

Pyro Electric Studies on Dye Doped TGS Crystals For Ir Detector and Laser Applications

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Abstract

Triglycine sulphate (TGS) crystals were grown by slow evaporation process. The stability of TGS single crystal was improved by doping organic dyes. The structural, optical properties, pyroelectric properties and dielectric properties of the doped crystals were analyzed. The FTIR spectra of all grown crystals have been recorded in the range of 400 - 4000 cm^{-1} using Bruker FT-IR 8400 spectrophotometer by KBr pellet technique. To determine the lattice parameters, powder X-ray diffraction analysis was performed by X-ray diffractometer system with Cu- K_{α} ($\lambda = 1.54178\text{\AA}$) radiation at room temperature with an operating voltage 40 kV and the tube current was 30 mA. In the present work, optical transmission and absorption spectra were recorded by Systronics UV-Double beam spectrometer in the wavelength range 190 to 1100 nm. The results for doped TGS crystal are compared with the results of the pure TGS crystals.

Introduction

The study of Ferro electricity has been closely linked with device applications [1]. The pyroelectric properties of ferroelectrics make them very suitable for thermal detection. This can be used to detect any radiation that results in a temperature change of the crystal [2]. They also have useful features at room temperature operation TGS has been the most extensively studied material for thermal detector applications. The presence of hysteresis loop makes them possible to use ferroelectrics as memory elements in computers [3]. The ferroelectric materials can be used as a thermo static non-linear dielectric element. They can be used to measure pressure and can also be used as frequency multiplier [4].

The potential barrier which a system must overcome in order to create a (crystalline) nucleus in the ideally homogeneous mother phase and which determines the rate of nucleation is defined as homogenous nucleation, by the interface energy. TGS crystals are at present the only ferroelectric crystals [5], which can be grown easily in bulk form needed for IR imaging applications; for which (010) plates of size $(2 \times 1) \text{ cm}^2$ are required (fig.1). There are problems associated with the growth of bulk transparent TGS crystals by traditional technique, due primarily to formation of spurious nucleation and irregular growth rate.

The purpose of the present investigation on nucleation is mainly to determine the induction period of pure and methyl orange doped TGS solutions under those conditions, which are present during the growth of large TGS crystals [6]. A quantitative experimental investigation of nucleation is extremely complicated. This is due primarily to the small sizes of the nuclei; which as yet make it impossible to observe them directly and measure the condensation parameters [7].

