

INVESTIGATION OF THE DYNAMIC POLARIZATION OF FERROELECTRICS

V. V. DEM'YANOV and S. P. SOLOV'EV

Branch of Karpov Physico-chemical Institute

Submitted June 9, 1967

Zh. Eksp. Teor. Fiz. 53, 1858-1871 (December, 1967)

Certain dynamic effects of the polarization of single-crystal and polycrystalline BaTiO<sub>3</sub>, due to the presence of a domain structure, were investigated experimentally in the frequency range up to 1.5 × 10<sup>10</sup> Hz. A dependence of the dispersion frequencies of ε' on the domain dimensions is established in accordance with the theoretical conclusions obtained on the basis of the volume model of domain oscillators. It is shown that the dynamic susceptibility of ferroelectrics is due to displacements of the domain boundaries (κ<sub>dis</sub>) and to elastic-ion polarization, and the nonlinearity and reversibility of ε', the dispersion of ε', and the reversal of polarization are connected only with κ<sub>dis</sub>.

1. INTRODUCTION

THE dynamic polarization of ferroelectrics has attracted attention of many investigators in connection with possible practical applications of many effects connected with it. Several models were proposed<sup>[1-5]</sup> to explain the effects observed in the frequency range up to 5 × 10<sup>10</sup> Hz, particularly the low-frequency nonlinearity of ε' and the dispersion of this nonlinearity, as well as the nonlinearity and reversibility of ε' at high frequencies, microwave dispersion, etc. However, the experimental data accumulated to date do not confirm the full validity of any particular model, and the absence of a unified theoretical approach to the polarization (weak fields) and polarization reversal (strong fields) even within the framework of a single mechanism make it difficult to understand the dynamic polarization of ferroelectrics.

Historically, the most widely used model is the one borrowed from the previously developed theory of dynamic magnetization of ferromagnets<sup>[6]</sup>, based on the assumption that the polarization and polarization-reversal processes in ferroelectrics are determined essentially by the domain structure, and the presence of the anomalously large susceptibility of ferroelectrics is due to effects of domain wall displacement (DWD); the domain walls being regarded as flat membranes oscillating in the external field<sup>[3,5,7]</sup>.

This model was used to explain the polarization in weak fields and microwave dispersion<sup>[3,5,7,8]</sup>, and also the reversal of polarization of materials such as BaTiO<sub>3</sub> in strong alternating fields<sup>[9-13]</sup>. However, the approximate agreement between the resonant frequency calculated on the basis of the flat domain wall model and the experimentally observed center of the microwave dispersion of BaTiO<sub>3</sub><sup>[14-17]</sup> was obtained under the assumption that the DWD makes a 100% contribution to the susceptibility, and also by using too low a value of the spontaneous polarization P<sub>S</sub> (16 in place of 26 μCoul/cm<sup>2</sup><sup>[3,7]</sup>) and average domain dimensions 10<sup>-2</sup> cm in<sup>[3]</sup>, 10<sup>-3</sup> cm in<sup>[7]</sup>, and 0.5 × 10 cm in<sup>[5]</sup>, whereas in real single-crystal and polycrystalline BaTiO<sub>3</sub> samples the domain dimensions range from 10<sup>-2</sup> to 10<sup>-5</sup> cm<sup>[9-12,18,19]</sup>. Elimination of these and a few other "stretched points" leads to an overestimate

of the frequency obtained in<sup>[3,5,7]</sup> for the center of the dispersion region, by approximately one order of magnitude compared with the experimentally observed one (see the table).

It seems to us that the noted tendency of overestimating the resonant frequency is an inevitable consequence of the low effective mass of the oscillating plane domain wall, whereas actually the DWD is the result of a change of the polarization within the volume of the entire domain, which thus should be regarded as a vibrating element with an appreciably larger effective mass.

In this case the volume of a favorably oriented domain V in a weak external field E increases by ΔV as a result of the transverse displacement of its boundaries<sup>[9-13,19]</sup>, so that the susceptibility of the crystal is κ = κ<sub>C</sub> + κ<sub>dis</sub>. Here κ<sub>C</sub> is the susceptibility of the crystal along the c axis, and the κ<sub>dis</sub> = ΔP<sub>dis</sub>/E, where ΔP<sub>dis</sub> = P<sub>S</sub>θΔV/V is the polarization increment due to the boundary displacement, and θ is a constant that takes into account the distribution of the c-axes of the domains in the crystal (see<sup>[6]</sup>). It turns out that in case of small lateral wall displacements the behavior of the oscillating volume of the domain in an external field can be described by the same linear equation of motion as was used in<sup>[3,7]</sup> to describe the domain wall-oscillator. Now, however, the coefficients of this equation should be normalized not to a unit area of the domain wall, but to a unit of the corresponding volume.

The application of the methods employed in<sup>[7,20]</sup> to the volume model of the domain-oscillator gives an expression for the resonant frequency of the domain that agrees better with experiment (see the table):

Theoretical and experimental values of the resonant frequencies for BaTiO<sub>3</sub>

d, cm	Resonant frequency f <sub>0</sub> = ω <sub>0</sub> /2π, Hz		
	Data of [7]	From formula (1)	Experiment
10 <sup>-6</sup>	3 · 10 <sup>11</sup> ÷ 10 <sup>12</sup>	10 <sup>11</sup> ÷ 3 · 10 <sup>11</sup>	} ~ 2 · 10 <sup>9</sup> (Fig. 1, 3) } ~ 3 · 10 <sup>8</sup> (Fig. 1, 2) } 2 · 10 <sup>6</sup> (Fig. 2)
10 <sup>-5</sup>	10 <sup>11</sup> ÷ 3 · 10 <sup>11</sup>	10 <sup>10</sup> ÷ 3 · 10 <sup>10</sup>	
10 <sup>-4</sup>	3 · 10 <sup>10</sup> ÷ 10 <sup>11</sup>	10 <sup>9</sup> ÷ 3 · 10 <sup>9</sup>	
10 <sup>-3</sup>	10 <sup>10</sup> ÷ 3 · 10 <sup>10</sup>	10 <sup>8</sup> ÷ 3 · 10 <sup>8</sup>	
10 <sup>-2</sup>	3 · 10 <sup>9</sup> ÷ 10 <sup>10</sup>	10 <sup>7</sup> ÷ 3 · 10 <sup>7</sup>	
10 <sup>-1</sup> *	10 <sup>9</sup> ÷ 3 · 10 <sup>9</sup>	10 <sup>6</sup> ÷ 3 · 10 <sup>6</sup>	

