

Phase Transition and Nonlinear Susceptibility in SrTi¹⁸O₃

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Ferroelectric phase transition and dielectric response of oxygen isotope-exchanged SrTiO₃ were investigated. The non-linear dielectric response of SrTi¹⁸O₃ measured under dc bias field, χ_3/χ_1^4 gave strong decrease around T_c . This corroborates the fluctuation controlled quantum ferroelectric phase transition despite its smearing due to quenched random fields. These results suggest that phase transition of SrTi¹⁸O₃ excludes the possibility of random-bond random-field cluster glass mechanism and support the phase transition mechanism as suggested by the present authors for this material.

Key words: strontium titanate, perovskite, isotope exchange, ferroelectricity, quantum paraelectricity

1. INTRODUCTION

The ferroelectric phase transition in BaTiO₃ is generally considered to be the classical example of a displacive soft mode type phase transition describable by anharmonic lattice dynamics. The question of the possible existence of a displacive to order-disorder crossover close to the paraelectric-ferroelectric phase transition is however still open.

Contrary to BaTiO₃, SrTiO₃ is known as a prototype quantum paraelectric whose displacive soft mode is impeded to completely slow down by the quantum fluctuation. SrTiO₃ is known to show a ferroelectric-like behavior by the application of uni-axial pressure or electric field. Chemical substitution of Ca for Sr is well known method to induce a ferroelectricity[1]. Such an impurity doping method invokes an additional effect other than the purposed effects as shrinkage of the lattice and enhanced random field, which prevent us from obtaining the true nature of the material. Isotope exchange is an ideal experimental method to investigate the effect of mass in the property, especially for phase transition. There are quite many reports on the cation isotope experiments for oxides, but those on the anion isotope exchange are few. Among isotopes which are commercially available, enrichment of the oxygen isotope is of the highest, 99 %. Therefore, using this isotope one can draw a definite conclusion on the "isotope effect" among oxide materials. In our previous reports[2-24], we have shown that oxygen isotope exchanged SrTiO₃ (STO18) shows a ferroelectricity at

25 K. However, STO18 was found to exhibit quite curious properties of huge dielectric constant of larger than 170000[3], quite large effects of amplitude of electric signal and bias, and the residual polarization above T_c [3,4,9]. Most of these abnormal phenomena are attributable to the domain state properties, *i.e.*, large domain wall contribution to the dielectric response.

These results imply that long range ferroelectric domains do not glow below T_c . Zhang *et al.*[23] proposed that STO18 is a homogeneous quantum ferroelectric with mixed displacive and order-disorder signatures through the dielectric measurements and SHG[24].

In this paper we will reconfirm the random-field induced domain state in STO18 through the analysis of bias dependence of the dielectric susceptibility measurements.

2. EXPERIMENTAL

Sample was prepared by the same method as previously reported[2,4]. Sample of SrTiO₃ in parallelepipeds $7 \parallel [001] \times 2 \parallel [1\bar{1}0] \times 0.2 \parallel [110]$ was subjected the oxygen isotope exchange. The exchange rate was 99 %. Measurement of the dielectric susceptibility was carried out in the temperature range 2 to 300 K using HP 4182A LCR meter. The amplitude of the test signal was fixed at 40 V/m. Measurement of the dielectric susceptibility under the bias of 0 to 200 kV/m at a constant temperature was measured below 50 K.

3. RESULTS AND DISCUSSION

As reported in our previous papers, STO18 crystal shows a rounded peak of ac susceptibility and small dispersion around " T_c "[2-5]. Such behaviors are characteristics of the relaxor like lead mignoniobates (PMN). The key issue to the relaxor is the appearance of polar clusters in the paraelectric phase, which are correlated by the fluctuations of weak random-field (RF). In cubic relaxors like PMN the dipole interaction between polar clusters is proposed to be at the origin of a random-bond random-field dominated glassy transition[25]. Therefore, a cluster glass defines the ground state of PMN at $T < T_c$ instead of domain state. The purpose of this work is to decide between a ferroelectric and glassy phase transition by a conventional susceptibility measurements.

