DYNAMICS OF DOMAINS
IN $(CH_3NH_3)_5Bi_2Br_{11}$ CRYSTALS*

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The nucleation and movement of the 180° domain walls in $(CH_3NH_3)_5Bi_2Br_{11}$ crystals has been investigated by means of liquid crystals. The various shapes of domains during the polarization reversal has been observed and discussed, considering that the type of nucleation is the controlling factor in the propagation of the walls.

PACS numbers: 77.80.Dj

1. Introduction

The alkylammonium halogenobismuthate, $(CH_3NH_3)_5Bi_2Br_{11}$ (MAPBB), crystallizes at room temperature in the orthorhombic symmetry (space group $Pca\,2_1$) with the c-orthorhombic axis being the polar one [1, 2]. The crystal undergoes two second order phase transitions; at $T_c = 312$ K from paraelectric (space group $Pcab$) to ferroelectric phase and at 77 K the structural phase transition. The X-ray diffraction studies showed that the loss of polarity at T_c is related to the motion of the methylammonium cations [3, 4]. The Raman studies of MAPBB [5–7] have reported that ferro-paraelectric phase transition can be considered as an order–disorder transition.

For observing optically indistinguishable 180°-domains in MAPBB crystals the nematic liquid crystal (NLC) method [8, 9] and the scanning electron microscopy [10, 11] have been used. It has been found that the domain structure in as-grown crystal, observed on the crystal plate normal to c, the polar direction, is elongated in the b-crystallographic direction. Połomska et al. [8] succeeded in observing the domains moving under an electric field and investigated the field dependence of the switching time.

Here we communicate the results of our observations of peculiarities of the domain dynamics in MAPBB crystals using the NLC-method. Domain structure has been observed using the method described in Ref. [12].

2. Experimental results

For observation of the ferroelectric domains we used the NLC of MBBA (p-methoxybenzylidene-p-n-butylaniline). The samples of MAPBB crystals grown from the aqueous solution were cut perpendicularly to the ferroelectric c-axis and polished. After supplying a sample (coated with NLC) with suitable transparent electrodes, the electric field could be applied and continuous direct observations of the domains during the polarization reversal were carried out using a polarization microscope.

Evolution of domains during polarization reversal for the three values of an electric field is shown in Fig. 1. The studies were carried out on the same crystal plate but with alternately changed polarity of the electric field, because the initial black-white contrast between domains becomes poorer and vanishes gradually after several re-polarization cycles. After each series of experiments, the monodomain state was obtained by applying the dc-electric field of 200 kV/m during 5 min.

Figure 1 illustrates only qualitative changes of a domain structure under the influence of an electric field. The difference in switching time (as a result of the internal bias field E_b) for opposite field directions for examined crystal sample is about several percent in a weak electric field and decreases at higher electric field strengths. However, in the field ranges given in the text, the same type of domains for opposite field directions has been registered.

It has been shown that the process of polarization reversal in a single crystal is accomplished by the nucleation and subsequent growth through the 180° domain wall of a single domain. The first nucleation was obtained with +80 kV/m applied field for 3 min. The electric field of an order of nucleation field creates plate-like elongated in the b-direction domains (Fig. 1 region 1; negative nucleation field −90 kV/m). In this range of electric field sidewise wall motion is quite non-uniform, because the walls are impeded by defects within the crystal. The velocity shows large anisotropy; for +80 kV/m the average velocity is 2×10^{-4} mm/s in the fast b-direction and 1.8×10^{-5} mm/s in the perpendicular slow one. The switching time is of the order of several minutes or even a few hours for various samples.

For an electric field strength of above 110 kV/m the individual nucleated domains have the form close to a circle, but an anisotropy of the domain wall motion results in the lenticular domains (Fig. 1 region 2). Their domain wall movement is not restrained by defects and a smooth motion of domain walls is observed. In this range, the electric field is sufficient to reverse the polarity of the whole crystal sample, with the switching time τ_s of the order of several seconds.

