PHYSICAL REVIEW B VOLUME 40, NUMBER 10 1 OCTOBER 1989

# Cluster and domain-wall dynamics of ferroelectric $Sr_{1-x}Ca_xTiO_3$

W. Kleemann and H. Schremmer
*Angewandte Physik, Universität Duisburg, 4100 Duisburg, Federal Republic of Germany*
(Received 26 June 1989)

The dielectric permittivity of the $xy$-type random-field system $Sr_{0.942}Ca_{0.058}TiO_3$ is measured at frequencies $30 < f < 10^7$ Hz and temperatures $7.5 < T < 200$ K. At all temperatures a Debye-type, monodispersive process dominates with relaxation times $\tau \sim 10^{-5}$ s. It is attributed to off-center $Ca^{2+}$ dipole dynamics, which also determines the low-$T$ ferroelectric bulk relaxation. At $T < T_c \sim 35$ K an additional polydispersive Cole-Cole–type domain-wall relaxation is observed. Its large spectrum of relaxation times centered around $\tau \sim 10^{-3}$ s gives rise to glasslike behavior at low $T$. Experiments with external electric fields competing with the built-in random fields are discussed.

Solid solutions of $Sr_{1-x}Ca_xTiO_3$ ("Sr-Ca-Ti-O") with $x < 0.1$ are known[1,2] to undergo smeared second-order phase transitions (PT) into ferroelectric (FE) domain states. These are induced by random fields (RF), which are believed to be due to both dipolar and strain interactions of the order parameter with randomly distributed $Ca^{2+}$ and $Ca^{2+}$-$V_0$ centers. The polarization lies within the $(001)_c$ plane, but by virtue of weak fourfold in-plane anisotropy with easy axes $[110]_c$ and $[1\bar{1}0]_c$ the $xy$-type symmetry is broken.[1] This leads to four types of domains with mesoscopic coherence length in the spontaneous low-temperature ($T \lesssim 35$ K) domain state. However, by application of moderate electric fields along one of the easy axes the polarization can be switched and nearly saturated with negligible delay ($\tau < 1$ s) at whatever low $T$. This behavior strongly contrasts with that of $K_{1-x}Li_xTaO_3$ ("K-Li-Ta-O"), $0.022 < x \lesssim 0.1$, which is known[3] to form FE domain states with very large cubic anisotropy and, hence, random electret properties.

It is clear that the different domain mobilities found for Sr-Ca-Ti-O and K-Li-Ta-O must be connected with different dynamics of the dopant ions involved. $Li^+$ in $KTaO_3$ is known[4] to form off-center dipoles with large reorientation energies, $\Delta E/k_B \sim 1000$ K. This implies strong RF and, hence, domain immobility at low $T$. On the other hand, the RF in Sr-Ca-Ti-O seem to be weak and easily overcome by an external electric field in the sense discussed by Andelman and Joanny.[5] Hence, fairly small activation energies of $Ca^{2+}$ dipoles may be anticipated in $SrTiO_3$.

It is one aim of this paper to elucidate the dynamics of the dielectric permittivity of Sr-Ca-Ti-O, which is expected to contain bulk and domain-wall contributions. Indeed, both processes are found to be clearly discernible. The wall response is characterized by a broad distribution of relaxation times, which is consistent with the observed[2] small nonergodicity of the low-$T$ state upon field cycling. External fields are, however, not sufficient to unsmear the PT by field cooling (FC) contrary to what was recently observed on K-Li-Ta-O with $x = 0.063$.[6] This will be discussed in the second part of this Rapid Communication.

The dielectric permittivity ($\epsilon'$ and $\epsilon''$) is measured on Sr-Ca-Ti-O with $x = 0.058$ (Ref. 1) using a Hewlett-Packard 4192A impedance bridge at frequencies $30 < f < 10^7$ Hz and temperatures $7.5 < T < 200$ K. The samples are typically of size $2.5 \times 1 \times 0.4$ mm$^3$ with the shortest edge parallel to the easy axis $[110]_c$ and to the applied ac and dc fields. Data obtained on samples with other concentrations will be presented elsewhere.

