

GROWTH AND CHARACTERIZATION OF PURE AND GLYCINE DOPED TRIS THIOUREA NICKEL SULPHATE (TTNS) SINGLE CRYSTALS

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Abstract

Single crystals of Nickel Thiourea Sulphate(NTS) plays an important role in ample of applications such as Opto-electronics, Lasers, UV-filters etc. However the crystal with good transparency and controlled parameters is challengeable one amidst the scientific community. Hence in the present work pure and Glycine doped Tris Thiourea Nickel Sulphate (TTNS) crystals were grown by slow evaporation method. The grown crystals were characterized structurally, spectroscopically optically and mechanically. X-ray diffraction studies proved the crystalline nature of the grown compound and it belongs to orthorhombic structure. FTIR analysis confirmed the presence of various functional groups in the grown crystal. Mechanical behaviour has been studied by Vickers Microhardness test. Optical properties has been obtained by UV-Vis analysis.

Keywords: TTNS crystals, FTIR, Opto-electronics, orthorhombic, Microhardness.

1. INTRODUCTION

Nonlinear Optical (NLO) materials play a vital role in optical modulation, fiber optic communication and optoelectronic since they are capable of producing higher values of the original frequency. A continuous effort has been taken in growing organic, inorganic and semi-organic materials with high damage threshold, wide transparency range and high nonlinear coefficient which make them suitable for device fabrication [1, 2]. Ligands like Thiourea, allylthiourea, thiocyanate and thiosemicarbazide with S and N donors are capable to combine with metal to form stable complexes through coordinated bonds. Metal-organic compounds have attracted much more attention for their stable physico-chemical properties and mechanical intension [3]. Among the semi organic NLO materials, metal complexes of thiourea, have a low UV cut off wavelength which is applicable for frequency conversion and second harmonic generation [4]. Thiourea molecules are an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds. The nonlinear optical properties of some of the complexes of thiourea, such as bis(thiourea) cadmium chloride(BTCC), Tris(thiourea) zinc sulphate(ZTS), Tris(thiourea) Magnesium sulphate (MTS), Tris(thiourea) cadmium sulphate (CTS), Zinc–Magnesium Tris(Thiourea) Sulphate (ZMTS) [5] have gained significant attention in the last few years, because both organic and inorganic components in them contribute specifically to the process of second harmonic generation. Nickel sulphate hexahydrate crystals are used in Missile approach warning systems and sensors in spaceships. In the present study, we have grown Glycine doped Tris Thiourea Nickel Sulphate (TTNS) single crystals and investigated the effect of Glycine on the properties of TTNS. The results obtained are reported here and discussed.

2. EXPERIMENTAL

2.1. Synthesis and Crystal growth

The TTNS salt was synthesized by dissolving Nickel Sulphate hexahydrate and Thiourea in the ratio of 1: 3 in distilled water.

The required quantity of Nickel Sulphate hexahydrate and Thiourea was estimated from the following reaction.



The solution was stirred with magnetic stirrer for nearly 2 hours at room temperature. The prepared solution was filtered using filter paper so that all the impurities could be removed. The filtered solution was allowed to evaporate at room temperature. After 30 days, TTNS crystal was harvested. For the growth of Glycine doped TTNS, 0.75 mol% of glycine was added to the solution containing nickel sulphate hexahydrate and Thiourea. The doped crystals were harvested in 30 days. The photographs of the grown crystals are shown in Fig.1.

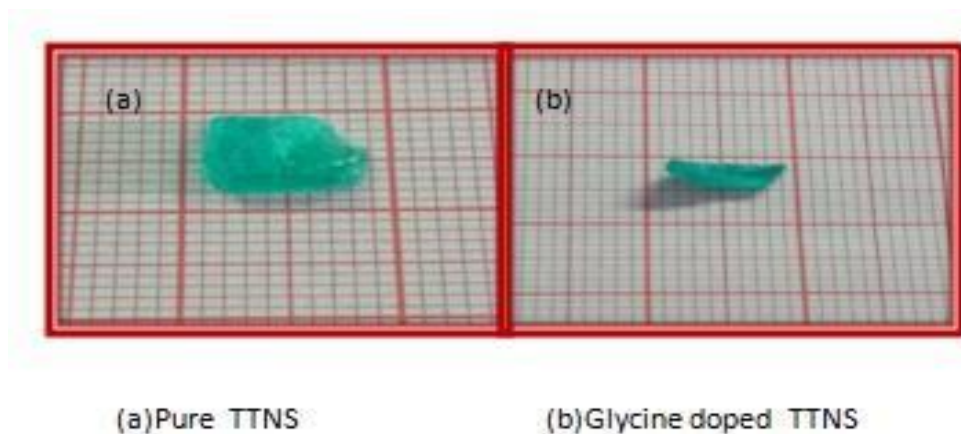


Fig.1 Photograph of the grown pure and Glycine doped TTNS crystals

3. CHARACTERIZATION

3.1. Powder X-Ray diffraction analysis

The Powder X-Ray diffraction patterns were obtained using the powder X-Ray diffractometer. The unit cell parameters of the grown crystals reveal that the crystals belong to Orthorhombic system. The lattice parameters of the grown TTNS and TFGNS crystals are given in Table 1.