In the range of electric field strength (130–150) kV/m domain walls move irregularly because new nucleation centres appear adjacent to moving walls and in the bulk. We found the boundaries to be often of zigzag-type as a result of preferential formation of new nuclei, that appear along b-direction (Fig. 1, region 3). Here the wall displacement rate is found to increase substantially (2–10 times).
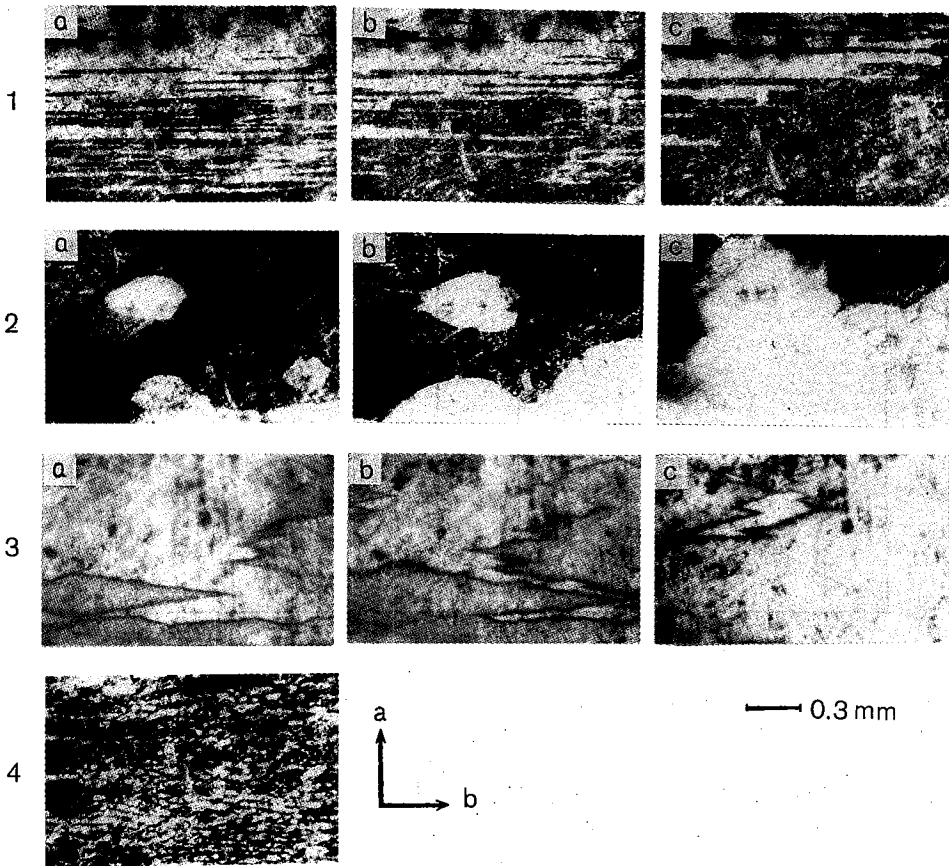
Fig. 1. Evolution of domains after applying of dc-electric field E [kV/m]: (1) -90; (2) $+120$; (3) -140; (4) $+160$; time from the moment of switching electric field: (1) a — 8 min; b — 16 min; c — 25 min; (2) a — 4 s; b — 8 s; c — 15 s; (3) a — 1 s; b — 2 s; c — 3 s.

But the data are not reproducible because the process of nucleation is not the same in every cycle.

For electric fields above 150 kV/m switching takes place mainly through the forward growth of many small domains. The nucleated domains grew sidewise only a short distance to the next such a domain. A number of nucleated domains increases with the time of application of electric field and is so large that it prevents measurements of the sidewise movement of the domain walls. The photograph showed in Fig. 1, region 4 was taken when the switching process was initiated, after the $+160$ kV/m electric field was applied to the monodomain sample. The switching time of 68 ms (measured by VHS camera) was too small to take another photograph during the same polarization cycle.

