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Studies On Glutamic Acid Doped TGS Single Crystals

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ABSTRACT
Effect of 10 mol% Glutamic acid doping on the properties of triglycine sulphate has been studied. Glutamic acid 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 dielectric studies were carried out to identify the phase transition temperature and the dielectric behavior. 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 glutamic acid.
Key words :TGS crystals, glutamic acid doping, dielectric constant, dielectric loss, AC conductivity, DC conductivity

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I. INTRODUCTION

Amino acid family of crystals over the years been subjected to extensive investigation by several researchers for their non linear optical properties [1]). The crystal of many inorganic derivatives of amino acids provides excellent crystals such as triglycine sulphate, L-arginine phosphate accepted for the fabrication of devices[2]. Triglycine sulphate (TGS) is well known ferro electric material and it is widely used in fabricating thermal detectors, vidicons and image systems due to its second-order phase transition at room temperature and h igher pyroelectric co-efficients as well [3-5]. The major drawback in TGS crystal is depolarization of the device performance. To overcome this, organic and inorganic dopants have been tried. The organic and inorganic dopants in TGS have solved the problem of depolarization. In L-alanine added TGS, the presence of extra methyl group in the place of a hydrogen atom resulted in stabilization of the structure[6-9]. The added advantage of doping results in reduced dielectric permittivity and hence the pyroelectic figure of merit was higher that's the undoped TGS [10-12]. Even though doping enhances the characteristics of TGS, it could not alleviate the proliferation of microbes.

Since glycine and co-substituted amino acids are rich in nutrient and hence reducing their shelf life. In order to overcome this microbial problem, the partial substitution of phosphate in TGS was tried and it gives rise to enhanced characteristic and shelf life timme of the solution. 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 [13] . Many authors investigated the effecct of doping of various amino acids on TGS [14-16]. The effect of organic dopants on TGS and rare earth ions dopant with TGS have also been investigated[17-19]. 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 glutamic acid as dopant because glutamic acid 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 glutamic acid addition on the growth and properties of TGS crystal.

II. EXPERIMENTAL

Synthesis of TGS

Triglycine sulphate (TGS) was synthesized [20] by taking glycine and sulphuric acid in the molar ratio 3:1. Glycine reacts with sulphuric acid as follows:

$3(NH_2CH_2COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3H_2SO_4$ …(1)

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. The doped samples were prepared by mixing 10 mol% of glutamic acid with TGS. Impurity contents in TGS were minimized by successive recrystallization process.

An important step to obtain good quality crystals is the use of high purity chemicals and hence analytical reagent (AR) grade of sulphuric acid, glycine and glutamic acid were used. The technique followed for the growth of glutamic acid doped TGS single crystals was solution method with slow evaporation technique. In accordance with the solubility data, the saturated solution of glutamic acid doped TGS was prepared in water at room temperature and maintained with continuous stirring by using a magnetic stirrer for about two hours to ensure homogeneous concentration over the entire volume of the solution. The homogeneous saturated solution was kept in glass vessels covered with perforated filter paper for slow evaporation. Repeated recrystallization was carried out to obtain good quality and transparent crystals. Seed crystal technique was also used to harvest large-size crystals. A photograph of the harvested glutamic acid doped TGS crystal is displayed in Figure 1. The growth period was 25-30 days.

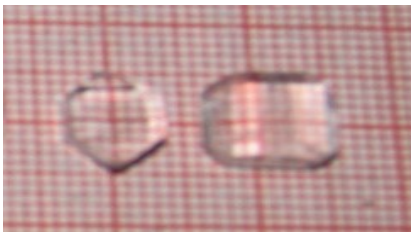

Fig. 1: Photograph of pure and 10 mol% glutamic acid doped TGS single crystals

Electrical Measurements

The important property of the solid material is its electrical conductivity. The electrical conductivity of a solid is due to the mobility of electrons or ions or imperfections which are charged. In the case of semiconducting materials, the conductivity is due to the movement of electrons and holes. The flat surfaces of the cylindrical crystals were coated with good quality graphite to obtain a good conductive surface layer. A travelling microscopic (Least count = 0.001 cm) was used to measure the dimensions of the crystals. The percentage porosity was calculated using the relation.

$$P=1 - D_o/D_x \quad \ldots\ldots\ldots\ldots \quad (2)$$

Where D_o is the measured density of the crystal and D_x is the density of the bulk crystal. D_o was estimated by measuring the mass and volume of the crystal and using the relation [21].

$$D_o=m/v=m/(\pi r^2 h) \quad \ldots\ldots\ldots\ldots \quad (3)$$

Where m is the mass, r is the radius and h is the thickness of the crystal.