The appearance of sharp and strong peaks confirms the good crystallinity of the grown crystal. The powder XRD patterns of the grown crystals are shown in Fig. 2.

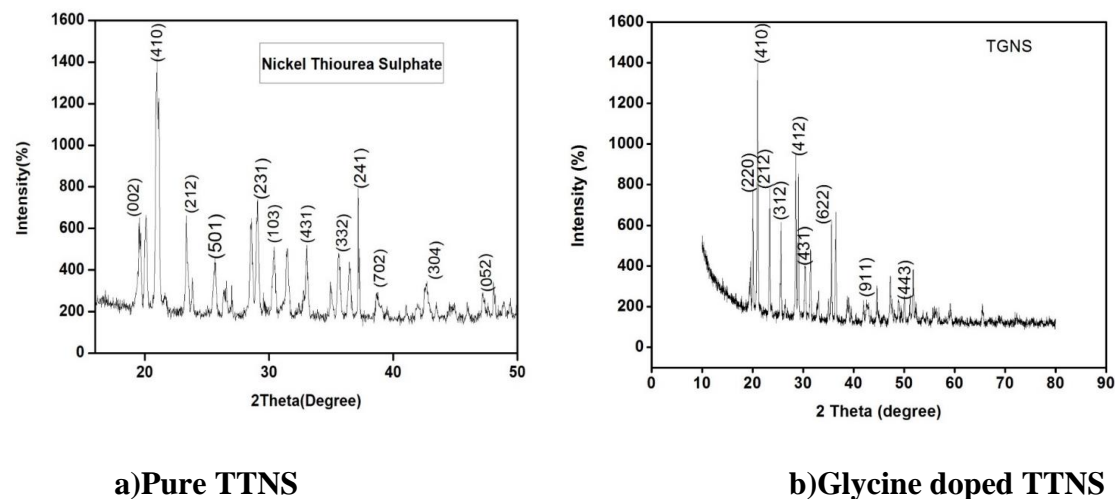


Fig. 2: XRD Pattern of the grown Pure and Glycine doped TTNS crystals

Table .1: Lattice parameters of the TTNS and TTGNS crystals

Crystal	a (Å)	b (Å)	c (Å)	Angle	Cell Volume (Å ³)	Crystal system
Pure TTNS	19.070	10.420	8.98	$\alpha=\beta=\gamma=90^\circ$	1764.41	Orthorhombic
TTGNS	19.069	10.420	8.978	$\alpha=\beta=\gamma=90^\circ$	1784.39	Orthorhombic

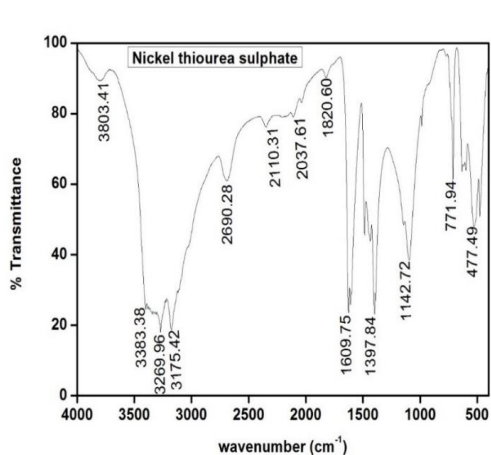
3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectrum was recorded in the wavenumber range 500-4000 cm^{-1} . The presence of Glycine in TTNS crystal was analyzed from the FTIR spectra of the grown crystals. The comparison of assignments observed in FTIR spectra are given in the Table. 1.

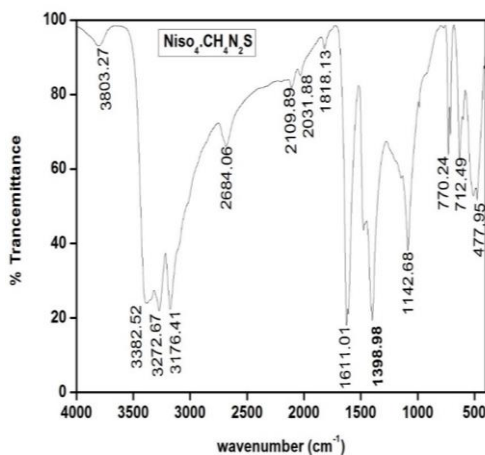
Fig.3 shows the FTIR spectra of pure and Glycine doped TTNS crystals.

