PECULIARITIES OF THE IMPURITY DISTRIBUTION IN FERROELECTRIC LAYER-DOPED TGS - TGS + Cr CRYSTALS

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In the last two decades, influenced by the success of semiconductor superlattice and quasi-matching (SHG) theories, the ferroelectric superlattice has become a hot topic in materials science and photoelectronics. Ferroelectric superlattices can consist of two types of ferroelectric materials or of ferroelectric and non-ferroelectric materials, composed alternately layer by layer, forming so-called heterostructures [1,2]. However, most of them consist of the same type of material, such as single crystals, in which the domain structure is modulated, for example, by periodic external influences or changes in the concentration of dopant impurities.

All physical properties associated with a third-rank tensor in a superlattice will be modulated by domains, while the properties associated with even-rank tensors remain constant. It is precisely the modulated physical properties that make such a material particularly favorable for use in nonlinear optics and acoustics. Properties described by the odd-rank tensor, such as nonlinear optical coefficients, electro-optical coefficients, and piezoelectric coefficients, are no longer constant in the crystal: instead, they change sign from the positive domain to the negative domain. Consequently, they become periodic functions of spatial coordinates.

Interest in ferroelectric superlattices lies not only in the area of their fundamental research, but also in practical applications. Some of these superlattices are used in new optical and acoustic devices compatible with modern electro-optical technology. It is possible in principle to obtain regular domain structures in any ferroelectrics, because a multi-domain structure is more advantageous. But in reality, ferroelectric superlattices with a regular domain structure, which find practical application in nonlinear optics, were obtained on high-temperature crystals of lithium niobate and tantalate [1, 2]. In this regard, the creation of a regular laminar domain structure with 180-degree domains on ferroelectric crystals grown from solutions is almost never carried out, although such crystals can serve both as model objects for fundamental research and as functional material for practical implementation.

The aim of this work was to obtain layered ferroelectric triglycine sulfate single crystals (TGS-TGS+Cr) doped with a non-isomorphic impurity of trivalent chromium ions, to study the profile distribution of chromium impurities over the crystals volume and corresponding domain structure.

The formation of layered structures directly during crystal growth is one of the ways to obtain regular inhomogeneous structures in crystals. Obtaining of TGS-TGS+Cr crystals was carried out by sequentially growing layers of changed composition by alternately immersing the crystal in liquid media of various compositions - pure and with impurities. With the method of periodic immersion, it becomes possible to obtain layered structures with fairly sharp differences in composition in adjacent layers and the possibility of obtaining layers whose thickness can vary over a wide range, because it is determined solely by the growth time (at a given growth rate). The crystals were obtained at temperatures below the Curie point. Elucidation of the mechanism of the influence of spatial changes in composition on the domain structure and characteristics of ferroelectric crystals can only be carried out under the condition of a precision study of the inhomogeneous distribution of impurities over the volume of the crystal. Despite the large number of developed modern techniques, many of them turned out to be inapplicable for research in TGS-TGS+Cr crystals. This is due to the fact that in most methods for carrying out such studies, the creation of a high vacuum is required, in which samples of doped TGS crystals, as practice has shown, change color and transparency, which indicates a violation of the crystal structure.

Performed at the Institute of Crystallography named after. A.V. Shubnikov Federal Scientific Research Center "Crystallography and Photonics" of the Russian Academy of Sciences, X-ray fluorescence analysis (XRF) and the use of probe microscopy methods made it possible to obtain data on the width of the bands, impurity concentration and the character of the impurities distribution profile in layered TGS-TGS+Cr crystals. Note that XRF is a non-destructive method and used to monitor the content of impurities of various elements with high accuracy and localization. At studying layered crystals difficulties arose due to the fact that the area of illumination of the sample with exciting X-ray radiation should be smaller than the width of the bands with different impurity contents. Piezoresponse force microscopy (PFM) and scanning capacitive force microscopy (SCFM) were used to detect the boundary between doped and pure bands. As our previous studies have shown [3] it possible to successfully detect such boundaries in TGS–TGS+Cr crystals, both on poly- and single-domain areas of the surface. Thus, Figure 1 shows images of the boundary of the doped and pure bands for the crystal under study, obtained by the PFM and SESM methods. At the boundary of the bands there is a sharp change in the morphology of the domain structure, in addition, SESM demonstrates a change in contrast in the pure and doped bands.

