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Effect of Doping on the Morphology of Tris(thiourea) Zinc Sulphate Nonlinear Optical Single Crystal

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Abstract: Tris(thiourea) zinc sulphate (ZTS) single crystals were grown from aqueous solution by slow evaporation technique. The cell parameters and morphology studies were carried out using single crystal XRD. The various functional groups present in ZTS has been confirmed by FTIR analysis. The UV-Vis spectrum revels the optical properties of the grown crystal and band gap energy is found to be 4 eV. The photoluminescence spectrum shows the maximum emission of ultraviolet light at 360 nm. The thermal stability of the grown crystal has been analyzed by TG/DTA and the compound has good thermal stability up to 240°C. The mechanical properties have been studied using Vicker's microhardness test and the second harmonic generation of efficiency were determined by Kurtz and Perry technique. The laser damage threshold of ZTS single crystal was determined (14.85 MW/cm^2) using Nd:YAG laser. The effect of cadmium chloride doping on the morphology of the ZTS single crystal has been analyzed.
Key words: Single crystal, Solution growth, Powder XRD, photoluminescence, thermal analysis.

1. Introduction

Nonlinear optical (NLO) materials are receiving great attention and substantial progress has been made in the development of laser technology, optical data storage and optical information processing. Nonlinear optical materials are important for the fabrication of photonics and optoelectronic device [1, 2]. The organic materials can have a very high nonlinear susceptibilities compared with inorganic, but these organic material have low optical transparencies, poor mechanical and thermal properties, low laser damage threshold and inability to produce large size single crystals. Inorganic NLO materials typically have excellent thermal and mechanical properties but possess relatively modest optical nonlinearities because of the lack of extended π -electron delocalization [3, 4]. The semiorganic crystal has good thermal and mechanical property with high nonlinear optical property. These materials have the potential for combining the high optical nonlinearity and chemical flexibility of organic materials with the thermal stability and mechanical robustness of inorganic materials [5-7]. In the present work semiorganic NLO material ZTS have been synthesized and morphology, mechanical, thermal and optical properties have been evaluated. Direct band gap energy of ZTS was calculated using UV-Vis analysis. The emission of light in visible and UV region was studied in Photoluminescence spectrum. The effect of 1wt. % of dopant (cadmium chloride) on the ZTS morphology has been studied.

2. Experimental analyzes

2.1 Synthesis of NLO Material

The ZTS salt was synthesized using thiourea (AR grade) and zinc sulphate (AR grade) in the ratio 3:1. The reaction is followed by-

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

The synthesized colorless crystalline salt of ZTS was obtained immediately.

2.2 Growth of ZTS single crystal

The ZTS synthesized salt was dissolved in distilled water. The solution was stirrer well for more than 5 hours. The solution was allowed to evaporate at room temperature. The good quality single crystals of dimension 7×6×4 mm^3 were harvested within a month shown in Fig 1.

Simultaneously 1 wt. % of cadmium chloride was doped in the ZTS solution (CC-ZTS) and single crystals with size of 8× 6× 6 mm^3 were obtained within three weeks. The grown crystals are shown in Fig.2.

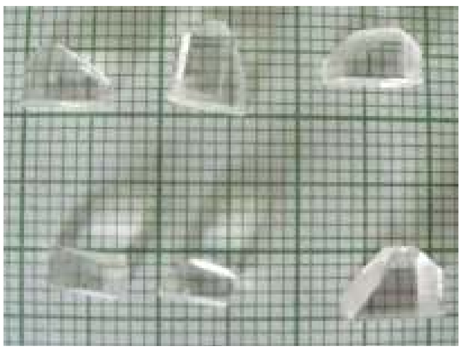


Fig.1 As Grown single crystal of ZTS.

Fig.2 As Grown single crystal of CC-ZTS.

3. Results and Discussion

3.1 X-ray powder diffraction

The synthesized salt of ZTS has been subjected to X-ray powder diffraction analysis using D8 advance and Bruker X-ray diffractometer (Fig.3). The sample was subjected to intense x-ray of wavelength 1.544 Å (Cu Kα). The sample was scanned for 2θ range (15.100 - 61.820º) and at scan rate of 2 min. The X-ray powder diffraction shows the crystalline nature of the synthesized material. The grain size of the synthesized ZTS salt was calculated by using Scherer's formula.

