

Optical, photoconductivity, dielectric and thermal studies of L-arginine doped zinc thiourea chloride crystal for photonics applications

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In present studies, L-arginine doped zinc thiourea chloride (LAZTC) crystal has been grown by slow solution evaporation technique. The cell parameters of LAZTC crystal were determined using the single crystal X-ray diffraction technique. The incorporation of L-arginine in ZTC has been confirmed by means of Fourier transform infrared analysis. The high optical transparency of the grown crystal has been examined under the UV-visible study. The wide optical band gap of LAZTC crystal is found to be 5.25 eV. The photoluminescence study of grown crystal has been investigated in the range of 300 to 700 nm. The negative photoconducting nature of LAZTC crystal has been investigated by means of photoconductivity studies. Thermal stability of LAZTC crystal was evaluated by thermogravimetric and differential thermal analysis. The dielectric measurements confirmed the lower dielectric characteristics of LAZTC crystal.

Keywords: Crystal growth, X-ray diffraction, Dielectric studies, Optical studies, Thermal studies, Photoconductivity

Introduction

In recent years, emphasis has been centred on materials exhibiting high non-linearity with impressive properties for their potential applicability in the field of integrated optical devices, frequency conversion and optoelectronic devices.¹ Zinc thiourea chloride (ZTC) is the influential semiorganic crystal resembling the orthorhombic crystal symmetry displaying good mechanical and structural stability with better optical and non-linear properties.² Amino acids offer large non-linearity and promising optical properties as it possesses proton donor amine group (NH_3^+) and proton acceptor carboxyl group (COO^-). The improved physicochemical, electrical and non-linear parameters of bis-thiourea cadmium chloride and zinc thiourea sulphate (ZTS) doped with different amino acids have been reported in literature.³⁻⁶ The influence of glycine on different properties of ZTC has been reported by Hussaini *et al.*⁷ Dhumane *et al.* reported the studies on L-alanine doped ZTC crystal.⁸ Recently, we reported the studies on optical and electrical properties of L-cysteine doped ZTC crystal.⁹

L-Arginine is a promising amino acid, as second harmonic generation efficiency of 1, 3 and 5 mol-% L-arginine doped ZTC crystals was found to be 1.04, 1.14 and 1.21 times higher than that of ZTC crystal respectively.¹⁰ The small quantity of L-arginine has highly influenced the crystal morphology of ZTC and ZTS crystals. L-Arginine can substantially enhance the optical transparency and mechanical properties of ZTC and ZTS crystals, which are extremely important for device fabrication.^{11,12} However, to the best of the authors' knowledge, growth and investigation of different characteristic properties of 1 wt-% L-arginine doped ZTC (LAZTC) crystal were not encountered in literature. This paper discusses the systematic analysis of structural, UV-visible, photoluminescence (PL), photoconductivity, dielectric and thermal characterisation studies of LAZTC crystal for its effective usability for electro-optic applications.

Experimental

The parent compound ZTC has been synthesised by dissolving zinc chloride and thiourea in double distilled deionised water with stoichiometric ratio of 1:2. The synthesised ZTC salt was successively recrystallised three times to eliminate the possible impurities from the compound. The precisely measured 1 wt-% of L-arginine was gradually introduced to supersaturated solution of ZTC with continued stirring. The saturation of LAZTC was agitated for 5 h to achieve the homogeneity throughout the aqueous solution. The filtered solution of LAZTC was kept for slow evaporation in a constant

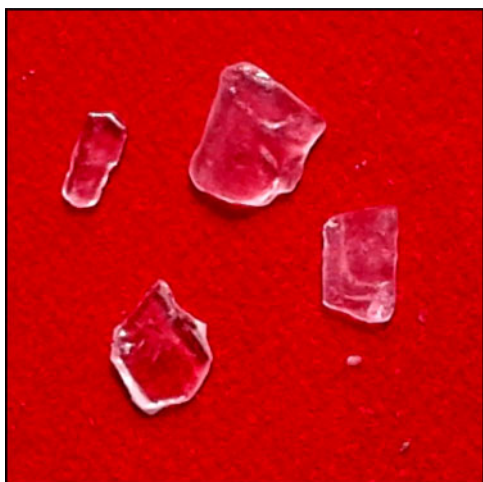
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1 As grown LAZTC crystals

temperature bath of accuracy $\pm 0.01^\circ\text{C}$ maintained at 38°C . The purity of the synthesised salt has been achieved by repetitive recrystallisation. Optically transparent as grown LAZTC crystals are shown in Fig. 1.

