Indian Journal of Pure & Applied Physics
Vol. 53, April 2015, pp. 234-238

Growth and characterization of TGS single crystal doped with $NiSO_4$ grown by Sankaranarayanan-Ramasamy method

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Received 20 February 2014; revised 19 July 2014; accepted 4 February 2015

Unidirectional <001> $NiSO_4$ doped triglycine sulphate (TGS) single crystal of 15 mm in diameter and 150 mm in length was successfully grown in aqueous solution by Sankaranarayanan-Ramasamy (S-R) method. The characterization of the grown crystal was made by powder X-ray diffraction, UV-Vis. spectroscopy, Fourier transform infrared spectroscopy (FTIR), Vicker's microhardness studies. The X-ray diffraction analysis revealed a monoclinic structure for the grown crystal. UV–Vis. analysis showed high transmittance for the doped TGS crystal in the entire visible region. FTIR spectrum verified the presence of various functional groups in the grown specimen. Vicker's microhardness studies of the doped TGS crystal showed that it is harder than pure TGS crystal. The density of the doped crystal was found to be higher than that of the undoped one.

Keywords: Transmittance, Growth from solution, X-ray diffraction, $NiSO_4$ dopant, TGS crystal

1 Introduction

Triglycine sulphate [$(NH_2CH_2COOH)_3$. H_2SO_4] (TGS) is an interesting material for its wide range of applications[1]. TGS has found many applications in pyroelectric vidicon tubes operating at room temperature and is one of the interesting ferroelectric materials which find applications in the fabrication of infrared detectors, capacitors, transducers and sensors[2]. Pyroelectric sensors based on TGS are uniformly sensitive to radiations over wide wavelength range from ultra-violet to far-infrared, and operate at room temperature as compared to quantum detectors, which require cooling. TGS is one of the very few ferroelectrics known to exhibit a second-order phase transition and hence offers possibilities for the observation of genuine critical phenomenon very close to the Curie temperature. It is order–disorder-type ferroelectric with a transition from ferroelectric to paraelectric phase at 49°C, having high pyroelectric coefficient and low dielectric constant values[3].

Crystal growth conditions of pure TGS crystal has been studied intensively[4-10]. Undoped TGS crystals have some disadvantages such as the ferroelectric domains possess high mobility at room temperature, easy depolarization by electrical and thermal means, microbial contamination with time during the growth and low Curie point. These disadvantages can be overcome by adding suitable impurities to the lattice sites of TGS crystals[11-13].

The ferroelectric properties of the TGS family crystals by doping with various amino acids have been investigated[9,14].

The growth of doped TGS crystals has been undertaken by many researchers to prevent depolarization with temperature, due to its low Curie temperature, so as to enhance internal bias, transition temperature and pyroelectric properties. To allow this, a variety of dopants like alanine, valine, histidine, etc. have been incorporated to TGS crystals[4,15,16].

The pyroelectric properties, crystal quality and depolarization effect of TGS have been improved by doping organic molecules. However, the crystal quality is affected due to the internal stress generated in the crystal. The ferroelectric properties of these modified crystals L-, D-, and DL-methionine-doped TGS[17] TGSN[18,19], DBTGS[20], ADP-,KDP doped TGSP[21], KCl-doped TGS[22], all L-form amino acids except L-tyrosine doped TGS[23], LGLM-TGS[24], IDA-TGS[25], NaBr-doped TGS[13], $LiSO_4$-doped TGS[26], CdS added TGS[27], KBr doped TGS[28], iminodiacetic acid doped TGS[29], dye doped TGS[30] are reported to be better than those of pure TGS crystal.

In the present investigation, TGS crystal doped with 0.5 mol% of $NiSO_4$ was grown from aqueous solution in <001> direction using Sankaranarayanan-

Ramasamy S-R technique. S-R method has several advantages over other conventional solution growth methods such as possibility to grow crystals unidirectional and ability to convert 100 % of solute to crystal.

2 Experimental Details

TGS single crystal doped with $NiSO_4$ (0.5 mole%) was grown from an aqueous solution by SR method. An aqueous solution of TGS was prepared using analar reagent (AR) grade of glycine and concentrated sulphuric acid in the molar ratio of 3:1. The solvent used in this work was deionized water. The chemical reaction for obtaining TGS salt is given below:

$$3(NH_2CH_2COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3(H_2SO_4)$$

The solution was transferred to big tray and allowed for rapid evaporation. Within a week, 80% of the solvent was evaporated and the synthesized TGS crystals were collected. The crystallized salt was again dissolved in triple distilled water and then re-crystallized. A transparent and good quality seed was selected for growing bulk TGS-$NiSO_4$ crystal by SR method. The details of the S-R set-up have been given elsewhere[31]. A (001) TGS disk shape seed with 2 mm thick and 5 mm diameter was cut from the already grown crystal and carefully mounted at the bottom of the ampoule. It was so fitted not to allow other faces to grow. Then, the TGS-$NiSO_4$ (0.5 mole %) solution at 25°C (room temperature) was slowly added to the growth ampoule after filtration. The temperature of the bottom ring was set to 25°C while the upper one was set to 28°C. A small hole was made on the cover of the ampoule for evaporation of the solvent. Solvent evaporation from the solution surface provided the growth condition for the seed. After 60 days, cylindrical shape $NiSO_4$ doped TGS single crystal of 15 mm diameter and 150 mm height was grown in <001> direction as shown in Fig. 1.

