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Growth and Investigation Studies of Pure and Glycine Doped Zinc Tris-thiourea Sulphate (ZTS) Single Crystals

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Abstract: Zinc Tris-thiourea Sulphate (ZTS) belongs to the family of semiorganics nonlinear optical materials. Good quality single crystal of pure and doped ZTS have been grown by slow evaporation solution growth technique at room temperature. The grown crystals have been subjected to FTIR and UV visible spectra studies. The Fourier Transform Infrared analysis confirms the presence of functional groups and zinc coordination in grown crystals. The UV visible spectrum revels that grown crystals were transparent in the entire visible region. These investigations indicated that impurity played an important role in the changes of the transmittance of ZTS crystals.

Keywords: Nonlinear optical materials, Crystal growth, Slow evaporation solution growth, Second harmonic generation, Amino acid doped ZTS, FTIR and UV VIS analysis.

I. INTRODUCTION

Semiorganic NLO crystals are expected to possess the advantages of both inorganic and organic materials. “Semiorganics” are salts in which are combined with the favorable mechanical and thermal properties of an inorganic counterion. While recent work has demonstrated that organic crystals can have very large nonlinear susceptibilities relative to inorganic crystals, their use is impeded by their low optical transparencies, poor mechanical properties, low laser damage thresholds, and pure processibility. In contrast, purely inorganic NLO materials typically have excellent mechanical and thermal properties but often possess relatively modest optical nonlinearities due to their lake of extended π-electron delocalization.

Furthermore, inorganic crystals grown from high-temperature melts typically may have lower laser damage thresholds and more optical inhomogeneities throughout their bulk due to impurities, internal stresses, and defects resulting from the extremely non equilibrium growth conditions. In semiorganics, polarizable organic molecules are stoichometrically bond within an inorganic host; e.g. an organic ion-inorganic counterion salt, such as L-arginine phosphate or an organic ligand-metal ion complex, such as zinc tris (thiourea) sulphate (ZTS). Imparting ionic character to large NLO-response organic molecules via complexation and /or salt formation works to improve the mechanical and optical properties of the crystals of these materials and also provides a high degree of design flexibility for NLO effects. A further benefit of this approach is that semiorganics are prepared by crystallization from near-ambient temperature solvents. Zinc (thiourea) sulphate (ZTS) belongs to the family of semiorganics nonlinear optical (NLO) materials. ZTS can be grown from aqueous solutions at moderate temperatures. This crystal crystallizes in the non-Centro symmetric orthorhombic space group Pca21. The lattice parameters are reported to be a=11.13Å, b=7.785Å, and c=15.466Å. In the early nineties, ZTS crystal drew considerable interest as a potential candidate for second harmonic generation (SHG) and use as an electro-optic modulator.

II. EXPERIMENTAL PROCEDURE

A. Synthesis

Zinc tris (thiourea) sulphate (ZTS) was synthesized according to the chemical reaction:

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

ZTS salt was synthesized by thiourea and zinc sulphate heptahydrate in the molar ratio 3:1. The component salts were very well dissolved in deionized water which was throughly mixed using a magnetic stirrer, and the mixture was heated at 50°C till a white crystalline salt of ZTS was obtained.