\*Single-domain sample—single crystal.

$$f_0 = \frac{P_s}{2\pi d} \left[ \frac{20C' \kappa_c}{M_{\text{eff}} \kappa_{\text{dis}}} \right]^{1/2}, \quad (1)$$

where  $d$  is the average dimension of the domains,  $M_{\text{eff}}$  the effective mass of the domain-oscillator, and  $C'$  a constant determined by the coefficients of the expansion of the thermodynamic potential and dependent on the shape of the domains.

The present paper is devoted to an experimental study of the processes of dynamic polarization of ferroelectrics of the  $\text{BaTiO}_3$  type and to an interpretation of the obtained data on the basis of the domain-oscillator model.

An analysis of this model allows us to predict several effects which are obtained qualitatively also from the flat-wall model<sup>[3,7]</sup> and are due to the dynamic interaction of the electromagnetic field with the ferroelectric.

1. The inverse proportionality of  $f_0$  to  $d$ , which follows from (1), should lead to:

a) A dependence of the frequency of the start of the microwave dispersion on the dimensions of the domains in single-crystal and in polycrystals, and apparently also on the dimensions of the crystallites in polycrystalline samples.

b) A shift of the microwave dispersion of the single crystal towards the low-frequency region (in the limit towards the resonant frequency of the sample) when a bias field is applied to the crystal, for in this case the domains should increase until a single-domain state is reached in an appreciable part of the crystal.

c) A dependence of the region of the low-frequency dispersion of  $\epsilon'$  in large measuring fields on the dimensions of the sample.

2. Such properties of ferroelectrics as the nonlinearity and the reversibility of  $\epsilon'$ , the microwave dispersion, and the reversal of polarization processes should be characteristic of multidomain crystals or crystallites, and are due to the large contribution made to the susceptibility by the displacement of the domain boundaries ( $\kappa_{\text{dis}}$ ) as a result of a change in the volume of the domains.

3. In a crystal whose single-domain state is achieved by decreasing the dimensions to a value at which no further breakdown into domains takes place, and consequently there are no moving boundaries,

$\kappa_{\text{dis}} = 0$  and the total susceptibility should be due only to the mechanism of elastic-ionic polarization, and there should be no nonlinearity or reversibility of  $\epsilon'$ , microwave dispersion, or processes of polarization reversal.

4. It can also be assumed that the experimental data presented below confirm the fact that there should be no difference in a homogeneous crystal between the susceptibilities in the so-called "free" and "clamped" states, and the high piezoelectric properties of ferroelectrics can become manifest only in connection with the single-domain state of the crystal or the crystallites.

5. Some of the effects considered in Items 1 and 2 can be observed in irradiated ferroelectric crystals (see<sup>[21]</sup>), since irradiation effectively influences their domain structure<sup>[22,23]</sup>.

## 2. EXPERIMENTAL PROCEDURE

At frequencies up to 150 MHz, we used the ordinary procedure of measuring  $\epsilon'$  and  $\tan \delta$  with the aid of Q-meters and measuring bridges, but the main results were obtained with the aid of a microwave measurement procedure developed by us and described in<sup>[21,24]</sup>. The use of this procedure made it possible essentially, for the first time, to solve two very important methodological problems that determine the reliability and reproducibility of the obtained results:

1) The feasibility of performing the measurements with one sample, in the range of greatest interest for ferroelectrics from 0.15 to 15 GHz, and with the aid of a single procedure based on the use of standard and non-standard coaxial measuring lines.

2) The performance of measurements of the frequency dependences of  $\epsilon'$  and  $\tan \delta$ , to an arbitrary degree of detail, for a single setting of the sample, making it possible to obtain reliable experimental data on sufficiently small single crystals.

Up to 1.5 GHz, the measurements were made with the aid of two generators, and the frequency spacing between the experimental points was not limited, since the use of a previously obtained short-circuit curve at these frequencies makes it possible to perform measurements with accuracy not worse than 5–10% for  $\epsilon'$  and 10–20% for  $\tan \delta$ . At higher frequencies, up to 15 GHz, switchable generators were used, usually not more than eight, for each frequency.

The ferroelectric ceramic samples were prepared by cutting cylindrical posts with subsequent fusing of silver electrodes on the polished ends. The sample diameters were 1.0 and 0.5 mm and the heights were from 0.1 to 1.0 mm. The single-crystal  $\text{BaTiO}_3$  samples were cleaved from single-crystal plates, on which the electrodes were deposited beforehand by fusing or sputtering of silver. The effective diameter of most single crystals obtained in this manner was  $\sim 0.5$  mm at height 0.2–0.5 mm.

