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## LETTER TO THE EDITOR

## A new monoclinic phase and features of stress relief in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ solid solutions

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### Abstract

We analyse the possibilities of elastic matching and effective internal stress relief at the coexistence of polar phases in ferroelectric  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  compositions close to the morphotropic phase boundary. The important role of the polydomain (twinned) monoclinic phase in this stress relief over wide concentration and temperature ranges is discussed. A new link between phase boundaries in the phase diagram, reported by Noheda *et al* (Noheda B, Cox D E, Shirane G, Guo R, Jones B and Cross L E 2001 *Phys. Rev. B* **63** 014103), and optimal domain volume concentrations, calculated in the present work, is revealed.

In recent experimental studies [1–3] of the ferroelectric  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PZT) system, great emphasis is placed on the existence of a new monoclinic phase with the symmetry group  $Cm$ , which is a subgroup of both the tetragonal  $P4mm$  and rhombohedral  $R3m$  groups [4]. As follows from high-resolution synchrotron x-ray powder diffraction measurements [3] on a series of highly homogeneous PZT samples, the  $Cm$  phase is stable over certain ranges of molar concentration  $x$  and temperature  $T$ , and phase coexistence over a fairly wide  $T$ -range is typical of various compositions (for example, at  $x = 0.45, 0.46, 0.51$ ). Despite complex structural studies and the presentation of a new PZT phase diagram [3], questions regarding an elastic interaction between the ferroelectric phases and the effectiveness of internal stress relief have not yet been resolved and are of independent interest. Furthermore, the lack of PZT single crystals grown over a wide  $x$ -range remains a barrier to the understanding of the features of the phase coexistence and electromechanical behaviour around the morphotropic phase boundary. The purpose of the present work is to shed light on the elastic matching of the phases in PZT solid solutions and to indicate the role of the  $Cm$  phase in such matching.

The concept of the zero-net-strain plane (ZNSP) was earlier applied [5] for description of the first-order tetragonal–rhombohedral phase transition in PZT. We analysed interfaces separating the polydomain  $P4mm$  phase (two types of  $90^\circ$  domain, i.e. mechanical twins) and the single-domain or polydomain  $R3m$  phase (up to four types of  $71^\circ$  ( $109^\circ$ ) domain which are

mechanical twins). It was shown that the unit-cell parameters of the  $P4mm$  and  $R3m$  phases, coexisting in different compositions, obey conditions [5, 6] for ZNSPs despite differences in processing.

In the present work we study the elastic matching of the phases in PZT solid solutions whose unit-cell parameters were determined in the recent experimental work [3]. Consider a single crystal or an individual ceramic grain which is supposed to be diphasic, i.e. undergoing one of the following three first-order phase transitions:  $P4mm-R3m$ ,  $P4mm-Cm$ , and  $R3m-Cm$ . Introduce a rectangular coordinate system  $(X_1, X_2, X_3)$  whose axes are parallel to the axes of the perovskite unit cell in the paraelectric  $Pm3m$  phase. Single-domain states of the above-mentioned ferroelectric phases are associated with unit-cell vectors  $(a, b, c)$  that are oriented by taking into account the shear [2] and rotation [5, 6] angles along certain directions of the coordinate system  $(X_1, X_2, X_3)$ . So, in the  $P4mm$  phase we distinguish the  $90^\circ$  domains with  $(a_t, b_t, c_t)$  lying along  $([100], [010], [001])$  and  $([010], [001], [100])$  and having volume concentrations  $n_t$  and  $1 - n_t$ , respectively. The  $R3m$  phase can be split into  $71^\circ$  ( $109^\circ$ ) domains, and one of the four types of such adjacent domains is described by the vectors  $(a_r, b_r, c_r)$  which are approximately oriented as  $([100], [010], [001])$ . In the  $Cm$  phase there are domains with vectors  $(a_m, b_m, c_m)$  having approximate orientations  $([110], [1\bar{1}0], [001])$  and  $([011], [01\bar{1}], [100])$  and volume concentrations  $n_m$  and  $1 - n_m$ , respectively. In accordance with the definitions of distortions of the unit cells, domain (twinned) regions, or polydomain phases [5–7], the distortion matrices of the  $P4mm$ ,  $R3m$ , and  $Cm$  phases may be written as

