

Intermediate monoclinic phase and elastic matching in perovskite-type solid solutions

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This paper is devoted to the study of elastic matching of phases coexisting in systems of perovskite-type solid solutions close to morphotropic phase boundaries. Determined are different interfaces that separate single-domain or polydomain phases in $(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ single crystals and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ceramic grains. These interfaces are parallel to so-called zero net strain planes. Some results of recent experimental studies of the crystal structure and electromechanical properties are analyzed in connection with the revealed simplification of the domain structure in the intermediate monoclinic phase of $(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ single crystals. The important role of the monoclinic phase in relieving stress at the phase coexistence in both the systems is considered. Links between optimal domain volume concentrations derived from unit-cell parameters' behavior are discussed on the basis of concepts of the polarization rotation path proposed by Fu and Cohen [Nature (London) **403**, 281 (2000)].

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I. INTRODUCTION

In the last decade, heterogeneous ferroelectrics and related materials attracted attention due to the presence of intermediate phases. These phases appear, for example, in single crystals of PbZrO_3 (ferroelectric $3m$ phase over a narrow temperature range),^{1,2} KCN (ferroelastic $2/m$ phase induced by hydrostatic pressure or thermal cycling),³ $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ (unique intermediate antiferroelectric $\bar{4}2m$ phase in boracite-type single crystals and “seagull” shape domains of the ferroelectric $mm2$ phase induced ephemerally at $\bar{4}3m-\bar{4}2m$ interfaces),⁴⁻⁶ etc. Of particular interest are perovskite-type piezoelectric $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) ceramics and relaxor-based $(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ (PZN-PT), and $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ single crystals. The three last systems of solid solutions are intensively studied not only because of their remarkable ferroelectric and piezoelectric properties (see, e.g., Refs. 7–11), but also as materials in which intermediate monoclinic phases have been recently discovered.¹²⁻¹⁵ Close to the well-known morphotropic phase boundary,⁷ the monoclinic phase can coexist with either the rhombohedral $R3m$ phase or the tetragonal $P4mm$ one over certain ranges of temperature T , molar concentration x (that occurs in PZT ceramic grains¹⁴), or electric field E (as follows from results¹⁵⁻¹⁷ of structural studies of PZN-PT single crystals). The electric field \mathbf{E} applied to crystal samples of the above-mentioned perovskite-type solid solutions influences their behavior and crystallographic features. For example, a ferroelectric incommensurate phase¹⁸ is observed at cooling the $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ samples from the paraelectric $Pm3m$ phase under the field \mathbf{E} . The ferroelectric monoclinic Cm phase¹⁹ appears in $0.65\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-0.35\text{PbTiO}_3$ single crystals previously poled under the field \mathbf{E} applied along a perovskite unit-cell axis $[001]$.

Our recent analysis of elastic matching and features of relieving stress in PZT solid solutions reveals a link²⁰ between phase boundaries in the x,T diagram, proposed by Noheda *et al.*,¹⁴ and interfaces, which separate the coexisting

phases. Different variants of the elastic matching of two polydomain or twinned phases were considered by using concepts^{6,21,22} of the zero net strain plane (ZNSP). The interfaces lying along the ZNSP's obey conditions for complete stress relieving and the vanishing of an excessive elastic energy associated with the interaction of the coexisting phases. As for the PZT system, a line of the ZNSP's at the coexistence of the above-mentioned $P4mm$ phase and the intermediate Cm one is practically parallel²⁰ to the $P4mm-Cm$ boundary in the x,T diagram from Ref. 14. Such a novel and original example of the elastic matching as well as recent experimental data^{15-17,19} prompt us to describe some effects at the phase coexistence in PZN-PT single crystals where the intermediate monoclinic Pm phase is observed under the applied electric field \mathbf{E} at room temperature. In this connection the present paper is aimed at the study of the peculiarities of the elastic matching of the above-mentioned phases in the vicinity of the morphotropic phase boundary in PZN-PT single crystals ($x \approx 0.08$) and at the generalization of results on elastic matching in perovskite-type solid solutions.