B. Seed Preparation

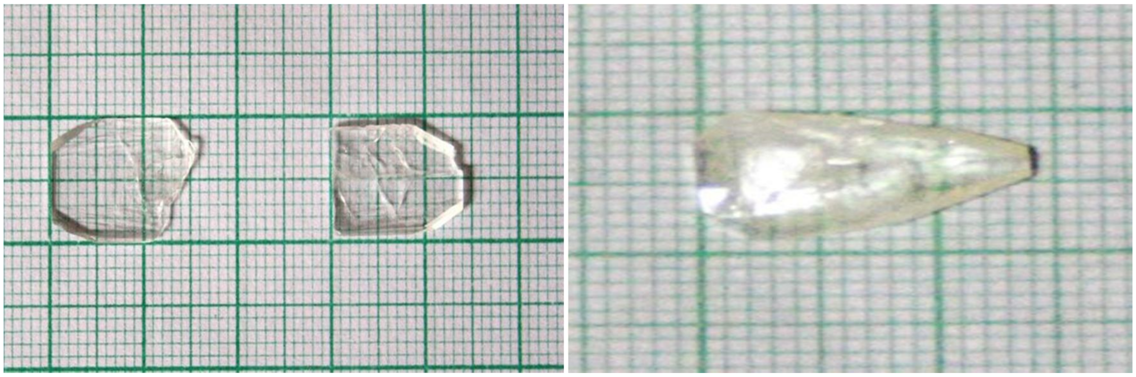
The synthesized ZTS salt was dissolved in deionized water and the solution was prepared in a slightly saturated condition. The solution was constantly stirred for two hours using a magnetic stirrer. The solution was filtered using high quality filter paper (Whatmann). Then the filtered solution was poured into a pertidish, and closed by plastic paper. The seed crystals were grown after a period of one week. Good quality seed crystals were taken for the growth of large-size crystals by slow evaporation technique. The quality of the grown crystals very much depends on the quality of the seed crystals used. A seed used to grow a large single crystal must be free from inclusions and cracks.

C. Growth of ZTS Crystals

The impurity content of the synthesized salt was minimized by repeated recrystallization processes. Then, the synthesized salt was taken as the raw material of the growth of ZTS. The raw material was poured into 100ml water up to the saturated solution was prepared. Meanwhile, the solution was continuously stirred by using a magnetic stirrer. Finally, the saturated solution of ZTS called “mother solution” was prepared, and it was poured into another 100ml beaker. The seed crystal obtained earlier was hunged inside the mother solution using a nylon thread and allowed to grow. The period of growth ranged from 40 to 50 days. After the completion of growth, the crystals were harvested from the solution (Fig.1a.)

D. Growth of glycine doped ZTS crystals

The growth of 3mol% glycine doped ZTS crystal was carried out by slow evaporation technique at room temperature. The saturated solution of ZTS was prepared, and it was poured in to a beaker. The measured amount of 3 mol% of glycine was added and the beaker was tightly closed with a thick plastic paper so that the evaporation could be minimized. After 20 days, well-grown crystals of 3mol% glycine doped crystals were harvested from the solution (Fig.1b.)



