Formation of a quasi-equilibrium domain structure of crystals of the TGS group near $T_c$

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Abstract

In the temperature range $\Delta T \approx 321$ K ÷ 322 K, the kinetics of the nonequilibrium domain structure of triglycine sulphate crystals, both pure and with specially introduced defects, has been studied by means of piezoresponse force microscopy technique. The temporal change in the domain structure as a set of regions with a scalar order parameter of $P(r,t) = +1$ and $-1$ for oppositely polarized domains was analysed by the behaviour of the space-time correlation function $C(r,t) \approx (P(r,t)P(0,t))$. At different distances from the Curie point $T_c$, the characteristic length $L_c$, as a scale measure of the average domain size, increases with time according to the power law $L_c(t) \approx (t-t_0)^\alpha$. A decrease of the exponent $\alpha$ with distance from $T_c$ can be a consequence of the transition of the domain structure of TGS crystals from a non-conservative state to a conservative one.

Keywords: Piezoresponse atomic force microscopy, Triglycine sulfate, space-time correlation function, Characteristic length, Time dependences, Power law


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1. Introduction

Triglycine sulphate (NH$_2$CH$_2$COOH)$_2$H$_2$SO$_4$ - TGS, its isomorphs (triglycine selenate, triglycine fluoroberyllate), their deuterated analogues, as well as their modifications doped with various impurities, are some of the best materials for pyroelectric applications. But they are of no less interest as convenient model objects for studying structural phase transitions [1–5], the domain structure [4–14], the influence of a weak magnetic field on non-magnetic ferroelectric materials [15–18], the manifestation of ferroelectric properties under conditions of limited geometry [19–22], etc.

The study of any physical properties of ferroelectrics and, in particular, these crystals is impossible without a detailed analysis of the role of the domain structure in the behaviour of these properties, especially near $T_c$, where it is anomalous. Therefore, in this work, the kinetics of the formation of a domain structure (DS) of several crystals of the TGS group was studied at an insignificant (no more than 1 K), distance from the phase transition temperature $T_c$, at which point this structure occurs, being in a significantly non-equilibrium state during the initial moments of time.

The choice of the temperature range was also dictated by the fact that in this critical region, which is quite close to the point of phase transition, where fluctuation effects can still be noticeable, and the thickness of the domain walls can be comparable to the width of the domains, such studies were practically not carried out. Earlier [7–10], the behaviour of DS of only nominally pure TGS crystals was studied after their exposure in the paraelectric phase followed by a rapid cooling into the ferroelectric phase to temperatures spaced from the Curie point by $\Delta T_c > 2$ K. At temperatures closer to the phase transition, the formation of a quasi-equilibrium DS was studied only in [6] and [11, 12] during its visualization, respectively, by the method of nematic liquid crystals and atomic force microscopy. There are no data on such studies of TGS crystals with defects of a known type in the literature.

The objectives of this work were to find out: 1) whether the behaviour of the studied crystals near $T_c$ is consistent with that established for TGS crystals at a significant distance from $T_c$ [7–10]; 2) to what extent this behaviour corresponds to the general regularities of the ordering processes of various two-phase systems [23] after their transition from an disordered high-symmetric phase to an ordered low-symmetric one.

Obtaining objective results in the studies of crystals of the TGS group is not an easy task, since not only crystals grown under different conditions and having different post-growth history, but even samples from different growth pyramids of the same crystal have different domain structures. The static and dynamic properties of the domain structure of TGS crystals also significantly depend on the presence of any defects in them [5]. And if an impurity (such as L,$\alpha$-alanine) enters non-uniformly into the volume of the growing crystal, then the DS can be different even within the same growth pyramid [24]. Differences in the experimental techniques used and in the measurement conditions also play a significant role.

The symmetry of the ferroelectric phase of the TGS crystal is simple (the space group P2$_1$ of the monoclinic syngony), but its 180° domain structure is diverse and geometrically complex. Five typical configurations of antiparallel domains can be observed in nominally pure TGS crystals [25]. Four of them are characteristic of freshly grown crystals, and the fifth, the most typical striped (lamellar) domain structure (type E, according to [25]), studied in this paper, occurs in an aged TGS crystal after its annealing in the paraelectric phase and subsequent transfer to the ferroelectric phase. At the same time, small lenticular domains of the opposite sign can be incorporated into the lamellae, fully or partially growing along the polar direction. These are type A and type B according to the classification [25] (Fig. 1).

