FIELD-DEPENDENT DIELECTRIC PERMITTIVITY IN DISORDERED DIELECTRICS LIKE $KTaO_3$:Li AND $KTaO_3$:Nb

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We calculate the field-dependent susceptibility $\chi(E,T)$ of disordered dielectrics with dipole impurities of $KTaO_3$:Li and $KTaO_3$:Nb. The calculations had been carried out in the framework of our random field method. They had shown that the coefficients $\chi_{nl}^{(k)}(T,n)$ in the power series of susceptibility $\chi(E,T) = \sum_{k=0}^{\infty} \chi_{nl}^{(k)} E^{2k}$ diverge at the same temperature $T = T_m$ that depends on the concentration of impurity dipoles. We compare the predictions of our theory with experimental data for $KTa_{1-x}Nb_xO_3$ ($0.0075 \leq x \leq 0.05$). The fair coincidence between theory and experiment shows that our theory can describe the main peculiarities dependence of the observed nonlinear dielectric susceptibility as a function of temperature, electric field, and concentration.

Incipient ferroelectrics like $KTaO_3$ doped by Li, Nb, Na and $SrTiO_3$ doped by Ca attract much attention of scientists as model disordered systems with a lot of unusual properties dependent on the dopants concentration. In particular, the above dopants due to their off-center position at the corresponding site of a host dielectric can be considered as some electric dipoles embedded into this host lattice. As the content x of such dipoles grows, the substance sequentially undergoes the transition from the state of dipole glass (DG) with short-range polar order to the mixed ferroglass (FG) phase with coexistence of short- and long-range orders and finally that to the ferroelectric (FE) phase with long-range order only. Although much efforts have been spared both in experiment and theory of such doped dielectrics (see, e.g., [1, 2]), some questions are still remain opened. One of the most interesting questions is related to nonlinear dielectric susceptibility. This is because this quantity is known to be more sensitive (than linear susceptibility) to the details of a possible ordering of dipoles. For example, the investigation of nonlinear (in dc field) dielectric susceptibility $\varepsilon_{\rm NL}$ in the DG state in the vicinity of the freezing temperature T_g ($T < T_g$ is the temperature interval of DG existence) is very important to answer the question if DG is a truly equilibrium phase with "normal" phase transition, to say with the divergence of linear and nonlinear permittivities at $T = T_g$ or it is rather a metastable state with long-time (up to infinity) relaxation modes (see [3] and references therein).

At $T = T_g$, the cusp-like anomaly along with conventional maximum in linear permittivity $\varepsilon_{\rm L}$ appears at $T = T_m$. This occurs because the disordered dielectric loses its ergodicity at $T = T_g$ due to the quenching of a disorder in the impurity dipole subsystem. In ordinary ferroelectrics like $BaTiO_3$, the maximum of $\varepsilon_{\rm L}$ corresponds to the ferroelectric—paraelectric phase transition and so $T_m = T_c$. For this case, the calculations on the base of the phenomenological Landau theory lead to the divergency of both $\varepsilon_{\rm L}$ and $\varepsilon_{\rm NL}$ at $T = T_c$. But such a mean field approach is not correct for disordered dielectrics at least in their DG and FG phases. Thus, to explain the properties of $\varepsilon_{\rm NL}$ in the above substances, the

calculations beyond the mean field approximation are needed. This need may be corroborated by theoretically unexplained measurements [4—6] of the nonlinear dielectric behaviour in $KTa_{1-x}Nb_xO_3$ ($0.0075 \leq x_{Nb} \leq 0.05$), $K_{1-x}Na_xTaO_3$ ($0.08 \leq x_{Na} \leq 0.24$), $Sr_{1-x}Ca_xTiO_3$ ($0.003 \leq x_{Ca} \leq 0.058$) performed during last years. The aim of these measurements was to study the competition between order and disorder at low impurity concentrations. In the intermediate concentration range ($0.0018 \leq x_{Ca} \leq 0.02$, $0.0075 \leq x_{Nb} \leq 0.02$ and $0.12 \leq x_{Na} \leq 0.20$), the critical divergence of nonlinear susceptibility was revealed at $T = T_m$ with critical exponent close to that for true ferroelectric phase transition. This seems to give an evidence in favor of a conventional ferroelectric long-range order, which can be described in the mean field approximation.

