Growth and Characterization of Pure and Phosphoric Acid Doped Triglycine Sulfate Crystal by the S-R Method

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In the present work, triglycine sulfate (TGS) and phosphorus-doped TGS (TGSP) crystals were grown from an aqueous solution by a new technique called the S-R method. XRD spectra of the grown crystals were used to determine their crystal parameters. Optical transmission of the TGSP crystal was found to be higher than that of the TGS crystal. Fourier transform infrared spectroscopy (FTIR) studies of the grown crystals confirmed the functional groups present in the samples. Raman spectroscopy was employed to investigate the presence of phosphate ions in the grown TGSP crystal. Hardness determination of the crystals revealed a lower value for TGSP compared to TGS. Surface etching of the crystals were carried out, and the etch pits appearing on the TGSP crystal surface were found to be deeper and larger than those appearing on the TGS crystal surface.

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I. INTRODUCTION

Triglycine sulfate (TGS) crystal (\((\text{HCHNH}_2\text{COOH})_3\cdot\text{H}_2\text{SO}_4\)) is one of the well known ferroelectric materials which shows a second order ferroelectric transition at the Curie temperature of 49 °C [1]. At \(T > T_c\) the crystal structure is centrosymmetric, and in the paraelectric phase it shows 2/m monoclinic symmetry. The crystal belongs to the polar group 2 of the monoclinic system at \(T < T_c\). In this state, the crystal is in a ferroelectric phase and polarizes along the \(b\) axis [2]. Lattice constants of this crystal are \(a = 9.40\ \text{Å}, \ b = 12.62\ \text{Å}, \ c = 5.71\ \text{Å}, \ \text{and} \ \beta = 110^\circ 32'\) [3].

TGS crystal is an important material due to its ferroelectric property at room temperature which makes it suitable for infrared detection [4]. phosphorus-doped TGS (TGSP) hat is TGSP? Please explain. crystal is a ferroelectric material with a Curie temperature of 51 °C and is suitable for use in infrared detectors at room temperature. It has a monoclinic structure in both the ferroelectric and paraelectric phases. The replacement of sulfate ions by phosphate ions during the crystallization of TGSP crystal decreases the presence of microscopic impurities and prevents depolarization due to a lapse of time. It has been shown that TGSP crystal is a suitable material for pyroelectric applications [3]. This crystal has

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been grown by conventional solution growth methods [2, 3].

In the present investigation, a new solution growth method called S-R, after the names of Sankaranarayanan and Ramsamy, has been employed to grow TGS and TGSP single crystals along the 001 direction. The S-R method has several advantages over other conventional solution growth methods, such as the possibility to grow crystals unidirectionally and the ability to convert 100% of the solute to crystal. This reduces the amount of the solution necessary to grow a crystal in comparison with the conventional method, in which a large quantity of solution is normally used. This method has been used to grow a number of crystals such as benzophenon, KDP, and TGS [5–9]. The grown TGS and TGSP crystals were studied by XRD, UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, microhardness measurements, and chemical etching methods.

II. EXPERIMENT

II-1. Experimental set-up

The schematic diagram of the experimental set up is shown in Fig. 1. It consists of two ring heaters, one at the bottom (around the seed crystal) and the other at the top (around the solution surface) that provide the necessary temperature difference. The top heater provides the necessary temperature for solvent evaporation while the bottom one is kept at room temperature. The later one was moved upwards depending on the growth rate of the crystal. Each of the heaters was connected to a temperature controller equipped with a thermocouple to set the desired temperature. The entire S-R set-up was placed in a water bath in order to avoid thermal fluctuations.
II-2. Growth of pure TGS crystal

TGS solution was made by mixing glycine and sulfuric acid in the molar ratio of 3:1. The following is the chemical equation [10].

$$3(\text{NH}_2\text{CH}_2\text{COOH}) + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4.$$ 

For synthesizing TGS material, room temperature solution evaporation method was used. According to the solubility curve, the amount of TGS material needed for preparation of the saturated solution at room temperature was dissolved in deionized water. Therefore, based on the above reaction, the required amount of glycine and sulphuric acid was calculated and the solution was prepared. After filtration by filter paper, the prepared solution was placed at room temperature in a dust free place. The container surface was covered by a cellophane paper and the solution was allowed to evaporate through small pores made on it. After one week, transparent TGS crystals grew, out of which a suitable one was selected to be used as a seed. Figure 2 shows the selected seed.

![TGS seed crystal](image)

FIG. 2: TGS seed crystal.

Initially, the (001) face of the seed was cut and polished to the size of the bottom of the ampoule. It was then mounted in such a way that the (001) face was facing towards the saturated solution of TGS. The TGS saturated solution in deionized water at 28 °C was transferred into the growth vessel after filtration using a membrane filter of 0.45 µm porosity. The initial temperature of the top and bottom portions of the ampoule were set as 31 and 28 °C, respectively. A small hole was made on the cover of the ampoule for evaporation of the solvent. A cylindrically shaped TGS crystal with 20 mm diameter and
120 mm length was grown in the [001] direction within 40 days. Figure 3 shows the as grown and the cut and polished TGS crystal.

