

# Effect of amino acids doped TGS crystals for IR detectors

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Amino acids (L-Glutamic acid, L-Tartaric acid) doped Triglycine sulphate (TGS) crystals are grown by solution growth technique. Slow cooling as well as slow evaporation methods were employed to grow these crystals. The concentration of dopants in the mother solution was varied from 0.1 mol% to 10 mol%. The solubility data for all dopants concentration were determined. There is variation in pH value and hence, there is habit modifications of the grown crystals were characterized. Dielectric studies reveal slight distortion of lattice parameter for the heavily doped TGS crystals. TGA–DTA studies reveal good thermal stability. The dopants increase the hardness value of the material and it also depends on the concentration of the dopants. The detailed results on the spectral parameters, habit modifications and constant values have been presented.

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## 1. Introduction

Modern technology is largely based on materials such as semiconductors, superconductors, piezo-electrics, ferroelectrics, and infrared sensitive crystals [1]. Preparation of single crystals of such materials has resulted in the importance of crystal growth in theoretical and experimental aspects. 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. The ferroelectric property of TGS was first discovered by Matthias et al 1956 [2].

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. TGS has a complex chemical and crystallographic structure [3]. It becomes the object of active research for two reasons; firstly, it is one of the very few ferroelectrics known to exhibit a second order phase transition and hence offers possibilities for the observation of genuine critical phenomenon very close to the Curie temperature; secondly it is an order-disorder ferroelectric [4]. These crystals are grown from aqueous solutions and are useful in infrared detection due to their interesting physical properties [5].

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. 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. 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 [6]. In the present study, an investigation was made on the solubility and metastable zone width for pure and amino acid doped (L-Glutamic acid, Tartaric acid) TGS saturated solutions [7]. The results of the investigations form a basis for the growth of bulk TGS crystals. 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 [8].

### 1.1 Crystal structure and properties of TGS

TGS is a colourless, odourless and acidic salt; it is synthesized by reacting  $\alpha$ -amino acid with sulphuric acid in the molar ratio of 3:1. Its density is 1.65 - 1.68 g/cm<sup>3</sup>. TGS belongs to the monoclinic system with the space group  $P_{21}$  number of formula units per unit cell is 2. Wood et al (1957) proposed the parameters of the unit cell as  $a = 9.47 \text{ \AA}$ ,  $b = 12.69 \text{ \AA}$ ,  $c = 5.71 \text{ \AA}$  and  $\beta = 110 \text{ \AA}$ . Above the Curie temperature ( $T = 49^\circ \text{C}$ ), the monoclinic system and belongs to the centro-symmetric crystal class  $P_{21/m}$ [9]. So the spontaneous polarization is then lost. Below  $T_c$ , the mirror plane disappears and the crystal belongs to the polar point group  $P_{21}$  of monoclinic system. The first detailed investigation of crystal structure was carried out [10]. TGS may be called glycine-di-glycinium sulphate with chemical formula

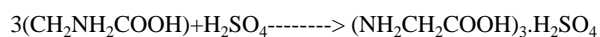


Of the three-glycine group contained in the asymmetric unit, two assume a completely planar configuration and the third on assume partially planar configuration. They are connected by a hydrogen bond between oxygen atoms [11]. The bonds between two planar groups II and III are responsible for ferroelectric transition. 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.

## 2. Determination of solubility and metastable zone width

### 2.1 Synthesis of the salt

TGS was synthesized by taking the annular grade glycine ( $\text{CH}_2\text{NH}_2\text{COOH}$ ) and concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ) Glycine and sulphuric acid were taken in the ratio 3:1 respectively [12]. 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  $60^\circ\text{C}$ . Again the crystallized salt was dissolved in Millipore water and then recrystallized. By this way, the impurity content of TGS 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  $60^\circ\text{C}$  for 2 days prior to loading the crystallizer.

### 2.2 Experiment

Recrystallized salt was used to study the solubility of pure and amino acid doped (L-Glutamic acid, L-Tartaric acid) for three different temperatures 35, 40 and  $45^\circ\text{C}$ . A sealed container charged with millipore water and the solute, maintained at a constant temperature, was used to determine the equilibrium concentration [13]. The solution was stirred continuously for 24 hours. The content of the solution was analyzed gravimetrically. Fig. 1 shows the solubility curve for TGS crystal at different temperatures.