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

Where D is the grain size, β is the full with off maximum and θ is the diffraction angle, from the diffraction pattern shown below, θ = 16.436, β =0.0019 rad, λ = 1.544 Å and yielding a particle size of D = 77 nm.

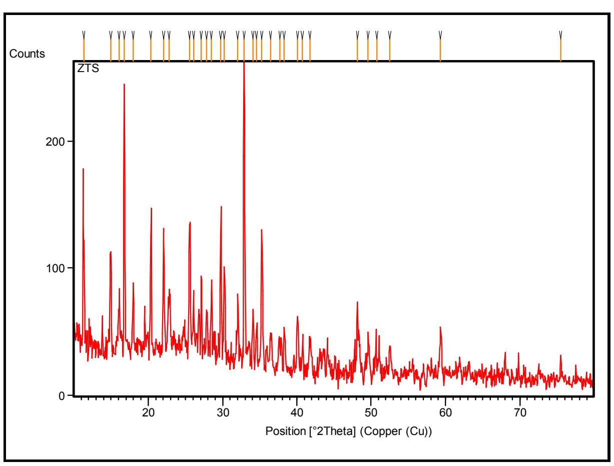


Fig.3 X-ray powder diffraction pattern of ZTS.

3.2 Single crystal XRD analysis

The single crystal XRD analysis for ZTS and CC-ZTS crystals were carried out using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer with $M_0K\alpha$ (λ= 0.717 Å) radiation. From the XRD data, it was observed that the ZTS and CC-ZTS belong to orthorhombic system. The cell dimensions are presented in table 1. There is no remarkable change in the cell parameter for cadmium chloride doped ZTS single crystal but surface morphology changes has been observed (Figs. 4&5). There are four well developed planes in the ZTS single crystal that are ($0\bar{1}0$), ($\bar{1}0\bar{1}$),(100), ($00\bar{1}$) are developed. Due to the 1 wt. % dopant of cadmium chloride in the ZTS solution there is change in morphology and some new planes are developed such as (102), ($\bar{1}0\bar{2}$).

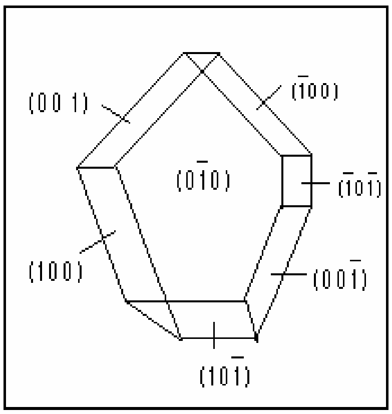


Fig.4 Morphology of ZTS.

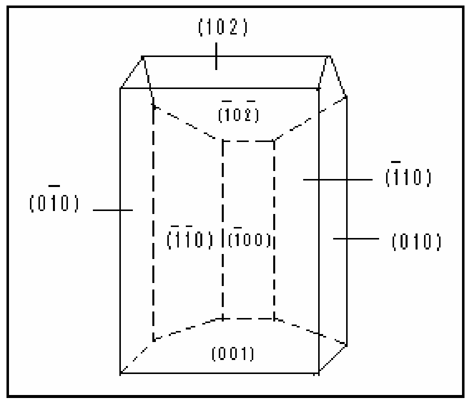


Fig.5 Morphology of CC-ZTS.

Table.1 Cell parameters of ZTS & CC-ZTS.

Crystal	a (Å)	b (Å)	c (Å)	V $(Å)^3$	α =β=γ	Crystal system
ZTS	9.6047	13.2751	6.5106	830	90°	Orthorhombic
CC-ZTS	9.605	13.2316	6.446	819.17	90°	Orthorhombic

3.3 FTIR spectral studies

The FTIR spectrum was recorded in the range of 400-4000 cm^{-1} for ZTS using KBr pellet technique (Fig.6). From the spectrum, the peak at 3192 shows the presence of NH_2 symmetric stretching vibration. The band at 1625 cm^{-1} shows the N-H bending vibrations [8]. The peak 714 and 1400 cm^{-1} are assigned to symmetric and asymmetric C=S stretching vibration [9]. The peak 617 and 1122 cm^{-1} represent conforms the presence of sulfate ion in the grown crystals.