Some of the measurements were made on specially chosen polycrystalline samples with different sizes of the crystal grain. The size of the crystallites was determined by standard x-ray diffraction methods (see<sup>[25]</sup>). Crystallites with dimensions exceeding  $10^{-4}$  cm were identified by the number of spots on the diffraction rings of the x-ray pattern obtained by

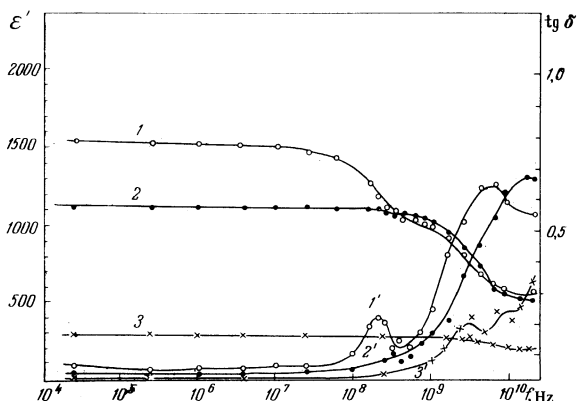


FIG. 1. Dependence of the start of the microwave dispersion of  $\epsilon'$  (1, 2, 3) and the maximum of  $\tan \delta$  (1', 2', 3') of polycrystalline  $\text{BaTiO}_3$  on the size of the crystallites ( $d_c$ ): 1, 1' -  $d_c = 50 - 300 \mu$ ; 2, 2' -  $d_c = 1 - 10 \mu$ ; 3, 3' -  $d_c < 1 \mu$ .

photography with Cu radiation, and the dimensions of the smaller crystallites were determined from an analysis of the width and the shape of the lines recorded with the URS-50IM diffractometer.

All the results presented below were reproduced by us not less than four times in independent experiments on different samples, but the set of points on any of the presented curves corresponds to a single sample.

### 3. EXPERIMENTAL RESULTS

#### 1. Influence of the Crystallite Dimensions on the Microwave Dispersion of Polycrystalline BaTiO<sub>3</sub>

Figure 1 shows the frequency dependences of  $\epsilon'$  and  $\tan \delta$  for two different samples of polycrystalline BaTiO<sub>3</sub>, and also for a pyroceram (sitall) based on PbNb<sub>2</sub>O<sub>6</sub>, having crystallite grains of greatly varying size. Curves 1 and 1' correspond to the frequency dependence of a BaTiO<sub>3</sub> sample with very large crystallite grains, 50–300  $\mu$ , in which domains can exist having the same dimensions as in single crystals, i.e.,  $10^{-2}$  cm and less<sup>[9-12,18,19]</sup>.

The second sample, corresponding to curves 2 and 2', had crystallite dimensions on the order of several microns. If it is assumed that the domains cannot be larger than the crystallites, then the dimensions of the oscillator-domains in this sample should not exceed  $10^{-4}$  cm.

The third, pyroceramic sample had in its amorphous matrix crystallites with dimensions much smaller than  $10^{-4}$  cm, and consequently the domain dimensions in this case should also be much smaller than  $10^{-4}$  cm.

All samples exhibited the characteristic temperature dependence of  $\epsilon'$  and  $\tan \delta$  in the vicinity of the Curie point.

From the plots of  $\epsilon'$  and  $\tan \delta$  on Fig. 1, it is obvious that the start of the region of the microwave dispersion depends on the dimensions of the crystallite grain. Comparing curves 1 of Figs. 1 and 2, we reach the conclusion that the start of the dispersion  $\epsilon'$  in the large-grain sample and in the single crystal approximately coincide (frequency region  $10^8$  Hz); this can be

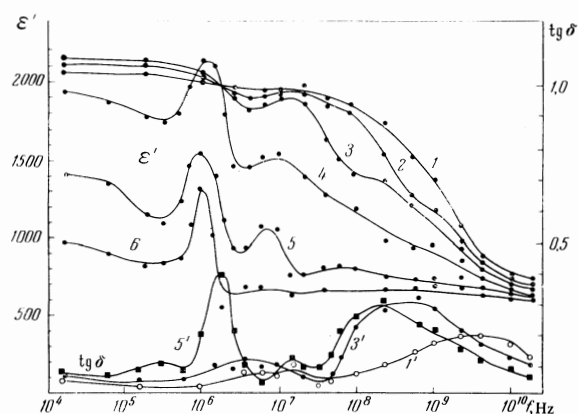


FIG. 2. Dependence of the start of the dispersion of  $\epsilon'$  (1–6) and of the maximum loss  $\tan \delta$  (1', 3', 5') of a single-crystal BaTiO<sub>3</sub> sample of  $\sim 0.5$  mm diameter and  $\sim 0.2$  mm height on the displacement field ( $E_0$ ): 1, 1' –  $E_0 = 0$ , 2 –  $E_0 = 200$  V/cm, 3, 3' –  $E_0 = 600$  V/cm, 4 –  $E_0 = 1.5$  kV/cm, 5, 5' –  $E_0 = 10$  kV/cm, 6 –  $E_0 = 35$  kV/cm.

attributed to the presence in the large crystallites of domains having the same dimensions ( $10^{-2}$ – $10^{-3}$  cm) as in single crystals<sup>[19]</sup>.

The anomaly of the  $\tan \delta$  curves is another feature of the microwave dispersion, as already pointed out in<sup>[21]</sup>. In the same paper there is also a description of the effect of the shift of the start of the microwave dispersion in large-grain polycrystalline BaTiO<sub>3</sub> under the influence of irradiation with fast electrons, which leads to the breaking up of the domains and consequently to an increase of their resonant frequency. Thus, the results of<sup>[21]</sup> and the data of Fig. 1 offer convincing evidence in favor of the presence of a dependence of the start of the dispersion of  $\epsilon'$  in BaTiO<sub>3</sub> on the domain dimensions in single crystals or in crystallites.

