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NONLINEARITY AND CONTROLLABILITY OF DIELECTRIC PERMITTIVITY

Among the various materials used in electronics, an important place is occupied by the functional (smart) dielectrics. In this paper, we study dielectric nonlinearity and the possibility of an electrical control over the permittivity. In ionic compounds, this nonlinearity is conditioned by different electronegativities of neighboring ions, while the controllability of permittivity is determined by a change in the rigidity of atomic bonds under a controlling electric field influence. The relevance of this problem is due to the fact that microelectronics uses very thin dielectric layers, in which the electrical strength increases significantly allowing the use of nonlinearity. Moreover, in ferroelectrics, the electric field activates the orientation of domains, which significantly increases the permittivity, and, conversely, decreases it, when the reorientation of domains is suppressed by a bias electric field. The rate of nonlinear change in permittivity and its electrical control are important for use in electronics. So, the applicability limits of these properties are assessed using dielectric spectroscopy.

Keywords: dielectric nonlinearity, dielectric parameters control, controlled capacitors, dielectric spectroscopy.

1. Introduction

It is generally accepted that the main parameters characterizing dielectric materials, namely, permittivity, piezoelectric modulus or pyroelectric coefficient, do not depend on the electric field strength, which is consistent with their original definition. It was assumed that electrical, mechanical, and other reactions are linearly related to external effects, while the main parameters characterizing the dielectric should be independent of the electric field strength. As a rule, the possibility of changing these parameters in a strong external electric field was not taken into account.

However, it is advisable not to take a nonlinearity into account only in the case of not very high electric fields, which are usually used in electrical engineering. But, the attitude to the nonlinearity of dielectrics can be changed in micro- and nanoelectronics, where even a voltage equl to several volts applied to very thin dielectric layers leads to high field strengths in the film, which leads to a significant change in the permittivity due to a disproportionate change in the polarization of the dielectric relative to the magnitude of the applied electric field. For the account for or the possible use of a nonlinearity in films, a positive factor is that the electrical strength of dielectrics in thin layers increases tens and hundreds times, which allows avoiding the phenomenon of electrical breakdown. Therefore, the dielectric nonlinearity can be an important phenomenon in microelectronics, since micron-thick dielectrics are widely used in epitaxial structures. In this case, the nonlinearity manifested in a strong electric field can be used long before the critical level of electrical breakdown. However, it should be noted that, with the rare exception of ferroelectrics, in ordinary bulk dielectrics, even the observation of a nonlinear dependence $\varepsilon(E)$ requires the application of a very high electric field. In connection with the subject of this work, the term "permittivity" is used hereinafter, rather than the commonly used term "dielectric constant", since it is a change in this parameter with the electric field strength, temperature, and frequency that is being investigated: $\varepsilon(ET, \varpi)$.

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At the same time, functional (smart) dielectrics are quite remarkable, are notable for their parameters, usually considered as constant for electrical insulating materials, turn out to be significantly dependent on the electric field, and can even be controlled electrically. For example, such important properties as piezoelectricity and pyroelectricity can be induced by a strong electric field and even can be applied un the case of dielectrics with large permittivity. In this case, the electrically induced piezoelectric modulus or pyroelectric coefficient is fundamentally related to the dielectric nonlinearity. Indeed, in a strong electric field the pyroelectric coefficient can be induced proportionally to the electric field strength E, while the induced piezoelectric modulus is proportional to E^2.

The point is that the dielectric nonlinearity depends on the dielectric polarizability which is quantitatively described by a permittivity., That is why others characteristics (electrothermal and electromechanic) are also dependent on it. For example, the linear dependence of the permittivity on the electric field also means a linear dependence of the elastic deformation (strain x) of the crystal, which corresponds to the inverse piezoelectric effect $x = dE$, where d is the piezoelectric modulus for an electrically open circuit, while for an electrically closed circuit it is necessary to use other linear coefficients $x = gP$, where g is the piezoelectric coefficient. But in a strong field, the piezoelectric coefficient depends on the square of the applied voltage: $d \sim E^2$. As shown in [1], even some basic principles can sometimes be changed under the influence of a strong electric field. For example, it is known that there are 21 symmetry classes of noncentrosymmetric crystals, but only 20 of them are linear piezoelectric; however, this only unaccounted class in a strong electric field still exhibits an odd (but nonlinear) piezoelectric effect, proportional not to E, but to E^3 (however, not to E^2, as the even electrostriction effect). Thus, in electric strong fields, all non-centrosymmetric dielectrics have a nonlinear piezoelectric effect.

To assess the possibilities of using nonlinear and controllable properties of functional dielectrics, it is necessary to consider this aspect in connection with the main mechanisms of electric polarization, and, at the same time, to establish the frequency limits of using nonlinear and controllable dielectric devices. For this purpose, the dielectric spectroscopy is used in this work, as one of the methods for studying the polarization of dielectrics, allowing to estimate its nonlinearity, controllability, and, especially, their inertia. This method allows us to separate various polarization mechanisms in the frequency range, as well as to determine their "dielectric contributions". It is especially important that dielectric spectroscopy allows one to obtain the relaxation time characterizing certain polarization mechanisms by studying the temperature-frequency dependences of the permittivity: $\varepsilon(\omega, T)$.

From the point of view of technical applications, the dielectric nonlinearity and the related controllability of permittivity by electric voltage are used in many devices: electromechanical drives [2], electrically controlled delay lines, acoustoelectronic modulators [3], and electrically tunable piezoelectric filters [4]. Thus, controllability of the parameters of electronic devices is of considerable scientific and practical interest. In this case, electrical control over the dielectric permittivity is due to the nonlinearity of polarization and is used in tunable capacitors, microwave filters, phase shifters, etc. [5]. Moreover, control over the absorption and reflection of microwave radiation by electrically adjusting the dielectric components of a microwave-absorbing composite can be used to protect military facilities from radars. In all these cases, it is most appropriate to study the mechanisms of dielectric permittivity to explain the field dependences and other parameters of conventional and functional dielectrics.

Dielectric nonlinearity and the possibility of electrical control oner the permittivity value significantly expand the possibilities of technical application of functional dielectrics. The paper examines models of physical mechanisms that explain the nonlinearity of the permittivity. One of the tasks to be solved is to estimate the frequency limits of using this nonlinearity and to establish frequency limits for using nonlinear and controllable properties of various dielectrics.

2. General Description of Dielectric Nonlinearity

Electric polarization is a consequence of the electric field applied to the dielectric: $P = \varepsilon_0 \chi E$, where e_0 is the electric constant and χ is the permittivity. Polarization can also be described by electric induction: $D = \varepsilon_0 E + P$, where the first term includes the vacuum induction $\varepsilon_0 E$ so that the permittivity accounts for both components: $\varepsilon = 1 + \chi$.

The nonlinearity of electric polarization described by the dependence $\varepsilon(E)$ can manifest itself as an increase in the permittivity in an electric field ($d\varepsilon/dE > 0$) or as its decrease in the electric field ($d\varepsilon/dE < 0$). A special case is the control over the permittivity by additionally applying a control electric field to the dielectric, called a bias field.

The physical mechanisms of nonlinearity and controllability of permittivity are determined by the features of the electric polarization and can be determined both by the reaction of all charged particles of the dielectric to the electric fields acting on it, and also by the reaction of a cluster of many dielectric particles, or by the reorientation of ferroelectric domains. In any case, the nonlinearity of the dielectric polarization is determined not only by the chemical composition of the material, but also by the structural features of a particular dielectric. Due to the huge variety of dielectric structures and differences in the mechanisms of electric polarization, it is very difficult to give a universal description of the nonlinearity. So, it is necessary to consider each specific case.

However, it is possible to propose a very general approach to the description of the dielectric nonlinearity in solids based on their symmetry [2]. Namely, the dependence $\varepsilon(E)$ can be expanded into a rapidly converging series. Then the first terms of this series can be analized:

$$\varepsilon(E) = \varepsilon + \varepsilon_1 E + \varepsilon_2 E^2 + \varepsilon_3 E^3 + \varepsilon_4 E^4 + \dots \quad (1)$$

Next two different approximations will be considered.

