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Growth and Studies of Glycine doped Zinc Tris Thiourea Sulphate (GZTS) Single Crystals

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ABSTRACT

Good optical quality single crystals of pure and glycine doped zinc tris thiourea sulphate (ZTS) were grown from aqueous solution by slow evaporation technique at ambient temperature. The grown crystals were subjected to various studies such as powder X-ray diffraction, UV-Vis spectral analysis, Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA)-Differential scanning calorimetry (DSC) studies and second harmonic generation (SHG). Powder X-ray diffraction of pure and glycine doped samples reveals some minor structural variations. Changes in intensity patterns and slight shift in peak positions are observed because of doping. The UV-vis spectrum shows that the materials have wide optical transparency in the entire visible region. The SHG efficiency of the crystals was found to increase substantially with increase in glycine concentration. The presence of dopant has been confirmed and analyzed by FTIR. TGA and DSC analysis confirmed that the thermal stability of grown crystal is increasing with the doping concentration of glycine. Mechanical properties of the grown pure and glycine doped crystals were studied by using HMV-2T microhardness testor.

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Introduction

Nonlinear optical (NLO) materials are capable of frequency conversion and gaining much importance in many applications such as optical computing, laser sensing, photonic devices, optical memories and optical switching [1]. Zinc tris thiourea sulphate (ZTS) is a good NLO semiorganic material for second harmonic generation (SHG) and it combines the advantages of both organic and inorganic materials. ZTS possesses very high laser damage threshold, low angular sensitivity, wide range of transparency and dielectric constant at higher frequencies [2-3]. ZTS is 1.2 times more nonlinear than KDP and possesses orthorhombic structure with space group $Pca2_1$ [4-5]. The amino acids play an important role in the field of NLO crystals [6] and are used as dopants in order to enhance the material quality such as nonlinear optical properties. Glycine is the simplest and natural amino acid having hydrogen atom as it side chain. The pK value of carboxyl group of glycine is 2.3 and that of amino group is 9.6 [7]. The effect of sodium chloride on the properties of ZTS single crystals and influence of $MgSO_4$ doping on the properties of zinc tris-thiourea sulphate (ZTS) single crystals have been reported in our recent investigation [8-9]. In the present investigation, synthesis and single crystal growth of pure and glycine doped ZTS from aqueous solution by slow evaporation method is reported. The grown crystals were characterized by FTIR, UV-Vis spectral analysis, powder X-ray diffraction analysis, TGA-DSC, microhardness studies, and second harmonic efficiency and their results are reported in this paper.

Experimental work

The calculated quantity of analar grade starting materials such as zinc sulphate **($ZnSO_4.7H_2O$)** and thiourea **($CS[(NH_2)_2]$)** were dissolved separately in deionised (DI) water at room temperature. The solutions of zinc sulphate and thiourea were then mixed in the molar ratio of 1:3. A white precipitate was formed by mixing which was heated slowly along with solution at a constant stirring to avoid precipitation of other phases. After 2 hours of stirring, the saturated homogeneous solution was prepared by using the magnetic stirrer. The saturated solution was filtered twice with whattman filter paper before it was subjected to evaporation [10-11]. The solution was kept covered to avoid dust incorporation and left undisturbed for days together by monitoring continuously. Crystals of appreciable size was obtained at the end of the 15th day.

Glycine doped ZTS (GZTS) crystal was also grown by adding 1 mol % of glycine. Transparent colourless GZTS crystal was harvested at the end of the 20th day. The single crystals of pure and glycine doped ZTS were subjected to various characterizations viz., FTIR, UV-vis spectral analysis, powder X-ray diffraction analysis, TGA-DSC, microhardness studies and second harmonic efficiency measurements. The as grown pure and glycine doped ZTS crystals are shown in the figure 1. (a) and (b) respectively.

