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Synthesis and Characterization of Copperdoped Urea Thiourea Single Crystal Developed By Slow Evaporation Method

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ABSTRACT: A single crystal of Copperdoped urea thiourea has been grown successfully from its aqueous solution. The grown crystals have been subjected to X-ray diffraction studies to identify the morphology and structure. The TGA studies showed the thermal properties of the crystals. The functional group of the grown crystals was found by UV - Visible double beam spectra, FT-IR analysis, NMR and XRD studies.

KEYWORDS: Urea, Thiourea, Copper Sulphate, Urea Thiourea Copper (CuTU), X-Ray diffraction, UV-Vis, FT-IR, NMR, TGA, NLO and micro hardness.

I. INTRODUCTION

Crystals are the inevitable materials for the modern technology. Without crystals, there would be no electronic or photonic industry etc. Crystal growth is a multidisciplinary subject covered with physics, chemistry, chemical engineering, metallurgy, crystallography etc. The strong influence of single crystals in the present technology is evident from the recent achievements in the above mentioned fields. Hence, in order to achieve high performance from the crystallographic objects, good quality single crystals are needed. The search for new frequency conversion materials over the past decade has led to the discovery of many organic and inorganic materials with high nonlinear susceptibilities. Recent interest is centred on inorganic crystals because pure inorganic materials have excellent mechanical and thermal properties. The rapid development of optical communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel semi organic systems of considerable potential and high performance [1-21]. There are three major stages involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices [1-15]. In this paper, the method of crystal growth with emphasis on low temperature solution growth technique was described.

II. EXPERIMENTAL METHOD

2.1 SYNTHESIS

1g of urea, 9g of thiourea and 5g of copper sulphate were dissolved in 30 ml of double distilled water. The solution was thoroughly mixed using a magnetic stirrer. A crystalline substance was formed. The Urea Thiourea Copper Sulphate solution was prepared in water and maintained at 30°C with continuous stirring to ensure homogeneous temperature and concentration. The solution was kept at 30°C for five days in order to get hard copper doped thiourea urea single crystal.

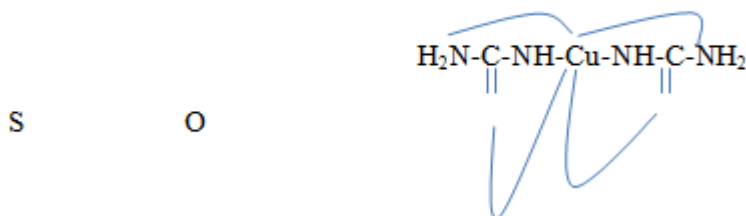
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Crystal growth large single crystals can be grown from slow evaporation solution growth. Single crystals of urea thiourea copper are grown by slow evaporation of the saturated aqueous solution at room temperature. Good quality single crystals were grown within seven days.



Molecular structure of CuTU

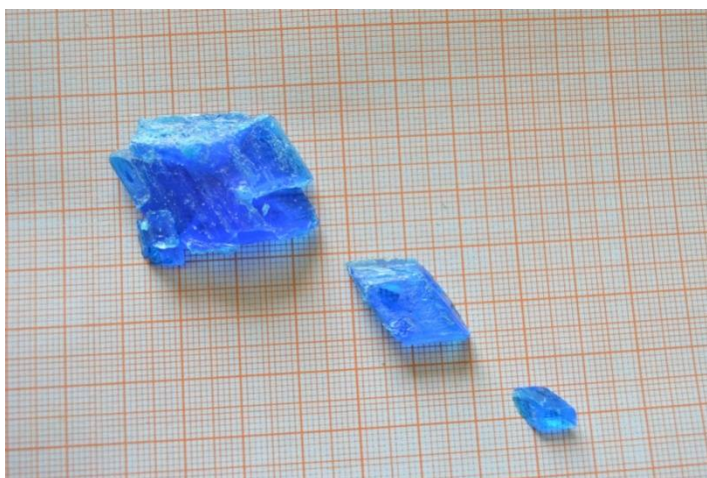


Fig.1-Shape of CuTU

2.2 UV-VIS SPECTRAL ANALYSIS

The optical transmittance range and transparency cut-off wavelength are the main requirements for device applications.