After holding an electrically free TGS crystal in the paraelectric phase ($T > T_c = 322$ K) and its subsequent cooling into the ferroelectric phase, a nonequilibrium DS as a set of very small domains occurs in it. For energy reasons [4], such a domain structure gradually enlarges over time [5]. This process can be studied within the framework of phase ordering kinetics [23], an approach used to describe the behaviour of various systems subjected to quenching (rapid cooling) from a homogeneous phase to a phase with broken symmetry. Here 180° ferroelectric...
DS is considered as a two-phase system described by the scalar long-range order parameter $P(r,t)$ [26], which takes values “+1” and “–1” in antiparallel domains. Its evolution at $T = \text{const}$ can be analysed using the space-time correlation functions $C(r,t) = \langle P(r,t)P(0,t) \rangle$ [6–9].

In this work, the functions $C(r,t)$ were calculated for domain patterns visualized by means of piezoresponse force microscopy technique during the evolution of the DS of TGS crystals in the temperature range $321 \text{ K} \leq T < T_c = 322 \text{ K}$. The main questions were the following: 1) the time dependence and the equilibrium value of the characteristic scale length $L_c$ of the average domain size, 2) the features of the order parameter $P(r,t)$, which determine the form of the dependence $L_c(t)$, 3) the scaling of the correlation function, 4) the effect of defects on the quantitative parameters of the evolution of the domain structure.

2. Experimental

Crystals of pure TGS (crystal growth conditions and its properties are described in articles [12, 27]), as well as TGS with impurity ($L,\alpha$-alanine – ATGS, chromium – TGS-Cr, phosphorus – TGSP) and radiation (X-ray irradiation – XR-TGS) defects were studied. All doped crystals were grown at temperatures below $T_c$. The TGS crystal was grown from a solution with the concentration of $L,\alpha$-alanine in it of 10 mol%. The TGS-Cr crystal was grown from a solution containing 1 mol% salt of $\text{Cr}_2(\text{SO}_4)_3\cdot6\text{H}_2\text{O}$. The TGSP crystal was grown from a solution of a mixture of triglycine sulphate and triglycine phosphate salts taken in a ratio of 1:1 [28]. Radiation defects were generated by irradiation of nominally pure TGS with CuK$\alpha$ X-rays (quantum energy of 30 keV, total dose of 240 kR). High concentrations of $L,\alpha$-alanine, and chromium impurities, as well as high X-ray radiation doses, can suppress the dynamics of domains in TGS, which was unacceptable for the purposes of this work. Therefore, relatively “soft” samples were selected from these crystals with a dielectric constant at the Curie point $\varepsilon_{\text{max}} > 1\cdot10^3$ and with an internal bias field $E_b \leq 500 \text{ Vcm}^{-1}$, which made it possible to observe the evolution of the emerging DS in them.

The samples of the studied crystals were polar $b$-cleavages with an average size of $5\times5\times1 \text{ mm}$. Domain images were recorded in the contact mode of piezoelectric force microscopy (PFM) using a Solver P47 Pro microscope by applying an alternating electric field with an amplitude of 1 V and a frequency of 150 kHz to a NSG11/TiN cantilever (tip curvature radius 35 nm, force constant 11.5 N·m$^{-1}$, resonance frequency 255 kHz). The measurements were carried out in air at constant parameters (temperature, humidity, pressure) of the environment. The temperature of a specimen was regulated and monitored using a homemade controller mounted on the head of the microscope. The samples were preheated from $T_1 = 293 \text{ K}$ to $T_2 = 333 \text{ K}$ and, after holding for half an hour at $T_2$, they were cooled at a rate of 1 K min$^{-1}$ to $T_3 = 324 \text{ K}$. Then, the cooling rate was decreased to 0.1÷0.2 K·min$^{-1}$ in order to minimize the time required for the stabilization of the temperature of observation ($T_{ob}$) with an accuracy of about ± 0.05 K. Each scan at a fixed $T_{ob}$ was carried out on the same area of the sample surface. The recording of images of the domain structure ended when the lateral displacement of the domain walls did not exceed the measurement error of the domain size (2%).

In our measurements, the cooling of the samples into the ferroelectric phase was not a real quenching, as, for example, in [7], but, nevertheless, both the phase transition and the initial state of the crystals were obviously not
equilibrium. The amplitude PSM images of the DS were converted into a digital format for further calculations in a program specially compiled in the MATHCAD package. The obtained domain images, as well as the calculated graphs of the correlation functions $C(r,t)$, were not subjected to any additional processing, the expediency of which was discussed in [29].