Results and discussion

Powder XRD analysis

Powder X-ray diffraction analysis of pure and 1 mol % glycine doped ZTS crystals were carried out using Rigaku diffractometer with CuKα radiation of wavelength 1.5418 Å. The powder XRD pattern of pure and doped ZTS crystals is shown in figs. 2a and 2b. All the observed reflection lines in XRD pattern are indexed and the unit cell parameters were calculated. The calculated lattice parameter values are a=11.12 Å, b=7.773 Å, c =15.499 Å, $\alpha = \beta = \gamma = 90^{\circ}$ for pure ZTS and a=11.13 Å, b=7.774 Å, c =15.489 Å, $\alpha = \beta = \gamma = 90^{\circ}$ for 1 mol % glycine doped ZTS. These values are found to be in good agreement with the literature values [12-13]. Peak shift and minute change in peak intensities were observed in X-ray

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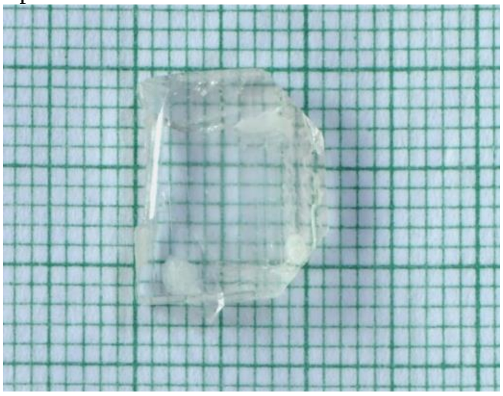
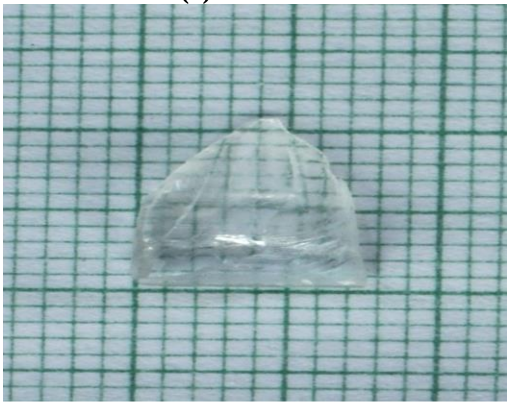
diffraction patterns. The XRD analysis confirmed that the grown crystals belong to the structure of orthorhombic system with space group Pca21.



(a) Pure ZTS



(b) 1 mol % glycine doped ZTS

Figure 1. As-grown Crystals of ZTS: (a) Pure and (b) 1 mol % glycine doped

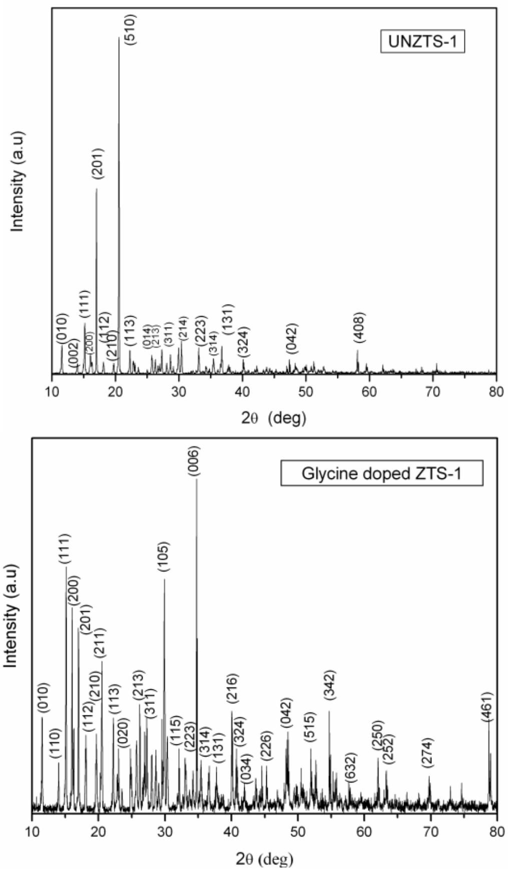


Figure 2. XRD pattern of (a) pure ZTS crystal (UNZTS-1) and (b) 1 mol % glycine doped ZTS crystal

