



Growth and characterization of Pure and Glycine doped Zinc thiourea chloride (ZTC)

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ABSTRACT

Single crystals of pure and Glycine-doped Zinc Thiourea Chloride (ZTC) were grown by slow evaporation technique. 1 molar percent of Glycine was added in saturated ZTC solution. The chemical composition of the crystals were determined by Fourier transform infrared (FTIR) analysis. The unit cell parameters and crystal structure were determined by single crystal X-ray diffraction. The UV-visible absorption spectra of pure and Glycine-doped ZTC showed excellent transmittance from 300 nm to 1100 nm. The thermal stability of the grown crystals was studied by thermo-gravimetric analysis (TGA). The second-harmonic generation efficiencies were studied by Kurtz and Perry powder SHG test and observed an enhancement in the SHG efficiency of Glycine-doped ZTC. Micro hardness study was also carried out on the samples to study the mechanical stability of the grown crystals.

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1. Introduction

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. This effort has also brought its fruits in applied aspects of nonlinear optics. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of inorganics has been found to be overwhelmingly successful in the recent past.

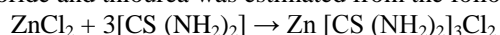
Thiourea, which is otherwise centrosymmetric, yields excellent noncentrosymmetric materials and typifies this approach [1]. Metal complex of thiourea, commonly called semi-organics, include the advantages of both organic and inorganic part of the complex. A variety of crystals of this class have been grown by several groups. Some of them viz., Bis thiourea zinc chloride doped potassium dihydrogen phosphate[2], Glycine doped cadmium thiourea sulphate[3], and L-Lysine doped Zinc thiourea sulphate[4] have been reported. Zinc thiourea chloride (ZTC) is a potential semi-organic NLO material, which exhibits a low angular sensitivity and hence useful for type-II second harmonic generation (SHG) [5–7]. Growth of ZTC single crystals using slow evaporation technique [8], slow cooling technique [9] and potassium chloride doped ZTC [10] has been reported.

Though the SHG efficiency of ZTC is reported to be less than that of ZTS [11], it has promising crystal growth characteristics. The nucleation parameters of ZTC, which are essential for the growth of bulk crystals, have been investigated [8].

The importance of amino acids in NLO applications is in the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in a non-centrosymmetric space group. In solid state, amino acids containing one de-protonated carboxyl group (COO⁻) and a protonated amino group (NH⁺₃). This dipolar nature exhibits peculiar physical and chemical properties of amino acids making them ideal candidates for use in NLO. Glycine is the simplest of all amino acids in the crystalline form, having three different polymorphs in which the molecules exist in the dipolar form. The effect of Glycine and L-Alanine on the optical properties of ZTC [12-14] single crystals have already been reported. In this work, we obtained ZTC crystals doped with Glycine by slow evaporation at room temperature and investigated the optical, thermal, and mechanical properties through various characterization studies such as X-ray diffraction, UV-vis, FTIR, thermal, mechanical and NLO.

2. Crystal growth

The ZTC salt was synthesized by dissolving Zinc chloride and thiourea in the ratio 1:3 in deionized water. Single crystals of ZTC and Glycine doped ZTC were grown employing slow evaporation techniques. The solution was stirred with magnetic stirrer at room temperature. The required quantity of Zinc chloride and thiourea was estimated from the following reaction.



The calculated amount of salt was dissolved in the deionized water by constant stirring till the super saturation stage was achieved. The purity of the synthesized salt was increased by successive recrystallization process. After 30 days, a well-defined, transparent colorless ZTC crystal of was harvested. For the growth of Glycine doped ZTC crystals, 1 mol % of Glycine was added to the solution of ZTC. Single crystals with good transparency were harvested in 30 days. The photographs of the grown crystals are shown in Fig (1a) and (1b).



Fig.1 (a) The Photograph of Pure ZTC crystal



Fig.1 (b) The Photograph of Glycine doped ZTC crystal

3. Characterization

3.1. Single crystal X-ray diffraction Analysis

The ENRAF NONIUS CAD4 diffractometer was used to determine the unit cell parameters of the grown crystals. The values revealed by X-ray analysis for pure and Glycine doped ZTC crystals are shown in Table.1 which is in good agreement with the reported data [13].

