

Crystal Growth, Morphology, Spectral and Optical Studies of Tris (thiourea) Zinc Sulphate - Nonlinear Optical Material

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Abstract

The Nonlinear Optical (NLO) material Tris (thiourea) zinc sulphate (ZTS) was grown by slow evaporation method. The unit cell parameter and morphology were determined by single crystal XRD. The molecular structure of ZTS was identified by FTIR analysis. The optical properties of ZTS were determined by UV-Vis spectral studies. The photoluminescence spectrum of ZTS shows the strong emission in ultraviolet region at 360 nm. The thermal behaviors were identified by TG/DTA analyzes and the melting point is 240°C. The hardness of the material is measured by micro hardness test. The SHG efficiency was confirmed by powder technique. The Laser damage threshold value of ZTS single crystal was found to be 20.15 MW/Cm². The effect of L-histidine doping on the morphology of the ZTS single crystal has been studied.

Keywords: Nonlinear Optical Material, Photoluminescence Single Crystal, SHG

1. Introduction

The nonlinear optical materials have lot of applications in various fields such as optical modulation, frequency doubling device, color display, optical data storage and submarine communications etc¹⁻³. The organic NLO possess high second order optical nonlinearity, lower laser damage threshold but poor mechanical and thermal properties⁴⁻⁵. Inorganic materials have high mechanical and thermal properties but it has poor optical nonlinearity⁶. The semi organic materials are the combination of organic and inorganic materials. This material has high mechanical, thermal and large nonlinear coefficient^{7, 8}. In the present work, the growth of pure and amino acid (L-histidine) doped ZTS crystals were grown by slow evaporation techniques. The effect of L-histidine doping on the ZTS, a remarkable morphology change has been observed. The structural, physical, optical, thermal and mechanical properties of ZTS single crystal have been studied.

2. Experimental Techniques

2.1 Synthesis of NLO Material

The thiourea and zinc sulphate was taken in 3:1 ratio.



The thiourea and zinc sulphate was dissolved in distilled water and kept separately. The zinc sulphate solution was transferred into the thiourea solution. Immediately ZTS salt was precipitated in the solution then the product was separated and dried.

2.2 Growth of Single Crystal

The synthesized salt of ZTS was thoroughly dissolved in distilled water. The solution was kept at room temperature for crystallization. The single crystal of the size 13 x 12 x 3 mm³ was grown within 25 days (Figure 1). Simultaneously 1wt. % of L-histidine doped ZTS (L-HZTS) solution was prepared and allowed for crystallization. The grown

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crystals of size $15 \times 10 \times 6 \text{ mm}^3$ were harvested in the period of one month (Figure 2).

3. Result and Discussion

3.1 Powder XRD

The synthesized salt of ZTS was subjected to powder XRD using D8 advance and Bruker X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.544\text{\AA}$). The sharp peaks show the good crystalline nature of the sample (Figure 3). The average grain of the ZTS were calculated using Scherer's equation

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where D is the average grain size and β is the full width half maximum. For the diffraction pattern shown below,

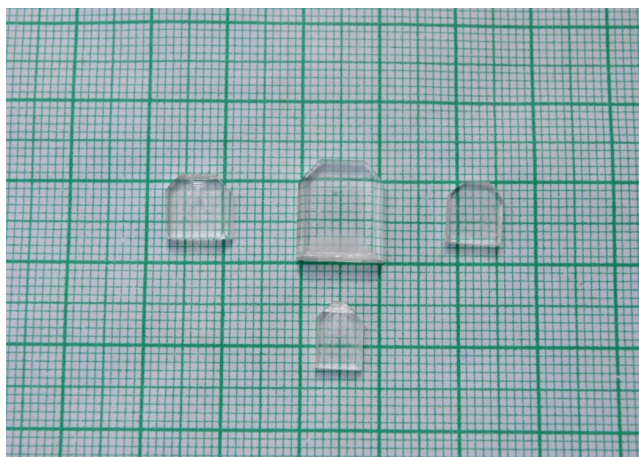


Figure 1. Grown single crystal of ZTS.

