New Nonpiezoelectric Dielectrics with Very High Dielectric Permeability and Small Conductivity

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It is shown that a combination favoring polarization of the internal field by means of relaxation polarization of ions leads to a very high dielectric permeability in a wide range of frequencies (up to very high) with freedom from spontaneous polarization and other piezoelectric effects. We obtained nonpiezoelectric dielectrics with $\epsilon \approx 1000$ and with small conductivity.

ONE of the authors in cooperation with A. I. Demeshina has earlier discovered relaxation polarization, giving a very high dielectric permeability at low frequencies (50-20,000 cycles per second). This was found in polycrystalline dielectrics made of rutile (TiO_2) containing small impurities of oxides of the alkali earth metals[1].

In the present work the problem was to bring about experimental conditions in a solid dielectric such that the internal field associated with the polarization[2] would be associated with an ionic relaxation displacement which would have a sufficiently small time of relaxation. At the same time, the dielectric permeability was to be very high even at high frequencies. The basic difficulty in this program consists in bringing about the possibility of comparatively large ionic displacements while still preserving the perovskite structure, which is favorable for polarization.

If one adds ions of bismuth, which have the same radius (1.2 *A*) as ions of strontium, to strontium titanate, then the ions of bismuth are able partly to displace ions of strontium without changing the crystal structure. Also, owing to the differences of valence (ions of strontium are divalent, ions of bismuth are trivalent) the electrical neutrality of the lattice can be maintained only if holes are formed with the specified fractional substitution, as is the case in solid solutions of the substitutional type. Ia. M. Ksendzov showed that the presence of holes is very probable. Breaking up the lattice of the perovskite type can lead to the appearance of ionic relaxation polarization.

Experimental work in this direction has showed that dielectrics of strontium titanate in the presence of a small addition of bismuth trioxide actually possess very high relaxation polarization, and moreover this is quite clearly expressed. Their dielectric permeability remains very high up to very high frequencies*. In Figs. 1 and 2 are curves of the dependence of the dielectric permeability ϵ and of the tangent of the angle of dielectric losses, $\tan\delta$, on temperature with various frequencies for one of the new dielectrics. The shape of these curves is characteristic of relaxation polarization: an increase of frequency displaces the maximum of $\tan\delta$ and ϵ toward the direction of high temperatures. The presence of clearly expressed temperature maxima in ϵ and $\tan\delta$ is an indication that the relaxation polarization is not affected by other processes, for example, by an increased conductivity. The falling part of the curve $\epsilon = f(T)$ corresponds to a dielectric permeability with a zero frequency ϵ_0 which decreases with rising temperatures. With sufficiently low temperature the dielectric permeability is reduced in value and approaches the elastically dependent polarization ϵ_∞ ($\sim$200-250).

The series of experiments showed that the new dielectrics, in spite of the temperature maximum of ϵ, cannot be put into the class of piezoelectrics, because of the following characteristics: 1) the temperature maxima of ϵ and $\tan\delta$ shift with increasing frequency toward the direction of high temperature; 2) nonlinearity of polarization is absent and the dielectric permeability is independent of field strength; 3) dielectric hysteresis is absent. The presence of the temperature maximum of ϵ corresponds to "classical relaxation polarization." This was observed earlier in such an evident form only in polar liquids and some polar polymers, but it was not brought out in such high values of ϵ.

The circumstance that the conductivity of the strontium-bismuth titanates (SBT) is relatively very small makes it possible to estimate from the experimental data in Figs. 1 and 2 several of the dielectric parameters, for example, the coefficients of the internal field, the activation energy of ionic relaxation, and so on.

If one does not take into account the differences between the fields acting on various ions, then one can introduce and average field *E*, which is equal to

* We discovered similar, but more weakly expressed, properties in the dielectric systems calcium titanate-bismuth titanate and barium titanate-bismuth titanate.

