Kinetics of phase transitions in solid solutions of ferroelectric perovskites

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(Received 19 July 1994; revised manuscript received 7 November 1994)

The dynamics of interphase boundaries at first-order phase transitions in ferroelectric solid solutions are considered. The width and velocity of the interphase boundary as functions of concentration are calculated for the ferroelectric perovskite solid solutions K(Ta,Nb)O$_3$ (KTN) and Pb(Zr,Ti)O$_3$ (PZT), which are taken as examples. It is shown that the velocity depends very strongly on concentration in the vicinity of the phase transition.

Perovskite solid solutions constitute an important group of oxide crystals with broad ranges of technologically important dielectric, piezoelectric, ferroelectric, superconducting, and electrooptic properties.[1-4] Some of them have recently attracted attention as very firm ceramics, as substances having very large electro-optic coefficients, and as materials applied in the development of integrated micromechanical, transistor, memory, and optical devices.[1-4] The mechanical and electrical properties of the perovskite solid solutions depend strongly on concentrations of their components. In many of these materials ferroelectric phase transitions are of first order. As a result of the concentration change in the solid solution, the first-order phase transition becomes a second-order one at a tricritical point.[5-8] At the concentration range where the transition is of first order, there exists an interphase boundary which separates the paraelectric and ferroelectric phases. Most of the work on ferroelectric perovskite solid solutions was focused on the study of their equilibrium properties, while we emphasize here the importance of looking into phase transition kinetics due to its large sensitivity to composition changes of the solid solution. In this paper we propose a theory of the interphase dynamics at ferroelectric phase transitions in perovskite solid solutions. We calculate the dependence of the width and velocity of the interphase boundary on concentrations using the experimental data for KTa$_{1-n}$Nb$_n$O$_3$ (KTN) and PbZr$_{1-n}$Ti$_n$O$_3$ (PZT) as examples. We show that the velocity of the interphase boundary is very sensitive to concentration changes near the phase transition.

It is well known that concentrated KTN undergoes the same sequence of structural phase transitions as pure KNbO$_3$, but at progressively lower phase transition temperatures as the concentration of Nb is reduced.[6] At large concentrations of Nb these mixed crystals exhibit the concentration-temperature phase diagram which looks like the pressure-temperature one: the temperature ranges of stability of the tetragonal and orthorhombic phases decrease with increasing concentration of Ta and the phase transition temperature T_c moves to lower temperatures with increased Ta concentration. There is a tri-

critical concentration at which the character of the transition changes from first order to second order. Thus, there is a range of concentrations and temperatures at which the paraelectric-ferroelectric interphase boundary exists. At a constant temperature and pressure the interface exists for concentrations $n_0 < n < n^*$, where n^* and n_0 are the concentrations corresponding to the stability limit of the ferroelectric phase and to the stability limit of the paraelectric phase, respectively; $n^* < n_t$, n_t is the tricritical concentration of Ta. The phase transition concentration n_c is the concentration at which the depths of the two minima of the paraelectric and ferroelectric phases are equal. For the description of first-order ferroelectric transitions in perovskites we use the Landau expansion

$$F = \int [f + D(\nabla P)^2]dV, \tag{1}$$

where F is the free energy and f is the free energy density given by

$$f(n,T,P) = f_0 + \frac{1}{2}A(n,T)P^2 - \frac{1}{4}B(n)P^4$$
$$+ \frac{1}{6}C(n)P^6; \tag{2}$$

f_0 is the free energy density for the paraelectric phase, and D is the positive coefficient of the inhomogeneity term. For $B > 0$ and $C > 0$, Eq. (2) describes a first-order phase transition. For $B < 0$ a second-order phase transition takes place. If $B = 0$, a tricritical point is reached. $A = A'(n)[T - T_0(n)]$, where T_0 is the temperature of the stability limit of the paraelectric phase. It follows from the experimental data[6] that A' increases linearly with increasing concentration of Ta. The coefficient C has the same behavior,[7] while T_0 and $(T_c - T_0)$ decrease; T_c is the phase transition temperature. We can write the coefficient B as follows:

