Nonlinear Response of Dielectric Properties of Nano-domains in SrTi^{18}O$_3$

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Ferroelectric SrTi^{18}O$_3$ shows typical behaviors of 'domain state', *i. e.*, large amplitude and bias dependence of ε' and large relaxation of plarization. The size of nanosize ferroelectric domains in SrTi^{18}O$_3$ was calculated based on the bias dependence of ε' to be a few tens of nanometers.

Keywords: strontium titanate, single crystal, isotope exchange, nanosize ferroelectric domain

1. INTRODUCTION

Despite of having been studied for about half a century, strontium titanate, SrTiO$_3$, still continues to show its amazing new properties and to attract interests of both theorists and experimentalists. One of the new results that have been discovered in it recently is the oxygen isotope exchange-induced ferroelectricity [1-4] at cryogenic temperatures. Itoh and Wang have found that ferroelectricity could be induced in SrTiO$_3$ via substituting ^{16}O with ^{18}O up to ~33% [2]. By analyzing the dielectric constant data, the origin of the oxygen isotope exchange-induced ferroelectricity has been recognized as the heavier isotopic-exchange-stabilized quantum fluctuation [4]. Nevertheless, different from the typical ferroelectrics such as BaTiO$_3$ and PbTiO$_3$, the dielectric properties of the oxygen isotope exchanged SrTiO$_3$, SrTi(^{16}O$_{1-x}$^{18}O$_x$)$_3$, shows abnormal behaviors: residual polarization, and *DE*-loop are observed at temperatures above T_c; the real part of the dielectric constant depends strongly on the amplitude of the test signal; the relaxation of the remnant polarization shows non-logarithmic variation; and so

on [3,4]. We have suggested that these are indications that the low temperature state of the oxygen-isotope exchanged SrTiO$_3$ is the random-field-induced domain state. In this paper, we shall describe the bias dependence of the dielectric constant of SrTi(^{16}O$_{1-x}$^{18}O$_x$)$_3$ (x = 0.84) at cryogenic temperature and try to estimate the size of the ferroelectric clusters.

2. EXPERIMENTAL

Sample is (110)-oriented with size 7×3×0.3 mm whose axes are along perovskite cubic [001], [1-10], and [110] directions, respectively. The substitution of ^{16}O with ^{18}O was carried out by heating the sample in the ^{18}O$_2$ atmosphere, and followed by annealing in vacuum-sealed quartz glass[5]. The oxygen isotope exchange rate x was determined by weight increment to be 84%. The dependence of the dielectric constant (ε) on the bias field (E) was measured isothermally by using an HP4284A LCR meter at frequency f = 10 kHz within temperature range 2 K $\leq T \leq$ 50 K.
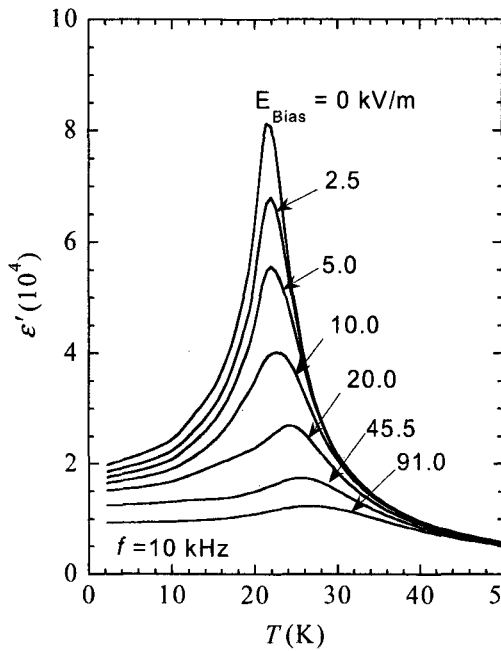
3. RESULTS AND DISCUSSIONS
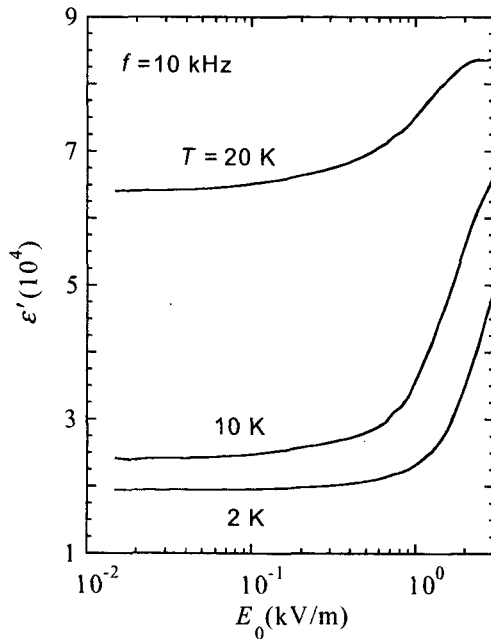
Fig.1   Bias dependence of ε' for STO18-84.

