

Synthesis and characterization of some single crystals of thiourea urea zinc chloride

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Abstract Thiourea Urea Zinc (II) Chloride (TUZC), a new semiorganic non-linear optical material has been synthesized. The solubility studies have been carried out at room temperature. Single crystals of different proportions of TUZC have been grown by slow evaporation of saturated aqueous solution at room temperature. The FTIR and UV spectral bands have been compared with urea, thiourea and *bis* Thiourea Zinc Chloride (BTZC). The TG curve showed a two steps mass loss on heating the compound between 30 and 800 °C corresponding to two exothermic DTA peaks at 181–183 and 250–252 °C.

Keywords TUZC · Solubility · UV · FTIR · Non-linear optical material · TG · DTA

Introduction

Urea crystals have attracted the attention of both theoretical and experimental scientists due to their non-linear optical piezoelectric properties. Urea is representative of one class of materials, which are applicable to photonics and reference material in the diffusive mixing of organic solution (DMOS) experiment in microgravity carried out by NASA. They are potentially very useful materials for frequency doubling of near IR laser radiation single crystals of the material have very high laser damage threshold. Non-linear optics is playing a major role in emerging photonic and optoelectronic technologies. New non-linear optical frequency conversion materials have a significant impact on laser technology and optical data storage. Non-linear optical (NLO) materials showing second harmonic generation (SHG) have been in demand over the last several decades due to the technological importance in the fields of optical communication, signal processing and instrumentation [1–3]. The non-linearity [4] of urea is comparable with that of another important commercial NLO material potassium dihydrogen phosphate (KDP). The materials explored for NLO application were mostly inorganic until the last decade. However, the fact is that inorganic materials have lower probability for centric structures and consequently researchers focused their attention on organic materials. Thiourea is an interesting inorganic matrix modifier because of its large dipole moment [5] and its ability to form an extensive network of hydrogen bonds. It belongs to the orthorhombic crystal system. However, most of the thiourea complexes crystallize in centro symmetric form at room temperature and do not show SHG.

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Only a few of thiourea complexes viz, zinc thiourea sulphate [1, 6, 7], ATCC, cadmium thiourea acetate [8], *bis* thiourea cadmium chloride [9], thiourea doped glycine phosphite [10], thiourea doped TGS [11], dichloro tetrakis thiourea nickel [12], *bis* thiourea zinc acetate [13], *bis* (thiourea) cadmium formate [14], potassium thiourea chloride [15] and potassium thiourea bromide [16] crystallize in non-centro symmetric structure and show SHG. The research for new and efficient NLO materials has resulted in the development of a new type of materials called semiorganic crystals. TG-DTA, microscopic, optical and spectral studies are very important methods for materials characterization. Therefore, many authors have used these methods for investigation of various materials [17–30]. These facts have prompted us to undertake a systematic investigation of various thiourea urea zinc (II) chloride single crystals, synthesized and grown by slow evaporation technique at room temperature and also characterized them by thermal, optical and spectral studies as well as determining their solubility.

Experimental

Single crystals of various proportions of thiourea urea zinc (II) chloride (hereafter abbreviated as TUZC) were prepared at room temperature by slow evaporation of aqueous solution containing 1:1:1, 2:1:1, 3:1:1 and 4:1:1 of thiourea, urea and zinc chloride (Merck, Mumbai). Care was taken to minimize mechanical and thermal variations. Colourless, bright and transparent crystals were obtained.

Thermogravimetric and differential thermal analyses of various proportions of TUZC were carried out on a NET-ZSCH STA 409C thermal analyzer in nitrogen atmosphere. The samples were heated between 30 and 800 °C at a heating rate of 10 K/min.

UV spectral analyses were carried out on a double beam spectrometer in the range of 200–400 nm.

A Bruker IFS 66 V spectrometer was used to record the FTIR spectra of the compound, employing KBr pellet technique in the frequency range 400–4,000 cm^{-1} .

To determine the solubility, the saturated solutions of the salts were prepared individually. Then the empty mass of silica crucible was weighed. 5 mL of saturated solution was taken in a crucible and it was also weighed to determine the solubility in 100 mL of water.

Results and discussion

Solubility

The literature survey indicates that the organic urea, thiourea salts as non-linear optic. The salts used for the

experiments were Analar Merck grade. The salts were re-crystallized using double distilled water. The obtained fine powder crystals were air dried at room temperature. Preliminary experiments were performed in different growth conditions to optimize the most acceptable to our growth parameters including the starting temperature of crystallization, purity, orientation of the seed crystal and concentration of the encouraging agent.