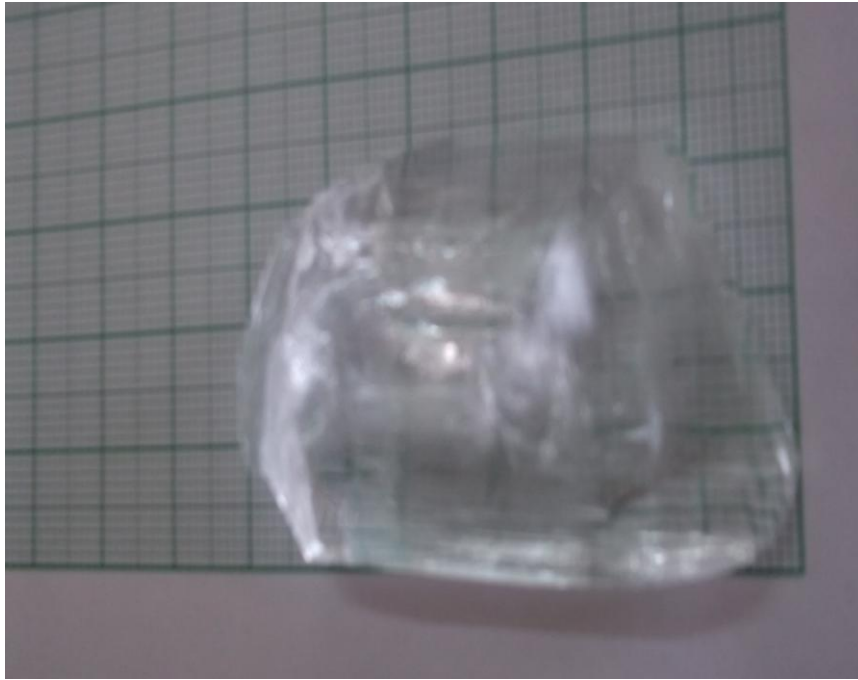


Figure 1: Xylenol dye doped TGS crystal

Triglycine sulphate $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$ crystals are very important because of their application as room temperature IR detectors and imaging systems[8]. The ferroelectric property of TGS was first discovered by Matthias et al 1956. This crystal has the most rectangular hysteresis loop and it has high pyroelectric coefficient and low dielectric constant. These properties make it a ferroelectric of great interest [9].

In TGS, the spontaneous electrical polarization is along the [010] crystallographic direction, which is sensitive to the temperature variation. In recent years, there has been considerable development in infrared detectors, with the aim of achieving the highest performance. To further enhance the device parameters, TGS has been doped

with amino acids. For the fabrication of thermal detectors and imaging systems, large size TGS crystals of wide b-plane are required, for which studies on fundamental growth parameters such as the solubility, metastable zone width are very essential [10]. There are many reports on ferroelectric studies on TGS such as the pyroelectric, dielectric properties etc., but investigations on the basic growth parameters such as the solubility and metastable zone width of pure and doped TGS are very scarce [11].

In the present study, an investigation was made on the solubility and metastable zone width for pure and methyl orange doped TGS saturated solutions [12]. The results of the investigations form a basis for the growth of bulk TGS crystals [13]. The effect of seed of different orientations on the habit of c and the change of morphology while doping with amino acids has also been investigated [14].

Crystal Structure and Properties of TGS

TGS [(NH₂CH₂COOH)₃.H₂SO₄] is a colourless, odourless and acidic salt [15]; it is synthesized by Glycine acid with sulphuric acid in the molar ratio of 3:1 [16]. Its density is 1.65 - 1.68 g/cm³ TGS belongs to the monoclinic system with the space group P₂₁ number of formula units per unit cell is 2. Above the Curie temperature (T = 47°C), the monoclinic system and belongs to the centro-symmetric crystal class P_{21/m}. So the spontaneous polarization is then lost [17]. Below T_c, the mirror plane disappears and the crystal belongs to the polar point group P₂₁ of monoclinic system.

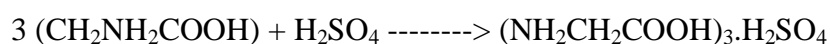
The first detailed investigation of crystal structure was carried out. TGS may be called glycine-di-glycinium sulphate with chemical formula



Of the three-glycine group contained in the asymmetric unit, two assume a completely planar configuration and the third on assume partially planar configuration [18]. They are connected by a hydrogen bond between oxygen atoms. The bonds between two planar groups II and III are responsible for ferroelectric transition [19]. Above the Curie temperature, glycine I molecule is splitted. Reversal of the polarization in the material is largely associated with the rotation of the glycine I group about the crystallographic "a" axis to change into mirror image [20].

Synthesis of The Salt

TGS was synthesized by taking the analar grade glycine (CH₂NH₂COOH) and concentrated sulphuric acid (H₂SO₄) Glycine and sulphuric acid were taken in the ratio 3:1 respectively. The required volume of concentrated sulphuric acid was diluted with millipore water. Then the calculated amount of glycine salt was slowly dissolved in the diluted sulphuric acid. This solution was heated until the crystallized. Extreme care was taken while crystallizing the salt to avoid oxidation of glycine; solution temperature was always maintained below 60°C [21]. Again the crystallized salt was dissolved in Millipore water and then recrystallized. By this way, the impurity content of TG was minimized. The reaction between glycine and sulphuric acid is given below



The solution has then been filtered with 0.2 micron porosity nuclear filter after due preheating. This solution was maintained at 60°C for 2 days prior to loading the crystallizer.