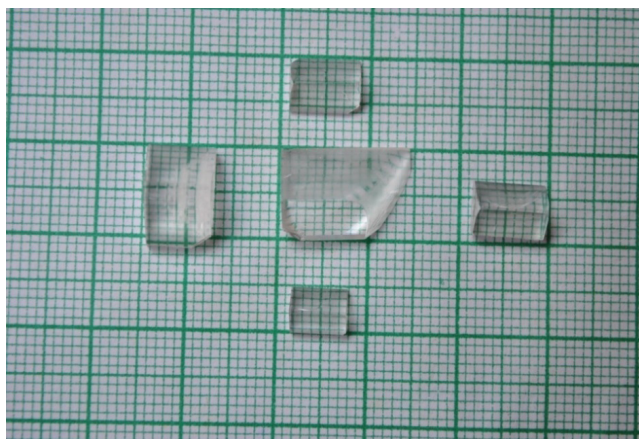


Figure 2. Grown single crystal of L-HZTS.

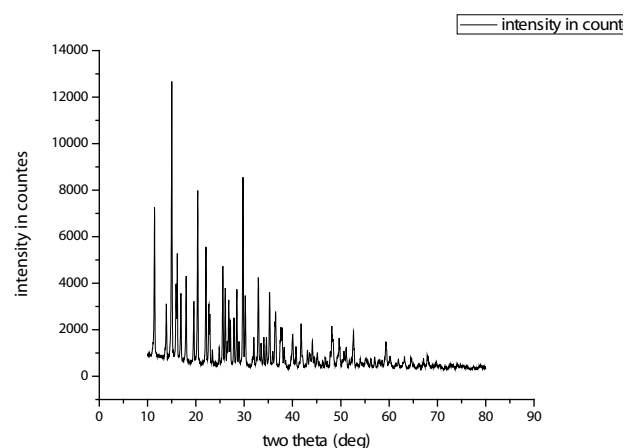


Figure 3. Powder XRD pattern of ZTS.

$\theta = 7.5$, $\beta = 0.00349$ rad, and $\lambda = 1.544 \text{\AA}$, yielding a particle size $D = 41 \text{ nm}$.

3.2 Single Crystal XRD

The grown single crystals (ZTS and L-HZTS) have been subjected to single crystal XRD using an ENRAF NONIOUS CAD-4 automatic X-ray diffractometer with $\text{MoK}\alpha$ radiations ($\lambda = 0.717 \text{\AA}$) to determine the morphology and unit cell dimension (Table 1). The crystal system of ZTS and L-HZTS belongs to orthorhombic. The morphology of ZTS and L-HZTS were shown in Figure 4 and Figure 5 respectively. In the morphology of ZTS single crystal, there are four well developed prominent planes (010), $(\bar{1}00)$, (010) and $(00\bar{1})$ are identified as shown in the (Figure 4). Due to the effect of L-histidine doped in ZTS (L-HZTS), the single crystal morphology shows some new planes $(10\bar{2})$, $(\bar{1}0\bar{2})$ and (111) (Figure 5). However, due to doping there is no remarkable change in the cell parameter and properties of single crystals.

3.3 FTIR Spectral Studies

The FTIR spectrum was recorded in the range of $400\text{--}4000 \text{ cm}^{-1}$ (Figure 6). The NH_2 symmetric stretching at

Table 1. Lattice parameters value of ZTS and L-HZTS

Crystal	a($\text{\AA}$)	b($\text{\AA}$)	c($\text{\AA}$)	V($\text{\AA}^3$)	$\alpha=\beta=\gamma$
ZTS	7.815	11.182	15.492	1353	90°
L-HZTS	7.812	11.112	15.501	1342	90°

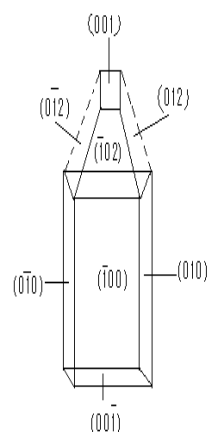


Figure 4. Morphology of ZTS.

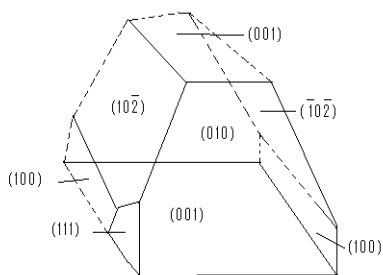


Figure 5. Morphology of L-HZTS.

