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AFM characterization of domain structure of ferroelectric TGS crystals on a nanoscale

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Abstract

Atomic force microscopy has been used for the study of the surface topography and domain structures of triglycin sulfate (TGS) crystals. The images of various types of domains at the polar (0 1 0) surfaces of as-cleaved TGS crystals have been obtained (in contact mode and resonant mode). The crystals grown old, after annealing, γ-irradiated by various doses, were studied. It has been found that the surface relief of crystals after annealing differs from that of crystals grown old and irradiated: in the first case the peak-to-peak value is nearly constant whereas in the second case it varies in wide limits. The parameters of domain structure were determined. These parameters have been shown to be different for crystals grown old, crystals after annealing and irradiated crystals. It has been shown that, after cantilever scanning after a long period in different AFM modes the TGS surface experiences a partial polarization reversal.

Keywords: Ferroelectrics; Domains; Atomic force microscopy

1. Introduction

Atomic force microscopy (AFM) is successfully applied to the investigation of ferroelectric crystals [1–4]. However, interpretation of the images obtained in different AFM modes is still complicated because of insufficient knowledge of the mechanism of their formation and difficulties in the separation of various "irregular" domain structure configuration and topographic surface relief. To investigate the domain surface microrelief and to reveal the peculiarities of the images obtained in the different AFM modes, the crystal of TGS has been selected for investigation. This model crystal with the cleaved surface being perpendicular to the polar direction has been intensively studied on a macroscale. Analysis of the images obtained in different modes (in contact, lateral force and resonant mode) makes it possible to study the domain structure on a nanometer scale. We managed to observe the process of domain repolarization under probe tip influence during scanning process both in contact and resonant modes.

2. Experimental

TGS crystals ($(NH_3CH_2OO)_3$ H_2SO_4) were grown at the Institute of Crystallography by

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isothermal evaporation method at temperatures $T > T_c$ (49.5°C). The samples prepared in different conditions have been investigated. The series of samples comprised aged crystals of weak unipolarity with lens-like domains oriented by the long axis along the *a*-axis of the crystal. Another series of samples was γ-irradiated by Co^{60} with a dose of 0.8 Mrad. They showed a high density of domain boundaries of different configuration.

TGS crystal surface images were obtained in different AFM modes (in contact, lateral force and resonant mode) using the AFM microscope 'Solver NT-MDT'. In every case, the as-cleaved crystal surfaces in air have been investigated. The contact and lateral force modes, a Si_3N_4 cantilever of 85 μm length with 120 kHz resonance frequency and a tip radius of 50 nm was used; in the resonant mode conducting Si cantilevers (NT-MDT) of 90 μm length with 165 kHz and tip radius of 20 nm were used.

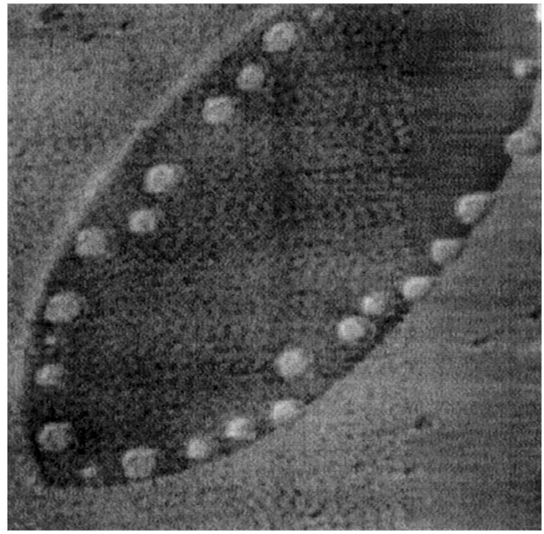


Fig. 1. Contact mode. 3000 × 3000 nm² lateral force image of an aged TGS crystal (old domain).

