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Formation of phase states in $PbFe_{0.5}Nb_{0.5}O_3$: Description based on multiminima models

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Two ferroelectric phase transitions are observed in the $PbFe_{0.5}Nb_{0.5}O_3$ crystal. The first is between the cubic and tetragonal phase, the second is between the tetragonal and monoclinic phases. To describe phase transitions and emerging phases, a statistical model is proposed, based on the composition of two multi-minimum models — a six-minima model for the Pb cation and an eight-minima model for the Nb cation. Adjusting the model parameters, makes it possible to reproduce all the characteristic features of the thermodynamic behavior of the crystal. The most interesting is the formation of a ferroelectric, complexly ordered monoclinic phase with Cm symmetry. It is shown that the mentioned monoclinic phase arises due to the fact that the first-order phase transition to the rhombohedral ferroelectric phase occurs in the presence of an „external field" of tetragonal symmetry. The contribution of the subsystems of Pb and Nb cations to the features of the dielectric and structural properties of the crystal is estimated.

Keywords: ferroelectric relaxors, phase transitions, multiminima models, ferroelectric monoclinic phase.

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1. Introduction

Lead ferroniobate $PbFe_{0.5}Nb_{0.5}O_3$ (PFN) is a triple perovskite — a multiferroic having both ferroelectric and magnetic properties [1,2], and its solid solutions are a promising basis for dielectric, piezoelectric, pyroelectric and magnetoelectric materials [3–9]. Properties of triple perovskites $PbB'_{0.5}B''_{0.5}O_3$, (B' — In, Sc, Yb; B'' — Nb, Ta) to which PFN belongs, very strongly depend on the degree of ordering of the cations B' and B''. With a high degree of ordering, $PbB'_{0.5}B''_{0.5}O_3$ have an distinct ferroelectric or antisegnetoelectric phase transition (PT), whereas with strong disordering, relaxation properties are observed: a strongly blurred maximum of dielectric susceptibility χ, the temperature $T_{\max}$ of which increases with the frequency of the measuring field f [10–14]. On PFN X-ray diffractogramms, superstructural reflections indicating the presence of a long-range order in the distribution of Fe^{3+} and Nb^{5+} ions along the nodes of the crystal lattice are absent [15,16]. As a result, PFN in most works is considered a ferroelectric relaxor [1,4,6,8,17]. However, the blurring of the maximum $\chi(T)$ in PFN ceramics with low conductivity is very small, and the dependence of $T_{\max}(f)$ is practically absent. In addition, unlike classical ferroelectric relaxors, two macroscopic structural PTs are observed in PFN: the first — between the phases of the paraelectric cubic (phase C, $Pm\bar{3}m$, O_h^1) and ferroelectric tetragonal (phase T, P4mm, C_{4v}^1) at $T \approx 376\,K$, and the second — between ferroelectric phases tetragonal and monoclinic (phase M, Cm, C_s^3) at $T \approx 356\,K$ [15,16]. This data, as well as the results of the study of the dielectric properties of single crystals PFN [18], allow us to assume that PFN is not a relaxor, but an ordinary ferroelectric, and the often observed relaxor-like dielectric properties are due to the influence of defects or impurities.

Among the phases realized in PFN, the most interesting is the appearance of the monoclinic phase of symmetry Cm ($p_1 > p_2 = p_3$), where p_i ($i = 1, 2, 3$) — components of the polarization vector. Such a phase is quite rare, in terms of theoretical research, it is quite complex, so up to a certain point, very little attention was paid to it. However, after detecting this phase in the immediate vicinity of the morphotropic interphase boundary ($\sim 48\%$) in the PZT system ($PbZr_{1-x}Ti_xO_3$) between the rhombohedral (R) and tetragonal (T) ferroelectric (FE) phases [19] interest in it has increased dramatically.

In the work [20], based on the phenomenological theory using the decomposition of the thermodynamic potential (TP) in a series by degrees of a small order parameter (OP), it was shown that in the vicinity of the N-phase multicritical point, this phase is unstable, it is „covered with" stable phases: either T and R, or rhombic. In [21,22], also on the basis of the phenomenological theory, significantly complicated by taking into account the terms of higher degrees in the decomposition of TP and restrictions on the coefficients of decomposition, $T - x$ diagrams were obtained in which this phase is stable. However, such complications have led to the fact that it is almost impossible to give any clear physical interpretation of how and due to what such diagrams can be implemented. So, the question of how such a monoclinic phase is formed remains open. The purpose of this work is to develop a model capable, within the framework of a single approach, to investigate and describe the formation of the entire set of phase states (PS) observed in PFN, as well as to identify the factors responsible for the appearance of this complexly ordered FE-phase. Among other things, this makes it possible to find out how the structural basis is formed, on which the magnetic properties are realized in the future.

