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# STUDIES ON THERMAL, OPTICAL, DIELECTRIC AND NON LINEAR PROPERTIES OF L-LYSINE DOPED ZINC THIOUREA SULPHATE (ZTS) METAL COMPLEXES CRYSTALS

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## ABSTRACT

Amino acids are interesting materials as they contains the carboxyl, amino and hydroxyl groups which provide the ground state charge asymmetry of the molecule required for second order nonlinearity. In the present manuscript the influence of L-Lysine on the thermal, optical, photoluminescence, dielectric and non linear optical properties of Zinc thiourea sulphate crystals has been studied. The pure zinc thiourea sulphate (ZTS) and ZTS compound doped with L-Lysine have been grown by slow evaporation techniques at room temperature. The TG/DTA study shows that grown crystals have been thermally stable up to $197^0$C which is satisfactory result for coherent light sources applications. The red shift has been noticed in the photoluminescence studies at different excitation energy. The SHG efficiency has been found same as that of pure ZTS by the kurtz perry powder technique. The presence of Zinc element in the grown crystals has been confirmed by atomic absorption spectroscopy technique.

The optical transmittance of ZTS doped with L-lysine has been increased and shift the cutoff wavelength towards UV vis region. The optical transmission method were used to calculate the various optical parameters such as optical band gap ( Eg), extinction coefficient (K), absorption coefficient (α), linear refractive index (n), complex dielectric constant (εc) and optical conductivity (σop) of pure and L- Lysine doped ZTS crystals over the spectral range of 200nm-900nm. The optical band gap of doped ZTS is found to be 3.74eV. The calculated values of all above optical parameter of L-Lysine doped ZTS have been strongly favourable for the photonic and optoelectronic devices applications.

***KEYWORDS:*** Crystal Growth, Non linear optical material, Refractive index, photoluminescence

## 1. INTRODUCTION

The optoelectronic and photonic technology development is mainly due to the progress in crystal growth technology. Over the years several studies have been made a great efforts to develop a new semi organics non linear optical material due their wide and unlimited applications in the domain of optical devices such as frequency conversion, high speed information processing, optical communication and optical storage devices, frequency shifting, light valves optical switches, laser technology, telecommunication industries, signal processing devices etc.[1-5] Today, organometallic nonlinear optical materials have been focussed for their applicability in photonic and optoelectronic devices, because they posses higher mechanical strength, large nonlinearity thermal and chemical stability.Therefore the quest and demand for semi organic non linear crystals analysis always remains high. [6-7]

Recently several thiourea metal complexes have been reported which have better physic-chemical properties than KDP. [8-10]. The structural, UV Visible, microhardness, thermal, non linear optical properties of thiourea coordinated metal complexes like Zinc thiourea sulphate (ZTS) and zinc thiourea chloride (ZTC) have been studied. [11-13] As per the reports available in the literature the amino acid and its complexes with semiorganic compounds are promising material for optical second harmonic generation (SHG) and high laser damage threshold, wide transparency window, low UV cut off, and high NLO coefficients. Many amino acids have been used as dopants to deduce the physico chemical properties of Zinc thiourea sulphate (ZTS) and Zinc thiourea chloride (ZTC) [14-16]. Dhumane N R et al reported the influence of glycine on the properties of ZTS crystals. [17] .The L-Threonine added a ZTS crystal has 2.44 times NLO efficiency than the pure ZTS crystal has been noticed by Kanagasabapathy K. et al. [18]. Dr. Josheph Prakash et al investigated the growth and morphological and micro hardness properties of pure and L-Lysine doped ZTS metal complex. [19] As on date no systematic optical parametric studies in detail of pure and doped ZTS have been conducted. In addition to this the effect of L-Lysine on thermal, optical photoluminescence and NLO properties remains to be investigated.

