# GROWTH AND CHARACTERIZATIONS OF SINGLE CRYSTALS OF PURE AND L-ALANINE DOPED ZINC TRIS-THIOUREA SULPHATE

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**Abstract:**
The Pure Zinc Tris-Thiourea Sulphate and L-alanine doped ZTS single crystal grown at temperature 37℃ and 24℃ temperature by employing slow evaporation technique and further have been analyzed by various characterization techniques. The good transparency is achieved by slow evaporation method. The crystals were confirmed by single crystal X-ray diffraction analysis using Bruker D8-Advanced Diffractometer. From that structure of crystal and lattice parameter and also observed the change in particle size. Band gap is calculated using UV-Visible absorption spectra recorded by double beam UV-Visible spectrophotometer (Systronics-AU-2701) in the wavelength range 200-1000 nm .The functional groups were identified by using FT-IR Spectrophotometer with ATR (Shimatzu Japan- ISWL) in the wave number range 500-4500 cm-1. The uniform distribution of particles confirmed from SEM study which reveals the cubical morphology.
**Keywords:** slow evaporation, Zinc Tris-Thiourea sulphate, X-ray diffraction.

**Introduction:**
Recent years thiourea molecules are an appealing chemical matrix modifier as having large dipole moment and capability to form an network of hydrogen bonds.[1-4] The bis zinc chloride,), potassium thiourea bromide, tris-zinc sulphate (ZTS) and bis (thiourea) cadmium chloride (BTCC possesses nonlinear optical properties have focus major attention in the last few years since organic and inorganic both components in Thiourea contribute in particular to the process of second harmonic generation. The combination of centrosymmetric thiourea with inorganic salt gives non centrosymmetric complexes, which shows the nonlinear optical properties.[5-6] For second harmonic generation Zinc thiourea sulphate (ZTS) will acts as superior nonlinear optical semi organic material. It has low angular sensitivity, at higher frequency low dielectric constant, high laser damage threshold and extensive range of transparency. The X-ray structural determination shows a zinc ion terahedrally coordinating three planar thiourea molecules and one oxygen from a sulfate .There is also extensive inter- and intramolecular hydrogen bonding between N-H's and the sulphate O's and this feature most likely gives rise to the noncentrosymmetry, which is an essential property for second harmonic generation.[7-19]

**Experimental Work:**
**Preparation of Zinc Tris-thiourea Sulphate Salt:**
The ZTS Salt has been synthesized from Zinc sulphate heptahydrate and Thiourea taking in the 1:3 molar ratios. Take 1 mole means 28.756 gm Zinc sulphate heptahydrate and 3 mole means 22.836gm Thiourea. Prepare the solution in 100 ml distilled water by continuously adding 28.756 gm Zinc sulphate heptahydrate and when it dissolves completely then add 22.836gm Thiourea. The solution of Zinc sulphate heptahydrate and thiourea in molar ratio 1:3 are reacting under continuous stirring at room temperature ($\sim 36^0$c) .To avoid precipitation of other phases the mixture is stir vigorously.
The reaction is takes place as:
$$ZnSO_4.7H_2O + 3CS(NH_2)_2 \longrightarrow Zn[CS(NH_2)_2]_3SO4+7H_2O$$
According to above reaction we get the resultant precipitate of Zinc Tris-Thiourea Sulphate. On filtering and drying the solution we get precipitate of ZTS .In this way we get the salt of ZTS.
**Preparation of saturated solution of Zinc Tris-Thiourea Sulphate:**
Take 100 ml double distilled water as a solvent and stir it. Simultaneously add ZTS salt until equilibrium condition occurs. Then filter the solution using watmann filter .We get clear, transparent, saturated solution of ZTS. Keep this solution at room temperature for slow evaporation process after 4 to 6 days and the nucleation is takes place .there is formation of seed crystal.After 25 to 27 days we get transparent, colorless, grown ZTS crystal. Crystal size of grown crystal is 0.9×0.5×0.2mm
**Preparation of L-Alanine Doped ZTS Single Crystal**
Take 1 mole % L-Alanine for the doping in ZTS solution. For the synthesis of L-Alanine doped ZTS crystal Take 50 ml double distilled water. Add 2.25 gm L-Alanine in the solution of ZTS Separately. The solution was stirred thoroughly for 3 hours. Filter the solution using watmann filter paper. Keep this solution at room temperature upto 6 to 8 days for slow evaporation process. By the nucleation there is formation of crystal. And after 30 to 35 days we get transparent, colorless, grown ZTS crystal. We observed

crystal size of grown crystal is 0.9×0.6×0.3mm.