Results and discussion

Single crystal X-ray diffraction

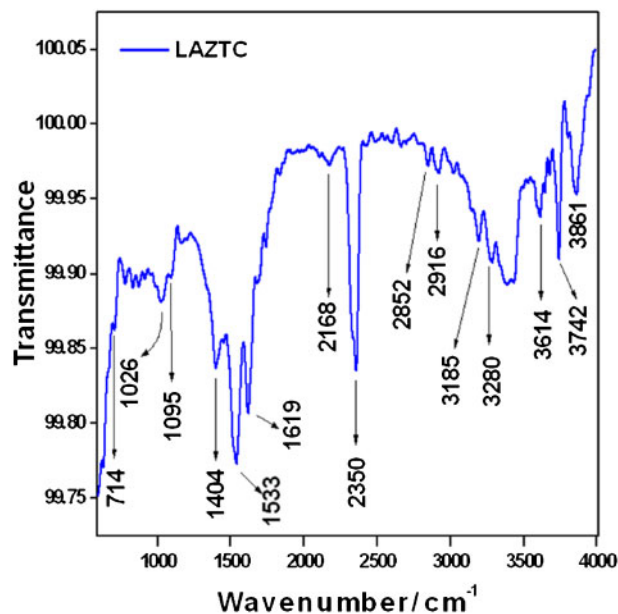
The grown crystal has been characterised by single crystal X-ray diffraction (XRD) using the Enraf Nonius CAD4 X-ray diffractometer. The XRD data revealed that LAZTC crystal occupied the orthorhombic crystal symmetry with slight change in cell parameters of ZTC crystal. L-Arginine, owing to basic nature, has strong tendency to perturb the geometrical morphology of the ZTC crystal. In the present study, the increase in volume of ZTC crystal with addition of L-arginine was observed, which agrees with the results reported by Sweta *et al.*¹¹ The similar results were also observed with L-arginine doped ZTS crystal.¹² The lattice parameters of ZTC and LAZTC crystal are discussed in Table 1.

Fourier transform infrared spectral analysis

The functional groups of the solid LAZTC crystal have been identified using the Bruker α -ATR instrument in the range of $600\text{--}4000\text{ cm}^{-1}$. The recorded Fourier transform infrared (FT-IR) transmittance spectrum of the grown crystal is shown in Fig. 2. The absorption at 3861 cm^{-1} corresponds to the C–H bond stretching vibration. The N–H stretching vibration is observed at 3280 cm^{-1} . The O–H bond stretching vibrations are observed at wavenumbers 2852, 2916, 3614 and 3742 cm^{-1} . The vibrations observed at wavenumber 3185 cm^{-1} contributed to the NH_3^+ antisymmetric stretching of ammine associated with L-arginine in ZTC. The C–H bond stretching vibration is observed at 2350 cm^{-1} . The $\text{N}\equiv\text{C}$ bond stretching vibration occurs at wavenumber 2168 cm^{-1} . The NH_2 bending vibration is attributed at 1619 cm^{-1} . The absorption peak at 1533 cm^{-1} corresponds to the COO^- stretching

Table 1 X-ray diffraction data

Crystals	Cell parameters/Å	Cell volume/Å ³	Crystal system
ZTC	$a=5.9, b=12.77, c=13.02$	978	Orthorhombic
LAZTC	$a=5.92, b=12.82, c=13.11$	995	Orthorhombic