The present investigation deals with the influence of L-Lysine on optical, thermal, dielectric, and NLO properties of pure ZTS single crystals. The optical parameters such as optical band gap (Eg), extinction coefficient (K), absorption coefficient ($\alpha$), linear refractive index (n), complex dielectric constant ($\varepsilon_c$), and optical conductivity ($\sigma_{op}$) were calculated. In this point of view, the optical absorption studies, FT-IR, TGA/DTA, Photo luminance, atomic absorption spectroscopy, dielectric and NLO studies have been carried out and the experimental results are discussed to explore its effective optical device applicability.

## 2. SYNTHESIS AND CRYSTAL GROWTH:

The Zinc (Tris) Thiourea Sulphate (ZTS) is a metal organic compound has been synthesized by dissolving high purity analytical reagent (AR) grade Zinc Sulphate heptahydrate and thiourea in molar ratio 1:3 in double distilled water. The homogeneous mixture was obtained by continuous stirring with help of magnetic stirrer for five hours and filtered by using whattman paper in a beaker. The beaker containing the solution was kept for evaporation to get white crystalline ZTS crystals. The purity of ZTS materials has been increased by appropriate recrystallization.

In the saturated solution of zinc thiourea sulphate $\{Zn [CS (NH_2)_2]_3SO_4\}$, the organic impurity L-Lysine ($C_6H_{12}N_2O$) were mixed in different molar percent (1, 2 and 3 mol%) and stirred well for 4hrs. The solution of L-Lysine doped ZTS was filtered in large size beakers. All the beakers closed by the thin transparent paper and kept at room temperature in vibration free space for slow evaporation. The nucleation of ZTS crystals were observed after 4 days where as the nucleation of L-lysine doped ZTS were observed after 25 days. It indicates that the nucleation period of L-Lysine doped ZTS crystals have been greater than pure ZTS crystals. It was also observed that the growth rate of Pure ZTS crystals is higher than L-Lysine doped ZTS crystals. The Pure and L-lysine doped ZTS crystals of adequate size with good transparency were harvested in 40 days as shown in fig.1

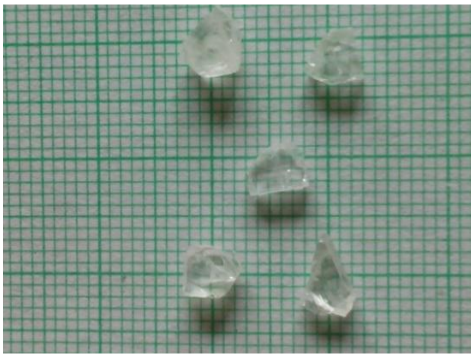

**Fig.1** *The photograph of grown pure ZTS and L-Lysine doped ZTS crystals*

## 3. RESULTS AND DISCUSSION

The FT-IR spectrum of L-Lysine doped crystal was recorded in the range of 400-4000 cm-1 at the resolution of $\pm 2$ /cm using Perkin Elmer Rx1 spectrometer. The thermal stability of the L-Lysine doped ZTS crystal was recorded by employing Perkin Elmer Diamond TG/DTA instrument. The photoluminescence of the grown crystals has been studied using a Cary Eclipse Win FLR EL07073870 Instrument with fluorescence emission in the wavelength range 220nm-1100nm. The NLO properties of the grown material confirmed by Kurtz and Perry technique employing Nd: YAG laser source. The optical transmittance was recorded by Shimadzu UV-2450 spectrophotometer in the range 200-900 nm. The dielectric measurement was performed by Gw Instek Lcr-819 meter. The elemental analysis was performed by atomic absorption spectroscope.

