Ferroelectric domains of a new type: closed loop domains at twinning boundaries

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The ferroelectric crystal guanidine alumosulfate hexahydrate, $[C(NH_2)_3]\cdot[Al(H_2O)_6][So_4]_2$ (GASH), is known to belong to the class $3m(C_{3V})$ over its entire range of existence and to lack a paraelectric phase. It decomposes when it reaches the Curie point [see, for example, F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon, New York, 1962 (Russ. transl. Mir, Moscow, 1965). The 180° GASH domains are optically indistinguishable. The domain structure has accordingly been studied by a decoration method [B. Hilczer *et al.*, Phys. Status Solidi **a28**, k101 (1975), and F. Suda *et al.*, J. Phys. Soc. Jpn. **45**, 916 (1978)] and by an electroluminescence method {I. S. Zheludev *et al.*, Kristallografiya **7**, 147 (1962) [Sov. Phys. Crystallogr. Vol. 7, 121 (1962)]}.

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In some experiments in which liquid crystals were used to decorate the domains in GASH crystals[5] we have observed, in addition to the ordinary 180° domains, some domains of a new type, which have not been observed previously in any ferroelectric. In a plane perpendicular to the polar axis fo the crystal (the z axis) these domains are narrow loops (1-μm or less thick) of substantial length (10^2–10^3 μm). They begin at one edge of the crystal and wind their way across the entire surface, ending up at the same or at another edge of the crystal or forming closed configurations of arbitrary shape (Fig. 1). The patterns of the observed domains on opposite surfaces of a sample (from 0.2 to 3 mm thick) oriented perpendicular to the z axis are absolutely identical; i.e., the walls of these domains run parallel to P_s.

In a static field of the appropriate sign along the z axis, the domains begin to expand nearly symmetrically in both directions. When the field is reversed before the complete sample has been put in a single domain, the domain walls begin to move opposite each other; coalescing along the line of the initial position, they can no longer be observed. In sinusoidal fields $E_{z\sim}$ a loop begins to change position when the threshold field E_t (which depends on the initial perimeter of a domain) is reached; at this point, the loop begins to elongate in proportion to the field (Fig. 2). With a further increase in the field amplitude $E_{z\sim}$ and, correspondingly, in the perimeter, the domain becomes unstable and begins to break up into separate closed loops, whose length decreases with increasing $E_{z\sim}$. On occasion we observe, at a constant amplitude $E_{z\sim}$, large fluctuational oscillations (up to tens of microns) in individual parts of a loop domain which are not associated with the field period. These oscillations are preceded by a rupture of the domain at these regions, followed by the formation of new closed loop domains. Domains of this type are found most frequently near the edges of the

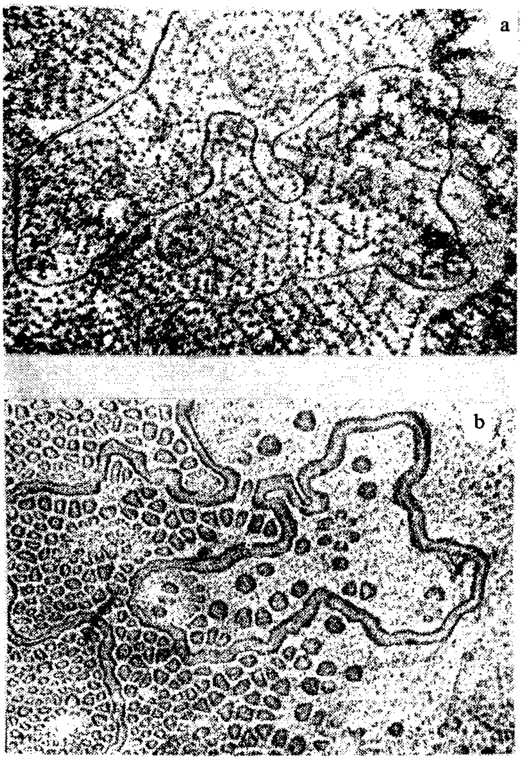

FIG. 1. a—Domain structure of a z-cut GASH crystal in a field $E_{z\sim} = 150$ B, $f = 500$ Hz. The sample is 1 mm thick. The structure was visualized with the help of smectic liquid crystals. Visible here are a loop domain and ordinary 180° domains; b—the same part of the crystal after the application of a field $E_z = 100$ V for 5 s.

crystal, near the boundaries of growth pyramids, and near other structural inhomogeneities.