2.3 THERMAL ANALYSIS

Thermo Gravimetric Analysis (TGA) gives the information regarding the phase transition and different stages of decomposition of the crystal system.

2.4 FT-IR SPECTRAL ANALYSIS

FT-IR Spectroscopic studies were effectively used to identify the functional groups present in the synthesized compound and to determine the molecular structure.

2.5 NMR

¹H NMR CHEMICAL SHIFTS

Molecular structure of the grown crystal was investigated by ¹H NMR spectroscopy. The ¹H NMR spectrum indicates the presence of different proton environments in the title crystal.

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¹³C NMR CHEMICAL SHIFTS

¹³C NMR spectrum arises in the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied fields strength.

III. RESULTS AND DISCUSSION

3.1. X-RAY DIFFRACTION ANALYSIS

Single crystal X-ray diffraction study was performed for the grown CuTU crystal. It was found that CuTU crystal belongs to orthorhombic system ($\alpha = \beta = \gamma = 90^\circ$). Lattice parameter values of CuTU are compared with reported TU in Table 1. In the case of doped sample, a slight variation in the cell parameters is observed, which may be due to the incorporation of urea and thiourea ligands. This analysis revealed that the induction of urea and thiourea ligand in the CuTU crystal does not change the crystal system though there is a small change in the lattice parameters. The powder sample of CuTU was scanned over the range 10-80° at a rate of 1° per minute and the powder X-ray diffraction patterns were indexed using Check cell software (Fig. 3). The Lattice parameter (a) was calculated by selecting the (102) plane using the formula [2],

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

Sample	System	2θ(degree)	FWHM	hkl	Lattice parameter (Å)	
					Calculated	Reference
TU	Orthorhombic	23.25	0.16	200	7.644	7.644
		20.81	0.16	020	8.527	8.559
		32.57	0.24	002	5.493	5.492

Sample	System	2θ(degree)	FWHM	hkl	Lattice parameter (Å)	
					Calculated	Reference
CuTU	Orthorhombic	27.108	0.2455	200	3.2867	3.3012
		22.244	0.4402	020	3.9931	4.0781
		18.684	0.3072	002	4.7453	4.8234

