

The equation of state for metal-doped ferroelectrics within the Weiss model

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This paper presents a theoretical model for describing the thermodynamic properties of doped ferroelectric crystals based on a modified Weiss mean-field approach. Accounting for quadrupole and octupole terms in the expression for the effective field within the Weiss model makes it possible to move from the Langevin equation to the Landau–Ginzburg equation. Furthermore, the coefficients of the Landau–Ginzburg equation can be expressed in terms of the physical parameters of the crystal lattice. For these parameters, analytical expressions are proposed that describe their change when adding dopants in ceramic matrix composites. Perovskite barium titanate ceramics with a variety of inclusions is considered as an application example of the developed method. The obtained agreement between the analytical and experimental results for barium titanate ceramics with lanthanum/magnesium/zirconium dopants gives us hope of the applicability of the present theory to the calculation of other doped ferroelectrics as well.

Keywords: Ferroelectrics; doped ceramics; Weiss theory; Ising model; barium titanate; lanthanum; magnesium; zirconium.

1. Introduction

Cooling based on caloric effects, in comparison with the widespread vapor compression, has a higher efficiency, environmental friendliness, and also the ability to interact with micro-objects.^{1–4} The most promising of the caloric effects, in our opinion, is the electrocaloric effect (ECE),³ which consists in reversible changing of thermal properties (temperature, entropy, heat capacity) under application or removal of an electric field. Ferroelectric materials have the highest ECE at temperatures close to the phase transition, where the temperature dependence of the dielectric constant is the strongest. Despite the existence of various approaches to enhancing the electrocaloric effect,^{5,6} progress in the design of modern cooling systems involving ECE is significantly constrained by the lack of materials with a high ECE magnitude at room temperatures. One of the possibilities to obtain ferroelectrics with desired properties is doping, when one atom in the crystal lattice is replaced by the dopant. From a practical point of view, ceramic films based on barium titanate BaTiO₃ (BTO) have the greatest prospects. Near the phase transition from paraelectric cubic to the ferroelectric tetragonal phase, crystalline BTO has a notable ECE reaching 1.6K at relatively low voltages of 1 MV/m, e.g., see Ref. 7. The phase transition temperature for pure BTO is close to 400 K. For the employment of such a ceramic material as a working body of the solid-state cooler, this temperature must be reduced to room temperature. The addition of various metals to the BTO ceramics leads to both a decrease in the

Curie temperature T_0 and a decrease in the maximum ECE values. Every percent of lanthanum reduces T_0 by about 20–35 K,⁸ magnesium by 30–35 K,⁹ and zirconium by 3–5 K.^{10,11}

Unfortunately, the calculation of the properties of the doped material proves to be an extremely difficult problem. The existing methods for finding homogenized physical characteristics¹² do not work properly. This is due to both the nonlinearity of the equations and the fact that doping is not a purely mechanical process, but the one that results in a qualitative change in the crystal lattice. To describe the thermal properties of ferroelectrics considering their physical parameters, the Ising or Weiss models are usually employed.

Initially, both theories were intended to describe second-order phase transitions.^{13–15} However, when using the Ising model, the consideration of nonlinear terms in the expression for the mean field made it possible to describe quite accurately phase transitions of the order–disorder type as well.¹⁶ The Weiss approach relies on the universal Boltzmann distribution for dipoles, while the Ising approach uses statistical sum to find the polarization. The three-dimensional Ising model is currently not fully developed, so its one-dimensional version¹⁶ is treated. The existing shortcomings of both models have led to the fact that the simpler semi-empirical Ginzburg–Landau–Devonshire (GLD) model has become most widely used in describing BTO. In this model, the free energy is a polynomial with respect to the components of the polarization vector. In the scalar case, this approximation

includes only the polarization modulus, and it is this case that we consider here. This special case of the GLD model is called the Ginzburg–Landau (GL) model. The polynomial coefficients in the GL model are quantities that are determined from experimental data. Moreover, these coefficients depend on the measurement conditions, in particular, it is necessary to distinguish between isothermal and adiabatic coefficients GL.¹⁷

Let us recall that in the Weiss and Ising mean-field models the parameters had a clear physical meaning. In view of this, of undoubted interest is finding a relationship between the parameters of the Weiss and Ising models and the GL coefficients. For the Ising model, such a dependence was obtained earlier in Refs. 16,18,19. Below, we demonstrate that both theories give the same averaging equations, although they initially have coefficients that depend differently on the physical parameters of the cell. Meanwhile, the main aim of our study is to modify the Weiss mean-field approach to describe the properties of doped displacement-type ferroelectric crystals, which include barium titanate. Lanthanum (La), magnesium (Mg), and zirconium (Zr) are considered as an example of a dopant material.