DC Electrical Measurements

The DC electrical conductivity measurements were carried out to an accuracy of ± 1% for all the sample prepared using the conventional two-probe technique in a way similar to that followed in the literature[22,23].

DC resistance of the crystal was measured at various temperatures ranging from 30-60°C by the conventional two-probe technique using a million megohmmeter. The observations were made while cooling the sample. Temperature was controlled to an accuracy of ±0.5°C.

The DC electrical conductivity (σ_{dc}) was calculated using the relation,

$$\sigma_{dc}=d/(RA) \quad \ldots\ldots\ldots\ldots \quad (4)$$

Where R is the measured resistance, d is the thickness of the sample and A is the area of the face in contact with the electrode. The resistances of the crystals were measured using a thousand Meg ohmmeter. The observations were made while cooling the sample.

AC Electrical Measurements

In the presence of applied electric field dielectric materials have permanent dipoles or induced dipoles. One of the basic electrical properties of solids is the dielectric constant. Dielectric constant is a number relating to the ability of a material to carry alternating current to the ability of vacuum to carry alternating current. The capacitance created by the presence of the material is directly related to the dielectric constant of the material.

Another important property of a dielectric material is its ability to support an electrostatic field while dissipating minimal energy in the form of heat. When an electrical field acts on any matter the late dissipates a certain quantity of electrical energy that transforms into heat energy. This phenomenon is commonly known as “the expense” or loss of power, meaning an average electric power dissipated in matter during a certain interval of time.

The amount of power losses in a dielectric under the action of the voltage applied to it is commonly known as dielectric losses. When considering dielectric losses we usually mean the losses precisely under an alternating voltage. The lower the dielectric loss the more effective is a dielectric material.

rameter both for the material of a dielectric and an insulated portion. When a dielectric is subjected to an alternating field E there will be a phase lag between the applied field and the displacement, Hence the dielectric constant is described as a complex quantity.

$\varepsilon_1=\varepsilon' - i\varepsilon''$ . . . . . (5)

$\varepsilon''/\varepsilon'=\tan\delta$ . . . . . (6)

Where tan δ is called the dielectric loss.

The measurement of dielectric constant and dielectric loss as a function in frequency and temperature is of interest both form theoretical point of view and from the applied physics. Dielectric constant can be measured by determining the change in the capacitance of specially designed condenser when the dielectric is inserted between the plates of the condenser. The dielectric constant determines the share of the electric stress which is absorbed by the material without any dielectric breakdown. Practically the presence of a dielectric between the plates of a condenser enhances the capacitance. This effect makes materials with high dielectric constant useful in capacitor technology. This enhancement of capacitance provides the basic experimental method for the measurement of dielectric constant. Various 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 solids[24-26].

The capacitance (C_p) and dielectric loss factor (tan δ) of the crystal were measured at various temperatures ranging from 303-360K using an LCR meter APLAB by the parallel plate capacitor method with two different frequencies, viz. 100 Hz, 1 kHz, The sample was annealed in the holder assembly at ~350K before making observations. The observations were made while cooling the sample. Temperature was controlled to an accuracy of ±0.5K. The real part of the dielectric constant (ε') of the crystal was determined by using the relation:

$\varepsilon'=C_p h/(\varepsilon_o \pi r^2)$ . . . . . (7)

Where ε_o is the permittivity of free space and is equal to 8.854 x 10^{-12} F/m, r is the radius and h is the thickness of the crystal. The imaginary part of the dielectric constant was calculated using the relation:

$\varepsilon''=\varepsilon' \tan\delta$ . . . . . (8)

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 δ) were measured using the conventional two probe technique [14-16] various temperatures ranging from 303 to 360 K using an LCR meter (Model APLAB with two frequencies, namely 100Hz and 1 kHz). The dielectric constant was calculated using the relation:

$$\varepsilon' = \frac{C_{cry} - C_{air}(1-(A_{crys}/A_{air}))}{C_{air}} \times (A_{air}/A_{crys}),$$

Where, C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of electrode.

The AC electrical conductivity was determined by using the relation:

$\sigma_{ac}=\varepsilon_o \varepsilon' \omega\tan\delta$, ... (9)

where εo is the permittivity of free space(8.85 x 10-12 Farad/m) and ω is the angularfrequency (ω = 2 π f , f = 100 Hz& 1kHz).

