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DYNAMICS OF DOMAINS IN $NaNO_2$ CRYSTALS*

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Growth and shrinkage of domains in sodium nitrite crystals are investigated in a wide range of electric fields using the liquid crystal method. The rhombic shape of domains in the growing process and the lenticular shape of domains in the shrinking process are observed and discussed.

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1. Introduction

While studying dynamics of the domain walls in sodium nitrite crystals it is found out that the domain structure differs in as-grown and treated by electric field samples [1, 2]. As-grown samples usually have a lamellar elongated in c-direction domain structure. When the crystals are put in an electric field, the rhombic shape domains arise, with the domain walls parallel to the (101) and $(10\bar{1})$ planes, which coincide with the natural cleavage planes of $NaNO_2$ crystals.

Theoretical calculations based on the Zhirnov type continuum theory for static domains [3] and the kinematic wave theory for moving domains [4] successfully explain the lamellar domain structure, but fail to explain the orientation of the walls of rhombic domains, predicting the lenticular or elliptical shapes of the growing domains in the electric fields.

Here we communicate the results of our observations of peculiarities of domain dynamics in $NaNO_2$ crystals using the nematic liquid crystal — (NLC) method [5] in a wide range of the external electric fields.

2. Experimental results

The crystal of sodium nitrite has perfect (101) and $(10\bar{1})$ cleavage planes, which are parallel to the spontaneous polarization P_s (Fig. 1a). To prepare sample plates perpendicular to P_s, a slender rhombic prism was cleaved from a crystal prepared by slow cooling of the melt, then cut and polished. For observation of ferroelectric domains we used the NLC mixtures of MBBA (p-methoxybenzylid-

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ene-*p*-*n*- butylaniline) and EBBA (*p*-ethoxybenzylidene-*p*-*n*- butylaniline). After supplying a sample (coated with NLC) with suitable transparent electrods, the electric field can be applied and continuous direct observations of the domains during the polarization reversal were carried out using a polarization microscope.

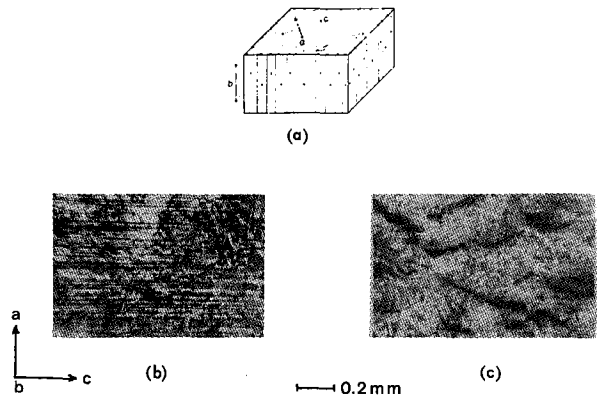

Fig. 1. Domain structure of $NaNO_2$. a) A schematic model; side faces are the cleavage ones and the arrows represent P_s; b) Lamellar shape of domains elongated in *c*-direction; c) Moving domain walls after applying of dc-electric field to the monodomain sample.

Figure 1b shows the lamellar elongated in *c*-direction domain structure observed in as-grown crystals. After making the crystal single domained further switching in weak fields creates rhombus-like domains. Their domain wall motion under the influence of the electric field is quite non-uniform. After applying the dc-electric field the sidewise wall velocity reaches its maximum value, then it decreases down to a constant value. In the weak electric fields of the order of the nucleation field the wall stops at some distance from an initial position. These stopped domain walls are always parallel to the cleavage planes. It suggests that the defects and their diffusion influence the orientation of the domain walls during the polarization reversal.

Using the etching method Sawada et al. [6] observed linear arrays of closely located etch pits of dislocations, distributed approximately parallel to the edges of the rhombus. Through the interaction of domain walls with dislocations, domain walls are put in energetically more favourable positions and therefore a far stronger external electric field is required for the polarization reversal.

Evolution of the domains in the growing and shrinking process for three values of an electric field is shown in Fig. 2. The studies were carried out on the same crystal plate. After each series of the experiments, the monodomain state is obtained. For the electric field of the order of nucleation field (+0.2 MV/m for this sample Fig. 2a), the domain walls moved slowly being approximately parallel to (101) and ($10\bar{1}$) planes and they finally stopped. Only higher electric fields can cause a further movement of these walls.