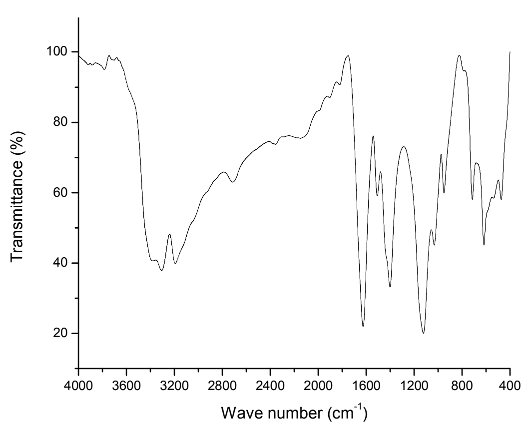


Fig.6 FTIR spectrum of ZTS.

3.4 UV-Vis spectral studies

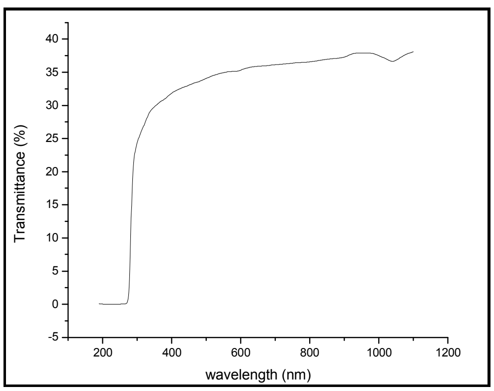
The UV- Vis spectral transmission study was carried out using Perkin Elmer lambda UV-Vis spectrophotometer in the range 190 to 1100 nm (Fig.7). The ZTS single crystal (3 mm thickness) has 35 % of transmission in the entire visible and IR region with lower cutoff wavelength at 280 nm. The optical transmittance window of ZTS shows 300–1100 nm which is suitable for nonlinear optical application. The absorption coefficient was calculated using the relation

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right)$$

Where α is absorption coefficient, d is the thickness of the sample and t is the transmittance of light. As a direct band gap material, the crystal under study has a absorption coefficient (α) obeying the following relation for high proton energies (hν).

$$\alpha = \frac{A\left(h\nu - E_g\right)^{\frac{1}{2}}}{h\nu}$$

Where E_g is the optical band gap of the crystal and A is a constant. The plot of $(\alpha h\nu)^2$ versus hν is shown in Fig. 8. E_g was evaluated by extrapolation of the linear part [10]. The band gape energy of ZTS was found to be 4 eV.



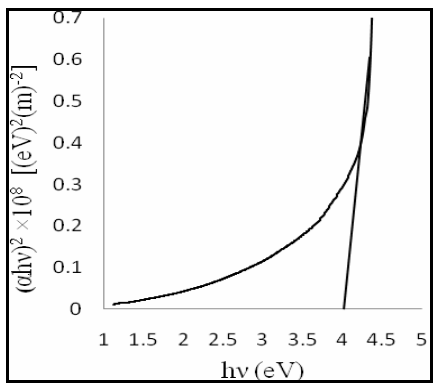
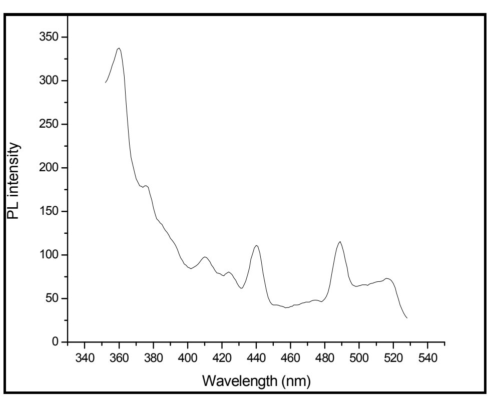


Fig.7 UV-Vis transmittance spectrum of ZTS.