Figure 1 shows $\epsilon'$ vs $\log_{10} f$ for $30 < f < 10^5$ Hz at various temperatures between 100.2 K (curve 1) and 7.5 K (curve 7). A relatively sharp drop around $f_0 \sim 3$ kHz and flat behavior at $f \ll f_0$, respectively, hints at essentially monodispersive Debye-type relaxation,

$$\epsilon = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1 - i\omega\tau) , \qquad (1)$$

whose $T$ dependence is determined by both the static permittivity $\epsilon_s$ and the relaxation time $\tau$. This is confirmed by Fig. 2, which shows the familiar Cole-Cole plots, $\epsilon''$ vs $\epsilon'$. Their half-circle shapes are nearly perfect at $T \gtrsim 35$ K (curves 1–4), but become slightly oblate at lower temperatures (curves 5–7). The deviations from pure Debye-

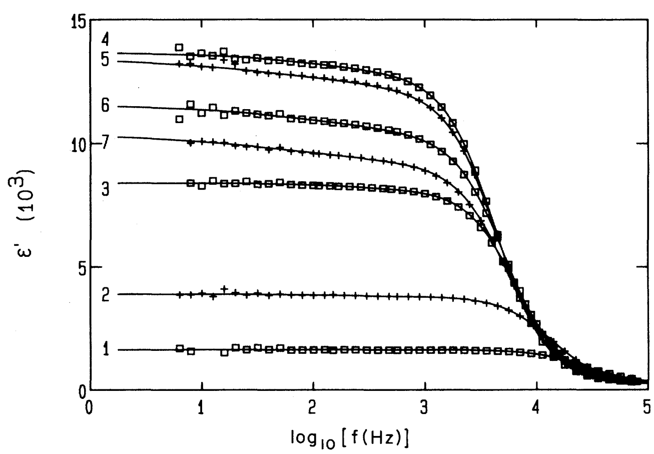


FIG. 1. $\epsilon'$ vs $\log_{10} f$ measured on $Sr_{0.942}Ca_{0.058}TiO_3$ at 100.2 (curve 1), 68.0 (curve 2), 55.1 (curve 3), 34.9 (curve 4), 26.5 (curve 5), 14.2 (curve 6), and 7.5 K (curve 7). The solid lines are best fits to Eqs. (2) and (3) with fit parameters partially shown in Table I.

 

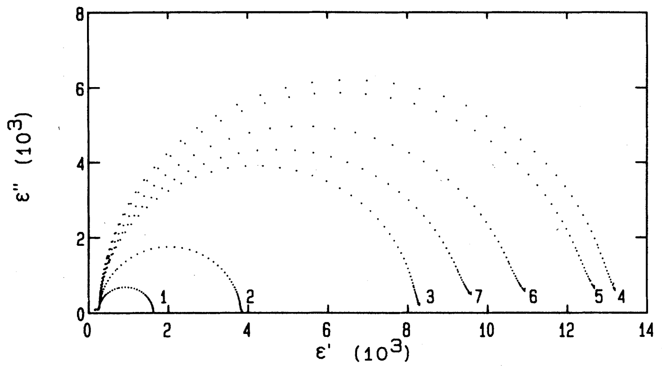


FIG. 2. Cole-Cole plots $\epsilon''$ vs $\epsilon'$ of $Sr_{0.942}Ca_{0.058}TiO_3$ for various temperatures as specified in Fig. 1.

