Local elastic properties of layered ferroelectric TGS crystals

A.L. Tolstikhina[1], R.V. Gainutdinov[1], A. K. Lashkova[1], D. A. Zolotov[1], B.S. Roschin[1], V. E. Asadchikov[1], V.N. Shut[2], S.E. Mozzharov[2], I.F. Kashevich[3]

[1] *Institute of Crystallography. A.V Shubnikov Federal Research Center "Crystallography and Photonics" RAS, Moscow, Russia*
[2] *Vitebsk State Technological University, Vitebsk, Belarus*
[3] *Vitebsk State University named after P.M. Masherova, Vitebsk, Belarus*

* corresponding authore-mail :kashevich@tut.by

Abstract

A technique for studying the local elastic properties of inhomogeneous ferroelectrics has been proposed by the example of growth striations in triglycine sulfate crystals, layer-by-layer doped with chromium and L-α-alanine impurities. The data on the width and impurity compositions of stripes were obtained by X-ray fluorescence analysis and X-ray topography. The positions of the boundaries of the stripes emerging at the surface and the domain structure morphology were determined by the methods of correlation electrical atomic-force microscopy. Local elastic properties (Young's modulus) in pure and doped stripes of the crystals with profile distributions of chromium and L-α-alanine were measured by the AFS method for the first time. It was found that Young's modulus in doped stripes is smaller than in pure ones.

Keywords: triglycine sulfate crystals, Young's modulus, impurity composition, atomic-force microscopy.

Introduction

Ferroelectric crystals of the triglycine sulfate (TGS) family have a significant pyroelectric effect and are used to create thermal sensors and radiant energy receivers, for example, to detect infrared (IR) and microwave radiation [1, 2]. The properties of a TGS crystal substantially depend on the introduced impurities; therefore, work is still ongoing to study the effect of various additives to the solution and crystallization conditions on them. Recently, profile doping techniques have been used to control the properties of ferroelectrics, which demonstrate new possibilities [3-5].

This work continues the series of studies of TGS crystals with a profile periodic distribution of nonpolar and polar impurities [6]. Theoretical modeling of the properties of device elements based on uniaxial ferroelectrics with a composition gradient is based on knowledge of the physical properties of the crystal. Mechanical properties are classified as important.

The aim of this paper was to study the mechanical properties by the ACC method in "pure" and doped stripes of TGS crystals with the profile introduction of nonpolar and polar impurities (Cr3+ and L-α-alanine).

Experimental

We studied TGS-TGS+Cr crystals obtained by periodically growing crystals in solutions of various compositions - nominally pure and containing an impurities of chromium ions and L-α-alanine. The method and device for growing such crystals are given in the work [7].

To study the elastic properties of TGS crystals with impurities microindentation is usually used [8]. In our case, the choice of atomic force microscopy (AFM) was due to the small size of the streaky structures (from 100 to 700 μm) and the possibility of independent control of the width of

the transition region between the stripes with impurity modulation extrema using piezoresponse force microscopy (PFM) and scanning capacitive force microscopy (SECM).

The complexity of the task is due to the technical difficulties of precise positioning of the probe relative to the middle of alternating bands with and without impurities (the maximum scanning area of most AFMs does not exceed 100 μm).

The surface of the samples was studied using an NTEGRA Prima scanning probe microscope (NT-MDT). The search for the boundaries of the bands with and without impurities was carried out by the PFM and SECM methods using silicon cantilevers (HA_FM/Pt, beam B, Tipsnano, Estonia) coated with Pt, with the following characteristics: resonant frequency f = 140 kHz, rigidity ktip = 3.5 N/m , the tip rounding radius R < 30 nm.

To study the mechanical properties, much more rigid cantilevers were used, which makes it possible to achieve a force value at which surface deformation occurs, namely cantilevers (HA_HR, beam A, Tipsnano, Estonia) with the following characteristics: f = 380 kHz, ktip = 34 N/m, R < 10 nm. Distance dependences of the force were measured in the AFM contact mode at the center of each of the bands (doped and pure) in order to eliminate the effect of possible impurity diffusion near their boundaries (Figure 1).