Fig.2   Amplitude dependence of ε' for STO18-84.

Figure 1 shows the temperature dependence of the dielectric constant for SrTi(^{16}O$_{0.16}$^{18}O$_{0.24}$)TiO$_3$ (STO18-84). It is clearly shown that the peak temperature increases up to 30 K and the dielectric
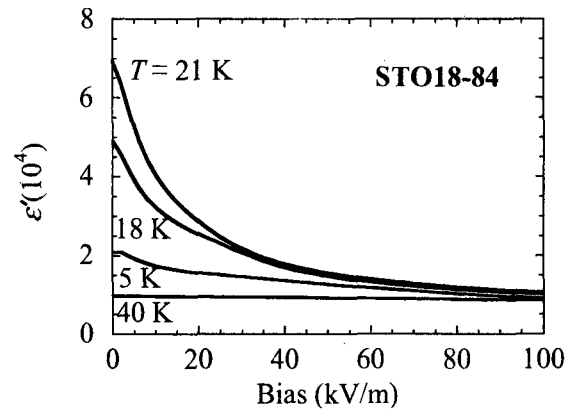

Fig.3 Bias field dependence of the dielectric constant ε' at several temperatures T

constant decreases with the increase in temperature. The behavior of the ε' vs bias field is qualitatively reproduced by using a statical model, which gives a conclusion that a formation of the single domained ferroelectric phase appears at the higher bias field side [4]. Figure 2 shows the amplitude dependence of the ε' for STO18-84. It is clearly shown that smaller amplitude gives a constant ε', but larger one gives an abrupt increase in ε'. These behaviors are attributed to the depinning of the ferroelectric nanodomains by the larger electric field.

From the dielectric constant measurement, it is known that the ferroelectric transition temperature is T_c= 21.4 K [4]. In figure 3, the bias dependence of the dielectric constant is shown. At T = 5 K, ε' shows a weak dependence on E. However, as T approaches T_c, the bias dependence becomes stronger. At T = 21 K ($\sim T_c$), the dependence is the strongest, ε decreases with E sharply. As T further increases to higher than T_c, the bias dependence of ε' becomes weaker again, and at T = 40 K, almost no bias dependency is observed. The behavior is very similar to that of small amount of Ca-doped SrTiO$_3$: (Sr$_{1-x}$Ca$_x$)TiO$_3$ [6,7].

Conventionally, ε' vs. E follows a polynomial expression involving only even powers of E that describes the non-linear bulk response

$$\varepsilon' = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4 \qquad (1)$$

where ε_1, ε_2, and ε_3 denote the linear, non-linear, and higher-order dielectric constants, respectively. However, the expression (1) can not fit our data well as shown in

figure 2 by dotted line. As the dielectric properties of the SrTi($^{16}O_{1-x}{}^{18}O_x$)$_3$ and (Sr$_{1-x}$Ca$_x$)TiO$_3$ systems show a high similarity [1-7], and they share the same parent material: SrTiO$_3$, we suggest that the Langevin-type approach [8], which have successfully explained the ε vs. E behavior of (Sr$_{0.993}$Ca$_{0.007}$)TiO$_3$ single crystal [6], also applies to SrTi($^{16}O_{1-x}{}^{18}O_x$)$_3$. According to the Langevin-type approach, for a system with a) ferroelectric clusters embedded in the paraelectric background, and b) the polarization of a cluster possesses four possible equivalent directions, due to cluster reorientation, the total static polarization parallel to the applied field E is

$$P_t = P_s \tanh(EP_s L^3 / 2k_B T) \tag{2}$$

where P_t: total static polarization; P_s: local polarization, L: cluster size, and k_B: Boltzmann's constant. The dielectric constant is given by differentiating P_t with respect to the bias field E. Thus, the total response of the dielectric constant to the bias field can be written as

$$\varepsilon' = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4$$
$$+ \sum_{n=1}^{m} (P_n^2 L^3 / 2\varepsilon_0 k_B T)[\cosh(P_n L^3 E / 2k_B T]^{-2} \tag{3}$$