Table – 1

Single XRD data of pure and Glycine doped ZTC crystals

Pure ZTC	Glycine doped ZTC
a = 13.013A°	a = 13.022A°
b = 12.767A°	b = 12.758 A°
c = 5.891A°	c = 5.887A°
V = 978.71A° ³	V = 975.21A° ³
Orthorhombic	Orthorhombic
Space group- Pnma	Space group- Pnma

3.2. FT-IR analysis

The presence of Glycine in ZTC crystal was qualitatively analyzed from the FTIR spectra of the grown crystals and compared with each other. Fig.2 (a) and 2(b) shows the FTIR spectra of pure and doped crystals. The spectrum was recorded using KBr pellet technique in the frequency region 400-4000cm⁻¹ using PERKIN ELMER RX1 Fourier Transform Infrared spectrometer. The FTIR spectrum contains all the characteristic bands corresponding to different molecular groups present in the sample. The comparison of assignments of various internal modes observed in these FTIR spectra with thiourea are given in the Table.2. The bands observed in the 3000-3500 cm⁻¹ region in the FTIR spectra are characteristics of NH₂ asymmetric and symmetric stretching vibrations and are in agreement with other compounds containing thiourea molecule [15-18]. There is a strong NH absorption peak at around 3200 cm⁻¹ in the spectrum of the doped crystals, which may increase with doping. As Glycine is doped, more NH stretch vibrations are introduced resulting in a stronger NH absorption peak. The strong band at 1627cm⁻¹ of thiourea corresponds to a band at 1617.37cm⁻¹ of pure ZTC and 1626.64cm⁻¹ of Glycine doped ZTC, which is attributed to the NH₂ bending vibration. The peaks at 1472cm⁻¹ and 740cm⁻¹ assigned to the C=S stretching vibration in thiourea

is shifted to 1406.74cm⁻¹, 1405.75cm⁻¹ and 709.08 cm⁻¹, 709.38 cm⁻¹ in the pure and doped crystals. So, the doping of ZTC crystal with Glycine is indirectly established through the shift in the peaks.

Table – 2

FT-IR spectral data of Thiourea, pure and Glycine doped ZTC crystals

Wavenumber (cm ⁻¹)			Assignments
Thiourea	Pure ZTC	Glycine doped ZTC	
3280	3287.70	3322.33	Asymmetric NH ₂ stretching
3167	3192.50	3205	Symmetric NH ₂ stretching
1627	1617.37	1626.64	NH ₂ bending
1472	1406.74	1405.75	Asymmetric C=S stretching
1089	1097.71	1098.90	Asymmetric N-C-N stretching
740	709.08	709.38	Symmetric C=S stretching

