

# Growth and Spectroscopic studies of Pure and L-Proline doped ZTS crystal (with Taxol)

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## Abstract

Single crystals of Zinc thiourea sulphate (ZTS) doped with L-Proline were grown by solution growth method at appropriate temperature with Taxol solution. The Fourier transform infrared spectroscopy study confirms the assimilation of L-Proline in the ZTS crystal. The doped crystals are optically better and more transparent than the pure ones. Results are given analysed and discussed.

Keywords: Crystal, X-ray diffraction; Growth from solutions; ZTS; Nonlinear optic materials, Taxol.

## 1. Introduction

In modern era several studies with organic, inorganic and semi organic molecules and materials acknowledged as nonlinear optics (NLO) are studied and also reported.

The nonlinear (NLO) responses in molecules in solution and solids are of superior importance in many fields of research (1, 6). Thiourea molecules have noticing inorganic material specifications due to its large dipole moment and they are capable to form and extensive association of hydrogen bonds (8). The nonlinear optical properties of some of the multifaceted thiourea, such as Tris (thiourea) cadmium sulphate, potassium thiourea

bromide have significant consideration (13, 16 & 25), because both organic and inorganic components in it throw in specifically implied to the process of second harmonic generation (SHG). The centro symmetric thiourea molecule, when mingled with inorganic salt yield NLO complexes (3). Hence, center of attention is only on new types NLO materials which combined the advantages of organic and inorganic material called semi organic materials.

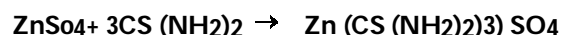
Two types of semi organic material include organic and inorganic salts and metal organic coordination complexes (13,14, 17, 18, 19, 21 & 22). Zinc (Tris) thiourea sulphate (ZTS) is a good nonlinear optical semi organic material for second harmonic generation. ZTS has wide range of transparency and low dielectric constant at elevated frequencies (5).

ZTS possesses orthorhombic structure with Pca21 space group (15). The growth and various studies of doped and undoped ZTS crystals have been reported in a number of publications (4, 7, 9, 10, 12, 20, & 24). In this paper we report the results of our work on the growth of pure and (L-Proline) doped ZTS crystal along with the characterization by X-ray diffraction (XRD), FTIR, UV-Visible and NLO studies.

## 2. Experimental

### 1. Synthesis and Crystal Growth

The ZTS salt was synthesized by dissolving high purity AR grade Zinc sulphate and thiourea in the ratio 1:3 in water. The solution was stirred by a magnetic stirrer. White crystalline ZTS salt was attained instantaneously. ZTS salt was produced according to the reaction (2).



Single crystals of ZTS and L-Proline doped ZTS were grown solution growth techniques at room temperature (32°C - 35°C). Transparent colorless ZTS crystals of size 15 x 13 x 2 mm<sup>3</sup> were grown in 17-18 days. For the growth of L-Proline doped ZTS crystals, 1 mol percent of L-Proline was added to the solution of ZTS with Taxol. Single crystals of size 11 x 9 x 2 mm<sup>3</sup> with good transparency were grown in 31 -34 days as shown in Figure 1.

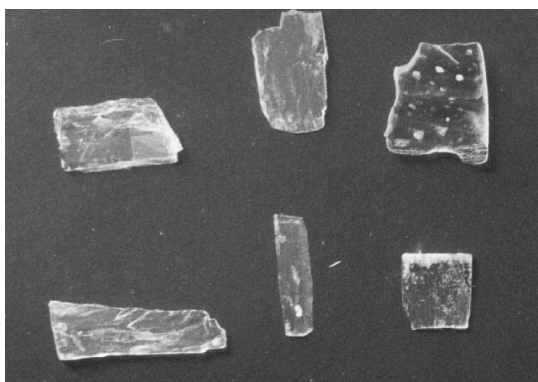


Fig 1. The photograph of grown pure ZTS and L-Proline doped ZTS crystals

### 3. Characterisation

The grown crystals have been analyzed by different categorization techniques. The grown single crystal of pure and amino acid doped ZTS with Taxol was confirmed by single crystal X-ray diffractometer (5). The functional groups were identified by using Fourier Transform Infrared spectrophotometer. The optical properties of the crystals were examined using UV-Vis spectrometer.