Experiment

Recrystallized salt was used to study the solubility of pure and xylenol orange doped TGS for three different temperatures 35, 40 and 45°C. A sealed container charged with millipore water and the solute, maintained at a constant temperature, was used to determine the equilibrium concentration. The solution was stirred continuously for 24 hours. The content of the solution was analyzed gravimetrically. The results are presented in figure.

In Triglycine sulphate, glycine is one of the amino acids. The substitution of another dye – xylenol orange - in the place of glycine has been found to improve the crystal properties by the way of contributing to effective internal bias in these crystals which, in turn, inhibits ferroelectric switching giving permanently poled single domain crystal. This improved the device characteristics and hence xylenol mixed crystals. The spontaneous polarization of ferroelectric crystal originates from the dipole moment of each dipole within the crystal. Some molecules with higher dipole moments can be introduced into the polar lattice of TGS crystal in such a way that their polar orientation tends to coincide with the bulk polarization. Thus, the pyroelectric properties of the crystal may be improved.

Results and Discussion

X-Ray Analysis

The grown crystals have been characterized by powder X ray diffractometer. Fig.2 represents the powder X-ray pattern of the grown TGS. The system is found to exhibit monoclinic structure with the space group P_{21} and the lattice parameters of pure TGS crystal are $a = 9.581 \text{ \AA}$, $b = 11.450 \text{ \AA}$ and $c = 4.936 \text{ \AA}$ which are in good agreement with the literature. TGS pure and doped crystals were cleaved into small pieces. The radiation used was $\text{MoK}\alpha$, monochromatized by graphite. Cell parameters were measured from 30 reflections and after refining the orientation matrix and cell parameters by least squares. The following data have been obtained for TGS crystal both pure and doped from the single crystal XRD analysis.

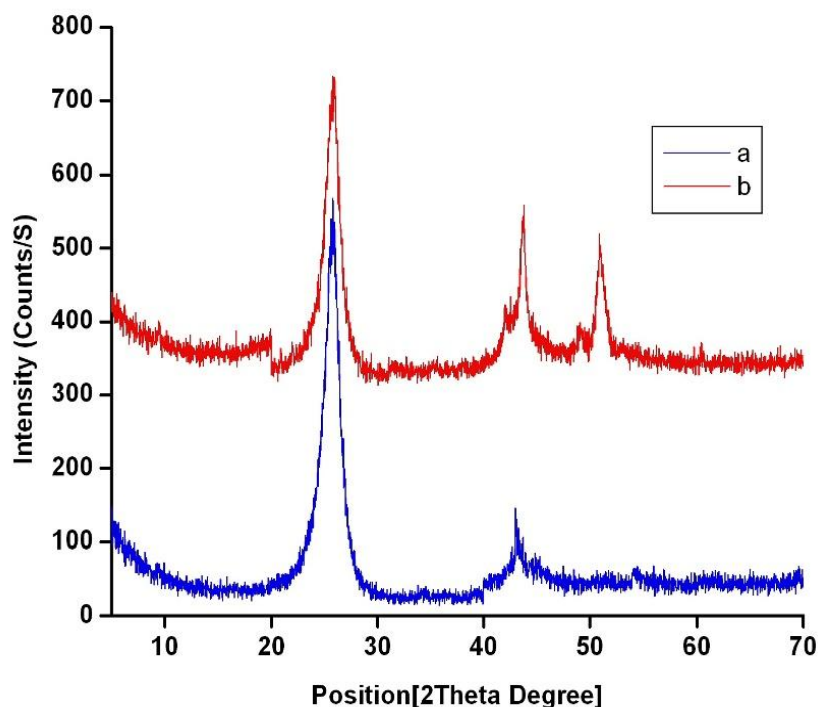


Figure 2: XRD of (a) Pure and (b) Xyleneol doped TGS Crystal

FTIR Studies

The presence of dopants in the crystal was qualitatively investigated by the FTIR studies. The infrared spectra were obtained with a BRUKER IFS 66V FTIR spectrometer using the KBr pellet technique. The FTIR data for pure and dye doped TGS. The NH, OH and CH absorptions smeared into a continuum which occurs at a higher frequency (3100 cm^{-1}). The absorption around 1500 cm^{-1} refers to the normal band position for unionized C=O and hence TGS is not in the Zwitter ion form. The strong absorption in the $1015 - 1175\text{ cm}^{-1}$ region is evidently due to the sulphate part of the molecule.