3167 cm^{-1} in thiourea is shifted to 3190 cm^{-1} in ZTS¹². The band at 3370 cm^{-1} corresponding to asymmetric stretching vibration of NH_2 group¹⁰. The N-H bending vibrations for primary amine of ZTS at 1629 cm^{-1} . The peak at 714 cm^{-1} and 1401 cm^{-1} shows the symmetric and asymmetric C=S stretching vibration respectively¹¹. The vibrations peak at 613 cm^{-1} and 1127 cm^{-1} confirms the presence of sulfate ion. The observed frequencies and their assignment are listed in Table 2.

3.4 Optical Studies

The UV-Vis spectral transmittance of ZTS single crystal with 2 mm thickness was studied using a Lambda UV-Vis Spectrophotometer (Figure 7). The lower cut off wavelength for ZTS is 260 nm and the transmittance percentage is 45 %. The optical window (260-1200 nm) in the visible and IR region enables good for NLO application. The direct optical band gap of ZTS was determined as 4.2 eV using Tauc's plot as shown in Figure 8.

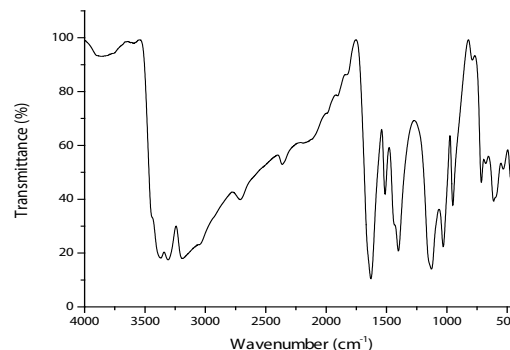


Figure 6. FTIR spectrum of ZTS.

Table 2. Comparison of IR band with thiourea

Wavenumbers		Assignment [12,13]
Thiourea [14]	ZTS	
3167	3190	vs (NH_2)
3376	3370	vas(NH_2)
1627	1629	$\delta(\text{NH}_2)$
1417	1401	vas (C=S)
	1512	v(N-C-N)
740	714	vs (C=S)

v - Stretching, δ - bending, s- symmetric, as- asymmetric

3.5 Photoluminescence Spectral Studies

Photoluminescence (PL) is the process of emission of light when photons are excited from ground state. The photoluminescence spectrum of ZTS was recorded using Cary eclipse photoluminescence spectroscopy with an excitation wavelength of 330 nm (Figure 9). The spectrum shows that the strong emission of ultraviolet is observed at 360 nm corresponding energy is 3.5 eV (Figure10). The peak at 445 nm has week emission of violet with energy of 2.5 eV. The peak at 490 nm has the week emission of blue light with energy of 2.8 eV which is suitable for photonic device applications.

3.6 TG/DTA Analyses

The TGA/DTA analysis of ZTS was carried out using *SII Nanotechnology TG/DTA 6200* in the nitrogen atmosphere (Figure11). The TGA curve shows that the ZTS has good thermal stability up to 240°C with the major weight loss

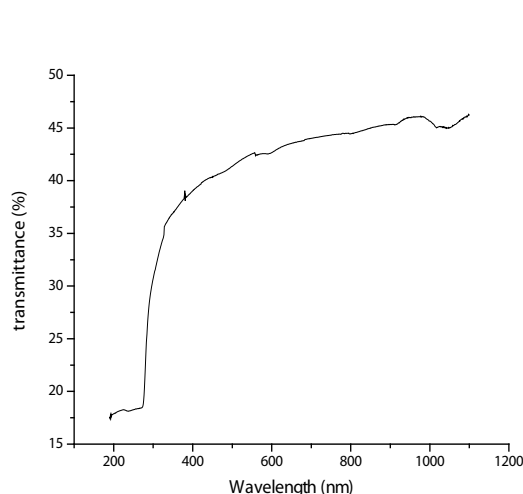


Figure 7. UV-vis transmittance spectrum of ZTS.

