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Research Article

Synthesis, Growth, and Electrical Transport Properties of Pure and $LiSO_4$-Doped Triglycine Sulphate Crystal

Farhana Khanum and Jiban Podder

Department of Physics, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

Correspondence should be addressed to Jiban Podder, jpodder@phy.buet.ac.bd

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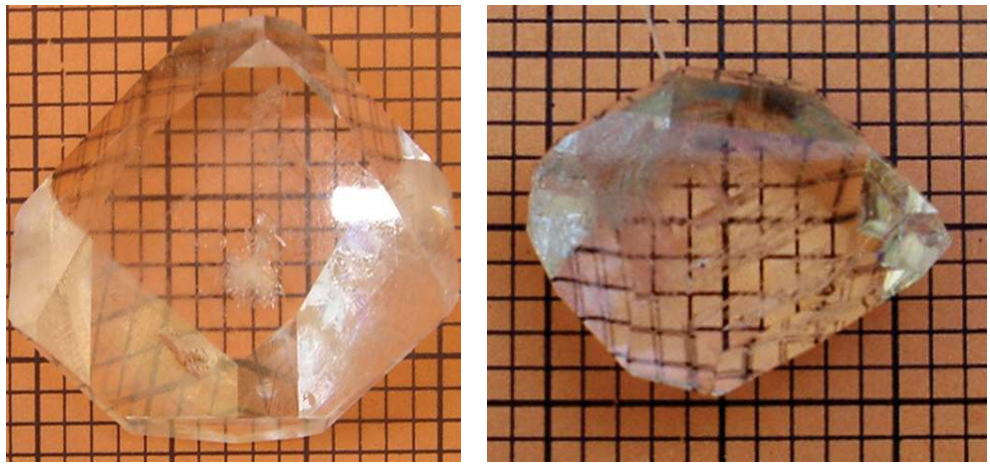
Pure triglycine sulphate (TGS) and $LiSO_4$-doped TGS crystals were grown from aqueous solution by natural evaporation method. The grown crystals were characterized by UV-vis spectroscopy, electrical conductivity (σ_{dc}) measurement, dielectric studies, microhardness, and thermogravimetry/differential thermal analysis. Pure TGS and $LiSO_4$-doped TGS crystals were found highly transparent and full faced. The direct current conductivity is found to increase with temperature as well as dopant concentrations. Curie temperature remains the same for pure and doped crystals, but dielectric constant and dielectric loss increase with dopant concentration. The Vicker's microhardness of the $LiSO_4$-doped TGS crystals along (001) face is found higher than that of pure TGS crystals. Etching studies illustrate the quality of the doped crystal. The experimental results evidence the suitability of the grown crystal for optoelectronic applications.

1. Introduction

Triglycine sulphate, $(NH_2CH_2COOH)_3\ H_2SO_4$, crystal is considered as one of the potential materials for its wide range of applications, namely, UV tunable laser, second harmonic generation, and pyroelectric infrared sensors due to its high pyroelectric coefficient, optical transmission, and reasonably low dielectric constant [1–4]. It is a hydrogen-bonded ferroelectric crystal having a typical second-order phase transition at Curie temperature of 49°C [5–7]. TGS has a major disadvantage that it depolarized by thermal, mechanical, and electrical means. In order to overcome this difficulty, several studies have been attempted with different organic and inorganic dopants to achieve effective internal bias to stabilize the domains and desired pyroelectric and ferroelectric properties of TGS crystals [8–13]. Alkali halides such as NaBr and KBr-doped TGS crystals were grown, and the effects of the dopant have been investigated [14, 15]. Metal ion dopants have been added to modify the properties of TGS crystal [16, 17]. In the literature, only limited information is available about the behavior of TGS doped with Lithium [18]. Lithium reacts with water easily and noticeably with less energy than other alkali metals. Li^{+1} ion has 90 pm ionic radius, so it can easily reside into the lattice site of the TGS crystal and it can modify the electrical, mechanical, thermal, and surface morphology of TGS crystals. In the present work, $LiSO_4$ is used as a dopant to see its effect on the property of TGS crystal.

