Growth, structural, optical and thermal studies of L-Threonine added Zinc(Tris) Thiourea Sulphate single crystals

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Single crystals of Zinc tris-thiourea Sulphate (ZTS) and L-Threonine added Zinc tris-thiourea Sulphate were grown from aqueous solution by slow evaporation method. The cell parameters of the grown crystals were estimated by single crystal X-ray diffraction technique. The powder X-ray diffraction patterns were recorded and indexed for further confirmation of crystalline nature of grown crystals. The presence of functional groups has been confirmed by FTIR analysis. The UV-Vis absorption spectra have been recorded to find the cut-off wavelength. The TGA/DTA and DSC studies show the thermal behavior of the grown crystals. Microhardness study on the crystal samples revealed that the hardness number (H_v) increases with applied load for all the grown crystals. The second harmonic generation of ZTS and L-Threonine added ZTS crystals was observed by Kurtz Perry powder method using Nd:YAG laser. The crystal perfection and quality have been identified by etching studies.

(Received December 1, 2011; accepted February 20, 2012)

Keywords: Crystal growth; Crystal structure; X-ray Diffraction; Nonlinear material

1. Introduction

The search for efficient and new materials on nonlinear optical processes has been very active since the discovery of second harmonic generation (SHG) in quartz crystal by Franken et al [1]. Nonlinear optical (NLO) materials are expected to play a major role in photonics including optical information processing, telecommunication sensor protector applications, optical data storage, etc. Some organic compounds exhibit large NLO response, in many cases, order of magnitude larger than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. In this stimulating context, organic nonlinear materials have been recognized as forefront candidate for fundamental and applied investigations involving, in a joint effort, chemists, material scientists and optical engineering [2-6]. Over past two decades, there has been remarkable interest in growth and characterization of nonlinear optical material crystals [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 physio-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 π-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 in organic 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 possess 1.2 times more nonlinear efficiency than KDP [17-19]. ZTS belongs orthorhombic crystal structure with space group$Pca2_1$ [20, 21]. Most of the amino acids individually exhibit the NLO property due to donor amino group NH^{3+} and acceptor carboxyl group COO^- and intermolecular charge transfer is also possible [20]. Therefore, amino acids can be used as dopants and it was observed that there is enhancement in the material properties such as nonlinear and ferroelectric properties [3]. L-Threonine is an important polar aminoacid, which shows higher SHG than other amino acids [22]. The effect of several dopants on structural and physical properties of metal complexes of thiourea and KDP has been reported [19, 23, 25]. Semi-organic nonlinear optical (NLO) crystals are formed by amino acids with inorganic materials possess the advantages of high optical nonlinearity of the organic amino acids [26]. In the present investigation, ZTS has been added with amino acid L-Threonine, in order to improve its SHG efficiency, so that they can be used as better alternative to pure ZTS for optoelectronics applications. In the present study, ZTS and 1mole% L-Threonine added ZTS were synthesized and bulk crystals were grown by slow evaporation method. Also the grown crystals have subjected to various characterizations such as single crystal X-ray diffraction, Powder XRD, FTIR, UV/Visible spectroscopy, Microhardness and etching studies. The TGA, DTA and Differential scanning calorimetry (DSC) analyses and Kurtz-Perry powder test also performed on the grown crystals.

2. Experimental

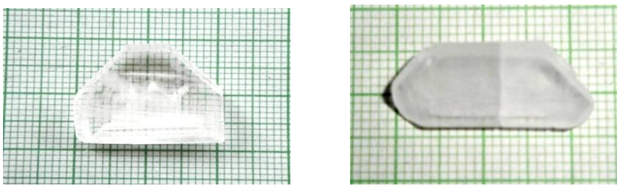
2.1. Synthesis and crystal growth

ZTS salt was synthesized by stoichiometric incorporation of Analar grade Thiourea (99% Merck) and zinc sulfate heptahydrate (99% Merck). The thiourea and zinc sulfate heptahydrate were taken in the ratio 3:1 and the calculated amounts of thiourea and zinc sulfate heptahydrate were dissolved in the double distilled water of resistivity 18 MΩcm (Millipore). The ZTS compound was prepared according to the following reaction,

$$3CS(NH_2)_2 + ZnSO_4.7H_2O \rightarrow Zn[CS(NH_2)_2]_3SO_4 + 7H_2O$$

The synthesized substance was purified by the repeated recrystallization process. A saturated growth solution was prepared and kept at room temperature for slow evaporation. Good quality single crystal with regular shape and size 20×18×6 mm^3 was harvested within 20 days with approximate growth rate of 0.5 mm/day. For the growth of

L-Threonine added ZTS crystals, 1 mole% of L-Threonine ($C_4H_9NO_3$) was added to the ZTS solution and single crystal of size 21×10×7 mm^3 with good transparency was obtained as shown in the Fig. 1.