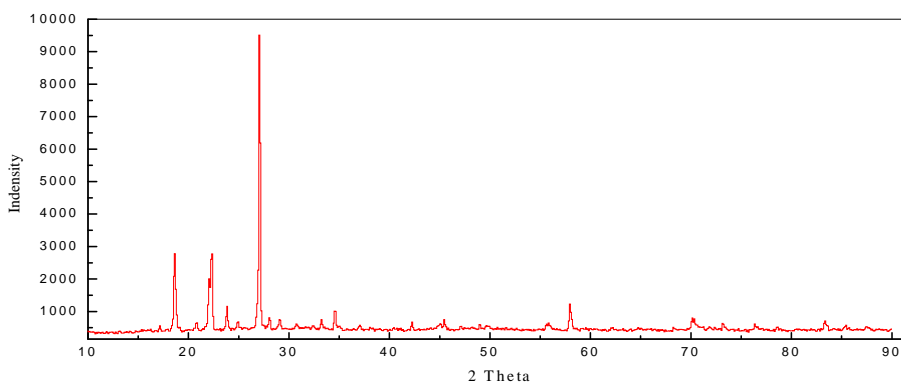


Fig.2-XRD pattern of CuTU

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3.2. FOURIER TRANSFORMS INFRARED SPECTROSCOPY

The FTIR spectra of urea thiourea coppergrown crystals are shown in figure3. In the higher wavelength region, the peak at 3480 cm^{-1} is assigned to C-H, N-H stretching vibration. The region 34750 cm^{-1} and 3110 cm^{-1} with strong intensity represents N-H stretching mode. The broad envelope positioned in between 3460 cm^{-1} and 2681 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH_2 group. The peak at $2935 - 2910\text{ cm}^{-1}$ with medium intensity refers C-Asymmetric stretching. Combinational overtones extend to the bands from $2410 - 2320\text{ cm}^{-1}$. The peak at 1730 cm^{-1} indicating the C=O stretching mode of vibration. The NH_2 bending vibrations occur at $1610, 1603$ and 800 cm^{-1} . The peak at 1540 cm^{-1} is due to NH_2 bending vibration. The peaks at $1470-1420\text{ cm}^{-1}$ corresponds to the C=S stretching. The C-C stretching mode of vibration occurs in 1290 cm^{-1} peak. The peak at 1200 cm^{-1} gives rise to C-N stretching mode of vibration. The spectra show absorption bands in the region of 1140 cm^{-1} and 1038 cm^{-1} which are due to in-plane C-H bending vibration. The band 1100 cm^{-1} signifies the N-H symmetric bending. The bands at 830 cm^{-1} and 800 cm^{-1} revealed that C-N deformation mode. The ring deformation occurs at the peak 810 cm^{-1} . C=O deformation is identified by the band at 670 cm^{-1} . C-H out-of plane bending peaks obtained at 660 cm^{-1} and 648 cm^{-1} . The bands $631-628\text{ cm}^{-1}$ represents C-C deformation. The absorption bands in the region of $480-461\text{ cm}^{-1}$ are due to N-C stretching vibration. The assignments confirm the presence of various functional groups present in the material. The absorption around 1600 cm^{-1} is NH_2 bending and this band would be shifted into lower wavelength region 1618 cm^{-1} . Our investigations were well compared with earlier reports [10-21].

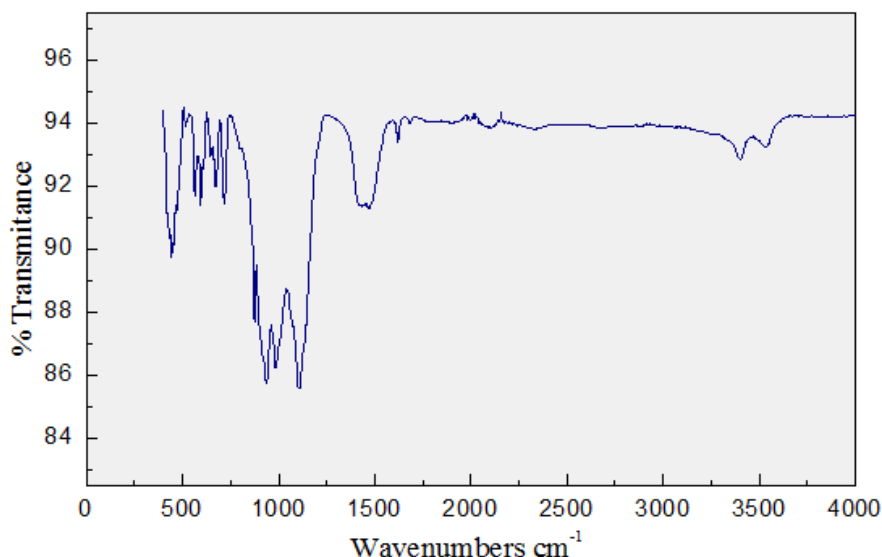


Fig.3-FT-IR Spectrum of CuTU

Table. 1-IR Spectrum data's

Crystal	Wavenumber (cm^{-1})	Band Assignment
CeNTU single Crystal		

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3.3 UV- VISIBLE STUDIES

The UV-Visible spectrum of the single crystal CuTU indicates low absorption in the entire visible and near infrared region of the crystals. This is a desirable property for NLO applications since a wider optical transparency in these regions enhances the frequency conversion efficiency in the corresponding wavelengths.

The lower cut off wavelengths of CuTU single crystal were found to be 315, 357 nm and 376 nm respectively. The good optical transmittance in the entire visible region and the lower cut off wavelength (λ_{cut}) was observed as this is due to $\pi-\pi^*$ transition in the compounds. The band gap energy ($E_g = hc/\lambda$) was found to be 5.63 eV for pure and copper urea thiourea crystals. The large transmission in the entire visible region and short cut off wavelength enables it to be a potential material for second and third harmonic generation.

Crystal	Wavelength (nm)	% Transmittance
CuTU	315	90.2
	357	114.5
	376	187.9

3.4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

NMR spectrum of CuTU was recorded using FT-NMR spectrometer. CuTU crystal was powdered and dissolved in deuterated dimethyl sulfoxide (DMSO). FT-NMR spectrum recorded for CuTU is shown in Figure 4. A chemical shift at 8.198- 8.219 ppm is due to O=C-NH proton. The chemical shift at 7.065 - 7.085 ppm is assigned to =C-NH-C proton. Chemical shift at 6.734 - 6.754 ppm is due to =C-, H-N-C=O. A chemical shift at 5.593 ppm is due to =C-H proton [12]. A chemical shift at 3.88 is due to -C=S. The above values confirm the structure of CuTU.

