

Effect of L-threonine on the optical properties of (tris) thiourea zinc sulphate (TTZS) single crystal

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Abstract

The growth of L-Threonine 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-Threonine was doped in saturated TTZS solution. The effect of L- Threonine on SHG property was studied by Kurtz and Perry powder SHG test. The higher enhancement in SHG efficiency was observed at 1mole% L-Threonine doped TTZS. Hence, the growth 1mole% L- Threonine doped TTZS 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: TTZS crystals; XRD; FT-IR; UV-Vis; TGA; DTA; Mechanical Hardness Test; Dielectric Studies

1. Introduction

The modern world is witnessing many revolutionary advancements in all aspects of science and technology. Every new day is suppressing its predecessor by some new achievements that originate from novel ideas leading towards the exploration of new materials for use in emerging fields, which were hitherto unknown. Over the past two decades, there has been remarkable interest in the growth and characterization of nonlinear optical material crystals [1-6]. It is widely accepted that NLO materials play 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 as well as visible region and stable physico thermal performance are needed for these applications [11-12]. Inorganic NLO materials have good 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 crystals in order to obtain superior NLO crystals 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].

Tris thiourea zinc sulphate (TTZS) is a promising semi-organic NLO material for second harmonic generation from metal complexes of thiourea. TTZS is 1.2 times more nonlinear than KDP [17-19]. TTZS possesses an orthorhombic structure with space group Pca21 [20, 21]. Most of the amino acids individually exhibit the NLO property. An α -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 an α -carbon atom. This tetrahedral array of four different groups about α -carbon confers optical capability on the amino acid.

By nature an amino acid only exhibits zwitterionic nature when it is in solution form with a neutral pH. LTH on the other hand, exhibits a zwitterionic nature even while in its powder form. In the dipolar form of an amino acid, the amino group is protonated ($-\text{NH}_3^+$) and the carboxyl group is dissociated ($-\text{COO}^-$). L-Threonine is an important polar amino acid which shows higher SHG than other amino acids. In the present investigation, TTZS and L-Threonine doped TTZS were grown. Also the grown crystals were subjected to various characterisations such as single crystal XRD, Powder XRD, FT-IR, UV/Vis spectroscopy, TGA/DTA, Dielectric and SHG studies.

2. Synthesis and Crystal Growth

TTZS salt was synthesized by dissolving AR grade zinc sulphate and thiourea in 2D water in the ratio 3:1. The synthesized salt was purified by repeated recrystallization. A saturated solution of TTZS was prepared at room temperature and 1 mole% of L-Threonine was added to it.

The synthesized salt of 1 mole% L-Threonine doped TTZS was dissolved in 2D water. The purity of salt was obtained by repeated re-crystallization. A super saturated solution of 1 mole% L-Threonine doped TTZS was prepared at 32°C by constant stirring for about 5 - 6 hours and then filtered using whatman filter paper. The solution was then kept in a constant temperature bath of accuracy $\pm 0.01^\circ\text{C}$ at 40°C. Good quality transparent seed crystals were obtained 24 hours later. (Fig 1)



Fig. 1: L-Th Doped Seed Crystals

A seed crystal thus obtained was suspended by nylon thread in a beaker containing the mother solution. The slow evaporation technique was employed for growth of bulk crystal. A good quality transparent crystal was harvested within 23 days.

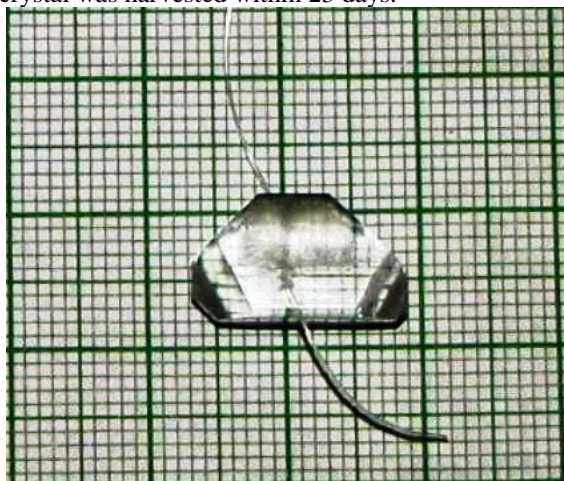


Fig. 2: A single L-Threonine Doped TTZS Crystal

3. Material Characterization

In order to ascertain the non-linear property and quality of the grown crystals, the following characterizations were performed on them:

3.1. Single Crystal XRD Analysis

Single crystal X-ray diffraction analysis of pure and 1 mole% L-Threonine doped TTZS Crystals were carried out. Their respective lattice parameter values are presented in the table 1 below.