### 3.1 FOURIER TRANSFORMS INFRARED (FT-IR) SPECTRAL STUDIES

The Fourier transform infrared spectroscopic analysis is used to determine the chemical functional groups in the sample. The functional groups of zinc thiourea sulphate doped with L- lysine have been recorded using a Perkin Elmer Rx1 infrared spectrometer model in the frequency region between 4000 and 400 cm–1 as shown in figure 2. The symmetric and asymmetric stretching modes of $NH_2$ grouping of zinc coordinated thiourea has been observed at absorption peaks at3200cm-1 and 3396cm-1 whose position are not same as that of pure ZTS peaks. The absorption peak at 1120 $cm^{-1}$ is due to sulphate ion. This confirms coordination with thiourea and L-Lysine amino acids. **[19]** The strong absorption peak at 1628 $cm^{-1}$ is corresponds to $NH_2$ asymmetric bending vibrations. N-C-H symmetric, C=S asymmetric stretching vibrations are also seen at 1506cm-1 and 1385cm-1 respectively. The absorption peak noticed at lower frequency 617cm-1. The stronger absorption peaks NH stretch vibration is recorded due to the addition of L-Lysine in ZTS. Hence FTIR spectra indirectly establish the presence of L-lysine in the lattice of ZTS crystal.

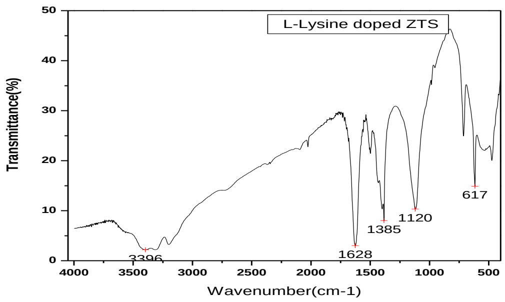


**Fig. 2** *FTIR Spectrum*

**3.2 THERMO GRAVIMETRIC/ DIFFERENTIAL THERMO GRAVIMETRIC ANALYSIS (TG/DTA)**

Thermo gravimetric and differential thermal analyses give complete idea regarding phase transition of crystallization and different stage of decomposition of the grown crystal system. The thermo gravimetric (TG) and differential thermal analysis (DTA) of L-Lysine doped ZTS crystal were investigated between $30^0$C – 1000 $^0$C in the nitrogen atmosphere at the heating rate of $10^0$C/min using Perkin Elmer Diamond thermal analyzer. The TG/DTA curves of L-Lysine doped ZTS crystals are shown in figure 3. From the TG curve, the L-Lysine doped ZTS crystal have very good thermal stability up to 197°C which is found to be less than the pure ZTS ($233^0$C) [20].The decrease in thermal stability level may be due to presence of organic compound thiourea and high thermal instability of L-Lysine in pure ZTS crystals. [21] The grown crystals do not contain the water molecule because there is no weight loss around $100^0$C. The decomposition starts only after this stability level and the phase transition remains unaltered till the material melts. It undergoes a sharp endothermic peak at $232^0$C is assigned to the melting point of the crystals and corresponding to phase transition. The sharpness of the peak showed good degree of crystallinity of the samples. The major weight loss of L-Lysine doped ZTS crystals may be due to liberation of volatile substances probably sulphur oxide and other impurities in the compound. The material is completely decomposed up to $800^0$C followed by the various decomposition of material such as combustion of organic matter such as CO and $NO_3$. The decrease in decomposition temperature and melting point is due to the effect of amino acids on metal complexes ZTS crystals. [22].