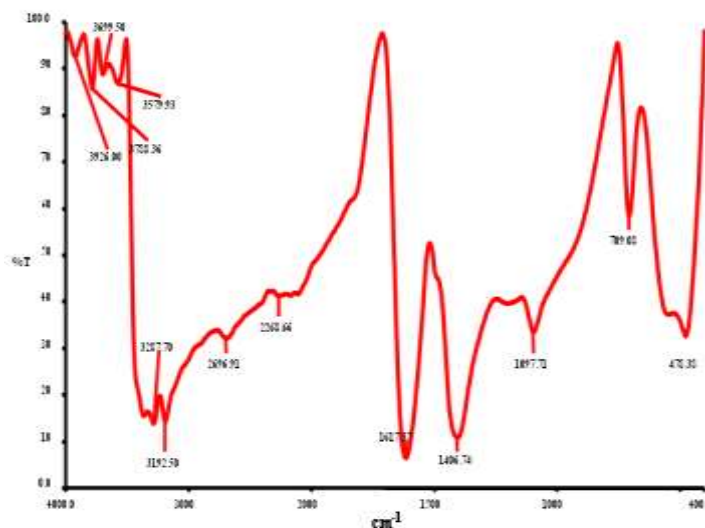


Fig. 2(a) FT-IR Spectrum of ZTC crystal

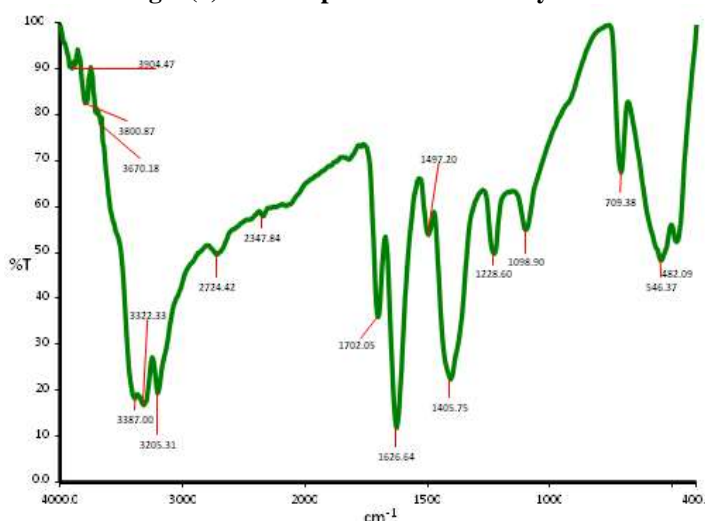


Fig. 2(b) FT-IR Spectrum of Glycine doped ZTC crystal

3.3. UV-Visible transmittance study

An optical material can be defined as a solid that presents events when interacts with light in the range of wavelengths of 200 nm (ultraviolet) to 3 μm (near infrared). The UV-Vis spectrum of pure and Glycine doped ZTC crystals were recorded in the range of 190-1100nm using LAMBDA-35 UV-Vis spectrophotometer. Optical transmission spectra of Glycine with ZTC as shown in Fig. (3) has a good transparency in between

300 and 1100 nm. The lower cutoffs of both pure and doped crystals occur at 275nm. Glycine doped ZTC has minimum of 70% transmission which is higher than that for pure ZTC. The increased transparency in the visible region for Glycine doped ZTC crystal enables the achievement of high second harmonic transmission for Nd:YAG laser.

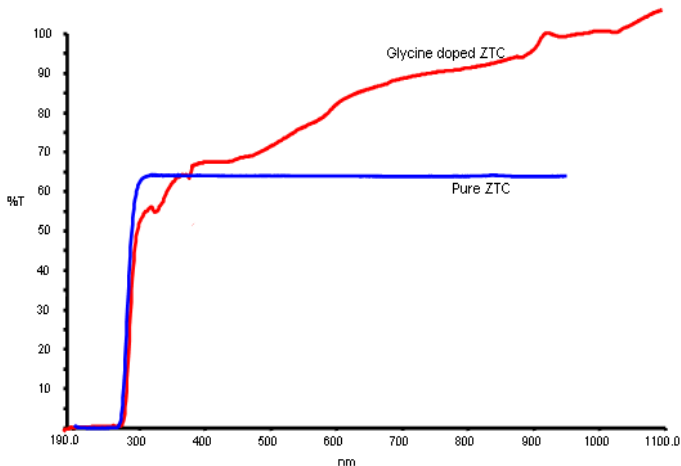


Fig. (3) UV-Vis spectrum of pure and Glycine doped ZTC crystals

3.4. Thermal analysis

The thermograms of pure and Glycine doped ZTC crystals were recorded by using TAQ-500 analyzer. In TGA, Fig.4(a) shows that the sample pure ZTC is stable till 160.97°C, then it begins to degrade with 18% weight loss till 247.91°C after which a weight loss of 48.29% was observed from second endothermic peak to 354.50°C. From Fig.4(b) it is observed that for Glycine doped ZTC crystal there is weight loss of about 13.99% between the temperature range 172.75°C and 235.23°C. It may be attributed to the liberation of volatile substances such as the dopant Glycine and the hydrogen of thiourea molecule [15]. The weight loss of about 26.12% near the temperature of 375°C may be due to the removal of sulphur of thiourea from the Zinc co-ordination [19]. Since there is no weight loss up to 172.75°C, this Glycine doped ZTC crystal may be exploited for NLO applications upto the temperature of 172.75°C.