$$\|N_t\| = n_t \begin{pmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_c \end{pmatrix} + (1 - n_t) \begin{pmatrix} \cos \varphi_t & 0 & -\sin \varphi_t \\ 0 & 1 & 0 \\ \sin \varphi_t & 0 & \cos \varphi_t \end{pmatrix} \begin{pmatrix} \varepsilon_c & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_a \end{pmatrix} \quad (1)$$

$$\|N_r\| = \begin{pmatrix} \mu_a & \mu & \mu \\ \mu & \mu_a & \mu \\ \mu & \mu & \mu_a \end{pmatrix} \quad (2)$$

and

$$\|N_m\| = n_m \begin{pmatrix} \eta_a & \eta_{ab} & \eta_{ac} \\ \eta_{ab} & \eta_b & \eta_{bc} \\ \eta_{ac} & \eta_{bc} & \eta_c \end{pmatrix} + (1 - n_m) \begin{pmatrix} \cos \varphi_m & 0 & -\sin \varphi_m \\ 0 & 1 & 0 \\ \sin \varphi_m & 0 & \cos \varphi_m \end{pmatrix} \begin{pmatrix} \eta_c & -\eta_{bc} & -\eta_{ac} \\ -\eta_{bc} & \eta_b & \eta_{ab} \\ -\eta_{ac} & \eta_{ab} & \eta_a \end{pmatrix} \quad (3)$$

respectively. The unit-cell distortions  $\varepsilon_a, \varepsilon_c$  from equation (1),  $\mu_a, \mu$  from equation (2), as well as  $\eta_a, \eta_b, \eta_c, \eta_{ab}, \eta_{ac}$ , and  $\eta_{bc}$  from equation (3) are written in terms of the unit-cell parameters of the ferroelectric phases considered and the paraelectric  $Pm3m$  phase. The distortion matrix of the  $Pm3m$  phase is assumed to be a unit matrix. The angles

$$\varphi_t = \arccos[2\varepsilon_a\varepsilon_c/(\varepsilon_a^2 + \varepsilon_c^2)] \quad \varphi_m = \arccos[2\eta_a\eta_c/(\eta_a^2 + \eta_c^2)]$$

are introduced in equations (1) and (3), respectively, which enables us to take into consideration a rotation of crystallographic axes [6, 7] of the adjacent domains in the  $(X_1OX_3)$  plane, because  $\varepsilon_a \neq \varepsilon_c$  in the  $P4mm$  phase and  $\eta_a \neq \eta_c$  in the  $Cm$  phase.

In order to analyse the possibilities of elastic matching of the coexisting phases, their distortion matrices (1)–(3) are taken in pairs and substituted into formulae [5, 6]. According to these formulae the elastic matching along ZNSPs obeys the conditions

$$\det \|D\| = 0 \quad (4)$$

and

$$D'_{ij} = D_{ij}^2 - D_{ii}D_{jj} \geq 0 \quad (i \neq j). \quad (5)$$

The matrix elements used in formulae (4) and (5)

$$D_{ij} = \sum_{k=1}^3 (N_{ik}^{(2)} N_{jk}^{(2)} - N_{ik}^{(1)} N_{jk}^{(1)}) \quad (6)$$

are defined as sums of differences between second powers of the distortion matrix elements. For example,  $\|N^{(1)}\| = \|N_m\|$  and  $\|N^{(2)}\| = \|N_t\|$  for the elastic interaction of the *Cm* and *P4mm* phases. Interfaces oriented along ZNSPs are described by normal vectors  $\mathbf{n}_1(h_1k_1l_1) \perp \mathbf{n}_2(h_2k_2l_2)$  in the coordinate system ( $X_1, X_2, X_3$ ) where

$$h_{1,2} = D_{11}/D_{1,2} \quad k_{1,2} = (D_{12} \pm D'_{12})/D_{1,2} \quad l_{1,2} = (D_{13} \pm D'_{13})/D_{1,2} \quad (7)$$