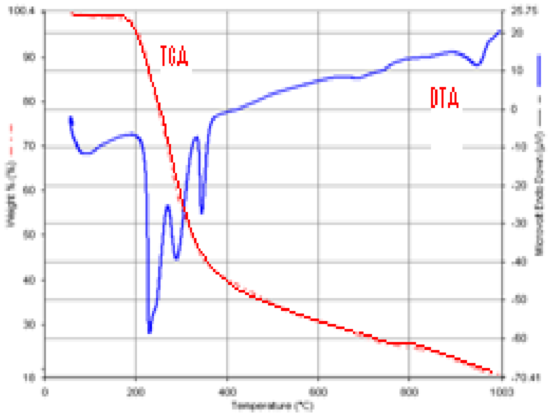


**Fig. 3** *TG/DTA curve*

**3.3 UV- VISIBLE STUDIES**

The UV spectroscopic studies of L-Lysine doped ZTS crystals have been carried out for the investigation of optical properties over the wide range of wavelength 200-900nm of the grown crystals using a Shimadzu UV-2450 spectrophotometer. The other optical parameters such as band gap (Eg), extinction coefficient (K), absorption coefficient (α) linear refractive index (n) ,complex dielectric constant ($\varepsilon_c$), and optical conductivity ($\sigma_{op}$) were calculated which required for designing of optical devices.

**3.3.1 OPTICAL TRANSMITTANCE**

The optical transmittance spectra for the Pure ZTS and L-Lysine doped ZTS is shown in Figure 4. From the optical transmittance curve, it is noticed that the transmittance of pure ZTS (77.76%) is less than L-Lysine doped ZTS (86.91%) Therefore the L-Lysine doped ZTS crystal shows a superior transmittance in the visible and IR region. The lower cut-off wavelength of L-Lysine doped ZTS (261nm) is found less than pure ZTS (267nm). Therefore the doping of amino acid has been increased range of transmission energy. The addition of L-Lysine in ZTS has lowered the cut off wavelength as well as enhanced the transmittance of pure ZTS. [23]. The wide and higher range of transparency and lower cutoff wavelength of doped ZTS indicates its suitability for SHG and optoelectronics device applications. [24] The optical absorption coefficient (α) has been obtained using the formula $\alpha=2.303\log(1/T)/t$ [25] The high transmittance and the low absorbance and reflectance of the material over a wide range of Wavelength indicates that the L-Lysine doped ZTS materials can be used as anti-reflection coating in solar thermal devices and nonlinear applications [26]

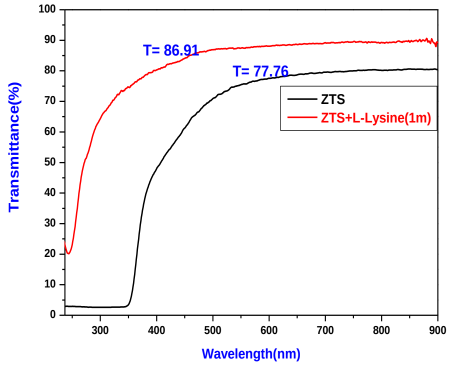


**Fig. 4** *Transmittance spectrum*

### 3.3.2 COMPLEX DIELECTRIC CONSTANT

The complex dielectric constant ($\varepsilon_c$) characterizes the optical properties of the crystals and is calculated using the expressions as $\varepsilon_c = \varepsilon_r + \varepsilon_i$, where εr and $\varepsilon_i$ are the real and imaginary parts of dielectric constant. The real part of the dielectric constant is expressed as $\varepsilon_r = n^2 - k^2$ and imaginary dielectric constant is given as εi = 2nk [25] The variation of complex dielectric constant with wavelength is depicted in figure 5. The real part is related with the degree of change in speed of light where as the imaginary part gives that how a dielectric absorbs energy from electric field due to dipole motion. The complex dielectric constant of doped ZTS has been significantly less than the pure ZTS. The lower range of complex dielectric constant (2.2-3.8) over the transmission range of the material really counts for the induced polarization in the material to exhibit NLO activity. This indicates that the lower value of dielectric constant with wide band gap of doped ZTS crystal suggests the suitability of optoelectronic devices.