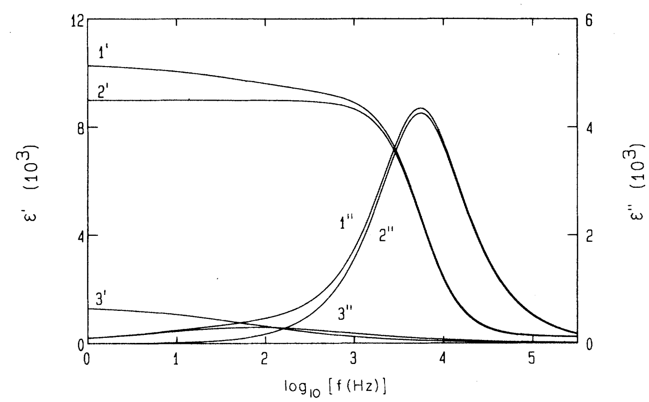


FIG. 3. $\epsilon'$ and $\epsilon''$ vs $\log_{10}f$ measured at 7.5 K and fitted to Eqs. (2) and (3) by solid curves 1′ and 1″, respectively, each of which is decomposed into a Debye-type (curves 2′, and 2″) and a polydispersive term (curves 3′, and 3″) (see text).

type dispersion are easily recognized in Fig. 1, where $\epsilon'$ vs $\log_{10}f$ reveals a finite slope at $f < f_0 \sim 10^3$ Hz. This effect is most pronounced in the low-$T$ limit.

Obviously, polydispersive behavior is encountered. Tentatively, this might be described by the well-known Cole-Cole permittivity relation,[7]

$$\epsilon = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/[1-(i\omega\tau)^{1-\alpha}] \quad (2)$$

where $0 < \alpha < 1$ determines the width of the distribution function $g(\tau)$. However, fitting our data to but one function of this type with one set of parameters ($\epsilon_\infty$, $\epsilon_s$, $\tau$, and $\alpha$) proves to be unsatisfactory. This indicates that Sr-Ca-Ti-O as a whole does *not* behave like a glass as, e.g., $Eu_{0.55}Sr_{0.45}S$.[8] Inspection shows that one has rather to consider *two* superimposed contributions as shown in Fig. 3 for our $T = 7.5$ K data of $\epsilon'$ and $\epsilon''$ vs $\log_{10}f$ (curves 1′ and 1″, respectively). They are perfectly fitted to an eight-parameter expression,

$$\epsilon = \bar{\epsilon} + \bar{\bar{\epsilon}}, \quad (3)$$

where both $\bar{\epsilon}$ and $\bar{\bar{\epsilon}}$ obey Cole-Cole–type characteristics, Eq. (2). The dominating term $\bar{\epsilon}$ is nearly Debye-type, $\bar{\alpha} \sim 0$ (curves 2′ and 2″), whereas $\bar{\bar{\epsilon}}$ is strongly polydispersive, $\bar{\bar{\alpha}} \sim 0.5$ (curves 3′ and 3″). Its amplitude achieves about 15% of that of $\bar{\epsilon}$ at low $T$.

The high quality of the curves best fitted to the data shown in Fig. 1 justifies the ansatz of Eq. (3). Table I shows the best-fit parameters obtained for some of them. Clearly, for $T > 50$ K the $\bar{\bar{\epsilon}}$ contribution is negligible, whereas $\bar{\epsilon}$ represents a classical Debye relaxator. In particular, $\bar{\tau}$ obeys an Arrhenius-type function, $\bar{\tau} = \bar{\tau}_0 \exp(\Delta E/k_B T)$, with $\bar{\tau}_0 = 3\times10^{-6}$ s and $\Delta E/k_B = 140$ K as shown in Fig. 4. It is attributed to the behavior of off-center $Ca^{2+}$ ions on $Sr^{2+}$ sites, which thus occupy similar, but much shallower potential wells than $Li^+$ in $KTaO_3$.[4] Very typically, in the ferroelectric phase, $T \lesssim 40$ K, $\bar{\tau}$ remains essentially constant. This is a consequence of the polarization of the surrounding host material, which collectively responds to an external ac field and thus blocks a further freezing of the individual $Ca^{2+}$ dipoles. The relatively large attempt time $\bar{\tau}_0$ in the paraelectric regime seems to be characteristic of large polarization clouds rather than of single off-center $Ca^{2+}$ ions. When approaching $T_c \sim 35$ K, the Debye relaxator nearly diverges ($\epsilon' > 10^4$) and thus simultaneously characterizes the percolating cluster at the ferroelectric PT. It may then be interpreted as a highly overdamped lattice oscillator undergoing extreme critical slowing down to $f \sim 5\times10^3$ Hz as is typical of the competition between thermal and RF fluctuations near the PT.[9]

