



## A study on the growth and characteristic properties of L-Arginine doped ZTS single crystal

J. Felicita Vimala<sup>1</sup> and J. Thomas Joseph Prakash<sup>2,\*</sup>

<sup>1</sup>Department of Physics, DIET, Mayanur, Karur, Tamilnadu, India.

<sup>2</sup>Department of Physics, H.H. The Rajah's College, Pudukkottai-1, Tamilnadu, India.

### ARTICLE INFO

#### Article history:

Received: 16 January 2013;

Received in revised form:

5 March 2013;

Accepted: 5 March 2013;

#### Keywords

Growth from solutions;

Second harmonic Generation;

Nonlinear optical (NLO) materials;

Amino acids doped ZTS.

### ABSTRACT

In order to get good-quality crystals, method of slow evaporation was adopted to grow pure and L-Arginine doped Zinc (tris) Thiourea sulphate (ZTS) single crystals. The grown crystals are semiorganic non linear in nature whose lattice parameter values were found out using single x-ray diffraction analysis. The different functional bond frequencies associated with the crystals, decomposition temperature, and weight loss were found out from Fourier transform infra-red (FTIR) spectroscopic analysis, differential thermal analysis (DTA), and thermo-gravimetric analysis (TGA) respectively. The optical behavior, mechanical stability and etching nature were also analysed. The SHG efficiency of the grown crystals was measured through NLO studies.

© 2013 Elixir All rights reserved.

### 1. Introduction

Crystal growth is a frontier area of science and technology, which plays a major role in the technology of photonics. Rare earth complexes have distinct properties such as optical, electrical and magnetic and are closely related to their electronic configurations. Such materials act as a new type of functional materials having potential use in the fields of photoluminescence, electro-luminescence, laser, etc. Non-linear optical (NLO) materials have received constant attention due to the practical application in the field of optoelectronics. The NLO properties of some complexes of thiourea have attracted significant attention because both organic and inorganic components in it contribute specifically to the process of SHG [1-3]. The nonlinear optical properties of some complexes of thiourea [4-6] have gained significant attention in the last few years. The centrosymmetric thiourea molecule, when combine with inorganic salt yield non symmetric complexes, which has the nonlinear optical properties [7].

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 [8-10]. ZTS possesses orthorhombic structure with space group Pca21 [11, 12]. The effects of several dopants on structural and physical properties of metal complexes of thiourea have been reported [10, 13]. Most of the amino acids individually exhibit the NLO property. In solid state, amino acid exists as dipolar ion in which carboxyl group is present as carboxylate ion. Due to this dipolar nature, amino acids have a physical property which makes them ideal candidates for NLO applications [14]. Semiorganic nonlinear optical (NLO) crystals formed by amino acids with inorganic materials possess the advantages of high optical nonlinearity of the organic amino acids. A series of studies on amino acid doped semiorganic compounds [15-17] as potential NLO crystals have been

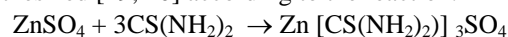
reported. The effect of the addition of L-Arginine in ZTS has been already reported [18].

In the present investigation ZTS has been doped with L-Arginine, in order to improve its SHG efficiency so that it can be used as better alternative to pure ZTS for optoelectronics applications. The L-Arginine 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-Arginine doped ZTS is very much higher than pure ZTS. Therefore, the 1mole% L-Arginine doped ZTS crystal was grown by slow evaporation technique at room temperature and its characterization and findings have been reported.

### 2. Experimental

#### 2.1. Crystal growth

Slow evaporation technique was employed for the growth of ZTS crystals. The Raw material for the growth of ZTS was synthesized by dissolving high purity AR grade Zinc sulphate and thiourea in the molar ratio 1:3 in de-ionized water. The solution was stirred by magnetic stirrer. ZTS salt was synthesized [19, 20] according to the reaction:



The component salts were well dissolved in de-ionized water and it was thoroughly mixed using a magnetic stirrer and the mixture was heated at 50°C till a white crystalline salt of ZTS was obtained. Temperature was maintained at 50°C to avoid decomposition. To synthesize L-Arginine doped ZTS crystals, the parent material (ZTS) was recrystallized and 1mol % of L-Arginine was added to the solution of ZTS separately and the same procedure was followed as for undoped ZTS crystal. Transparent colorless ZTS crystals of size 14 × 12 × 2 mm<sup>3</sup> were harvested in 18 days and L-Arginine doped ZTS crystals of size 7 × 6 × 2 mm<sup>3</sup> with good transparency were harvested in 30 days as shown in Fig.1(a) and Fig.1(b).



