Journal of Crystallization Process and Technology, **2011, 1, 49-54**
doi:10.4236/jcpt.2011.13008 Published Online October 2011 (http://www.SciRP.org/journal/jcpt)

Crystallization and Characterization of Triglycine Sulfate (TGS) Crystal Doped with $NiSO_4$

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Received August 24th, 2011; revised September 26th, 2011; accepted October 5th, 2011.

ABSTRACT

Nickel sulfate doped triglycine sulfate crystals have been grown by natural evaporation method. The chemical composition of the pure triglycine sulfate crystals and the presence of nickel ion in doped triglycine sulfate crystal were confirmed by Energy Dispersive X-ray analysis. The functional groups of the grown crystals have been identified by the Fourier Transform Infrared spectroscopy. The structural studies on the grown crystals were carried out by X-ray Diffraction analysis. All the grown crystals are found in monoclinic structure and the lattice parameters of pure TGS crystal are $a = 9.6010$ *Å*, $b = 12.5600$ *Å and* $c = 5.4500$ *Å. The lattice parameters are slightly distorted due to the incorporation of nickel ion into the lattice sites of the TGS crystal.*

Keywords: *Triglycine Sulfate*, *Solution Growth*, *Energy Dispersive X-ray*, *Fourier Transform Infrared Spectroscopy*, *Microhardness*

1. Introduction

Crystals of triglycine sulfate $(NH_2CH_2COOH)_3\ H_2SO_4$ (TGS), are known as ferroelectric materials [1,2]. It is also known as pyroelectric material which finds application in the fabrication of infrared detectors, pyroelectric vidicon tube operating at room temperature, in the fabrication of capacitors, transducers and sensors [3,4]. In the ferroelectric phase, the Curie temperature, T_c, is 49˚C and the crystal systems in monoclinic with space group P_{21}. The lattice parameters of pure TGS are a = 9.41 Å, b = 12.64 Å, c = 5.7 Å and $\beta = 110.13˚$ [5]. The presence of organic dopants like L-alanine, L-lysine with low concentration raises the internal bias field and makes the crystal permanently poled [6-8]. Rare earth metal ions such as La^{3+}, Ce^{3+} and Nd^{3+} are found to modify the morphology and coercive field [9]. Alkali halides such as NaBr and KBr doped TGS crystals were grown and the effect of the dopant on the growth, structural, mechanical and dielectric properties have been investigated [10,11]. However the investigations on TGS doped with $NiSO_4$ is not studied in details. In general transition metals possess a high density, a high melting point and boiling point. The transition metals and their compounds are used for their catalytic activity. This activity is ascribed due to their ability to adopt multiple oxidation states. The objective of the present work is to see the effect of transition metal like nickel (Ni^{+2}) ion as dopant on growth, structural, optical, mechanical and electrical properties of TGS crystals.

2. Experimental

2.1. Materials

- AR grade glycine
- Concentrated sulfuric acid
- De-ionized water
- Nickel Sulfate

2.2. Equipment

The crystals were grown by natural evaporation process. Energy Dispersive X-ray (EDX) analysis was performed by Quanta Instect S-12919 system. Functional group and bonding nature were determined qualitatively by Fourier Transform Infrared (FTIR) analysis. The FTIR spectra of all grown crystals have been recorded using a Shimadzu FTIR 8400 spectrophotometer by KBr pellet technique. To determine the lattice parameters, powder X-ray diffraction (XRD) analysis was performed by Philips X'-pert PRO X-ray diffractometer system with CuK_α (λ =

1.54178 Å) radiation at room temperature (25˚C) with an operating voltage 40 kV and the tube current 30 mA. Optical transmission spectra were recorded by a Shimadzu UV-160 spectrometer in the wavelength range 190 nm to 1100 nm.

