Influence of L-Leucine on Structural, Thermal, Fluorescence and Non-linear Optical Oproperties of Zinc Thiourea Sulphate Single Crystal

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Abstract— The L-Leucine (L-L) mixed zinc thiourea (tris) sulphate (ZTS) crystal is grown by slow solution evaporation method and characterized with single and powder XRD, FT-IR, TG/DTA, photo luminance analyses and SHG test. The crystalline nature of L-LZTS crystal has been determined by means of powder XRD analysis. The functional group of grown crystal has been identified by means of FT-IR analysis. The thermal stability of L-LZTS crystals is found up to 200 ^{0}C without phase transition. The photoluminescence study has been carried out to know the electron transition at an excitation wavelength of 290 nm. The second harmonic generation (SHG) of L-LZTS was confirmed by Kurtz powder method.

Key Words—: Non linear optical crystal, ZTS Crystal, L-Leucine, Crystal growth

INTRODUCTION

The nonlinear optical (NLO) single crystals are demanded in many fields, such as microelectronics, optoelectronics, as well as photonics [1]. Therefore, the extensive studies have been carried out for design and development of all class of NLO materials. The uses of organic and inorganic NLO materials for device application are impeded by their poor mechanical and thermal properties and low laser damage threshold as well as relatively modest optical nonlinearities. Due to these difficulties, the search for new frequency conversion materials has led to the growth of many semi organic materials. These materials with excellent optical mechanical and thermal properties have been studied extensively for their possible device applications in various technological fields. [2-6]. Among the large number of semi organic materials, zinc (tris) thiourea sulfate (ZTS) is a promising semi-organic NLO material. It has orthorhombic crystal structure with space group Pca21 and better SHG efficiency than KDP [7-10]. It is also reported that the additives like amino acids and metals affects the morphology and physical properties of the ZTS crystals and enhance the NLO activities [11]. Recently, the amino acids such as L-Lysine, L-Alanine, L-Proline, L-Threonine and γ-glycine doped ZTS has been reported to be promising NLO active materials [12-17]. However, so far the growth of L-Leucine doped ZTS (L-LZTS) single crystal and its properties has not yet been reported in the literature. The L-Leucine is a branched-chain amino acid which possesses an aliphatic side-chain that is non-linear and exhibits zwitterionic form at neutral pH. [18]. In the present investigation, L-LZTS crystal has been grown by slow evaporation method at room temperature and subjected to powder XRD, fourier infrared transform (FTIR), TGA/ DTA, photoluminence (PL) studies and SHG efficiency test

SYNTHESIS AND GROWTH

The zinc thiourea (tris) sulphate (ZTS) salt was synthesized by dissolving high purity AR grade thiourea and Zinc sulphate in distilled water in molar ratio 3:1. The supersaturated solution of ZTS was prepared at room temperature by constant stirring up to six hours and then the 0.1, 0.2 and 0.3 mole% of L-Leucine was added in the supersaturated solution and continues the stirring for four to five hours and the mixture filtered by Whattman filter paper. The solution was allowed to evaporate at room temperature in dust free space and good quality colourless transparent crystals of L-LZTS. A good quality transparent, colorless crystal was harvested in the period of 35 days as depicted in fig.1.

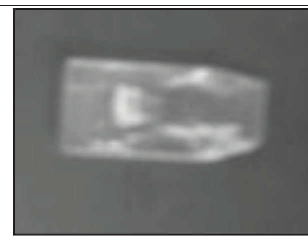

Fig.1. Photograph of L-LZTS

RESULT AND DISCUSSIONS:

X ray Diffraction Analysis

The powder X-ray diffraction pattern of L-LZTS contains was recorded using the XPERT-PRO diffractometer (Cukα, λ=1.540598A^0) and the sharp peaks are illustrated in fig.2. The pattern was used to confirm the identity, crystalline nature and unit cell parameters of the grown crystals. A microscopic variation in the d-spacing has been observed in the pure and L-LZTS sample. The single crystal X-ray diffraction analysis of L -LZTS crystals was also carried out by using D8 Venture BRUKER diffractometer to determine unit cell dimension. The lattice parameter of L-LZTS crystal are a= 7.81 A^0, b=11.17A^0 and c=15.52 A^0 and α=90^0, β =90^0, γ =90^0. The cell volume of L-LZTS is found to be 1354 (A^0)^3. Therefore it is noticed that L-LZTS crystal belongs to orthorhombic crystal system. The calculated lattice parameter values of L-LZTS are good agreement with the pure ZTS crystal [2]. From single crystal X-ray analysis, it is confirmed that dopant does not changes the basic structure of crystal.