II. POLYDOMAIN PHASES AND THEIR ELASTIC MATCHING

A. Distortion matrices and zero net strain planes

In order to analyze elastic effects at the phase coexistence let us consider a stress-free PZN-PT single crystal undergoing a structural phase transition over some ranges of x and/or E . Orientations of individual ferroelectric domains as components of mechanical twins in each phase are given by unit-cell vectors $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ in a rectangular coordinate system $(X_1X_2X_3)$, and axes of this system are assumed to be parallel to the perovskite unit-cell vectors in the paraelectric cubic $Pm3m$ phase. These domains are separated by stress-free planar walls whose orientations are determined in accordance with results of works by Fousek and Janovec.²³ Four types of 71° (109°) domains of the rhombohedral phase are characterized by unit-cell vectors $(\mathbf{a}_{ri}, \mathbf{b}_{ri}, \mathbf{c}_{ri})$ and volume concentrations n_{ri} , where $i=1, 2, 3$, and 4. The vectors $(\mathbf{a}_{ri}, \mathbf{b}_{ri}, \mathbf{c}_{ri})$ are arranged by taking into account unit-cell

shear angles^{24,14} approximately along the following directions:²⁵ ([100], [010], [001]) ($i=1$), ($[\bar{1}00]$, [010], [00 $\bar{1}$]) ($i=2$), ([0 $\bar{1}0$], [$\bar{1}00$], [00 $\bar{1}$]) ($i=3$), and ([010], [$\bar{1}00$], [001]) ($i=4$). The volume concentrations of these domain types are described by two parameters,¹ $0 \leq u_r \leq 1$ and $0 \leq g_r \leq 1$, in accordance with formulas $n_{r1} = (1 - u_r)(1 - g_r)$, $n_{r2} = (1 - u_r)g_r$, $n_{r3} = u_r(1 - g_r)$, and $n_{r4} = u_r g_r$. In the tetragonal phase one can distinguish two types of 90° domains with unit-cell vectors (\mathbf{a}_{ij} , \mathbf{b}_{ij} , \mathbf{c}_{ij}) lying along ([100], [010], [001]) ($j=1$, volume concentration $0 \leq n_t \leq 1$) and ([010], [001], [100]) ($j=2$, volume concentration 1

$-n_t$). The monoclinic phase induced by the electric field $\mathbf{E} \parallel [OX_3] \parallel [001]$ is divided into four types of domains¹⁵ with unit-cell vectors (\mathbf{a}_{mk} , \mathbf{b}_{mk} , \mathbf{c}_{mk}), where $\mathbf{c}_{mk} \parallel [001]$ and $k = 1, 2, 3$, and 4 (Fig. 1). Volume concentrations of these domain types in the monoclinic phase are expressed¹ in terms of two parameters, $0 \leq f_m \leq 1$ and $0 \leq v_m \leq 1$, as follows: $n_{m1} = f_m v_m$, $n_{m2} = (1 - f_m)v_m$, $n_{m3} = f_m(1 - v_m)$, and $n_{m4} = (1 - f_m)(1 - v_m)$. According to definitions for distortions of the single-domain and polydomain regions,^{21,22} distortion matrices of the rhombohedral, tetragonal, and monoclinic phases are written as

$$\|\mathbf{N}_r\| = \begin{pmatrix} \mu_a & \mu(2g_r - 1) & \mu(2u_r - 1)(2g_r - 1) \\ \mu(2g_r - 1) & \mu_a & \mu(2u_r - 1) \\ \mu(2u_r - 1)(2g_r - 1) & \mu(2u_r - 1) & \mu_a \end{pmatrix}, \quad (1)$$

$$\|\mathbf{N}_t\| = n_t \begin{pmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_c \end{pmatrix} + (1 - n_t) \begin{pmatrix} \cos \varphi_t & 0 & -\sin \varphi_t \\ 0 & 1 & 0 \\ \sin \varphi_t & 0 & \cos \varphi_t \end{pmatrix} \begin{pmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_a \end{pmatrix}, \quad (2)$$