UV – Visible spectral analysis

The UV- visible spectrum of as-grown pure and glycine doped ZTS single crystals were recorded using Lambda 35 model UV- Visible spectrometer in the spectral range 190 – 1100 nm. The absorption spectra showed that the grown crystals have lower cut off wavelength of less than 297 nm. The forbidden energy gap was estimated from the values of λ using the relation $E_g = hc/\lambda$. The estimated forbidden energy gap of pure and 1 mol % glycine doped crystals are 4.182 eV and 4.465 eV. The absorption and transmission spectra of as-grown crystals are shown in fig.3 and 4. The grown crystals have shown good transmission in UV as well as in visible region. The wide range of transparency in as-grown crystals is added advantage in the field of opto electronic applications.

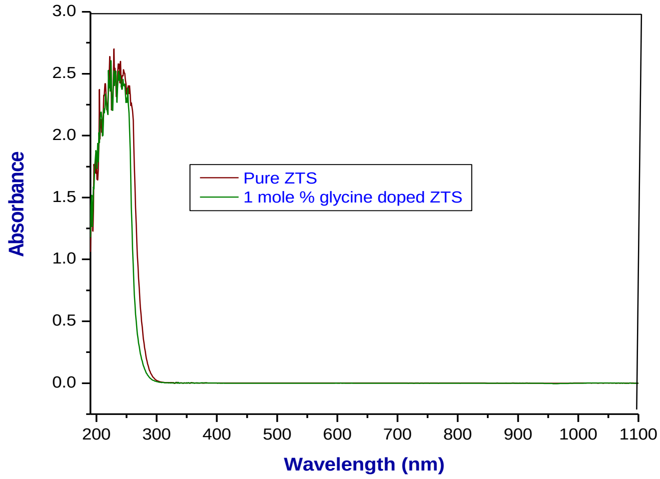


Figure 3. Absorption spectra of pure ZTS and 1 mol % glycine doped ZTS crystal

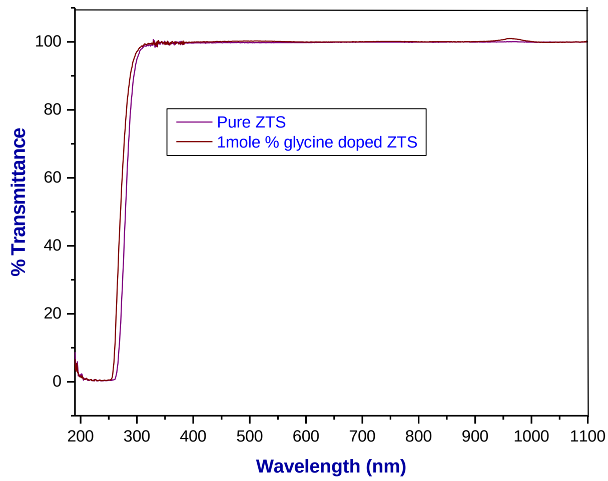
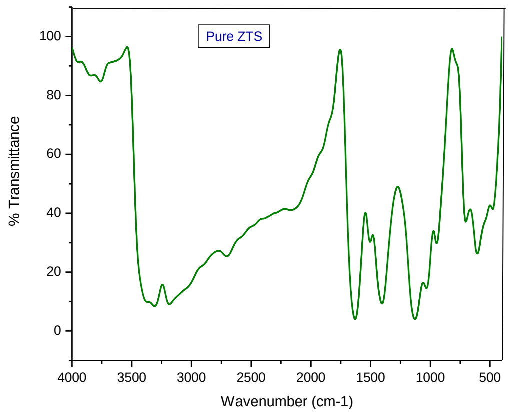