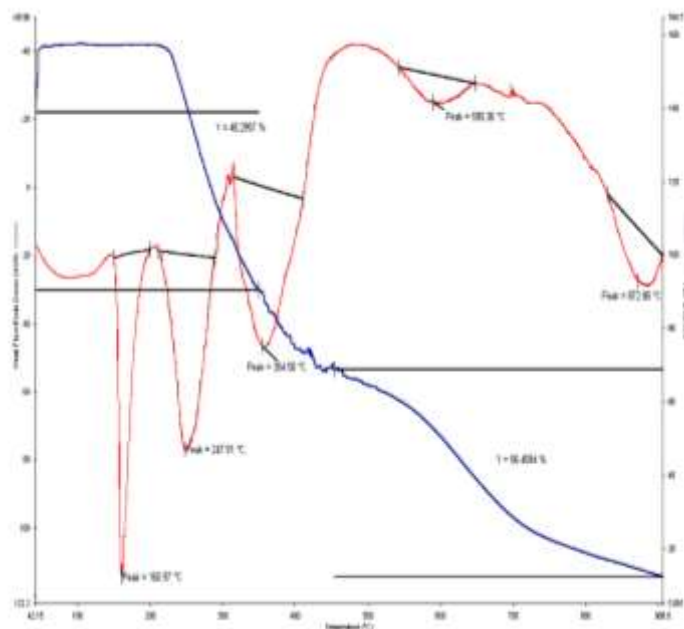


Fig.4 (a) Thermogram of pure ZTC Crystal

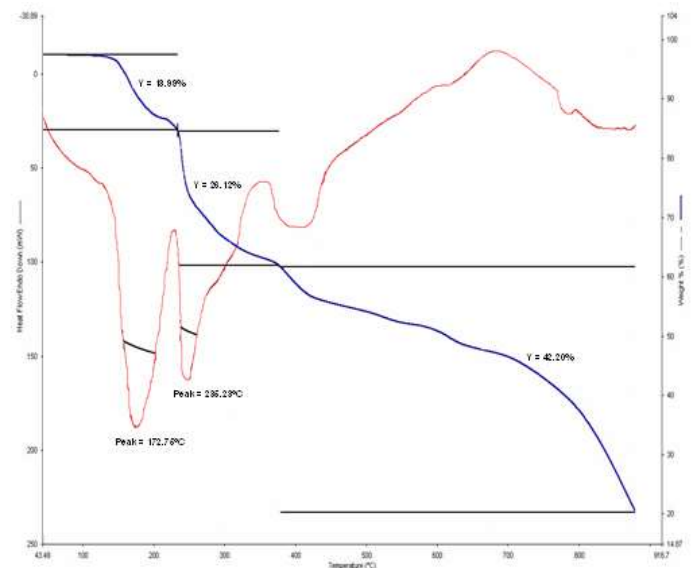


Fig.4 (b) Thermogram of Glycine doped ZTC Crystal

3.5. Microhardness measurement

Microhardness testing is to be performed on single crystals to evaluate the mechanical properties and to examine the suitability of the material for devices by measuring the resistance of the lattice against the applied load [20]. Hardness was measured using Leitz-Wetzler hardness tester. Microhardness measurements were made on the smooth surface of the as grown pure and Glycine doped ZTC single crystal. Load P was varied between 25 and 100g by keeping the time of indentation constant (10s) for all trials and the diagonal length of indentation was measured. The Vickers hardness number of the materials Hv is determined by the relation, $H_v = 1.8544 * (P/d^2) \text{ kg/mm}^2$

Where P is the applied load in kg and d is the diagonal length of indentation impression in mm. The fig.5 shows the plot of hardness number variation with applied load. From the profile, it is observed that the hardness number increases with increasing load. However, the hardness value of Glycine doped ZTC crystal is found to be greater than that of the pure ZTC crystal. For the same range of applied loads the microhardness measurement clearly shows that the inclusion of amino acid has improved the mechanical stability of Glycine doped ZTC crystal.

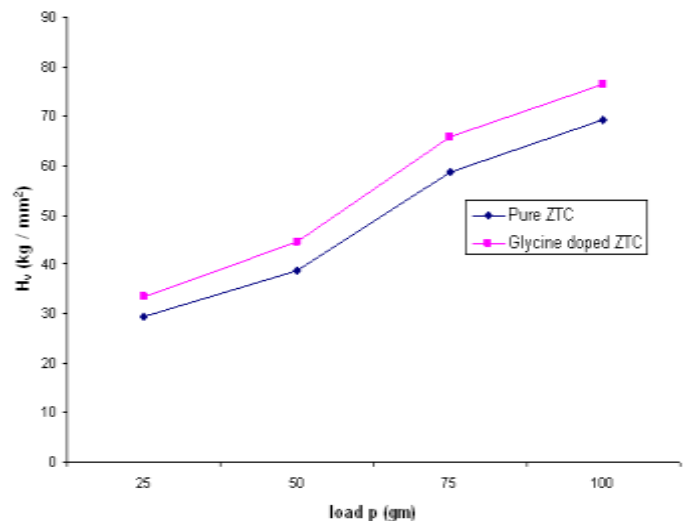


Fig.5 Vickers Hardness Vs load for pure and Glycine doped ZTC Crystals

3.6. SHG efficiency

The second harmonic generation signal in the pure and doped ZTC crystals were examined by the Kurtz powder technique [21]. A high intense beam from the Nd:YAG laser with the wavelength of about 1064nm was allowed to be incident on the samples. The SHG signal generation was confirmed by the emission of green radiation from the crystals. From the analysis it was found that the SHG output relative efficiency was 5mv for pure ZTC and 11mv for the Glycine doped ZTC samples. Comparing the above values the measured SHG efficiency of Glycine doped ZTC sample was found to be about 2.2 times greater than that of pure ZTC sample.

