



Synthesis, Growth and Characterization of new Semi Organic Single Crystal: Urea Copper Sulphate (UCS)

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ABSTRACT

Good quality of semi organic single crystals of a urea copper sulphate (UCS) was grown from solution by slow evaporation technique at room temperature. Good optical quality single crystals with dimensions $15 \times 11 \times 3 \text{ mm}^3$ were obtained. The grown crystal had been confirmed by single X-Ray Diffraction Method. UV -Vis absorption, studies reveals that the grown crystal was optically transparent through the visible range. The vibrational frequencies of various functional groups in the crystals had been derived from Fourier transform infrared spectrum. Dielectric studies have been made. Dielectric studies give information about the charge transport mechanism of a material. The optical absorption studies indicate that for the sample, optical transparency window is quite wide, making it suitable for NLO applications.

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Introduction

Urea crystal is the first organic crystal successfully used in an optical parametric oscillator [1]. It has large non linear optical coefficients, high birefringence, high laser damage threshold and non linear optical applications in UV because of its transparency range extending to 200nm in the short wavelength limit [2] and it also serve as a better crystal compared to KDP for its nonlinear optical coefficient [3].

The urea molecule is planar in crystal structure and the oxygen atom of urea has more electro negativity compared to the nitrogen atom due to the lone pair of N atom with π - electron on carbonyl results, causing a decrease in the electron density around the N atoms. Due to the charge transfer among the C,H and N molecules, the H^+ ions become weaker and O^- become stronger. Complex formation with Urea is possible in two ways. One through the N molecule, and the other through the O atom, which leads to ionic and adduct complexes respectively [4]

The structure and spectroscopic properties of metal-urea complexes have been reviewed. The metal-urea complexes are interesting group of compounds with which to investigate the metal-oxygen and metal-nitrogen chemical bonds and the effect of metal interaction on the structure and properties of Urea-Metal-Amide complexes are of great significant to the pharmaceutical and medical sciences, for instance antimicrobial and antiviral properties, and could be effective against diseases [5,6].

2. Experimental Procedure

2.1. Synthesis and Crystal Growth

UCS was synthesized using AR grade copper (II) sulfate pentahydrate and urea in a stoichiometric ratio of 1:1. The reactants were dissolved in deionised water, thoroughly mixed using a magnetic stirrer for 3 hours. The solution was tightly covered with a perforated polythene sheet and kept at a

constant temperature. The crystallization took place in a period of 10 – 15 days. After continuous recrystallisation and filtration, optically good quality single crystal have been harvested. Photograph of the as grown UCS crystal is shown in Fig.1.

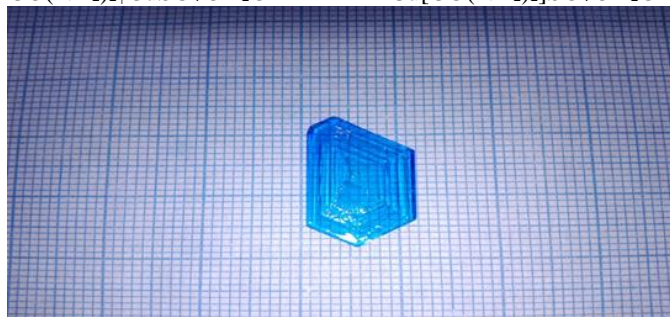
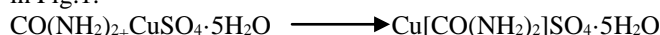


Figure 1. Photograph of grown UCS

3. Results and Discussion

3.1 Single Crystal X-Ray Diffraction Analysis

The grown crystals were subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 X ray diffractometer to determine the cell parameters and it reveals that the UCS crystal crystallizes in Triclinic system having lattice parameters were found to be $a = 5.97 \text{ \AA}$, $b = 6.12 \text{ \AA}$, $c = 10.75 \text{ \AA}$, and $\alpha = 77.43^\circ$ $\beta = 82.37^\circ$ $\gamma = 72.66^\circ$, $V = 365 \text{ \AA}^3$. [7]

3.2 FTIR Analysis

The FTIR spectrum of the grown crystals was recorded in the range $400 - 4000 \text{ cm}^{-1}$ using IFS BRUKKER 66V spectrophotometer and the resultant spectrum is shown in the figure 2. The C=O stretching vibration is found to be around 1609.67 cm^{-1} . The peak at 1419.67 cm^{-1} represents the asymmetric vibrations of N-C-N respectively. The band due to the NH_2 symmetric vibration is at 3372.68 cm^{-1} . The band at 1787.12 cm^{-1} in the spectrum is assigned to NH_2 bending