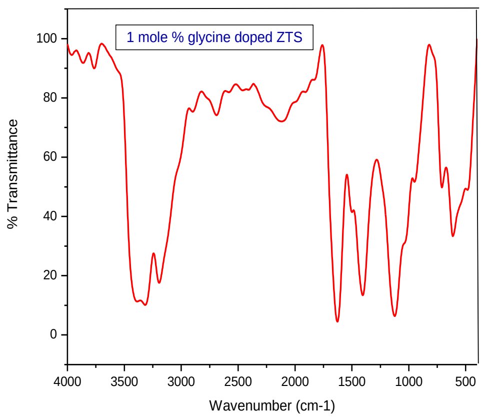
Figure 4. Transmittance spectra of pure ZTS and 1 mol % glycine doped ZTS crystal

Fourier transform infrared spectra

The presence of functional groups and modes of vibration of grown pure and glycine doped ZTS crystals were recorded using Perkin Elmer spectrum FTIR spectrometer by KBr pellet technique in the range of 400 – 4000 cm^{-1}. The FTIR spectra of grown crystals are shown in fig. 5a and 5b. The presence of sulphate ion in the coordination sphere of pure ZTS is evident from its peak at about 490 cm^{-1} and 948 cm^{-1}. The absorption band observed at 717 cm^{-1} can be assigned to be C=S stretching vibration. The spectra of pure and glycine doped ZTS shows a broad envelope lying between 2750 cm^{-1} and 3500 cm^{-1} arising out of symmetric and asymmetric modes of NH_2 group of zinc coordinated thiourea. The absorption band at 1627 cm^{-1} in the spectra of pure ZTS corresponds to the NH_2 bending vibration. The peak was observed at 3170 cm^{-1} assigned to the NH_2 symmetric stretching vibration. The absorption band observed at about 3376 cm^{-1} corresponds to the NH_2 asymmetric stretching vibration. IR spectra of ZTS compared with 1 mol % of glycine doped ZTS, shows slight shift in absorption bands. This shift in absorption bands may be due to incorporation of glycine in ZTS[14-16].



(a) Pure ZTS



(b) 1 mol % glycine doped ZTS

Figure 5. FTIR spectrum of (a) pure ZTS crystal and (b) 1 mol % glycine doped ZTS crystal.

Thermal analysis

The thermal stability of pure and glycine doped ZTS were also identified by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) SDT Q600 analyser in the range 0 - 1000˚ C at a heating rate of 20˚ C/ min and are shown in fig. 6a and 6b, and 7a and 7b respectively . The DSC reveals exactly the same changes shown by TGA. The sharp endothermic peaks of pure and 1 mol % glycine doped ZTS crystals in DSC at 244.10˚ C and 248.35˚ C indicates the melting point of the materials. The TGA traces show the different stages of decomposition. The pure and 1 mol % glycine doped ZTS crystals are found to be thermally stable up to 236.92˚ C and 239.08˚ C respectively. This clearly indicates that the materials can be exploited for NLO applications up to stable temperature. The first stage of pure ZTS TGA curve shows that there is 43.30% of weight loss in the temperature range from 238.83˚ C – 246.74˚ C due to the liberation of volatile substance sulphur oxide in the compound and it appears to be the major stage of decomposition. From 1 mol % glycine doped ZTS TGA curves, it is observed that there are maximum weight losses of about 40.97% in the temperature range from 239.08˚ C – 248.96˚ C. Beyond 564.95˚ C and 593.60˚ C the weight loss is very little for pure and glycine doped ZTS crystals. The residues are found at about 7.87% and 10.37% of initial mass. From TGA-DSC study, it is concluded that the thermal stability of doped ZTS is greater than undoped ZTS as the effect of glycine dopant.