First of all the solubility of the salts were determined and presented in Fig. 1.

From this solubility of urea in 100 mL of water was found as 108.09 and that of thiourea was 29 g. Similarly, the solubility of 0.5, 0.66, 0.75 and 0.9 TUZC was 85, 38.5, 33.3 and 26.4 g, respectively (Fig. 1). It was observed that the solubility decreases with increase in proportion of thiourea.

Morphological studies

The organic substance urea is found to have tetragonal structure, when the crystal appeared in needle shaped. Thiourea is crystallized and has orthorhombic structure. As urea and thiourea having similar structure corresponding to the formula $(\text{NH}_2)_2 \text{C}=\text{O}$ and $(\text{NH}_2)_2 \text{C}=\text{S}$. Since the presence of sulphur atom in thiourea has orthorhombic structure, the morphological studies of various proportions of TUZC crystals were carried out. The morphology of the various proportions of TUZC single crystals is given by means of photographs (Fig. 2). The above different morphology suggest that the symmetry planes of both urea and thiourea are affected each other and this may bring about considerably non-linear properties wide range. Therefore, the series of single crystals may be used as laser crystals.

UV spectral studies

The UV spectra of urea, thiourea and 0.5, 0.66, 0.75 and 0.9 TUZC were taken on a double beam spectrophotometer in the range of 200–400 nm and shown in Fig. 3. The observed absorption bands have been given in Table 1. Here, the absorption band of 0.5, 0.66, 0.75, 0.9 TUZC were compared

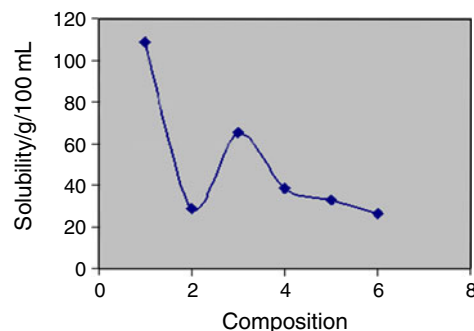


Fig. 1 Solubilities of urea, thiourea, various proportions of TUZC

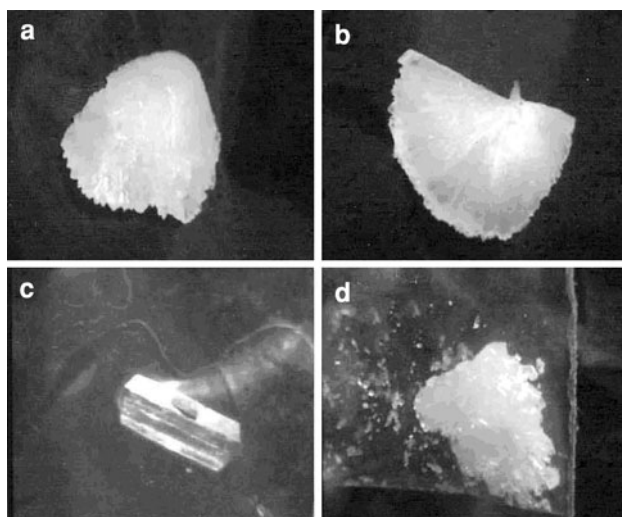


Fig. 2 Morphology of **a** 0.5 TUZC, **b** 0.66 TUZC, **c** 0.75 TUZC, **d** 0.9 TUZC

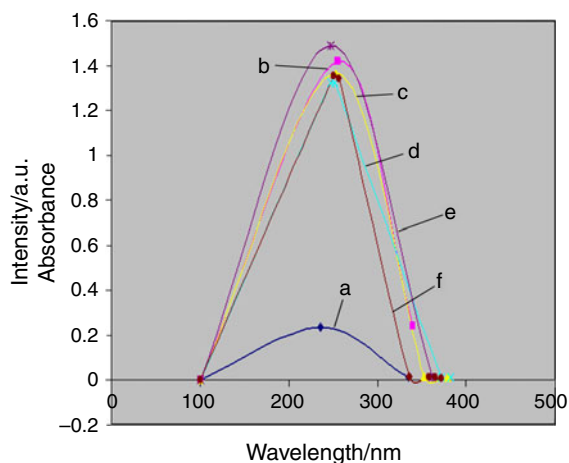


Fig. 3 UV Spectra of **a** urea, **b** thiourea, **c** 0.5 TUZC, **d** 0.66 TUZC, **e** 0.75 TUZC and **f** 0.9TUZC

