CHAPTER 3

GROWTH AND CHARACTERIZATION OF ADP ADMIXTURED TGS CRYSTALS

3. 1 Introduction

Ferroelectric materials are the important class of electronic materials having wide application in the electronic and optical industries such as fabrication of capacitors, detectors, transducers and sensors. The pyroelectric properties of ferroelectric materials make them more suitable for thermal detectors. With increasing demand for pyroelectric detectors, growth of single crystals of pyroelectric detector material in bulk becomes inevitable. Triglycine sulphate crystal \([(\text{NH}_2\text{CH}_2\text{COOH})_3\cdot\text{H}_2\text{SO}_4, \text{TGS}]\) is a well known pyroelectric material which has been studied intensively, and is used in infra-red detection techniques as commercial products (Sun et al 1999, Amin et al 1984, Loiacano et al 1982). It also finds applications in burglar alarms, medical vidicons, FTIR instrumentation, earth observation camera and in pyro-electric detector. Even though TGS has a complex chemical and crystallographic structure, it becomes the material of active research for two reasons.

(i) It is one of the few ferroelectrics, which exhibit second order phase transition. It offers the possibility of observing the critical phenomena very close to the phase transition temperature.

(ii) It is an order-disorder type ferroelectric material.
TGS crystal is monoclinic below and above the Curie temperature (49°C) and has a second order ferroelectric phase transition at the Curie point and it is an order disorder type ferroelectric (Sun et al 1999). The cell parameters are $a = 9.1583\text{Å}$, $b = 12.6445\text{Å}$, $c = 5.7254\text{Å}$ and $\beta = 105.53^\circ$ (Meera et al 2000). Above the Curie point, it belongs to centrosymmetric point group $P2_1/m$ of the monoclinic system and hence the spontaneous polarization is lost. Below $T_c$, spontaneous polarization $P_s$ arises along the b-axis, putting it into the polar point group $P2_1$ of the monoclinic system. The molecular mechanism for the ferroelectric transition was explained on the basis of glycine molecules present in the lattice (Lines and Glass 1977). The possibility of hydrogen bonds involved in phase transition is less significant since deuterization has no effect on the dielectric properties. But the dominant role in the transition is more likely due to the dynamics of nitrogen atom in the glycine-I molecules. The unit cell of TGS is constructed through the coupling of hydrogen bonds between three glycine molecules and hence coupled modes can be a more likely mechanism. TGS family crystals possess equal number of positive and negative domains well below $T_c$ and macroscopically the mirror plane exits. TGS crystals possess a natural cleavage plane perpendicular to the b-axis, which is the polar axis. Spontaneous polarization strength and pyroelectric coefficient of TGS crystal depends on the growth rate along the polar axis (Arunmozhi et al 1998). Thus cleaved sections give proper orientation for use in infrared detectors and pyroelectric vidicons.

3.2 Crystal structure of TGS

The ferroelectric activity of TGS was discovered by Matthias et al (1956). Glycine commonly crystallizes in two forms. One is a structure in which two carbon atoms and two oxygen atoms are approximately coplanar, while the nitrogen atom is significantly displaced out
of plane. In the other structure, all carbon, nitrogen and oxygen atoms are close to planar. The first detailed investigation on the crystal structure was carried out by Hoshino et al (1959) using three dimensional X-ray diffraction data shown in figure 3. 1.

Fig. 3. 1 Crystal structure of TGS viewed along c-axis
The molecular group of glycine crystallizes as asymmetric units, of which two assume a complete planar configuration and third assumes a partial planar configuration. The two planar groups, glycine-II and glycine-III are connected by a hydrogen bond between oxygen atoms and are perpendicular to the polar axis (b-axis), which is responsible for the ferroelectric property. Above the Curie temperature, polarization reversal associated with the rotation of glycine-I group about the crystallographic a-axis occurs (Whatmore 1986). The completely planar groups are monoprotonated, having taken the protons from the H$_2$SO$_4$, and they are best designated as glycinium ions, while the partial planar group (GII) assumes the Zwitter ion configuration. Hence this compound has got another name as glycine di-glycinium sulphate with the chemical formula \((\text{NH}_3^+\text{CH}_2\text{COO}^-)(\text{NH}_3^+\text{CH}_2\text{COOH})_2\text{SO}_4^{2-}\). In the case of deuterated TGS, it is not possible to completely replace the hydrogen with deuterium. There are seventeen hydrogen atoms in each TGS molecule. Among the seventeen, eleven are active except the six which are in contact with the carbon atom. These eleven active hydrogen atoms can be substituted with deuterium (Fang et al 1989).

