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Short-term fluctuations of BaTiO₃ dielectric dispersion

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ABSTRACT

A short-time decrease of the dispersion frequency by three orders of magnitude and its subsequent return to previous value was observed during investigations of dielectric dispersion of BaTiO₃ single crystal under influence of measuring electric field only. It is suggested that possible mechanism of this phenomenon is related to the dynamics of screening processes.

Introduction

The results of investigations of dielectric dispersion of high-quality BaTiO₃ single crystals both in ferroelectric and paraelectric phases are rather contradictory. It was experimentally determined that the frequency of the dispersion (the frequency position of the ε'' maximum) in some cases is located in the kHz region [1, 2], and in other cases is higher than 10^9 Hz [3, 4]. Computer simulations of the dielectric response of 90-degree domain walls of different configuration [5] gives the value of the frequency about 10^{12} Hz. There are papers in which the existence of the dielectric dispersion in paraelectric phase was not found [4], but in the others it was demonstrated that the dispersion has rather large amplitude [1, 2]. In spite of numerous early and recent theoretical papers, there is still no generally accepted opinion about the mechanism of the dielectric dispersion in BaTiO₃.

In the present paper we report about one more peculiarity of the dielectric dispersion in BaTiO₃, – the short-term changes of the dispersion frequency.

For the measurements BaTiO₃ single crystal grown from the seed and then cut across the drawing direction was used. Silver paste electrodes were deposited on the polished surface of the cuts. Electrode area was 28,5 mm², the sample was 1,6 mm thick. External contacts contacted with surface of the electrodes with constant pressing force ≈30 g in order to minimize the contribution of the ferroelastic effect. The sample was aged during several years and was not polarized. The measuring field amplitude did not exceed 1,5 V. The check increase of the measuring field amplitude up to 20 V did not change the measurement results and indicate the electrical rigidity of the crystal caused by growing procedure.


The measurements were carried out on broadband dielectric spectrometer "Novocontrol Concept 40" at a room temperature. The duration of each frequency sweep from 10^5 to $2 \cdot 10^7$ Hz was about 2,5 min.

Experimental results and discussion

Under the conditions of practically constant room temperature we occasionally observed short-term reversible changes of the dielectric dispersion. The example of such fluctuation with increasing and decreasing of the dispersion frequency is shown on Fig. 1.

It is seen from Fig. 1 that between the frequency sweeps (3–5 minutes) the frequency of the dispersion at first spontaneously decreased by several orders of magnitude, then slightly shifted to higher (Fig. 1a) or lower (Fig. 1b) frequencies and finally returned to its initial value. The frequencies of the $\varepsilon''(\log f)$ peaks are higher than the resonance frequencies of the sample.
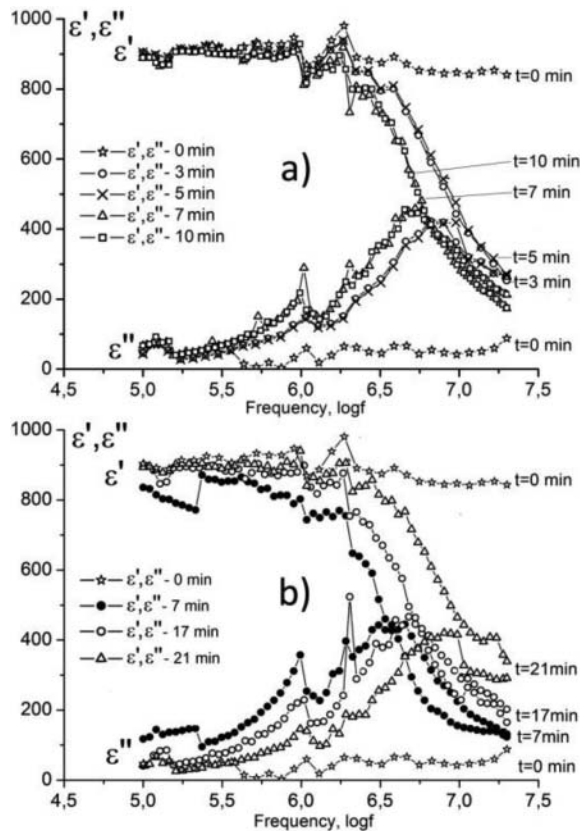
Figure 1. Occasional short-term reversible changes of the dielectric dispersion curves of BaTiO$_3$ single crystal at room temperature. (a) t = 0 – initial dispersion curve, t = 3, 5, 7, 10 min demonstrate the changes of the dispersion with time. (b) t = 0 – initial dispersion curve, t = 7, 17, 21 min demonstrate the changes of the dispersion with time.

