Research Paper www.ijcps.com

International Journal of
Chemical and Pharmaceutical Sciences
2013, June., Vol. 4 (2)

ISSN: 0976-9390
IJCPS

Synthesis and Characterization of Bisurea-Thiourea Mixed Crystal

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ABSTRACT

Bisurea-thiourea mixed crystal (BUTMC) via solution growth by using urea, thiourea and deionised water is starting materials. The functional groups and vibrational frequencies were identified using FTIR spectral analysis. Thermogravimetry (TG) and differential analyze (DTA) were used to examine the behavior of bisurea-thiourea mixed crystal. Using TG-DTA analyses, the decomposition temperature was obtained. X-ray diffractogram of the crystal has been recorded and various planes of reflection are obtained.

Keywords: Bisurea-thiourea mixed crystal, Solution growth, TG-DTA, XRD

1. INTRODUCTION

The need of non-linear optical materials is much more then other material because of their applications in photonics and optoelectronics Krishnan H (2008 p 3313). Organic NLO crystals are attracted the attention because of the low cost and flexibility of molecular design, which are need for applications with using suitable donor-acceptor organic materials are often formed by weak Vanderwals and hydrogen bonds and hence possess a high thermal stability . However, these organic crystals have certain limitation such as poor mechanical strengths and thermal stability Rajasekaran R (2000 p 365). To overcome these problems, combinations of organic compounds leads to find a new class of materials for electronic industries, called organic mixed crystals Qui J (2006 p 191). Urea is representative of one class of materials which are applicable to photonics and served as a model and reference material in the DMOS (Diffusive Mixing in Organic Solutions) experiment in microgravity carried out by NASA Angelimary P A (2001 p 1231). Recently metal complexes of thiourea have been explored. Example of these complexes is zinc thiourea sulphate (ZTS) Gopinath S (2012 p 27), cadmium thiourea chloride (CTC) Boomadevi S (2002 p 159) and zinc thiourea chloride (ZTC) Sing P (2004 p 42) . Literature survey shows that urea-metanitro benzoic acid, urea-hydrogen peroxide compounds have been done [Kumar K (2006 p 217), Rajasekaran R (2003 p 273)]. However, there is no reference in literature regarding the work of bisurea-thiourea mixed crystal. This paper reports the synthesis and characterization of bisurea-thiourea crystal through FTIR and TG-DTA studies.

2. EXPERIMENTAL

Solution **1** 10g of urea was dissolved in 8ml of distilled water.

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

Solution **3** (BUTMC) 10g of urea, 5g of thiourea was dissolved in 16ml of distilled water.

The crystal growth solutions should be in equilibrium at room temperature (30ºC) 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 hours. The undissolved material collected at the bottom of the same flask and the clean solution was transferred to another flask and it is slightly heated above 5°C. So that the undissolved material gets completely dissolved. After dissolving, filtration of the solution which plays a vital role (i.e. chemical purity of the solution) during growth is preformed. The filtration of the solution was preformed the size of Buckner funnel is taken and placed over it perforated disc. It is then fitted in a filtration flask connected to suction pump. The rate of filtration through conical flask considerably increased using a perforated filter paper. Thus purified solution has prepared. While transferring the solution, temperature of

the growth chamber was brought down to 2ºC 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 (30ºC), 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 Solution 2 and 3. The solubility of synthesized BUTMC has been determined in deionised water. Infrared spectroscopic studies were carried out on the grown crystals in order to understand the structure and bonding in them. The FTIR spectrum of BUTMC has recorded on a Shimadzu spectrometer using KBr pellet technique in the wavelength range 400-4000cm^{-1}. The thermogravimetric and differential thermal analysis of BUTMC was made by employing Netzsch STA 409 thermal analyzer at a heating rate of 10ºC/min under nitrogen atmosphere. The powder X-ray diffraction pattern of the grown crystal was recorded using Cu Kα radiation (λ = 1.5418 Aº). SEM micrographs of the crystal was recorded, using Hitachi scanning electron microscope model S-450, operated at 15KV, after coating sample with layer (100Aº) using Hitachi vaccum evaporator model HVS 5GB.