3.3 Nature of transition in TGS

The phase transition in TGS is order-disorder type transition. The basic feature of an order-disorder type of transition is the existence of rotatable dipoles, or ions with two equilibrium positions, which become ordered below a critical temperature (Jona and Shriane 1962). A qualitative picture of the phase transition dynamic was proposed by Itoh and Mitsui (1973). The resonance frequencies suggest that above $T_c$, glycine II and glycine III are chemical equivalents. These points to the fast exchange of the glycinium-glycine roles of these two ions owing to proton transfer in the symmetric double-well of the hydrogen bond. Below $T_c$,
glycine II and glycine III become inequivalent as the proton minima develop unequal depths. Above $T_c$, glycine I in all probability describes a thermally activated hopping motion between equivalent potential wells on either side of the b-mirror plane. This motion carrying most of the polarization is therefore of order-disorder character. Below $T_c$, the pseudo centres of symmetry and pseudo mirror plane disappear. The sites of glycinium II and glycinium III are not equivalent. The polar glycine I occupies one of its possible sites preferentially, producing dipole moment in the ‘b’ plane.

3.4 Effect of dopants in TGS family crystals

Ferroelectric properties of TGS have been found to be influenced by many dopants. Single crystals of solid solution such as TGFb : DTGFb, TGSe : DTGSe, TGS : TGSe have been extensively studied (Keve et al 1971, Bye et al 1974, Loiacano et al 1982, Amin et al 1984). Cesium added L-alanine doped TGS crystals has been reported to be a promising material for infrared applications (Banan et al 1992). Ferroelectric behavior of TGS in the presence of metal ions like $\text{Cu}^{2+}$, $\text{Mg}^{2+}$ and $\text{Cr}^{3+}$ was studied by Gaffar et al 1989). The effect of divalent ions doping in TGS resulted in decrease in the energy gap of doped crystals (EI-Fadl 1999). Doping of cobalt (II) phosphate in TGSP crystal resulted in good quality crystal with stabilized domain structure (Prokopova et al 2001). The presence of rare earth ions like Ho, Tm and Yb in TGS solution resulted in the decrease of $T_c$ (Mihaylova et al 1996). The growth and ferroelectric properties of EDTA added TGS have been investigated by Meera et al (2005). In the case of light rare earth ion doping, the crystal structure remains unaltered (Mihaylova and Byrne 2000). A systematic study has been made on the growth, morphology and ferroelectric properties of TGS crystals doped with light rare earth ions like La, Ce and Nd (Muralidharan et al 2002).
Deuterated TGS crystals have also been studied extensively and it has been found that deuteration increases the coercive field making the switching process more difficult (Drozhdin and Kuyantsev 1998). Growth and characterization of L-tyrosine, thiourea, guanidine, I-threonine, dl-threonine and I-methionine doped TGS crystals have been studied extensively (Meera et al 2000, Meera et al 2004, Sun et al 1999, Meera et al 2004).

In triglycine sulphate, glycine itself is one amino acid. The substitution of another amino acid in the place of glycine has been found to improve the crystal properties by contributing to internal bias in these crystals, which in turn, inhibit ferroelectric switching, giving a permanently poled single domain crystal. Many authors have investigated the effect of various amino acids on TGS crystals. The effect of various amino acids like L-alanine (Bye et al 1972, Nakatani 1990, Aravazhi et al 1997a), L-valine (Aravazhi et al 1997b), L-arginine, L-asparagine (Arunmozhi et al 1997) and L-aniline (Ravi et al 1995) on TGS showed improvement in the ferroelectric properties of the TGS crystals. Effect of rare-earth metal dopants on the growth and properties of TGS single crystals was studied by Muralidharan et al (2002). Amino acids with structure similar to glycine have been doped with TGS and the resultant crystal showed improved ferroelectric properties (Ravi et al 1995). Growth aspects of ADP admixed TGS crystals have been reported in our earlier work (Balu et al 2007). Growth of 20 mole % ADP doped TGS single crystals using slow cooling technique was studied by Arunmozhi et al. (2002), hitherto no reports on the growth of ADP admixed TGS single crystals by slow evaporation technique. In the present studies, various weight percentage of ADP was added in TGS and crystals were grown in the ferroelectric phases by a slow evaporation technique. This investigation was carried out to study the effect of antiferroelectric ADP of different concentration on the growth, structural, optical, mechanical and dielectric properties of TGS crystal.
3. 5 Material Synthesis

