CHAPTER 3

Thermal properties of Glycine phosphite single crystals

3.1 Introduction

The α-aminoacid glycine forms addition compounds with several inorganic materials, especially inorganic acids. Some of them exhibit ferroelectric / ferroelastic phase transitions with interesting dielectric and elastic properties. The familiar ferroelectrics in this category include triglycine sulphate (TGS), triglycine selenate (TGSe), triglycine fluroberyllate (TGFB) etc. [1]. A few betaine compounds have also been investigated for their ferroelectric, antiferroelectric and ferroelastic properties. The most well studied in this class is betaine phosphite [(CH3)3NCH2COOH3P03] which exhibits atleast two phase transitions at 355K and 216K, with the lower temperature leading to a ferroelectric phase [2]. Glycine phosphite [NH3CH2COOH3PO3], abbreviated as GPI, is a recently developed ferroelectric crystal in this category, which has been explored for its ferroelectric phase transitions [3].

Glycine phosphite is a representative hydrogen bonded ferroelectric crystal of phosphorous acid with an aminoacid, similar to betaine phosphite. Both these crystals are characterized by a typical layered structure [3, 4]. These crystals belong to the monoclinic system with similar space groups $P2_1/a$ and $P2_1/c$ for GPI and BPI respectively. The main structural difference between GPI and BPI lies in that the phosphate chains are oriented parallel and perpendicular to the $b$-axis in BPI and GPI.
respectively. The GPI crystal has unit cell dimensions $a = 9.792 \text{ Å}$, $b = 8.487 \text{ Å}$, $c = 7.411 \text{ Å}$ and $\beta = 100.43^\circ$ and has four molecules per unit cell [3]. Spontaneous polarization of GPI appears along the $b$-axis.

The main structural feature of this crystal is that its atomic arrangement has a typical layer organization. Planes built by the phosphoric entities alternate with planes containing the organic group. These two layers develop parallel to the $bc$-planes and are separated by a distance of $a/2$. Inside the phosphoric layers, the $\text{H(HPO}_3\text{)}^-$ groups form an infinite chain along the crystallographic $c$-axis to which the amino acids are attracted by strong hydrogen bonds. The projection of the crystal structure, as viewed along the $b$-axis is given in Fig. 3.1. The phosphite anions are mutually linked by two kinds of strong double well potential hydrogen bonds (of lengths 0.2482nm and 0.2518nm) with equally populated wells at room temperature. The phosphite layers as interconnected by glycine ions forming three hydrogen bonds (of lengths 0.2861nm, 0.2875nm and 0.2899nm) to the phosphite oxygens via -NH$_3$ group from one side and single bond (of length 0.2598nm) via acidic oxygen from the opposite side.

Dielectric measurements performed on GPI crystal along the $b$-axis (polar axis for the monoclinic crystal) reveal a large anomaly in dielectric constant ($\varepsilon$) at 224.7 K, giving a clear indication of the transition temperature [5, 6]. The maximum value of spontaneous polarization $P_s$ along its polar axis is about $5 \times 10^{-23} \text{ Cm}^{-2}$, which is considerably smaller in comparison to other crystals of the family as BPI [2]. The $b$-axis of GPI is perpendicular to infinite chains of hydrogen bonded phosphite anions, similar to that observed in KDP family crystals [7]. Hence, the ordering of hydrogen bonds along the $c$-axis results in the appearance of
spontaneous polarization along the $b$-direction. Also any change in the phosphite layers which can appear as a result of proton ordering in the hydrogen bond, will influence the glycine orientation.

Fig. 3.1: Projection of crystal structure of GPI when viewed along the $b$-axis (Circles, in decreasing order of size represent N, O, C and H atoms respectively)

The activation energy for GPI crystal is estimated to be $\Delta E = 17$ kJ/mol which is more than three times higher than other ferroelectric crystals in which the mechanism of paraelectric-ferroelectric phase transition is connected only with the ordering of protons in the strong hydrogen bonds. This suggests that the dynamics of the organic sub lattice (glycinium cations) of GPI could play a vital role in the long range ordering of the crystal. With the slowing of the glycine $\text{NH}_3^+$ group rotations.
the ordering of these protons takes place as seen in EPR measurements [8], as a result of which the GPI crystal undergoes a phase transition at 224 K. Several macroscopic and microscopic properties of GPI have been investigated by researchers to elucidate the mechanism underlying the phase transition [6, 8, 9-12]. However, investigations on the thermal properties of this crystal have not been reported.

