Phase diagram of mixed system of ferroelectric relaxors in the random field theory framework

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We suggest a random field based model for calculation of physical properties of mixed ferroelectric relaxors. Our model naturally incorporates the different orientations of electric dipoles (related to different solid solution components) as well as the contribution of nonlinear and correlation effects of random field. We calculate the transition temperature $T_c$ as well as concentrealional and temperature dependence of order parameters. The equations for these quantities have been derived. The theory has been applied for description of the systems (PSN)$_{1-x}$(PST)$_x$ with different degree of order as well as for (PMN)$_{1-x}$(PT)$_x$ systems. We show, that higher $T_c$ value for more disordered (PSN)$_{1-x}$(PST)$_x$ system at $0 \leq x < 0.5$ is related to larger nonlinearity coefficient of PSN in comparison with that of PST. We determine the morphotropic region of temperatures and concentrations for (PMN)$_{1-x}$(PT)$_x$. The observed phase diagram of both aforementioned mixed ferroelectric relaxors is in pretty good coincidence with the results of our numerical calculations.

I. INTRODUCTION

The ferroelectric relaxors like PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN), PbSc$_{1/2}$Ta$_{1/2}$O$_3$ (PST), PbSco$_{1/2}$Nb$_{1/2}$O$_3$ (PSN), Pb$_{1-x}$La$_x$Zr$_{0.55}$Ti$_{0.45}$O$_3$ at $x = 0.08-0.09$ (PLZT 8-9/65/35) have been widely investigated in the last years [1]. In spite of this the mechanisms of unusual properties of these materials (like Vogel-Fulcher (V-F) law in dynamic dielectric permittivity, nonergodic behaviour, the distribution of different properties maxima in broad temperature range ($\Delta T \sim 100$ K for PMN relatively to the temperature of permittivity maximum)) are still under discussion. The presence of random field related to substitutional disorder, vacancies of lead and oxygen, impurity atoms is firmly established in the relaxors. Since this field has to influence the local properties of material, its distribution was shown to result in V-F law [2], anomalies of nonlinear dielectric permittivity [3], distribution of relaxation times and non-Debye behaviour of dynamic dielectric permittivity [4]. The model [5] for quantitative description of relaxor ferroelectrics is based on the supposition that the random field destroys ferroelectric long range order which could appear at $T \leq T_d$ where $T_d$ is Burns temperature ($T_d \sim 600$ K for the most of relaxors). As a result, mixed ferroglass phase with coexistence of long and short range order or dipole glass state (both of them with non-ergodic behaviour) can appear. In the case of PLZT the reference phase is PZT, its ferroelectric long range order is destroyed completely (at $x_{La} = x \geq 0.07$) or partly (at $x < 0.07$) by random field of impurity La ions. The degree of disorder can be controlled by special technological conditions which decrease the number of random field sources in the relaxors PST, PSN and in other representatives of 1:1 family. In the case of PMN (1:2 family relaxor) it appeared impossible to increase the degree of order with the help of technological treatment. However, this can be done by addition of PbTiO$_3$ (PT) (see e.g. [6] and ref. therein). In particular, measurements had shown that in solid solution (PMN)$_{1-x}$(PT)$_x$ there is morphotropic phase transition between rhombohedral and tetragonal phases at $x_r \approx 0.35$. For $x > x_r$ normal ferroelectric behaviour is present. Still missing theoretical description of this mixed system phase diagram seems to be necessary to clarify the physical nature and mechanisms of relaxor ferroelectrics behaviour. On the other hand the solution of these problems is important due to giant electrostriction related to high dielectric response which result in extremely high value of electromechanical coefficient ($k \sim 0.92$ for (PMN)$_{0.9}$(PT)$_{0.1}$ single crystals). These anomalous properties made mixed ferroelectrics very attractive for application in electromechanical transducers, actuators, sonars etc. [7,8]. Another mixed system (PSN)$_{1-x}$(PST)$_x$ is also prospective for aforementioned applications [9]. Both phase diagram of these relaxors and the behaviour of PSN and PST with different degree of disorder exhibit the puzzles which have not been solved up to now. The most interesting problem is the increase
of transition temperature $T_c$ in PSN and its decrease in PST as disorder increases. The observed dependence $T_c(x)$ at $0 \leq x \leq 1$ for solid solution of PSN and PST with different degree of order had shown [10,11,12] that aforementioned peculiarity exists in wide range of the components concentrations, namely $T_c^{\text{dis}}(x) > T_c^{\text{ord}}(x)$ at $x \leq 0.5$. The experimental and theoretical investigations of anomalies of dielectric response (the existence of low and high temperature maxima obeyed to V-F and Arrhenius law respectively) of PbSc$_{0.5}$(Nb$_{0.2}$Ta$_{0.3}$)O$_3$ single crystals have been performed recently [13]. In this work we propose the method of calculation of mixed systems phase diagram. The method bases on the random field theory framework.