2.3. Material Synthesis

Glycine and concentrated sulphuric acid were mixed in 3:1 molar concentrations. Synthesized TGS salt was obtained by heating the solution of TGS at 50˚C. Temperature as low as 50˚C was maintained in order to avoid decomposition of the salt. The reaction takes place with the formation of the following compound:

$$\begin{aligned}&3\left(NH_2CH_2COOH\right)+H_2SO_4\\&\rightarrow\left(NH_2CH_2COOH\right)_3\cdot H_2SO_4\end{aligned}\qquad(1)$$

After preparing the solution, the solution was transferred to a big tray and was allowed to rapid evaporation. Within 7 days 80% of the solvent was evaporated and the synthesized TGS crystals were collected. An example of the different planes in TGS crystal has schematically shown in **Figure 1**.

2.4. Crystal Growth

The crystallized salt was again dissolved in triple distilled water and was then re-crystallized. This process was repeated three times to improve the purity of the material. The seed crystals were prepared by natural evaporation method. Good quality and defect free seed crystals were selected to grow bigger size crystal. To obtain doped TGS crystal, 0.5 mole% and 1 mole% $NiSO_4$ were added to the saturated mother solution. Seed crystals were suspended with nylon thread within the solution of the beaker. Fully transparent and good quality crystals were obtained within 30 days. The pure TGS crystals and $NiSO_4$ doped TGS crystals are found colourless. The grown crystals are shown in **Figure 3**.

2.5. Growth Rate Investigation

The growth rate of the grown crystals was determined by weighing method [12]. The growth rate is determined by

$$G_s = m - m_0/m_0\Delta t \qquad (2)$$

where m_0 is the initial mass of the crystal, m is the final mass and Δt is the growth time.

A graph for mass growth rates vs. time for pure TGS and $NiSO_4$ doped TGS are shown in **Figure 2**. Initially the growth rate was found rapid within two weeks and then growth became steady. The growth rate was de-

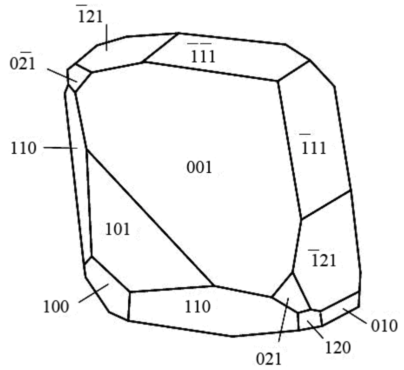

Figure 1. Typical morphology of a naturally grown TGS crystal.

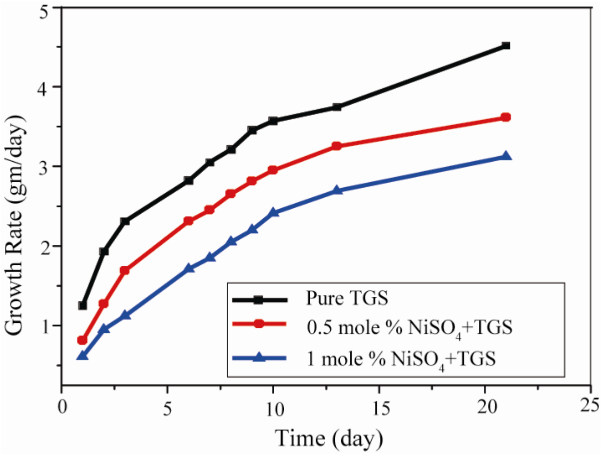

Figure 2. Variation of mass growth rates for pure and $NiSO_4$ doped TGS crystal.

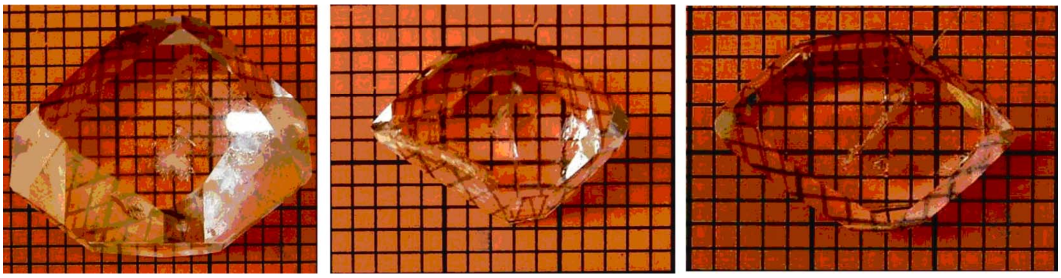
(a) (b) (c)

