

Effect of N-719 Dye Doping in Tri-Glycine Sulphate Single Crystals- A Potential Candidate for Optical Materials

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Single crystals of Pure Tri-Glycine Sulfate (PTGS) and 0.05 mol% N-719 Dye-Doped Tri-Glycine Sulfate(DTGS) have been successfully grown by slow evaporation solution growth technique. An investigation of dye doping's effect on structural and optical properties has been investigated. Powder XRD analysis of both PTGS and DTGS confirms the crystal structure and demonstrates very good crystalline quality. The FTIR analysis provides conclusive evidence regarding the existence of multiple functional groups in addition to the incorporation of dye into TGS. The optical and band gap analysis have been carried out using a UV-Visible spectrophotometer. A 270 nm excitation wavelength has been employed to acquire the PL spectra. TGS is a semi-organic material, exhibiting non-linear optical characteristics and depicting good properties in ferroelectricity and pyroelectricity. It is also a good piezoelectric material and can be used as an alternative to other energy sources.

Keywords: Ferroelectric, Non-Linear Optical (NLO), Piezoelectric, Powder XRD, Single Crystals

1 Introduction

As our global population has been growing, the energy demand has been rising. While renewable sources such as solar energy, wind energy, and bioenergy hold a good future, current research endeavors have also been dedicated to harnessing the untappable potential of vibrations and motions, transforming what was once wasted into a valuable and sustainable energy source. For this, piezoelectric materials have generally been employed, which can generate charge from the applied mechanical stress. With the advancement of technology, modern electronics like ICs have significantly reduced their power consumption, operating at levels as low as tens of milliwatts. As a result, piezoelectric devices have been used in body motion sensors and various trackers due to their efficiency in harnessing energy from bodily movements¹⁻³.

In this study, single crystals of pure TGS (PTGS) and N-719 dye-doped TGS (DTGS) have been grown by slow evaporation solution growth method in the constant water bath (Fig. 1). TGS, an organic-inorganic hybrid material, exhibits piezoelectric, ferroelectric, and pyroelectric properties, finding widespread use in piezoelectric motors, sensors and actuators, portable electronics, medical imaging

devices, MEMS, etc. It has a monoclinic structure with a $P2_1$ space group. TGS has been reported to exhibit a curie temperature of 49.3°C in numerous studies⁴.

TGS material generally gets depolarized with time, making them less efficient for device applications. So, to increase its properties amino acid doping has generally been employed, thereby increasing its overall efficiency⁵. The optical properties have been further enhanced with the interaction of the dye with the TGS matrix, improving the optical nonlinearity of the material⁶. Dyes, being an organic aromatic compound, have possessed water solubility and demonstrated a remarkable capacity for absorbing and

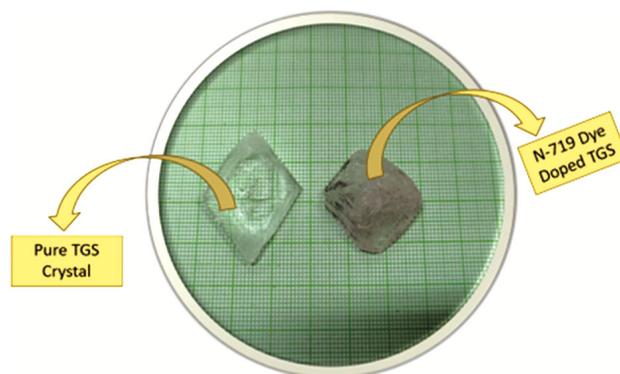


Fig. 1 — Photographs depicting single crystals of PTGS and 0.05 mol% N-719 DTGS.

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emitting visible light. In addition to affecting the optical properties, dyes have also affected the thermal, mechanical, and electrical properties of the materials. These parameters have been a must for device fabrication. The inclusion of dye enhanced the range of applications in displays, electro-optical devices, and solid-state dye lasers, expanding their versatility and potential.