FIG. 3: TGS crystal grown by the S-R method, a) as grown, b) cut and polished ingots.

III. GROWTH OF H₃PO₄ ADDED TGS (TGSP) CRYSTAL

A suitable seed crystal from those prepared for the growth of pure TGS crystal was selected and inserted at the bottom of the ampoule in such a way that its (001) plane was facing towards the saturated solution of TGSP. The required solution for TGSP growth was prepared according to following chemical composition [2].

\[3\text{NH}_2\text{CH}_2\text{COOH} + (1-x)\text{H}_2\text{SO}_4 + x\text{H}_3\text{PO}_4 \rightarrow (\text{NH}_2\text{CH}_2\text{COOH})_3(\text{H}_2\text{SO}_4)_{1-x}(\text{H}_3\text{PO}_4)_x\]

where \(x\) represents phosphoric acid molar portion in solution. In this study, the molar ratio is estimated (calculated) as \(x = 0.25\).
For preparing this solution, the weighted amounts of glycine, sulfuric acid, and phosphoric acid were dissolved in deionized water with molar ratios of 0.25 : 0.75 : 3. Then, the TGSP solution saturated at room temperature was slowly added to the growth ampoule after filtration with a membrane filter of 0.45 µm porosity. The temperature of the bottom ring was set to 27 °C (room temperature) while the upper one was set to 4 °C higher. A small hole was made on the cover of the ampoule for evaporation of the solvent. Solvent evaporation from the solution surface provided the growth condition for the seed. After 35 days, a cylindrically shaped TGSP crystal with 20 mm diameter and 100 mm length grew in the [001] direction. Figure 4 shows the as grown TGSP crystal inside the ampoule as well as the cut and polished samples.

FIG. 4: TGSP crystal grown by S-R method (a) inside growth ampoule, (b) cut and polished ingots.
IV. RESULTS AND DISCUSSION

IV-1. Powder X-ray diffraction analysis

The TGS and TGSP crystals were analyzed by the X-ray diffraction (XRD) technique using an X-ray diffractometer (Advance Model D8) with high intensity CuKα radiation ($\lambda = 1.5406$ Å), and the collected data were used to estimate the lattice parameters which are presented in Table I. The data reveal a monoclinic structure for the grown crystals. The lattice parameters of the two crystals show a significant difference in spite of the low incorporation of H$_3$PO$_4$ into the crystal lattice. Similar observations on alanine and phosphate added TGS crystals have been reported by others [11, 12]. It is clearly seen in the table that the lattice parameters of TGS crystal decreased upon doping with H$_3$PO$_4$ while the monoclinic angle $\beta$ increased. Figure 5 represents the XRD patterns of pure and H$_3$PO$_4$ added TGS crystals.

**TABLE I: Lattice parameters of the TGS and TGSP crystals.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS</td>
<td>9.37</td>
<td>12.63</td>
<td>5.72</td>
<td>110.31</td>
</tr>
<tr>
<td>TGSP</td>
<td>9.33</td>
<td>12.61</td>
<td>5.66</td>
<td>110.65</td>
</tr>
</tbody>
</table>

IV-2. Optical transmission studies

Figure 6 presents a comparison between the transmittance of 1 mm thick [001] directional TGS and TGSP crystals measured by a Shimadzu spectrophotometer model UV-1650 pc for the wavelength range 200–1100 nm. From the spectrum, it is observed that the transmittance percentage of the TGSP crystal is higher than that of the TGS crystal. The lower UV-cutoff wavelength is around 226 nm. The same cutoff wavelength was reported by Pandian et al. [13] for pure TGS crystal grown by the S-R method but with lower transmission (< 65%) compared to the present work.

V. FOURIER TRANSFORM INFRARED ANALYSIS (FTIR)

TGS and TGSP crystals were studied using a Shimadzu FTIR model 8400 spectrophotometer in order to analyze the presence of the H$_3$PO$_4$ dopant in the TGSP sample qualitatively. The crystals were powdered and mixed with KBr pellets for obtaining the FTIR spectra. Figures 7(a) and 7(b) display the FTIR spectra of the TGS and TGSP crystals, respectively. The pure TGS crystal shows a broad and strong absorption band in the range 2300–3800 cm$^{-1}$ for the O-H stretching of hydrogen bonded carboxyl groups and the N-H stretching of the NH$_3^+$ group. The C=O stretching vibration of the carboxyl group appears as a sharp band at 1707 cm$^{-1}$. The C-H bending vibration appears at 1620 cm$^{-1}$. The N-H bending vibration is present at 1499 cm$^{-1}$. A strong band at 1350 cm$^{-1}$ arising
from C-O stretching is also observed. The asymmetric and symmetric S=O stretching frequencies can be assigned to frequencies 1424 and 1620 cm\(^{-1}\), respectively. The torsional oscillation of the NH\(^3+\) group appears at 62.99, 57.12, and 50.5 cm\(^{-1}\).

