



Crystal growth, Comparison of Vibrational and Thermal properties of Semiorganic Nonlinear Optical Materials

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Abstract

Single crystals of Urea Thiourea Mercuric Sulphate (UTHS) and Urea Thiourea Magnesium sulphate (UTMS), semi organic nonlinear optical materials, have been grown from a low-temperature solution growth technique by slow evaporation method using water as solvent. Good quality single crystals were grown within three weeks. The nonlinear nature of the crystals was confirmed by SHG test. The UV-Vis spectrum shows the transmitting ability of the crystals in the entire visible region. FTIR spectrum recorded and vibrational assignments were made. The degree of dopant inclusion was ascertained by AAS. The TGA-DTA studies show the thermal properties of the crystals.

Key words: UTHS, UTMS, NLO crystals, UV-VIS, FTIR, AAS, TGA, DTA, SHG.

Introduction

Non linear optical materials generating second harmonic frequency play an important role in laser technology and optical fiber communication[1-2]. To have proper transmission and reception, communication link is essential. Organic material posses good optical transmission characteristics[3]. To be useful in this technology the materials should possess large second order optical nonlinearities, short transparency cutoff wavelength and thermal stability. Organic materials possess good optical non-linearity but they are thermally unstable. Inorganic materials are having excellent mechanical and thermal properties with moderate non-linearities. In the last two decades much progress has been made in the development of NLO organic materials, having large nonlinear optical coefficients. But organic materials are soft and difficult to polish since they are constituted by weak van der Waals and hydrogen bonds with conjugated π electrons. Moreover these materials have more absorption in UV region. In view of these problems, the search for new frequency conversion materials has led to the discovery of many semi organic materials. They posses large non linearity, high resistance laser induced damage and low angular sensitivity[4-5].

Semi organics are formed by combining organic molecules of high polarizability with mechanically strong and thermally stable inorganic molecules. These materials combine the chemical flexibility and nonlinearity of organics and favorable physical properties of inorganics[6-7]. Here, an attempt is made to grow and characterize single crystals of urea thiourea magnesium sulphate (UTMS) and urea thiourea mercuric sulphate (UTHS) by slow evaporation.

Experimental

2.1 Synthesis

The required quantities of urea, thiourea and magnesium sulphate, mercuric sulphate dissolved separately in double distilled water. The solution was thoroughly mixed using a magnetic stirrer. A crystalline substance was formed. The synthesized substance was purified by repeated crystallization process.

The UTMS and UTHS solutions were prepared in water and maintained at 30⁰ C with continuous stirring to ensure homogenous temperature and concentration over the entire volume of the solution. On reaching the saturation the content of solution analyzed gravimetrically. This process was repeated for every 5⁰ C in water from 30 to 50⁰ C. The solubility curve is shown in Fig. 1

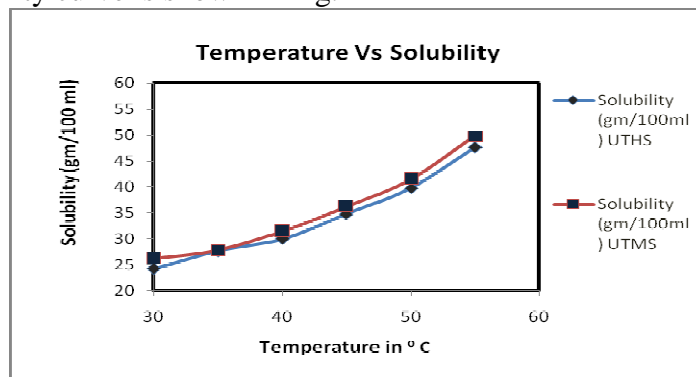


Fig. 1 The solubility graph of UTHS and UTMS

2.2 Crystal Growth

From the solubility test, both UTMS and UTHS are more soluble in water. The required quantities of the component salts were very well dissolved in double distilled water and thoroughly mixed for about 4 hours and 7 hours, respectively, using a magnetic stirrer to ensure homogeneous temperature and concentration throughout the volume of the solution. The P_H of the solutions are maintained at 4 and 4.5, respectively. The saturated solution was covered with transparent polythene paper and left undisturbed for slow evaporation. Good quality single crystals of UTMS and UTHS were grown within three weeks and are shown in Figure 2a and 2b.