In our study, N-719 dye has been employed in the TGS matrix. The exceptionally reduced scattering points within single crystal positions make them ideal contenders for incorporating dye molecules. N-719 dye has been an important dye that is used for energy materials, DSSCs, and organic photovoltaic materials⁷. It has the chemical formula $C_{58}H_{86}N_8O_8RuS_2$. The purpose of dye doping has been to explore the influence of dye on both the structural and optical properties of pure TGS, aiming to enhance its suitability for device applications⁸. This has been particularly important for TGS, as they have strived for cost-effectiveness and less power consumption. To the extent of our understanding, this research represents the initial investigation demonstrating the integration of N-719 dye within the TGS matrix.

2 Materials and Methods

The slow evaporation solution approach was deployed to grow the single crystals of PTGS and DTGS. The growth process took place in a constant water bath set at a temperature of 40° C. To initiate the growth process, a molar ratio of 1:3 was maintained between sulfuric acid and glycine. A clear and homogenous solution was obtained by adding the reactants to de-ionized water while continuously stirring for 7 hours. Filtration was then employed to remove impurities, if there during the synthesis process. The filtered homogenous solution was then poured into another beaker to keep it in the constant water bath. The beaker was wrapped with a transparent plastic sheet on top to prevent the entry of any impurity into it. Also, small pinholes were made on top keeping in mind the rate of evaporation. After 9 days, TGS crystals were observed to have settled at the bottom of the beaker. DTGS was also grown by the same method, but to this 0.05 mol%, N-719 dye was added as a dopant. Dye-doped crystals were also obtained in 8 days.

For structural analysis, both samples were crushed into a fine powder using a mortar pestle and were subjected to powder XRD. A Rigaku MiniFlex 600 X-ray diffractometer was employed to get the XRD

pattern for both samples. The confirmation of the functional groups was performed through FTIR spectroscopy using the ATR method, employing the Nicolet iS50 FTIR Tri-detector spectrometer. Shimadzu UV-2600i spectrophotometer was used for optical band-gap studies. The PL spectra were recorded with an excitation wavelength of 270nm using FL 8500 Perkin Elmer spectro-fluorometer.

3 Results and Discussion

3.1 X-Ray Diffraction Analysis

Powder XRD analysis was conducted on both PTGS and DTGS. The sample was scanned from 10° to 50°, having a step size of 0.02° at a rate of 0.3 seconds/step. Sharp diffraction peaks were obtained for both samples showing good crystalline perfection. Figure 2. displayed the variation of peak intensity corresponding to various hkl planes for both pure and dye-doped samples. This intensity variation depicted the successful incorporation of dye into a pure TGS matrix. Also, slight peak shifting could be seen in both samples, which might be due to the presence of strain in the lattice as heavy dye molecules were incorporated into the TGS lattice. Checkcell refinement confirmed this, indicating slight variations in the lattice parameters for both PTGS and DTGS. The acquired data closely aligned with the JCPDS data number (00-015-0947) for TGS, exhibiting a close resemblance. These variations are documented in Table 1. The crystals were found to possess a monoclinic structure with the $P2_1$ space group.

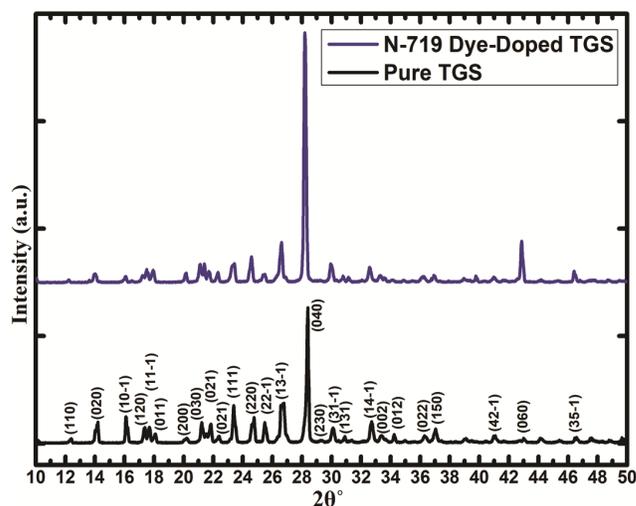


Fig. 2 — Powder XRD patterns of as-synthesized PTGS and N-719 DTGS.

