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# Pressure as a probe of dielectric properties and phase transition of doped quantum paraelectrics: $Sr_{1-x}Ca_xTiO_3$ $(x=0.007)$

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Pressure is shown to have a very strong influence on the glass-like (relaxor) dielectric response of $Sr_{1-x}Ca_xTiO_3$ $(x=0.007)$, or SCT (0.007), reducing the dielectric susceptibility and lowering the glass transition temperature, $T_m$, at the very rapid rate of ~35 K/kbar. Above 0.5 kbar there is complete suppression of the transition and relaxor state and evolution of a quantum paraelectric state at low temperatures. These effects can be understood in terms of the increase of the ferroelectric soft mode frequency, $\omega_s$, with pressure which strongly reduces the polarizability, and thereby the correlation length, $r_c$, for dipolar interactions. It is estimated that above 0.5 kbar $r_c$ becomes significantly smaller than the average separation between neighboring $Ca^{2+}$ ions (2.1 nm) leading to loss of overlap and correlations between adjacent nano-domains and loss of the relaxational character of the dielectric response. While pressure lowers $T_m$, the application of a dc biasing electric fields raises $T_m$ and can reinstate a ferroelectric state at modest pressures. The interplay between pressure and dc field provides insights into the physics. The very large pressure and field effects observed are attributed to the small characteristic energies of the crystal in the quantum regime.

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## I. INTRODUCTION

The physics of random dipolar impurities in highly polarizable ionic dielectric crystals has been a subject of continuing interest. Here the best examples are dipolar impurities in the two incipient soft mode ferroelectrics $KTaO_3$ and $SrTiO_3$ where the very high polarizability of the host lattice, associated with the soft ferroelectric (FE) mode, not only renormalizes the dipole moment of the impurity, but also functionally changes the dependence of the dipole-dipole interaction energy on the spacing between dipoles.[1,2] In this case, a long-range ordered FE state occurs if the impurity concentration exceeds a critical value; below this value, a dipolar-glass-like (relaxor) state forms.

A particularly interesting material system in these regards is $Sr_{1-x}Ca_xTiO_3$ (or SCT) in the limit of small *x*, which has been the subject of extensive research.[3–5] $Ca^{2+}$ might be expected to substitute for $Sr^{2+}$ at the *A* site in the $ABO_3$, perovskite lattice; however, the evidence is clear that the $Ca^{2+}$ impurity in $SrTiO_3$ is dipolar.[3–5] Its ionic radius (0.99 Å) is considerably smaller than that of $Sr^{2+}$ (1.12 Å), making it possible for the $Ca^{2+}$ to occupy an off-center position at the $Sr^{2+}$ site, thereby producing random electric field and strain coupling to the polarization. Alternatively, some of the $Ca^{2+}$ may substitute at the $Ti^{4+}$ site resulting in the formation of an oxygen vacancy $(V_o)$. The dipolar impurity would then be the $Ca_{Ti}:V_o$ pair defect. However, recent theoretical results on $KTaO_3$ strongly favor metal ion at the *A* site over (dopant: $V_o$) pair hopping as responsible for the small activation energies found in experiments.[6]

The present paper deals with a fixed SCT composition, $x=0.007$, or SCT (0.007) for short. Extensive dielectric and optical studies were performed on this composition by Kleemann and co-workers.[4,5] The results suggest that SCT (0.007) exhibits an inhomogeneous polar low-temperature state with evidence for ordering at two length scales.[4] On the shorter length scale, quasi-first-order Raman scattering by soft $(TO_1)$ and hard $(TO_2$ and $TO_4)$ polar modes gave evidence of Ca-induced FE microregions, or polar nanodomains, whose size is determined by temperature-dependent correlation radius, $r_c$, and the crystal exhibits the dipolar glass response of a relaxor ferroelectric. The longer length scale ordering is deduced from field-dependent linear birefringence measurements and is attributed to the presence of large random-field-correlated domains that relax independently and behave like switchable superparaelectric moments whose size increases with increasing temperature.[4]

Because the soft FE mode frequency of $SrTiO_3$ is known to be a strong function of pressure[7] and because the characteristic energies of the crystal are small in the quantum regime, it was felt that the application of hydrostatic pressure would lead to significant changes in the dielectric response and phase behavior of this crystal and thus provide new insights into the physics. Indeed, as will be described below, the present results reveal an unusually high sensitivity of the response to pressure leading to fast suppression of the transition temperature and vanishing of both the transition and the frequency dispersion by ~0.5 kbar. We also investigated the influence of a biasing dc field on the response. Section II provides a brief description of the experimental details followed by presentation and discussion of the results in Sec. III. Section IV provides some concluding remarks.

## II. EXPERIMENTAL DETAILS

The single crystal used came from the same material and was prepared as for the earlier 1-bar dielectric studies.[4,5] A

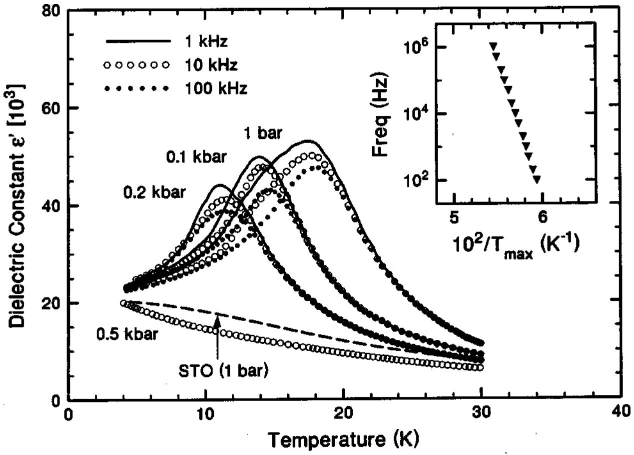

FIG. 1. The dielectric $\epsilon'$ $(T)$ response of SCT (0.007) at different pressures showing the frequency dispersion, which vanishes at 0.5 kbar. Also shown for comparison in the frequency-independent response of pure $SrTiO_3$ (STO) at 1 bar. The inset is an Arrhenius plot of the $T$ dependence of the relaxational frequency (=inverse relaxation time) at 1 bar.