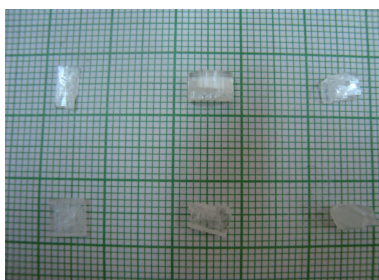


Fig. 2a Single crystals of UTMS



Fig. 2b Single crystals of UTHS

Characterization

3.1 Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy (AAS) is one of the most widely used quantitative analytical methods. AAS is used for quantitative determination of metals and metalloids down to absolute amounts as low as 10⁻¹⁴g. AAS determines the presence of metals in liquid samples. Metals include Fe, Cu, Al, Zn, Mg, Hg, and many more. It also measures the concentrations of metals in the samples. To determine the mole percentage of dopants incorporated in the grown doped crystals, finely powdered doped crystals weighing about 100mg are dissolved in 10 ml of dilute acid and then subjected to AAS. The results of AAS are presented in Table 1. The amount of dopant incorporation was found to be far below its original concentration in their respective solution. The low percentage of incorporation of dopants into the crystal may be due to large difference between the ionic radii.

Table 1: Atomic Absorption Spectra Estimate for dopants

Samples	% of dopants
UTMS	0.09
UTHS	0.004

3.2 UV-Vis spectral studies

The optical transmission spectrum is recorded using UTHS and UTMS crystals of suitable size in the wavelength range of 200 – 2000 nm using VARIAN spectrophotometer. The UV-visible-near infrared transmission spectrum of UTMS and UTHS crystals are shown in Figure 3a and 3b, respectively. The significant absorption was found at 235 nm. The lower cut off wavelength is below 250 nm, which is an advantage in semi organic non linear materials. The absorbance of the crystal over inorganic material is less than one unit in the entire visible region. The transparent nature in the visible region is a desirous property for NLO application and enables the crystals to be good candidate for optoelectronic applications. Interestingly, both UTMS and UTHS are transparent in entire visible and infrared regions.

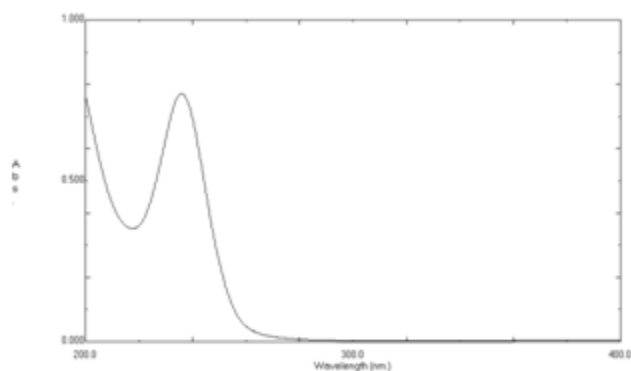


Fig 3a UV-VIS spectrum of UTMS crystal

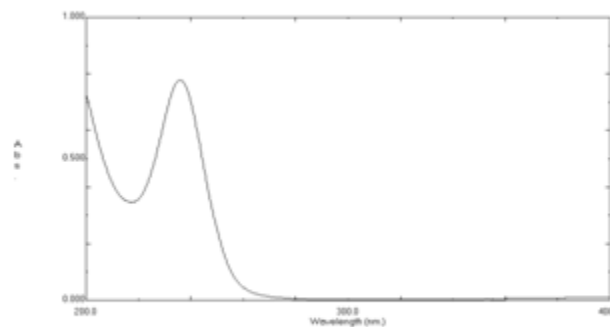


Fig 3b UV-VIS spectrum of UTHS crystal

3.3 Second Harmonic Generation testing (SHG)

The SHG conversion efficiency of the crystal was carried out using the Nd:YAG laser beam of wavelength 1064 nm, using Kurtz Powder technique. The second harmonic generation was confirmed by the emission of green radiation of wavelength of 532 nm. Second harmonic generation efficiency of UTMS and UTHS are compared with KDP and it is found to be $1/4^{\text{th}}$ and $1/6^{\text{th}}$ of KDP material, respectively

3.4 Thermogravimetry

Thermogravimetry (TGA) when complemented with differential thermal analysis (DTA) and differential scanning studies (DSC) gives valuable information about decomposition patterns of materials and weight loss can be got. Simultaneous TGA and DTA were carried out for the UTMS and UTHS crystals. A powder sample of 3.08 mg and 3.02 mg was used for the analysis in the temperature range of 28°C to 1100°C with a heating rate of 20 K/min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in Fig. 5a, 5b and 5c.