and

$$\|\mathbf{N}_m\| = v_m \begin{pmatrix} \eta_a & 0 & \eta(2f_m - 1) \\ 0 & \eta_b & 0 \\ 0 & 0 & \eta_c \end{pmatrix} + (1 - v_m) \begin{pmatrix} \cos \varphi_{ab} & -\sin \varphi_{ab} & 0 \\ \sin \varphi_{ab} & \cos \varphi_{ab} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \eta_b & 0 & 0 \\ 0 & \eta_a & \eta(2f_m - 1) \\ 0 & 0 & \eta_c \end{pmatrix}, \quad (3)$$

respectively. The unit-cell distortions from Eqs. (1)–(3) are expressed in terms of the unit-cell parameters a_r, ω_r of the rhombohedral phase, a_t, c_t of the tetragonal phase, a_m, b_m, c_m , and ω_m of the monoclinic phase, and a_0 of the cubic phase as follows: $\mu_a = a_r \cos \omega_r / a_0$, $\mu = a_r \sin \omega_r / a_0$, $\varepsilon_a = a_t / a_0$, $\varepsilon_c = c_t / a_0$, $\eta_a = a_m \cos \omega_m / a_0$, $\eta_b = b_m / a_0$, $\eta_c = c_m / a_0$, and $\eta = a_m \sin \omega_m / a_0$. The angles $\varphi_t = \arccos[2\varepsilon_a \varepsilon_c / (\varepsilon_a^2 + \varepsilon_c^2)]$ and $\varphi_{ab} = \arccos[2\eta_a \eta_b / (\eta_a^2 + \eta_b^2)]$ from Eqs. (2) and (3) are introduced in order to take into consideration a rotation of crystallographic axes^{6,20,21} of adjacent domains in the tetragonal phase or domain pairs in the monoclinic phase because $\varepsilon_a \neq \varepsilon_c$ or $\eta_a \neq \eta_b$, respectively.

The elastic matching of the coexisting polydomain phases along ZNSP's obeys conditions^{21,22}

$$\det \|\mathbf{D}\| = 0 \quad (4)$$

and

$$D'_{pq}{}^2 = D_{pq}^2 - D_{pp}D_{qq} \geq 0 \quad (p \neq q). \quad (5)$$

Matrix elements used in formulas (4) and (5) are written in the general form as

$$D_{pq} = \sum_{w=1}^3 (N_{pw}^{(2)} N_{qw}^{(2)} - N_{pw}^{(1)} N_{qw}^{(1)}), \quad (6)$$

where $N_{pw}^{(1)}$ and $N_{pw}^{(2)}$ are elements of the distortion matrices from Eqs. (1)–(3). Orientations of the interfaces separating the phases are described by normal vectors $\mathbf{n}_1(\mathbf{h}_1 \mathbf{k}_1 \mathbf{l}_1) \perp \mathbf{n}_2(\mathbf{h}_2 \mathbf{k}_2 \mathbf{l}_2)$, where the Miller indices represent ratios

$$\mathbf{h}_{1,2} = D_{11} / D_{1,2}, \quad \mathbf{k}_{1,2} = (D_{12} \pm D'_{12}) / D_{1,2},$$

$$\mathbf{l}_{1,2} = (D_{13} \pm D'_{13}) / D_{1,2}. \quad (7)$$

The ratios given by formulas (7) depend on the matrix elements from Eq. (6) as well as on their combinations, such as D'_{pq} from formula (5) and $D_{1,2} = [D_{11}^2 + (D_{12} \pm D'_{12})^2 + (D_{13} \pm D'_{13})^2]^{1/2}$. If at least one of the conditions (4) and (5) is not satisfied, the interfaces become strained and may be approximated by second-degree surfaces^{1,22} in a series of cases.