(a) (b)

Fig. 1. Photographs of (a) pure ZTS and (b) L- Threonine added ZTS crystals.

3. Material characterization

The grown crystals were subjected to single crystal XRD studies using a Kappa ApexII Nonius CAD4 diffractometer with MoK$_\alpha$ radiation (λ=0.71073 Å) to determine unit cell dimension. The powder XRD pattern of the grown crystal was recorded between 10°–80° in steps of 2° employing CuK$_\alpha$ radiation(λ=1.5406 Å) using Bruker Germany Powder X-ray Diffractometer. The optical absorption spectra of the grown crystals were recorded using Perkin Elmer Lambda 35 Model UV-Visible spectrophotometer in the wavelength region 200–900 nm. The FTIR spectra of pure and L-Threonine amino acid added ZTS were recorded by Alpha Bruker spectrometer using KBr pellet technique in the wavelength range 4000–400 cm^{-1}. The nonlinear property in ZTS and L-Threonine added ZTS compounds was confirmed by shining Nd: YAG laser of wavelength 1064 nm. The qualitative measurement of the second harmonic conversion efficiency was determined using powder technique developed by Kurtz and Perry. In order to estimate the thermal behaviour, simultaneous thermo gravimetric analysis and differential thermal analysis of pure and L-Threonine added ZTS were carried out using Universal V4.5A TA instruments, Model : Q600 SDT Thermal Analyzer in the temperature range: RT to 800°C (SiC furnace) and DSC was carried using TA–Q20 Differential Scanning Calorimeter. The microhardness studies were carried out on the grown crystals using Vicker's Microhardness tester attached with an optical microscope (Micro-Duromet 4000E Hardness apparatus). Optical microscope in the reflection mode was used to observe the etch patterns on the (100) plane of the grown crystals.

4. Results and discussion

4.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction analysis of pure and 1mol% L-Threonine added ZTS crystals were carried out and their respective lattice parameter values are presented in the Table 1.

Table 1. Lattice parameter values of the grown crystals.

Crystal	a(Å)	b(Å)	c(Å)	V(Å^3)	α = β = γ
Pure ZTS	11.14	7.77	15.50	1341.6	90°
L-Threonine added ZTS	11.12	7.76	15.44	1332.3	90°

Pure and 1mole% of L-Threonine added ZTS crystals belong to orthorhombic system with space group $Pca2_1$. The decrease in unit cell volume may be attributed to the replacement of some units of thiourea molecule with

L-Threonine molecule in the crystal lattice of ZTS. These values are very close to the corresponding JCPDS (76-0778) values of pure ZTS with very nominal changes due to doping [6].

4.2. Powder X-ray diffraction analysis

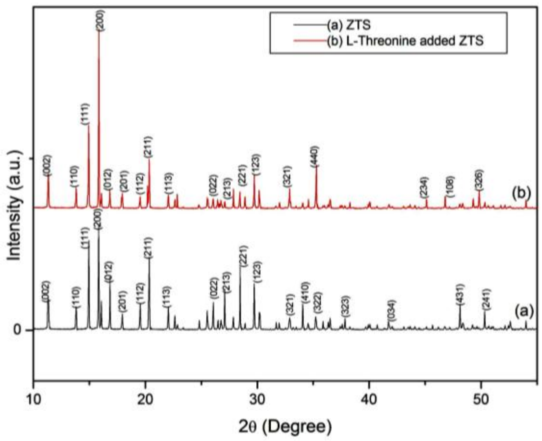


Fig. 2. Powder XRD patterns of (a) pure ZTS and (b) L-Threonine added ZTS.