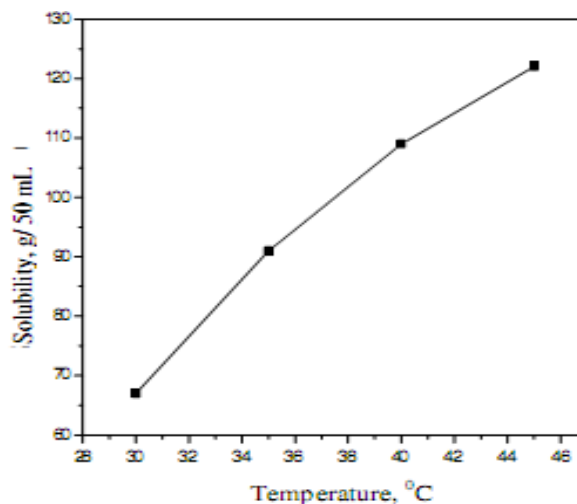


Fig. 1. Solubility curve solubility curve for pure TGS Crystal.

### 2.3 Metastable zone width measurements

A 100 ml glass beaker was used as nucleation cell. The nucleation cell was placed in a cryostat and the temperature was thermostatically controlled to an accuracy of  $\pm 0.05^\circ\text{C}$ . The solutions were stirred by means of a motor. Recrystallized salt of TGS and Millipore water were used in the present study [14]. Aqueous solutions of pure and doped TGS were prepared by dissolving the required amount of TGS salt in 100 ml of millipore water at a temperature slightly higher than their respective saturation temperatures. The solution was continuously stirred for at least 24 hours before use. The stability of the solutions was evaluated by means of the traditional polythermal measurements of the metastable zone. It was observed that metastable zone width decrease with increase of temperature as shown in the Fig. 2. In the polythermal method (Zaitseva et al 1995), the solution was cooled from the overheating temperature until a first visible crystal appeared in the volume or at the bottom of the crystallizer.

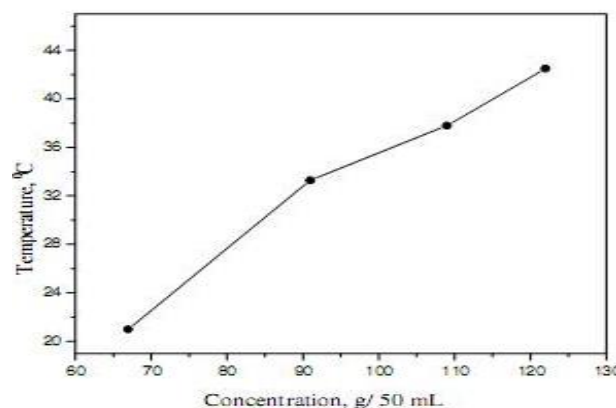


Fig. 2. Metastable zone width curve for pure TGS.

### 3. Thermal studies on amino acids doped Tgs crystals

To analyze the thermal stability and to confirm the melting point of the material, the Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out using PL-STA 1500 thermal analyzer at a heating rate of  $20^{\circ}\text{C min}^{-1}$  in air.

There are two stages of decomposition of the pure TGS crystal (Fig. 3). The crystal is thermally stable upto  $226^{\circ}\text{C}$ . The first stage of decomposition of the crystal begins from  $240^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ . The TG trace of the crystal shows weight loss of 11.66% in the first stage of decomposition and it corresponds to the evolution of hydrogen gas. The decomposition temperature of the second stage ranges from  $251^{\circ}\text{C}$  to  $296^{\circ}\text{C}$ . In the second stage of decomposition, 75 % of the sample is decomposed. The oxygen and carbon gases have been evolved in the second stage leaving behind sulphur which remains as the residue. A residual mass of 12.75 % remains undecomposed.

Fig. 4 shows that L-Glutamic acid doped TGS melts at a temperature around  $125^{\circ}\text{C}$  and it undergoes in irreversible endothermic transition around  $210^{\circ}\text{C}$  followed by another endothermic occurred at  $290^{\circ}\text{C}$ . The TGA curve shows that there was a weight loss of about 13 % in the temperature range  $190^{\circ}\text{C} - 350^{\circ}\text{C}$  due to the liberation of volatile substances, probably carbon dioxide or ammonia. Prolonged heating up to  $900^{\circ}\text{C}$  does not produce any endothermic peaks in the DTA curve and TGA shows a total weight loss of only 13 % at  $900^{\circ}\text{C}$ .