For UTMS there is no loss of weight observed around 100°C showing the absence of any absorbed water molecules in the sample. There is a sharp endotherm at 228.73°C which has no corresponding weight loss in the TGA trace. Hence, this endotherm is assigned to melting of this compound. Major weight loss occurs in two stages between 242°C and 300°C. The first stage weight loss corresponds to 73.58% at 242.05°C another weight loss follows at 298.64°C corresponds to 82.23%. The weight loss in this range may be due to decomposition of thiourea present in UTMS. In the case of UTHS crystal also there is no weight loss around 100°C shows the absence of water molecules. There is sharp endotherm at 221°C which has no corresponding weight loss. The weight loss at 231°C is about 80%. The increase in decomposition temperature compared to

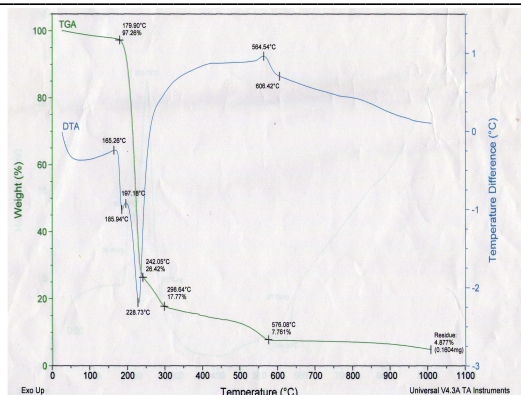


Fig. 5a Thermogram of UTMS crystal

the decomposition temperature of thiourea which is 182°C may be due to the formation of metal complex. This shows the thermal stability of UTMS than that of UTHS crystal. The thermogravimetry study shows that the UTMS crystal is thermally more stable than UTHS crystal.

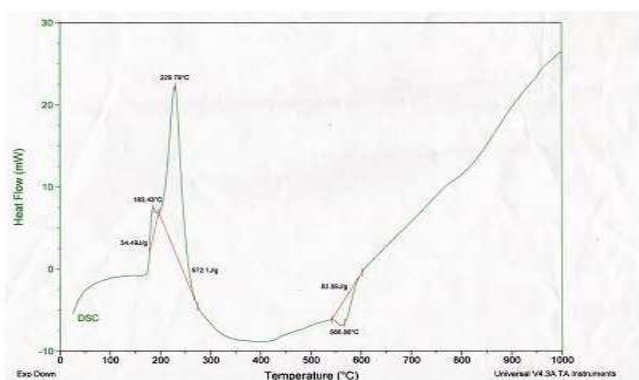


Fig. 5b Differential Scanning Calorimetry(DSC)