We show that the difference in PSN and PST behaviour can be calculated in the random field theory framework with different degree of order had shown [10,11,12] that appearance of coherently oriented dipoles. Their fraction tends to order system via indirect dipole-dipole interaction over soft mode of reference phase, while all other random electric field sources try to disorder the materials. The competition between these tendencies can lead to appearance of coherently oriented dipoles. Their fraction $L$ can be calculated in the random field theory framework on the base of equation

$$L = \int_{-\infty}^{+\infty} \langle \tilde{i} \rangle f(\tilde{E}, \tilde{L})d\tilde{E}$$

(1)

where $f(E, L)$ is random field $E$ distribution function.

As the matter of fact $L$ is a dimensionless order parameter, which expressed through single dipole moment $\langle \tilde{i} \rangle = \langle \frac{d\tilde{r}}{dx} \rangle$ ($d^*$ is effective dipole moment related to Lorenz field parameter, see [14] for the details) averaged over possible orientations and random field distribution function. In the case of two-orientation dipoles ($l_z = 1, l_x = l_y = 0$) $\langle l_z \rangle = \tanh(d^*E_z/kT)$, Eq.(1) can be rewritten as

$$L_z = \int \tanh \left( \frac{d^*E_z}{kT} \right) f(E_z, L_z)dE_z$$

(2)

For the completely ordered system which is usually described by a mean field approximation $f(E, L) = \delta(E - E_0L)$, where $E_0$ is mean field value ($d^*E_0 = kT_{cmf}$), so that Eq.(2) gives well-known expression for order-disorder ferroelectrics: $L_{mf} = \tanh(d^*E_0L_{mf}/kT)$ and $T \to T_{cmf}$ at $L_{mf} \to 0$.

For the considered case of mixed system of ferroelectric relaxors A$_{1-x}$B$_x$ two types of electric dipoles $d^*_1$, and $d^*_2$ and order parameters $L_1$, and $L_2$, must be considered. In such a case the random field is induced by both type of dipoles and its distribution function $F$ depends on both order parameters, i.e. $F = f(E, L_1, L_2)$. Therefore $L_{1z}$ and $L_{2z}$ can be written in the form of Eq.(2) with this distribution function and with $d^*_1$ and $d^*_2$ in the Eqs. for $L_{1z}$ and $L_{2z}$ respectively, $z$ and $z'$ being the directions of 1 and 2 types electric dipoles orientations.

The most of the disordered system characteristics are included into random electric field distribution function $f(E, L)$. This distribution function has been calculated in the statistical theory framework allowing for contribution of electric dipoles, point charges and dilatational centers as the random field sources [14]. Linear, nonlinear and spatial correlation effects contribution of the random field was taken into account in [15]. Allowing for these effects for the materials with cubic symmetry (see [15]) in supposition that the considered electric dipoles are the main sources of random field and introducing $\cos(l_1l_2) \equiv \cos(zz')$ one can obtain the following equations for two order parameters:

$$L_1 \equiv L_{1z} = \int_{-\infty}^{+\infty} \tanh \frac{d^*_1(\varepsilon_z + \alpha_3^{(1)} \varepsilon_z^3)}{kT} f_1(\varepsilon_z, L_1, L_2)d\varepsilon_z,$$

$$L_2 \equiv L_{2z'} = \int_{-\infty}^{+\infty} \tanh \frac{d^*_2(\varepsilon_{z'} + \alpha_3^{(2)} \varepsilon_{z'}^3)}{kT} f_2(\varepsilon_{z'}, L_1, L_2)d\varepsilon_{z'}.$$ 

