Effect of l-aspargine on Structural, Photoluminescence and Photoconductive propereties of Triglycine Sulphate single crystals

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Abstract

Effect of 1 mol% L-aspargine doping on the properties of triglycine sulphate has been studied. L-aspargine doped triglycine sulphate single crystals have been grown from aqueous solutions by low-temperature solution growth method. The practical substitution of an optically active molecule in the place of glycine molecule causes an internal bias field, which makes the crystal permanently polarized. The crystallinity of the grown crystals was examined by powder X-ray diffraction analysis. Optical transmittance shows that the L-aspargine doped TGS possesses higher transparency compared to pure TGS. High intense luminescence for the L-aspargine doped TGS single crystal is observed from the photoluminescence study. The Positive photoconductivity nature is observed for both undoped and L_aspargine doped TGS and it was studied under different conditions such as dark, light and also under room temperature.

Key words

TGS, l-aspargine, PXRD, SXRD, UV-Visible, Photoluminescence, Photo current

I. Introduction

Triglycine sulphate (TGS) is known as important material in the fabrication of IR detectors as this crystal possessess both pyroelectric and ferroelectric properties at room temperature [1–5]. Pyroelectric sensors based on TGS are uniformly sensitive to radiations in wavelength range from ultraviolet to far-infrared [4-6]. It also finds application in burglar alarms, medical videocon tubes operating at room temperature, FTIR instrumentation and in pyroelectric detector. Hoshino et al. studied its Curie temperature (47 °C), in which because of second order ferroelectric phase transition, its space group changes from P21 to P21/m [7-9]. From the molecular structure of Triglycine sulphate it has two kinds of glycine group, glycinium ions and zwitter ions. Such configuration of glycine ions interconnected by short O–H··· O hydrogen bonds are regarded as particularly important for the ferroelectric behavior of this crystal [10,11]. TGS has a tendency for spontaneous polarization which takes place along the b-axis. All the three glycine groups I–III participate in the polarization reversal in TGS crystal [12]. This is major drawback of this crystal and hence studies dealing with the influence of various doping with TGS to improve its properties are of particular interest.

TGS crystals are known to depolarize by thermal, electrical or mechanical means [13]. An efficient way to stabilize the single domain state is practiced by doping an optically active molecule into TGS. The small amount of an optically active molecule in the place of glycine molecule causes an internal bias field, resulting in a permanent polarization [14].

The effect of organic dopants on TGS and rare earth ions dopant with TGS have also been investigated[17-17]. In recent years, the interest in studying the undoped and doped TGS crystals has increased because of their promise in various devices. In the present work we have chosen the amino acid l_aspargine as dopant because l_aspargine ions are expected to play a partial role for the spontaneous polarization in TGS crystal thereby increase the dielectric constant and Tc due to its intrinsic dipole moment. The objective of the present work was to investigate the effect of l_aspargine addition on the growth and properties of TGS crystal.

I. Experimental

Undoped and L_aspargine doped Triglycine sulphate (TGS) was synthesized by taking high purity glycine $(CH_2NH_2COOH)_3$ and concentrated sulfuric acid (H_2SO_4) in the molar ratio of 3:1. Initially proportionate amount of glycine is taken in a beaker and dissolved in deionised water and stirred until it attains saturated condition. After preparing saturated solution of glycine, concentrated sulfuric acid is added dropwise with continuous stirring for 4 h to get homogeneous solution and filtered. After 15 days, the synthesized salt of TGS is obtained. Glycine reacts with sulfuric acid and expected reaction is as follows:

$$3(CH_2NH_2COOH)+H_2SO_4 \rightarrow (CH_2NH_2COOH)_3 \cdot H_2SO_4$$

The synthesized salt of TGS was again dissolved in deionised water and then recrystallized by natural evaporation process. This process was repeated two times to improve the purity of the material. Well defined and transparent crystals of dimension up to $20\times22\times4$ mm^3 were formed within 22 days. Finally, 1 mol% of L-aspargine was added in the two time recrystallized saturation solution of TGS and it was stirred for four hours. After filtering, the solution was kept for evaporation in an isolated place, free from dust and mechanical jerk. In the span of 10 days a transparent crystal with average size of $27\times25\times6$ mm^3 was harvested. The compound Triglycine sulphate consists glycine and sulfuric acid. Due to presence of glycine there is a large possibility for the fungus formation in the solution. This may leads to the inclusion and the quality of the crystal will be poor. The presence of L-aspargine in the TGS solution avoids the formation of fungus and enhances the growth rate. The photograph of the as-grown single crystals of undoped and 1 mol% L_aspargine doped TGS is shown in the Figure 1.

