

TRIGLYCINE SULPHATE DYNAMICS OF DOMAINS IN RELATION WITH TEMPERATURE AND BIAS FIELD

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Abstract. Triglycine sulphate crystal (TGS) is a hybrid organic-inorganic ferroelectric crystal with a large electronic band-gap, transparent in visible spectra. It has large applications in electronics, as thermal IR detector. Pure and doped TGS crystals of 3-5 cm linear dimensions were grown at constant temperature in the paraelectric phase (52 °C), by slow solvent evaporation. Pure TGS samples show non-reproducible values of permittivity and losses in the ferroelectric phase after the “excursion” in the paraelectric phase. Walking up and down the crystal temperature, using a special program, the permittivity and losses were automatically recorded and analyzed. There is a continuous decrease of permittivity towards an equilibrium value during a long period of time. Previous AFM measurements from the literature have revealed peculiar aspects of domain dynamics. The relaxation process of permittivity was considered according to the equation $\epsilon_r = A - B \exp(-t/\tau)$. However, surprisingly, there is not a unique relaxation time τ . For the first 500 sec (or so), the relaxation time is $\tau \approx 7$ minutes, while between the next time decades 1.000 - 10.000 - 100.000 sec, it is approximately 1 hour and 8 h respectively. The process is related with the ferroelectric domain’s dynamics, which are more or less strongly pinned by dislocations or some other lattice defects.

Keywords: Perovskite; First-principles calculations; Electronic properties; Elastic properties

1. Introduction

Triglycine sulphate crystal, TGS for short, with the chemical formula $(\text{NH}_2\text{CH}_2\text{COOH})_3 \text{H}_2\text{SO}_4$ is a hybrid organic-inorganic material. It is a ferroelectric crystal which undergoes a typical second order ferroelectric transition around 49.2°C. It has important applications in electronics devices, as IR detector, gas sensor, etc, having a great figure of merit versus other crystals or PZT ceramics [1]. Pyroelectric vidicon tubes use crystals of the TGS family as target materials [1,2]. Doped crystals have usually more stable ferroelectric parameters, lower dielectric constants and lower losses, i.e., higher figures of merit [3,4].

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Pure TGS crystals show non-reproducible values of permittivity, crossing up and down the Curie Point. Much higher values of permittivity (and losses) are found in the ferroelectric phase after such an “excursion” [3,4]. Lower and stable parameters of the ferroelectric samples could be found only after several months of relaxation [4-6].

Ferroelectric parameters, permittivity and losses, pyroelectric coefficient and spontaneous polarization are usually measured in the literature only by increasing temperature [7]. It is quite well known from the literature, that returning to the ferroelectric phase the domain structure is not reproducible [8-11]. There appear a huge number of small ferroelectric domains, which give the most part of the permittivity in the first stages. Then, domains coagulate in time, reducing the domains wall length, whose oscillation under the small measuring ac electric field is responsible for the permittivity decrease in time [12].

The evolution (relaxation) of the dielectric constant and losses of pure TGS samples, during the transient period of time, after the returning in ferroelectric phase shall be presented in this paper.

2. Crystal growth and sample preparation.

The basic TGS substance was synthesized from aminoacetic and sulphuric acid. Two fractional recrystallizations were performed in order to improve the substance quality [13, 14]. Middle fraction of the first crystallization was used for the second recrystallization, in order to eliminate presumed impurities with segregation coefficients higher and lower than one. Only middle fraction from the second recrystallization was used for crystal growth.

TGS single crystals of 3–4 cm linear dimensions were grown by slow solvent evaporation in the paraelectric phase at 52°C, during 50÷60 days. Our previous growth experiments [14] and some literature data [15] have indicated that TGS crystals grown in paraelectric phase have improved structure and ferroelectric properties.

Samples of about 1 mm thick and approximately 0.8 cm² surface, cleaved from the grown crystals, were carefully polished on a silk plate using 10 % water in glycerine. Silver paint electrodes were used for electric contacts.

3. Experimental measurements and results.

3.1. Permittivity and losses in successive runs.

Essential ferroelectric parameters, permittivity ϵ_r and losses $\tan \delta$ were measured between 31°C and 66°C with a self-acting bridge HIOKI 3511-50 at 1 kHz. The measured sample was placed in a special support, inside of an air thermostat (error

less than $\pm 0.1^\circ\text{C}$), following a special temperature program. Experimental data were on line registered, every 10 seconds, by the computer.