Table 2: Vibrational frequency assignment of pure and Glycine doped TTNS crystals

Frequency in wavenumber		Assignments
Pure TTNS cm ⁻¹	TTGNS cm ⁻¹	
3803.41	3803.27	Asymmetric NH ₂ stretching
3383.38	3382.52	Asymmetric NH ₂ stretching
3269.96	3272.67	Asymmetric NH ₂ stretching
3175.42	3176.41	Symmetric NH ₂ stretching
2690.28	2684.06	O-H stretching
2110.31	2109.89	CH ₂ rocking
2037.61	2031.88	CH ₂ rocking
1609.75	1611.01	Asymmetric NH ₂ bending
1397.84	1398.98	Asymmetric (C=S) Stretching
1142.72	1142.68	NH ₂ rocking
771.94	770.24	Symmetric (C=S) stretching
477.49	477.95	Symmetric(N-C-N)bending



a) Pure TTNS



b) Glycine doped TTNS

Fig .3 : FTIR Spectrum of the Pure and Glycine doped TTNS crystals

3.3.Vickers micro hardness test

Hardness of the material is a measure of resistance that offers to deformation. Microhardness was measured from 25 g to 100 g load using microhardness tester, filtered with a Vickers pyramidal indenter. The hardness of the material was calculated by the relation

$$H_v = 1.8544(P/d^2) \text{ Kg mm}^{-2}$$

Where P is the applied load and d is the mean diagonal length of the indenter impression. The variation of microhardness values with applied load is shown in Fig.4. Pure and Glycine doped TTNS crystal exhibits reverse indentation size effect (RISE) in which the hardness value increases with the increasing load [6]. The work hardening coefficient (n) value was determined by least square fitting method from the graph of Log P versus Log d as shown in Fig.5. The work hardening coefficient (n) for pure and Glycine doped TTNS crystals are 3.45 and 5.22

respectively. According to Onitsch [6], 'n' lies between 1 and 1.6 for hard materials and it is above 1.6 for soft materials.

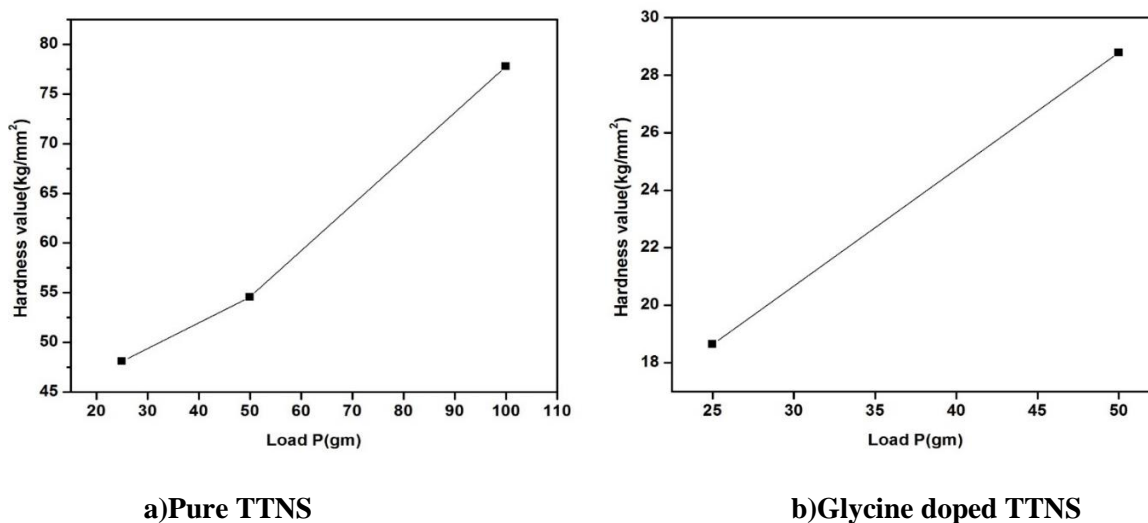


Fig. 4: Variation of hardness with the applied load for pure and Glycine doped TTNS crystal