To explain the nature of these domains and their behavior in an electric field, we recall that the symmetry of the domain structure (and of the translational-twin structure) in a specific phase of any crystal is determined by the symmetry of the actual or hypothetical initial phase of this crystal. The symmetry of the hypothetical initial phase—a paraelectric paraphase—of GASH must be the $3m$ supergroup. Cubic supergroups should be eliminated, since GASH is definitely a uniaxial ferroelectric (only 180° domains are present, and there is no other than 180° switching). Some other possible symmetry groups of the initial phase are $\bar{3}m$ *and* $\bar{6}m2$ (they were predicted several years ago[6]). Of the latter two, the first leads to no distinctive features in the domain structure. For the second, the ferroelectric phase should contain, along with ferroelectric domains, twins which are not distinguishable on the basis of those properties which are described by the first- and second-rank polarization tensors but which are distinguished by the signs of the elastic coefficients $(s_{14} = s_{24} = \frac{1}{2} s_{56})$ and their piezoelectric coefficients $(d_{31} = d_{32}, d_{33}, d_{24} = d_{15})$. The switching of ferroelectric do-

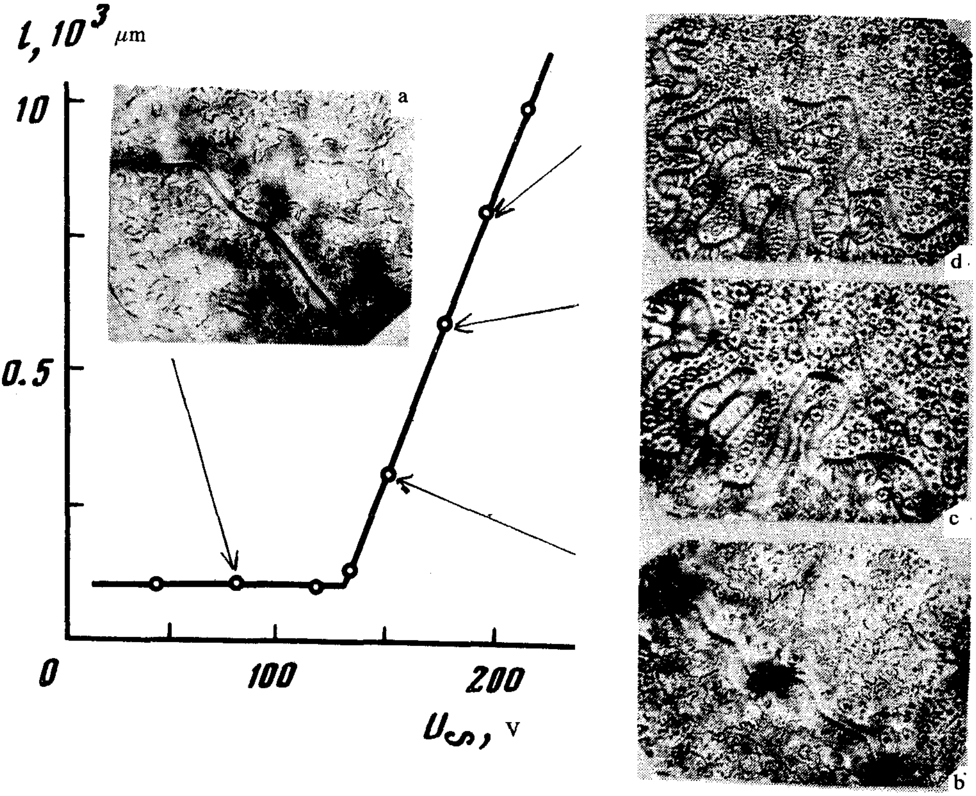

FIG. 2. Change in the length of a loop domain under the influence of a field $E_{z\sim}$ ($f = 500$ Hz), and views of a part of a loop domain in the corresponding field. The visualization was carried out with nematic liquid crystals.

