



PHYSICS

## EFFECT OF L-ALANINE ON THE OPTICAL PROPERTIES OF ZINC (TRIS) THIOUREA SULFATE (ZTS) SINGLE CRYSTAL

N.R. Dhumane, S.S. Hussaini, Kunal Datta, Prasanta Ghosh and Mahendra D. Shirsat\*

*Intelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad -431 004(MS) India*

### Abstract

The growth of L-Alanine doped Zinc (tris) Thiourea Sulfate single crystal from aqueous solution by low temperature solution growth has been reported in the present investigation. The 1, 2 and 3mole% L-Alanine was doped in saturated ZTS solution. The effect of L-Alanine on SHG property was studied by Kurtz and Perry powder SHG test. The higher enhancement in SHG efficiency was observed at 1mole% L-Alanine doped ZTS. Hence, the growth 1mole% L-Alanine doped ZTS was carried. The grown crystal was characterized by single crystal X-ray analysis, FT-IR, UV-visible spectroscopy and thermal study by TGA and DSC analysis.

**Keywords:** Crystal growth; Low temperature solution growth; Semi organic NLO material; L-Alanine

### Introduction

The modern world is witnessing revolutionary advancements in the various aspects of science and technology. Every new day is suppressing its predecessor by some new achievements that require novel ideas leading towards the exploration of new materials for emerging fields, which were hitherto unknown. Over past two decades, there has been remarkable interest in growth and characterization of nonlinear optical material crystals [1-6]. It is widely accepted that NLO material plays a major role in applications such as telecommunications, optical data storage and optical information processing [5-8]. Second order nonlinear optical materials are used in optical switching, frequency conversion and electro-optical applications especially in Electro Optical modulators [9-10]. In addition to large second order susceptibilities, good transmission in UV and visible region and stable physico thermal performance are needed for these applications [11-12]. Inorganic NLO materials have large mechanical strength, thermal stability and good transmittance, but modest optical nonlinearity due to the lack of extended  $\pi$ -electron dislocation [13-15]. Purely organic NLO material have large nonlinearity compared to inorganic material but low optical transparency, poor mechanical and thermal strength and low laser damage threshold [16]. Thus the research is focused on semi organic NLO material crystal in order to obtain superior NLO crystal by combining the advantages of organic and inorganic materials. The semi organic NLO materials have been attracting much attention due to high nonlinearity, chemical flexibility, high mechanical and thermal stability and good transmittance [16].

Zinc (tris) Thiourea Sulfate (ZTS) is a promising semi-organic NLO material for second harmonic generation from metal complexes of thiourea. ZTS is 1.2 times more nonlinear than KDP [17-19]. ZTS possesses orthorhombic structure with space group  $Pca2_1$  [20, 21]. Most of the amino acids individually exhibit the NLO property. A  $\alpha$ -amino acid consists of an amino group, a carboxyl group, a hydrogen atom and a distinctive R group (side chain), all of which bonded to a  $\alpha$ -carbon. This tetrahedral array of four different groups about  $\alpha$ -carbon confers optical activity on amino acid. Amino acids in solution at neutral pH are predominantly dipolar ions (or zwitterions) rather than unionized molecules. In dipolar form of an amino acid, the amino group is protonated ( $-NH_3^+$ ) and the carboxyl group is dissociated ( $-COO^-$ ). Alanine is simplest amino acid having only methyl group as its side chain [22].

The effects of several dopants on structural and physical properties of metal complexes of thiourea and KDP have been reported [19, 23, and 24]. Semiorganic nonlinear optical (NLO) crystals formed by amino acids with inorganic materials possess the advantages of high optical nonlinearity of the organic amino acids.

In the present investigation ZTS has been doped with various molar percents of amino acid, L-Alanine, in order to improve its SHG efficiency so that it can be used as better alternative to pure ZTS for optoelectronics applications. The L-Alanine was added in 1, 2 and 3mole% in ZTS and compound salts were subjected to Kurtz Perry powder test, it was observed that the SHG efficiency of 1mole% L-Alanine doped ZTS is 1.74 times more than pure ZTS. Therefore, the 1mole% L-Alanine doped ZTS crystal was grown by low temperature solution growth, slow evaporation

