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INVESTIGATION ON SYNTHESIS, CHARACTERIZATION AND THIRD ORDER NLO PROPERTIES OF UNDOPED AND AMINO ACID DOPED ZTS CRYSTALS FOR NONLINEAR OPTICAL APPLICATIONS

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ABSTRACT

Undoped and amino acid (L-Valine) doped zinc tris (thiourea) sulphate (ZTS) crystals were grown by low temperature slow evaporation solution technique. The cell parameters of grown crystals have been determined by single crystal X-ray diffraction study. The presence of functional groups was studied by FT-IR analysis. The optical transmission analysis shows that the grown crystals have good transparency over the entire visible region from 300 nm. Photoluminescence spectrum of the title materials showed violet emission. The thermal stability of the grown crystals was checked by TG/DTA. The second harmonic generation test for the grown crystals was performed by Kurtz and Perry experimental setup. Third order nonlinear optical (NLO) response of the grown crystals has been examined using a Z-scan technique.

KEYWORDS

Optical materials, X-ray diffraction, FT-IR, Photoluminescence and Z-scan technique.

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INTRODUCTION

Nonlinear optical (NLO) crystals have attracted the eye of scientists and technologists due to their potential applications in photonics as well as optical information processing[1], high-energy lasers for inertial confinement fusion research, color display, electro-optic switches and frequency conversion[2]. In recent years, efforts are created to develop Ultraviolet lasers for, optoelectronics, photonics, infrared and medical applications.

The nonlinear optical property of amino acid crystals has contributed to the great progress that has been created within the development of coherent Ultraviolet sources. Organic crystals exhibit special properties of high optical nonlinearity and low cutoff wavelength in the Ultraviolet region and the organic NLO crystals have bound limitations like poor mechanical and thermal stability. To overcome these issues, a mixture of organic and inorganic hybrid compounds has been established. These compounds represent a replacement class of materials remarked as semiorganic materials. Semiorganic crystals have combined the inorganic deformed polyhedron with the asymmetric conjugate organic molecules[3]. Recently, semiorganic crystals with large nonlinear susceptibility, superior optical transparency with high hardness have been recognized. Semiorganic complex of thiourea (TU) with good optical nonlinearity mixed with the physical austerity of an inorganic compound has been useful for device applications.

Zinc tris (thiourea) sulphate (ZTS) is a nonlinear optical semiorganic crystal having potential application in frequency conversion and electro-optic devices. ZTS crystal goes to the orthorhombic crystal system with the space group Pca21[4]. The advantage of the title materials is its low angular sensitivity in the phase-matching direction in frequency doubling experiments.

Recently, amino acid family crystals are playing a significant role in the field of NLO[5]. The amino acid may be used as a dopant in order to enhance the nonlinear optical property of the material. A number of researchers have reported that amino acids doped ZTS crystal exhibits excellent optical properties and moderate thermal stability[6-8]. L-Valine is an organic material under the amino acid family. It is one of the naturally arising hydrophobic amino acids. L-Valine exists in a zwitter ionic form combined with anionic, cationic and overall neutral constituents. Hence, L-Valine mixed semiorganic material will be of special interest as a basic building block to develop several complex crystals with improved NLO properties. Since ZTS is a semiorganic material, the addition of L-Valine might enhance the NLO properties. It is with this intention this piece of work is carried out.

In the present investigation, the effect of L-Valine on structural, optical, thermal, Photoluminescence, NLO properties of undoped ZTS single crystals has been studied. The optical constants were calculated and the experimental results are discussed to explore its suitability for optical device applications.

EXPERIMENTAL PROCEDURE

Synthesis and crystal growth

Undoped crystal of ZTS was synthesized by Analar grade Thiourea (99% Merck) and zinc sulphate (99% Merck) mixed in a stoichiometric ratio. Thiourea and zinc sulphate were taken in the molar ratio 3:1. The calculated molar ratio of thiourea and zinc sulphate were dissolved in double deionized water which was thoroughly mixed using a magnetic stirrer for 2 hours continuously and the mixture was heated at 45˚C to avoid decomposition. The saturated solution was then filtered into a clean beaker and kept closed with a perforated foil sheet to facilitate the evaporation process slowly. Transparent colorless undoped ZTS crystals were obtained after a time span of 32 days.

L-Valine doped ZTS crystal was also grown by adding 0.5 mol% of L-Valine in the saturated undoped ZTS solution. Transparent and colourless L-Valine doped ZTS crystals were obtained after a time span of 40 days. The photographs of as grown undoped and L-Valine doped ZTS crystals are shown in Figure No.1a and 1b.

RESULTS AND DISCUSSIONS

Single Crystal XRD analysis

The unit cell parameters of the grown crystals were carried out using ENRAF NONIOUS CAD4 X-Ray diffractometer equipped with Mokα radiation (λ= 0.71073 Å). The single crystal X-Ray diffraction analysis provides information regarding the crystal structure. It was observed that both the crystals belonging to the orthorhombic system having space group $Pca2_1$. The values of the unit cell parameters of the grown crystals are given in Table No.1.

The observed unit cell parameter values coincide well with the reported values[6]. A slight increase in the unit cell parameters may be assigned to the lattice strain resulted due to the doping of L-Valine which causes an increase in cell volume from $V_{undoped}$ = 1359 $Å^3$ to $V_{doped\ ZTS}$ = 1364 $Å^3$ and it is confirmed that dopant does not change the basic structure of crystals.

Vibrational spectroscopy

The FT-IR spectra were recorded within the wave number range of 400-4000 cm^{-1} using PERKIN ELMER RXI FTIR spectrophotometer by KBr pellet technique. The FT-IR spectra of undoped and L-Valine doped ZTS were carried out to analysis the functional groups present in the grown crystals. The observed FT-IR spectra are given in Figure No.2.