#### 3.1. Single XRD Studies

The single X-ray diffraction studies have been carried out to confirm the crystalline nature and to determine the crystal parameters of the grown ZTS. From the XRD data

it is observed that both pure and doped L-Proline crystals are orthorhombic in nature. The calculated crystal parameter values of pure and L-Proline doped ZTS are presented in table 1. In the case of doped sample, a slight variation in the cell volume is pragmatic.

**Table 1. Single-crystal XRD data:  
Pure and L-Proline doped ZTS crystals**

	Pure ZTS	L-Proline doped ZTS
Cell parameters a	7.797 Å	7.790 Å
b	11.144 Å	11.152 Å
c	15.512 Å	15.518 Å
	$\alpha = \beta = \gamma = 90^\circ$	
Volume	V= 1348 Å <sup>3</sup>	V= 1349 Å <sup>3</sup>
System	Orthorhombic	
Space group	Pca21	---

#### 3.2. UV Studies

The UV-VIS spectrum analysis has been evaluated using UV-Vis spectrophotometer. The UV-VIS spectrum gives restricted information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron from the ground state to higher energy states. Optical transmission spectrum of the ZTS was recorded. The recorded optical transmission spectrum was shown in Figure 2. The transmittance is found to be upper limit in the entire visible and IR regions.

When we consider the percentage of transmission we detect that for all L-Proline doped ZTS crystals the transmission has been increased to nearly 75% in the visible region. From the spectrum it is observed that the transmittance percentage of L Proline

doped ZTS is 15-18 % higher than that of the pure grown crystal. The crystal shows a superior transmittance in the intact visible region (16).

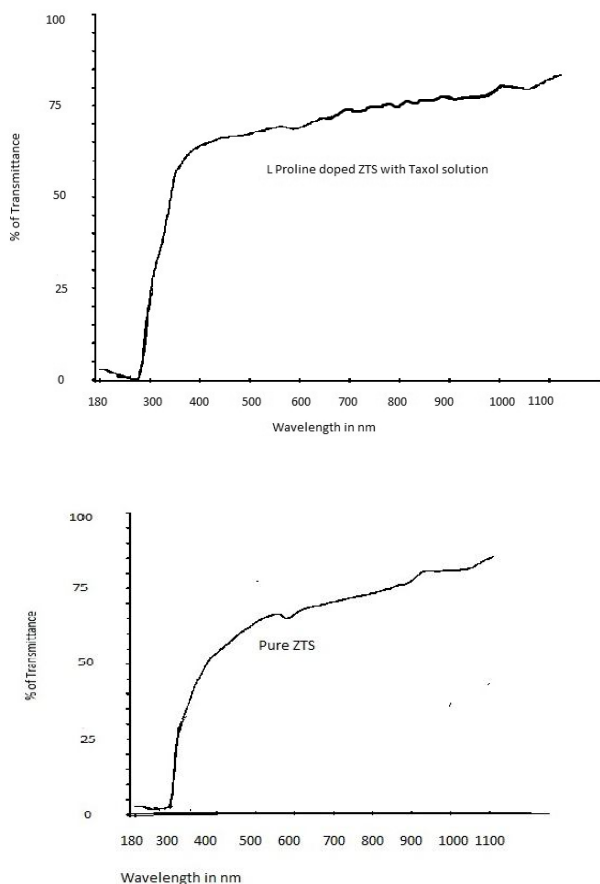


Fig 2. UV Vis spectra for the pure and L-Proline doped ZTS

### 3.3 FTIR studies

FTIR spectrum of pure and L-Proline doped ZTS crystal was found using Fourier Transform Infrared (FTIR) spectrometer. The recorded FTIR spectrum of pure and L-Proline doped ZTS crystal is shown in Figure 3. The broad band lies in the range 2710 – 3400  $\text{cm}^{-1}$  corresponds to symmetric and asymmetric vibrations of