In PFN, cations that may be responsible for the appearance of FE-state (i.e. ferroactive cations) — these are Pb^{2+} and Nb^{5+} (ferroactive means cations capable, under appropriate conditions, of creating acentric anionic blocks (octahedra, cuboctahedra) by forming asymmetric cation-anionic bonds inside an anionic polyhedron). The most important role of the Pb cation in the formation of the FE-PS, especially the T phase, is confirmed by the fact that the substitution of Pb for Ca or Ba leads to a significant decrease in the temperature of PT between phases C and T [23]. At the same time, the degree of decrease in the temperature of PT with an increase in their concentration (at least at low concentrations) is almost the same for both Ca and Ba. This means that the decrease in the temperature of the PT is not associated with a change in particle size, but is due to the replacement of the ferroactive Pb cation with ferrodeutral cations in this compound Ca and Ba. In turn, the activity of the Nb cation is manifested in the fact that it contributes to the appearance of FE-states, therefore, the temperatures of the PT in PFN are higher than in the isostructural, close in crystal chemical parameters, $PbFe_{0.5}Ta_{0.5}O_3$ (PFT), in which the phase transitions with C$-$T and T$-$M are observed at 240$-$270 and 200$-$220 K respectively [24]. Also, in the system $(1-x)$PFN$-x$PbTiO$_3$ replacement of the cation $(Fe/Nb)^{4+}$ with the cation Ti^{4+} in the area of small x is accompanied by a relatively small increase in the PT temperature of C$-$T and a sharp decrease in PT temperature T$-$M [18,25]. This indicates that it is the Nb cations that play an important role in the formation of the M phase.

According to structural studies of PFN [16], the Fe and Nb cations are located in the nodes B of the perovskite ABX_3 disordered, and the cubic phase is characterized by a noticeable disorder in the arrangement of the Pb cation inside the cuboctahedral cavity. It is noted that the potential relief for Pb inside the cavity is quite complex. According to [16], the most likely option seems to be with six minima, but other options — with eight and twelve minima — according to the authors, it is impossible to exclude.

Certain information about the specifics of the PFN compound structure can be obtained by estimating the lattice parameters and the lengths of cation-anion bonds. In [26] it was shown that in the compounds $AB_{0.5}B'_{0.5}O_3$ with a perovskite structure, the cubic lattice constant is defined as follows:

$$a = 2\,\frac{n_A\frac{L_A}{\sqrt{2}} + \frac{1}{2}n_BL_B + \frac{1}{2}n_{B'}L_{B'}}{n_A + \frac{1}{2}n_B + \frac{1}{2}n_{B'}}$$

where L_A, L_B, $L_{B'}$ — equilibrium (unstressed) distances $A-$O, $B-$O, $B'-$O, respectively, n_A, n_B, $n_{B'}$ — valence of cations A, B, B'. According to [27], $L_{\mathrm{PbO}} = 2.83\,\text{Å}$, $L_{\mathrm{TiO}} = 2\,\text{Å}$, $L_{\mathrm{NbO}} = 2.01\,\text{Å}$, $n_{\mathrm{Pb}} = 2$, $n_{\mathrm{Fe}} = 3$, $n_{\mathrm{Nb}} = 5$. In this case $a = 4\,\text{Å}$ (in experiment [16] — 4.01 Å). From here it can be seen that the Pb$-$O, Fe$-$O, Nb$-$O bonds in the crystal are practically not deformed. It should be noted that this circumstance plays an important role in the fact that, despite the difference in charges, the Fe and Nb cations are disordered [28,29]. The presence of disorder in the arrangement of Fe and Nb cations, the absence of deformation of Fe$-$O, Nb$-$O bonds and the fact that the lengths of these bonds coincide make it possible to consider the cation B as a kind of averaged (Fe/Nb)-cation. The tolerance factor t for PFN can be defined as follows:

$$t = \frac{L_{\mathrm{PbO}}}{0.5\sqrt{2}(L_{\mathrm{FeO}} + L_{\mathrm{NbO}})} = 0.98 \approx 1.$$

With $t \gtrsim 1$ connection $A-$O are compressed, and the bonds $B-$O — are stretched, at $t \lesssim 1$ the bonds $A-$O are stretched, and the links $B-$O — are compressed. The stretching of $B-$O bonds can contribute to the appearance of FE-states, and their compression — the appearance of either rotational or (less often) antisegnetoelectric ordering. In the case of $t \approx 1$, in the presence of corresponding ferroactive cations, complexly ordered FE-states can be formed, resulting from the competition of ordering subsystems of cations located at the nodes A and B.