A broad envelope positioned between 2713 cm^{-1} and 3376 cm^{-1} occurring out of the symmetric and asymmetric modes of the NH_2 group zinc coordinated thiourea[9]. The absorption band observed at 1600 cm^{-1} in undoped ZTS and 1602 cm^{-1} in L-Valine doped ZTS are assigned to the NH_2 bending mode of vibrations. C=S stretching vibrations of the symmetric and asymmetric are observed in the bands 1398 cm^{-1} and 700 cm^{-1} for undoped ZTS and 1400 cm^{-1} & 704 cm^{-1} for L-Valine doped ZTS. The absorption at 1510 cm^{-1} is due to N–C–N stretching vibrations for undoped ZTS and 1512 cm^{-1} for L-Valine doped ZTS. The presence of sulphate ion is confirmed by the absorption band at 400 cm^{-1} for undoped ZTS and 405 cm^{-1} for L-Valine doped ZTS[10]. All these vibrations for undoped and L-Valine doped ZTS assigned and listed in Table No.2. There is a slight shift in the absorption bands of L-Valine doped ZTS compare to undoped ZTS and this shift in the absorption bands is also attributed to the incorporation of L-Valine in ZTS.

Linear Optical Analysis

UV-Vis transmittance spectra were recorded by PERKIN ELMER LAMBDA 35 UV-Vis spectrophotometer within the wavelength range of 190 nm to 1100 nm. The optical transmission spectra for the undoped and L-Valine doped ZTS are indicated in Figure No.3.

From the optical transmittance curve, it is noticed that added the transmittance of undoped ZTS (70 %) is less than L-Valine doped ZTS (90 %). The percentage of transmittance of L-Valine doped ZTS crystal is very high, is an advantage for these crystals to be employed in the field of optoelectronic devices[11]. Both undoped and L-Valine doped ZTS crystals possess a wide transparency window in the entire visible region ranging from 380 nm to 700 nm. L-Valine doped ZTS crystal shows a superior transmittance in the visible region. Transparency in the visible region with a lower cut off at 300 nm is some of the characteristic features of an NLO material. Both the grown crystals have the same UV cut-off wavelength at 300 nm. It concludes that doping L-Valine into the crystal lattice of ZTS is not affecting the cut-off wavelength and optical character of undoped ZTS crystals.

Estimation of optical band gap, extinction coefficient and refractive index

The optical absorption coefficient of the grown crystals (α) was calculated by

$$\alpha = \frac{2.3026 \log(\frac{1}{T})}{d} \quad \text{--------------------- (1)}$$

Where, T and d are the transmittance and thickness of the crystal (1 mm) respectively. As a direct band gap material, the title material with 'α' gives the following relation

$$h\nu\alpha = A(h\nu - E_g)^n \quad \text{---------------------(2)}$$

"A" is the constant, E_g and h are the optical band gap and Planck's constant respectively and "ν" is the incident photon frequency. The exponent "n" depends on the type of transition. The values of "n" represented by ½, 2, 3/2 for direct allowed indirect allowed and direct forbidden transitions. In the present manuscript, n is taken as ½. The optical band gap was estimated by plotting $(\alpha h\nu)^2$ vs hν (Tauc's plot Figure No.4).

From Figure No.4, the values of the optical band gap for the undoped and L-Valine doped ZTS are 4.5 eV and 5 eV respectively. This increase in the band gap value may be due to the chelation of L-Valine in undoped ZTS. L-Valine doped ZTS crystal with wide optical band gap indicates its suitability for optoelectronic devices like LED and laser diodes[12].

The various other optical constants were estimated using the following relation. The extinction coefficient (K) is found by the relation:

$$K= \frac{\alpha\lambda}{4\pi} \quad \text{---------------------- (3)}$$

Where, λ is called as the wavelength. The extinction coefficient as a function of photon energy is indicated in Fig. 5 for undoped and L-Valine doped ZTS. An exponential decay is observed in the extinction coefficient as the photon energy increases (Figure No.5).

The reflectance (R) of the crystal is calculated by

$$R = \frac{1\pm\sqrt{(1-\exp(-\alpha t)+\exp(\alpha t))}}{(1+\exp(-\alpha t))} \quad \text{---- (4)}$$

and the refractive index (n) is given by

$$n= \frac{-(R+1)\pm\sqrt{(-3R^2+10R-3))}}{2(R-1)} \quad \text{---- (5)}$$

The reflectance was also plotted as a function of photon energy and shown in Figure No.6 for undoped and L-Valine doped ZTS.

The refractive index was calculated from the equation (5) and the plot of wavelength vs refractive index (Figure No.7) for undoped and L-Valine doped ZTS.

From Figure No.7, it is noticed that the refractive index (n) decreases with the increase in wavelength. The refractive index of L-Valine doped ZTS crystal with wavelength at 1100 nm in Figure No.7 was found to be 1.59 and for undoped ZTS with wavelength at 1100 nm, it was 1.68. Therefore, the refractive index of L-Valine doped ZTS is less than undoped ZTS crystals which confirmed the optical transmission of doped ZTS crystal is higher than undoped ZTS.

The high transmission, low reflectance and low refractive index of L-Valine doped ZTS makes the materials a suitable one for antireflection coating in solar thermal and nonlinear optical device applications[13]. Hence, this material may prove useful in the fabrication of optoelectronic and nonlinear optical devices.

Photoluminescence analysis

Photoluminescence emission spectra of the crystals were recorded using a Perkin Elmer LS-55 spectrometer within the wavelength range of 400 to 700 nm at room temperature. The optical emission activities of the material are essential for applications in the field of medical investigations to determine the chemical, biochemical, interfaces, surfaces, impurity levels. It is also used to gauge alloy disorder and interface roughness. The room temperature PL spectrum was recorded with an excitation wavelength of 300 nm for both undoped and L-Valine doped ZTS crystals (Figure No.8).

The PL spectrum of undoped and L-Valine doped ZTS crystals shows a sharp violet emission at 425 nm. The emission occurring between 370 nm and 500 nm is also associated with vacancy sites and defect concentrations[14]. A marked enhancement in the PL intensity was observed in the L-Valine doped ZTS crystal which is due to the considerable increase of vacancy concentration[15]. An intensive peak broadening is observed at the emission point which is attributed to increased S^{2-} vacancies which are created during doping of L-Valine. This results in the increase of vacancy related defects (F-centers). Hence, it could be concluded that doping L-Valine increases the intensity and the sharpness of the violet band in the PL spectrum.