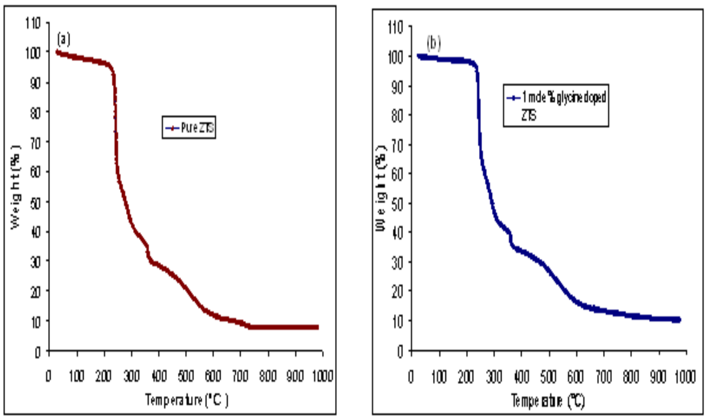


Figure 6. The TGA curve of ZTS: (a) Pure and (b) 1 mol % glycine doped

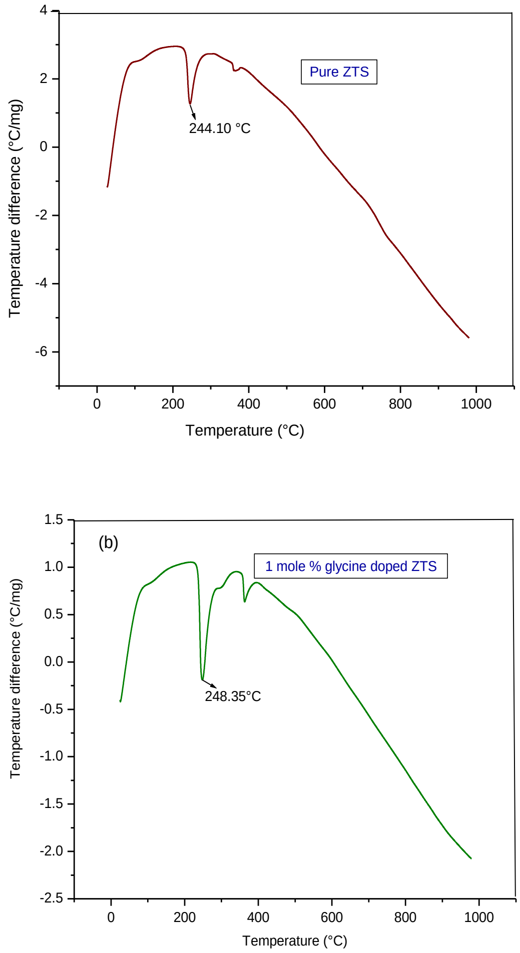


Figure 7. The DSC curve of ZTS: (a) Pure and (b) 1 mol % glycine doped

Second harmonic generation (SHG) efficiency

The SHG efficiency of pure and glycine doped ZTS crystals were determined by Kurtz-Perry powder technique. The harmonic output was generated by irradiating the powder samples using Q-switched Nd-YAG laser with wavelength of 1064 nm. The SHG was confirmed by the emission of green radiation (532 nm) and it is a potential material for frequency conversion [17-18]. From the obtained results, it is clear that the SHG efficiencies of pure and 1 mol % glycine doped ZTS are 3.78 and 3.96 times greater than KDP. The increase in SHG efficiency with addition of glycine is due to fact that the glycine has zwitter ion that is NH_3^+ and COO^- group. The enhancement in SHG efficiency of glycine doped is due to the optically active amino group which may get added in the structure and increase in non-Centro symmetry and hence increase its SHG efficiency.

