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Abstract

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ON FEATURES OF THE DOMAIN STRUCTURE OF FERROELECTRICS REVEALED BY ELECTRON-MICROSCOPIC VISUALIZATION

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Until the present time, studies of the domain structure of ferroelectrics have been carried out with the aid of ordinary polarizing microscopes at low magnifications (tens and hundreds). Taking into account the exceptionally important role of ferroelectric domains for understanding their physical properties and for elucidating the very nature of ferroelectric phenomena, the use of electron microscopy appears promising for refining our ideas about the regularities of domain orientation, about the features of their boundaries, and about their sizes.

As our investigations have shown, visualization of the domain structure of ferroelectrics is possible with the aid of a transmission microscope when the replica method is used. In this case, however, the replicas must convey the fine structure of the electric field. This proved possible owing to the presence of natural relief on the surface of a polydomain ferroelectric crystal, caused by mechanical stresses at domain boundaries due to the interaction of their electric dipoles. The use of a transmission electron microscope with colloid and carbon replicas (in some cases shadowed with chromium (1)) enabled us to observe the domain structure on barium titanate and Rochelle salt crystals at magnifications of up to 25,000 times.

It appears possible to observe the domain structure of ferroelectrics both on replicas taken directly from untreated crystals and on replicas taken from etched crystals. It should be noted that the latter method can be applied not only to the study of the orientation of domains as such, but also to determining the direction of spontaneous polarization in the domains, since the different ends of the domain dipoles are etched chemically in different ways (2).

The $BaTiO_3$ crystals were etched by us in concentrated hydrochloric acid for 5–10 min. After etching, the specimens were washed with water, then with alcohol, and dried. The state of the etched crystal was examined in an optical microscope in order to compare the domain pattern before and after etching of its surface. Colloid or carbon replicas were then taken from the object. Carbon was

Fig. 1a

Figure 1: Fig. 1a

Fig. 1b

Figure 2: Fig. 1b

deposited on $BaTiO_3$ in vacuum. The thickness of the films studied, determined by their color on glass (different shades of brown), was 300–500 Å. The films were separated from the object mechanically after they had been strengthened with gelatin or collodion. The best results were obtained with shallow etching, which made it necessary to shadow the replicas with chromium at an angle of 15–20°.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Colloidal replicas were obtained by applying a drop of a 1% solution of collodion in amyl acetate to the etched crystal. The film was then reinforced with gelatin. The colloidal films were always shadowed with chromium. In addition to barium titanate, replicas of Rochelle salt were made by the latter method. Before the replicas were taken, the Rochelle salt was etched with water, usually for 0.5 min at a temperature of about 10°.

Proof that etching does indeed reveal the domain structure is provided by the fact that, using three sections of a Rochelle-salt crystal (x-, y-, and z-sections), we observed the domain structure only on the x-sections. It is known that only on these sections is the domain structure observed optically. A second check was the taking of replicas from the x-section of Rochelle salt at a temperature above the upper Curie point (30°), on which no domain structure was found.

The study of the domain structure of $BaTiO_3$, carried out by optical methods ([3]–[5]), showed its rather complex arrangement and led to the conclusion that the width of such neighboring regions, in which the direction of spontaneous polarization makes an angle of 90° with respect to one another and the vector of spontaneous polarization lies in the plane of the plate (the so-called a-domains), is of the order of 10^{-4} cm.

In Fig. 1a one such region is shown, photographed in an electron microscope

Fig. 2

Figure 3: Fig. 2

Fig. 3

Figure 4: Fig. 3

Fig. 4a

Figure 5: Fig. 4a

($BaTiO_3$, etched with HCl for 8 min, colloidal replica, 8000×). In this figure two facts attract attention. The first is that the boundaries between two regions (the dark bands in the figure) are very substantial and are approximately 10^{-5} cm.

Although the indicated magnitude of the boundary between a-domains does correspond to its theoretical value given in Little' s work (^{4}), the large width of the indicated domain periods may in part be explained by other factors as well. Such "broadening" of a-domain boundaries may be explained, in particular, by etching, by significant mechanical stresses at the domain boundaries, and by the block structure of ferroelectric crystals (which will be discussed below).

Another interesting fact seen in Fig. 1a is that the etch figures within one region have intermediate boundaries between them, oriented at an angle of 45° to the main ones. The presence of these additional boundaries, as will be shown below, is connected with the division of a large a-region into smaller regions with antiparallel orientation of the spontaneous-polarization vector.