Thermal Stability analysis

TG/DTA analysis was carried out using EXSTAR6200 thermal analyzer at a heating rate of 20°C/ min in a nitrogen atmosphere for a temperature range of 30°C-850°C. The recorded TG/DTA thermograms for undoped and L-Valine doped ZTS crystals are shown in Figure No.9a and Figure No.9b.

The percentage of weight loss of the material as a function of temperature is measured in TGA. The absence of water of crystallization in the molecular structure is represented by the absence of weight loss around 100 °C[16]. Since there is no weight loss within the temperature ranges of 0-230°C, undoped ZTS and L-Valine doped ZTS are thermally stable till 230°C. The TGA curve also shows different phases of decomposition. The first phase of weight loss begins at 223.04°C for undoped ZTS and at 223.86°C for L-Valine doped ZTS which is ascribed to the decomposition as well as the evaporation of a part of the title materials. The second stage of weight loss at 312.22°C and

310.31°C for undoped and L-Valine doped ZTS respectively. The TGA curves exhibit that maximum weight loss takes place in the temperature range 232°C – 310°C due to the liberation of volatile substance like sulphur oxide in the title material and this seems to be the major stage of decomposition[10].

DTA curve for undoped ZTS shows a sharp endothermic transition at 239 °C further an endothermic peak observed at 354°C. DTA curve for L-Valine doped ZTS shows the endothermic transition at 250°C and 370°C. The first endothermic peak accompanied by a weight loss denotes the decomposition point of the crystals. It can be noted that L-Valine doped ZTS is more thermally stable than the undoped ZTS. The decomposition temperature of undoped ZTS is 239°C and that of L-Valine doped ZTS is 250°C. The sharpness of the endothermic peaks in DTA curve suggests a good degree of crystallinity of the materials. The absence of other peaks before the decomposition point of the samples confirms that there is no other transition taking place in the material and this ensures the thermal stability of the material for possible applications in lasers. Thus, L-Valine doped ZTS crystal with better thermal stability can be more preferred than undoped ZTS for optical limiting applications.

Nonlinear optical analysis (Z–scan technique)

The nonlinear optical parameters were studied by a Z-scan technique using He–Ne laser (λ = 632.8 nm) and focused by a lens of 23 cm focal length. Z-scan measurements are performed in two different modes i.e. (i) open aperture and (ii) closed aperture. The measurement in open aperture mode provides information regarding the nonlinear absorption coefficient (β) and the closed aperture mode helps us to estimate the third order nonlinear refractive index (n_2). The Real part of the third-order susceptibility [Re $\chi^{(3)}$] is directly proportional to the nonlinear refractive index and the nonlinear absorption coefficient is connected to the imaginary part [Im $\chi^{(3)}$]. The sample was moved across the focal region (-z to +z) along the direction of propagation of the laser beam through an aperture and intensity of the laser source was determined by a digital power meter attached to the detector.

In the closed aperture, the transmittance of the title materials through the aperture is observed in the far field as a function of the Z–position. He –Ne laser whose wavelength λ = 632.8 nm was employed as the source of the light and focused by a lens of 23 cm focal length and a polished title compound of 1mm thickness was employed for this measurement. The experiment was performed by placing the title materials in the laser beam at various positions with respect to the focus and assessing the corresponding light transmission of the grown crystal. A spatial distribution of the temperature at the crystal surface is produced due to the localized absorption of a tightly focused beam passing through the absorbing title materials. Therefore, a spatial variation of the refractive index is produced which behaves as a thermal lens leading to the phase distortion of the propagating laser beam. Figure No.10a and Figure No.11a shows the closed aperture Z- scan curve for undoped ZTS and L-Valine doped ZTS crystals respectively.

The peak to valley transmission difference can be evaluated using the following equation[17,18].

$$\Delta T_{p-v} = 0.406\,(1-S)^{0.25}\,|\Delta \phi| \qquad \text{---- (6)}$$

Where,

$S = [1-\exp(-2r_a^2/\omega_a^2)]$ represents the aperture linear transmittance, r_a is denoted as the aperture radius and ω_a is the radius of the beam at the aperture. The third order nonlinear refractive index was determined by the relation

$$n_2 = \frac{\Delta \phi}{K I_0 L_{eff}} \qquad \text{---------------------- (7)}$$

Where K=2π / λ which is the wave number, I_0 is the laser beam intensity at Z= 0 (0.1473kWcm^{-2}). $L_{eff} = [1-\exp(-\alpha L)]/\alpha$, is the effective thickness of the title material depending on the linear absorption coefficient (α) and L are the thickness of the sample (1 mm).

For open aperture, a lens replaces the aperture to accumulate the entire laser beam transmitted through the sample. Fig. 10b and Fig. 11b shows the open aperture Z scan curve for undoped ZTS and L-Valine doped ZTS crystals respectively.

The nonlinear absorption coefficient (β) was estimated by

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad \text{---------------------- (8)}$$

Where, ΔT is the one peak point at the open aperture Z-scan curve. The nonlinear susceptibility of grown crystals was determined by the equations

$$Re\chi^{(3)}\ (esu) = 10^{-4}(\varepsilon_0 C^2 n_0^2 n_2)/\pi\ (cm^2/W)$$

$$Im\chi^{(3)}\ (esu) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)/4\pi^2\ (cm/W)$$

Where, ε_0 is the permittivity in the vacuum and C is the velocity of light, n_0 is the linear refractive index of the sample. Thus, the third order nonlinear susceptibility can be calculated by

$$\chi^{(3)} = \sqrt{(Re\chi^{(3)})^2 + (Im\chi^{(3)})^2} \quad \text{--------- (9)}$$

The negative refractive index shows the self-defocusing effect of the grown crystals[19]. This may be an added advantage for the application of optical sensors like night vision devices. The negative β value indicates that the complex shows the saturable absorption[20,21].

The measurement details and the results of the nonlinear parameters such as nonlinear optical susceptibility $\chi^{(3)}$, nonlinear refractive index (n_2) and third order nonlinear absorption coefficient (β) have been evaluated which are presented in Table 3 and Table 4.

From Table 4, it is clear that L-Valine doped ZTS crystal possesses a high third order nonlinear susceptibility when compared to the undoped ZTS crystal. The high value of $\chi^{(3)}$ is owing to the π-electron cloud transfer from the donor to the acceptor, which can constitute the molecule highly polarized[22].

