Phase transition in triglycine sulfate by piezoelectric response force microscopy and dielectric spectroscopy

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Many studies were performed for a better understanding of the phase transition in triglycine sulfate (TGS) well known as ferroelectric organic compound. The material undergoes second – order phase transition at about 49.5°C. From the three glycine molecules (G1, GII, GIII) forming the unit cell the non – planar GI molecule is responsible for the polarization and shows a complex dynamics much faster than that performed by the other glycine molecules [1]. Despite a large number of works on the investigation of phase transition in TGS, the mechanism by which a spontaneous dipole moment is created, is still not fully understood, the processes of the appearance of polar state at cooling and destruction of ferroelectric domains upon heating remain unstudied at the nanoscopic level. The narrowest region near Tc remained the least studied [2,3].

The phase transition in TGS has been studied in this work by means of dielectric spectroscopy and piezoelectric force microscopy (PFM). The TGS dielectric spectra were measured in a wide frequency range. The total dielectric spectra of TGS crystal measured near phase transition temperature is presented in the Figure 1. At least two characteristic times can be clearly revealed from this spectra; 300 kHz and 40 GHz. An attempt was made to combine the molecular dynamics data [1] in TGS near phase transition temperature with dielectric dispersion and observed in PFM structure transformation features.

The images obtained by PFM *in situ* reflected the evolution of TGS surface structure during the phase transition (Fig. 2). The formation of surface polarized structure in the form of elongated thin lamellas was recorded at T ≈ 49.5°C under conditions of slow cooling the sample. The width of lamellas is $w_1 \approx 50 \pm 10$ nm (light contrast), $w_2 \approx 74 \pm 10$ nm (dark contrast) (Fig. 2a). When the temperature drops to 49.2°C, the lamellas become enlarged, their width and its dispersion increase to $w_1 \approx 105$-291 nm, $w_2 \approx 137 - 342$ nm (Fig.2b). The regions with a light contrast occupy ~ 50% of the total image area at T ≈ 49.5°C and ~ 62% at 49.2°C. The domains coalesce upon further cooling to 48.7°C and below, gradually increasing in size, while a slight predominance of one sign over the other remains.

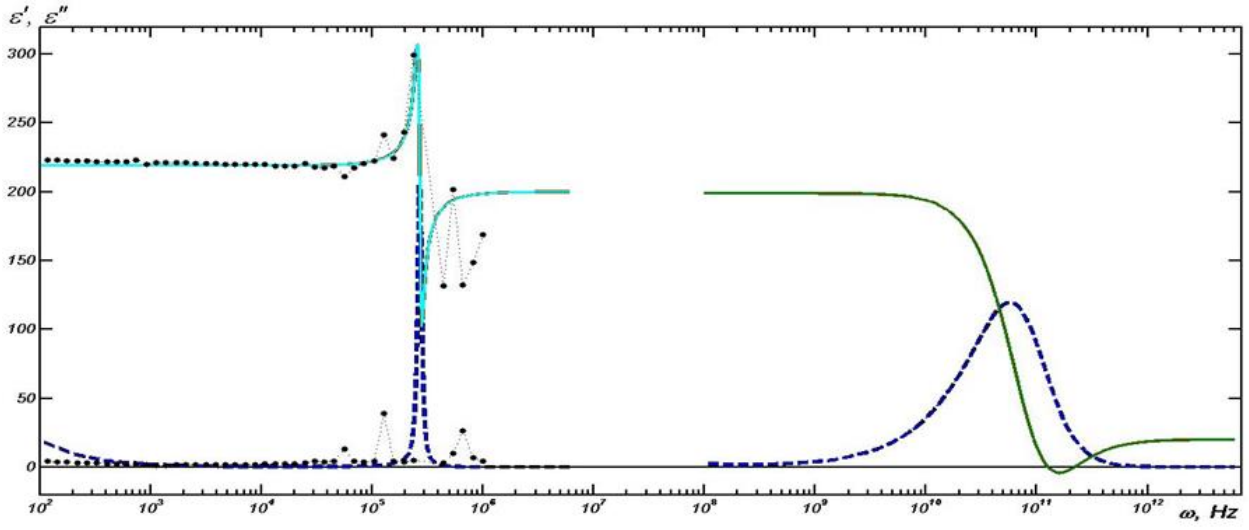

Figure 1. Dielectric spectra of TGS in the hole investigated frequency region.

To the right of the images of domain structures, their two-dimensional amplitude Fourier spectra are shown. The Fourier transformation of the phase images showed that a quasiperiodic one-dimensional domain structure is formed in the immediate vicinity of phase transition point $Tc-1°C < T < Tc$, which is characterized by the repetition of bands of the same width with a small random dispersion around the mean value. Notably, obvious features of the quasi-periodicity of domain structure disappear at a distance from the phase transition point by a degree or more, the width of the domains and the dispersion of width values from the mean value increase significantly.

The calculation of two-dimensional correlation functions made it possible to determine the period of the structure and analyze the temperature dynamics of the TGS crystal in this region. The quasi-periodicity of structure is become apparent most clearly at $T \approx Tc - 0.2°C$.