1.1. Classical Weiss mean-field theory for ferroelectrics

Under the action of a constant electric field \mathbf{E} atoms in the crystal lattice of a ferroelectric are oriented so that their dipole moments tend to become parallel to the field direction. As a result of the establishment of the equilibrium, polarization \mathbf{P} arises, which is co-directional with the electric field. According to the Weiss mean-field theory,¹³ the field of forces acting upon the dipole moment of a ferroelectric atom in a unit cell can be reduced to the sum of the external electric field \mathbf{E} and some additional field. The latter takes into account the effect of adjacent ferroelectric atoms on a given atom and is proportional to its polarization \mathbf{P} . This assumption means that not only the applied electric field acts on an individual dipole, but so do other dipoles of the system. In other words, the effective electric field \mathbf{E}_{ef} in a ferroelectric is the sum of the true electric field \mathbf{E} and the additional field $\beta\mathbf{P}$: $\mathbf{E}_{\text{ef}} = \mathbf{E} + \beta\mathbf{P}$, where β is some positive constant (Lorentz factor) characterizing the properties of a given ferroelectric. More precisely, the effective field can be represented as a series^{16,18,19}

$$\mathbf{E}_{\text{ef}} = \mathbf{E} + \beta\mathbf{P} + \gamma\mathbf{P}^3 + \delta\mathbf{P}^5 + \dots, \quad (1)$$

which is limited only to the written out terms. Here, γ, δ, \dots are some constants associated with the quadrupole, octupole, etc. moments of a given ferroelectric. The presence of the above coefficients significantly expands the range of applicability of mean-field theories.¹⁶ In particular, Eq. (1) allows to describe first-order phase transitions that is absent in the standard Weiss theory. The collinearity of \mathbf{E} and \mathbf{P} in (1) holds only for the cubic and tetragonal phase. Because the ECE reaches its maximum near the phase transition between

these phases,^{7,20} then for its description it is sufficient to restrict consideration to (1).

The unit volume of a ferroelectric contains N unit cells with a constant dipole moment p_0 . By the unit cell, we consider the minimum set of atoms, which is periodically repeated. The origin of the spherical coordinate system (r, ϑ, ϕ) is placed at an arbitrary point. The problem of interest is to investigate the electric field at this point. The polar axis is directed along the external field \mathbf{E} (see, Fig. 1). In the presence of an external field, the distribution of dipole moments of unit cells is found from the Boltzmann law

$$dN = ce^{-U/k_B T} dV, \quad (2)$$

where c is the normalization constant determined from the condition $\int dN = N$ and $k_B = 1.38 \times 10^{16}$ erg/K is the Boltzmann constant. Let U be the potential energy of the cell in the considered field of forces. In a rigorous formulation, U depends on a huge number of parameters and the qualitative behavior of this function is known. This energy contains the term $U_0 = -p_0 E \cos \vartheta$ depending only on the angle ϑ . The explicit form of the function U is unknown, in what follows we consider the potential energy equal to U_0 , $U = U_0$. The error that arises with such a replacement can be estimated by comparison with experimental data. Then, after finding the constant c , let us keep in (2) the dependence only on the angle ϑ . Thus, the distribution (2) can be rewritten as follows:

$$dN = \frac{2\alpha N}{\sinh \alpha} e^{\alpha \cos \vartheta} \sin \vartheta d\vartheta. \quad (3)$$

In the above, the notation $\alpha = p_0 E_{\text{ef}} / (k_B T)$ is introduced. In contrast to (2), the quantity dN corresponds to the number of molecules — the angles between their axes and the direction of the field lie in the range from ϑ to $\vartheta + d\vartheta$. Therefore, as the deviation of the molecules distribution from the uniform one determined by (3) increases, the field strength E increases as well and the temperature decreases. This is easy to understand seeing as the temperature rises, the energy of the thermal motion increases, disturbing the order of the distribution.