(a) Pure ZTS (b) Glycine doped ZTS

Figure 1: Photograph of the pure and glycine doped ZTS grown crystals

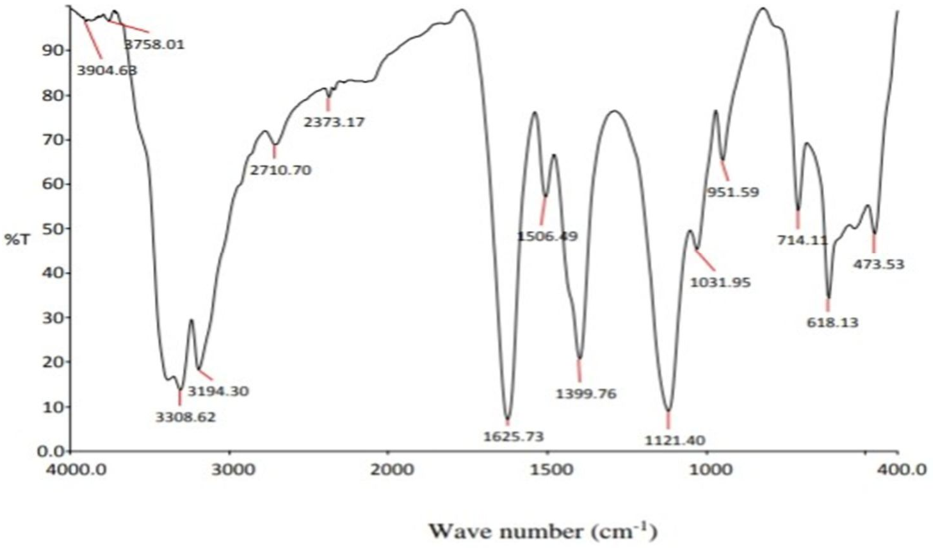
III. CHARACTERIZATION

A. FTIR Spectrum Analysis of Pure and Glycine Doped ZTS

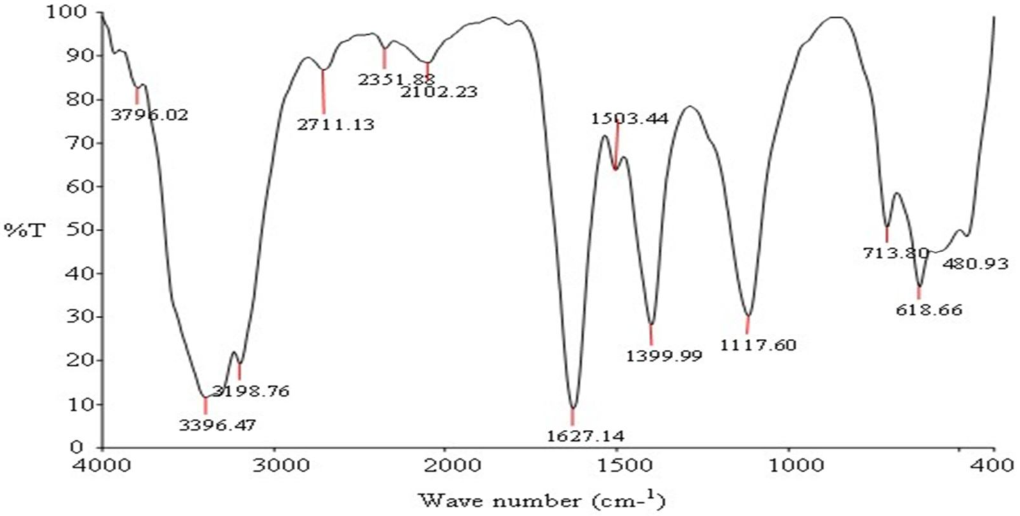
Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups present in synthesized material. The presence of functional groups and modes of vibration of pure and 3mol% glycine doped ZTS crystals are recorded using Perkin-Elmer FTIR spectrometer by KBr pellet technique in the wavenumber range of 400 – 4000 cm^{-1}. The FTIR spectra of grown pure and 3mol% glycine doped ZTS crystals are shown in fig. 2a and 2b. The comparison of assignments observed in FTIR spectra are given in the Table. 1. The Fourier transform infrared (FTIR) spectrum of ZTS is shown in fig.2a. In ZTS complex, there are two possibilities by which the coordination of zinc with thiourea can occur. It may occur either through nitrogen or sulphur of thiourea. The bonds observed in the 3000- 3500cm^{-1} region in the FTIR spectra, at 3194.30 and 3308.62 cm^{-1} are characteristics of NH_2 asymmetric and symmetric stretching vibrations are in agreement with other compounds containing thiourea molecule $CS(NH_2)_2$. The strong bond observed at 1625.73 cm^{-1} in the ZTS complex corresponds to a bond at 1628 cm^{-1} of thiourea, which is attributed to the NH_2 deformation vibration similar to those of some metal thiourea complexes. The bond at 1477 cm^{-1} assigned to the N-C-N stretching vibration in thiourea is shifted to 1506.49 cm^{-1} in the ZTS complex. This shift may be due to the greater double bond character of the C-N bond on complex formation. The bond observed at 1384 and 1399.76 cm^{-1}in the complex correspond to the 1414 cm^{-1} bond of thiourea due to the NH_2, N-C-N, and C=S stretching vibrations.

The sharp and intense band absorption of ZTS at 714.11vibrations of the C-N bond is expected in 460-730 cm^{-1} range. The three bonds at 473.53, 618.13 and 714.11 cm^{-1} are assigned to C-N deformation vibration. The shift in the frequency bond at low frequency region also indicates the presence of a sulphur-metal bond in ZTS.

