggest that the crystal belongs to orthorhombic system (Madhurambal and Mariappan, 2010).

## UV-vis Spectral Analysis

A transmission spectrum is very important for NLO material because a non-linear optical material can be practically used only if it has wide transparency window. The optical transmission spectrum of UTNS was recorded in the range 200 – 1100 nm using Shimadzu –UV 1800 spectrometer. There is no absorption band at 300 to 1100 nm (Fig.4). The sample has a good transmittance and lower cut off wavelength falls below 300 nm. Wide and good optical transmittance over entire visible region enables it to be a potential applicant for optoelectronic applications (Senthilkumar and Ramachandraraja, 2012).

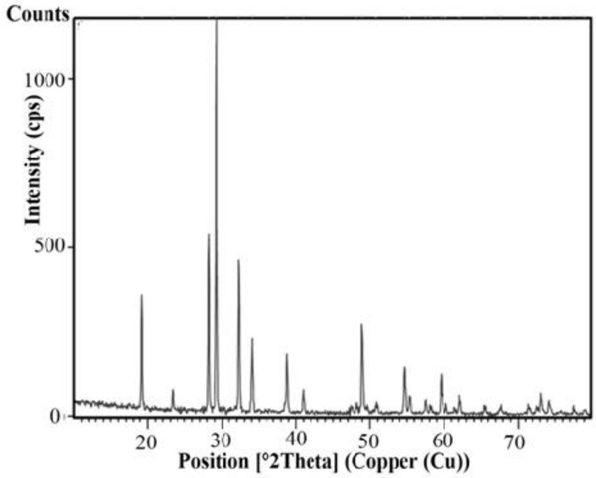



**Fig.3. Powder XRD pattern of UTNS Crystal**

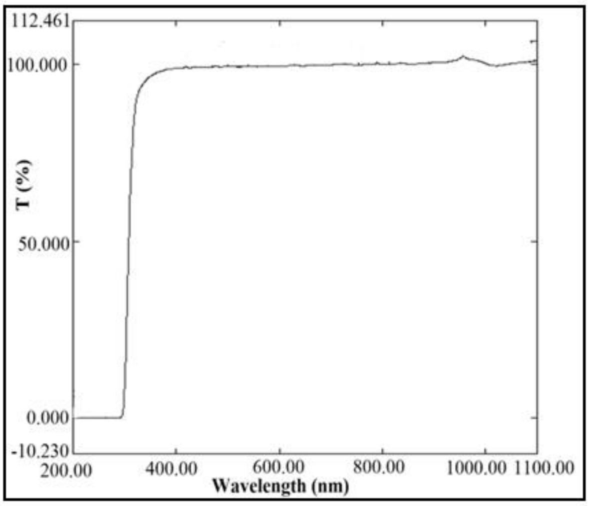



**Fig.4. UV-vis spectrum of UTNS Crystal**

## Thermal Analysis

The Thermogravimetry (TG) and Differential Thermal Analysis (DTA) of UTNS crystal was carried out using a NETZSCH - STA 449 F3 JUPITER model thermal analyzer. A powder sample was used for the analysis in the temperature range of 30 to 1000 °C with a heating rate of 20 °C / min in a nitrogen atmosphere. From the TG curve (Fig.5); it is observed a no loss of weight at around 100 °C. This confirms the absence of water molecule in the sample. The horizontal portions (plateaus) indicate the regions where there is no weight change up to 230 °C. The thermal stability of the UTNS crystal around is 230 °C (stage I). Then thiourea starts to decompose into carbon nitrogen sulphur and carbon sulphur (Madhurambal, 2013).