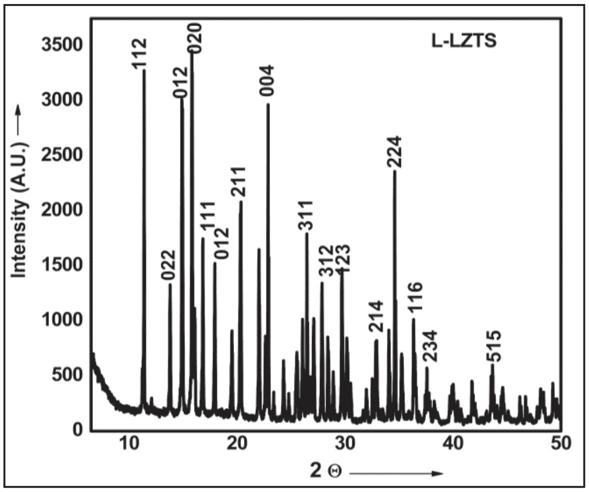

Fig.2. Powder XRD pattern of L-LZTS

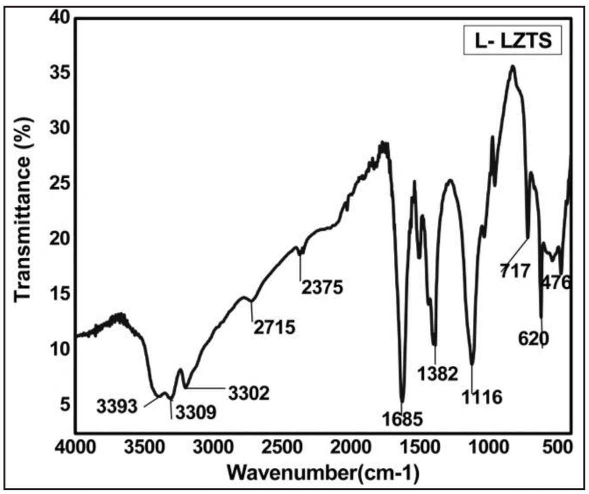

Fig.3. FTIR spectrum of L-LZTS

FT-IR Studies

The FT-IR spectra (Fig. 3) of L-LZTS crystal was recorded in range 400-4000 cm^{-1} using PERKIN ELMER RX1 spectrophotometer. The transmission spectra noticed the shifting of absorption peaks which confirms the incorporation of L-Leucine in ZTS crystal. The absorption observed at 476.83 cm^{-1} corresponds to the C-S-N symmetric bending vibration. The symmetric and asymmetric C=S stretching vibrations are observed at 717 cm^{-1} and 1382 cm^{-1}. The C-N stretching vibration appeared at frequency 1116 cm^{-1}. The absorption band at 1685 cm^{-1} corresponds to N-C-N stretching vibrations. The O-H stretching vibration of carboxyl group is observed at 2715 cm^{-1}. The NH_2 bending and asymmetric stretching vibrations are evident at 2375 cm^{-1} and 3302 cm^{-1}. This shows the shifting in characteristic vibrational frequencies of L-LZTS towards higher side, confirms the addition of L-Leucine in grown crystal.

TG/DTA Studies

The thermo gravimetric analysis of L-LZTS crystal has been carried out between 30^0C – 1000 ^0C in the nitrogen atmosphere at the heating rate of 10 ^0C/min. The TG/DTA analysis provides the information regarding chemical decomposition, phase transition, melting point and the weight loss of the grown crystals. From the graph (Fig. 4), it is noticed that the melting point of L-LZTS crystal is at 236 ºC and it is thermally stable up to 196 ºC without any phase transition. The melting point of L-LZTS is slightly decreased than pure ZTS (238^0C) due to the addition of amino acid [18]. The complete decomposition of sample occurs between 196ºc and 800ºc The rapid weight loss in the temperature range 238 - 400 ºC is due to the liberation of volatile substances like sulphur oxide in the compound [19]. The zero weight loss around 100^0c confirmed the non hygroscopic nature of the crystal. The absence of phase transition till the material melt indicates the thermal stability and purity of the compound insures the suitability for laser applications.