**Result and Conclusion:**
**Characterization:**
The grown crystals were subjected to different characterization viz. Powder XRD, FT-IR analysis, UV-visible spectral studies and dielectric constant measurement by transmission line wave guide method.
**a) Powder X- ray Diffraction Analysis**
Single crystal X-ray diffraction analysis for the grown crystal has been carried out to identify the cell parameters by using Bruker D8-Advanced Diffractometer in the 2 θ range of 20-80 degree which was operated at 40 KV and 30 mA. with CuKα radiation ($\lambda$=1.5406 Å) and The XRD patterns ZTS are shown in Fig.(a),Fig (b) and Fig (c). It is confirmed that, each crystal posses orthorhombic structure and have definite cell parameters. The XRD Data used to estimate the particle size of the grown sample . It is found that the grown crystal belongs to orthorhombic crystal system with space group Pca21 and the lattice parameters of Pure ZTS at Temp 37°C $a$ = 7.797Å, b= 11.144Å and c= 15.512 Pure ZTS at Temp 24°C $a$ =7.795 Å, b=11.147 7Å and c= 15 Å . L-Alanine doped ZTS at Temp 37°C $a$ =7.799 Å, b= 11.141Å and c=15.471 Å
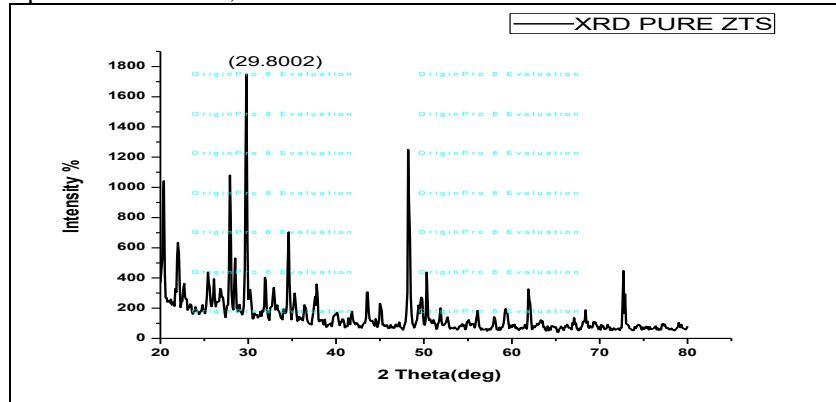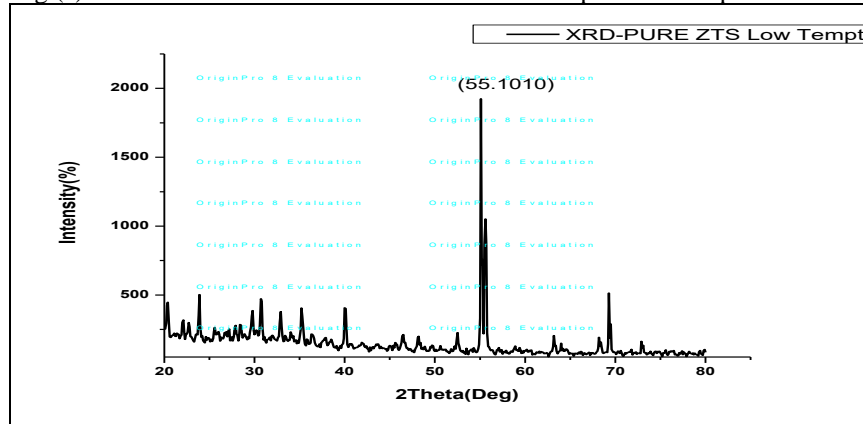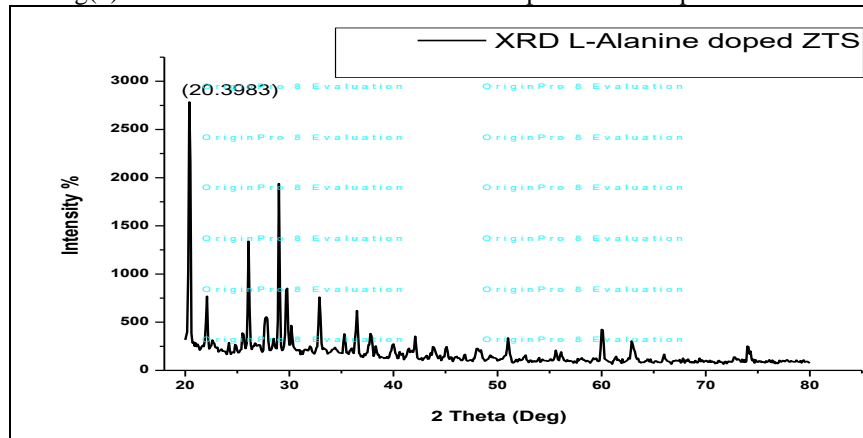