3. Results and discussion

Figures 2–4 show the correlation functions $C(r)$ and the corresponding images (50×50 μm) of domains of TGS, LATGS, and XR-TGS crystals during the initial and final stages of the evolution of their domain structures at two temperatures below $T_c$. Correlation functions were calculated for directions close to [001] and [100].

For comparison, Figures 5–7 show similar information for TGS, TGSF, and TGS-Cr crystals, but at a distance from the phase transition point $\Delta T_c = 4.0$ K, since, as shown in [13, 14], the evolutionary kinetics of the domain structure should depend on the depth of cooling into the ferroelectric phase.

The initial domain structures, especially near $T_c$, are ensembles of many small irregularly shaped domains, which are predominantly elongated in a direction close to [100]. In pure TGS, the domain structure is lamellar, while in doped and irradiated crystals it is more complex, with more rugged domain boundaries. Over time, the domain structures of all the crystals under study become larger, but their main topographic features are preserved, and the question is, how statistically similar are they to the original ones? The domain enlargement in all crystals includes: 1) the disappearance of small domains located inside large domains of the opposite sign; 2) the contraction and disappearance of the protrusions along ~[100] direction; 3) contraction of large domains in the longitudinal (~[100]) direction. As a result, domains expand along the lateral (~[001]) direction, and their boundaries become smoother and less curved. These features of the evolution of the domain structure of pure TGS, noted earlier in [8–10], are more pronounced with distance from $T_c$, where the domains are larger. In crystals with defects (especially with radiation ones),
Fig. 3. The correlation functions $C(r)$ and correspondent domain pictures for a LATGS crystal at $\Delta T_c = 0.3$ K (a, c) and $\Delta T_c = 0.8$ K (b, d) for two time moments after phase transition, and for directions [001] (a, b) and [100] (c, d).

Fig. 4. The correlation functions $C(r)$ and correspondent domain pictures for a XR-TGS crystal at $\Delta T_c = 0.3$ K (a, c) and $\Delta T_c = 0.8$ K (b, d) for two time moments after phase transition, and for directions [001] (a, b) and [100] (c, d).
these regularities are less pronounced, since the defects, pinning the domain walls, impede their “spontaneous” displacements.

The mechanism of the observed temporal change of domains is formally explained by the action of electric field forces equivalent to the surface tension forces, the value of which is determined in our case by the curvature of the domain walls [23, 30]. The relaxation kinetics of the already existing domain structure is effected by the movement of the domain walls due to near-wall nucleation and the subsequent two-dimensional growth of nuclei whose sizes are larger than a critical one [31]. The initial nucleation that leads to the appearance of new domains is most likely insignificant in the absence of an external electric field. However, any displacement of the domain wall leading to local switching of polarization in any way must be caused by the action of a local electric field $\mathbf{E}_{\text{loc}}$, which in the general case is the sum of the external electric field $\mathbf{E}_{\text{ext}}$, the depolarizing field $\mathbf{E}_{\text{dep}}$, and the screening field $\mathbf{E}_{\text{scr}}$: $\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{dep}} + \mathbf{E}_{\text{scr}}$ [14] and in absence of an external field $\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{dep}} + \mathbf{E}_{\text{scr}}$. 

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**Fig. 5.** The correlation functions $C(r)$ and correspondent domain pictures for a TGS crystal at $\Delta T_c = 4.0$ K for two time moments after phase transition and for directions [001] (a) and [100] (b).

**Fig. 6.** The correlation functions $C(r)$ and correspondent domain pictures for a TGSP crystal at $\Delta T_c = 4.0$ K for two time moments after phase transition and for directions [001] (a) and [100] (b).

**Fig. 7.** The correlation functions $C(r)$ and correspondent domain pictures for a TGS-Cr crystal at $\Delta T_c = 4.0$ K for two time moments after phase transition and for directions [001] (a) and [100] (b).
The depolarizing field $\vec{E}_{\text{dep}}$ is the field of bound charges of spontaneous polarization, and the field $\vec{E}_{\text{scr}}$ is created as a result of either external or internal (bulk) screening. The external screening field arises as a result of the adsorption of charged particles on the surface of a ferroelectric crystal and their redistribution in the external medium. The volume screening is a result of the redistribution of charge carriers in the bulk of the ferroelectric and of the reorientation of dipole defects. The depolarizing field can be compensated completely only by volume screening, the delay of which is the cause of the jump-like motion of DWs [31, 32]. For a real ferroelectric, under the conditions of a real experiment, there is no reason to believe that the local fields are the same in the neighbouring domains, and it can be assumed that it is their difference that triggers the processes of motion of DWs, i.e. near-wall polarization reversal. The defects, pinning the domain walls, firstly, cause non-monotonicity of their displacements and, secondly, determine, along with the temperature [13, 14], the average speed of their movement that leads to a reduction in the duration of the process of changing the domain structure of the ferroelectric.