On the other hand, it had been shown that, at a low concentration of impurities,

$$T_m(x) \approx (x - x_{cr})^{1/2}, \tag{1a}$$

where x_{cr} is equal to 0.0018 (Ca); 0.008 (Nb); 0.12 (Na). This quantity is a threshold value of impurity content such that long-range ferroelectric order never appears at $x < x_{cr}$, and DG state can exist in the substances under consideration. For large x, the disordered dielectric behaves to the great extent similarly to a conventional ordered ferroelectric. In this case,

$$T_m(x) \sim x \tag{1b}$$

as in the mean field approximation. For the considered systems, the linear dependence (1b) was observed at $x_{Nb} > 0.05$, $x_{Na} > 0.24$ and $x_{Ca} > 0.058$. At first glance, the experimental data for nonlinear susceptibility and the observed $T_m(x)$ dependence in the form of Eq. (1a) contradict each other. The aim of this paper is to show that there is no real contradiction since the considered intermediate concentration range corresponds to the FG phase with mixture of long- and short-range polar orders. To show this, we calculate the nonlinear susceptibility of above disordered dielectrics using our random local field method.

The dielectric susceptibility is the first derivative of polarization $\mathbf{P} = nd^*\mathbf{L}$ in the external static electric field $\mathbf{E}$:

$$\chi_{\alpha\beta} = nd^* \left(\frac{\partial L_\alpha}{\partial E_\beta}\right)\Bigg|_{E_{1\beta}\to 0}, \quad \alpha, \beta = x, y, z. \tag{2}$$

Here, $n = \frac{x}{a^3}$ is the concentration of impurity electric dipoles, $d^* = \gamma d \frac{\varepsilon_0 - 1}{3}$ is the effective dipole moment of the impurity, γ is the Lorenz factor, a and ε_0 are the lattice constant and static permittivity of a host lattice, respectively. The quantity $\mathbf{L}$ in Eq.(2) characterizes the number of coherently oriented dipoles. In our random field theory, we calculate it by the self-consistent averaging of a dipole moment of a single impurity with a distribution function of random fields. This function incorporates the results of averaging over random spatial configurations of impurities (generally speaking, not only dipoles) as well as over permissible orientations of the impurity dipole in a host dielectric. This procedure leads to the following expression for $\mathbf{L}$ [7]:

$$\mathbf{L} = \int_{-\infty}^{\infty} \langle l(E+\varepsilon)\rangle f(\mathbf{E}, \mathbf{L}) d^3\varepsilon, \tag{3}$$

where $f(\mathbf{E}, \mathbf{L})$ is the distribution function of the random field $\mathbf{E}$, calculated in [7] and $\langle l(E+\varepsilon)\rangle$ is a quantum statistical (thermal) average of the dimensionless dipole moment $\mathbf{l} = \frac{\mathbf{d}^*}{d}$ of a single impurity. For simplicity and without loss of generality, we will consider below electric dipoles with two permissible orientations only ($l_z = \pm 1$, $l_x = l_y = 0$). Note, that off-center ion Nb^{5+} in $KTaO_3$ has eight possible orientations. It turns out [1] that this model is exactly reducible to that with two possible dipole orientations but with different dipole moment: $d_8 = d_2\sqrt{3}$. Also, for our purposes (see, e.g., [1, 7]), it is sufficient to use the Gaussian limit for the (partial) distribution function of the random field of impurity dipoles. This limit occurs for $nr_c^3 > 1$ (r_c is a host lattice correlation radius) [1]. In this case, the distribution function has the form:

$$f(\varepsilon, L) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left[i\rho(\varepsilon - E_0 L) - C\rho^2\right] d\rho, \tag{4}$$

where $\varepsilon \equiv \varepsilon_z$, $L \equiv L_z$, and

$$E_0 = \frac{4\pi n d^*}{\varepsilon_0}, \quad C = \frac{16\pi}{15}\left(\frac{d^*}{\varepsilon_0 r_c^3}\right)^2 n r_c^3. \tag{5}$$