Fig.8 Tauc's plot of ZTS crystal.

3.5 Photoluminescence spectral studies

Photoluminescence is a process in which a substance absorbs photons and then re-radiates photons. The photoluminescence study of ZTS was carried out using a Cary eclipse photoluminescence spectroscopy with an excitation wavelength of 330 nm (Fig.9). From PL spectrum the peak at 355 nm has maximum ultraviolet emission with energy of 3.5eV (Fig.10).the violet emission at 440 nm with a band gap energy of 2.8 followed by a blue emission at 490 nm corresponding energy of 2.5 eV.



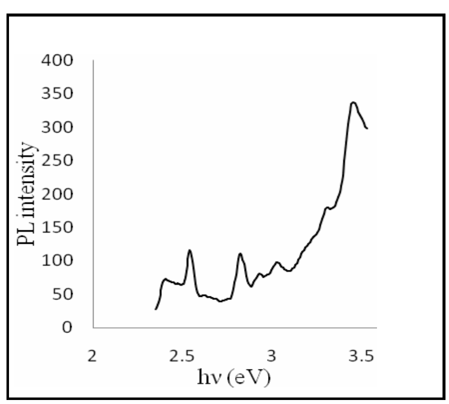


Fig. 9 PL spectrum of ZTS.

Fig. 10 PL spectrum of ZTS in eV.

3.6 Thermal analysis

The Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) where carried out using SII Nanotechnology TG/DTA 6200 for a sample weight of 6.329 mg with a temperature range 28℃ - 600 ℃ at a heating rate of 10℃/min (Fig 11). The TGA curve shows that the compound ZTS has good thermal stability up to 240°C as there is no weight loses below that temperature and major weight loss of about 40 % in the temperature range 242°C - 320°C due to the liberation of volatile substance like sulphur oxide. The DTA curve shows that the melting point of ZTS is 241°C. The DTA curve shows that the first endothermic transition takes place at 247°C followed by second endothermic transition takes place at 367°C.

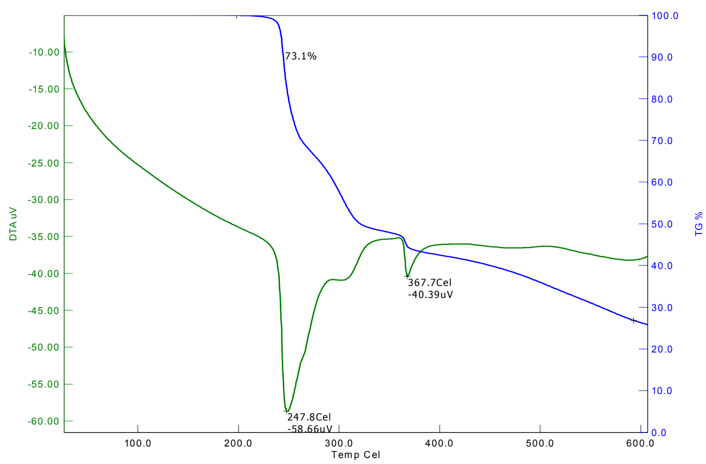


Fig.11 TGA-DTA curve of ZTS.

3.7 Measurement of microhardness

Microhardness measurement of ZTS was carried out using Shimadzu HMV-2 fitted with Vickers pyramidal indenter and attached to an incident light microscope Vickers micro hardness studies were carried out to find the mechanical stability of the crystal [11]. The microhardness test was carried out in the prominent plane ($0\bar{1}0$) of the crystal. The indentations were made using a Vickers pyramidal indentor for a various load from 2 to 50 grams. Hardness number increases with increasing load (Fig 12).

$Hv=1.8544\ P/d^2\ kg/mm^2$

Where Hv is the Vicker's hardness number, P is the applied load in grams and d is the average diagonal length of the Vicker's impression after loading. From Meyer's law $P=ad^n$ connected to a applied load (P) and diagonal length (d) of the indentation. Where n is a arbitrary constant and n is the work hardening coefficient 'n' was calculated. Draw a graph was drawn between logP vs logd. The work hardening coefficient was found by taking slop in the straight line. The work hardening coefficient 'n' was found to be 3.2 reveals that the material has good mechanical strength (Fig 13).