(3)

Here $\alpha_3^{(1,2)}$ is coefficient of nonlinearity of the reference phase, its dimensionality being $\varepsilon^{-2}$ (see [15]).

$$f_1(\varepsilon_z, L_1, L_2) = \frac{1}{2} \int_{-\infty}^{+\infty} \exp(-\rho^2_{z} \eta_1) \cos \left[ \rho_z \left( \varepsilon_z - (1 - x) \frac{T_{cm} f_2}{d_2^*} L_2 \cos(l_1 l_2) - z \frac{T_{cm} f_1}{d_1^*} L_1 \right) \right] d\rho_z,$$

(4)

$$f_2(\varepsilon_{z'}, L_1, L_2) = \frac{1}{2} \int_{-\infty}^{+\infty} \exp(-\rho^2_{z'} \eta_2) \cos \left[ \rho_{z'} \left( \varepsilon_{z'} - (1 - x) \frac{T_{cm} f_2}{d_2^*} L_2 - z \frac{T_{cm} f_1}{d_1^*} L_1 \cos(l_1 l_2) \right) \right] d\rho_{z'},$$
\[ \eta_1 = \cos^2(l_1 l_2) \xi_1 + \xi_2; \quad \eta_2 = \xi_1 + \cos^2(l_1 l_2) \xi_2; \quad \xi_1 = \frac{16\pi}{15} \frac{d_1^2}{\varepsilon_1^2} n_1; \quad \xi_2 = \frac{16\pi}{15} \frac{d_2^2}{\varepsilon_2^3} n_2. \]

In Eq. (4) \( \xi_1 \) and \( \xi_2 \) describe the width of random field distribution functions with Gaussian form related, respectively, to the first and second types of dipoles, their concentrations being \( n_1 = \frac{\beta_1}{a_1^2} \) and \( n_2 = \frac{\beta_2(1-x)}{a_2^2} \) (\( \beta_1 \) is fraction of unit cells in which dipoles exist); \( \varepsilon_{1,2}, a_{1,2} \) and \( r_{c,1,2} \) are respectively dielectric permittivity, lattice constants and correlation radii of A and B relaxors reference phase. Note, that the difference between distribution functions \( f_1 \) and \( f_2 \) is related to the different orientations of the dipoles which manifests itself in the presence of \( \cos(l_1 l_2) \) multiplier; \( f_1 = f_2 \) if \( \cos(l_1 l_2) = 1 \).

The polarization of mixed system \( P \) can be expressed via \( L_1 \) and \( L_2 \) as follows
\[ \vec{P} = x \frac{\beta_1 a_1^2 L_1}{d_1^2} + (1 - x) \frac{\beta_2 a_2^2 L_2}{d_2^2}. \] (5)

**III. PHASE DIAGRAM OF MIXED SYSTEM**

The phase diagram has to describe the dependence of the temperature \( T_c \) at which order parameters arise on concentration. The \( T_c(x) \) dependence can be obtained from Eqs. (3), (4) in the limit \( L_1 \to 0, L_2 \to 0 \). One can see from (4), that in such a limit the distribution functions \( f_1 \) and \( f_2 \) can be represented in the form:
\[ f_{1,2}(\varepsilon, L_1, L_2) = f_{01,2}(\varepsilon_1) - k_{1,2} \left( \frac{df_{1,2}}{d\varepsilon_1} \right)_{L_1 = L_2 = 0}, \]
\[ i = z, z', \]
\[ k_1 = (1-x) \frac{T_{cm,f_2} L_2}{d_2^2} \cos(l_1 l_2) + x \frac{T_{cm,f_1} L_1}{d_1^2}; \]
\[ k_2 = (1-x) \frac{T_{cm,f_2} L_2}{d_2^2} + x \frac{T_{cm,f_1} L_1}{d_1^2} \cos(l_1 l_2), \]
\[ f_{01,2}(\varepsilon_i) = \frac{1}{2\sqrt{\pi} n_{1,2}} \exp \left( -\frac{\varepsilon_i^2}{4n_{1,2}} \right). \] (8)