As it was shown in [30,31], the FE transitions in $PbTiO_3$ and $KNbO_3$ are mainly of PT type „order-disorder" and are caused by the redistribution of Pb and Nb cations by six and eight crystallographically equivalent positions (CEPs), respectively. At the same time, for both $PbTiO_3$ and $KNbO_3$, the factor $t \approx 1$ ($L_{\mathrm{TiO}} = 1.97\,\text{Å}$, $L_{\mathrm{KO}} = 2.85\,\text{Å}$ [27]) is the same as for PFN. Accordingly, the situation, i.e. the location of the nearest particles and the distance between them, for Pb cations in the cuboctahedral cavity and Nb in the anionic octahedron PFN is close to the situation for Pb and Nb cations in $PbTiO_3$ and $KNbO_3$. This suggests that in PFN, the potential relief for the Pb cation may have six CEPs, and for the Nb cation — eight CEPs. Such a choice of composition of multiminimum models, among other things, is due to the fact that the main ordered FE-phase described by the 6-minimum model — is the phase T, the main ordered FE-phase described by 8-minimumthe model — phase R, and the phase M under consideration can be obtained by a superposition of phases T and R.

So, a model for the study of statistical and thermodynamic properties of PFN can be presented in the following form. Pb cations located in the cuboctahedral cavity have six CEPs, and (Fe/Nb) cations located in octahedra have eight CEP. The interaction between subsystems is described by an expression bilinear in order parameters characterizing the polarization of each of the subsystems. PT of the type „order–disorder" are associated with the redistribution of the corresponding particles in six and eight CEPs. A similar approach using the composition of two 8-minima models to describe the PT in the cryolite $K_3WO_3F_3$ was used in [32].

The scenario of the formation of phase states in PFN based on the proposed model is as follows. If „turns off" interaction between subsystems with six and eight CEPs, then when the temperature decreases, first in the subsystem with six CEPs, the first kind of PT should occur from the cubic to the tetragonal FE-phase, and then in the subsystem with eight CEPs, the first kind of FP should also occur from the cubic to the rhombohedral FE-phase. „The inclusion of" interaction leads to the fact that when the PT enters the phase T, along with the OP characterizing polarization in the subsystem of six CEPs, the OP characterizing polarization in the subsystem of eight CEPs appears, and the transition to the rhombohedral phase turns into PT „in the external field of" tetragonal symmetry, therefore the rhombohedral the phase becomes monoclinic. The fulfillment of these conditions is the basis for the selection of model parameters.

The analysis of the statistical properties of the model is carried out within the framework of the mean field approximation. As noted in [33], this approach is convenient to apply to systems with little-studied interaction, while checking qualitative ideas about the nature of PT.

2. Model description

As an object of research, we consider a perovskite crystal with the general structural formula ABX_3 with a cubic lattice of symmetry Pm$\bar{3}$m containing two subsystems of — Pb and (Fe/Nb) cations. The Pb cation subsystem has six CEPs, slightly offset in the directions of type [001] from the center of the cuboctahedral cavity (6-min. model) (Fig. 1, *a*), and the subsystem of cations (Fe/Nb) in octahedra has eight CEPs shifted in the directions of the type [111] (8-min. model) (fig. 1, *b*) from the center of the octahedron. In the symmetric, cubic phase, all six and eight CEPs are filled with the corresponding particles equally, and FP is associated with a violation of the equivalence of probability in their filling, which is accompanied by a change in the symmetry of the lattice.

The nonequilibrium thermodynamic potential (TP) for PFN in the Gorsky–Bragg–Williams approximation [34,35] per one formula unit can be represented as

$$F_0 = F_6 + F_8 + H_{\text{int}}, \tag{1}$$

where F_6 — TP6-min. models describing the ordering in the Pb cation subsystem,

$$F_6 = \frac{1}{6}\left[A_6\left(\sum_{i=1}^{3}\varepsilon_i^2\right) + B_6\left(6\gamma_1^2 + 2\gamma_2^2\right)\right] + T\sum_{k=1}^{6} n_k \ln n_k, \tag{2}$$

$$n_{1,2} = \frac{1}{6}\left(1 + 2\gamma_1 \pm \varepsilon_1\right),$$

$$n_{3,4} = \frac{1}{6}\left(1 - \gamma_1 + \gamma_2 \pm \varepsilon_2\right),$$

$$n_{5,6} = \frac{1}{6}\left(1 - \gamma_1 - \gamma_2 \pm \varepsilon_3\right),$$

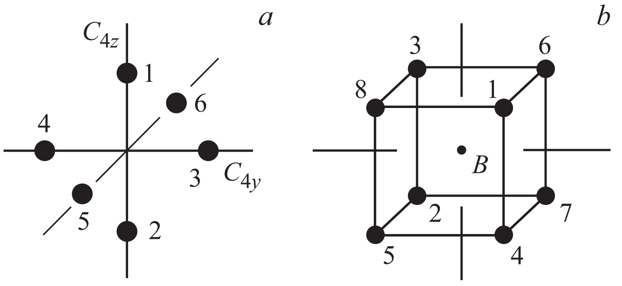

Figure 1. Location and numbering of CEPs inside anionic: *a*) cuboctahedron; *b*) octahedron.

