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Highlights

Optics & Laser Technology ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Investigation of optical and electrical properties of L-Cystein doped zinc thiourea chloride (ZTC) crystal for nonlinear optical (NLO) applications

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- The L-Cystein doped zinc thiourea chloride (ZTC) crystal grown using slow evaporation technique.
- The SHG efficiency found to 1.96 times that of pure ZTC.
- The crystal has high transparency in UV visible region.
- The lower dielectric characteristics indicate high optical quality of crystal.
- The thermal studies of the crystal are discussed.

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Investigation of optical and electrical properties of L-Cystein doped zinc thiourea chloride (ZTC) crystal for nonlinear optical (NLO) applications

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ABSTRACT

The single crystal of L-Cystein doped zinc thiourea chloride (ZTC) has been grown by slow evaporation technique. The optical study revealed that the doped ZTC crystal has high transmission with lowest cut off wavelength of 306 nm. The optical band gap was found to be 4.2 eV. The transition band gaps were studied using the photoluminescence spectrum. The incorporation of L-Cystein in ZTC was estimated qualitatively by FT-IR analysis. The presence of dopant was confirmed by energy diffraction X-ray analysis (EDAX) analysis. The lower dielectric characteristics of doped ZTC crystal were scrutinized by dielectric measurements. The high thermal stability of grown crystal was ascertained by TG/DTA analysis. The Second harmonic generation (SHG) efficiency measured using Nd-YAG laser is 1.96 times that of pure ZTC.

1. Introduction

In recent years, great efforts had been made to develop new organic, inorganic, and semiorganic nonlinear optical (NLO) materials due to their widespread applications in technologies like lasers, optoelectronics, frequency conversion, high-speed information processing, optical advantage of both inorganic (high thermal and mechanical stability) and organic (broad optical frequency range and second harmonic conversion efficiency) materials. Among thiourea metal complex zinc thiourea chloride (ZTC), zinc thiourea sulphate (ZTS), cadmium thiourea chloride (BTCC), copper thiourea chloride (CTC), bisthiourea zinc acetate (BTZA) and cadmium thiourea acetate (BTCA) are reported and possess moderate SHG efficiency [1–3]. The zinc thiourea chloride (ZTC) is a potential semiorganic NLO material and crystallizes in the non centrosymmetric orthorhombic space group. In the field of nonlinear optical crystal, amino acids play a vital role as they exhibit natural chiral properties and crystallize in the noncentrosymmetric space groups, which are an essential criterion for NLO applications. Optically active amino acids show high efficient optical second harmonic generation (SHG) and are promising candidates for laser and optical communication technology. Since isometrically pure and optically active substances always meet the symmetry requirements for optical second harmonic generation, there is considerable variation in efficiency for the generation of SHG, ranging from almost zero to greater than that of potassium dihydrogen phosphate crystals. The influence of L-Arginine on SHG efficiency of ZTC had been reported by Balu et al. [4].The growth and characterizations of L-Alanine and Glycine doped ZTC crystals had also been reported by our group [5,6]. L-Cystein [$C_3H_7NO_2S$], the smallest naturally occurring amino acid with a thiol group, offers a high degree of chirality due to the presence of three different functional groups. The L-Cystein occurs in both the nonionic and Zwitter ionic forms under involvement of all three functional groups. It has Zwitter ionic state in aqueous solution as well as in solid state [7]. In literature no reference has been observed in attempting L-Cystein doping in ZTC crystal. In the present communication, attention is focused on the effect of optical and dielectric properties of ZTC with addition of amino acid L-Cystein.