III. 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 diploes and space charge polarizations can be understood very easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids [27-29] 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 glutamic acid 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 [30]. The temperature dependence of dielectric constant (εr) obtained for the grown crystals for 100 Hz and 1 KHz frequency in Fig. 2.

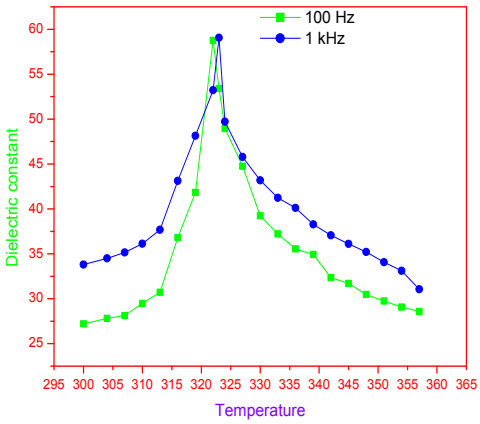

Fig. 2: Variation of dielectric constants with temperature for pure and 10 mol% glutamic acid doped TGS single crystals

The temperature dependence of dielectric loss (tan δ) obtained for the frequency 100 Hz and for 1 KHz is presented in Fig. 3. 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 Tc 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 Tc the dielectric constants decreases suddenly and obey Curie-Wess law. Variation of εr 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 εr at low temperature is mainly due to the expansion and electronic and ionic polarization [31,32]. At higher temperatures, the increase is mainly attributed to the thermally generated charge carriers and impurity dipoles.

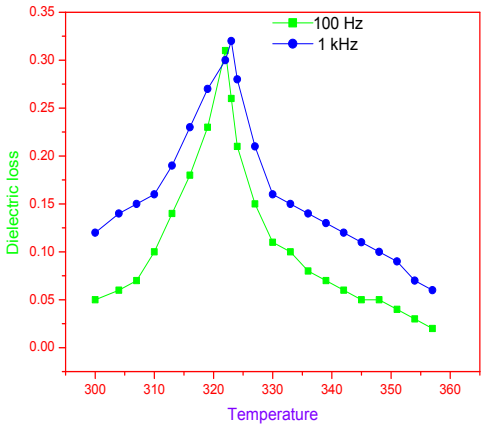

Fig. 3: Variation of dielectric loss with temperature for pure and 10 mol% glutamic acid doped TGS single crystals

The AC conductivity shows the same behavior (Fig.4). Fig. 5. shows the temperature dependence of DC conductivity (σdc), 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[33,34].

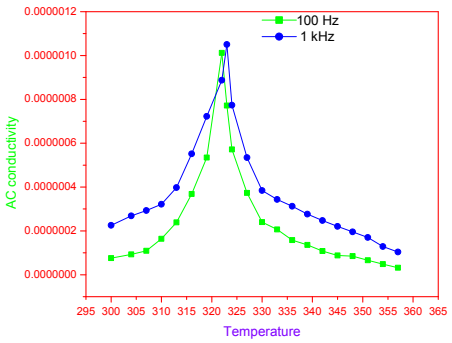

Fig. 4: Variation of AC conductivity with temperature for pure and 10 mol% glutamic acid doped TGS single crystals

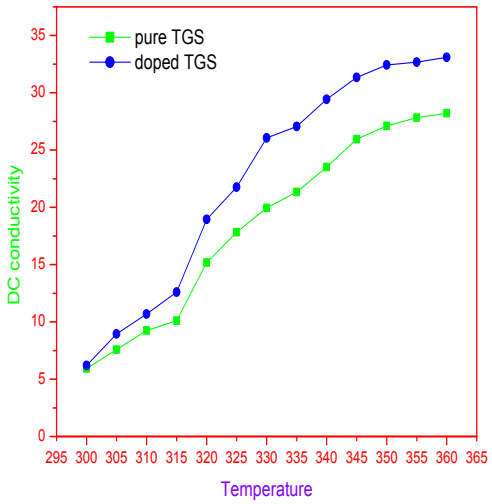

Fig. 5: Variation of DC conductivity with temperature for pure and 10 mol% glutamic acid doped TGS single crystals

Conclusions

Single crystals of pure and 10 mol% glutamic acid doped Triglycine sulphate (TGS) were grown by slow evaporation method. The grown crystals are transparent and with well defined external appearance. Capacitance and dielectric loss tangent (tan δ) 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 δ 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 glutamic acid. DC electrical conductivity was also measured at various temperatures and found to increase with increasing temperature.

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