

Magnetic-field- and alloying-induced wetting of the ferroelectric domain structure in some smart materials

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Wetting of the ferroelectric domain walls is studied in external magnetic fields and for composition changes in (Ba,Sr)TiO₃ and Pb(Zr,Ti)O₃. We discuss the sensibility of a domain structure to concentration of alloying element in perovskite ferroelectrics. A considerable magnetic-field- and concentration-induced variation of the ferroelectric domain size and the paraelectric layer width is demonstrated. The concentration-temperature ‘‘phase diagram’’ showing the range of the wetting existence is calculated. [S0163-1829(99)51634-2]

Smart materials feature appropriately configured actuators, sensors, and control algorithms which enable materials to respond autonomously to external stimuli.¹ They have the ability to modify their band structure or the domain structure, in response to an external change, such as temperature, hydrostatic pressure, and electric or magnetic field. Phase transition is a common feature of most widely used functionally smart materials. It arises from a change in the external environment leading to a change in the property parameters of the materials. With a change of temperature, pressure, external fields, or composition a solid phase may be wet by another solid phase.² In ferroelectrics two-domain regions of opposite polarization may exist and a paraelectric phase can wet domain walls in a ferroelectric phase below a first-order phase transition.³ In this communication we show that domain-structure wetting can be produced by composition sampling or by an external magnetic field in smart materials of the perovskite type. The ferroelectric state in perovskites may be governed by alloying or by an external magnetic field.⁴⁻⁷ We consider ferroelectric perovskites as candidates for wetting of domain walls: Ba_{1-n}Sr_nTiO₃ (BST) and PbZr_nTi_{1-n}O₃ (PZT), n is the atomic fraction of the component of the solid solution. Their properties were shown to be well described in terms of the Landau free-energy density expansion:^{8,9}

$$f = f_0 + \frac{1}{2}AP^2 - \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + f', \quad (1)$$

where f_0 is the free-energy density in the paraelectric phase, f' contains terms depending on an external electric and/or magnetic field. For $B > 0$ and $C > 0$ Eq. (1) describes a first-order phase transition in zero external electric field. $A = A'(T - T_0)$, where T_0 is the temperature of the stability limit of the paraelectric phase, differing from the transition temperature T_c . The magnetic field H cannot affect elastic

strains because of the absence of magnetostriction in the material. Therefore it does not change the order of the phase transition but shifts its temperature.⁸ The magnetic-field shift of the phase transition occurs due to the magnetoelectric effect^{6,7} and its field dependence is described by the sum of the quadratic and quartic power terms in H according to experimental data:⁶ $f' = -\frac{1}{2}gP^2H^2 - \frac{1}{2}hP^2H^4$, where $A'CG/B^2 = 6.27 \times 10^{-4} \text{ KT}^{-2}$, $A'Ch/B^2 = 6.28 \times 10^{-7} \text{ KT}^{-4}$, where g and h are magnetoelectric coefficients. The sign of the shift of the phase transition in BaTiO₃ (Ref. 6) and in KTaO₃ (Ref. 7) is determined by the fact that the increase of the magnetic field leads to the increase of the transition temperature. For further calculations we use the following experimental data: in BST— $A'(n=0) = 7.41 \times 10^{-5} \text{ K}$,⁸ $B(n=0) = 6.8 \times 10^{-13} \text{ cm sec/g}$,⁸ $C = 2.28 \times 10^{-22} \text{ cm}^2 \text{ sec}^4$,⁸ $n_t = 0.6$,⁸ $dT_0/dn = -358 \text{ K/n}_{\text{Sr}}$,⁸ $D = 3.35 \times 10^{-16} \text{ cm}^2$,⁹ in PZT— $dT_0/dn = 333 \text{ K/n}_{\text{Ti}}$, $(A'C/B^2)_0 = 3.37 \times 10^{-3}$,¹⁰ $(C/B^2)_0 [d(B^2/C)/dn] = 16.84 \text{ K}^{-1}/n_{\text{Ti}}$.¹⁰ According to the experiment^{8,10} A', B, C are linear functions of n in the concentration range under consideration. Consequently, we explicitly include the composition dependence into the free-energy density expansion in Eq. (1), where we assume, according to,^{8,10} that

$$A' = A'(0) + \left(\frac{dA'}{dn} \right)_0 n;$$

$$B(n) = B(0) + \left(\frac{dB}{dn} \right)_0 n = b(n_t - n),$$

which implies $B(0) = bn_t$, n_t is the tricritical concentration, and $(dB/dn)_0 = -b$,

$$C(n) = C(0) + \left(\frac{dC}{dn} \right)_0 n; \quad T_0(n) = T_0(0) + \left(\frac{dT_0}{dn} \right)_0 n.$$