Triglycine sulphate [TGS, \((\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4\)] is colourless, odorless and acidic. Its density is 1.65 g/cm\(^3\). TGS was synthesized (Matthias et al 1956) by taking analar grade glycine (\(\text{CH}_2\text{NH}_2\text{COOH}\)) and concentrated sulphuric acid (\(\text{H}_2\text{SO}_4\)) in the molar ratio 3:1. The required volume of concentrated sulphuric acid was diluted with triple distilled water. Then the calculated amount of glycine was added and dissolved in diluted \(\text{H}_2\text{SO}_4\). Glycine reacts with sulphuric acid as follows:

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

This solution was heated until the salt crystallizes. Extreme care was taken during crystallization of the salt to avoid oxidation of glycine and the solution temperature was maintained below 50°C. The crystallized salt was further purified by successive recrystallization process.

3. 6 Growth of ADP admixed TGS crystals

A saturated solution of TGS at 35°C was prepared using twice recrystallized salt. The solution was filtered using a high quality Whatman filter paper. Then, 5, 10 and 15wt % of ADP were added to the TGS saturated solutions in separate containers. The solutions were loaded in the constant temperature bath set at 35°C. Slow evaporation technique was employed for the growth. Transparent single crystals were harvested from the mother solution after a typical growth period of 20 days. The TGS crystals grown with ADP of concentration 5, 10 and 15wt % in TGS solution have been hereafter called as ADPTGS (5wt %), ADPTGS (10wt %) and ADPTGS (15wt %). As grown crystals of pure and ADP admixed TGS crystals are shown in
figures 3.2 and 3.3 respectively. The grown crystals were subjected to structural, optical, dielectric and mechanical studies.

![As grown crystal of pure TGS](image)

**Fig. 3.2 As grown crystal of pure TGS**

![As grown crystals of ADPTGS](image)

**Fig. 3.3 As grown crystals of (a) ADPTGS (5wt %); (b) ADPTGS (10wt %); (c) ADPTGS (15wt %).**
3. 7 Characterization studies

Characterization of the grown crystals facilitates the assessment on the quality of crystal and their feasibility for device applications. TGS, being a technologically important material, has elicited a large degree of characterization studies. Extensive studies have been made on these crystals in order to improve the physical, chemical, optical, mechanical and dielectric properties. The crystallinity of the grown crystals has been verified by powder XRD. The calculated lattice parameter values from powder XRD pattern are in good agreement with the single crystal XRD data, which are in very good agreement with the reported literature values (Hoshino et al 1959). The infrared spectra were taken using JASCO FTIR-410 spectrophotometer using KBr pellet technique to analyse qualitatively the presence of ADP in the sample. Transparent and good quality crystals were selected for optical transmission and dielectric studies. A Varian Cary 5E UV-Vis-NIR spectrophotometer had been used for spectral transmission studies. Dielectric measurements were carried out by conventional two probe method using a LCR bridge in the temperature range 35-65°C at a constant frequency of 1 kHz. Microhardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indenter.

3. 8 Results and discussion

3. 8. 1 Single crystal XRD analysis

Nonius CAD-4 / MACH 3 diffractometer, with MoKα radiation (λ=0.71073 Å) was employed to obtain the accurate cell parameters of pure and ADP admixed TGS crystals at room temperature. These were obtained from least-squares refinement of the setting angles of 25 reflections. The dimensions of the single crystal used for the analysis were of the order of
0.3 mm × 0.3 mm × 0.3 mm. From the data, it is observed that pure and ADPTGS crystallizes in monoclinic system and the calculated unit cell parameters are listed in Table 3.1.