2.1. Solubility

The solubility test was carried out using deionised water. The commercially available urea and thiourea was used for solubility study and growth, after repeated recrystallization processes. The salts used for the experiments are Analar Merck grade. The solubility experiment was carried out in constant temperature bath (accuracy ±0.001K) for the temperatures 303K, 305K and 307K. The temperature dependence of solubility of BUTMC is shown in Fig 1. The growth experiments were performed by using deionised water in the help of solubility curve, by slow evaporation technique.

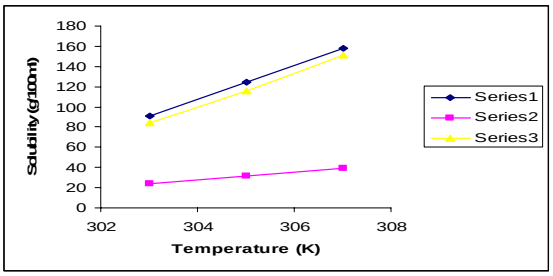

Figure - 1: Solubility of urea, thiourea and BUTMC in water.(Series 1 – urea; Series 2 – Thiourea; Series 3 - BUTMC)

3. RESULTS AND DISCUSSION

3.1. FTIR Spectral Analysis

Figure 2 shows the IR spectrum of BUTMC. Though it was very complex, the presence of broad bands at 3415cm-^{1} (NH stretching vibration) Malyajdas S (2006 p 555), 1433 cm^{-1} (C=S stretching vibration of thiourea) 1632cm^{-1} (C=O stretching vibration of urea) 1093cm^{-1} (CN stretching vibration of urea and thiourea) Madhurambal G (2004 p 125) were evident. Absorption bands observed at 2000-2700cm^{-1} also confirms the formation of title compound, because delocalization of π electrons of urea and thiourea occur at these regions. These bands are not observed in single crystals of urea and thiourea.

Table - 1: FTIR Assignments For Urea, Thiourea and BUTMC

Urea (cm^{-1})	Thiourea (cm^{-1})	BUTMC (cm^{-1})	Assignment
3455	3362	3415	ν_s NH_2
1625	---	1632	ν_s C=O
---	1478	1433	ν_s C=S
1064	1093	1093	ν_s CN
---	732	724	δ_s C=S

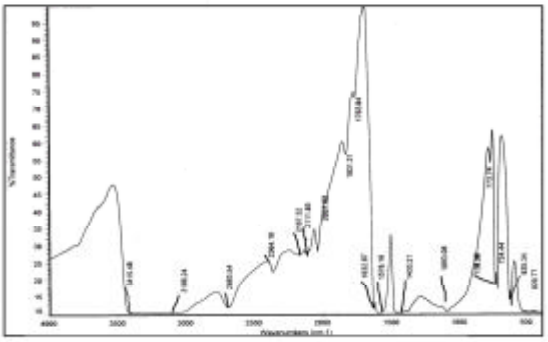

Figure -2: FTIR Spectrum of bisurea - thiourea crystal.

3.2. Thermal Analysis

The TG and DTA of BUTMC is shown in Fig 3. The TG curve indicates a two step weight loss on heating the compound between 30-800ºC. The following decomposition pattern is formulated for BUTMC.

Step **1**

.....H–HN–CO–NH–H.....S=C(NH_2)$_2$.....H–HN–CO–NH–H..... → $4NH_3 + CO$

Step **2**

–NH–CO–NH_2 → $H_2S + N_2 + C$

Four molecules of ammonia and a molecule of carbon monoxide are lost on heating the compound from 200-400ºC. This accounts for 45.65% weight loss observed in the TG curve. This indicates the higher percentage of urea in

BUTMC. Thiourea in BUTMC is stable up to about 450ºC. After that, thiourea begins to split. This accounts for 30.77% weight loss observed in the TG curve. This process consisted of two stages, as can be inferred from the position of exothermic peaks in the DTA curve. In the first stage from 200-400ºC, the exothermic peak at 352.1ºC was attributed to the removal of urea which combined weakly with thiourea.