Powder XRD pattern of L-Threonine added ZTS crystal is compared with that of pure ZTS crystal (Fig.2). The Bragg's reflections were indexed for pure and doped ZTS crystals using the cell parameters. The Diffraction Curves show some interesting features. They consist of a set of prominent peaks corresponding to (002), (111), (200), (012), (211), (113), (221), (321), (034), (431) and (241) planes. In the L-Threonine added ZTS, the peak intensities of reflections (200), (321) and (440) have been increased with doping, the peak intensities of reflections (012),(211), (113), (022) and (221) have been reduced with doping. The peaks (034) and (431) are disappeared in the doped system and few new peaks (440), (234), (108) and (326) are also appeared due to doping. Comparing the powder XRD patterns of pure and L-Threonine added crystals,there is a small shift in the doped XRD pattern of ZTS. This confirms the incorporation of L-Threonine in the ZTS crystal lattice. The observed values are in good agreement with the reported values [6]. From single crystal X-ray analysis, it is confirmed that dopant does not changes the basic structure of crystal [18,21]. The slight change in unit cell volume may be due to change in pH of the solution due to the addition of amino acid [20].

4.2. FTIR studies

The FTIR analysis was carried out using Alpha Bruker FTIR spectrometer by KBr pellet technique in the range 400-4000 cm^{-1}. The FT-IR spectra of pure ZTS and 1mole% L-Threonine added ZTS are shown in Fig. 3(a) and Fig. 3(b) respectively. In the 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 broad band lying in the range 2710–3377 cm^{-1} corresponds to symmetric and asymmetric vibrations of NH_2 group. The NH_2 bending vibration is observed at 1625 cm^{-1} [18]. The symmetric and asymmetric C=S stretching vibrations are observed in the bands 713 cm^{-1} and 1400 cm^{-1}. The absorption at 1502 cm^{-1} arising out due to N-C-N stretching vibration. The presence of sulphate ion is confirmed by the absorption band at 618 cm^{-1} and 1115 cm^{-1} [14]. The other characteristic vibrational frequencies are assigned in Table 2. So FTIR spectra indirectly establish the presence of L-Threonine in the lattice of ZTS crystal.

Table 2. Comparison of IR bands of 1mole% L-Threonine added ZTS with pure ZTS crystals.

ZTS Wavenumber cm^{-1}	1mole% L-Threonine added ZTS Wavenumber cm^{-1}	Assignments
478.00	480.50	δ_s(C-S-N)
619.04	618.84	ν_{as}(N-C-S)
713.03	712.92	ν_s(C=S)
1115.22	1116.09	ν_s(C-N)
1400.39	1400.07	ν_{as}(C=S)
1502.78	-	ν(N-C-N)
1626.09	1625.49	δ(NH_2)
3195.80	-	ν_s(NH_2)
3321.43	3313.78	ν_s(NH_2)

ν-stretching, **δ**-bending, ***s***-symmetric, as-asymmetric.

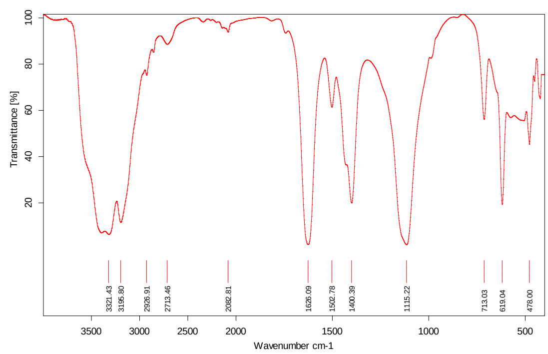


Fig. 3(a). FTIR Spectrum of pure ZTS crystal.

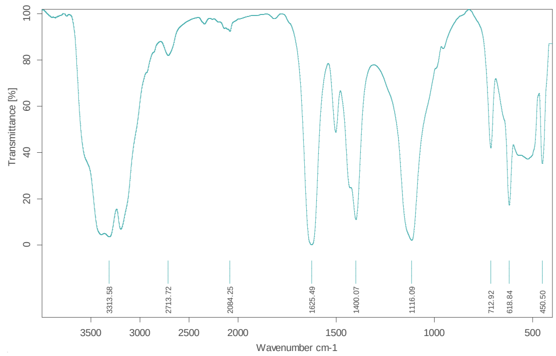


Fig. 3(b). FTIR Spectrum of L-Threonine added ZTS crystal.

