Role of surface states in polarization reversal of the ferroelectric lead germanate

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The influence of the electrical boundary conditions on the switching process and the stability of the ferroelectrical domain structure in a lead germanate crystal is investigated.

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We want to call attention to the unusual behavior of the uniaxial ferroelectric lead germanate in an external electric field.

Lead germanate $Pb_5Ge_3O_{11}$ is a collinear (pure) ferroelectric with spontaneous polarization $P_s = 4.3\ \mu C/cm^2$ at 20 °C. At 177 °C, the crystal transforms into the paraelectric state via a second-order phase transition ($P3 \rightarrow P\bar{6}$). Its domains are optically distinguishable due to the difference in the sign of their optical activity. The specific rotation ρ is equal to 5.5 °/mm at room temperature.[1]

In our investigations of repolarization processes in lead germanate, the external electric field was applied to the specimen through external dielectric gaps 0.2–1 mm thick, artificially created with the help of glass interlayers, with ferroelectric specimens up to 10 mm thick. The electrodes consisted of glass with a conducting coating made of SnO_2. The behavior of the gaps on the one hand permits introducing a controllable impedance for the ferroelectric-electrode interface and, on the other, slowing down the polarization reversal to times that are convenient for recording intermediate (polydomain) states of the domain structure. Under these conditions, complete switching of polarization was observed (Fig. 1) in constant electric fields up to 18 kV/cm (the value of the field at which the polarization reversal began to depend on the past history of

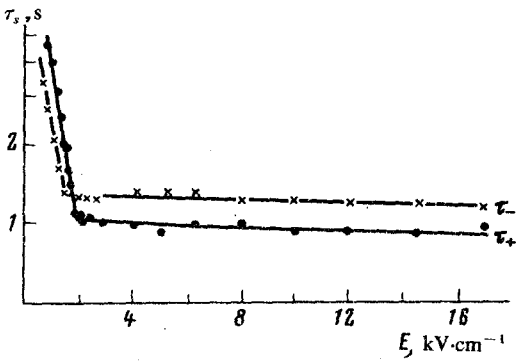

FIG. 1. Dependence of the switching time τ_s on the magnitude of the external field E.

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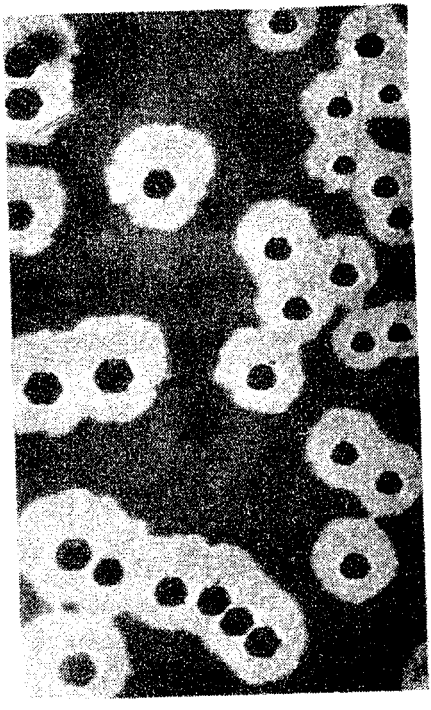

FIG. 2. View of a typical domain structure of lead germanate crystal. Nucleation of domains on etching grooves on the surface of the specimen.

the specimen). The polarization reversal was recorded optically according to the difference in the angle of rotation by the optical activity in domains with different sign. Figure 2 shows the typical form of the domain structure of the crystal. With switching through the dielectric gap, domain nuclei appear on any defects on the surface of the specimen and field inhomogeneities in the gap. Figure 2 shows the formation of domain nuclei during polarization reversal on etching grooves on the surface of the specimen.

The results of the investigations performed can be summarized as follows: when a field of sufficient magnitude is applied, the polarization is completely switched, in spite of the presence of the dielectric gaps, and when the field is switched off, neither the single-domain nor any intermediate state of the domain structure (when the field is switched off before the polarization process is completed) is destroyed after the field is removed, irrespective of whether the condition of zero potential is satisfied on the electrodes. This indicates that there is enough time for the bound charges from spontaneous polarization, which appear at the boundaries of the ferroelectric during the polarization process, to be cancelled out during polarization reversal by free charges from the bulk of the crystal, since the specimen is loated in the gap. The compensation (screening) time corresponds to the Maxwellian screening time $\tau_M = \epsilon\rho = 5\times10^{-11} - 10^{10} = 0.5$ s at $T = 290$ K. The time for complete switching,

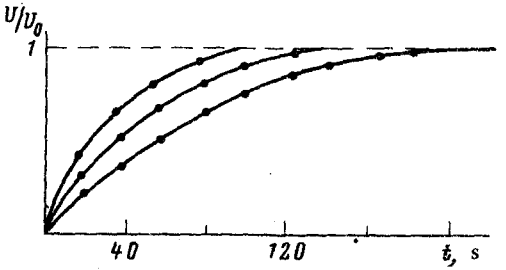

FIG. 3. Time dependence of a switched volume of the specimen (obtained from the dielectric hysteresis loop at 0.05 Hz, $E = 10$ kV/cm) with different aging time (τ_{age}) after single-domain formation by a field $E = 10$ kV/cm: 1) $\tau_{age} = 5$ min; 2) $\tau_{age} = 15$ min; 3) $\tau_{age} = 30$ min.