to urea and thiourea. The absorption band ($\pi-\pi^*$ and $n-\pi^*$ transition) were shifted to longer wavelength compared to urea and slightly lower than thiourea. This is because the π^* orbital are stabilized by hydrogen bonding between urea and thiourea. This may be due to the greater polarity of π^* orbital compared to π orbital. Thus, smaller energy required for such transition and absorption shows a red shift.

FTIR spectral studies

The FTIR Spectra of the various proportions of TUZC crystal were recorded on a Burkert IFS 66 V FTIR Spectrometer using KBr pellet technique in the range of 400–4000 cm^{-1} as shown in Figs. 4, 5, 6 and 7. The observed assignments have been summarized in Table 2. Here, the characteristic vibrations of TUZC in IR region

Table 1 Comparison of absorption of urea, thiourea with TUZC

Crystals	Absorbance	Wavelength/nm
Urea	0.013	335
	0.236	236
Thiourea	1.416	255
	0.010	379
0.5 TUZC	0.017	352
	1.362	253
	0.011	382.5
	0.014	371.5
0.66 TUZC	1.324	251.5
	1.324	247.5
	1.490	247
0.75 TUZC	0.008	371.5
	0.010	364.5
	0.010	358.5
	0.013	336
	1.343	256.5
	1.353	251

have been compared with those of urea, thiourea and bis thiourea zinc chloride [31]. The high frequency γ_s (NH_2), γ_{as} (NH_2) absorption bands in the region 3100–3400 cm^{-1} in the spectra of thiourea were shifted to higher frequencies. This confirms the formation of metal thiourea complex indicating that nitrogen to zinc bonds is not present and the bonding must be between sulphur and zinc atoms. It can be seen from the Table 2 that the symmetric, asymmetric stretching of γ_s C=S, γ_{as} C=S vibrations at 740 and 1417 cm^{-1} of thiourea 1406 and 715 cm^{-1} of BTZC were shifted to lower frequencies 714.77, 714.69, 714.60, 714.22 cm^{-1} and 1406, 1405.13, 1409.67 cm^{-1} (except 0.66 TUZC) in 0.5, 0.75 and 0.9 TUZC, respectively. Similarly, the γ_s (C–N) stretching vibration at 1089 cm^{-1} in thiourea was shifted to higher frequencies 1103.31, 1100.83, 1101.83 and 1100.72 cm^{-1} in 0.5, 0.66, 0.75 and 0.9 TUZC. It is understood that the binding of zinc with thiourea is through sulphur. The formation of S–Zn bond was expected to increase the contribution to the highly polar character of thiourea molecule, resulting in a stronger double bond character for the nitrogen to carbon bond and a stronger single bond for the carbon to sulphur. The bands were observed at 1495.88, 1494.40, 1495.71 and 1495.39 cm^{-1} in 0.5, 0.66, 0.75 and 0.9 TUZC and it corresponds to 1471, 1496 cm^{-1} band of thiourea, BTZC assigned the γ_s N–C–N stretching vibration. This increase in frequency (compared to thiourea) may be attributed to a stronger double bond character of the carbon to nitrogen on complex formation. Similar observations have been reported in Tris Thiourea Zinc Sulphate (ZTS). The bands (γ_s C=O) were observed at 1818.04, 1818.30 and