2 Spectrum (FT-IR) of LAZTC

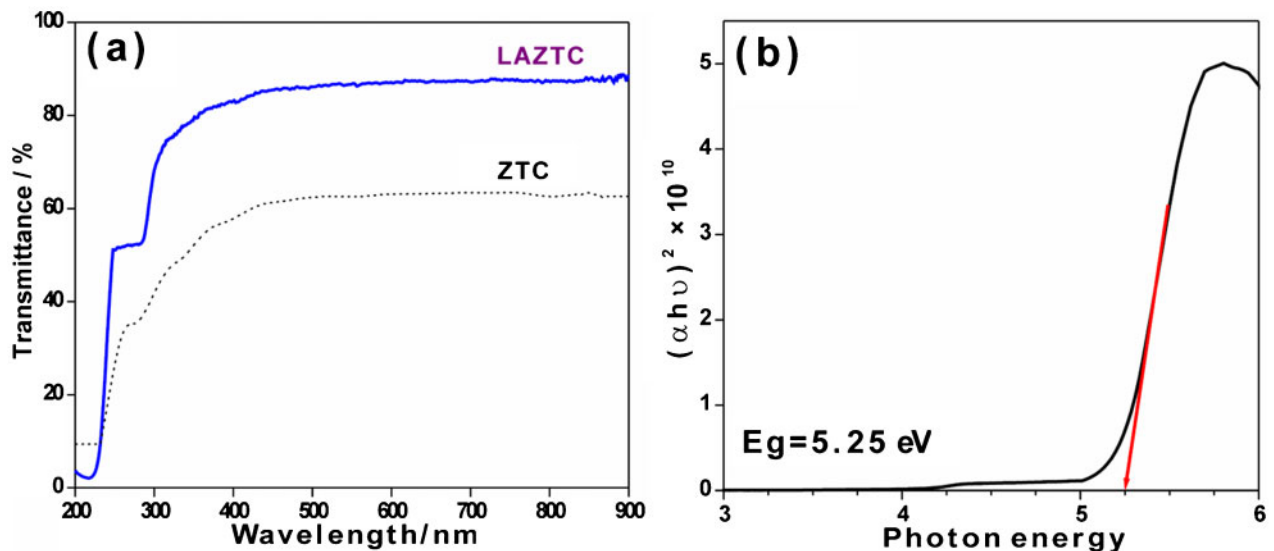
of carboxyl group associated with L-arginine. The C=S bond stretching vibrations are observed at 714 and 1404 cm^{-1} . The C–C–N stretching is evident at 1095 cm^{-1} . The absorption peak at 1026 cm^{-1} is attributed to C–N bond stretching vibration. The characteristic vibrational frequencies of ZTC and LAZTC crystal are illustrated in table 2. The shift in the vibrational frequencies of ZTC and prominent COO^- and O–H bond stretching vibrations strongly evidences the incorporation of L-arginine in ZTC crystal.

UV-visible studies

The optical transparency of the LAZTC crystal has been assessed using the Shimadzu UV-2450 spectrophotometer in the range of 200–900 nm. The recorded transmittance spectrum shown in Fig. 3a revealed that LAZTC crystal is optically transparent up to 82% in entire visible spectrum, which is appreciably higher than pure ZTC crystal. The lower cutoff (235 nm) of LAZTC crystal is due to electronic transition ($n\rightarrow\pi^*$) offered by the nitro group of L-arginine incorporated in ZTC.¹³ The high transmittance and lower cutoff wavelength of LAZTC crystal are essential optical parameters for

Table 2 Vibrational assignments of ZTC & LAZTC crystal

Wavenumber (cm^{-1})		
ZTC ²	LAZTC	Vibrational assignments
713	714	C=S stretching
1103	1095	C–C–N stretching
1404	1404	C=S stretching
1612	1619	NH_2 bending
	2168	$\text{N}\equiv\text{C}$ stretching
	2852, 2916, 3614	OH stretching
	3185	NH_3^+ antisymmetric stretching