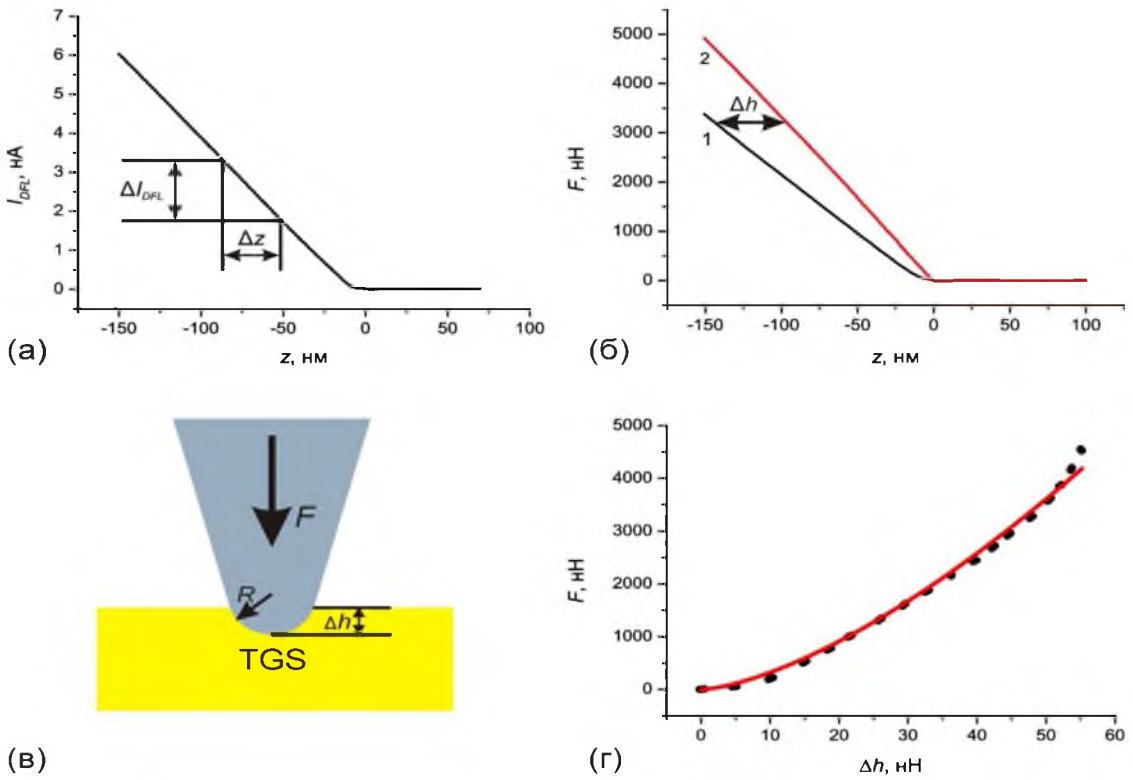

Figure 1. Young`s modulus determination by the AFM method: (a) dependence of photodiode mismatch current on the piezo scanner displacement for the reference sample, (b) the force exerted by the tip on the surface as a function of piezo scanner displacement for (1) deformable and (2) reference samples, (c) sample surface deformation under cantilever tip, and (d) dependence of the force applied to the sample on the tip penetration depth into the surface.

Before measurements, an initial topographic image of the surface was obtained in the intermittent-contact mode, still free from destruction under the influence of a rigid cantilever. Then the atomic force microscope was switched to the contact mode, and the dependence of the force on the distance was measured. For each of the bands, force curves were obtained at 25 surface points, which were then averaged. The movement between the points was carried out in the absence of

contact between the cantilever tip and the surface in order to avoid its destruction or modification due to hard contact with the tip. After measuring the force curves in the crystals, reference force curves were obtained on a test non-deformable sample of an optically polished lithium niobate crystal.

Results and discussions

Figure 2a shows the averaged dependences of the acting force on the scanner displacement for pure (curve 1) and doped (curve 2) stripes. A difference in the slopes of dependences measured for stripes with and without impurity is observed. This fact indicates a difference in the mechanical properties in the TGS + Cr and TGS stripes.

The dependences of the force applied by the cantilever tip on the penetration depth were calculated for each stripe from the obtained data (Fig. 2b). Experimental curves 1 and 2 correspond to pure and doped stripes, respectively. The reference sample was an optically polished lithium niobate crystal.