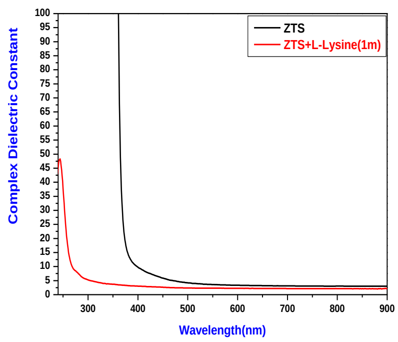


**Fig. 5** Plot *of Complex Dielectric Constant as a function of wavelength*

### 3.3.3 OPTICAL BAND GAP

The plot of optical band gap against the photon energy is depicted in figure 6. The optical band gap ($E_g$) was calculated by using the relation given as follows $(\alpha h\upsilon)^2 = A(h\upsilon - Eg)$.where A is a constant, $E_g$ is the optical band gap and hυ is incident photon energy. The optical band gap pure and doped ZTS crystals were determine using the Tauc's extrapolation plot shown in figure 9. The optical band gap of pure ZTS and L-Lysine doped ZTS crystals have been reported form the graph 3.35eV and 3.74 eV respectively. The optical band gap has been increased due to the addition of L-Lysine in pure ZTS crystal. The doped ZTS material with wide optical band gap indicates its suitability for UV tunable lasers and optoelectronic applications. [27-28]

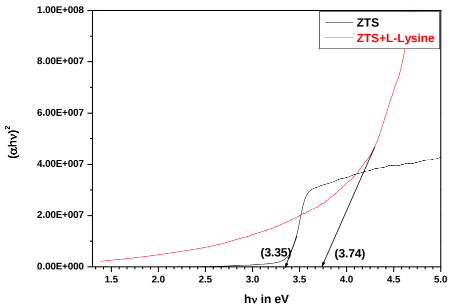


**Fig. 6** *Plot of optical band gap as a function of photon energy*

### 3.3.4 EXTINCTION COEFFICIENT

The extinction coefficient also called absorption index is a measure of the fraction of the light lost due to scattering and absorption per unit distance of the medium. The extinction coefficient was calculated using the relation K= λα/2π [29] The variation of extinction coefficient with wavelength is shown in figure 7. From the curve, the absorption index has been low at the lower wavelength for both pure and doped ZTS materials. The variation of extinction coefficient is found to be linear decreasing with respect to wavelength even for low values of absorbance. It is found to be gradually rising with respect to wavelength for doped ZTS crystals.

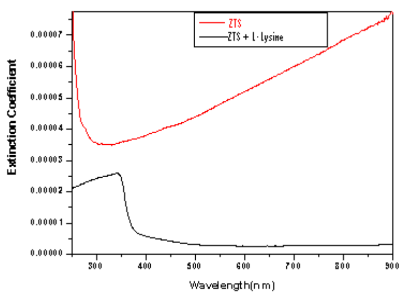


**Fig. 7** *Plot of Extinction Coefficient as a function of wavelength*

### 3.3.5 OPTICAL CONDUCTIVITY

The variation of optical conductivity $\sigma_{op}$ as a function to photon energy (hυ) is shown in the Figure 8. The optical conductivity $\sigma_{op}$ of the material is related to the absorption coefficient and refractive index and it is determined using the relations $\sigma_{op} = \alpha\eta c/4\pi$ . where c is the velocity of light and $\eta$ is the refractive index. [26] The optical conductivity trace indicates that the optical conductance increases with the increase of photon energy. The higher order of optical conductivity at higher photon energy (Fig.8) confirms the better conversion efficiency of the L-Lysine doped ZTS material for second harmonics generation.

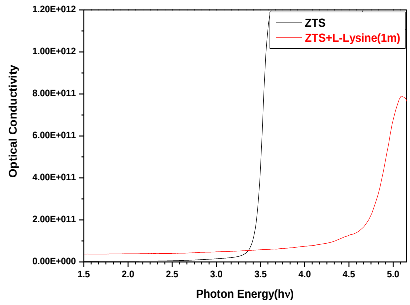


**Fig. 8** *Plot of Optical Conductivity as a function of photon energy*

### 3.3.6 REFRACTIVE INDEX

The refractive index is a fundamental physical property of a substance, used to detect a particular substance with its concentration and purity. Figure 9 shows the plot of refractive index as a function of wavelength. The refractive index decreases abruptly in the UV region and it remains constant in the visible region for pure and doped ZTS crystals. The refractive index of L-Lysine doped ZTS crystal was calculated by using the fundamental equations and it is found to be 1.468 (700nm) and for pure ZTS it is 1.718 (700nm). Therefore the refractive index of L-Lysine doped ZTS is less than pure ZTS crystals confirmed that the optical transmission of doped ZTS crystal is more than the Pure ZTS.