\* Corresponding Author, *Email:* mdshirsat\_bamu@yahoo.co.in, Tel.: +91-240-2403385, Fax: +91-240-2403113

technique at the temperature of 32°C. The X-ray diffraction study shows orthorhombic structure of grown crystal. The presence of different functional groups in the grown crystal after addition of L-Alanine was analyzed by FTIR analysis. The optical studies were carried out using the UV-Visible analysis. The grown crystal has also been subjected to Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

## Experimental

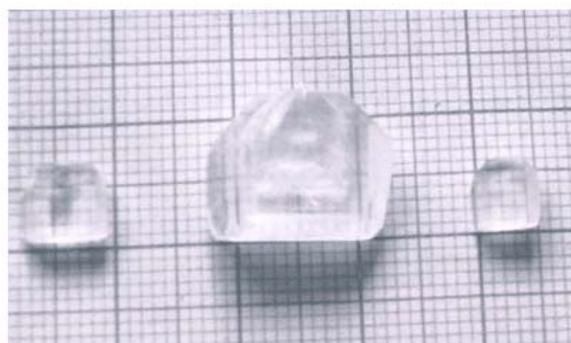
### Synthesis

ZTS salt was synthesized by dissolving AR grade zinc sulfate and thiourea in deionized water. The synthesized salt was purified by repeated re-crystallization. Saturated solution of ZTS was prepared at room temperature in three different beakers and 1, 2 and 3mole% of L-Alanine was added in these three beakers respectively. The synthesized salt was tested for SHG by Kurtz and Perry powder test. We observed enhancement of SHG efficiency in ZTS when it is doped with L-Alanine. The enhancement of SHG efficiency was higher for 1mole% L-Alanine doped ZTS. Hence 1mole% L-Alanine doped ZTS crystal was grown by low temperature solution growth method.

### Crystal growth

The synthesized salt of 1mole% L-Alanine doped ZTS was dissolved in deionized water. The purity of salt was obtained by repeated re-crystallization. A super saturated solution of 1mole% L-Alanine doped ZTS was prepared at 32°C by constant stirring up to five to six hours and then filtered by whatmann filter paper. Then this solution was loaded in constant temperature bath with an accuracy  $\pm 0.01^\circ\text{C}$  set at 32°C. After twenty four hours the good quality transparent seed obtained from same solution was suspended in beaker containing solution by nylon thread. Slow evaporation technique was employed for growth of bulk crystal. A good quality transparent crystal was harvested within 23 days. Figure 1 shows the photograph of grown crystal.

Figure 1: Photograph of Grown Crystals



## Characterizations

Initial testing for enhancement of SHG property was studied by Kurtz and Perry powder SHG test at Department of Inorganic and Physical chemistry, Indian Institute of Science, Bangalore. The grown crystal was characterized by various characterization viz. single crystal X-ray analysis, FT-IR analysis, UV-visible spectral study and thermal study by TGA and DSC.

## Results and Discussion

### SHG Measurement

The study of NLO conversion efficiency of grown crystal has been carried out in accordance with the classical powder method developed by Kurtz and Perry [25]. It is an important and popular tool to evaluate the conversion efficiency of NLO materials. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 4.5 mJ, and a pulse width of 8 ns with a repetition rate of 10 Hz were used. The crystals of 1, 2 and 3mole% L-Alanine doped ZTS was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect the intensity of 532nm component, and to eliminate the fundamental wavelength. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube. The generation of second harmonic was confirmed by the emission of green light. A sample of ZTS, also powdered to the same particle size as the experimental sample, was used as a reference material for the present measurement. The SHG conversion efficiency of L-Alanine doped ZTS was found to be enhanced than that of pure ZTS. The optical signal generated from sample is converted into electrical signal and was measured on oscilloscope. The measured output for pure ZTS and 1, 2, 3mole% L-Alanine doped ZTS were 35mV, 61mV, 55mV and 57mV respectively. This indicates that SHG conversion efficiency of 1mole% L-Alanine doped ZTS is greater than pure ZTS and other molar concentrations of L-Alanine in ZTS. Thus the maximum enhancement in SHG efficiency is 1.74 times than that of pure ZTS for 1mole% L-Alanine doped ZTS crystal. The enhancement in SHG efficiency of L-Alanine doped ZTS is due to the optically active amino group which may get added in the structure and increases its non-Centro symmetry and hence increasing its SHG efficiency.