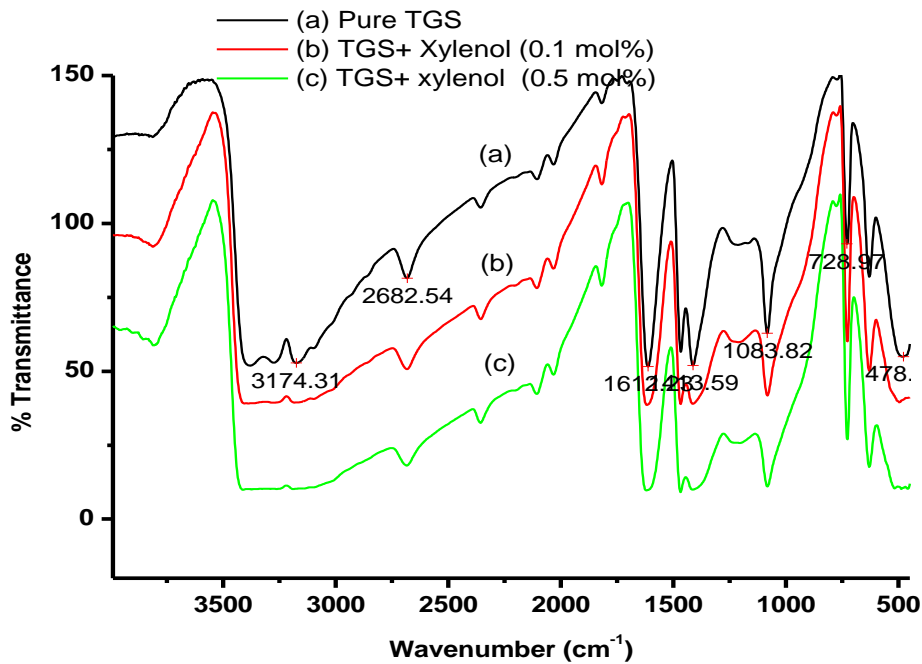


Figure 3: FT-IR Spectra of pure and Xylenol doped TGS Crystals

The doping with xylenol orange causes much broadening of the peaks in the spectra compared to the pure TGS crystal. The spectra also reveal reduction in the crystal hardness as a result of dopant incorporation - this has been evident from the hardness measurements for pure and doped crystals. It is inferred that the modes due to polar groupings, for example COOH, COO are more broadened compared to the modes of non-polar groupings illustrating that the doped crystals reject more degree of interaction for the polar groupings rather than for non-polar groupings.

Poling of The Crystals

The domain wall contribution to the free energy will affect most of the macroscopic properties of ferroelectrics. Consequently the starting point for the experimental study of a ferroelectric is the preparation of single crystals, which are both single domains electrically and untwined crystallographically. Electric poling was achieved by cooling the crystal from the paraelectric phase into the ferroelectric phase in an applied field parallel to the crystallographic axis under constant electric field (E) conditions, the voltage applied to the electrode sample being 3.5 KV/cm. The single domain state was then thermodynamically stable in an unstressed crystal since depolarization fields were neutralized by charge flow in the external circuit. The poling apparatus is shown in figure 4. The amplitude and duration of the voltage required for poling vary substantially between materials.