The wetting phenomenon induced by alloying or by applying external magnetic field should start in the range of coexistence of the two phases on approaching the tricritical point.¹¹ The free energy is as follows:

$$F = \int [f + D(\nabla \vec{P})^2] dV, \quad (2)$$

where D is the positive coefficient of the inhomogeneity term. The variation of polarization across a domain wall is obtained by minimization of the functional (2) and by solving the Euler-Lagrange equation:

$$\frac{\partial^2 P}{\partial x^2} - \frac{\partial f}{\partial P} = 0. \quad (3)$$

The profile of the ferroelectric domain wall at a first-order phase transition is given by¹²

$$P = \frac{P_0 \sinh(x/\Delta)}{[k + \cosh^2(x/\Delta)]^{1/2}}, \quad (4)$$

where Δ is the domain wall width, k and the equilibrium value of polarization P_0 are given by

$$\Delta = \frac{2}{B} \left[\frac{2DC}{1 - 4\alpha + (1 - 4\alpha)^{1/2}} \right]^{1/2}, \quad (5)$$

$$P_0^2 = \left(\frac{B}{2C} \right) [1 + (1 - 4\alpha)^{1/2}]; \quad \alpha = \alpha(n, H, T), \quad (6)$$

$$k = \frac{1 + (1 - 4\alpha)^{1/2}}{-1 + 2(1 - 4\alpha)^{1/2}}. \quad (7)$$

Equation (4) is a solution of Eq. (3) for boundary conditions

$$\lim_{x \rightarrow \pm\infty} P = P_0, \quad \lim_{x \rightarrow \pm\infty} \frac{dP}{dx} = 0. \quad (8)$$

In the tricritical point according to Ref. 13, the shape of the domain wall is

$$P = P_0 \frac{1}{\left[\frac{3}{2} \coth^2(x/\Delta) - \frac{1}{2} \right]^{1/2}}. \quad (9)$$

Equation (9) converts to Eq. (4), when $k = \frac{1}{2}$, $P_0 = \sqrt[4]{(A/C)}$, and $\Delta = \sqrt{(2D/A)}$:

$$P = P_0 \frac{\sinh(x/\Delta)}{\left[\frac{1}{2} + \cosh^2(x/\Delta) \right]^{1/2}}. \quad (10)$$

In Figs. 1 and 2 the domain wall shapes $P(x/\Delta)$ are shown for BST and for PZT. The paraelectric phase layer is surrounded by two ferroelectric domains with opposite directions of polarization. The appearance of a paraelectric layer in the ferroelectric domain wall is the wetting of the domain wall by the paraelectric phase.³ The existence of a paraelec-

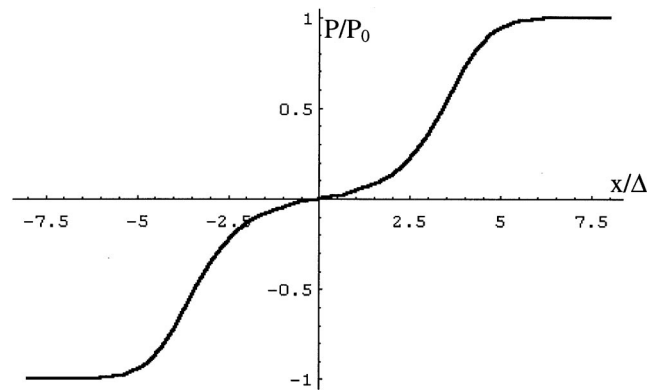


FIG. 1. Polarization as a function of distance x/Δ in BST with Sr concentration equal to 1.1%. The domain wall width Δ is given by Eq. (5).

tric layer is demonstrated in Fig. 2(a) by presentation of the first derivative of Eq. (4). The minimum on this curve illustrates the existence of a paraelectric layer. In Fig. 2(b) the wetting in PZT is shown at a constant temperature for two concentrations of Zr: $n = 5\%$ (curve I) and $n = 5.07\%$ (curve II). Curve I gives a larger paraelectric layer than curve II. The wetting can therefore happen at a constant temperature by changing the concentration. Thus, in addition to the range of temperature, there is a range of concentration, in which the wetting appears. Consequently, concentration can be the critical parameter for the wetting existence as well, i.e., the situation is different from the known one,³ where the only