4.3 UV–Visible spectral analysis

The single crystals are mainly used for optical applications. Thus the study of optical transmission range of grown crystal is important. The optical absorption spectra were recorded using Perkin Elmer Lambda 35 UV-Visible spectrophotometer in the wavelength region 200–900 nm with high resolution. The absorption spectra show the grown crystals have lower cutoff wavelengths at around 268 nm. Near the UV region, absorption arises from electronic transition associated within the thiourea units of ZTS. The orbital P electron delocalization in thiourea arises from the mesomeric effect. This P electron dislocation is responsible for its nonlinear optical response and absorption in near UV region [27]. Thus grown crystal has good transmission in UV as well as in visible regions. The wide range of transparency of grown crystal is an added advantage in the field of optoelectronic applications [28]. The absorption spectrum of pure ZTS and 1mole% L-Threonine added are shown in Fig. 4. Both the crystals are having same cut off wavelength at 268 nm. It concludes that the adding of L-Threronine in ZTS is not affecting the cut off wavelength and optical transmission property of pure ZTS [18,19,25]. The wide range of transparency in UV, visible and IR regions enables good transmission of the second harmonic frequency of Nd:YAG laser. This is an added advantage in the field of optoelectronic applications.

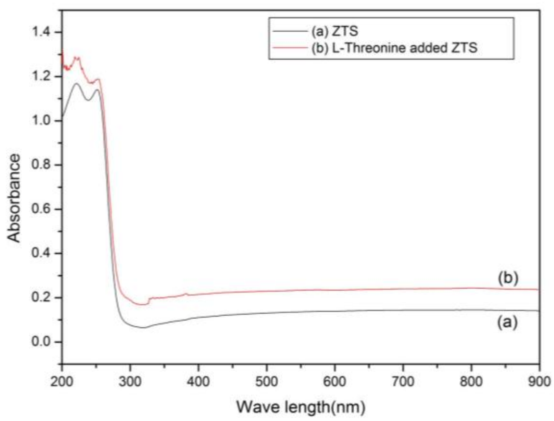


Fig. 4. UV-Visible absorption spectra of (a) pure ZTS and (b) L-Threonine added ZTS crystals.

4.4 Thermal analysis

4.4.1Thermo gravimetric analysis

The chemical decomposition, phase transition temperature, melting point and the weight loss of the grown crystals were determined by thermo gravimetric analysis and differential scanning calorimetry. The thermo gravimetric analysis (TGA) was carried out by using Universal V4.5A TA instruments, Model: Q600 SDT Thermal Analyzer in the temperature range 25 °-800 °C at a heating rate of 25 °C /min. The experiment was performed in nitrogen atmosphere. DTA curve of ZTS shows that pure ZTS melts at 239.72 ºC which is also confirmed by the earlier report [27]. There is a sharp endothermic transition at 249.27 ºC. Further endothermic peaks are observed at 300 ºC and 359.81 ºC. The TGA curve shows that the sample undergoes a complete decomposition between 230 ºC and 800 ºC. The weight loss in the temperature range 231 ºC–280 ºC is due to the liberation of volatile substances like sulphur oxide in the compound [14]. The melting point of L-Threonine added ZTS is found to be at 236.90 ºC. When L-Threonine is added with ZTS, the melting point of ZTS is decreasing slightly. There is no major weight loss up to 234 ºC. So the crystal is thermally stable up to 234ºC. It is observed that there is maximum weight loss in the temperature range 236.90 ºC–348.47 ºC compared with subsequent stages. A total weight loss of about 60.8 % occurs only at 600 ºC. This shows the thermal stability of the crystal. A weight loss about 75 % of pure ZTS occurs at 630 ºC. It concludes that the thermal stability of ZTS decreasing with doping of L-Threonine. There is no phase transition till the material melts, this increases the temperature range for the use of crystal in NLO application. The absence of water in molecular structure is confirmed by the absence of weight loss around 100 ºC. There is no decomposition up to melting point, this insures thermal stability of material for possible application in lasers. Fig. 5 shows TGA-DTA curve of (a) pure ZTS and (b) L-Threonine added ZTS crystal.

4.4.2 Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) of pure and L-Threonine added ZTS crystals were carried out in nitrogen inert atmosphere between 0 and 700 ºC. The DSC trace shows exactly the same change as shown by thermo gravimetric analysis. From the study of both thermograms it is clear that the melting point of grown crystals are 249.27 ºC for pure ZTS and 236.90 ºC for L-Threonine added ZTS respectively.