The FTIR spectra of 3mol% glycine doped ZTS shows (fig.2b) a broad envelope lying in between 2750 and 3500cm^{-1} arising out of symmetric and asymmetric modes of NH_2 group of zinc coordinated thiourea. The absorption band at 1627.14 cm^{-1} in the spectra of 3 mol% glycine doped ZTS corresponds to NH_2 bending vibrations. The absorption peak observed at 1503.44 cm^{-1} corresponds that of N-C-N stretching vibration. The absorption band at 1399.99 cm^{-1} assigned to the C=S asymmetric stretching vibration. The presence of sulfate ion in the coordination sphere is evident from peaks at about 500 and 1000cm^{-1}. Comparison of IR spectra of ZTS and 3 mol% glycine doped ZTS shows slight shift in absorption bands. This shift in absorption bands may be due to addition of glycine in ZTS. The shoulder at around 2000cm^{-1} is assigned to the hydrogen bonding of NH_3^+ and COOH group.



(a) Pure ZTS



(b) Glycine doped ZTS

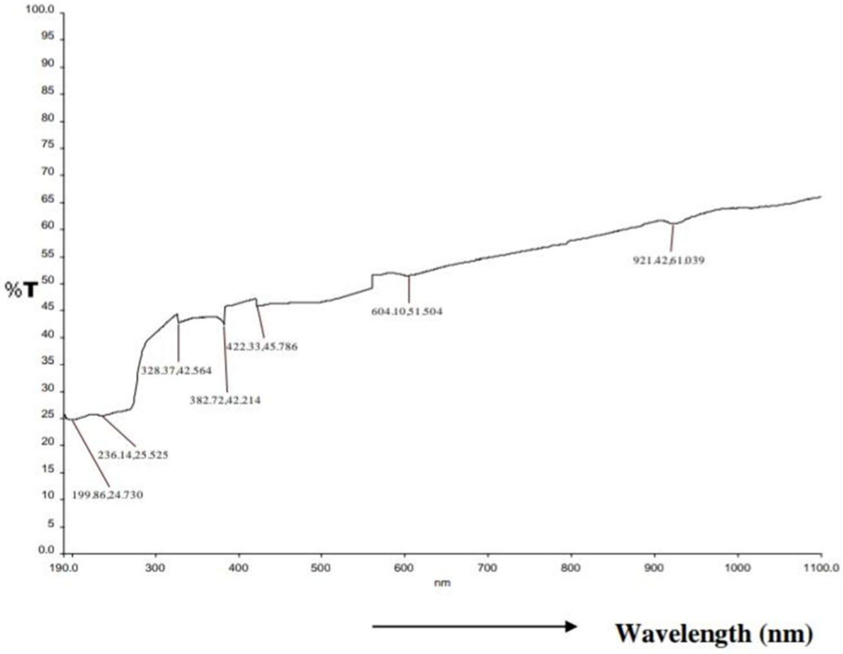
Figure 1: FTIR Spectrum of the pure and glycine doped ZTS crystals

Table1.
Vibrational frequency assignments observed in FTIR spectra of grown pure and glycine doped ZTS crystals