$(110)_c$-oriented sample plate with the long edges parallel to $[001]_c$ was polished to optical quality and subsequently etched in boiling orthophosphoric acid in order to remove surface layers of about 0.1-mm thickness. After this procedure the sample reaches its final sizes, $0.46\times2.6\times6.5\ \mathrm{mm}^3$. This geometry favors an oriented state with the tetragonal $c$ axis parallel to the long edges, i.e., parallel to $[001]_c$. The polished broad faces become $\{110\}$ oriented in the low-temperature tetragonal phase and were equipped with copper-gold electrodes. The $Ca^{2+}$ concentration, $x=0.007$, of this sample was determined from the antiferrodistortive phase transition temperature of 125 K. The dielectric permittivity (both real $\epsilon'$ and imaginary $\epsilon''$ components) was measured with a Hewlett-Packard model 4192*A* impedance bridge as a function of temperature (4–293 K), hydrostatic pressure (0–6 kbar) frequency $(10^2-10^6\ \mathrm{Hz})$, and biasing dc electric fields (0–500 V/cm). The ac electric field amplitude was below 1 V/cm to minimize nonlinearities in the dielectric response. Pressure was generated in a conventional high-pressure apparatus using gaseous and solid He as the pressure transmitting media. The temperature dependence was measured during a slow drift of less than 1 K/min.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. 1-bar dielectric response

The dielectric response of SCT (0.007) at ambient pressure (1 bar) was first studied by Bednorz and Müller[3] (for $x=0.00\,75$) and later in more detail by Bianchi *et al.*[5] Figure 1 shows the real part of the dielectric constant, $\epsilon'$, vs temperature for our sample measured at different frequencies with the amplitude of the ac driving field fixed at 0.6 V/cm. The results are in close agreement with the earlier work.[3,5] The rounded $\epsilon'$ $(T)$ peak and the frequency dispersion in $\epsilon'$ $(T)$ at and below the peak temperature, $T_m$, were taken to be evidence of a percolative transition into a random-field ferroelectric domain state,[5] but they are also the signatures of a relaxor state.[2,4] In what follows much of our emphasis will be on the relaxational response.

We envision each $Ca^{2+}$-induced dipolar entity surrounded by a polarized region of the soft $SrTiO_3$ host lattice, forming a nanodomain whose size is determined by the $T$-dependent $r_c$ of the host. Because of the soft ferroelectric mode nature of the host, on cooling from high $T$ these nanodomains grow as $r_c$ increases, increasing their dynamic correlations.[2,4] (See Sec. III F below). However, for this dilute sample, these correlations do not become large enough to precipitate a global, long-range ordered FE state at low $T$. Rather, they exhibit a dynamic slowing down of their orientational motion, resulting in the frequency dependent peak in $\epsilon'$ $(T)$, a dynamic glasslike transition temperature, and the frequency dispersion on the low-$T$ side of the peak. At sufficiently low $T$ all such motion freezes, and the dispersion vanishes as shown below ~4 K. Dispersion is also exhibited by the imaginary part of the dielectric function $\epsilon''$ $(T)$ in the transition region.[5]

The flipping of the orientation of the Ca-induced nanodomains between equivalent potential minima (at zero bias) is a thermally activated process. We find that the relaxational kinetics for SCT (0.007) obey a simple Arrhenius expression over the rather small changes in $T_m$ with frequency for the present results (inset, Fig. 1). The results show the expected increase of the activation energy $E$, with field strength (not shown), but the magnitudes of $E$ (~100 meV) and the preexponential (attempt frequency $>10^{30}$) are unphysically large. This is a feature that is generally observed in fitting the relaxational kinetics of relaxors to a simple Arrhenius law.[2,8] When data are taken over a sufficiently broad frequency range, deviations from this law are generally observed for relaxors.[2] In such cases the kinetics are found to be well fit by the Vogel-Fulcher (VF) equation, which yields more realistic values for the fitting parameters.[2,8] In the present case, the dielectric data do not extend over a sufficiently broad frequency range to use the VF equation.

### B. Influence of pressure on the dielectric response

Pressure has a very strong influence on the dielectric response of SCT (0.007), as shown in Fig. 1. First, we note the large shift of the glass transition temperature $(T_m)$ to lower temperatures with very modest pressures. The slope $dT_m/dP$ is $\approx -35$ K/kbar, a very large effect. Second, there is a decrease in the amplitude of the peak with increasing pressure. These effects are characteristic of relaxors and can be explained in terms of soft mode and relaxor physics.[2] There has been considerable interest in the properties of relaxors and the mechanism for the ferroelectric-to-relaxor crossover in $ABO_3$ ferroelectrics with random site disorder. It has been shown that for these systems pressure favors the relaxor state over the normal FE state.[2]

The results in Fig. 1 also show the complete suppression of the "transition" and, thus, the relaxor state, with pressure. The 0.5-kbar data show no evidence of an approaching transition in either $\epsilon'$ or $\epsilon''$ (not shown). The 2- and 4-kbar results in Fig. 2 confirm the complete suppression of the relaxor