3 Results and Discussion

3.1 Powder X-ray diffraction analysis

TGS-$NiSO_4$ single crystal was analyzed by X-ray diffraction (XRD) technique using X-ray diffractometer (Advance Model D8) with high intensity Cuk_α radiation (λ=1.5406Å). XRD pattern of 0.5 mol% $NiSO_4$ crystal doped TGS is shown in Fig. 2. The data reveal a monoclinic structure for the grown crystal. The calculated unit cell parameters of the grown TGS-$NiSO_4$ single crystal along with those of pure TGS crystal [20] are listed in Table 1. The lattice parameters of the two crystals show significant difference in spite of low incorporation of $NiSO_4$ into

Fig. 1 — Grown TGS-$NiSO_4$ crystal by SR Method after cutting

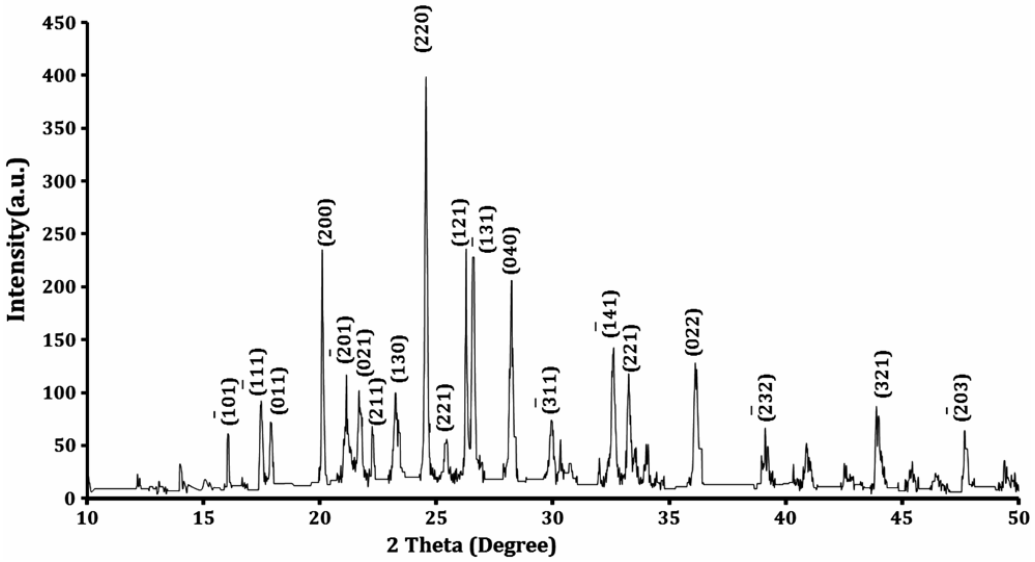

Fig. 2 — XRD pattern of TGS-$NiSO_4$ crystal

the crystal lattice. The lattice parameters of TGS crystal have increased upon doping with $NiSO_4$ (Table 1). The monoclinic angle β has increased too. This increment may be attributed to the presence of dopant into the TGS crystal.

3.2 Fourier transform infrared analysis (FTIR)

TGS-$NiSO_4$ crystal has been studied using Shimadzu FTIR model 8400 spectrophotometer in order to analyze the presence of $NiSO_4$ dopant in the doped sample qualitatively. The crystal was powdered and mixed with KBr pellets for obtaining the FTIR spectrum. The spectrum of the doped crystal is shown in Fig. 3. It shows a broad and strong absorption band in the range 3158 - 1864 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 1701 cm^{-1}. The C-H bending vibration appears at 1490 cm^{-1}. The N-H bending vibration is present at 1422 cm^{-1}. A strong band arising from C-O stretching is also observed at 1126 cm^{-1}. The asymmetric S=O stretching frequency can be assigned to frequency 1305 cm^{-1}.