$\text{NH}_2$  group. Very strapping absorption at 950  $\text{cm}^{-1}$  is owing to sulphate ion. The FTIR spectra of doped crystals show a strong NH absorption peak at about 3200  $\text{cm}^{-1}$ . When ZTS is doped with L-Proline more NH stretch vibrations are pioneer due to doping and as a result the NH absorption peak becomes strapping. So FTIR spectra indirectly ascertain the presence of L-Proline in the ZTS crystal.

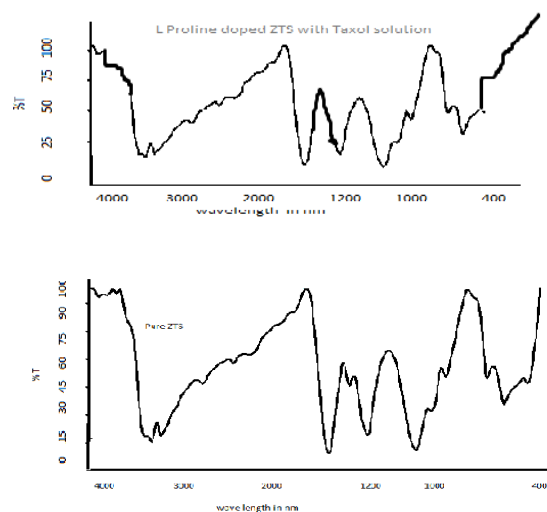


Fig 3. FTIR spectra of pure and L-Proline doped ZTS

### 3.4 Second Harmonic Generation Efficiency (SHG)

The second harmonic generation (SHG) conversion efficiency of ZTS was measured by powder Kurtz system (11). The crystal was grounded into a fine powder and compactly crammed between two transparent glass slides. Nd: YAG laser emitting a fundamental wavelength of 1064 nm was allowed to smack the sample cell specification. The SHG output 546 nm (green light) was finally detected. The powdered material of potassium dihydrogen phosphate (KDP) was used in the experiment as a reference material. Second harmonic generation efficiency of the doped L-Proline crystal almost same as the pure ZTS. ZTS material

is nearly 1.2 times more nonlinear than KDP one (23).

#### 4. Conclusion

Good optical quality pure ZTS and L-Proline doped ZTS with Taxol single crystals have been grown by solution growth method at room temperature. The lattice parameters have been found by single crystal X-ray diffraction technique. The FT-IR spectrum elucidates that the various functional groups present in the grown crystal. The optical absorption spectrum specifies that the absorbance is less than one unit between 300 and 1200 nm. This indicates the absence of any overtones or combination modes above 250 nm and absorbance due to electronic transition between 300 and 1100 nm (24,25).

The studies on the NLO property confirmed the second harmonic conversion efficiency of the crystal to be better than KDP by nearly 1.2 times. Taxol has thermal and spectroscopic (fluorescence, IR, NMR, and circular dichroism) analyses provided evidence of complex formation that was stable in the solid state but weak in solution, suggesting an explanation for the observed precipitation on dilution.

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#### Profile

I am K.Senthil Kannan M.Sc (Gold medalist), M.Phil, B.Ed, P.G.D.C.A., M.B.A., M.A., D.C.H., C.I., (Ph.D) and passed SLET (UGC) in the first attempt and having more than 6 years of research experience and more than one decade of

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Published two books and more Papers in National and International level.