### Single crystal x-ray diffraction analysis

To determine unit cell parameter Single crystal X-ray diffraction analysis was carried out by Brukers Axs (Kappa Apex) diffractometer. The observed unit cell parameters are  $a = 11.159 \text{ \AA}$ ,  $b = 7.792 \text{ \AA}$ ,  $c = 15.527 \text{ \AA}$ , cell volume =  $1350.2 \text{ \AA}^3$  and  $\alpha = \beta = \gamma = 90^\circ$ . The

crystal belongs to orthorhombic system with space group  $Pca2_1$ . From single crystal X-ray analysis it is confirmed that dopant does not changes the basic structure of crystal [19, 21]. The slight increase in unit cell volume may be due to change in pH of the solution due to the addition of amino acid [20].

**FT- IR spectral studies**

The FTIR analysis was carried out by Perkin Elmer Spectrum FTIR spectrometer by KBr pallet technique in the range  $450-4000\text{cm}^{-1}$ . The FT-IR spectra of pure ZTS and 1mole% L-Alanine doped ZTS is shown in Figure 2 and Figure 3 respectively. In ZTS complex, there are two possibilities by which the coordination with metal can occur. It may be either through nitrogen or through sulfur. From spectra, the N-H absorption bands in the high frequency region in thiourea were not shifted to lower frequencies on formation of metal thiourea complex, thus coordination of thiourea occurs through sulfur in ZTS [19, 20]. The NH, C=S and N-C-N stretching vibrations were also seen. The comparison shows slight shift in characteristic vibrational frequencies of 1mole% L-Alanine doped ZTS with respect to pure ZTS [26]. This confirms the addition of L-Alanine in grown crystal.

Figure 2: FTIR Spectra of Pure ZTS Crystal

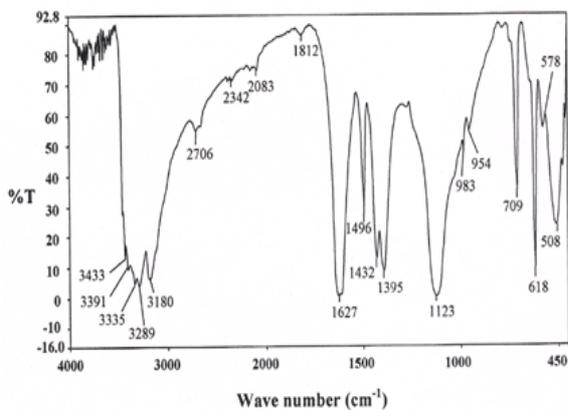
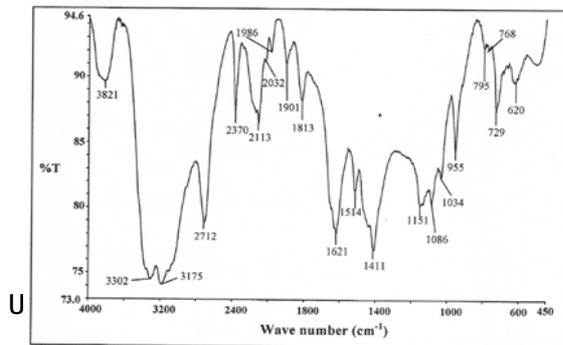


Figure 3: FTIR Spectra of L-Alanine doped ZTS Crystal



carried out by Shimadzu UV 1600 UV-vis. spectrometer in a range 200 nm to 1100 nm. The absorption spectrum of 1mole% L-Alanine doped ZTS

is shown in Figure 4. The window in Figure 4 shows UV spectrum of pure ZTS for comparison. The absorption spectrum reveals that the crystal has lower cutoff wavelength at around 290 nm. The absorption near UV region is associated electron with transition within thiourea units of ZTS. Doping of 1mole% L-Alanine in ZTS does not destroy the transparency of the crystal. From spectra it has also been observed that the lower cutoff wavelength is almost the same for L-Alanine added ZTS and pure ZTS crystals [27]. The wide range of transparency in UV, visible and IR region enables good transmission of the second harmonic frequencies of Nd: YAG laser. This is an added advantage in the field of optoelectronic applications.