B. Results of calculations

Some interesting features of the elastic matching of the ferroelectric phases along the ZNSP's in PZN-PT single crystals are listed in Table I and below. Our calculations were made by using the room-temperature unit-cell data from papers by Noheda *et al.*¹⁵ (rhombohedral and monoclinic phases, $x=0.08$) and by Kuwata, Uchino, and Nomura²⁴ (tetragonal phase, $x \approx 0.09$).²⁷ Calculated field dependencies of

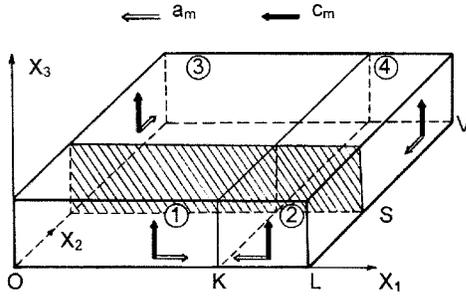


FIG. 1. Schematic arrangement of domains of the monoclinic phase induced by the electric field $\mathbf{E} \parallel [001]$ in $(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ single crystals. The directions of the unit-cell vectors \mathbf{a}_{mk} and \mathbf{c}_{mk} are marked by arrows. $f_m = |OK|/|OL|$ and $v_m = |LS|/|LV|$ are parameters determining the volume concentrations of the domain pairs (1,3) and (1,2), respectively. The (010) domain wall is shown as a shaded plane separating the domain pairs (1,2) and (3,4).

the optimal domain volume concentrations are characterized by slight sensitivity to changes in the above-mentioned concentration parameters u_r and g_r in the rhombohedral phase and f_m in the monoclinic one. Any variations of these parameters over a range $[0, 1]$ lead to changes in the calculated values of $v_{m,\text{opt}}$, $v'_{m,\text{opt}}$, $n_{t,\text{opt}}$, and $n'_{t,\text{opt}}$ up to 1% only. This circumstance is caused by a negligible influence of the shear unit-cell distortions of several domains on the elastic matching of the polydomain phases. Such influence is expressed in fairly small off-diagonal elements depending on u_r , g_r , or f_m and making the distortion matrices (1) and (3) whose elements are finally compared in accordance with formulas (4)–(6).

Table I contains two sets of values of the volume concentrations that range from 0 to 1. Their values were found without taking into account energy of the electrostatic interaction “domain field.” However, this interaction becomes very important in the tetragonal phase split into 90° domains with spontaneous polarization vectors $\mathbf{P}_{s1} \parallel OX_3$ and $\mathbf{P}_{s2} \parallel OX_1$. It implies that increasing the magnitude of the electric field E at the phase transition monoclinic \rightarrow tetragonal gives rise to a wide propagation of the domains with $\mathbf{P}_{s1} \parallel OX_3$, and such behavior corresponds to the calculated $n_{t,\text{opt}}(E)$ dependence only. Contrary to $n_{t,\text{opt}}(E)$, the $n'_{t,\text{opt}}(E)$ dependence is to be omitted because $n'_{t,\text{opt}} \rightarrow 0$ as the magnitude of the electric field E increases.

III. ROLE OF THE INTERMEDIATE MONOCLINIC PHASE IN HETEROPHASE STATES

A. PZN-PT single crystals under the electric field $\mathbf{E} \parallel [001]$

The results of our calculations of the optimal domain volume concentrations at the coexistence of the rhombohedral and monoclinic phases shed light on peculiarities^{15–17,28} of behavior of PZN-PT single crystals in the vicinity of $E = E_0 = 15$ kV/cm. As shown in Table I, optimal values $v_{m,\text{opt}} \approx 1$ and $v'_{m,\text{opt}} \approx 0$ correspond to a simplification of the domain structure in the monoclinic phase. Apparently, at $E \geq 15$ kV/cm crystal samples contain either domain pairs