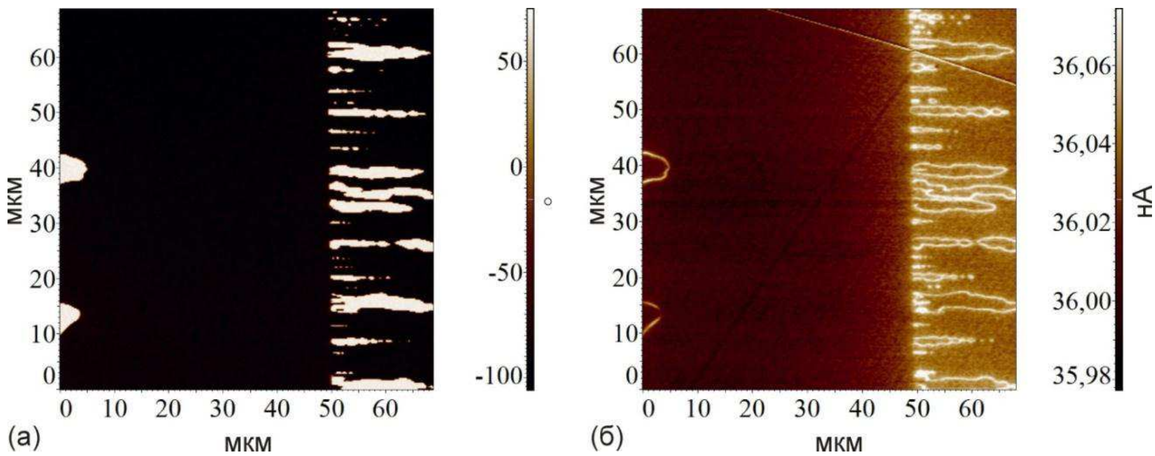

Figure 1 – Image of a section of the surface of a TGS−TGS+Cr crystal with a TGS band on the left and a TGS+Cr on the right: (a) PFM, (b) SESM.

Control of the boundary position in combination with XRF data on the width of the bands allows one to measure the force curves approximately in the middle of both pure and doped bands. The results of studying the profile distribution of chromium ion impurities in TGS-TGS+Cr crystals by X-ray diffraction, obtained in [3], are presented in Figure 2.

It has been established that the impurity in the crystal is distributed according to a sinusoidal law. A correlation has been revealed between the formation of a regular domain structure and the nature of the impurity distribution for layered TGS-TGS+Cr crystals. The formation of domain walls occurs predominantly 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 outline.

Similar results were obtained for lithium niobate crystals [4]. However, the question of the mechanisms of this phenomenon has not yet been clarified. Therefore, in the future it is planned to conduct practical studies and theoretical calculations on the effect of the impurity gradient on the formation of the domain structure and develop recommendations for obtaining RDS in ferroelectric crystals grown from solutions.

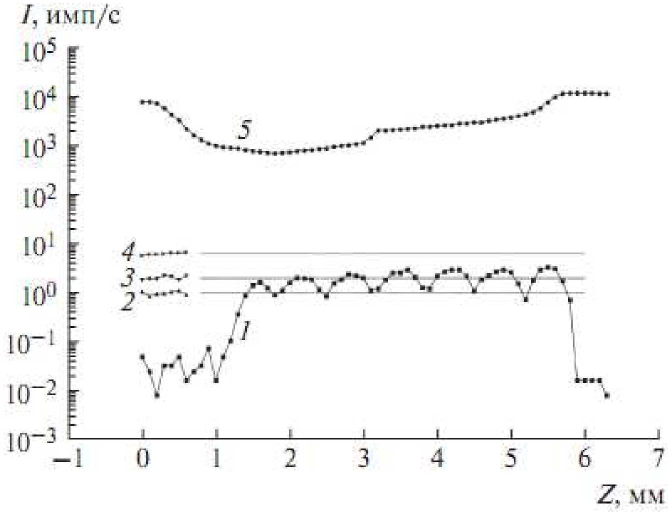

Figure 2 - Dependences of the intensities of the fluorescent radiation output of the CrKα line (1) and the radiation transmitted through the TGS−TGS + Cr crystal (5) and on the vertical position of the crystal. The dependences shown by triangles were obtained from calibration measurements of ruby rystals with chromium ion concentrations of 0.05 (2), 0.12 (3) and 0.7 (4) wt. %. The dotted line shows the corresponding mean intensity values calculated from the calibration measurements for each concentration. Z – measurement area, mm [3].

Besides within the framework of testing the growth modes of layered ferroelectric single crystals of triglycine sulfate doped with chromium, based on the study of the absolute supersaturation of solutions with varying degrees of purification, the role of one of the mechanisms of spontaneous nucleation in the process of growing such crystals was clarified. The methods of X-ray fluorescence analysis and X-ray topography made it possible to estimate the degree of uniformity of the impurity in the bulk of the crystals, as well as to determine the width of the doped and pure layers, which subsequently simplified the study of domain boundaries using microscopic methods.

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