The electric field of +0.5 MV/m (Fig. 2c) is sufficient to reverse the polarity of the whole crystal sample (with the switching time $t_s = 10$ s). Also the domains

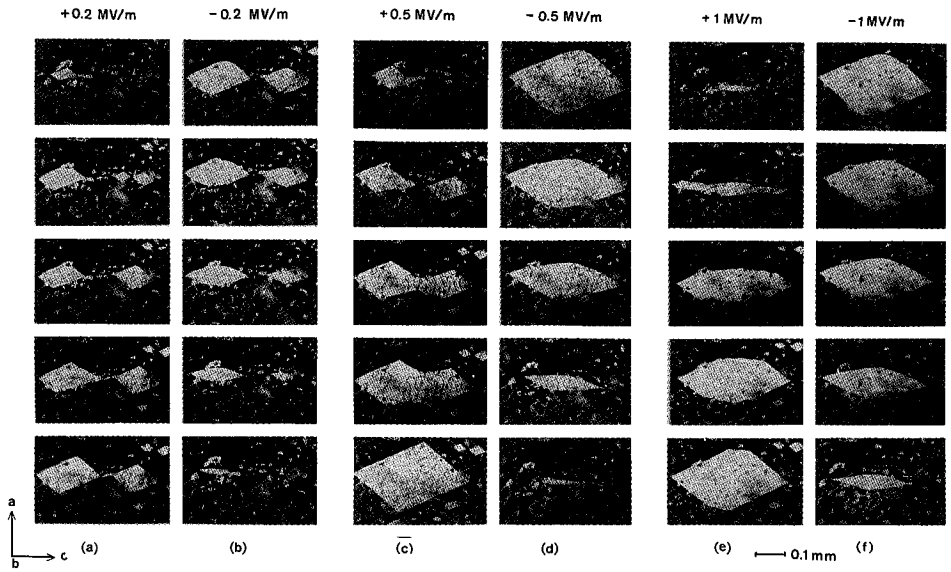

Fig. 2. Sequence of domain pattern photographs showing evolution of domains after applying of dc-electric field: 0.2 MV/m, 0.5 MV/m, 1 MV/m; (a), (c), (e) — during the growing process; (b), (d), (f) — during the shrinking process.

having the walls parallel to cleavage planes grow, except from the sites, where the local velocity of the domain walls increases and thus, this domain wall become rounded (Fig. 2c).

For the electric field of +1 MV/m (Fig. 2e) domains have complicated shapes, the preference in the domain wall orientation is not so strickly observed. Domain boundaries may be composed of the densely zigzag planes, each of which are the {101} planes.

Figure 2(b,d,f) shows evolution of the domains for three values of the electric fields of the opposite direction (negative ones) which cause shrinking of the domains previously nucleated and growing in the positive electric fields. The domains attain regular shape being nearly lenticular and a smooth motion of the domain walls is observed.

In order to explain such peculiarities of the domain shape, we measured the velocity of the sidewise domain motion in both polarities of the electric fields (Fig. 3). As the local velocity of the wall in this range of the electric fields is anisotropic and inhomogenous, the average velocity is measured at the same wall shift from the initial position. It is found out that the sidewise motion velocity is much higher in the case of negative electric fields causing shrinking of the white domains in Fig. 2(b,d,f). It means that the walls in these cases move in effective higher fields, which manifests itself by the smooth motion of the domain walls, as they are not restrained by defects.

Such peculiarities of the domain wall motion can be explained taking into

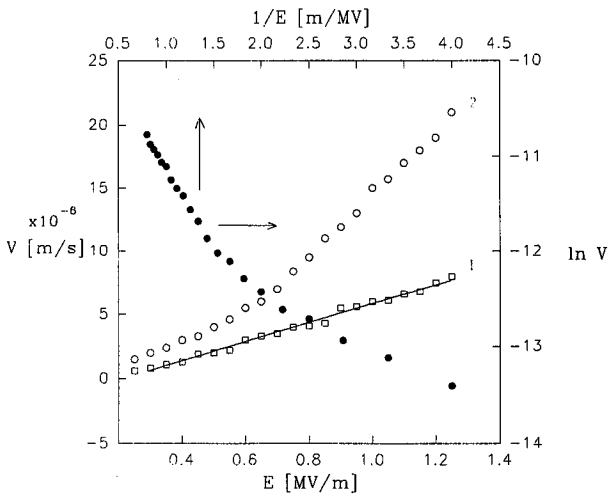

Fig. 3. Wall motion velocity versus applied electric field during: the growing process (curve 1), the shrinking process (curve 2). The plot ln V as a function $1/E$ is taken from curve 2.

account that the velocity of the domain wall is determined by the magnitude of the electric field on the boundary of growing domains. For the moving wall it must be taken into account the existence of the depolarization field, which is not fully compensated by the external and bulk screening and acts as the driving field [7].

