

# GROWTH, SPECTRAL AND SECOND ORDER NLO STUDIES OF UNDOPED AND THIOUREA DOPED UREA L-TARTARIC ACID

C. Anbulakshmi<sup>1</sup>, P.Selvarajan<sup>2</sup>, S.Selvaraj<sup>3</sup>

<sup>1</sup>Research Scholar, Reg. No. 12434, Department of Physics and Research Centre, MDT Hindu College, Tirunelveli-627010, Tamilnadu, India.

<sup>2</sup>Associate Professor of Physics, Aditanar College of Arts and Science, Tiruchendur - 628216, Tamilnadu, India.

<sup>3</sup>HOD and Associate Professor of Physics, MDT Hindu College, Tirunelveli-627010, Tamilnadu, India.

(Affiliated to Manonmaniam Sundaranar University, Abishekapatti-627012, Tirunelveli, Tamilnadu, India)

Received: June 14, 2018

Accepted: July 25, 2018

## ABSTRACT

*Slow evaporation technique was adopted to grow the undoped and thiourea doped urea L-tartaric acid crystals. When thiourea was added as the dopant, the morphology and other properties seem to be altered. Solubility of the grown crystals was measured by gravimetric method. X-ray diffraction (XRD) studies reveal that the grown single crystals crystallize in orthorhombic structure. Functional groups have been identified by Fourier Transform Infra Red spectral studies. The transmittance of the samples was found using UV-visible spectral studies. The second Harmonic generation (SHG) efficiency of the crystals was found by Kurtz and Perry technique.*

**Keywords:** Solution growth; doping; single crystal; XRD; SHG; NLO; FTIR; transmittance

## 1. Introduction

The need of nonlinear optical (NLO) single crystals are very much useful in the fields of second harmonic generation, fiber optic communication, electro-optic modulation etc, [1, 2]. The search for new materials with high optical nonlinearities is an important area due to their practical applications such as optical communication, optical computing, optical data processing, data storage, laser fusion reaction, remote sensing, color display and medical diagnostics [3]. Urea is an NLO material and is hydrogen bonded, which leads to enough delocalization, yet it has strong localized features such as  $\pi$  electrons in the carbonyl groups which contribute significantly to nonlinear response. It has high a nonlinear coefficient, a high birefringence and a high laser damage threshold [4, 5]. It is reported that urea molecule forms an extensively hydrogen bonded host structure and the phase diagram of urea dicarboxylic acid has been reported in the literature [6-8]. Urea is observed to be combining with L-malic acid and L-tartaric acid to form interesting NLO materials [9,10]. Krishnan *et al.* have reported about the growth and studies of urea succinic acid crystal [11]. L-tartaric acid and its compounds form an important class of materials as they exhibit interesting electrical and optical properties. Molecular salts composed of L-tartaric acid and basic compounds have been synthesized. Some of the reported L-tartaric acid compound crystals are urea-tartaric acid, L-cysteine tartrate, cobalt tartrate, holmium tartrate, calcium tartrate, etc [12-15]. Urea tartaric acid is an additive compound formed by small organic molecules of urea and the chiral molecule of L-tartaric acid. The crystal structure of urea L-tartaric acid is stabilized by a strong hydrogen bond in three dimensional networks, between urea and tartaric acid and this crystal is more rigid and is expected to enhance the optical nonlinearity due to cross linking of multidirectional hydrogen bonds or multi bond character in C-N and C-O bonds [16]. It is believed that if an organic salt like thiourea is added into urea L-tartaric acid (ULTA) crystals, interesting properties may be obtained. Hence the aim of this paper is to report the results of solubility, growth, XRD studies, FT-IR studies, and SHG studies of the grown undoped and thiourea doped ULTA crystals.

## 2. Synthesis, solubility and crystal growth

Analar Reagent (AR) grade of urea and L-tartaric acid were purchased commercially and used for the synthesis of urea L-tartaric acid salt. Urea and L-tartaric acid were taken in the molar ratio of 1:1 and dissolved in the solvent of double distilled water to get the saturated solution. The solution was heated until the synthesized salt of urea L-tartaric acid (ULTA) was obtained. During the synthesis, temperature of the solution was maintained at 50 °C in order to avoid the oxidation of the sample. To prepare the thiourea doped urea L-tartaric acid salt, 1 mole% of thiourea was added into the aqueous solution of urea L-tartaric acid and this solution was heated at 50 °C till the doped sample was obtained. Solubility studies were carried out using a hot plate magnetic stirrer and a digital thermometer by gravimetric method. The solubility of

both the samples were measured at temperatures 30 °C, 35 °C, 40 °C, 45 °C, 50 °C, 55 °C, 60 °C in water. The solubility curves are presented in figure 1. From the solubility curves, it is observed that the urea L-tartaric acid in water has the more solubility and thiourea doped ULTA sample has the less solubility compared to undoped one. For both the samples, solubility is found to be increasing with increase of temperature and hence the samples have positive temperature coefficient of solubility. Single crystals of the synthesized salts were grown by solution method. The grown crystals are shown in the figure 2.

