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Growth and Characterization of a New Non-Linear Optical Crystal: Urea Thiourea Zinc Chloride

G. MADHURAMBAL† and M. MARIAPPAN*
Department of Chemistry, R.V.S. College and Technology
Kallikuppam, Thiruvettakudi Post, Karaikal-609 609, India
E-mail: mmari_101@yahoo.com; mmari101@gmail.com

Urea thiourea zinc chloride (UTZC) a new semi-organic non-linear optical material has been synthesized. Single crystals of UTZC have been grown by slow evaporation of saturated aqueous solution at room temperature. The spectral bands have been compared with urea, thiourea, *bis* thiourea zinc chloride (BTZC).

Key Words: Urea thiourea zinc chloride crystals, Non-linear optical material.

INTRODUCTION

Non-linear optics playing a vital role in the emerging photoelectronic technologies. New non-linear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical data storage. The search for new and efficient NLO materials has resulted in the development of a new class of materials called semi-organics. These materials have the potential for combining the high optical non-linearity and chemical flexibility of organic materials with the thermal stability and mechanical robustness of inorganic NLO materials[1]. Thiourea possess a large dipole moment and it forms a number of co-ordination compounds like *bis* thiourea cadmium chloride (BTCC)[2] and *tris* thiourea zinc sulphate (ZTS)[3], antimony thiourea bromide monohydrate (ATBM)[4] which are potential materials for frequency doubling of the near IR laser radiation. Single crystals of these materials have very high laser damage threshold[5]. In general crystals of the type $M[tu]_2X_2$, where M = Cd, Co, Hg, Pb, Ti, Zn; tu = thiourea and X = halogen, have been found to exhibit good NLO properties[6]. Motivated by these considerations urea thiourea zinc chloride (UTZC) crystals was synthesized by slow evaporation technique at room temperature.

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†Department of Chemistry, A.D.M. College for Women, Nagapattinam-611 001, India; E-mail: madhumaniam@yahoo.com

EXPERIMENTAL

Solution 1: 10 g of urea was dissolved in 8 mL of distilled water.

Solution 2: 10 g of thiourea was dissolved in 30 mL of distilled water.

Solution 3 (0.1 UTZC): 1 g of urea, 9 g of thiourea and 5 g of zinc chloride was dissolved in 27 mL of distilled water.

Solution 4 (0.25 UTZC): 2.5 g of urea, 7.5 g of thiourea and 5 g of zinc chloride was dissolved in 25 mL of distilled water.

The crystal growth solutions should be in equilibrium at room temperature (30 ºC) and should not contain any spurious nuclei. The procedure adopted can be explained by taking solution **1**, a saturated solution at a temperature slightly higher than initially required was prepared and filtered through a hot sintered glass flask. The solution was stirred by using magnetic stirrer for about 6 h. The undissolved material collected at the bottom of the same flask and the clean solution was transferred to another flask and heated slightly above 5 °C. The undissolved material would completely dissolve. After dissolving, filtration of the solution which plays a vital role (*i.e.* chemical purity of the solution) during growth is preformed.

When the filtration of the solution was preformed, the size of Buckner funnel is taken and placed over the perforated disc. The rate of filtration through conical flask considerably increased using a perforated filter paper. While transferring the purified solution, temperature of the growth chamber was brought down to 2 ºC above the saturation temperature (32 °C), doing so the seed crystal may dissolve slightly as the solution was under saturated. Since periphery of the crystals dissolve in this case clear and clean, seed will be remaining. The temperature of the solution was adjusted to saturation temperature (30 ºC), the seed dissolution stops. After that the flask was covered with polyethylene sheets, in which small holes were bored to allow slow evaporation. Similar procedure was adopted for solutions **2**, **3** and **4**. The time was recorded until the nucleation starts and appearance of visible nuclei was taken as the induction period. It was observed that for all the single crystals, the induction period decreased from 0.1 to 0.25. The mixed crystals obtained had different morphology. The morphological sizes of the 0.1 and 0.25 UTZC were $2.4 \times 0.3 \times 0.3$ cm^3 and $0.8 \times 0.7 \times 0.7$ cm^3, respectively (Figs. 1-4).

