

Effect of amino acid doping on the dielectric properties of triglycine sulphate (TGS) crystals

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Abstract

Effect of amino acid (proline) doping on the dielectric properties of triglycine sulphate has been studied. Pure and proline doped triglycine sulphate (TGS) were grown from aqueous solution by solution growth technique at room temperature. The dielectric studies were carried out to identify the phase transition temperature and the dielectric behavior. The present study shows that there is an increase in the Curie temperature for the doped crystals.

Keywords: TGS crystals, proline doping, dielectric properties.

Introduction

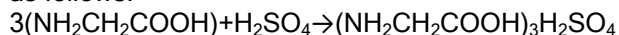
Ferroelectric triglycine sulphate (TGS) is one of the most extensively studied ferroelectric materials, which finds wide application as room temperature IR detector. It also finds application in burglar alarms, medical vidicon tubes operating at room temperature, FTIR instrumentation and in pyroelectric detector. It undergoes a second-order phase transition at Curie temperature (322 K) from ferroelectric to paraelectric. The crystal structure of TGS is monoclinic below and above Curie temperature (Hoshino *et al.*, 1959). The space group transforms from non-centrosymmetric P_{21} in the ferroelectric phase to centrosymmetrical $P_{21/m}$ in the paraelectric phase. The cleavage plane is generally expressed as the b-plane and the spontaneous polarization ($P_s=2.8\mu\text{C}/\text{cm}^2$) arises along the crystallographic b-axis (Landolt-Bornstein, 1969). However, the TGS has a disadvantage that it depolarizes by thermal, electrical or mechanical means. An efficient way to stabilize the single domain state is practical by doping an optically active molecule into TGS. 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 (Nakatani, 1973). Many authors investigated the effect of doping of various amino acids on TGS (Bye *et al.*, 1972; Aravazhi, 1997a,b; Meera *et al.*, 2000). The effect of organic dopants on TGS and rare earth ions dopant with TGS have also been investigated (Mihaylova & Stoyanov, 1996; Meera *et al.*, 2001; Muralidharan *et al.*, 2002; Theresita Shanthy *et al.*, 2009; Selvarajan *et al.*, 2008). In recent years, the interest in studying the pure and doped TGS crystals has increased because of their promise

in various devices. In the present work we have chosen the amino acid proline as dopant because proline ions are expected to play a partial role for the spontaneous polarization in TGS crystal thereby increase the dielectric constant and T_c due to its intrinsic dipole moment. The objective of the present work was to investigate the effect of proline addition on the growth and dielectric properties of TGS crystal.

Experimental procedure

Growth of TGS

Triglycine sulphate (TGS) was synthesized (Theresita Shanthy *et al.*, 2009) by taking glycine and sulphuric acid in the molar ratio 3:1. Glycine reacts with sulphuric acid as follows:



The required amount of sulphuric acid was diluted with doubly distilled water. Then, the calculated amount of glycine was added and dissolved in diluted H_2SO_4 . The solution was heated until the salt got recrystallized. Extreme care was taken during recrystallization to avoid the oxidation of glycine. Hence, the solution temperature was always maintained below 60°C . The recrystallized

TGS salt was dissolved in doubly distilled water. In this way the natural impurity content of TGS salt was minimized. A saturated solution of TGS at room temperature was prepared using twice crystallized salt. The solution was filtered using a high quality filter paper. The amino acid proline (5 and 10 wt%) was added to the saturated solution, till the equilibrium was attained. The solution was kept in glass vessels covered with perforated filter paper for slow evaporation at room temperature. Slow evaporation technique was employed for crystal growth. Good quality transparent crystals were harvested after 25 days. The grown crystals were shown in Fig.1.

Fig. 1. Photograph showing the pure and proline added TGS crystals grown (from left: pure TGS, 5 & 10 wt% proline added)



The sample crystals cleaved perpendicular to the polar axis with thickness about 4 mm having graphite coating on the opposite faces was placed between two brass electrode and thus parallel plate capacitor was formed. The capacitance and dielectric loss ($\tan \delta$) were measured using the conventional two probe technique (Joseph John *et al.*, 2007; Joseph John & Mahadevan, 2008) at various temperatures ranging from 300 to 357 K using an LCR meter (Model APLAB with two frequencies, namely 100Hz and 1 kHz). The dielectric constant was calculated using the relation:

$$C_{\text{cry}} - C_{\text{air}}(1 - (A_{\text{cry}}/A_{\text{air}}))$$

$$\epsilon_r = \frac{C_{\text{cry}} - C_{\text{air}}(1 - (A_{\text{cry}}/A_{\text{air}}))}{C_{\text{air}}} \times (A_{\text{air}}/A_{\text{cry}}), C_{\text{air}}$$

