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Domain state properties of $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ single crystals

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Experimental results reveal that the dielectric permittivity depends strongly on the amplitude of the ac test signal, and the polarization varies with time in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ single crystals. These characteristics are attributed to the occurrence of a domain state in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$. Data analysis suggests that $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is a system with quenched random-field disorder. The origin of the random fields and the physics in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ are discussed.

Defects such as random impurities, dislocations, vacancies, etc., are unavoidable in any real system. The understanding of the effects of these defects on the phase transition is essential for any meaningful comparison of theories and experiments. By considering the energetics of domain formation following the fluctuations in the random field, Imry and Ma¹ were able to show that for a Heisenberg or a xy system with a continuous symmetry of order parameter, an ordered state is unstable against an arbitrarily small random field. That is, instead of a long-range order, the system will break up into domains, a state that is called a "domain state".² Much succeeding theoretical work has been devoted to the lower critical dimensionality d_1 of random systems. If $d < d_1$, no long-range order can occur and the system will show a domain state. Aharony has predicted that in systems with a continuous order-parameter symmetry or a small anisotropy, $d_1 = 4$.³ This means that irrespective of the dimension of all the real Heisenberg or xy systems with a sufficiently small anisotropy, the long-range order will be destroyed. Experimentally, the physical properties of the domain states have been extensively studied for diluted antiferromagnets such as $\text{Fe}_{1-x}\text{Zn}_x\text{F}_2$ (Ref. 4), $\text{Fe}_{1-x}\text{Mg}_x\text{Cl}_2$ (Ref. 5), $\text{Mn}_{1-x}\text{Zn}_x\text{F}_2$,⁶ and so on, in which, domain states evolve, if the low-temperature state is achieved via field cooling. Excess magnetization, stored in the antiferromagnetic domain walls, signifies and provides a quantitative measurement of the domain states. There are a few reports on the Jahn-Teller structural system $\text{DyAs}_x\text{V}_{1-x}\text{O}_4$,⁷ however, the existence of spontaneous twinning makes it a complicated

system.² Up to now, no ferromagnetic system containing quenched random fields has been convincingly established. Ferroelectric systems that contain quenched off-center dipoles, like $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$, and $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ seem to be promising candidates for studying the influence of quenched local random fields on the physical properties of the domain states.² Nevertheless, due to the coexistence of random dipolar fields and random strain fields, there is always vagueness in explanations. Here, we report on features of ^{18}O -isotope-exchanged SrTiO_3 crystals; the dielectric permittivity depends strongly on the amplitude of the ac test signal, and the polarization varies with time. We attribute these characteristics to the occurrence of a domain state in the samples. The nearly identical atomic radius of ^{16}O and ^{18}O , and the simple crystallographical structure make it easier to get to the fundamental physics of the domain states.

Recently, our group has successfully demonstrated that besides A-site doping,^{8,9} the application of electric field¹⁰ or uniaxial stress¹¹ ferroelectricity can be induced in quantum paraelectric SrTiO_3 by the following means: oxygen isotope.¹² A dielectric permittivity peak around 23 K was detected in a 93% ^{18}O -isotope-exchanged SrTiO_3 (STO18) sample.¹² Below the peak temperature T_c , a hysteresis loop in D vs E and the splitting of the Raman active mode was clearly observed, indicating that the permittivity peak corresponds to the evolution of ferroelectricity in STO18. The succeeding work on partially ^{18}O -isotope-exchanged samples, $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$, confirms that there exists

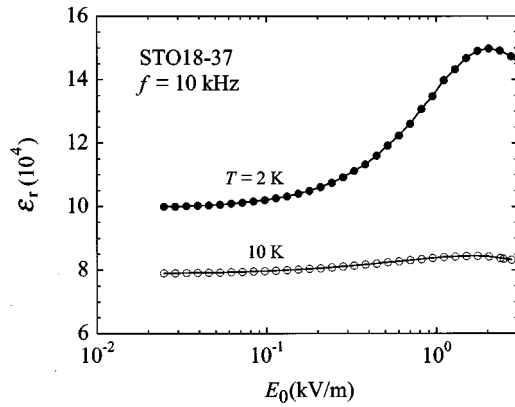


FIG. 1. Variation of permittivity ϵ_r with the amplitude E_0 of the ac test signal for STO18-37 at 2 K, and 10 K ($f = 10$ kHz).