Comparison of the data shown in Fig. 1 makes it possible, in addition, to conclude that the displacement of the domain boundaries contributes to the polarization of the samples at low frequencies. Indeed, if we start from the fact that the end of the region of the microwave dispersion of  $\epsilon'$  corresponds to total elimination of this contribution, then this contribution amounts to  $\sim 60$ – $70\%$  in large-grain BaTiO<sub>3</sub> (curve 1) and also in multidomain single crystals (Fig. 2), to  $\sim 45\%$  in fine-grain samples (curve 2), and  $\sim 15\%$  in the sitall ceramic. Such a behavior can be explained on the basis of the 3 and 3' greatly different number of single-domain formations in the chosen samples. In particular, crystallites with dimensions  $< 1 \mu$  in the sitall sample should be predominantly single-domain, as a result of which the contribution of  $\kappa_{dis}$  to the total susceptibility is small. Regardless of the results presented in Fig. 1, this conclusion is favored also by the very small ( $\sim 5\%$  at 50 kV/cm) reversibility of  $\epsilon'$  of the third sample, and the absence from it of low-frequency nonlinearity and of a hysteresis loop.

#### 2. The Problem of the Single-domain Crystal

Figure 2 shows the results of an investigation of single crystals in a wide range of frequencies at differ-

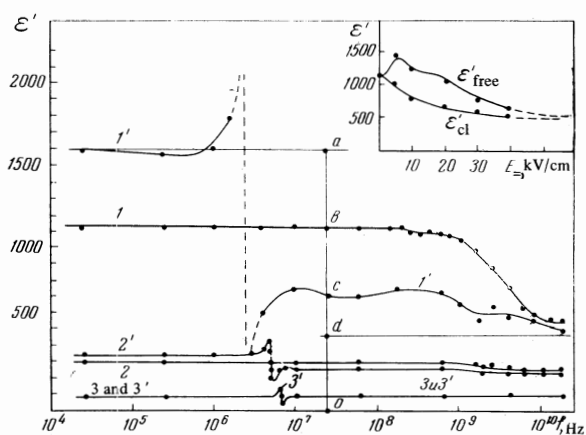


FIG. 3. Frequency dependences of  $\epsilon'$  of unpolarized polycrystalline samples (1, 2, 3) and of samples polarized with a field 20 kV/cm (1', 2', 3'); the sample diameter is  $\sim 0.5$  mm and the height 0.4 mm. The crystallite dimensions ( $d_c$ ) are as follows: 1, 1' – BaTiO<sub>3</sub>,  $d_c = 1$ – $10 \mu$ ; 2, 2' – pyroceram based on PbNb<sub>2</sub>O<sub>6</sub>,  $d_c \sim 1 \mu$ ; 3, 3', pyroceram,  $d_c \ll 1 \mu$ . The insert shows the dependence of  $\epsilon'$  for BaTiO<sub>3</sub> with  $d_c = 1$ – $10 \mu$  on the displacement field, with  $\epsilon'_{free}$  measured at 0.1 MHz and  $\epsilon'_{cl}$  at 50 MHz.

ent degrees of their polarization by a constant field. These results can be regarded as proof of the correctness of certain conclusions of formula (1), and above all of the conclusion that the constant field shifts the start of the microwave dispersion in multidomain single crystals toward lower frequencies (towards is resonant frequency). This shift is due to the enlargement of the domains and to corresponding reduction of their resonant frequency. Comparing curves 1–6, we can state that with increasing displacement field, the region of microwave dispersion actually shifts first towards the UHF and then to the radiofrequencies,  $\sim 10^6$  Hz. It is seen from curves 4, 5, and 6 that the shift of the dispersion region in fields of  $\sim 1.0$  kV/cm stops at the resonant frequency of the crystal, since its dimensions determine the maximum possible dimension of the domain.

The shift of the microwave dispersion towards the resonant frequency of the crystal is also evident on the plots of  $\tan \delta$  (1', 3', and 5'). In addition, the simultaneous growth of  $\tan \delta$  in the regions  $10^6$ – $10^7$  Hz (increasing domains) and  $10^9$  Hz (decreasing domains) demonstrates clearly the growth of certain domains at the expense of others. A confirmation of this conclusion can also be the observed shift of the start of the dispersion of polycrystalline BaTiO<sub>3</sub> towards the resonant frequencies of the crystallites, as shown in Fig. 4 (curves 5 and 2').

Unlike Devonshire<sup>[1]</sup>, according to whom the susceptibility of a homogeneous crystal at frequencies

much higher than resonant should exceed by several times the high-frequency susceptibility, the results of our experiment (Fig. 3 and curves 4, 5, 6 of Fig. 2) can be interpreted in such a way that the concept of "free" and "clamped" susceptibilities are apparently not the properties of a homogeneous crystal, and are a manifestation of certain dynamic regularities in the polarization of inhomogeneous multidomain crystals of the ferroelectric.

Indeed, curves 1 and 1' of Fig. 3, for unpolarized and polarized BaTiO<sub>3</sub> respectively, offer evidence of a  $\sim 45\%$  contribution of  $\kappa_{\text{dis}}$  (the ordinate segment bd) and simultaneously of a difference, by an approximate factor of 2, between the susceptibilities of the "free" sample (ordinate ao) and the "clamped" one (ordinate oc). For the fine-grain pyroceramic sample, which has a much smaller contribution of  $\kappa_{\text{dis}}$ ,  $\sim 15\%$ , this difference turns out to be much smaller ( $\sim 20\%$ , see curves 2 and 2' of Fig. 3). Curves 3 and 3' correspond to another pyroceramic sample, in which no effects of boundary displacement are observed, owing to the single-domain character of the crystallites; we see that in this sample there is practically no difference between the susceptibilities in the "free" and "clamped" states.

It is interesting to note that pyroceramic crystals cannot be polarized in any other way except by transforming from the cubic phase to the tetragonal one with simultaneous application of a large bias field. This confirms the conclusion that reversal of polarization of the crystal is possible only via the boundary-displacement mechanism, i.e., the reversal of polarization of single-domain regions, in which breakdown into domains is impossible, is apparently impossible in realistic fields.