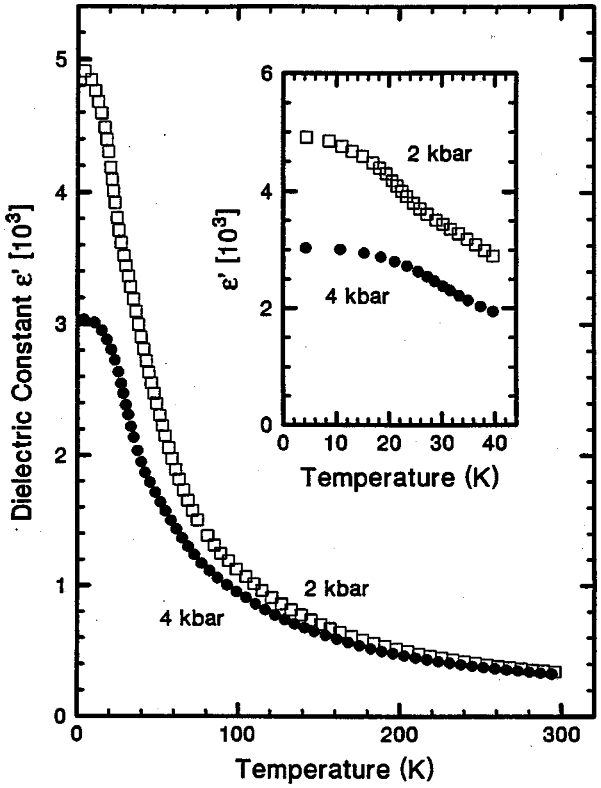

FIG. 2. The frequency-independent $\epsilon'$ $(T)$ response of SCT (0.007) at 2 and 4 kbar. The inset is an expanded view of the behavior at low temperature.

state and reveal the emergence of a quantum paraelectric state—a state characterized by a high $\epsilon'$ that is independent of temperature over a substantial temperature range at the lowest temperatures. Pure $SrTiO_3$ (STO) exhibits such a state below ~3 K at 1 bar,[9] which is also seen in other materials.[2] Accompanying the suppression of the relaxor state is the vanishing of the frequency dispersion in the response, as seen and as expected.[1,2]

Figure 3 compares the $\epsilon'$ $(T)$ response of SCT (0.007) and pure STO at 0.5 kbar. The major difference occurs below ~30 K, where $\epsilon'$ $(T)$ of SCT (0.007) rises more rapidly with decreasing $T$—an effect that we attribute to increased correlations among the polar nanodomains as well as to a lower soft mode ($TO_1$) frequency. Above 30 K the two responses appear very similar, but there is a systematic difference, $\epsilon'$ of SCT (0.007) being slightly higher over most of the temperature range covered. This is clearly revealed by the differences in the $1/\epsilon'(T)$ responses as shown.

### C. Temperature-pressure phase diagram

Figure 4 shows the temperature-pressure phase diagram for SCT (0.007). The crystal is in the paraelectric state at temperatures above 20 K for all pressures. At lower temperature and low pressure the $\epsilon'$ $(T)$ response is relaxorlike. Using $T_{\max}$ at 10 kHz versus pressure to separate the paraelectric and relaxor FE states, the relaxor state is confined to the triangular region from 0 to 18 K and between ambient and 0.5 kbar. Over the limited range of the data, the results in

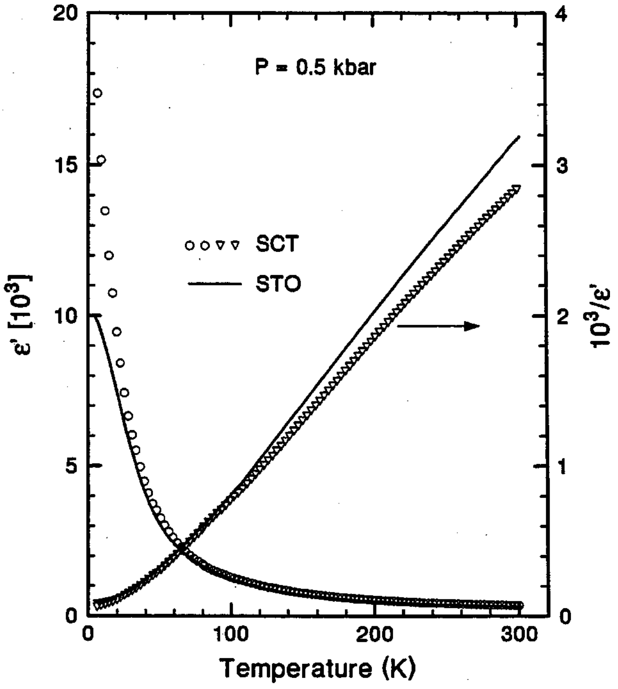

FIG. 3. The $\epsilon'$ $(T)$ and $1/\epsilon'$ $(T)$ response of SCT (0.007) at 0.5 kbar. The responses of pure $SrTiO_3$ (STO) at the same pressure are shown for comparison.

Fig. 4 show that $T_m$ decreases linearly with pressure, suggesting a finite slope as $T_m \rightarrow 0$ K (broken line). For an equilibrium phase transition, the third law of thermodynamics requires that $T_c$ vanishes with an infinite slope, i.e., $dT_c/dP \rightarrow -\infty$ as $T_c \rightarrow 0$ K. For a glasslike transition, on the other hand, residual configurational entropy as $T_m \rightarrow 0$ K allows for a finite $dT_m/dP$.[2] Although the data in Fig. 4 do not cover a sufficient range to draw a definitive conclusion, they are suggestive of a glass transition.