In order to explain such peculiarities of the domain shape, we have measured the velocity of the sidewise domain motion in positive electric fields. As the local

velocity of the wall is anisotropic and inhomogeneous, the average velocity was measured at the same wall shift from the initial position. To obtain the relevant time interval, required for the wall to move through a known distance, a stop watch was used in the range of weak electric field and VIIS camera in strong electric fields, respectively.
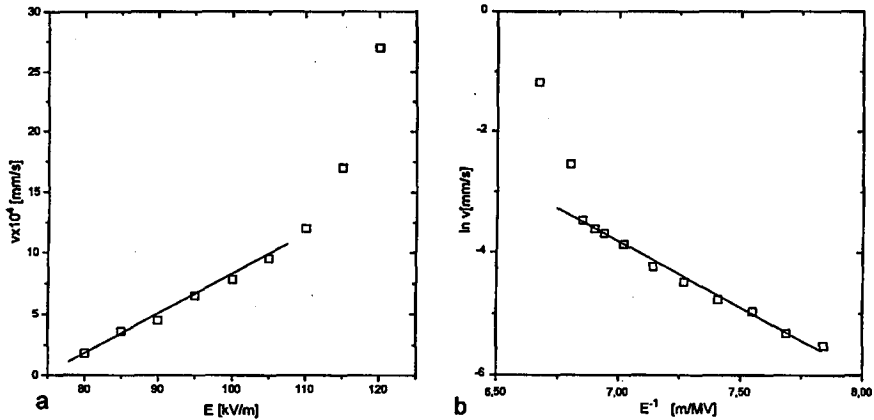

Fig. 2. An average wall motion velocity V versus electric field E (a). Plot of $\ln V$ versus $1/E$ (b).

The data obtained are illustrated in Fig. 2. For weak electric fields (plate-like domains) the field dependence of the average wall velocity V is approximately linear, thus we determined the sidewise switching mobility $\mu = V/E = 3 \times 10^{-5}$ m^2/(MV s). In electric fields higher than 110 kV/m (lenticular domains) the data are well approximated by exponential field dependence described by the following relation

$$v = V_\infty \exp(-\delta/E)$$

with the activation field of domain wall motion $\delta = 2.09$ MV/m.

Measurements made on a different crystal, or on the same being at different stage of aging process, can produce values of δ different from that given above as much as 50%.

This proves that many factors (as value of bias field, number of defects, domain sizes) play an important role in the polarization reversal process.

3. Discussion

The peculiarities of domain structure dynamics can be explained assuming that the mechanism of domain growth is similar to the mechanism of crystal growth [13, 14]. The theory of crystal growth assumes that at weak oversaturation the growth of the crystal is due to the one-dimensional nucleation steps at the phase boundary. This proceeds as layer after layer growth of crystal by the motion

of these steps along the boundary. In this case the linear dependence of growth velocity is observed and crystals with regular faces are obtained.

At large oversaturation the crystal is growing through two-dimensional nucleation at the phase boundary. Due to the disorder nature of this process the velocity of growth is proportional to the rate of nucleation, thus exponential dependence of the growth velocity is observed and no preference in crystal orientation is to be seen.

By analogy with the theory of crystal growth it is assumed that the switching process is determined by the oversaturation degree, which corresponds in ferroelectrics to the magnitude of an electric field acting on the domain boundary.

This model satisfactorily explains the domain pattern evolution in lead germanate and gadolinium molybdate crystals [15]. Our investigations confirmed such considerations, as well. Observations of domain dynamics confirmed that mechanism of the domain growth in weak electric fields (Fig. 1 region 1) is suitable for the one-dimensional nucleation steps at the boundary. The residual domains, which always exist in ferroelectrics or cylindrical domains anchored to the dislocation lines, can play the role of step sources [16]. The anisotropy of the surface energy must lead to the preferable motion of steps along one direction thus, layer after layer growth of domains of preferable orientation (parallel to the crystallographic *b*-axis) takes place. The field dependence of the sidewise motion velocity of these walls is linear. Domain structure is similar in as-grown and trained by weak electric field samples.

