Methods of theoretical researches the non-linear electrophysical properties of solid dielectrics with compound crystalline structure

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Abstract. Methods quasiclassical kinetic theory investigate the phenomena of nonlinear ion-relaxation polarization in solid dielectrics with a compound structure of the crystal lattice. As a particular case, the mechanism of nonlinear proton-relaxation polarization in hydrogen-bonded crystals (HBC), classified according the electrophysical properties as proton semiconductors and dielectrics (PSD), is theoretically studied. Generalized kinetic equation and spectra of complex permittivity (CP), which allow to describe the nonlinear properties of dielectric losses in HBC in range of ultra-low temperatures (1-10 K) and low fields (100 kV/m - 1000 kV/m), and in range of ultra-high temperatures (550-1500 K) and strong fields (10 MV/m - 1000 MV/m). The scientific and practical significance of received results consists in development of the theoretical basis of algorithm for computer prediction of materials properties and parameters that are functional elements of technological schemes of industrial installations and systems.

Introduction
The hydrogen bonded-crystals (HBC) [1] classified by type and properties of crystal lattice as layered crystals (layered silicates, crystalline hydrates), and by electrophysical properties as proton semiconductors and dielectrics (PSD) are of scientific-practical interest for modern electrotechnical, electrochemical and electric power industries [2-10]. HBC is characterized by the presence of a hydrogen sublattice in their structure and the proton conductivity property connected with the diffusion transfer of hydrogen ions (protons) along hydrogen links towards to the lines of force of external electric field [11]. Materials of this class are used as: memory elements for computer chips; nonlinear converters of optical signals [2-8]; regulators of laser radiation parameters (KDP, DKDP); electric insulation elements of the conductive parts of thermal electric power station electrical generators [9]; fuel cells in hydrogen energetics [10] etc.

Of practical interest are materials of functional elements of technological systems, which work in extreme conditions: ultra-low temperatures (near helium); strong electric fields and ultrahigh temperatures (near breakdown); intensive (coherent) laser radiation; strong magnetic fields, etc.

In the low-temperatures range (50-100 K), according to the results of experimental and theoretical studies [11,12,14], mechanism of relaxation polarization in the HBC is realized, mainly, due to the tunnel proton transport through a potential barrier (nonlinear quantum diffusion polarization). In the
high temperatures range (450-550 K) nonlinear volumetric charge polarization takes place [11,13,15,16] due to the mixed type relaxers transfer: thermally activated transitions of Bjerrum ionization defects between layers of water molecules and quantum transitions protons.

**Research objective and research methods**
Nonlinear electrophysical processes in the PSD caused by: nonlinear volume-charge polarization, in the sufficiently high temperatures range \( T \approx 350-550 \) K [15, 16]; tunnel migration polarization, at low \( T \approx 70-100 \) K and ultralow \( T \approx 4-25 \) K temperatures [11-14]; structural rearrangement of the hydrogen sublattice during spontaneous polarization of ferroelectrics (KDP, DKDP), near the temperature of phase second order transition [17, 18]. All these phenomena are not sufficiently studied at the theoretical level, there is no unified universal theory equally suitable for mathematical description and computer prediction of the proton conductivity mechanisms in HBC in any temperature range, field strengths and electromagnetic radiation intensity.

Low-temperature (tunnel) maxima \( \text{tg}_6(T) \) in HBC [19] can not be measured at all.

The purpose of the paper is to develop a generalized pattern based on theoretical research of nonlinear electrophysical properties of dielectrics materials with a compound crystal structure (ceramics, ferroelectrics, mica and etc.). The generalized nonlinear kinetic equation in this model will be composed by methods of quasiclassical kinetic theory [20,21] on basis of the balance equation of number of ions, moving in the multiwell potential field, perturbed by external polarizing field [16,20,22].