Sample	Cell Parameters (Å)			Vol (Å ³)	Syst em $\alpha=\beta=\gamma=90^\circ$
	a	b	c		
Pure TTZS	11.120	7.806	15.478	1344	Orthorhombic
L-Th doped TTZS (1 M)	11.129	7.777	15.565	1341	Orthorhombic

Table 1: Comparison of Lattice Parameters

Both pure and 1 mole % l-threonine Doped TTZS crystals belong to the orthorhombic system with space group Pca21. The decrease in unit cell volume of l-threonine doped TTZS may be attributed to the replacement of some units of thio urea molecule with l-threonine molecule in the crystal lattice of TTZS.

From single crystal X-ray analysis, it is confirmed that dopant does not changes the basic structure of crystal (18, 21). There is a slight change in unit cell volume may be due to change in pH of the solution due to the addition of amino acid (20).

3.2. Powder XRD Analysis

The powder X-ray diffraction pattern of l-threonine doped TTZS crystal is compared with that of pure TTZS crystal (fig 3). The Bragg's reflection was indexed for pure and doped TTZS crystals using the cell parameters. The diffraction curves show some interesting features. Comparing the powder XRD patterns of pure and l-threonine doped crystals, the maximum intensity peak is shifted to the right hand side in the doped XRD pattern of TTZS. This confirms the incorporation of L-Threonine in the TTZS lattice. The observed values are in good agreement with the reported values (6).

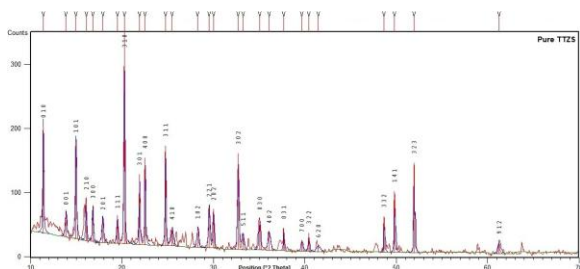


Fig. 3: Powder XRD pattern of pure TTZS

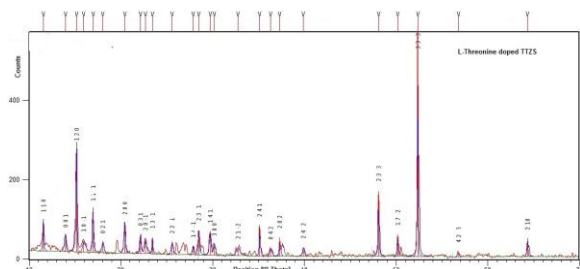


Fig. 4: Powder XRD pattern of L-Th doped TTZS

3.3. FT-IR Studies

The FT-IR analysis was carried out by Perkin Elmer Spectrum FTIR spectrometer by KBr pallet technique in the range 450-4000cm⁻¹. The FT-IR spectra of pure TTZS and 1 mole% L-Threonine doped TTZS are shown in Figure 5 and 6 respectively.

