

$\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$: An XY Quantum Ferroelectric with Transition to Randomness

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A series of twenty homogeneous $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ mixed crystals has been measured dielectrically between 4.2 and 300 K. In the tetragonal phase, the dielectric constant perpendicular to the c axis becomes peaked above $x_c = 0.0018$, the quantum mechanical onset for displacive ferroelectricity. The polarization $\perp c$ can be switched between the two equivalent a axes, i.e., the system is an XY , $n = 2$, quantum ferroelectric. Above $x_r = 0.016 \pm 0.002$, the $\epsilon(T)$ peaks round in a distinct manner which we attribute to the onset of a random-field-induced domain state.

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Pure SrTiO_3 is a quantum paraelectric. Its low-temperature dielectric constant, perpendicular to the c axis, increases to about 30 000 upon cooling, and then remains temperature independent below 3 K because of quantum fluctuations.¹ Application of stress perpendicular to the c axis induces *uniaxial* ferroelectricity perpendicular to the c and stress axes. This was shown in beautiful dielectric and Raman experiments by Uwe and Sakudo.² Thus, in principle, the onset of uniaxial $n = 1$ quantum ferroelectricity (QF) can be achieved by uniaxial stress. The $n = 1$ QF case was first realized by Samara in applying hydrostatic pressure to KH_2PO_4 , an $n = 1$ case, causing T_c to vanish at a critical pressure p_c .³ The $n = 3$ case was then observed in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ mixed crystals by Höchli and co-workers for $x_c = 0.008$.⁴ This system exhibits ferroelectricity in the whole range from x_c to $x = 1$.

Here, we report on results of SrTiO_3 crystals doped up to 12% with Ca^{2+} ions which show several novel features: Above a critical concentration $x_c = 0.0018$, the quantum mechanical critical point, the crystals become ferroelectric with polarization axes along pseudocubic $[110]$ and $[\bar{1}\bar{1}0]$ directions perpendicular to the c axis oriented $\parallel [001]$. The polarization can be switched between the two, i.e., the system is an XY , $n = 2$ ferroelectric with quartic anisotropy. Upon increase of the Ca concentration at $x_r > 0.016 \pm 0.002$, the peaks in dielectric constant round, a phenomenon which we attribute to the onset of a random-field domain state. Much effort has recently been devoted to the lower critical dimensionality d_1 of random systems. If the dimensionality d of a system is below d_1 , no long-range order can occur and the system will show a domain state. For random fields, d_1 has been investigated theoretically, and is 4 in Heisenberg and XY isotropic systems for the classical short-range and dipolar cases.^{5,6} In the quantum regime, d_1 is lowered by 1, to 3, in the absence of

random fields,⁷ but is again 4 when they are present.⁸ The experiments reported here suggest that for the dipolar XY random-field case with sizable quartic anisotropy, $d_1 > 3$ in the classical regime.

$\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ single crystals ($x = 0.0$ to 0.12) were grown by the flame-fusion and the zone-melting techniques.⁹ Electron microprobe analysis was used to determine the chemical composition and to check the uniform Ca distribution, which proved to be homogeneous with fluctuations Δx of ± 0.0005 lying in the range of counting statistics.

Capacitance and conductance measurements were performed mainly at 1591.5 Hz on a Wayne Kerr (B 642) bridge with an applied measuring field of 200 mV peak to peak. The platelets cut from the crystals were approximately $6 \times 2 \times 0.3$ mm³ in size. Electrodes of copper covered with gold were prepared by vacuum deposition and extended to the edges of the large faces. Because of the high dielectric constants measured as compared to air, corrections of the data with respect to boundary effects were assumed to be unnecessary. An earlier set of measurements showed the dielectric constant to be dependent on sample thickness and strains. Even well-annealed crystals did not show a clearly peaked ferroelectric $\epsilon(T)$ curve in the concentration range of 0.0020 to 0.0075, when their thickness was smaller than 0.2 mm. Unetched SrTiO_3 crystals show surface layers of approximately 0.1 mm.¹⁰ It is well possible that this is the reason for the rounding effects observed in thin samples.

First dielectric constants ϵ for the mixed and (100)-oriented crystals were measured in thermal equilibrium between 300 and 4.2 K. In the case of pure SrTiO_3 , ferroelectricity was found to be suppressed because of nonvanishing zero-point motion.¹ As can be seen from Fig. 1, below 10 K, ϵ no longer depends on T . With increasing Ca content x , $\epsilon(T)$ of the mixed crystals is found to rise.