2. Experimental

The ZTC salt was synthesized using the AR grade zinc chloride and thiourea in molar ratio 1:2. The Calculated amount of salt was dissolved in the deionised water and allowed to evaporation at room temperature. The ZTC salt was dissolved in deionized water to achieve the supersaturated solution. The amino acid L-Cystein was doped in1, 2 and 3 weight% to the supersaturated solution of ZTC and stirred for four hours at constant speed to achieve the homogeneity throughout the volume. This doped solution is filtered and kept for evaporation at room temperature. The purity of L-Cystein doped ZTC is achieved by successive recrystallisation. The good quality transparent seed crystals were harvested within

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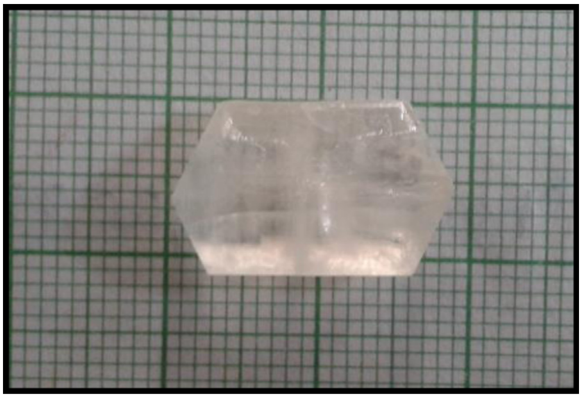

Fig. 1. Photograph of L-Cystein doped ZTC.

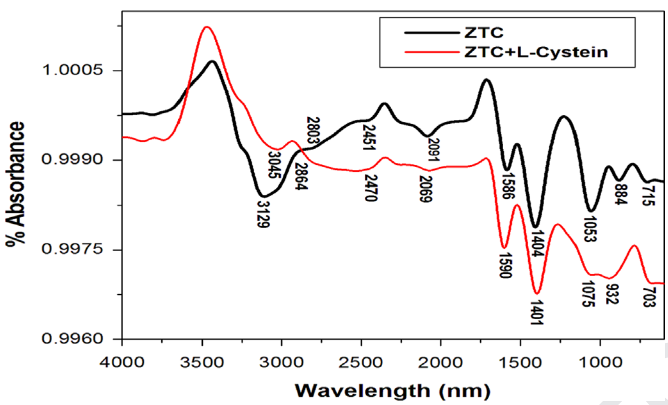

Fig. 2. FT-IR spectrum of L-Cystein doped ZTC.

15 days. The single bulk crystal of 2 wt% L-Cystein doped ZTC was grown by slow evaporation technique is shown in Fig. 1.

3. Result and discussion

3.1. SHG efficiency test

The SHG efficiency of L-Cystein doped ZTC was determined using the Kurtz and Perry powder method [8]. To elaborate, the SHG demands specific molecular alignment of the crystal to be achieved facilitating nonlinearity in the presence of a dopant. The inclusion of complexation alters the molecular alignment which is imperative for enhancing SHG [4]. The NLO behavior was confirmed from the output of the bright green emission from the powder sample. The measured output signals for pure and doped ZTC crystals were 5 mV and 9.8 mV, respectively. The SHG efficiency of Doped ZTC crystal is 1.96 times greater than that of pure ZTC.

3.2. Fourier transform infrared (FT-IR) analysis

The FT-IR spectrum was recorded using Bruker Alpha-T in the region 4000–600 cm^{-1} is shown in Fig. 2. The specific peaks of ZTC occur at 1586, 1404, 1053, 713 cm^{-1}which are in good agreement with the reported work [9]. The major band of C=S symmetric stretching is observed at 932 cm^{-1}.The C–O stretch band is observed at 1075 cm^{-1} for doped ZTC. The C–S asymmetric stretching vibration is observed at 1404 cm^{-1} and 1401 cm^{-1} for pure and doped ZTC crystal. The characteristic $-NH_2$ bending of ZTC is observed at 1586 cm^{-1}. The absorption peak at 1590 cm^{-1} is assigned to $-NH_2$ bending of doped ZTC. The N=C=S bond

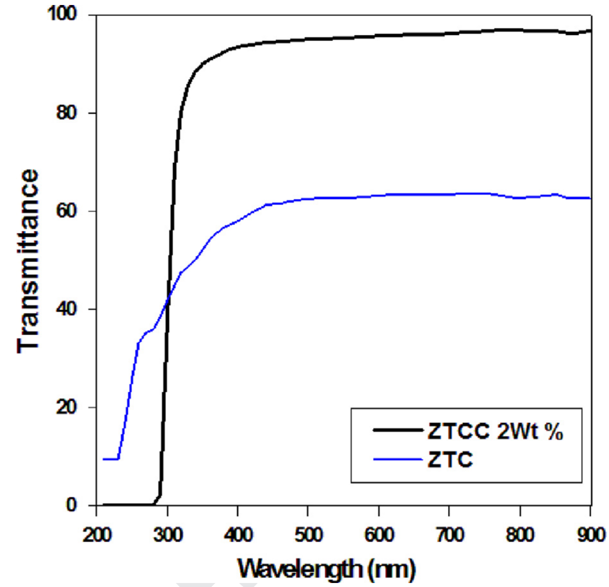

Fig. 3. UV transmittance spectrum.