Defining the quantum paraelectric (QPE) region by the onset of a nearly temperature-independent $\epsilon'$ at the lowest temperatures, the dashed line separates the paraelectric and QPE regions. Thus, as the hydrostatic pressure increases from ambient, there is a rapid suppression of the relaxor state

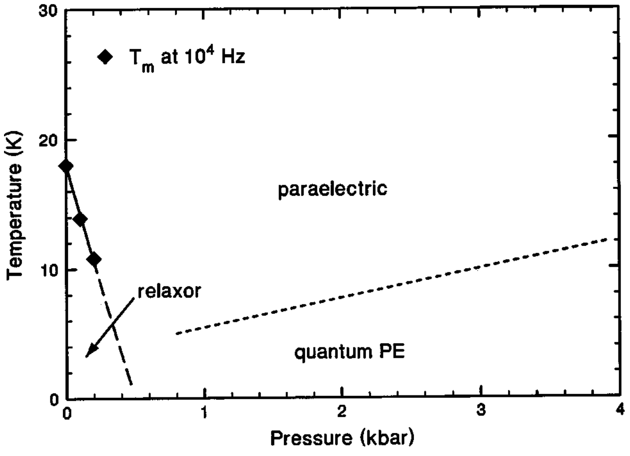

FIG. 4. Temperature-pressure phase diagram for SCT (0.007).

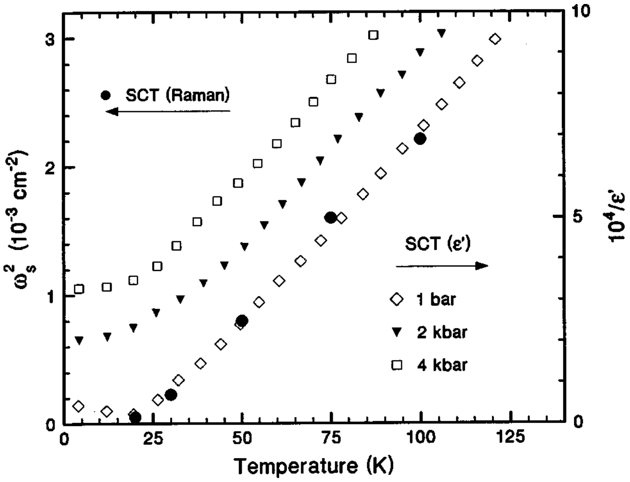

FIG. 5. Comparison of the temperature dependences of the square of the soft mode frequency, $\omega_s$ (Ref. 4), and $1/\epsilon'$ responses at 2 and 4 kbar, which also reflect the $T$ dependences of $\omega_s^2$ at these pressures.

followed by a slow expansion of the QPE state. The dashed line in Fig. 4 does not, of course, represent a true phase boundary; it merely represents the experimental finding that the range over which $\epsilon'$ becomes nearly independent of $T$ at low temperatures expands with increase $P$, a common observation for ferroelectrics in the quantum regime.[2]

### D. Temperature and pressure dependences of the susceptibility in the paraelectric phase

Kleemann *et al.*[4] deduced the 1-bar temperature dependence of the FE soft mode frequency ($\omega_s$) of the same crystal from Raman scattering measurements. For soft mode FEs, $\epsilon'$ and $\omega_s$ are related by a Lyddane-Sachs-Teller relationship such that $\omega_s^2\epsilon' \approx$ const. Figure 5, which is a coplot at 1 bar of $\omega_s^2(T)$ and our $(1/\epsilon')(T)$ data, shows that this relationship is well-obeyed for the SCT (0.007) crystal, i.e., the temperature dependence of $\omega_s$ determines that of $\epsilon'$. Similarly, we expect the pressure ($P$) dependence of $\omega_s$ to determine the pressure dependence of $\epsilon'$, as has been demonstrated for many soft mode systems.[7] Thus, the $P$ dependence of $1/\epsilon'(T)$ in Fig. 5 represents the $P$ dependence of $\omega_s^2 T$) also.

Figure 6 compares isothermal $\epsilon'$ at 10 kHz versus $P$ at temperatures between 50 and 293 K. In this temperature range $\epsilon'$ is independent of frequency. The data at $T \geqslant 100$ K were recorded versus decreasing $P$ after cooling from room temperature at 6 kbar. However, isothermal measurements for both increasing and decreasing pressure showed no hysteresis in this temperature range. The 50-K data were deduced from isobaric $\epsilon'$ ($T$) plots. $\epsilon'$ ($P$) at 200 and 293 K decreases nearly linearly with increasing $P$ over the modest pressure range of the data. The initial logarithmic derivatives, $(\partial \ln\epsilon'/\partial P)_T$, are $-0.021$ and $-0.032$ per kbar at 293 and 200 K, respectively. The slope at 293 K compares favorably with the slope $-0.022$/kbar for pure $SrTiO_3$ at 298 K.[10] At lower temperatures the dependence of $\epsilon'$ on pressure becomes much stronger and increasingly nonlinear, as shown.

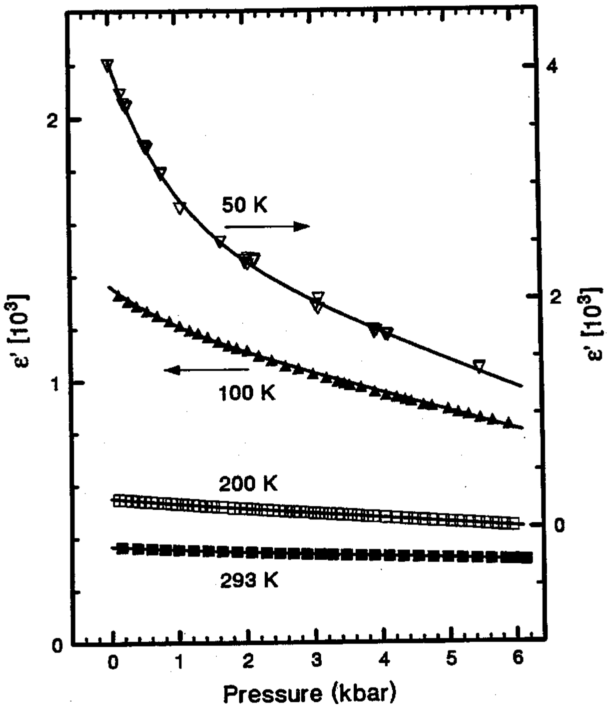

FIG. 6. Isothermal pressure dependence of $\epsilon'$ of SCT (0.007).