Thus, we see that on going from curves 1, 1' to curves 3, 3' the difference between the values of  $\epsilon'$  in the "free" and "clamped" states practically vanishes simultaneously with the increase of the role of the single-domain crystallites. Similar conclusions follow also from an examination of curves 4, 5 and 6 of Fig. 2, which show the equalization of  $\epsilon'$  in the "free" and "clamped" crystal when the field causing the single-domain structure is increased. We can therefore regard it as experimentally established that a connection exists between the domain boundary displacement and the difference in the susceptibilities of the "free" and "clamped" crystal. It is also clear from the foregoing that this property cannot be ascribed to homogeneous (ideally single-domain) crystals of the ferroelectric.

### 3. Separation of the Displacement and Resonance Effects

The experimental separation of the effects due to the displacements (multidomain crystal) and resonance (single-domain crystal) is essential for more detailed and deeper study of the dynamic phenomena in polarization of ferroelectrics. An example of such a separation are the results shown in Fig. 3, on the basis of which we discussed above the meaning of the concepts of "free" and "clamped" constants  $\epsilon'$ .

Thus, the procedure for separating the resonance effects reduces to a study of powders or polycrystals with very small ( $\sim 10^{-5}$  cm) crystallite grains. Ap-

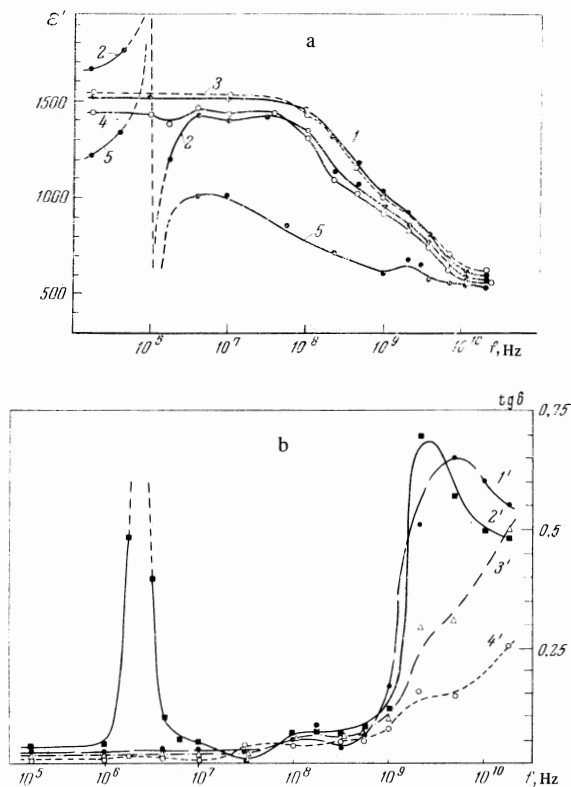


FIG. 4. Frequency dependences of  $\epsilon'$  (a) and  $\tan \delta$  (b) for BaTiO<sub>3</sub> samples with  $d_c = 50 - 300 \mu$ : 1, 1' - unpolarized solid; 2, 2' - polarized with a 3 kV/cm and solid; 3, 3' - unpolarized and composite; 4, 4' - polarized with a field 3 kV/cm and composite; 5 - polarized with a 40 kV/cm field and solid.

parently the practice of producing single domains in single crystals by means of a field or the use of specially grown "single-domain" crystals is not suitable for the study of resonance phenomena alone, since it is impossible to get rid in such crystals of the displacement effects, and actually the difference between the susceptibilities in the "free" and "clamped" states of the crystal can serve as a good indicator of the number of domains in it.

To study effects connected only with the displacement of the domain boundaries, to the contrary, it is necessary to use multidomain crystals. In such crystals, in measuring fields which do not cause growth (enlargement) of the domains from one electrode to the other, the resonance phenomena are practically unnoticeable. Since polycrystalline samples usually contain both multidomain and single-domain crystallites, the resonance phenomena will become manifest even in the case of an insignificant polarizing field.

If the measurements are made of composite (doubled) samples polarized in different directions, then if the dimensions of the halves are sufficiently equivalent it is possible to get rid of the piezoresonant activity of the sample as a whole. It should be noted that the use of composite samples for waveguide microwave methods of ferroelectric investigations (see, e.g., [17]) is apparently the only method of investigating their reversible characteristics. In this connection, it is useful to call attention to effects connected with the use of composite samples.

Figure 4 shows the frequency dependences of  $\epsilon'$  and  $\tan \delta$  for polycrystalline BaTiO<sub>3</sub>, curves 1 and 1' corresponding to the usual unpolarized sample, and 2 and 2' to the same sample but polarized with a field  $\sim 10$  kV/cm. Curves 3 and 3' show the frequency dependence of  $\epsilon'$  and  $\tan \delta$  for a composite sample made of the same piece of ceramic, without application of the bias field, while curves 4 and 4' show the same relations in the presence of a bias field  $\sim 10$  kV/cm on the intermediate electrode between the samples.

In addition to the effects already discussed in connection with the data of Figs. 2 and 3, notice should be taken of the greatly differing results obtained for the frequency dependences of  $\epsilon'$ , and particularly  $\tan \delta$ , in ordinary and composite samples. The appreciable reduction in the microwave losses in the polarized composite sample, and also the corresponding decrease in the anomaly of the  $\tan \delta$  curve, can be attributed to partial compensation of the piezoresonant activity of the single-domain crystallites, produced by the bias field in oppositely polarized parts of the sample.

A compensation of the same kind can be observed in composite samples, even if they are not polarized in opposite directions. Whereas the entire sample is apparently compensated as a whole, there may be no such compensation for single-domain crystallites of definite size. This may cause  $\tan \delta$  to increase anomalously at certain frequencies, or else to be cancelled out by the piezoactivity of such regions, the shift of one of the parts of the composite sample to the opposite electrode frequently changing the alternation of the anomalies of  $\tan \delta$ . Such an effect is seen on curves 2' and 4' in the frequency region  $3 \times 10^9$  Hz, and in the case of sufficiently strong bias fields the piezoactivity of the single-

domain regions becomes noticeable on the  $\epsilon'$  curve (see curve 5 in the region  $3 \times 10^9$  Hz).