In the first run, ϵ_r and $\tan\delta$ were measured on an “aged” sample (three-month relaxation). The temperature was increased and decreased at the same pace $0.2^\circ\text{C}/\text{min}$, with a break of one hour at 66°C . The result of the first run is presented in fig.1, together with the reverse of permittivity. Walking down the temperature, through the Curie Point, the peak value of permittivity increases about three times.

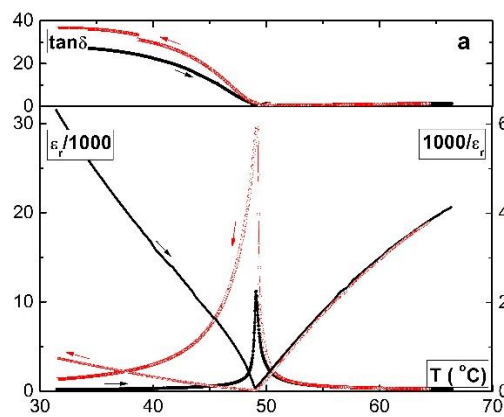


Fig.1. Permittivity and losses of pure, “tree months aged” TGS crystal, measured in the first run. Higher values of both permittivity and losses in the ferroelectric phase can be noticed.

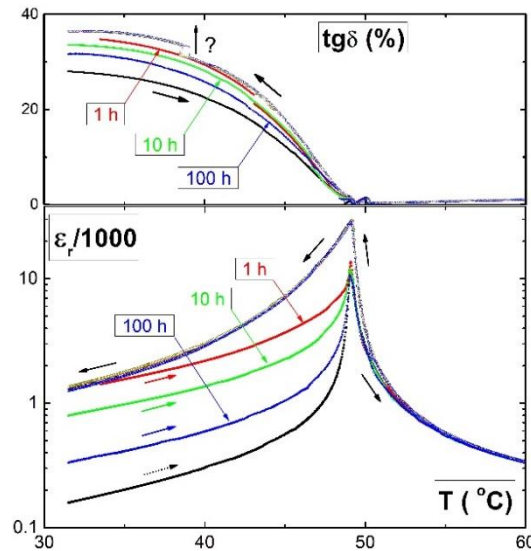


Fig.;2. Permittivity and losses in successive cycle runs at several intervals marked on the curves.

Based on previous relaxation measurements of permittivity [8], we have realized that the returning, permittivity has a continuous relaxation in the ferroelectric phase.

The second run started at 36°C, after 1 h break, the third one after 10 h break and the fourth after 100 h break. Results of the four successive measurements can be seen in fig.2. The lowest curves of ϵ_r and $\tan\delta$ in fig 2 correspond to the increase of the temperature in the first run (sample relaxed 3 month).

The highest curve values correspond to the returning curves, which are the same for all runs. How fast relaxes the permittivity in several temperature ranges is an open problem to analyze. The whole cycle of a run lasts about (3+1+3) hours. Returning time in the ferro phase of about 1.5 hours is comparable with the time break at the starting point of the second run. However, the relaxation seems to be considerable faster between 45°C and the transition point, at least for the first hours. It seems that the “ageing” of 100 h (about 4 days) of the sample at 31°C is not enough to reach the equilibrium value.

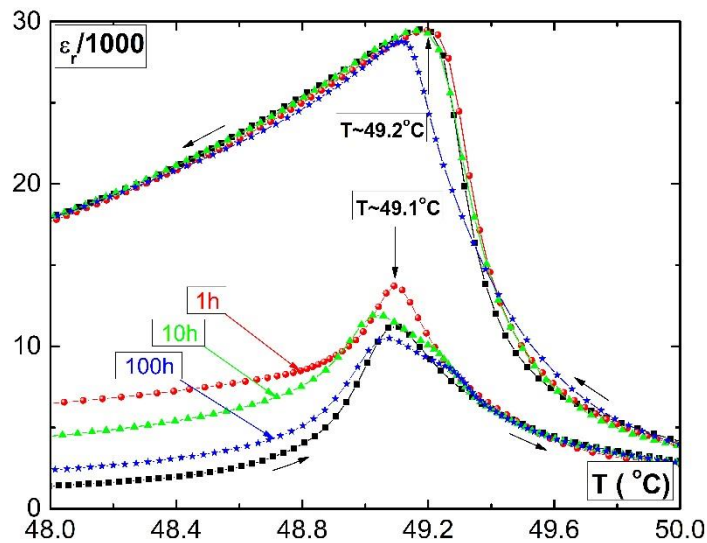


Fig.3. The dielectric constant in a narrow temperature interval around the Curie Point in the four successive runs. The time marked on the curves shows the waiting time at 31°C starting point.