F_8 — TP8-min. models describing the ordering in the subsystem of cations (Fe/Nb)

$$F_8 = \frac{1}{8}\left[A_8\left(\sum_{i=1}^{3}\varphi_i^2\right) + D_8\left(\sum_{i=1}^{3}e_i^2\right) + G_8\xi^2\right] + T\sum_{i=1}^{8} p_i \ln p_i, \tag{3}$$

$$p_{1,2} = \frac{1}{8}\left[1 + e_1 + e_2 + e_3 \pm (\xi + \varphi_1 + \varphi_2 + \varphi_3)\right],$$

$$p_{3,4} = \frac{1}{8}\left[1 + e_1 - e_2 - e_3 \pm (\xi + \varphi_1 - \varphi_2 - \varphi_3)\right],$$

$$p_{5,6} = \frac{1}{8}\left[1 - e_1 + e_2 - e_3 \pm (\xi - \varphi_1 + \varphi_2 - \varphi_3)\right],$$

$$p_{7,8} = \frac{1}{8}\left[1 - e_1 - e_2 + e_3 \pm (\xi - \varphi_1 - \varphi_2 + \varphi_3)\right],$$

$$H_{\text{int}} = h\left(\sum_{j=1}^{3}\varepsilon_j\varphi_j\right),$$

where A_6, A_8, B_6, D_8, G_8 — functions of constants characterizing paired interactions as direct, and indirect, through the subsystem of anions, between the same type, and h — between different types of particles (all of them, in fact, are phenomenological parameters of the theory); n, p — functions characterizing the probabilities of filling the CEP; the sign „+" refers to odd numbers, and the sign „–" — to even numbers; the variables ε, γ, φ, e, ξ act as order parameters (OP), ε and φ are transformed by the irreducible representation of T_{1u} in the same way as the polarization vector, and characterize the polarization in cuboctahedra and octahedra, respectively, $\gamma \in E_g$ and is transformed as a uniaxial strain tensor, $e \in T_{2g}$ and is transformed as a shear strain tensor, $\xi \in A_{2u}$ and is transformed as a third-rank tensor of the form xyz. The order parameters ε and φ actually determine the polarization, and OP γ and e — uniaxial and shear deformations of the crystal. The equilibrium values of these OPs can be found by solving a system of equations of state

$$\frac{\partial F}{\partial \varepsilon_i} = 0, \quad \frac{\partial F}{\partial \gamma_i} = 0, \quad \frac{\partial F}{\partial \xi_i} = 0, \quad \frac{\partial F}{\partial e_i} = 0, \quad \frac{\partial F}{\partial \varphi_k} = 0 \quad (4)$$

and choosing the solution that corresponds to the absolute minimum F_0, given the values A_6, A_8, B_6, D_8, G_8, h, T.

By selecting the relationships between the model parameters, a relatively realistic description of the set of phase transformations in PFN crystals is obtained. When $A_8 = 3.6A_6$, $D_8 = 0.335A_8 = 1.206A_6$, $G_8 = 0$, $B_6 = 0.15A_6$, $h = 0.07A_6$, the sequence _of phases and PT looks like this. Cubic phase $Pm\bar{3}m$ ($|\varepsilon| = |\varphi| = |\gamma| = |e| = \xi = 0$) loses stability with respect to the appearance of OP ε_1, φ_1, at $A_6/T = -0.925$.

The condition $G_8 = 0$ means that the interaction characterized by OP ξ is small compared to others. The conditions $B_6 \lesssim 0$, $D_8 \lesssim 0$ mean the presence of a small „softness" in OP γ and e, symmetry conjugate tensors of uniaxial and shear deformations.