4. Conclusion

The Growth and properties of pure and Glycine doped ZTC single crystals grown by slow evaporation method have been investigated. The unit cell parameters and crystal structure were determined by single crystal X-ray diffraction. The FTIR spectra revealed all the characteristic bands corresponding to different molecular groups present in the sample. Transmission spectra revealed that the crystals have an extended transparency down to UV. Thermogravimetric analysis showed that the Glycine doped ZTC crystal is thermodynamically more stable than pure ZTC. The hardness values of ZTC are lesser than amino doped ZTC crystal. The SHG output efficiency of Glycine doped ZTC sample was found to be about 2.2 times greater than that of pure ZTC sample. The promising crystal growth characteristics and the properties of the grown crystals prove them to be attractive materials for harmonic generation of Nd:YAG lasers.

References

[1] Venkataramanan, V., Maheswaran, S., Sherwood, J.N. and Bhat, H.L. (1997). *J. of Cryst. Growth*. 179(3-4): 605.
 [2] Fernando Loretta, T. Josephine Rani, P. Selvarajan, S. Perumal, S. Ramalingom, *World J. Sci. and Tec.* 1(3) (2011)01-06
 [3] M. Lawrence, J. Thomas Joseph Prakash, *Spectrochimica Acta Part A* 91 (2012) 30– 34

[4] J. Thomas Joseph Prakash, M. Lawrence, *International J. of Comp. Appl.* (0975-8887) Volume 8– No.3, October 2010.
 [5] P.A. Angeli Mary, S. Dhanuskodi, *Cryst. Res. Technol.* 36 (2001) 1231.
 [6] Rajasekaran, R., Kumar, R.M., Jayavel, R. and Ramasamy, P. (2003). *J. of Cryst. Growth*. 252(1-3):317.
 [7] Rajasekaran, P., Ushasree, P.M., Jayavel, R. and Ramasamy, P. (2001) *J. of Cryst. Growth*. 229(1-4): 563.
 [8] R. Rajsekaran, K.V. Rajendiran, R.M. Kumar, R. Jayavel, R. Dhanasekaran and P. Ramasamy, (2003), *Materials Chem. and Phy.* 82(2): 273.
 [9] K. Parasuraman, K. Sakthi Murugesan, R. Uthrakumar, S. Jerome Das, B. Milton Boaz; *Physica B*. 406 (2011) 3856–3860.
 [10] L.Ruby Nirmala, J.Thomas Joseph Prakash, *Spectrochim Acta A* 102 (2013)297-300.
 [11] M. Oussaid, P. Becker, C. Carabatos-Nedelec, *Phys. Stat. Sol. (B)* 207 (1998) 499.
 [12] S.S. Hussaini, N. R. Dhumane, V. G. Dongre, M. D. Shirsat (2008) *Optoelectronics and Adv. Materials – Rapid Communications*, 2(2):108-112.
 [13] N.R. Dhumane, S.S. Hussaini, V.G. Dongre, P. Ghugare; M.D. Shirsat (2009) *Appl. Phy. A: Materials Science & Processing* 95(3):727-732.
 [14] M. Lawrence, J. Thomas Joseph Prakash, *Elixir Crystal Growth* 41 (2011) 5623-5628.
 [15] V. Winterfeld, G.Z. Schaack, *Phys. B* 26 (1980) 303.
 [16] K.T. Kim, J.J. Kim, *Ferroelectrics* 105 (1990) 243.
 [17] V. Venkataramanan, M.R. Srinivasan, H.L. Bhat, *J. Raman Spectrosc.* 25 (1994)805.
 [18] S. Abraham, G. Aruldas, *Spectrochim. Acta A* 51 (1995) 79.
 [19] D. Parikh, D.J. Dave, B.B. Parekh, M.J. Joshi, *Bull Mater. Sci.* 30, 105 (2007).
 [20] J.B. Quinn, G.D. Quinn, *J. Mater. Sci.* 32 (1997) 4331.
 [21] S.K. Kurtz, T.T. Perry, *J. Appl. Phys.* 39 (1968) 3798.