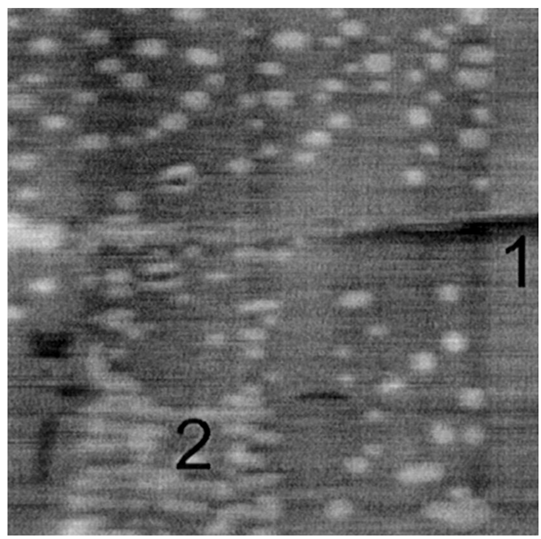
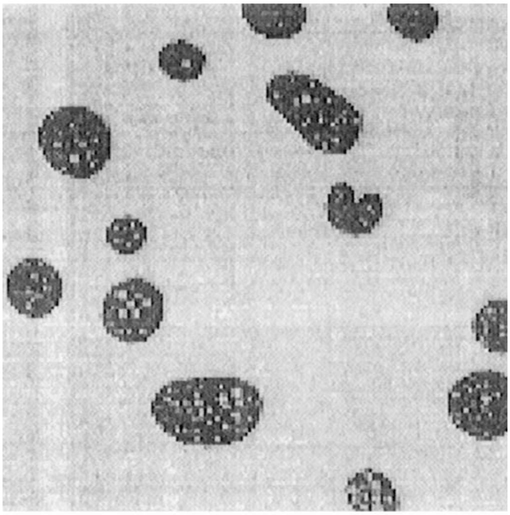


Fig. 2. Contact mode. 1200 × 1200 nm² topographic image of an aged γ-irradiated TGS crystal ($D = 0.8$ Mrad, Co^{60}). (2) marks the part of the surface with partial repolarization after additional scanning.

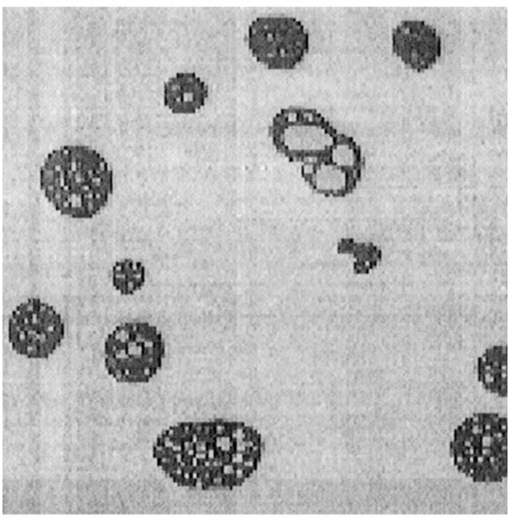
3. Results and discussion

In Fig. 1 the image of an area of aged and weakly unipolarized crystal surface obtained in the lateral force mode is shown. One can see a classical lens-like domain oriented with the long axis of the lens parallel to the crystallographic *a*-axis. Its size is 1800 nm (along the short axis) and about 4000 nm (along the long axis). The domain is well distinguished in the surrounding matrix having the opposite polarization. Inside the walls of the domain round islands of different polarity of 100–150 nm diameter can be seen. They may act as domain nuclei in further repolarization. They can continue the ousting of the smaller domain component under natural aging and/or crystal repolarization in the electric field parallel to the spontaneous polarization of the larger domain component. One can notice, that in the topographic image the large lens-like domain cannot be clearly seen whereas in the lateral force mode (Fig. 1), it exhibits a clear contour.

In Fig. 2 the topographic image of irradiated crystal surface (contact mode) is depicted, where one can see domains of irregular form of linear size from 40 to 160 nm. They appear after many times of scanning the cantilever on surface. Cantilever scanning along the *X*-axis yields domains elongated in the *X*-direction. It is seen for example, in the lower left corner of the figure (2) where scanning



A



B

Fig. 3. Resonant mode. Phase image of a γ-irradiated TGS crystal. ($D = 0.8$ Mrad). (A) single scanning; (B) after 40-min scanning, the smaller domain component has partially repolarized. All images are $6100 \times 6400\ \text{nm}^2$ in size.

was carried out more often than on the rest of the surface of the crystal (1). The distance in relief depth between the appeared domains and the matrix having the opposite polarization was 0.7–0.8 nm. It is interesting to note that all the new formations have the form of protuberance on the domains of different sign.