Here, we emphasize that the most probable random field value E_0 (mean field) is originated from the indirect dipole-dipole interaction via the host-lattice soft phonon mode (see [1]), so that only this indirect interaction of constant sign is in response for the "creation" of $E_0 \neq 0$. In other words, the above indirect interaction tends to order the dipoles thus trying to establish an overall long-range order in the system. This fact is reflected mathematically in the fact that $E_0 \neq 0$ for impurity

dipoles only. The other sources of the random field (like point charged defects, elastic dipoles) would also contribute to the distribution function, but $E_0 = 0$ for them. The contribution of such nondipole defects is to the width of distribution $C^2 = \sum_i C_i^2$, where C_i is the contribution of the i-th type of nondipole defect [7]. Substitution of Eq. (4) into Eq. (3) and integration over dE yields

$$L = \lambda\tau \int_0^\infty \exp(-y^2) \frac{\sin(\lambda y(\xi + L))}{\sinh\left(\frac{\pi\lambda\tau y}{2}\right)} dy, \tag{6}$$

where we introduced the following dimensionless variables:

$$y = \rho\sqrt{C}, \quad \tau = \frac{T}{T_{cmf}}, \quad \xi = \frac{E}{E_0}, \quad \lambda = \frac{E_0}{\sqrt{C}}. \tag{7}$$

Here,T_{cmf} is the transition temperature in the mean field approximation.

Equation (6) is a self-consistent equation for L, i.e. it has L on left and right hand sides. To derive the explicit expression for susceptibility (Eq (2)), we should keep this fact in mind while performing the differentiation over E. This procedure yields

$$\frac{4\pi}{\varepsilon_0}\chi = \frac{Q}{1-Q}, \tag{8a}$$

$$Q = \lambda^2\tau \int_0^\infty e^{-y^2} \frac{y\cos\left[\lambda y(\xi + L)\right]}{\sinh\left(\frac{\pi\lambda\tau y}{2}\right)} dy. \tag{8b}$$

Equations (6) — (8) constitute the closed set of equations to describe the dependence of dielectric susceptibility on temperature, external static electric field, and impurities concentration. Linear susceptibility is determined by (8b) as $\xi = 0$, and nonlinear (in dc-field) susceptibility corresponds to $\xi \neq 0$.

In principle, Eqs. (8) give an analytical expression for nonlinear dielectric susceptibility for an arbitrary magnitude of the external dc field. However, in the experiment very frequently (see, e.g., [4, 5]) it is necessary to analyze the dielectric susceptibility for small fields as the power series

$$\chi(E,T) = \chi_{\rm L}(T) - \chi_{\rm NL}^{(1)}(T)E^2 +$$

$$+\chi_{\rm NL}^{(2)}(T)E^4 + ... + \chi_{\rm NL}^{(k)}(T)E^{2k} + ..., \tag{9}$$

where $\chi_{\rm NL}^{(k)}$ is the so-called k-th order nonlinear susceptibility. To obtain this expansion from our expressions (6), (8), we expand L in (6) in power series in the dimensionless external field ξ. This expansion contains only odd powers of ξ and has the form

$$L_{mf} \approx A\xi + B\xi^3 + C\xi^5 + \dots . \tag{10}$$

The explicit form of expansion (9) may be obtained from Eq. (10) by its substitution into Eqs. (8) with the subsequent equating of the terms at the same degrees of ξ. This gives the following expression for dielectric susceptibility:

$$\frac{4\pi}{\varepsilon_0}\chi \approx \frac{\lambda^2\tau J_0}{1-\lambda^2\tau J_0} - \frac{1}{2}\xi^2 \frac{\lambda^4\tau J_1}{(1-\lambda^2\tau J_0)^4} +$$

$$\frac{5}{12}\xi^4 \frac{\lambda^6\tau J_1}{(1-\lambda^2\tau J_0)^6}\left[\frac{J_2}{J_1}\frac{1}{10} + \frac{\lambda^2 J_1\tau}{1-J_0\lambda^2\tau}\right],$$

$$J_k = \int_0^\infty \frac{y^{2k+1}\exp(-y^2)dy}{\sinh\left(\frac{\pi\lambda y\tau}{2}\right)}, \quad k = 0, 1, 2. \tag{11}$$

The same procedure allows also us to obtain higher coefficients in the expansions of L and χ. It is seen from Eq. (11) that all coefficients diverge at $\tau = \tau_m \equiv \frac{T_m}{T_{cmf}} = \frac{1}{\lambda^2 J_0(\tau_m)}$ that depends on the impurities concentration. These coefficients define completely the temperature dependence of linear (first term) and nonlinear susceptibilities of any order.