RESULTS AND DISCUSSION

The FTIR Spectrum of the UTZC crystal was recorded using a Bruker IFS 66V FTIR Spectrometer using KBr pellet technique in the range of 4000-400 cm^{-1}. The observed assignments have been tabulated in Table-1. The characteristic vibrations of UTZC in IR region have been compared with those of urea, thiourea, *bis* thiourea zinc chloride[7]. The high frequency γ_s (NH_2), γ_{as} (NH_2) absorption bands in the region 3400-3100 cm^{-1} in the

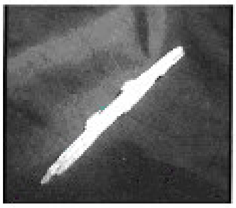

Fig. 1 Urea

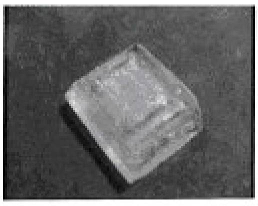

Fig. 2. Thiourea

Fig. 3. 0.1 UTZC

Fig. 4. 0.25 UTZC

TABLE-1
COMPARISON OF ABSORPTION IR BANDS OF UTZC WITH UREA, THIOUREA AND BTZC

Wavenumber (cm^{-1})					
Urea	Thiourea	BTZC	0.1 UTZC	0.25 UTZC	Assignment
–	411	424	–	–	δ_s (S-C-N)
–	469	474	474	476	δ_s (S-C-N)
508	494	511	585	–	δ_{as} (N-C-N)
–	740	715	–	713	γ_s (C=S)
790	–	–	781	–	δ_s (C=O)
1008	–	–	–	1011	γ_s (C-N)
–	1089	1101	1155	1154	γ_s (C-N)
–	1417	1406	–	1404	γ_{as} (C=S)
1454	–	1442	1455	1442	γ_{as} (C-N)
–	1471	1496	–	1501	γ_s (N-C-N)
1631	1627	1630	1626	1628	δ_{as} (NH_2)
–	3167	3202	–	3212	γ_s (NH_2)
3320	3280	–	3369	3355	γ_{as} (NH_2)
3422	–	3411	3463	3431	γ_{as} (NH_2)

spectrum of urea, thiourea were shifted to higher frequencies. This formation of metal thiourea complex indicating that nitrogen to zinc bonds is not present and the bonding must be between sulphur and zinc atoms[8] (Table-1). The asymmetric stretching of γ_{as} C=S vibrations at 740 and 1417 cm^{-1} of thiourea 1406 and 715 cm^{-1} of BTZC (except 0.1 UTZC, this may be due to the lower concentration of thiourea in UTZC) were shifted to lower frequencies 713 and 1404 cm^{-1} in 0.25 UTZC. Similarly, the γ_s (C-N) stretching vibration at 1008 cm^{-1} in urea, 1089 cm^{-1} in thiourea is shifted to higher frequencies 1011, 1101, 1155 cm^{-1} in both crystals of 0.1 and 0.25 UTZC. It is understood that the binding of zinc with thiourea is through sulphur[7-10]. 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 band was observed at 1501 cm^{-1} in 0.25 UTZC and it corresponds to 1496 cm^{-1} band of thiourea assigned to the γ_s N-C-N stretching vibration. This increase in frequency 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)[11]. The bands (γ_{as} C=O) were observed at 781 cm^{-1} in 0.1 UTZC and 1011 cm^{-1} in 0.25 UTZC indicate that the binding of urea with thiourea.

Conclusion

(i) The crystals of 0.1 and 0.25 urea thiourea zinc chloride (UTZC) were synthesized and its solubility analyzed in the room temperature. It was observed that the solubility decreases with increase in thiourea proportion. (ii) Single crystals of UTZC have been grown by slow evaporation technique at room temperature. (iii) The functional groups present in the grown crystal have been confirmed by FTIR spectral studies that binding of thiourea with zinc chloride occurs through sulphur.

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