Where, C_{cry} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{cry} is the area of the crystal touching the electrode and A_{air} is the area of electrode. The AC electrical conductivity (σ_{ac}) was calculated using the relation $\sigma_{\text{ac}} = \epsilon_0 \epsilon_r \omega \tan \delta$ where ϵ_0 is the permittivity of free space (8.85×10^{-12} Farad/m) and ω is the angular frequency ($\omega = 2\pi f$, $f = 100 \text{ Hz}$ & 1 kHz).

The resistances of the crystals were measured using a thousand Meg ohmmeter. The observations were made while cooling the sample. The dimensions of the crystals were measured using a traveling microscope. The DC conductivity (σ_{dc}) of the crystal was calculated using the relation $\sigma_{\text{dc}} = d / (RA)$ where d is the thickness of the sample, A is the area of the sample and R is the measured resistance.

Results and discussion

The term dielectric applies to the material properties governing the interaction between matter and electromagnetic field. Induced or permanent electric polarization or magnetization of matter as a function of static or alternating electric, magnetic or electromagnetic field constitutes the dielectric properties of the material. The dielectric constant is one of the basic electrical properties of solids. Various polarization mechanisms in solids such as atomic polarization of the lattice, orientational polarization of dipoles and space charge polarizations can be understood very easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids (Wagner & Hantemann, 1950; Rao & Somakula 1965; Govinda & Rao, 1975) These investigations help in detecting the structural phase transitions taking place in solids when abrupt changes in dielectric properties are observed. Particularly, the presence of a dielectric between the plates of a condenser enhances the capacitance. The effect makes material with dielectric constant useful in capacitor technology.

The magnitude of the dielectric constant depends on the degree of polarization charge displacement in the crystals. The electronic exchange of the number of ions in the crystals gives local displacement of electrons in the direction of applied field that gives polarization. Ferroelectric domains are areas of such local dipole alignment with an associated net dipole moment and net

polarization. In presence of an applied electric field, domains that are aligned with the direction of the field will grow at the expense of the less well aligned domains. Thus the observed enhancement in the dielectric constant at low frequency could be attributed to the multi-domain state of the proline doped sample. As the frequency increases, a point will be reached where the space charge cannot sustained and comply with the external field giving rise to diminishing values of dielectric constant. Above this frequency the domain wall motion contribution to dielectric constant was nearly the same for pure and doped crystals (Parimalaselvi *et al.*, 2010).

The temperature dependence of dielectric constant (ϵ_r) obtained for the grown crystals for 100 Hz frequency is provided in Fig.2a and for 1 KHz frequency in Fig. 2b. The temperature dependence of dielectric loss ($\tan \delta$) obtained for the frequency 100 Hz is presented in Fig.3a and for 1 KHz in Fig. 3b. The dielectric constant and the dielectric loss values increases with the increase in temperature for both the frequencies up to the transition temperature and then decreases. The doped crystals have higher dielectric constant values compared to that of pure TGS. Increase in dielectric constant of doped TGS crystals at transition temperature attributed to free charge carriers created by the dopant.

The Curie point T_c for all the samples was not found to be the same. A small shift in temperature is found for doped TGS crystals. The dielectric constant is small at lower temperature, which increases with temperature and rises sharply up to the Curie point for both the frequencies. Above T_c the dielectric constants decreases suddenly and obey Curie-Wess law. Variation of ϵ_r with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The variation of ϵ_r at low temperature is mainly due to the expansion and electronic and ionic polarization. At higher temperatures, the increase is mainly attributed to the thermally generated charge carriers and impurity dipoles. The AC conductivity shows the same behavior (Fig.4a and 4b).

Fig. 5. shows the temperature dependence of DC conductivity (σ_{dc}), It can be seen that, for all TGS systems the DC conductivity increases with the increase in temperature. The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases. The addition of impurity further increases the electrical conduction in the temperature region considered. The conduction region is considered in the present study seems to be connected to mobility of vacancies.