First, the nonlinearity of *centrosymmetric* dielectrics is characterized only by the coefficients at even degrees of the field (i.e., at E^2, E^4, ...), while, at the odd degrees of E, all coefficients are equal to zero. In view of the rapid convergence of series (1), it is quite sufficient to consider only the first significant term of the series ($\varepsilon_2 E^2$); in this case, the coefficient ε_2 is associated with the differential nonlinearity N_ε:

$$\begin{aligned}&\varepsilon(E) = \varepsilon + \varepsilon_2 E^2; \quad N_\varepsilon = \frac{1}{\varepsilon}\frac{\partial\varepsilon(E)}{\partial E};\\ &\varepsilon_2 = \frac{1}{2E}\frac{\partial\varepsilon\,(E)}{\partial E} = \frac{\varepsilon N_\varepsilon}{2E}.\end{aligned} \quad (2)$$

At that, the effect of a sinusoidal voltage on a centrosymmetric nonlinear dielectric leads to the emergence of odd harmonic components of the electric current. Note also that quadratic dependence of the permittivity on the electric field also means the same dependence of a deformation induced by the electric field (strain x). This is a phenomenon of electrostriction: $x = RE^2$, where R is the electrostriction coefficient for an electrically open circuit (while, for an electrically closed circuit, the strain is $x = RQ^2$, where Q is another electrostriction coefficient).

Second, to describe the nonlinearity in the case of *non-centrosymmetric* dielectrics, both types of coefficients are important: for even and odd degrees of the electric field in series (1). When considering the rapidly converging series, it is enough to take only the first (odd) coefficient into account, and to express the differential nonlinearity N_ε as:

$$\begin{aligned}&\varepsilon(E) = \varepsilon + \varepsilon_1 E; \quad N_\varepsilon = \frac{1}{\varepsilon}\frac{\partial\varepsilon(E)}{\partial E};\\ &\varepsilon_1 = \partial\varepsilon(E)/\partial E = \varepsilon N_\varepsilon.\end{aligned} \quad (3)$$

The effect of a sinusoidal voltage on the non-centrosymmetric medium leads to the emergence of even harmonic components of the electric current. The linear dependence of the permittivity on the electric field means also a linear dependence of the field-induced strain which corresponds to the converse piezoelectric effect $x = dE$, where d is the piezoelectric module for the electrically open circuit (while, for the electrically closed circuit, it needs to use the linear ratio $x = gP$, where g is the piezoelectric coefficient).

In principle, nonlinearity in the form of a change in $\varepsilon(E)$ should be observed in all dielectrics. However, in most of them, nonlinearity should be considered, only when a large electric field is applied to the dielectric: 10^7–10^{10} V/m, while the dielectric strength in solid dielectrics usually is within the limits: $E_{br} = 10^8$–10^9 V/m (at that, in thin films, E_{br} reaches 10^{11} V/m). It is worth to note here that the *optical* nonlinearity is observed in any dielectric, but only when a very powerful laser beam acts on the crystal. As a result of this nonlinearity, this beam self-focuses inside the dielectric due to the fact that orbital electrons bound in atoms have a very low inertia and have time to participate in electrical polarization at a huge frequency of light. In this case, electrical breakdown at optical frequencies does not interfere with the manifestation of the nonlinearity, since avalanches of free electrons, which are the main cause of conventional electrical breakdown, do not have time to form. Therefore, in a strong electric field created by a giant laser pulse (when the strength of this field becomes close to the internal fields acting between atoms), the nonlinearity of optical polarization turns out to be sufficient for observation and important applications, being the physical basis of nonlinear optics.

In electronics, with the advent of high technology, it has become possible to obtain high-quality thin dielectric layers whose electrical strength is three orders of magnitude higher than that of bulk dielectrics. Consequently, the electrical breakdown strength in thin layers increases significantly, so that even in conventional dielectrics their nonlinearity can be significant. However, in electrical engineering, in most dielectrics used, the electrical breakdown occurs before they have time to exhibit noticeable nonlinearity. Another example of the application of dielectric nonlinearity and controllability in electronics is the $\varepsilon(E)$ change in ferroelectrics. In them, during phase transitions from the paraelectric to the polar state, the forces of neighboring atoms interactions are practically compensated; therefore, any external influence, including the applied electric field E, leads to an $\varepsilon(E)$ significant dependence. The permittivity in ferroelectrics is usually very high ($\varepsilon \sim 10^3$–10^4), while the dielectric nonlinearity $N_\varepsilon \sim \partial\varepsilon/\partial E$ is proportional to E^3. In this case, the electrical controllability of permittivity in ferroelectric and paraelectric can be used in the electric field close to 10^5 V/m, which is significantly less than the electric breakdown field in them.

Nevertheless, as already noted, in most usual insulators, their nonlinearity manifests itself at an electric field strength that is close to the electric breakdown field. In this respect, the functional dielectrics differ significantly from conventional insulators in that their parameters respond to increasing the electric field strength long before a possible electrical breakdown. In any case, the consideration of the electrical controllability by the parameters of functional dielectrics should be preceded by a study of the microscopic mechanisms of polarization that determine such control.

3. Dielectric Nonlinearity Modeling

The manifestation of nonlinear properties of a dielectric may be different, since it depends on the features of the polarization mechanisms. In this case, the possibility of a dielectric nonlinearity becomes clear already when discussing elementary models describing the polarization. Three types of polarization mechanisms are considered below.

1) Electric polarization has a quasi-elastic nature: that is, an electric field applied to a dielectric displaces electrons and ions that are quite rigidly but elastically, bound in the dielectric structure (or changes the stable orientation of its own dipoles), thereby violating the energetically favorable unpolarized state. In this case, a stressed state arises in the dielectric structure, leading to the emergence of a restoring force, which, in the linear case, is proportional to the magnitude of the deviation of polarization objects from their equilibrium state. Violation of this proportionality leads to a dielectric nonlinearity (in this case, usually $d\varepsilon/dE > 0$).

2) Electric polarization has a thermally stimulated nature, which is possible for those electrons and ions which are weakly bound in local nanosized regions in the dielectric structure (they are capable of chaotically jumping into different localized states under the action of thermal motion). This mechanism also takes place for dipole dielectrics, where permanent dipoles chaotically change their orientation under the action of the thermal motion. The electric field leads to an asymmetry of these orientations that causes the thermal dipole polarization. Nonlinearity for the listed polarization mechanisms is characterized by the dependence $d\varepsilon/dE < 0$.

3) Microregions – polar clusters – consisting of many self-oriented dipoles, as well as the ferroelectric domains lead to the electric polarization. In this case, the nonlinearity can be characterized by both a significant increase in the permittivity with increasing the magnitude of the applied field: $d\varepsilon/dE \gg 0$, and its substantial decrease: $d\varepsilon/dE \ll 0$.

It is advisable to begin the consideration with some *elementary models.*

The main parameter that determines the nonlinearity and controllability of smart dielectrics is their dielectric permittivity, which characterizes the processes of electrical polarization. When an electric field is applied to a dielectric, it causes a small displacement x between nearby charged particles, creating a microscopic electric moment: $p = qx$. Particles with an electric charge q that participate in the polarization process are: electrons that move from equilibrium positions in atoms, ions that deviate from equilibrium in a crystal lattice, and dipoles that change their orientation under the influence of an electric field. It is assumed that the induced electric torque is proportional to the applied local field: $p = \alpha F = qx$, where α is the polarizability, which, if we use a microscopic approach to the polarization phenomenon, is similar to the dielectric susceptibility χ, which is included in the macroscopic relation $P = \varepsilon_0 \chi E$. At the microscopic level, it is the nature of the dependence of the polarizability α on the internal electric field F that ultimately determines the nonlinearity and controllability of macroscopic parameters in the dielectric.

Since the polarizability α is microscopic analog of macroscopic parameter susceptibility χ, from a microscopic point of view, the dielectric nonlinearity should be described by a series corresponding to the description of nonlinear dielectric constant (1):

$$\alpha'_e\,(F) = \alpha_0 + \alpha_1\,F + \alpha_2\,F^2 + \alpha_3\,F^3 + ..., \qquad (4)$$

where F is the microscopic Lorentz field, defined as $F = \frac{\varepsilon+2}{3}E$, while the permittivity and polarizability are related by the equation $\frac{\varepsilon+2}{\varepsilon-1} = \frac{\sum n_k \alpha_k}{3\varepsilon_0}$, where n_i is the concentration of charged particles with polarizability α_i.