The tetragonal phase P4mm, characterized by a set of OPs ε_1, φ_1, γ_1, becomes stable at $A_6/T = -0.905$. The temperature of PT between the cubic and tetragonal phases C and T is determined by the equality of their thermodynamic potentials. According to the calculated data, this is the case at $A_6/T = -0.91$, and in the experiment such an PT is observed at 376 K. Comparing these data, we can estimate the value of A_6, it turns out to be equal to -342.2 K. The phase T loses stability relative to the appearance $\varepsilon_2 = \varepsilon_3$, $\varphi_2 = \varphi_3$, $e_2 = e_3$, e_1, ξ at $T = 353$ K ($A_6/T = -0.969$). Monoclinic phase Cm (ε_1, $\varepsilon_2 = \varepsilon_3$, φ_1, $\varphi_2 = \varphi_3$, γ_1, $e_2 = e_3$, e_1, ξ) appears when $T = 359$ K ($A_6/T = -0.955$), and PT between tetragonal and monoclinic phases T and M occurs at $T = 357$ K ($A_6/T = -0.958$).

3. Discussion of results

Phase C is stable at $T > 370$ K, phase T is stable in the area of $353 < T < 378$ K, and the phase M is stable at $T < 359$ K. Phases C and T have a area of coexistence $\sim 8°$, and the phases T and M — $\sim 6°$. PT of the first order between phases C and T occurs at $T_{\text{tr}} = 376$ K and is accompanied by „jumps" of OP $\Delta\varepsilon_1 = 1.67$, $\Delta\varphi_1 = 0.43$, $\Delta\gamma_1 = 0.41$. For comparison, the maximum OP values in a ferroelectrically fully ordered phase T — $\varepsilon_{1\,\max} = 3$, $\varphi_{1\,\max} = 1$, $\gamma_{1\,\max} = 1$. It follows that $\Delta\varepsilon_1 \approx 0.5\varepsilon_{1\,\max}$, $\Delta\varphi_1 \approx 0.4\varphi_{1\,\max}$, $\Delta\gamma_1 \approx 0.4\gamma_{1\,\max}$. In the tetragonal phase, the redistribution of the Pb cation by six CEPs, and the (Fe/Nb) cation — eight CEPs lead to the occurrence of polarizations, in the cuboctahedron — $p_{16} \approx (1/3)\varepsilon_1$ and in the octahedron —$p_{18} \approx \varphi_1$. The appearance of OP γ_1 is accompanied by the appearance of uniaxial deformations η_1, while $\eta_1 = m\gamma_1$, where $\eta_1 = (2u_{11} - u_{22} - u_{33})/\sqrt{6}$, $u_{22} = u_{33}$ (u_{ii} — diagonal components of the homogeneous strain tensor). In the tetragonal phase of PFN uniaxial deformations are very small, $c/a = 1.01$ [16]. This means that the coefficient m is small. The small value of m may be due to the fact that the octahedral crystal frame remains rigid relative to η_1, despite the presence of eight CEPs for cations (Fe/Nb). This is mainly due to the absence in the configuration space of 8-min. of a OP model transformed by an irreducible representation of E_g. Therefore, the redistribution of the Pb cation density over the six CEPs is accompanied by only minor deformations of the anionic cuboctahedron and small deformations of the octahedron. Accordingly, tetragonal deformations in the crystal are relatively weak, and mainly due to deformations of the octahedra $(Fe/Nb)_{0.5}O_6$, which make up the framework of the crystal structure.

Phase M occurs due to loss of phase stability T with respect to the appearance of OP $\varphi_2 = \varphi_3$, which generate a whole set of OP: $\varepsilon_2 = \varepsilon_3 \propto \varphi_2 = \varphi_3$, $e_2 = e_3 \propto \varphi_1\varphi_3 = \varphi_1\varphi_2$, $e_1 \propto \varphi_2\varphi_3$, $\xi \propto \varphi_1\varphi_2\varphi_3$. In its turn, the appearance of parameters of the order of e is accompanied by the appearance of homogeneous shear deformations $u_{12} = u_{13} \propto e_2$, $u_{23} \propto e_1$. At the same time, the „rigidity of" octahedra with respect to shear deformations is significantly reduced due to the interaction of u_{ij} with „soft" (i.e., because $D_8 < 0$) subsystem characterized by OP e. This circumstance leads to the fact that the appearance of OP φ_2 is accompanied by noticeable shear deformations of the octahedral crystal frame.

Transition between phases T and M at $T = 357$ K — is also a first kind PT, in which OP changes as follows: the OP values in the phase T —$\varepsilon_{1\text{t}} = 2.22$, $\varphi_{1\text{t}} = 0.56$, $\gamma_{1\text{t}} = 0.64$, and the OP values in phase M — $\varepsilon_{1\text{m}} = 2.26$, $\varepsilon_{2\text{m}} = 0.06$, $\varphi_{1\text{m}} = 0.7$, $\varphi_{2\text{m}} = 0.53$, $\gamma_{1\text{m}} = 0.65$, $e_{1\text{m}} = 0.34$, $e_{2\text{m}} = 0.42$, $\xi_{\text{m}} = 0.28$. Hysteresis during the transition between phases With and T will be less than 8°, and between phases T and M — less than 6°. According to experimental data [18], the temperature hysteresis at PT with $-$T is $\sim 6-7°$.

