AN INVESTIGATION ON DIELECTRIC AND THERMAL PROPERTIES OF PRISTINE AND L-LEUCINE DOPED ZINC TRIS (THIOUREA) SULPHATE CRYSTALS

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Abstract
Structural, dielectric and thermal properties of pure and L-Leucine doped zinc tris (thiourea) sulphate (ZTS) crystals have been studied in present investigation. The sample crystals have been grown by slow evaporation technique at room temperature. The thermal stability of doped ZTS crystal was determined by means of thermo gravimetric and differential thermal analyses. The dielectric characteristics of pure and doped ZTS crystals were investigated using dielectric studies.

Keywords- Crystal growth, Thermal properties, Dielectric constant

1. Introduction

ZincTris-Thiourea Sulphate (ZTS) is one of the semiorganic nonlinear materials for type II second harmonic generation (SHG) [1-3]. It is a novel organometallic crystal with potential application in electro-optic modulation, device fabrication and laser fusion experiments. It belongs to orthorhombic system with the space group Pca21 and point group mm2. Although the crystal growth, kinetics and characterization of ZTS have been extensively investigated [2,4–8], a systematic investigation of the effect of a new organic dopant, L-Leucine, an amino acid, on ZTS crystal growth medium has not been reported yet.

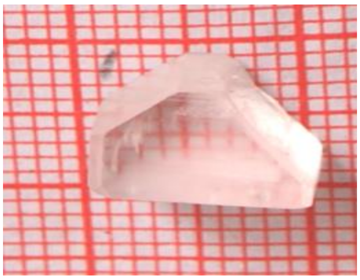
Interestingly, the amino acids that contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino (-NH2) group could have the potential for nonlinear optical (NLO) applications [9]. Moreover, amino acids are shown to exhibit improved material properties when added as impurities [14]. It has also been shown that L-Leucine forms several complexes, which are promising materials for SHG [15-16]. Hence, in this paper we report the investigations on the growth of pristine and L-Leucine doped ZTS crystal along with various characterization techniques at room temperature for NLO applications.

2. Experimental Procedure

Material synthesis and crystal growth

The ZTS salt was synthesized by stoichiometric incorporation of Analytical Reagent (AR) grade zinc sulphate heptahydrate and thiourea in the molar ratio 1:3. The component salts were dissolved in double Distilled water 0DDW) and thoroughly mixed using a magnetic stirrer and the mixture was heated at 45 °C till a white crystalline salt of ZTS was obtained. Temperature was maintained at 45 °C to avoid decomposition.

After successive recrystallization processes, crystals were grown by slow evaporation solution growth technique. Doping of L-Leucine was done during the crystallization process. The crystallization took place in 25–30 days and the macroscopic defect-free, good quality transparent and colorless crystals were harvested . Figure 1a and 1b show the picture of as - grown pristine and L-Leucine doped crystals respectively.



(a) (b
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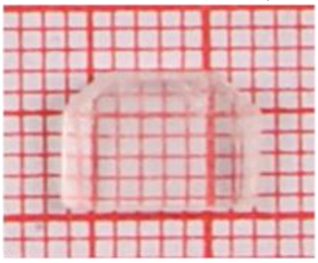