and

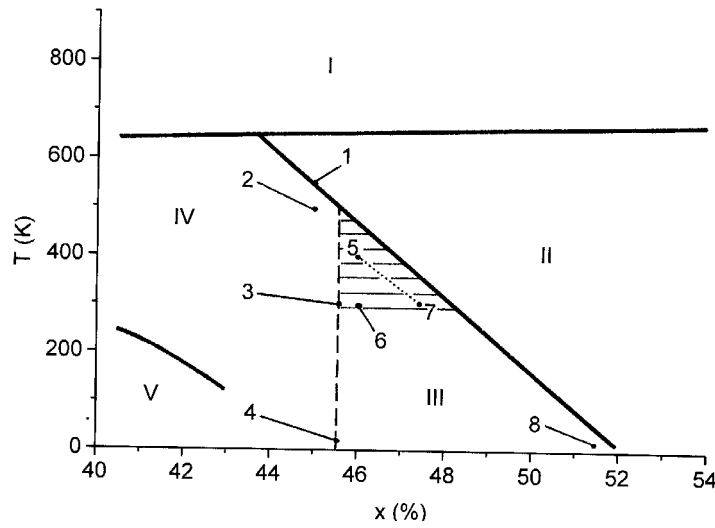
$$D_{1,2} = [D_{11}^2 + (D_{12} \pm D'_{12})^2 + (D_{13} \pm D'_{13})^2]^{1/2}.$$

If conditions (4) and (5) are not satisfied, the interfaces are strained and approximated by second-degree surfaces in a series of cases. A further description of such surfaces is obtained, in accordance with the results from [5, 7].

Our study of the elastic interaction of the above-mentioned phases in the PZT system produced table 1 and figure 1. Unit-cell behaviour provides the elastic matching of the ferroelectric phases for complete (i.e. along ZNSPs) or very considerable stress relief. Orientations of the corresponding interfaces are determined according to formulae (4)–(7) with perovskite axes as  $\{0kl\}$ . Our calculations show that the slightly strained interfaces separating practically

**Table 1.** Elastic matching of phases in  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  solid solutions. All unit-cell parameters used for calculations were taken from experimental data [3]. Optimal domain volume concentrations given in the fifth column were calculated by using formulae deduced from equation (4) consistently with condition (5).

Coexisting phases	$x$	$T$ (K)	Distortion matrices	Optimal domain volume concentrations corresponding to the elastic matching along ZNSPs	Conditions for slightly strained interfaces (if no ZNSPs are determined)	Points in figure 1
<i>P4mm, R3m</i>	0.45	550	(1), (2)	$n_{t,opt} = 0.691$ or $n'_{t,opt} = 0.309$	—	1
		500		$n_{t,opt} = 0.698$ or $n'_{t,opt} = 0.302$	—	2
<i>R3m, Cm</i>	0.45–0.46	300	(2), (3)	$n_{m,opt} = 0.700$ or $n'_{m,opt} = 0.300$	—	3
		20		$n_{m,opt} = 0.724$ or $n'_{m,opt} = 0.276$	—	4
<i>P4mm, Cm</i>	0.46	400	(1), (3)	$n_{t,opt} = 1, n_{m,opt} = 1$ or $n'_{t,opt} = 0, n'_{m,opt} = 0$	—	5
		300		—	$n_t \rightarrow 1, n_m \rightarrow 1$ or $n'_t \rightarrow 0, n'_m \rightarrow 0$	6
	0.47–0.48	300		$n_{t,opt} = 1, n_{m,opt} = 1$ or $n'_{t,opt} = 0, n'_{m,opt} = 0$	—	7
	0.51–0.52	20		—	$n_t \rightarrow 1, n_m \rightarrow 1$ or $n'_t \rightarrow 0, n'_m \rightarrow 0$	8



**Figure 1.** A fragment of the  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  phase diagram [3] around the morphotropic phase boundary. I, II, III, IV, and V denote the  $Pm\bar{3}m$ ,  $P4mm$ ,  $Cm$ ,  $R3m$ , and  $R3c$  phases, respectively, the shaded area represents the region of the coexistence of the  $P4mm$  and  $Cm$  phases. Points 1–8 correspond to different variants of the elastic matching of the adjacent single-domain or polydomain phases in accordance with results of our calculations from table 1.

single-domain phases (see points 6 and 8 in figure 1) can be either planar boundaries [8] or conical surfaces [5] with negligibly small curvature. Absolute values of the corresponding internal stresses appearing at such phase coexistence become orders of magnitude lower than  $c_{fgij}^E |\xi_{ij}^s|$  where  $c_{fgij}^E$  are elastic moduli of the single-domain crystal which are measured at the electric field  $E = \text{constant}$ ,  $\xi_{ij}^s$  are spontaneous strains of the coexisting single-domain phases. Because of the lack of experimental data on elastic properties of the PZT single-domain crystals, known experimental values of elastic moduli of the related perovskite single-domain  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  crystals [9] are taken for these estimations.