In the higher electric fields (Fig. 1, region 2) the switching is accomplished through arising a few round section domains and the domain wall velocity exponentially depends on the applied electric field.

The different field dependences of the wall velocity in the different field ranges are explained in terms of the difference in the mechanism of the nucleation, on the existing wall. One can assume that the mechanism of the sidewise wall motion in moderate electric field is determined by the two-dimensional nucleation process of statistically independent nuclei [17]. It has been shown [18] that the electric field dependence of the probability for the nucleation of reversed domains can be of the form $\exp(-\text{const}/E)$, if E is not too great. This field dependence is of the same form as that found for the sidewise wall motion, where $V = V_0 \exp(-\delta/E)$ and therefore suggests that the nucleation rate rather than the growth rate is the controlling factor in the propagation of a wall. Thus the domains are formed with shapes depending only on the anisotropy of the activation field δ (defined in exponential law $V(E)$) and that δ is proportional to the wall energy density σ according to Miller–Weinreich model [19].

Domain pattern evolution presented in Fig. 3 can illustrate the above-mentioned considerations. When the weak electric field (-80 kV/m) is applied to the previously partly switched sample in higher electric field ($+120$ kV/m, Fig. 3a) the further switching occurs by nucleation and movement of the plate-like domains along the *b*-direction (Fig. 3b).

On the basis of kinematic wave theory [20] it was possible to explain the lenticular shape of domains growing under an electric field in TGS [21] and
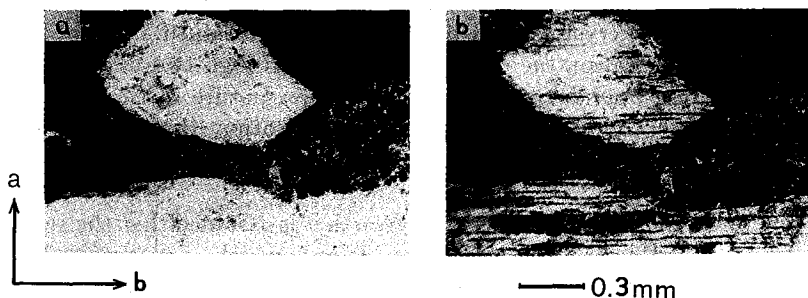
Fig. 3. The pattern of the domain structure arising during the switching; a) initial domain structure formed in electric field sufficient to create lenticular domains, b) plate-like domains formed in electric field of the order of nucleation field (further switching occurs by movement of plate-like domains).

NaNO$_2$ [22] crystals. It seems that such considerations can be adopted in the case of MAPBB crystals as well.

A marked increase in the wall displacement rate observed for electric field above 140 kV/m (zigzag-shape domain walls; Fig. 1, region 3) can be connected with appearance of new nucleation sites especially adjacent to the moving domain walls. Nucleated domains grow and become joined with pre-existing domains.

In order to explain this behaviour we must take into consideration that the probability of nucleation is defined by the field strength at the boundary of growing domains. Shur at al. [23] pointed out that for a quickly moving domain wall the existence of depolarization field, which is not fully compensated by the external and bulk screening, must be taken into account. It gives rise to increase in the internal field before a moving domain wall and hence increase in the probability of nucleation.

Observations of moving zigzag-shaped domain walls pointed out that the sidewise movement of domain walls does not seem to be a completely coherent process, but rather by a polarization reversal in individual chains along the polar axis. Each chain switches as a result of large fluctuations of opposite polarization, expanding rapidly along the polar axis. This multistep mechanism considerably lowers the barrier against the sidewise domain wall motion.

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