

Dynamics of Hydrogen Bonds in TGS Crystals Observed by Means of Measurements of Pyroelectric Currents Induced by Linear Changes of Temperature

M. TRYBUS*, T. PASZKIEWICZ AND B. WOŚ

Rzeszów University of Technology, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

The study of pyroelectric response of monocrystalline TGS cubic specimens to changes of temperature induced by linear and pulse heating of three mutually perpendicular pairs of cube sides demonstrated a complicated structure of signals. We attribute their forms to the activation of various hydrogen bonds between glycine G1, G2, and G3 molecules. In the case of pulse heating the pyroelectric signal is observed also in the paraelectric phase.

DOI: [10.12693/APhysPolA.132.161](https://doi.org/10.12693/APhysPolA.132.161)

PACS/topics: 77.70.+a, 77.84.Fa, 77.80.B-

1. Introduction

Triglycine sulfate (TGS) is a hybrid organic-inorganic crystal. Due to its ferroelectric properties at room temperature, it is one of the most comprehensively studied ferroelectric materials for infrared, non-cooled thermal detectors. The material undergoes second order phase transition at about 49°C. Crystals are monoclinic in both polar and non-polar phases. In the ferroelectric phase, the polarization vector is directed along vector \mathbf{b} , which is perpendicular to the plane defined by the vectors \mathbf{a} and \mathbf{c} (henceforth we shall refer it to the b-side). The vector \mathbf{b} determines the ferroelectric \mathbf{b} axis. Keeping in mind that pyroelectric effect in \mathbf{b} axis direction is strong and may veil subtle contributions of hydrogen bonds that may be present in vicinity of the critical temperature T_c , we decided to perform pyroelectric measurements in two orthogonal directions perpendicular to the ferroelectric \mathbf{b} axis. The way to apply our chosen method of measurements is to use samples of TGS in the form of a cube. Such form makes measurements of electric current in three nonplanar directions easy and repeatable under controlled conditions. With the use of the setup described in our papers [1, 2], ferroelectric samples can be stimulated by linear changes of temperature with desired parameters. We used a pair of micro-Peltier cells for heating or cooling of pairs of parallel sides of cubic samples. Before each measurement our TGS samples were heated from about 30°C to 55°C and then cooled back down to 30°C. This way, each initial measurement was performed on aged TGS samples while all successive measurements were conducted on freshly rejuvenated samples. We studied the behavior of three cubic samples, but we only present the results for the sample for which the dynamics of the signal measurements were the best.

We induced the response of samples to linear changes of their temperature.

2. Experiment

Single crystals of TGS were grown from an aqueous solution of stoichiometric quantities of the aminoacetic and sulphuric acids, using the static method of water evaporation, as described in numerous publications. Colorless, transparent crystals of good optical quality were obtained. The ferroelectric \mathbf{b} axis of the samples was oriented using natural cleavage of single crystals. After mechanical treatment, samples with width, length, and thickness of about 5×10^{-3} m were fabricated. Silver electrodes were attached to the sample sides. Such fabricated samples were used for pyroelectric measurements with the use of a sample holder and measuring system as described in [1]. Pyroelectric response to the linear excitation was measured in the case of cubic samples in two orthogonal directions lying in b-side. We denote such arbitrary selected measurements directions by the letters x and y . It should further be noted that in our experiments the crystalline \mathbf{a} and \mathbf{c} axes were not precisely oriented.

3. Results and discussion

Pyroelectric current induced in TGS single crystal in direction of ferroelectric \mathbf{b} axis is very sharp and rather strong in close proximity of T_c . This may obscure subtle phenomena which can be unmasked for other directions. This motivated us to perform similar experiments for cubic samples in two directions perpendicular to ferroelectric \mathbf{b} axis. We observed very weak signals — more than 2.5 orders of magnitude weaker than those measured in \mathbf{b} axis direction at the same temperature conditions (linear heating and cooling). We discovered two correlated processes that seem to supplement each other. We note the following sequences of events for cubic samples:

1. when sample goes from ferroelectric to paraelectric phase (heating), for direction:

*corresponding author; e-mail: m_trybus@prz.edu.pl

x : local maximum (at 47.8 °C) → local minimum (49.1 °C) → local maximum (50.8 °C),
 y : global maximum (at 49.9 °C),
 b : global maximum (at 49.9 °C);

x : global minimum (at 46.9 °C),
 y : local minimum (at 48.2 °C) → local maximum (47.1 °C) → local minimum (46.3 °C),
 b : global minimum (at 46.6 °C).

2. when sample goes from paraelectric to ferroelectric phase (cooling), for direction:

Typical results of measurements obtained in our experiment are presented in Figs. 1 and 2.