Frequency dependencies of the real ε' and imaginary ε'' parts of complex dielectric permittivity ε^* ($\varepsilon^* = \varepsilon'\text{-}i\varepsilon''$) were fitted by the Havriliak-Negami expression

$$\varepsilon^*(\omega)-\varepsilon_\infty = \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_0)^b\right]^c}, \tag{1}$$

where τ_0 is the mean relaxation time, $\Delta\varepsilon = \varepsilon_0$ and ε_∞ is the relaxation strength (ε_0-ε_∞ are the low- and high-frequency limits of dielectric permittivity) and ω is the angular frequency. The parameters b and c ($0\leq b$, $bc \leq 1$) describe the symmetric and asymmetric broadening of the relaxation time distribution, respectively. The $\varepsilon'(f)$ and $\varepsilon''(f)$ data at T = const are well fitted by the Debye relationship ($b = c = 1$) and the relaxation times are very close, as shown in Table 1.

The minimum value of the mean relaxation time was $4{,}66\cdot10^{-8}$ s which corresponds to the characteristic frequency of the dispersion $\approx3{,}42$ MHz. It was reported earlier [3] that this frequency is $\approx 3{,}2$ GHz for BaTiO$_3$ single crystals in ferroelectric phase. As seen from the Fig. 1, ε_0 is the same for initial and anomalous dispersion; ε_∞ and ε_0 are not time dependent. The averaged value of the measure of dispersion n = $(\varepsilon_\infty/\varepsilon_0) \approx 0{,}13$ is significantly lower than typical values reported for BaTiO$_3$ single crystals: n $\approx 0{,}45$ [3] at T<T$_C$ (T$_C$ is the Curie temperature), n $\approx 0{,}47$ [6] and $0{,}35$ [7] for ceramic samples of BaTiO$_3$ at 20°C. Such considerable spontaneous fluctuations of the dispersion need to be clarified.

There are examples of changes of dielectric dispersion in solid dielectrics after artificial incorporation of the defects into the lattice by γ-rays (corundum ceramics) [8], accelerated electrons [9] and neutrons [10] (BaTiO$_3$ ceramics). In the first case it was reported that the characteristic frequency of the dispersion significantly decreased, in the last two cases ε_0 values changed significantly, while the characteristic frequency remained the same or increased.

The shape of the dispersion curve in ferroelectrics is also sensitive to the amplitude of the measuring field. Exceeding of the threshold of the domains switching in BaTiO$_3$ dramatically increases ε_0 value and decreases the characteristic dispersion frequency by orders of magnitude [11, 12].

Our experimental conditions exclude the reasons mentioned above. At our opinion, they may be related to the changes of the state of the main relaxation oscillator responsible for the dispersion – the domain wall, or with changes in screening conditions.

Let us consider each of these possible reasons separately using the information about the structure of BaTiO$_3$.

Table 1. Fitting parameters of the Havriliak-Negami analysis (Eq. 1) of the experimental data presented on Fig. 1 (a, b).