Electrons, ions, and dipoles moving under the influence of an electric field in a confined space can acquire electrical moment through various mechanisms. First, dielectric nonlinearity will be considered for *quasi-elastic* polarization, where the charged particles are tightly bound in the structure, so, the electric field causes only a very small deviation from their equilibrium state. Nevertheless, in this case, all particles of the dielectric participate in the polarization process, that gives a significant integral effect on the permittivity with possible manifestations of dielectric nonlinearity and controllability. The second type of polarization mechanisms, called *thermally activated* polarization, occurs, when electrons, ions, or dipoles are weakly bound in the structure (usually, they are located near the structural defects). Thermal chaotic jumps of such particles can have a noticeable effect on the polarization: localized in the nanoregions, these particles actively change their position between the points of their localization, moving over a distance of lattice parameter dimension (i.e., moving over a distance that is thousands of times greater than in the case of quasi-elastic polarization). Therefore, during thermally activated motion of charged particles, their average displacements δ significantly exceed the small deviations x of main structural units of a crystal during their elastic polarization. In this case, the coordinated thermal jumps of weakly bound charged particles between different local positions can have a significant impact on the dielectric permittivity and its nonlinearity.

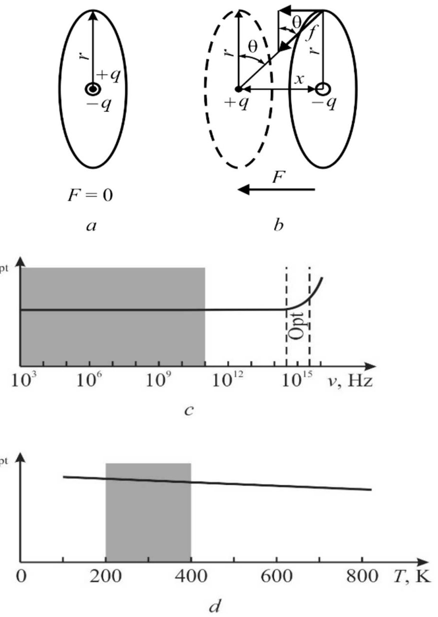


Fig. 1. Simple explanation of electronic (optical) polarization: model consisting of one electron and nucleus (*a*); shift of orbital in local field F (*b*); frequency dependence of electronic permittivity (*c*); temperature dependence of electronic permittivity (shaded areas show the ranges of technical interest in electronics) (*d*)

Next, the most important elementary mechanisms of polarization will be briefly discussed in order to assess their capabilities in terms of the dielectric nonlinearity. Note that, despite the simplicity of the models under consideration, they are the basic mechanisms underlying much more complex concepts of dielectric nonlinearity and controability.

Electronic quasi-elastic polarization is a mechanism common to all dielectrics. The analysis of its simplified model gives the polarizability value $\alpha_e \sim \sim r_e^3$, where r_e is the radius of the electronic shell, Fig. 1, a, b. When the electric field is applied to an atom, its electronic shell (conventionally shown by a circle of radius r_e) is displaced relative to the nucleus by a distance x, that leads to the polarization: $p = qx$, where q is the orbital charge, x is the displacement of the shell relatively core. This field-induced reversible and quasi-elastic displacement determines the electronic polarizability $\alpha_e = p/F$. It is the nonproportionality of this displacement to the magnitude of the electric field that leads to a nonlinearity. In the SI system $\alpha_e = 4\pi\varepsilon_0 r_e^3$ [2], but it is more convenient to use the Gaussian system, where $\alpha_e \sim r_e^3$.

To evaluate the nonlinearity, dependence, $\alpha_e \sim\sim r_e(F)$ should be presented as a series (4), where a few initial coefficients are:

$$\alpha_0 = r^3, \quad \alpha_1 = 0, \quad \alpha_2 = \frac{3}{2}\frac{r^7}{q^2}; \quad \alpha_3 = 0, \\ \alpha_4 = \frac{1}{8}\frac{r^9}{q^4}, \quad \alpha_5 = 0, \tag{5}$$

where q is the charge of the electronic shell. For the assessment, it is enough to use only the first nonzero coefficient of this series (after the main value α_0), since the nonlinearity is noticeable only in a very large electric field (this can be experimentally realized only in powerfull laser beam). All coefficients at the odd degrees of field F are zero (this result is expected for the symmetric model shown in Fig. 1, *a*). In this case, the nearest non-zero coefficient is positive: $\alpha_2 > > 0$. This means that, in the strong electric fields, the electronic polarizability $\alpha_e \sim r_e(F)$ increases; as a result, the dielectric permittivity $\varepsilon(E)$ also increase as the optical refractive index $n = \sqrt{\varepsilon}$.

Electronic nonlinearity arises, because the Coulomb force f, which returns the electronic shell to the unpolarized state after the guiding field is switched off, changes quadratically (according to the r^{-2} law as the force of attraction of electrons to the nucleus), while the displacement x induced by the guiding field increases only linearly (proportional to the field F). As a result, with an increase in the electric field, the electronic shell stretches what leads to an increase in polarizability. Thus, as the electron moves away from the nucleus, the electron shell becomes more susceptible to a displacement. An increase in $\alpha_e(F)$ correspondingly leads to an increase in the permittivity $\varepsilon(E)$. Indeed, at optical frequencies (when only the electron polarization is possible), the laser beam becomes self-focusing in any solid dielectric (which is considered as a lens effect of the self-focusing of the optical beam).

Ionic quasi-elastic polarization means that ions in an rigid, but elastic lattice are displaced by an electric field from their equilibrium position, which leads to the appearance of an induced electric moment $p = qx = \alpha_i F$. With such a displacement of the ions, a quasi-elastic restoring force arises, which, after the turning off the electric field, quickly returns the ions to their undisturbed position. This mechanism is the characteristic only of those dielectrics, in which the ionic nature of interatomic bonds is strongly expressed.

To calculate the polarizability α_i of the ionic quasi-elastic polarization, a simple model can be used, shown in Fig. 2, *a*, *b*. Unlike the previous case, a noncentrosymmetric model is chosen, similar to a two-ion molecule, but these two ions can also represent two sub-lattices (cationic and anionic) inserted into one another and, thus, forming an ionic crystal. This model involves the Coulomb attraction of ions, where the repulsive force is caused by the interpenetration of electronic shells.

The energy of ions attraction depends on the distance a between them: $\frac{q^2}{4\pi\varepsilon_0 a}$, while the energy of their repulsion is described by a power function $\frac{d}{r^n}$. The result of the calculations is $\alpha_i = \frac{4\pi\varepsilon_0 a^3}{(n-1)}$ in SI, while, in the Gauss system, $\alpha_i = \frac{a^3}{(n-1)}$. It follows that the ionic polarizability α_i by order of magnitude is similar to the electronic polarizability α_e.

The ionic polarization nonlinearity is assessed using the series coefficients, where, as in the previous model, it is sufficient to account for the first non-zero coefficient:

$$\alpha_0 = \frac{a^3}{n-1}; \quad \alpha_1 = \frac{a^5\,(n+4)}{q\,(n-1)^2}. \tag{6}$$

If we compare this result with the nonlinear electronic polarization (5), it should be noted that, in this case, the first-odd coefficient α_1 is positive. So, there is no need to consider the next even coefficient α_2 or more due to the very rapid convergence of the series and the evaluative nature of the calculations. As for the magnitude of the nonlinearity caused by various mechanisms of lattice polarization, it depends on the strength of the bonds of neighboring atoms, i.e., on the nature of chemical bonds of these atoms. In a stable lattice, the Coulomb forces of interatomic attraction are compensated by the Pauli (quantum) forces caused by the overlap of electronic shells, which is of the same nature for all crystals. Therefore, in a non-equilibrium polarized state, under the influence of an electric field, the covalent and ionic crystals become, as it were, like “polar crystals”, acquiring the properties of piezoelectric, pyroelectric and other polar effects. It is obvious that the force of attraction of ions decreases in proportion to the permittivity. Note that, in crystals with high dielectric permittivity, the nonlinearity is also increased. Really, in the ionic paraelectrics and biased ferroelectrics, the nonlinearity can become very high, as will be discussed below.

