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Crystal growth and comparison of vibrational and thermal properties of semi-organic nonlinear optical materials

S GUNASEKARAN[1], G ANAND[2,*], R ARUN BALAJI[3], J DHANALAKSHMI[4] and S KUMARESAN[2,5]

[1]Periyar University, Salem 636 011, India
[2]Faculty of Sciences, Arulmigu Meenakshi Amman College of Engineering, Vadamavandal 604 410, India
[3]Department of Physics, Rajiv Gandhi College of Engineering, Sriperumbadur 602 105, India
[4]Department of Chemistry, Kamaraj College of Engineering and Technology, Virudhunagar 626 001, India
[5]Present address: School of Advanced Sciences, Materials Division, VIT University, Vellore 632 014, India
*Corresponding author. E-mail: geayea21@gmail.com

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Abstract. Single crystals of urea thiourea mercuric sulphate (UTHS) and urea thiourea mercuric chloride (UTHC), semi-organic nonlinear optical materials, were grown by low-temperature solution growth technique by slow evaporation method using water as the 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 showed the transmitting ability of the crystals in the entire visible region. FTIR spectrum was recorded and vibrational assignments were made. The degree of dopant inclusion was ascertained by AAS. The TGA–DTA studies showed the thermal properties of the crystals.

Keywords. Urea thiourea mercuric sulphate; urea thiourea mercuric chloride; nonlinear optic crystals; ultraviolet–visible; Fourier transform infrared; atomic absorption spectroscopy; thermogravimetric analysis; differential thermogram analysis; second harmonic generation.

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1. Introduction

Nonlinear optical materials generating second harmonic frequency have a significant impact on laser technology, optical communication and optical storage technology [1,2]. High-performance electro-optic switching elements for telecommunications

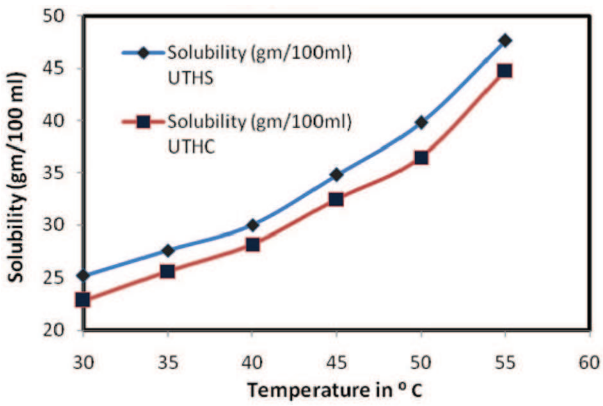


Figure 1. Solubility curve of UTHS and UTHC.

and optical information processing are based on materials with high nonlinear optical properties. The search for new frequency conversion materials in recent years has concentrated on semi-organic complexes. The metal-organic materials have the potential for combining the high optical nonlinearity and flexibility of organics with temporal, thermal stability and excellent transmittance of inorganics [3–7].

Recently, the metal complexes of thiourea are being explored. Among the semi-organic NLO materials, metal complexes of thiourea received much attention as they have low UV cut-off wavelength and possess better nonlinearity than KDP. They have higher values of laser damage threshold and can be used in frequency doubling and laser fusion experiments [4]. In this paper, we are presenting a preliminary report on the growth and characterization of two semi-organic single crystals, urea thiourea mercuric chloride (UTHC) and urea thiourea mercuric sulphate (UTHS), by slow evaporation technique.

2. Experimental method

2.1 *Synthesis*

The required quantities of urea, thiourea and mercuric chloride were dissolved 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 UTHC solution was prepared in water and maintained at 30°C with continuous stirring to ensure homogeneous temperature and concentration. On reaching saturation, the content of solution was analysed gravimetrically. This process was repeated for every 5°C in water from 30 to 50°C. The UTHS solution also was formed by following the same procedure. The solubility curve is shown in figure 1. The solubility curve shows that both UTHS and UTHC have positive solubility temperature gradients.

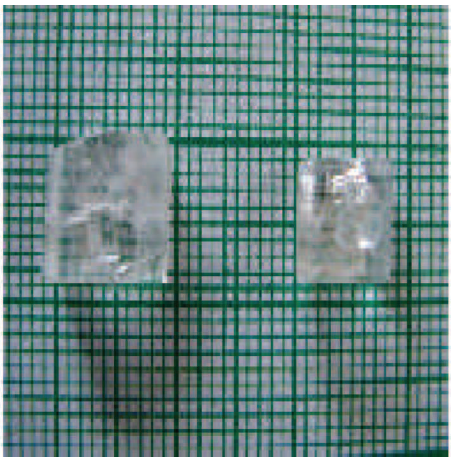


Figure 2. Single crystals of UTHC.