**Thermal analysis**

The chemical decomposition, phase transition temperature, melting point and the weight loss of the grown crystals were determined by means of thermo gravimetric analysis and differential scanning calorimetry. The thermo gravimetric analysis (TGA) was carried out by using TAQ-500 analyzer in the temperature range 25 - 800°C at a heating rate 25°C / min. The thermo gram is shown in Figure 5. The TGA trace shows the different stages of decomposition. The first stage of decomposition starts at 183.93°C and at about 292.97°C it appears to be the major stage of decomposition. But there is no weight loss below 183.93°C, hence the crystal is completely devoid of any entrapped solvent in the lattice of the crystal. This clearly indicates that the material can be exploited for NLO application up to 183.93°C. The DSC analysis of 1mole% Alanine doped ZTS was carried out between 40°C and 220°C in nitrogen inert atmosphere. The DSC curve is shown in Figure 6. From the differential scanning calorimetric curve (DSC) it was confirmed that there is no phase transition for the material up to temperature range 40°C to 183.93°C.

Figure 4: UV visible Spectra of L-Alanine doped ZTS Crystal

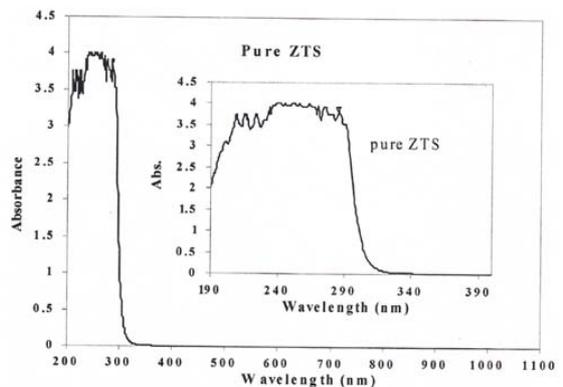


Figure 5: TGA Thermogram of L-Alanine doped ZTS Crystal

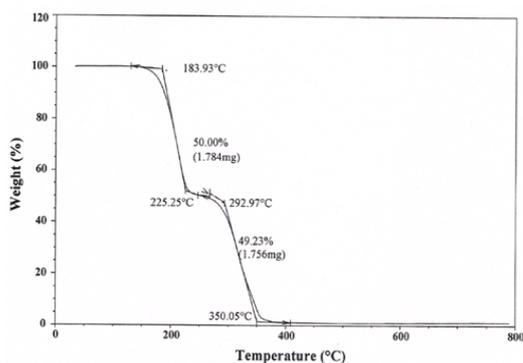
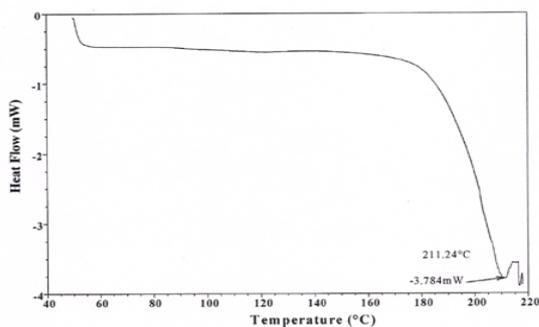


Figure 6: DSC curve of L-Alanine doped ZTS Crystal



## Conclusions

The L-Alanine doped ZTS crystal was grown from solution by slow evaporation technique. The Kurtz and Perry powder SHG test shows that 1mole% L-Alanine doped ZTS has SHG efficiency 1.74 times that of pure ZTS. Single crystal X-ray diffraction confirms that there is no change in basic structure of ZTS. FT-IR study confirms the presence of all functional groups. UV-visible study shows that grown crystal has wide range of transparency in UV and entire visible region. TGA analysis shows that the grown crystal has very good thermal stability up to 183.93°C. Thus the 1mole% L-Alanine doped ZTS crystal is going to play vital role in the field of optoelectronics and laser technology.

## Acknowledgment

The authors are thankful to the University Grants Commissions, New Delhi, India for providing financial assistance. We thank Prof. P. K. Das, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore (India), Dr. Babu Varghese, SAIF, Indian Institute of Technology, Chennai (India) for extending their facilities for characterizing the crystal.

## References

1. D. Prem Anand, M. Gulam Mohamed, S.A. Rajasekar, S. Selvakumar, A. Joseph Arul Pragasam, P. Sagayaraj, *Mater. Chem. Phys.* 97 (2006), 501- 505.