2. Experimental Methods

2.1. Synthesis and Crystal Growth. Analar Reagent (AR) grade glycine and concentrated sulphuric acid (H_2SO_4) were dissolved in deionized water in the molar ratio of 3 : 1, and the solution was heated at 50°C to obtain synthesized TGS salt. The synthesized salt was again dissolved in triple distilled water and then recrystallized by natural evaporation process. This process was repeated three times to improve the purity of the material. The seed crystals of pure TGS were prepared by natural evaporation method. Good quality and defect-free seed crystals were suspended with nylon thread within the solution of the beaker to grow bulk-size crystal. To obtain doped TGS crystal, 1 mole % $LiSO_4$ was added to the saturated mother solution. Highly transparent and full-faced crystals were obtained within 4 weeks. The pure and



(a) (b)

Figure 1: (a) Pure TGS (b) 1 mole % $LiSO_4$-doped TGS Crystal.

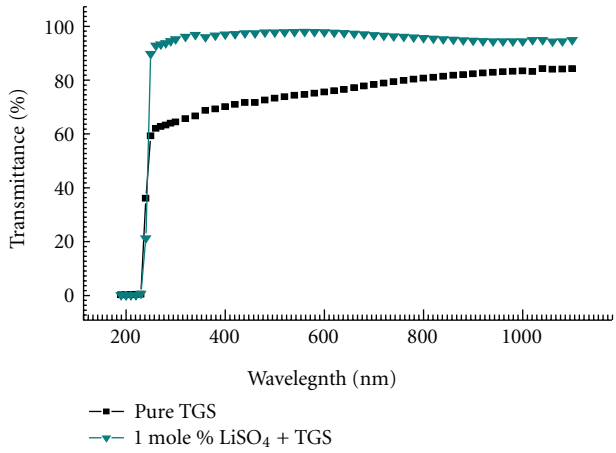


Figure 2: UV-visible transmittance spectra for pure and $LiSO_4$-doped TGS Crystals.

$LiSO_4$ doped TGS crystals are found colourless and shown in Figure 1.

3. Results and Discussion

3.1. Optical Transmission Studies. The optical transmission spectra of the grown crystal were carried out in the range of 190 to 1100 nm covering the entire near-ultraviolet, visible, and near infrared region using SHIMADZU UV-160 Spectrometer to find the transmission range about the suitability of this grown crystal for optical applications. An optically polished $10 \times 10 \times 2\,mm^3$ single crystal was used for this study. The transmission spectra are shown in Figure 2. The transmittance in the visible region is found nearly about 84% for pure TGS and ~94% for $LiSO_4$-doped TGS crystal. A strong absorption and the UV cut off wavelength is found to be at 230 nm for both pure TGS and $LiSO_4$-doped TGS crystal, and it reveals the good optical quality of the grown crystal. High transmission in the whole visible region for $LiSO_4$-doped TGS crystal shows the suitability of this grown crystal for use of UV tunable laser and second harmonic generation (SHG) device applications. Using the formula $E_g = hc/\lambda$, the band gap is calculated to be 5.404 eV, which is in good agreement with the reported literature [19].

3.2. D.C. Electrical Conductivity. For D.C. electrical measurement, crystal samples were prepared in the form of thin plates of 2 mm thickness. The samples were elevated far from the seed portion to ensure the homogenicity and optical quality and free from any noticeable defects. The conducting silver paste is applied on the two opposite (001) faces of crystal samples. Two connecting leads were taken out from the two opposite faces using thin Cu wire. Temperature versus D.C. electrical conductivity (σ_{dc}) is shown in Figure 3. It is seen that, the DC electrical conductivity increases with increase in both the temperature and 1 mole % $LiSO_4$ doping concentration, which is in good agreement with the reported literature [20]. The increase of conductivity with the increase in temperature observed for pure TGS and $LiSO_4$-doped TGS crystals was due to the temperature dependence of the proton transport.

3.3. Dielectric Studies. Crystal samples for dielectric studies were prepared in the similar way of DC electrical measurement. The dielectric constant of the pure TGS and $LiSO_4$-doped TGS crystals was calculated as function of temperature at 1 kHz and shown in Figure 4. Curie point, T_c, (para-ferroelectric phase) was observed at 49°C for pure and $LiSO_4$-doped TGS crystals. The dielectric constant is small at low temperature, but it increases with temperature and rises sharply up to the T_c.