It should be noted that the small high-$f$ permittivity, $\bar{\epsilon}_\infty \sim 200$, is not sensitive to the PT. Apart from a very high-$f$ infrared contribution ($f \sim 10^{13}$ Hz[10]), a remnant $SrTiO_3$-like[10] dispersion step, $\Delta\epsilon' \sim 100$, is observed at $f = 5\times10^6$ Hz. This shows no anomalies at $T_c$ and may be interpreted as the response of the $SrTiO_3$ matrix embedding the percolating FE cluster.

TABLE I. Fit parameters of $\epsilon'$ and $\epsilon''$ data shown in Figs. 1 and 2 fitted to Eqs. (2) and (3).

| $T$ (K) | $10^{-3}\bar{\epsilon}_s$ | $\bar{\epsilon}_\infty$ | $10^5\bar{\tau}$/s | $\bar{\alpha}$ | $10^{-3}\bar{\bar{\epsilon}}_s$ | $\bar{\bar{\epsilon}}_\infty$ | $10^3\bar{\bar{\tau}}$/s | $\bar{\bar{\alpha}}$ |
|---|---|---|---|---|---|---|---|---|
| 7.5 | 9.0 | 224 | 2.9 | 0.02 | 1.4 | 0.1 | 2.3 | 0.49 |
| 26.5 | 12.0 | 172 | 3.6 | 0.02 | 1.5 | 0.2 | 2.0 | 0.51 |
| 34.9 | 12.8 | 255 | 3.7 | 0.02 | 0.9 | 0.1 | 1.5 | 0.33 |
| 68.0 | 3.8 | 258 | 1.2 | 0.01 | 0.1 | 0.1 | 1.3 | 0.15 |
| 100.2 | 1.6 | 230 | 0.6 | 0.03 | 0.0 | 0.0 | · · · | · · · |

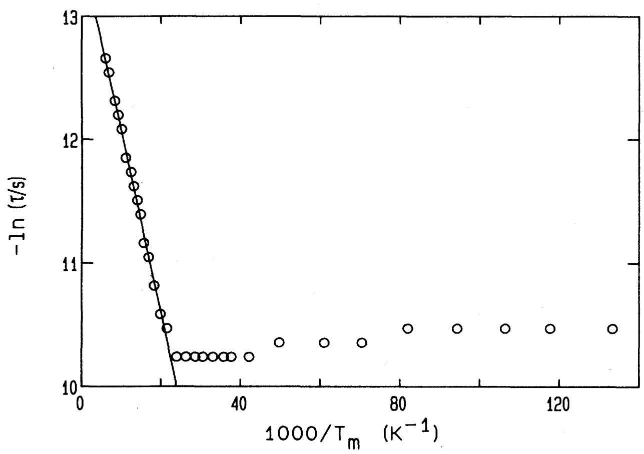


FIG. 4. Arrhenius plot of the relaxation time of the Debye-type contribution to the permittivity of $Sr_{0.942}Ca_{0.058}TiO_3$ (see text).