$$B = b(n_t - n), \tag{3}$$

where b does not depend on n; in the pure KNbO$_3$, $n = 0$, i.e., $B_0 = bn_t$. Equation (3) is explained as

follows. A well-defined interphase boundary exists unless the concentration is not very close to the tricritical point. When the concentration approaches the tricritical point, the order parameter of the low-temperature phase goes to zero, and the interphase boundary width becomes infinitely thick and finally disappears. The difference between the phase transition temperature T_c and the temperature corresponding to the stability limit of the paraelectric phase T_0 decreases with increasing concentration of Ta and this is a manifestation of the fact that the character of the phase transition changes from first order to second order. Assuming a linear concentration dependence we have $A' = A_0' + \frac{dA'}{dn}n$, where $\frac{dA'}{dn} = 4.875 \times 10^{-5}$ K/n_{Ta} (Ref. 6) and $T_0 = T_0^0 + \frac{dT_0}{dn}n$ [where $T_0^0 = T_0$ ($n = 0$)], where $\frac{dT_0}{dn} = -562.5$ K/n_{Ta},[6] $C = C_0 + \frac{dC}{dn}n$, $\frac{dC}{dn} = 2.33$ K/n_{Ta},[7] $A_0' = 2.6 \times 10^{-5}$ 1/K,[9] $B_0 = 1 \times 10^{-12}$ CGSE,[9] and $C_0 = 5.4 \times 10^{-22}$ CGSE.[9] We take $n_t = 0.75$ instead of 0.55 (Ref. 6) because the interphase boundary also exists at $n = 0.65$ (Ref. 10) and at $n = 0.68$ $(T_c - T_0) = 3.5$ K.[11] The dependence $D(n)$ is negligible because D is proportional to the square of the lattice parameter[12] that changes negligibly compared to the other above composition effects at the concentration range under consideration.[1] We can obtain n_0, n_c, and n^* from $\alpha_0 = 0$, $\alpha_c = \frac{3}{16}$, and $\alpha^* = \frac{1}{4}$, where $\alpha = \frac{AC}{B^2}$, i.e., from the minimization of the free energy density and from the conditions for stability limits of the phases.

By changing the Ta concentration one can induce the motion of the ferroelectric interface. The above dynamics are described in terms of the time evolution of the polarization P:

$$\frac{\partial P}{\partial t} = -\Gamma \frac{\delta F}{\delta P}, \tag{4}$$

where Γ is the kinetic coefficient which is assumed to depend noncritically on a temperature, pressure, and concentration. The functional derivative $\frac{\delta F}{\delta P}$ tends to restore the value of P to its thermal value. When displaced away from the equilibrium state by changing the concentration of Ta the system will relax back to it. The kinetics of the relaxation towards equilibrium may be described in terms of the time evolution of the polarization [Eq. (4)]. The corresponding equation of motion in the x direction is as follows:

$$\frac{\partial P}{\partial t} + \Gamma \left[A(n,T)P - B(n)P^3 + C(n)P^5 \right]$$
$$- 2\Gamma D \frac{\partial^2 P}{\partial x^2} = 0. \tag{5}$$

Equation (5) is therefore the equation of motion for the polarization and it is a mean-field representation of the nonequilibrium interphase boundary kinetics. Now we look for a steady-state solution of Eq. (5) for which, in the moving reference frame of the interphase boundary, the profile of polarization P is time independent, i.e., letting $s = x - vt$:

$$2\Gamma D \frac{d^2 P}{ds^2} + v \frac{dP}{ds} - \Gamma \left[A(n,T)P - B(n)P^3 + C(n)P^5 \right]$$
$$= 0. \tag{6}$$