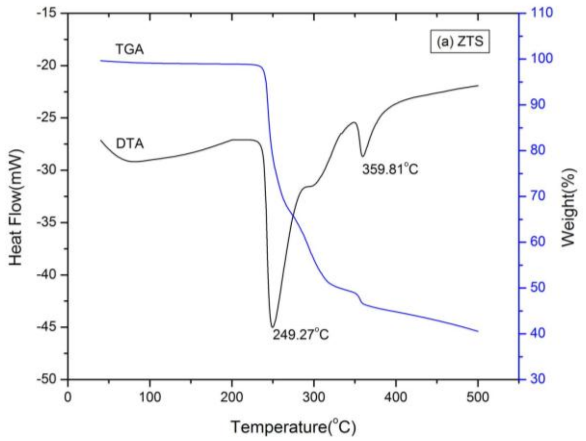


Fig. 5(a). TGA-DTA curve of pure ZTS.

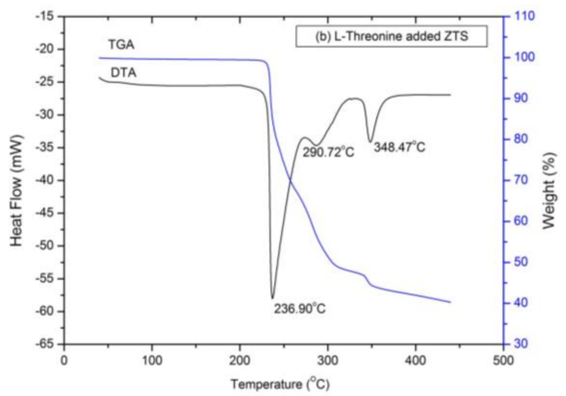


Fig. 5(b). TGA-DTA curve of L-Threonine added ZTS.

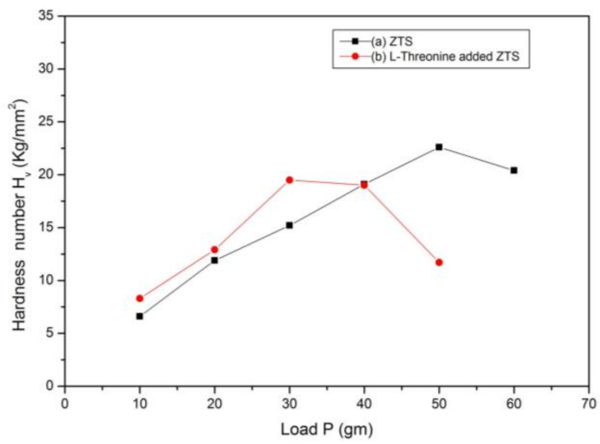


Fig. 6. Plot of Vicker's Hardness number against load of pure and L-Threonine doped crystals.

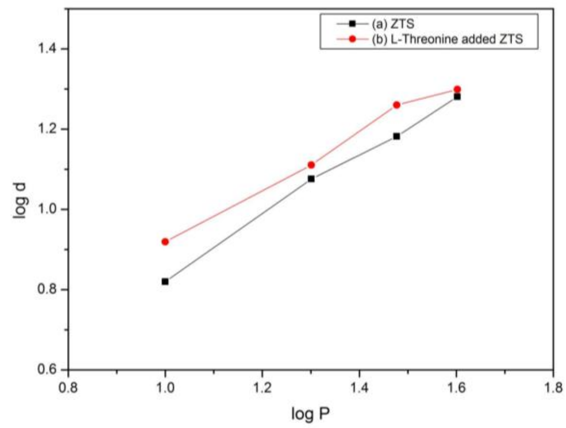


Fig. 7. Plot of log P against log d.

4.5. Microhardness studies

Hardness of a material is a measure of its resistance it offers to local deformation. In this study, indentations were made on (100) plane of pure and aminoacid added ZTS crystals using a Vicker's indenter for various loads with dwell time 3s. For each load, several indentations were made and the average diagonal length (d) was measured to calculate the microhardness using the following relation,

$$H_v = 1.8544\ P/d^2 \quad Kg/mm^2$$

where H_v is the Vicker's hardness number, P is the applied load in kg and d is the diagonal length of the indented impression in mm. A plot drawn between Hardness value H_v and load P is shown in the Fig. 6.