All of the $\epsilon'$ ($P$) effects in Fig. 6 are well-known properties of soft mode systems.[7] From $\omega_s^2\epsilon' =$ const we have, for the $P$ dependence of $\omega_s$,

$$(\partial \ln \omega_s/\partial P)_T = -1/2(\partial \ln\epsilon'/\partial P)_T. \tag{1}$$

Taking the initial $\epsilon'$ ($P$) slopes in Fig. 6, we find that $(\partial \ln \omega_s/\partial P)_T$, i.e., the fractional change in $\omega_s$, increases from 1.05%/kbar at 293 K to 2.85%/kbar at 100 K, to ~40%/kbar at 50 K, rates that are typical of perovskites well above $T_0$.[7]

The $T$ dependence of $\epsilon'$ in the high temperature paraelectric phase of $ABO_3$ ferroelectrics usually obeys a Curie-Weiss law, $\epsilon' = C/(T-T_0)$ over a wide $T$ range. Here $C$ is the Curie constant and $T_0$ is the Curie-Weiss temperature. Relaxors, however, show large deviations from this law starting well above $T_m$. In fact, such deviations set in upon the nucleation of the polar nanodomains, i.e., at the so-called Burns temperature, $T_{\mathrm{Burns}}$, and increase with decreasing $T$ as the size of the domains and their correlations increase.[2] It has been found that the $\epsilon'$ ($T$) response of relaxors above $T_m$ can be generally represented by the power law expression,[2]

$$(\epsilon' - \epsilon'_\infty) = C(T-T_m)^{-\gamma}, \tag{2}$$

where $\epsilon'_\infty$ is the limiting high temperature value of $\epsilon'$. At $T > T_{\mathrm{Burns}}$, $\gamma \rightarrow 1.0$, and Eq. (2) is simply the Curie-Weiss law. However, below $T_{\mathrm{Burns}}$, $\gamma$ can reach values up to 2.0. Although there appears to be no unambiguous justification for a $\gamma = 2.0$ for relaxors, a $\gamma = 2$ regime is predicted on the basis of lattice dynamical models solved within the framework of quantum statistical mechanics to describe the deviation from Curie-Weiss behavior in the quantum displacive limit (i.e., $T_c \equiv 0$ K) of ferroelectrics.[2,3,11,12] In this case the deviation

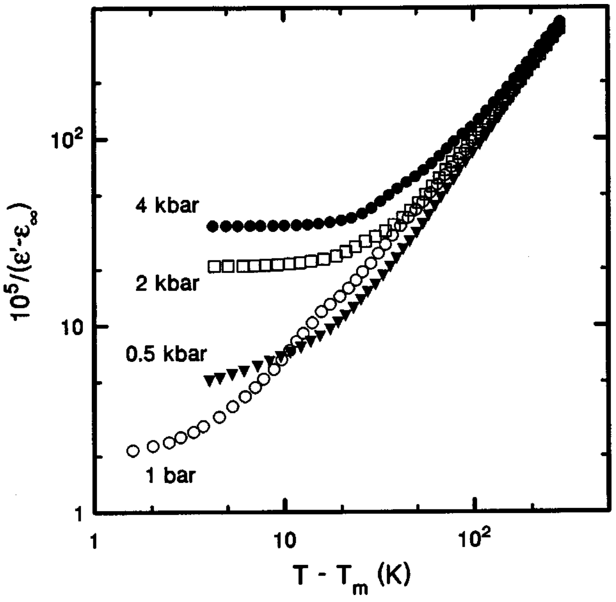

FIG. 7. Log-log plot of the temperature dependence of the $\epsilon'$ response of SCT (0.007) at different pressures as suggested by Eq. (2).

from $\gamma=1$ is attributed to quantum fluctuations. This prediction has been met for systems exhibiting equilibrium phase transitions[2] as well as for the $Sr_{1-x}Ca_xTiO_3$ system in the extreme dilute limit.[3,11]

Figure 7 shows double-logarithmic plots of $(\epsilon' - \epsilon'_\infty)^{-1}$ vs. $(T - T_m)$ for SCT (0.007) at 1 bar and elevated pressure. Taking $\epsilon'_\infty = 100$ and $T_m = 18$ K, the 1-bar results yield $\gamma=1.23$, which is comparable to $\gamma \approx 1.3$ for a SCT (0.0075) sample measured by Bednorz and Mueller.[3] Assuming $T_m = 0$ K at 0.5 kbar (see Fig. 3), the data in Fig. 7 yield $\gamma=1.44$, and at 2 kbar $\gamma=1.18$. Thus, these results suggest that $\gamma$ increases with decreasing $T_m$ (as observed for quantum ferroelectrics), but it does not reach a value of 2.0 as $T_m \rightarrow 0$ K (unlike quantum ferroelectrics).[2]

