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Growth and characterization of pure and L-Alanine doped Zinc Tris-thiourea Sulphate (ZTS) single crystals

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Abstract-The pure and L-Alanine doped Zinc (Tris) Thiourea sulphate crystals were grown successfully by slow evaporation method at room temperature. The concentration of dopants in the mother solution was varied from 1 mol% to 3 mol%. There is a drastic change morphology due to doping which is reflected in the X- Ray diffraction pattern. The Fourier transform infrared spectroscopy study confirms the incorporation of L-Alanine into ZTS crystal. The doped crystals are optically better and more transparent than the pure one. The dopant increases the hardness value of the material and it also depends on the concentration of the dopant. Kurtz and Perry method was employed to measure powder SHG efficiency of undoped and doped single crystals. The grown crystals were also subjected to etching studies and the results are discussed.

Index Terms: **Crystal morphology, Growth from solutions, nonlinear optic materials, X-ray diffraction**

I. INTRODUCTION

In the last decade, nonlinear optical (NLO) crystals have been found to have enormous applications in many fields such as optical communications, optical information processing, optical computing, optical disk data storage, laser fusion reactions, color display, medical diagnostics, etc. The nonlinear (NLO) responses induced in various molecules in solution and solids are of great interest in many fields of research [1,2]. Thiourea molecules are an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [3]. The nonlinear optical properties of some of the complexes of thiourea, such as bis (thiourea) cadmium chloride (BTCC), bis (thiourea) zinc chloride (BTZC), tris (thiourea) zinc sulphate (ZTS), tris (thiourea) cadmium sulphate (CTS), potassium thiourea bromide (PTB) have gained significant attention in the last few years [4-6], because both organic and inorganic components in it contribute specifically to the process of second harmonic generation. The centrosymmetric thiourea molecule, when combine with inorganic salt yield noncentrosymmetric complexes, which has the nonlinear optical properties [7]. A series of studies on semi organic amino acid compounds such as L-arginine phosphate [8], L-histidine hydro bromide [9], L-cystine hydrochloride [10], L-valine hydrochloride [11] as potential NLO crystals have been reported. Zinc (tris) thiourea sulphate (ZTS) is a good nonlinear optical semi organic material for second harmonic generation. ZTS has high laser damage threshold, low angular sensitivity, wide range of transparency and low dielectric constant at high frequencies [12]. ZTS is 1.2 times more nonlinear than KDP [13]. ZTS possesses orthorhombic structure with $Pca2_1$ space group [14]. The growth and various properties of undoped and amino acid doped ZTS crystals have been reported by a number of researchers [15-21]. In this manuscript we report the growth of pure and amino acid (L-Alanine) doped ZTS crystal with the characterizations such as X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectral study, UV-Visible study and Micro hardness studies.

II. EXPERIMENTAL

CRYSTAL GROWTH

The material of the title compound was synthesized in the aqueous medium from zinc sulphate and Thiourea in 1:3 stoichiometric ratio according to the following chemical reaction. To avoid decomposition, low temperature was maintained during preparation of the solution in the deionized water.

$$ZnSO_4 + 3CS(NH_2)_2 \rightarrow Zn[CS(NH_2)_2]_3SO_4$$

The solution was stirred with magnetic stirrer. White crystalline ZTS adduct was obtained immediately. In order to eliminate the adduction temperature was maintained at 50°C. Single crystals of ZTS and L-alanine doped ZTS were grown by employing slow evaporation technique. Transparent colorless ZTS crystals were obtained in 20

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days. For the growth of L-alanine doped ZTS crystals, 1 mol percent of L-alanine was added to the solution of ZTS. Single crystals with good transparency were harvested in 30 days. The as grown undoped and L-Alanine doped ZTS crystals are shown in Figure 1(a) and 1(b).

