Growth, Structural and Nonlinear Optical Characterization of Nickel Chloride doped Zinc Tris-thiourea Sulphate Single Crystals

K. Kanagasabapathy[a*], S.Vetrivel[b] and R. Rajasekaran[c]

[a] PG & Research Department of Physics, A. A. Govt. Arts College, Villupuram, Tamilnadu, India.
[b] PG & Research Department of Physics, Govt. Arts College, Tiruvannamalai, Tamilnadu, India
[c] Thiru. Kolanjiappar Government Arts College, Vriddachalam,Tamilnadu, India.

Abstract – **Zinc Tris–Thiourea Sulphate (ZTS) and Nickel chloride doped Tris Thiourea Zinc(II) Sulphate single crystals were grown from aqueous solution by slow evaporation technique. The unit cell parameters of the grown crystals were evaluated by single crystal X-ray diffraction analysis. The powder X-Ray diffraction patterns were recorded and indexed for further confirmation of crystalline nature of grown crystals. The incorporation of Nickel entered into ZTS crystals was confirmed from SEM-EDX analysis. UV-Visible transmission spectra have been recorded to find the cut-off wavelength of grown crystals in non-linear applications.The nonlinear optical properties of pure and doped ZTS crystals were confirmed by Kurtz Perry powder method using Nd:YAG laser source.**

Keywords: Growth from solution; ZTS; XRD; SEM-EDX; Second Harmonic Generation; Nonlinear optical material.

I. INTRODUCTION

In the recent years, the semi-organic NLO materials have been attracting much attention due to high nonlinearity, chemical flexibility, good transmittance, high mechanical and thermal stability. Among the semiorganic NLO materials, metal-complexes of thiourea family have been investigated actively [1-2]. Zinc Tris-thiourea Sulphate (ZTS) is an interesting semi-organic nonlinear optical (NLO) material [3]. Metal ion doped materials are currently receiving a great deal of attention due to the rapid development of laser diodes [4-5]. Doping influences the mechanical, electrical, optical properties and surface morphology depending upon the nature of the host material and the dopant [6-7]. The effect of metal doping on the physical and NLO properties of potassium hydrogen phthalate (KHP) and zinc tris- thiourea sulphate (ZTS) crystals have been studied [8-9].

In the present work, attempts have been made to further improve the crystalline perfection and to study the influence of Nickel chloride(Ni^{2+}) doping on the physicochemical properties of ZTS crystals grown by slow evaporation method from aqueous solution and its structural and nonlinear optical behavior have been reported.

II. EXPERIMENTAL PROCEDURE

ZTS compound was synthesized by stoichiometric incorporation of analar grade Thiourea (99% Merck) and zinc sulphate heptahydrate (99% Merck). Thiourea and zinc sulphate heptahydrate were taken in the ratio of 3:1 and were dissolved in deionised water of resistivity 18.2 MΩcm. The ZTS compound was prepared according to the following reaction,

$$3(CH_4N_2S) + ZnSO_4.7H_2O \rightarrow Zn[(CH_4N_2S)]_3 \cdot SO_4 + 7H_2O \quad … \quad (1)$$
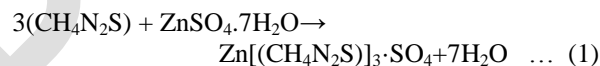
The synthesized salt was further purified by repeated recrystallization process. Using the purified ZTS, saturated growth solution was prepared and allowed it for slow evaporation. Good optical quality single crystal with regular shape and size $11 \times 9 \times 6$ mm^3 was harvested within 20 days. For the growth of Nickel doped ZTS crystals, 1 mol% of Nickel Chloride was added to the solution of ZTS, single crystals of size $10 \times 6 \times 7$ mm^3 with good transparency were grown in 35–40 days. The as-grown crystals of pure and metal ions doped ZTS crystals are as shown in Figs.1(a-b) respectively.
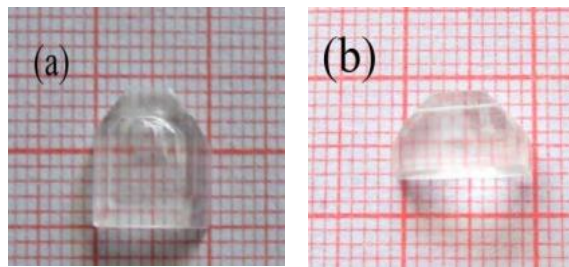

Fig. 1 As grown crystals of ZTS (a) Pure (b)Nickel chloride doped .