The time transformation of the obtained images of the domain structure, which to a certain extent reflect its evolution towards equilibrium, can be considered as the transition of the system from a disordered to an ordered state and analysed using the space-time correlation function $C(r,t) = \langle P(r,t) P(0,t) \rangle$ [7–9, 23], which is the average product of the values of the scalar order parameter $P(r) = \pm 1$ (where +1 corresponds to $+P_s$ and −1 to $-P_s$) for two fragments of the image, shifted by $r$ relative to each other. The equal-time function $C(r,t = \text{const})$ indicates the degree of similarity between these fragments at a given time. The similarity of one and the same fragment taken at various moments in time can in principle also be detected using the correlation function. Thus, it is possible to investigate both spatial and temporal correlations of DS during its evolution.

The dependences of the function $C(r,t)$ upon $r$ both for initial and final times of domain pictures recording, shown in Figures 2a, 4a,b and 5a–7a, indicate to quasiperiodicity of domain patterns along ~[001] direction. As for the ~[100] direction (Figures 2c,d–4c,d and 5b–7b) the clear oscillations of $[C(r)]_{[100]}$ curves take place mostly in the vicinity of $T^*_c$, as well during the initial stage of evolution when there is a sufficient number of domains which dimensions along this direction not exceed the size of the scanned area. Absolute values of the correlation function show that during evolution the spatial correlation of domain configurations increases with time, as well as when moving away from $T^*_c$ towards lower temperatures. In the crystals with defects in which the domain walls are less mobile, the absolute values of $C(r,t)$ and, consequently, the spatial correlation of domain patterns do not significantly change both upon time and temperature.

Earlier in [12], for the temperature range $321 \text{ K} < T < T^*_c = 322 \text{ K}$, the time dependences of some parameters of the domain structure of a pure TGS crystal during its evolution after the phase transition were found from domain pictures. It was shown, particularly, that the average linear dimensions of domains along the [001] and ~[100] directions obey the power law: $\langle w \rangle \sim t^\alpha$, where the exponent $\alpha$ varies upon temperature from 0.45 to 0.93. Here for all TGS crystals under investigation the time dependences (Figures 8 a–d) for the characteristic scale length $L_c(t)$ were found, i.e. the distance at which the absolute value of the correlation function $C(r = L_c,t) = 0.5$ occurred. These dependences also obey the power law $L_c(t) \sim (t - t_c)^\alpha$, known from [23] for various thermodynamic systems undergoing phase ordering. The values of exponent $\alpha$ are in good agreement with those from [12].

For a nominally pure TGS, the exponent $\alpha \approx 0.5$ at a distance from $T_c$ by 0.3–0.5 K (in Fig. 9 this region is highlighted by a dotted oval), showing that under these conditions the crystal behaves like a system with a non-conservative macroscopic order parameter [23]. This result is in good agreement with the result of [15], where it was shown within the framework of the Ginzburg–Landau theory, that near the critical point the evolution of the non-equilibrium 180° domain structure to thermodynamic equilibrium occurs in such a way that the correlation radius and, consequently, the sizes of domains of the ferroelectric grow according to the law: $\sim r^{0.5}$. 

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Near the Curie point ($\Delta T_c \approx 0.1–0.2$ K), the exponent $a$ for TGS is close to 1 and the same values of $a \approx 1$ are demonstrated by LATGS and XR-TGS crystals, but in the range $\Delta T_c \approx 0.3$ K. The reason for such a strong discrepancy between the experimental and model behaviour of $a$ [8, 9, 23] may be due to the fact that in the immediate vicinity of the transition point, the volumes of the polar medium components (the domains themselves and the regions separating them, interpreted as domain walls) are close in size [6, 11, 35], and between two phases of the system (domains of different signs) there are no sharp boundaries, whose existence is an obligatory element of the model approach [23]. It can be assumed that the kinetics of not only the enlargement of the domain structures of the studied crystals, but probably also of other two-phase systems in the immediate vicinity of the phase transition point is not described by existing theoretical models [23] and requires additional research.