In this chapter, we give a systematic study of the variations in thermal parameters- thermal diffusivity ($\alpha$), thermal effusivity ($\epsilon$), thermal conductivity ($K$) and heat capacity ($c_p$) - of GPI single crystal along the three principal directions, when the crystal undergoes the para-ferroelectric phase transition, employing an improved photopyroelectric (PPE) technique [13]. Details of the experimental results obtained and discussion of the results are outline in the following sections.

### 3.2 Sample preparation

Single crystals of glycine phosphite are grown by the slow cooling of an equimolar solution of glycine [NH$_2$CH$_2$COOH] (AR grade) and orthophosphorous acid [H$_3$PO$_3$] solution (Aldrich). Prior to growth, GPI was re-crystallized for nearly 4-5 hours to yield purified materials. Slow cooling from a temperature of about 35°C to 29°C at a rate of 0.02°C / hour is achieved with a programmable temperature controller having a cooling rate of 0.01°C / hour. Crystals as large as 50 x 35 x 30 mm$^3$ have been grown by this method. Transparent good quality crystals so obtained are used in the present investigations.

The crystallographic directions of the crystal are identified by X-ray diffraction technique (XRD). The complete morphology of GPI crystal has been
generated using XRSHAPE software after measuring the interfacial angles using a contact goniometer and is given in Fig. 3.2. The crystallographic $b$ and $c$ axes are selected as the crystal physical $Y$ and $Z$-axes respectively but the crystal physical $X$-axis lies in the (010) plane making an angle 10.43° to the crystallographic $a$-axis ($\beta = 100.43^\circ$). The coordinate system chosen for measurement is not orthogonal, such that the (100) plane is normal to the crystallographic $a$-axis.

![Diagram of crystal morphology](image)

**Fig. 3.2: Complete morphology of Glycine phosphite (GPI) single crystal**

The oriented crystals are cut with a slow speed diamond wheel saw such that they have faces perpendicular to the [100], [010] and [001] directions or the crystallographic $a$, $b$- and $c$-axes respectively. The samples are carefully polished, initially with water and finally with alumina powder, to get good surface finish. The samples prepared for the photopyroelectric measurements have a thickness of $\approx 0.3$mm. The density of the sample is measured to be 1.722 gcm$^{-3}$. A very thin layer of carbon black from a benzene flame has been carefully coated on to the illuminated surface of each sample to enhance its optical absorption.
3.3 Experimental details

An improved photopyroelectric technique has been used to determine the thermal parameters of GPI single crystal. In this measurement, a thermally thick pyroelectric detector film is attached to one side of the sample, which is also thermally thick and the combination is mounted on a thermally thick backing medium. The other side of the sample is illuminated by an intensity-modulated beam of light, which gives rise to periodic temperature variations by optical absorption. The thermal waves so generated propagate through the sample and are detected by the pyroelectric detector.

A 120mW He-Cd laser of wavelength $\lambda = 442\text{nm}$ (KIMMON), intensity modulated by a mechanical chopper has been used as the optical heating source. Polyvinylidene difluoride (PVDF) film of thickness 28µm, both sides coated with Ni-Cr film, with pyroelectric coefficient $P = 0.25 \times 10^{-8} \text{Vcm}^{-1}\text{K}^{-1}$ is used as the pyroelectric detector. The detector is supported on a thermally thick backing medium, made of copper. The sample-detector-backing assembly has been enclosed in a chamber whose temperature can be varied and controlled as desired. The signal output is measured using a lock-in amplifier (SR 830). The frequency of modulation of the light is kept above 30Hz to ensure that the detector, the sample and the backing medium are thermally thick during the measurements. The thermal thickness of the GPI sample in this experiment has been verified by plotting the PPE amplitude and phase with frequency at different temperatures between room temperature and 180 K, along three principal directions are given in figures 3.3(a), 3.3(b), 3.4(a), 3.4(b), 3.5(a) and 3.5(b) respectively.
Measurements have been carried out illuminating the three cut sample faces so that the propagation of the thermal wave is along one of the symmetry axes. Measurement of the PPE signal phase and amplitude enable one to determine the thermal diffusivity (defined as $\alpha = K / \rho c_p$, $\rho$ being the density) and effusivity (defined as $e = (K\rho c_p)^{1/2}$) respectively [13]. From the measured values of $\alpha$ and $e$, $K$ and $c_p$ of the sample are determined. A careful calibration of the experimental set up and procedure has been done prior to carry out the measurements, as described in detail in Chapter 2 of this thesis. The measurements as a function of temperature have been made at a heating rate of approximately 0.5 Kmin$^{-1}$ and data collected in every 1K interval normally and at closer intervals near the transition point. The temperature is measured with a platinum sensor placed close to the sample inside the chamber.