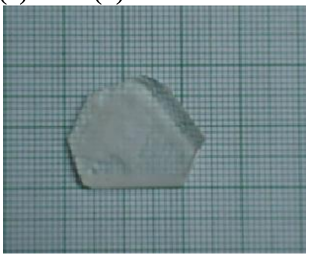

Fig.1 (a) Grown ZTS crystal

Fig.1 (b) Grown L-Alanine doped ZTS crystal

III. CHARACTERIZATION

The Grown single crystals of pure and L-alanine doped ZTS have been analyzed by different characterization techniques. The crystals were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The functional groups were identified by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm^{-1}. The optical properties of the crystals were examined between 200 and 1200 nm using LAMBDA-35 UV-Vis spectrometer. The mechanical properties of the grown crystals have been evaluated using a Leitz Weitzler hardness tester fitted with a diamond pyramidal indenter.

IV. RESULTS AND DISCUSSION

SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

The single X-ray diffraction studies have been carried out to estimate the lattice parameters of the grown sample. The structure was solved by the direct method using SHELXL program. From the XRD data it is observed that both pure and L-alanine doped ZTS crystals crystallize in orthorhombic system. The calculated lattice parameter values of pure and L-alanine doped ZTS are presented in table.1. The results of the present work are in good agreement with the reported values [22]. In the case of doped sample, a slight variation in the cell volume is observed which is due to the incorporation of the dopant.

Table.1 Single-crystal XRD data for pure and L-alanine doped ZTS crystals

Cell Parameters	Pure ZTS	L-alanine doped ZTS
Unit Vectors and Length of the Interfacial angles	a = 7.797 Å	a = 7.799 Å
	b = 11.144 Å	b = 11.147 Å
	c = 15.512 Å	c = 15.471 Å
	$\alpha = \beta = \gamma = 90°$	
Volume	V = 1348 $Å^3$	V = 1345 $Å^3$
System	Orthorhombic	
Space Group	$Pca2_1$	

FOURIER TRANSFORM INFRARED ANALYSIS

The infrared spectroscopy is effectively used to identify the functional groups of the samples. FT-IR spectra of pure and L-alanine doped ZTS are provided in Fig.2. The broad band in between 2709.09 and 3378.63cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH_2. The presence of sulphate ions is evident by its peak around 707.29 cm^{-1}. The absorption band observed at 1627.86 cm^{-1} in the spectrum can be assigned to the bending vibration. The absorption bands at about 1503.54 cm^{-1} and 948.52 cm^{-1} can be assigned to the N-C-N stretching vibration. The FT-IR spectrum of pure ZTS crystal is observed to be almost similar to that of L-alanine doped ZTS crystal, but the shift in some absorption peaks suggest that the dopants have entered into the lattice of ZTS crystal. The characteristic vibrational frequencies of the spectra have been assigned according to the data reported [23]. The FTIR spectra of doped crystals show a strong NH absorption peak at about 3189.82 cm^{-1}. When ZTS is doped with L-alanine more NH stretch vibrations are introduced due to doping and as a result the NH absorption peak becomes stronger. So, FTIR spectra indirectly established the presence of amino acid, L-alanine in the lattice of ZTS crystal.