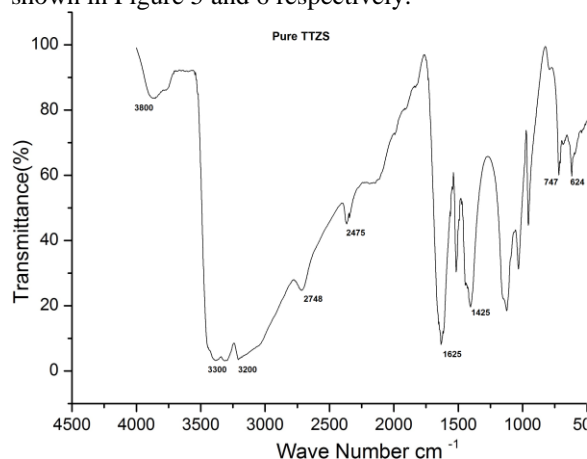


Fig.5: FT-IR Spectrum of Pure TTZS Crystal

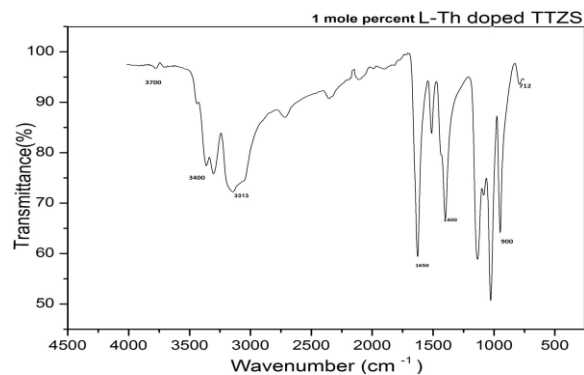


Fig.6: FT-IR Spectrum of L-Th Doped TTZS Crystal

In TTZS complex, there are two possibilities by which the coordination with metal can occur. It may be either through nitrogen or through sulphur. From the spectra given in table 2, 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 TTZS [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 1 mole% l-threonine doped TTZS with respect to pure TTZS [26]. This confirms the addition of l-threonine in grown crystal.

The broad band lying around 3200 to 3800 cm⁻¹ corresponds symmetric stretching of NH₂ group. The NH₂ bending vibration is observed at 1625.4 cm⁻¹. The symmetric and asymmetric C=S stretching vibrations are observed in the bands 713 cm⁻¹ and 1400 cm⁻¹. The presence of sulphate ion is confirmed by the absorption band at 618cm⁻¹ and 1115 cm⁻¹. The additional peaks observed in the second graph confirm the incorporation of l-threonine molecules in the TTZS lattice. Hence the FT-IR spectra indirectly establish the presence of l-threonine in the lattice of TTZS crystal.

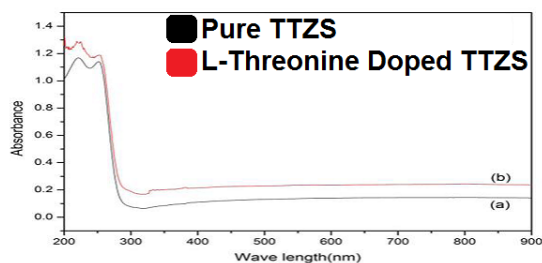
TTZS Wave Number (Cm ⁻¹)	L-Th doped TTZS Wave Number (Cm ⁻¹)	Assignments
3321	3313	Symmetric stretching(NH ₂)
1626	1625.4	NH ₂ bending
1400.3	1400	C=S Stretching (Asymmetric)
713	712	C=S Stretching (Symmetric)
619.04	618	N-C-S Asymmetric stretching
955	900	N-C-N Stretching

Table 2: Comparison of IR bands

3.4. UV-Vis 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 that 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 TTZS. The orbital P electron delocalization in thiourea arises from the mesomeric effect. This P electron de-localization is responsible for its nonlinear optical response and absorption in the near UV region [27]. The crystals thus grown have good transmission in their UV as well as visible regions. The wide range of transparency of grown crystals is an added advantage in the field of optoelectronic applications [28]. The absorption spectrum of pure TTZS and 1 mole% l-threonine doped are shown in Fig. 7. Both the crystals were found to have the same cut-off wavelength at 268 nm. It concludes that the doping of L-Threonine in TTZS is not affecting the cut off wavelength and optical transmission property of pure TTZS [18, 19, 25]. The wide range of transparency in UV, visible



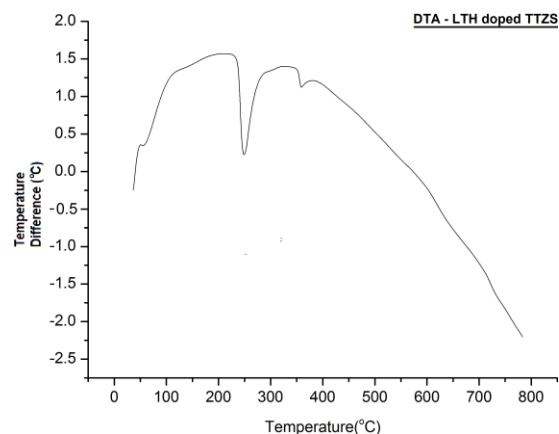
and IR regions enables good transmission of the second harmonic frequency of Nd:YAG laser.