Substituting Eqs. (4)- (8) into (3) and performing the integration, one obtains the following system of equations for \( T_c(x) \) calculation:
\[ L_1 = \left[ (1-x) T_{cm,f_2} L_2 \Delta \cos(l_1 l_2) + x T_{cm,f_1} L_1 \right] \frac{I_1}{k T_c}; \]
\[ L_2 = \left[ (1-x) T_{cm,f_2} L_2 + x \frac{T_{cm,f_1} L_1 \cos(l_1 l_2)}{\Delta} \right] \frac{I_2}{k T_c}; \] (9)
\[ I_{1,2} = \int_{-\infty}^{\infty} f_{01,2}(\varepsilon) \frac{(1-3\varepsilon^2 \alpha_1^{(1,2)} d_2^2)}{\cosh^2(l_1 l_2/k T_c)(\varepsilon + \alpha_3^{(1,2)} \varepsilon)}, \]
\[ \Delta = \frac{d_2^2}{d_1^2}. \] (10)

Integrals \( I_1 \) and \( I_2 \) depend on components concentrations since the distribution function width (see Eq. (8)) depends on \( x \) and \( T_c \).

![Graph](image-url)

**a**

![Graph](image-url)

**b**

FIG. 1. Concentrational dependence of dimensionless transition temperature \( \tau_c = \frac{\tau_c(x)}{T_{cm,f_2}} \) for the case \( d_1 \parallel d_2 \), \( \alpha_1^{(1)} = \alpha_2^{(2)} = 0.6 \) (solid line); 0.7 (dashed line); 0.8 (dotted line); \( \alpha_0^{(1)} = \alpha_0^{(2)} = 1 \) (a); \( \alpha_0^{(1)} = \alpha_0^{(2)} = 3 \) (b).

The condition of the system (4) solvability leads to following equation for \( T_c \):
\[ T_c^2 - C_2(T_c) T_c + C_1(T_c) = 0; \] (11)
\[ C_1(T_c) = (1-x) x I_1 I_2 T_{cm,f_1} T_{cm,f_2} (1-\cos^2(l_1 l_2)); \]
\[ C_2(T_c) = x I_1 T_{cm,f_1} + (1-x) I_2 T_{cm,f_2}. \] (12)

The dependencies \( C_{1,2}(T_c) \) are related to those of \( I_{1,2} \) integrals (see Eqs. (3)), so that (12) is complicated non-linear equation for \( T_c \). It will be solved numerically.
Factor \((1 - \cos^2(l_1 l_2))\) reflects the dependence on orientations of the \(d_1^*\) and \(d_2^*\) dipoles. It equals \(\frac{2}{3}\) in the case when the dipoles 1 and 2 are oriented, respectively, along [001] and [111] type of direction. This factor is zero as \(\cos(l_1 l_2) = \pm 1\) when the dipoles are parallel or antiparallel to each other. In the latter case the system (12) reduces to single equation \(T_c = C_2\). One can see, that in general case there is at least two \(T_c\) values and the largest one has to describe the mixed system behaviour. It is seen from Eqs. (11), (12), (10), (8), that \(T_c\) depends on several parameters - coefficients of nonlinearity, distribution function half-width and electric dipole moments ratio. To illustrate the influence of these parameters on \(T_c(x)\), we depicted in Fig.1 the dimensionless transition temperature \(\tau_c = T_c(x)/T_{cm/f2}\) for the case when \(d_1 \parallel d_2\) (i.e. \(T_c = C_2\)) for several values of dimensionless parameters. It is seen that increase of \(\alpha_0^{(1,2)}\) and \(\Delta = d_1^*/d_2^*\) increases the rate of \(T_c(x)\) decrease. The influence of dipole moments ratio is more pronounced with decrease of the second component concentration.

\[
\begin{align*}
T_c(PSN) &= I_2 T_{cm/f2}, \\
T_c(PST) &= I_1 T_{cm/f1}.
\end{align*}
\]