3.4 Results and discussion

Figures 3.6(a), 3.6(b), 3.7(a), 3.7(b), 3.8(a) and 3.8(b) show the variation of PPE amplitude and phase of GPI single crystal along the $a$-, $b$- and $c$- axes of the crystal. It is seen that, in all the three directions, PPE amplitude and phase reflect the para-ferroelectric phase transition at 224 K.

Figures 3.9, 3.10 and 3.11 show the variation of thermal diffusivity and thermal effusivity with temperature along the $a$-, $b$- and $c$- axes of GPI single crystal.
Fig. 3.3(a): Variation of PPE amplitude with frequency of GPI crystal along the a-axis

Fig. 3.3(b): Variation of PPE phase with frequency of GPI crystal along the a-axis
Fig. 3.4(a): Variation of PPE amplitude with frequency of GPI crystal along the $b$-axis

Fig. 3.4(b): Variation of PPE phase with frequency of GPI crystal along the $b$-axis
Fig. 3.5(a): Variation of PPE amplitude with frequency of GPI crystal along the c-axis

Fig. 3.5(b): Variation of PPE phase with frequency of GPI crystal along the c-axis
Fig. 3.6(a): Temperature variation of PPE amplitude of GPI crystal along the a-axis.

Fig. 3.6(b): Temperature variation of PPE phase of GPI crystal along the a-axis.
Fig. 3.7(a): Temperature variation of PPE amplitude of GPI crystal along the $b$-axis

Fig. 3.7(b): Temperature variation of PPE phase of GPI crystal along the $b$-axis
Fig. 3.8(a): Temperature variation of PPE amplitude of GPI crystal along the \(c\)-axis

Fig. 3.8(b): Temperature variation of PPE phase of GPI crystal along the \(c\)-axis
Fig. 3.9: Variation of thermal diffusivity and thermal effusivity with temperature of GPI crystal along the $a$-axis

Fig. 3.10: Variation of thermal diffusivity and thermal effusivity with temperature of GPI crystal along the $b$-axis
Fig. 3.11: Variation of thermal diffusivity and thermal effusivity with temperature of GPI crystal along the c-axis

As seen in figures, the thermal diffusivity follows the same pattern as PPE phase and decreases up to the point of para-ferroelectric phase transition at $T = 224K$, in agreement with the already reported value of transition temperature. At the transition temperature, there is a peak and there after thermal diffusivity steadily decreases with temperature. The thermal effusivity exhibits an opposite behaviour. It increases with temperature up to the transition point. At the transition temperature, there is a minimum in the thermal effusivity value but thereafter it increases steadily with temperature. Taking into account, the various limitations of the measurements, the overall uncertainties in the values of $\alpha$ and $e$ are estimated to be $\pm 1\%$.

Figure 3.12 shows the variation of heat capacity of GPI single crystal as a function of temperature. The phase transition in GPI is reflected clearly in the
temperature variation of heat capacity as a clear anomaly at the transition point. These heat capacity results agree with the DSC measurements reported earlier [6]. As we can see, there is no direction dependence for heat capacity.