stretching in the doped ZTC is assigned to absorption peak cited at 2069 cm^{-1}. The absorption observed at 2470 cm^{-1} and 2451 cm^{-1} is assigned to S–H bond stretching. The broad envelope positioned between 2864 cm^{-1} and 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of $-NH_2$ group of pure and doped ZTC crystals. Thus thiourea complex formation and its coordination with the amino acid have been confirmed.

3.3. Optical studies

The optical transmission spectra of the grown crystals were recorded using Shimadzu UV-2450 Spectrophotometer in the range of 200–900 nm is shown in Fig. 3. The L-Cystein doped crystal showed high transmittance of 90% in entire visible region and lower cut off wavelength of 306 nm imperative for laser frequency conversion applications. The optical band gap (E_g) can be evaluated from the transmission spectra [10] using the relation

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

where A is a constant, E_g the optical band gap, h the Planck's constant and n the frequency of the incident photon. The optical band gap of doped ZTC crystal is found to be 4.2 eV and is shown in Fig. 4. The lower absorption and high optical band gap is most desirable for UV tunable laser materials [10]. The extinction coefficient of doped ZTC crystal was observed to be decreasing with wavelength represented in Fig. 5 which confirms semiconducting nature of material [11]. The refractive index (RI) was calculated using the formula reported by Bakr et al. and plotted in Fig. 6 [12]. It was found to be 1.12 at 632 nm. The lower RI procured by doped ZTC crystal makes it more suitable than pure ZTC for antireflection coating in solar thermal devices and optical device fabrications [11]. The variation of complex dielectric constant and optical conductivity is shown in Figs. 7 and 8, respectively. The low dielectric constant and enhanced optical conductivity of doped ZTC is better for frequency conversion [11]. Hence, this crystal can be used for UV tunable laser, NLO and SHG device applications effectively.

3.4. Photoluminescence studies

The photoluminescence (PL) studies were carried to evaluate lower concentration of defects and transitional band gaps.

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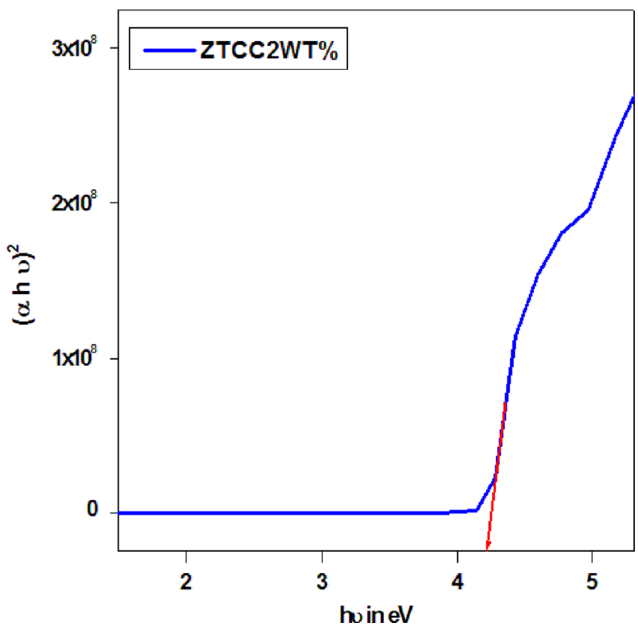

Fig. 4. $(\alpha h\nu)^2$ vs. $h\nu$ (eV).

