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Abstract

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MIGRATION POLARIZATION CAUSED BY THE MOTION OF IONS ALONG DISLOCATIONS

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The relaxation polarization of ceramics is associated with the presence of defects in the crystalline phase and with the existence of phase-boundary interfaces possessing different specific conductivities ([1–4]).

Let us consider the influence of the motion of ions along dislocations on the polarization of the crystalline phase, assuming for simplicity that ions of one kind, for example positive monovalent ions, collect at the dislocations, their concentration per unit volume of the crystal being equal to N. The dislocations are surrounded by a cloud of negative ions distributed in the crystal and neutralizing the positive charge. It has been established that, during motion along dislocations, impurity ions possess anomalously high mobility ([5]); this gives grounds for considering the displacement of positive ions along dislocations, regarding the negative ions in the crystal as immobile.

Let us choose a group of dislocations of the same length L, directed along a homogeneous electric field, and determine the average value of the dipole moment arising when positive ions are displaced under the action of the field.

The distribution of positive ions along a dislocation is determined by the Boltzmann formula $n(x) = n_0 \exp[-\varphi(x)/kT]$, where x is the displacement of an ion in the direction of the electric field relative to the beginning of the dislocation; $n(x)$ and n_0 are the numbers of ions per unit length of dislocation at the point x and at the beginning of the dislocation, respectively; $\varphi(x)$ is the potential energy of the ion ($x = 0,\ \varphi(0) = 0$); k is the Boltzmann constant and T the temperature. Neglecting the interaction of ions with one another and introducing the notation $a = qE/kT$, where q is the charge of the positive ion and E is the electric-field strength, the distribution of ions along the dislocation may be written in the form $n(x) = n_0 \exp(ax)$.

The average electric moment $\bar{\mu}$, calculated per one positive ion, is equal to

$$\bar{\mu} = q\left\{\int_0^L (x - L/2)[n(x) - n_c]\,dx\right\} \Big/ \left\{\int_0^L n(x)\,dx\right\} =$$

$$= q\left\{\int_0^L (x - L/2)n(x)\,dx\right\} \Big/ \int_0^L n(x)\,dx, \tag{1}$$

where n_c is the mean number of ions per unit length of dislocation. Introducing the substitution $x - \frac{1}{2}L = \frac{1}{2}Lz$, we reduce expression (1) to the form

$$\bar{\mu} = q\frac{L}{2}\int_{-1}^{+1} z\exp\left(\frac{aL}{2}z\right)\,dz \Big/ \int_{-1}^{+1} \exp\left(\frac{aL}{2}z\right)\,dz = q\frac{L}{2}\mathcal{L}\left(\frac{aL}{2}\right), \tag{2}$$

where $\mathcal{L}(aL/2)$ is the Langevin function. In weak fields, for small $\beta = aL/2$, the Langevin function is expanded in the series $\mathcal{L}(\beta) = \beta/3 - \beta^3/45 + \cdots$. Consequently, in weak electric fields, when

$qEL/2kT < 1$, the mean dipole moment $\bar{\mu}$ per one positive ion moving along a dislocation extended in the direction of the electric-field vector is

$$\bar{\mu} = \frac{qL}{4}\frac{qLE}{3kT}. \tag{3}$$

In strong fields, as $\beta \to \infty$, the Langevin function tends to unity, and $\bar{\mu} = qL/2$. However, strictly speaking, when calculating $\bar{\mu}$ in the case of strong electric fields, the interaction of ions should be taken into account.

Whether an electric field is strong or weak depends on the length of the dislocation, which is limited by the sizes of the crystallites in the ceramic. The sizes of crystallites in various ceramic materials are of the order of a micron or tens of microns. For a dislocation length $L = 1\,\mu$, fields with intensity $E < 500$ V/cm will be weak, and if $L = 10\,\mu$, then fields with $E < 50$ V/cm are weak.