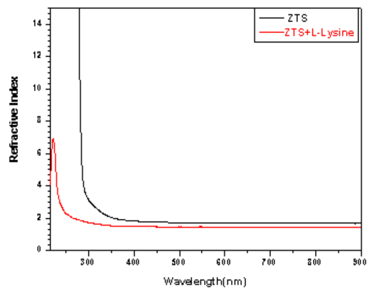


**Fig. 9** *Plot of refractive index as a function of wavelength*

### 3.4 PHOTOLUMINESCENCE STUDIES

The L-Lysine doped ZTS single crystals were subjected to photoluminescence measurement with excitation wavelength.240nm. The graph shown in figure 10 reflects that there are no excitation peaks at lower wavelength in the violet and green region. S. Aripponammal et al reported the excitation peaks in the violet and green region of the electromagnetic spectra for pure ZTS crystals [30]. But in the present work for excitation wavelength, the peaks are appeared in red region. The PL spectra of grown crystals show prominent weak red emission peaks at 638nm. The emission band at around 400nm is attributed to $S^{2-}$ vacancies in pure ZTS [31] which is absent in doped ZTS. This may be due to the influence of L-Lysine in pure ZTS crystals.

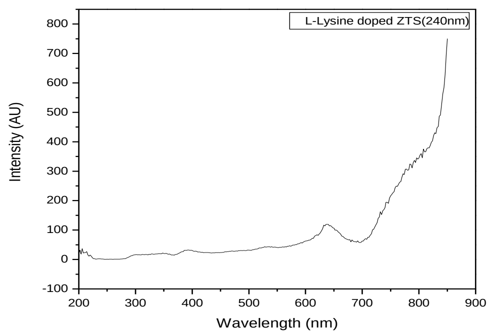


**Fig. 10** *Photoluminescence spectrum*

### 3.5 DIELECTRIC STUDIES

The dielectric properties are correlated with electro-optic properties of the crystals [13]. The dielectric constant ($\varepsilon_r$) was calculated by using the relation, $\varepsilon_r = Ct/A\varepsilon_0$, where $\varepsilon_0$ is the permittivity of the free space, C is the capacitance and A is the area of cross section of the sample. The variation of dielectric constant against frequency at room temperature for the grown crystals is shown in figure 11. The graph reveals that the dielectric constant is higher at lower frequencies and then decreases with increasing frequency and unaltered at a higher frequency region. The dielectric constant of L-Lysine doped ZTS crystal is found to be high at lower frequency. The large value of dielectric constant at low frequency is mainly due to the contribution of electronic, ionic, dipolar and space charge polarization. The intrinsic nature and imperfection of the materials will decide the space charge polarization. The increase in the dielectric constant at a low frequency is attributed to space charge polarization. When the electric charge carriers cannot follow the alternation of ac electric field applied beyond a certain critical frequency, the dielectric constant decreases with increasing frequency and remains constant.[32 ]