Curve	Fig. 1(a)				Fig. 1(b)		
	3 min	5 min	7 min	10 min	7 min	17 min	21 min
τ_0, s	$2{,}08\cdot10^{-8}$	$1{,}98\cdot10^{-8}$	$2{,}88\cdot10^{-8}$	$2{,}86\cdot10^{-8}$	$4{,}66\cdot10^{-8}$	$3{,}49\cdot10^{-8}$	$2{,}42\cdot10^{-8}$
ε_∞	159,83	157,72	109,37	120,14	71,41	88,89	90,16
$\Delta\varepsilon = \varepsilon_0$-$\varepsilon_\infty$	754,09	757,98	802,79	788,16	797,38	814,80	818,41
b	1	1	1	1	0,98	1	1
c	1	1	1	1	1	0,95	0,75
n = $\varepsilon_\infty/\varepsilon_0$	0,21	0,21	0,14	0,15	0,09	0,1	0,11
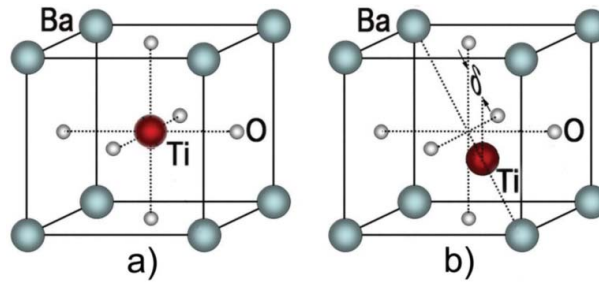
Figure 2. The structure of BaTiO$_3$ unit cell in paraelectric phase: (a) – centrosymmetrical, (b) – polar. δ is the diagonal shift of Ti^{4+} ion. $\delta = 0,19(5)$ Å at T = 35 K, $\delta = 0,16(5)$ Å at T = 70 K [15].

In spite of the long-term studies of structure of BaTiO$_3$ single crystals there is still no agreement concerning the structure of its unit cell. Experiments carried out in 1946 [13] formed the basis of the microscopic displacive models [14]. It was accepted that each Ti^{4+} ion is located in the middle of the oxygen octahedron and the unit cell is centrosymmetrical (Fig. 2a) in the cubic phase. In the tetragonal phase Ti^{4+} ion is shifted in 001 direction. This idea was later on extended to the other structures (at temperature decrease) where Ti^{4+} ion was shifted in 011 direction (rhombic phase) and in 111 direction (rhombohedral phase).

However, these measurements later began to raise doubts [15] and then their fallibility has been shown [16]. X-ray investigations showed the reliability of cluster model [17] where Ti^{4+} ions are shifted along 111 direction in all structural phases. It has been shown [18] that in case Ti^{4+} ion is shifted along the 111 direction the energy is lower than in case when the ion is located in the centre of the octahedron. Based on this fundamental statement, the structural element which determines the properties of the crystal should be the supercell (cluster) of eight polar unit cells (Fig. 2b). Principal feature of this supercell is that only four out of eight Ti^{4+} ions are displaced at phase transitions. At the same time, possible position of Ti^{4+} ions in 64 directions makes the supercell extremely labile for the defects of the unit cell. The width of the domains in the structure built from supercells should be about several nanometers [19].

In the studied frequency range namely the movement of the domain wall should be considered as the main mechanism of the dispersion. In this case the problem is to discover the reasons of its sudden "slowing down". Well known theories of the dispersion consider the number of such reasons with reference to the model of the unit cell where Ti^{4+} is shifted in 010 and 001 directions in tetragonal phase. As far as we know, there aren't any dispersion theories for the alternative displacive model where Ti^{4+} is shifted in 111 direction in all structural phases [18]. Nevertheless, well developed formalism, on our opinion, could be extended on the supercell model.

The presence of lattice disorder which is typical even for the perfect samples gives rise to a broad spectrum of remarkable physical phenomena including pinning, oscillatory and sliding motions of the domain wall, appearance of the dynamic phase transitions and other self-organized critical states. Causes for such peculiarities are irregular random bonds and random fields due to interaction of the defects with spontaneous polarization and thermal excitations [20]. The domain wall curves between the pinning defects, with a radius of curvature determined by the material parameters and the

applied electric field [21]. Temporary change of the configuration of the domains and migration of the defects in mechanically free samples should change the dynamic properties of the domain wall, i.e. the dielectric dispersion cannot be regarded as rigid quantitative property of the sample. The shifting rate of the domain wall, the dynamics of the screening and, therefore, the dispersion are determined by the current condition of the sample.