Fig. 4 FTIR Spectrum of 0.5 TUZC

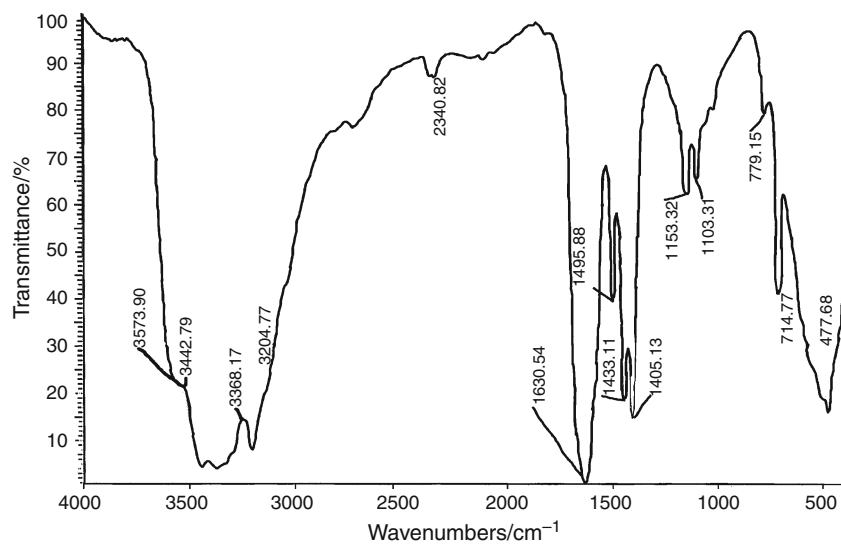


Fig. 5 FTIR Spectrum of 0.66 TUZC

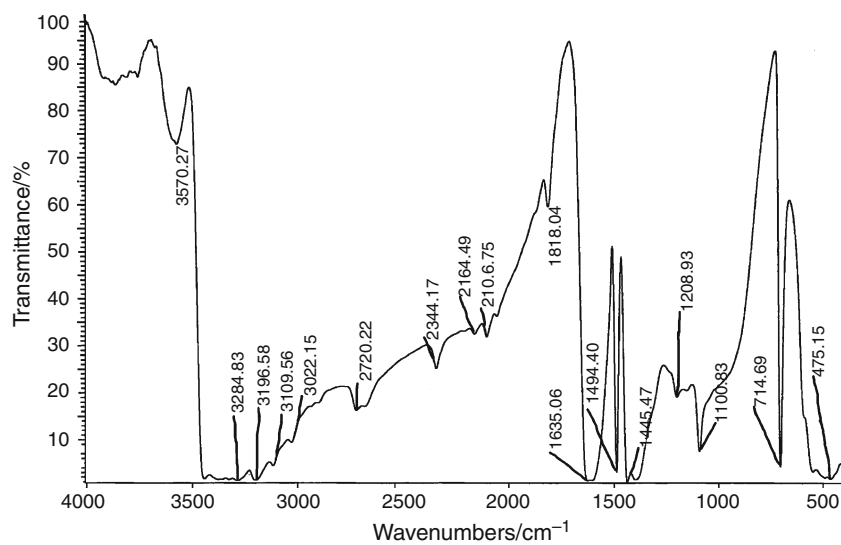


Fig. 6 FTIR Spectrum of 0.75 TUZC

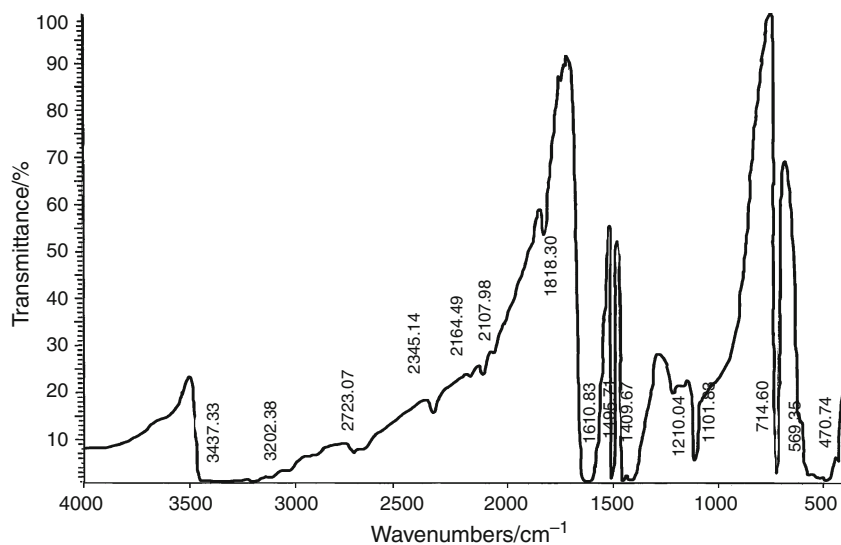
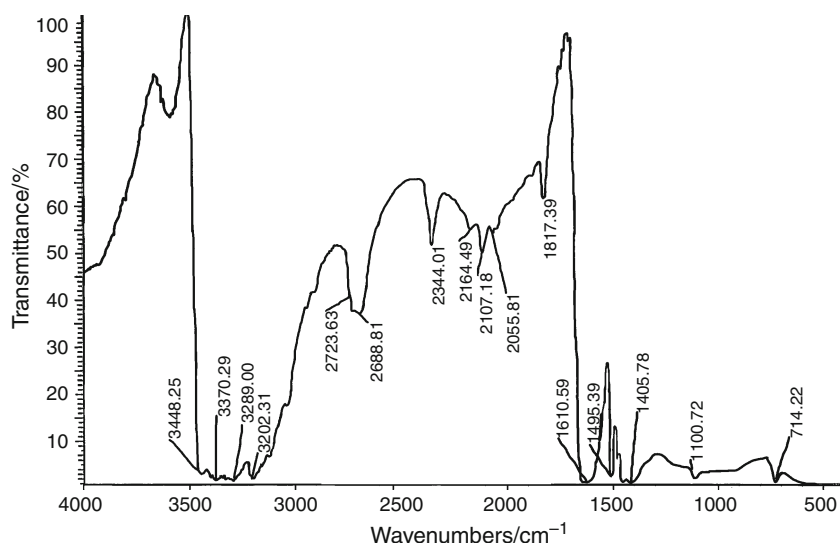