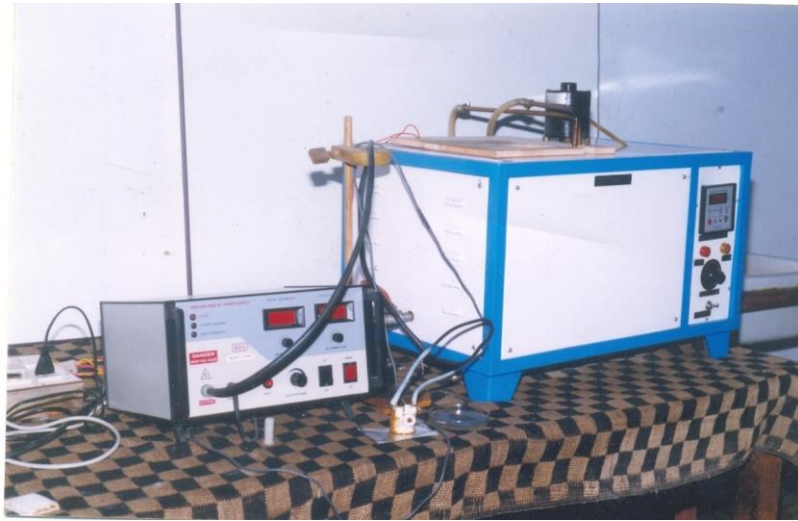


Figure 4: Poling Apparatus With Sample Holder

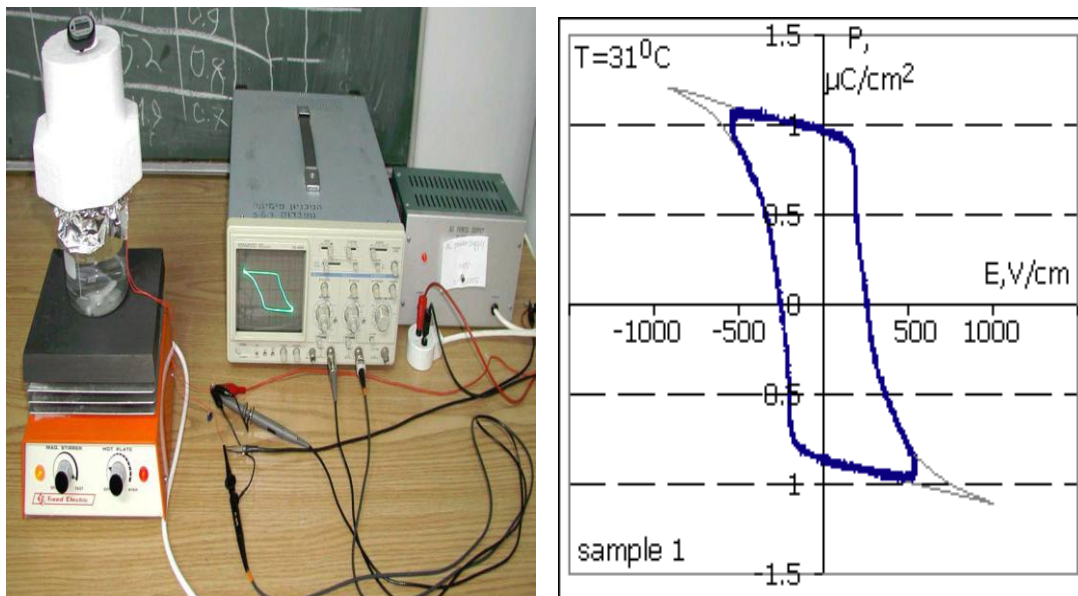


Figure 5: A hysteresis loop illustrating the coercive field E_c , spontaneous polarization P_s and the remanent polarization P_r

Some materials will pole easily and if used in large signal switching applications may not even require a preliminary poling cycle. A hysteresis loop (fig.5) illustrating the coercive field E_c , the spontaneous polarization P_s and the remanent polarization P_r .