Figure 3. (a) Pure TGS, (b) 0.5 mole% $NiSO_4$ doped TGS and (c) 1 mole% $NiSO_4$ doped TGS crystal.

creased with dopant concentrations. The incorporation of transition metal Ni^{2+} ion hence promotes the nucleation behaviour of pure TGS by chemical complexions. Ni^{2+} ion as a smaller cation has a stronger interaction with water molecules in the coordination sphere and might play an important role in modifying the growth behaviour. Hence by increasing the addition of Ni^{2+} metal ions into the solution, increasing the induction period (time taken for the formation of a critical nucleus) for nucleation. As a result, the nucleation rate is decreased due to adsorption of Ni^{+2} ion on the available surfaces (*i.e.* kinks sites) of the growing nuclei. In such way Ni^{+2} is expected to act as a growth inhibitor in the doped crystals.

3. Characterization

3.1. Energy Dispersive X-ray Analysis

The EDX has been performed to identify the elements present in the crystals. The EDX spectra of pure and $NiSO_4$ doped TGS are shown in **Figure 4**. The atomic and weight percentages of the elements are shown in **Table 1**. From the analysis it is found that Ni^{2+} ion is incorporated into the interstitial slits of the TGS crystal.

3.2. FTIR Spectroscopy

The FTIR spectra have been recorded in the range 400 to 4000 cm^{-1} and the spectra of pure TGS and doped TGS are shown in **Figure 5**. The pure TGS crystal shows a broad and strong absorption band in the range 2380 - 3800 cm^{-1} for the O-H stretching of hydrogen bonded-carboxyl groups and the N-H stretching mode of NH_3 group. The C=O stretching vibration of carboxyl group appears as a sharp band at 1685 cm^{-1}. The C-H bending vibrations appear at 1493.93 cm^{-1}. The N-H bending vibrations are present at 1408.10 cm^{-1}. A strong band arises from C-O stretching is also observed at 1118.76 cm^{-1}. The asymmetric S=O stretching frequencies can be assigned to frequency 1309 cm^{-1}. The torsional oscillation of NH_3 groups appears at 619, 572.8 and 501.5 cm^{-1} respectively. All the observations clearly confirm the presence of the functional groups in the grown crystals, which is in good agreement with the reported values [13]. The strong peak at 2350 cm^{-1} is due to combination of the asymmetrical NH_3 bending vibration and the torsional oscillation of the NH_3 group [14]. The existence of these small shifts and sharp band are expected due to the presence of Ni^{+2} in the crystals.

Table 1. Data for atomic and weight percentage of the elements.

	Pure TGS		1 mole% $NiSO_4$ doped TGS	
Element	Atomic%	Weight%	Atomic%	Weight%
C	39.47	32.93	39.88	32.58
N	15.66	15.24	14.06	13.39
O	43.12	47.93	42.81	46.5
S	1.75	3.89	3.07	6.70
Ni	-	-	0.18	0.73
Total	100	100	100	100