**Solutions for a prototype system**
Theoretical investigating of kinetics phenomena connected with the ion-relaxation polarization and conductivity in dielectrics with a compound crystal lattice will be based upon the one-dimensional equation of the diffusional ion transport (in HBC – protons) [21]

\[
q \frac{\partial N}{\partial t} + \frac{\partial \jmath}{\partial x} = 0.
\] 

Based upon (1), modeling the current density of ions in the form [22]

\[
\jmath_k(x; t) = q \left\{ \nu_{mob}(x; t) \cdot N(x; t) - \frac{\partial}{\partial x} \left( D_{diff} (x; t) \cdot N(x; t) \right) \right\}
\] 

Where \( D_{diff}(x; t) = \sum_{l=0}^{\infty} \frac{1}{(2l)!} D_{diff}^{(2l)} \cdot \xi^{2l}(x; t) \cdot \nu_{mob}(x; t) = \left[ \sum_{l=0}^{\infty} \frac{1}{(2l+1)!} \cdot \mu_{mob}^{(2l+1)} \cdot \xi^{2l}(x; t) \right] \times E(x; t) \),

\[ D_{diff}^{(2l)} = a^{2l} W^{(2l)}, \]

\[ \mu_{mob}^{(2l+1)} = \frac{q a^{2l} W^{(2l+1)}}{k_b T}, \]

\[ \zeta(x; t) = \frac{q E(x; t) \tau}{2 k_b T} < 1 \] [22], we get a generalized nonlinear kinetic equation of the Fokker-Planck equation type [22]

\[
\frac{\partial N}{\partial t} = \frac{\partial^2}{\partial x^2} \left( D_{diff} (x; t) \cdot N(x; t) \right) - \frac{\partial}{\partial x} \left( \nu_{mob}(x; t) \cdot N(x; t) \right). 
\] 

The kinetic coefficients \( W^{(2l)}(T) \), \( W^{(2l+1)}(T) \) in approximations in \( 2l, 2l+1 \) by parameter \( \zeta(x; t) \) calculated in [22] in temperature functions. The solution of the equation (3) will be done for the blocking electrodes model \( \jmath_k(0; t) = \jmath_k(d; t) = 0 \), where \( d \) – the crystal thickness [11]:
\[
\left[ v_{mob}(x; t) \cdot N(x; t) - \frac{\partial}{\partial x} \left( D_{diff}(x; t) \cdot N(x; t) \right) \right]_{v=[0, d]}
\] (4)

The initial condition has the form \( N(x; 0) = N_0 \) \([1],[11]\). The equation (3) is solved in complex with the Poisson equation \([11]\)

\[
\frac{\partial E}{\partial x} = \frac{q}{\varepsilon_\infty} \cdot (N(x; t) - N_0)
\] (5)

In equation (5): \( N_0 \) — equilibrium concentration of the particles (ions); \( \varepsilon_\infty \) — high-frequency dielectric constant. Boundary conditions for equation (5) are taken in the form

\[
\int_0^d E(x; t) \, dx = V_0 \cdot \exp(\text{i} \omega t), \text{ where } V_0 = E_0 d, \omega \text{— amplitude and frequency of EMF } [11].
\]

Solution of equation (3) in general case is done by method of successive approximations in infinite power series in powers of dimensionless comparison parameter \( \xi_0 = \frac{qE_0 a}{2k_B T} < 1 \). Then

\[
N(x; t) = \sum_{s=0}^{\infty} N^{(s)}(x; t) \cdot \xi_0^s.
\] (6)

More detailed investigations of the scheme for solving equations (3), (5), by the method of successive approximations (6) come to the search for the linking dependencies of this approximation \( n^{(s)}(x; t) \), from the previous approximation.

**Theoretical part**

The detailed theoretical researches of the nonlinear kinetic phenomena during the proton relaxation in HBC, made on basis of linearizing system equations (3), (5), allowed to install the generalized expressions for polarization determined in the approximation \( r \) by frequency \([23]\)

\[
p^{(r)}(r) = \frac{2^{2+s}}{qN_0 \cdot W^{(0)}(T) \cdot \gamma^s} \sum_{n=0}^{\infty} C^{(a+r)}(n) \times \frac{\exp (\text{i} r \omega t)}{1 + i \omega r} \times \sin^2 \left( \frac{\pi n}{2} \right).
\] (7)

The function \( C^{(a)}(n) \) and non-dimensional parameters \( \Xi_0 < 1, \gamma = \frac{qE_0 W^{(i)}}{W^{(0)}} < 1 \) were investigated in work \([23]\).