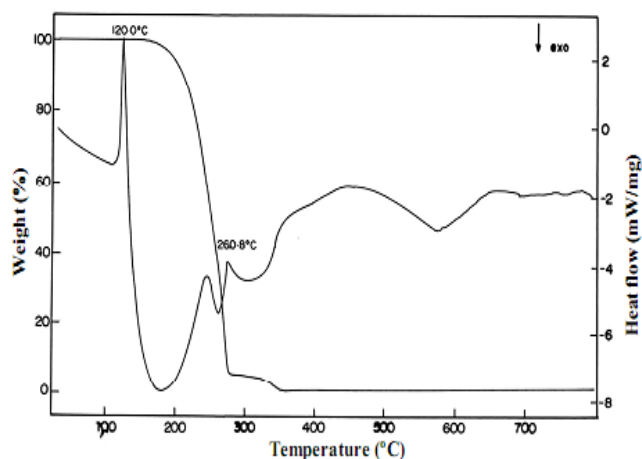


Fig. 3. TG-DTA curve of pure TGS crystal.

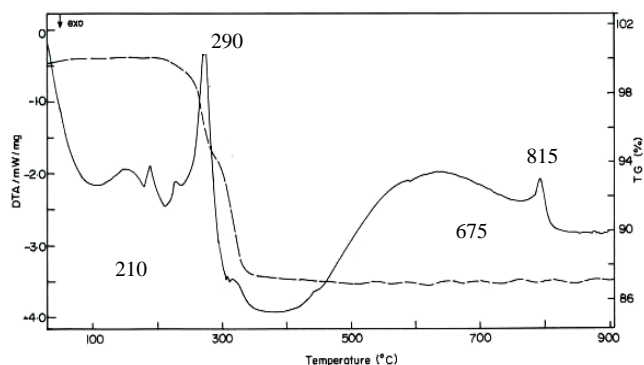


Fig. 4. TG-DTA curve of amino acid (L-Glutamic acid) doped TGS crystal.

DTA studies were carried out on amino acid (L-Tartaric acid) doped TGS single crystals. Powder samples were prepared by crushing single crystal using mortar and pestle. Experiments were performed using simultaneous TG-DTA (SETRAM STA 409C) analysis by heating the sample at  $20^{\circ}\text{C/min}$  in the temperature range between 25 and  $900^{\circ}\text{C}$  under nitrogen atmosphere. The DTA curve (Fig. 5) of L-Tartaric acid doped TGS shows major peaks at 106, 192, 205.4, 272.6 and  $770^{\circ}\text{C}$  respectively. However the DTA curve reveals two more events at 560 and  $798^{\circ}\text{C}$  respectively and these peaks are not accompanied by the weight loss. They might be attributed to high temperature phase transition of TGS. In addition, a significant splitting appears in the DTA peak at  $192.1^{\circ}\text{C}$  [15].

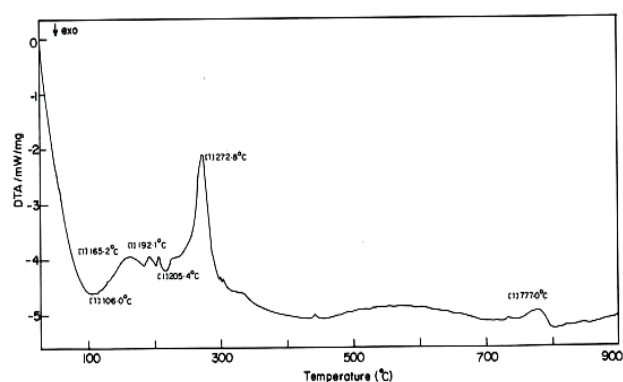


Fig. 5. DTA curve of amino acid (L-Tartaric acid) doped TGS crystal.

The satellite peak might correspond to the low temperature structural phase transition of TGS. DTA results of L-Tartaric acid doped (0.1 mol %) TGS samples are very much comparable with the pure TGS results except small deviations in the peak positions. Another significant observation was that the intensity of the major peak ( $272.6^{\circ}\text{C}$ ) which splits into two peaks reversal when compared to pure samples. The results suggested that the phase stability of the L-Tartaric doped TGS might have

been improved when compared to the pure TGS sample that occurred in a higher decomposition temperature. The total mass loss was 2.774 % and comparable to pure TGS sample contrary to the above results.

The L-Glutamic acid doped TGS sample do not show any splitting in the major DTA peak (290° C) at least up to the resolution limit of the instrument. The above results were very significant in two different aspects (i) that the dopant L-Tartaric acid is actually substituted in the crystal lattice. (ii) The result suggests the TGS phase stability improved in the presence of L-Glutamic acid. However, further studies with various doping level is required for conforming their observations. Fig. 2 shows that the loss of water molecule occurs at 106° C, it was exothermic reaction and crystallization of salt occurs at 272.6° C and decarboxylation from doped TGS occurred at 205.4° C, these are due to exothermic reactions.

