

Thermal, UV and FTIR spectral studies of urea–thiourea zinc chloride single crystal

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Abstract A single crystal of urea–thiourea was grown by slow evaporation of aqueous solution at room temperature. The bright and transparent crystals obtained were characterised by TG–DTA, UV and FTIR spectral analyses. A fitting decomposition pattern for the title compound was formulated on the TG curve which shows a two stage mass loss between 200 and 750 °C. DTA curve shows exothermic peaks supporting the formulated decomposition pattern in this temperature range. The UV and FTIR spectra show the characteristic absorption, vibration frequencies due to urea–thiourea zinc chloride crystals. Detailed structural analysis of the compound is under progress.

Keywords Solution growth · Urea–thiourea zinc chloride single crystal · TG–DTA · UV · FTIR

Introduction

Nonlinear optical (NLO) materials have a significant impact on laser technology, optical communication and optical storage devices. The search for new frequency conversion materials over the past decade has led to the discovery of many organic materials. Organic material

possesses large nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness [1–3]. Urea is representative of one class of materials which are applicable to photonics and served as a model compound and reference material in the DMOS (Diffusive Mixing of Organic Solutions) experiment in microgravity carried out by NASA [4]. Many authors investigated various organic and organometallic compounds due to their very important roles in chemical, biological, electrical and environmental sciences and also examined their various properties [5–30]. Recently, metal complexes of thiourea have been explored. Example of these complexes is zinc thiourea sulphate (ZTS), cadmium thiourea chloride (CTC) and zinc thiourea chloride (ZTC). These crystals have better nonlinear properties than KDP [31–34]. Literature survey shows that urea metanitro benzoic acid, urea hydrogen peroxide compounds have been studied. However, there is no reference in literature regarding the work of urea–thiourea zinc chloride (UTZC) crystal. UTZC is one of the new semi organic nonlinear crystals having good second harmonic generation (SHG) efficiency. This article reports the synthesis, and characterisation of UTZC crystal using UV and FTIR spectral and TG–DTA studies. A detailed structural analysis of the compound is under progress will be published in our next article.

Experimental details

A single crystal of UTZC was prepared at room temperature by slow evaporation of aqueous solution containing equimolar proportion of urea and thiourea (Merck, Mumbai). Care was taken to minimise mechanical and thermal variations. Colourless, bright and transparent crystal

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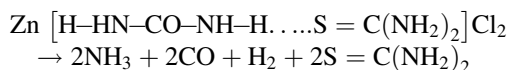
with an average size of $0.9 \times 0.8 \times 0.8$ mm was obtained. The crystal was characterised as follows; the thermogravimetric and differential thermal analyses of UTZC was carried out using a NETZSCH STA 409C thermal analyser in nitrogen atmosphere. The sample was heated between 30 and 800 °C at a heating rate of 10 K/min. UV spectral analysis was carried out by using a double beam spectrometer. A Burkert 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} . A detailed structural analysis of the compound will be published in future.

Results and discussion

Thermal studies

The TG and DTA curves of UTZC are shown in Fig. 1. The TG curve indicates a two step mass loss on heating the compound between 30 and 800 °C. The following decomposition pattern is formulated for UTZC:

Step 1



Step 2



Two molecules of ammonia, carbon monoxide, carbon dioxide and a molecule of hydrogen, thiourea is lost on heating the compound from 180 to 400 °C. This accounts for 44.17% mass loss observed in TG curve. The theoretical mass loss of urea is much closed to experimental mass loss. The remaining portion of UTZC very slowly decomposed to up to 750 °C. High mass loss indicates the presence of urea in UTZC. In UTZC, urea is stable up to 180 °C. Above 180 °C, urea in UTZC decomposes into two molecules of ammonia, carbon dioxide and a molecule of hydrogen. Urea is slowly vaporises at 400 °C. Afterwards, thiourea in UTZC begins to split to hydrogen sulphide, ammonia and nitrogen and carbon residue. This accounts for 30.25% mass loss observed in the TG. This is consistent with the TG curve. The thermogravimetric study thus confirms the formation of the title compound in the stoichiometric ratio and the decomposition pattern of UTZC. The DTA curve depicted in Fig. 1 shows exothermic peaks at 128.8, 237 and 311.6 °C corresponding to the first stage decomposition. The second peak and a broad exothermic peak at 595 °C are due to the decomposition of thiourea in UTZC.