Fig. 7 FTIR Spectrum of 0.9 TUZC**Table 2** Comparison of absorption IR bands of TUZC with urea, thiourea and BTZC

Wave number/cm ⁻¹							
Urea	Thiourea	BTZC	0.5 TUZC	0.66 TUZC	0.75TUZ	C0.9TUZC	Assignment
–	411	424	–	–	–	–	δ_s (S–C–N)
–	469	474	477.68	475.15	470.74	–	δ_s (S–C–N)
508	494	511	–	–	–	–	δ_{as} (N–C–N)
–	–	–	–	–	569.75	–	δ_s (C=O)
–	740	715	714.77	714.69	714.60	714.22	γ_s (C=S)
790	–	–	–	779.15	–	–	δ_s (C=O)
1008	–	–	–	–	–	–	γ_s (C–N)
–	1089	1101	1103.11	1100.83	1101.83	1100.72	γ_s (C–N)
–	1417	1406	1405.13	–	1409.67	1405.72	γ_{as} (C=S)
1454	–	1442	1443.11	1445.57	–	–	γ_{as} (C–N)
–	1471	1496	1495.88	1494.40	1495.71	1495.39	γ_s (N–C–N)
1631	1627	1630	1630.54	1635.06	1610.83	1610.59	δ_{as} (NH ₂)
–	–	–	–	1818.04	1818.30	1817.39	γ_s (C=O)
–	–	–	–	2106.75	2107.98	2107.18	γ_s (N=C=O)
–	–	–	2340.82	2344.17	2345.14	2344.01	γ_{as} (N=C=O)
–	–	–	–	2720.22	2723.67	2732.63	γ_s (SH)
–	3167	3202	3204.77	3196.58	3202.31	3202.31	γ_s (NH ₂)
–	–	–	–	3284.83	–	3289.10	γ_s (NH ₂)
3320	3280	–	3368.17	–	–	3370.29	γ_{as} (NH ₂)
3422	–	3441	3442.79	–	3437.33	3448.25	γ_{as} (NH ₂)
–	–	–	3573.00	3570.27	–	–	γ_{as} (NH ₂)

1817.39 cm⁻¹ in 0.66, 0.75 and 0.9 TUZC indicated that the presence of urea was in TUZC. Besides the formation of new bands at 2106–2108 cm⁻¹ (γ_s N=C=O), 2340–2344 (γ_{as} N=C=O) and 2720–2723 (γ_s SH) in 0.66, 0.75 and 0.9 were observed and that led to the confirmation of the cyclic structure of urea in this complex.

TG-DTA analyses of various proportions of TUZC

The TG and DTA curves of 0.5, 0.66, 0.75 and 0.9 TUZC are shown in Figs. 8 and 9. The TG curves indicate a two step mass loss on heating the compounds between 30 and 800 °C.