2. M.D. Shirsat, S.S. Hussaini, N.R. Dhumane, V.G. Dongre, *Cryst. Res. Technol.* 43 (2008), 756 –761.
3. S.S. Hussaini, N.R. Dhumane, V.G. Dongre, P. Karmuse, P. Ghughare, M.D. Shirsat, *J. Opt. Elect. Adv. Mater. (Rapid Commun.)* 1 (2007), 707- 711.
4. S.S. Hussaini, N.R. Dhumane, V.G. Dongre, P. Karmuse, P. Ghughare, M.D. Shirsat, *J. Opt. Elect. Adv. Mater. (Rapid Commun.)* 2 (2008), 108- 112.
5. K. Meera, R. Muralidharan, R. Dhanasekaran, Manyum Prapun, P. Ramasamy, *J. Cryst. Growth.* 263 (2004), 510 - 516.
6. R. Mohan Kumar, D. Rajan Babu, D. Jayaraman, R. Jayaval, K. Kitmura, *J. Cryst. Growth.* 275 (2005), e1935 - e1939.
7. Pricilla Jeyakumari, J. Ramajothi, S. Dhanuskodi, *J. Cryst. Growth.* 269 (2004), 558 -564
8. A.S. Haja Hameed, C.W. Lan, *J. Cryst. Growth.* 270 (2004), 475 – 480.
9. S.S. Hussaini, N.R. Dhumane, V.G. Dongre, M.D. Shirsat, *J. Materials Science-Poland* 27 (2009), 365- 372.
10. Shaokang Gao; Weijun Chen; Guimei Wang; Jianzhong Chen, *J. Cryst. Growth.* 297(2006), 361- 365
11. P. Joseph Ginson, J. Philip, K. Rajarajan, S.A. Rajasekar, A. Joseph Arul Pragasam, K. Thamizharasan, S.M. Ravi Kumar, P. Sagayaraj, *J. Cryst. Growth.* 296 (2006), 51 – 57.
12. P. M. Ushasree, R. Muralidharan, R. Jayavel, P. Ramasamy, *J. Cryst. Growth.* 210 (2000), 741 – 745.
13. H.Q. Sun, D.R. Yuan, X.Q. Wang, X.F. Cheng, C.R. Gong, M. Zhou, H.Y. Xu, X.C. Wei, C.N. Luan, D.Y. Pan, Z.F. Li, X.Z. Shi, *Cryst. Res. Technol.* 40 (2005), 882 – 886.
14. J. Ramajothi, S. Dhanuskodi, K. Nagarajan, *Cryst. Res. Technol.* 39 (2004), 414 – 420.
15. S. Aripnammal, S. Radhika, R. Selva, N. Victor Jeya, *Cryst. Res. Technol.* 40 (2005), 786 – 788.
16. Min-hua Jiang; Qi Fang, *Adv. Mater.* 11(1999), 1147- 1151
17. M. Oussaid, P. Becker, M. Kemiche, C. Carabatos-Nedelec, *Phys. Stat. Sol. (b)* 207(1998), 103 – 110.
18. P.M. Ushasree, R. Jayaval, C. Subramanian, P. Ramasamy, *J. Cryst. Growth.* 197(1999), 216- 220.
19. P.M. Ushasree, R. Jayaval, P. Ramasamy, *Mater. Sci. Eng. B* 65 (1999), 153 – 158.
20. P.M. Ushasree, R. Jayaval, P. Ramasamy, *Mater Chem Phys.* 61 (1999), 270 - 274.
21. G. Arunmozhi, M. de E. Gomes, S. Ganesamoorthy, *Cryst. Res. Technol.* 39 (2004), 408 - 413.
22. Lubert Stryer. *Biochemistry*, W. H. Freeman and Company: New York 1995.

23. V. Kannan, R. Bairava Ganesh, R. Sathyalakshmi, N.P. Rajesh, P. Ramasamy, *Cryst. Res. Technol.* 41(2006), 678 – 682.
24. S.Selvakumar, Julius J. Packiam, S.A. Rajasekar, A. Ramanand, P. Sagayaraj, *Mater. Chem. Phys.* 89 (2005), 244-248.
25. S.K. Kurtz, T.T. Perry, *J. Appl. Phys.*39 (1968), 3798 – 3813.
26. Mary P. Angeli, S. Dhanuskodi, *Cryst. Res. Technol.* 36 (2001), 1231-1237.
27. N.R.Dhumane, S.S.Hussaini, V.V.Nawarkhele, M.D. Shirsat, *Cryst. Res. Technol.* 41 (2006), 897 –901.