**IV. MIXED SYSTEM OF 1:1 FAMILY RELAXORS: (PSN)\(_{1-x}\)(PST)\(_x\)**

The behaviour of this solid solution components (PSN and PST) is strongly different: the increase of the degree of disorder leads to increase of \(T_c\) for PSN and to decrease of \(T_c\) for PST. At the first glance the latter seems to be more reasonable while the PSN behaviour is puzzling since it is common wisdom that random field decreases \(T_c\). On the other hand the increase of random field value can result into appearance of nonlinear and correlation effects. These effects have to be dependent on the value of nonlinearity coefficient of the material. Keeping in mind that PSN and PST contain scandium, niobium and tantalum oxygen complexes, one can conclude that coefficient of nonlinearity for PSN should be larger than that for PST. This is because this coefficient for niobium oxygen complexes was shown to be several times larger than that for tantalum \([16]\). The value of nonlinearity coefficients for PSN and PST was extracted from observed \(T_c\) values with the help of formulas (11), (12) at \(x = 0\) (PSN) and \(x = 1\) (PST). One can see, that in both cases \(C_1(T_c) = 0\) and \(C_2(T_c) = C_2\).

**FIG. 2. Phase diagram of mixed relaxors (PSN)\(_{1-x}\)(PST)\(_x\) for disordered (open symbols) and ordered (solid symbols) ceramic samples, taken from \([10,11,12]\). Solid and dashed lines - theory respectively for aforementioned and 10\% larger \(\Delta\) value with \(\alpha_0^{(1)} = 0, \alpha_0^{(2)} = 0, 3, \alpha_0^{(1')} = \alpha_0^{(2')} = 0\) for disordered and ordered materials.**

**FIG. 3. Fraction of coherently ordered dipoles in (PSN)\(_{1-x}\)(PST)\(_x\).**

\(a)\) solid line - \(L_{2ord}(x = 0)\); dashed line - \(L_{2disord}(x = 0)\); dotted line - \(L_{1ord}(x = 1)\); dotted-dashed line - \(L_{1disord}(x = 1)\)

\(b)\) solid line - \(P_{ord}(x = 0, 3)\); dashed line - \(P_{disord}(x = 0, 3)\); dotted line - \(P_{ord}(x = 0, 8)\); dotted-dashed line - \(P_{disord}(x = 0, 8)\).

The fitting of observed \(T_c\) values (see e.g. \([10]\) and ref. therein) for more disordered PSN and PST made it possible to obtain dimensionless coefficient of nonlinearity \((\alpha_0\)
$= \alpha_3(kT_{cmf2}/d_1^2))$ for PSN $a_{00}^{(2)} = 0.3$ and $a_{00}^{(1)} = 0.098$ for PST along with distribution function dimensionless half-width $(g_1 = \frac{1}{kT_{cmf1}/d_2}; \xi_0 = \frac{16\pi}{kT_{cmf1}/d_2}; \beta = \frac{\sqrt{2}}{\pi})$ $g_2$(PSN) $= 0.425$, $g_1$(PST) $= 0.499$. Note, that while introducing dimensionless values we took into account, that parameters of reference phase for PSN and PST are close to each other. Allowing for the fact that $T_{cmf}$(PSN) $\approx T_{cmf}$(PST) $\approx T_{cmf}$(PST) [17] one comes to conclusion that $\frac{\alpha_3}{\alpha_2}$ $= 0.89$ for more disordered relaxors. The same fitting of $T_c$ values observed in more ordered PSN and PST [10,11] leads to $\alpha_0^{(1)} = \alpha_0^{(2)} = 0$, $q_1 = 0.477$, $q_2 = 0.457$ and $\Delta_0 = 0.88$. The obtained parameters made it possible to calculate $T_c(x)$ both for more disordered and ordered (PSN)$_{1-x}$(PST)$_x$ mixed system without additional fitting parameters. To simplify the calculations we supposed the same orientations of $d_1$ and $d_2$ dipoles. The comparison of calculated and measured [10-12] $T_c(x)$ values is shown in Fig.2. We used two different values of $\Delta$ to show, that the concentration $x$, at which $T_c$(disordered) $= T_c$(ordered) is sensitive to the parameter values. One can see that the theory describes the observed values pretty good, allowing for the distribution of measured $T_c$ values related to different experimental conditions (see [10] and ref. therein).