The solution of Eq. (6) for the interface boundary conditions has the kink form[13]

$$P = \frac{P_0}{\sqrt{1 + \exp(\frac{s}{\Delta})}}, \tag{7}$$

where P_0 is the equilibrium value of polarization,

$$P_0^2 = \frac{B(n)}{2C(n)} \left(1 + \sqrt{1 - 4\alpha}\right), \tag{8}$$

and Δ is the width of the interphase boundary given by

$$\Delta = \frac{[3DC(n)]^{\frac{1}{2}}}{B(n)\sqrt{1 - 2\alpha + \sqrt{1 - 4\alpha}}}. \tag{9}$$

The boundary moves with the velocity v, given by

$$v = \frac{\sqrt{2}}{3} \frac{\Gamma(D)^{1/2}B(n)}{\sqrt{C(n)}} \frac{(8\alpha - 1 - \sqrt{1 - 4\alpha})}{\sqrt{1 - 2\alpha + \sqrt{1 - 4\alpha}}}. \tag{10}$$

Equation (7) describes the kink profile of the moving interphase boundary separating the paraelectric and ferroelectric phases. Thus, the above motion of the interphase boundary is a nonlinear phenomenon. The nonlinear kinetics given by (7) results from the nonlinear expression for the free energy density (2) which describes a first-order ferroelectric phase transition. Therefore, for small disturbances of external conditions the system does not necessarily relax linearly and the rate of the phase transition is described by the nonlinear kinetics equation (5). The interphase boundary preserves its shape (7) during the propagation because of the competition of the two terms: the homogeneous part of the free energy density tends to make the interphase boundary infinitely sharp, while the inhomogeneous part of Eq. (5) has opposite tendency. At first, the paraelectric and ferroelectric phases are at equilibrium. Let us change the concentration of Ta slightly; for example, we increase the concentration of Ta by a small amount over the critical concentration n_c. The ferroelectric phase then becomes metastable, while the paraelectric phase is stable. As a result of the interphase boundary motion, the space occupied by the paraelectric phase is increased, while the space occupied by the ferroelectric phase decreases. If we now lower n_{Ta} slightly, the paraelectric phase becomes metastable. As a result, the interphase boundary moves towards the region occupied by the paraelectric phase.

It is seen from (9) and (3) that at $n = n_t$, i.e., in the tricritical point, the interphase boundary width tends to infinity. In Fig. 1 the interphase boundary Δ is shown as a function of n_{Ta} in KNbO$_3$ at $\Delta T = T_0^0 - T = 1$ K. At this temperature the ratio between the limited concentrations of the range of existence of the interphase boundary is 12.5. The maximal width of the interphase boundary is twice as large as the minimal one. This means that when ΔT increases, the width grows but remains finite. In Fig. 2 the concentration dependence of the interface velocity v is demonstrated at the same temperature. We see that, at $n_c = 1.76\%$, $v = 0$. A change of n above or below n_c induces the interface motion towards the paraelectric or ferroelectric phase, respectively. This means that the fer-
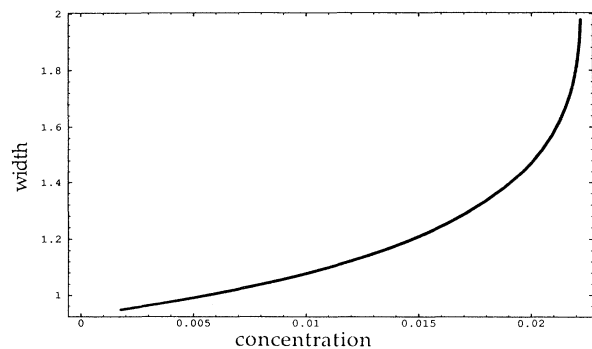
FIG. 1. The interphase boundary width Δ as a function of the concentration of Ta, n, in KTN at $\Delta T = T_0^0 - T = 1$ K. The width is given in units of $\frac{(3DC)^{\frac{1}{2}}}{B}$.