Let us now describe the resulting dipole moment per unit volume of the body, i.e., its polarization P . The vector \mathbf{P} is assumed to be parallel to the effective field \mathbf{E}_{ef} . Hence, its value must be equal to the sum of the projections of the moments of all N atoms in the direction of the polar axis. The total dipole moment dN of atoms whose axes lie between θ

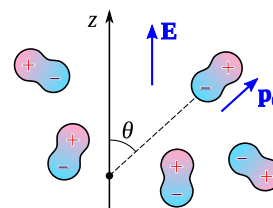


Fig. 1. The schematic representation of the dipole polarization for ferroelectric ceramics.

and $\vartheta + d\vartheta$ is $p_0 dN$, and its projection onto the polar axis is $p_0 \cos \vartheta dN$. Then, the polarization of the system can be represented as $P = \int p_0 \cos \vartheta dN$, or^{13,21}

$$P = p_0 N \left(\coth \alpha - \frac{1}{\alpha} \right). \quad (4)$$

Equation (4) for $\beta = 0$ was first obtained by Langevin, and the function $L(\alpha) = \coth \alpha - 1/\alpha$ is called the Langevin function.

1.2. GL equation

For small values of the parameter α , the Langevin function can be expanded in the Maclaurin series

$$L(\alpha) = \frac{\alpha}{3} - \frac{\alpha^3}{45} + \frac{2\alpha^5}{945} + \dots \quad (5)$$

At low electric fields, as it is easy to check when using the series (5), the Langevin equation (4) turns into the GL equation

$$E = aP + bP^3 + cP^5, \quad (6)$$

whose coefficients are

$$a = \frac{3k_B T}{p_0^2 N} - \beta, \quad b = \frac{9}{5} \frac{k_B T}{p_0^4 N^3} - \gamma, \quad (7)$$

$$c = \frac{297}{175} \frac{k_B T}{p_0^6 N^5} - \delta.$$

The coefficient a in (6) linearly depends on temperature T and can be written as $a = a_0(T - T_0)$. Here, $a_0 = 1/\varepsilon_0 C$ is some constant, T_0 is the Curie–Weiss temperature, i.e., the temperature of appearance of the metastable paraelectric phase, C is the Curie constant, and ε_0 is the electric constant. Because the quantities $\{a_0, b, c, T_0\}$ are well established for many ferroelectrics, we write out the relations connecting them and the parameters of the Weiss model $\{\beta, \gamma, \delta, p_0, N\}$

$$a_0 = \frac{3k_B}{p_0^2 N}, \quad T_0 = \frac{p_0^2 \beta N}{3k_B}, \quad (8a)$$

$$\beta = a_0 T_0, \quad p_0^2 N = \frac{3k_B}{a_0}. \quad (8b)$$

The relative dielectric susceptibility $\chi = 1/\varepsilon_0 \partial P / \partial E$ in the GL model has the following form:

$$\chi = \frac{1}{\varepsilon_0 (a + 3bP^2 + 5cP^4)}, \quad (9)$$

At temperatures exceeding the Curie temperature, Eq. (9) can be rewritten approximately as

$$\chi = \frac{1}{\varepsilon_0 a_0 (T - T_0)}. \quad (10)$$

Note that the relation (10) makes it possible to determine with sufficient accuracy the parameters a_0 and T_0 from the known

experimental temperature dependencies of the dielectric constant. The important point is that the GL coefficients in (7) have exactly the same form as the analogous coefficients obtained from the Ising model when passing to the GL model.^{16,18,19} Both sets of coefficients include the parameters $\{\beta, \gamma, \delta\}$ in the same way. The powers of N and p_0 are also identical. The only difference is in the numerical factors in front of the degrees of temperature T . The numerical factors differ the most (by a factor of 9) in the coefficient b . Nonetheless, this discrepancy does not lead to a noticeable variation in the GL coefficients, as the indicated multipliers stand in front of small values. Finally, it is worth to emphasize that in the classical GL model the coefficients b and c do not depend on temperature.

1.3. Determination of the GL coefficients for doped ferroelectric

Let us proceed to consider doped ferroelectrics, in which some of the atoms from the initial material M_m are replaced by additive atoms M_i . Hereinafter, the subscripts m and i refer to the matrix (initial ferroelectric) and inclusion (doping material), respectively. The quantities characterizing the properties of doped ferroelectric will be written without the subscripts. If we denote by v the fraction of substituted atoms, then the fraction of the original atoms is $1 - v$. We suppose that the substituted atoms are arranged fairly evenly and the original sample can be divided into many subdomains (a set of unit cells). The concentration of inclusions is the same and is equal to v in each of these subdomains.