### E. Effects of dc biasing electric fields

Bianchi *et al.* demonstrated the strong influence of dc bias on the dielectric response so for SCT (0.007) at 1 bar.[5] We find equally strong field effects at elevated pressures. Figure 8 shows the responses at 0.1 and 0.2 kbar, which are qualitatively similar to what is observed at 1 bar.[5] The large suppression of the peak amplitude $\epsilon'_{\max}$ and the shift of $T_m$ to higher temperatures are the expected behaviors for quantum ferroelectrics, and result from field stabilization of the local potential of a dipolar entity making one of its potential minima deeper and the other shallower [inset in Fig. 8(a)]. Thus, more thermal energy is needed to overcome the deeper barrier and induce the transition. Additionally, the field aligns and clamps the polarization of the sample, reducing its small signal ac susceptibility. These effects are well known from Landau free energy theory, which predicts that $T_m$ increases with field strength as $E^{2/3}$. Bianchi *et al.*'s 1-bar data confirm this prediction for $E > 50$ V/cm. Our results with bias at high pressure are not as extensive as those of Bianchi *et al.*, but they are in close agreement with the latter. The inset in Fig. 8(b) compares our 0.2 kbar $\Delta T_m$ versus $E$ results with the 1-bar data.[5] Another feature to note is the fact that these very large biasing field effects occur only in the quantum regime. They vanish above 25–30 K, as shown in Fig. 8.

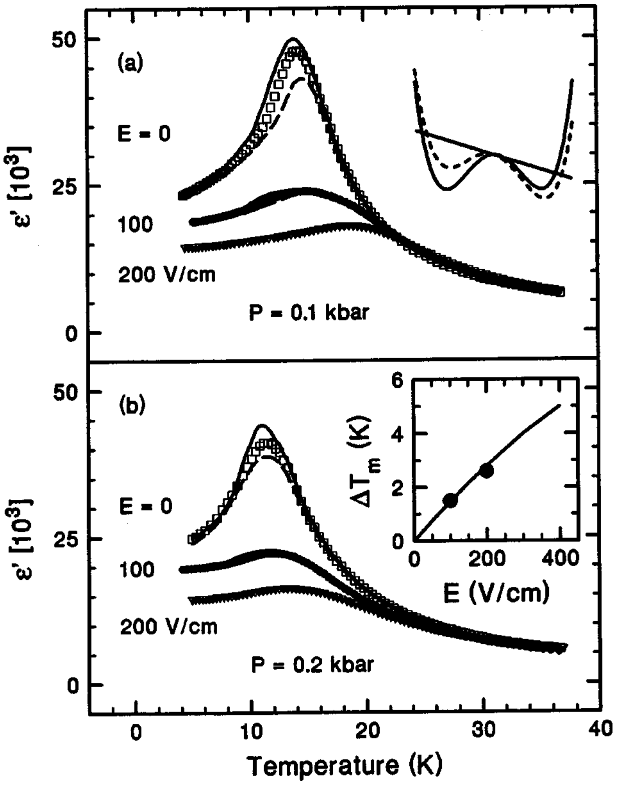

FIG. 8. The influence of dc bias on the $\epsilon'$ $(T)$ response of SCT (0.007) at 0.1 and 0.2 kbar. The inset in (a) depicts the effect of bias on the potential for the hopping of dipolar entities. The inset in (b) shows the shift of the glass transition temperature $T_m$ with field for SCT (0.007) at 1 bar (solid line, Ref. 5) and at 0.2 kbar (solid circles).

In the case of relaxors, additional biasing field effects can be expected and are observed. Cooling a relaxor in the presence of a dc field aligns its polar nanodomains increasing their sizes and correlations, effectively canceling the influence of random fields and reducing the frequency dispersion in the relaxor state. At sufficiently high fields, which are still very modest in the quantum regime, the domains can become sufficiently large so as to percolate the whole sample and lead to the onset of long-range order and a normal FE transition. This is a field-induced nano-to-macro domain transition. Evidence of such a transition in relaxors has come from dielectric response and TEM measurements.[2]

Evidence for these effects can be seen in our pressure results (Fig. 8). The relaxor nature of the response at low bias is evident. The dispersion is essentially gone at the very modest field of ~300 V/cm. Taking $\Delta T_f$, the difference between $T_m$ at $10^6$ and $10^2$ Hz, as a measure of the strength of the relaxor character of the response, we find that $\Delta T_f$ decreases from 1.8 K at 0 V/cm to 0 K by ~300 V/cm. The vanishing of the dispersion in $T_m$ at high bias is a reflection of the transition acquiring normal ferroelectric character, as expected.[2]

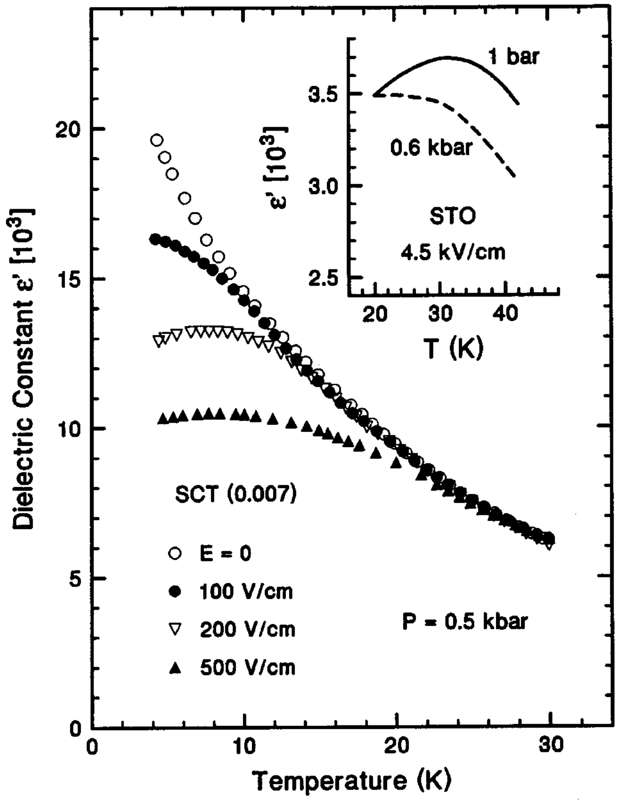

FIG. 9. The influence of dc bias on the $\epsilon'$ $(T)$ response of SCT (0.007) at 0.5 kbar. The inset shows the $\epsilon'$ $(T)$ response of pure $SrTiO_3$ (STO) at a bias of 4.1 kV/cm.