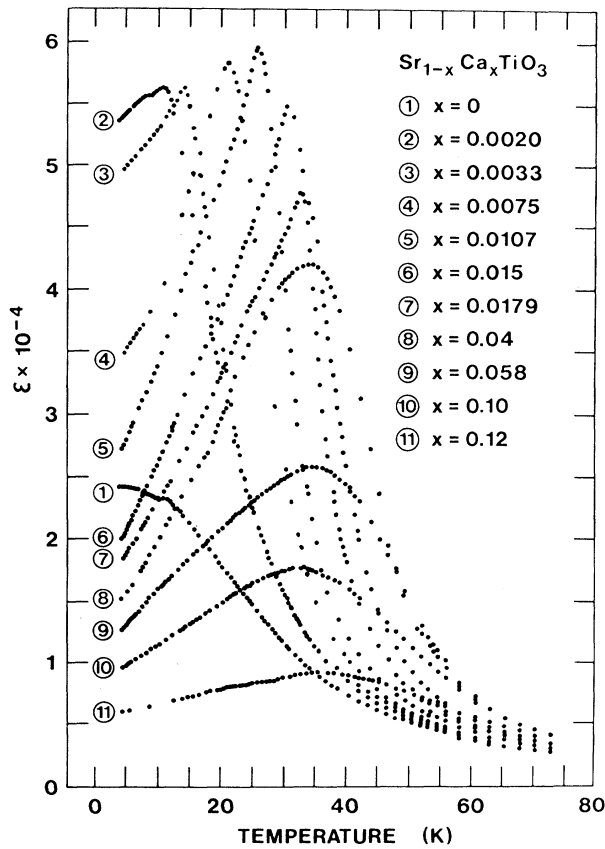


FIG. 1. Temperature dependence of the dielectric constant $\epsilon_{[100]}$ of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ crystals with x between 0.0 and 0.12.

At $x = 0.002$, a maximum indicates that $T_c \neq 0$. At $x > 0.016$, the transition becomes diffusive, a behavior often observed in solid solutions.¹¹ The spread of the transition temperature over a certain range can be assigned to either compositional fluctuations or structural disorder.^{4,12} However, T_m as deduced from the minimum value of $1/\epsilon$ vs T is found to become independent of the concentration for $x > 0.016$. The rounding of the $\epsilon(T)$ curves between the quantum mechanical critical point at $x_c = 0.0018$ and $x = 0.0075$ occurs where the dependence of T_c is steepest, actually proportional to $(x - x_c)^{1/2}$ as shown in Fig. 2(a). Thus, macroscopic compositional fluctuations have greatest influence, and the less-pronounced peaks may be attributed to this case. In Fig. 2(c), the temperature width ΔT at 90% of ϵ_{\max} is plotted ($\Delta T = T_{0.9\epsilon(\max)} - T_{\epsilon(\max)}$ for $T_{0.9\epsilon(\max)} > T_{\epsilon(\max)}$). One clearly sees a decrease till $x_r = 0.016 \pm 0.002$ from where on ΔT increases linearly. At this same concentration, the effective slope of $1/\epsilon(T)$ shows a minimum, Fig. 2(b), and the T_m curves break away from the $(x - x_c)^{1/2}$ law of quantum fer-