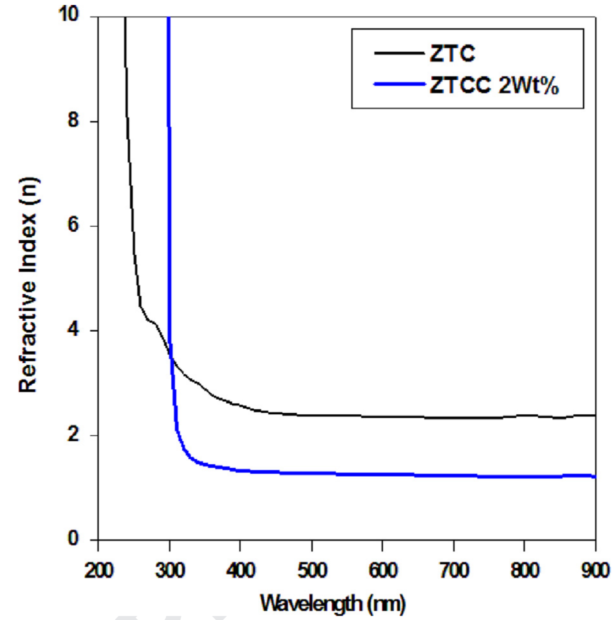

Fig. 6. Refractive index wavelength.

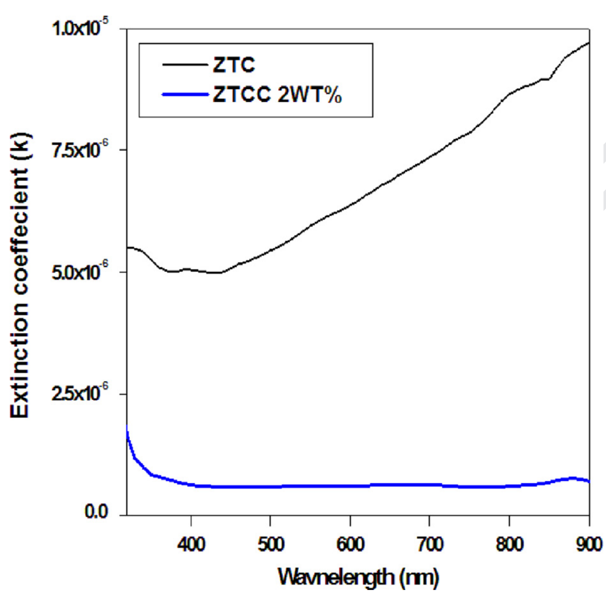

Fig. 5. Extinction coefficient vs. wavelength.

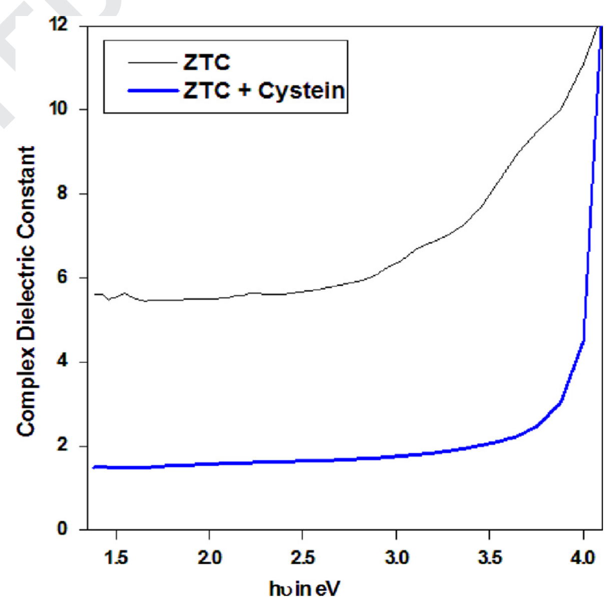

Fig. 7. Complex dielectric constant vs. $h\upsilon$ (eV).

The impurity on absorption of light gives rise to bound excited state from which it returns to its ground state abiding in the analysis of colour centre creation mechanism [3]. The recorded PL spectrum of doped ZTC crystal is shown in Fig. 9. The sample had been excited at 254 nm, four major peaks were observed. The high energy violet emissions were observed at 396 nm and 412 nm corresponding to energies 3.13 eV and 3 eV. The two shoulder blue emissions were observed at 483 nm and 457 nm. The emission of energy 2.2 eV in green band at 539 nm can be attributed to the relaxation of polarization defects formed by the strained sites attached to oxygen vacancies. In metal complexes the defects due to oxygen vacancy plays important role in lattice distortion and its surrounding [3].The sharp PL intensity confirms low transitional band gaps and high optical quality of doped ZTC crystal substantiating it for NLO applications.