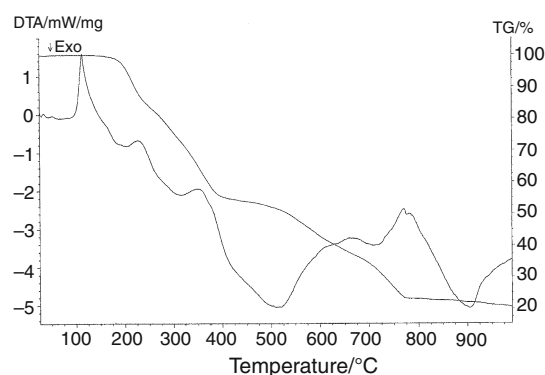


Fig. 1 TG–DTA curves of urea–thiourea zinc chloride

UV spectral analysis

The UV spectra for urea, thiourea and UTZC are shown in Figs. 2, 3, and 4. The observed bands have been given in Table 1. In UTMC, the $\pi-\pi^*$ absorption band shifted to longer wavelength compared to urea. This is because of the formation of hydrogen bond between $>\text{C}=\text{O} \dots \text{N}-\text{H}$ (of urea, thiourea) increase the bond length of $>\text{C}=\text{O}$ and thus

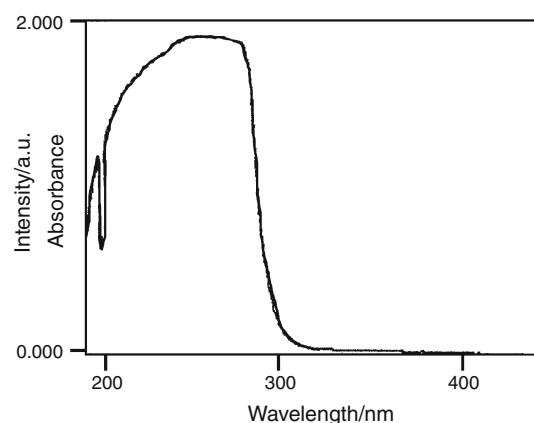


Fig. 2 UV spectrum of urea

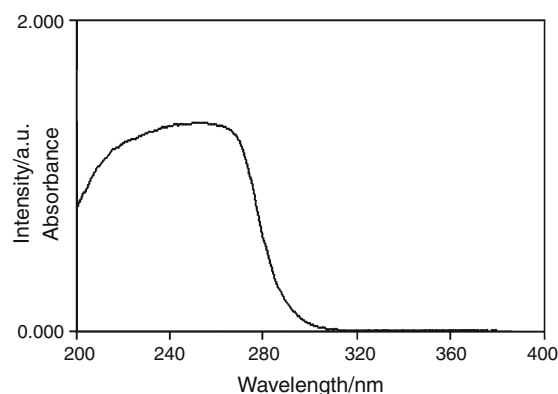


Fig. 3 UV spectrum of thiourea

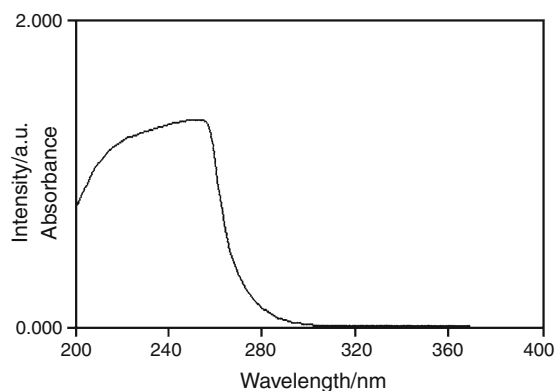


Fig. 4 UV spectrum of urea–thiourea mixed crystal

Table 1 Comparison of absorption band of urea, thiourea with UTMC

Crystals	Absorbance	Wavelength/nm
Urea	0.013	335
	0.456	236
Thiourea	1.416	255
UTZC	0.012	362
	0.013	352
	1.368	245

smaller energy required for this transition and hence the absorption shows the red end of the spectrum. Similarly, $n-\pi^*$ transition also shifted to higher wavelength due to less stable non-bonded electron in UTZC.