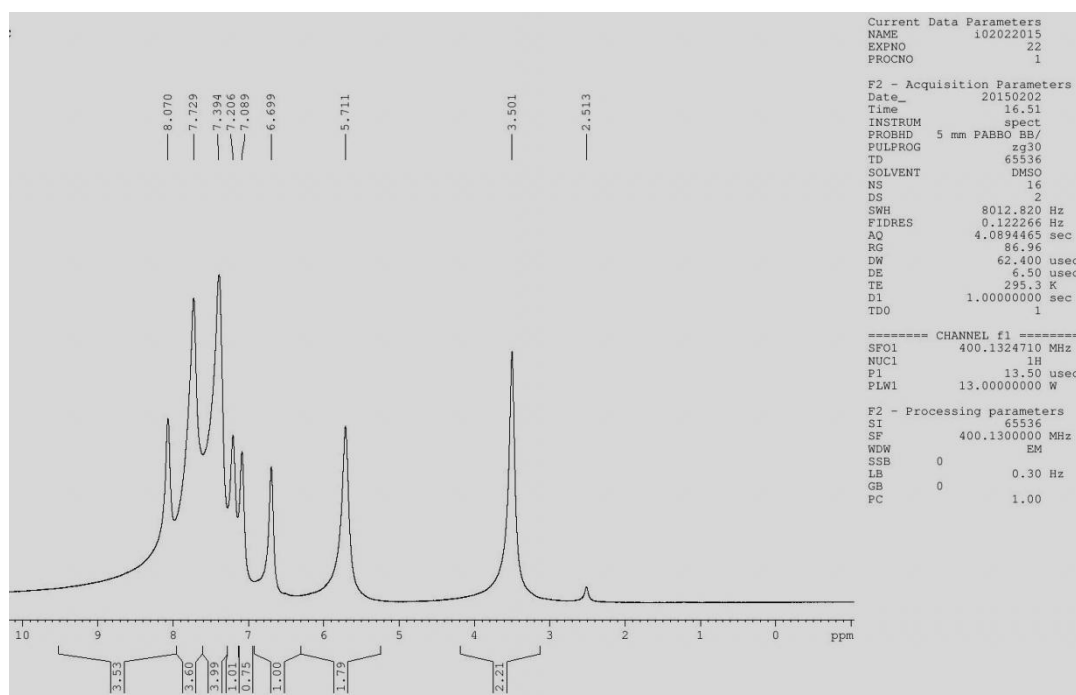


Fig.4-NMR Spectrum of CuTU

3.5 THERMAL ANALYSIS

TGA analysis of the CuTU crystal was carried out in the temperature range 10- 900°C. The recorded thermogram is shown in figure 5. From TGA curve it is observed that the weight loss start from 300°C. There is 8.5 %

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weight loss between 320°C to 350°C. This weight loss is due to the liberation of NH₃. There is 15.4 % weight loss between 555°C and 695°C. This weight loss is due to the liberation of CO. There is 22.2 % weight loss at 830°C. This weight loss is due to the liberation of H₂S. This endothermic event is in good agreement with the TGA trace [21].