The calculations of $L_1$ and $L_2$ on the base of Eq.(1) had shown, that $L_2 > L_1$ both for more disordered and ordered relaxors, the values of $L$ for ordered ones being larger than those for more disordered samples. The nonzero values of $L_1$ and $L_2$ in whole range of the components concentrations give evidence that each component is in mixed ferro-glass phase (see also [13]).

which is proportional to these materials polarization. For two relaxors solid solution at $x = 0.3$ and $x = 0.8$ we performed the calculations of dimensionless polarization (in the units of $P_0 = \frac{d_1^2}{\alpha_2}$) on the base of Eq.(6) (keeping in mind that $d_1 \parallel d_2$ and $\beta_1 = \beta_2$) and showed the results in Fig.3b. It is seen that increase of $x$ leads to increase of polarization $P(x)$ of more ordered samples is larger than $P(x)$ of disordered samples.

V. MIXED SYSTEM (PMN)$_{1-x}$(PT)$_x$

This system is a solid solution of relaxor ferroelectric PMN (component 2) and normal ferroelectric PbTiO$_3$ (component 1). In fact, the phase diagram of this system can be calculated similar to that in the previous section, with some details different.

First, due to the existence of normal ferroelectric phase transition in PbTiO$_3$ at $T_c = 763$ K which can be calculated in a mean field approximation, $T_{cmf1} = 763$ K. Second, the distribution function of random field in ordinary ferroelectrics is known to be $\delta$-function because of negligibly small random field in the system, so that $\xi_1 = 0$ in Eq.(3). Note, that in such a case PT component contributes to random field distribution via PT mean field written as $xT_{cmf1}L_1/d_1^2$ (see Eqs.(3)). The number of electric dipoles $n_1 = x/a_3$ where $a$ is PT lattice constant.

FIG. 5. Temperature dependence of the fraction of coherently ordered dipoles in PMN (solid line) and PT (dashed line).

It is important to emphasize that PMN relaxor state was considered as mixed ferroglass phase with coexistence of long and short range order. The peculiarities of nonlinear dielectric permittivity of PMN (see [18]) speak in favour of this statement. Keeping in mind that the dipoles in PMN and PT are oriented, respectively, along [111] and [100] type of directions, we calculated $T_c(x)$ on the base of Eqs.(1), (2) with $\cos(l_1l_2) = \frac{1}{\sqrt{3}}$. It
appeared possible to neglect the contributions of non-linear and correlation effects because they do not improve the fitting of calculated and measured $T_c(x)$ dependence. The results of numerical calculations are reported in Fig.4. Fitting parameters $g_2 = 0.51$ and $\Delta = \frac{1}{10}$ were obtained from observed $T_c$(PMN), $T_c$(PT) and $\frac{\partial T_c}{\partial x} = \frac{1}{3}$, i.e. $\frac{\partial P}{\partial T} = \frac{1}{3}$, so that only 11% of unit cells in PMN have electric dipoles because $\beta_1 = 1$. One can see that our calculation describes pretty good observed $T_c(x)$ dependence.

To find the change of mixed system symmetry with variation of concentration of components, we performed the calculations of $L_1$ and $L_2$ temperature and concentration dependence. We start with calculations for PMN ($x = 0$) and PT ($x = 1$) using the aforementioned parameters (see Fig.5). The comparison of solid and dashed lines in Fig.5 shows clearly the difference of the behaviour of order parameters in mixed ferroglass phase (PMN) and normal ferroelectric phase (PT). The calculation of $L_2(T)$ at $T \to 0$ had shown that $L_2(T=0) \approx 0.58$, so that the contribution of long range order is large enough in low temperature region in PMN.

FIG. 6. Temperature dependence of the components with rhombic ($P_2$) and tetragonal ($P_1$) symmetry of dimensionless polarization in (PMN)$_{1-x}$(PT)$_x$. Solid line - $P_2(x = 0.1)$; dotted line - $P_1(x = 0.3)$; dashed line - $P_1(x = 0.1)$; dotted-dashed line - $P_2(x = 0.3)$.