Fig.7: UV Spectrum of pure and LTH doped TTZS

3.5. Thermal Analysis

Thermal analysis was carried out using SDT Q 600 V 8.3 build 101 simultaneous DTA/TGA analyzer in nitrogen atmosphere. Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out for the sample of weight 1.0180 mg in a temperature range of 200-1000°C at a heating rate of 20°C/min in nitrogen atmosphere.

Fig.8: DTA graph for LTH doped TTZS



In the DTA graph of pure TTZS crystal, we can see that the substance undergoes a sharp endothermic transition at 244.10°C. Again it undergoes a second endothermic peak at 353.01°C thus indicating that a major decomposition of the material has happened. The sharpness of the endothermic peak talks of the good crystallinity of the material. When l-threonine is doped with pure TTZS and then subjected to DTA testing, it was found to exhibit the first endothermic peak at 251.99°C and the second at 354.43°C. As we compare the DTA testing for pure and doped samples, the melting point of the doped sample was found to be higher than its pure counterpart. Also, the temperature at which total decomposition is attained is more for the doped sample.

From the TGA analysis carried out for pure TTZS sample, it was observed that the crystal had good thermal stability up to 235.77°C as there is no weight loss below that temperature.

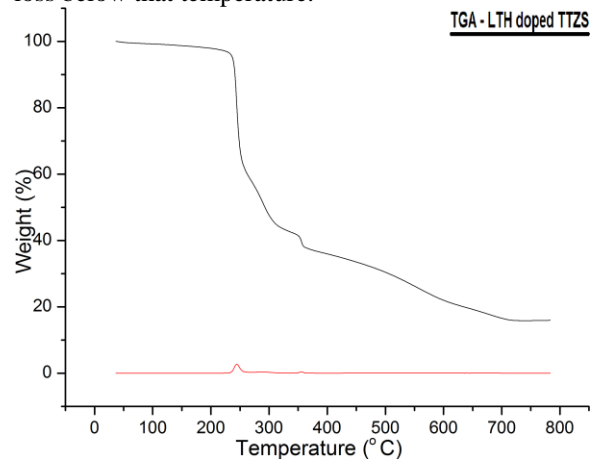


Fig. 9: TGA Graph for LTH doped TTZS

At 600°C however, the major weight loss of TTZS sample was observed to be about 81.4%. Residual weight loss of the sample was observed to happen at the temperature 789°C. Whereas for l-threonine doped TTZS sample, it was observed that the crystal loses its thermal stability at 240.37°C, and major weight loss of about 83.37% happens at the temperature of 625°C. Residual weight loss of the sample was observed at the temperature 800°C.

It can be seen from DTA curves of pure and l-threonine mixed TTZS samples that the melting point of doped sample is slightly greater than the pure one. Hence it was concluded that the thermal stability of TTZS slightly increases with the doping of 1 mole % of l-threonine.

3.6. Dielectric Studies

Dielectric properties are correlated with the electro-optic property of the crystals [14–16]. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. The dielectric constant and dielectric loss was measured using HIOKI 3532-50 LCR HITESTER. The selected samples were cut using a diamond saw and polished using paraffin oil.

Two opposite surfaces across the breadth of the TTZS and l-threonine doped TTZS samples were treated with good quality silver paste in order to obtain good ohmic contact. The studies were carried out and the capacitance, dielectric loss ($\tan \delta$) and ac conductivity of the sample as a function of frequency (100 Hz – 5 MHz) and temperature (in the range of 40, 80, 120 and 160°C) were measured.

The dielectric constant was calculated using the relation $\epsilon_r = Cd/\epsilon_0 A$, where ϵ_0 is the permittivity of the free space, C is the capacitance, d is the thickness of the sample and A is the area of cross section. The variation in the dielectric constant with frequency at different temperatures is illustrated in fig 10 below.