3 a transmittance spectrum and b Tauc's plot of LAZTC

applications in second harmonic generation transmission devices.¹⁴ The transition of electron in different energy state unfolds the presence of energy band gap (E_g) in LAZTC crystal, which can be evaluated using the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ where α is the absorption coefficient and $h\nu$ is the incident photon energy.¹⁵ The Tauc's extrapolation plot shown in Fig. 3b was drawn to determine the band gap of grown crystal. The band gap of LAZTC crystal is found to be 5.25 eV, which is appreciably higher than pure ZTC (4.3 eV).¹⁶ The wide optical band gap of LAZTC crystal indicates its large transmission and vitalises its stringent requirement for optoelectronic device applications.¹⁵

Photoluminescence studies

The PL studies were recorded in the visible range of 300–700 nm using the HIOKI 3540 spectrophotometer at room temperature. The optical emission behaviours of the material are essential for applications in the field of biochemical, medical and chemical researches to assess the surfaces, interfaces and impurity levels and to gauge alloy disorder and interface roughness.^{13,17} The PL emission spectra of LAZTC, shown in Fig. 4, enable to analyse the electronic transition occurring due to absorption of light by intrinsic impurities causing colour centred emissions. The excitation wavelength used for the present study is 532 nm, and the emission behaviour was studied at 254 nm in visible region. The LAZTC crystal expressed prominent single violet emission at 391 nm, which may be due to the protonation of amino group to carboxyl group. Further, a mild shoulder peak is observed at ~459 nm, which evidences the rotation of carboxyl group around the central C–C bond.¹⁸

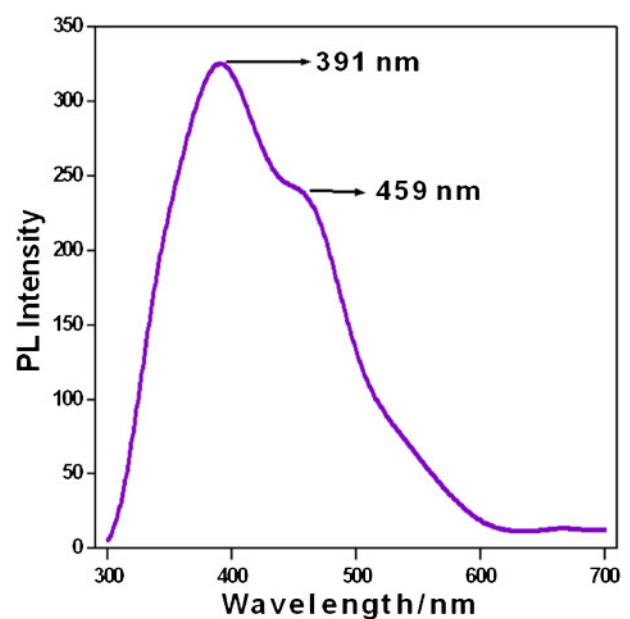
Photoconductivity studies

The photoconductivity studies of LAZTC crystal were studied by connecting the sample crystal in series to DC power supply and Keithley-480 picoammeter. The electrical contacts were made by microscopic probes connected at a distance of 0.3 cm on crystal surface, and voltage was applied in the range of 5 to 100 V. The applied voltage was increased in steps of 5 V to record the dark current I_d and photo current I_p produced by the LAZTC crystal. The crystal sample under study was