Conclusions

Single crystals of pure and proline added Triglycine sulphate (TGS) were grown by slow evaporation method. The grown crystals are transparent and with well defined external appearance. Capacitance and dielectric loss

Fig.2a. Variation of Dielectric constant with temperature at 100 Hz

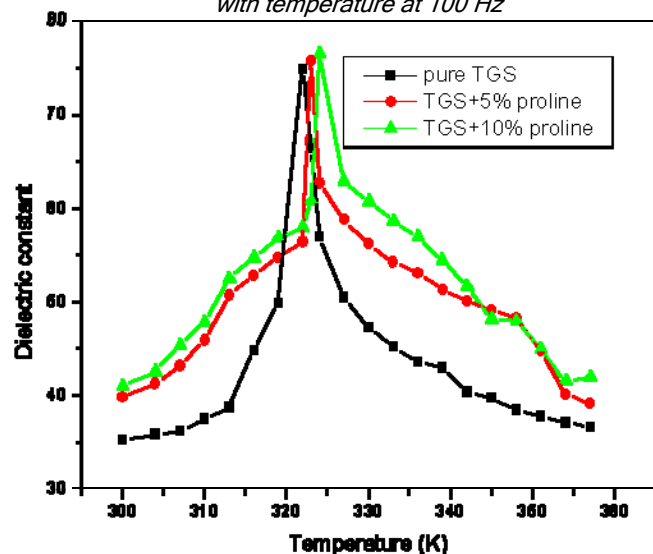


Fig.2b. Variation of Dielectric constant with temperature at 1 kHz

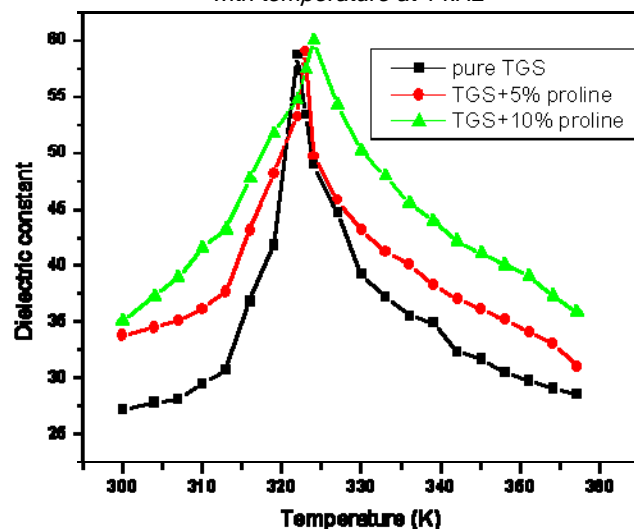


Fig.3a. Variation of Dielectric loss with temperature at 100 Hz

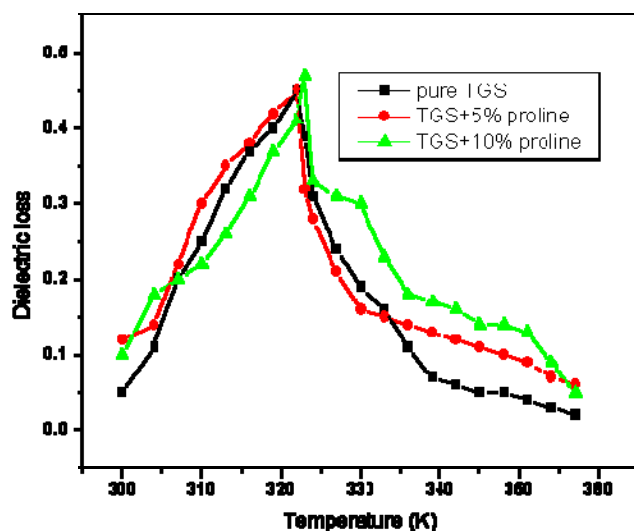


Fig.3b. Variation of Dielectric loss with temperature at 1 kHz

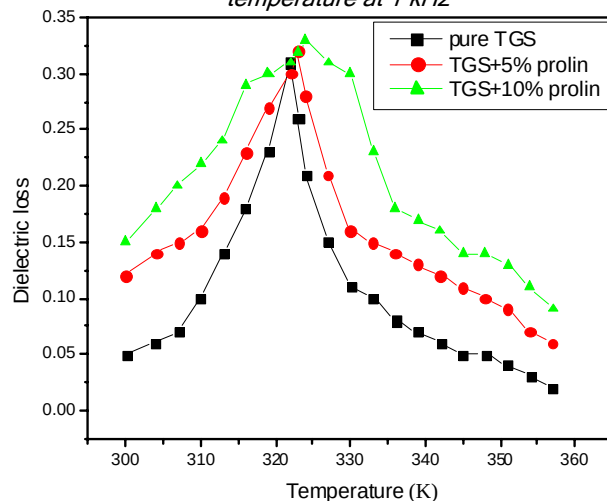


Fig.4a Variation of AC conductivity with temperature at 100 Hz

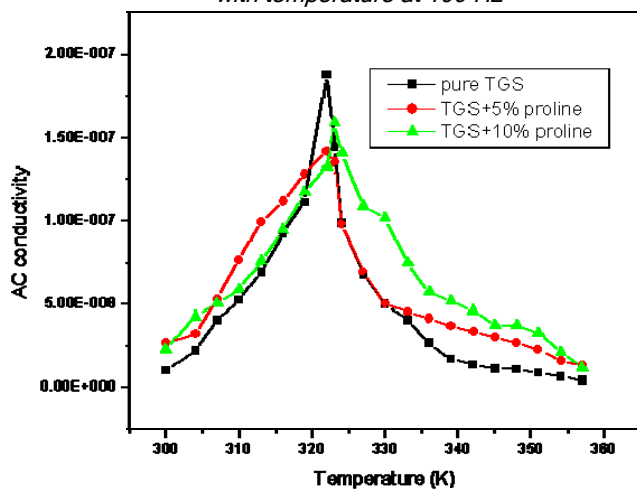