Generalized model of quasi-elastic electronic-ionic polarization is based on the idea of a “soft” (or “compliant”) ion, which is especially characteristic of the anions. In fact, quasi-elastic polarization involves highly mobile outer electronic orbitals, the displacement of which in an electric field can be determined both by the displacement of electrons from the nucleus (inside each ion) and by the general interaction of valence electrons with all ionic lattice. The first mechanism corresponds to the fastest electronic (optical) polarization, the low inertia of which is determined by the small mass of electrons (this determines the frequency response, shown in Fig. 1, *c*, $_{\varepsilon}$ with a dielectric contribution $\varepsilon_e = 2$–5 and a high dispersion frequency of up to 10^{16} Hz). The limiting frequency of the second polarization mechanism, which is actually also determined by the displacement of valence electrons, but *associated* with the ionic lattice, is limited to the infrared frequency range of 10^{12}–10^{14} Hz, as shown in Fig. 2, *c*, but the dielectric contribution of which can be in wide limits: the ε_i might be up to 10^4. This polarization and its nonlinearity are decisively influenced by the difference in the electronegativity of neighboring ions: the ion with increased electronegativity shifts the shared electrons in the pair toward itself; so, its working charge becomes more negative, and the ion with lower electronegativity acquires a correspondingly increased positive charge. Together, these ions create a mixed covalent-ionic bond, characterized by a non-uniform distribution of the electronic density along the interionic bonds, which contributes to the manifestation of the nonlinearity.

Thermally activated polarization, generally speaking, is observed predominantly in crystals containing a significant concentration of structural defects. Loosely bound electrons and ions are localized around them, and, in some cases, the crystal lattice contains its own dipoles – polar molecules with a constant (hard) intrinsic electric moment p_0, the orientation of which in the applied field leads to a polarization. In this case, charged nanosized formations localized in the crystal lattice can also be classified as quasi-dipoles, Fig. 3, *a*, *b*; usually, their occurrence is caused by structural defects. Their concentration ($n_0 \sim 10^{20}\text{cm}^{-3}$) is approximately thousands times less than the concentration of basic structural particles ($n \sim 10^{23}\text{cm}^{-3}$). However, the local polar moments of nanosized inclusions can create the electric polarity, which is thousands times higher than the elementary moments caused by the displacement of ordinary crystal particles.

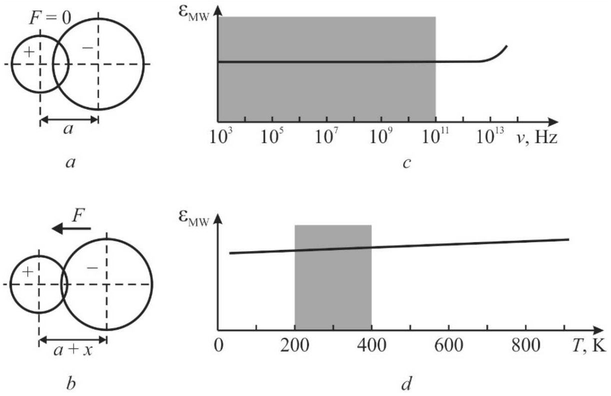


Fig. 2. Ionic polarization: simplest model consisting of one positive and one negative ion (*a*); deformation x in local field F (*b*); frequency dependence of the ionic permittivity (*c*); ionic permittivity temperature dependence (shaded areas show the range of technical interest) (*d*)

Various orientations of quasi-dipoles are stimulated by thermal chaotic vibrations. At that, the applied electric field increases the probability of a reorientation of quasi-dipoles and induces their polarization in the direction of the applied field.

Thermally activated ionic polarization occurs in the process of thermal chaotic motion in the crystal lattice; in this case, weakly bound ions must overcome the potential barrier U to obtain a new localization, Fig. 3, *a*. The average distance between these positions is of the order of lattice constant ($\delta \sim 10^{-6}$ cm). Typically, these chaotic jumps of many loose ions do not lead to their self-polarization, but an applied electric field disrupts their uniform distribution, which leads to a polarization. In this case,

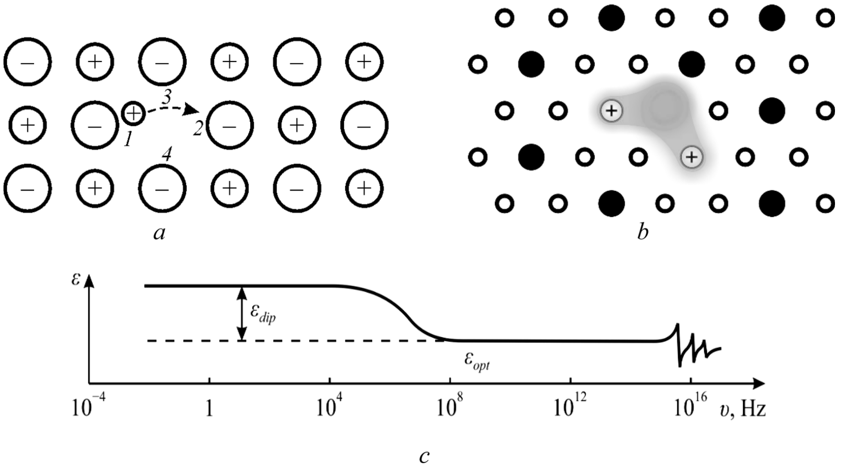


Fig. 3. Thermally activating ionic (*a*) and electronic (*b*) polarization: polar cluster in cubic ionic crystal, where small positive ion of impurity localizes nearby one (*1*) of possible six (in volume) negative ions but has ability to jump in other position (*2*) (*a*); polar cluster in titanium dioxide planar lattice model, where the oxygen anionic vacancy is located at intersection of electronic clouds; O – oxygen, O^{-2}; • – Ti^{+4}; ⊕ – Ti^{+3} (*b*); dielectric spectra showing contributions $\varepsilon_{\rm dip}$ to the permittivity from dipoles thermally activated orientation (*c*)

the number of free ions generating the total polar moment is limited, which ultimately leads to a nonlinearity, since the number of non-oriented ions decreases, as the electric field increases.

The probability of the jumping of a particle to overcome the potential barrier is $\exp(-U/k_{\rm B}T)$, where $k_{\rm B}$ is the Boltzmann constant. The Debye frequency of thermal vibrations of ions in the lattice is ν. So, the number of ions, which can jump over the potential barrier, is $n_{12} = n_{21} = = \frac{n_0}{6}\nu e^{-\frac{U}{k_{\rm B}T}}$. In the applied electric field, the height of potential barrier is reduced by value $\Delta U = \frac{qF\delta}{2}$. At that, the electrically induced moment is $P = \Delta nq\delta$, where $\Delta n = n_{12} - n_{21}$. Calculation [6] showed that the polarizability of the thermal ionic polarization is $\alpha_{iT} = = \frac{q^2\delta^2}{12kT}$. The nonlinearity of the ionic thermal polarization in a strong electric field should arise in the case where the electrical field causes the flip-over of ions through the potential barrier: $\alpha_{iT}\left(F\right) = \frac{q\delta}{6F}\tanh\frac{\Delta U}{kT}$.

Passing to series (4), the hyperbolic tangent series $\frac{\Delta U}{kT}$ follows: $\tanh\frac{\Delta U}{kT} = \frac{\Delta U}{kT} - \frac{1}{3}\left(\frac{\Delta U}{kT}\right)^3 + \ldots$. So, for the nonlinearity of the thermal ionic polarization, we obtain:

$$\alpha_0 = \frac{\left(q\delta\right)^2}{12kT}; \quad \alpha_1 = 0; \quad \alpha_2 = -\frac{\left(q\delta\right)^4}{144\left(kT\right)^2}. \tag{7}$$

This means that, in a strong electric field, the saturation of the polarization is observed, since the number of not yet oriented dipoles decreases; thus, the polarizability (and the dielectric constant) decreases. With a rare exceptions, the nonlinearity of the thermal ion polarization is observed in a very strong electric field (comparable to the breakdown voltage). However, if the crystal itself has an increased permittivity, rather a strong dipole-dipole interaction can occur, creating an artificial ferroelectric with very high nonlinearity: An example is the $K_{1-x}Li_xTaO_3$ solid solution, where $x = 0.1$–0.2 [2].