Analysis of Pyroelectric Studies

The doping of TGS with Xylenol orange has shifted the ferroelectric transition temperature (T_c) to a higher value. The shift observed at Curie temperature may be

due to simultaneous change in macroscopic polarization and increase in the electrical conductivity. The dipolar strength of Xylenol orange is larger compared to pure TGS as a result of large electron repulsion from $(\text{CH}_3)_2\text{CH}$ group. So, Xylenol orange doped TGS is found to have maximum pyroelectric coefficient compared to pure

TGS. The doping of dye in the place of glycine makes the crystal set-up an inherent bias field by which the depolarization phenomenon of the crystal can be prevented. In the case of xylenol orange, due to the extra methyl group in the molecule which prevents its rotation within the lattice, the dipolar molecule is fixed with respect to the crystal structure and the polarization does not disappear at a temperature close to T_c which keeps the crystal permanently polarized. The internal bias is produced by two factors; one is the change in the dipolar moment at the site of the dopants and other is the displaced charge in the cells around the doped cells. The second factor has greater influence. The xylenol orange doped TGS exhibited a maximum pyroelectric coefficient at 52°C .

Dielectric Studies

The temperature dependent dielectric constant of xylenol orange doped TGS crystals were measured using Hioki LCR Hi-Tester in the frequency range from 300Hz to 50MHz at different temperatures. In order to ensure good electrical contact between the crystal and the electrodes, the sample was coated with silver paint and mounted between the two electrodes. The capacitance of the parallel plate capacitor formed by the electrodes, with the sample as a dielectric medium, was measured. The variation of capacitance was recorded in the frequency range 300Hz to 50 MHz at different temperatures. The dielectric constant of the material was calculated for different frequencies from the measured capacitance values. The plot of dielectric constant versus applied frequency is shown in Fig 6. It is observed that dielectric constant has high values in the low frequency region and there after decreases with the applied frequency. The very high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientation, electronic and ionic polarization, and the low value at higher frequencies may be due to the loss of significance of these polarizations gradually.

The most commonly measured small signal electrical property is the dielectric permittivity ϵ_r also often referred as the dielectric constant. ϵ_r in polar materials is rarely a constant, but varies with the applied field, stress and temperature and other parameters. When a dielectric material is subjected to an electric field, the net polarization of the medium is altered. The dielectric constant and dielectric loss may be obtained from a measurement of the real and complex admittance of a crystal. These measurements are particularly straightforward with impedance bridges, which separate the conductance and capacitance of the crystals. Unpoled crystals have been used for the measurement and this is mainly used for the identification of phase transitions and the recording of transition temperature. Any strain or inhomogeneities in the crystal tend to broaden the phase transition so that there is no apparent discontinuity in dielectric permittivity (ϵ_r).

Conclusion

In the present investigation, the molecules of dye such as xylenol orange, whose molecular structures are CH_3 (CH) (NH_2) COOH, have been introduced in the TGS crystal. These materials with larger asymmetric molecules stimulated us to study their influence on the basic growth parameters such as solubility and stability. Synthesized TGS salt has been used for the preparation of solution. The dopants xylenol orange were added to the saturated TGS aqueous solution till the equilibrium was achieved.

The pyroelectric studies it was found that doping the crystals with xylenol orange enhanced the pyroelectric coefficient and the ferroelectric transition temperature (T_c). Dielectric studies on the samples reveal a low permittivity of the doped crystals were suitable for IR detector applications. The FTIR studies reveal a broadening of peaks for the doped samples confirming the presence of dopants in the crystal. The substitution of dye - in the place of glycine has been found to improve the crystal properties by the way of contributing to effective internal bias in these crystals which, in turn, inhibits ferroelectric switching giving permanently poled single domain crystal. This improved the device characteristics and hence xylenol orange crystals. The spontaneous polarization of ferroelectric crystal originates from the dipole moment of each dipole within the crystal. Some molecules with higher dipole moments can be introduced into the polar lattice of TGS crystal in such a way that their polar orientation tends to coincide with the bulk polarization. Thus, the pyroelectric properties of the crystal may be improved. The NLO property in these molecules is due to the virtual electron excitation occurring in the individual molecular or polymeric units. Organic dyes and polymeric materials possess lower dielectric constants and faster response time.

Acknowledgements

We gratefully acknowledge financial supports from the Department of Science & Technology-Science and Engineering Research Board [DST-SERB-FAST TRACK, PS-20/2009(SR)], New Delhi, India.

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