Table No.1: Unit cell values of undoped ZTS and L-Valine doped ZTS crystals

S.No	Specimens	Unit cell parameters			Cell volume [Å^3]	α =β=γ
		a [Å]	b [Å]	c [Å]		
1	Undoped ZTS	7.811	11.185	15.556	1359	90°
	L-Valine doped ZTS	7.813	11.199	15.584	1364	90°

Table No.2: Functional group assignments of undoped ZTS and L-Valine doped ZTS

S.No	Undoped ZTS (cm^{-1})	L-Valine doped ZTS (cm^{-1})	Bond Assignments
1	3202	3204	ν_s (NH_2)
2	2357, 2710	2360, 2713	Hydrogen bonding interaction of COOH in Crystal lattice
3	1798, 1894	1800, 1897	ν (C=O)
4	1600	1602	δ (NH_2)
5	1510	1512	ν_s (N–C–N)
6	1398	1400	ν_{as} (C=S)
7	1120	1122	ν_s (C–N)
8	995	1000	ν_s (C–N)
9	700	704	ν_s (C=S)
10	598	604	ν_{as} (N–C–S)
11	400	405	δ_s (N–C–S)

ν_s – Symmetric stretching, ν_{as} – Asymmetric stretching, δ - bending,
δ_s – Symmetric bending, ν – Stretching.

Table No.3: Measurement details of the Z-scan measurement

S.No	Parameters	Present work
1	Laser beam wavelength (λ)	632.8 nm
2	Lens focal length (f)	23 cm
3	Spot-size diameter in front of the aperture (ω_a)	2 cm
4	Aperture radius (r_a)	5 mm
5	Incident intensity at the focus (z = 0)	0.1473 kW cm^{-2}
6	Effective thickness (L_{eff})	6.46 x 10^{-7} m

Table No.4: The results of the nonlinear optical parameters

S.No	Parameters	Undoped ZTS	L -Valine doped ZTS
1	Nonlinear refractive index (n_2) x 10^{-8} cm^2/ W Nonlinear absorption coefficient (β) x 10^{-3} cm / W Real part of the third order nonlinear optical susceptibility [Re $\chi^{(3)}$] x 10^{-6} esu Imaginary part of the third order nonlinear optical susceptibility [Im $\chi^{(3)}$] x 10^{-6} esu Third order nonlinear optical susceptibility [$\chi^{(3)}$] x 10^{-6} esu	 -5.28 -6.69 3.13 1.64 3.2	 -6.69 -7.27 3.34 1.57 4.8

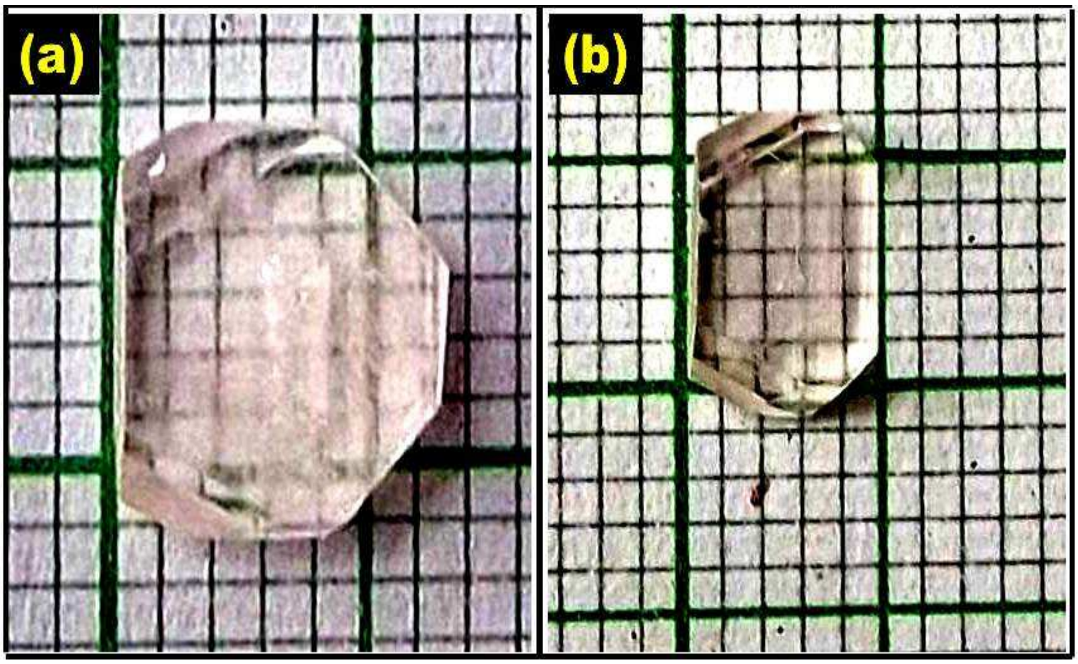

Figure No.1: (a) As grown undoped ZTS crystal (b) As grown L-Valine doped ZTS crystal