Thermally activated electronic polarization occurs, when a dielectric near its structural defects has weakly attached electrons, which can be localized in two or more equivalent positions separated by potential barriers. Typically, these electrons are captured by crystal defects or impurity ions, which create nanoregions with an uneven charge density distribution. When there is no external electric field, these electrons or holes jump from one place to another one. But if the electric field is turned on, such chaotic jumps of electrons do not create a volumetric electric moment. The influence of an external field coordinates unilateral jumps and generates an electric polarization.

Figure 3, *b* shows a model of thermal electronic polarization in rutile ($Ti^{+4}O_2^{-2}$), where two trivalent titanium ions Ti^{+3} compensate for one anion vacancy. In some sense, this model is equivalent to the ionic thermal polarization. At that, the calculation of the polarizability and nonlinearity is carried out in a similar way, as Eq. (7). The polarizability of the electronic thermal polarization is equal to $\alpha_{et} = \frac{e^2\delta^2}{12kT}$, where the distance δ separates the two locations of electrons localization. This polarization can make a significant contribution to the dielectric permittivity; for example, in pure ceramic rutile at room temperature $\varepsilon \approx 100$, being caused by the quasi-elastic electronic and ionic polarization. However, in the doped rutile, due to the thermal electronic polarization, the permittivity can increase up to $\varepsilon \approx 2000$, depending on the concentration of anionic defects. In this case, in a strong electric field, the dielectric nonlinearity manifests itself as a decrease in the permittivity with increasing the voltage.

Dipole thermally activated polarization. Randomly oriented dipoles in a polar dielectric usually do not form a general electric moment, if there is no external electric field. However, after the turning-on of the electric field, some of the dipoles become one-sided oriented, which leads to the electric polarization. The stronger the electric field, the greater the number of oriented dipoles and the greater the dipole polarization. The electric moment calculated per one molecule equals to $p = \alpha_{dt}F$, where α_{dt} is the dipole polarizability, and F is the local field. In a weak external field, i.e., under the condition $p_0F \ll k_\mathrm{B}T$, the polarizability is determined by the formula $\alpha_{dt} = \frac{p_0^2}{3kT}$. Using expansion (4), we can find the nonlinearity coefficients of the thermal dipole polarization:

$$\alpha_0 = \frac{p_0^2}{3kT}; \quad \alpha_1 = 0; \quad \alpha_2 = -\frac{p_0^4}{45k^3T^3}; \quad \alpha_3 = 0\ldots. \tag{8}$$

This is a completely expected result, since the participating of quasi-dipoles in ionic or electronic thermal polarization can be represented by electric moments $p_i = q\delta$ or $p_e = e\delta$: therefore, formulas (7) and (8) have a similar form. Since, in polar dielectrics, $\alpha_2 < 0$, their dielectric permittivity in a strong electric field decreases. However, in most of these dielectrics, their nonlinearity manifests itself only near a voltage close to the electrical breakdown.

Nevertheless, a peculiar property of dipole ferroelectrics in their disordered (paraelectric) phase is the significant nonlinearity, which is realized in a completely acceptable field (10^4–10^5 V/m), but only when the crystal temperature is close to that of the ferroelectric phase transition. It should be noted that, in such paraelectrics, the polarization mechanism only to a some extent resembles the model of thermally activated dipole polarization discussed above, since the above simple model did not involves the interaction between dipoles.

Summarizing the reasoning about elementary polarization models, we can conclude that quasi-elastic electric polarization is associated with electrostriction, i.e., the applied electric field leads to the expansion of the dielectric along the direction of the applied field and, therefore, weakens the elastic coupling of neighboring particles. In a strong electric field, this expansion leads to a quadratic dependence of the elastic displacement of particles on the electric field. Due to the small mass of moving particles and their strong coupling, the natural frequency of quasi-elastic processes is very high, and, therefore, the manifestation of the polarization nonlinearity is practically inertia-free, and also weakly depends on the temperature, Fig. 1, c, d and Fig. 2, c, d. On the contrary, the thermally activated polarization is characterized by a strong dependence of all parameters on the temperature, while the dielectric nonlinearity is due to the fact that only a limited number of particles participate in the polarization; therefore, when they gradually become oriented, the number of non-oriented particles is depleted. So, the saturation occurs, and the dielectric constant decreases with increasing electric field. The delay of these processes usually occurs at radio frequencies, Fig. 3, *c*.

4. Large Dielectric Nonlinearity of Ferroelectric Materials

It is assumed that ferroelectrics and related materials have a unique arrangement of their interatomic bonds, which causes a strong nonlinear response to the action of an electric field. To explain this feature, in the models shown in Fig. 4 on the left, the nonpolar covalent and ionic bonds of the crystal are compared with the polar *mixed* covalent-ionic bonds that can form a ferroelectric. This structure of interatomic bonds is a consequence of the structural compensation of the different electronegativity of neighboring ions, whose charges are somewhat changed. It is this feature that gives ferroelectrics special electrical, mechanical, thermal and optical properties which differ significantly from the ordinary dielectrics.

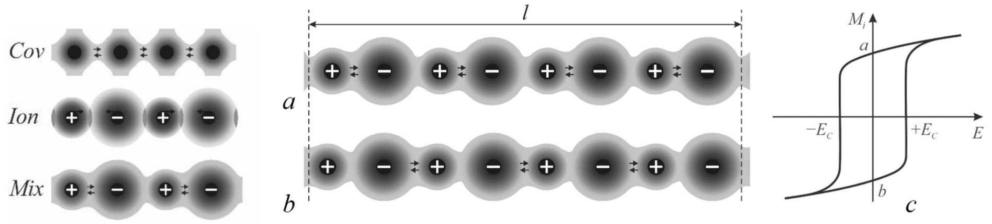


Fig. 4. Simple presentation of polar-sensitive structures: shown on the left are non-polar covalent and ionic bonds as well as polar mixed bonding; shown on the right are polar bonds of opposite orientations; correspondent *a* and *b* directions are shown in hysteresis loop (*c*)

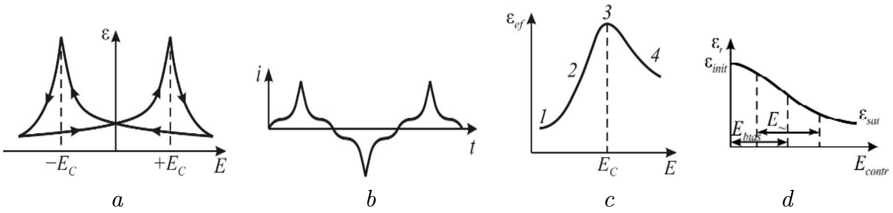


Fig. 5. Nonlinear effects in ferroelectrics: nonlinearity in strong alternating field corresponding to hysteresis loop in Fig. 4, *c* with coercive field E_c (*a*); effective non-linearity (*b*); current in ferroelectric variable capacitor (*c*); reversible nonlinearity in bias electric field (*d*)

In ferroelectrics, polar bonds under the action of an applied electric field can be reoriented that leads to a strong nonlinear response: on the right of Fig. 4, the models *a* and *b* demonstrate the orientation of internal bonds in two opposite cases. In a weak electric field, both of these structures are stable and characterized by a coercive field E_c, measured by studying the dielectric hysteresis loop. The switching phenomenon occurs, if the applied electric field exceeds the coercive field (Fig. 4, *c*) that is used in ferroelectric memory devices.