Details of the temperature variation, up and down measured permittivities are presented in fig.3. Relaxation, with a considerable increase around the peak values (2 times) is remarkable. The reverse of the same permittivities, measured also on the same narrow range of temperature are presented in fig.4.

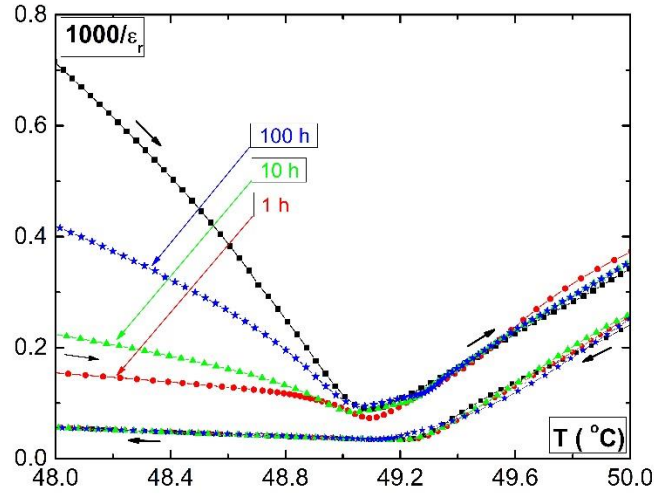


Fig.4. The reverse of the dielectric constant in a narrow temperature interval around the Curie Point in the four successive runs

3.2. Relaxation at constant temperature.

Permittivity measured crossing down the Curie point, in the temperature range 35÷45°C, is about 2 times higher than the permittivity measured with the temperature increase, in the first run (see fig2). The Curie constant ratio in para and in ferroelectric phase is approximative ≈ 2.6 , i.e., higher than two, the value predicted by the thermodynamic and Landau theory. The same ratio for returning curves become smaller than one (about 0.15) and cannot be explained by the theory.

In order to make clear what happens in a much longer run, we have used the same measuring assembly, to register both permittivity decay and losses evolution in time at 36°C constant temperature (see fig.5). The relaxation process was considered to be fitted with some kind of relation:

$$\varepsilon_r = A - B \cdot \exp(-t/\tau) \quad (1)$$

similar to the previous analysis [8]. However, surprisingly, the process could not be described by only one time relaxation. For the first ≈ 500 sec. the relaxation time was $\tau_1 = 7$ min. (similar in fig 5, ref. [8]), while between 8 min. (0.13 h) and 9 hours it was $\tau_2 \approx 1$ hour and other τ_3 was for the next (III) interval.

Data were represented in the next equation in order to estimate constants A_i and τ_i

$$\varepsilon_r = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + \dots \quad (2)$$

The experimental data show as in fig.5. Three domains can be considered for the time scale, with typical constants (see also ref. 8).

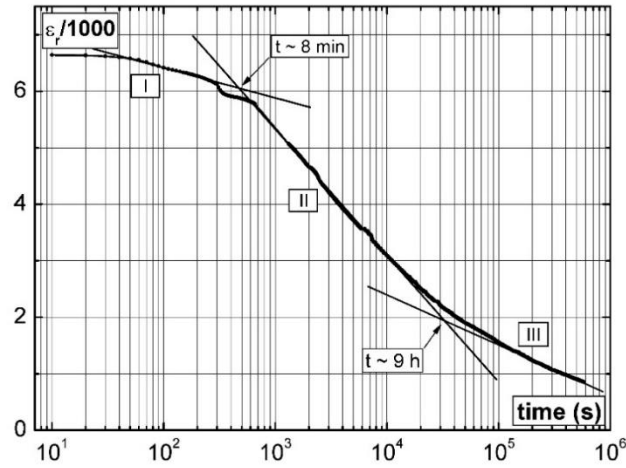


Fig.5. The permittivity decreases at 36°C during 7 days. The tree periods of time (I), (II), (III) correspond to several mechanism of dielectric relaxation.

