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Nucleation near the tricritical point of $BaTiO_3$

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Time-resolved polarization measurements on $BaTiO_3$ for pressures between 1 atm and the tricritical pressure $P_t \equiv 32$ kbar reveal a delay between the application of an electric field and the rise of polarization towards its equilibrium, ferroelectric value. The delay decreases exponentially with the difference between applied electric field and the field at which the equilibrium ferroelectric-paraelectric transition occurs. A model which includes long-range elastic and dipole interactions present in single crystals gives a qualitative description of the delay time.

$BaTiO_3$ constitutes an excellent laboratory for the study of nonequilibrium phenomena near first-order phase transitions. By varying the temperature (T), pressure (P), and applied electric field (E), the transition can be made either continuous at a line of critical points[1,2] or second order beyond a tricritical point.[3,4] At the Curie temperature, the coupling of the polarization to the lattice leads to a tetragonal strain of $c/a = 1.01$ at $P = 1$ atm and $T = 298$ K, and this strain decreases with increasing pressure.[5] Recent time-resolved x-ray scattering and polarization measurements reveal a finite delay time for the electric-field-induced transition at atmospheric pressure.[6] The delay time decreases exponentially with excess field ΔE, which is the difference between the applied field and the equilibrium value of the field at the transition for a given temperature. In order to determine the dependence of the delay time on the tetragonal strain, we have performed time-resolved polarization measurements as a function of pressure up through the tricritical point. The critical field, where the transition becomes continuous, and the jump in polarization at the phase transition extrapolate to zero at the temperature and pressure expected for the tricritical point on the basis of previous work.[3] The delay time is still observed at pressures approaching the tricritical pressure P_t, but it decreases much more rapidly with increasing ΔE. These results are in disagreement with most theories for the decay of metastable states;[7,8] but a model which takes account of the strain interactions present in single-crystal systems such as $BaTiO_3$ gives a qualitative description of our data.[9]

Time-resolved polarization measurements were made using a Sawyer-Tower circuit on $BaTiO_3$ crystals grown by the Remeika method[10] as discussed in Ref. 6. Care was taken to cut, etch, and electrode the crystals according to established methods so as to minimize problems of surface phases and clamping effects. Measurements were made on undoped and doped crystals, partially and fully electroded crystals, and weakly (Au) and strongly bonding (Cr–Au) electrodes with no qualitative differences. The results shown in the figures are for crystals containing 0.2 at.% Fe for charge compensation and Au electrodes which were between 500 and 1000 Å thick and 2 mm in diameter. Measurements were made up to $P = 35$ kbar using a Teflon cell container in a conventional piston cylinder device with a freshly prepared 50:50 mixture of *n*-pentane-isoamyl alcohol.[11] The temperature was varied by cooling the pressure plate in a bath of either dry-ice alcohol or liquid nitrogen, and the temperature was measured with a Chromel-Alumel thermocouple placed next to the sample in the Teflon cell.

To establish the P-T-E phase diagram for the ferroelectric paraelectric phase transition, a train of alternating positive and negative pulses (10-msec duration, spaced 30 msec apart) was applied to the crystal, and the polarization was measured during the last 2 msec of the pulse as a function of pulse amplitude and pressure at $T = 294$ K. The results are shown in Fig. 1, where they are compared with similar measurements made on a different sample in a two stage oven as a function of temperature at one atmosphere. The jump in polarization is much smaller near the phase transition at $T = 294$ K and $P = 20.4$ kbar than it is at $T = 391$ or 393 K at $P = 1$ atm. Over a narrow range of pressure the jump in polarization decreases to zero, and the critical field at $T = 294$ K is $E_c = 1900$ V/cm which is about one-third of the value observed at $P = 1$ atm ($E_c = 5500$ V/cm).[5] The phase diagram obtained from a series of similar measurements is shown in Fig. 2, where the results are compared with previous measurements in the P-T plane.[3,4] Our results agree well with those of Samara[3] who also used crystals grown by the Remeika method. The phase boundary reported by Clarke and Benguigui[4] is displaced because crystals grown from a TiO_2 melt have a Curie temperature 15 K