![Graph of Heat Capacity vs Temperature]

**Fig. 3.12:** Variation of heat capacity with temperature of GPI single crystal

Figure 3.13 shows the temperature variation of thermal conductivity along the three symmetry axes ($a$, $b$ and $c$) of GPI. Thermal conductivity exhibits significant anisotropy as is evident from Fig. 3.13. A study of anisotropy in thermal conductivity enables one to draw important conclusions regarding intermolecular forces in the crystal. With such an intention, we have plotted the thermal conductivity ellipsoids for the $b$-$c$, $a$-$c$ and $a$-$b$ planes.
Fig. 3.13: Variation of thermal conductivity with temperature of GPI single crystal

The characteristic representation of quadric for thermal conductivity is given by [14]

$$ K_{ij} \tilde{n}_i \tilde{n}_j = 1 $$

(3.1)

where $K_{ij}$ are the thermal conductivity tensor and $\tilde{n}_i$ are the direction cosines.

When we refer to the principal axes, we have

$$ K_1 n_1^2 + K_2 n_2^2 + K_3 n_3^2 = 1 $$

(3.2)

$K_1, K_2$ and $K_3$ are always positive and hence this represents the thermal conductivity ellipsoid.

Figures 3.14(a), 3.14(b) and 3.14(c) represent the projection of the thermal conductivity quadric lying in the $b$-$c$, $a$-$c$ and $a$-$b$ planes, when viewed along the $a$-, $b$- and $c$ axes of the crystal respectively.
Fig. 3.14: Projection of the thermal conductivity quadric lying in the $b$-$c$, $a$-$c$ and $a$-$h$ planes when viewed along the $a$-, $b$- and $c$- axis of the crystal respectively.
The thermal conductivity ellipsoid is a prolate one, both above and below the para-ferroelectric phase transition temperature for the $b$-$c$ and $a$-$c$ planes, whereas for the $a$-$b$ plane, it is similar to a spheroid, inferring that the values of $a$- and $b$-axes thermal conductivities have close values, as expected, whereas the $c$-axis thermal conductivity is much smaller.

The difference between $b$ and $c$ axes thermal conductivities can be attributed to the orientation dependence of the intermolecular forces in the crystal. It is seen that the maximum thermal conduction occurs in the direction of predominant covalent bonding, which is along the $b$-axis, whereas minimum thermal conduction occurs in a direction perpendicular to the chains of glycine molecules connected by hydrogen bonding. The nature of the temperature dependence is similar for all the three directions.

Anisotropy in thermal conduction can be explained as follows. In the structure of GPI, planes containing infinite chains of phosphite $H\left(HPO_3\right)_n^-$ anions alternate with those built by the organic cations. These two types of layers are parallel to the crystallographic $b$-$c$ plane, i.e. they are arranged alternatively in the $a$-direction. This layer arrangement corresponds to the direction of weak coupling in the crystal. Within the phosphite layers, $H\left(HPO_3\right)^-$ groups are mutually linked by hydrogen bonds forming infinite chains extending along the crystallographic $c$-axis. The inter-molecular and intra-molecular interactions, which are also hydrogen bonded, are stronger along the $b$-axis. Correspondingly, thermal conductivity is high in this direction. So, the orientation dependence of the strength of the hydrogen bonds in the system may be responsible for the observed anisotropy in thermal conductivity.
A recent report [15] on the thermal expansion coefficient $\alpha$ of GPI in the para electric phase shows a relatively large thermal expansion coefficient along the $c$-axis, corresponding to the weak hydrogen bonded direction, while the strong intermolecular forces along the $b$-direction supports its low value in this direction. This is good agreement with the ultrasonic investigation of elastic constants of GPI crystal, reporting similar anisotropy in elastic properties with the stiffness constant $C_{12}$ (corresponding to $b$-axis) being high, while $C_{11}$ and $C_{33}$ are low, in accordance with the bonding scheme in the crystal lattice [12].

We can thus conclude by saying that the results on the temperature variation of thermal properties of GPI are in tune with other measurements [6,12] confirming the occurrence of an order-disorder type para-ferroelectric phase transition at 224K in GPI crystals.

### 3.5 Conclusions

The four thermal parameters of glycine phosphite single crystals have been evaluated by photopyroelectric measurements. Correlation between crystal structure of GPI explains the high values of elastic constant along crystallographic $b$ direction and smaller values along the $a$ and $c$ axes. The variation of these thermal parameters across the phase transition temperature reveals an order-disorder type paraelectric to ferroelectric phase transition at 224 K.
References