(1,2) or (3,4) (see Fig. 1), and no displacements of (010) domain walls separating these pairs are expected. Due to the simplification of the domain structure the unit-cell vectors \mathbf{b}_{mk} are arranged to be parallel to either the OX_1 ($k=3,4$) or the OX_2 ($k=1,2$) axis all over the crystal sample. The above-mentioned domain-wall displacements at $E < E_0$ are accompanied by strains ξ_{pq}^i induced because of an inequality of unit-cell parameters $a_m \neq b_m$. Estimations based on formulas from Ref. 29, where the displacements of 90° domain walls in grains of ceramic BaTiO_3 were studied, result in induced strains $|\xi_{pq}^i| \leq (a_m - b_m)/b_m$. Taking into account experimental dependencies¹⁵ $a_m(E)$ and $b_m(E)$ we finally have $|\xi_{pq}^i(E_0)| \leq 0.6\%$ that is comparable with the piezoelectric strain $\xi_{33} \approx 0.5\%$ measured¹⁷ on PZN-PT single crystals with $x = 0.08$.

In our opinion, specific jumps²⁸ in the piezoelectric coefficient $d_{31}(E)$ and elastic compliance $s_{11}^E(E)$ at $E \approx E_0$ are also caused by the simplification of the domain structure in the monoclinic phase. The relative changes in the values of these constants are several times less than at the field-induced phase transition which was observed²⁸ at $E \approx (20 \cdot \dots 25)$ kV/cm. At the same time, no jump in the dielectric permittivity $\epsilon_{33}^\sigma(E)$ was experimentally registered at $E \approx E_0$, and it may be explained in terms of the unit-cell vectors. The above-mentioned simplification does not affect the arrangement of the unit-cell vectors \mathbf{c}_{mk} : in all the domains of the monoclinic phase it remains $\mathbf{c}_{mk} \parallel \mathbf{E} \parallel [001]$. The spontaneous polarization vector \mathbf{P}_{sk} of the domain of the k th type rotates⁹ from the $[101]$ to $[001]$ unit-cell direction so that an angle between \mathbf{P}_{sk} and \mathbf{E} remains constant for $k=1, 2, 3$, and 4 and $E = \text{const}$. As a consequence, the dielectric response of each domain will be equal along the OX_3 axis at $E \approx E_0$.

It should be pointed out that appreciable changes in the strain-field loop $\xi_{33}(E)$ (Ref. 17) and the unit-cell parameter $c_m(E)$ (Ref. 15) are also observed in a vicinity of $E = E_0$. At $E \geq E_0$ and increasing the magnitude of the field, the $\xi_{33}(E)$ dependence is characterized by a considerable decrease in the slope that leads to a nonmonotonic field dependence of the piezoelectric coefficient $d_{33}(E) = d\xi_{33}(E)/dE$.³⁰ The coexistence of the rhombohedral and monoclinic phases in PZN-PT single crystals is to be considered together with the jump in $c_m(E)$ (Ref. 15) because of drastic changes in the matrix element $N_{m,33}$ from Eq. (3). This matrix element influences a set of elements D_{pq} from Eq. (6) and, therefore, leads to a redistribution of the stress field in the crystal sample. It is believed that such behavior of the unit-cell distortions and internal stress fields is consistent with results by Viehland³¹ on the jump in the unit-cell parameter c_m .

The coexistence of the monoclinic and tetragonal phases at $E=0$ was earlier postulated by Durbin *et al.*¹⁶ According to our current evaluations for $E \geq 0$ (see Table I), the ZNSP's are realized in both cases, i.e., when the new tetragonal or monoclinic phase appears. The ZNSP's corresponding to the phase transition tetragonal \rightarrow monoclinic at $E \approx 20$ kV/cm can take place if the optimal values of the parameters of the domain volume concentration in the monoclinic phase obey a condition

TABLE I. Elastic matching of phases in $(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ solid solutions. The electric-field vector \mathbf{E} is parallel to the perovskite unit-cell direction $[001]$.