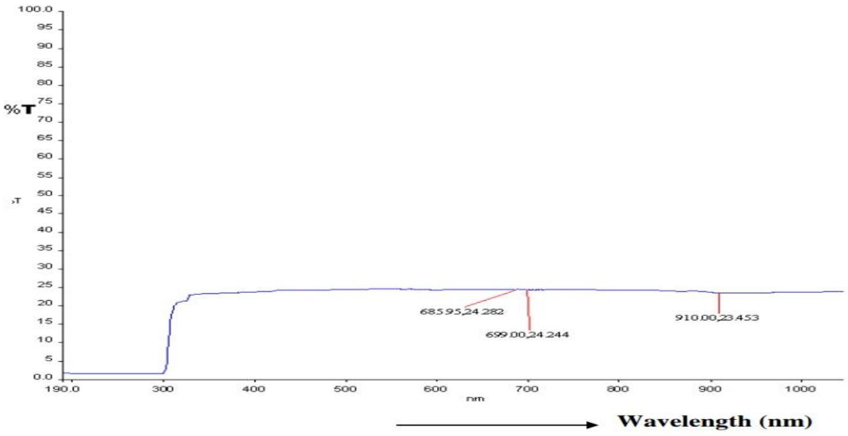
Frequency in wave number (cm^{-1})		Assignments
Pure ZTS	Glycine doped ZTS	
3758.01	3796.02	Asymmetric NH_2 stretching vibration
3308.62	3396.47	Asymmetric NH_2 stretching vibration
3194.30	3198.76	Symmetric NH_2 stretching vibration
2710.70	2711.13	O-H stretching vibration
2373.17	2351.88	CH_2 rocking vibration
1625.73	1627.14	NH_2 bending vibration
1506.49	1503.44	N-C-N stretching vibration
1399.76	1399.99	NH_2 rocking vibration, C=S asymmetric stretching vibration and N-C-N stretching vibration
1121.40	1117.60	C=S and C-N stretching vibration
714.11	713.80	Symmetric C=S stretching vibration
473.53	480.93	Symmetric N-C-N bending vibration

B. UV-visible Spectral Study of Pure and Glycine Doped ZTS Crystals

The UV-Visible transmittance spectrum was studied using Lambda -35 Spectrophotometer with a single crystal of 3mm thickness in the range of 190-1000nm. The recorded UV-visible transmittance spectra of the grown crystals of pure & glycine doped ZTS crystals were shown in Fig. 3a & 3b. The recorded UV-visible Absorption spectra of the grown crystals of pure & glycine doped ZTS crystals were shown in Fig. 4a & 4b. The pure ZTS crystal has sufficient transmission in the entire visible and IR region. The lower cutoff wavelength is around 300nm. The transmittance window in the visible region and IR region enables good optical transmission of the second harmonic frequencies of Nd: YAG laser. From the UV –visible spectrum of both pure and glycine doped ZTS, it is confirmed that the absorption of UV radiations reduced when glycine is doped.