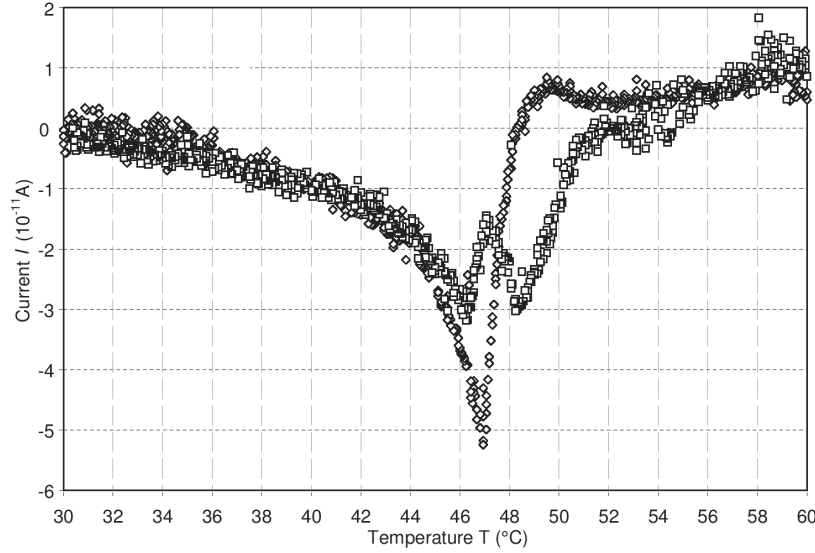


Fig. 1. Components of pyroelectric current recorded in x (\diamond) and y (\square) directions in linear heating experiment.

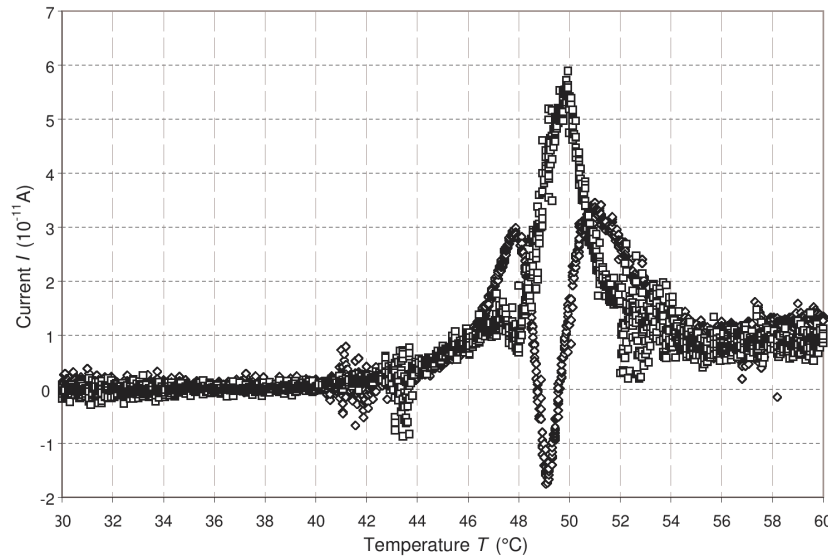


Fig. 2. Components of pyroelectric current recorded in x (\diamond) and y (\square) directions in linear cooling experiment.

It can be concluded that the occurrence of global extreme values of pyroelectric currents, related to the phase transition and recorded along b axis, are almost always preceded by local weak anomalies measured in directions x and y perpendicular to this axis. Hydrogen bonds between glycine molecules labeled G1, G2 and G3 as well as between G1 and SO_4 molecules are depicted in Fig. 3. Two glycine groups G2 and G3 are arranged almost perpendicular to the ferroelectric axis b . The length d_{12} of

the hydrogen bond H12 between glycines G1 and G2 and the length d_{13} of the bond H13 between molecules G1 and G3 as well as the length d_{23} of the bond H3 between G2 and G3 depend on temperature [3, 4]. The lengths d_{12} and d_{13} increases, whilst d_{23} decreases with growing temperature. Lengths d_{11} and d_1 of hydrogen bonds between N1 and O3 and N1 and O4 as well as between O11 and O1 increase with the rise of temperature.