3.2 Fourier Transform Infrared Spectroscopy

The FTIR spectrum talks about the type of bond present and also gives information about molecular structure. In this study, both PTGS and DTGS were exposed to infrared radiation, and the frequencies associated with the vibrational motion of the specific chemical bond got absorbed. The FTIR spectrum of both PTGS and DTGS is shown in Fig. 3. The spectra of PTGS and DTGS showed minimal variation, representing that process of doping did not impact the functional groups of PTGS. The transmittance (%) showed noticeable changes in both samples, providing evidence of the doping effect on the material. The spectral range spanning from 3370 cm^{-1} – 2800 cm^{-1} was associated with stretching vibrations of N-H in NH_3^+ and O-H in the COOH group. The stretching vibration at 1702 cm^{-1} was due to the C=O of the COOH group. COO⁻ ion stretching vibration was measured at 1614 cm^{-1} . The bending vibrations at 1536 cm^{-1} and 1495 cm^{-1} were due to the NH_3^+ group. Stretching vibrations of the S=O bond was responsible for the peak observed at 1300 cm^{-1} . The region between 1121 cm^{-1} and 976 cm^{-1} showed

characteristic vibrations of the sulfate group (SO_4^{2-}) ion. The range spanning from 612 cm^{-1} to 498 cm^{-1} showed torsional oscillations of the NH_3^+ group^{6,9}.

3.3 UV-Visible Spectroscopic Analysis

UV-Visible spectroscopy was utilized to analyze both PTGS and DTGS. Figure 4 displays the transmittance curves for both samples, with a Tauc plot included as an inset. Both the samples showed good transparency in the whole visible region, making them a potential optoelectronic candidate. In addition, the presence of characteristic peaks at 316 nm and 535 nm indicated the incorporation of N-719 dye into PTGS. The cutoff wavelength of PTGS was 254 nm while for DTGS was 249 nm. A decrease in cutoff wavelength indicated a broader range for optical transmittance, indicating improved optoelectronic properties of the material. The band-gap value for PTGS and DTGS was ascertained as 5.48 eV and 5.37 eV, respectively. So, dyedoping into PTGS enhanced the optical properties of the material¹⁰.

3.4 Photoluminescence Spectra Analysis

Photoluminescence study explains the emission of light from a material after it has absorbed photons, giving information about optical properties and energy levels. Both PTGS and DTGS were subjected to an excitation wavelength of 270 nm. On investigation, a sharp peak at 541 nm was obtained for PTGS while a broader and more intense peak was obtained for DTGS. The change in intensity and

Table 1 — Refined Lattice parameters for both PTGS and N-719 DTGS

Crystallographic Parameters	PTGS	DTGS
a, b, c (Å)	9.44, 12.58, 5.69	9.41, 12.65, 5.72
$\alpha=\gamma$ (degree)	90	90
β (degree)	110.11	110.31
Cell Volume (Å) ³	635.65	638.95