Above T_c, the dielectric decreases suddenly and obeys Curie-Weiss law. The rapid increase of dielectric constant may be due to space charge polarization of thermally generated carriers. The Curie temperature of pure TGS and $LiSO_4$-doped TGS remains the same. The increase in dielectric

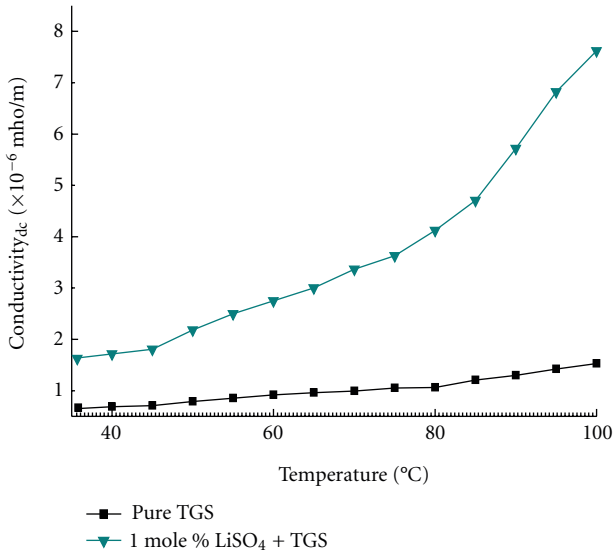


Figure 3: D.C. electrical conductivity for pure and $LiSO_4$-doped TGS crystals.

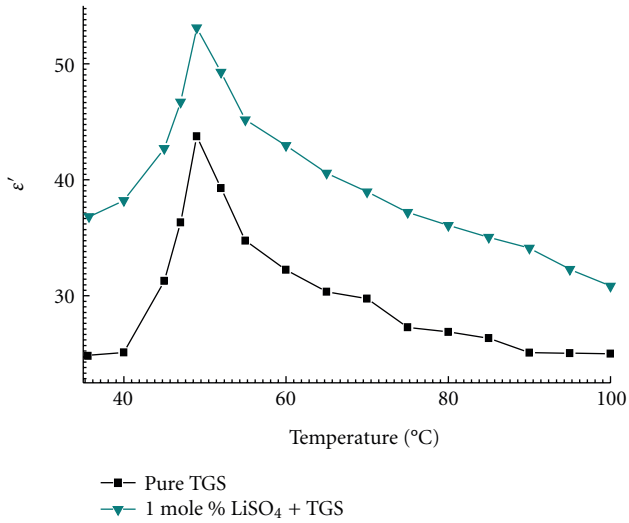


Figure 4: Graph for dielectric constant versus temperature of pure TGS and $LiSO_4$-doped TGS crystals.

constant for $LiSO_4$-doped TGS crystals may be due to incorporation of impurities into the TGS lattice [21]. The temperature dependence dielectric loss of pure TGS and $LiSO_4$-doped TGS crystals is shown in Figure 5.

The dielectric loss for the $LiSO_4$-doped TGS is higher than that of pure TGS crystal. The value of dielectric loss (tan δ) at room temperature is low that the grown crystals are of high quality.

3.4. Vicker's Microhardness Studies. The hardness of a material is related to its bond strength and crystallographic orientation. The important property of any device material is its mechanical strength, represented by its hardness. Vicker's microhardness indentations were made on the (001) face of the pure TGS and $LiSO_4$-doped TGS crystals at room temperature with the load ranging from 10 g to 100 g. The indentation time was kept as 6 sec for all the loads. Vicker's microhardness number, H_v, was calculated using the following equation:

$$H_v = \left[1.8544 \times \frac{P}{d^2}\right] \frac{\text{kg}}{\text{mm}^2}, \quad (1)$$

where P is the applied load in kg, d is the diagonal length of indentation impression in millimeter, and 1.8544 is a constant of a geometrical factor for the diamond pyramid. From Figure 6, it is seen that the hardness value of $LiSO_4$-doped TGS crystal is higher than the hardness of the pure TGS crystal. Maximum hardness number is found at 50 g. $LiSO_4$-doped TGS crystal is found to be much harder than pure TGS crystal thus confirmed the greater crystalline perfection.

3.5. Thermal Analysis. TG-DTA of pure TGS and $LiSO_4$-doped TGS crystals was carried out between 35°C and 600°C at a heating rate 10°C/min in nitrogen atmosphere. The

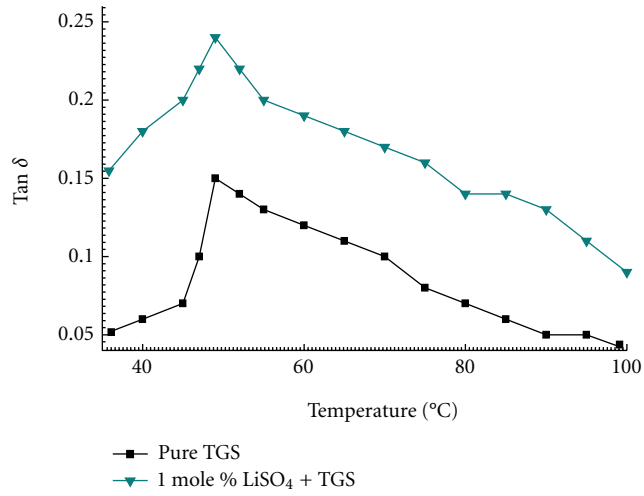


Figure 5: Graph for dielectric loss versus temperature of pure TGS and $LiSO_4$-doped TGS crystals.