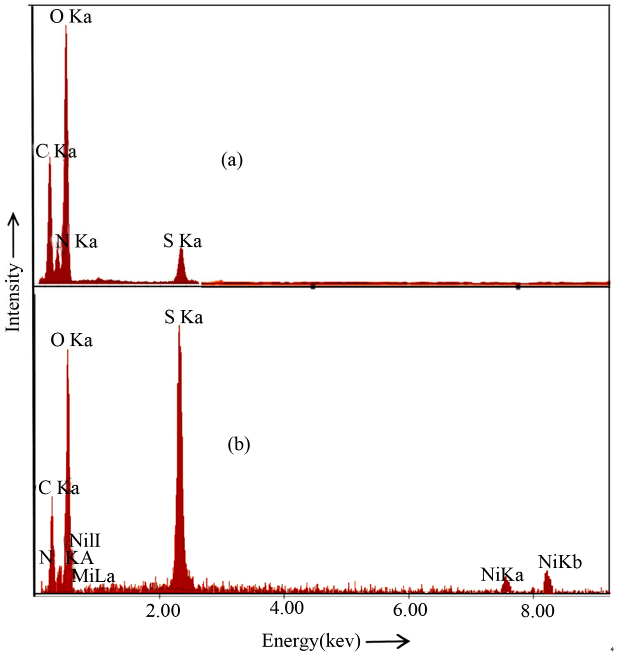

Figure 4. EDX spectra of (a) pure TGS (b) 1 mole% $NiSO_4$ doped TGS crystal.

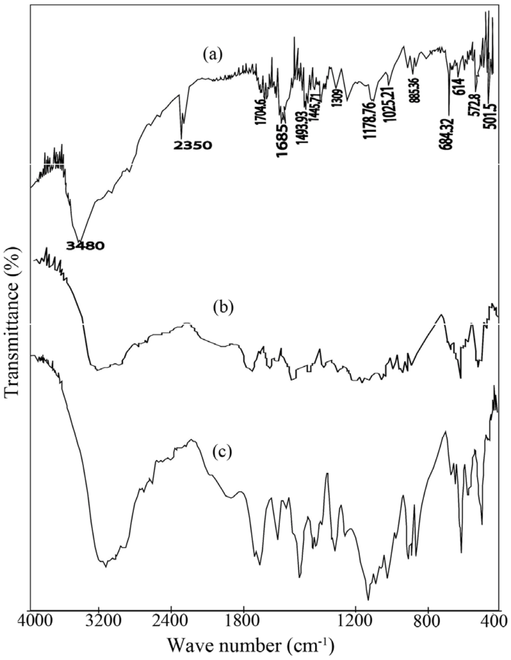

Figure 5. FTIR Spectra (a) pure TGS (b) 0.5 mole% $NiSO_4$ doped TGS and (c) 1 mole% $NiSO_4$ doped TGS crystal.

3.3. Powder X-ray Diffraction Analysis

Powder XRD pattern of pure and $NiSO_4$ doped (0.5 mole%, 1 mole%) TGS crystals are shown in **Figure 6**. The lattice parameters were calculated and presented in **Table 2**. From the data, it is observed that pure and $NiSO_4$ doped TGS crystals crystallize in monoclinic system. The values of lattice parameters for the pure TGS crystals are found to be in good agreement with the reported data [15].

It is observed that the lattice parameters are slightly deviated when TGS is doped with $NiSO_4$ (0.5 mole%, 1 mole%) which may be attributed to the presence of dopant into the TGS crystals. The XRD results confirm that the incorporation of Ni^{2+} ion into the TGS crystal lattice does not change the basic structure of the crystals.

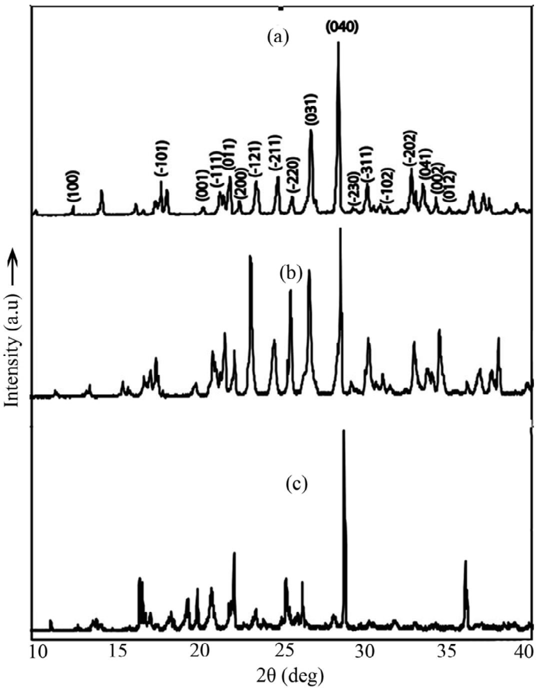

Figure 6. X-ray powder diffraction pattern of (a) pure TGS (b) 0.5 mole% $NiSO_4$ doped TGS and (c) 1 mole% $NiSO_4$ crystal.