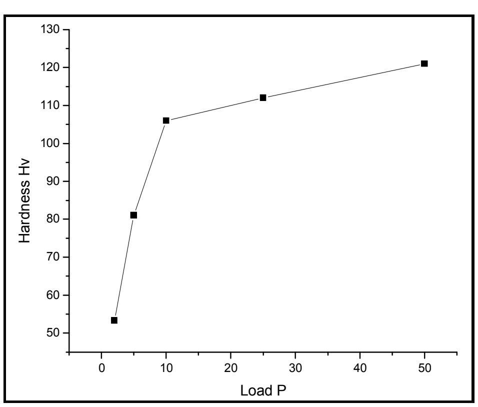


Fig. 12 Variation of hardness with load.

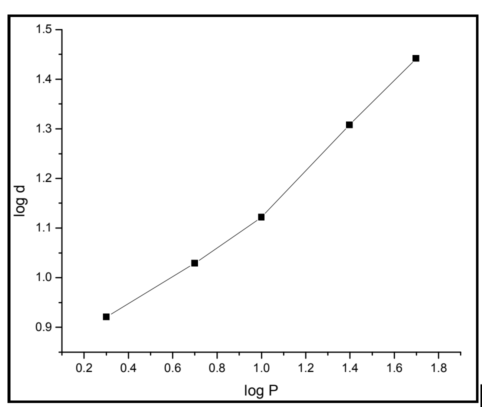


Fig. 13 Plot of LogP vs Logd.

3.8 Second harmonic generation (SHG)

The nonlinear optical property of ZTS crystal was studied by Kurtz and Perry technique. The crystal was grounded into a fine powder and densely packed between two transparent glass slides. A Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm (pulse width 8 ns) was allowed to striking the sample [12, 13]. The second harmonic generation in the crystalline sample was confirmed by the emission of green radiation (532 nm) emitted by sample. The SHG efficiency of the output signal is found to be 0.9 times that of KDP.

3.9 Measurement of laser damage threshold

The laser damage threshold were carried out using a Q-switched Nd:YAG laser emitting fundamental wavelength of 1064 nm with a pulse width of 6 ns. The crystal was exposed to the laser for a time period of 20 s for all measurements [14, 15]. The laser beam was focused on ($0\bar{1}0$) plane and allow striking the crystal. The input energy from 10 to 60 mJ was applied on the surface of the crystal and there is has no crack was observed. When beam with 70 mJ was applied, the crack was developed on the surface (Table 2). The laser damage threshold value of the ZTS crystal was found to be 14.85 MW/cm^2.

Table 2. Laser damage threshold value of ZTS single crystal

Input energy (mJ)	No. of Laser pulses	Laser exposure Time (s)	Observation
10	20	20	No damage
20	20	20	
30	20	20	
40	20	20	
50	20	20	
60	20	20	
70	20	20	Damaged

4. Conclusion

The single crystals of ZTS and CC-ZTS were grown by slow evaporation solution growth technique at room temperature. The grain size of the synthesized salt of ZTS was 77 nm measured using scherer's formula. Single crystal XRD analysis confirmed that ZTS and CC-ZTS crystals were belongs to orthorhombic system and some new planes were emerged such as (102), ($\bar{1}0\bar{2}$) in CC-ZTS crystal. The presences of functional groups were confirmed by FT-IR spectroscopic studies. The optical properties of ZTS were conformed by UV-Vis spectrum and have the lower cut of value 280 nm with band gap energy of 4 eV. The PL spectrum shows that strong emission of 355 nm in the ultraviolet region. The Vickers hardness studies shows that ZTS single crystal has good mechanical stability with work hardening coefficient 'n' was found to be 3.2. The SHG emission was confirmed by Kurtz and Perry technique with SHG emission of ZTS is 0.9 times that of KDP. The laser damage threshold energy of ZTS was found to be 14.85 MW/cm^2.

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