Development of birefringence imaging techniques under high electric fields

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Abstract. We developed a suitable sample stage that is optimized for birefringence imaging measurements at high electric fields (E ≃ 5 kV/cm) and low temperatures (T ≃ 20 K) to directly observe electric-field-induced ferroelectric domains in SrTiO3. As a result, a huge retardance area corresponding to the ferroelectric domains appears at E ≥ 2 kV/cm and T ≤ 60 K even though the paraelectric domains partially remain. Furthermore, the fast-axis direction drastically rotates by 90° at the ferroelectric phase transition temperature because of an electrostrictive effect in ferroelectrics. The phase diagram of the critical electric fields and temperatures agrees with previous reports obtained from dielectric and neutron scattering measurements.

A multi-critical phase transition in SrTiO3 is well known to occur at T = 105 K[1-4]. From multiple investigations of the lattice dynamics, the soft-mode behavior, and the dielectric constant, SrTiO3 below T = 105 K is known to belong to the incipient ferroelectricity class in which an electrically ordered state is suppressed by quantum fluctuations. A further phase transition related to the coherent paraelectric state was revealed at T ≃ 37 K from electron paramagnetic resonance in a Fe3+ doped sample[5, 6], Brillouin- and neutron-scattering measurements of the TA-phonon branches[6], and extended x-ray absorption fine structure (EXAFS) measurements in the Ti-O bond length fluctuations[6]. Furthermore, the dielectric permittivity was found to show anomalies that indicate electric-field-induced ferroelectricity above E ≃ 2 kV/cm and below T ≃ 40 K[7-10]. According to ref. 10, the electric-field-induced ferroelectricity is still characterized by a large amount of disorder due to quantum fluctuations. Therefore, it seems more appropriate to interpret the ordered state as an induced ferroelectric domain state. The phase transitions between the quantum paraelectric, coherent paraelectric and electric-field-induced ferroelectric states may be governed by tetragonal domains with quantum fluctuations[11]. It is necessary to observe the formation process of the ferroelectric domains at high electric fields and low temperatures to understand the quantum fluctuation effects at the electric-field-induced ferroelectric phase transition. In this paper, we report observations of the electric-field-induced ferroelectric domains in SrTiO3 using birefringence imaging techniques.

The change in the birefringence (∆n) under electric fields is known as the Pockels effect in ferroelectricity, i.e., ∆n is proportional to the electric fields. As demonstrated in previous studies[12, 13], retardance (δ) and fast-axis direction (ψ) images using birefringence imaging techniques are useful to investigate domain structures because δ levels are proportional to the

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degree of distortion and $\psi$ indicates not only optical anisotropy but also uniaxial stress in crystals. When the indices of refraction along the orthogonal optical principal axes are defined as $n_1$ (for the slow axis) and $n_2$ (for the fast axis) with $n_1 \geq n_2 > 1$, the birefringence $\Delta n$ is expressed as

$$\Delta n \equiv n_1 - n_2.$$  

In a material with $n_1 \neq n_2$, the transmitted light becomes elliptically polarized because the electric-field component of the light along the fast axis travels faster than that along the slow axis, leading to a phase shift between the two components[14]. The effect is described as a retardation between the electric-field wave components along the fast and slow axes. The relationship between $\Delta n$ and $\delta$ is given by

$$\delta \equiv \Delta n \cdot t,$$  

where $t$ is the optical-path length. The value of $\delta$ corresponds to the circumferential length around the Poincaré sphere from the polarization condition of the incident light to that of the transmitted light[14]. In this paper, we measured the $\delta$ and $\psi$ images at the same time under high electric fields and low temperatures. If a ferroelectric phase transition occurs, we expect $\delta$ to become very large and $\psi$ to give information about the polarization direction.