Fig (a): XRD Pattarn of Pure Zinc Tris-Thiourea Sulphate at Temperature 37°C
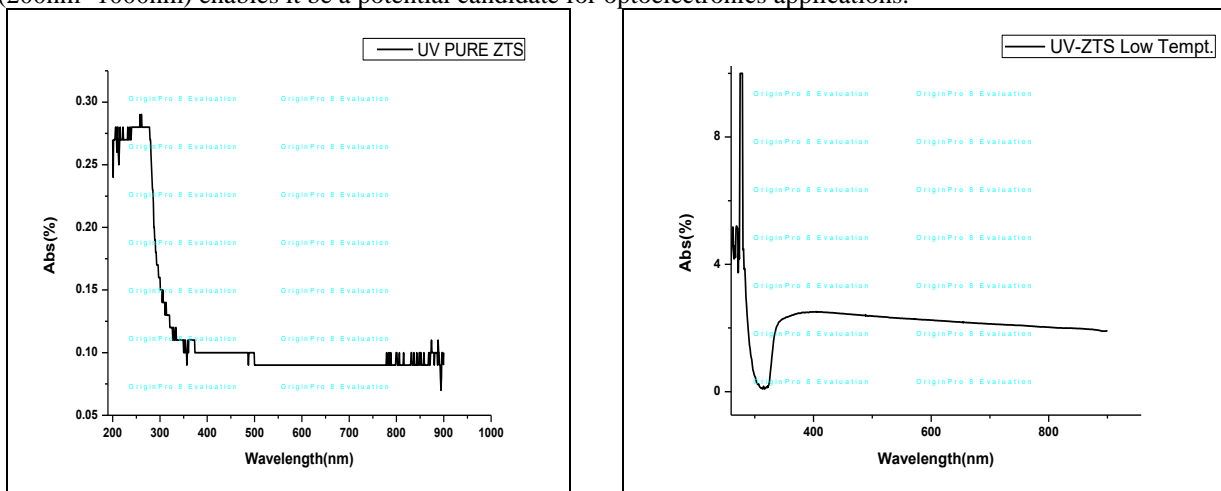


Fig(b): XRD of Pure Zinc Tris-Thiourea Sulphate At Temperature 24°C



Fig(c): XRD pattern of 0.5 mole% L-Alanine doped Zinc Tris Thiourea Sulphate

**b) UV-Visible Spectroscopy:**

UV-Visible absorption spectra of Pure Zinc Tris-Thiourea Sulphate At Temperature 37°C and 24°C were recorded by double beam UV-Visible Spectrophotometer (Systronics-AU-2701) in the wavelength range 200-1000 nm. The UV-visible absorbance spectra of Pure ZTS At Temp 37°C and Pure ZTS at temperature 24°C are shown in following fig. The absorption spectra reveal that these two crystals have lower cut off wavelengths at around 280 nm. The wide transmission in the entire visible region (200nm- 1000nm) enables it be a potential candidate for optoelectronics applications.



**Table : The Band Gap of Given crystal sample**

| Sample | Cut of Wavelength (nm) | Bandgap (eV) |
|---|---|---|
| Pure ZTS | 278 nm | 4.4 eV |
| Tempt. Change ZTS | 279 nm | 4.4eV |

**c) Fourier Transform Infrared Spectral Analysis:**

FTIR transmission spectra of Pure Zinc Tris-Thiourea Sulphate At Temperature 37°C and 24°C were recorded by FT-IR Spectrophotometer with ATR (Shimatzu Japan- ISWL) in the wavenumber range 500-4500 cm$^{-1}$. FTIR used to find the functional group, internal structure of the molecule and the nature of chemical bond of the compound which are present in crystal.[20] Fourier transform infrared spectral analysis is one of the most prominent and broadly used spectroscopic method for the analyzing the structure of the unknown components.