Table 2. Lattice parameters of pure and $NiSO_4$ doped TGS crystal.

Crystals	Lattice parameters (Å)			
	a	b	c	Volume (Å^3)
TGS	9.6010	12.5600	5.4500	604.1530
0.5 mole% $NiSO_4$+ TGS	9.3624	12.4877	5.6938	625.0225
1 mole% $NiSO_4$+ TGS	9.2589	12.3248	5.7044	611.1884

3.4. UV-Visible Spectroscopy

Good optical transmittance and lower cut off wavelength are very important properties for nonlinear optical (NLO) crystals. The thicknesses of all the samples were 2 mm. The transmission spectra of pure TGS and $NiSO_4$ doped TGS are shown in **Figure 7**. For pure TGS, a strong absorption peak corresponding to the fundamental absorption appears at 230 nm and the crystals show the transmittance of 84.26% which proves the good optical quality. The band gap was calculated using the formula

$$E_g = hc/\lambda \qquad (3)$$

The optical band gap is found to be 5.40 eV, which is in good agreement with the reported value in the literature [16]. For 0.5 mole% $NiSO_4$ doped TGS shows the transmittance of 70.08% and for 1 mole% $NiSO_4$ doped TGS shows the transmittance of 52.32%. $NiSO_4$ doped TGS crystal has lower transmission in compared to that of pure TGS crystal. The transmittance is decreased with the increase in dopant concentrations. The reduction of transmittance is expected due to the incorporation of cations into the superficial crystal lattice and forming defects centers.

3.5. Vicker's Microhardness Study

Hardness of a material is a measurement of the resistance, it offers to local deformation. Vicker's microhardness (H_v) is a measure of hardness of a material calculated from the size of an impression produced under load by pyramid shaped diamond indentor. The microhardness studies are carried out on the (001) plane of pure and $NiSO_4$ doped TGS crystals with the load ranging from 10 to 100 g. H_v was calculated from the following equation:

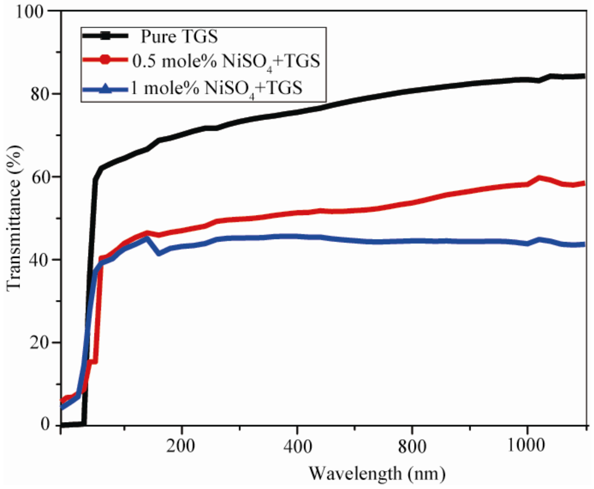

Figure 7. UV-Visible transmittance spectra of Pure TGS, TGS+ 0.5 mole% $NiSO_4$ and TGS+ 1 mole% $NiSO_4$ doped TGS crystals.

$$\mathrm{Hv} = 1.8544 P/d^2\ \mathrm{kg \cdot mm^{-2}} \qquad (4)$$

where, P is the applied load in kg and d is the diagonal length of indentation impression in millimeter and 1.8544 is a constant of geometrical factor for diamond pyramid. It can be seen from **Figure 8** that the doped crystal is harder than the pure crystal. Microhardness increases with dopant concentrations and for loads above 50 g, cracks started to develop. Micro hardness increases for the presence of Ni^{+2} into the lattice site of the crystals.

