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Observation of dynamics of hydrogen bonds in TGS crystals by means of measurements of pyroelectric currents induced by changes of temperature

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HIGHLIGHTS

- We measured pyroelectric current in three orthogonal directions of TGS samples.
- We discovered weak currents in directions perpendicular to ferroelectric *b* axis.
- We attribute this observation to dynamics of hydrogen bonds.
- Further experiments with samples oriented along crystallographic axes is required.

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ABSTRACT

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 I, II, III molecules. In the case of pulse heating the pyroelectric signal is observed also in the paraelectric phase. The applied measurement method is relatively simple but precise and can be realized in most of dielectric measurements laboratories.

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. TGS is a model uniaxial ferroelectric – attractive because of its excellent pyroelectric properties and high figures of merits. The material undergoes second-order, order-disorder phase transition at about 49 °C. Crystals are monoclinic in both polar and non-polar phases. Growth of single crystals is relatively easy, and properties of TGS are widely described in numerous papers.

The primitive vectors of the TGS crystalline lattice are denoted by **a**, **b**, **c**. The lattice constants of the TGS monoclinic unit cell are $a = 0.15$ Å, $b = 12.69$ Å, $c = 5.73$ Å, and $\beta = 105°$ [1]. In the ferroelectric phase, the polarization vector is directed along vector **b**, which is perpendicular to the plane defined by the vectors **a** and **c** (henceforth we shall refer it to the *b*-side). Vector **b** determines the *b* axis.

Using various methods, many authors investigated the phase transition and structural changes of TGS and its doped crystals. The aim of such investigations is to find structural origin of ferroelectricity and to explain mechanisms of the phase transition in TGS family. However, there are still questions about the trigger of phase transition in TGS.

Keeping in mind that pyroelectric effect in *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 *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 [2,3], ferroelectric samples can be stimulated by linear changes of temperature and temperature pulses with desired parameters (such as the duration, amplitude, or fill factor of the

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pulse). We used a pair of micro-Peltier cells for heating or cooling of pairs of parallel sides of cubic or plate shaped samples. The measuring system is shown in Fig. 1.

The dependence of the pyroelectric current response to changes of temperature of TGS was studied by several authors. Chynoweth [4] determined the pyroelectric signal as a function of temperature in both ferroelectric and paraelectric phases. He also observed a small pyroelectric signal above the Curie point. Chynoweth used the chopped light beam to generate pyroelectric signals which made the temperature of TGS specimens slightly higher than of an oven. White and Wieder induced the paraelectric response in ferroelectric TGS using microwaves [5]. Simhony and coworkers used rectangular [6] and step [7] infrared signals to obtain the temperature dependence of parameters of pyroelectric voltage response, namely of the initial slop, peak value, rise and fall times. Hadni and collaborators scanned the surface of TGS plate with a laser beam [8,9]. Measuring pyroelectric current, they observed motion of domain walls as well as location of domain nucleation centers. The domain structure in a plane perpendicular to ferroelectric *b* axis (henceforth referred to the *b*-side) of TGS plates was revealed in experiments of Bhide et al. [10]. These authors induced the pyroelectric signal with a laser beam which can be displaced over the crystal surface. They noted that there are limits to the resolution of small domains related to the size of the laser beam cross-section. Al-Allak and Dewsbery [11] studied the pyroelectric coefficient along the ferroelectric axis in a single domain crystal of TGS.

In all of the above described experiments, currents were directed along the *b*-axis. However, Fugiel studied the pyroelectric properties of TGS along the non-polar *c*-axis in the TGS [12]. In experiments performed by Fugiel et al., TGS crystals were placed in a constant electric field perpendicular to the ferroelectric axis [12–14].

Pyroelectric signals induced by means of the described methods depend on the topography and on the domain pattern of a surface under study. Hence, high resolution studies of ferroelectric materials are important for better understanding of nucleation and growth of ferroelectric domains. The domain structures of TGS were studied by various modes of Atomic Force Microscopy (cf. references given in [15–18]), Electrostatic Force Microscopy [19] and Piezoresponse Force Microscopy [20]. Using results of neutron and X-ray single crystal diffuse scattering, Hudspeth et al. proposed a microscopic mechanism of domains development [21,22].

We shall underline that our method of measuring pyroelectric currents [2] averages out effects of the surfaces topography as well as the distribution and time dependence of the surface charge. Such effects were observed in experiments described in papers [15–20] and in papers cited therein.

To avoid effects studied in papers [15–20] 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. Regarding the limited room for publication of redundant material, we did not decide to present results measurements for all our specimens. In the case of remaining two samples, measurements were repeatable and agree with results presented in the text. For this sample the dynamics of the signal measurements was the best.

2. Experiments

Single crystals of TGS were grown from an aqueous solution of stoichiometric quantities of the aminoacetic and sulfuric acids [2]. After mechanical treatment, samples with dimensions of about 5×10^{-3} m (width), 5×10^{-3} m (length) and 5×10^{-3} m (thickness) were fabricated. Silver electrodes were attached to the sample sides. They were used for pyroelectric measurements with the use of a sample holder and measuring system as described in Ref. [2].

2.1. Linear thermal excitation: b-sides are heated

Our former experiments were performed on plate-shaped specimens [2,3]. In order to compare the pyroelectric response of cubic and plate-shaped samples, we fabricated the reference sample of dimensions 5×10^{-3} m (width), 5×10^{-3} m (length) and 2×10^{-3} m (thickness). We used the same single crystal to fabricate both cubic and plate-shaped samples.

In case of cubic samples, one has to take into account the influence of samples' thickness on the difference of temperatures inside

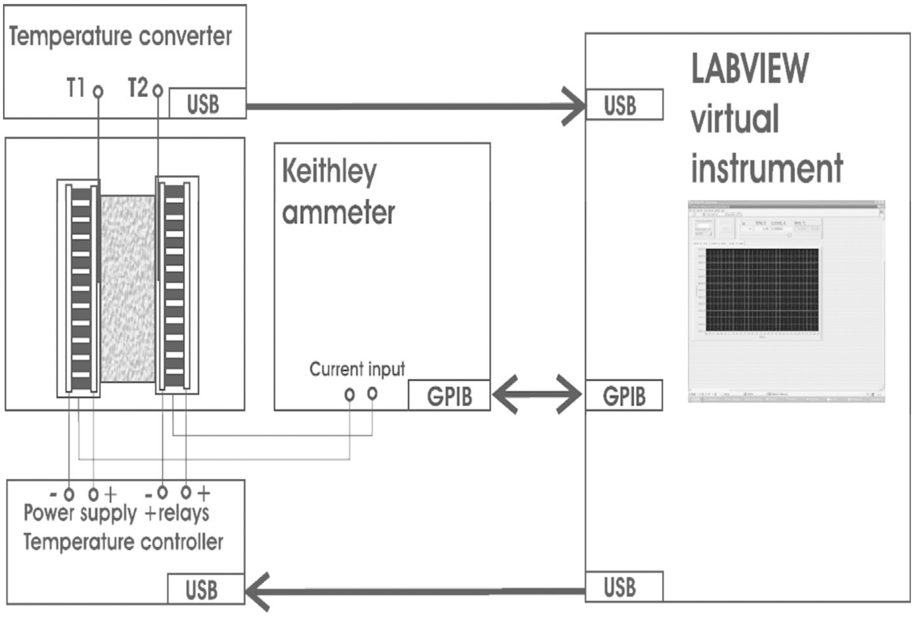

Fig. 1. Schematic view of the measuring system.