Figure 1 (a) Pure ZTS crystal and (b) L-Leucine doped ZTS crystal

3. Results and Discussion

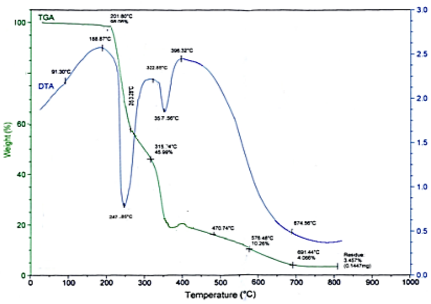
a) Thermal Studies

The TGA/DTA studies were carried out using SDTQ 600 V 8.2 (Universal V4.2 ETA) thermal analyzer in the temperature range 35 $^{\circ}$C - 1000 $^{\circ}$C at a heating rate 10 $^{\circ}$C/ min in the nitrogen atmosphere. Thermal analysis of grown crystals provides information regarding phase transition, water of crystallization and different stages of decomposition of the crystal. Thermal analysis of a material also provides useful information regarding the thermal stability of that material. The TGA–DTA curve of L-Leucine doped ZTS crystal is shown in Figure 2. It is observed from the TGA that the grown crystal was thermally stable up to 201 °C. The sharp and major endothermic peak observed around at 247 °C confirms the good crystalline nature and corresponds to the melting point of L-Leucine doped ZTS crystal. The endothermic peak at 367 °C might have been attributed due to liberation of volatile components and unstable nature of L-Leucine at high temperature. From the curve, the L-Leucine doped ZTS crystal has very good thermal stability up to 247 °C which is found to be greater than that of pure ZTS (240 °C) [13]. Thermo gravimetric and differential thermal analyses confirm the phase transition of crystallization and different decomposition stage of the grown crystal system [14,15].

Figure 2. TGA/DTA thermal curves of L-Leucine doped ZTS crystal

b) Dielectric Studies

Dielectric properties are related with the electric field distribution within solid materials. The dielectric constant of a material gives an insight into the nature of bonding. One of the broadly used parameters of the dielectric materials is the relative dielectric constant or relative permittivity. Dielectric constant and dielectric loss of the grown crystals were measured using the Agilient (4284A) precision LCR meter at different frequencies ranging from 10^2 to 10^6 Hz with a maximum resolution of 1 MHz. Contact faces of the crystal are coated by graphite or silver paint to obtain a good conductive surface layer. The samples were heated up to 80 ^{o}C. The dimensions of the crystals were measured using a travelling microscope or a screw gauge. Figure 3 and 4 show the variation of dielectric constant and dielectric loss of ZTS an L-leucine doped ZTS single crystal. The dielectric constant has higher values in the lower frequency region and it decreases with the increase of applied frequency. The high value of 'ξ' at lower frequency is due to the presence of space charge, orientational, electronic and ionic polarizations and low value at higher frequency may be due to the loss of significance of these polarizations gradually [16]. The dielectric constant of ZTS



increases by the incorporation of L-leucine with ZTS. The rate of increase in dielectric constant is found to increase with increase of mole percentage of L-leucine in ZTS. In accordance with Miller rule, the lower value of dielectric constant at higher frequency is a suitable parameter for the enhancement of SHG coefficient [17]. Fig.4 shows the variation of dielectric loss with frequency. The crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices because of low dielectric loss with high frequency for the samples [18]. The variation of dielectric constant and dielectric loss with frequency indicate that the grown crystals are of good quality i.e. the grown crystals are good-quality dielectric materials [19-21].

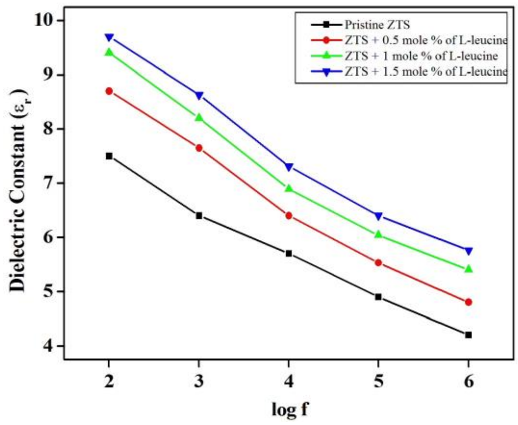


Figure 3. Plot of log f vs dielectric constant

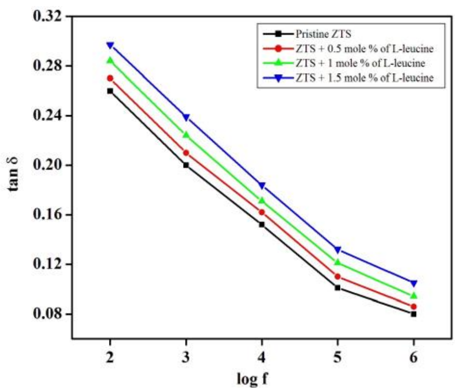


Figure 4. Plot of log f vs Dielectric loss

4. Conclusions

Good optical quality pristine ZTS and L-leucine doped ZTS crystals were grown using slow evaporation technique. From the TGA analysis, it is concluded that, the L-Leucine doped ZTS crystal has very good thermal stability up to 247 °C. The dielectric studies revealed that the grown crystal has low dielectric constant at high frequencies and is an essential property for any NLO material.

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