mains by a field E_z should not be accompanied by a switching of the twins; i.e., a ferroelectric domain of the same sign may exist on each side of a twinning boundary (this is a fundamental distinction from the case of the dicalciumstrontiumpropionate crystal, for which this twinning boundary coincides with a domain wall).

The loop domains may be nucleated by an electric field at twinning boundaries as they are at crystal defects. Since the twins in GASH are distinguished from each other only by their elastic and piezoelectric properties, the twinning boundaries in the basis plane can have an arbitrary orientation. This point explains the smooth contours of the twinning boundaries and of the domains that appear there. In an alternating electric field, the walls of such domains run parallel to twinning boundaries; the distance between the domain walls and the corresponding twinning boundary varies periodically at the field frequency. In a static electric field of the appropriate sign, it is energetically favorable for a loop domain to increase in size, i.e., for its width h to increase. Since there is no anisotropy of the walls in the basis plane, this broadening should occur at an identical rate dh/dt along the entire loop. For this reason, experiments reveal a similarity between the changing domain walls and the changing twinning boundary when a field of the appropriate sign is applied at any time. As the field E_z

increases, another process becomes energetically favorable: the growth of one domain through an increase in the dimensions of the twinning boundary, l, and the nucleation of new twins, at whose boundaries loop domains of width h appear. The energy advantage is proportional to $-hlEP$, where hl is the area of the domain in the basis plane, and the energy disadvantage is proportional to $\frac{1}{2}(s''_{ik} - s'_{ik}) \times \sigma_i \sigma_k S$, where S is the loop area $(S \sim l^2 \gg hl)$, s''_{ik} and s'_{ik} are the elastic compliances of the twins (in the case at hand, different components s_{14} should correspond to the twins), and σ_i and σ_k (e.g., σ_1 and σ_4) are elastic stresses produced by the presence in the crystal of macroscopic defects, an anisotropy of the thermal strain preceding the twinning plastic flow, an inhomogeneity of the thermal field near regions of electric breakdown, and other factors.[7]

A qualitative condition for the nucleation of a new twin is thus

$$a \Delta s_{14} \sigma_1 \sigma_4 l^2 - hlPE = 0, \tag{1}$$

where a is a coefficient, and $\Delta s_{14} = s''_{14} - s'_{14}$. We see that the perimeter of the twinning boundary, l, satisfies the proportionality $l \sim EhP / \Delta s_{14} \sigma_1 \sigma_4$, i.e., increases linearly with increasing electric field, in accordance with experiment (Fig. 2). On the other hand, condition (1) may be regarded as the definition of the threshold field E_t at which a loop having an initial perimeter l_0 begins to increase in size, i.e., $E_p \sim \Delta s_{14} \sigma_1 \sigma_4 l_0 / hP$. The existence of a definite threshold in the field has also been observed experimentally (Fig. 2). We wish to emphasize that the reason for the motion of the twinning boundaries in this case is their interaction with loop domains; i.e., a twinning boundary must move and change in length under the influence of the field E_z (for given stresses σ_1 and σ_4). This is a fundamental distinction between this case and the behavior of a similar twinning boundary in quartz or NG_4Cl. We may thus assume that the closed loop domains observed here actually form from ferrobielastic twinning boundaries, and of the two possible hypothetical paraphases of GASH preference should be given to $\bar{6}m2$. It has also been shown that it is possible to visualize twinning boundaries of this sort by means of liquid crystals in an electric field in cases in which the methods of crystal-optics are unsuitable. It has been found possible to control the shape and number of twinning boundaries of this sort by means of an electric field.

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