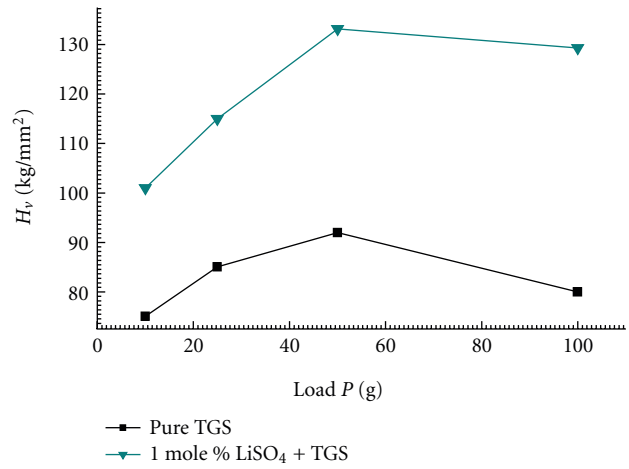


Figure 6: Variation of load versus Vicker's microhardness number (H_V).

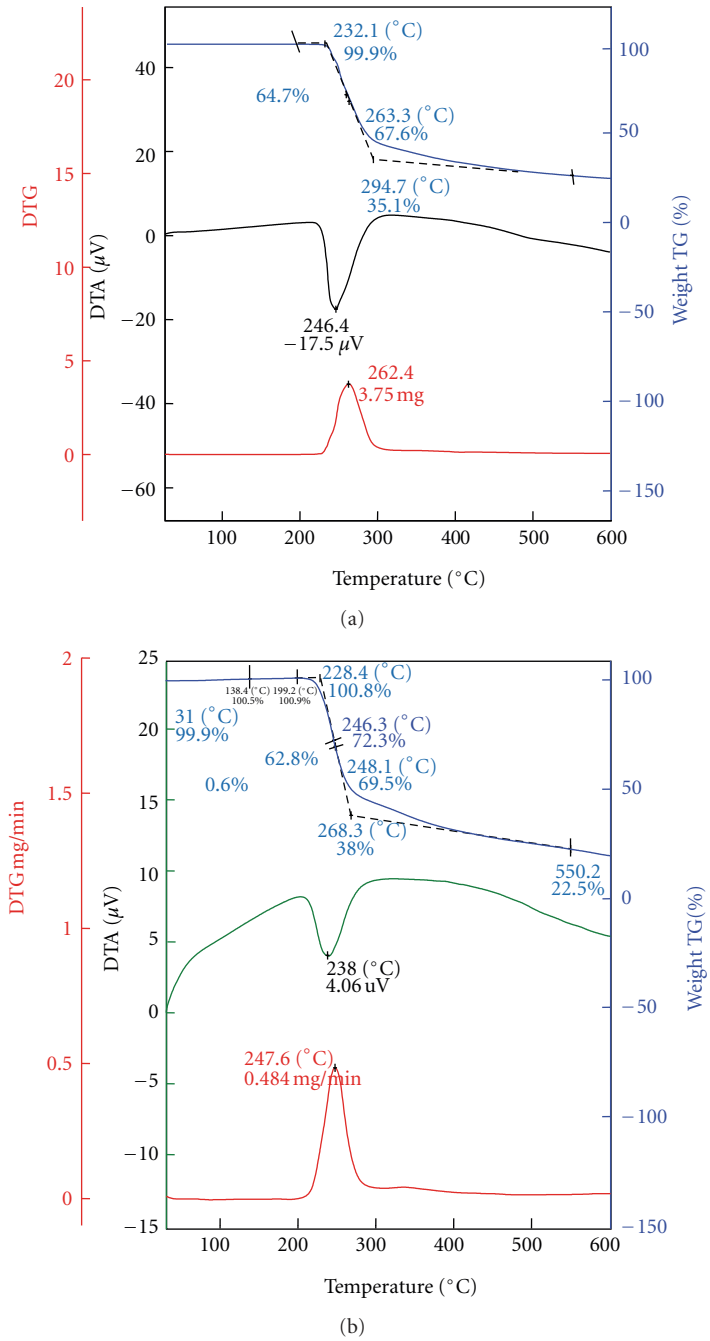
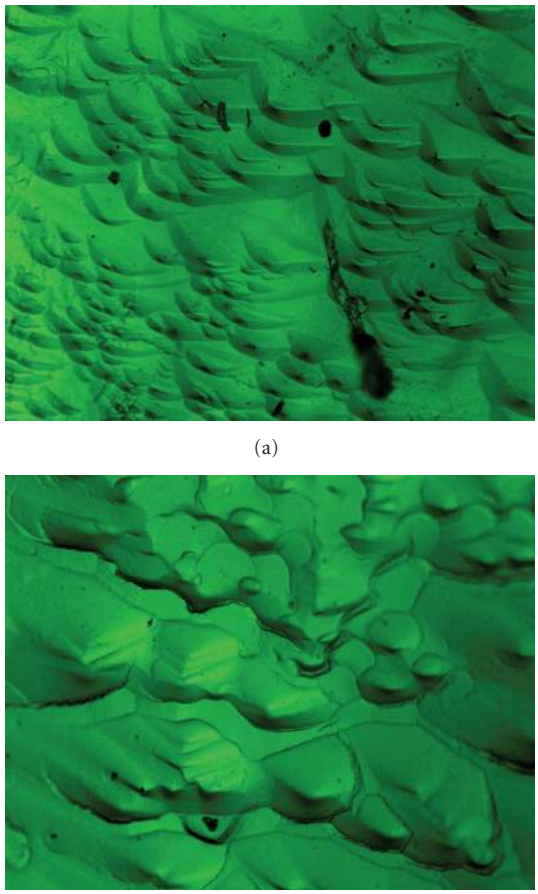