Investigations show the difference between fast dynamics of the atomic polarization in external field and slowed-down dynamics of the screening charges [22]. The theory on the velocity of planar 180 grad domain wall displacement [20] sets the relationship between the dynamics, the width of the domain wall and the velocity of its displacement. The domain wall uniformly moves under homogeneous external field in the frequency range under consideration. For the transparent, solid, non-charged, uniformly moving domain wall without nuclei, the relaxation time for the screening charges is $\tau = \varepsilon_{ii}/\lambda$, where ε_{ii} is the dielectric permittivity and λ is the electric conductivity of the screening layer. There won't be any delay for screening charges following the domain wall when $a \ll v\tau$ and $t > \tau$, where a is the wall width, v is the wall velocity, t is the time. When these relations are not satisfied, the delay of screening charges is essential and the wall depolarization field is screened by the instant free charges located at the electrode, and thus the measured value of the dielectric constant is lower.

As mentioned above, our experiments showed the decrease of the characteristic frequency of the dispersion by three orders of magnitude (Fig. 1) in comparison with data reported in [3, 4]. We should look for the explanation of this effect in varying of the parameters a, v and τ. The width of the domain wall $a = 0,5 \div 5$ nm in BaTiO$_3$, i.e. the variation of the width is no more than one order of magnitude. Slowing down of the domain wall would cause appearance of pinning points in the volume of the crystal, which is unlikely because the crystal was not affected to the strong influences. The most probable reason is the change of screening conditions. The fact of the sudden appearance of changed dispersion indicates its internal impulsive influence on the sample properties. The impulsive character of the effect in steady state allows us to relate it to the peculiarities of ferroelectric medium, for example, to the Barkhausen effect, i.e. spontaneous switching of the domain structure. On our opinion, it is caused by thermodynamically non-equilibrium mechanical condition of the sample. The latter, in our case, is probably formed by several repeated passes over the resonance frequencies (Fig. 1, logf = 6-6,25) and by the appearance of local areas of mechanical stress near microcracks on polished surface. As experimentally established in [23], the Barkhausen discontinuities are accompanied by impulsive conduction between the electrodes. The charges passing through the sample should change the steady state of the double screening layer [24]. The changes in the layer structure, which is related to the configuration of the domains, should change the surface conduction λ [25] and its relaxation time τ_0.

In order to check out the relation between the dispersion of the dielectric properties and the Barkhausen effect, the switching of the domains was made by the application of the reversible polarization field E = ± 3 kV/cm followed by $\varepsilon'(\log f; 22°C)$ measurements (Fig. 3).

Figure 3 illustrates significant decrease of the dispersion frequency down to ∼2,3 MHz (compare curves 1 and 2, 3 on Fig. 3) and decrease of ε_0; the measure of the dispersion n ≈ 0,71. Barkhausen jumps initiated by the repolarization remain for a long time until the thermodynamically stable state of the domain structure is reached. Smooth type of curves 2
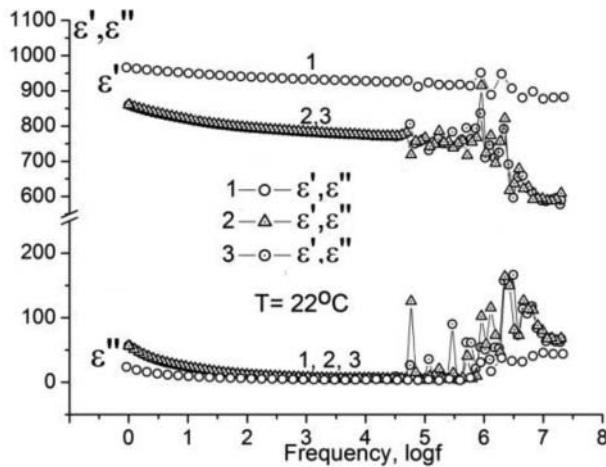
Figure 3. Transformation of the dielectric dispersion $\varepsilon',\varepsilon''$(logf) for BaTiO$_3$ single crystal before (1) and after the reversible polarization by the external field E $= \pm$ 3 kV/cm (2, 3).

and 3 at low frequencies up to 10^5 Hz is due to the integrating effect of the measurement system of the spectrometer, since according to [23] typical duration of the electric impulses due to the Barkhausen effect is $\sim 1\mu$s.

Time evolution of the dispersion formed by reversible polarization is presented on Figure 4.