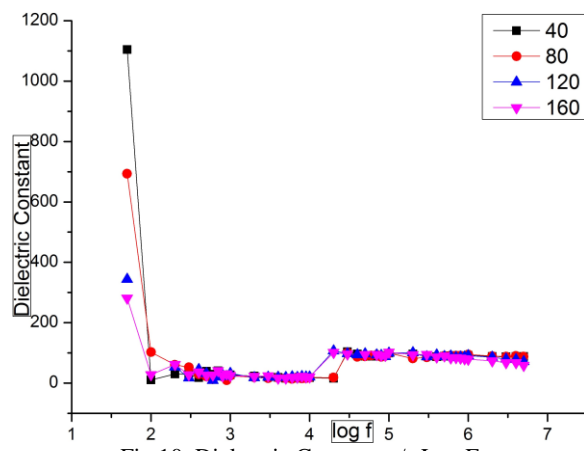


Fig.10: Dielectric Constant v/s Log F

The dielectric constant has maximum value in the lower frequency region and then decreases with the applied frequency. The decrease of dielectric constant with increasing frequency is normal dielectric behavior that may be due to the presence of

polarizations viz. Space Charge, Orientation, Electronic and Ionic polarizations.

Minimum value at higher frequencies is attributed to the slow loss of significance of these polarizations [17]. Higher values of dielectric loss at low frequencies originate from space charge polarization mechanism dipoles.

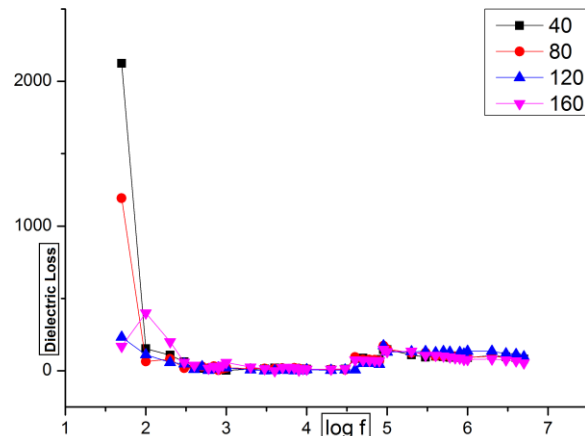


Fig.11: Dielectric Loss v/s Log F

The gradual decrease in dielectric constant and dielectric loss with frequency suggests that the grown crystals have varying relaxation times. The dielectric constant and electric susceptibility were found to remain unchanged by the incorporation of l-threonine into the Tris thiourea zinc sulphate crystals.

Usually the dielectric losses fall into two categories, they are intrinsic and extrinsic. Intrinsic losses are dependent on the crystal structure and can be described by the interaction of the phonon system with the ac electric field.

The AC electric field alters the equilibrium of the phonon system and the subsequent relaxation is associated with energy dissipation. These intrinsic losses set the lower limit of losses found in pure “defect-free” single crystals.

Extrinsic losses are associated with imperfections in the crystal, e.g., impurities, microstructural defects, grain boundaries, porosity, micro cracks and random crystallite orientation. Low value of dielectric loss suggests that the TTZS and l-threonine doped TTZS possesses enhanced optical quality with low density of defects.

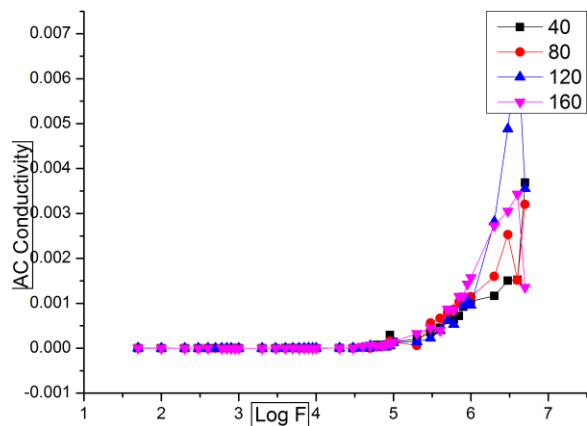


Fig.12: AC Conductivity v/s Log F

The AC conductivity patterns show a frequency independent plateau in the high frequency region and exhibits dispersion at lower frequencies. This behavior obeys the Universal Power Law which is denoted by $\sigma(\omega) = \sigma_0 + A\omega^n$ where σ_0 is the DC conductivity (frequency independent plateau in high frequency region), A is the pre-exponential factor and n is the fractional exponent between 0 and 1.