Coexisting phases	$(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$			$\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, Ref. 20						
	x	E (kV/cm)	Optimal domain volume concentrations corresponding to elastic matching along ZNSP's	x	T (K)	Optimal domain volume concentrations corresponding to elastic matching along ZNSP's				
Rhombohedral and tetragonal	0.09	0	$n_{t,\text{opt}}=0.620$ or $n'_{t,\text{opt}}=0.380^{\text{a}}$	0.45	550	$n_{t,\text{opt}}=0.691$ or $n'_{t,\text{opt}}=0.309^{\text{b}}$				
					500	$n_{t,\text{opt}}=0.698$ or $n'_{t,\text{opt}}=0.302$				
Rhombohedral and monoclinic	0.08	0	$v_{m,\text{opt}}=0.775$ or $v'_{m,\text{opt}}=0.225^{\text{c}}$	0.45	300	$n_{m,\text{opt}}=0.700$ or $n'_{m,\text{opt}}=0.300^{\text{d}}$				
					5	$v_{m,\text{opt}}=0.801$ or $v'_{m,\text{opt}}=0.199$	20	$n_{m,\text{opt}}=0.724$ or $n'_{m,\text{opt}}=0.276$		
					10	$v_{m,\text{opt}}=0.873$ or $n'_{m,\text{opt}}=0.127$	0.46			
					15	$v_{m,\text{opt}}=0.980$ or $v'_{m,\text{opt}}=0.020$				
					20	$v_{m,\text{opt}}>1$ or $v'_{m,\text{opt}}<0$, i.e., no ZNSP's are possible				
Monoclinic and tetragonal	0.08	0	Monoclinic \rightarrow tetragonal	0.46	400	$n_{t,\text{opt}}=1$ and $n_{m,\text{opt}}=1$ or $n'_{t,\text{opt}}=0$ and $n'_{m,\text{opt}}=0^{\text{f}}$				
							5	$n_{t,\text{opt}}=0.461$ or $n'_{t,\text{opt}}=0.539$		
	0.09	10								
								15	$n_{t,\text{opt}}=0.519$ or $n'_{t,\text{opt}}=0.481$	
								15	$n_{t,\text{opt}}=0.588$ or $n'_{t,\text{opt}}=0.412$	
								20	$n_{t,\text{opt}}=0.762$ or $n'_{t,\text{opt}}=0.238$	
								30 . . . 35	$n_{t,\text{opt}}\approx 1$ or $n'_{t,\text{opt}}\approx 0$	
								Tetragonal \rightarrow monoclinic		
								20	$v_{m,\text{opt}}=0.429$ or $v'_{m,\text{opt}}=0.571^{\text{g}}$	
								15	$v_{m,\text{opt}}=0.274$ or $v'_{m,\text{opt}}=0.726$	
10	$v_{m,\text{opt}}=0.245$ or $v'_{m,\text{opt}}=0.755$									
5	$v_{m,\text{opt}}=0.224$ or $v'_{m,\text{opt}}=0.776$									
0	$v_{m,\text{opt}}=0.217$ or $v'_{m,\text{opt}}=0.783$									

^aResults of calculations for $u_r=g_r=0$ or $u_r=g_r=1$ before the discovery of the field-induced monoclinic phase, see Ref. 26.

^bResults of calculations for $u_r=g_r=0$.

^cResults of calculations for $u_r=g_r=\frac{1}{2}$ and $f_m=\frac{1}{2}$.

^dIn the monoclinic phase there are domains with the unit-cell vectors (\mathbf{a}_{mk} , \mathbf{b}_{mk} , \mathbf{c}_{mk}) having approximate orientations ($[110]$, $[\bar{1}10]$, $[001]$) and ($[011]$, $[01\bar{1}]$, $[100]$) and volume concentrations n_m and $1-n_m$, respectively. The orientation of the unit-cell vectors in the rhombohedral phase corresponds to $u_r=g_r=0$.

^eResults of calculations for $v_m=1$ and $f_m=\frac{1}{2}$.

^fOnly single-domain phases are elastically matched along the ZNSP's.