The relation between the load and size of indentation is given by Meyer's law as $P = a\ d^n$, where P is load in kg, d is the diameter of recovered indentation in mm, a is constant and n is the work hardening coefficient. The plots between log P against log d for pure and L-threonine added ZTS crystals are shown in the Fig. 7. The slope of the straight lines of the figure gives the work hardening coefficient (n). The work hardening coefficient (n) for pure ZTS crystal is found to be 5.74 which is in good agreement with the reported value [14,24]. The obtained value of work hardening coefficient for 1mole% of L-Threonine added ZTS crystal is 4.53. Careful observations of Kishan Rao et al [31] on various materials have pointed out that n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. According to Onitsch [32], if n is greater than 1.6, the microhardness number increases with increase in load. Since the obtained values of n for pure and L-Threonine added ZTS crystals are more than 1.6, the grown crystals of this work belong to the category of soft materials and hardness number increases with the load and it is useful for non-linear optical applications.

4.6. Etching studies

To obtain the structural perfection and growth features of a grown crystal, etching studies can be used. The (100) plane of the pure and doped ZTS crystals has been completely immersed for 10s in the water etchant. Using optical microscope in the reflection mode, the features of the crystals have been analyzed which are shown in the Figs 8(a) and 8(b). From the figures, it is observed that the number of etch pits have been identified with identical shape. By increasing the etching time, the pattern remains the same but the size of the etch pits have been increases. The etch pit can be attributed to the initial dislocations formed at low angle boundaries or segregated impurities. The etch pits did not appear upon continuous etching suggesting that the pits were due to dislocations which is strongly correlated to the formation of inclusions in the crystals which can be originate from growth sector boundaries [4]. Also due to the liquid inclusions, there have been drastic changes in growth condition [13]. Hence, it is observed that the less number of dislocations shows the quality of the crystal.

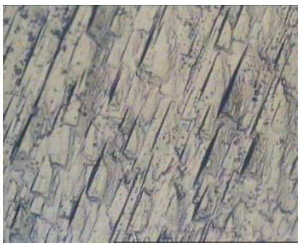


Fig. 8(a) Etch patterns on pure ZTS - 10s.

Fig. 8(b) Etch patterns on L-Threonine added ZTS-10s.

4.7 NLO property studies

Kurtz-Perry [33] powder SHG test was performed to study the NLO property of grown crystals.The crystalline powder was illuminated using Spectra-Physics Quanta-ray Prolab 170 Q-Switched Nd:YAG laser and Coherent Molectron powermeter, USA, using the first harmonics output of 1064 nm with a pulse width of 10 ns and a repetition rate of 10 Hz. The ZTS and L-Threonine doped ZTS powder samples were irradiated at 1064 nm by a Nd:YAG laser and the green light at 532 nm was observed. The output pulses were measured for powdered samples given Table 3.

Table 3. SHG output.

Input energy= 0.68 J/pulse

Sample	Second Harmonic Signal ouput (mJ)	SHG efficiency
Pure ZTS	1.6	1
L-Threonine added ZTS	3.9	2.44

The SHG efficiency of L-Threonine added ZTS crystal was found to be enhanced than that of pure ZTS crystal.Hence the L-Threonine added ZTS crystal has 2.44 times NLO efficiency than the pure ZTS crystal.

5. Conclusion

Optical quality single crystals of pure Zinc Tris(thiourea) Sulphate and L-Threonine added ZTS crystals were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction studies confirm that there is no change in basic structure of ZTS. The cell parameters show that pure and L-Threonine added ZTS crystals belong to orthorhombic structure. FT-IR study confirms the presence of all functional groups present in the grown crystals. UV-Visible study shows that the grown crystal has wide range of transparency in UV and entire visible region and cutoff wave length is around 268 nm. TGA analysis shows that the grown crystal has very good thermal stability up to 232 °C. Microhardness studies show that Hardness number (H_v) increases with the increase of loads. The values of work hardening coefficient of the grown crystals have been determined. The crystal perfections and quality have been identified by using the etching studies. SHG efficiency increases for L-Threonine added ZTS crystal by 2.44 times than pure ZTS crystal. Thus the 1mole% L-Threonine added ZTS crystal is going to play vital role in the field of optoelectronics and laser technology.

Acknowledgement

The authors acknowledge SAIF, IIT-Madras, B. S. Abdur Rehman University, Chennai, Department of Chemistry, Annamalai University, India, VIT University, Vellore and CIF, Pondicherry University, India for characterization facilities.

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