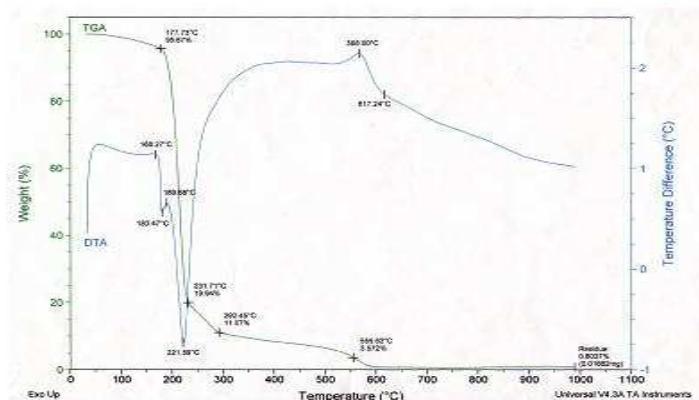


Fig. 5c Thermogram and Differential Thermogram

3.5 Comparison of UTMS and UTHS by FTIR spectral study

Infrared spectroscopy is effectively used to determine the molecular structure and the identification of the functional groups in the synthesized compound. FTIR spectrum was recorded using Bruker IFS 66V spectrophotometer by KBr pellet technique in the region 4000 – 400 cm^{-1} and shown in Figure 6a and 6b. The characteristic vibrational frequencies are assigned and compared with urea, thiourea[8]. The symmetric and asymmetric C=S stretching vibrations⁸ at 740 and 1417 cm^{-1} of Thiourea are shifted to 730 and 1412 cm^{-1} respectively. The N-H absorption bands in the high frequency region 3400 – 3000 cm^{-1} in the thiourea were not shifted to lower frequencies on the formation of metal-thiourea complex indicating that nitrogen to magnesium bonds are not present and bonding must be between sulphur and magnesium atoms. The band at 1473 cm^{-1} is assigned to N-C-N stretching vibration[9] and other characteristic Vibrational frequencies are assigned in Tab. 2.

Bonding through sulphur will increase the contribution from the resonance forms II and III, thus decreasing the bond order of carbon-sulphur link towards the value of a single bond, whilst that of the carbon-nitrogen bond approaches the value for a double bond. Hence, in such complexes, the CS stretching frequency should decrease and that of CN opposite effect is to be expected. The symmetric and asymmetric C=S stretching vibrations[9-10] at 740 cm^{-1} and 1470 cm^{-1} of thiourea are shifted to lower frequencies 712 cm^{-1} and 1401 cm^{-1} in UTHS crystals. In the case UTHS crystals they are shifted to 730 cm^{-1} and 1412 cm^{-1} respectively. In both the crystal the NH absorption bands in the high frequency regions 3400 – 3000 cm^{-1} (thiourea) were not shifted to lower frequencies on the formation of metal thiourea complex.