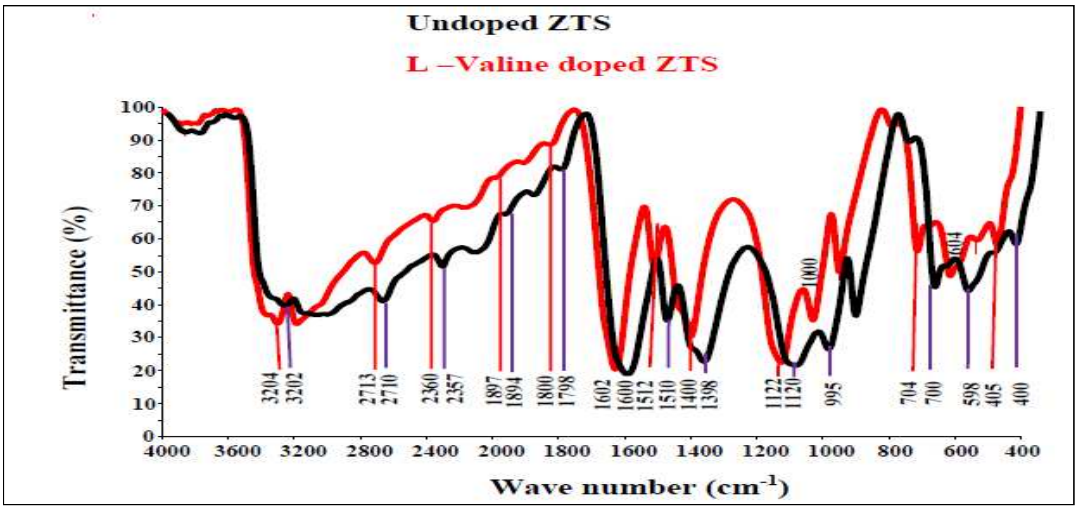

Figure No.2: FTIR Spectrum of undoped ZTS and L-Valine doped ZTS

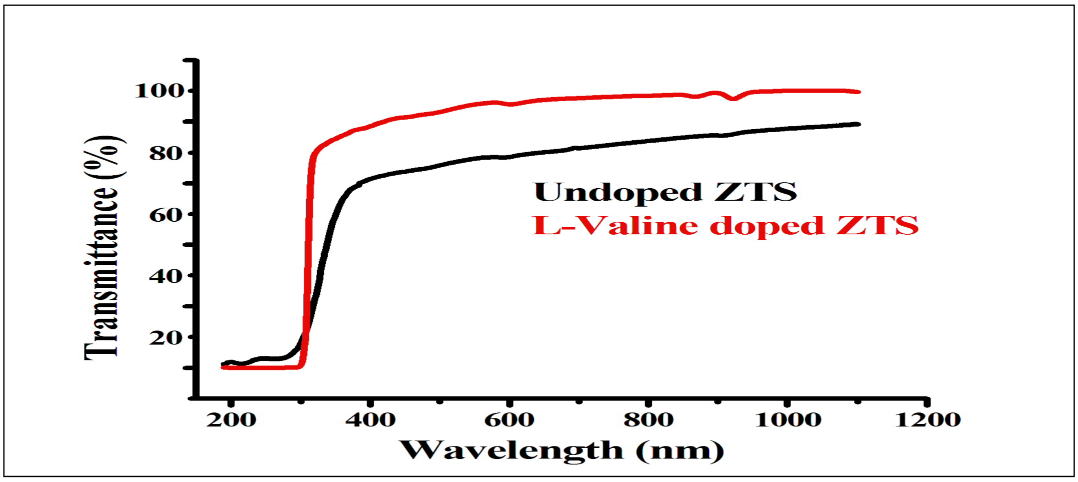

Figure No.3: UV-Visible spectra of undoped ZTS and L-Valine doped ZTS crystals

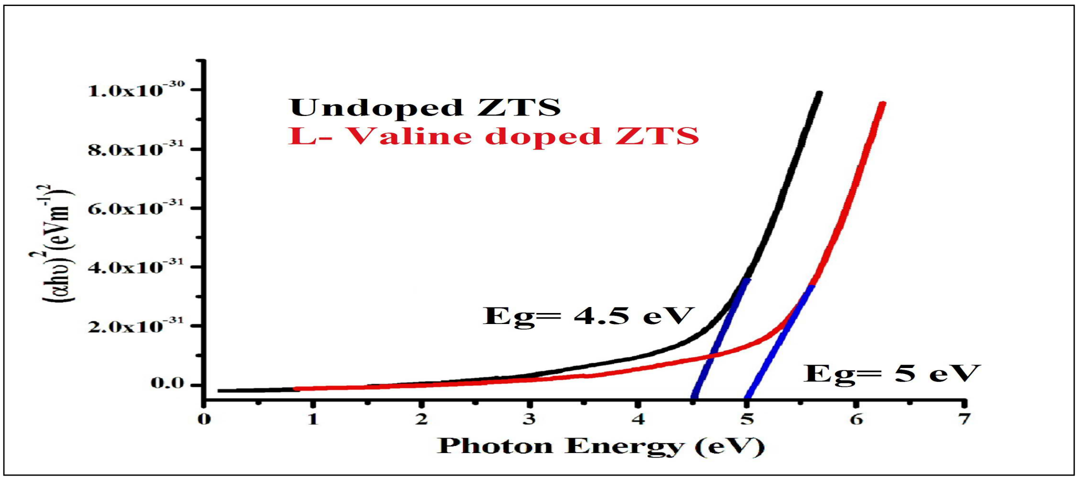

Figure No.4: Optical band gap of undoped and L-Valine doped ZTS crystals

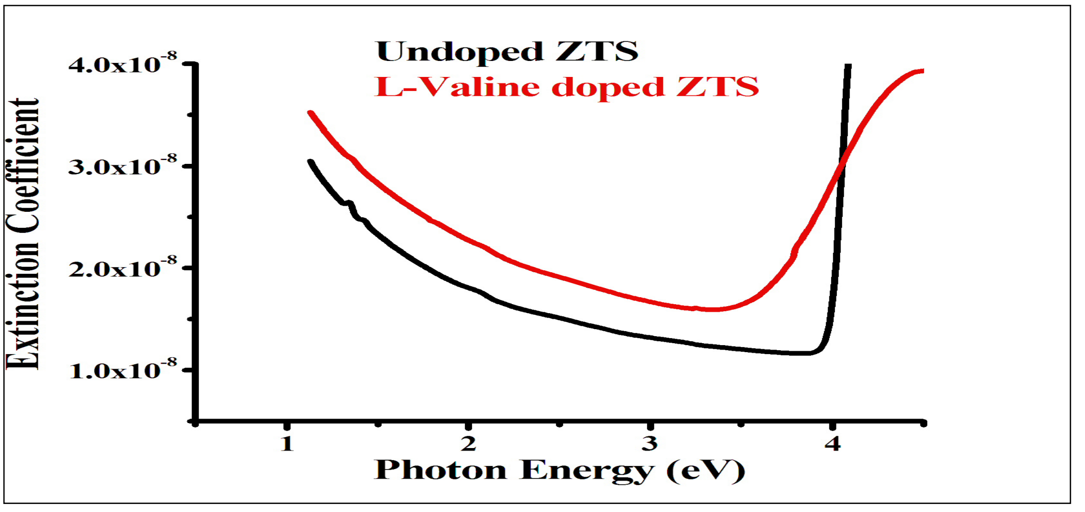

Figure No.5: Photon energy vs Extinction coefficient of undoped and L-Valine doped ZTS