Jaśkiewicz et al. [8] show that the depolarization field depends on the width of the domains, thus the walls of small domains in Fig. 2b move (in the electric field of -0.2 MV/m) at a velocity comparable with the velocity of domain walls in Fig. 2d (in the electric field of -0.5 MV/m).

3. Discussion

An interesting suggestion is put forward for explaining the domain structure dynamics in lead germanate and gadolinium molybdate crystals [9]. By analogy with the theory of crystal growth [10, 11] 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. The theory of crystal growth assumeds that at large oversaturation the crystal is growing from the melt, through a two-dimentional nucleation at the phase boundary. As the velocity of growth is proportional to the rate of nucleation, the exponential dependence of the growth velocity is observed and no preference in crystal orientation is to be seen. 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.

By analogy, it is supposed that the mechanism of domain wall motion in the strong fields is due to the two-dimentional nucleation and in the weak fields is due to the one-dimentional nucleation; where the residual domains, which always exist in ferroelectrics, can play the role of the step sources. This model satisfactorily explained the hexagonal shape of domains (connected with the three-fold symmetry of the polar axis) in lead germanate crystals in the weak fields and round shaped domains in the strong electric fields.

Taking into account these considerations it was possible to explain peculiarities of the domain structure evolution in electric fields in sodium nitrite crystals, as well. Observation of domain dynamics confirmed that mechanism of the domain growth in the examined range of electric fields is suitable for the one-dimentional nucleation.

1. The boundaries appearing parallel to the (101) and $(10\bar{1})$ planes may be explained by the fact that the strength of the bonding which acts across these faces is considered to be rather weak owing to its large interatomic distance [12].
2. The field dependence of the sidewise motion velocity is approximately linear when the field causes the growth of the domains (Fig. 3, curve 1).
3. In sites of a crystal, where the local velocity of domain wall diminishes, a domain wall expands through the "spiral growth" of steps along a rhombus shaped domain perimeter [2] (it can be seen in Fig. 2a). It seems there is a connection with a selective distribution of dislocations [6], thus the domain wall moves with the dislocations.
4. The additional confirmation of the unity of the process governing the crystal growth at small oversaturation and domain growth in the weak electric fields are a coincidence of the domain wall and the crystal face orientation. During the crystal growth at a small oversaturation the crystal pulled along the polar axis, has a shape of a rhombic prism with the side faces parallel to the cleavage planes. So it could be concluded that the domain boundaries of the rhombic shape are formed in connection with the characteristics of the crystal growth and they depend on a symmetry of the $NaNO_2$ crystal.

In the strong electric fields the polarization reversal is determined by the nucleation process of statistically independent nuclei [13] and their dynamics is not connected with a symmetry of the crystals. Thus the domains are formed with shapes depending only on the anisotropy of the wall energy. Our treatment indicates that such results are obtained in the shrinking process. The lenticular shape of domains observed in the shrinking process can be explained by the kinematic wave theory [1, 4].

According to the kinematic wave theory the shape of the wall is determined by an orientational dependence of V — the sidewise velocity of the domain wall. In the calculations of Hatano et al. [1] the field dependence of V is presented by the exponential law $V = V_\infty \exp(-\delta/E)$, thus the lenticular or elliptical shapes of domains are given.

Our investigations confirmed such considerations. The velocity of the domain

wall in the shrinking process (curve 2) can be approximated by the exponential law (the plot $\ln V = f(1/E)$ in Fig. 3).

4. Conclusions

It could be concluded that the domain boundaries of the rhombic shape do not result from the anisotropy of the wall energy, but are formed in connection with the characteristics of the crystal growth. The rhombic domains are created only in the weak electric fields below 1 MV/m for $NaNO_2$ crystals. We can pressume that the lenticular shape of domains resulting from the anisotropy of the wall energy could be observed in the process of growing domain in the range of the coercive field about 2 MV/m at room temperature. However it is impossible to apply such strong fields using the NLC method, because a conductive layer of SnO_2, deposited on the electrods, will be damaged.

The only solution could be the study of domain dynamics in $NaNO_2$ crystals in the range of the weak fields but at the temperature near T_c.

It should be added that similar results were obtained in studies of domain dynamics in TGS crystals [14]. An irregular shape of domain walls is to be observed in the weak fields due to the domain wall and defects interaction. The lenticular shapes of domains are observed in the electric field in the range of the coercive field.

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