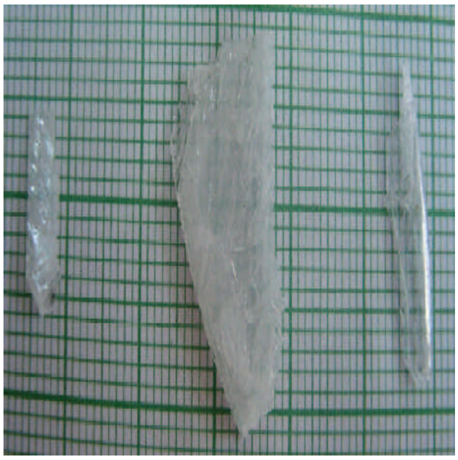


Figure 3. Single crystals of UTHS.

2.2 *Crystal growth*

Large single crystals can be grown from slow evaporation solution growth [6–8]. Single crystals of urea thiourea mercuric sulphate and urea thiourea mercuric chloride were grown by slow evaporation of the saturated aqueous solution at room temperature. pH of the UTHS solution was maintained at 4.5 and that of UTHC at 4.2. The solutions were mixed for about 7 h using a magnetic stirrer to get homogeneous temperature and concentration. The saturated solutions were collected in two different beakers covered with transparent polythene papers and left undisturbed for slow evaporation. Good quality single crystals were grown within three weeks. The single crystals of UTHC and UTHS are shown in figures 2 and 3.

3. 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^{-14} g. AAS determines the presence and concentration of metals in liquid samples. To determine the mole percentage of dopants incorporated in the grown doped crystals, finely powdered doped crystals weighing about 100 mg were 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 is found to be far below its original concentration in their respective solution. The low percentage of incorporation of dopants into the crystal may be because of the large difference between the ionic radii.

4. UV–Vis spectral analysis

The optical transmittance range and transparency cut-off wavelength are the main requirements for device applications. The optical absorption spectra of UTHC and

Table 1. Atomic absorption spectra estimate for dopants.

Samples	% of dopants
UTHS	0.004
UTHC	0.007

Table 2. Comparison of absorption IR bands.

Urea	Thiourea	UTMS	UTHC	UTHS	Assignments
	469				δ (S–C–N)
508	494	509	509	509	δ (N–C–S)
		631	614	624	ρ (C–H)
	740	730	712	730	ν (C=S)
	1089	1083	1079	1083	ρ (NH_2)
	1471	1473	1503	1473	ν (N–C–N)
1631	1627	1621	1617	1611	δ (NH_2)
	3167	3178	3178	3183	ν_s (NH_2)
3320	3280	3283	3278	3273	ν_s (NH_2)
3422	3376	3388	3368	3383	ν_{as} (NH_2)

UTMS – Urea thiourea magnesium sulphate, UTHC – urea thiourea mercuric chloride, UTHS – urea thiourea mercuric sulphate, ν – stretching, ρ – rocking, δ – bending, ν_s – symmetric stretching, ν_{as} – asymmetric stretching.

UTHS crystals were recorded using Varion Cary 5E UV–Vis NIR spectrophotometer in the range 200–400 nm with high resolution. The recorded spectra are shown in figures 4a and 4b. The UTHC and UTHS crystals had lower cut-off wavelengths around 236 nm which were comparable with UTMS crystal [9]. There was no absorption band beyond 236 nm, which confirmed the absence of any overtones and absorbance due to electronic transitions. The transmittance window in the visible region and IR region enabled good optical transmission of the second harmonic frequencies of Nd:YAG laser [10].

5. NLO property studies

Second harmonic generation test (SHG) was made on the UTHC and UTHS samples using Kurtz and Perry [11] technique. The source used was the Q-switched, mode-locked Nd:YAG laser emitting 1.06 μm fundamental radiation. The input laser beam was passed through an IR reflector and was then directed on the microcrystalline powdered sample packed in a capillary tube. Photodiode detector and oscilloscope assembly detected the light emitted by the sample. The emission of green light confirmed the second harmonic generation of the crystals. The powder SHG efficiency of UTHC and UTHS is 2/3rd and 1/6th of the standard NLO material KDP.