3.5. *Energy dispersive X-ray analysis (EDAX)*

Energy dispersive X-ray analysis was employed for characterizing the presence of doped element using a JEOL-2300 instrument. The energy peaks obtained for different elements were recorded as shown in Fig. 10. The presence of oxygen O, Cl, Zn, S, N peaks in EDAX spectrum confirmed the successful doping of L-Cystein in ZTC.

3.6. *Scanning electron microscope (SEM) investigations*

The grown crystal was exploited to SEM analysis using JD-2300 analysis System The quality of the grown crystal can be inferred to some extent by observing the surface morphology of the crystal. The recorded SEM picture Fig. 11 confirmed the formation of the pits and inclusions on the surface of the crystal, which may occur due to the temperature fluctuations during the growth process.

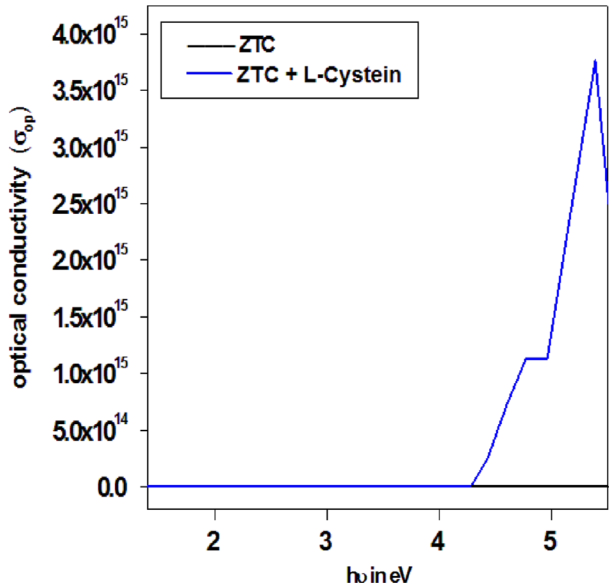

Fig. 8. Optical conductivity vs. $h\upsilon$ (eV).

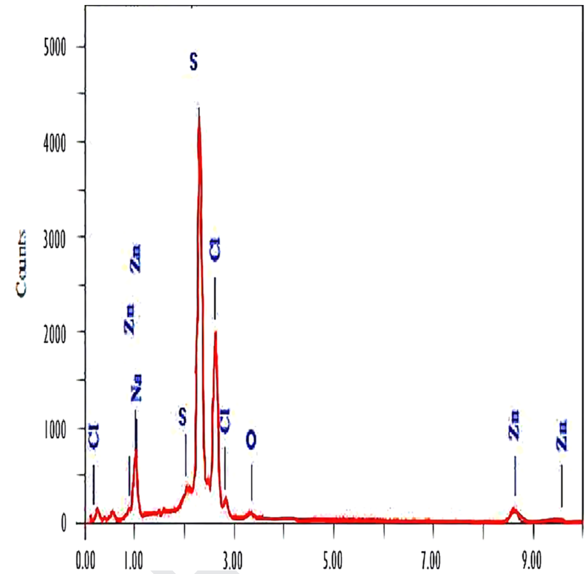

Fig. 10. EDAX spectrum of L-Cystein doped ZTC.