3.7. Mechanical Hardness Studies

Hardness of a material is a measure of the resistance it offers to any local deformation. In this study, indentations were made on (100) plane of pure and amino acid doped TTZS and l-threonine doped TTZS crystals using a Vicker’s indenter for various loads with dwell time 9 ns. For each load, several indentations were made and the average diagonal length (d) was measured to calculate the micro hardness using the following relation: $H_v = 1.8544 P/d^2 \text{ Kg/mm}^2$

where H_v is the Vicker’s hardness number, P is the applied load in kg and d the diagonal length of the indented impression in mm.

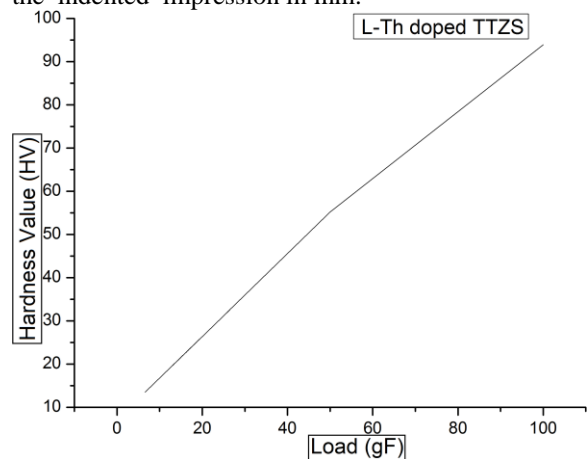


Fig. 13 – Load v/s Hardness Value

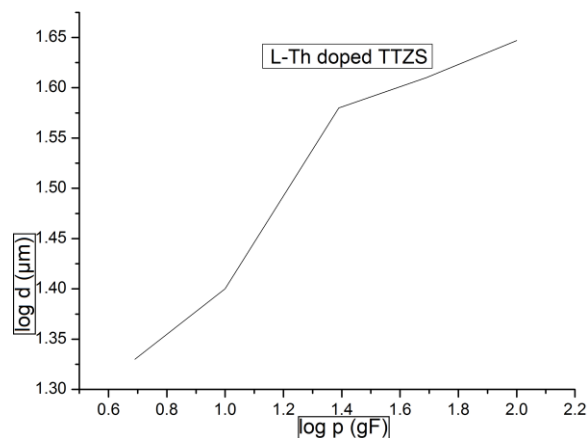


Fig. 14 – Log P v/s Log D

The relation between the load and size of indentation is given by Meyer’s law as $P = a \cdot d^n$, where P is the 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 and Log D for pure and l-threonine doped TTZS crystals are shown in Fig. 14.

The slope of the straight lines of the figure gives the work hardening coefficient (n). The work hardening coefficient (n) for pure TTZS crystal is found to be 5.74 which is in good agreement with the reported value of [14,24]. The obtained value of work hardening coefficient for 1 mole% of l-threonine doped TTZS crystal is 5.53. Careful observations by various researchers has 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 micro hardness number increases with increase in load. Since the obtained values of n for pure and l-threonine doped TTZS crystals are more than 1.6, the grown crystals belong to the category of soft materials. The hardness number is found to increase with the load. Therefore it would be useful in non-linear optical applications.

3.8. NLO 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 Moletron power meter, USA, using the first harmonics output of 1064 nm with a pulse width of 10 ns and a repetition rate of 10 Hz. The TTZS and l-threonine doped TTZS 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.

Input energy= 0.68 J/pulse	
Sample	SHG Output (mJ)
Pure TTZS	18.6
L-Threonine doped TTZS	20

The SHG efficiency of L-Threonine added TTZS crystal was found to be enhanced than that of pure TTZS crystal. Hence the L-Threonine added TTZS crystal has very good NLO efficiency than the standard KDP Crystals, which is usually taken as reference material to find relative efficiency.

4. Conclusion

Optical quality single crystals of pure Zinc Tris (thiourea) Sulphate and L-Threonine doped TTZS 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 TTZS. The cell parameters showed that pure and l-threonine doped TTZS crystals possess an orthorhombic structure. FT-IR study confirmed the presence of all functional groups present in the grown crystals. UV-Visible study showed that the grown crystals have a wide range of transparency in the UV and visible region spectra. The cutoff wave length was found to be around 268 nm. TGA analysis showed that the grown crystals have very good thermal stability up to 235.77°C. Also the SHG efficiency was found to increase for l-threonine doped TTZS crystal, which according to the data calculated above, is much greater than that of KDP crystals.

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6. References

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