In (7): \( T_n = \left( \frac{1}{T_{n,D}} + \frac{1}{T_M} \right)^{-1} \) — relaxation time for the relaxation mode number \( n \) \([24]\), where

\[
T_{n,D} = \frac{T_D}{n^2} \text{ — diffusional relaxation time for the mode number } n, \text{ and } T_D(T) = \frac{d^2}{\pi^2 D_{diff}^{(0)}(T)} \text{ — for the 1-st mode. }
\]

\[
T_M(T) = \frac{\varepsilon_0 \varepsilon_\infty}{\mu_{mob}(T) \cdot q N_0} \text{ — Maxwelle relaxation time.}
\]
Detailed analysis of the expression (7) allowed to establish theoretically, that in the app taking into account all the subsequent approximations of the perturbation theory in a parameter, starting from the second, results roximation $r=1$ (on the fundamental frequency of variable field), taking into account all the subsequent approximations of the perturbation theory $\gamma$ in a parameter, starting from the second, leads to noticeable deviations from the results of the linear kinetic theory [11], when calculating the components of the complex dielectric constant (CP) [24]

$$
\hat{a}^{(a)} = e_0 e_n \times \frac{\Gamma^{(a)}_1 - i \Gamma^{(a)}_2}{1 - \Gamma^{(a)}_1 + i \Gamma^{(a)}_2},
\hat{a}^{(a)} = e_0 e_n \times \frac{1}{1 - \Gamma^{(a)}_1 + i \Gamma^{(a)}_2}.
$$

(8)

$$
\text{Re}[\hat{a}^{(a)}] = e_0 e_n \times \frac{1 - \Gamma^{(a)}_1}{(1 - \Gamma^{(a)}_1)^2 + (\Gamma^{(a)}_2)^2},
\text{Im}[\hat{a}^{(a)}] = e_0 e_n \times \frac{\Gamma^{(a)}_2}{(1 - \Gamma^{(a)}_1)^2 + (\Gamma^{(a)}_2)^2}.
$$

(9)

In the meaning of Maxwelle relaxation, when $T_n \approx T_M$, we can write

$$
\text{Re}[\hat{a}_{1M}^{(a)}] = e_0 e_n \times (1 + \Gamma^{(a)}_{1M}) = e_0 e_n \times \left(1 + \frac{1}{1 + \omega^2 T_M^{-2}}\right),
\text{Im}[\hat{a}_{1M}^{(a)}] = e_0 e_n \times \Gamma^{(a)}_{2M} = e_0 e_n \times \frac{\omega T_M}{1 + \omega^2 T_M^{-2}}.
$$

(10)

In the meaning of diffusional relaxation, when $T_n \approx T_{nD}$, we can write

$$
\text{Re}[\hat{a}_{1D}^{(a)}] = e_0 e_n \times (1 + \Gamma^{(a)}_{1D}) = e_0 e_n \times \left(1 + \frac{4T_D}{\pi^2 T_M n^2} \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{n^4 + \omega^2 T_D^{-2}}\right),
\text{Im}[\hat{a}_{1D}^{(a)}] = e_0 e_n \times \Gamma^{(a)}_{2D} = e_0 e_n \times \frac{4T_D}{\pi^2 T_M} \sum_{n=1}^{\infty} \frac{1}{n^2 (n^4 + \omega^2 T_D^{-2})}.
$$

(12)

denoting $\alpha_1 = \frac{T_D}{T_M}, \alpha_2 = \frac{\alpha_D}{T_D}, \xi = \pi \sqrt{\frac{\alpha_2}{2}}$, finally we can rewrite the diffusional dispersions relations in the following transcendent form.
Proposed solution scheme of a generalized nonlinear kinetic equation (3) can be used in analytical studies of polarization processes in different electric and technical, so in other materials similar to HBC by the type of crystal structure and ionic conduction mechanism (ferroelectric crystals (KDP, DKDP), perovskites, ceramics, mica and etc.) [25-30].

**Summary**

1. Composed the generalized nonlinear kinetic equation (3), describing influence of nonlinearities on mechanism of proton-relaxation polarization in crystals with hydrogen bonds (HBC), in a wide range of temperatures (1-1500 K) and fields (100 kV / m-1000 MV / m).
2. For the first time, transcendental analytical expressions for diffusion dispersion relations during polarization in HBC are written - formulas (13), (14).
3. A mathematical model significant for practical applications has been developed, which can be used for theoretical studies of nonlinear polarization phenomena in other (similar to HBC) dielectric crystals with ionic conductivity (ferroelectric crystals (KDP, DKDP); ceramics, mica, etc.).

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