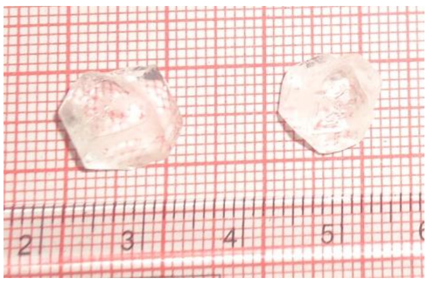


Fig. 1. Photograph of undoped and 1 mol% L_aspargine doped TGS

III. RESULT AND DISCUSSION

3.1. Single crystal X-ray diffraction studies

The lattice parameters of the both pure and 1 mol% L_aspargine doped TGS single crystal are obtained using the Enraf-nonious CAD 4/MACH 3 Diffractometer with Mo kα radiation (1.5440 Å) single crystal XRD instrument. The crystals of both pure and L_aspargine doped TGS are monoclinic with the space group P21 and obtained lattice parameters are shown in Table 1. The observed lattice parameters of L-aspargine doped TGS are nearly same compared to that of pure TGS. Hence the 1 mol% of dopant L_aspargine does not change the structure of parent compound (TGS) and this has been confirmed by the above lattice parameters. The similar results were observed in the case of KAP and DSHP crystal when it is doped with Cu_{2+} Zn_{2+} and Na_{2+} [18,19].

Table 1
Lattice parameters observed from single crystal X-ray diffraction.

Lattice Parameters	Undoped TGS	1 mol% of RS doped TGS
a (Å)	5.76 (3) Å	5.726 (3) Å
b (Å)	12.67 (3) Å	12.642 (3) Å
c (Å)	9.18 (18)Å	9.1518 (18) Å
α(deg)	90	90
β(deg)	105.407	105.49(2)
γ(deg)	90	90
Volume (A3)	646. 3 (4)Å^3	638.4(4) Å^3
Space group	P21	P21
System	monoclinic	monoclinic

3.2. Powder X-ray diffraction analysis

The grown crystals were subjected to powder x-ray diffraction analysis to confirm the crystallinity using X′Pert pro PANalytical diffractometer using nickel-filtered Cu-Kα radiation (0.15418 nm) as source and operated at 40 kV and 30 mA. Powder form of the undoped and 1 mol% L_aspargine doped TGS single crystal was taken for the powder x-ray diffraction analysis. The sample was scanned, 2θ ranging from 10° to 90° at room temperature. The indexed powder X-ray diffraction pattern of the grown crystal is shown in Fig. 2a & 2b. The obtained 2θ values are used for indexing using the 'TWOTHETA' software package. The well defined and sharp peaks signify the good crystalline nature of the compound, and the intensity of the peak is varied in L-aspargine doped TGS single crystal when compared to pure TGS crystal and it confirms the presence of L_asparginein the TGS crystal lattice. Powder XRD results show that the L-aspargine doped TGS crystal retains its original structure and it reveals that the dopant does not affect the structure of pure TGS. Similar results are observed in the case of L-lysine monohydrochloride dehydrate doped ADP single crystals and Amaranth doped TGS single crystals [20-22].

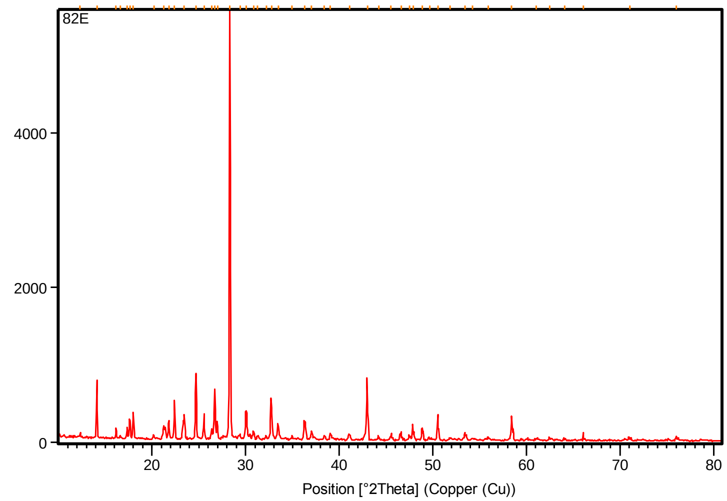


Fig. 2a. Powder XRD study of undoped TGS single crystal.