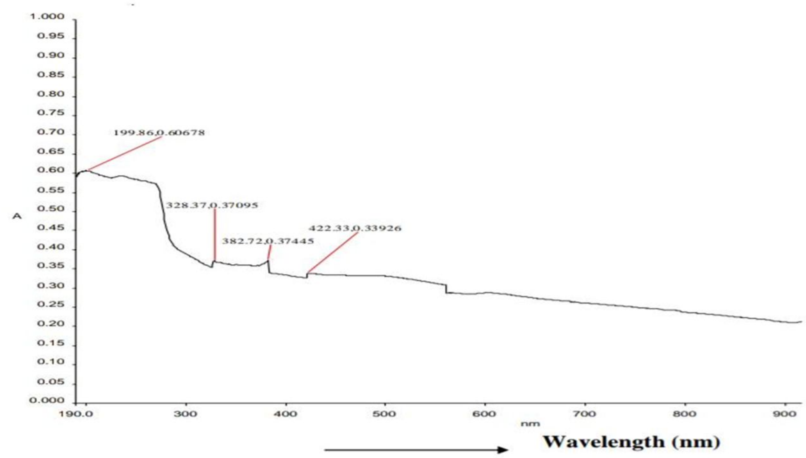


(a) Pure ZTS

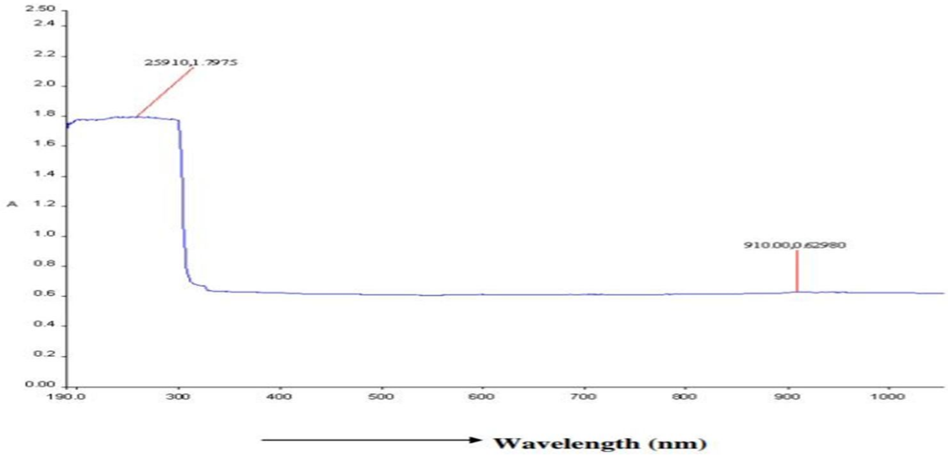


(b) Glycine doped ZTS

Figure 1: Transmittance Spectrum of the pure and glycine doped ZTS crystals



(a) Pure ZTS



(b) Glycine doped ZTS

Figure 1: Absorption Spectrum of the pure and glycine doped ZTS crystals

IV. CONCLUSION

Good quality single crystals of pure and 3 mol % glycine doped ZTS has been grown by slow evaporation solution growth technique at room temperature. The Fourier transform infrared (FTIR) analysis confirms the presence of functional groups and sulphur -zinc coordination in the grown crystals. The UV-visible spectrum reveals that the grown crystals were transparent in the entire visible region, which is the essential requirement for the NLO applications. The doping of 3 mol% glycine with ZTS enhances the transmittance of the pure ZTS crystals. All the above studies of the glycine doped ZTS crystal confirmed that it is a suitable material for various optoelectronic applications.

REFERENCES

[1] C. Krishnan, P.Selvarajan, T.H.Freeda, J.Crystal Growth 311 (2008) 141-146.
[2] M. Lawrence, J.Thomas Joseph Prakash, J. Spectrochimica Acta Part A 91 (2012) 30-34.
[3] K.Kanagasabapathy, R.Rajasekaran, Adv. Mater. Res. 584 (2012) 37-41.
[4] F.Helen, G.Kanchana, J.Pure & Appl. Phys. 52 (2014) 821-828.
[5] C.Krishnan, P.Selvarajan, T.H.Freeda, J. Mater. Lett. 62 (2008) 4414-4416.
[6] D.Prem Anand, S.Selvakumar, K.Ambujam, K.Rajarajan, M.Gulam Mohamed & P.Sagayaraj, Ind. J. Pure & Appl. Phys. 43 (2005) 863-868.
[7] J.H.Joshi, S.Kalainathan, D.K.Kanchan, M.J.Joshi & K.D.Parikh, J. Mater. Sci. Mater. In Elec. 30 (2019) 2985-2993.
[8] A.David Kalaimani Raj, S.Chidambaram, R.Manimekalai, Inter. J. Sci. Res. Phys. & Appl. Sci. 6 (4) (2018) 73-77.
[9] A.Kumaresh, R.Arunkumar, M.Arivanandhan, Y.Hayakawa, J. Crystal Growth 401 (2014) 874-877.
[10] P.Maliga, C.Senthamilselvi, Rasayan J. Chem. 9 (2016) 144-148.
[11] NR.Dhumane, SS.Hussaini, VG.Dongre, MD.Shirsat, Opt. Mater. 31 (2008) 328-332.
[12] M. Selvapandiyan and P. Sundaramoorthi, Opt. Mater. 64 (2013) 19151-19155.
[13] F. Helen & G.kanchana, Ind. J. Pure & Appl. Phys. 52 (2014) 821-828.
[14] N. N. Shejwal, Mohd Anisy, S. S. Hussainiz and M. D. Shirsat, Inter. J. Mod. Phys. B. 30 (2016) 1650159 (11 pages).
[15] K.Ambujam, K.Rajarajan, S.Selvakumar, I.Vetha. Pothekar Ginson, A.Joseph, P.Sagayaraj, J. Crystal Growth 286 (2006) 440-444.