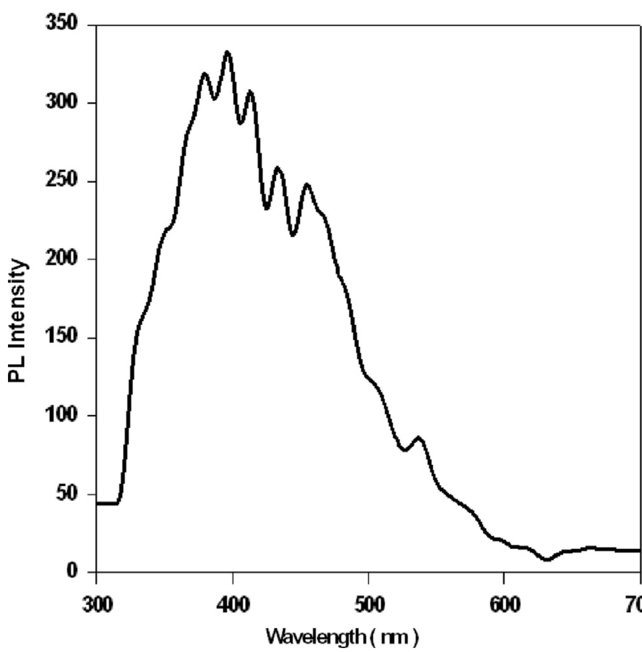

Fig. 9. PL spectra of L-Cystein doped ZTC.

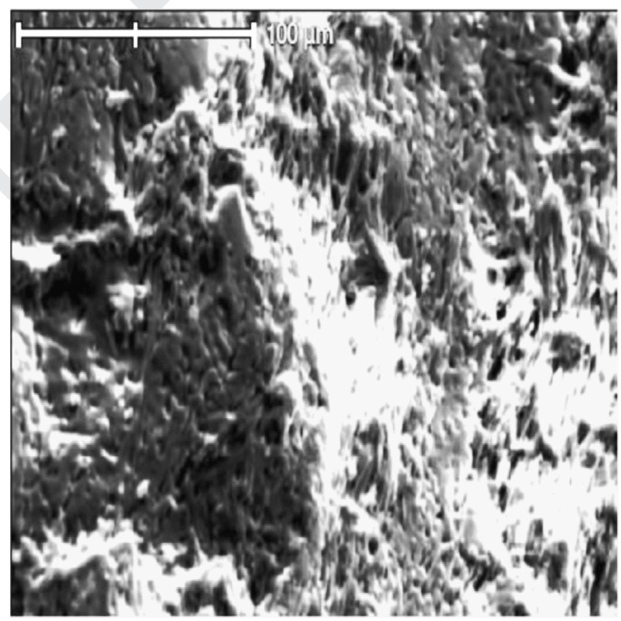

Fig. 11. SEM image of L-Cystein doped ZTC crystal.

3.7. Dielectric studies

The dielectric behavior of the doped and pure ZTC crystal were carried at room temperature using the Gwinstek LCR-819 cube meter with varying frequency range of 10 Hz to 1 kHz. The dielectric constant is calculated using the relation, $\varepsilon = Cd/\varepsilon 0A$ where, C is the capacitance, d is the thickness; A is the area of the sample. The frequency response of dielectric constant and dielectric loss for pure and doped ZTC crystal is shown in Figs. 12 and 13. The dielectric constant has high values in the lower frequency region and then decreases with the applied frequency. The high value of dielectric constant at lower frequencies may be due to the presence of polarizations mechanism namely space charge, orientation, electronic and ionic polarization. The low values of dielectric constant at high frequencies indicate high crystal perfection and low space charge polarization [13]. The dielectric loss as a function of frequency suggests that dielectric loss strongly depends on the frequency of the applied field suggesting low energy dissipation, high optical quality and least defects in crystal [13]. The lower dielectric characteristics indicate the grown crystal is efficient for NLO, optoelectronic, laser and SHG device applications [14]. The ac conductivity is of the order of 10^{24} inverse to that ac resistivity is of the order 10^{-18} shown in Fig. 14.

3.8. Thermal analysis

The thermal behavior of L-Cystein doped ZTC crystal was studied by thermograviemetric analysis (TG) and differential thermal analysis (DTA) at a heating rate of 20 °C/min in the region 100 °C to 400 °C to testify the weight loss and thermal stability. The resulting TG/DTA trace is shown in Fig. 15. The TGA trace of doped ZTC showed straight behaviour up to 200 °C, examination of DTA thermogram reveals an exothermic peak at 140 °C, which could be due to physically absorbed water. A steady weight loss of