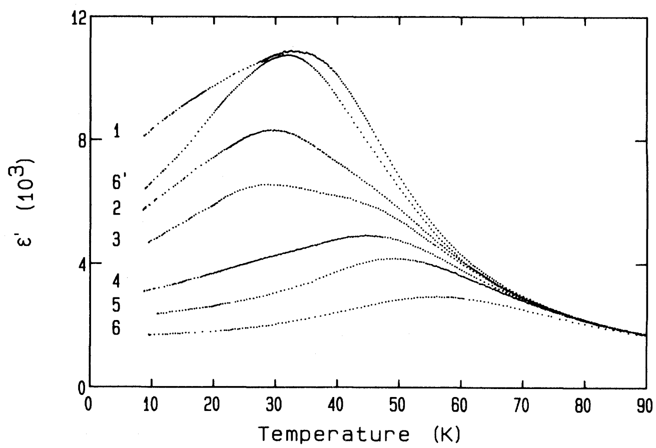


FIG. 5. Temperature dependence of $\epsilon'$ measured at $f=100$ Hz on field cooling with $E=0$ (curve 1), 160 (curve 2), 200 (curve 3), 280 (curve 4), 400 (curve 5), and 700 kV/m (curve 6) and on zero-field heating after field cooling with 700 kV/m (curve 6′).

The onset of the polydispersive contribution, $\bar{\bar{\epsilon}}$, starts gradually at $T \lesssim 50$ K in agreement with the smearing of the PT as conjectured from linear birefringence data.[2] From the distribution function of the Cole-Cole relaxator, $\bar{\bar{g}}(\tau)$,[8] we find $1/e$ widths of the relaxation time spectrum spreading from about one to four decades between 68 and 7.5 K. Hence, relaxation times of more than 0.1 s do occur in the low-$T$ limit.

The origin of the Cole-Cole relaxation is believed to be connected with the mesoscopic domain structure of Sr-Ca-Ti-O at low $T$. The displacements of the RF pinned domain walls respond as an extra relaxator apart from the $Ca^{2+}$ centered ferroelectric one. The hierarchy of potential barriers due to the RF fluctuations[11] gives rise to the observed broad width of $\bar{\bar{g}}(\tau)$.

The temporal response function,

$$\phi(t)=\int_0^\infty [\bar{g}(\tau)+\bar{\bar{g}}(\tau)]\exp(-t/\tau)d\tau\,, \tag{4}$$

contains contributions due to both relaxators discussed above. The dominating $\delta$ function, $\bar{g}(\tau)$, of the Debye relaxator yields the major contribution giving rise to a sudden drop of $\phi(t)$ within a few milliseconds. On the other hand, the broad distribution $\bar{\bar{g}}(\tau)$ of the Cole-Cole relaxator is expected[8] to yield stretched exponential relaxation in the limit $t \gg \bar{\bar{\tau}}$. However, since the width of $\bar{\bar{g}}(\tau)$ is less extreme than for typical spin glasses,[8] most of the glass-like relaxation presumable takes place on still relatively short time scales, $10^{-3} < t < 1$ s. Experiments are planned to check quantitatively these predictions.

The different relaxation mechanisms discussed above are also reflected by their response to external electric fields. Figure 5 shows several $\epsilon'$ vs $T$ curves measured at $f=100$ Hz upon FC with various electric fields, $\mathbf{E} \parallel [110]_c$. Curve 1, referring to $E=0$, shows the well-known[1] broadened peak indicating the smeared PT to appear at $T_c \sim 33$ K. FC with increasing $E$ gradually decreases the peak values of $\epsilon'$ from 11000 ($E=0$; curve 1) to 2500 ($E=700$ kV/m; curve 6). Additionally, upon increasing $E$, the peak first splits into a double-hump at $\sim 30$ and $\sim 45$ K ($E=200$ kV/m; curve 3). At higher fields the low-$T$ peak is gradually suppressed and the high-$T$ peak shifts to higher temperatures ($\sim 60$ K at $E=700$ kV/m; curve 6). The original $\epsilon'$ vs $T$ curve is nearly recovered after removing the cooling field at low temperatures and measuring upon zero-field heating (curve 6′). Appreciable hysteresis is only noticed in the low-$T$ range, $T < 30$ K.