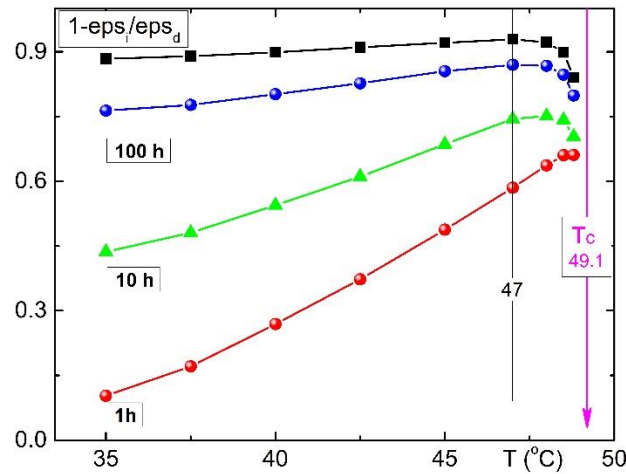


Fig.6. The relative variation of the dielectric constants with temperature, according to the equation: $1 - \varepsilon / \varepsilon_d = f(T)$, where ε_d is for down temperature measured permittivity which is the same for all curves.

The relative variation of the dielectric constants with temperature, according to the equation:

$$1 - \varepsilon / \varepsilon_d = f(T) \quad (3)$$

is presented in fig.6, where ε represent several increasing permittivity values and ε_d the down returning values, which are reproducible for all curves.

Between 47°C and $T_c=49.1^\circ\text{C}$ (fig. 6), there are $\approx 2^\circ\text{C}$ near the transition point where linear dependence become curved. This unexpected effect is a result of a special effect which take place in the boundary between the domains of opposite directions [18].

4. Discussions.

Relaxation of the dielectric constant is an intriguing subject, still not elucidated. The unusual increase of permittivity in the ferroelectric phase, after the “excursion” in the paraelectric phase appears to be correlated with the ferroelectric domain reconstruction [9-11]. The relaxation process of permittivity, described by the eq. (1), does not seem adequate. The semi-log representation in fig.5, suggest three periods of time, having probable several mechanisms of relaxation. In the region (I), up to about 8 minutes, the slow relaxation process described by eq.2, has a relaxation time close to our previously estimated one $\tau \sim 7$ minute [8]. This is probable the mean time of free charges relaxation in the body of the ferroelectric sample, when the depolarization field is created.

The evolution of the ferroelectric domain topography after their formation is based on the increase of larger domains, on the expense of the smaller ones. As a consequence, the total wall length substantially decreases. Usually the a.c. electric field, used to measure the dielectric constant (of about ~ 1 V/cm) is quite small and the domain configuration cannot be changed significantly during one period. There are only small oscillations of the domain walls, which give an important contribution (up to 80 %) to the permittivity, versus the whole measured value [12]. The simultaneous decrease of the domains wall length decreases also the permittivity. This is the basic concept of the phenomena [12]. The physical support of the relaxation mechanism is not well understood yet.

Scanning force microscopy was used [11] in order to study the ferroelectric domains evolution, after crossing down the Curie Point. The AFM images [11] confirm the extension of larger ferroelectric domains on the expense of the smaller ones.

The domains evolution after the heat treatment (crossing down the Curie point) was observed on TGS samples with the nematic liquid crystals in ref. [9, 10]. Ferroelectric domain width was measured in time. In a double-log scale, two straight lines cross each other after 9 hours (see fig.5 in ref. [9]. There is a slowing down effect of the domain enlargement. This is similar to knee point we have found in fig.5 of permittivity decrease, after about 9 hours time. Similar behavior after 500-600 minutes was also found in ref. [16].

The relative variation of the permittivity versus temperature $1 - \varepsilon / \varepsilon_d = f(T)$ is linear, except the last 2 Celsius degree near the Curie Point, where Landau theory might not be valid [17]. The curve obtained after 1 hour rest at 31 °C has the highest slope variation. Very new recent data, ref [18] and [19] shows special phenomena happened 2°C or 3°C near the Curie point.

5. Conclusions.

Pure TGS crystals of high quality were grown by slow solvent evaporation in the paraelectric phase at 52 °C. Crystals show unstable permittivities (ε_r) and losses ($\text{tg}\delta_\varepsilon$), crossing up and down the Curie point, due to ferroelectric domain reconstruction.

Permittivity and losses were measured on a large temperature interval (31°C to 61°C) in four successive cyclic runs, with the time breaks of 1 h, 10 h, 100 h, at the starting point 31°C temperature. The relative permittivity variation $1 - \varepsilon / \varepsilon_d = f(T)$ was linear, except around 2°C, near the Curie Point.

In seven days of continuous permittivity measurements at 36°C constant temperature, it was found that the permittivity relaxation has not a unic relaxation time according to the usual concept. There is probably a distribution of such relaxation times, due to pinned effect of ferroelectric domains by several lattice defects, like dislocations, or some other defects. Three mechanism of permittivity relaxation are suggested to be active in the permittivity decrease in time at constant temperature.

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