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Effect of glycine on the optical properties of Zinc Thiourea Chloride (ZTC) single crystal

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Zinc thiourea chloride (ZTC) is a well known semiorganic NLO material for various optoelectronics applications. On the other hand amino acids play a vital role in the field of optical nonlinearity due to the presence of NH_2 and COOH groups. Hence it is of interest to use amino acids as dopant in the nonlinear optical materials so as to study the change in optical property of nonlinear materials. In the present investigation we have grown Glycine doped ZTC crystal and its optical properties were studied. The second harmonic generation (SHG) efficiency test of Glycine doped ZTC salt was carried out by the Kurtz Perry powder technique. We observed increase in SHG efficiency of ZTC after addition of Glycine, and it was found that the SHG efficiency of ZTC salt increases by 9 times when it was doped with 3 mole % Glycine. We have observed a 9 time enhancement in SHG efficiency of Glycine doped ZTC crystal when it was doped with 3mole% of Glycine. The incorporation of Glycine in ZTC was confirmed by the FTIR and EDAX analysis. The effect of Glycine on the optical transmission in the visible and ultra violet regions were studied by the UV-Visible spectral spectra. The thermogravimetric analysis suggests that incorporation of Glycine in the ZTC decreases thermal stability of the grown crystal.

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1. Introduction

There has been remarkable advancement in various aspects of material science and technology. Non linear optics (NLO) has emerged as one of the most attractive field of current research in view of its vital application in many areas such as optical modulation, optical switching and frequency conversion [1-7]. Second order nonlinear optical materials have recently attracted much attention because of their potential application in emerging optoelectronics technology [8-12]. Due to large flexibility in molecular design and high nonlinear Optical (NLO) efficiency, there has been significant progress in basic research on organic polymers and organometallic solid materials. NLO properties of organo metallic materials are currently under intense investigation, triggered by potential application in optoelectronics because of the inherent advantages of both organic and inorganic materials.

Some intuitive understanding of the advantages of NLO properties of thiourea co-ordination compound was found in literature [13-15]. Some of the examples of these complexes are Zinc thiourea sulfate (ZTS), Zinc thiourea chloride (ZTC), Bis thiourea cadmium chloride (BTCC), Biscadmium Formate (BTCF), Copper thiourea chloride (CTC) and Cadmium thiourea acetate. All these crystals posses higher nonlinearity than KDP, higher laser-damaged threshold, polarizibility and wide spectral transmission window, hence may be used for various NLO applications such as electro-optic modulation, optical data storage and frequency conversion applications [16-23].

In the field of nonlinear optical crystal, amino acids are playing vital role. Many members of amino acids exhibit nonlinear optical properties. Some of the amino acids are used as dopants as they enhance the nonlinearity due to the presence of NH_2 and COOH groups. A series of semiorganic crystals of amino acids such as L-arginine phosphate, L-arginine tetrafluoroborate, and L- histidine tetrafluoroborate, L-arginine dehydrate, hippuric acids crystals, L-alanine and L-threonine Acetate etc, were reported [24-28].

Zinc thiourea chloride $\{Zn\ [CS\ (NH_2)_2]_2Cl_2\}$ is a potential semiorganic nonlinear optical material and crystallizes crystallizes in the non-centrosymmertic orthorhombic structure. Its second harmonic generation (SHG) efficiency was reported to be less than Zinc thiourea sulfate (ZTS) crystal [19]**.** The growth of bulk single crystals of this material with enhanced SHG efficiency has been the subject of intense research in order to use them for device applications. The ZTS and ZTC crystals were doped with phosphate [29, 30]. The tri glycine sulphate (TGS) crystals were also doped with amino acids and their properties were studied [31-32]. However, to the best of our knowledge there is no report on the doping of amino acid into thiourea metal complexes. In the present investigation, we have grown the Glycine doped ZTC crystal with improved nonlinearity. It has been observed that the addition of Glycine in ZTC increases its SHG efficiency and as the doping concentration increases the SHG also increases. The highest increase in SHG efficiency was observed when 3mole% Glycine was added in under saturated solution of ZTC and it was 9 times more than pure ZTC. Therefore, the single crystal was grown from the 3mole% Glycine doped ZTC solution by slow evaporation solution growth method. The grown crystal was subjected to optical, structural and thermal characterizations to study its possible use in optoelectronics and Laser based applications. The Powder X-ray diffraction confirmed the orthorhombic structure. The incorporation of Glycine in crystal bonding was confirmed by FTIR spectra. The EDAX analysis has also been carried out to confirm the presence of dopant in the material of grown crystal. The UV-Visible absorption spectrum was obtained to observe the change in the optical absorption of ZTC crystal after addition of Glycine. The thermal study of grown crystal was carried out using thermogravimetric analysis (TGA).