Very probably the 30-K peak of $\epsilon'$ is primarily due to both ferroelectric cluster *and* domain-wall dynamics. Field-induced domain alignment and ferroelectric saturation then drastically suppress this peak and the entire low-$T$ permittivity. Incomplete restoration of the domain state and accidental metastability, depending on the sample probed,[2] explain the slight irreversibility after removing the field. On the other hand, the 45–60-K peak of $\epsilon'$ is believed to reflect the off-center $Ca^{2+}$ dynamics. Their local potential wells are stabilized by the external field. This causes the $\epsilon'$ peak to shift to higher $T$ as $E$ increases.

In contrast with K-Li-Ta-O ($x=0.063$),[6] sharp spikes of $\epsilon'$ have never been observed in Sr-Ca-Ti-O ($x=0.058$) upon zero-field heating *after* FC. Sharp PT due to field alignment of dipolar impurities are, hence, not achievable. Very probably this is a consequence of the low-$T$ immobility of the $Ca^{2+}$-$V_O$ centers. On the other hand, their invariable static dipolar *and* quadrupolar RF make the domain-state configuration approximately reversible upon field cycles as evidenced by linear birefringence and $\epsilon'$ measurements (not shown).

Principally, unsmearing of the PT should also become possible via the Adelman-Joanny mechanism[5] by FC through $T_c$. Here we assume no principal differences in the behavior of RF Ising or *anisotropic xy* systems. However, an external field breaks the symmetry of the paraelectric phase, and hence tends to smear the expected[1] second-order PT in a trivial way. In order to evidence unsmearing of the PT in Sr-Ca-Ti-O, at least partially, one should try to drastically reduce the inherent RF strengths. This might be feasible by field alignment of the $Ca^{2+}$-$V_0$ centers at elevated temperatures allowing for $O^{2-}$ migration, $T \sim 1000$ K. Compensation of the remaining RF, mainly due to the random strain fields of both on-site $Ca^{2+}$ ions *and* $Ca^{2+}$-$V_0$ centers, should then be possible by moderate external fields, similarly as in K-Li-Ta-O.[6] Experiments towards these ends are currently underway.

We are very grateful to J. G. Bednorz and K. A. Müller for kindly providing the samples used in this investigation and for helpful discussions. This work was supported by the Deutsche Forschungsgemeinschaft.

[1]J. G. Bednorz and K. A. Müller, Phys. Rev. Lett. **52**, 2289 (1984).
[2]W. Kleemann, F. J. Schäfer, K. A. Müller, and J. G. Bednorz, Ferroelectrics **80**, 297 (1988).
[3]W. Kleemann, S. Kütz, and D. Rytz, Europhys. Lett. **4**, 239 (1987).
[4]F. Borsa, U. T. Höchli, J. J. van der Klink, and D. Rytz, Phys. Rev. Lett. **45**, 1884 (1980).
[5]D. Andelman and J. F. Joanny, Phys. Rev. B **32**, 4818 (1985).
[6]H. Schremmer, W. Kleemann, and D. Rytz, Phys. Rev. Lett. **62**, 1896 (1989).
[7]K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
[8]J. J. Baalbergen, T. S. Ong, A. J. van Duyneveldt, and J. C. Verstelle, J. Phys. (Paris) Colloq. **49**, C8-1065 (1988).
[9]J. Villain, J. Phys. (Paris) **46**, 1843 (1985); D. S. Fisher, Phys. Rev. Lett. **56**, 416 (1986).
[10]M. Maglione, S. Rod, and U. T. Höchli, Europhys. Lett. **4**, 631 (1987).
[11]T. Nattermann and I. Vilfan, Phys. Rev. Lett. **61**, 223 (1988); T. Nattermann, Y. Shapir, and I. Vilfan (unpublished).