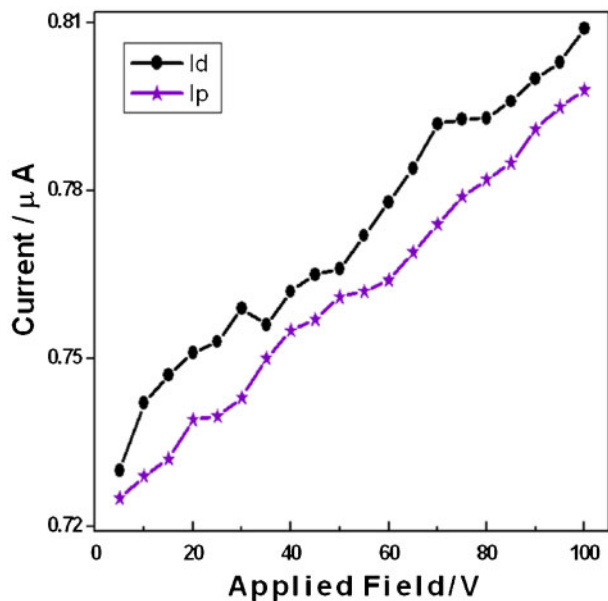
protected from all the possible radiation to measure the dark current, while the variation of photo current was measured by illuminating the crystal sample by halogen lamp (100 W). The nature of I_d and I_p with increasing voltage is depicted in Fig. 5. As photo current has less magnitude than dark current at every applied voltage; it evidences the negative photoconductivity by LAZTC crystal, which resulted due to decrease in lifetime as well as reduced traffic of charge carriers in the presence of radiation.¹⁹ In accordance to the Stockmann model, the energy state with high seizing cross-section close to the valence band traps electrons from the conduction band and holes from the valence band decrementing the mobility of charge carriers, which is key mechanism responsible for negative photoconductivity.²⁰

Dielectric studies

The frequency F dependent dielectric response of pure ZTC and LAZTC crystals has been studied at room temperature using the Gwinstek-819 LCR metre. The

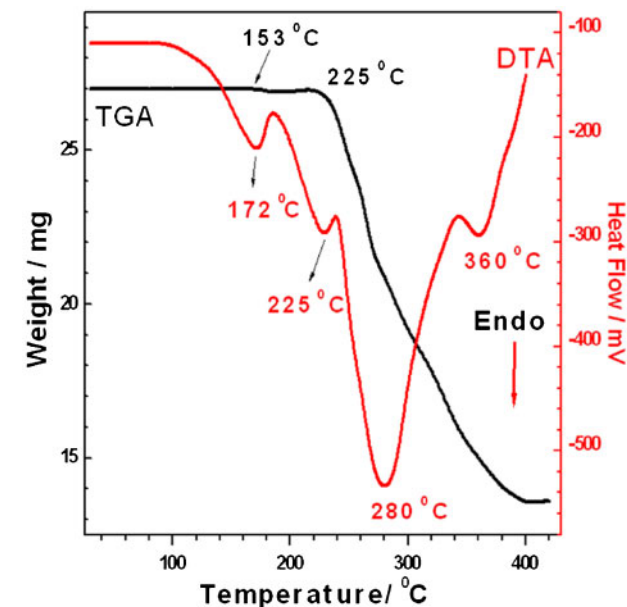
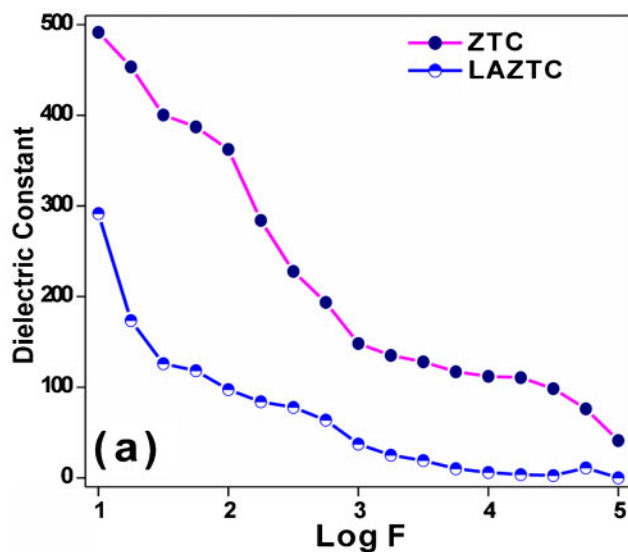