τ_s, decreases with increasing external field up to some value whose order of magnitude coincides with τ_m and remains essentially unchanged with further increase in the field (Fig. 1).

We should note one more important characteristic of the domain structure created in the crystals investigated under these conditions by the external field. With time, the single-domain and any intermediate state of the domain structure become more stable. This is manifested as an increase in the external field required to destroy the domain structure (Fig. 3). The observed effect is analogous to the aging effect, observed in other well-known ferroelectrics, but, in the latter,[2-3] the aging process is accompanied by a restructuring of the domain structure, while in lead germanate, not only is the domain structure not restructured but, on the contrary, it is consolidated. The characteristic aging time of lead germanate T_{age}, as is evident from Fig. 3, greatly exceeds τ_m.

It would appear that we are looking at mutually exclusive phenomena. On the one hand, switching of the polarization in an external field indicates the absence of complete screening of the external field. On the other hand, the conservation of the single-domain or any intermediate state indicates complete screening of spontaneous polarization. This contradiction can be explained as follows. Assume that there are local states on the surface of the ferroelectric with sufficiently high density, whose energies are situated near the Fermi energy, making it possible to change their charge state. When the external constant electric field is switched on through the dielectric gap, the field is first redistributed uniformly over the crystal. Under the action of this field, the carriers begin to move toward the surface of the ferroelectric and over the Maxwellian time completely screen the external field. The carriers arriving at the surface are trapped into local states. However, the capture process is of a random nature, so that some locations on the surface have more charge than other locations. A fluctuation potential arises, and correspondingly, a nonuniform electric field appears near the surface. This means that nuclei of phases, corresponding to opposite orientation of the spontaneous polarization, appear on the surface of the crystal. At this time, the change in the sign of the field leads to rapid polarization reversal due to the growth of many nuclei of the corresponding phase. If after the polarization reversal the external field is switched off, then due to repulsion the randomly positioned charges begin to redistrib-

ute themselves with the thermal ejection time over the empty surface states in order to decrease the fluctuation potential.[4] In this case, nuclei with opposite sign begin to disappear over a time $\tau_{age} > \tau_m$ and with time it will be increasingly more difficult to reverse the polarization of this crystal. Since the thermal ejection time depends exponentially on the temperature, the consolidation time of the domain structure will also depend exponentially on the temperature, which is in fact observed experimentally.[5]

We have thus observed that the ferroelectric in a capacitor with gaps will switch if it has a finite conductivity, which will permit screening internally the spontaneous polarization. We have assumed that this is a common phenomenon for all real ferroelectrics, and for this reason, we performed analogous measurements on the ferroelecric TGS, whose conductivity is small ($\leqslant 10^{-11}\ \Omega \cdot cm^{-1}$, measured in fields of 10 kV/cm) at room temperature.[6] Under analogous conditions, the polarization reversal in this crystal occurs in a manner similar to lead germanate with times comparable to the Maxwell time for the TGS crystal ($\sim 10^3$ s).

[1]H. Iwasaki, K. Sugii, N. Niizeki, and H. Toyoda, Ferroelectrics **3**, 157 (1972).
[2]S. L. Rapoport and L. I. Lontsova, Kristallografiya **15**, 384 (1970) [Sov. Phys. Crystallogr. **15**, 327 (1970)].
[3]V. P. Konstantinova and Ya. Stankovskaya, Kristallografiya **16**, 158 (1971) [Sov. Phys. Crystallogr. **16**, 123 [1971)].
[4]E. V. Chenskiĭ and Yu. Ya. Tkach, Zh. Eksp. Teor. Fiz. **79**, 5, 1809 (1980) [Sov. Phys. JETP **52**, 915 [1980)].
[5]V. Ya. Shur, V. V. Letuchev, and Yu. A. Popov, Fiz. Tverd. Tela **24**, 2854 (1982) [Sov. Phys. Solid State **24**, 1618 (1982)].
[6]M. Polomska, B. Hilczer, and M. Michalczyk, Ferroelectrics **39**, 1217 (1981).

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