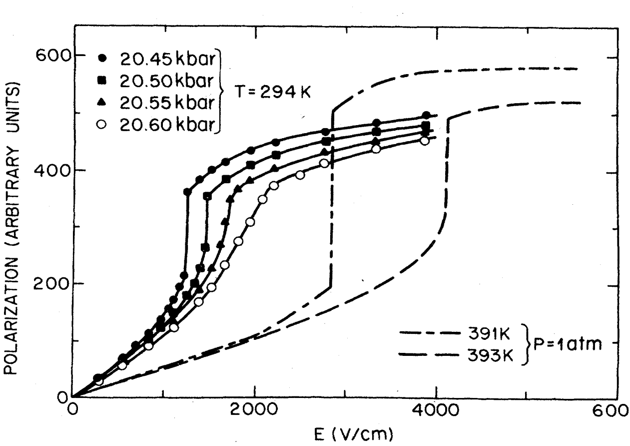

FIG. 1. Comparison of polarization vs applied electric field near the PE-FE phase boundary at atm and 20.4 kbar.

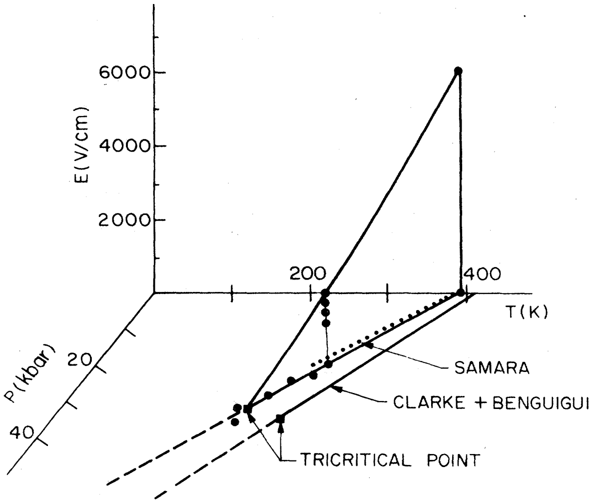

FIG. 2. Pressure-temperature-electric field phase diagram for the PE-FE transition in BaTiO$_3$ showing the line of critical points terminating at the tricritical point.

higher. However, the qualitative features are unchanged. The tricritical point is estimated to be at $P_t = 32$ kbar and $T = 235$ K in the flux grown crystals. The critical voltage and the jump in polarization both scale with the reduced pressure: $(P_t - P)/P_t$.

Figure 3(a) shows representative oscilloscope traces of the polarization as a function of time for three pressures: 1 atm, 20.50 kbar, and 27.4 kbar. At the onset of the voltage pulse at $t = 0$ the polarization rises rapidly and saturates at some intermediate value. At all three pressures the field-induced first-order transition to the ferroelectric (FE) phase occurs after a well-defined time. The jump in polarization and the final value of the polarization decreases with increasing pressure. Figure 3(b) displays the variation of the delay time with excess field ΔE for representative samples at $P = 1$ atm and at $P = 20$ kbar. The line through the points at $P = 1$ atm is obtained from x-ray scattering measurements of the delay time, and it is in reasonable agreement with the values from the polarization measurements. There are variations of 20% in the slope from sample to sample under otherwise identical conditions, but the magnitude is approximately three times larger at high pressure. The slope appears to scale inversely with the reduced pressure.

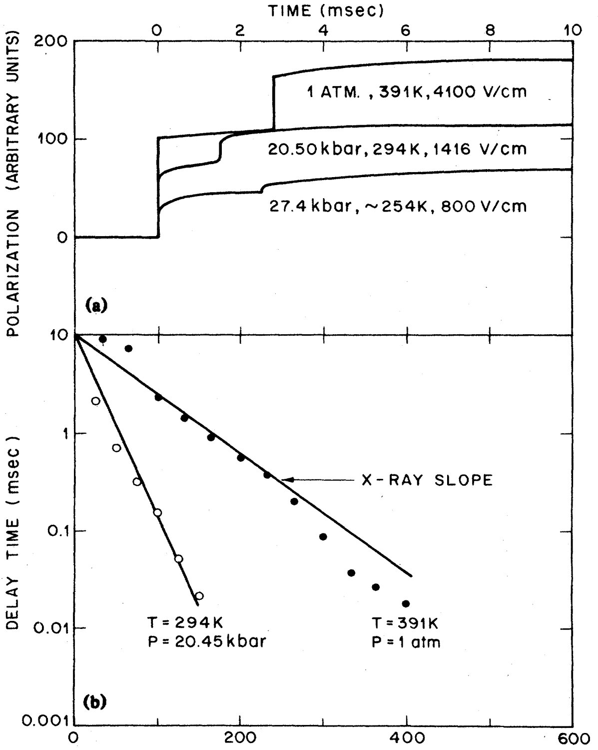

FIG. 3. (a) Comparison of polarization vs time for three different pressures showing a well defined delay time. (b) Delay time vs excess field at 1 atm and at 20.45 kbar.