The unique constancy of the optimal volume concentrations  $n_{t,opt}$  and  $n_{m,opt}$  (or  $n'_{t,opt}$  and  $n'_{m,opt}$ , respectively) and the various ZNSPs at the 'single-domain  $R3m$  phase–polydomain  $P4mm$  phase' and 'single-domain  $R3m$  phase–polydomain  $Cm$  phase' interfaces are realized over a narrow concentration range ( $\Delta x \approx 0.01$ ) and a very wide temperature range ( $\Delta T > 500$  K) (see table 1). In both cases of phase coexistence, complete stress relief depends on the domains (twins) of the  $P4mm$  and  $Cm$  phases being characterized by similar anisotropies of their spontaneous strains. However, splitting the  $R3m$  phase into  $71^\circ$  ( $109^\circ$ ) domains<sup>1</sup> does not break the established constancy of the volume concentrations: the  $n_{t,opt}$ ,  $n'_{t,opt}$ ,  $n_{m,opt}$ , and  $n'_{m,opt}$ , calculated by using the matrices from equation (1) and  $\|N_r^*\|$ , deviate from the corresponding values given in table 1 by less than 1%. The  $n'_{t,opt}$ -values, corresponding to the ZNSPs at the  $P4mm$ – $R3m$  phase transition, are in good agreement with our earlier evaluations [5], which used unit-cell parameters measured on different PZT ceramic samples long before

<sup>1</sup> In this case the distortion matrix from equation (2) is modified and written as

$$\|N_r^*\| = \begin{pmatrix} \mu_a & N_{12,r} & N_{13,r} \\ N_{12,r} & \mu_a & N_{23,r} \\ N_{13,r} & N_{23,r} & \mu_a \end{pmatrix}$$

where the off-diagonal elements  $N_{ik,r} = \mu f_{ik}$ , the  $f_{ik}$  are functions of volume concentrations of the  $71^\circ$  ( $109^\circ$ ) domains (see, e.g., reference [7]), and  $-1 \leq f_{ik} \leq 1$ .

the discovery of the  $Cm$  phase [1–3]. It should also be added that earlier experimental studies of the coexistence of the  $P4mm$  and  $R3m$  phases were carried out [10] on grains of  $PbZr_{0.53}Ti_{0.47}O_3$  ceramics. The authors of [10] came to the conclusion that  $90^\circ$  domain structures developed within the grains, and proposed a model of the adjacent domains of the coexisting phases. According to this model, the coexistence region is characterized as a laminated structure of domains whose unit-cell vectors form a sequence [010], [111], [001], [111], [010], [111], ... (i.e. the  $P4mm$  and  $R3m$  phases alternate). The presence of such  $90^\circ$  domains (orientations [010] and [001] for perovskite axes) attests to their leading role in stress relief at the  $P4mm$ – $R3m$  phase coexistence.

The similarity of the anisotropies of the unit-cell spontaneous strains is finally revealed at the morphotropic phase boundary, i.e. at the  $Cm$ – $P4mm$  boundary in the PZT phase diagram proposed by Noheda *et al* [3]. Our results show that the  $Cm$  and  $P4mm$  phases remain practically single domain for elastic matching along the ZNSPs or slightly strained interfaces, and this effect occurs over wide concentration and temperature ranges (see table 1). It should be noted that the line linking points 5 and 7 (figure 1) and corresponding to the ZNSPs at the coexistence of the  $Cm$  and  $P4mm$  phases is oriented practically parallel to the  $Cm$ – $P4mm$  phase boundary found in reference [3]. It is reasonable to expect these interesting features of the elastic matching at phase coexistence in PZT solid solutions to be subjects of further experimental study. For the present, the data from table 1 agree with suppositions [3] regarding the active role of non- $180^\circ$  domains in stress relief at the coexistence of the ferroelectric phases in PZT and indicate additional possibilities of elastic matching of the single-domain phases. The results of our present study demonstrate the importance of the role of the new monoclinic phase, providing very favourable conditions for elastic matching in the vicinity of the morphotropic phase boundary.

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