Fig. 1(a) The Photograph of Pure ZTS crystal



Fig. 1(b) The Photograph of L-Arginine doped ZTS crystal

### 3. Characterizations

The grown crystals were characterized by various characterizations viz. single crystal X-ray analysis, FT-IR analysis, UV-visible spectral study, thermal study by TGA and DTA, Vickers hardness study and etching analysis. The enhancement of SHG property was confirmed by Kurtz and Perry powder SHG test.

#### 3.1. X-ray diffraction analysis

To confirm the crystallinity and to determine the lattice parameters of the grown samples the single crystal X-ray diffraction study has been carried out using ENRAF NONIUS CAD4 diffractometer. The structure was solved by the direct method using SHELXL program. From the XRD data it is observed that both pure and L-Arginine doped ZTS crystals are orthorhombic. The calculated lattice parameter values of the grown crystals are presented in table 1. The results of the present work are in good agreement with the reported values [18]. In the case of doped sample, a slight variation in the cell volume is observed.

**Table 1**  
Single-crystal xrd data of pure and l-arginine doped zts crystal

Pure ZTS	L-Arginine doped ZTS
a = 7.797 Å	a = 7.796 Å
b = 11.144 Å	b = 11.129 Å
c = 15.512 Å	c = 15.489 Å
$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$
V = 1348 Å <sup>3</sup>	V = 1344 Å <sup>3</sup>
Orthorhombic	Orthorhombic
Space group-Pca2 <sub>1</sub>	Space group-Pca2 <sub>1</sub>

#### 3.2. FTIR studies

FTIR spectrum of pure and L-Arginine doped ZTS crystals was recorded using KBr pellet technique in the frequency region 400-4000 cm<sup>-1</sup> using PERKIN ELMER RX1 Fourier Transform Infrared spectrometer. The recorded spectrum is shown in Fig.2(a) and 2(b). In the FTIR spectrum of ZTS, the intensity 3190.23 cm<sup>-1</sup> is due to N-H stretching vibration of the NH<sub>2</sub> group of thiourea. The C=S stretching vibrations occurs at 1622.01 cm<sup>-1</sup>. The peaks at 1505 and 1402.09 cm<sup>-1</sup> are due to NH<sub>2</sub> bending vibration. C-N vibration is a peak at 1121.35 cm<sup>-1</sup>. The peaks at 709.41 and 470.32 cm<sup>-1</sup> are tentatively assigned to Zn-S vibrations. So, the crystal is devoid of covalent bonded water to Zinc.

In the FTIR spectrum of L-Arginine doped ZTS, the intensity 3191.64 cm<sup>-1</sup> is due to N-H stretching vibration of the NH<sub>2</sub> group of thiourea. The C=S stretching vibrations occurs at 1627.07 cm<sup>-1</sup>. The peaks at 1502.43 and 1403.17 cm<sup>-1</sup> are due to NH<sub>2</sub> bending vibration. C-N vibration is a peak at 1116.96 cm<sup>-1</sup>. The peaks at 712.15 and 480.43 cm<sup>-1</sup> are tentatively assigned to Zn-S vibrations. So the L-Arginine doped ZTS crystal is devoid of covalent bonded water to Zinc. The spectrum of L-Arginine doped ZTS displays nearly similar features as that of ZTS. An examination of the peak position illustrates substantial shifts for the peaks as shown in Table 2. This is the clear indication for the presence of amino acid, L-Arginine in the lattice of ZTS crystal.