3.6. Dielectric Study

For the dielectric studies, the crystal samples were prepared in the form of thin plate of 2 mm thickness. The prepared samples were transparent and free from any noticeable defects. The conducting silver paste is applied on the two opposite faces of crystal samples. Two connecting leads were taken out from the two opposite faces using thin Cu wires. The variation of dielectric constant of the pure and $NiSO_4$ doped TGS crystals at 1000 Hz and at different temperatures is displayed in **Figure 9**. The T_c was observed at 49˚C. The dielectric constant is found small at low temperature and increases sharply with temperature up to the T_c. Above T_c, the dielectric constant decreases and obeys Curie-Weiss law. The rapid increase of dielectric constant may be due to space charge polarization of thermally generated carriers. The T_c of pure TGS and $NiSO_4$ doped TGS remains same. Dielectric constant increases with dopant concentrations. The increase in dielectric constant for $NiSO_4$ doped TGS crystals may be due to frittering of domains owing to incorporation of impurities into the lattice [17].

4. Conclusions

The pure TGS and $NiSO_4$ doped (0.5 mole% and 1 mole%) TGS crystals are found with good quality, full faced and colourless. The mass growth rates were found slower for the doped crystal compared to that of pure TGS crystal. The chemical composition of the pure TGS crystal and the presence of Nickel within doped crystal were confirmed by EDX study. No systemic variation was observed in the values of lattice parameters when TGS crystals are doped with $NiSO_4$. The transmission percentage of $NiSO_4$ doped TGS is lower than pure TGS and the transmission decreases with increase in dopant concentrations. The Vicker's microhardness value increases with dopant concentrations. This increase in the microhardness of doped TGS crystals may be attributed to the incorporation of impurities into the lattice sites of the crystals. The incorporation of impurities in filling the interstitial hole most probably enhances the strength of bonding with the host materials and hence increasing the hardness.

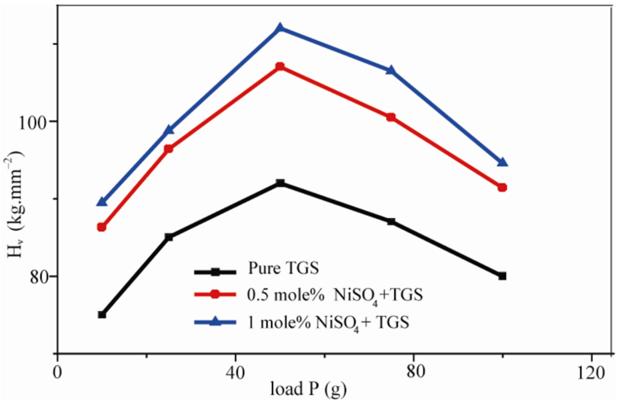

Figure 8. Variation of load versus Vicker's microhardness number (H_V).

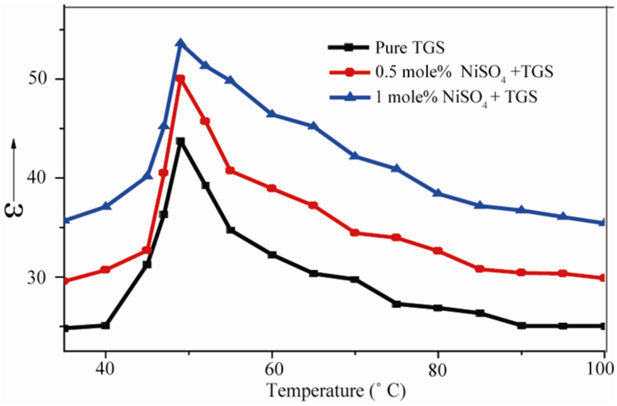

Figure 9. Dielectric constant vs. temperature of pure TGS and $NiSO_4$ doped TGS crystals.

5. Acknowledgements

The authors are grateful to Dr. Md. Abdul Gafur, Senior Engineer, BCSIR Laboratory, Dhaka, Bangladesh for UV-vis and Microhardness measurements and Dr. Dilip Kumar Saha, Chief Scientific Officer, AECD for XRD analysis.

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