#### 6.REFERENCES

1. Aggarwal, M.D., Choi, J., Wang, W.S., Bhat, K., Lal, R.B., Shield, A.D., Penn, B.G., Frazier, D.O. J.Crystal Growth 204 (1999)179.
2. Andreetti, G.D., Cavalca, L., Musatti, A. Acta Crystallogr, sect. B 24 (1968) 683.
3. Anie Roshan, S., Joseph, C., Ittachen, M.A. Matter.Lett.49 (2001)299.
4. Dhumane, N.R., Hussaini, S.S., Dongre, V.G., Mahendra, Shirsat, D. Optical Materials, Volume 31, Issue 2, October-December 2008, Pages 328-332.
5. Dhumane, N.R., Hussaini, S.S., Nawakhele, V.V., Shirsat, M.D. Cryst. Res. Technol. 41 (2006)897.
6. Elmert, D., Velsko, S., Davis, L., Wang, F., Loiaceono, G., Kennedy, G. IEEE. J. Quantum Electron. 25 (1989) 179.
7. Gupte Sonal S. Pradhan Ranjit D. J Appl Phys 2002;91:3125-8.
8. Hellwege, K.H., Hellwage, A.M. Landolt-Bornstein Group I I 14 (1982) 584.
9. Krishnan, C., Selvarajan, P., Freeda, T.H. Journal of Crystal Growth, Volume 311, Issue 1, 15 December 2008, Pages 141-146.
10. Krishnan, C., Selvarajan, P., Freeda, T.H., Mahadevan, C.K. Physica B: Condensed Matter, Volume 404, Issue 2, 28 February 2009, and Pages289-294.
11. Kurtz, S.K., Perry, T.T., J. Appl. Phys., 39 (1968) 3798.
12. Marcy Ho, Warren LF, Webb MS, Ebberts CA, Velsko SP, Kenndy GC, et al. J Appl Opts 1992; 31: 5051-60
13. Marcy, H.O., Warren, L.F., Hebb, M.S., Ebberts, C.A., Visko, S.P., Kennedy, C.G. J. Appl.Opt. 31 (1992) 5051.
14. Meera, K., Muralidharan, R., Dhanasekaran, R., Prapun Manyum, Ramasamy, P. J.cryst. Growth 263 (2004)510.



15. Oussaid, M., Becker, P., Carabatos Nedelac, C.  
Phys. Status Solidi B 207 (1998) 499.
16. Oussaid, M., Becker, P., Kemiche, M. C.  
Carabatos-Nedlec, Phs. Stat. Sol.B 207 (1998) 103.
17. PricillaJeyakumari, A., Ramajothi, J.,  
Dhanuskodi, S., J.Cryst.Growth 269 (2004)558.
18. Rajasekaran, R., Ushasree, P.M., Jayavel, R.,  
Ramasamy, P. J.cryst. Growth 229 (2001)563.
19. Ramajothi, J., Dhanuskodi, S., Nagarajan, K.  
Cryst. Res. Technol. 39 (2004) 414.
20. Sumil Verma, Singh Wadhawan, MK. Suresh,  
VK., Pramana, CH. J Phys 2000; 54:879-88.
21. Sun, H.Q., Yuan, D.R., Wang, X.Q., Cheng,  
X.F., Gong, C.R., Zhou, M., Xu, H.Y., Wei,  
X.C., Luan, C.N., Pan, D.Y., Li, Z.F., Shi, X.Z.  
Cryst.Res. Technol. 40 (2005) 882.
22. Ushasree, P.M., Muralidharan, R., Jayavel,  
R., Ramasamy, P. J. Cryst. Growth 218 (2000) 365.
23. Ushasree, P.M., Muralidharan, R., Jayavel,  
R., Ramasamy, P. J. Cryst. Growth 210 (2000) 741.
24. Venkataramanan V. Subramanian CK. Bhat HL. J  
appl Phys 1995; 77:6049-51.
25. M. Lawrence, Dr. J. Thomas Joseph Prakash  
International Journal of Computer Applications  
0975 – 8887, Volume 8, October 2010.