2. Experimental

2.1 Synthesis and growth

The salt of ZTC was synthesized by mixing annalar grade thiourea and Zinc chloride in stoichiometric ratio (1:2) with de-ionized water of resistivity 18.2MΩ cm^{-1}. The under saturated solution of ZTC was prepared at temperature 35^{o}C. This solution was kept in three different beakers and 1, 2 and 3 mole% Glycine was added to the respective beakers of ZTC solutions. These solutions were kept in constant temperature bath at temperature of 35 ^{o}C for evaporation in order to get salts. The compound salts were subjected to SHG test. We have observed enhancement in SHG efficiency for 1, 2, and 3 mole% addition of Glycine. However, the highest enhancement (9 times more than pure ZTC) was for 3mole% Glycine doped ZTC. Then seed crystals were grown from the solution of 3-mole% Glycine doped ZTC and a seed crystal free from any macro defects was selected for bulk growth. A single bulk crystal was harvested after 30 days. The grown crystal was subjected to various characterization techniques. The photograph of grown crystal is shown in Fig. 1.

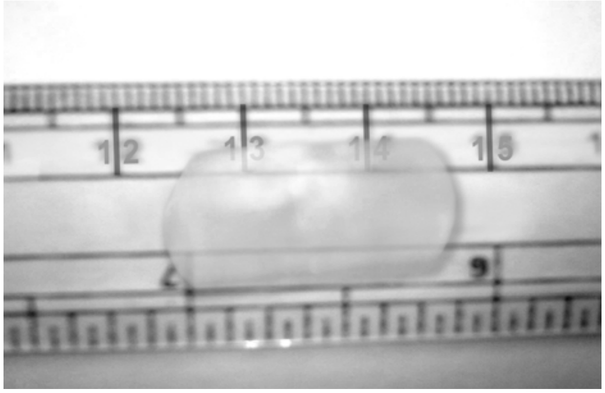

Fig. 1. Glycine doped ZTC crystal.

2.2 Characterization

The grown crystal was characterized by SHG efficiency test, Powder X-ray diffraction, FTIR analysis, Energy dispersive X-ray analysis (EDAX), UV-visible spectral studies and thermal analysis by thermogravimetric analysis (TGA).

3. Results and discussion

3.1 SHG efficiency

The Kurtz's powder SHG test was carried out to study the enhancement in SHG efficiency of Glycine doped ZTC crystal in comparison with pure ZTC. The Glycine was added in three different mole percent viz. 1, 2 and 3mole% to undersaturated solution of ZTC. The crystalline powder of pure and Glycine doped ZTC were illuminated by Nd: YAG laser of wavelength 1064 nm with input beam energy of 3mJ/pulse with pulse width of 8ns and repeatition rate of 10Hz. The second harmonic signals generated in the crystalline sample were confirmed from emission of green radiation by the sample. The photomultiplier tube was used as detector. We have observed out put voltage of 5 mV and 45 mV for pure ZTC and 3mole% Glycine doped ZTC respectively. This indicates that the SHG efficiency of 3 mole% Glycine doped ZTC is 9 times more than pure ZTC. This increase in SHG of ZTC with addition of Glycine is due to the fact that the Glycine has Zwitter ion i.e.NH_2 and COOH group. The Glycine has more dipole moment because of the presence of polar amino group [33]. ZTC reacts with Glycine, which an amino acetic acid, the optically active amino group may get added in the structure and increases its non-centrosymmetry and hence increasing its SHG efficiency. Hence Glycine doped ZTC crystal with enhanced SHG efficiency can be used as the active media in 1) Efficient Second harmonic generators 2) tunable parametric oscillators and 3) broadband electro-optic modulators.

3.2 Powder X-ray diffraction

The powder X-ray diffraction of grown Glycine doped ZTC crystal was carried out by using the panalytical XPert PRO powder X-ray diffractrometer employing CuKα radiation (λ=1.5418 A^{o}). Using the simulated hkl values and experimental d values, the lattice parameters were estimated which indicate that ZTC crystal retained its orthorhombic structure even after the addition of Glycine. The comparison of cell parameters and cell volume of pure and Glycine doped ZTC is shown in Table1. The X-ray diffraction pattern is shown in Fig. 2.

