Unusual orientation of domain walls in the uniaxial ferroelectric crystal LiH$_3$(SeO$_3$)$_2$

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A stable domain configuration with inclined boundaries has been observed in the uniaxial ferroelectric lithium trihydroselenite crystal.

The geometry of the domain structure of the crystal and the possible number of orientations of the spontaneous polarization vector and, therefore, of the orientation of domains are determined by the symmetry of the starting and asymmetric phases. Uniaxial ferroelectric materials must therefore be separated into domains with antiparallel spontaneous polarization vectors (180° domains). The absence of bound charges at the boundary between domain walls (div **P** = 0) in this case is energetically favorable, i.e., the domain walls are parallel to the spontaneous polarization vector of the crystal.[1] Precisely this type of domain structure is observed in nearly all uniaxial ferroelectric materials (but not ferroelectric-semiconducting materials).[2]

We have observed a fundamentally different domain structure in the uniaxial ferroelectric crystal LiH$_3$(SeO$_3$)$_2$ (LHS).

This ferroelectric crystal, which has been known for more than 20 years, has an unusually high (for hydrogen-containing crystals) spontaneous polarization (15 μC cm^{-2}) and remains in the ferroelectric phase with a symmetry *Pn* up to the melting point (383 K). The crystal can be transferred to the paraelectric state with a symmetry *P*2$_1$/*n* by applying hydrostatic pressure. The temperature of the hypothetical phase transition under atmospheric pressure is 420 K.[3] The LHS crystal has recently again attracted attention as a possible candidate for applications.[4]

Until now, it has not been possible to observe the domain structure of the LHS crystal. We made use of the effect of decoration of the surface of the ferroelectric crystal by a nematic liquid crystal (NLC).[5] The LHS crystal has a perfect cleavage surface (the *b* cut), along which lies the spontaneous-polarization vector, in accordance with the symmetry. The orientation of the spontaneous-polarization vector has been established to within 1°.[6] A thin NLC layer was deposited on the cleavage face of the crystal and a black and white contrast, corresponding to the pattern of the domain structure, was observed in polarized light under a microscope.

From the photomicrograph of the static domain structure of the LHS crystal shown in Fig. 1a it is evident that the domain walls in the crystal are not parallel to the spontaneous polarization vector, and form an angle of ~18° to it. The orientation of the domain walls approximately ($\pm$ 1°) corresponds to the crystallographic *c* axis. The application of a constant electric field, ~10^2 V/cm, along the polar axis transforms the crystal into a single-domain state, and the contrast vanishes in this case. Upon removal of the external field the single-domain state does not remain in the short-
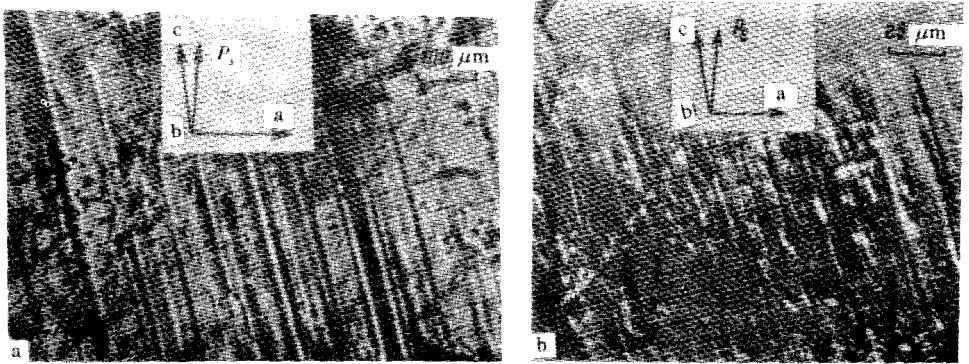
FIG. 1. Domain structure of the LHS crystal. (a) Visualization with the help of NLC, (b) visualization by the SEM method (accelerating voltage 3 kV).

circuited crystal, and the domain structure with inclined boundaries is restored. Visualization of the domain structure on the polar cut and the a cut of the crystal leads one to conclude that the domains in the crystal form a semiperiodic layered structure.

To obtain unequivocal results concerning the nature of the domain structure of the crystal, we have also used the method of scanning electron microscopy (SEM). The contrast produced in this case is due to the modulation of the emission of secondary electrons by the domain structure of the crystal.[7] The pattern of the domain structure obtained by the SEM method (Fig. 1b) for the same b cut of the crystal is similar to the pattern obtained by decoration with NLC. It should be noted that the SEM method is generally used to analyze polar cuts of ferroelectric crystals. The contrast observed in our case in the nonpolar b cut of the crystal has a number of distinctions. In particular, only some regions of the domain walls can be identified, and there is no inversion of the contrast near the equilibrium potential of the sample. The indicated features of the contrast can apparently be explained by the interaction of slow, secondary electrons with the nonuniform field created by the spontaneous polarization in the region of the domain walls.

On the basis of the experiments and symmetry considerations we assume that a bound charge is present near the domain walls, which accounts for the additional internal scattering fields in the crystal. In contrast to ferromagnets, the energy of elastic interation, along with the energy of scattering fields, can play a large role in ferroelectric materials. However, in the LHS crystal, the spontaneous striction is quadratic and cannot play a determining role in the orientation of domain walls. We can only point out that the piezoelectric anisotropy of the asymmetric phase of the crystal is such[8] that the boundary between two adjacent walls, which is oriented along the crystallographic c axis, is subjected to a very small strain; i.e., the orientation of the domain walls which is observed experimentally may turn out to be the most energetically favorable.

[1] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Nauka, Moscow, 1982.
[2] J. C. Burfoot and G. W. Taylor, Polar Dielectrics and Their Applications, Macmillan Press, 1979.
[3] G. A. Samara, Phys. Rev. **173**, 605 (1968).
[4] A. Shaulov and W. A. Smith, Ferroelectrics **49**, 223 (1983).
[5] N. A. Tikhomirova, L. I. Dontsova, S. A. Pikin, and L. A. Shuvalov, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 37 (1979) [JETP Lett. **29**, 34 (1979)].
[6] L. A. Shuvalov, V. N. Anisimova, N. R. Ivanov, and I. A. Velichko, Kristallografiya **17**, 1253 (1972) [Sov. Phys. Crystallogr. **17**, 1101 (1972)].
[7] R. Lebihan and M. Maussion, C. R. Acad. Sc. B **272**, 1010 (1971).
[8] D. Berlincourt, W. R. Cook Jr., and M. E. Rander, Acta Cryst. **16**, 163 (1963).