Simple models of nucleation and growth at a first-order transition do not give a well-defined delay time. In the Kolmogorov model, the fraction of the sample transformed at a time t is given by

$$Q(t) = 1 - \exp\left[-\int_0^t C_n R(s) V(t-s)^n ds\right] , \qquad (1)$$

where $R(s)$ is the nucleation rate, V the growth rate (domain wall velocity) of a nucleus growing in n dimensions, and C_n a dimension constant.[12] If $R(s)$ and V are assumed to be independent of time, then $Q(t)$ has the familiar S shape as a function of time. The inclusion of a critical size which a nucleus must reach before sustained growth can occur does not by itself lead to a finite delay time;[13] rather, a model is needed in which the nucleation rate is essentially zero at short times or in which the rate increases rapidly by some feedback mechanism at longer times. In our experiment the system is initially in equilibrium at a temperature above the Curie point, and there is a single minimum in the curve of free energy versus order parameter (polarization) at $\phi = 0$. The sudden application of an electric field shifts the free-energy curve to one with a metastable minimum at a small value of ϕ and a second stable minimum at a larger value of ϕ. There are at least three models of homogeneous nucleation which can lead to finite periods of time before observable growth of the stable ferroelectric phase occurs. After a sudden change in P, T, or E, there is some transit time before a steady-state population is established in the metastable minimum and consequently a finite time before statistical fluctuations produce a steady-state population of critical nuclei. In other words, the nonequilibrium dynamics is dominated by the finite time τ_e for equilibration with the heat bath. While τ_e can be substantial (10^{-2}–10^6 sec) for the crystallization of glasses,[8] τ_e for BaTiO$_3$ must be less than the time ($\frac{1}{2}$ μsec) required for sound to travel across the electrode diameter.

A second model which yields a delay time is based on the assumption that the state of the system is represented by a single dynamical variable (e.g., net polarization) subject to a potential which minimizes the system's equilibrium free energy. Both this model and elaborations[7] designed to account, to lowest order, for gradient terms in the free-energy yield delay times decreasing as $(\Delta E)^{-1/2}$—a form inconsistent with the data shown in Fig. 3.

A model which does agree with our measurements is based on the strong coupling between the polarization and the tetragonal strain (c/a ratio).[9] Within a Landau theory (which gives an accurate parametrization of the static behavior in this material) the transition is driven first order by strong coupling between the polarization and the strain. Under clamped conditions, the transition would be of second order occurring at a temperature $T_0 < T_c$. Consequently, a nucleus of the FE phase can only exist if the polarization is accompanied by a spontaneous strain.

It is now apparent that even if the paraelectric phase is metastable ($E > E_c$), nucleation of small FE regions will be strongly hindered because of the internal stresses by the strain mismatch between the two phases. Moreover, unlike the case of short-range coupling, the strain mismatch cannot be accommodated at the surface of a nucleus. The strain energy will grow proportional to the *volume* of FE phase transformed. Close to the critical line, an individual nucleus of *any* finite size will be *unstable* and tend to shrink. In order for homogeneous nucleation to occur, the process must be cooperative. On account of the long-range nature of strain interactions, individual nuclei of semimicroscopic size v_c are coupled to the average strain in the sample, which is in turn proportional to the fraction transformed. We assume that the nuclei are in local thermodynamic equilibrium, but that they are large enough so that $v_c \Delta F >> kT$ [here $\Delta F(s)$ is the difference in free energy per unit volume of the FE and PE phases under the condition of fixed average strains]. Fluctuations of individual domains into the FE phase will occur, but initially thermal population will be very small. However, once a small population of ferroelectric domains has been established, further nucleation into the FE phase will be enhanced because ΔF is reduced by the induced strain field. Provided the initial condition that $v_c \Delta F/kT >> 1$ is satisfied, this feedback mechanism leads to a step-function-like growth of the order parameter with time; the delay time t_0 decreases exponentially with ΔE. This model is in qualitative agreement with the time resolved x-ray and polarization measurements, but a quantitative comparison must await a microscopic derivation of the various parameters.

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