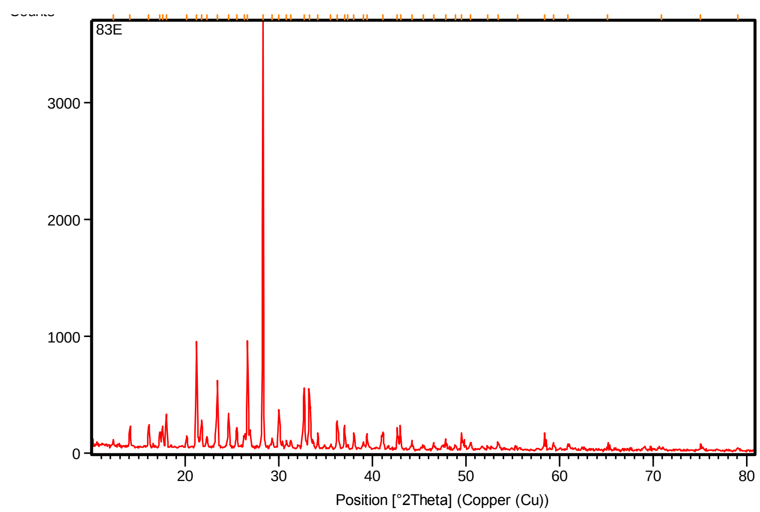


Fig. 2b. Powder XRD study of 1 mol% L-aspargine doped TGS single crystal.

3.3. UV–Vis analysis

UV–Visible analysis provides the information about optical properties of materials, electronic band structures, localized states and types of optical transitions. The material possesses lower cut off in the transmittance in between 200 and 500 nm, it can be used for effective optical applications. The material with lower cut off provides wider optical window [22-25]. UV–Vis transmittance spectra were recorded for the grown crystals with 1 mm thickness samples using Perkin Elmer UV–Vis –NIR Spectrophotometer in the range between 200 and 1100 nm. The measurement is carried out on the grown crystals of undoped and 1 mol% L_aspargine doped TGS with fine polished plane of (001). The observed assorbtion and transmittance spectrum is shown in Fig. 3a & 3b. The L_aspargine doped TGS shows 87% transmittance while the pure TGS shows 84% transmittance. The grown crystal of both pure and RS doped TGS has good transmission in the entire visible and IR region and the lower cutoff is found at 335 nm. Since the crystal has good optical transmittance and lower cutoff wavelength, it can be used for effective optical applications.