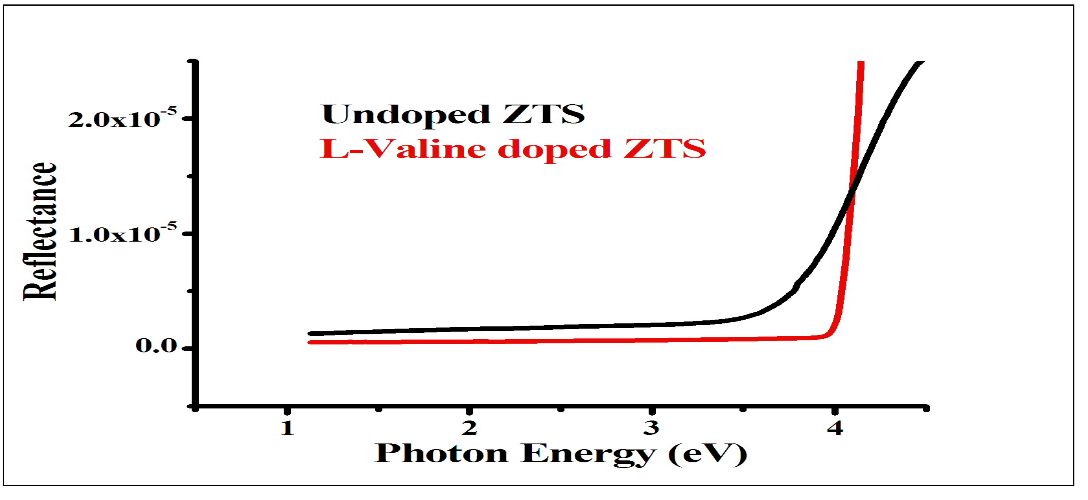

Figure No.6: Photon Energy vs Reflectance of undoped and L-Valine doped ZTS crystals

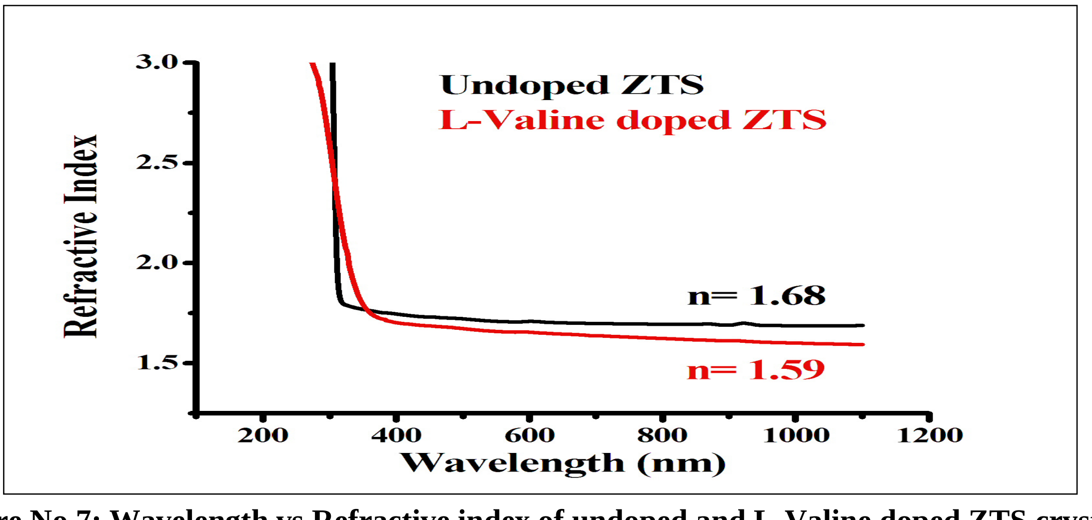

Figure No.7: Wavelength vs Refractive index of undoped and L-Valine doped ZTS crystal