For a dislocation to which the field is directed at an angle ϑ, the magnitude of the mean projection of the moment on the direction of the electric-field vector, $\bar{\mu}_E$, is

$$\bar{\mu}_E = \bar{\mu}\cos\vartheta = \frac{qL}{2}\mathcal{L}\left(\frac{qLE\cos\vartheta}{2kT}\right)\cos\vartheta. \tag{4}$$

In ceramic specimens, dislocations with equal probability may be oriented in any direction. Averaging (4) over all possible directions of the dislocations, in the case of weak fields, for the mean projection of the moment on the direction of the electric field, instead of (3) we obtain an expression containing the coefficient $\overline{\cos^2\vartheta} = 1/3$,

$$\bar{\mu}_E = \frac{1}{3}\frac{qL}{4}\frac{qLE}{3kT}. \tag{5}$$

In the case of strong fields, averaging gives the coefficient $\overline{|\cos\vartheta|} = 1/2$, and

$$\bar{\mu}_E = \frac{1}{2}qL/2.$$

Assuming that all dislocations have the same length, and multiplying μ_E by the concentration of ions N moving along the dislocations, we obtain the polarization P, caused by the motion of ions along dislocations in a constant electric field,

$$P = \bar{\mu}_E N = \frac{1}{3}\frac{qL}{4}\frac{qLE}{3kT}N. \tag{6}$$

If, however, the lengths of the dislocations differ substantially, then, assuming that the number of ions per unit length of dislocation does not depend on L, we obtain

$$P = \frac{1}{3}\frac{q}{4}\frac{\langle L^3\rangle}{\langle L\rangle}\frac{qE}{3kT}N, \tag{7}$$

where $\langle L^3\rangle$ is the mean value of the cube of the dislocation length, and $\langle L\rangle$ is the mean dislocation length.

If a ceramic capacitor has remained for a long time in a constant electric field, so that the polarization has reached a stationary value, then after the plates are short-circuited the field in the capacitor, in the absence of space charges, decreases to zero, and relaxation of the polarization P, caused by the motion of ions along dislocations, occurs. The decrease of P with time t can be determined by considering the diffusion of ions along dislocations and solving the equation

$$\partial n/\partial t = D\,\partial^2 n/\partial x^2, \tag{8}$$

where D is the diffusion coefficient of ions along the dislocation.

The solution of (8) may be sought in the form of a sum of a series

$$n(x,t) = n_c + \sum_{m=1}^{\infty} n_m(x,t), \quad \text{where} \quad n_m(x,t) = A_m \cos\frac{m\pi x}{L}\exp\left[-D\left(\frac{m\pi}{L}\right)^2 t\right], \tag{9}$$

each term of which decreases with its own relaxation time

$$\tau_m = 1/D(m\pi/L)^2. \tag{10}$$

At the moment the capacitor plates are short-circuited, at $t = 0$, for a dislocation along which an electric field had been directed,

$$n(x,0) = n_c + \sum_{m=1}^{\infty} A_m \cos\frac{m\pi x}{L} = n_0 e^{ax}. \tag{11}$$

Only terms with odd m contribute to the polarization; for them

$$A_m = \frac{2}{L}\int_0^L n(x,0)\cos\frac{m\pi x}{L}\,dx = -\,2n_c\frac{a^2}{a^2+(m\pi/L)^2}\,\mathrm{cth}\left(\frac{aL}{2}\right), \tag{12}$$

and the mean value of the dipole moment per ion at $t = 0$ is

$$\bar{\mu}_m = \frac{q}{n_c L}\int_0^L \left(x - \frac{L}{2}\right) A_m \cos\frac{m\pi x}{L}\,dx = -\frac{2q}{n_c L}\frac{A_m}{(m\pi/L)^2}. \tag{13}$$

The relative contribution to the polarization of the term with index m is obtained by dividing (13) by (2) and taking (12) into account:

$$\frac{\bar{\mu}_m}{\bar{\mu}} = 8\,\frac{(aL)^2}{(aL)^2+(m\pi)^2}\,\frac{1}{(m\pi)^2}\,\frac{\mathrm{cth}(aL/2)}{\mathcal{L}(aL/2)}. \tag{14}$$

In the case of weak fields $\mathrm{cth}(aL/2) \simeq 2/aL$, $\mathcal{L}(aL/2) \simeq {}^1/_3\, aL/2$, and

$$\frac{\bar{\mu}_m}{\bar{\mu}} \simeq 8\,\frac{(aL)^2+12}{(aL)^2+(m\pi)^2}\,\frac{1}{(m\pi)^2} \simeq \frac{96}{(m\pi)^4} = \frac{0.985}{m^4}. \tag{15}$$

Consequently, in weak fields practically all the polarization is due to the first term with $m = 1$, whose contribution to the polarization is 98.5%. The contribution of the next essential term with $m = 3$ is only 1.22%, and all the remaining terms give 0.28%.