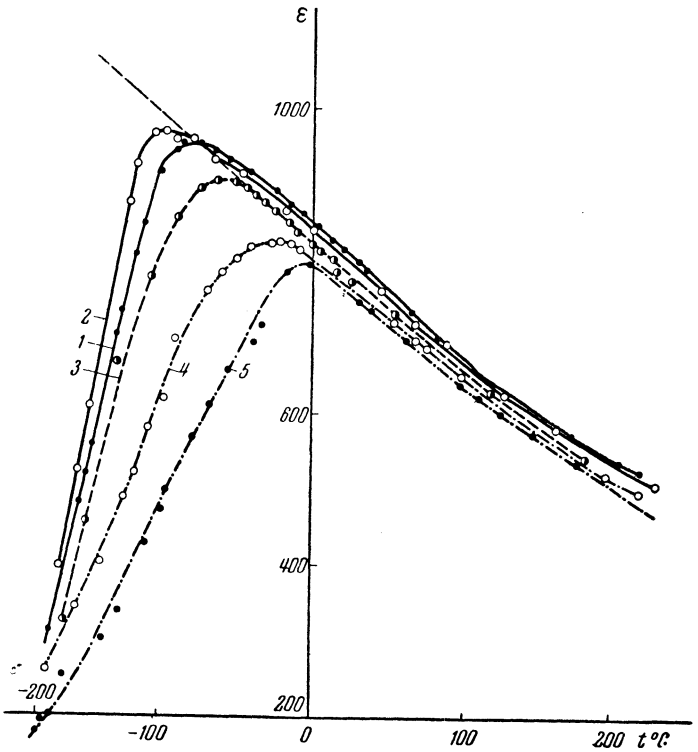

FIG. 1. The dependence of ϵ on the temperature, using various frequencies for the dielectric SVT.
1 -- $f = 5000$ cycles, *2* -- $f = 50$ cycles, *3* - $f = 50$ kc, *4* -- $f = 1$ mc, *5* -- $f = 10$ mc.

$$E = E_{ave} + \beta_1 I' + \beta_2 I_0, \qquad (1)$$

where E_{ave} is the average macroscopic field, I' is the electrical moment of the unit of volume, dependent on the relaxation polarization and I_0 is the same for the elastic (electronic and ionic) polarization. Then the condition for a maximum in $\tan\delta$ will have the following form:

$$(\omega\tau)' = \frac{\varepsilon_\infty - 1 + (4\pi/\beta_1)}{\varepsilon_0 - 1 + (4\pi/\beta_1)} \sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}}, \qquad (2)$$

where $\tau = (2\nu)^{-1} \exp(U/kT)$, U is the potential barrier which the relaxing particles surmount and ν is their frequency of oscillation in position. It is essential that the condition (2) does not include the coefficient of the internal field β_2, which was created by the elastic polarization.

It is possible to show that an approximate condition for a temperature maximum in ϵ has the following form:

$$(\omega\tau)'' \approx \frac{\varepsilon_{max} - \varepsilon_\infty}{2U\varepsilon_{max} \operatorname{tg}\delta''} kT_1, \qquad (3)$$

where $\tan\delta''$ relates to the temperature T_1 of maximum ϵ and to the frequency ω, and k is Boltzman's constant.

Expressions (2) and (3) correspond to the assumption that all the weakly bound ions take the same relaxation time. It is well known from experimental data that ϵ_0 and ϵ_∞ can be expressed through the effective "elastic" polarizability of the unit volume α_{eff} and the relaxation polarizability of the unit volume $\alpha' = n' q^2 \varkappa^2 / 12\, kT$ (q is the charge of the relaxing ion, $\varkappa$ is its displacement and n' is the number of weakly bound ions in 1 cm^3)

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{4\pi(\alpha_{eff} + \alpha')}{1 - (\beta_2\alpha_{eff} + \beta_1\alpha')}, \qquad (4)$$

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi\alpha_{eff}}{1 - \beta_2\alpha_{eff}}. \qquad (5)$$

The combination of Eqs. (2) and (5), and also an estimate of the size of α_{eff} from additional considerations, makes it possible to estimate U, β_1,

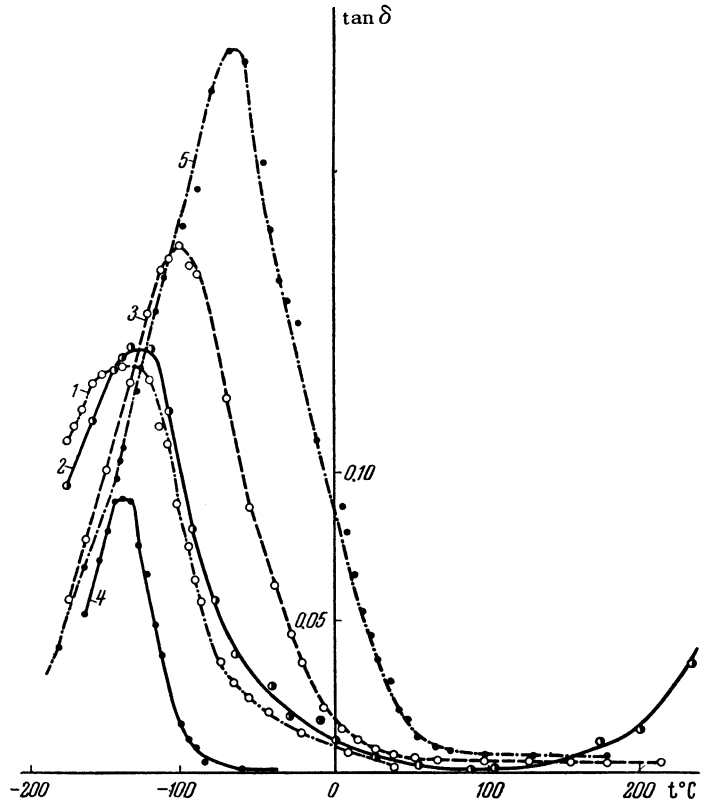

FIG. 2. The dependence of tan δ on temperature, using various frequencies for the dielectric SVT.
1 -- $f = 5000$ cycles, *2* -- $f = 50$ kc, *3* -- $f = 1.5$ mc, *4* -- $f = 50$ cycles, *5* -- $f = 10$ mc.