Table 1 — Unit cell parameters of pure TGS [20] and TGS-$NiSO_4$ (present work)

Sample	Crystal System	a (Å)	b (Å)	c (Å)	B
TGS[20]	monoclinic	9.15	12.69	5.73	105°6′
TGS-$NiSO_4$	monoclinic	9.317	12.743	5.835	105°23′

The torsional oscillation of NH^{3+} group appears at 614, 568 and 500 cm^{-1}. All the observations clearly confirm the presence of the functional groups in the grown crystal. The FTIR spectrum of $NiSO_4$ doped TGS crystal when compared with that obtained by Khanum and Podder[32] for pure TGS crystal reveals a small shift towards the lower wavenumbers which is attributed to the presence of Ni^{+2} in the crystal. In addition, the close resemblance between the FTIR pattern of the grown TGS-$NiSO_4$ crystal and that of the pure TGS crystal[24] suggests that the crystal structures of the two crystals are identical. This indicates that the crystal has retained its structure even upon doping with $NiSO_4$.

3.3 Density measurement

Density of the doped crystal was measured by floating method[33]. It was found to be 1.701 g/cc which is higher than that of pure TGS crystal[34] (1.69g/cc). It may be attributed to the incorporation of dopants in the interstitial positions of the sample hence increasing the crystal mass and so the density.

3.4 UV–Vis. analysis

To determine the optical transmittance range and hence to know the suitability of doped TGS single crystal for optical applications, the UV–Vis. transmittance spectrum was recorded using a Shimadzu spectrophotometer (model UV-1650 pc). Figure 4 shows a comparison between the transmission spectra of the S-R grown[6] TGS, and $NiSO_4$-doped TGS (present study) crystals.

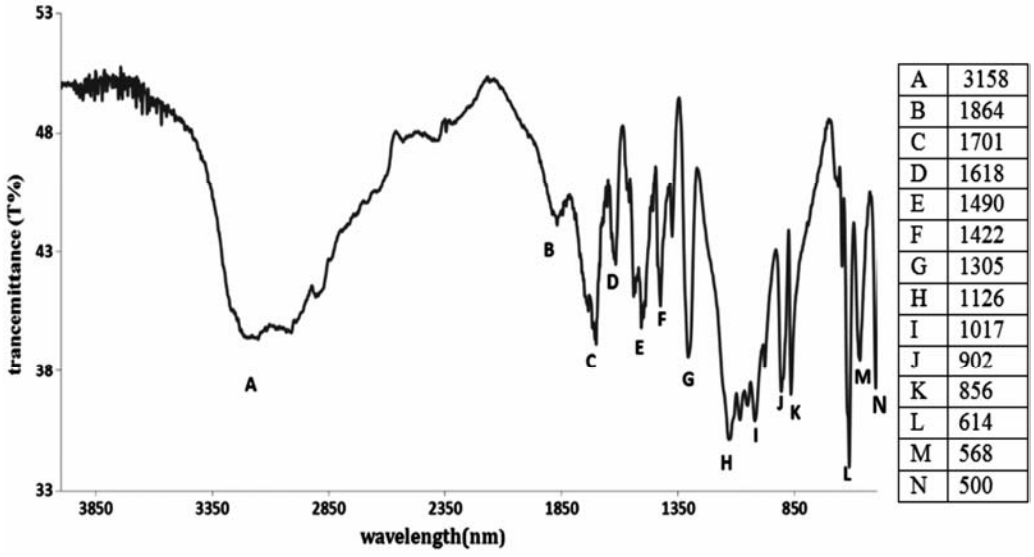

Fig. 3 — FTIR spectrum of TGS-$NiSO_4$ crystal

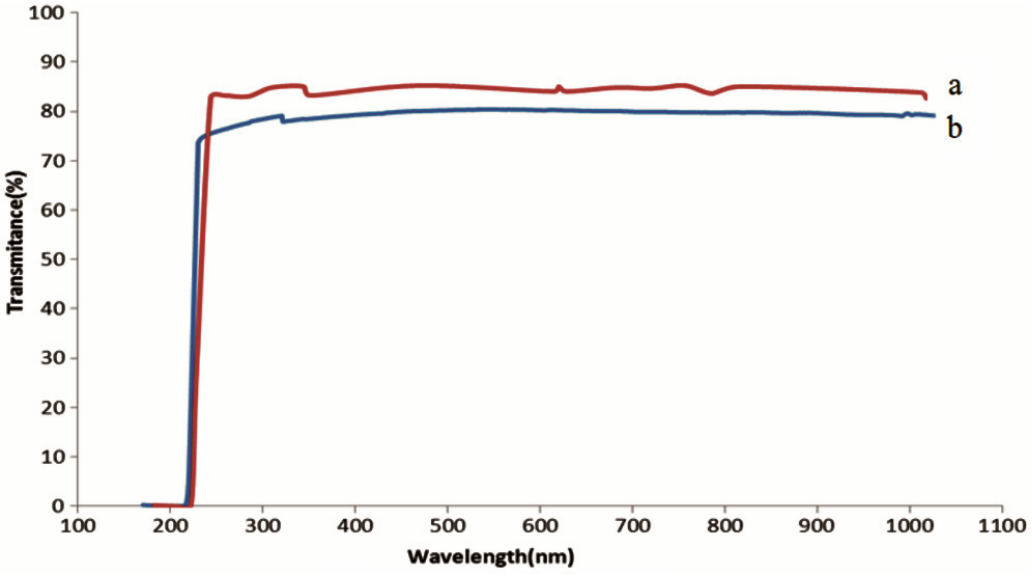

Fig. 4 — UV-Vis. spectra of (a) Pure TGS [6] and (b) TGS-$NiSO_4$ crystals grown by S-R method