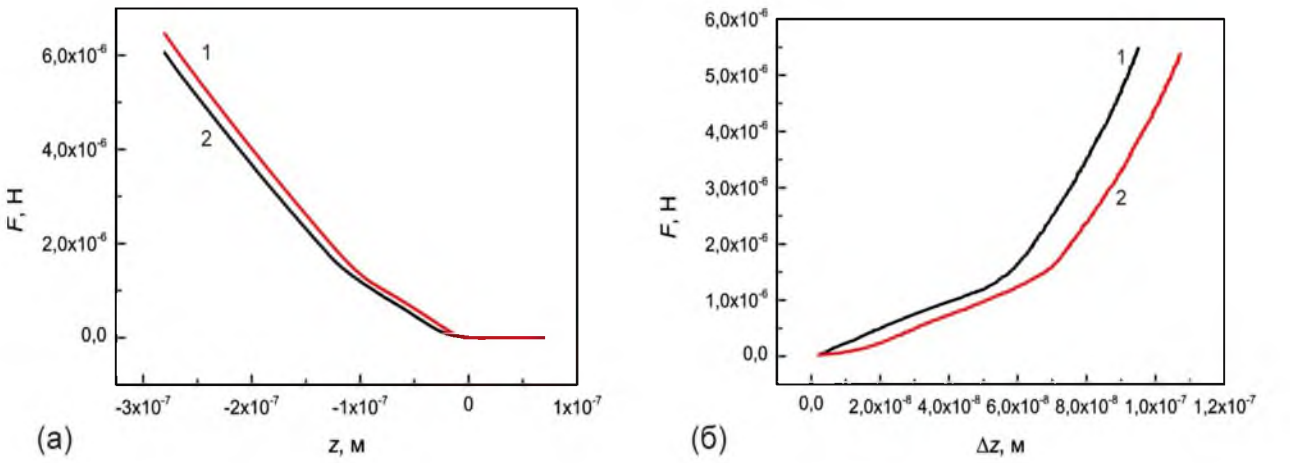

Figure 2. Young's modulus in the TGS–TGS + Cr sample: (a) the force exerted by the tip on the surface as a function of piezo scanner displacement for the (1) TGS and (2) TGS + Cr stripes and (b) dependence of the force applied to the sample on the penetration depth of the tip into surface for the (1) TGS and (2) TGS + Cr stripes.

The approximation of obtained dependences made it possible to determine Young's moduli in the stripes with and without impurity; the latter were found to be E_{doped}= 0.96 GPa and E_{pure} = 1.2 GPa respectively; i.e., the difference amounts to 20–25%. The estimation of measurement error 3 SD (standard deviation) does not exceed 5%, which indicates reliability of the data on the difference between Young's moduli for pure and chromium-doped stripes. Thus, even a small content of Cr^{3+} impurity results in a significant difference in the mechanical characteristics of pure and doped stripes.

The results of the study showed the TGS–TGS + LATGS crystals to be single-domain. For this reason, it is impossible to separate doped and pure stripes based on domain-structure morphology. However, the surface areas with a clearly pronounced change in contrast are observed; the boundaries between these areas are fairly straight and smooth. A detailed study of these boundaries showed them to be parallel to the crystal growth face. A spatial modulation with a period of about 200 μm is observed during displacement perpendicular to the boundaries, which agrees well with the XRD data.

Conclusion

Thus, mechanical characteristics (Young's modulus) were measured by atomic force spectroscopy in pure and doped bands of crystals with a profile distribution of chromium and L-α-alanine impurities for the first time. It was found that the Young's modulus in stripes with impurities is lower than in pure ones, namely, in stripes with chromium impurities, the difference was 20–25%, while with L-α-alanine impurities it was 12–14%. In "pure" TGS stripes, Young's modulus is two times higher for TGS–TGS + LATGS crystals than for TGS–TGS + Cr crystals. This may be due to the fact that a crystal with a polar impurity of L-α-alanine experiences strong mechanical stresses; however, additional studies are required to confirm this hypothesis. Thus, the profile introduction of an impurity affects not only the domain structure, optical and electrical characteristics of crystals, but also their mechanical properties.

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