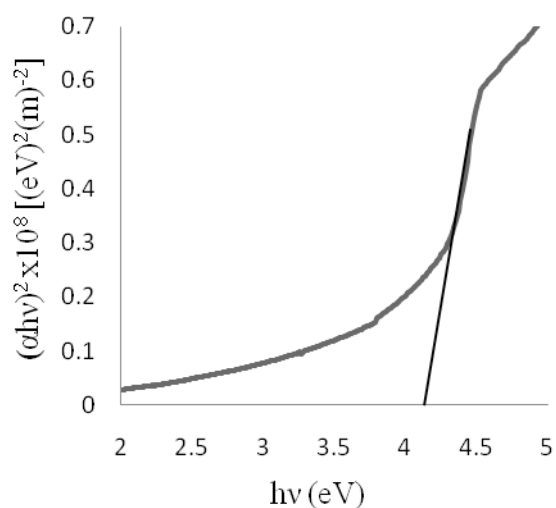


Figure 8. Tauc's plot of ZTS crystal.

about 52 % is observed in the temperature ranges 240-320°C. The DTA curve shows the melting point of ZTS is 240°C. The DTA shows that the first endothermic transition at 243°C is due to the liberation of volatile substance like sulphur oxide followed by second endothermic transition takes place at 364°C. The sharpness of the melting curve indicates well crystalline of the sample.

3.7 Measurement of Microhardness

Microhardness measurement of ZTS was carried out using shimadzu hmv-2 micro hardness tester to measure

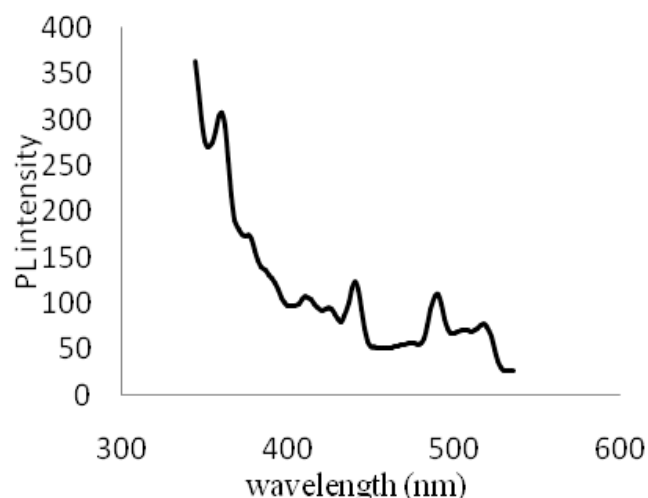


Figure 9. PL Emission of ZTS.

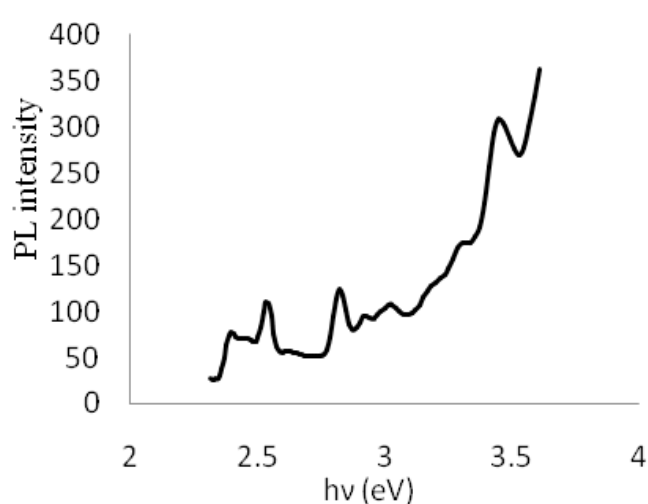


Figure 10. PL Emission of ZTS in eV.

the mechanical strength of the material. For various loads 2 to 50 grams hardness measurements was performed⁹.

$$H_v = 1.8544 P/d^2 \text{ kg/mm}^2$$

The grown crystal with well developed face ($\bar{1}00$) was selected for micro hardness study. A graph is plotted between the hardness number (HV) and load (P). Hardness number is increases with increasing load (Figure12). The work hardening coefficient (n) of the material is related to the load (P) by the relation $P = ad^n$, where n is the Meyer's index and 'a' is an arbitrary constant. A graph was plotted

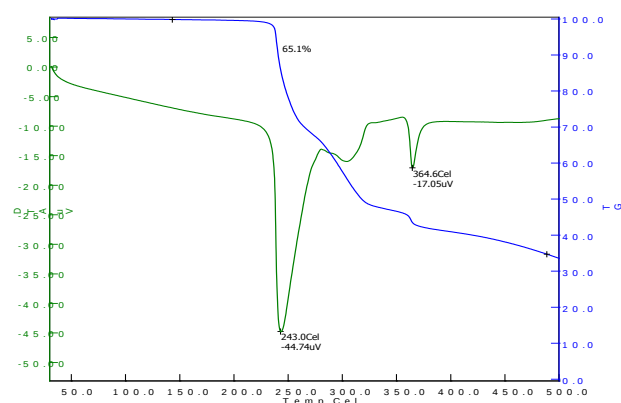


Figure 11. TGA-DTA curve of ZTS.