III. RESULTS AND DISCUSSION

Structural Analysis.

a) Single Crystal X-ray diffraction studies:

Single crystal X-ray diffraction studies of pure and 1 mol% Nickel Chloride doped ZTS crystals were carried out

using a Kappa Apex II Nonius CAD4 diffractometer and their unit cell parameters are : a = 11.14 Å , b = 7.77 Å , c = 15.50 Å , cell Volume = 1341.65 $Å^3$, α = β = γ = 90° for ZTS crystal and a = 11.16 Å , b = 7.78Å , c = 15.53 Å , cell Volume =1349.59 $Å^3$ and α = β = γ = 90° for 1mol% of Nickel chloride doped ZTS crystals. All the grown crystals belong to orthorhombic system with space group $Pca2_1$ and point group mm2. The cell parameter values are in good agreement with the data available in JCPDS (Card No.76-0778) for pure ZTS with very nominal changes due to doping [10]. From single crystal X-ray analysis, the presence of dopants has marginally altered the lattice parameters without affecting the basic structure of crystal [5], [11].

b) Powder X-ray diffraction Studies:

Powder XRD patterns of the grown crystals were recorded using Bruker Powder X-ray diffractometer. The Bragg's reflections in the powder XRD patterns (Fig. 2) were indexed for pure and Nickel chloride doped ZTS crystals.
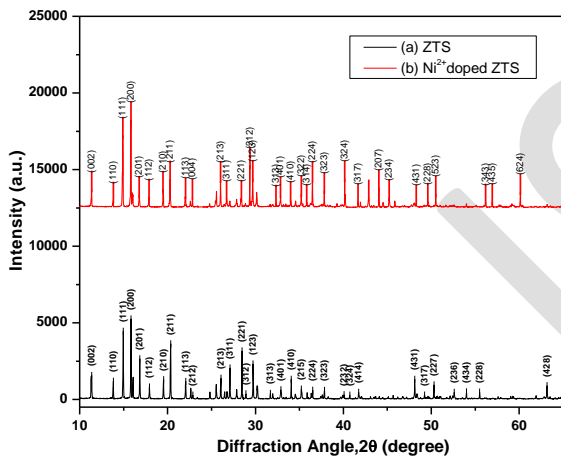

Fig. 2 Powder XRD patterns of ZTS crystals (a) Pure (b) Ni^{2+} doped

It is observed that the relative intensities have been changed and a slight shift in the peak position was observed as a result of doping. The most prominent peaks with maximum intensity of the XRD patterns of pure and doped specimens are quite different. These observations could be attributed to strain in the lattices. Appearance of sharp and strong peaks confirms the good crystallinity of the grown sample. The prominent well-resolved Bragg's peak at specific 2θ angle reveals the high perfection of the grown crystal. The observed values are in good agreement with the reported values [10].

EDX Analysis.

In order to confirm the presence of metal ions in ZTS crystal, the samples of grown crystals were subjected to

Energy Dispersive X-ray analysis using JEOL JSM 5610 LV Scanning Electron Microscope . The presence of Nickel in the doped specimen was confirmed from EDX analysis and the concentration of the incorporated Nickel into the ZTS crystalline matrix can be clearly seen in Figs.3(a-b). Surface analysis at different sites reveals that the incorporation of Nickel was not uniform over the whole crystal surface.
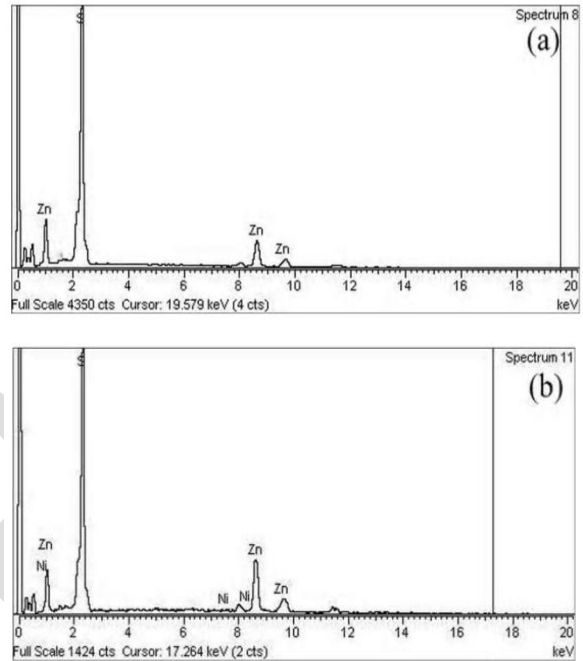

Fig.3 EDX Spectra of ZTS crystals (a) Pure (b) Ni^{2+} doped

The amount of Ni^{2+} incorporation into ZTS lattice is given in Table 1.