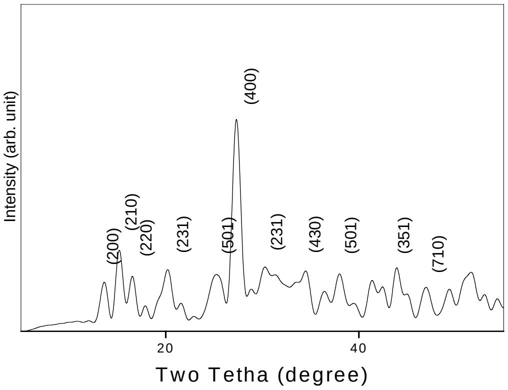

Fig. 2. Powder XRD pattern (the numbers assigned to various peaks are values of hkl indexes)

Table 1. Lattice Parameter values of pure and Glycine doped ZTC crystals.

Sample	a (A°)	b (A°)	c (A°)	V ($A^{\circ 3}$)
Pure ZTC	13.012	12.768	5.890	978.64
Glycine doped ZTC	13.021	12.762	5.895	974.76

3.3 Fourier transform infrared spectroscopy (FTIR) analysis

In order to analyze the presence of Glycine in the crystal qualitatively, Fourier transform infrared spectra study was carried out. The spectrum was recorded in the wavelength range 450-4000 cm^{-1} using Perkin Elmer FTIR spectrometer. The FTIR spectra of pure ZTC and Glycine doped ZTC crystal is shown in Fig. 3(a, b). The broad envelope positioned in between 2726.58 cm^{-1} and 3500 cm^{-1}corresponds to the symmetric and asymmetric modes of NH_2 stretching [18]. In spectra of Glycine doped ZTC crystal, the band in the region of 3763cm^{-1} and 3918 cm^{-1} may be due to the incorporation of added NH_2 group of Glycine. The broad envelope between 1821.64 cm^{-1} to 2324.47cm^{-1} was observed in the Glycine doped ZTC crystal only; it may be attributed to C-N out of phase stretching occurred due to the addition of Glycine.

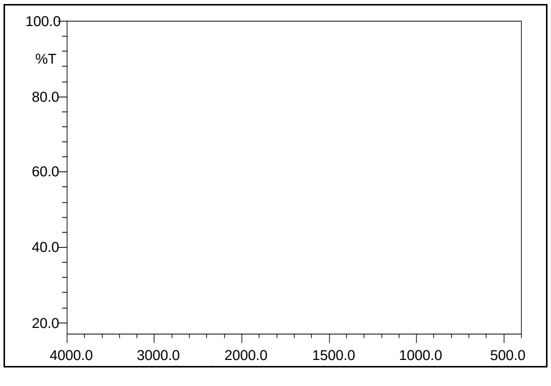

Fig. 3(a). FTIR spectrum of pure ZTC Crystal.

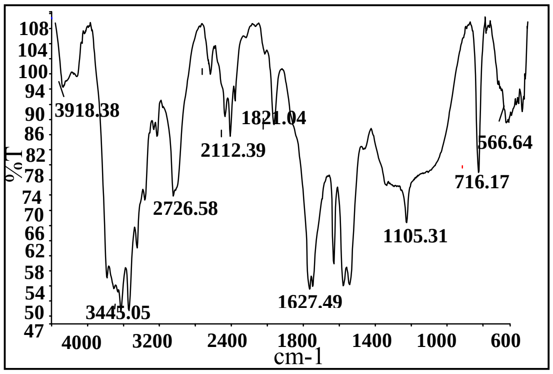

Fig. 3(b). FTIR spectrum of Glycine doped ZTC Crystal.

3.4 Energy dispersive analysis (EDAX)

Energy dispersive X-ray analysis (EDAX) is important tool for determining the elements present in the crystals. In the present investigation a small amount of material of the sample was subjected for EDAX analysis using JEOL-6360 Scanning Electron Microscope. The energies of different elements present in the salt of grown crystal such as C, N, O, S and Zn are 0.277Kev, 0.392Kev, 0.52Kev, 2.307Kev and 8.630Kev respectively. The additional nitro group may be seen near the energy of 1Kev. The EDAX spectrum of Glycine doped ZTC crystal is shown in Fig. 4, which also confirms the incorporation of Glycine in the grown crystal.

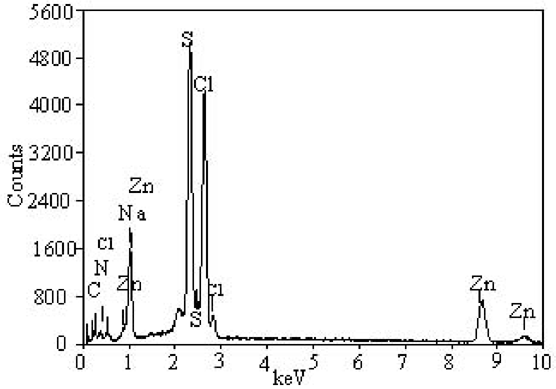

Fig. 4 EDAX spectrum of Glycine doped ZTC Crystal.