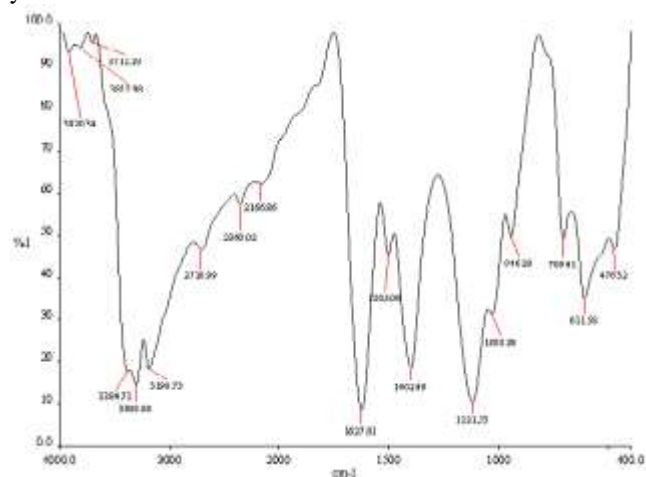


Fig.2(a). FTIR Spectrum of ZTS crystal

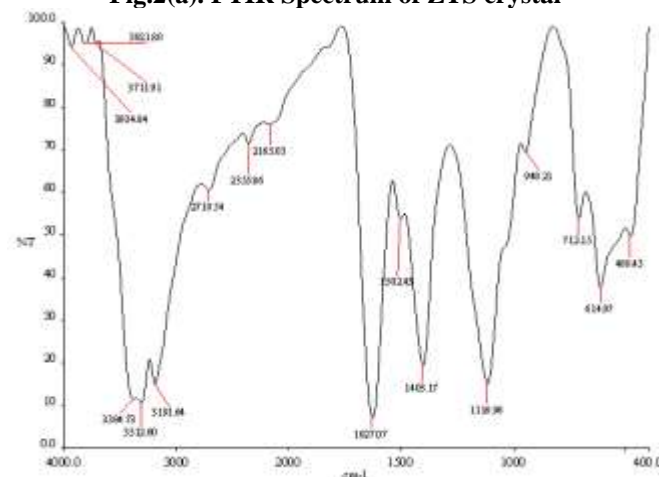


Fig.2(b). FTIR Spectrum of L-Arginine doped ZTS crystal

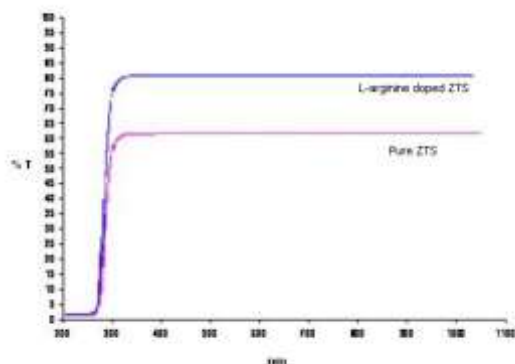
**Table 2**  
FTIR data comparison of pure and l-arginine doped ZTS single crystal

Pure ZTS (cm <sup>-1</sup> )	L-Arginine doped ZTS (cm <sup>-1</sup> )	ASSIGNMENT
3190.23	3191.64	N-H stretching
1622.01	1627.07	C=S stretching
1505	1502.43	NH <sub>2</sub> bending
1402.09	1403.17	NH <sub>2</sub> bending
1121.35	1116.96	C-N vibration
709.41	712.15	Zn-S vibrations
470.32	480.43	Zn-S vibrations

#### 3.3. Optical studies

To find the transmission range of the grown samples, the UV-Visible spectrum analysis has been carried out using LAMBDA-3 UV-Vis spectrophotometer in the wavelength

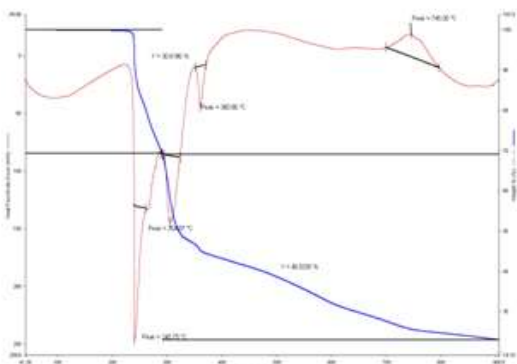
range of 200-1200 nm. The recorded spectrum is shown in Fig.3. The transmittance is found to be maximum in the entire visible and infrared regions. When we consider the percentage of transmission we observe that for L-Arginine doped ZTS crystals the transmission has been increased from 60% to 80% in the visible region. From the spectrum it is observed that the transmittance percentage of doped ZTS crystal is 20% higher than that of the pure grown crystal. The lower cutoff at 270 nm for both pure and doped ZTS crystals attest the usefulness of this material for optoelectronic applications and the second harmonic generation of the Nd:YAG laser.