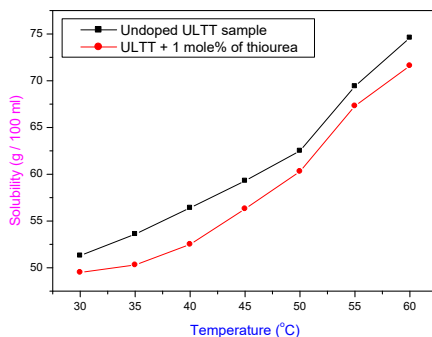


Fig. 1: Solubility curves for undoped and thiourea doped urea L-tartaric acid samples

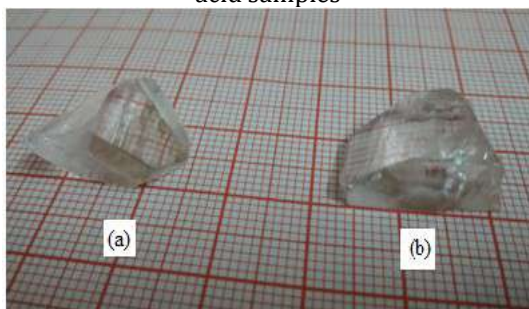


Fig.2: Harvested crystals of (a) undoped and (b) thiourea doped urea L-tartaric acid

### 3. Crystal structure and lattice constants

X-ray Diffraction (XRD) helps to determine the arrangement and the spacing of atoms and hence to determine the lattice parameters of crystalline material. The grown crystals were subjected to single crystal XRD studies using a single X-ray diffractometer (Bruker-Nonius MACH3/CAD4) and the structural data were obtained. Single crystal XRD analysis indicates that the grown crystals crystallize in orthorhombic structure. The space group of the samples is observed to be  $P2_12_12_1$ . The obtained lattice parameters of the samples are provided in the table 1. The values lattice parameters obtained here for undoped urea L-tartaric acid crystal are found to be in good agreement with the reported data in the literature [17]. The molecular weight of the grown undoped ULTA crystal is found to be 210.14. The density of the crystals is determined using the relation  $\rho = MZ/NV$  where M is the molecular weight of the crystal, Z is the number of molecular units per unit cell which is equal to 4, N is the Avagadro's number and V is the volume of the unit cell. The calculated values of the density of undoped and thiourea doped ULTA crystals are 1.637 g/cc and 1.623 g/cc respectively.

Table 1: Unit cell constants for undoped and thiourea doped urea L-tartaric acid crystals

Sample	Unit cell parameters	Volume ( $\text{\AA}^3$ ) <sup>3</sup>
Undoped Urea L-tartaric acid crystal	a = 9.794(3) $\text{\AA}$ b = 5.062(4) $\text{\AA}$ c = 17.198(2) $\text{\AA}$ $\alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ$	852.26(3)
Urea L-tartaric acid crystal + 1 mole % of thiourea	a = 5.078(5) $\text{\AA}$ b = 9.816(3) $\text{\AA}$ c = 17.223(4) $\text{\AA}$ $\alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ$	858.49(2)

#### 4. FTIR studies

Fourier Transform Infrared (FTIR) spectroscopy is particularly useful for the study of molecules. For qualitative analysis, the absorption or the lack of absorption in specific frequency regions can be correlated with specific vibrational modes of atoms in a molecule. Fourier Transform Infrared (FTIR) spectrum of sample was recorded using a Shimadzu spectrometer with KBr pellet technique in the range of 4000 to 400  $\text{cm}^{-1}$ . The FTIR spectrum of thiourea doped urea L-tartaric acid is shown in figure 3. By the interpretation of FTIR spectra it is possible to show that certain functional groups are present and certain others are absent in the material. The broad band in the range 3400-3100  $\text{cm}^{-1}$  is attributed to stretching modes of NH and OH. The peaks at 2974 and 2528  $\text{cm}^{-1}$  are corresponding to CH stretching vibrations. The peak at 1632  $\text{cm}^{-1}$  is attributed to C=O stretching vibration mode of tartaric acid. The band 1133  $\text{cm}^{-1}$  is due to CN stretching vibration. The peak 1406  $\text{cm}^{-1}$  is corresponding to C-O stretching of urea. The complete FTIR spectral bands/peaks are given assignments in accordance with the data reported in the literature [18] and are provided in the table 2.