3.5 UV-Visible spectral study

The UV-Visible spectral study was carried out using Perkin Elmer Lambda 35 UV Spectrophotometer and spectrums of pure and Glycine doped ZTC crystal are shown in Fig. 5. The absorption spectra revealed that the grown Glycine doped ZTC crystal has lower absorption peak shifted to 236 nm. The increased transparency in the visible region for Glycine doped ZTC crystal enables the achievement of high second harmonic transmission for Nd:YAG laser. Hence it can be used as better alternative to pure ZTC in optoelectronics applications.

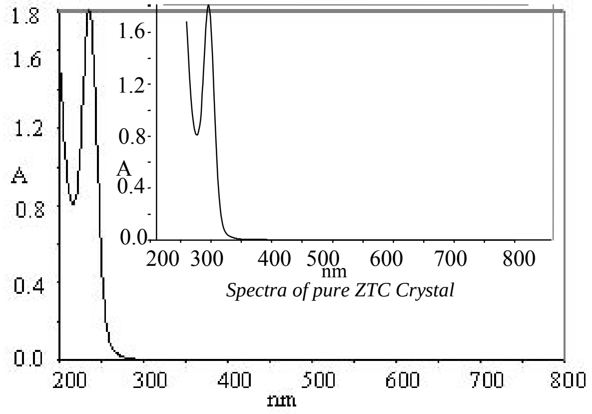

Fig. 5. UV-Vis absorbance spectra of Glycine doped ZTC Crystal.

3.6 Thermogravimetric analysis (TGA)

Thermo gravimetric analysis of grown Glycine doped ZTC crystal was carried out using TAQ-500 thermo gravimetric analyzer between temperature limit 25°C to 800°C at a heating rate of 25°C/min in a nitrogen inert atmosphere. The resulting thermogram and DTG trace is shown in Fig. 6. There is weight loss of about 50% between the temperature range 227.88°C to 303.50°C. It may be attributed to the liberation of volatile substances such as the dopant Glycine and the hydrogen of thiourea molecule. The weight loss near the temperature of 382°C may be due to removal of sulphure of thiourea from the Zinc co-ordination. There is another weight loss of 26.10% between temperature limits of 515.72°C to 620.52°C. Although there are the different weight losses at different temperature throughout the thermogram, there is no weight loss before 227.88ºC. It is due to the fact that the amino acids become unstable at lower temperature which weakens the grown crystal and as result the dehydration process takes place early in comparison of pure ZTC [34], hence this Glycine doped ZTC crystal is thermodynamically stable up to the temperature of 227.88°C and may be exploited for NLO applications upto this temperature.

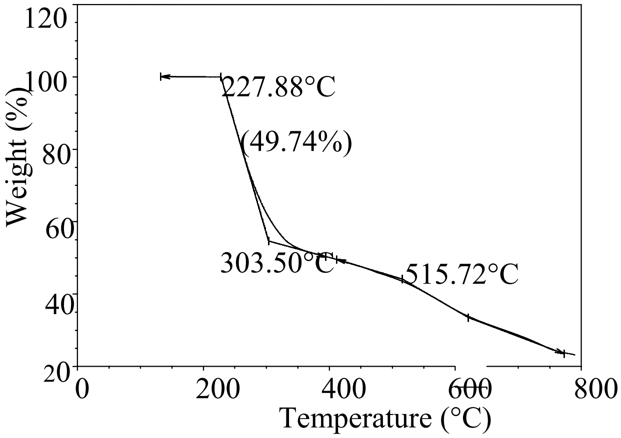

***Fig.6 .** TGA thermogram of Glycine doped ZTC Crystal*

5. Conclusions

The Glycine doped ZTC single crystal was grown and its optical study was carried out. The SHG test exhibit the enhancement in SHG efficiency of ZTC by the addition Glycine. The highest increase in SHG efficiency was found (9 times more than pure ZTC) when 3mole % Glycine was doped in to pure ZTC. The FTIR and EDAX spectra confirmed the incorporation of Glycine. The Powder X-ray diffraction analysis shows that ZTC retains its orthorhombic structure even after addition of Glycine, as there were very small changes in the cell parameters. The UV-Visible absorption spectra reveals that the Glycine doped ZTC crystal has low cut-off wavelength at 236 nm, which is better than pure ZTC. The thermogravimetric analysis (TGA) suggests that when Glycine is doped in ZTC crystal, it becomes thermally less stable and dehydrate faster at a comparatively lower temperature.

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