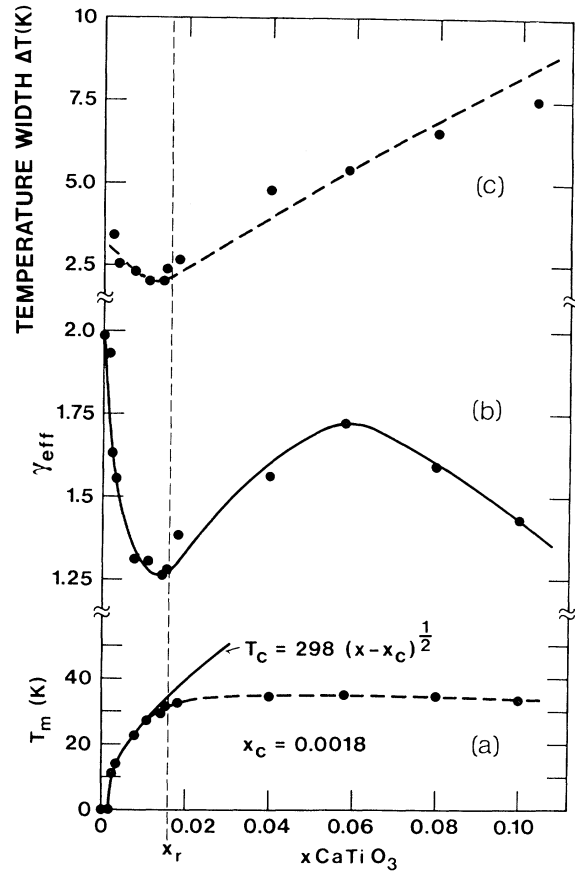


FIG. 2. (a) Temperature T_m at ϵ_{\max} as a function of CaTiO_3 concentration x . The solid line indicates the $(x - x_c)^{1/2}$ law for QF. (b) Effective susceptibility exponent γ_{eff} as a function of x . (c) Temperature width $\Delta T = T_{0.9\epsilon(\max)} - T_{\epsilon(\max)}$ measured at 90% of ϵ_{\max} as a function of x .

roelectrics. This law was predicted theoretically⁷ and observed experimentally in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$.⁴

A first possibility was that the whole system is random and x_r is the concentration where ferroelectric domains become smaller than the thickness 0.03 cm of the sample. To exclude this possibility, we further measured $\epsilon(T)$ parallel to the [010] axis where the sample dimension for $x = 0.0107$ was ten times the thickness, i.e., 0.3 cm. For both cases, the same peak value of $\epsilon(T)$ was obtained. This size independence indicates that we are observing true quantum ferroelectric behavior perpendicular to the c axis of the platelets. Indeed, measuring $\epsilon(T)$ along the latter axis showed the relatively low dielectric constant of 7600, being temperature independent below 10 K similar to pure SrTiO_3 . Therefore, the system can polarize spontaneously but in two spatial directions below x_r , and $T_m = T_c$ in that range. Thus, it is an XY, $n = 2$ quantum fer-

roelectric. We recall that $\text{Tb}_2(\text{MoO}_4)_3$ is a classical XY improper ferroelectric resulting from piezoelectric coupling.¹³ Because our crystals are tetragonal above T_c , a quartic anisotropy in dielectric constant was expected. We found that we could polarize the crystals along the tetragonal a axes by applying electric fields, and switch P between them below T_c . It should be noted that the a axes are $\langle 110 \rangle$ and not $\langle 100 \rangle$ pseudocubic directions. Figure 3 shows the dielectric constant measured for such a polarized crystal. Its peak value is 110 000, the second highest reported to date for mixed crystals, the highest being 160 000 at the cubic-to-tetragonal ferroelectric transition in $\text{KTa}_{0.9}\text{Nb}_{0.1}\text{O}_3$ by Kind and Müller.¹⁴

Since we observe polarizations across (110) platelets, i.e., along $[110]$ directions as well as parallel to the surface along $[1\bar{1}0]$, we can exclude the ferroelectricity observed as being due to strains introduced perpendicular to the thinnest sample

dimension by the polishing-etching procedure. Furthermore, such $[110]$ strain would result in a polarization along the c axis $\parallel [001]$, and in (100) platelets a polarization $\parallel [010]$ should appear,² whereas we find $P \parallel \langle 110 \rangle$. Therefore, Ca doping is microscopically quite different from applied uniaxial stress.

Smolensky's group has conducted extensive research in disordered high-temperature cubic systems,¹¹ and found rounded $\epsilon(T)$ curves which they called "diffusive transitions;" the rounding was attributed to compositional fluctuations. Ionic replacement and site disorder lead to both compositional fluctuations and random electric fields. In the latter case, from renormalization group studies for $d = n = 3$ systems, in the classical regime, $d_1 = 4$ (Refs. 5 and 6) is expected, which also agrees with the experimental observations.¹¹ In contrast, in the cubic $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, $n = 3$ compounds, the transition is ferroelectric in the *whole range* above x_c (Ref. 4) till $x = 1$.¹⁵ Here, if we replace Ta^{5+} by Nb^{5+} with practically the same effective charge and ionic radii, it is the different mass which entails a different soft-mode frequency and therefore a different T_c .¹⁶