Vibration. The NH_2 rocking appears at 863.18 cm^{-1} is due to out of plane bending vibrations [8, 9]. The band at 3119 cm^{-1} assigned to stretching vibration of O-H group [10]. The stretching vibration mode of S-O group found at 1103.33 cm^{-1} . The bending vibration of S-O group were identified at 615.32 cm^{-1} [11]. The vibration mode of metal ion Cu^{2+} may be observed at Cu-O-H vibration is assigned to 863.18 cm^{-1} .

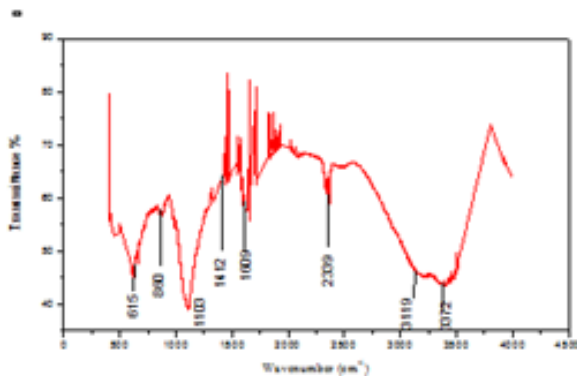


Figure 2. FTIR spectrum

3.3. Optical absorption of UCS

The optical absorption spectral analysis of the grown crystal was carried out between 190-900 nm using VARIAN CARY SE Spectrometer and is shown in Fig 3. There is very low absorbance in the entire visible region and shows maximum absorption at UV region. This is one of the most desirable properties of the crystals for the device fabrication. The UV cut-off wavelength of the crystal was found to be at 220 nm.

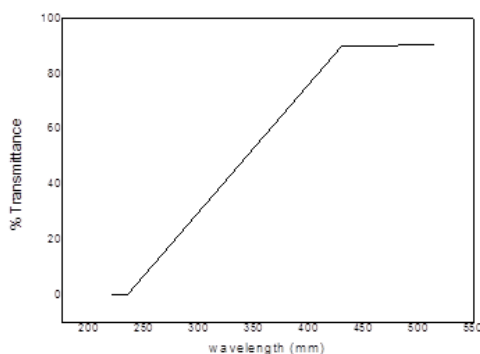


Figure 3. UV transmission spectrum

3.4. Micro hardness studies

Micro hardness is one of the important parameters, studied before any crystal is considered as suitable for device application. The hardness of a material is a measure of its resistance to plastic deformation [12]. The micro hardness measurement of UCS was recorded at room temperature, using the Economet (Model VH1MD) hardness tester, with Vickers's Pyramidal diamond indenter. The UCS crystal was held firmly by forming a mould. A diamond indenter was pressed into the selected surface of the grown UCS crystal for the applied load from 10 to 100 g and a dwell time of 10 s. The Vickers's micro hardness was estimated using the relation, $H_v = 1.8544 P/d^2 \text{ (kg/mm}^2\text{)}$

Where, H_v is the Vicker's hardness number, P is the indentation load in kg and d is the diagonal length of the impressions in mm. A graph has been plotted between the hardness number (H_v) and applied load (P) for the corresponding planes, as shown in Fig.4. It is evident from the graph that the microhardness of the crystal increases with the

increase in applied load due to weak bonding forces among the molecules of UCS crystals. For all the planes, the same trend was observed. The increase in the microhardness with increasing load is in agreement with the reverse indentation size effect. The values of UCS crystal calculated and are found to be below 1.6. These values indicate that UCS belongs to the hard material category [13]. Fig 5 shows log P vs log D .