It can be easily checked that the higher order terms omitted in Eq. (11) also diverge at $\tau = \tau_m$ and their critical indices increase with increasing the nonlinear susceptibility order. Because of this, the contribution of these higher order terms to susceptibility becomes especially important in the vicinity $\tau = \tau_m$ so that series (11) may even diverge. In such a case of not small fields, it is more reasonable to calculate the field dependence of susceptibility directly from Eqs. (6) and (8) without expansion in power series. On the other hand, the analysis of experimental data obtained at $\tau \approx \tau_m$ on the base of Eq. (9) may lead to large inaccuracy of critical indices due to a strong contribution of nonlinear terms of higher orders. It should be emphasized here that the temperature $\tau = \tau_m$, where linear and nonlinear susceptibilities diverge, corresponds to the equilibrium (i.e. zero field) phase transition temperature. This

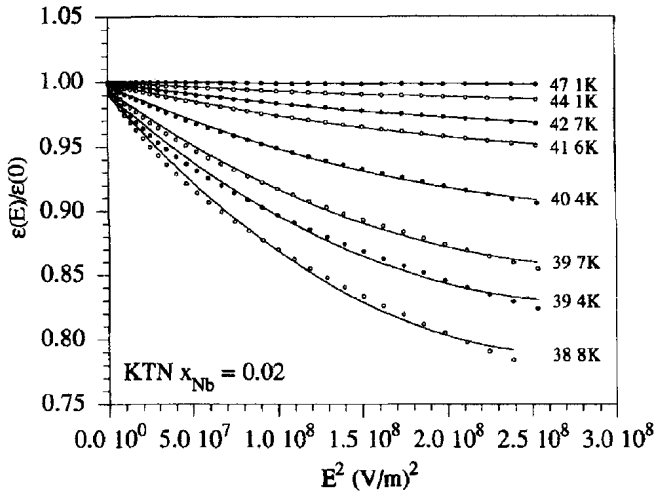

Fig. 1. Normalized dielectric susceptibility as a function of the squared dc electric field in a $KTa_{1-x}Nb_xO_3$ ($x_{Nb} = 0.02$) crystal at different temperatures [7]

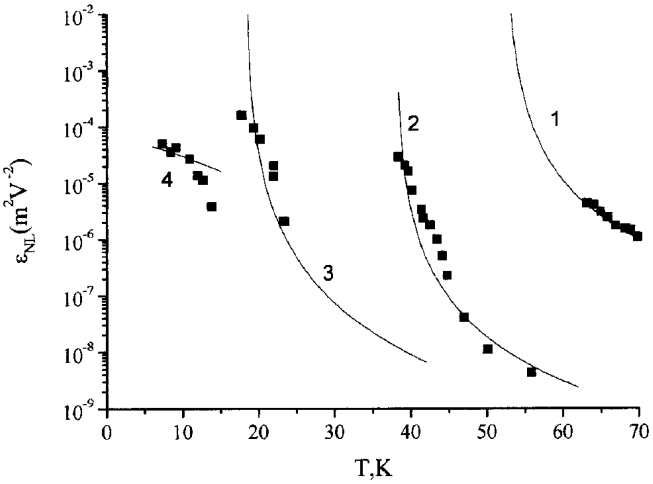

Fig. 2. Temperature dependence of first order nonlinear susceptibility for $KTa_{1-x}Nb_xO_3$ for different Nb concentrations x = 0.05 (*1*); 0.02 (*2*); 0.015 (*3*); 0.0075 (*4*). Points are experimental data [7], solid lines – theoretical calculations with the following values of λ: 4 (*1*); 2.404 (*2*); 1.8848 (*3*); 1.661 (*4*)

temperature can be obtained from (6) in the limit $L \to 0$ (of course at $\xi = 0$ also). In this case, we have

$$L - \lambda^2 \tau_m L \int_0^\infty \frac{y \exp(-y^2) dy}{\sinh\left(\frac{\pi \lambda \tau_m y}{2}\right)} = 0 \qquad (12a)$$