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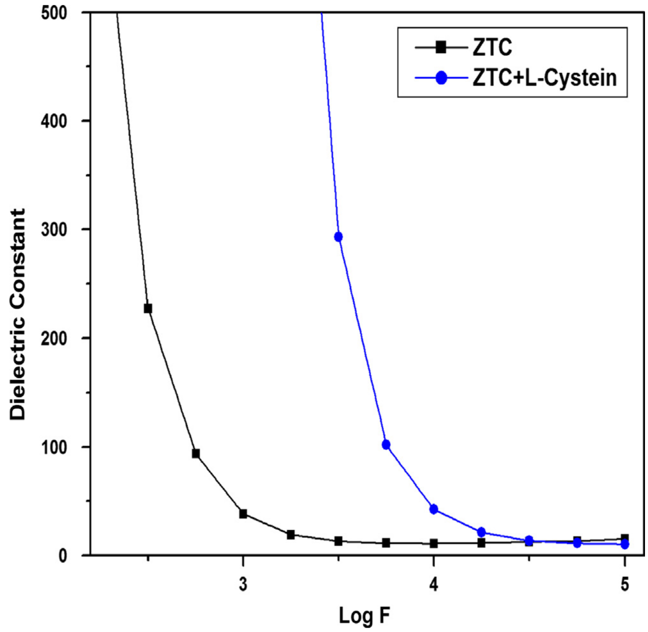

Fig. 12. Dielectric constant vs. log F.

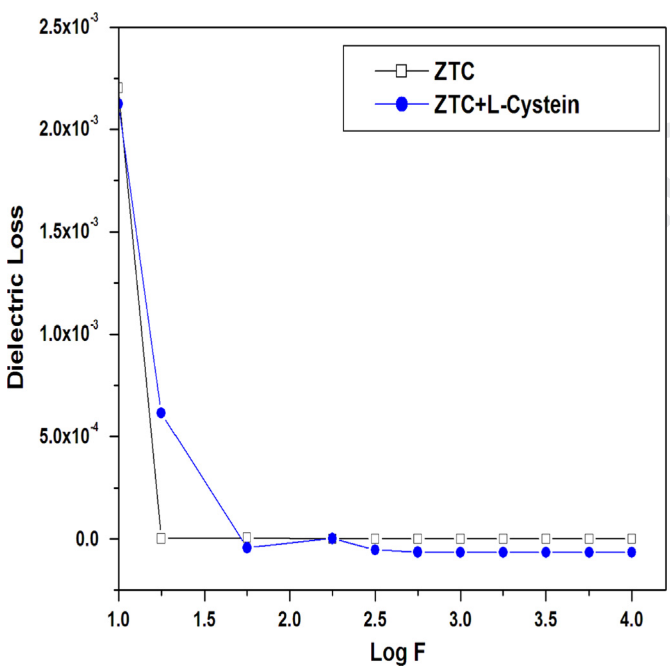

Fig. 13. Dielectric loss vs. log F.

11.25 mg was observed up to 300 °C which may be due to the decomposition of volatile substances such as sulphurdioxide. At higher temperature above 300 °C, the residue observed to be decomposing with high rate, accompanied by a weight loss of 5 mg. The recorded endoderm valley at 150 °C may be due to isomorphic transformation as there is no corresponding weight loss in TGA trace. The thermal studies affirm the grown crystal may be exploited for NLO applications up to 200 °C.

4. Conclusion

Optical quality single crystal of L-Cystein doped ZTC was grown by slow evaporation technique. The optical study shows that the L-Cystein doped crystal has wide optical window with lower cut