where n denotes the number of cluster types. For $m = 1$(that is, there only exists one type of cluster embedded in the paraelectric background), the fitting is greatly improved compared to only considering the bulk response, however, derivation from the experiment data is still significant (Figure 4, broken line). If assume $m = 2$, the fitting is nearly perfect (Figure4, solid line). This hints at that there exist two types of clusters in the paraelectric background. According to the best-fit parameters to expression (3), cluster sizes L are summarized in figure 3 with L_1 and L_2 represent the cluster size of the first type and the second type, respectively. L_1 is about 20 nm and almost temperature independent. Whereas, L_2 is about 30 nm near 2 K and increases with increasing temperature to ~50 nm at 10 K, and then keep this value until ~T_c. No obvious change of both L_1 and L_2 were observed in the vicinity of T_c. For (Sr$_{0.993}$Ca$_{0.007}$)TiO$_3$ single crystal, the two types of cluster have been ascribed to be "hard" and "soft" clusters, which corresponds to Ca^{2+} centered polar cluster and, probably, coherent acoustic quantum state, respectively [6]. In SrTi($^{16}O_{0.16}{}^{18}O_{0.84}$)$_3$, because of the same valence charge and ionic size of $^{16}O^{-2}$ and $^{18}O^{-2}$,

there is no off-center ion related random field is expectable. In addition, the existence of the coherent acoustic quantum state, which has been suggested by Müller *et al* [9], was questioned by a number of experimental and theoretical results [10], thus the two kinds of cluster in SrTi($^{16}O_{0.16}{}^{18}O_{0.84}$)$_3$ seems to have different origins to that in (Sr$_{0.993}$Ca$_{0.007}$)TiO$_3$. It is considerable that the extrinsic oxygen vacancy forms one of the sources of random fields in SrTi($^{16}O_{1-x}{}^{18}O_x$)$_3$ [3,4]. Notice that, in the present study, the substitution of ^{16}O with ^{18}O is not 100%. Therefore, the competing of the Ti-^{16}O interaction (paraelectric-like) with the Ti-^{18}O
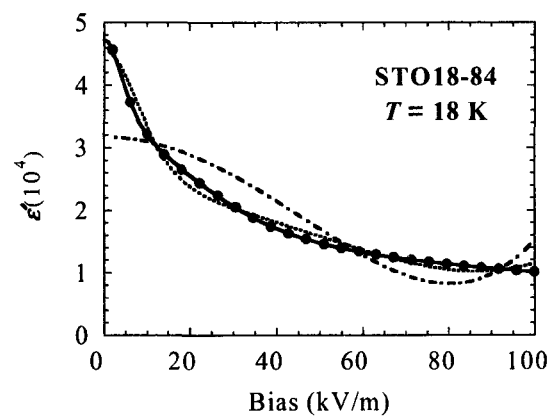

Fig 4   Fitting curves for various models. Solid circles: experimental data. Dotted line: bulk response; broken line: bulk response + one cluster; solid line: bulk response + two clusters.

interaction (ferroelectric-like) may form another kind of random field. In addition, the relaxation rate of the monodomain samples is slower than that of the multidomain samples, and the twin boundaries formed at the zone-boundary phase transition around 105 K [11] also appear to be a source of the random fields in SrTi($^{16}O_{1-x}{}^{18}O_x$)$_3$. We conjecture that, the different type of clusters in SrTi($^{16}O_{0.16}{}^{18}O_{0.84}$)$_3$ might be related to the different kind of random fields that have been suggested above. Unfortunately, the correspondence between the type of clusters and the kind of random fields is still unclear only according to the simple model used, and it seems that the usage of a more sophisticated model considering the distribution of the cluster size is necessary.
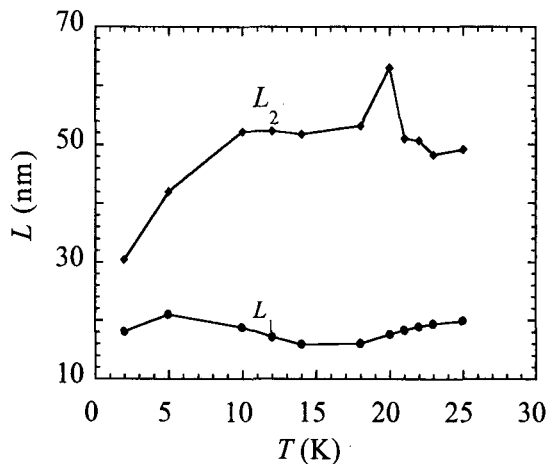
Fig.5   Variation of the best-fit parameters with temperature.

4. CONCLUSIONS

The Langevin-type approach has been used to analyze the bias field dependence of the dielectric constant for a structurally single-domained single crystal: SrTi(^{16}O$_{0.16}$^{18}O$_{0.84}$)$_3$. It was found that there exist two different dissipative clusters, and the size of the clusters was in the order of a few tens of nanometers.

5. ACKNOWLEDGEMENTS

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