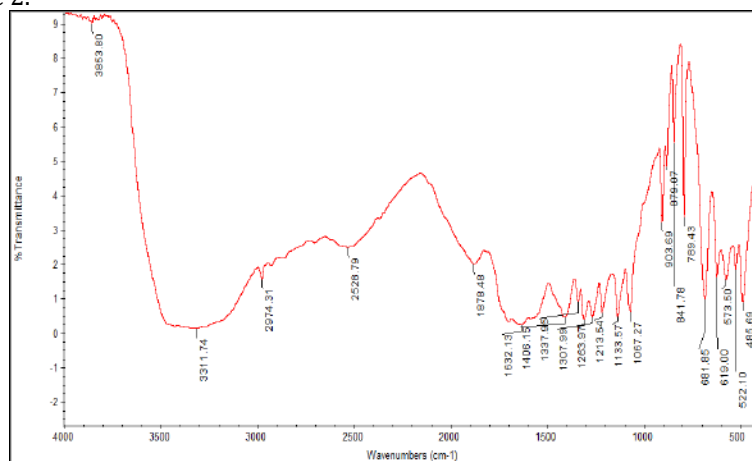


Fig. 3: FTIR spectrum of thiourea doped urea L-tartaric acid crystal

Table 2: FTIR spectral assignments for thiourea doped urea L-tartaric acid crystal

FTIR peaks/bands ( $\text{cm}^{-1}$ )	Assignments
3400-3100	NH <sub>2</sub> and OH stretching
2974	CH stretching
2528	CH stretching
1878	Combination band
1632	C=O stretching of tartaric acid
1406	C-O stretching of urea
1307	CH bending
1263	C-C stretching
1213	C-C stretching
1133	CN stretching
1067	C-O bending
841	C-C bending
573	C-O wagging
522	NH <sub>2</sub> torsion
485	NH <sub>2</sub> rocking

#### 5. Optical transmittance

The UV-visible transmission spectra of the samples were recorded on a SHIMADZU UV-240 IPC spectrophotometer in the range of 190-1100 nm. The transmittance was studied for the cut and polished face of the grown crystals [19]. A crystal of thickness of about 1.2 mm has been used for this study. The

recorded UV-visible transmittance spectra of the grown crystals are presented in the figure 4. From the results, the lower cut-off wavelength for both the samples is observed to be at 242 nm and the percentage of transmission for undoped ULTA crystal is noticed to be about 75% and that for thiourea doped ULTA crystal is observed to be about 70% in the visible region. The spectrum indicates that the crystals have wide optical transmission window. The results indicate that the transmittance for thiourea doped ULTA crystal is less than that of undoped sample.

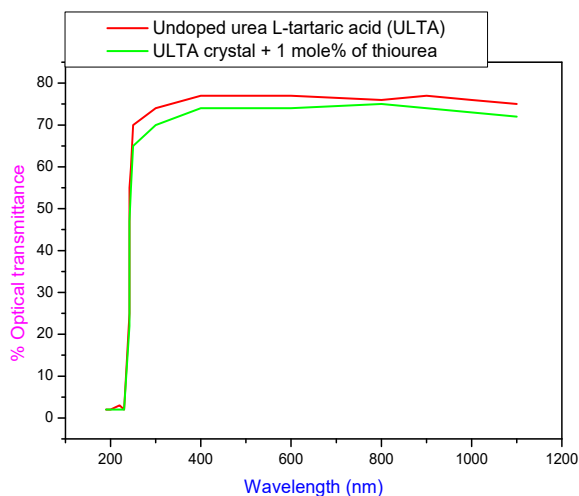


Fig. 4: FTIR spectra of undoped and thiourea doped urea L-tartaric acid crystals

## 6. Second order NLO studies

In order confirm nonlinear optical property, microcrystalline form of pure and thiourea doped ULTA crystals were subjected to Kurtz-Pery test [20]. The powdered sample was illuminated using Spectra Physics Quanta Ray DHS2-Nd: YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repetition rate 10 Hz. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation by the crystal. The SHG radiations of 532 nm green light was collected by a photomultiplier tube and the optical signal incident on the PMT was converted into voltage output at the CRO. Second harmonic output of 26.55 mJ was obtained from the undoped ULTA sample for an input energy of 0.70 J. The powdered potassium dihydrogen phosphate (KDP) was used as the reference material in the SHG measurement and the output was found to be 8.91 mJ. Thus, the relative SHG efficiency for undoped ULTA crystal is found to be 2.97 times that of KDP sample. Similarly, the relative SHG efficiency for thiourea doped ULTA crystal is found to be 3.2 times that of KDP. As given in the table 3, when the SHG values of undoped and thiourea doped ULTA samples are compared with that of urea, it is found that SHG value of undoped ULTA crystal is slightly less than and SHG value of thiourea doped ULTA crystal is slightly more than that of urea. When ULTA crystal is doped with thiourea, it is possible that the SHG efficiency is improved and hence thiourea doped ULTA crystal is better material for NLO applications.