^gResults of calculations for $n_t=1$ and $f_m=\frac{1}{2}$.

$$v_{m,\text{opt}}\approx v'_{m,\text{opt}}\approx \frac{1}{2}. \quad (8)$$

It is more likely that the domain arrangement, shown in Fig. 1 and satisfying Eq. (8) and condition $f_{m,\text{opt}}\approx 1/2$, corresponds to pseudotetragonal symmetry as mentioned by Noheda *et al.*¹⁵

B. Comparison of heterophase states in PZN-PT and PZT solid solutions

Our earlier results²⁰ on the optimal domain volume concentrations in the PZT system are listed in Table I for com-

parison and generalization. Unit-cell parameters' behavior over the x and T ranges close to the morphotropic phase boundary does not give rise to considerable differences between the optimal domain volume concentrations at the rhombohedral-tetragonal phase coexistence and the optimal domain volume concentrations at the rhombohedral-monoclinic phase coexistence. This fact is in agreement with concepts⁹ on the polarization rotation path linking the $[111]$ and $[001]$ perovskite unit-cell directions by the shortest way, i.e., when the spontaneous polarization vector of the intermediate monoclinic phase in PZT is parallel to $[\mathbf{hh}1]$. Appar-

ently, the fairly simple “transition” $[\mathbf{hh}1] \rightarrow [001]$ does not result in striking differences between the related linear unit-cell distortions of the monoclinic and tetragonal phases, and, as a consequence, a condition $n_{r,\text{opt}} \approx n_{m,\text{opt}}$ holds true.

The rhombohedral-tetragonal phase coexistence in PZT and PZN-PT (Ref. 26) solid solutions at $E=0$ is characterized by approximately equal $n_{t,\text{opt}}$ and $n'_{r,\text{opt}}$ values. The elastic matching of these phases in both the systems is associated with the similar anisotropy of the unit-cell spontaneous strains $\xi_{11,t^s} = \varepsilon_a - 1$ and $\xi_{33,r^s} = \varepsilon_c - 1$ in the tetragonal phase and with the slight effect of the rhombohedral shear unit-cell spontaneous strains $\xi_{pq,r^s} = \mu$ [see Eqs. (1) and (2)] on the internal stress field. The electric field $\mathbf{E} \parallel [001]$ applied to monoclinic PZN-PT samples affects their unit-cell parameters¹⁵ and, undoubtedly, the anisotropy of the unit-cell spontaneous strains $\xi_{11,m^s} = \eta_a - 1$, $\xi_{22,m^s} = \eta_b - 1$, and $\xi_{33,m^s} = \eta_c - 1$ [see Eq. (3)]. The effect of the electric field on the coexistence of the monoclinic and adjacent phases in PZN-PT consists of changes in domain structures and internal electric and elastic fields, and these changes promote the formation of ZNSP's.

At $E \rightarrow 0$, revealed is an interesting link between the optimal volume concentrations of domain pairs of the monoclinic phase of PZN-PT. As shown in Table I, the $v_{m,\text{opt}}$ and $v'_{m,\text{opt}}$ values at the rhombohedral-monoclinic phase coexistence are practically equal to $v'_{m,\text{opt}}$ and $v_{m,\text{opt}}$, respectively, where the two last values are related to the monoclinic-tetragonal phase coexistence. In both cases the phase coexisting with the monoclinic phase is assumed to be single domain. The above-mentioned values of the optimal volume concentrations are solutions of Eq. (4) and obey the following conditions written in terms of elements of the distortion matrices (1)–(3):

$$\begin{aligned} N_{m,11}(v_{m,\text{opt}}) &\approx N_{r,11}, & N_{r,1q} &\rightarrow 0, \\ N_{m,1q}(v_{m,\text{opt}}) &\rightarrow 0 \quad (q=1,3) \end{aligned} \quad (9)$$

or

$$\begin{aligned} N_{m,22}(v'_{m,\text{opt}}) &\approx N_{r,22}, & N_{r,2q} &\rightarrow 0, \\ N_{m,2q}(v'_{m,\text{opt}}) &\rightarrow 0 \quad (q=2,3) \end{aligned} \quad (10)$$

for the rhombohedral-monoclinic phase coexistence or

$$\begin{aligned} N_{m,11}(v_{m,\text{opt}}) &\approx N_{t,11}, & N_{t,1q} &\rightarrow 0, \\ N_{m,1q}(v_{m,\text{opt}}) &\rightarrow 0, \quad (q=1,3) \end{aligned} \quad (11)$$