Assume that for the doped material, the average value of the cell dipole moment p_0 and the associated constant β is the weighted average of their values in the matrix and in the inclusion

$$\beta = (1 - v)\beta_m + v\beta_i, \quad p_0 = (1 - v)p_{0m} + vp_{0i}. \quad (11)$$

The relation (11) means that the average dipole moment of the unit cell depends linearly on the percentage of doping. For an ideal mechanical substitution of atoms, the parameter β_i is the Lorentz factor for the inclusion material, and the relation (11) is exact. But for real materials, the value of β_i simply shows how strong the influence of neighboring cells on the effective field in a given cell decreases, and is weakly related to the Lorentz factor.

Further, it is necessary to determine the third parameter N for finding the coefficient a and its dependence on temperature. The number of specified structural elements in one mole of a substance is the Avogadro constant N_A . We remind that barium titanate ceramics and lanthanum/magnesium/zirconium additives are selected to demonstrate the developed approach. Hence, the ratio of the numbers N_i and N_m is equal to the ratio of molar masses of lanthanum titanate $\mu_i = 234.77$ g/mol and barium titanate $\mu_m = 233.192$ g/mol

$$N_i = N_m \frac{\mu_m}{\mu_i}, \quad N = N_m \left(1 + v \frac{\mu_m - \mu_i}{\mu_i} \right). \quad (12)$$

The difference in the parameters N_i and N_m is tenth of a percent for not too large values of v , and this difference between the parameters can be neglected in the first approximation. For doping with other metals, for example, with magnesium and zirconium the parameters N_i and N_m are noticeably different from each other, and they cannot be replaced by one. The molar masses of barium, zirconium ($\mu_{iZr} = 91.224$ g/mol), and magnesium ($\mu_{iMg} = 24.34$ g/mol) vary significantly. Therefore, we must use (12) to find N number. As a result, we obtain the final expression for a_0 and T_0

$$a_0 = \frac{3k_B}{[(1-v)p_{0m} + vp_{0i}]^2 N},$$

$$T_0 = \frac{[(1-v)p_{0m} + vp_{0i}]^2 [\beta_m(1-v) + \beta_i v] N}{3k_B}. \tag{13}$$

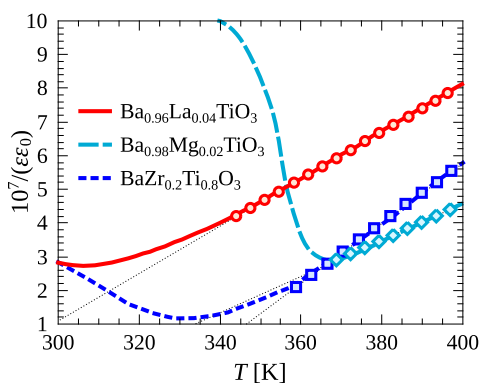


Fig. 2. The temperature dependence of the inverse dielectric permittivity. The symbols mark the regions of linear interpolation to determine a_0 and T_0 .

These equations express the coefficients a_0 and T_0 for doped ferroelectrics in terms of analogous coefficients for the matrix and inclusion materials. It is easy to check that the formulas (13) for a_0 and T_0 completely coincide with the expressions that follow from the Ising model under the assumptions (11), (12) about the dipole moment and the number of dipoles. This brings us to the important conclusion that, despite different physical ideas underlying the Weiss and Ising mean field models, these models result in identical formulas for the mixture material.

2. Results and Discussion

A comparison with the available experimental data for $Ba_{1-v}La_vTiO_3$, $Ba_{1-v}Mg_vTiO_3$, and $BaZr_vTi_{1-v}O_3$ ceramics⁸⁻¹⁰ has been made to validate the obtained theoretical expressions (13). Following the standard procedure, from the temperature dependence of the inverse dielectric constant (see Fig. 2) on the basis of (10), the coefficients a_0 and T_0 as a function of the percentage of doping with lanthanum, magnesium, and zirconium are built in Fig. 3. The only unknown parameter in (13) is the ratio p_{0i}/p_{0m} . Its value was evaluated under condition of the best agreement of the developed theory with experimental data. The calculations were carried out with parameters, as displayed in Table 1.

The coefficients a_0 and T_0 calculated from the experimental data coincided with a high degree of accuracy with those predicted on the basis of the Weiss mean-field theory. The agreement with the experimental data takes place up to a dopant concentration of 10%. Changes in the properties of lanthanum-doped barium titanate ceramics at lanthanum concentrations larger than 10% were also noted in Ref. 22.