Fig. 8 Curves of **a** 0.5, **b** 0.66, **c** 0.75 and **d** 0.9 TUZC

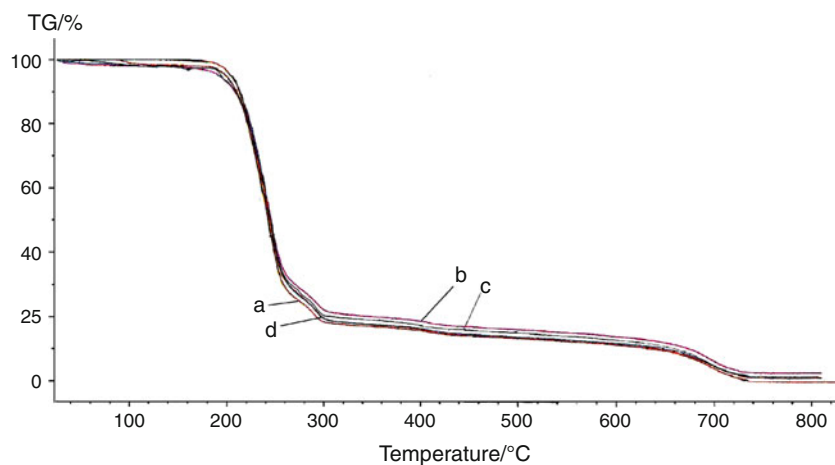
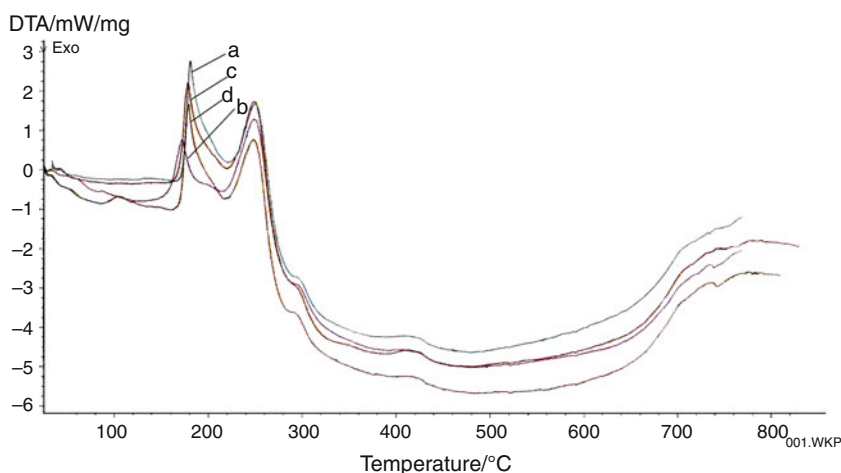


Fig. 9 DTA curves of **a** 0.5, **b** 0.66, **c** 0.75 and **d** 0.9 TUZC



Urea and thiourea are lost at 180–300 °C. This accounts for 80 to 82% mass loss observed in (0.5, 0.66, 0.75 and 0.9 TUZC) on the TG curves. The theoretical mass loss of compounds is in good agreements with experimental mass loss. The remaining portion of TUZC very slowly decomposed up to 740 °C. This accounts for 10.40, 10.41, 10.33 and 10.22% mass loss observed on the TG curves. The thermogravimetric study thus confirms the formation of the title compound in the stoichiometric ratio and the decomposition pattern of TUZC.

The DTA curves presented in Fig. 9 show exothermic peaks at 181, 182, 183 and 183 °C in 0.5, 0.66, 0.75 and 0.9 TUZC, respectively, corresponding to the first stage decomposition. The second broad exothermic peaks at 250, 251, 253 and 253 °C are due to decomposition of thiourea in TUZC. Thus, the DTA curves also confirm the formulated decomposition pattern of the compounds.

Conclusions

- (1) 0.5, 0.66, 0.75 and 0.9 TUZC crystals were synthesized and their solubility was determined at room

temperature. It was observed that the solubility decreases with increase in thiourea proportion.

- (2) Single crystals of various proportions of TUZC have been grown by slow evaporation technique at room temperature.
- (3) The absorption bands ($\pi-\pi^*$ and $n-\pi^*$ transition) shifted to lower wavelength compared to thiourea indicate the presence of hydrogen bond between urea and thiourea.
- (4) The functional groups present in the grown crystal have been confirmed by FTIR spectral studies proved that the binding of thiourea with zinc occurs through sulphur.
- (5) Different morphologies of the different TUZC suggest that the symmetry planes of both urea and thiourea are affected each other and this may bring about considerably non-linear properties wide range.

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