These effects are apparently one of the main causes of the appreciable discrepancy between the results of microwave measurements obtained by different authors with the aid of different methods and on different samples.

#### 4. Relation between the Displacement Polarization and Elastic Deformations in Ferroelectric Crystals

The role of the foregoing piezoresonant phenomena in the microscopic values of the sample is not limited to the effects shown in Fig. 4. In particular, when explaining the results presented below, it becomes necessary to assume the presence of a dynamic connection between the displacement polarization ( $P_{dis}$ ) and the piezoresonant phenomena causing mechanical deformations ( $u_{ij}$ ) of the crystal. Indeed, in a polarized polycrystalline sample there should appear considerable piezoactivity of the single-domain formations that are present prior of the polarization and are produced under the influence of the polarized field ( $E_{\pm}$ ); this is an additional cause of the increase of the boundary displacement in the remaining multidomain crystallites, compared with the displacements induced only by the measuring field in the unpolarized sample. This process can be regarded as excitation of elastic-deformation waves by the single-domain crystallites; these waves excite the entire sample via the skeleton of the intercrystallite partitions and, replacing the energy state of the domains, intensify the displacements of their boundaries.

From this point of view, the increase of  $\epsilon'_{free}$  (see the insert of Fig. 3) during the initial stage of polarization can be attributed to the predominance of the contribution of the "deformation" displacements over the processes that stop the displacements in crystallites that become single-domain. In the case of large displacement fields, the decrease of  $\epsilon'_{free}$  due to the single-domain formation in the crystallites prevails and  $\epsilon'$  approaches  $\epsilon'_{cl}$ .

At frequencies higher than the mechanical resonance, this correlation between the boundary displacements and the deformations of the sample vanishes, and  $\epsilon'_{cl}$  should depend only on the field. Therefore an experimental study of the  $\epsilon'_{free}(E_{\pm}, u_{ij})$  and  $\epsilon'_{cl}(E_{\pm})$  dependences makes it possible to determine the degree of

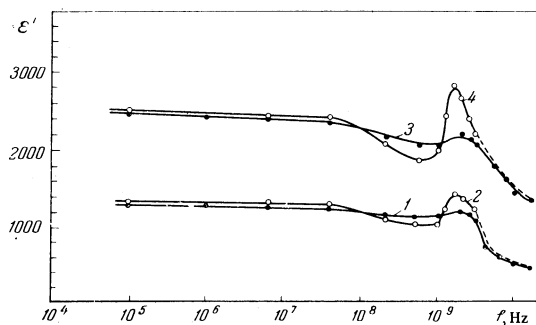


FIG. 5. Frequency dependences of  $\epsilon'$  for the piezoceramic TsTS-6 (1, 2) and for Ba(Ti<sub>0.8</sub>Sr<sub>0.2</sub>)O<sub>3</sub> (3, 4) at a measuring field amplitude 0.01 V/cm (1, 3) and 10 V/cm (2, 4).

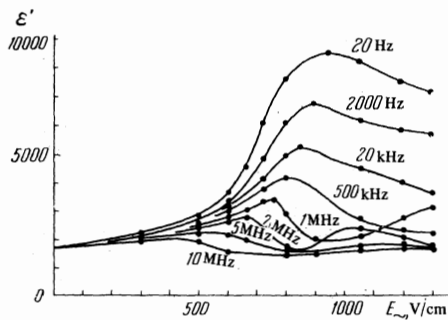


FIG. 6. Dependence of  $\epsilon'$  of a single-crystal  $\text{BaTiO}_3$  sample of  $\sim 0.5$  mm diameter and  $\sim 0.2$  mm height on the amplitude of the measuring field.

the aforementioned correlation of  $P_{\text{dis}}$  and  $u_{ij}$ , as well as the character of the relation between these quantities. The relation between the deformations of the sample and its displacement polarizations can be attributed to the low-frequency nonlinearity and the anomalously large permittivity of the ferroelectrics in appreciable measuring fields (see, e.g., Fig. 6 below).

Inasmuch as  $u_{ij} = CP_1^2$ <sup>[1,19]</sup>, the deformations of the crystal will increase like the square of the increasing measuring field, and the dielectric constant  $\epsilon'_{\text{dis}}$  induced by them should increase in proportion to the amplitude of the deformation, from which follows obviously a nonlinear  $\epsilon'_{\text{dis}}(E_{\sim})$  dependence. The vanishing of the correlation between the deformations of the crystal and the displacements of the domain boundaries should, in accord with the data of Fig. 7, lead to the appearance of a low-frequency dispersion of  $\epsilon'_{\text{dis}}$  and to a dependence of the start of this dispersion on the dimensions of the sample.

The aforementioned relation between  $P_{\text{dis}}$  and  $u_{ij}$  apparently plays an important role also at microwave frequencies, but it is manifest qualitatively in a manner different than at the frequencies of the free oscillations of the crystal. The difference should consist in the fact that the appreciable piezooscillations of the single-domain crystallites can intensify the displacements of the boundaries only in neighboring multidomain crystallites subtended by the elastic-deformation wave during a time on the order of the period of the microwave oscillations exciting the single-domain crystallites. This should result in anomalies on the plot of  $\epsilon'$  and  $\tan \delta$  against the frequency; these anomalies were already reported in<sup>[21]</sup>. It is clear that the excitation of the displacements by local piezodeformations in the microwave region is not connected with the elastic deformation of the entire sample, and can therefore be observed in unpolarized samples.

To check on the foregoing assumptions, special measurements were made. Figure 5 shows the frequency dependences of  $\epsilon'$  of two piezoceramic samples TsTS-6 and TBS-20 of  $(\text{Ba}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ , in which the effects discussed above are most clearly pronounced, because the elastic constants of these materials are large and the technology of preparing the ceramics ensures the production of homogeneous crystallites with dimensions  $\sim 10^{-4}$  cm, which correspond in accordance with formula (1) to resonance frequencies  $10^9 - 3 \times 10^9$  Hz.