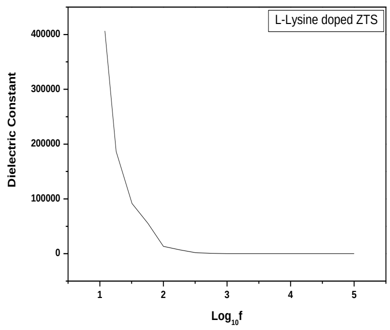


**Fig. 11** *Plot of Dielectric constant as a function of frequency*

The variation of the dielectric loss of the L-Lysine doped ZTS with different frequency at room temperature is represented in figure 12. It is clear from graph that the value of dielectric loss is high in lower frequency region and decreases with increasing frequencies and no dielectric loss for higher frequency. The characteristic of the low dielectric loss with high frequency suggests that the sample possesses enhanced optical quality with lesser defects.[ 33] The low value of dielectric loss indicates that the L-Lysine doped ZTS single crystals have defects less and optically more transparent material. For a material to be a potential candidate for NLO applications, dielectric loss (tan δ) must also be kept as low as possible. From the graph, it is clear that the doped ZTS crystal exhibit very low dielectric loss at high frequencies and can be used for NLO applications effectively [34].

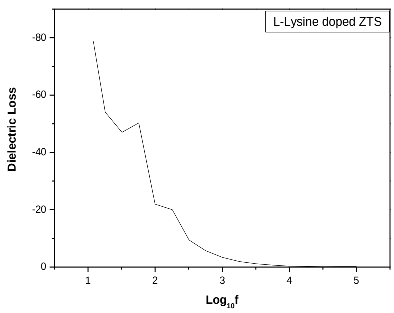


**Fig. 12** *Plot of Dielectric loss as a function of frequency*

### 3.6 ATOMIC ABSORPTION SPECTRAL ANALYSIS

Atomic absorption spectroscopy (AAS) is a spectra analytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. The technique is used for determining the concentration of a particular element in a sample to be analyzed. The atomic absorption study was carried out to confirm the presence of metal in the grown crystal. As per the test results, the sodium (Na) and iron (Fe) element is found to be less than 1ppm in the grown crystal. The Zinc (Zn) is to be found in a grown crystal sample above the detection limit. The extra element is not found in the sample. The pure and doped ZTS crystal does not have any metal impurity other than Zinc metal.

### 3.7 NLO STUDIES

The second harmonic generation (SHG) conversion efficiency was measured by powder Kurtz and Perry powder technique [35]. The fine powder of pure and doped ZTS crystal was filled into capillary tube and the Laser beam of wavelength 1064nm with 8ns pulse width was allowed to incident on it. The green light emission (532nm) was noticed at the output detected by the photomultiplier tube. This confirms that the frequency of output light has been double than the incident light. Therefore the L-Lysine ZTS crystal generates second harmonic generation. The Second harmonic generation efficiency of the L-lysine doped ZTS crystal almost same as the pure ZTS.

## 4. CONCLUSION

The L-Lysine doped ZTS single crystals were obtained by slow evaporation solution growth technique at room temperature. The FT-IR spectrum shows that the amino, sulphate and other functional groups present in the grown crystal confirms the incorporation of L-Lysine in ZTS structure. In the spectra of L-Lysine ZTS there is a shift in the frequency band in the low-frequency region which reveals that thiourea forms sulfur-to-zinc bonds in the ZTS crystal. In addition to that the presence of Zinc element was confirmed by atomic absorption spectroscopic study. TGA/DTA analysis shows that the grown crystal has very good thermal stability up to $197^0$C which good for Laser application. The second harmonic generation (SHG) efficiencies of grown crystals have similar to pure ZTS crystal. A Photoluminescence study reveals that the doped ZTS have a red emission of radiation. The high transmittance and the low absorbance and reflectance as well as low refractive index of the material over a wide range of wavelength indicates that the L-Lysine doped ZTS materials can be used as anti-reflection coating in solar thermal devices and nonlinear applications The low value of dielectric loss and dielectric constant with wide band gap indicates that the L-Lysine doped ZTS single crystals have defects less and optically more transparent material. Thus the L-Lysine doped ZTS crystals exhibited properties may be used as potential candidates in the field of optoelectronics and laser technology.

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