1. Materials and Methods

Birefringence images were obtained using a WPA-100 ellipsometer (Photonic Lattice, Inc.), which was employed to accurately characterize the polarization via the adoption of the Stokes parameters ($S_0, S_1, S_2, S_3$). Furthermore, a polarimeter with a 6-W LED white light source exhibiting a circular polarization at $S_3/S_0 \simeq -1$ was used with an irradiation area equal to $100 \times 136$ mm$^2$. The wavelength was monochromated using three types of wavelength filters ($\lambda = 523$ nm, 543 nm, and 575 nm). Therefore, the light’s energy density was very low, resulting in negligible increases in sample temperatures due to irradiation light. To simultaneously obtain $\delta$ and $\psi$ images at 384 × 288 pixels, the polarizer and wave plate generated by the autocloning techniques were arranged between the CCD camera and objective lens, with the Stokes parameters ($S_0, S_1, S_2, S_3$) at the respective pixels given by a four-detector method[15]. As demonstrated in ref. 12, we need to correct the retardance and the fast-axis direction ($\delta C$ and $\psi C$) in $\delta \simeq 0$ compounds. However, if the retardance is beyond the inherent upper limit of birefringence ($\delta > \lambda/2$), the converted retardance and fast-axis direction ($\delta_{CV}$ and $\psi_{CV}$) are obtained using the multi-$\lambda$ mode as verified in ref. 13.

To observe the electric-field-induced ferroelectric phase transition at low temperatures, the SrTiO$_3$(110) substrate was prepared from a commercial substrate of superconducting thin films (Shinkosha Co., ltd.). To obtain a large monodomain below the structural phase transition temperature, the substrate size was $7.0 \parallel [001] \times 2.0 \parallel [110] \times 0.333 \parallel [110]$ mm$^3$ as mentioned by Müller[16].

2. Results and Discussion

Birefringence imaging measurements in a ferroelectric substrate under electric fields ($E$) up to $E \sim 5$ kV/cm at room temperature were reported by Jellison et al.[17]; however, there are no commercial products of suitable sample stages for applying high electric fields ($E > 2$ kV/cm) and decreasing temperatures ($T < 40$ K). Therefore, we assembled a sample stage that is optimized for the birefringence imaging measurements to observe the formation process of the electric-field-induced ferroelectric phase transition in SrTiO$_3$.

From the birefringence measurements in the SrTiO$_3$(110) substrate at $E = 0$ V/cm, $\psi_C$ rotates at $T_a = 103.8(5)$ K and a structural phase transition from cubic to tetragonal occurs
at $T_c = 105.0(3) \, K$[12]. To collect the birefringence images under high electric fields, external electric fields ($E = 1.3 \, kV/cm$, $2.5 \, kV/cm$, $3.9 \, kV/cm$, and $5.2 \, kV/cm$) were applied at 125 K and then the temperature ($T$) was decreased to 20 K while maintaining $E$ (the electric poling process). Figures 1(a) and 1(b) show the corrected retardance ($\delta_C^{575}$) images under $E = 0 \, V/cm$ at 125 K and 20.4 K, respectively. These experimental data at $E = 0 \, V/cm$ are highly reproducible and agree well with the previous results[12]. Even though there is no huge retardance that indicates the ferroelectricity, a homogeneous retardance that provides the tetragonal monodomain was observed. Figure 1(c) shows the converted retardance ($\delta_C^{543}$) image under $E = 5.2 \, kV/cm$ at 20.8 K. As can be seen in Fig. 1(c), three types of domains appear: a huge retardance area in the lower part, a $\delta_C^{543} \sim 0$ area in the middle part, and a tetragonal domain area in the upper part. The boundary line between the upper and middle parts appears along the projection of [111] on (110). Figures 2(a) and 2(b) show the corrected fast-axis direction ($\psi_C^{575}$) images under $E = 0 \, V/cm$ at 125 K and 20.4 K, respectively. When $T$ decreases from 125 K to 20 K, $\psi_C^{575}$ changes from $E \parallel [001]$ to $E \parallel [110]$. Figure 2(c) shows the converted fast-axis direction ($\psi_C^{543}$) image under $E = 5.2 \, kV/cm$ at 20.8 K. In the upper

Figure 1. The corrected ($\delta_C^{575}$) or converted ($\delta_C^{543}$) retardance images at (a) $E = 0 \, V/cm$ and $T = 125 \, K$, (b) $E = 0 \, V/cm$ and 20.4 K, and (c) $E = 5.2 \, kV/cm$ and 20.8 K for a SrTiO$_3$ (110) substrate. In panel (c), $E$ is applied at 125 K, and then $T$ decreases with the poling process. The squares indicate the sample analysis areas. The thickness of the substrate is $t = 0.333 \, mm$.