FTIR spectral studies

The FTIR spectra for urea, thiourea and UTZC are shown in Figs. 5, 6 and 7. The various absorption bands in FTIR spectra and the corresponding assignments are given below.

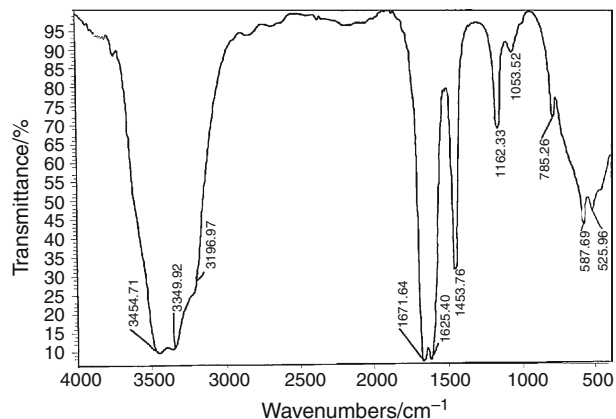


Fig. 5 FTIR spectrum of urea

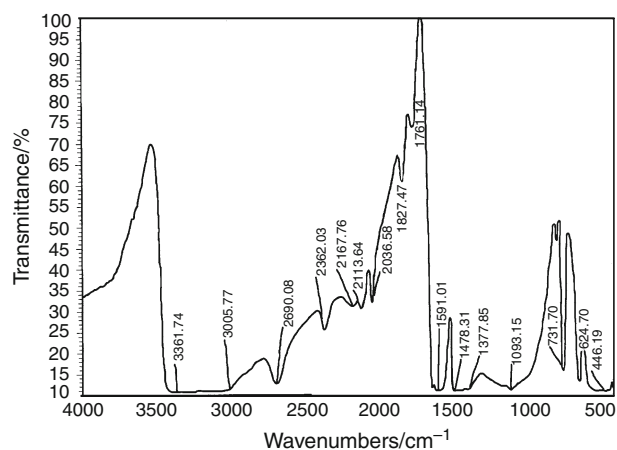


Fig. 6 FTIR spectrum of thiourea

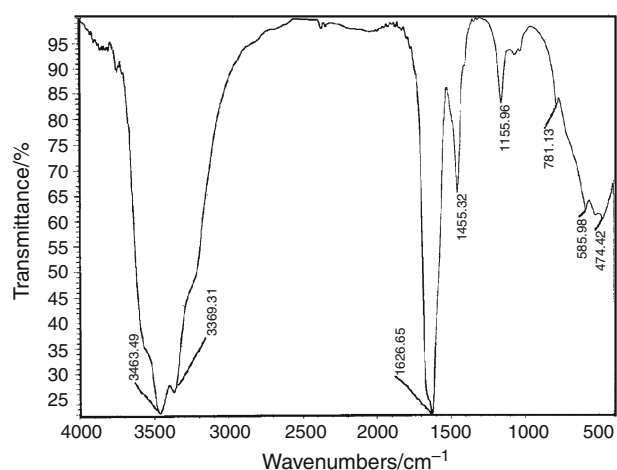


Fig. 7 FTIR spectrum of urea–thiourea zinc chloride

The frequencies at 3369.31 cm^{-1} are due to symmetric stretching N–H vibration of UTMC. $\delta_s\text{C}=\text{S}$ and $\nu_{as}\text{C}=\text{S}$ bending and asymmetric stretching appear at 781.13 and 1455.32 cm^{-1} , respectively. The weak band appearing at 1155.96 cm^{-1} is due to ν_{CN} symmetric stretching vibration. The rocking mode of $\text{N}=\text{C}=\text{N}$ found as a peak at 474.42 cm^{-1} . FTIR spectra show the characteristic vibration frequencies of urea and thiourea. This conforms the formation of UTZC.

X-ray diffraction study

The X-ray diffraction data and XRD pattern of UTZC is given below in Table 2 and Fig. 8. The American chemical Society for Testing and Materials (ASTM) data of urea and thiourea also represented.