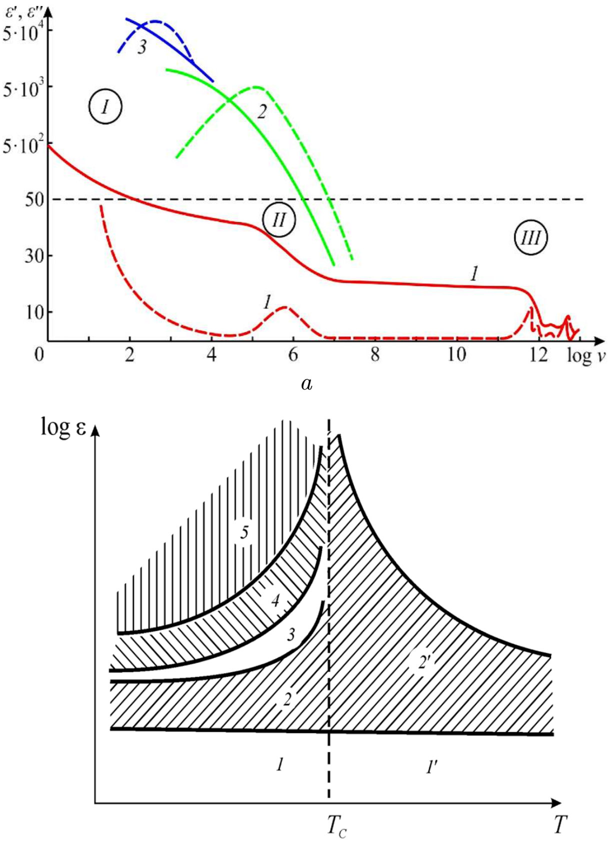
Nonlinear ferroelectrics can make many manipulations with electrical signals possible: their modulation, detection, amplification, *etc.*, Fig. 5. The nonlinearity of the electrical properties of ferroelectrics can be briefly explained as follows. usually, the electrical induction in a dielectric is proportional to the electric field; $D \sim \varepsilon E$, this means that the electrically induced polarization is linearly related to the electric field $P \sim \chi E$, where $\varepsilon = 1 + \chi$. However, in ferroelectrics and some paraelectrics, this linear dependence does not hold, since their permittivity depends on the electric field strength: $\varepsilon = \varepsilon(E)$ due to $\chi = \chi(E)$. The ratio of polarization to the electric field is determined by the permittivity: $\varepsilon = 1 + P/\varepsilon_0 E$. In the case where $\varepsilon \gg 1$ (which is typical of ferroelectrics), we can assume that $\varepsilon \approx P/\varepsilon_0 E$, where the polarization consists of two components: the induced lattice polarization and polarization conditioned by domains orientation: $P = P_{\rm ind} + P_{\rm or}$. The dependence $\varepsilon(E)$, as seen in Fig. 5, *a*, has the sharp maxima in the region of the coercive field E_c due to the intense domain switching. As a result, during one period of the sinusoidal voltage, the permittivity passes through its peak values twice, Fig. 5, *a*, so, the electric current in the nonlinear capacitor shows a large deviation from the usual sinusoidal Shape, Fig. 5, *b*.

By averaging the permittivity over one period, the *effective* permittivity $\varepsilon_{\rm ef}$ can be obtained, the dependence of which on the electric field is characterized by a curve with a maximum, Fig. 5, *c*, reminiscent of the maximum instantaneous values of $\varepsilon_{\rm start}$ shown in Fig. 5, *a*. In region *1* of the dependence $\varepsilon_{\rm ef}(E)$, i.e., with a relatively small electric field, the dependence $\varepsilon_{\rm ef}(E)$ is practically absent, since the electric field strength is not enough to cause the orientation of domains. Therefore the permittivity $\varepsilon_{\rm ef}$ is determined only by $P_{\rm ind}$. Further, in region *2* of the $\varepsilon_{\rm ef}(E)$ dependence, the permittivity increases rapidly due to the onset of domain orientation, so, the domain polarization $P_{\rm or}$ is added to $P_{\rm ind}$. In a strong electric field, the dependence $\varepsilon_{\rm ef}(E)$ exhibits a large maximum $\varepsilon_{\rm max}$ in region *3*, Fig. 5, *c*, since all domains are already involved in the polarization. If the electric field in region *4* is further increased, the effective permittivity decreases, because the contribution of P_{or} no longer increases, although the electric field strength E continues to increase. The onlinearity due to the domain repolarization can be described by the coefficient $K_{\mathrm{ef}} = \varepsilon_{\max}/\varepsilon_{\mathrm{start}}$; in ceramic nonlinear capacitors K_{ef} reaches 20, but, in single crystals, it can exceed 100, however, in thin ferroelectric films and composites the nonlinearity is an order of magnitude less [5].

In addition to the discussed effective nonlinearity, the variable capacitors exhibit *reversible* nonlinearity, Fig. 5, *d*, that can be used in the devices which allow the capacitance value to be controlled by an electric field. In this case, the electric bias field prevents the orientation of domains, reducing their repolarization, which leads to a decrease in the dielectric constant and its saturation to value $\varepsilon_{\mathrm{sat}}$. In this case, the controllability coefficient of such a dielectric "varactor" $K_{\mathrm{ef}} = \varepsilon_{\mathrm{init}}/\varepsilon_{\mathrm{sut}}$ is usually equal to 2, but, sometimes, it can reach ~10. Reversible nonlinearity is used to control the value of capacitance using a biasing electric field, and the efficiency of control can be significantly higher, if a tunable capacitor is included in the resonant circuit. This technique can be used to phase or amplitude modulate of RF signal. Unlike effective nonlinearity, the reversible nonlinearity can be applied over a very broad frequency range.

Physical mechanisms of ferroelectric nonlinearity and controllability, shown in Fig. 5 can be explained by the dielectric spectra studying of ferroelectrics, Fig. 6, that are rather interesting for applications.

Many ferroelectrics have been studied in this work, but the TGS crystal (triglycine sulfate $= (\mathrm{NH_2CH_2}\cdot(\mathrm{COOH})_3\mathrm{H_2SO_4})$, whose properties most closely correspond to Landau's theoretical model for the order-disorder phase transition, is chosen here as an illustrative example. In a strong electric field (curves *2* and *3* in the region **I** in Fig. 6), the dielectric dispersion in the TGS was studied under conditions of complete switching of ferroelectric domains, creating a larger effective permittivity $\varepsilon_{2\mathrm{ef}}$, compared to the permittivity measured in a weak electric field and shown in curve *1*. In a strong electric field, the main dispersion $\varepsilon_{2\mathrm{ef}}$ is observed at relatively low frequencies: in this case, the maximum effective loss coefficient $\varepsilon_{2\mathrm{ef}}$ is seen at a frequency of about 500 Hz, but some vibration of switched domain walls can be observed up to frequencies of the order of one megahertz.



a

b

Fig. 6. Dielectric permittivity dispersion: *a* – in TGS where ε' is shown by solid curves and ε'' by dotted curves): low frequencies, strong electrical fields (**I**), radiofrequency region, weak fields (**II**); infrared frequencies, weak fields (**III**); *b* – temperature dependence of main polarization mechanisms contribution to permittivity in ferroelectrics with displace type phase transition: electronic polarization (*1′*, *1*); "soft phonon" contribution (*2′*, *2*); domain walls dynamical polarization (*3*); electromechanical polarization (*4*); domain switching in strong electrical fields (*5*)

From the data obtained by measurements in a strong electric field, it follows that the control of domain reorientation, leading to a hysteresis dependence (such as shown in Fig. 4, *c*), is possible only at low frequencies up to 1 kHz. Note that in strong electric fields several mechanisms of polarization in ferroelectrics are involved, including faster polarization occurring in polar clusters localized in domain boundaries. As can be seen in Fig. 6, curves *2* in region **I**, the contribution of this mechanism is an order of magnitude smaller than that shown by curves *3*, and can be detected by high-frequency filtering of the response while simultaneously switching low-frequency domains. This means that the nonlinear characteristics shown in Fig. 5, a, b, c, can only be used at relatively low (sound) frequencies. As for the controlling characteristics presented in Fig. 5, d, then, due to the faster mechanism of polarization of clusters, they can be used at radio frequencies [6].

All other studies of TGS crystals were carried out in a weak electric field. In this case, three frequency regions of ε_2 dispersion are visible. The first appears at low frequencies (region **I**), and the second at radio frequencies (region **II**). Both of them are explained by the movement of domains in a weak electric field: the first dispersion means that domains can partially change their orientation even in a low-frequency electric field. As for the second dispersion $\varepsilon_2(\nu)$, which demonstrates a maximum of ε''_2 at a frequency of about 10^6 Hz, it corresponds to domain wall oscillations. The last, third dispersion $\varepsilon_2(\nu)$ in the far infrared region **III** is due to vibrations of the TGS crystal lattice.