The 0.5-kbar results present an interesting case. As noted earlier, at this pressure the relaxor state is completely suppressed and the sample is in a dispersion-free quantum paraelectric state—a state akin to that of undoped $SrTiO_3$ at 1 bar. The application of bias to these two crystals in this state produces qualitatively similar results. First, there is a large suppression in the magnitude of $\epsilon'$ in the quantum regime as shown in Fig. 9. Second, it is known from early work[13,14] that a sufficiently large field can induce ferroelectricity with a very broad and shallow $\epsilon'$ $(T)$ peak in $SrTiO_3$ (Fig. 9, inset; note the highly expanded $\epsilon'$ axis) with an accompanying reduction in crystal symmetry. The present 0.5-kbar data on SCT (0.007) hint at the existence of such a field-induced transition. The 200-V/cm data in Fig. 9 reveal a broad $\epsilon'$ $(T)$ peak at ~8 K. At 500 V/cm there is still evidence of a peak in $\epsilon'$ $(T)$, but, unfortunately, $\epsilon'$ is further suppressed and the peak is even broader.

The results in Fig. 9 show an important difference between our SCT (0.007) sample and pure $SrTiO_3$. Whereas the latter requires fields of kilovolts/cm to induce the FE state, or at least a peak in $\epsilon'(T)$ (4.5 kV/cm in the inset in Fig. 9), this state can be induced in the SCT (0.007) crystal at fields that are an order of magnitude smaller. We believe this is a reflection of the presence of Ca-induced polar nanodomains in the latter putting it closer to its FE instability limit. We also note (inset) that at 0.6 kbar, a field of 4.5 kV/cm is not sufficient to induce ferroelectricity in STO.[14]

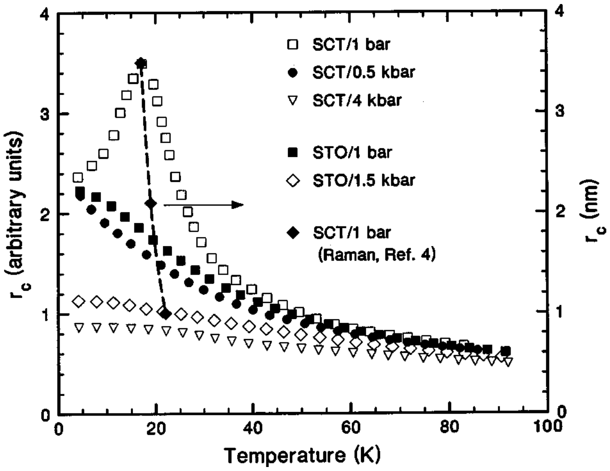

FIG. 10. Temperature dependence of the correlation length for dipolar interactions in SCT (0.007) and pure $SrTiO_3$ (STO) at different pressures deduced from the dielectric response. Also shown are 1-bar results for SCT (0.007) deduced from Raman measurements.

### F. Unique aspects of the incipient ferroelectric $SrTiO_3$ host

As already noted, a unique aspect of the SCT (0.007) crystal is the presence of the dipolar Ca-induced nanodomains in an incipient FE host, $SrTiO_3$. The very low, but finite, frequency $\omega_s$ of the soft mode of this crystal at low temperatures makes the polarizability $(\sim 1/\omega_s)$ very large. This polarizability is further enhanced, and $\omega_s$ is renormalized, by the presence of the dipolar entities.

The low frequency of the soft FE mode (a long wavelength TO phonon) is determined by the near cancellation of the short-range forces by the Coulombic forces, and increases rapidly with pressure[7] leading to a large decrease in the correlation length $r_c$ $(\propto 1/\omega_s \propto \sqrt{\epsilon'})$.[2] Figure 10 shows the temperature dependence of $r_c$ for SCT (0.007) at different pressures deduced from the dielectric data, and compares the behavior to that of pure STO. The strong enhancement of $r_c$ with decreasing $T$ on approaching $T_m$ at 1 bar for SCT (0.007), and the strong decreases of $r_c$ with pressure at low temperatures, are evident. The corresponding decreases in the correlation volumes are, of course, huge, and this result is at the heart of the interpretation of the present results.

Deducing $r_c$ from dielectric data gives relative, and not absolute, values of $r_c$. Thus, $r_c$ in Fig. 10 is given in arbitrary units. Kleemann *et al.*[4] deduced a quantitative value of the radius of the average polar cluster $(=r_c)$ for SCT (0.007) at 1 bar from analysis of the Raman line shape and intensity over a limited temperature range. Their analysis showed that $r_c$ increases from 1 nm at 22 K to 3.5 nm at 17 K (Fig. 10 read against the right ordinate). These results allow us to scale the $r_c(T)$ results deduced from the dielectric data for comparison. This scaling was done by equating the present arbitrary $r_c$ value at $T_m$ (~17 K) to Kleemann *et al.*'s value (3.5 nm) at the same temperature at 1 bar. Accordingly the scale of the left ordinate in Fig. 10, though in arbitrary units, matches the scale (in nm) of the right ordinate. It is immediately noticeable that, although both sets of 1-bar $r_c(T)$ data show the rapid decrease of $r_c$ with increasing $T$ from $T_m$, Kleemann *et al.*'s $r_c$ falls off much more rapidly than is suggested by the dielectric data. The cause of this discrepancy is not clear.