FIG. 2. The interphase boundary velocity v as a function of the concentration of Ta, n, in KTN at $\Delta T = T_0^0 - T = 1$ K. The velocity is given in units of $\frac{2^{\frac{1}{2}}}{3}\frac{\Gamma(D)^{1/2}B}{C^{\frac{1}{2}}}$.

roelectric phase grows at the expense of the paraelectric one and vice versa. The curve $v(n - n_c)$ for $n > n_c$ is sharper than $v(n_c - n)$ for $n < n_c$: $v \propto (n - n_c)^a$, where $a \approx 1.35$ and $v \propto (n_c - n)^b$, $b \approx 0.8$. The exponents a and b are determined by least squares fitting. This asymmetry resembles the experimental observed asymmetry of the temperature dependence of the interface velocity on supercooling and superheating in PbTiO$_3$.[14] The interface width and velocity are very sensitive to the change of concentration. These effects are much stronger than the variation of the phase transition temperature with concentration. Indeed, the maximum relative change of the phase transition temperature in the range of concentrations under study is approximately equal to 50%, while at a narrow range of concentrations, e.g., 9%–10%, the increase in width is about 100%. The increase in the concentration in 0.2% leads to the 200% growth of the interface velocity at $n > n_c$. Such a large sensitivity of the velocity to composition changes can provide a new method of studying the solid solutions. By varying the concentration of a component of the perovskite solid solution its growth can be controlled and the kinetics of the first-order phase transition can be governed. Thus, Fig. 2 can serve as the diagram of growth of the two phases in KTN. For each solid solution such a diagram can be constructed. The present consideration can be also extended for the study of the kinetic behavior of other perovskite solid solutions including antiferroelectric ones, for example, (Ba,Sr)TiO$_3$,[7] Pb(Zr,Ti)O$_3$,[5] and Co-doped BaTiO$_3$,[8] because of the analogous concentration dependences of their dielectric properties. Using the experimental data for PZT,[5] we obtain that $v \sim (n - n_c)^a$, where $a = 1.54$ for $n > n_c$, and $v \sim (n_c - n)^b$, where $b = 0.92$ for $n < n_c$. Therefore we see a noticeable differ-
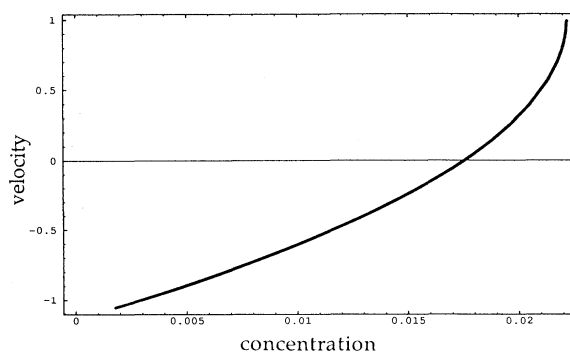
ence between the concentration dependences of the two velocities in KTN and PZT allowing us to identify the kinetics of the two materials.

The obtained results may be also useful for the superconducting perovskite solid solutions undergoing first-order ferroelectric phase transitions. In recent years the approach presented above was applied to study, both experimentally and theoretically, the temperature- and magnetic-field-induced dynamics of ferroelectric interphase boundaries.[14–16] The measurements on the temperature-induced dynamics are in agreement with the suggested consideration.[14,15] In addition, there are measurements on the temperature-induced interface dynamics in ferroelectric BaTiO$_3$, PbTiO$_3$, SbSI and antiferroelectric NaNbO$_3$ (Refs. 17–24) using the polarization microscope technique. Such interphase boundaries are known in a number of alloys undergoing martensitic transformations; these transformations are also diffusionless.[25] The similarity between the two types of phase transitions[26] can be useful in describing the kinetics of martensitic transformations.

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