In the emerging phase M, the polarization in cuboctahedra is directed near the C_4 axis ($\varepsilon_{1\text{m}} \gg \varepsilon_{2\text{m}} = \varepsilon_{3\text{m}}$), and in octahedra — closer to the axis C_3 ($\varphi_{1\text{m}} > \varphi_{2\text{m}} = \varphi_{3\text{m}}$, but the difference is $\varphi_{1\text{m}} - \varphi_{2\text{m}}$ is small). The shear deformations of the octahedra $u_{12} = u_{13} \propto e_2$, $u_{23} \propto e_1$ also differ slightly from each other. When the temperature decreases, the OP values change as follows. For $T = 271$ K — $\varepsilon_{1\text{m}} = 2.85$, $\varepsilon_{2\text{m}} = 0.02$, $\varphi_{1\text{m}} = 0.96$, $\varphi_{2\text{m}} = 0.93$, $\gamma_{1\text{m}} = 0.925$, $e_{1\text{m}} = 0.88$, $e_{2\text{m}} = 0.9$, $\xi_{\text{m}} = 0.85$. Hence it can be seen that in cuboctahedra the polarization became even closer to the C_4 axis, and in octahedra — noticeably closer to the C_3 axis (i.e., to the direction of type [111], i.e., to $\varphi_{1\text{m}} \approx \varphi_{2\text{m}} = \varphi_{3\text{m}}$). The components of the octahedron shear deformations are also almost equal, since $e_{2\text{m}} = e_{3\text{m}} \approx e_{1\text{m}}$. Considering that the structural motif of PFN is mainly formed by the subsystem of octahedra forming the framework of the structure, it can be concluded that the structure of the monoclinic phase M becomes very close to rhombohedral — so close that it can be characterized as pseudorombohedral. This conclusion is quite consistent with the results of structural studies of [16].

4. Investigation of dielectric properties

Based on this model, it is possible to estimate the effect of a subsystem of ferroactive particles with several CEPs on the dielectric properties of the crystal. This effect will be most pronounced in the vicinity of the PT between the cubic and tetragonal phases. In the presence of an external field directed along the axis C_4, the TP of the system can be represented as

$$F_0(E) = F_0 - a_1\varepsilon_1 E - a_2\varphi_1 E,$$

where $a_1\varepsilon_1 = Z_{\mathrm{Pb}}\cdot e(n_1 - n_2)d_6 = 1/3Z_{\mathrm{Pb}}\cdot ed_6\cdot\varepsilon_1$ — the dipole moment created by the distribution of the Pb^{2+} cation over six CEPs; $a_2\varphi_1 = 1/2Z_{\mathrm{Nb}}\cdot e\cdot 4(p_1 - p_2)d_8/\sqrt{3} = 1/2Z_{\mathrm{Nb}}\cdot e(d_8/\sqrt{3})\varphi_1$ — the dipole moment created by the distribution of the Nb^{5+} cation over eight CEPs; d_6, d_8 — distances from the centers of the cuboctahedron and octahedron to one of six or eight CEPs, respectively, F_0 is defined by the expression (1), $n_{1,2}$, $p_{1,2}$ — expressions (2) and (3).

The average polarization of a volume unit p is equal to

$$pv_{\mathrm{c}} = -\partial F_0(E)/\partial E = a_1\varepsilon_1 + a_2\varphi_1,$$

where v_{c} — the volume of the unit cell.

The equilibrium OP values $\varepsilon_1(E)$, $\varphi_1(E)$, $\gamma_1(E)$ are found when solving a system of equations of state

$$\partial F_0(E)/\partial\varepsilon_1 = \partial F_0(E)/\partial\gamma_1 = \partial F_0(E)/\partial\varphi_1 = 0.$$

After performing the corresponding calculations, it is possible to obtain in the cubic phase C

$$\chi_{\mathrm{C}}(T) = \frac{G}{F_{\varepsilon\varepsilon\mathrm{C}}F_{\varphi\varphi\mathrm{C}} - h^2T^2}\left(F_{\varphi\varphi\mathrm{C}} + g^2F_{\varepsilon\varepsilon\mathrm{C}} + 2ghT\right), \quad (5)$$

$$F_{\alpha\beta K} = \frac{\partial^2 F}{\partial\alpha\partial\beta}\Big|_{\mathrm{K}},$$

where K — phase designation, α, β — order parameters in phase K,

$$G = \frac{a_1^2}{\varepsilon_0 v_{\mathrm{c}} k_{\mathrm{B}}}, \quad g = \frac{a_2}{a_1}, \quad a_1 = Z_{\mathrm{Pb}}e\frac{d_6}{3},$$

$$a_2 = \frac{1}{2}Z_{\mathrm{Nb}}e\frac{d_8}{\sqrt{3}} \quad Z_{\mathrm{Pb}} = 2, \quad Z_{\mathrm{Nb}} = 5,$$