The presented data make it possible to estimate the speed of the polarization response to an alternating electric field. Detailed results on the dielectric dispersion are generalized for ferroelectrics with a displacement-type phase transition, Fig. 6, b; in this case, area *5* corresponds to areas *2* and *3* in Fig. 6, a, characterizing the dielectric nonlinearity shown earlier in Fig. 5.

In paraelectrics, the reversible nonlinearity is very important (Fig. 5, d): it can be used even in the microwave range. The temperature dependence of permittivity at ultrahigh frequencies is represented by region *2′* in Fig. 6, b, which corresponds to region above the ferroelectric Curie point T_c. It is noteworthy that, in the paraelectrics, there are no low-frequency polarization processes which can introduce hysteresis and dielectric losses in the microwave range. Therefore, the paraelectric can be used as a tunable and nonlinear dielectric up to the frequency range of 10^9–10^{11} Hz.

The electrical control over the permittivity value of paraelectrics can be described as follows. Curie–Weiss law $\varepsilon = C/(T-\theta)$, seen in Fig. 6, b, region *2′*, can be obtained in Landau theory, in which thermodynamic potential for ferroelectrics is written in a form: $\Phi(T,P) = \Phi_0(T) + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \ldots$, where α and β are the coefficients. Considering that electrical field is defined as derivative $\partial\Phi/\partial P$, above expression can be rewritten as $E = \alpha P + \beta P^3$. So inverse susceptibility $\chi^{-1} = \partial P/\partial E = \alpha + 3\beta P^2$ defines the permittivity $\varepsilon \approx \chi$, since $\varepsilon = 1 + \chi$ and in ferroelectrics $\varepsilon \gg 1$. In the paraelectric phase, where first term in the Landau polynomial is negative ($\alpha > 0$ at $T > \theta$), permittivity decreases in strong electrical field, because $\varepsilon \sim \partial P/\partial E$. General formula [2], which accounts for both ε-nonlinearity and ε-temperature dependence is:

$$\varepsilon(T,E) = \frac{C}{(T-\theta)}\left[1 + 3\,\beta\varepsilon_0^3 E^2 \frac{C^3}{(T-\theta)^3}\right]^{-\frac{1}{3}}, \qquad (9)$$

where C is Curie–Weiss constant; θ is Curie–Weiss temperature, β is coefficient at term P^4 in Landau expansion. It is seen that in the non-polar phase dielectric nonlinearity is the higher the closer temperature to phase transition point. For further analysis, expression (9) should be presented in a form of rapidly convergent series:

$$\varepsilon(T,E) \approx \frac{C}{T-\theta} - \frac{K}{3}\frac{C^4E^2}{(T-\theta)^4}\frac{2}{9} + \frac{2}{9}K^2\frac{C^7E^4}{(T-\theta)^7},$$

where $K = 3\,\beta\varepsilon_0^3$. From this expression, temperature coefficient permittivity $TC\varepsilon$ and the dielectric nonlinearity N can be determined:

$$N = \frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial E} \approx -\frac{2}{3}\frac{KC^3}{(T-\theta)^3}E + \frac{2}{3}\frac{K^2C^6}{(T-\theta)^6}E^3. \qquad (10)$$

These relations are illustrated graphically in Fig. 7.

Parameter $TC\varepsilon$ depends on the electric field, and nonlinearity N depends on temperature. At a certain temperature, a maximum of negative nonlinearity is observed, which is of primary interest in connection with the choice of operating modes of microwave variable capacitors for use in technical devices. From (10) we can find the field strength $E_{\max}$ at which the nonlinearity is greatest: $E^2_{\max} = (T-\theta)^3/3KC^3$. This parameter characterizes the paraelectric "stiffness" and determines the operating voltage range. In practice, this voltage must be reduced, which is caused by the need to increase the reliability of the device (the operating voltage should be significantly lower than the electrical breakdown voltage), as well as the need to reduce the power of the microwave signal (which leads to overheating of nonlinear dielectric).

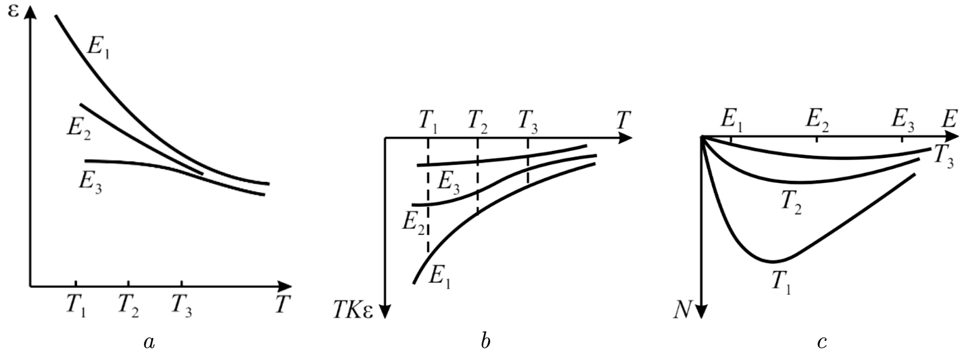


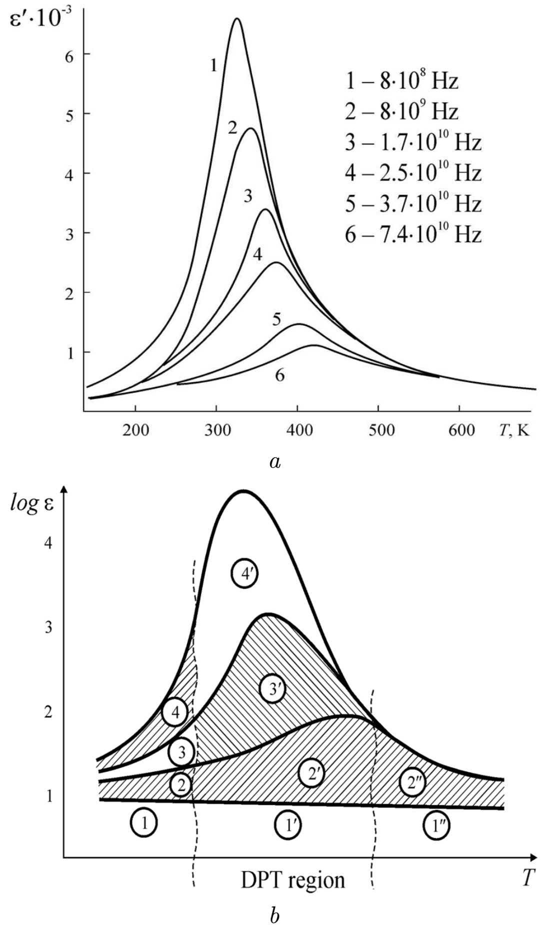
Fig. 7. Nonlinearity of permittivity in paraelectrics: permittivity dependence on temperature and bias field (*a*); temperature dependence $TC\varepsilon$ (*b*); non-linearity dependence on temperature and bias field (*c*)

Due to a low inertia of the controlling mode and high resistance to radiation, the variable microwave capacitors are very promising for use as parametric amplifiers, modulators of microwave signals, phase shifters, etc. At cryogenic (helium) temperatures, potassium tantalate ($KNbO_3$) is the most promising for use, since at helium temperatures it has a fairly low level of dielectric losses, and at liquid nitrogen temperatures, strontium titanate ($SrTiO_3$) is a suitable material for variable capacitors. At ambient temperatures, suitable variable capacitors can be made from ferroelectric solid solutions of (Sr, Ba)TiO_3 and (Sr, Pb)TiO_3 in the paraelectric phase. In this case, the control (bias) voltage is significantly lower than the electrical breakdown voltage .