Fig. 4b. Variation of AC conductivity with temperature at 1 kHz

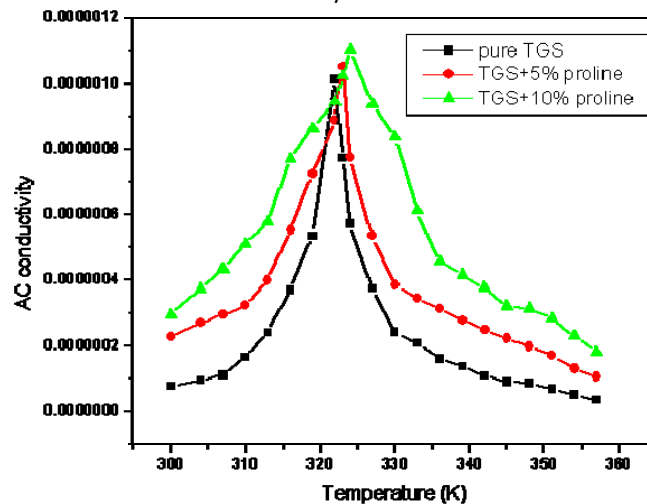
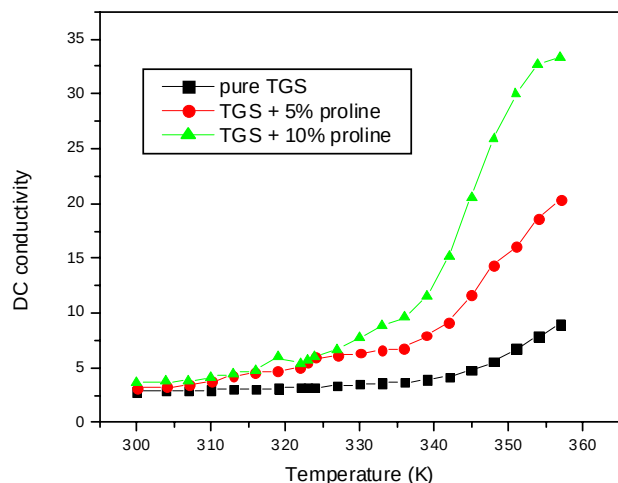


Fig.5. Variation of DC electrical conductivity with temperature



tangent ($\tan \delta$) measurements were carried out for the grown crystals at various temperatures ranging from 300 to 357 K using an LCR meter with frequencies of 100 Hz and 1 kHz. Dielectric constant and AC electrical conductivity were determined from the measured capacitance and $\tan \delta$ values. The shift in the Curie temperature from 322 to 324 K in the doped crystals is due to the presence of high polarization capacity of proline. DC electrical conductivity was also measured at various temperatures and found to increase with increasing temperature.

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