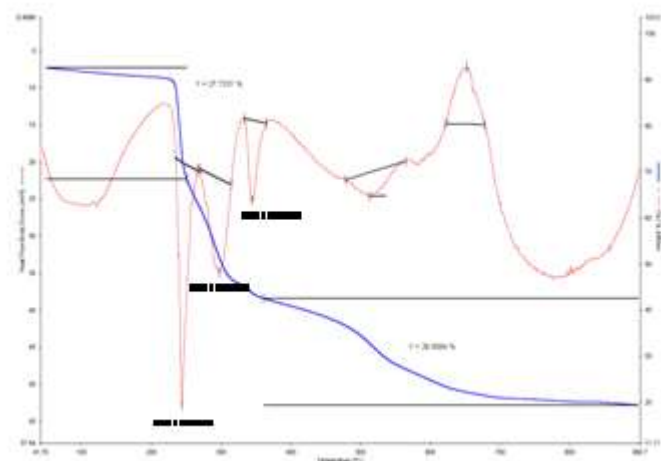
**Fig.3 UV-Vis spectrum of ZTS and L-arginine doped ZTS crystal**

### 3.4. Thermal Analysis

The weight loss and thermal stability of the samples were analysed by using TAQ-500 analyser at a heating rate of 25°C/min for temperature range 50 to 900°C in nitrogen inert atmosphere. The recorded thermograms are shown in Fig.4(a) and Fig.4(b). It reveals that in the case of L-Arginine doped ZTS crystals, the weight loss of about 27.72% takes place in the region 249.25°C and 309.42°C and for pure ZTS crystals weight loss of about 30.62% takes place in the region 240.75°C and 304.87°C. There is no weight loss upto 100°C, ensuring the absence of water in the crystal structures. The first weight loss is due to decomposition of both the compounds and the second weight loss is due to organic compound evaporation and liberation of volatile substances like sulphur dioxide [21]. The sharpness of the endothermic peak shows good degree of crystallinity of the grown crystal. In the DTA curve the first endothermic peak has been observed at 249.25°C for L-Arginine doped ZTS crystal and at 240.75°C for pure ZTS crystal. The doped crystal is more stable than pure ZTS crystal. Comparing the melting points of pure and doped crystals, it is evident that both the grown crystals are stable upto 240°C and are best suitable for NLO applications.



**Fig.4(a) Thermogram of pure ZTS Crystal**



**Fig.4(b) Thermogram of L-Arginine doped ZTS Crystal**

### 3.5. SHG efficiency measurement

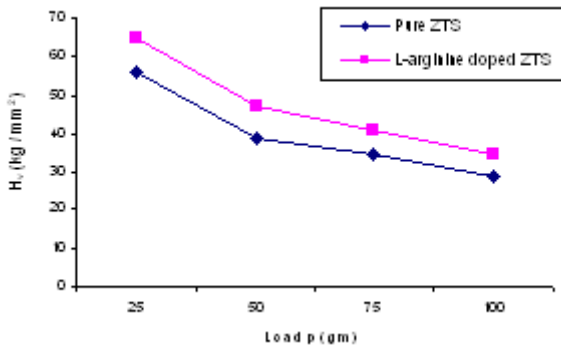
The second harmonic generation (SHG) conversion efficiency of the grown crystals was measured by Kurtz and Perry powder technique [22]. The grown crystals were ground into fine powder and densely packed between two transparent glass slides. A Q switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm, pulse energy 3 mJ/pulse, pulse width 8 ns and repetition rate 10HZ was allowed to strike the sample cell. The emission of green light confirmed the SHG efficiency of pure and doped ZTS crystals. The optical signal generated from the sample was recorded using an oscilloscope. The measured outputs were 28mV and 51mV for pure ZTS L-Arginine doped ZTS crystals. KDP was used as the reference material with SHG efficiency of 21mV. Since, the SHG efficiency of the doped crystal is 1.82 times higher than pure ZTS and 2.42 times higher than KDP, the L-Arginine doped ZTS crystal is best suitable for NLO applications.