#### 4. Dielectric studies on pure and amino acids doped TGS crystals

The extended portions of the crystals were removed completely and the crystals were more ground to proper thickness and polished. Each sample was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A 4279A, multi frequency LCR meter (Hawlett-Packard) was used to measure capacitance (C) of the sample as a function of frequency.

Fig. 6 shows the variation of dielectric constant with frequency measured at room temperature for Pure, L-Glutamic acid and L-Tartaric acid doped TGS crystals. The dielectric constants were maxima at low frequency and decreases with increase in frequency. L-Tartaric doped crystals have higher dielectric constant for purer and other dopants. The increase in the dielectric constant at low frequency is attributed to space-charge polarization (Munn and Ironside 1993).

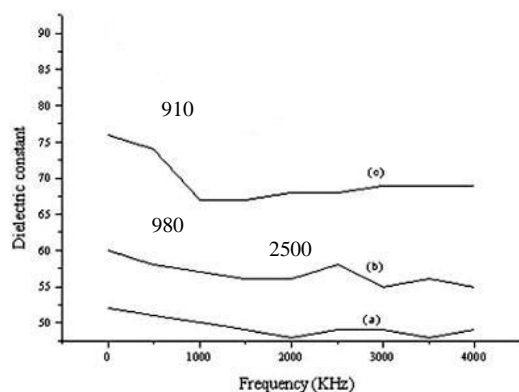


Fig. 6. Dielectric studies on (a) Pure TGS (b) L-Glutamic acid doped TGS crystal and (c) L-Tartaric acid doped TGS crystal.

#### 5. Results and discussion

The number of nuclei appearing in a unit volume per unit time depends very strongly on supersaturation and there exists a critical supersaturation below which there is practically no nucleation, and above which nucleation proceeds vigorously enough to be detected experimentally. This critical deviation from equilibrium defines the metastability boundary. The doping of amino acids (L-Glutamic acid, L-Tartaric acid) affects the basic growth parameters. It is observed that the solubility decreases while doping. This is in accordance with the common ion effect, where reducing the solubility accelerates the growth process. The results are the average of three reproducible observations. The introduction of dopants in the TGS solution has enhanced the rate of formation of nuclei; which in turn has decreased the metastable zone width.

In Triglycine sulphate, glycine is one of the amino acids. The substitution of another amino acid, L-Glutamic acid 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 L-Tartaric acid 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.

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 L-Glutamic acid, L-Tartaric acid were added to the saturated TGS aqueous solution till the equilibrium was achieved; the equilibrium concentration of these additives at 40° C were found to be in the range 5-6 g/100 ml for L-Glutamic acid, L-Tartaric acid in saturated TGS solution. The pH of the solution was then adjusted to 2.4. 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 into the crystallizer. After completion of the growth run, the crystals were removed from the solution and slowly cooled to room temperature

A projection of the crystal structure of TGS along the c-axis shows the (010) face to be constructed from layers of glycine and sulphate units, with alternating layers of glycine. These layers are linked c- in the [010] direction by hydrogen bonds between the glycine and sulfate units in adjacent layers. The doping of crystals affects the growth rate and morphology. In the case of L-Tartaric doped TGS crystal the growth rate in the [101] direction was restrained, leading to a wide (101) plane; the crystal was thinner than pure TGS. While doping with L-Glutamic acid growth rate along (010), (001) and (100) were less compared to that of pure TGS crystal. The

doping of L-Glutamic acid, L-Tartaric acid affects the possible replacement of the glycine molecule in the TGS thereby affecting the growth rate. The L-Tartaric acid molecules that are bigger in size than glycine molecules are difficult to substitute in glycine site thereby giving rise to a lesser growth rate. In the case of L-Glutamic acid doped TGS (ATGS) crystal, a series of strains are seen on one side of the [010] direction. This is attributed to the asymmetry of the L-Tartaric acid molecules, which are bigger in size than that of the glycine molecules and difficult to be incorporated in the glycine site.

## 6. Conclusion

The solubility and stability of pure and amino acid doped TGS crystals have been experimentally investigated. It has been found that while doping with amino acids both the solubility and stability were reduced. This has been attributed to the increase in the rate of formation of nuclei while doping with amino acids. The effect of seeds of different orientations on the habit of the crystal has been investigated. It has been found that while using a (001) seed the crystal ends with a wide b-plane - a suitable one for IR imaging applications.

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