The polarization of mixed system was calculated with the help of Eq.(6), which incorporates the contribution of the first and second type of dipoles, i.e. $\vec{P}(x) = \vec{P}_1(x) + \vec{P}_2(x)$. The concentrations at which $|\vec{P}_1(x)| = |\vec{P}_2(x)|$ correspond to coexistence of two types of symmetry in the mixed system, i.e. to appearance of morphotropic region in phase diagram. Temperature dependence of dimensionless $|\vec{P}_1|$ and $|\vec{P}_2|$ for several $x$ values is depicted in Fig.6.

The most interesting feature in the Fig.6 is the existence of the curves crossover at some $T = T_{cr}(x)$ for $x = 0.3$. This means that $|P_1| = |P_2|$ at $T = T_{cr}(x)$ (morphotropic region), $|P_1| > |P_2|$ at $T > T_{cr}(x)$ or $|P_1| < |P_2|$ at $T < T_{cr}(x)$, i.e. mixed system has the symmetry of component 1 or component 2 respectively. For (PMN)$_{1-x}$(PT)$_x$ the value $T_{cr}(x = 0.3)$ = 275 K and $T_{cr}(x = 0.4)$ = 460 K, therefore $T_{cr}$ increase with concentration increase (see dashed line in Fig.4). On the base of this consideration we discern the symmetry of mixed (PMN)$_{1-x}$(PT)$_x$ system in Fig.4 (pseudo-cubic like PMN and tetragonal like PT) which is in agreement with observed one [6].

One can see from Fig.6 the absence of the curves crossover, i.e. morphotropic region at $x = 0.1$. Since the compositions with small concentration of PT ($x \approx 0.1$) are important for applications (see [7,8]), we depicted in Fig.7 the fraction of coherently ordered dipoles and the components of polarization with tetragonal (solid line) and pseudo-cubic (rhombohedral) symmetry (dashed line) at $T = 0$.

FIG. 7. Concentrational dependence of order parameters at $T = 0$ with pseudo-cubic (rhombohedral) (dashed lines) and tetragonal (solid lines) symmetry expressed via fraction of coherently ordered dipoles (a) and via contributions to polarization (b).
It is seen from Fig.7b that tetragonal component linearly increases with PT concentration increase whereas pseudo-cubic component has a maximum at \( x \approx 0.135 \). This maximum origin can be related to the competition between increase of \( L_2 \) (see dashed line in Fig.7a) and \( (1-x) \) decrease with \( x \) increase (see Eq.(6)). Because of pseudo-cubic symmetry, both the polarization maximum and maxima of dielectric response, piezoelectric and electromechanical coefficient can be expected at \( x = 0.135 \). This concentration is a little larger than \( x \approx 0.1 \) where the high values of aforementioned properties were observed [7,8].

VI. CONCLUSION

We propose a model for calculation of ferroelectric order parameters and phase diagram of mixed relaxors. The physical background of the model is influence of random electric field of mixed system on its properties. Randomly distributed electric dipoles were supposed to be the main sources of the field. The contribution of non-linear and spatial correlation effects of random field was taken into account. We carried out the specific calculations for mixed PSN-PST and PMN-PT systems. The solution of the puzzle of larger transition temperature of more disordered \((PSN)_{1-x}(PST)_x\) system in the region \( 0 \leq x < 0.5 \) was shown to be related to non-linear and correlation effects contribution which has to be larger in PSN. The obtained concentrational dependence of transition temperature and polarization of solid solution \((PMN)_{1-x}(PT)_x\) revealed the existence of morphotropic region with coexistence of rhombic (pseudo-cubic) and tetragonal symmetry phases, its concentration being dependent on temperature. The maximal contribution of pseudo-cubic symmetry polarization at \( x = 0.135 \) was supposed to be related to high values of electromechanical coupling coefficient, observed at \( x \approx 0.1 \) in the mixed system. The developed theory describes pretty good observed phase diagram of PSN-PST and PMN-PT mixed relaxor systems.

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