$e = 1.6\cdot 10^{-19}\,\mathrm{C}$, $v_{\mathrm{c}} = 4^3\cdot 10^{-30}\,\mathrm{m}^3$, k_{B} — Boltzmann constant (J/K), $\varepsilon_0 = (4\pi\cdot 9\cdot 10^9)^{-1}$ (C/V · m), in this case $G = 1311\,\mathrm{K}$, $g = 1.375$.

In the tetragonal phase T, characterized by OPε_1, γ_1, φ_S,

$$\chi_{\mathrm{T}}(T) = \frac{G}{S_{\mathrm{T}}}\left[F_{\varphi\varphi\mathrm{T}}F_{\gamma\gamma\mathrm{T}} + g^2(F_{\varepsilon\varepsilon\mathrm{T}}F_{\gamma\gamma\mathrm{T}} - F^2_{\varepsilon\gamma\mathrm{T}}) + 2ghTF_{\gamma\gamma\mathrm{T}}\right], \quad (6)$$

$$S_{\mathrm{T}} = F_{\varphi\varphi\mathrm{T}}F_{\gamma\gamma\mathrm{T}}F_{\varepsilon\varepsilon\mathrm{T}} - F^2_{\varepsilon\gamma\mathrm{T}}F_{\varphi\varphi\mathrm{T}} - h^2T^2F_{\gamma\gamma\mathrm{T}}.$$

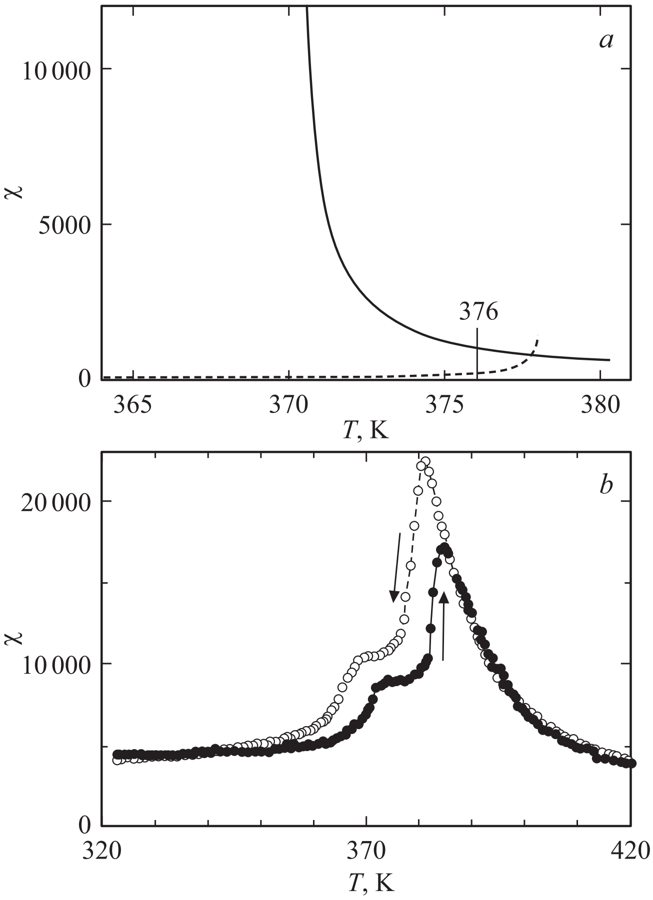

Figure 2. Dependences of the dielectric susceptibility of PFN on temperature: *a*) dependences $\chi_{\mathrm{C}}(T)$ (solid line) and $\chi_{\mathrm{T}}(T)$ (dashed), determined by the ratios (5) and (6), marked the temperature of the first order of PT between phases C and T; *b*) dependence $\chi(T)$ measured on a single crystal PFN [18].

Graphs of dependencies $\chi_{\mathrm{C}}(T)$ and $\chi_{\mathrm{T}}(T)$, determined by the relations (5), (6) are shown in Fig 2,*a*.