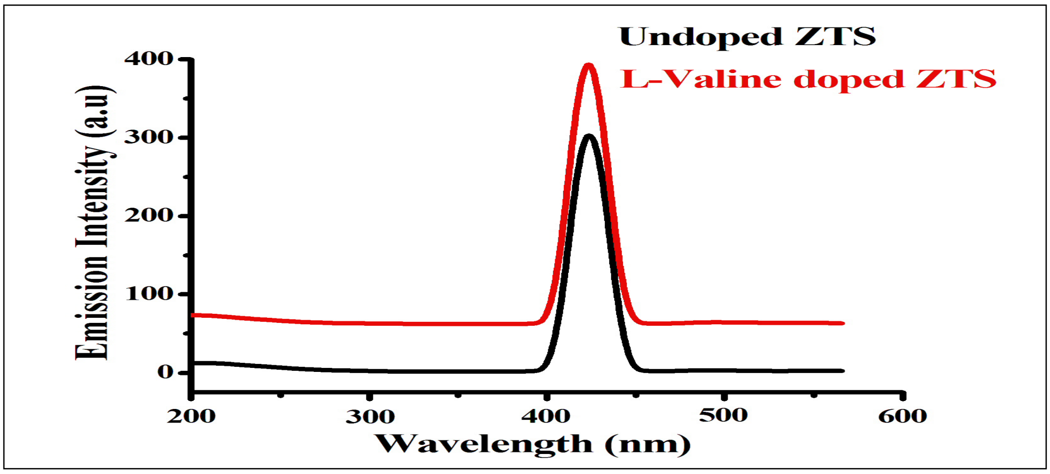

Figure No.8: Photoluminescence spectrum of undoped and L-Valine doped ZTS

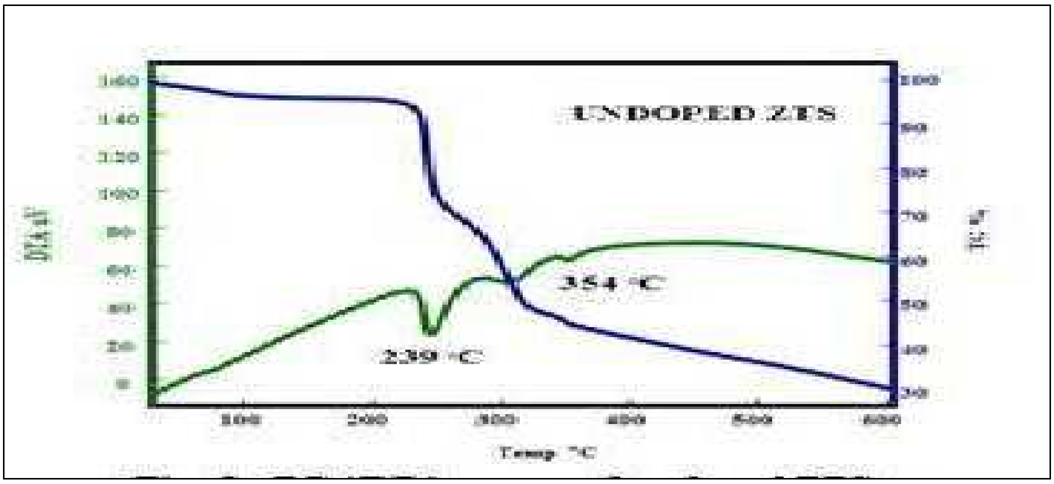

Figure No.9a: TG/DTA curve of undoped ZTS

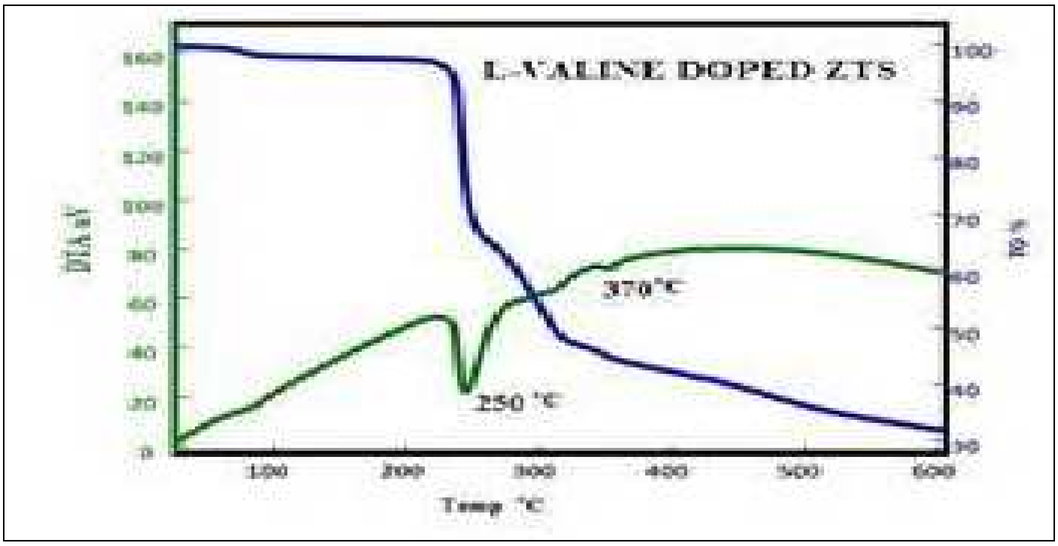

Figure No.9b: TG/DTA curve of L-Valine doped ZTS

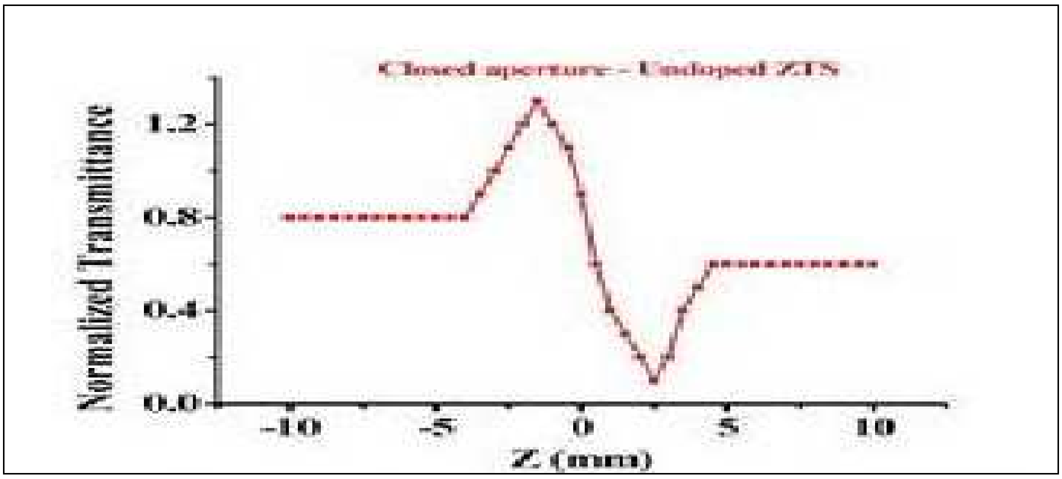

Figure No.10a: Closed aperture curve of undoped ZTS

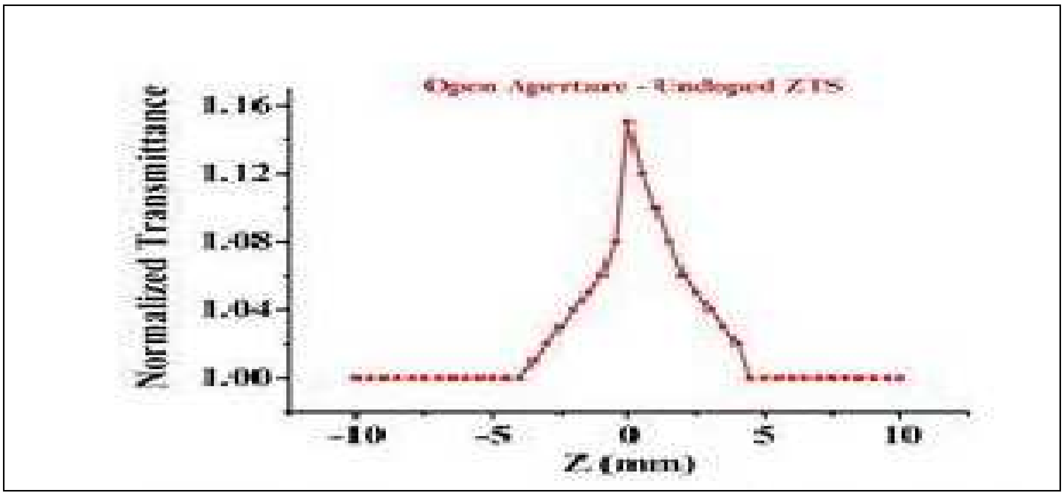

Figure No.10b: Open aperture curve of undoped ZTS

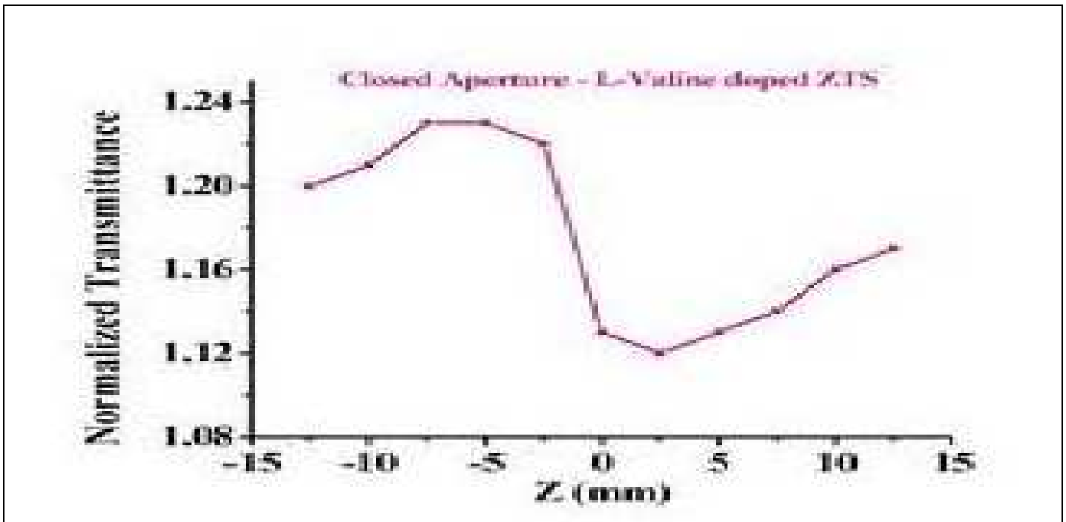

Figure No.11a: Closed aperture curve of L-Valine doped ZTS

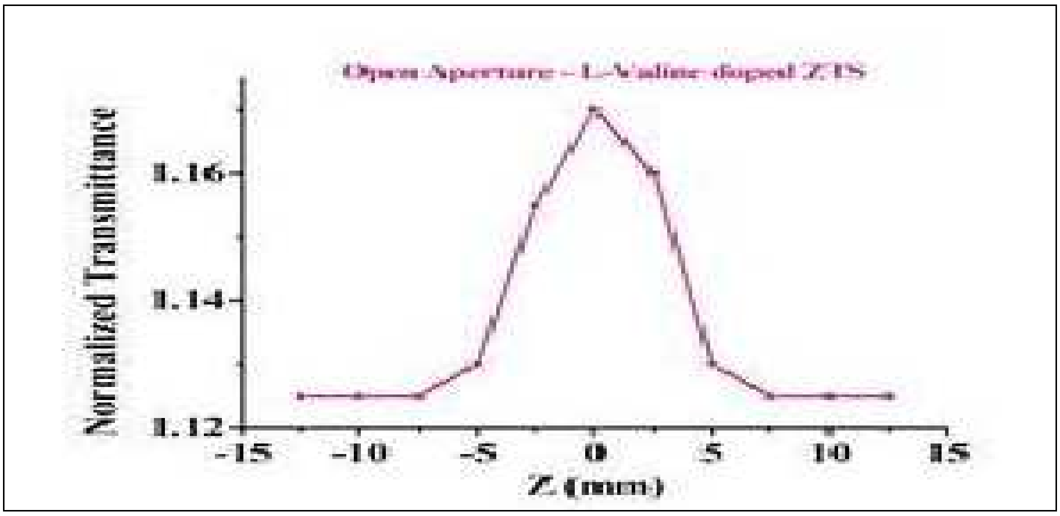

Figure No.11b: Open aperture curve of L-Valine doped ZTS

CONCLUSION

Undoped and L-Valine doped ZTS semiorganic nonlinear optical crystals were grown by low temperature solution technique. The single crystal X-ray analysis confirmed that the grown crystals belong to the orthorhombic system with space group $Pca2_1$. The presence of functional groups and modes of vibration of grown crystals were affirmed by FT-IR analysis. UV-Vis optical study shows a superior optical transmission nature of L-Valine doped ZTS crystal in the entire visible region than undoped ZTS crystal and the optical band gap of ZTS was found to increase from 4.5 eV to 5 eV on the addition of L-Valine. The optical investigation indicated the transparency of the grown crystals and confirmed its suitability for optical device fabrication. Optical constants were estimated and the variation of reflectance with respect to wavelength, extinction coefficient with respect to photon energy was studied. PL spectrum shows the sharp emission peaking around 425 nm corresponds to violet emission and a change in the intensities was noted. TG/DTA studies showed the grown crystals are thermally stable till 230°C. SHG efficiencies of grown crystals have enhanced due to the addition L-Valine in ZTS and hence L-Valine doped ZTS crystals are efficient candidates for frequency-doubling phenomena. Closed aperture Z–scan study reveals the negative refractive index showing the defocusing nature. This is the most required properties for optical limiting applications and open aperture Z-scan study reveals the saturation absorption. The third order nonlinear properties confirmed its suitability for nonlinear optical devices such as optical switching. The superior transparency, photoluminescence activity, wide band gap and third order nonlinear optical behavior along with fine melting point suggest that L-Valine doped ZTS crystal could be a suitable material for the nonlinear optical application.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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