a critical concentration x_c , above which ferroelectricity evolves.¹³ The composition dependence of $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ can be well explained by the quantum-mechanical “vector model” proposed by Schneider *et al.*¹⁴

The importance of the mass on the evolution of ferroelectricity in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ has been experimentally confirmed, yet the origin for the evolution is not clear and several contradictions in the experimental results attracted our attention. For STO18, a heat anomaly, which was considered to correspond to a three-dimensional phase transition and closely related to the evolution of ferroelectricity at 23 K, was not observed. Furthermore, temperatures at which the *DE* loop and/or the pyroelectricity become unobservable are more than 10 K higher than T_c . The significant discrepancy between the temperatures that characterize the evolution of ferroelectricity clearly hints at the unusual nature of the low-temperature state in ^{18}O -isotope-exchanged SrTiO_3 . To understand the physics of the system, two measurements, the relaxation of the polarization and the dependence of the dielectric permittivity on the amplitude (E_0) of the ac test signal, were performed.

Samples used in the present study were cut from a SrTiO_3 single-crystal lump, with edges parallel to pseudocubic [100] directions. After polishing and etching processes, the samples were heated in $^{18}\text{O}_2$ gas to undergo the oxygen iso-

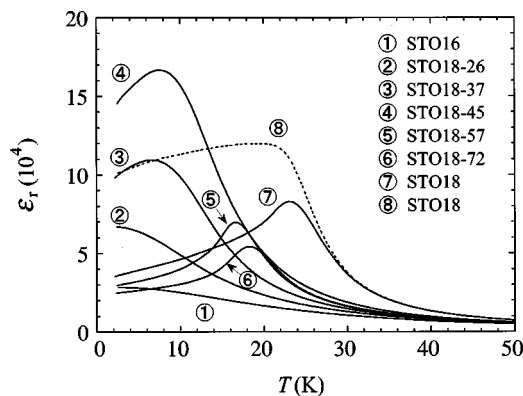


FIG. 2. Temperature dependence of ϵ_r for all the samples measured under $E_0 = 0.04$ kV/m and $f = 10$ kHz on warming. ϵ_r for STO18, measured under $E_0 = 3.2$ kV/m, is shown in broken line for comparison.

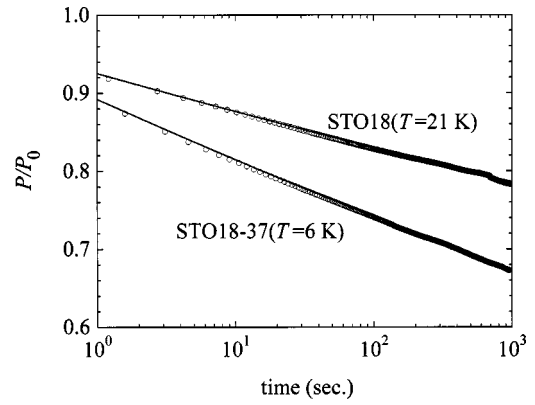


FIG. 3. Normalized remnant polarization versus time t of STO18-37 and STO18 after field-cooling with $E = 10$ kV/m at $T \cong T_c - 2$ K. The solid lines are best fits to the relation (1).

tope exchange. In this way, seven samples with an exchange rate x of 0 (STO16), 0.26 (STO18-26), 0.37 (STO18-37), 0.45 (STO18-45), 0.57 (STO18-57), 0.72 (STO18-72), and 0.93 (STO18), respectively, were obtained. The detailed description for the preparation of the samples can be found in our early reports.^{12,13} Gold electrodes were prepared by vacuum deposition onto the large faces. The dielectric permittivity was measured at a temperature range $2.2 \text{ K} \leq T \leq 300 \text{ K}$ using an HP4284A LCR meter. Variation of the polarization with time was observed by using a Keithley 6157A electrometer.