When using ferroelectric materials at ultra-high frequencies, it is important that the permittivity and its temperature dependence be minimal with maximum nonlinearity. However, as can be seen from equation (9), the nonlinearity is proportional to the permittivity raised to the power of 3, and the electric field in which the nonlinearity has a maximum depends on the Curie–Weiss temperature as $(T-\theta)^{3/2}$. Therefore, various technical requirements for the use of microwave paraelectric varactors (high thermal stability, high nonlinearity and low losses) are difficult to reconcile, but some compromise solutions are possible if paraelectrics are used in the form of thin films. As for the possibilities of controlling the permittivity using oriented deformation in thin layers, we note that a new direction, “Engineering of elastic deformations” [6], is currently being created, which allows changing the local symmetry of the crystal and obtaining completely new properties in thin films.

To summarize the discussion about functional dielectrics, which have a high dielectric nonlinearity, we can conclude that they belong to solids with a weakly stable electrical structure, prone to phase transitions. Typically, the nearest neighboring particles of a crystal are considered to interact strongly, while the interaction of more distant particles can be neglected. However, near a structural phase transition, the interaction of nearby particles apparently compensates for each other, and against this background, the interaction of particles located at greater distances from each other turns out to be dominant. During such transitions, an anomalous increase in the role of collective motions occurs: strong anomalies in the heat capacity and the coefficient of thermal expansion are observed, while in ferroelectrics the dielectric constant at the Curie point tends to infinity. During a displacement-type phase transition, a large decrease in the frequency of transverse optical vibrations is observed in the center of the Brillouin zone: in paraelectrics this is a “soft” phonon mode with a frequency $\nu = A(T-\theta)^{1/2}$. The influence of an external electric field leads to a more rigid structure, increasing this frequency with a corresponding decrease in dielectric constant.

In relaxor ferroelectrics, which are necessarily represented by solid solutions with an inhomogeneous distribution of ions of different valences, in addition to the above-mentioned “soft” phonon modes, some other polarization effects are added. For example, this is the existence of polar clusters (generated by local charge compensation) interacting with each other in a finely balanced structure which is extremely sensitive to the action of an electric field. The fact is



a

b

Fig. 8. Relaxor ferroelectrics dielectric spectrum: PMN permittivity at high frequencies (*a*); temperature dependence of dielectric contributions from basic polarization mechanisms (*b*): electronic (optical) polarization (*1*, *1′*, *1″*); lattice (ionic, phonon) polarization (*2*, *2′*, *2″*); domain walls polarization in polar phase (*3*), polar clusters re-orientations (*3′*); polarization of inter-phase boundaries (*4*, *4′*); DPT is diffuse phase transition

that, in a relaxor ferroelectric, similar structural positions are occupied by the cations of different valences: for example, such disordering of the composition [7] is observed in a crystal of lead-magnesium niobate (PMN = $\mathrm{PbMg_{1/3}Nb_{2/3}O_3}$), which in a general structural formula $\mathrm{ABO_3}$ has alternating ions $\mathrm{B^{+2}}$–$\mathrm{B^{+5}}$.

Relaxor ferroelectrics have a high permittivity over a wide temperature range; this property is very important for applications in many electronic devices (micromechanics and microdrivers). The displacement produced by these actuators is determined by the permittivity value of the relaxor ferroelectrics (note that nonlinearity also depends on this parameter). Therefore, to assess the limitations on operating rate of electronic devices based on relaxors, the frequency dispersion of the dielectric constant of relaxors is studied in a broad range of frequencies, Fig. 8.

The large values of $\varepsilon_{\max}$ in these materials are observed over a brode temperature range; dielectric spectroscopy should help one to explain their features. At optical frequencies, the dielectric constant does not have significant temperature anomalies, slowly decreasing with increasing temperature, regions *1*, *1′*, *1″* shown in Fig. 8.

Lattice (ionic) polarization of relaxor ferroelectrics, which is limited to regions *2*, *2′* *2″* indicates the presence of a “soft mode” in the vibrations of the crystal lattice, but it does not have such a decisive dielectric contribution as in the case of displace type ferroelectrics (see Fig. 6, *b*). Polarization of the inter-phase boundaries, shown in section *3′* of Fig. 8, *b*, makes the main contribution to the permittivity of relaxor ferroelectrics in the region of the diffuse phase transition (DPT). These boundaries between the fluctuating polar and nonpolar phases gradually, as the temperature decreases, become the interfaces between ferroelectric domains, and, therefore, behind the dotted lines of section *3′* this resembles the dispersion of microwave domains, already common for ferroelectrics (see Fig. 6, *a*).

The key mechanisms that determine the outstanding properties of relaxor ferroelectrics are due to the presence in their structure of polar clusters with highly polarizable boundaries, the dielectric contributions of which are designated in Fig. 8, *b* by numbers *3*, *3′* and *4*, *4′*. At radio frequencies and, in the near microwave range in the applied electric field, a reorientation of polar clusters occurs, which corresponds to region *4′* in Fig. 8, *b*. Beyond these boundaries, a dotted line is shown characterizing the dielectric contribution, region DFT 4, as well as the electromechanical (piezoelectric) mechanism of polarization of ferroelectric domains. The technical advantages of relaxor ferroelectrics are due precisely to the mechanism of reorientation of polar clusters, which can lead to the permittivity values of up to $\varepsilon \sim 40.000$ and more. Microwave spectroscopy, the main results of which are presented in Fig. 8, *a*, allows us to evaluate the speed capabilities of the use of devices with relaxators in electronic applications.

Thus, the low-frequency mechanism of permittivity dispersion in the relaxor ferroelectrics is explained by the strong electromechanical coupling of “softly polarized” polar regions, and microwave ε-dispersion is due to “frozen paraelectricity” at the boundaries between polar regions (as in ferroelectric domains). The response time of devices based on relaxor ferroelectrics is determined by dielectric dispersion mechanisms. The electromechanical contribution to the permittivity can be the dominant factor for speed and is determined by the speed of sound in the relaxor ferroelectric, so the speed of the corresponding devices depends on the size of the relaxor elements used.

In this way, dielectric spectra make it possible to evaluate the frequency limits of application of devices based on the use of redactor ferroelectrics.

5. Conclusions

The main parameters describing the electrical, electromechanical, and electrothermal properties of dielectrics are usually assumed to be independent of the electric field strength. However, in the functional dielectrics, this dependence is strongly expressed and can be used in the development of electrically controlled and nonlinear devices. In this paper, we have analyzed the dielectric nonlinearity and the possibility of electrical control over the permittivity in connection with various mechanisms of electrical polarization. By modeling elementary polarization mechanisms and using experimental methods of dielectric spectroscopy, we have studied the physical nature of nonlinear permittivity and its electrical controllability, which is becoming relevant at present for thin layers of dielectrics used in microelectronics. Particular attention is paid to the high dielectric nonlinearity of paraelectrics and relaxor ferroelectrics. The dielectric spectroscopy method is used to estimate the inertia of the described phenomena and to understand the mechanisms of dielectric nonlinearity and controllability. The above considerations and data provide a basis for predicting the development of devices with controlled dielectrics, as well as assessing their capabilities and prospects.

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НЕЛІНІЙНІСТЬ ТА КЕРОВАНІСТЬ ДІЕЛЕКТРИЧНОЇ ПРОНИКНОСТІ

Серед різноманітних матеріалів, що використовуються в електроніці, важливе місце займають функціональні (розумні) діелектрики. У цій статті ми досліджуємо діелектричну нелінійність і можливість електричного контролю за допомогою діелектричної проникності. В іонних сполуках ця нелінійність зумовлена різною електронегативністю сусідніх іонів, тоді як керованість діелектричної проникності визначається зміною жорсткості атомних зв'язків під керуючим впливом електричного поля. Актуальність даної проблеми зумовлена тим, що в мікроелектроніці використовуються дуже тонкі шари діелектрика, в яких значно підвищується електрична міцність, що дозволяє використовувати нелінійність. Крім того, в сегнетоелектриках електричне поле активує орієнтацію доменів, що значно збільшує діелектричну проникність, і, навпаки, зменшує її, коли переорієнтація доменів пригнічується електричним полем зміщення. Швидкість нелінійної зміни діелектричної проникності та її електричний контроль важливі для використання в електроніці, тому межі застосовності цих властивостей оцінювали за допомогою діелектричної спектроскопії.

Ключові слова: діелектрична нелінійність, контроль діелектричних параметрів, керовані конденсатори, діелектрична спектроскопія.