At the temperature of the first order of PT between phases C and T($T_{\mathrm{tr}} = 376\,\mathrm{K}$) the value of $\chi_{\mathrm{C}}(T_{\mathrm{tr}}) \approx 1049$, and $\chi_{\mathrm{T}}(T_{\mathrm{tr}}) \approx 235$, i.e. when cooling, given the PT, there should be a decline of $\chi(T)$ from 1049 to 235. However, given the presence of hysteresis $\sim 7^\circ$, the picture will be different. When cooled, in the cubic phase $\chi_{\mathrm{C}}(T \approx 371\,\mathrm{K}) \approx 6800$, and in tetragonal — $\chi_{\mathrm{T}}(T \approx 371\,\mathrm{K}) \approx 111$, i.e. there will be a decline of $\chi(T)$ from 6800 to 111. When heated, in the tetragonal phase $\chi_{\mathrm{T}}(T \approx 378\,\mathrm{K}) \approx 806$, and in cubic — $\chi_{\mathrm{C}}(T \approx 378\,\mathrm{K}) \approx 812$, i.e. at $T \approx 378\,\mathrm{K}$ there will be a hardly noticeable „jump“ from 806 to 812.

Comparing the results of the calculation of $\chi(T)$ with the experimental data in Fig. 2 shows that they are quite comparable at the qualitative level, and differ significantly from each other in quantitative characteristics. However, it should be borne in mind that the calculations took into account the contribution only from the subsystem of ferroactive cations responsible for the formation of polarization instabilities, and the contributions to χ from subsystems of anions and Fe cations that make up the background were not taken into account, and this contribution even far from the phase transitions of $\sim 3000-4000$ (fig. 2, *b*). Against such a background, the contribution from the ferroactive cation subsystem can manifest itself only in the immediate vicinity of the stability loss temperatures, i.e. at $T \approx 370\,\mathrm{K}$ and $T \approx 378\,\mathrm{K}$. Therefore, even a very rough, additive accounting of the contribution from background particles noticeably brings the calculated and experimental results closer, and when taking into account the interaction of background and ferroactive particles, the results will be quite comparable. In addition, it should be borne in mind that many estimates — in particular, the magnitude of the dipole moment — are made very approximately, and since the susceptibility depends on the square of the dipole moment, the error in the magnitude of this parameter is noticeably reflected in the calculation results.

5. Conclusion

The paper considers one of the possible mechanisms for the formation of phase states in a $PbFe_{0.5}Nb_{0.5}O_3$ crystal. A statistical model is proposed on the basis of which the whole set of structural phase transformations in this crystal is described. By selecting the parameters of the model, it turned out to be possible to reproduce all the characteristic features of its thermodynamic behavior at a qualitative level. Namely: the presence of ferroelectric and ferroelastic instabilities, as a result of which two first-order PTs are realized between paraelectric cubic and FE-tetragonal, between FE-tetragonal and FE-complex ordered monoclinic phases, as well as the formation of corresponding condensates of order parameters. The key point for the formation of such a monoclinic phase is that the first-order PT into the rhombohedral FE-phase occurs in the presence of the „external field“ tetragonal symmetry.

The calculated values of the temperature intervals between the PT and the values of the temperature hysteresis accompanying the PT are close to those observed. In addition, the features of the dielectric properties at the PT between phases C and T at the qualitative level also correspond to what is observed experimentally. Thus, based on the assumption of the presence of two cationic subsystems with six and eight CEPs, it turned out to be possible to reproduce the entire set of features of the thermodynamic behavior of the PFN crystal.

When studying the thermodynamic properties of the system at a qualitative level, the interaction between the cationic and anionic subsystems was not explicitly taken into account. This is due to the fact that such accounting will lead to a standard renormalization of the model parameters, and since these parameters are selected according to certain criteria, then the renormalized parameters will have to meet the same criteria, i.e. such accounting will not bring anything new. However, taking into account the interaction with the anionic subsystem turns out to be important for understanding the specifics of the structural changes observed in the crystal. Thus, the appearance of OP ε, φ, γ, e, ξ is due to the redistribution of cations over the corresponding sets of CEPs, which is accompanied by deformation of anionic polyhedra. At the same time, the main contribution to the formation of the crystal structure is made by the octahedron subsystem, which forms the framework of the structure. As it was shown earlier, in the phase T tetragonal deformations of octahedra should be small, and in the monoclinic phase, local deformations of octahedra should be large and close to rhombohedral. Accordingly, in the T phase Tetragonal deformations in the crystal structure are relatively weak, and in the M phase rhombohedral deformations are much more pronounced, which gives reason to characterize this phase as pseudorombohedral [16].

In addition, taking into account the interaction with the anionic subsystem plays an important role in estimating the friction constants and considering the piezoelectric effect, as well as for a more correct assessment of the values of dielectric susceptibility and dipole moment. The latter is due to the fact that it is necessary to take into account not only the dipole moment due to the distribution of cations over the CEPs, but also the dipole moment resulting from a noticeable distortion of the anionic polyhedra [16].

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Conflict of interest

The authors declare that they have no conflict of interest.

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