It is observed from Fig. 4 that the TGS crystal transmittance decreases upon doping with $NiSO_4$. The reduction of transmittance is expected due to the incorporation of cations into the superficial crystal lattice and formation of defects centers. High transmission in the whole visible region for $NiSO_4$-doped TGS crystal shows the suitability of using this grown crystal in UV tunable laser and second harmonic generation (SHG) device applications.

Using the formula $Eg = hc/\lambda$, the band gap is calculated to be 5.85 eV which is higher than that of pure TGS crystal reported by Khanum and Podder[26]. A strong absorption, i.e. the UV cut -off wavelength is found to be at 212 nm for $NiSO_4$ doped TGS crystal, which is lower than that for pure TGS crystal [7]which reveals the good optical quality of the grown crystal.

3.5 Vicker's microhardness studies

The mechanical properties of the grown crystal have been studied by Vickers hardness test on the (001) plane of the grown crystal using Leitz-Weitzlar hardness tester fitted with a diamond indenter. Hardness is a measure of materials' resistance to localized plastic deformation. It plays a key role in device fabrication[19]. Vicker's microhardness indentations were made on the (001) surfaces of the grown crystals of TGS and TGS-$NiSO_4$ at room temperature using the loads of 10, 25 and 50 g. The micro-hardness was calculated using the relation:

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

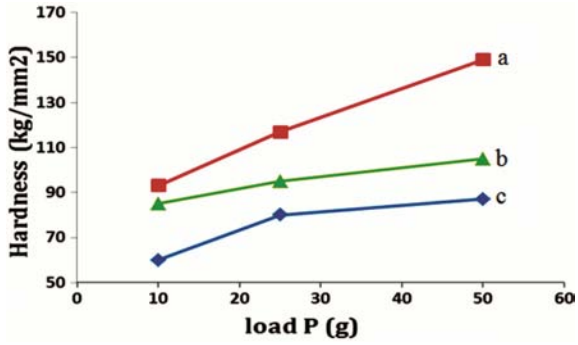

Fig. 5 — Load dependence of microhardness of TGS-$NiSO_4$ crystals grown (a) by S-R method, (b) by conventional method[32] and (c) pure TGS crystal grown by S-R method[8]

where P is the applied load and d is the diagonal length of the indentation impression. The measurement was done at different points on the crystal surface and the average value was taken as H_v for a given load. The Vickers hardness for pure and $NiSO_4$- added crystals as a function of load is shown in Fig. 5. The hardness value of $NiSO_4$-TGS has been found to be higher than that of the pure TGS crystal. Vickers hardness increased with increasing the applied load up to 50 g at which multiple cracks were observed around the indentation mark to develop.

The higher hardness number of TGS-$NiSO_4$ crystal as compared to that of pure TGS one can be attributed to the incorporation of Ni^{+2} into the lattice site of the crystals [32]. The presence of Ni^{2+}cations in the crystal lattice causes increasing the stability of the crystal and hence increasing its hardness. Figure 5 also shows

that the crystal grown by S-R method is harder than the one grown by conventional method. Higher hardness value of the TGS-$NiSO_4$ crystal by SR method indicates that greater stress is required to form dislocation in this crystal thus confirming its greater crystalline perfection.

4 Conclusions

Single crystal of TGS with $NiSO_4$ (0.5 mole %) as additive has been grown from aqueous solution by SR method. The X-ray diffraction analysis revealed a monoclinic structure for the grown crystal. The lattice parameters of doped crystal were found to be higher than those of undoped one. The FTIR analysis confirmed the functional groups presence in the grown doped TGS crystal. Density of $NiSO_4$ added TGS crystal was found higher than that of undoped one which may be attributed to occupation of interstitial positions of TGS crystal by the dopants. According to UV-Vis. analysis, the transmittance in the visible region is found to be nearly about 80.4% for $NiSO_4$- doped TGS crystal which is an indication of the good optical quality of the grown crystal. In addition, having wide transmittance range, starting in the UV region and extending up to the near infrared region through visible region, introduces the grown doped TGS crystal to be a good indication for using as an optical device. The hardness value of TGS-$NiSO_4$ has been found to be higher than that of pure TGS crystal.

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