β_2 and α', using experimental data. For the low temperatures (and low frequencies) $U \sim 1$ ev, while with high temperatures (and high frequencies) $U \sim 0.2$-0.3 ev. The coefficient $\beta_1 \sim 0.01$, $\beta_2 \sim +5$. The small value of β_1 confirms the assumption that the concentration of lattice defects, which governs the relaxation polarization, is small. The high value of dielectric permeability is determined by the simultaneous effect of the large internal field created by elastic polarization (β_2 is large and positive) and relaxation polarization. A more detailed analysis of the experimental data says that the new dielectrics have at least two collections of relaxation times: a diffuse collection of longer relaxation times and a concentrated collection of short relaxation times. Calculation using the two specified collections of relaxation times allows one to explain the intrease of tan δ_{max} with frequency and also several other facts.

As has been pointed out above, the electrical conductivity of the new dielectrics is extremely small (Fig. 3).

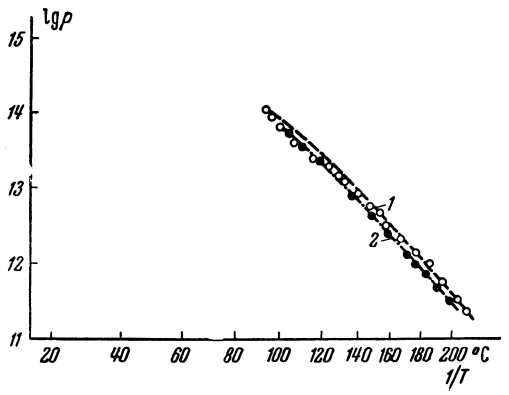

FIG. 3. The dependence of the resistivity ρ on temperature for the dielectric SVT. *1* -- forward direction. *2* -- reverse direction.

At low temperatures a large drop of current, dependent on the accumulation of space charge, occurs with time. In addition to this, if the specimen remains at room temperature with the voltage applied until the current is practically constant,

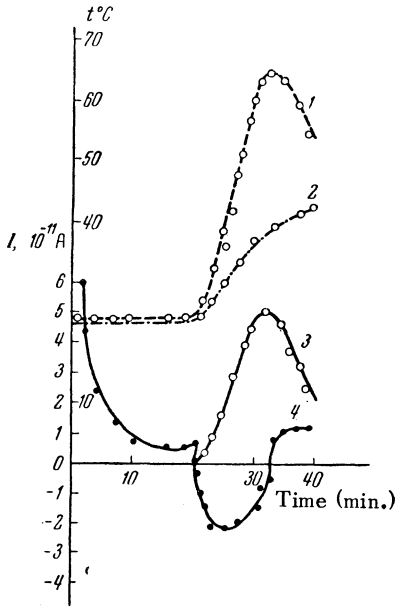

FIG. 4. The dependence of current and various electrode temperatures on time for the dielectric SVT. *1*--temperature on the "hot" electrode, *2*--temperature of the "cold" electrode, *3*--the difference in temperature of the electrodes, *4*--current through the sample.

and then the specimen is heated, the current changes its sign. Specially prepared samples showed that the reverse current can be determined by the rapidity of change of the temperature difference of the electrodes. The corresponding curves are in Fig. 4. One can think that with a change of temperature gradient in the sample with time, a reverse thermal diffusion current arises, determined by the recombination of space charge. In view of the small direct current conductivity, this reverse current can exceed the direct current, and the total current changes sign.

[1] G. I. Skanavi and A. I. Demeshina, J. Exptl. Theoret. Phys. (U.S.S.R.) 19, 3 (1949).

[2] G. I. Skanavi, Elektrichestvo 8, 15 (1947); J. Exptl. Theoret. Phys. (U.S.S.R.) 17, 399 (1947).

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The Shape of the Dispersion Signal in Nuclear Magnetic Resonance with Strong High-Frequency Magnetic Fields

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Approximate solutions are given for the system of equations which describe the behavior of the components of the magnetization vector in a strong high-frequency magnetic field for intermediate relaxation times; both symmetrical and asymmetrical sinusoidal modulation are considered. The approximation is investigated and the limits of its applicability indicated. The solution is used to derive expressions for the longitudinal and transverse relaxation times. The theoretical conclusions are found to be in agreement with the results of experimental studies.

INTRODUCTION

THE shapes of the dispersion and absorption signals in nuclear magnetic resonance depend on the relaxation times (longitudinal and transverse), which are characteristics of the internal fields, and on the external conditions (the strength of the high-frequency magnetic field, the amplitude, frequency and wave-shape of the modulating magnetic field, etc.). Although numerous analyses of the signal shape have been given in the literature [1-10] there are still many experimentally encountered cases which have not been considered.

The present paper is concerned with the signal shape when a "strong" high-frequency magnetic