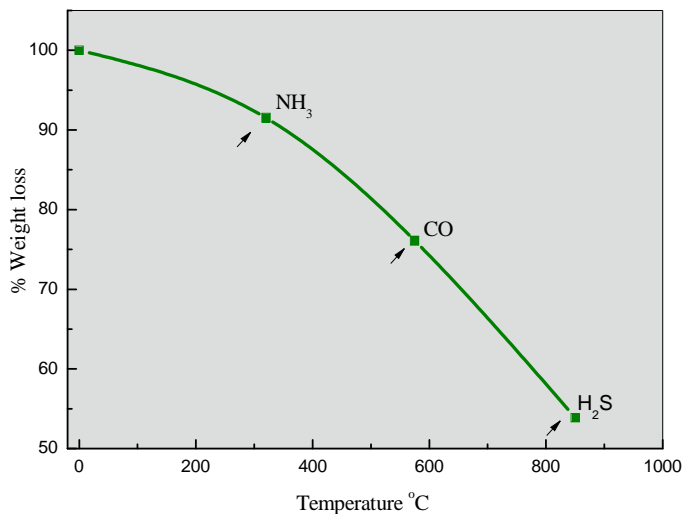


Fig. 5. Thermogravimetric analysis for the determining the weight loss

3.6 MICRO HARDNESS STUDIES

Hardness of the material is a measure of resistance that offers to deformation. The transparent polished crystal free from cracks was selected for hardness measurements. The indentations were made on the flat surface with the load ranging from 10 to 100 g using Shimadzu make-model-HMV-2 fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vicker's hardness (Hv) was calculated from the relation [21],

$$Hv = \frac{1.8544P}{d^2} P/d^2 \text{ kg/mm}^2$$

Where, P is the applied load and d the average length of the diagonal of the indentation mark. With P in g and d in μm, the units of Hv turned out to be kg/mm². The variation of micro hardness with applied load for the prominent (102) plane of the CuTU crystal is shown in Fig. 6. It is found that the hardness values increases with the increase of the applied load. This behaviour of increasing micro hardness with the load known as reverse indentation size effect (RISE) [21], which is also attributed due to existence of distorted zone near crystal medium interface, effect of vibrations, specimen chipping etc., and the plastic deformation is dominant. At low loads or strains, plastic deformation of crystals mainly involves the nucleation of dislocations along a particular slip system. The RISE effect can be qualitatively explained on the basis of the depth of penetration of the indenter [21]. At small loads, the indenter penetrates only the surface layers and therefore, the effect is shown sharply at the early stages. When the applied load increases, the penetration depth also increases and the overall effect must be due to the surface and inner layers. When only one slip system is active during plastic deformation at low loads, the number of active parallel glide planes during indentation is low. Therefore the nucleating dislocations rapidly propagate into the material without experiencing substantial mutual interaction stress between them. Consequently in this stage, indentation depth increases proportionally with applied pressure.

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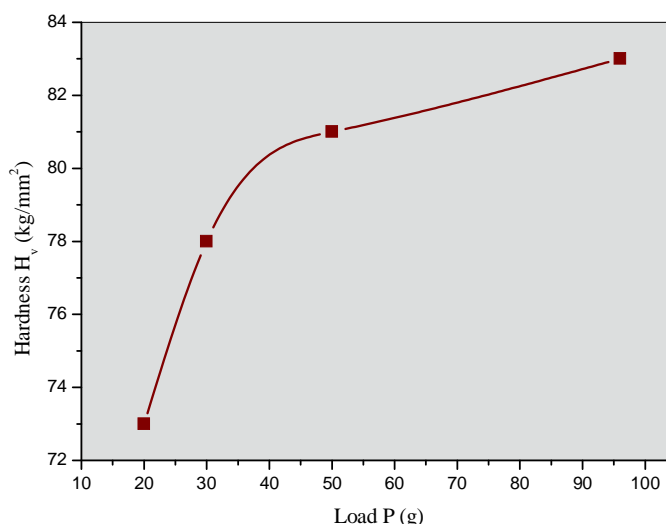


Fig. 7 : Variation of hardness number with load

3.7 NLO STUDIES

The second harmonic signal, generated in the crystals was confirmed from the emission of blue radiation by the crystals. The NLO SHG values of the CuTU single crystals were determined and compared to the reported SHG value of pure KDP[21].

Crystal	Second harmonic signal output (mJ)	SHG efficiency (compared to SHG efficiency of pure KDP)
CuTU	1.20	0.52

IV. CONCLUSIONS

The good quality single crystals of urea thiourea copper were successfully grown by slow evaporation method at room temperature. The UV-Vis spectra showed that the crystals had a wide optical window, no absorbance and good optical transmittance in the entire visible region. FT-IR analysis confirmed the presence of functional groups in the grown crystals. TGA thermogram revealed the thermal stability of the materials. The powder X-Ray diffraction study confirms the lattice parameter values. The good optical quality and their suitability for NLO applications. Kurtz-Perry powder SHG test was employed to determine the SHG efficiency of the samples and the values were compared to the reported SHG efficiency of pure KDP.

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