4 Photoluminescence emission spectrum



5 Field dependent photoconductivity of LAZTC

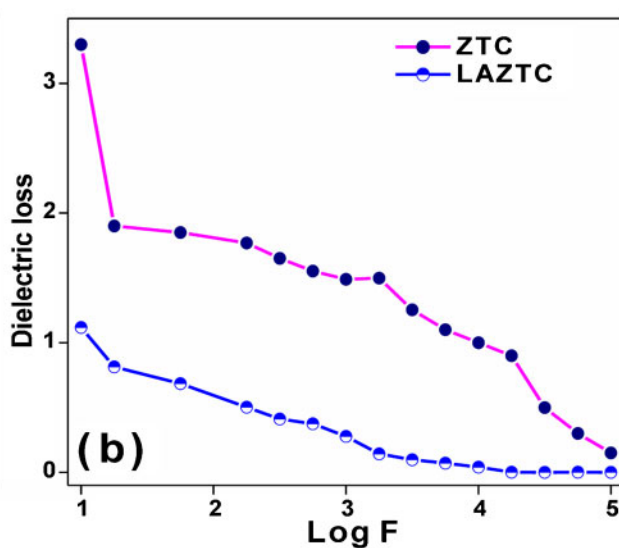
higher values of dielectric constant ($\epsilon_r = Cd/\epsilon_0 A$) at lower frequencies are attributed due to active polarisation mechanism (electronic, ionic and space charge), while the magnitude of dielectric constant decreases subsequently in high frequency domain as polarisation activity cannot sustain at higher frequencies.²¹ From Fig. 6a, it is obvious that the dielectric constant of LAZTC crystal is relatively lower than pure ZTC, which substantiates its suitability for microelectronics, photonics and non-linear optical (NLO) applications.^{22,23} The dissipation factor of electromagnetic energy and optical quality of the material medium can be understood by assessing the frequency response of dielectric loss, depicted in Fig. 6b. The lower dielectric loss of LAZTC crystal than pure ZTC indicates its superior optical quality and least amount of intrinsic defects.²⁴ The LAZTC crystal with lower dielectric constant and dielectric loss dominates over ZTC, suggesting its vital importance for electro-optic device applications.²³



7 Thermogravimetric-differential thermal analysis curve of LAZTC

Thermal studies

The thermal stability of the grown crystal has been analysed by simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) performed using the TQA-500 thermal analyser in the homogeneous nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$. The thermal behaviour of LAZTC crystal was studied in the range of 30 to 400°C , and the TG-DTA curve is displayed in Fig. 7. The TG analysis curve revealed that the LAZTC crystal is stable up to 225°C , which gives the clear evidence of purity of LAZTC and absence of water molecules, while the slight decomposition at 153°C occurs due to low temperature resistivity of amino acids.⁷ The DTA curve evidences the three melting stages of LAZTC crystal. The endothermic peak at 172°C indicates the preliminary melting of volatile substances like sulphur thiourea in LAZTC compound. Further mild endothermic peak at 225°C corresponds to



6 a dielectric constant versus log F, and b dielectric loss versus log F

the initiation of decomposition of LAZTC crystal. The sharp endothermic peak observed at 280°C corresponds to the major weight loss of LAZTC crystal and final melting point of LAZTC crystal. The rapid decomposition was observed beyond 360°C. As LAZTC crystal can sustain decomposition up to 225°C beyond the melting point; this substantiates its suitability for NLO device fabrication.

Conclusion

The LAZTC crystal has been successively grown by slow solution evaporation technique. The XRD analysis confirmed the orthorhombic structure of LAZTC crystal. The functional groups of LAZTC crystal were identified by means of FT-IR spectral analysis. The UV studies revealed that doping of L-arginine favoured high optical transparency (82%) in visible region, wide band gap (5.25 eV) and large transmission up to 235 nm, which substantiates its suitability for photonic device applications. The PL study confirmed the single violet emission at 391 nm by LAZTC crystal. The dominance of I_d over I_p signifies the negative photoconducting nature of LAZTC crystal. Thermal studies revealed that LAZTC crystal sustains decomposition up to 225°C, which is vital for device fabrication. The lower dielectric properties of LAZTC crystal are vital for microelectronics and photonics applications. The above studies validate usability of LAZTC crystal for distinct electro-optic applications.

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