Tagantsev and Glazounov[26] have recognized the importance of nonlinear coefficient $a_3 = \chi_3/\chi_1^4$. The scaling theory of non-classic continuous phase predicts vanishing of a_3 at a ferroelectric transition. a_3 is constant for a classic mean-field transition as described in Landau-Devonshire approximation. However, divergence of a_3 is expected at a freezing transition as observed in dipole glasses. The criteria are helpful when identifying disorder-dominated transitions as being glassy or ferroelectric. For example, $\text{BP}_{1-x}\text{BPI}_x$ [27] is glassy and SBN ferroelectric[28].

Non-linearity coefficient can be determined by various ways. Through the measurement of the dielectric susceptibility at constant temperatures under dc bias sweeping, it is easy to evaluate a_3 .

In a system with a centrosymmetric paraelectric state, a series of expansion polarization is given by

$$P = \epsilon_0 (\chi_1 E - \chi_3 E^3 + \chi_5 E^5 \mp \dots) \quad (1)$$

which is assumed to be the inverse of the equation of state

$$E = AP + BP^3 \mp \dots \quad (2)$$

where $A = (\epsilon_0 \chi_1)^{-1}$ and $B = \chi_3 / (\epsilon_0^3 \chi_1^4) \equiv a_3 / \epsilon_0^3$. Using χ_1 , χ_3 , and χ_5 , the dielectric susceptibility under bias field is given by

$$\chi(E) = \chi_1 - 3\chi_3 E^2 + 5\chi_5 E^4 \quad (3)$$

Figure 1 shows the temperature dependence of the linear susceptibility χ_1 , the nonlinear susceptibility χ_3 , and of the nonlinearity parameter $B = \chi_3 / (\epsilon_0^3 \chi_1^4)$.

Contrary to the Ca-doped system (SCT), where off-centered Ca ion can play a role of chemical impurities with fixed dipole moment and helps the nucleation of clusters, STO18 system can not be described by the polar clusters embedded in the paraelectric background because STO18 is a homogeneous system. As already confirmed in the

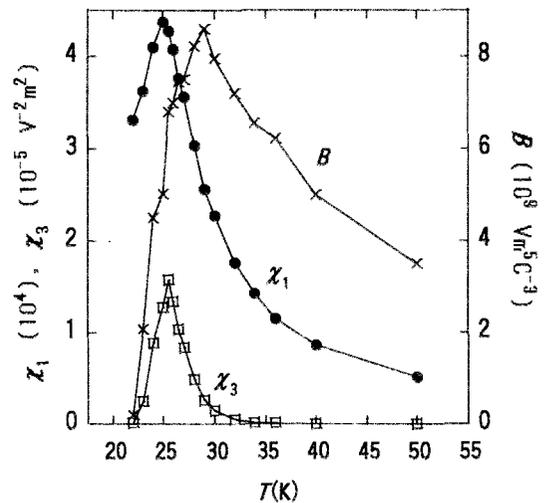


Figure 1 Temperature dependence of the linear susceptibility χ_1 (●), the nonlinear susceptibility χ_3 (□), and of the nonlinearity parameter $B = \chi_3 / (\epsilon_0^3 \chi_1^4)$. Solid lines are a guide for eye.

SCT[29], Langevin-type approach is possible to describe the picture polar clusters, where rigid clusters with field-independent sizes and dipole moments were assumed. However, in homogeneous STO18, such rigid cluster is lacking. An additional external bias field for STO18 does not rotate the cluster polarizations but grow the polar regions, whose initial orientation matches best with the field direction.

The nonlinearity coefficient increases within $28 < T < 50$ K and steeply decreases in the critical regime $23 \leq T \leq 28$ K. This behavior may be explained as follows. In the random bond glass with or without weak random field, a_3 should show a peak near $T \approx J/k$ or should diverge at a freezing temperature $T_f = J/k$ [30]. The variation of B with temperature may have such background. However, the decrease in B in the critical region may support the fluctuation-controlled ferroelectric transition. The finite value of B at T_c confirms that the transition finally becomes destroyed as a consequence of RFs. Based on these results, STO18 does not belong to the family of relaxor systems with a quasi-continuous order parameter like PMN. Quite recent studies on the ferroelectric soft mode by neutron inelastic and quasi-elastic scattering on STO18 support the present results[31]. Detail of the "phase transition" mechanism is to be reported in future. Origin of the RFs is to be solved by the NMR measurements for ^{47}Ti and ^{49}Ti , as reported for BaTiO_3 system[32].

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