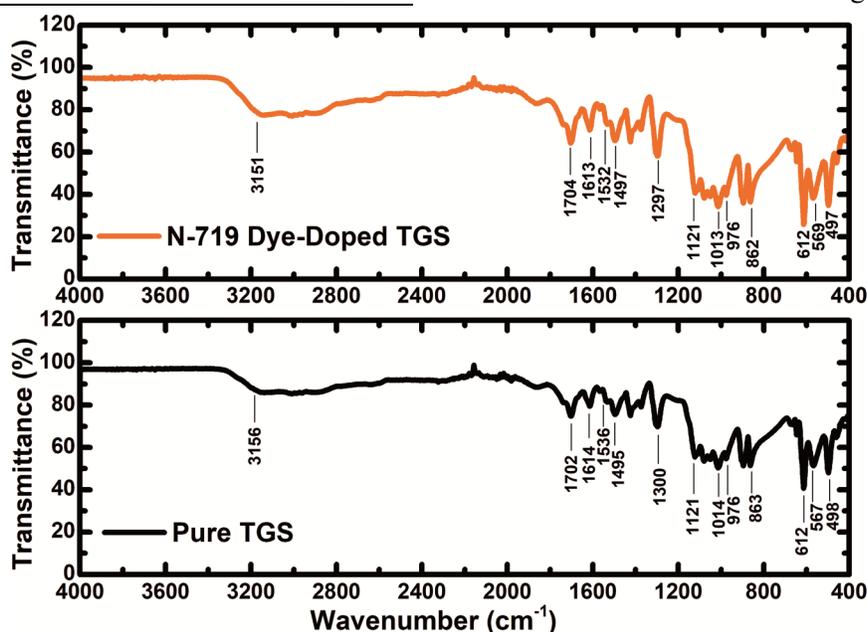


Fig. 3 — FTIR spectra of PTGS and N-719 DTGS.

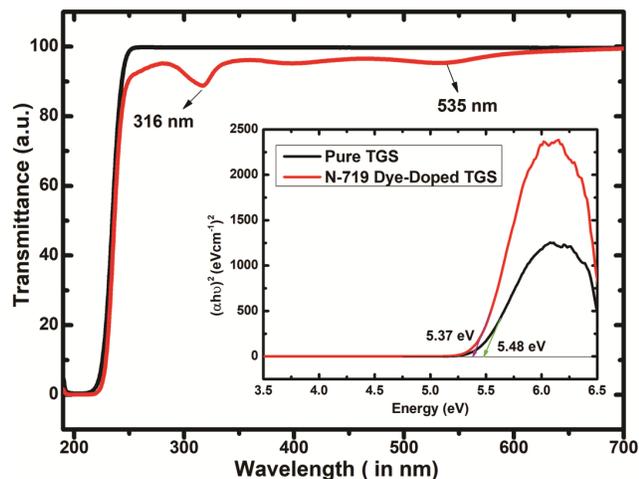


Fig. 4 — UV-Visible spectra of PTGS and DTGS with Tauc plot as inset.

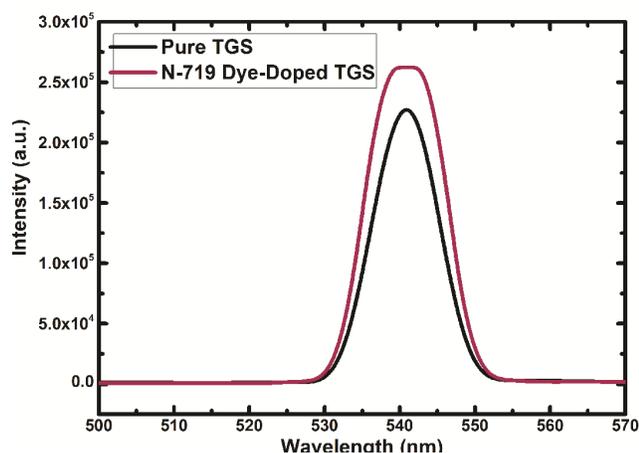


Fig. 5 — Photoluminescence spectra of as-grown PTGS and N-719 DTGS.

broadness may have been attributed to the doping of N-719 dye into the TGS lattice. These two peaks exhibited green color emission. PL spectra of both PTGS and DTGS are shown in Fig. 5.

4 Conclusion

Both PTGS and DTGS have been successfully grown by the slow evaporation method.

Characterizations have been performed to gain insights into their structural and optical properties. XRD has confirmed the monoclinic structure with the $P2_1$ space group. Peaks intensity variation in XRD confirms dye incorporation into PTGS. FTIR spectroscopy has been employed to determine the functional groups of both samples. The variation in transmittance (%) with a slight shifting in peaks confirms dye inclusion into PTGS. The optical analysis of both samples has been further checked via UV-Visible and PL spectroscopy. The decreased cutoff wavelength in DTGS has shown a broader range of optical transmittance, indicating better optoelectronics properties. Overall, the introduction of doping has resulted in notable advancements in optical properties.

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