It is observed from Fig. 7(b) that the IR spectrum of the TGSP crystal closely
FIG. 6: Transmission spectra of TGS and TGSP crystals.

resembles that of the TGS crystal, suggesting that the crystal structures of the two crystals are similar [14]. In addition, two more peaks in the FTIR diagram of TGSP crystal, marked as O and P, appearing at 441.5 and 468.10 cm\(^{-1}\) are observed. Socrates has suggested that these additional peaks are due to bending vibrations of the phosphorus and oxygen bonds, which clearly confirms the presence of phosphorus in the TGSP sample [15]. Therefore, it can be deduced that phosphate ions are present in the crystal lattice.

In order to more precisely investigate the presence of PO\(_4\) ions in the grown TGSP crystal, Raman spectroscopy was carried out on this sample.

VI. RAMAN SPECTROSCOPY

. Figure 8 represents the Raman spectrum of the TGSP sample. Two relatively high and intense peaks are observed at 961 cm\(^{-1}\) and 962 cm\(^{-1}\), which may be related to the vibration modes of the PO\(_4\) and SO\(_4\) ions, respectively. The peak appearing at 1027 cm\(^{-1}\) is also due to a vibration mode of PO\(_4\) ions. SO\(_4\) ion vibration modes are observed at 431 cm\(^{-1}\) and 627 cm\(^{-1}\). C-CO, C-O, and C-C bonds have appeared at 550 cm\(^{-1}\), 648 cm\(^{-1}\), and 874 cm\(^{-1}\), respectively. The stretching vibration of NH\(_3\) can be observed at 1027 cm\(^{-1}\), 1097 cm\(^{-1}\), and 1623 cm\(^{-1}\). The peak observed at 1421 cm\(^{-1}\) is due to the symmetric vibration of CO\(_2\). The vibration modes due to CH\(_2\) binding appear at 1448 cm\(^{-1}\), 3142 cm\(^{-1}\), 3022 cm\(^{-1}\), 2968 cm\(^{-1}\), and 2737 cm\(^{-1}\). The C=O vibration mode appears at 1663 cm\(^{-1}\). Therefore, Raman studies of the TGSP sample help to reveal the
FIG. 7: FTIR spectra of (a) TGS and (b) TGSP crystals.

presence of phosphate ions in the grown crystal.

VII. MICRO-HARDNESS MEASUREMENTS

Vicker’s microhardness indentations were made on the selected surfaces of the grown crystals of TGS and TGSP at room temperature (27 °C) using a Buehler hardness tester with the loads of 10, 25, and 50 g. Each load was used to make an indentation several times in order to obtain an average value for the microhardness, $H_v$, using the following equation:

$$H_v = 1.8544P/d^2 \text{ (kg mm}^{-2}\text{)},$$

where $H_v$ is the Vicker’s microhardness number, $P$ is the applied load and $d$ is the diagonal length of the indentation impression. The value 1.8544 is a geometrical constant factor for the diamond pyramid. Multiple cracks were observed to develop around the indentation mark when applying test loads above 25 g. Figure 9 shows the load dependence of the
microhardness of the TGS and TGSP crystals of the [001] face. TGS crystal is found to be harder than TGSP crystal. Ravi et al. have reported the same observation and stated that the decrease in the microhardness was proportional to the phosphate ion concentration in the TGSP crystal [16]. The lower hardness number of TGSP can be attributed to the loosely packed lattice on phosphate substitution. This in turn, is due to the higher solubility of TGSP in water.
VIII. ETCHING STUDIES

The etching studies revealed the structural perfection and growth features of the grown TGS and TGSP single crystals. The [001] face of TGS and TGSP crystals were subjected to etching with deionized water as etchant at room temperature. For this purpose, the surface of the crystal was completely immersed in water etchant for 10s. Figures 10(a) and 10(b) show the TGS and TGSP crystal planes after etching. Generally, after chemical etching of a crystal plane, some areas of hollow and projection are seen on the surface called etch pits and etching spots, respectively [17]. The etch pits which appeared on the TGSP surface were deeper and larger than those on the TGS crystal surface, indicating that the solubility of TGS has been increased by the presence of the phosphoric acid additive.

FIG. 10: (a) TGS and (b) TGSP crystal planes after etching.

IX. CONCLUSIONS

The pure and H$_3$PO$_4$ added TGS crystals were grown by the S-R method in the [001] direction. Lattice parameters of the grown crystals have been calculated from powder X-ray diffraction studies. The transmission spectrum showed that both the crystals were highly transparent in the entire UV-Vis region. TGSP crystal showed higher transmittance than TGS. FTIR analysis revealed the functional groups present in the samples. Phosphorus and oxygen bonds were distinguished in the FTIR spectrum of TGSP crystal confirming the presence of the H$_3$PO$_4$ dopant in the sample. Raman spectroscopy of the TGSP samples also confirmed the presence of phosphate ions in the doped sample. TGSP crystal showed lower hardness than TGS, which is attributed to the reduction in the interatomic binding in the phosphate-substituted crystal. The etch pits which appeared on the TGSP crystal surface were deeper and larger than those appearing on the TGS crystal surface, which indicates that the solubility of TGS has been increased by the presence of the phosphoric acid additive.
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References