Formation of domain configurations of doped layered TGS ferroelectric crystals

A.L. Tolstikhina[1], R.V. Gainutdinov[1], A. K. Lashkova[1], D. A. Zolotov[1], B.S. Roschin[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 comprehensive study of the growth striped structure of triglycine sulfate crystals doped layer by layer with an impurity of chromium ions has been carried out. Data on the width and impurity composition of the bands were obtained by X-ray fluorescence analysis and X-ray topography. The obtained data on the impurity growth structure are compared with the character of the domain structure studied using the nematic liquid crystal method. It is established that the impurity in the crystal is distributed according to a sinusoidal law. A correlation was found between the formation of a regular domain structure and the nature of the impurity distribution for layered TGS-TGS+Cr crystals. It has been established that the formation of domain walls occurs mainly in areas corresponding to a change in the impurity concentration gradient, and in places where the sign changes from positive to negative, smooth walls are formed, and from negative to positive, the domain boundary has a jagged, uneven contour.

Keywords: triglycine sulfate crystals, configuration of domain walls, impurity composition, X-ray fluorescence analysis.

Introduction

Ferroelectric crystals with a specially formed domain structure have unique properties and are in demand, in particular, for electrooptical applications. Controlling the shape of domains and properties of domain walls is a key issue for these applications. Numerous studies show that the addition of an impurity, its concentration, and distribution over the crystal volume lead to significant changes in the optical, electrical, and elastic properties near domain walls and affect the domain dynamics. However, there is still no unified idea of the mechanisms of interaction between impurity and domain structures. When elucidating the conditions for the formation of a regular 180° domain structure in high-temperature ferroelectrics with a layered impurity structure, it was found that there is a one-to-one correspondence between the growth bands and the domain configuration. The authors of [1–3] found that the formation of periodic domain structures in lithium niobate depends on the concentration gradient of the yttrium impurity. The same results were obtained in [4, 5] for LiTaO3 optical superlattices. It was shown in [2–3] that domain walls are always located in the place where the concentration gradient of the dissolved substance of the yttrium impurity Y changes sign from plus to minus or vice versa. The domain wall located at the concentration minima is very sharp, while the domain wall located at the concentration maxima is diffuse.

In these works, the mechanism of the gradient of the critical impurity concentration for the formation of domains with a regular periodic structure was proposed. The origin of the thickness inequality between layers of positive and negative domains, as well as island-like domains in periodic domain structures, is interpreted based on this mechanism.

The aim of this work was to clarification the issues related to the influence of a regularly inhomogeneous periodic distribution of chromium ion impurities on the formation of the domain structure of triglycine sulfate (TGS-TGS+Cr) ferroelectric crystals grown from solutions, and, in particular, to obtain a regular 180-degree domain structure.

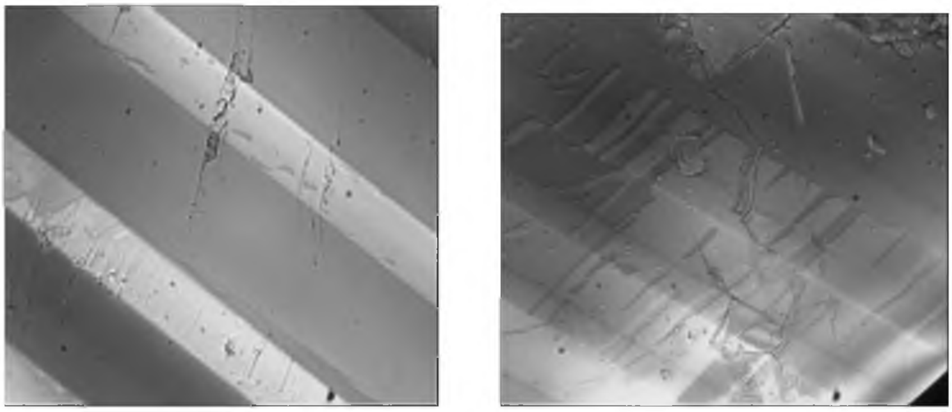
Experimental

We studied TGS-TGS+Cr crystals obtained by periodically growing crystals in solutions of various compositions - nominally pure and containing an admixture of chromium ions. The method and device for growing such crystals are given in the work [6].

Optical and X-ray topographic microscopy (RT) was used to visualize the impurity structure and evaluate its parameters. The spatial distribution of the impurity was studied by X-ray fluorescence analysis (XRF) and was performed at the Institute of Crystallography. A.V. Shubnikov Federal Research Center "Crystallography and Photonics" RAS.

Results and discussions

Figure 1 shows examples of the domain structure of different sections of the TGS-TGS+Cr crystal obtained by this method.



a) b)

Figure 1. Domain structure (method of nematic liquid crystals) of layered TGS-TGS+Cr crystals (dark layers are impurity) with different orientations of polarization vectors and impurity concentration gradient:
a - parallel orientation, b - 90-degree orientation

The darker bands in Fig. 1, in turn, also represent the growth layers of the crystal doped with a chromium impurity. From the morphology of these growth layers, it is also possible to judge the growth processes, since they repeat the shape of the crystallization front. The similarity of the shapes of the domains and growth layers in Fig. 1 by the morphology of the domains also makes it possible to judge the growth processes.

Of interest is a section of the domain structure (Figure 1.b). A feature of the domain structure of a crystal with a 90-degree orientation is the disappearance of the regular structure on the (100) face, despite the presence of pronounced growth layers.