The possibility of probe tip influence on the surface under investigation is known for contact mode of AFM. In resonant mode this influence is assumed to be weaker. However, our results show that when the time of tip acting on the surface increases, this acting can produce noticeable changes of surface domain ferroelectric structure in resonant mode too. In Fig. 3 the image of irradiated crystal obtained in resonant mode in phase contrast conditions is given. The domains of various forms can be seen. Inside these domains the areas of opposite polarization are revealed. Under these conditions of topographic imaging the domains are revealed as the surface areas with different relief depths as in the contact AFM mode. After many times of surface scanning a continuous change of the kind of domain is observed, namely its partial repolarization. So it can be seen that in the condition of "soft" resonant mode, active interaction between the tip and the surface takes place too.

Because of this, the question about stability of the TGS surface modified in this way arises. In Fig. 4A–C one can see different stages of changes in the non-irradiated crystal surface aged under scanning in contact mode with $F \sim 10^{-7}$ N. These new formations are revealed in the form of both protuberance and cavity with respect to the initial matrix. However, these new formations are unstable and after 12 h they start to disappear (Fig. 4D).

4. Conclusions

The characteristics of the TGS crystal domain structure vary widely depending on the sample history. The size of the step between the antiparallel domains and the width of the wall are minimal for domains formed shortly before or in the process of the study by AFM. Both the contact and the resonant modes cause repolarization of the TGS ferroelectric crystal after long scanning. As a result, if an optimum scanning mode is found and the samples are specially treated, a domain structure of specified configuration could be formed on the ferroelectric surface.

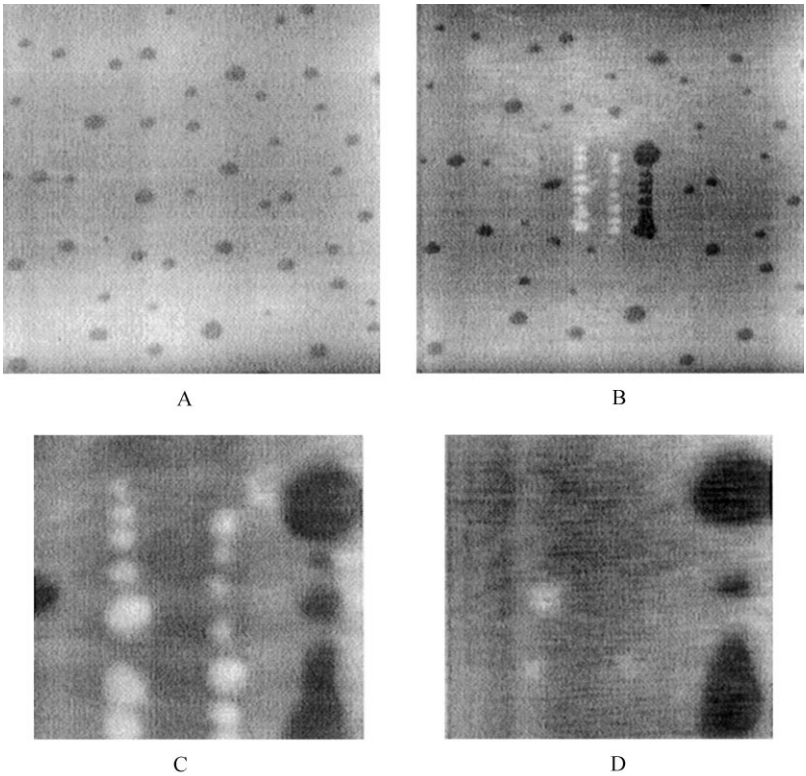


Fig. 4. Contact mode. Topographic image of an aged crystal surface: (A) single scanning; (B), (C) partial repolarization of the surface after 1 h scanning; (D) image of the same area after a 12-h annealing at room temperature. The initial surface has been partially restored. (A, B) $3700 \times 3700\ \mathrm{nm}^2$, (C, D) $1000 \times 1000\ \mathrm{nm}^2$.

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