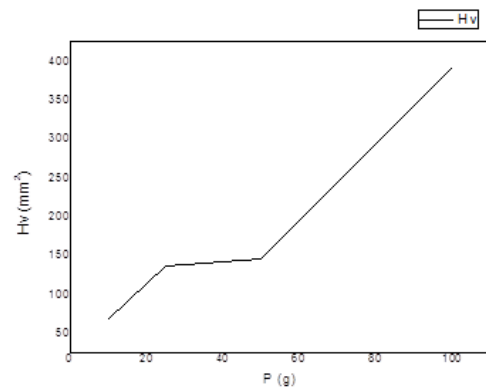


Figure 4. Load Vs Hv

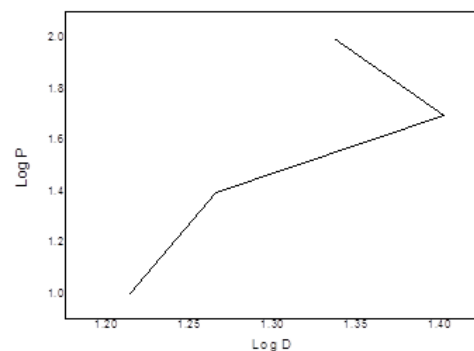


Figure 5. Log P Vs Log D

3.5. Dielectric studies

Dielectric studies give information about the charge transport mechanism of a material. To turn a crystal into capacitor medium electronic grade silver paste was coated on the opposite faces of the crystal for being used for taking measurements. The dielectric constant was calculated using the given formula

$$\epsilon_r = (Cd) / (\epsilon_0 A) \quad (1)$$

Where C is the capacitance, d is the thickness of the sample, A is the cross sectional area of the sample and ϵ_0 is the free space permittivity of the sample. Fig. 6 shows the variation of the dielectric constant vs frequency for the grown crystal. From the figure it is observed that the dielectric constant decreases with increase in frequency and attains the constant value at higher frequency. The dielectric constant is very high at a lower frequency. This may be due to the presence of all the four polarizations namely electronic, ionic, orientation and space charge polarizations [14]. Low value of the dielectric constant at high frequency may be attributed to the space charge polarization [15]. The dielectric loss was taken for the grown crystals with respect to frequency. Fig. 7 shows the variation of dielectric loss vs frequency for the grown crystal. The low value of dielectric loss at high frequency suggests that the crystal contains low level defects with enhanced optical quality and this is an important parameter for electro-optical device applications.

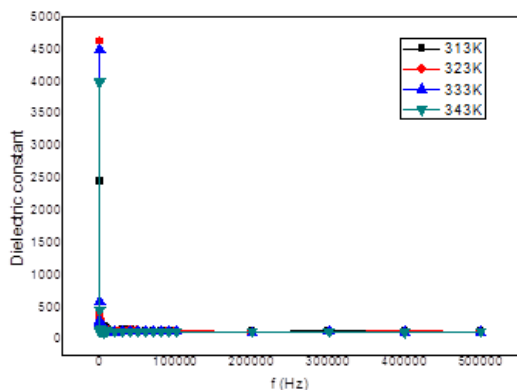


Figure 6. Frequency Vs Dielectric Constant

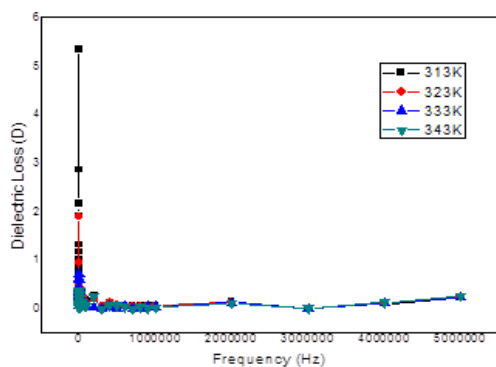


Figure 7. Frequency Vs Dielectric Loss

3.6. SHG Measurements

The Kurtz and Perry technique was used to find the nonlinear property of the crystal. Microcrystalline KDP material was used as a reference material with UCS for SHG measurements. A high intensity Nd:YAG laser beam with input pulse of 6.2mJ as an optical source was allowed into the powder samples. The second harmonics signal (532nm) 56mV and 126.3mV were obtained through KDP and UCS samples. Thus the SHG efficiency of the UCS crystal is 2.3 times higher than KDP crystal. This result confirms the non-centrosymmetric structure and NLO behaviour of the as-grown UCS crystal.

4. Conclusion

Single crystals of the semi-organic NLO UCS material, were grown from deionized water by slow evaporation technique. The unit cell parameters and morphology of UCS were evaluated by single crystal XRD. The functional groups of UCS compound were analysed using FTIR spectrum. The good optical absorption shown by UV-Vis-NIR proves the crystal suitable for optoelectronic applications. The powder

SHG efficiency of UCS is 2.3 times greater than KDP. The microhardness studies confirm the UCS crystal as a hard material. Dielectric studies were also taken and it proves the UCS crystal having low level defects with enhanced optical quality and this is an important parameter for electro-optical device applications.

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