Curves 1 and 2 for TsTS-6 correspond to measurement conditions at essentially different values of the power fed to the measurement line. At low values of the measuring field ( $E_{\sim} \ll 1$  V/cm) the amplitude of the deformation waves from the piezoactive single-domain crystal is small, and the effect of the displacement excitation should also be small, as is evidenced by the slightly noticeable rise in the region  $1.5 \times 10^9$  Hz on curve 1. Curve 2 corresponds to a measuring field  $E_{\sim} \sim 10$  V/cm, which should increase by several orders of magnitude the amplitude of the elastic deformations of the single-domain crystallites, a fact manifest in final analysis in the appreciable value of the rise of  $\epsilon'$  in the region  $1.5 \times 10^9$  Hz. A similar nonlinear effect is observed in a TBS-20 ceramic sample (curves 3 and 4).

From the point of view of these nonlinear effects we can understand the cause of a certain increase of  $\epsilon'$  in the pre-dispersion region, observed in certain investigations<sup>[14,21]</sup>, and the reason why Stanford's experiments could not be reproduced by using a different method of measurements as compared with that described in<sup>[14]</sup>. In fact, the use in<sup>[14]</sup> of the resonance of the transmitted power as a method of obtaining information on  $\epsilon'$  should lead to an appreciable increase of the measuring field in the sample (just as in a microwave cavity) and consequently to the effects shown on curves 2 and 4 (Fig. 5). The use of a procedure which is not connected with a resonant increase of the measuring field on the sample usually leads to the results shown on curves 1 and 3.

The foregoing singularities of the results of<sup>[14]</sup> do not influence the main conclusion of that paper, namely that with increasing temperature the resonance effects become stronger in the pre-dispersion region, but unlike Stanford, we relate this effect to the considerations advanced above concerning the relation between the piezoactivity of the single-domain regions (whose modulus of elasticity increases on approaching the Curie point<sup>[1,19]</sup>) with the displacement polarization in the neighboring multidomain crystallites.

In the measurements corresponding to curves 2 and 4 of Fig. 5 we verified, by comparing the results of the measurements in the continuous and pulsed modes, the possible influence of heating of the samples with increasing measurement power; the results showed the absence of heating.

The nonlinear effect at microwave frequencies, shown in Fig. 5, can be used in radio engineering.

## 5. Certain Features of Reversal of Polarization of Ferroelectrics

Figures 6 and 7 show the result of an investigation of the processes connected with the polarization reversal of  $\text{BaTiO}_3$  crystals. These results can be re-

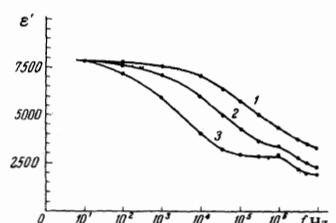


FIG. 7. Frequency dependence of  $\epsilon'$  in large measuring fields ( $\sim 1$  kV/cm) for single-crystal samples of  $\text{BaTiO}_3$  of  $\sim 0.2$  mm height and of diameter 0.1 mm (1), 0.5 mm (2), and 2 mm (3).

garded as a confirmation of the conclusion that the domain dimensions increase upon reversal of polarization, this being the principal cause (in accordance with formula (1)) of high-frequency relaxation of the contribution made to the susceptibility by the polarization-reversal displacements. From the family of curves of Fig. 6 it is seen that the maximum volume to which the domains can increase in phase with the deformations of the crystal and with a large measuring field decreases with increasing frequency. This can be seen from the decreasing contribution made to the dielectric constant by the polarization-reversal displacements of the boundaries and from the decrease of the instantaneous value of the field (corresponding to the maxima of  $\epsilon'$ ), at which the inertial lag of the growth of the domain dimension relative to the measurement field still does not appear.

Figure 7 shows the frequency dependences of  $\epsilon'$  of polarization-reversing BaTiO<sub>3</sub> single crystals of different size. It is seen from these relations that the region of low-frequency dispersion shifts towards higher frequencies with increasing sample dimension.

In connection with these results, it should be noted that the absence of unanimity on the part of the researchers concerning the limiting rate of polarization reversal, and the considerable discrepancies of the experimental data on the macroscopic quantities (switching current, rate of switching, etc.) used to calculate the mobility of the domain walls, can be attributed to ignoring the effect of the crystal dimensions. Indeed, an experimenter measuring a sample of  $\sim 0.1$  mm diameter will find that the "mobility" of the boundaries is larger in it than in a sample of  $\sim 2$  mm diameter, etc. Therefore the most correct macroscopic data on the dynamics of the boundaries can be obtained with the aid of optical research methods<sup>[9-13]</sup>, although in many cases the size effect must be taken into account also in optical measurements.

#### 4. BRIEF CONCLUSIONS

1. The processes of dynamic polarization and polarization reversal of ferroelectrics of the BaTiO<sub>3</sub> type were experimentally investigated in the frequency range up to  $1.5 \times 10^{10}$  Hz and were interpreted on the basis of the notions concerning the displacements of the main boundaries as a result of an oscillating variation of the domain volumes in the external field.

2. It is shown that the dynamic polarization of ferroelectrics is due essentially to effects of boundary displacements in inhomogeneous (multidomain) crystals and is accompanied by resonance effects in homogeneous (single-domain) crystals. In polycrystalline ferroelectrics, these effects appear simultaneously.

3. Connected with the boundary displacement effects are reversible and nonlinear dependences of  $\epsilon'$  and  $\tan \delta$  at low frequencies and at microwave frequencies, microwave dispersion, a hysteresis loop, and a difference between the values of the susceptibilities of the inhomogeneous crystal in the "free" and "clamped" states.