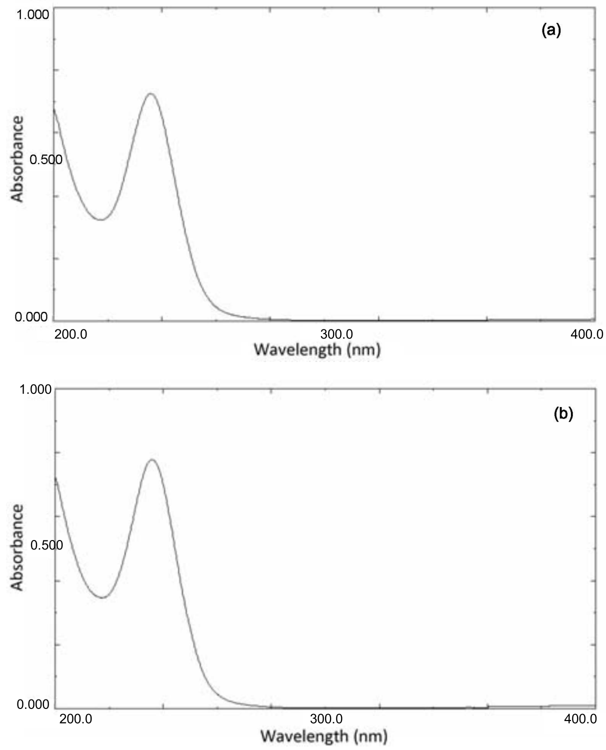


Figure 4. (**a**) Optical absorption spectrum of UTHC crystal and (**b**) optical absorption spectrum of UTHS crystal.

6. Thermal analysis

Differential thermogram analysis (DTA) and thermogravimetric analysis (TGA) give information regarding phase transition and different stages of decomposition of the crystal system [12]. TGA and DTA have been carried out for the grown UTHC and UTHS crystals in the temperature range of 25–1100°C with a heating rate of 20°C/min in the nitrogen atmosphere. Simultaneously recorded TGA and DTA curves of the samples are shown in figures 5a and 5b. There was no loss of weight observed around 100°C indicating the absence of water molecules in the samples. UTHC and UTHS are thermally stable up to 190 and 176°C, respectively. Below the decomposition temperature, there was no detectable weight loss and hence the crystals rejected solvent molecules during crystallization. Compound degradation took place above the decomposition temperature in different stages. From DTA curves it was confirmed that UTHC and UTHS underwent irreversible endothermic transition at 243.51 and 221.59°C corresponding to their melting points, respectively.

The melting points and decomposition temperature are higher than the ligand – thiourea. The increase in the decomposition temperature may be due to the formation of the metal complexes with $HgCl_2$ and $HgSO_4$. From these results it was

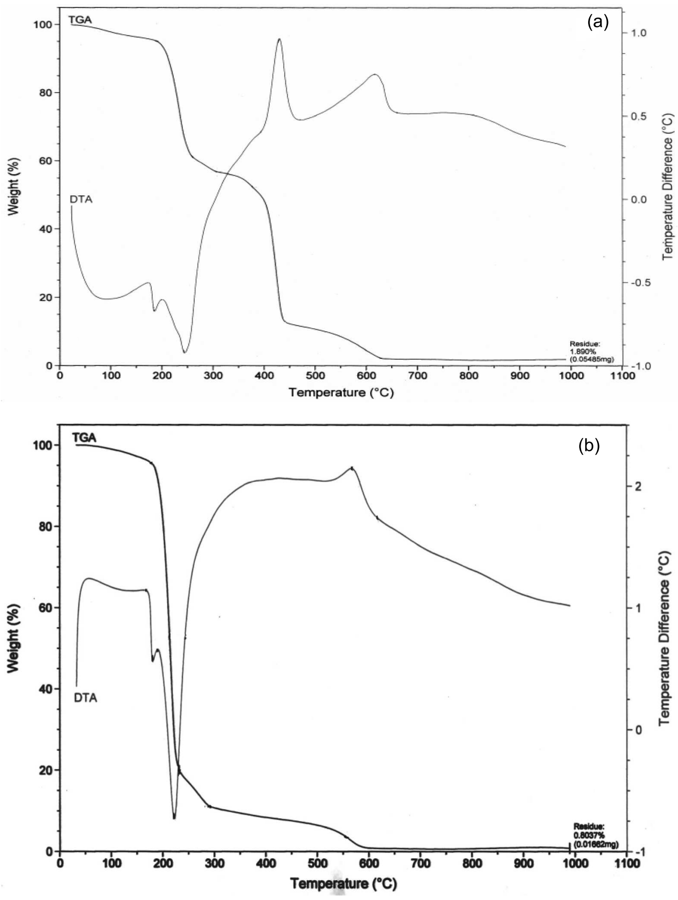
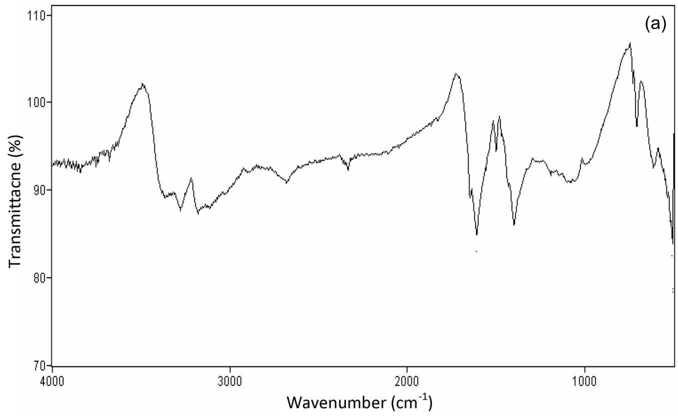