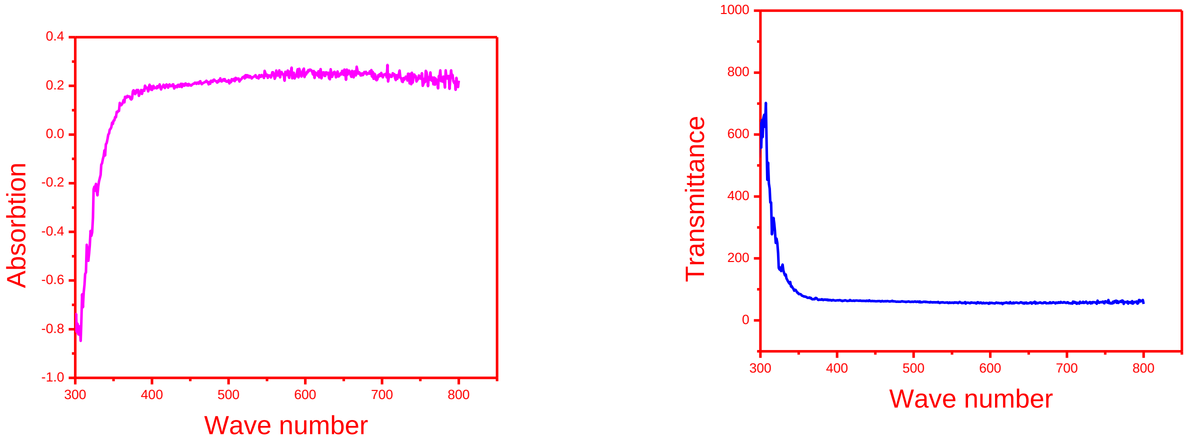
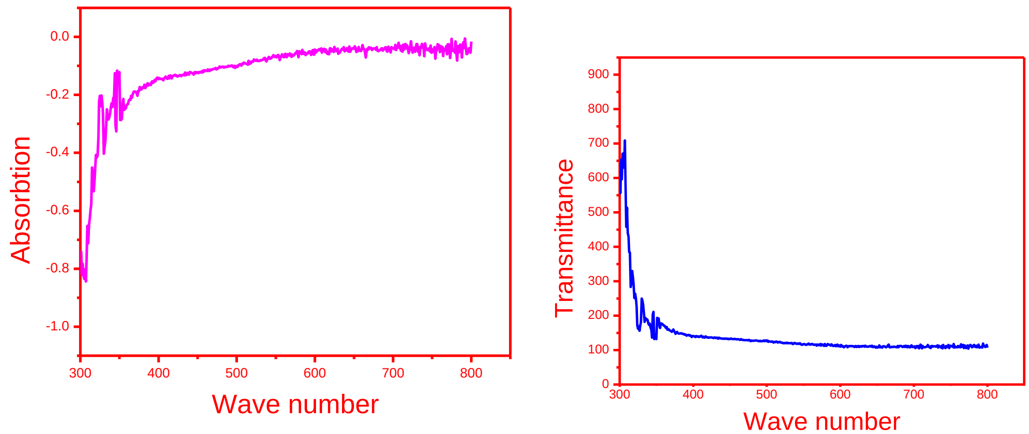


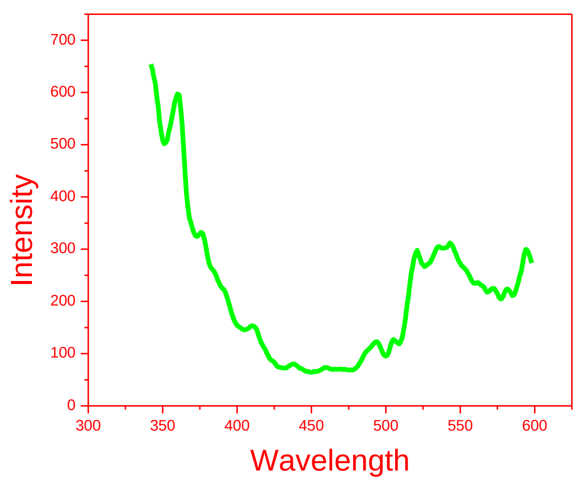
Fig 3a. Absorbance and Transmittance spectrum of undoped TGS crystal



3b. Absorbance and Transmittance spectrum of 1 mol% L-aspargine doped TGS crystal

3.4. Photoluminescence study

When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually, these excitations relax and the electrons return to the ground state. If radioactive relaxation occurs, the emitted light is called Photoluminescence. Photoluminescence intensity is highly dependent on the crystalline and structural perfection of the crystal [26]. Photoluminescence of undoped and L_aspargine doped TGS crystals is carried out using Shimadzu Spectrofluorophotometer RF-5031 PC Series with the slit width of 3 nm at room temperature. The powder sample of both undoped and 1 mol% doped TGS was excited at 310 nm and the emission spectrum was recorded between 300–700 nm and observed emission spectrum with inset excitation spectrum is shown in Fig. 4. An intense broad emission band appeared at 442 nm in both undoped and L_aspargine doped TGS. L-aspargine doped TGS possesses higher intensity emission peaks than pure TGS due to high crystalline perfection. The strong PL emission of the material may find potential applications in optoelectronic devices.