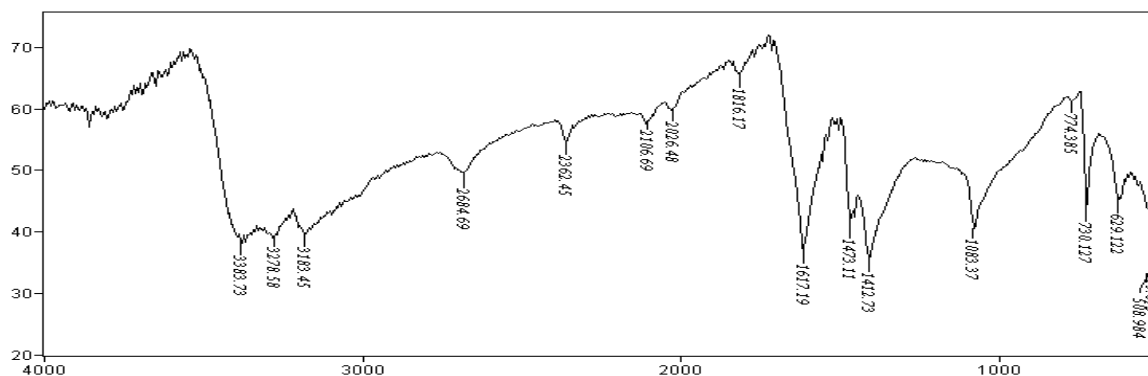


Fig 6a FTIR spectrum of UTMS crystal

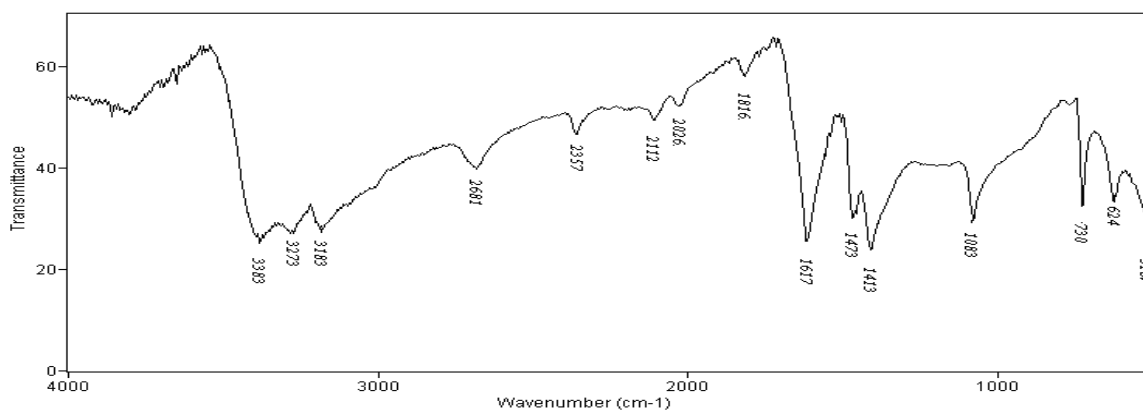


Fig 6b FTIR spectrum of UTHS crystal

Table 2 Comparison of Absorption IR bands of TUMS with Urea, Thiourea

Urea	Thiourea	UTMS	UTHS	Assignments
-	469	-		δ (S-C-N)
508	494	509	509	δ (N-C-S)
-	740	730	730	ν (C=N)
-	1089	1083	1473	ρ (NH ₂)
-	1417	1412	1611	ν _S (C=S)
-	1471	1473	-	ν (N-C-N)
1631	1627	1621	1611	δ (NH ₂)
3320	3167	3178	3183	ν _S (NH ₂)
3422	3280	3283	3273	ν _S (NH ₂)
	3376	3388	3383	ν _S (NH ₂)

Conclusion

Single crystals of UTMS and UTHS have been grown by slow evaporation technique at room temperature. Marginal change in the appearance of bands in the region between 2000 and 400 cm^{-1} in FTIR spectra of doped crystals confirms the incorporation of metal ions in the crystal lattice. Optical transmission studies confirm that UTMS and UTHS crystals are transparent in the entire visible region. TGA reveals that the pure sample is stable upto 185 °C without loss in weight whereas the doped samples have enhanced thermal stability upto about 240 °C and 220 °C, respectively. The present study is primarily aimed at the development of a newer variety of NLO crystals. The preliminary SHG efficiency studies and the optical and mechanical properties strongly favor the usage of these crystals in photonics technology. In addition, there are good chances of identifying entirely novel materials with promising properties.

References

- [1] X Q Wang, D Xu, D R Yuan, Y P Tian, W T Yu, S V Sun, Z H Yang, Q Fang, M K Lu, Y X Yan, F Q Meng, S Y Guo, G H Zhang and M H Jiang, *Mater. Res. Bull.*, **34**, 2003, (1999)
- [2] H O Marey, L F Warrn, M S Webb, C A Ebbbers, S P Velsko, G C Kennedy and G C Catella, *Applied Opts.* **31**, 5051 (1992).
- [3] G C Gunjan Purohit Joshi, *Indian J. Pure Appl. Phys.*, **41**, 922-927, (2003).
- [4] P M Ushashree, R Jayavel, C Subramanian and P Ramasamy, *J. Cryst. Growth*, 197, 216, (1999).
- [5] R Rajasekaran, P M Ushashree, R Jayavel and P Ramasamy, *J. Cryst. Growth*, 218, 365, (2000).
- [6] H O Marey, M J Rosker, L F Warren, P H Cunningham, C A Thomas, L A Deloach, S P Velsko, C A Ebbbers, J H Liao and M G Kanatzidis, *Opt. Lett.*, **20**, 252 (1995).
- [7] N J Long, *Angew. Chem.*, **34**, 21, (1995).
- [8] R.M. Silverstein, G. Clayton Basseler and T.C. Morrill, *Spectrometric Identification of Organic Compounds*, V-Edn, John Wiley & Sons, Inc. New York 1998.
- [9] K. Nakamoto, *IR spectra of Inorganic and Coordination Compounds II Edn.* Wiley & Sons, New York 1978.
- [10] S Gunasekaran, G Anand, R Arun Balaji, J Dhanalakshmi, S Kumaresan, G Anbalagan, *Int. J. Chem. Tech Res.*, Vol. 1, No. 3, pp. 649-653, (2009).