Figure 5. (**a**) Thermogram and differential thermogram of UTHC crystal and (**b**) thermogram and differential thermogram of UTHS crystal.

identified that UTHC had more thermal stability than UTHS. A complex formed with cadmium or mercury chlorides is more stable than the complex formed with cadmium or mercury sulfates [13]. The high melting point of semi-organic materials when compared with organic crystals arises because of the stronger bonding between the conjugation layers of thiourea molecules and metal ion [14].

7. FTIR spectral analysis

FTIR spectroscopic studies were effectively used to identify the functional groups present in the synthesized compound and to determine the molecular structure. To analyse qualitatively the presence of the functional groups in UTHC and UTHS crystals, FTIR spectra were recorded using Bruker IFS 66V spectrophotometer by KBr pellet technique in the region 4000–400 cm^{-1}. The recorded spectra are shown in figures 6a and 6b. The characteristic vibrational frequencies of the functional



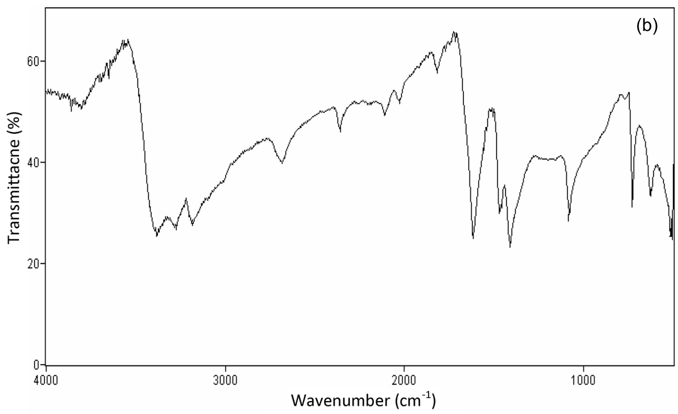


Figure 6. (**a**) FTIR spectrum of UTHC crystal and (**b**) FTIR spectrum of UTHS crystal.

groups of the crystal have been compared with urea, thiourea (Yamauchi *et al*, 1950) and UTMS [9]. Table 2 shows the vibrational assignments for UTHC and UTHS crystals.

In the metal complexes of thiourea, there are two possibilities by which the coordination of the metal with thiourea can occur. The coordination with metal may occur through either nitrogen or sulphur of thiourea [15]. Swaminathan and Irving [16] studied metal complexes of the type $M[tu]_2X_2$, where M is a metal, tu is thiourea and X is a halogen. Many metals were found to form metal–sulphur bonds. The symmetric and asymmetric C=S stretching vibrations in thiourea at 740 and 1470 cm^{-1} were shifted to 712 and 1401 cm^{-1} for UTHC crystals and 730 and 1413 cm^{-1} for UTHS crystals respectively, because of the addition of metal ion in the complex. This shows that the binding of metal with thiourea is through sulphur in both the crystals. The high-frequency N–H absorption bands in the region 3000–3400 cm^{-1} in the spectrum of thiourea were not shifted to lower frequencies on the formation of metal–thiourea complex in both UTHC and UTHS crystals. This indicates that nitrogen to metal bonds are absent and the bonding must be between sulphur and metal [17]. The band observed at 1503 cm^{-1} for UTHC corresponded to the 1470 cm^{-1} band of thiourea assigned to NCN stretching vibration. This increase in wavenumber may be due to the stronger double bond character of the carbon to nitrogen bond on complex formation. In the case of UTHS crystals it was observed at 1473 cm^{-1}. The peaks between 1700 and 2700 cm^{-1} were due to overtones and combination bands. The other characteristic vibrational wavenumbers are assigned in table 2.

8. Conclusions

The good-quality single crystals of UTHC and UTHS were successfully grown by slow evaporation method at room temperature. The degree of dopant inclusion was determined by AAS. The UV–Vis spectra showed that the crystals had a wide optical window, no absorbance and good optical transmittance in the entire visible region. The nonlinear optical studies confirmed the SHG property of the crystals. FTIR analysis confirmed the presence of functional groups in the grown crystals. The IR bands of the crystals were compared with urea, thiourea and UTMS. TGA and DTA thermogram revealed the thermal stability of the materials.

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