From the ASTM values, the different planes absorbed are identifies for all the mixed crystals and they are produced. Urea belongs to tetragonal and $D_{2D}^2\text{-P42}_1\text{M}$ and thiourea belongs to $D_{2H}^{16}\text{-P8MM}_1$ orthorhombic. From the

Table 2 X-ray diffraction data for urea–thiourea zinc chloride

<i>d</i> of urea/Å	<i>hkl</i> of urea	<i>d</i> of thiourea/Å	<i>hkl</i> of thiourea	<i>d</i> of UTZC/Å	<i>hkl</i> of UTZC
4.01	110	4.62	101	–	–
3.62	101	4.48	110	–	–
3.05	111	4.29	002	–	–
2.83	200	3.83	020	–	–
2.53	210	3.51	021	–	–
2.42	201	3.15	120	–	–
2.35	002	3.10	112	–	–
2.23	211	2.95	121	–	–
2.17	102	2.86	022	2.20	102
2.03	112	2.75	200	2.03	112
1.99	220	2.54	103	–	–
1.84	221	2.48	211	1.84	221
1.79	310	2.34	131	–	–
1.75	301	2.32	202	–	–
1.72	212	2.16	221	1.71	212
1.67	311	2.04	Indexed by BP	–	–
1.57	003	1.93		1.56	003
1.52	222			–	–
1.51	103			–	–
1.42	312			1.45	312
1.35	401			–	–
1.33	330			1.32	330
1.26	420			–	–
1.22	421			–	–
1.17	004			1.18,1.15	004
1.07	323			1.07	323

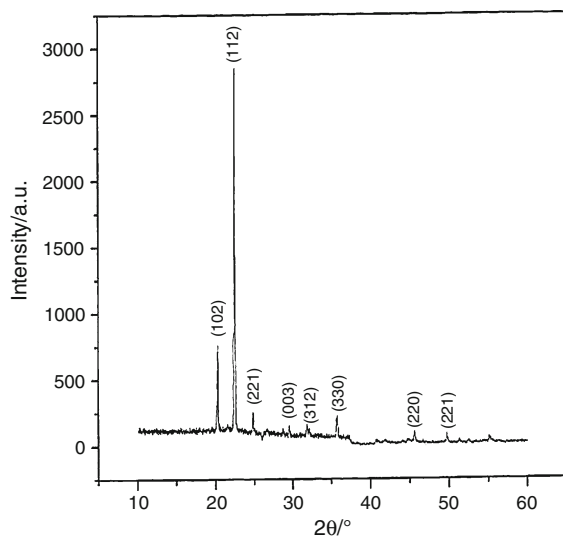
**Fig. 8** X-ray diffraction pattern of urea–thiourea zinc chloride

Table 2, it is understood that the number of planes absorbed decreased and *d* values are also decreased. This may be due to the overlapping of planes of urea crystals and

there-by-there is reorientation in the structure and this brings at different morphology of the crystals itself. This is very much striking phenomena observed and this mixed combinations of mixed crystals will produce a wide range of laser active crystals.

SHG efficiency

The optical absorption of the crystalline sample was recorded using Kurtz powder technique. The nonlinear property in UTZC crystal was confirmed by shining Nd:YAG laser ($\lambda = 1,046$ nm) on thin plate of the grown crystal. It is observed that green light is coming out of the crystal. The crystal was ground into powder and densely packed between two transparent glass slides. An Nd:YAG laser beam of wavelength 1,046 nm was made to fall normally on the sample cell. The transmitted fundamental wave was absorbed by a copper sulphate solution and second harmonic signal was detected by a photo multiplier tube and displayed on a storage oscilloscope. A UTZC crystal, powdered to the identical size was used as reference material in the SHG measurement. Although many

materials have been identified that have higher molecular non-linearities, the attainment of second order effects requires favourable alignment of the molecule within the crystal structure. The efficient SHG demands specific molecular alignment of the crystal to be achieved facilitating non-linearity in the presence of dopant. It has been reported that the SHG can be greatly enhanced by altering the molecular alignment through inclusion complexation.

Conclusions

Single crystal of UTZC was prepared at room temperature by slow evaporation of aqueous solutions. The bright and transparent crystal obtained was characterised. The TG and DTA studies confirm a two stage decomposition of the compound when heated between 180 and 750 °C. The UV spectral analysis confirms the formation of hydrogen bond between urea and thiourea. The FTIR spectra show characteristic vibrational frequencies of urea and thiourea. The detailed structural analysis of the compound under progress will help to understand the mechanism of the title compound.

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