Table 1
EDX data for the grown crystals

Crystal	Element	Weight %	Atomic %
Pure ZTS	S	54.85	71.46
	Zn	45.15	28.54
Ni^{2+} doped ZTS	S	54.69	71.46
	Zn	44.64	28.35
	Ni	0.67	0.19

Optical Studies.

Good optical transmittance and lower UV cutoff wavelengths are very important properties for NLO crystals [12]. Optical transmittance spectral analysis of the grown crystal was carried out between 200 and 900 nm using VARIAN 5000 UV-Vis-NIR spectrophotometer and is shown in the Fig. 4. It is clear from the spectra that the percentage of optical transmission for pure ZTS crystal is 73% at 800 nm and it increases for Nickel chloride (82%) doped ZTS crystals. Both of them have sufficient transmission in the entire visible region. Absorption in the

near ultraviolet region arises from electronic transitions associated within the sample. This is one of the most desirable properties of the grown crystals for the device fabrication. From the UV-Vis spectrum of ZTS, it is noted that there is a maximum transmittance in the entire visible region, which enables it to be a potential candidate for optoelectronic applications.

The band gap energy (E_g) can be calculated directly from the UV-cutoff wavelength by using the relation

$$E_g = hc / \lambda_{(cut)} \quad eV \qquad \dots \quad (2)$$

where E_g is band gap energy, $h = 6.626 \times 10^{-34}$ J / s, $c = 3 \times 10^8$ m/s, $\lambda_{(cut)}$ is the UV cut-off wavelength. The band gap energies were found to be from 4.613 eV to 4.647 eV. The pure and doped ZTS crystals were identified to be wide band gap material.
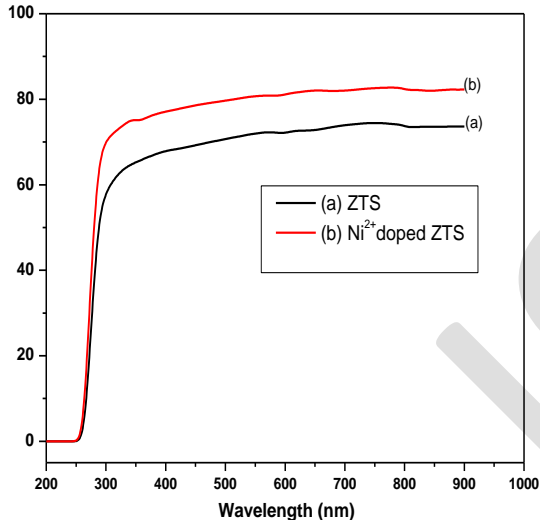

Fig. 4 UV-Vis transmission Spectra of ZTS (a) Pure (b) Ni^{2+} doped.

Second Harmonic Generation efficiency (SHG) Studies.

The second harmonic generation (SHG) efficiency was determined using powder technique developed by Kurtz and Perry [13]. For the SHG efficiency measurements, the output of a Q-switched, mode-locked Nd:YAG laser was used to generate about 2·8 mJ / pulse at 1064 nm fundamental radiation. A single shot mode of 8 ns laser pulse at a repetition rate of 10 Hz with a spot radius of 1 mm was used. The input laser beam energy 2·8 mJ / pulse was allowed to pass through an IR reflector and then directed on the micro-crystalline powdered sample packed in a capillary tube of diameter 0·154 mm. The photodiode detector and oscilloscope arrangement measured the light emitted by the sample. For the Nd:YAG laser, the fundamental beam of 1064 nm generates second harmonic signal of 532 nm (green light). The output pulses measured for the grown crystals are given in Table 2.

Table 2

SHG output signal voltages of pure and doped ZTS crystals

Samples	$I_{2\omega}$ (mV)	SHG Efficiency
ZTS	18	1.00
Ni^{2+} doped ZTS	21	1.17

IV. CONCLUSION

Optical quality single crystals of pure ZTS and Nickel chloride doped ZTS were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction confirms that there is no change in basic structure of ZTS while doping. It is confirmed that the grown crystals belong to orthorhombic structure. The prominent well-resolved peak at specific 2θ diffraction angle reveals the high crystalline perfection. SEM-EDX analysis confirms the presence of Nickel in the doped ZTS crystals. UV-Visible study shows that grown crystals have wide range of transparency in the UV and entire visible region and cut-off wave lengths were measured. The SHG efficiency increases to 1.17 times for Nickel doped ZTS crystal as compared with pure ZTS crystal. Thus, it is concluded that 1 mol% Nickel ions doped ZTS crystal will be suitable for optoelectronics applications.

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