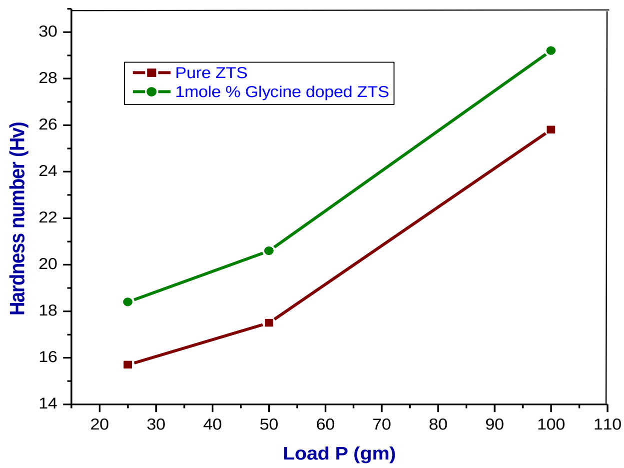


Figure 8. Load (P) vs Hardness number for Pure and 1 mol % glycine doped ZTS

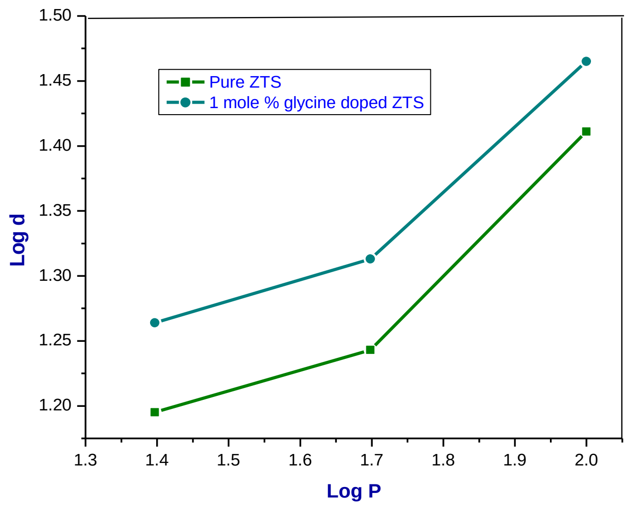


Figure 9. log P vs log d for Pure and 1 mol % glycine doped ZTS

Mechanical Studies

The Vicker's microhardness of the crystals carries information about the strength, molecular binding and yield strength of the materials. In the present study, mechanical properties of the grown pure and glycine doped crystals were studied by using HMV-2T microhardness testor. Before the indentations, the crystals were carefully washed to avoid the surface effect. The well polished and washed crystals were mounted on the platform of the microhardness tester. The loads of different magnitudes (25 gm-100 gm) were applied over a fixed interval of time. The indentation time was fixed as 5 seconds. Above 100 gm load, multiple cracks were developed on the surface of the crystals. The hardness number was calculated from the relation

$H_v = 1.854 (P/d^2)$ Kg/mm^2

Where,

H_v – Hardness number in Kg/mm^2

P – indentor Load in Kg and

D – diagonal length of the indented impression in mm

A graph is plotted between applied load (P) and hardness number (H_v) which provide a straight line (fig.8). The graph shows that the hardness number increases with the increase in load. By plotting the graph log P against log d, it also gives a straight line (fig.9). The slope of the straight line is the value of work hardening coefficient (n) of the grown crystals(n=1.76 and 2.22). This results confirmed that the grown crystals belong to the catagories of soft materials. Hardness study may suggest that the grown crystals are well suited for NLO applications below 100 gm of applied load.

Conclusion

Single crystals of pure and glycine doped zinc tris-thiourea sulphate (ZTS) were grown from aqueous solution by the slow evaporation method. The grown crystals are observed to be transparent and colourless with well defined external appearance. The functional groups of the grown pure and glycine doped ZTS crystals were identified from FTIR spectral analysis. The powder XRD analysis confirmed that the grown crystals belong to orthorhombic system. The second harmonic generation was confirmed by the emission of green radiation and it is a potential material for frequency conversion. The UV-Visible spectrums show that the grown glycine doped ZTS crystals have good optical transmittance in the entire visible region and it may be very useful for optoelectronic device fabrication. Glycine doped ZTS crystals have greater thermal stability due to addition of glycine in ZTS. Hardness study suggested that the grown crystals are well suited for NLO applications below 100 gm of applied load.

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