4. In a homogeneous crystal, and also in powder or in polycrystals consisting of single-domain formations, there are no boundary-displacement effects and only

resonance phenomena are observed, connected with the mechanism of elastic-ion polarization, which ensures values  $\epsilon'_c \sim 150$  at c-axis orientation, parallel to the external field (zero anisotropy energy),  $\epsilon'_a \sim 2000$  at c-axis orientation perpendicular to the external field (maximum anisotropy energy), and  $\epsilon'_{ac}$  values between 150 and 2000 at arbitrary c-axis orientation.

5. A homogeneous ferroelectric crystal should have, at all frequencies up to infrared dispersion, a constant susceptibility, and the difference between the susceptibilities of the "free" and "clamped" crystal can serve as an indicator of its inhomogeneity.

6. Microwave dispersion is observed only in inhomogeneous crystals, and a) the frequency limits of the dispersion region are determined by the maximum and minimum dimensions of the domains of the multi-domain crystal or crystallite;

b) the depth of the microwave dispersion  $\epsilon'$  is determined only by the contribution  $\kappa_{dis}$  to the total susceptibility of the sample;

c) in polycrystalline ferroelectrics, in which multi-domain and single-domain crystallites can exist, there is observed a strong relation between the piezodeformation of the single-domain regions and the boundary-displacement polarization in neighboring multidomain regions, leading to anomalies in the frequency dependences of  $\epsilon'$  and especially of  $\tan \delta$ , and also in a number of cases to a nonlinear dependence of  $\epsilon'$  on the magnitude of the external microwave field, something that can find use in microwave technology;

d) an increase of the external displacement field leads to a shift of the start of the microwave dispersion towards the resonant frequency of the single-crystal sample, and leads to a shift towards the resonant frequencies of the crystallites in a polycrystalline sample.

7. The experimental data on the microwave dispersion frequencies in ferroelectrics can be used to determine the domain dimensions and the crystallite dimensions, and also a few phenomenological constants.

8. The boundary-displacement effects can be investigated separately from resonant phenomena, and vice-versa.

9. In really attainable fields, the polarization reversal of ferroelectrics is possible apparently only via the mechanism of domain-boundary motion, and a crystal in which breakdown into domains is impossible cannot reverse polarization.

10. The start of the low frequency dispersion of  $\epsilon'$  in large measurement fields depends on the dimensions of the crystal (sample), a fact that must be taken into account in experimental studies of the dynamics of domain boundaries.

<sup>1</sup>A. F. Devonshire, *Phil. Mag.* 40, 1040 (1949) and 42, 1065 (1951).

<sup>2</sup>W. P. Mason and B. T. Matthias, *Phys. Rev.* 74, 1622 (1948).

<sup>3</sup>C. Kittel, *Phys. Rev.* 83, 458 (1951).

<sup>4</sup>Yu. M. Poplavko, *Izv. AN SSSR ser. fiz.* 29, 2020 (1965).

<sup>5</sup>R. E. Nettleton, *J. Phys. Soc. Japan* 21, 1633 (1966).

<sup>6</sup>W. Doring, *z. Naturf.* 3a, 373 (1948).

- <sup>7</sup>D. G. Sannikov, Zh. Eksp. Teor. Fiz. **41**, 133 (1961) [Sov. Phys.-JETP **14**, 98 (1962)].
- <sup>8</sup>N. P. Khuchua and L. F. Lychatkaya, Izv. AN SSSR ser. fiz. **28**, 708 (1964).
- <sup>9</sup>W. J. Merz, Phys. Rev. **95**, 690 (1954).
- <sup>10</sup>E. A. Little, Phys. Rev. **98**, 978 (1955).
- <sup>11</sup>R. C. Miller and A. Savage, Phys. Rev. **115**, 1176 (1959).
- <sup>12</sup>H. L. Stadler and P. J. Sachmanidis, J. Appl. Phys. **34**, 325 (1963).
- <sup>13</sup>J. Fousek and B. Brzezina, Izv. AN SSSR ser. fiz. **28**, 707 (1964).
- <sup>14</sup>A. L. Stanford, Phys. Rev. **124**, 408 (1961).
- <sup>15</sup>S. Ikegami, J. Phys. Soc. Japan **18**, 1203 (1963).
- <sup>16</sup>J. G. Powles and W. Jackson, Proc. Inst. Elect. Eng. **96**, 363 (1949).
- <sup>17</sup>M. M. Nekrasov and Yu. M. Poplavko, Izv. AN SSSR, ser. fiz. **28**, 714 (1964).
- <sup>18</sup>W. J. Tennery and F. R. Anderson, J. Appl. Phys. **29**, 755 (1958).
- <sup>19</sup>F. Iona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962.
- <sup>20</sup>V. A. Zhirnov, Zh. Eksp. Teor. Fiz. **35**, 1175 (1958) [Sov. Phys.-JETP **8**, 822 (1959)].
- <sup>21</sup>V. V. Dem'yanov and S. P. Solov'ev, Izv. AN SSSR ser. fiz. **31**, 1874 (1967).
- <sup>22</sup>N. A. Romanyuk and I. S. Zheludev, Kristallografiya **9**, 876 (1964) [Sov. Phys.-Crystallogr. **9**, 738 (1965)].
- <sup>23</sup>D. D. Glower and D. L. Hester, J. Appl. Phys. **36**, 2175 (1965).
- <sup>24</sup>V. V. Dem'yanov, V. M. Petrov, and S. P. Solov'ev, PTÉ No. 1, 1968.
- <sup>25</sup>S. S. Gorelik, L. N. Rastorguev, and Yu. A. Skakov, Rentgenograficheskii i elektronograficheskii analiz metallov (X-ray Diffraction and Electron-diffraction Analysis of Metals), Metallurgizdat, 1963.

Translated by J. G. Adashko