In strong fields $\mathrm{cth}(aL/2) \simeq \mathcal{L}(aL/2) \simeq 1$, and

$$\frac{\bar{\mu}_m}{\bar{\mu}} \simeq 8\,\frac{(aL)^2}{(aL)^2+(m\pi)^2}\,\frac{1}{(m\pi)^2} \simeq \frac{8}{(m\pi)^2} = \frac{0.81}{m^2}. \tag{16}$$

The contribution of the first term with $m = 1$ to the polarization decreases to 81%, while the role of all the remaining odd terms increases. The term with $m = 3$ contributes 9% to the polarization, and all the remaining terms 10%.

Thus, if after removal of a weak field the polarization decreases approximately according to an exponential law, then after the action of a strong field has ceased the law of polarization relaxation differs appreciably from an exponential one. The polarization decreases especially sharply in the first moments of time, and terms with $m > 1$ make a contribution to the time derivative of the polarization exceeding 50%.

When a voltage is applied, the law of growth of the polarization depends substantially on the electric-field strength. The change in the distribution of positive ions along the dislocation, along which an electric field of strength E is applied, is determined by the solution of the equation

$$\partial n/\partial t = D\,\partial^2 n/\partial x^2 - \mu E\,\partial n/\partial x, \tag{17}$$

which may be sought in the form of a series

$$n(x,t) = n_0 \exp(ax) + \exp\left(\frac{\mu E}{2D}x\right)\sum_{i=0}^{\infty} n_i(x,t), \tag{18}$$

where

$$n_i(x,t) = B_i \cos\sqrt{a_i/D - (\mu E/2D)^2}\,x\,\exp(-\alpha_i t) \tag{19}$$

and the relaxation time of the term with index i is

$$\tau_i = 1/\alpha_i = 1/D\left[(i\pi/L)^2 + (qE/2kT)^2\right]; \tag{20}$$

μ is the mobility of ions along dislocations, related to D by the Einstein relation $\mu/D = q/kT$.

In weak electric fields, the term containing E in expression (20) may be neglected for $i \geqslant 1$, and it reduces to (10). In addition, the terms of series (18) may be compared with the terms of sum (9), for which $m = i$. These terms are, to some extent, equivalent: at $t = 0$, i.e., at the instant the voltage is applied in the case of series (18) and the field is removed in the case of sum (9), they make equal relative contributions in absolute value to the polarization and have identical relaxation times. In studying polarization in a weak alternating electric field, this circumstance makes it possible to apply the superposition principle and, for example, to obtain for $\operatorname{tg}\delta$ the expression

$$\operatorname{tg}\delta = \frac{\dfrac{4\pi\gamma}{\omega} + 0.985(\varepsilon_c - \varepsilon_0)\displaystyle\sum_{m=1}^{\infty}\frac{1}{m^4}\frac{\omega\tau_m}{1+(\omega\tau_m)^2}}{\varepsilon_0 + 0.985(\varepsilon_c - \varepsilon_0)\displaystyle\sum_{m=1}^{\infty}\frac{1}{m^4}\frac{1}{1+(\omega\tau_m)^2}}, \tag{21}$$

where τ_m is determined by formula (10), γ is the specific through conductivity, ε_c and ε_0 are the static and high-frequency dielectric permittivities, and it is assumed that the difference $\varepsilon_c - \varepsilon_0$ is associated with the polarization caused by the motion of ions along dislocations.

The expression for $\operatorname{tg}\delta$ contains in the numerator a sum of terms that pass through a maximum, among which the principal role is played by the term with $m = 1$. Taking $L = 10^{-4}$ cm and assuming that at room temperature $D = 10^{-10}$ cm^2/s, from formula (10) one may estimate the relaxation time $\tau_1 = 10$ s and find the frequency ω_1 at which the first term passes through a maximum, $\omega_1 = 0.1$ rad/s. Consequently, the maximum in the frequency dependence of $\operatorname{tg}\delta$ (of the losses arising in ceramic specimens as a result of the motion of ions along dislocations) is located in the low-frequency region, with f of the order of 0.01 Hz, where it can easily be masked by the losses due to through conductivity. In the frequency region above ω_1, the terms with $m > 1$ lead to a slower decrease of $\operatorname{tg}\delta$ with frequency than is predicted by the Debye theory of relaxation losses, and than the decrease of $\operatorname{tg}\delta$ in the case of losses due to through conductivity.

Formula (21) has been derived under the assumption that the length of all dislocations is the same. Taking into account that dislocations have different lengths, one can obtain a theoretical dependence $\operatorname{tg}\delta(f)$ that agrees with the experimental one. This makes it possible to conclude that the dielectric losses of ceramic specimens are mainly due to migration polarization.

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Note: Figure translations are in progress. See original paper for figures.