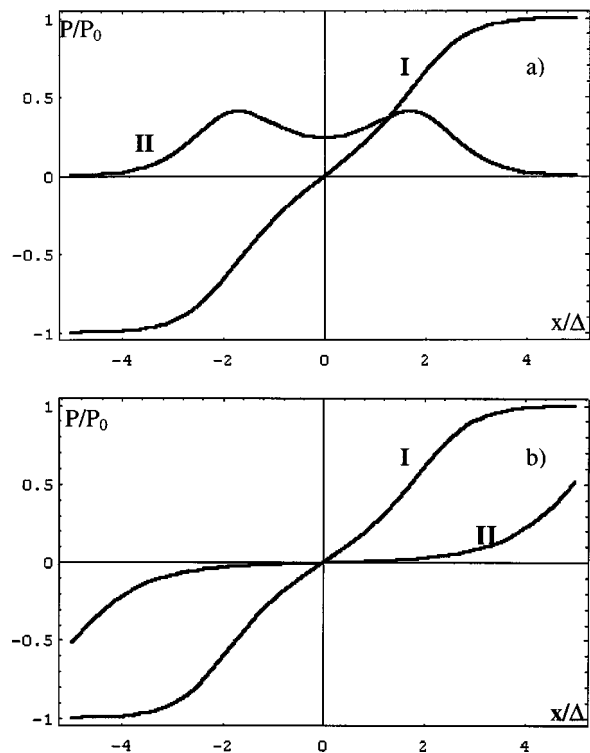


FIG. 2. (a) Polarization (curve I) and its first derivative as a function of distance x/Δ in PZT for $n_{Zr} = 2.2\%$. The domain wall width Δ is given by Eq. (5). (b) Polarization as a function of distance x/Δ in PZT for $n_{Zr} = 5\%$ (curve I) and $n_{Zr} = 5.07\%$ (curve II). The domain wall width Δ is given by Eq. (5).

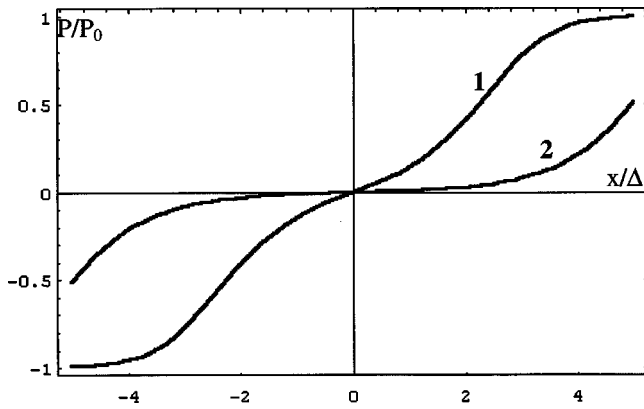


FIG. 3. Polarization as a function of distance x/Δ in BST at the magnetic field 10 T. The first curve is plotted at Sr concentration equal to 1.1% (curve 1), and the second at 1.12% (curve 2). The domain wall width Δ is given by Eq. (5).

critical parameter is temperature. In our case, there is a special concentration-temperature “phase diagram,” i.e., the geometric place of points of the wetting existence. The strong increase of the wetting layer on concentration in Fig. 2(b) is caused by the immediate proximity to the phase transition concentration. The shape of the interfaces between the paraelectric and ferroelectric phases is described by a kink solution

$$P = \frac{P_0}{[1 + \exp(\pm x/\Delta)]^{1/2}}. \quad (11)$$

Equation (11) is the second partial solution of Eq. (2) for boundary conditions of two paraelectric-ferroelectric interfaces:

$$+x \rightarrow \lim_{x \rightarrow +\infty} P = 0, \quad \lim_{x \rightarrow -\infty} P = P_0, \quad \lim_{x \rightarrow \pm\infty} \frac{dP}{dx} = 0. \quad (12)$$

$$-x \rightarrow \lim_{x \rightarrow -\infty} P = 0, \quad \lim_{x \rightarrow +\infty} P = P_0, \quad \lim_{x \rightarrow \pm\infty} \frac{dP}{dx} = 0. \quad (13)$$

The magnetic-field induced wetting is presented in Fig. 3 for BST at a constant temperature for two concentrations of Sr: $n = 1.1\%$ (curve 1) and $n = 1.12\%$ (curve 2). In the region close to the zero of polarization the curves in this figure form a plateau. This central plateau can be regarded as a sort of residue or nucleus of the paraelectric phase. Thus, the wetting of the ferroelectric domain wall takes place indicating the splitting of the domain wall into two interfaces separating the polarization-up and polarization-down regions.