Table 3.1

Lattice parameter values of pure and ADP admixed TGS crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TGS</td>
<td>9.159</td>
<td>12.624</td>
<td>5.723</td>
<td>105.59</td>
<td>661.71</td>
</tr>
<tr>
<td>ADPTGS (5 wt %)</td>
<td>9.133</td>
<td>12.615</td>
<td>5.735</td>
<td>105.56</td>
<td>660.745</td>
</tr>
<tr>
<td>ADPTGS (10 wt %)</td>
<td>9.161</td>
<td>12.635</td>
<td>5.73</td>
<td>105.58</td>
<td>663.243</td>
</tr>
<tr>
<td>ADPTGS (15 wt %)</td>
<td>9.169</td>
<td>12.659</td>
<td>5.74</td>
<td>105.57</td>
<td>666.244</td>
</tr>
</tbody>
</table>

3.8.2 Powder XRD analysis

The purified samples of the grown crystals have been crushed to a uniform fine powder and subjected to powder X-ray diffraction using a Rich Seifert powder X-ray diffractometer. The Kα radiations from a copper target (λ=1.5406 Å) were used. The specimen in the form of a thin film was scanned in the reflection mode in the 2θ range 10-60° at a rate of 1°/minute. From the diffraction pattern the d – spacing and hkl values for each diffraction peak in the spectrum were identified. Figures 3.4a-d represents the powder diffractogram for the grown crystals. From the powder diffraction data, the lattice parameters have been calculated which are in close agreement with the values obtained from single crystal X-ray diffraction.
Fig. 3. 4a Powder XRD pattern of pure TGS

Fig. 3. 4b Powder XRD pattern of ADPTGS (5 wt %)
Fig. 3. 4c Powder XRD pattern of ADPTGS (10wt %)

Fig. 3. 4d Powder XRD pattern of ADPTGS (15wt %)
3. 8. 3 FTIR studies

Infrared spectrum is an important record, which provides more information about the structure of a compound (Kalsi 1985, Dyer 1987). In the present study, FTIR spectra of pure TGS and ADPTGS (15 wt %) were recorded in the range of 4000-400 cm\(^{-1}\) using KBr pellet technique and are presented in figures 3. 5a and 3. 5b respectively.

The FTIR spectrum of pure TGS crystal (Fig.3.5a) shows a broad envelope between 2100 and 3800 cm\(^{-1}\). It includes the OH stretch of hydrogen bonded carboxyl groups, the asymmetric stretching mode of NH\(_3^+\) at 3163.28 cm\(^{-1}\) and CH\(_2\) stretching mode just below 3000 cm\(^{-1}\). The broadening that extends between 2800 and 2200 cm\(^{-1}\) includes overlapping of bands due to the stretching modes of hydrogen bonded NH\(_3^+\) overtones and combination bands. The absorption at 1708.36 cm\(^{-1}\) is assigned to C=O stretching of \(-\text{COOH}\) group. The CH\(_2\) bending modes of glycine are located at 1425.90 cm\(^{-1}\). The NH\(_3^+\) displays its characteristic bending modes at 1425.9 and 1503.18 cm\(^{-1}\). The strong absorption in the range 1023 - 1130 cm\(^{-1}\) is evidently due to the sulphate part of the molecule. The peaks observed at 613.17, 570.54 and 501.26 cm\(^{-1}\) are due to NH\(_3^+\) oscillation.

The FTIR spectrum of ADPTGS (15 wt %) crystal is shown in figure 3. 5b. Although it provides similar features as that of pure TGS spectrum, there is shifting observed for all the peaks suggesting that there is wide range of interactions for the groupings. The disappearance of the peaks at 1708.36, 1870.91, 868.98 and 570.54 cm\(^{-1}\) in the doped one was observed when compared to the pure TGS crystal. This may be due to the incorporation of ADP or other impurities in the TGS crystal. In addition the overtone band is well resolved and sharp (2358.55 cm\(^{-1}\)) when compared to pure TGS spectrum.
Fig. 3. 5a FTIR spectrum of pure TGS

Fig. 3. 5b FTIR spectrum of ADPTGS (15wt % crystal)
3.8.4 Dielectric measurements

To study the effect of ADP doping on the ferroelectric properties of TGS, dielectric measurements were performed. The samples cleaved perpendicular to the polar axis (b-axis) was used and the plates were polished and coated with an electronic grade silver paste, which acts as an electrode. Thickness of the prepared samples was 1mm and 1-2 cm² area. Dielectric measurements were made in the temperature range 35-65°C at a constant frequency of 1 kHz. The dielectric constant $\varepsilon_r$ was calculated using the relation $\varepsilon_r = C_d / \varepsilon_o A$, where $C$ is the capacitance, $d$ is the thickness of the crystal, $\varepsilon_o$ is the vacuum dielectric constant and $A$ is the area of the crystal. Figure 3.6 shows the temperature dependence of dielectric constant for pure and ADP admixed TGS crystals.