### 3.6. Microhardness measurement

Measurement of hardness is a non-destructive testing method to determine the mechanical behaviour of the materials. The Vicker's hardness value was calculated using the formula

$$H_v = \frac{(1.8544 * P)}{d^2} \text{ kg/mm}^2$$

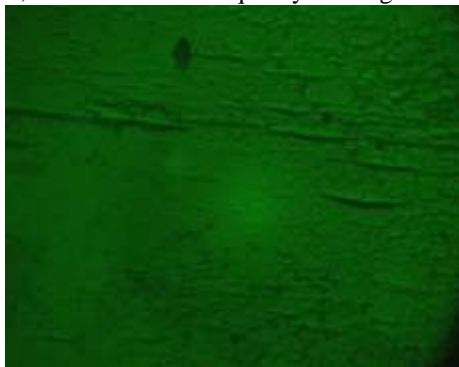
where  $H_v$  is the Vickers microhardness number,  $P$  is the applied load in kg and  $d$  is the diagonal length of the indentation impression in micrometer. The study was carried out using a LEITZ microhardness tester fitted with a Vickers diamond pyramidal indenter. A well polished crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied over a fixed interval of time. The indentation time was kept (10s) for all the loads. A graph has been plotted between hardness number ( $H_v$ ) and applied load ( $P$ ) as shown in Fig.5(a) and 5(b). In both pure and L-Arginine doped ZTS crystals the hardness decreases gradually with the increase of load and at higher concentration of impurity the hardness tends to saturate. This is because, in the solid state, L-Arginine exists as zwitterions. So, introduction of L-Arginine in the crystal lattice of ZTS creates ionic vacancy. All these defects, act as obstacles to dislocation motion, thus decreasing the hardness of the crystals. At higher concentration of impurity, the impurity-vacancy associates into larger aggregate. So, hardness saturates at higher concentration of impurity.



**Fig. 5 Plot of Load Vs Hardness of ZTS and L-Arginine doped ZTS crystal**

### 3.7. Etching Studies

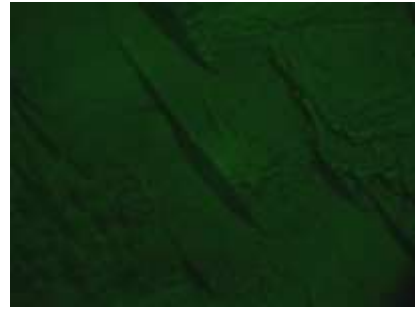
The crystal defects were revealed using chemical etching. Etching study on L-Arginine doped ZTS crystal was carried out using water as etchant. Etch pits were observed on the (1 0 0) plane when etched with water for 5, 10 and 15 secs. The capability of revealing etch pits by a solvent on different faces depends on the crystallographic orientation and hence corresponds to the symmetry of the crystal face on which the pit is produced. Using a Magnus MLX Microscope the features of the crystal has been analyzed which is shown in the Fig.6(a),6(b) and 6(c). From the figures, number of etch pits have been identified with identical shape. By increasing the etching time, the size and number of etch pits varies. The etch pits can be attributed to the initial dislocations formed at low angle boundaries or segregated impurities. When the crystal was etched for 10secs, well defined etch pits were observed rather than for 5 secs. Minimum patterns were observed for 15 secs etching time, which ensures the quality of the grown crystals.