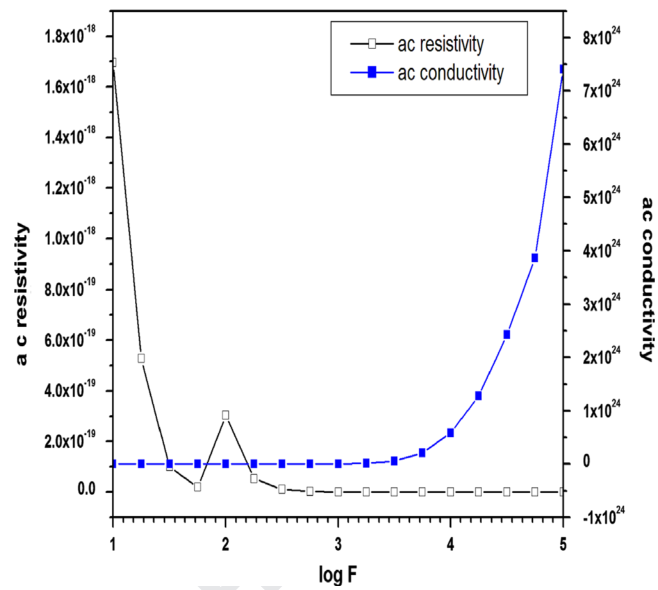

Fig. 14. ac resistivity and ac conductivity of doped ZTC crystal.

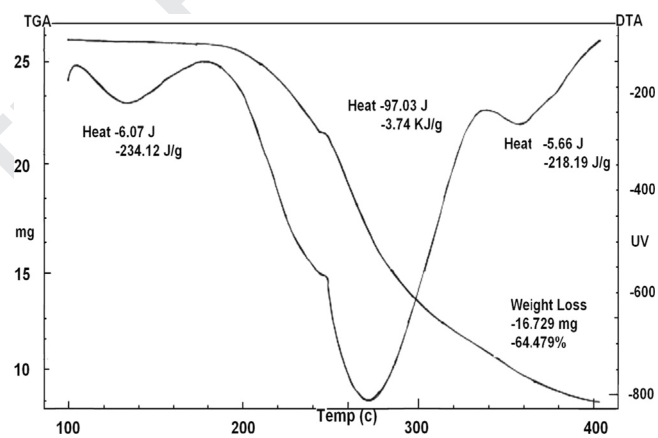

Fig. 15. Plot of TG/DTA curve.

off wavelength of 306 nm. The grown crystal has high optical band gap of 4.2 eV, lower refractive index and extinction coefficient. The L-Cystein doped crystal is thermally stable up to 200 °C. The decreased dielectric characteristics of doped ZTC crystal revealed low polarization mechanism and high crystal purity. The SHG efficiency of doped ZTC is 1.96 times that of pure ZTC. The optical, thermal and dielectric study of L-Cystein doped crystal substantiates its suitable for UV tunable lasers, optical device fabrication, solar thermal devices and NLO applications.

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References

[1] Suresh Sagadeva. Br J Sci Technol 2013;03:340–9.

[2] Suresh S, Mand P, Anand K. J Chem 2013;10:1155–9.

[3] Shahil Kirupavathy S, Stella Mary S, Srinivasan P, Vijayan N, Bhagavannarayana G, Gopalakrishnan R. J Cryst Growth 2007;306:102–10.
[4] Balu T, Rajasekaran TR, Murugakoothan P. Physica B 2009;404:1813–8.
[5] Ahlam MA, Ravishankar MN, Vijayan N, Govindaraj G, Siddaramaiah AP. Prakash Gnana. Nucl Instrum Methods Phys Res, Sect B 2012;278:26–33.
[6] Dhumne NR, Hussaini SS, Dongre VG, Ghugare P, Shirsat MD. Appl Phys A 2009;95:727–32.
[7] Hussaini SS, Dhumne NR, Dongre VG, Shirsat MD. Optoelectron Adv Mater 2008;02:108–12.
[8] Kurtz SK, Perry TT. J Appl Phys 1968;39:3798 (13).
[9] Rajasekaran R, Ushasree PM, Jayavel R, Ramasamy P. J Cryst Growth 2001;229:563–7.
[10] Vivek P, Murugakoothan P. Opt Laser Technol 2013;49:288–95.
[11] Sabari Girisun TC, Dhanuskodi S. Cryst Res Technol 2009;44:1297 (02).
[12] Bakr Nabeel A, Funde AM, Waman VS, Kamble MM, Hawaldar RR, Amalnerkar DP, Gosavi SW, Jadkar SR. J Phys 2011;76:519–31.
[13] Dhas SA Martin Britto, Bhagavannarayana G, Natarajan S. Open Crystallogr J 2008;1:42–5.
[14] Zion Delci, Devarajan Shyamala. Arunachalam Thayumanavan. J Cryst Process Technol 2013;3:5–11.

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