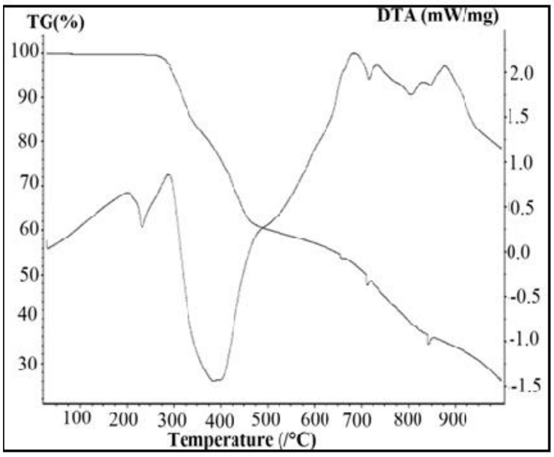
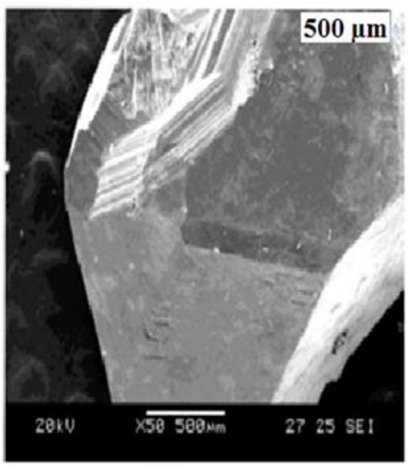



**Fig.5.TG/DTA-Curve of UTNS Crystal**

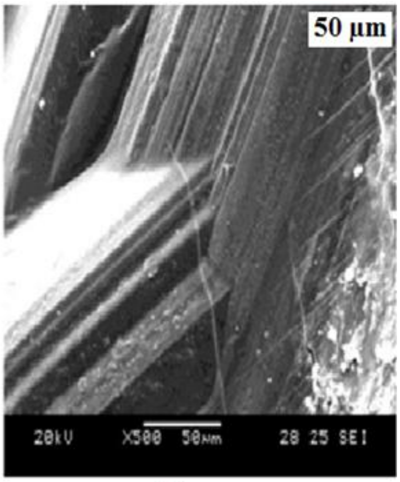
Decomposition occurs over several stages; 37% weight loss occurs between 230 to 460 $^oC$ (stage II). This represents the reaction temperature of the sample. Only 8% weight loss is observed at stage III (460 to 650 $^oC$). 19% weight loss at stage IV (650 to 840 $^oC$) and 10% weight loss, beyond 840 $^oC$ are evidenced. From DTA curve, UTNS crystal undergoes endothermic transition at 230 $^oC$ due to the melting. There is no phase transition till the material melts and this enhances the temperature range of the crystal utility in NLO applications (Lenin *et al*., 2007; Ravi Kumar *et al*., 2011). The Sharp DTA exothermic at 300 $^oC$ represents a phase change. Sharp and small endotherms above 700 $^oC$ indicate the crystalline rearrangements.

**SEM Analysis**

SEM analysis provided information's about its nature, suitability for device fabrication and also it is used to check the presence of imperfections. SEM analysis was carried out using JEOL JSM-5610 LV Scanning Electron Microscope. UTNS crystal exhibiting layered growth is seen from Fig.6a. It was observed that the basic units are arranged in different layers, which is a clear evidence for the stacking of fundamental units during the crystal growth. Microscopic observation of the habit faces reveals the presence of spreading micro-layer. Careful examination of the cross section of the crystal (Fig.6b) under the SEM shows the group that corresponds to step on the surface of parallel slip lines.




(a)




(b)

**Fig.6. SEM images of UTNS Crystal (a) X50 and (b) X500 magnifications**

They indicate that the atomic planes within the crystal have sheared with respect to one another resulting in a surface steps. It is generally found that the slip planes are closest packed structure in the crystal (Sivakumar *et al*., 2008).

**Conclusion**

A new single crystal of UTNS was grown by the slow evaporation method at room temperature. A Powder XRD analysis confirmed that the UTNS belongs to orthorhombic system. The presences of functional groups were identified by FTIR analysis. Good optical transmittance in the UV-vis spectrum reveals that UTNS crystal was a potential applicant for NLO applications. TG/DTA analysis is a very good tool to analyze the thermal stability of UTNS crystal up to 230 $^oC$. A topographical of the crystal was reported using the SEM analysis.

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