from (6) so that

$$1 - \lambda^2 \tau_m J_0(\tau_m) = 0. \qquad (12b)$$

In disordered ferroelectrics, the long range order parameter L develops in the transition from DG state to FG phase as the concentration of impurity dipoles grow. This transition can be obtained for $x \geq x_{cr}$ at $T_m \geq 0$ (see Eq. (1a)). Note that the freezing temperature T_g, where the disordered system loses its ergodicity (so that its behavior becomes nonergodic at $T < T_g$), may be considered as a transition one from the para-glass (Griffith) phase [9] to DG state for small concentrations $x < x_{cr}$ or to FG phase for $x \geq x_{cr}$. Up to now, there is no evidence about nonlinear susceptibility divergence at $T = T_g$ in disordered ferroelectrics neither in experiment nor in theory (see, e.g., [3]). The obtained divergency of linear and nonlinear susceptibilities at $T = T_m$ (see Eq. (16)) speaks in favour of the statement that the transition from DG to FG phase can be considered as equilibrium phase transition. The experiment confirms our theoretical findings.

Let us now compare the developed theory with experimental data. The most important result for all the above materials is the divergence of the first order nonlinear permittivity at $T = T_m$ with the critical index ν close to 4 at fixed E-fields and its electric field dependence at a fixed temperature that varies from $\sim E^2$ at $T > T_m$ to E^k at $T \to T_m$ ($k < 1$ both for $KTaO_3$:Nb and $SrTiO_3$:Ca [4—6] (see Fig. 1)). The anomalies in the calculated temperature dependence of the nonlinear permittivity (see Eq. (11)) are in a good agreement with experimental data (for $KTaO_3$:Nb $\nu \approx 4.05$ at $x = 0.02$, $\nu = 3.82$ at $x = 0.015$). At small concentration $x =$ 0,0075, the obtained value $\nu = 10.2$ may be related to the closeness of the concentration to the critical value so that the experimental error can be quite large. The poor accuracy for the obtained ν value for the sample with $x = 0.0075$ was stressed in also in [5].

The more detailed comparison with experimental data for $KTaO_3$ doped by different concentrations of Nb is reported in Fig. 2. The values of parameters λ for different concentrations of dopants were obtained on the basis of Eq. (12b) and experimental values of T_m allowing for $T_{cmf} \approx 60$ K. Note that the latter value corresponds to the dielectric susceptibility maximum position for $KTaO_3$:Nb with $x = 0.05$ because, for $x \geq 0.03$, the normal ferroelectric long-range order was shown to exist in the material [10]. One can see that the theoretical expression for the first-order nonlinear susceptibility given by the second term of Eq. (11) describes the experimental points fairly good. To fit our dimensionless expression with $\xi = \frac{E}{E_0}$ to experimental ε_{NL} that is the coefficient of E^2 with dimensions

m^2/V^2 so that $\varepsilon_{NL}(\text{exp.}) = \frac{\varepsilon_{NL}(\text{theor.})}{E_0^2}$, we used $E_0 = 130\,000$ V/m. This E_0 value made it possible to fit the dependence of the first-order nonlinear susceptibility on external electric field without any additional fitting parameters. To avoid unnecessary errors due to the truncation of power series (11) we calculated $\varepsilon(E)$ on the base of exact expressions (6), (8). The results of calculations are shown in Fig. 3. Keeping in mind that $\lambda = 2.404$ at $x = 0.02$ which we took from the fitting of $\varepsilon_{NL}(T)$ dependences (see Fig. 2), we obtained a surprisingly good agreement between the theory and experiment without any additional fitting parameters.

Let us now discuss briefly the dependence of λ-values extracted from the temperature dependence of nonlinear susceptibility on the Nb concentration. For the smallest concentration $x_{cr} > x = 0.0075$ where DG state has to exist, the value $\lambda = 1.661$ appeared to be smaller than $\lambda = \sqrt{\pi} = 1.7725$, the critical value of λ corresponding to $x = x_{cr}$ [7]. In such a case, λ has to be proportional to $\sqrt{x}$ for arbitrary x, as follows from Eqs. (5) and (7). One can see that the ratio of λ values extracted from $\varepsilon_{NL}(T)$ for different concentrations of Nb (see Fig. 2) indeed is close enough to the square root of the ratio of concentrations. The accuracy appeared to be about 90% or less that 50%, respectively, for the square root or simple ratio of the concentrations. The latter case can be expected when the other contributions from random field sources, e.g. point charges, dilatation centers, etc. to the random field distribution function width exceed the contribution of electric dipoles. Therefore, in $KTaO_3$:Nb, the contribution of the random field sources additional to electric dipoles can be not more than 10 %. It should be emphasized that, contrary to the case of Nb in $KTaO_3$:Li, these additional sources completely define the critical concentrations of Li-ions as well as the distribution function width [7, 10]. The physical origin of this difference is not clear now. To our mind, it may be related to the strong nonlinear coupling of Nb with surrounding oxygen ions [11]. The more detailed consideration of this reason and other possible ones of the revealed difference of random fields in $KTaO_3$ doped by Nb or Li is in progress now.