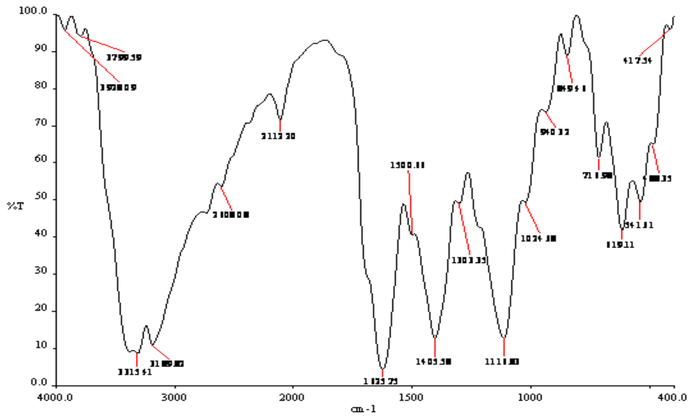

Fig. 2(a) FT-IR Spectrum of L-alanine doped ZTS

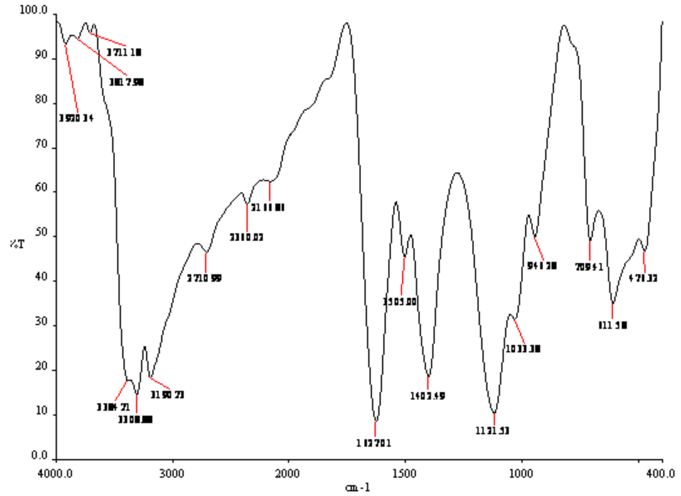

Fig. 2(b) FT-IR Spectrum of pure ZTS

OPTICAL TRANSMISSION STUDIES

For optical applications, the material considered must be transparent in the entire visible region. Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. To find the transmission range of ZTS crystal, the optical transmission spectrum for the wavelengths between 200 nm and 1200 nm was recorded. The recorded optical transmission spectrum of pure and L-alanine doped ZTS crystal is shown in Figure 3. The transmittance is found to be maximum in the entire visible and infrared regions. When we consider the percentage of transmission, we observe that for all L-alanine doped ZTS crystals the transmission has been increased much in the visible region. From the spectrum it is observed that the transmittance percentage of doped ZTS is higher than that of the pure grown crystal. The crystal shows a good transmittance in the entire visible region. The lower cutoff around 280 nm attest the usefulness of this material for opto-electronic applications and the second harmonic generation of the Nd: YAG laser and for the generation of the higher harmonics of the laser diodes.

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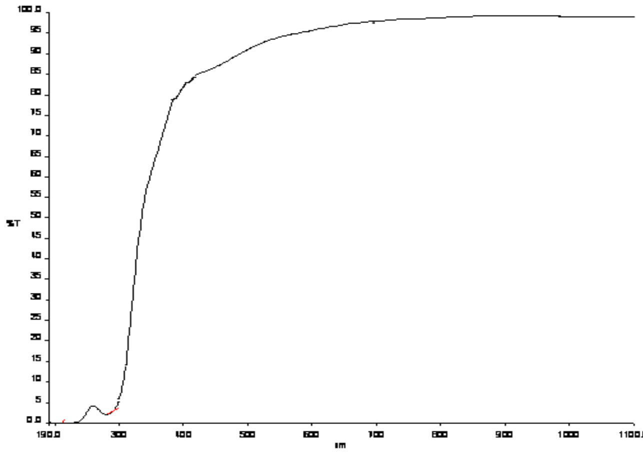