**Fig.6(a) (5 secs)**



**Fig.6(b) (10 secs)**



**Fig.6(c) (15 secs)**

**Fig. 6(a, b & c) Etching photographs of L-Arginine doped ZTS crystal**

### 4. Conclusion

Good optical quality pure ZTS and L-Arginine doped ZTS single crystals have been grown by slow evaporation method. The lattice parameters have been found out by single crystal X-ray diffraction technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The optical absorption spectrum reveals that the absorbance is less between 300 and 1100 nm. This illustrates the absence of any overtones or combination modes above 270nm and absorbance due to electronic transition between 300 and 1100nm. The Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. Hardness measurement shows that L-Arginine doped crystals are much harder than pure ZTS crystals. TG and DTA curves show that both the crystals are stable upto 240°C. The studies on the NLO property confirmed the second harmonic conversion efficiency of the crystals to be better than KDP. The crystal perfections and quality have been identified by using etching studies.

### References

- [1] R. Rajasekaran, P. M. Ushashree, R. Jayavel, P. Ramasamy, *J. Cryst. Growth*, 229 (2001) 63.
- [2] P. M. Ushashree, R. Jayavel, C. Subramanian, P. Ramasamy, *J. Cryst. Growth*, 218 (2003) 365.
- [3] S. Anie Roshan, Joseph Cyriac, M. A. Ittyachen, *Mater. Lett.*, 49 (2001) 299.
- [4] A. Pricilla Jeyakumari, J. Ramajothi, S. Dhanuskodi, *J. Cryst. Growth*, 269 (2004) 558–564.
- [5] M. Oussaid, P. Becker, C. Carabatos Nedelac, *Phys. Status Solidi.*, B 207 (1998) 499.
- [6] M. Daniel, M. Jeyarani Malliga, R. Sankar, D. Jayaraman, *Mater. Chem. Phys.*, 114 (2009) 18–22.
- [7] S. Anie Roshan, C. Joseph, M. A. Ittachen, *Mater. Lett.*, 49 (2001) 299.
- [8] M. Oussaid, P. Becker, M. Kemiche, C. Carabatos-Nedelec, *Phys. Stat. Sol. (b)* 207(1998), 103-110.
- [9] P. M. Ushashree, R. Jayaval, C. Subramanian, P. Ramasamy, *J. Cryst. Growth*, 197(1999), 216-220.
- [10] P. M. Ushashree, R. Jayaval, P. Ramasamy, *Mater. Sci. Eng. B* 65 (1999), 153-158.
- [11] P. M. Ushashree, R. Jayaval, P. Ramasamy, *Mater Chem Phys*, 61 (1999), 270-274.
- [12] G. Arunmozhi, M. de E. Gomes, S. Ganesamoorthy, *Cryst. Res. Technol.* 39 (2004), 408-413.
- [13] V. Kannan, R. Bairava Ganesh, R. Sathyalakshmi, N. P. Rajesh, P. Ramasamy, *Cryst. Res. Technol.* 41(2006), 678-682.
- [14] K. Ambujam, K. Rajarajan, S. Selvakumar, I. Vetha Potheher, Ginson P. Joseph and P. Sagayaraj, *J. Cryst. Growth*, 286 (2006) 440.
- [15] M. Lawrence, J. Thomas Joseph Prakash, *Spectrochimica Acta Part A*, 91 (2012) 30– 34.

- [16]N. R. Dhumane, S. S. Hussaini, Kunal Datta, Prasanta Ghosh J. and Mahendra D. Shirsat, Pure Appl. & Ind. Phys., Vol.1(1), 45-52 (2010).
- [17]J. Thomas Joseph Prakash, M. Lawrence, International J.of Computer Appls. (0975-8887) Volume 8– No.3, October 2010.
- [18]Moitra, Sweta Kar, Tanusree, Optical Materials, Volume 30, Issue 3, p. 508-512, November 2007.
- [19]M. Oussaid, P. Becker, M. Kemiche, C. Carabatosnedelec, Phys. Status Solidi B, 207 (1998) 103.
- [20]P. M. Ushasree, R. Jayavel, P. Ramasamy, Mater. Chem. Phys., 61 (1999) 270.
- [21]J. Ramajothi, S. Dhanuskodi, K. Nagarajan, Cryst. Res. Technol., 2004; 39: 414–20.
- [22]S. K. Kurtz, T. T. Perry, J. Appl. Phys., 39 (1968) 3798.