Figure 1 shows the variation of the dielectric permittivity (ϵ_r) with E_0 for STO18-37 measured at $T = 2$ K, 10 K and frequency $f = 10$ kHz. It is startling to notice that ϵ_r depends strongly on E_0 . The enhancement of ϵ_r by E_0 is considerable; however, it characterizes only the $T \leq 40$ K temperature range as shown by Fig. 2, indicating that the enhancement is closely related to the low-temperature polar state of the samples. This phenomenon is found to be a common feature of $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ samples. In Fig. 2, the temperature dependence of ϵ_r , measured under $E_0 = 0.04$ kV/m, is shown in the temperature range $2.2 \text{ K} \leq T \leq 50 \text{ K}$ for all the samples. For comparison, ϵ_r for STO18, measured under $E_0 = 3.2$ kV/m, is also shown (broken line). From the figure, the following points are clear: (1) ϵ_r is significantly enhanced by a high- E_0 at $T \leq 40$ K. For STO18-37, ϵ_r increases from $\sim 100\,000$ to $\sim 150\,000$ with increasing E_0 from 0.04 kV/m to 2.5 kV/m at around 2 K (Fig. 1), whereas virtually no dependence on E_0 of ϵ_r is observed in the temperature range $T > 40$ K. (2) The permittivity peak temperature T_c , measured under a high E_0 , is 2–3 K lower than that measured under a low E_0 . (3) In the low temperature side of T_c , the decrease of ϵ_r is reduced by a high E_0 . For STO18, the value of $[\epsilon_r(T_m) - \epsilon_r(2 \text{ K})] / \epsilon_r(T_m)$ is $\sim 60\%$ in the low- E_0 case (solid line) and only $\sim 17\%$ in the high- E_0 case (dashed line). Consequently, the permittivity peaks are smeared by the high E_0 .

The nonlinear dielectric responses to E_0 were observed in ferroelectrics^{15–17} and the results have been proposed to be related to the dynamics of various stable domainlike structures. However, it is noticed that, the E_0 used in Refs. 15–17 is two to three orders larger than that used in the present

TABLE I. Best-fit parameters to relation (1).

Sample	T (K)	E (kV/m)	α	τ (sec.)	ϕ
STO18–37	6	10	0.0410	0.14	1.00
STO18	21	10	0.0216	0.50	1.03

study; whereas the average $d\varepsilon_r/dE_0$ is much lower than the values in the present study. This fact signifies that the domain structure for $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is different from that for a ferroelectric. We speculate that the low-temperature state of $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is a domain state, a state with mesoscopic length scaled domain and sizeable domain-wall area. The E_0 -enhanced ε_r comes from the motion of domain walls, i.e., from the growth of the favorably oriented domains against the unfavorably oriented domains under the influence of a high enough external field. A similar phenomenon has been reported for $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ with $x=0.007$ at $T < T_c$.¹⁸ A linear birefringence and a dielectric property observations have yielded evidences of domain state achieved via smeared phase transitions for this sample.¹⁹ The origin of the E_0 -enhanced ε_r is suspected to lie in the depinning of the domain walls, which consist of large numbers of disordered configurations that are forced to align along an external field and responsible for the excess ε_r .

To have a deeper insight of the domain structure in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$, a variation of the polarization (P) with time (t) was investigated for two typical samples, STO18–37 and STO18. After slow cooling the samples in an electric field $E=10$ kV/m to $T \approx T_c - 2$ K, P was measured in a zero external field for periods up to $t=10^3$ s with temperature a constant. The results are shown in Fig. 3. A long-term nonexponential relaxation is observed for both samples. In the time interval measured, P decreases by $\sim 20\%$ and $\sim 14\%$ for STO18–37 and STO18, respectively.

Obviously, the field cooling of the samples creates an enhanced ferroelectric interaction, which decays in the absence of the external field. Compared to logarithmic, stretched-exponential, or simple power laws, the data in Fig. 3 are best fitted by the generalized power law²⁰

$$P/P_0 = A \exp\{-\alpha[\ln(t/\tau)]^\phi\}, \quad t \geq \tau. \quad (1)$$

The solid lines in Fig. 3 represent the best-fit results and the best-fit parameters, listed in Table I. The reasonable fitting of the generalized power law to the data in Fig. 3 signifies that $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is a system with quenched random-field disorder.²⁰ A smaller α and a longer relaxation time τ for STO18 than that for STO18–37 imply that the ferroelectric fluctuation in STO18 is stronger, probably due to a larger domain size.