or

$$\begin{aligned} N_{m,22}(v'_{m,\text{opt}}) &\approx N_{r,22}, & N_{t,2q} &\rightarrow 0, \\ N_{m,2q}(v'_{m,\text{opt}}) &\rightarrow 0 \quad (q=2,3) \end{aligned} \quad (12)$$

for the monoclinic-tetragonal phase coexistence. Conditions (9) and (11) correspond to a significant reduction in strains

induced in the two-phase sample along the OX_1 axis whereas conditions (10) and (12) correspond to the like reduction along the OX_2 axis.

To our best knowledge, links similar to $v_{m,\text{opt}} \leftrightarrow v'_{m,\text{opt}}$ were not mentioned in earlier papers on the elastic matching of phases in ferroelectrics and related materials. The change in the $v_{m,\text{opt}}$ and $v'_{m,\text{opt}}$ values implies mechanical switching of domain regions with $\mathbf{b}_{\text{mk}} \parallel [100]$ and $\mathbf{b}_{\text{mk}} \parallel [010]$ or with spontaneous polarization vectors lying in the (100) and (010) planes, respectively. A rotation of the spontaneous polarization vector \mathbf{P}_{sk} of the domain of the k th type occurs in PZN-PT along the rhombohedral-tetragonal path^{9,15} $[111] \rightarrow [101] \rightarrow [x0z] \rightarrow [001]$. The last sequence of the perovskite unit-cell distortions really corresponds to the pass of \mathbf{P}_{sk} from the (100) into the (010) plane and testifies to the correlation between the elastic matching of phases and the polarization rotation path of the individual domain.

Finally, the Miller indices (7) of the interfaces were evaluated for both systems of solid solutions in the vicinity of the morphotropic phase boundary. Despite different orientations of the unit-cell vectors $(\mathbf{a}_{\text{mk}}, \mathbf{b}_{\text{mk}}, \mathbf{c}_{\text{mk}})$ in the monoclinic phases of PZT (Refs. 13, 14 and 20) and PZN-PT (Ref. 15) as well as the specifics of domain structures in these phases, the ZNSP's orientations are approximated by the Miller indices $\{0kl\}$ in the perovskite axes. This result is true for all the optimal domain volume concentrations provided that their values belong to the range $[0,1]$ (see Table I). A detailed description of the evolution of the interfaces in polydomain PZN-PT single crystals under the electric field is of independent interest and may be carried out in the future.

IV. CONCLUSION

The present study of the elastic matching of phases in ferroelectric perovskite-type solid solutions has provided a better understanding of the features of various heterophase states in the vicinity of the morphotropic phase boundary. The current results of prognostication of different ZNSP's at the two-phase coexistence over certain (x,E) or (x,T) ranges suggest the following.

First, unit-cell parameters' behavior predetermines the outcome of the formation of various domain and heterophase structures. Information about these structures is very important for the interpretation of experimental results by Noheda *et al.*,¹⁵ Durbin *et al.*,^{16,17} and Paik *et al.*²⁸ In particular, the effect of the simplification of the domain structure in the monoclinic phase of PZN-PT single crystals on their electromechanical behavior at $E \approx 15$ kV/cm as well as the possibilities of completely relieving stress in two-phase states at $0 \leq E \leq 20$ kV/cm have no analogy with other known ferroelectrics. The link between the optimal domain volume concentrations of the monoclinic phase at the phase coexistence in PZN-PT and the slight differences between the optimal domain volume concentrations at the phase coexistence in PZT are successfully explained on the basis of concepts by Fu and Cohen.⁹

Second, proposed are different versions of the elastic matching of the single-domain and/or polydomain phases in PZN-PT single crystals under the electric field (see Table I),

and this subject is believed to be a good stimulus for further experimental studies. Third, despite structural distinctions,^{14,15} the monoclinic phases appearing as the intermediate ones close to the morphotropic phase boundaries favor the elastic matching along the ZNSP's in both systems of perovskite-type solid solutions.

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