The FTIR analysis of zinc-tris thiourea sulphate was carried out to investigate the presence of functional groups and their vibrational modes. The spectrum was recorded between the frequencies 600 and 4000 cm-1 using spectrum RXI spectrometer, the sample was prepared by using pellet technique with mixture of KBr as shown in the figure 5.12. In between the higher energy region 3789 to 2109 cm$^{-1}$, the (NH2) asymmetric stretching mode is observed at 3371 cm$^{-1}$. The (NH) stretching modes are observed at3260 & 3162 cm$^{-1}$. The (NH2) symmetric stretching mode is observed at 2852 cm$^{-1}$. The( N-H) bending vibrational mode ,(-N=N-) Streching mode .The (NH2) asymmetric bending mode is observed at 1514 cm$^{-1}$.The (CN) asymmetric stretching mode is observed at 1440cm$^{-1}$.The (CS) asymmetric stretching mode is observed at 1402 cm$^{-1}$.The (CN) symmetric stretching mode is observed at1085cm$^{-1}$.The (CS) symmetric stretching mode is observed at 715 cm$^{-1}$.[21]
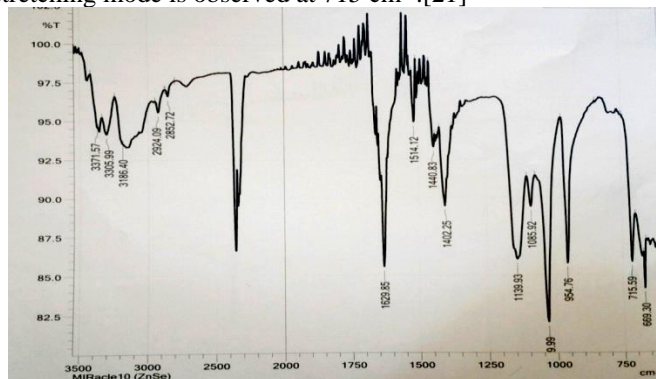


Fig. FTIR Spectra for Pure Zinc Tris Thiourea Sulphate At Temperature 37°C
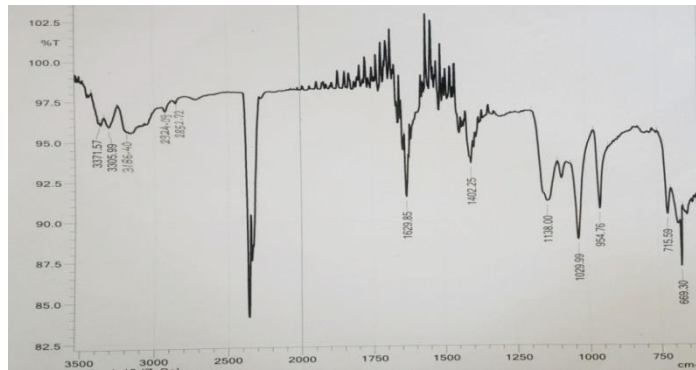
Fig. FTIR Spectra for Pure Zinc Tris Thiourea Sulphate At Temperature 24°C