The above-mentioned results suggest that the low-temperature state of $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is a domain state. In the image of the domain states, our previous^{12,13} and present results can be understood as follows. For STO16, it is well known that the ferroelectric fluctuation is suppressed by the quantum fluctuation. Via replacing ^{16}O with ^{18}O , the lattice is softened,¹³ thus the ferroelectric fluctuation is enhanced. When the exchange rate is low ($x < x_c$), compared to the quantum fluctuation, the ferroelectric fluctuation is still weak. Consequently, the formation of an ordered state at low

temperature is impeded and the effects of the ^{18}O -isotope exchange only manifests as a higher ε_r . On increasing x to above x_c , the ferroelectric fluctuation becomes stronger and tends to form an ordered state at low temperature. However, due to, probably, the existence of random fields and random interactions (see discussions below), the long-range order is broken and the domain states evolve. Because the lattice softens continuously with x , a larger size of domains in STO18 than that in STO18–37 is anticipated. Thus the decay of P in STO18 is slowed down (Fig. 3). The sizeable domain-wall areas, together with the uniformly polarized domains, control the response to external fields E . While the contributions from the domains dominate for a low E , the contributions from the domain walls become comparable to that from the domains for a high E , and a considerable enhancement of ε_r is observed. The still substantial contribution from the domain walls at ~ 2 K hints at a low-activation energy for the system. The fact that the enhancement of ε_r by E_0 is observed from $T > T_c$, rather than from $T = T_c$ (Fig. 2), signifies that the polar clusters form from temperatures far above T_c , like in the case of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ (Ref. 19). The persistence of the DE loop¹² and the pyroelectricity¹³ above T_c is a result of these ‘‘high- T polar clusters.’’

For $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$, $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$, $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, and so on, the domain states result from random dipolar and/or random strain fields that are introduced by A-site substitution.² Obviously, because of the negligible difference between the atomic radius of ^{16}O and ^{18}O (Ref. 12), ^{18}O -isotope exchange is not expected to create such kind of random fields, therefore, the origin of the domain state in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is different from that in A-site substituted SrTiO_3 and KTaO_3 . Very probably the extrinsic oxygen vacancies²¹ are the dominant sources of the random fields. Besides, substitution of ^{16}O by ^{18}O causes change in Ti-O interaction. Owing to experimental limit, we could not get a pure $\text{SrTi}^{18}\text{O}_3$. But according to our data,¹³ we can estimate that its T_c should be around 24 K. Compared to STO16, which has no T_c , the change in property is dramatic, signifying that the Ti-O interaction in $\text{SrTi}^{18}\text{O}_3$ is distinctly different from that in $\text{SrTi}^{16}\text{O}_3$. We consider that the competing of the Ti-O interaction from $\text{SrTi}^{16}\text{O}_3$ to that from $\text{SrTi}^{18}\text{O}_3$ is also part of the causes in the evolution of the domain states in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ samples. One may suspect that the twin boundaries formed at the zone-boundary phase transition around 105 K (Ref. 22) play a key role in determining the low-temperature state for the system. Our similar measurements performed on a twin-boundary-free $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ sample ruled out this possibility.²¹

Though at low temperature the absolute value of ε_r of $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is affected considerably by the domain-wall dynamics (Figs. 1 and 2), compared to our previous report,¹³ no qualitative changes are observed. The composition dependence of T_c and critical exponent γ express the same trends as before, only with a slight difference that $x_c = 0.33$ in the present study.

In conclusion, the experimental results shown in the present paper support that the low-temperature state of $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is a domain state induced by random fields. The origins of the domain states are attributed to the

extrinsic oxygen vacancies and the random Ti-O interaction-introduced by the ^{18}O -isotope exchange. We propose that the evolution of ferroelectricity in $\text{SrTi}(\text{}^{16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is closely related to the contest of the quantum fluctuation to the ferroelectric fluctuation.

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