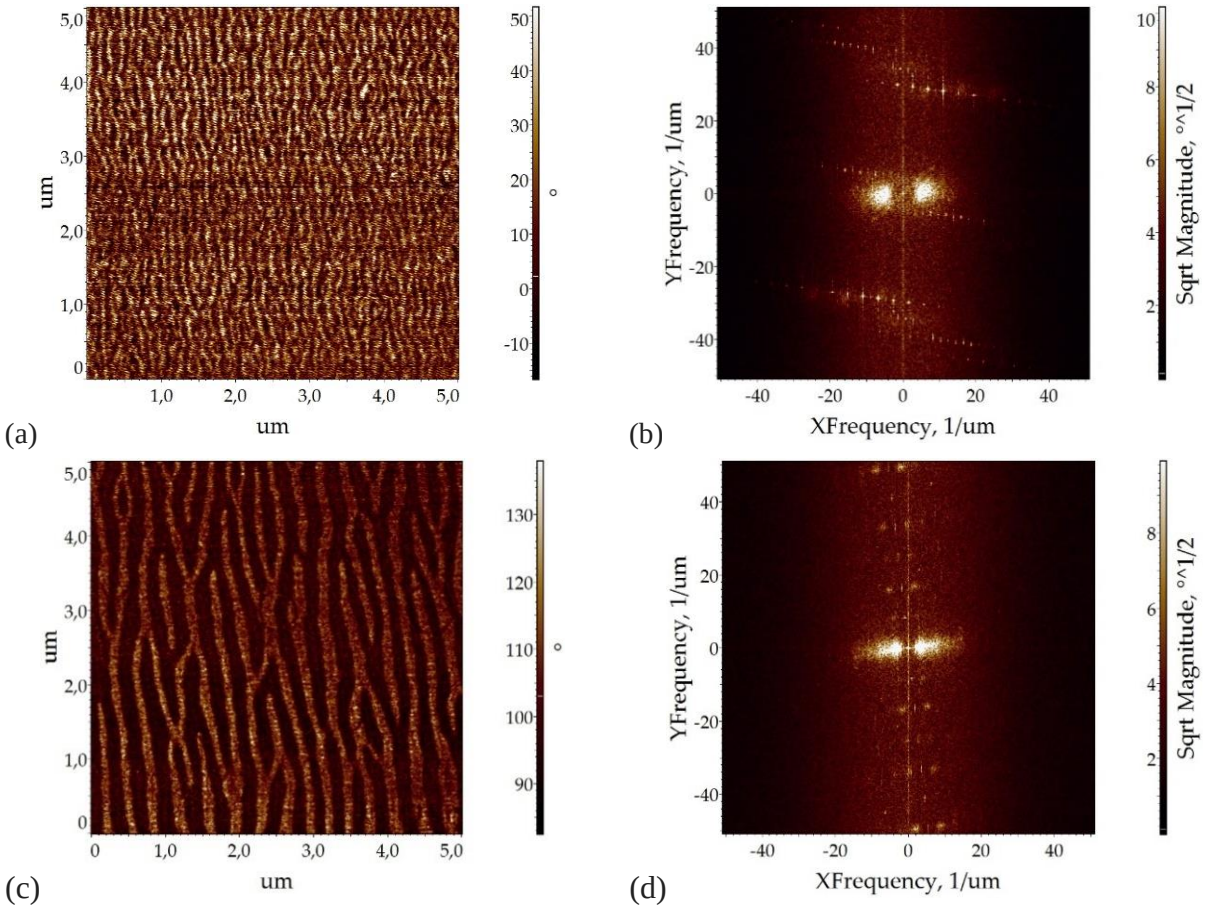

Figure 2. (a, b) PFM image of quasiperiodic structure of TGS crystal: (a) 49.5, (b) 49.2. (c, d) Corresponding two-dimensional amplitude Fourier spectra.

According to X-ray and neutron studies of TGS single crystals near Tc, diffuse scattering of Bragg reflections *0kl* is observed in the inverse space, which indicates correlation interactions at the local structure level: from one-dimensional zigzag chains of N^+H_3 groups aligned along *b* to three-dimensional ordering in network [4]. It is obvious that the processes observed here at the microscopic level are directly related to structural rearrangements occurring at the atomic level.

The correlation between the features of wide-band dielectric spectra and quasiperiodic structure of TGS crystal in the immediate vicinity of phase transition is discussed.

1. V. Tripadus, A. Radulescu, J. Piepe, at all., *Chemical Physics* **322**, 323 (2006).
2. E.Z. Luo, Z. Xie, J.B. Xu, et al., *Phys.Rev.B.* **61**, 203 (2000).
3. X.K. Orlik, V. Likodimos, L. Pardi, at al., *Appl. Phys. Lett*. **76**, 1321 (2000).
4. J.M. Hudspeth, D.J. Goossens, T.R. Welberry, et al., *J Mater Sci*. **48**, 6605 (2013).