Curve 3 on Figure 4 demonstrates the state of the dispersion after 180 hours and illustrates the process of increasing of ε'(logf, 22°C) value, which means that the sample has a tendency to transform into single domain state. We can consider this time interval as completion of some process, because no changes of the dispersion were observed after the next 570 hours (curve 4), except increased value of dielectric permittivity (curve 3), while the shape of dispersion curve 2 didn't change at all.

The result of the field influence on the sample volume (Figs. 2, 3) in comparison with the observed effect (Fig. 1) shows that the changes in the domain structure and the injection of
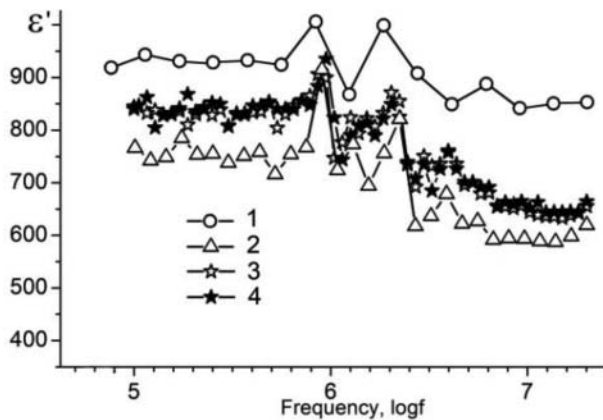
Figure 4. Time evolution of the dispersion formed by reversible polarization. Curves 1 and 2 are the curves 1, 2 from Figure 2. 3 – ε'(logf, 22°C) after 180 hours, 4 – after 750 hours.

free charge carriers (accompanying the field) visually change the dispersion. The tendency of this change and its time dependence, however, differ from characteristic parameters on Fig. 1.

Conservation of the constant value of ε_0 indicates (Fig. 1) that the initial domain structure is stable (or undergoes minimal transformation), i.e. that only a few Barkhausen impulses participate in the changes of the dispersion process. Manifestation of Barkhausen jumps is not observed on the decrease of the dispersion curve (compare to Fig. 2). These facts allow to suppose that in this case changes of the dispersion are determined by the changes in screening conditions in single [20] or double [24] surface layer. The observed increase of the effective relaxation time τ of screening charges indicates that the surface conductivity λ decreases dramatically, by several orders of magnitude. This possibility was experimentally demonstrated in [25]. Short-term conducting channel between the electrodes formed by the Barkhausen impulse [23] uniformly changes the screening conditions under the all electrode area and, respectively, the uniformity of the reaction of the volume on external alternating electric field. This supposition allows to explain the description of "hindered" relaxation curves (Fig. 1) by the Debye spectrum (Table 1).

In frame of the conceptions stated above, the reversible dispersion changes is a rather short (∼30 min) process. At the first stage of the process Barkhausen impulses induce thermodynamically nonequilibrium increase of the relaxation time τ. At the second stage the screening system returns to initial thermodynamically stable state.

The first stage is described by Fig. 1a, the second one – by Fig. 1b. Probably, we should expect some peculiarities of this stage (see curves 7 min and 17 min), – a discontinuity of $\varepsilon'(\log f)$ and $\varepsilon''(\log f)$ dependencies, that points to the temporary increase of polarizability and losses of the sample in some frequency interval. The mechanism of this effect still remains unclear.

Experimental curves presented in this study, obviously, give only time sections of the dispersion changes. The duration of frequency sweeps, strictly speaking, introduce an error into experimental results. Nevertheless, they are approximated by the Debye spectrum reasonably well (Table 1). The ratio of duration of the stages, apparently, depends on the present state of the sample and may be quantitatively studied only if the duration of frequency sweeps would be decreased and the highest frequency will be increased.

For the cluster model of the polar state in $BaTiO_3$ [18] the hypothesis about the change of screening mechanism should be corrected taking into account the possibility of changes of dynamical properties of cluster at its structural reorganization [2].

Conclusion

If the stated assumptions about the nature of the observed effect are correct, then the effect should be regarded as general one for different types of ferroelectric single crystals and for different geometries of samples, including nanometer films.

Acknowledgements

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