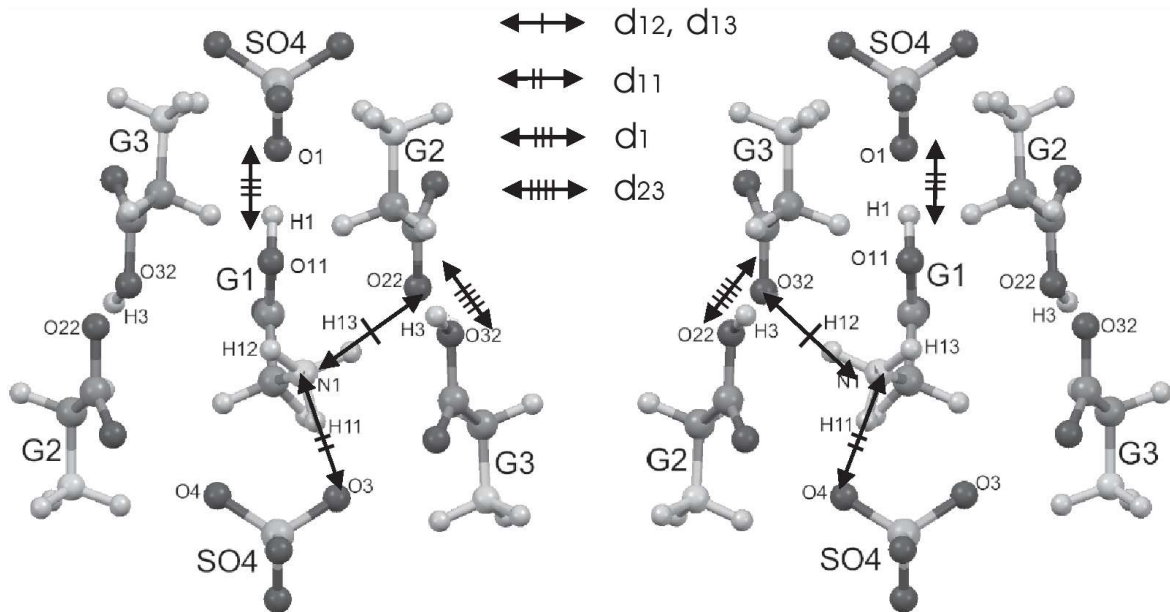


Fig. 3. Possible configuration of hydrogen bonds between G1 and surrounding molecules and the short hydrogen bond between G2 and G3 in ferroelectric phase [3, 4]. Looking from the left side: G1 respectively in right and in left position.

As the hydrogen bond between G1 and SO₄ gives very weak contribution to the polarization along *b* axis, we do not mention it in the following discussion. In the paraelectric phase ($T > T_c$), lengths d_{12} and d_{13} are sufficiently large, so molecules G2 and G3 do not influence the G1 molecules. The energy of thermal motion makes the probability of choosing each of two symmetrical positions of nitrogen atom of G1 group the same. Hence, the orientation of NH₃ group is disordered across the mirror plane. Therefore, the TGS crystal has the space group symmetry $P21/m$. No spontaneous polarization is present.

When temperature diminishes below T_c , length d_{23} of H3 bond increases. As a result, N1 atom may develop two equivalent bonds with oxygens O22 (bond H12) or O32 (bond H13). In the diffuse scattering of X-ray experiments, it was found that the position of H3 atom in G2–G3 bond is correlated with the orientation of G1 molecule [3, 4]. In the case of the right position of NH₃ group, H3 atom is covalently bonded with O32 atom, and N1 is hydrogen bonded to O22. In the case of the left position of NH₃, the H3 is bonded with atom O22, while N1 creates hydrogen bond with O32. Hudspeth [3] underlined that the dominant mechanism of interaction of G1 molecules is indirect via hydrogen bonds between G1 and G2 or G1 and G3, giving the zig-zag networks of interactions as illustrated in Fig. 6 of the papers by Hudspeth [3] and Hudspeth et al. [4]. As a result, the mirror plane disappears, the TGS structure has space group symmetry $P21$, and the crystal becomes polarized along the *b* axis. The selection of one of two possible configurations of hydrogen bond pairs H3–H12 and H3–H13 determines configuration of one of the remaining hydrogen bonds, i.e., H11.

4. Conclusions

Each of the above mentioned hydrogen bonds adds components of polarization vector along the *b* and *x* and *y* axes. These components are very weak in comparison with the component of polarization vector induced by nitrogen N1 atoms. Therefore, the only way to register such weak signals is to measure them in plane perpendicular to the polar axis *b*. Non-vanishing currents I_x and I_y measured in the mutually perpendicular directions perpendicular to polar *b* axis show that the listed hydrogen bonds are activated at different temperatures and these components of the induced polarization vectors have various orientations. We believe that our results are in agreement with the observations of Hudspeth [3] and Hudspeth et al. [4]. Our method seems to be a good tool for the deeper disclosure of weak effects accompanying the phase transition in TGS.

References

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