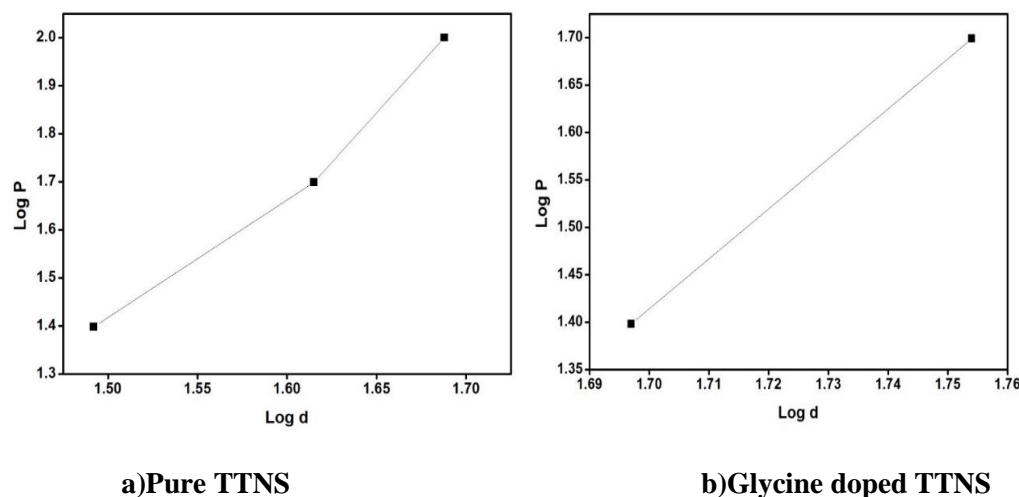


Fig. 5: Plot of Log P Vs Log d for pure and Glycine doped TTNS crystal

3.4. Optical Studies

Good optical transmittance and lower UV cutoff wavelengths are very important properties for NLO crystals [7]. Optical transmittance spectral analysis of the grown crystal was carried out between 200 and 1200 nm using VARIAN 5000 UV-Vis-NIR spectrophotometer and is shown in the Fig. 6. It is clear from the spectra that the percentage of optical transmission for pure TTNS crystal is 94% and it increases for Glycine (95%) doped TTNS 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 TTNS, 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

$$E_g = hc / \lambda(\text{cut}) \text{ eV} \quad \dots \quad (2)$$

where E_g is band gap energy, $h = 6.626 \times 10^{-34}$ J/s, $c = 3 \times 10^8$ m/s, $\lambda(\text{cut})$ is the UV cut-off wavelength. The band gap energies were found to be 4.48 eV and 4.53 eV for pure TTNS and glycine doped TTNS.

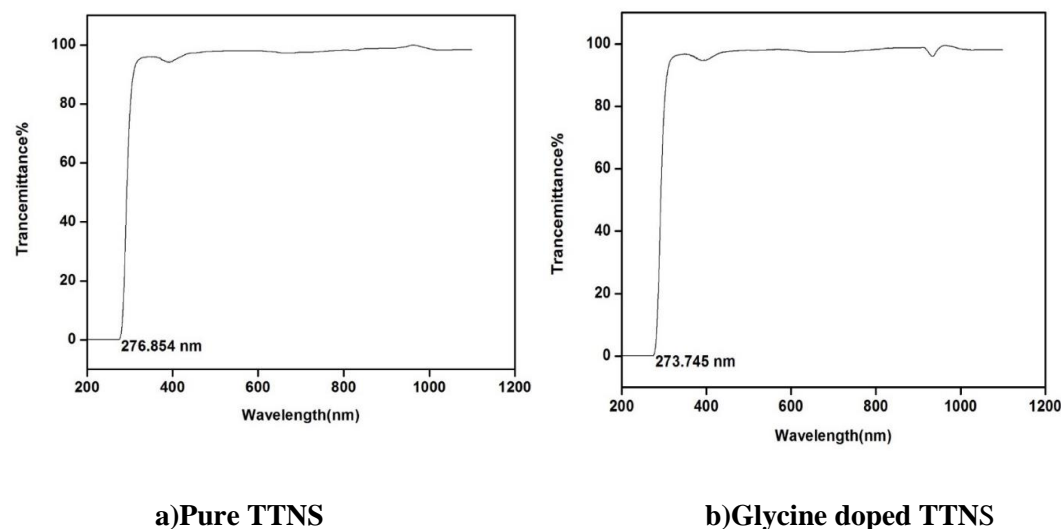


Figure. 6 : Transmittance spectrum of pure and Glycine doped TTNS crystal

Conclusion

Single crystals of pure and Glycine doped TTNS crystals were grown by slow evaporation technique at room temperature. Powder XRD analysis reveals that the grown crystal belongs to orthorhombic system. The functional groups were confirmed by FTIR analysis. Mechanical behaviour has been studied by Vickers microhardness test. The grown pure and Glycine doped crystals belongs to soft material category. The band gap energy was found from transmittance spectrum of UV-Vis analysis.

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