### d) Dielectric constant:

The dielectric behavior of pure ZTS crystal were carried at room temperature using the Gwin stek LCR-819 cube meter with varying frequency range of 10 Hz to 100 kHz. The dielectric constant is calculated using the relation, $\varepsilon = Cd/\varepsilon_0 A$ where, C is the capacitance, d is the thickness; A is the area of the sample. The frequency response of dielectric constant for pure and doped ZTS crystal is shown in fig.d. It shows that the dielectric constant has high values in the lower frequency region and decreases with the applied frequency. The high values of dielectric constant at lower frequencies may be due to the presence of polarizations mechanism namely orientation, space charge, electronic and ionic polarization. The low values of dielectric constant at high frequencies indicate high crystal perfection and low space charge polarization.
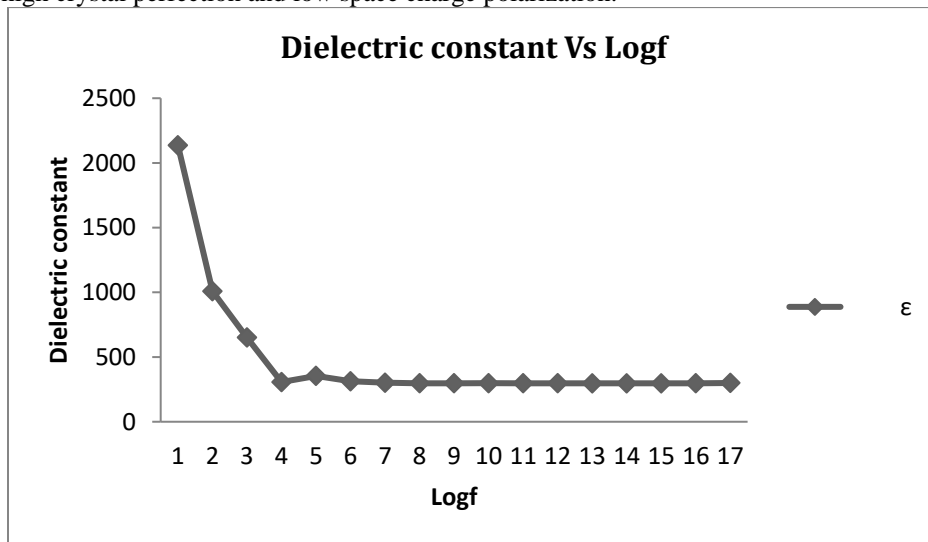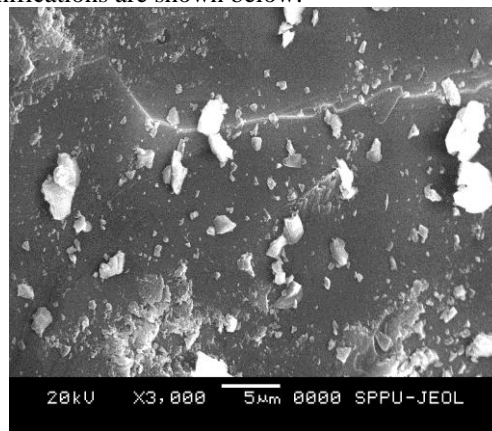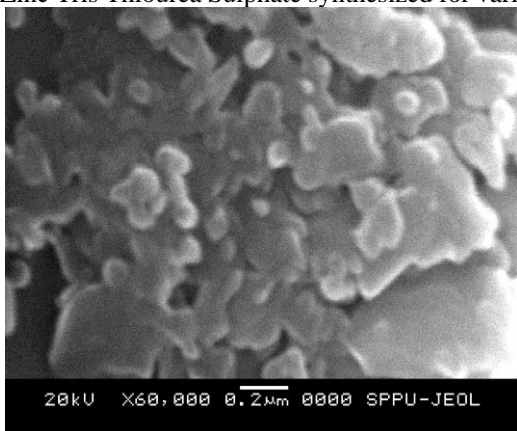


Fig.d. Frequency response of dielectric constant for pure and doped ZTS crystal.

### E) SEM Results:

The morphology of Zinc Tris Thiourea Sulphate single crystal particles was determined by SEM spectra. The spectra obtained with SEM of Zinc Tris Thiourea Sulphate synthesized for various magnifications are shown below:

## Conclusion:

The analysis of single crystals grown at 37°C of pure Zinc Tris-Thiourea Sulphate and L-alanine doped ZTS at 24°C has been carried out by different characterization techniques. Crystal is confirmed by single crystal X-ray diffraction. Single crystal ZTS is suitably grown by slow evaporation technique. As compare to other technique crystal grown by slow evaporation method shows good transferency. Also we get the structure of crystal and lattice parameter, and it is observed that the change in particle size .UV-Visible absorption spectra were recorded by double beam UV-Visible spectrophotometer (Systronics-AU-2701) in the wavelength range 200-1000 nm. From this by using cut off wavelength we calculate the band gap of given crystal sample. The functional groups were identified by using FT-IR spectrophotometer with ATR (Shimatzu Japan- ISWL) in the wave number range 500-4500 $cm^{-1}$. SEM shows the cubical morphology. It confirms the uniform distribution of particles.

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