Thus, the proposed theory explains the main features of the temperature and dc electric field dependences of nonlinear permittivity of the incipient ferroelectrics doped by the impurities with electric dipole moment like $KTaO_3$ with Nb. Since the temperature T_m in the considered disordered ferroelectrics corresponds to the transition from dipole glass to mixed ferroglass phase, the obtained both experimentally and theoretically

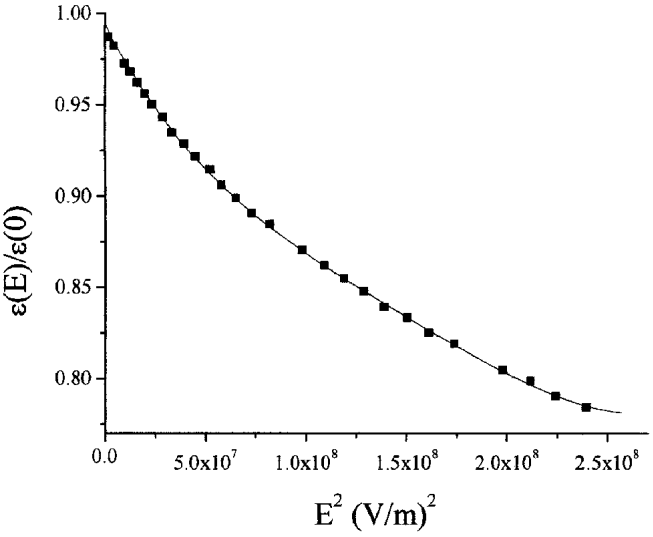

Fig. 3. External electric field dependence of $KTa_{0.98}Nb_{0.02}O_3$ susceptibility at $T = T_m = 38.8$ K, points are experimental data, solid line — theoretical calculations

closeness of the critical indices in the temperature dependence of χ_{NL} to those in conventional ferroelectrics can be a the result of the essential contribution of a long-range polar order to the FG phase. The revealed small contribution of random field sources such as point charges or dilatational centers which usually tend to destroy a ferroelectric long-range order is in a good agreement with the above statement. The theoretical and experimental findings in the considered disordered ferroelectrics give evidence that the transition from dipole glass to ferroglass phase is indeed an equilibrium phase transition.

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ПОЛЬОВА ЗАЛЕЖНІСТЬ ДІЕЛЕКТРИЧНОЇ СПРИЙНЯТЛИВОСТІ НЕВПОРЯДКОВАНИХ ДІЕЛЕКТРИКІВ ТИПУ $KTaO_3$:Li ТА $KTaO_3$:Nb

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Р е з ю м е

Обчислено польову залежність сприйнятливості $\chi(E,T)$ невпорядкованих діелектриків з дипольними домішками типу $KTaO_3$:Li та $KTaO_3$:Nb. Розрахунок був виконаний у рамках розробленого авторами раніше методу випадкового локального поля. Розрахунки показали, що усі коефіцієнти $\chi_{\rm NL}^{(k)}$ у степеневих рядах для сприйнятливості $\chi(E,T) = \sum\limits_{k=0}^{\infty} \chi_{\rm NL}^{(k)} E^{2k}$ розходяться при тій же самій температурі $T = T_m$, що залежить від концентрації дипольних домішок. Було порівняно наші теоретичні результати з експериментальними даними для $KTa_{1-x}Nb_xO_3$ $(0,0075 \le x \le 0,05)$. Досить добре узгодження між теорією та експериментом свідчить, що наша теорія здатна описати основні риси залежності спостережуваної нелінійної діелектричної сприйнятливості від температури, електричного поля та концентрації домішок.