Fig. 3(a) UV-Vis NIR Spectrum of L-alanine doped ZTS crystal

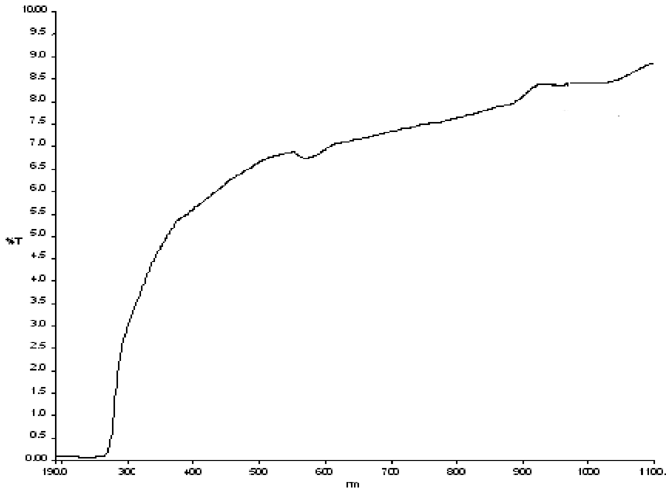

Fig. 3(b) UV-Vis NIR Spectrum of pure ZTS single crystal

THERMAL STUDIES

Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) give information regarding phase transition and different stages of decomposition of the crystal system. The TGA was carried out up to the temperature of 900°C at a heating rate of 20°C/min using a Perkin-Elmer thermal analyzer in nitrogen atmosphere. Fig. 4 shows the TGA & DTA spectra of L-alanine doped ZTS and pure ZTS crystals. Below 240°C there is no detectable weight loss and hence crystal rejected solvent molecules during crystallization, and hence there is no decomposition up to melting point and this confirms thermal stability of the material for possible application in Lasers. There is a sharp weight loss at 240°C without any intermediate stages, which is assigned as the decomposition point of the crystal and is greater than that of the undoped ZTS crystal (238°C). The TGA curve shows that the loss of weight occurred in two steps. The first weight loss of 30.67% is due to the decomposition of both the compounds and the second weight loss of 46% is due to the organic compound evaporation. From the DTA curve, three endothermic peaks are observed at 240°C, 300°C and 360°C which coincide with that of TG confirming the thermal stability of the crystal.

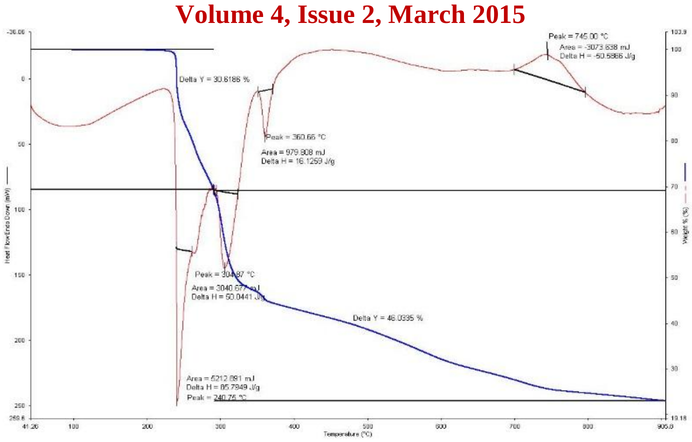

Fig.4a. TGA-DTA curves of L-alanine doped ZTS crystal

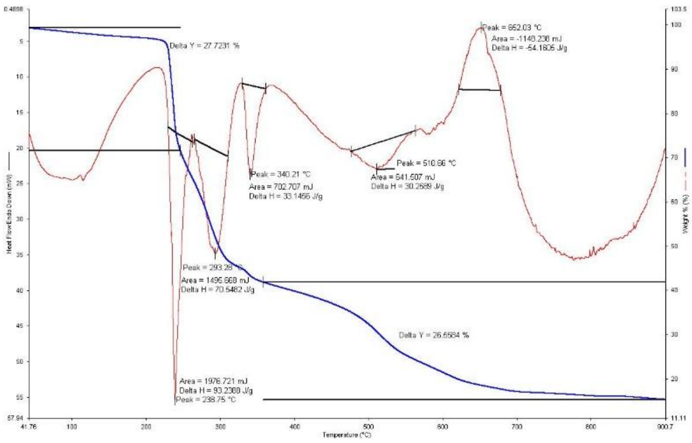

Fig.4b. TGA-DTA curves of pure ZTS crystal

MICROHARDNESS MEASUREMENT

Micro hardness of a crystal is its capacity to resist indentation. That is, hardness of a material is a measure of its resistance to local deformation. It is correlated with other mechanical properties like elastic constants and yield stress of materials. In the present work indentations are made on the pure and L-alanine doped ZTS crystals for five loads 5,10,15,20 and 25 g and indentation time given is 10s. For each load, several indentations are made and the average diagonal length is used to calculate the micro hardness number. Vickers hardness number is calculated using the relation