Figure 7: (a) TG/DTA for pure TGS. (b) TG/DTA for 1 mole % $LiSO_4$-doped TGS.

endothermic peak in DTA at 246.4°C for pure TGS and 238.0°C for $LiSO_4$-doped TGS are shown in Figure 7. TG curve shows that there is a sharp weight loss at 232°C for pure TGS and 228°C for $LiSO_4$-doped TGS crystals. The change in decomposition temperature is owing to incorporation of Li^{+1} ion impurities into the lattice.

3.6. Etching Studies. The etching studies reveal the structural perfection and growth features of grown single crystals. The (001) face of pure TGS and $LiSO_4$-doped TGS crystals were subjected to etching with water at room temperature. The surface of pure TGS and $LiSO_4$-doped TGS crystals were completely immersed for 10 s in the water etchant for etching. The features were analyzed using a Magnus MLX microscope shown in Figure 8. It was observed that the identical pyramidal-shaped etch pits were observed more in pure TGS than $LiSO_4$-doped TGS. The etch pits density is 6.1×10^3 cm^{-2} for pure TGS and 1.25×10^3 cm^{-2} for $LiSO_4$-doped TGS crystal. Less number of etch pits shows that the quality of the $LiSO_4$-doped TGS crystals is better than pure TGS crystal.



(a)

(b)

Figure 8: (a) Pure TGS (b) 1 mole % $LiSO_4$-doped TGS crystal.

4. Conclusions

The good quality of pure TGS and $LiSO_4$-doped TGS crystals was grown by natural evaporation method. The UV-visible spectra showed that the transmittance of $LiSO_4$-doped TGS is more than pure TGS crystal. DC conductivity increases with temperature and also with $LiSO_4$ concentration, which proves the incorporation of the dopant into the lattice sites. The Curie temperature, T_c, of pure and $LiSO_4$-doped TGS crystals remain the same. The Vicker's microhardness studies show that the (001) plane of $LiSO_4$-doped TGS crystal has higher hardness than the pure TGS crystal. Melting point is reduced due to $LiSO_4$ as observed by TG-DTA analyses. Etch pits decrease with dopant concentration, which proves that the quality of doped crystal is getting better than pure crystal by the minimization of dislocations and defects. The high optical transparency, thermal stability, low dielectric constant, and microhardness properties exhibit the optical quality and suitability of the as-grown TGS crystal doped with $LiSO_4$ for SHG and optoelectronic device applications.

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