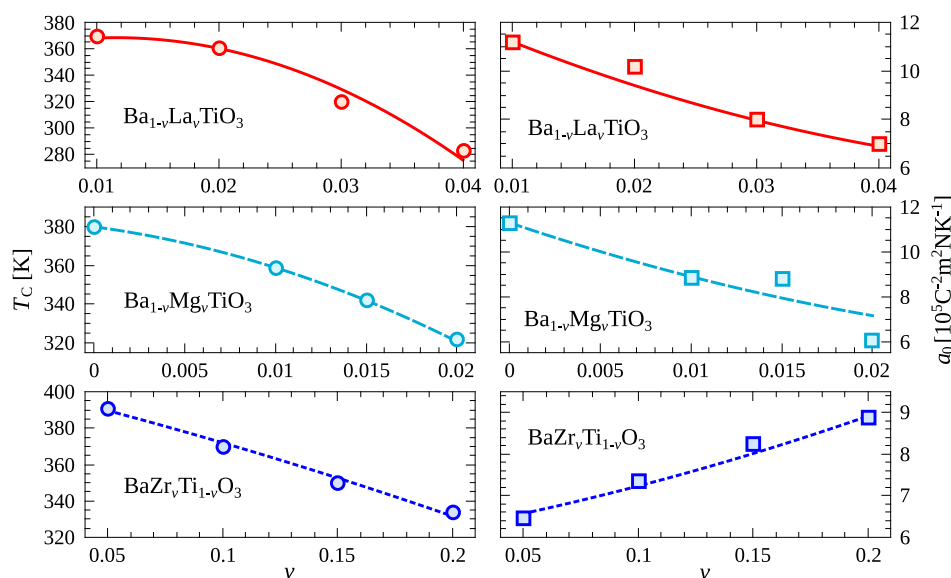


Fig. 3. (Left column) The Curie temperature T_0 as a function of the doping concentration of La, Mg, and Zr. (Right column) The dependencies of the coefficient a_0 on the La, Mg, and Zr doping concentration for $BaTiO_3$ matrix. The lines correspond to the theory presented in the text, and the symbols are experimental data.

Table 1. The estimated parameters of the Weiss model for doped barium titanate. In the calculations, the experimental data from Refs. 8–10 were used.

	p_{0i}/p_{0m}	$p_0^2 N$ [C ² /m]	β_m [m/F]	β_i [m/F]
Ba _{1-v} La _v TiO ₃	11	$3.07 \cdot 10^{-29}$	$4.85 \cdot 10^8$	$-6.88 \cdot 10^9$
Ba _{1-v} Mg _v TiO ₃	0.1	$6.91 \cdot 10^{-29}$	$2.43 \cdot 10^8$	$-5.07 \cdot 10^8$
BaZr _v Ti _{1-v} O ₃	8	$3.65 \cdot 10^{-29}$	$4.31 \cdot 10^8$	$7.12 \cdot 10^9$

Apparently, the order of replacement of barium by lanthanum in neighboring unit cells becomes significantly from such concentrations. For doping with magnesium, according to our estimates, the range of applicability of (13) is limited by $v < 0.04$.

In the simplest model, the dipole moment of a perovskite ferroelectric is determined by the displacement of the B-site ion, ξ , relative to the position at the center of the unit cell²³ and can be written as follows:

$$p_0 = \xi e_B, \quad (14)$$

where e_B is the charge of the B-site ion. Such an ion is the Ti ion in the BTO cell. The substitution of a titanium ion for another metal ion leads to a change in the charge e_B and in the displacement ξ . As a result, the dipole moment p_0 changes. In turn, the substitution of other ions leads, in the leading approximation, only to a change in the magnitude of the displacement. The probability of different substitution options in a given cell depends on whether there is a substituted ion in neighboring cells. Because each cell has 26 neighbors, the mathematical expectation of the number of substituted ions should exceed 1 at $v > 0.04$. In this way, the linear dependence (11) is valid for $v < 0.04$, when there is only one substituted atom in 26 neighboring cells with a high probability. If the probability of ion substitution does not depend on the number of substituted positions, then Eqs. (11) and (13) could also be applicable for large values of v . As the zirconium ion replaces the titanium ion, regardless of the presence of other dopants, the range of applicability of (11) and (13) for this case reaches $v = 0.2$. For lanthanum and magnesium ions, there are various options for substituting ions in the unit cell of barium titanate, so the range of applicability of the formulas (11) and (13) is much smaller ($v < 0.04$).