The values of $a$ decrease upon a decrease in temperature: for LATGS at $\Delta T_c = 0.5$ K and for XR-TGS at $\Delta T_c = 0.6$ K, they are close to the value of 0.33, which is characteristic for the evolution of systems with a conservative order parameter [6]. For pure TGS, $a$ decreases slower and its “conservative” value of $a \approx 0.3$ can presumably be achieved at $\Delta T_c \approx 2–3$ K, which, however, should depend on the quality, that is the degree of defectiveness of the crystal. Figure 9 shows the temperature dependence of the exponent $\alpha$ obtained for nominally pure TGS in this work, as well as its values according to the data of [8, 9, 11].

**Fig. 8.** Time dependences of the characteristic length $L_c$ for pure TGS: $\Delta T_c = 0.1$ K (a); $\Delta T_c = 1.0$ K (b) and for LATGS: $\Delta T_c = 0.3$ K (c); $\Delta T_c = 0.6$ K (d). Curves 1 – [001] and 2 – [100] directions.

**Fig. 9.** The values of the exponent $\alpha$ in the dependence $L_c(t) \sim (t - t_0)^{\alpha}$ at different distances from $T_c$: according to the data of this work – 1, according to the data of [8, 9] – 2.
9]. All experimental points, as can be seen from the figure, fit well on one curve, which probably indicates the objectivity of the results obtained. In the crystals with defects (LATGS, XR-TGS, TGSP, TGS-Cr) at a greater distance from \( T_c \) (3÷4 K) exponent \( \alpha \) tends towards a value of 0.2, which is characteristic for the evolution of inhomogeneous structures with defects during spinodal decay [17].

Theoretical and experimental studies of phase ordering in various systems give grounds to describe the development of the domain structure within the framework of the scaling hypothesis [8, 23]. The essence of this approach is that the domain structure (in a statistical sense) does not depend on time, when all lengths are scaled using the characteristic length \( L_c(t) \). It was shown [23] that the scaling properties of the growth kinetics of the emerged phases depend only on the spatial dimensionality of the system and are the same for systems either with defects or without them. In the present work, the scaling forms of the correlation functions \( C(r,t) = f(r/L_c(t)) \) were tested for all the crystals under study near the phase transition point. The examples of functions \( C(r,t) = f(r/L_c(t)) \), are shown in Fig. 10.

It can be seen that the scaled correlation functions for different time points on the initial section \( 0 \leq r/L_c \leq 2 \) of the graph decrease linearly according to the law \( f(r/L_c(t)) = 1 - k(r/L_c) \) with coefficients \( k = 0.54 \) for TGS and \( k = 0.57 \) for LATGS, close to the value 1/2, where 2 is the dimensionality of the system, and then begin to gradually dissipate. This behaviour is interpreted as Porod’s law [8, 23], which is characteristic for the field of both conservative and non-conservative scalar order parameters.

4. Conclusion

As a result of studying the formation of a quasi-equilibrium domain structure of ferroelectric crystals of the TGS group in a temperature range with the width of \( \Delta T_c = 1 \) K the following conclusions can be drawn:

1. During evolution of the DS the spatial correlation of domain configurations increases with time, as well as when moving away from \( T_c \) towards lower temperatures. In the crystals with defects in which the domain walls are less mobile, the absolute values of \( C(r,t) \) and, consequently, the spatial correlation of domain patterns do not significantly change both in time and temperature.

2. The characteristic length increases over time according to a power law with an exponent that is similar for the studied crystals. The decrease of the absolute values of the exponent, when moving away from the Curie point in the studied temperature range, is a consequence of the transition of the domain structure of TGS crystals during its evolution from a non-conservative state to a conservative one [18].

3. The correlation functions of domain patterns of all studied TGS crystals, presented at different times in a scaled form \( C(r,t) = f(r/L_c(t)) \equiv f(x) \), in the initial region \( 0 \leq x \leq 2 \) and near the temperature of the ferroelectric phase transition have a universal scaling form for the ordering kinetics of two-phase systems with a scalar order parameter: \( f(x) = 1 - 0.5x \).

4. The spontaneous evolution of the domain structure of crystals of the TGS group obeys the general laws of the ordering kinetics of two-phase systems of different nature not far but also near the phase transition temperature, that

Fig. 10. The dependencies \( C(r,t) = f(r/L_c(t)) \) over the time interval 2 ÷ 80 min at \( \Delta T_c = 0.1 \) K: TGS crystal, direction [001] (a); LATGS crystal, direction [001] (b)
is confirmed by the power-law time dependences of the characteristic sizes of the regions of two phases (domains) \( L(t) \), and the scaling behaviour of the domain structure.

**Authors contributions**

All authors made an equivalent contribution to the preparation of the publication.

**Conflict of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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