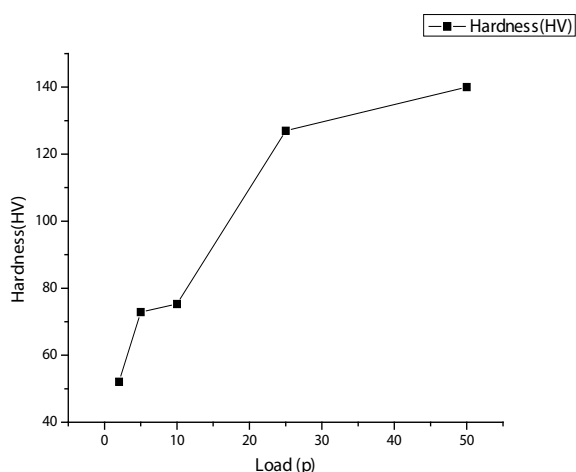


Figure 12. Variation load vs hardness.

between the logP and logd and straight line is obtained (Figure 13). The work hardening coefficient 'n' was found to be 4.6.

3.8 Measurement of SHG Efficiency

The high intensity laser with the wavelength of 1064 nm was allowed to strike the sample. The SHG efficiency was confirmed by the emission of green radiation (532 nm) emitted by sample and the SHG efficiency of ZTS is 0.6 times that of KDP.

3.9 Measurement of Laser Damage Threshold

The Laser damage threshold is a significant property of NLO material for applications¹³. This threshold mea-

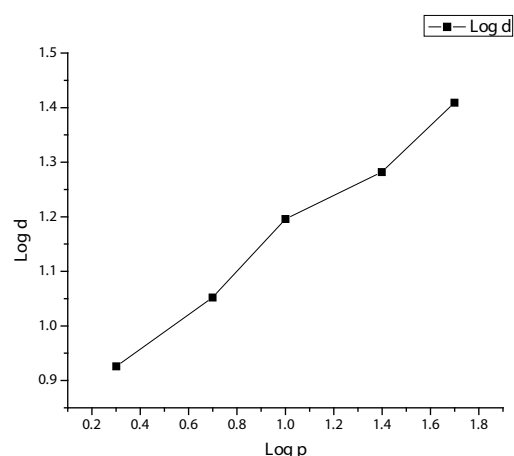


Figure 13. Plot of LogP vs Logd.

surement was carried out on the grown crystal using a Q-switched Nd: YAG laser operating at 1064 nm radiations with 6 ns pulse width and 10 Hz pulse rate. The Nd: YAG laser beam was passed along the $(\bar{1}00)$ direction of ZTS crystal. The laser damage threshold value of the ZTS crystal was found to be 20.15 MW/Cm² (Table 3). Compared with the laser damage threshold (12.44 MW/Cm²) of bis (thiourea) zinc acetate¹⁴.

4. Conclusion

The ZTS and L-HZTS single crystals were grown by solution growth technique. The Single crystal XRD confirmed that ZTS and L-HZTS crystals are belongs to orthorhombic system and the effect of dopant on the morphology change has been observed. The molecular structure of ZTS was confirmed by FT-IR analysis. The transmittance spectrum reveals that the crystal has a lower cutoff wavelength of 260 nm. The photoluminescence spectrum shows that the ZTS emitted ultraviolet fluorescence at 360 nm. The TG/DTA curves shows that the sample is highly stable up to 240°C. The Vickers hardness measurement

Table 3. The laser damage threshold value of ZTS Crystal

Energy (mJ)	No. of Laser pulses	Time (s)	Observation
20	20	20	No damage
40	20	20	
60	20	20	
80	20	20	
95	20	20	Damaged

shows that the work hardening coefficient 'n' is 4.6. The SHG efficiency was measured as 0.6 time that of KDP. The laser damaged threshold of ZTS is greater than bis (thiourea) zinc acetate.

5. References

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