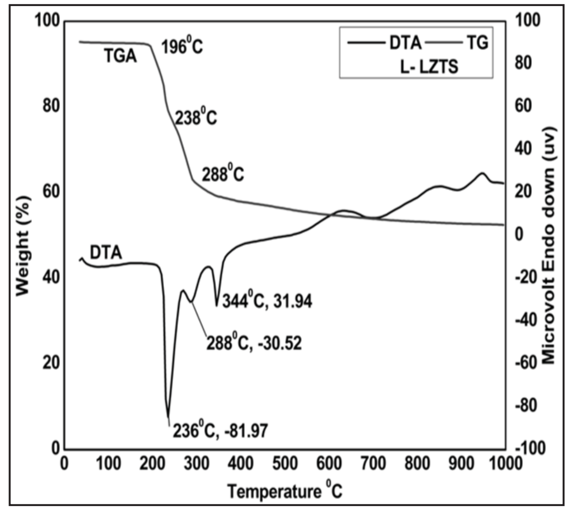

Fig.4. TG/DTA curves of L-LZTS

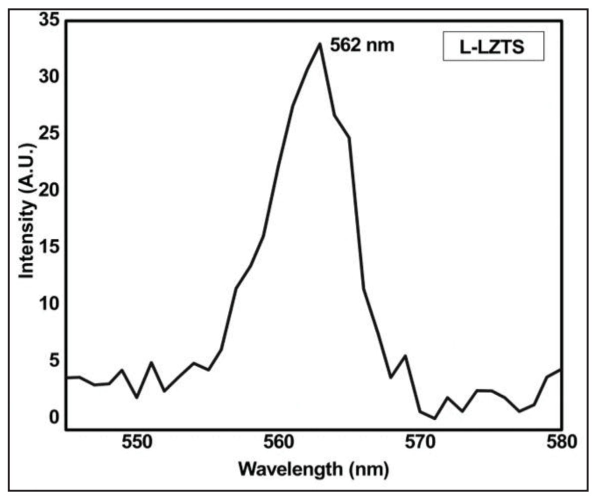

Fig.5.

Fig. 4 PL spectra of L-LZTS

Photoluminescence study

The photoluminescence study of L-LZTS crystal has been carried out in the wavelength range 220 nm-1100 nm with excitation wavelength 290 nm using a Cary Eclipse Win FLR EL07073870 Instrument. The photoluminence spectrum shown in fig.5 reveals that the high intensity peak is appeared at the wavelength 562 nm. However no emission peaks were observed in the ultraviolet and infrared region which confirms the inactive nature of crystal in ultraviolet and infrared region. The single peak confirms the good quality of L-LZTS crystal and utility of crystal in visible region.

SHG efficiency test

The Kurtz and Perry powder technique was employed to evaluate NLO efficiency of the L-LZTS crystal [20]. The fine powder of L-LZTS sample in capillary tube was subjected to an active Q-switched Nd: YAG laser beam of wavelength of 1064 nm. When the L-LZTS compound was illuminated by laser beam, the output optical signal of 532nm (green light) was detected. The measured output signal was 2.3mv for L-LZTS. This confirmed the non linear optical nature of the L-LZTS crystals.

CONCLUSION

Good quality single crystals of $_{L}$-Leucine doped zinc thiourea sulphate (L-LZTS) were grown by solution growth technique. The XRD study revealed that L-LZTS crystals are crystallized in orthorhombic system. The functional groups present in L-LZTS were ascertained using FT-IR spectral analysis. The TGA analysis show that L-LZTS crystal is thermally stable up to 200 ºC and sharp endothermic peak in DTA curve divulges that L-LZTS melts at 235 ºC temperature. In photoluminescence study, the single peak at 562 nm confirmed the good optical quality of L-LZTS crystal. The SHG test confirmed the Nonlinearity of grown crystal.

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