The data obtained can be explained on the basis of the hypothesis of the polarizing effect of the crystal composition gradient in the growth layers proposed in [7] and based on the Curie symmetry principle. The impurity concentration gradient vector can be considered as an action leading to polarization of the corresponding section of the crystal.

The methods of X-ray fluorescence analysis and X-ray topography made it possible to estimate the degree of uniformity of impurity incorporation in the volume of crystals, as well as to determine the width of the doped and pure bands, which further simplified the study of domain walls by microscopic methods. The results of studies of the profile distribution of the chromium ion impurity in TGS-TGS+Cr crystals by the XPA method are shown in Figure 2.

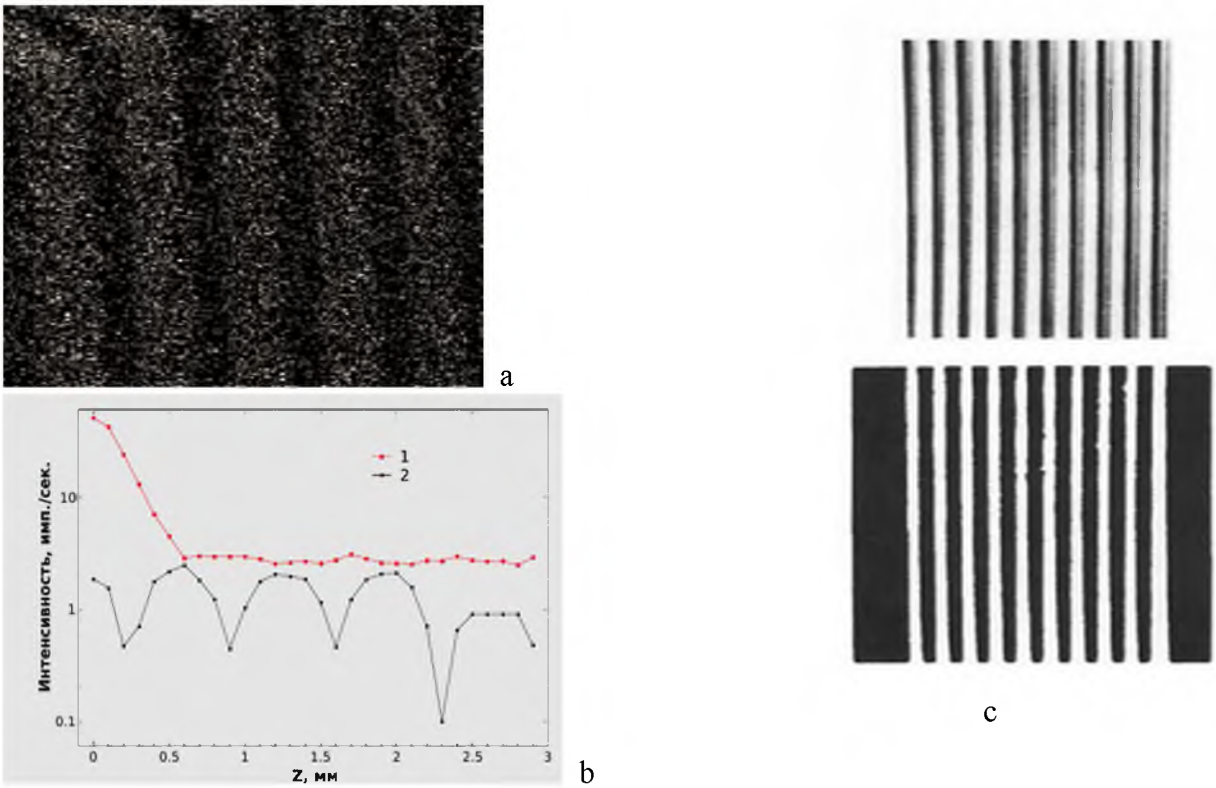


Figure 2. Images of striped TGS-TGS+Cr crystals, RT analysis (a) and the results of studying the profile distribution of chromium ion impurities in TGS-TGS+Cr crystals by XRD method (b). Surface impurity bands of rotational growth of a lithium niobate crystal (top) and the corresponding internal laminar ferroelectric domain structures (bottom) (c). [by 1]

Similarly, as for high-temperature crystals with a regular domain structure, it was found that in places of striped TGS-TGS+Cr crystals, where the concentration gradient changes sign, domain walls are formed, and where the gradient begins to increase, negative domains are formed, with a negative gradient - positive domains (Figure 2a,b). In addition, it was found that the structure of domain walls is different - there is an alternation of smooth walls and with a jagged structure. A sharp minimum of the impurity concentration corresponded to a smooth wall, and an extended maximum corresponded to a rugged, loose one. Apparently, the data obtained can also be explained on the basis of the mechanism of the gradient of the critical impurity concentration.

Conclusion

Thus, the obtained data on the impurity growth structure are compared with the character of the domain walls. The mechanisms of formation of domain configurations doped with nonisomorphic (chromium ions) impurities in layered crystals of triglycine sulfate are elucidated. A correlation was found between the formation of a regular domain structure and the nature of the impurity distribution for layered TGS-TGS+Cr crystals. It is shown that the formation of domain walls occurs mainly in areas corresponding to a change in the impurity concentration gradient, and smooth walls are formed in the places where the sign changes from positive to negative, and from negative to positive, the domain boundary has a jagged, uneven contour. Clarification of the mechanisms and conditions for the formation of domain walls will make it possible to obtain crystals with a given configuration of the domain structure.

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