As is known in Ref. 11, the width of the wetting layer diverges logarithmically as temperature, concentration, or magnetic field increases up to the critical value:

$$w = \Delta \ln\left(\frac{T_c - T}{T_c}\right). \quad (14)$$

The width w is determined by the distance between the two inflection points of the polarization function in Eq. (4).¹¹ Thus, the domain wall changes from its ferroelectric struc-

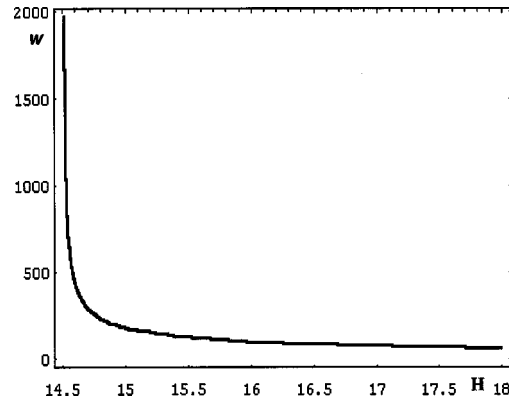


FIG. 4. The width of the paraelectric layer w as a function of an external magnetic field (in T) in BST at the phase transition temperature at $n_{\text{Sr}} = 2\%$. w is given in units of Δ_0 , where $\Delta_0 = \sqrt{8DC/B}$; $\Delta = \Delta_0 / (\sqrt{1 - 4\alpha} + \sqrt{1 - 4\alpha})$.

ture into a paraelectric one, which continues to involve and becomes at T_c a paraelectric layer bounded by two paraelectric-ferroelectric interfaces, with the width of the diverging paraelectric layer. The analogous effect has been observed in antiferromagnets in an external magnetic field:^{14,15} antiferromagnetic domain walls were “decorated” by paramagnetic nuclei. Thus, the nucleation of a new phase caused by a magnetic heterogeneity, such as 180° domain walls, turns out to be more probable than nucleation by reversal of spontaneous magnetization.

The magnetic field can fix the interphase boundary and change the dimension of the domain structure. We plot in Fig. 4 the magnetic-field dependence of the width of the wetting layer in BST at a constant temperature at $n_{\text{Sr}} = 2\%$. We see the decrease of the width when the magnetic field increases. The increase in the magnetic field decreases the paraelectric layer. It happens because the magnetic field acts as an ordering factor. Thus, the magnetic field hampers the splitting of the domain wall. Within the magnetic field range of about 40 T a paraelectric layer decreases in two or three orders of magnitude depending on the concentration and temperature chosen. This drastic change in the width of the paraelectric layer is explained by the critical dependence of the width w [Eq. (14)] characteristic of wetting phenomena. The magnetic-field effect leads to the essential redistribution of the bulk, domain wall, and interface energies and forma-

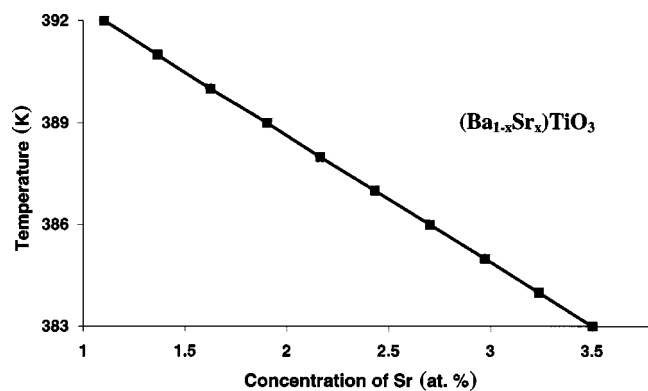


FIG. 5. The wetting existence curve in some range of concentration and temperature in BST.

tion of the domain and zero polarization structure of a new size. Magnetic field cannot be the critical parameter because its variation does not influence the phase-transition order and does not lead to the wetting.

In Fig. 5 we present a curve for the wetting existence in BST. The calculations give a curve of the wetting presence showing the range of concentration and temperature, in which the wetting takes place. We describe only a part of the curve for 383–392 °C and 1–3.5 %. In this range the geometric place of points of the wetting existence is well described by a straight line.

One additional note has to be done concerning the elastic effect on the phenomenon of the wall wetting. In our study the strain-dependent terms formally were not included in the free energy density. However, as has been shown in Ref. 3, strains suppress the effect of splitting of a domain wall. In spite of this fact, there are several circumstances that make our results valuable. The magnetic field does not influence the strain distribution because of the absence of magnetostriction effects in BST and PZT. Although the strain effects accompany phase transitions in perovskite ferroelectrics, the

parameters of the Landau functional were taken from experiments. Thus they include effectively the influence of elastic fields on formation of paraelectric nuclei. The same effect happens in the study of alloying effect on the wetting of domain walls. The elastic accommodation is effectively included in parameters of the functional and partially is accounted for by experimentally estimated derivatives dT_0/dn .

The formation of nuclei of the paraelectric phase should be signalized by an appearance of an additional resonance line of the spectrum. The nuclei can be also visualized within optical methods.¹⁵ The appearance of paramagnetic phase between two different time-reversed antiferromagnetic states (up-down and down-up) in Ref. 15 would be impossible due to elastic strains caused by magnetostriction.³ However, the wetting was observed in this case. This makes us optimistic regarding the observation of wetting in ferroelectric crystals.

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