$$Hv = 1.8554p/d^2 \text{ kg mm}^{-2}$$

Where p is the applied load in kg and d is the diagonal length of the indented impression in mm. Plots between the hardness values and the corresponding loads for doped ZTS crystals are drawn and they are provided in the Fig.5. From the results, it is observed that the hardness number increases as the load increases for both the samples. When the load increases, a few surface layers are penetrated by the indenter with increase in the load. The measured hardness is the characteristics of these layers and the increase in the hardness numbers is due to the overall effect on the surface and inner layers of the samples. Hardness number is found to be increasing with the doping concentration of L-alanine in the lattice of ZTS crystals. It is observed that scratching occurs in the crystals when the load is applied beyond 50g. Since the hardness number of doped crystal is more than that of pure ZTS crystal, doped ZTS crystal is harder than pure ZTS crystal. The increase of hardness for the doped ZTS crystal is due to the incorporation of L-alanine. The higher the hardness values, greater was the stress required to form dislocation, thus confirming greater crystalline perfection [24]. Both undoped and L-Alanine doped ZTS crystals come under soft materials category. These impurity defects in the lattice of ZTS crystals may act as obstacles to dislocation motion thus increasing the hardness of the crystals.

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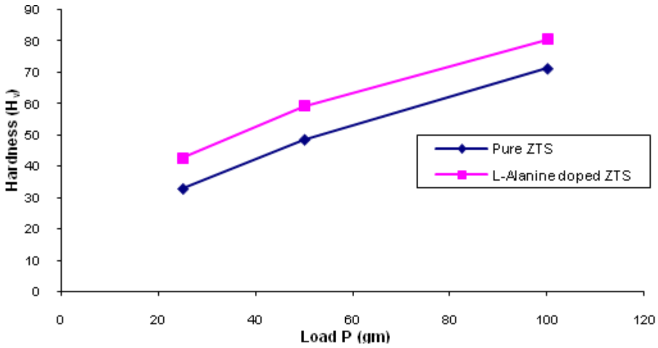

Fig. 5. Load vs Hv plot of undoped and L-Alanine doped ZTS crystal

V. NLO STUDIES

Kurtz and Perry method was employed to measure powder SHG efficiency of undoped and doped single crystals [25]. The grown crystals were ground into very fine powder and tightly packed in a micro capillary tube which served as the sample cell. Then it was mounted in the path of Nd:YAG laser beam of energy 1.8 mJ/pulse with pulse width of 10 ns and repetition rate of 10 Hz used to test the SHG efficiency. The NLO efficiency of ZTS crystal was found to be better than KDP which was used as the reference material [26]. The SHG efficiency of undoped and L-alanine doped ZTS crystals was found to be 1.2 and 1.5 times that of KDP crystal respectively. The emission of green radiation confirmed the enhancement of NLO property of the grown crystals. It has been reported that the SHG can be greatly enhanced by altering the molecular alignment through the inclusion of complexation [27].

VI. CONCLUSION

Good optical quality pure ZTS and L-alanine doped ZTS single crystals have been grown by solution growth method at room temperature. The lattice parameters have been found by single crystal X-ray diffraction technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The optical absorption spectrum reveals that the absorbance is minimum between 300 and 1100 nm. This illustrates the absence of any overtones or combination modes above 300 nm and absorbance due to electronic transition between 300 and 1100 nm. The Vicker's micro hardness was calculated in order to understand the mechanical stability of the grown crystals. Hardness measurement also shows that L-alanine doped crystal is much harder than pure ZTS crystal. The studies on the NLO property confirmed the second harmonic conversion efficiency of the crystal to be better than KDP.

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