Table 3: Data in connection with SHG measurement for undoped and thiourea doped ULTA crystals

Sl. No.	Name of the Sample	Output Energy (milli joule)	Input Energy (joule)
1	Undoped urea L-tartaric acid (ULTA)	26.55	0.70
2	KDP (Reference)	8.91	0.70
3	Thiourea doped ULTA sample	28.51	0.70
4	Urea	27.76	0.70

## 7. Conclusion

The single crystals of undoped and thiourea doped urea L-tartaric acid were grown by aqueous solution method. The grown crystals were subjected to single crystal XRD studies and it reveals that the grown crystals crystallize in orthorhombic structure. The crystal structure of the thiourea doped ULTA crystal has not been changed when compared to the pure ULTA crystal. Using the absorption peaks/bands of the FTIR spectrum, the functional groups such as  $\text{NH}_2$ ,  $\text{OH}$ ,  $\text{CH}$ ,  $\text{C}=\text{O}$ ,  $\text{C}-\text{N}$ ,  $\text{C}-\text{O}$  etc have been identified. From UV-visible spectra of the samples, the lower cut-off wavelength for both the samples is observed to be at 242 nm and the percentage of transmission for undoped ULTA crystal is noticed to be about 75% and that for thiourea

doped ULTA crystal is observed to be about 70% in the visible region. SHG efficiency for undoped ULTA crystal is found to be 2.97 times that of KDP sample and the relative SHG efficiency for thiourea doped ULTA crystal is found to be 3.2 times that of KDP. Since the samples have high SHG efficiency and high transparency in the visible region, they could be useful for NLO and opto-electronic applications.

### Acknowledgements

The authors like to thank the staff members of various research institutions like Cochin University (Cochin), Crescent engineering college (Chennai), St.Joshph's college (Trichy) for having helped us to collect the research data.

### References

1. D.S Chemla and J.Zyzz, Nonlinear optical properties of organic molecules and crystals Vol 1-2, Academic Press, New York (1987).
2. D.R. Yuan, N.Zhang, X.T. Tao, D.Xu, M.G.Liu, W.B.Hou, Y.H.Bing, J.Crystal Growth 166 (1996)545
3. T. Henningsen, N.B Singh, R.H Hopkins, R. Mazelsky, F.K Hopkins, D.O. Frazier, O.P Singh, Materials Letters 20 (1994) 203.
4. Zheshuai Lin, Zhizhong Wang, and Chungtian Chen, J. Chem. Phys. 118 (2003) 2349.
5. J. M. Halbout, IEEE. Jr. Quantum electron, 15 (1979) 1176-78.
6. W.R. Donaldson and C.L.Tang, Appl. Phy. Lett. 44 (1984) 25-28.
7. T. Raja Lakshmi, R. Danasekaran and P. Ramasamy, J. Materi. Sci. Let. 12 (1993) 1797-99.
8. Chadwick, K. Davey, R., Sadiq, G., Cross, W. and Pritchard, R., Cry. Engg. Comm, 11 (2009) 1412-414.
9. F. Q. Meng, M.K. Lu, Z. H. Yang, and H. Zeng, Mat. Let. 33 (1998) 265-268.
10. E. De Matos Gomes, V. Venkataramanan, E. Nogueira, M. Belsely, E. Proenca, Criado, M.J. Dianez, M.D. Estrada, S. Perez-Garrido, Syn. Metals 115 (2000)25-228.
11. S. Krishnan, C. Justin Raj and S. Jerome Das, J. Crystal Growth 310 (2008) 3313-3317.
12. Suryanarayana K, Dharmaparakash S. M. , Materials Letters 42 (2000)92-96.
13. Aakeroy C. B, Hitchcock P. B, Seddon K. R., J. Chemical Society, Chemical Communications, 115(1992) 553-555.
14. Dixit V. K, Vanishri S, Bhat H. L, de Matos Gomes E, Belsley M, Santinha C. Arunmozhi G, Venkataramanan V, Proena F, Criado A. J. Crystal Growth, 253(2003) 460-466.
15. Meng F. Q, Lu M. K, Chen J, Zhang S. J, Zeng H, Solid State Commun. 101(1997) 925-928.
16. A.S. Haja Hameed, C.W. Lan, J. Crystal Growth 270 (2004) 475.
17. F.Q. Meng, M.K. Lu, H. Zen, Cryst. Res.Tech., 31 (1996) 33-36.
18. P.R.Griffiths and J.A.De Hoseth, Fourier Transform Infrared Spectroscopy, Wiley,Chichester (1986).
19. S.Krishnan, C.Justin Raj, S.Dhinakaran, S.Jerome Das, Cryst. Res. Technol. 43(2008) 670.
20. S.K. Kurtz, T.T. Perry, J. Appl. Phys., 36 (1968) 3798-3813.