In Fig. 1b an image is shown of a wedge-shaped region (taken from a $BaTiO_3$ crystal etched with HCl for 5 min, carbon replica, at a magnification of 8000×), in which the dark and light bands correspond to domains in which the spontaneous-polarization vectors are antiparallel and perpendicular to the plane of the crystal (the so-called c-domains). These domains, whose width is hundredths of a micron, naturally cannot be resolved by ordinary optical methods.

In Fig. 2 an image is shown of the x-section of Rochelle salt (etching with H_2O, colloidal replica at a magnification of 8000×), the domain structure of which has been studied optically by a number of authors (^{6}, ^{7}). A characteristic feature of the pattern of this section of Rochelle salt is the presence of a network of peculiar channels within regions that are separated from one another by straight-line boundaries (in optical observations these regions are interpreted as separate domains). Such "blockiness" of the domains of Rochelle salt is, in our view, of considerable interest and deserves special consideration.

Let us turn to the consideration of the results of observing the domain structure

Fig. 4b

Figure 6: Fig. 4b

of $BaTiO_3$ from electron-microscopic images obtained by means of replicas taken from natural (unetched) faces of the crystal. As was already indicated above, the natural relief present on the faces of the crystal is in many cases quite sufficient for obtaining

very high-quality impressions. This natural relief arises because of spontaneous deformations (associated with electrostriction) of the domains, as a result of which surface deformations corresponding to the domains appear between them. These deformations, following along the domain boundaries, may be sufficient for electron-optical imaging of the domain structure without any chemical etching. To determine the depth of the electrostrictive deformations, we made stereo photographs in the electron microscope.

It is known that the spontaneous deformations of domains are proportional to the square of the spontaneous polarization. Depending on the value of the spontaneous polarization, the deformations at a given point of the crystal may be stronger or weaker. The disappearance of these deformations at the Curie point, observed by means of an optical metallographic microscope and on impressions, suggests that we are indeed observing the fine structure of the domains. Below the Curie point, optical inspection at these places reveals typical ferroelectric domains. We also noticed that in some crystals the local stresses are so strong that they cause inelastic deformations, likewise running along the domains. These deformations do not disappear at temperatures above the Curie point. Often in one and the same $BaTiO_3$ crystal there are both elastic and inelastic deformations, which perhaps depends on the amount of impurities in different places of the crystal, since the electrical properties of ferroelectrics and, consequently, the spontaneous and electrostrictive stresses are to a large extent determined by the local distribution of impurities.

A typical picture of the domain structure of $BaTiO_3$ (unetched, carbon impression) is shown in Fig. 3 at a magnification of 1000×. Of interest here is the presence of a regular series of small linear domains running at an angle of 45° (indicated by the arrow) and of junctions of regions with different directions of the polarization vector. This photograph was obtained at relatively low magnification, and the presence in it of sufficiently fine details, which escape ordinary optical visualization, is due to the peculiarities of formation of the electron-microscopic image (very great depth of focus, the shadowing effect, which improves the contrast, the quality of the carbon impression, which accurately records the relief, etc.). The same region is shown in Fig. 4a at a magnification of 8000×. At such high magnifications we can already see details of the shape of an individual domain, the rounding of its ends, and the regions of junctions between domains oriented in different directions. At still higher magnifications (Fig. 4b, magnification 25 000×) the boundaries between the domains and certain details of the structure of individual domains are seen quite clearly. The width of individual domains estimated from these photographs is approximately $3\text{–}5 \cdot 10^{-6}$ cm.

Thus, within regions which in optical microscopy are taken to be individual domains, we have succeeded in discovering a finer domain structure. The width of these domains is, at least, an order of magnitude smaller than that ordinarily assumed.

The presence of such a subdomain structure seems to us interesting for clarifying certain properties of ferroelectrics. In particular, it seems possible to explain, by the presence of such a fine domain structure, the rather large value of the dielectric permittivity (of the order of hundreds) determined from hysteresis loops on the portion of the loop corresponding to saturation fields. It may be thought that in these portions the polarization process is connected with reorientation of these small domains and, in particular, that those of them which are "stuck" at individual defects in the crystal (in the presence of sufficiently strong inelastic deformations at the domain boundaries, discussed above) can reorient only in very strong fields. The "block" structure of the crystal noted above will act in the same direction, since at the block boundaries the disturbances of the domain structure and its refinement may be quite strongly expressed.

In the recently published work (8), electron-microscopic images of domains of polycrystalline $BaTiO_3$ are presented.

In the present work, we studied details of the domain structure in single crystals of $BaTiO_3$ and Rochelle salt.

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