The advantage of the used model is that the Weiss parameters $\{\beta, p_0, \gamma, \delta\}$ can be considered as additive quantities, i.e., obeying the law (11). Note that the coefficient β with a change in v behaves differently when doped with zirconium and magnesium or lanthanum (see Fig. 4). This difference arises from the difference between the values of the coefficient a_0 found from the experimental data. It is explained by the relatively high probability of magnesium and lanthanum to replace not only titanium ions. Moreover, the coefficient N is uniquely determined by the molar mass of the substance. The GL coefficients $\{a, b, c\}$ are not additive, but can be recalculated using the Weiss parameters. The available experimental data are insufficient to find the coefficients $\{b, c\}$, and their theoretical values were not compared with the experimental ones.

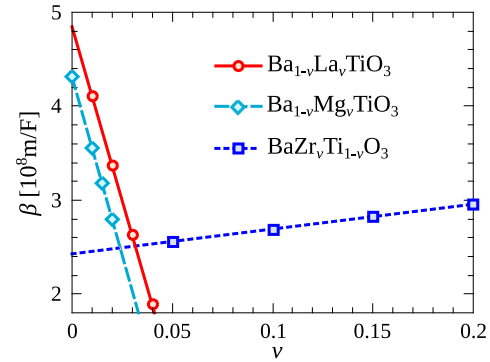


Fig. 4. The dependence of parameter β on the doping concentration.

It is important to mention that the simple Vegard's model can be applied to find the GL coefficients. Following this model, the free energies are summed up in proportion of the ferroelectric content.²⁴ Nonetheless, the Vegard's model gives significantly less accurate results than the adopted Weiss model reported in this paper. This fact can be explained by the following. At temperatures exceeding the phase transition temperature, the behavior of the dielectric permittivity of ferroelectrics ceases to depend on the electric field and can be described by the Curie–Weiss law (10). In this temperature range, different averaging approaches for dielectrics can be applied.¹² At low concentrations of inclusions, all formulas for finding the average value of a certain quantity X are represented as a series

$$X = (1 - v)X_m + vX_i + H_1(X_m, X_i)v(1 - v) + \dots \quad (15)$$

Here, $H_1(X_m, X_i)$ is some coefficient depending on the properties of the inclusion and the matrix. These terms are often sufficient to describe the dependence $X(v)$. For example, the experimental dependencies for the temperature T_0 of the well-studied ferroelectric barium–strontium titanate (Ba_{1-v}Sr_vTiO₃) were processed to obtain an approximate expression²⁵

$$T_0(v) = 382 - 340v + 100v(1 - v). \quad (16)$$

The last term in (16) describes the deviation from Vegard's law. For the barium–strontium titanate ferroelectric, the difference between the linear and parabolic interpolation (16) reaches 25 K. Therefore, interpolation according to the Vegard's law is not enough, and parabolic interpolation allows accurately approximating the experimental data. The approximating dependencies (13) proposed in this study are close to parabolic and give the possibility of finding the coefficient H_1 in (15) from Weiss parameters $\{\beta, p_0, \gamma, \delta\}$.

3. Conclusion

We have proposed a new theoretical approach to calculating the thermodynamic properties of doped ferroelectric material in the framework of the mean-field Weiss model. The theoretical results have been verified and illustrated for barium

titanate ceramics with lanthanum, magnesium, and zirconium inclusions. The dependence of the GL coefficients for a mixture on identical coefficients of its constituents is algebraic and for small concentration of inclusions v is linear in v , that is, it corresponds to the Vegard's model. As the concentration of the dopant increases, Vegard's law begins to be violated.

Our calculations demonstrate that the strongest deviation from the linear law is observed when doped with lanthanum, the weakest — when doped with zirconium. It should be stressed that, with a high degree of probability, zirconium replaces the titanium atom.^{26,27} As a result, the developed model makes it possible to describe the properties of zirconium-doped barium titanate ceramics even at a high doping percentage (20%). The coefficient β_i for this metal is positive, i.e., can be identified by the Lorentz coefficient. When doped with lanthanum, there are several options for substituting lanthanum atoms for atoms in the BTO unit cell.²² At high concentrations of lanthanum, the probability of substitution of any of the atoms of the unit cell may change due to the presence of a lanthanum atom in the neighboring cell. Moreover, the coefficient β_i turns out to be negative in this case. Magnesium-doped ceramics behave similarly. Apparently, the behavior of the coefficient a_0 for the three considered variants of doping differs precisely in the uniqueness and its absence. Despite different behaviors of the studied coefficients, the experimental data demonstrate a good agreement with the calculated dependencies, which proves the validity of the described approach.

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