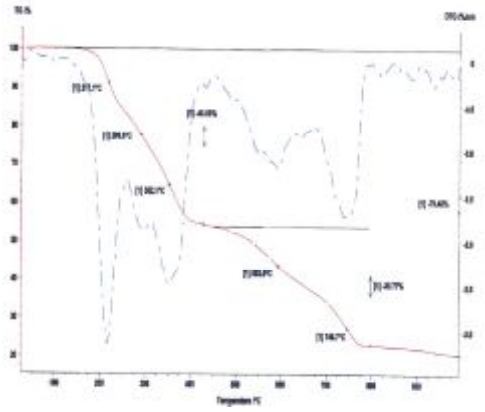

Figure -3: TG-DTA of bisurea - thiouera mixed crystal.

3.3. X-ray Diffraction Analysis and SHG Measurement

The XRD pattern of BUTMC has been compared with those of urea and thiourea. Major (110) and (020) peak with maximum intensity is shifted in BUTMC. XRD of BUTMC show a up shift of the peak positions compared with urea and thiourea. However, most of the peaks in the XRD peak are not resemble with that of urea and thiourea (Figure 4).

Table - 2: XRD data for bisurea-thiourea mixed crystal.

2θ	d	hkl Thiourea	hkl Urea	abc
12.5	3.5616	---	101	
17.6	2.5497	103, 122	210	
20.2	2.2326	---	211	
26.1	1.7522	---	301	
27.3	1.6808	---	311	a=b= 5.7013
30.0	1.5458	---	222	c= 5.0369
32.6	1.4309	---	312	
34.5	1.3611	---	401	
35.6	1.3242	---	330	
40.7	1.1822	---	431	
50.3	1.0012	---	221	
56.5	0.9328	---	003	

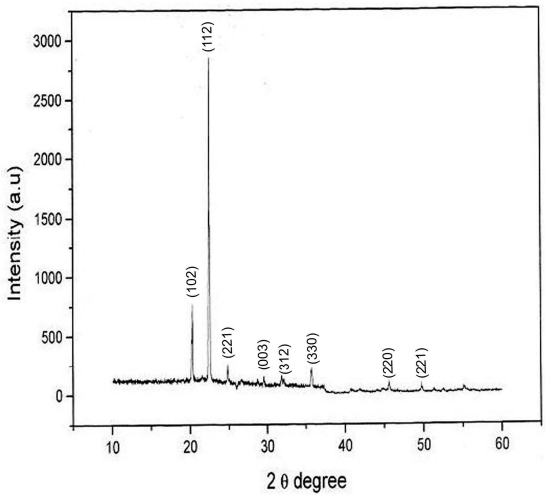

Figure - 4: XRD of bisurea - thiouera mixed crystal

The SHG experiment was carried out using powder technique. The BUTMC powder samples were irradiated at 1064nm by a Nd-YAG laser, and the green light was observed. An ADP crystal, powdered to the identical size was used as a reference material in the SHG measurement. Surface analysis of grown BUTMC using a Hitachi scanning electron microscope model S-450, showed a step like structure on the surface of BUTMC (Figure 5), which confirms the layer growth of BUTMC.

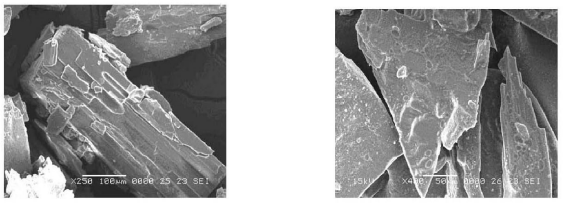

Figure - 5: morphology of bisurea-thiourea mixed crystal.

4. CONCLUSION

Optical quality mixed crystals of Bisurea-thiourea was grown by slow evaporation technique at room temperature. The solubility of Bisurea-thiourea mixed crystal has been determined in water. Functional groups present in Bisurea-thiourea mixed crystals are confirmed by FTIR analysis. Bisurea-thiourea crystals are thermally stable up to 200ºC.

The powder XRD pattern reveals the strong crystalline nature of the sample. X-ray analysis for the exact determination of the structure is in progress.

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