Examination of the results in Fig. 10 provides several insights into the physics of SCT (0.007). For this composition the average separation between $Ca^{2+}$ ions is ~2 nm. If percolation requires a full overlap of the correlation radii of adjacent polar nanodomains, then $r_c$ at the percolation limit must be equal to 2.1 nm.[4] The dielectric data in Fig. 10 suggest that at $T \gtrsim 50$ K, $r_c$ of SCT (0.007) is $<1$ nm and is essentially the same as that for pure STO, indicating that the nanodomains are nonoverlapping. Below this temperature, the larger $r_c$ causes the domains to overlap, interact, and increase their correlations, that reach a maximum at $T_m$, below which temperature dipolar motion slows down causing the polarizability and thereby $r_c$ to decrease.

At 0.5 kbar, an overlap of the nanodomains begins below ~30 K ($r_c \approx 1.1$ nm), with indications that $r_c$ may not reach the full percolation value of 2.1 nm even at the lowest temperatures, consistent with the observation that the transition is suppressed by this pressure. By 4 kbar $r_c < 1$ nm at all temperatures—there is no overlap or correlations among the polar domains, and the crystal is not unlike pure STO.

## IV. CONCLUDING REMARKS

The remarkably large pressure and bias field effects on the dielectric properties and phase behavior of SCT (0.007) are manifestations of the delicate balance between competing interactions in this system. At the heart of the physics of this crystal is the behavior of the FE ($TO_1$) soft mode. The quasi first-order Raman scattering results of Kleemann *et al.*[4] have identified the sum frequency, $2TO_1$, associated with the lattice and a low frequency $TO_1$ cluster (nanodomain) mode. Both of these $TO_1$ modes soften with decreasing *T*, their frequencies reaching about the same low, but finite, value ($\sim 7\ \mathrm{cm}^{-1}; \hbar\omega_s \approx 0.9$ meV) at $T_m$. The Raman results favor orthorhombic ($C_{2v}$) symmetry for the low temperature phase, i.e., below $T_m$, as well as for the polar nanodomains above $T_m$. This implies equilibrium tetragonal ($D_{4h}$)-to-orthorhombic phase transition for the crystal at $T_m$. However, at this time there is no confirming evidence, (e.g., from diffraction data) for a bulk phase transition. High resolution diffraction studies would be very desirable. The situation here is probably akin to that for dilute $KTa_{1-x}Nb_xO_3$ ($x \approx 0.01-0.02$) where Raman scattering results[15,16] gave evidence of long-range FE correlations (on the length scale of the wavelength of optical phonons) and lower symmetry below $T_m$, but high resolution x-ray diffraction[17] did not reveal evidence of a bulk phase transition. Thus, the issue is the length scale of the correlations—an issue that requires further study.

In this work we have emphasized the relaxational properties of SCT (0.007). The observed pressure and bias field effects can be understood in terms of a relaxor model, and at the heart of the physics is the strong dependence of the soft mode frequency on the various external variables. It is this dependence which determines the correlation length for interactions and correlations among the $Ca^{2+}$-induced polar nanodomains whose existence is a certainty. It will be interesting to investigate the influence of pressure on the susceptibility of SCT within a quantum scaling concept similarly as was done for the dependence on *E* and *T*.[18]

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[1] B. E. Vugmeister and M. D. Glinchuk, Rev. Mod. Phys. **62**, 993 (1990).

[2] G. A. Samara, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, New York, 2001), Vol. 56, pp. 239–483.

[3] J. G. Bednorz and K. A. Müller, Phys. Rev. Lett. **52**, 2289 (1984).

[4] W. Kleemann, A. Albertini, M. Kuss, and R. Lindner, Ferroelectrics **203**, 57 (1997).

[5] U. Bianchi, J. Dec, W. Kleemann, and J. G. Bednorz, Phys. Rev. B **51**, 8737 (1995).

[6] K. Leung, Phys. Rev. B **63**, 134415 (2001).

[7] G. A. Samara and P. S. Peercy, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1981), Vol. 36.

[8] K. B. Lyons, P. A. Fleury, and D. Rytz, Phys. Rev. Lett. **57**, 2207 (1986).

[9] K. A. Müller and H. Burkard, Phys. Rev. B **19**, 3593 (1979).

[10] G. A. Samara, Phys. Rev. **151**, 378 (1966).

[11] R. Morf, T. Schneider, and E. Stoll, Phys. Rev. B **16**, 462 (1977).

[12] J. Dec and W. Kleemann, Solid State Commun. **106**, 695 (1998).

[13] J. M. Worlock and P. A. Fleury, Phys. Rev. Lett. **19**, 1176 (1967).

[14] E. Hegenbarth and C. Frenzel, Cryogenics **7**, 331 (1967).

[15] W. Kleemann, F. J. Schäfer, and D. Rytz, Phys. Rev. Lett. **54**, 2038 (1985).

[16] J. Toulouse, P. DiAntonio, B. E. Vugmeister, X. M. Wang, and L. A. Knauss, Phys. Rev. Lett. **68**, 232 (1993).

[17] S. R. Andrews, J. Phys.: Condens. Matter **18**, 1357 (1985).

[18] W. Kleemann, J. Dec, and B. Westwanski, Phys. Rev. B **58**, 8985 (1998).