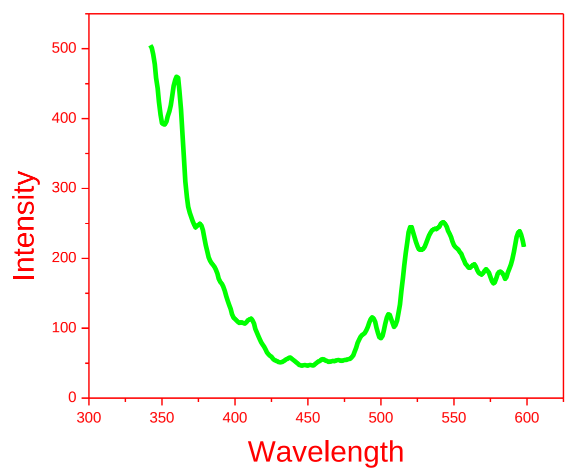


Fig. 4. Photoluminescence spectrum undoped and 1 mol% L-aspargine doped TGS crystal.

3.5. Photoconductive study

Photoconductivity is a phenomenon in which the electrical conductivity of the material increases due to the interaction of the electromagnetic radiation such as visible light, infrared radiation, and etc. Photoconductivity was carried out using KEITHLEY 6487 picoammeter in the presence of DC electric field at room temperature. Electrical contacts were made in both the undoped and 1 mol% L_aspargine doped TGS crystal with size of 10×5×3 mm^3. In order to have good conductivity, silver paint has been coated on the surface of both the samples. Then the sample was connected in series to a dc power supply with a Keithley picoammeter. To measure photo current, the sample was illuminated with the halogen lamp (20 w) by focusing a spot of light on the sample with the help of a convex lens. The applied field was increased from 0 to 5000 V/cm and the corresponding photo current and dark current were recorded for all the temperatures. The plot of photo current and dark current for both undoped TGS and L_aspargine doped TGS as a function of applied voltage with three different temperatures are shown in Fig. 5. It is observed that both undoped and 1 mol% L_aspargine doped TGS in all the temperatures show positive photoconductive nature and it is linearly increasing with applied field. The L_aspargine doped TGS shows higher photoconductive nature compared to undoped TGS and it confirms the presence of L_aspargine in the TGS crystal lattice.

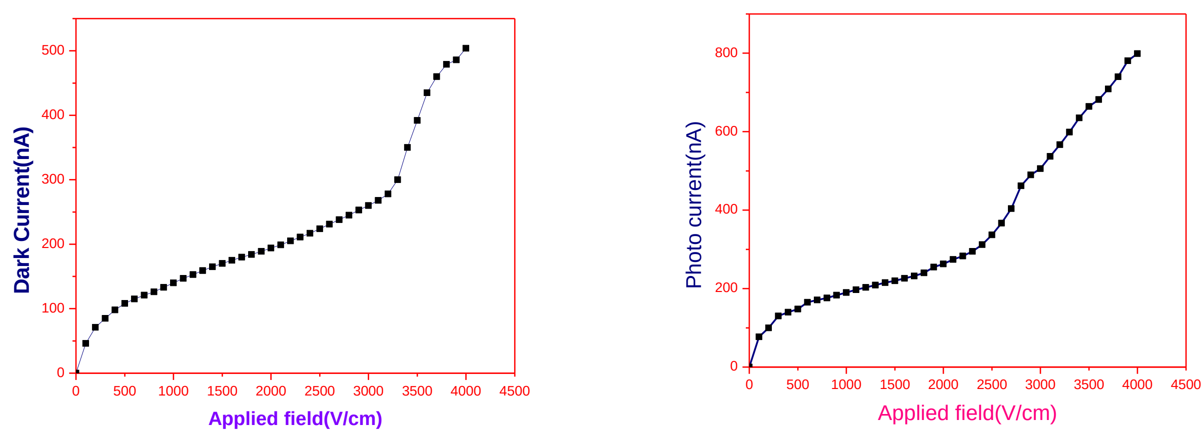


Fig 5. Photoconductivity study of undoped and l-aspargine doped TGS single crystals

IV. Conclusions

Single crystals of undoped and 1 mol% l_aspargine doped Triglycine sulphate (TGS) were grown by slow evaporation method. The grown crystals are transparent and with well defined external appearance. The enhancement in the optical transmittance in the case of

L_aspargine doped TGS is observed from UV–Visible analysis. From the photoluminescence study the high intensity luminescence emission is observed in the L-aspargine doped TGS crystal and resembles the good crystalline nature. Positive photoconductive nature is observed at Room for both undoped and L_aspargine doped TGS. The higher photoconductive nature is observed in L-aspargine doped TGS .

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