![Fig. 3.6 Temperature dependence of dielectric constant for pure and ADP admixed TGS crystals](image)

Fig. 3.6 Temperature dependence of dielectric constant for pure and ADP admixed TGS crystals
The Curie temperature $T_c$ are estimated from the figure 3.6 as 49 °C, 48.5 °C, 48.25 °C and 48 °C for pure and ADPTGS (5 – 15 wt %) crystals respectively. The decrease in the permittivity of pure TGS due to ADP doping was identified. The decrease in the permittivity in ADPTGS from pure TGS can be ascribed to the clamping of domains and pinning of dipoles by the dopant and the availability of extra protons for charge compensation due to the phosphate substitution in the lattice. The dielectric constant is small at low temperature, which increases with temperature and rises sharply at the Curie point. The rapid increase may be due to the space charge polarization of thermally generated carriers. Above $T_c$, the dielectric constant decreases suddenly. No distinct change in the ferroelectric nature of phase transition could be observed due to the doping of ADP. However a shift in $T_c$ to a lower point has been found to increase with increasing impurity concentrations. The shift in the $T_c$ values indicates that the distribution of dopants leads to micro regions in the crystal with different transition temperatures.

3.8.5 UV-Vis-NIR spectral analysis

Pure and ADP doped crystals were cut by wet thread crystal cutting machine and polished. Subsequently thin platelet sample of thickness 5 mm were prepared from the grown samples and subjected to optical transmission studies. The recorded transmittance spectra in the wavelength range 200 - 1200 nm are shown in figure 3.7. At about 230 nm a sharp fall in the transmittance to zero is observed and the crystals have sufficient transmission in the entire visible and IR region. It can meet the requirements of conventional optical systems. A strong absorption peak corresponding to the fundamental absorption appears at $\lambda = 230$ nm. Using the formula $E_g = 1240 / \lambda$ (nm), the band gap is calculated to be 5.39 eV.
3.8.6 Vickers hardness studies

The structure and composition of the crystalline solids are inviolably related to the mechanical hardness. Microhardness testing is one of the best methods of understanding the mechanical properties of materials such as fracture behavior, yield strength, brittleness index and temperature of cracking (Lawn 1975, Westbrook 1958). The mechanical strength of the grown crystals was estimated using Leitz Weitzler hardness tester fitted with a diamond indenter attached to Leitz incident light microscope. A smooth, flat surface was selected and subjected to this study. Indentations were made for various loads from 5 g to 25 g. Several trials of
indentation were carried out on the prominent face and the average diagonal lengths were calculated for an indentation time of 10 seconds. The Vickers microhardness number was calculated using the relation

$$H_V = 1.8544 \frac{P}{d^2} \text{ kg/mm}^2,$$

where $P$ is the applied load, $d$ is the diagonal length of the indentation impression and 1.8544 is a constant of a geometrical factor for the diamond pyramid. For loads above 25 g, cracks started developing around the indentation mark. It is due to the release of internal stress generated locally by indentation. The variation of load vs Vickers microhardness number for pure and ADP doped TGS crystals are shown in figure 3.8.

![Vickers hardness versus load for pure TGS and ADPTGS crystals](image)

**Fig. 3.8** Vickers hardness versus load for pure TGS and ADPTGS crystals
It can be seen from figure 3.8 that in pure TGS crystal the hardness increases with increase of the load. For ADPTGS crystals the hardness decreases with increase of the load and with increase in concentration. This may be the result of loosely packed lattice with reduced bond energy due to the introduction of ADP into the crystal. Out of these doped crystals, ADPTGS (5wt %) crystals has greater Vickers hardness than other crystals.

3.9 Conclusions

Optical quality single crystals of pure and ADP admixed TGS were grown by slow evaporation technique at room temperature. FTIR spectra confirm the presence of functional groups and the dopant qualitatively. The grown crystals have been characterized for its structural and optical perfection using single X-ray diffraction, UV – Vis - NIR spectral analyses. Since no distinct change in the nature of ferroelectric phase transition is observed in ADPTGS, it can be concluded that the antiferroelectric properties of ADP do not have an influence on the ferroelectric properties of TGS and ADP acts more like an impurity or dopant. Shift in $T_c$ shows that inhomogeneous dopant incorporation leads to micro regions in the crystal growth sectors with different transition temperatures. Microhardness studies showed that the hardness value decreases with increasing load for ADPTGS crystals.