In our XY system, we observe a transition from the QF state as in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ to one with a "diffusive character." This transition appears to be due to random electric fields introduced by Ca^{2+} doping in SrTiO_3 . The Ca^{2+} has the same charge as Sr^{2+} and will mainly occupy this site. Its ionic radius of 0.99 \AA is small compared to the Sr^{2+} of 1.12 \AA which sets up random strains e_{ij} coupling to the polarization with terms like $e_{ij}P_mP_n$. Alternatively, some of the Ca^{2+} may be located at Ti^{4+} sites. To balance the charge misfit, a next-neighbor oxygen can be vacant, V_0 , forming a $\text{Ca}^{2+}-V_0$ neutral center. Such $\text{Ca}^{2+}-V_0$ centers form dipoles and thus set up local electric fields. The ESR of $\text{Me}^{2+}-V_0$ centers in SrTiO_3 like $\text{Mn}^{2+}-V_0$ has been observed.¹⁷ In our case, we expect random-field XY behavior which has $d_1 = 4$ (Refs. 5,6); in $d = 3$ dimensions, this yields no ordering, i.e., a domain state as found above x_r . The observation of true QF below x_r is then a puzzle. Either the centers responsible for the random field are only formed above x_r or, if the effect is due to random strains, we shall have an effect of lower critical dimensionality crossover. Starting with x_c towards x_r , the system crosses over from true QF at x_c to classical behavior as T_c becomes different from zero. This is exemplified by the lowering of the measured effective susceptibility exponent from 2 towards 1, the classical regime, Fig. 2(b). This crossing over may

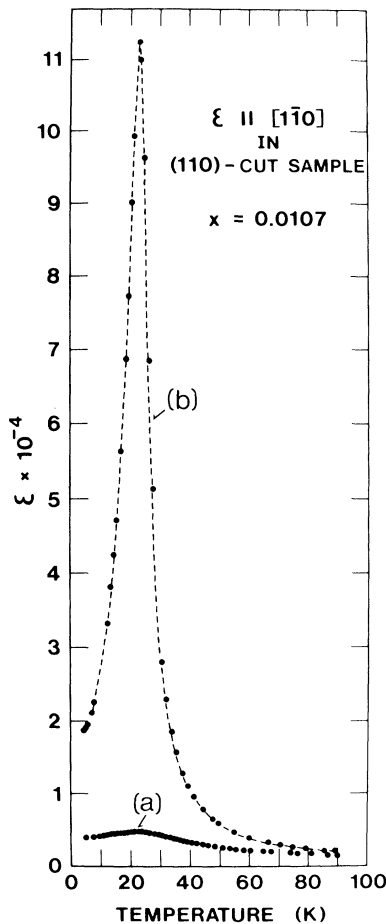


FIG. 3. $\epsilon_{[1\bar{1}0]}(T)$ curve (a) before and (b) after switching the polarization P . The applied field $E = 400 \text{ V/cm}$.

have the effect of changing the effective lower lattice dimensionality of the system from $d_1=3$ at x_c to $d_1=4$ at higher T_c . In fact, when $\gamma = 1.25 \pm 0.15$ the transition occurs.

As soon as $T_c \neq 0$ there must exist a regime very close to T_c where classical behavior is present. Schmelzer has considered this case of random quantum ferroelectrics in a most recent field theoretical study.¹⁸ The renormalized mass and the coupling constant become temperature dependent. He finds that the region of crossover seen experimentally is related to the Matsubara frequency cut-off, and the classical region is so small that it is not accessible experimentally. Therefore, in our experiments the rounding due to the random-field classical case is not observed, and true ferroelectric response is measured at finite electric fields for $x < x_r$.

For an isotropic random field system, $d_1=4$ in the quantum case as well. However, in our system, we certainly have a sizable quartic anisotropy: From Fig. 3, we obtain a dielectric constant anisotropy of 23 at 1.07% Ca^{2+} . The $\epsilon(T)$ peak of 110000 is clear evidence for a ferroelectric transition. With quartic anisotropy, a ferroelectric state in presence of random fields is possible⁶ with a first-order transition. For sufficiently large quartic anisotropy, the XY system decouples into two Ising systems which may have $d_1=2$ or 3.^{19,20} Then at sufficiently high random fields, the ferroelectric state can give way to a polar-glass state. However, at a spin-glass transition, $\chi(T)$ shows a frequency-dependent cusp. Our data were always more rounded the higher the Ca^{2+} content, and changed less than 5% by varying the frequency between 10 and 10^5 Hz.

In conclusion, the $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ mixed-crystal system shows XY -type quantum ferroelectricity above $x_c=0.0018$ along the a axes of the paraelectric parent phase with a transition to a random phase above $x_r > 0.016 \pm 0.002$. The nature of this transition is presently being investigated with other

methods.

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