Figure 2. The corrected ($\psi_C^{575}$) or converted ($\psi_C^{543}$) fast-axis direction at (a) $E = 0 \, V/cm$ and $T = 125 \, K$, (b) $E = 0 \, V/cm$ and 20.4 K, and (c) $E = 5.2 \, kV/cm$ and 20.8 K for a SrTiO$_3$ (110) substrate. In panel (c), $E$ is applied at 125 K, and then $T$ decreases with the poling process. The squares indicate the sample analysis areas. The thickness of the substrate is $t = 0.333 \, mm$. 
part, because the $\delta_{C543}^{543}$ and $\psi_{C543}^{543}$ images at $E = 5.2$ kV/cm are the same as the $\delta_{C575}^{575}$ and $\psi_{C575}^{575}$ images at $E = 0$ V/cm as shown in Figs. 1(b) and 1(c), the tetragonal paraelectric state was realized. In the lower part, however, the direction of $\psi_{C543}^{543}$ at $E = 5.2$ kV/cm rotates by $90^\circ$ and in the middle part that shows a gradual change. As a result, the large distortion that indicates the ferroelectricity may be generated in the lower part. In the middle part, it is likely that the tetragonal [100]-, [010]- and [001]-domains with paraelectricity overlap in (110) and then the retardance cancels out. After applying $E = 5.2$ kV/cm, the $\delta_{C575}^{575}$ and $\psi_{C575}^{575}$ images at $E = 0$ V/cm were measured between 20 K and 125 K again. Because these images agree well with those at $V_E = 0$ V before applying $E$, there are no problems with sample damage by applying $E$.

Figure 3(a) shows the $T$ dependence of the corrected retardance ($\delta_{C575}^{575}$) and corrected fast-axis direction ($\psi_{C575}^{575}$) at $E = 0$ V/cm. Furthermore, the $\delta_{C575}^{575}(T)$ and $\psi_{C575}^{575}(T)$ curves as shown in Fig. 3(a) are the same as those at $E = 1.3$ kV/cm and $2.5$ kV/cm. In a previous paper, the structural phase transition temperature ($T_c$) was defined as an inflection point of $\delta_{C575}^{575}(T)$, and $\psi_{C575}^{575}$ changes at $T_a$ corresponding to the minimum value of $\delta_{C575}^{575}(T)$ [12]. Therefore, the values of $T_c$ and $T_a$ were found to be constant below $E = 2.5$ kV/cm. Figure 3(b) shows the $T$ dependence of the corrected retardance ($\delta_{C543}^{543}$) and converted fast-axis direction ($\psi_{C543}^{543}$) at $E = 5.2$ kV/cm in the area A (the upper part), as shown by the squares in Figs. 1(c) and 2(c). Even though the $\delta_{C543}^{543}(T)$ and the $\psi_{C543}^{543}(T)$ curves at $E = 5.2$ kV/cm show small undulations, the values of $T_a$ and $T_a$ agree well with those at $E = 0$ V/cm within our experimental errors. Therefore, the tetragonal paraelectric state was found to be realized in the upper part at $E = 5.2$ kV/cm. As can be seen in Fig. 3, there are no anomalies of the $\delta_{C543}^{543}(T)$ and $\psi_{C543}^{543}(T)$ curves at the phase transition between the quantum paraelectric and the coherent paraelectric states at $T \simeq 37$ K.

To examine the electric-field-induced ferroelectric domains, we further analyzed the retardance and the fast-axis direction at $E = 5.2$ kV/cm in the lower part. Figure 4 shows the $\delta_{C575}^{575}(T)$ and $\psi_{C575}^{575}(T)$ curves at $E = 5.2$ kV/cm in the area B, as shown by the squares in Figs. 1(c) and 2(c). The transition temperatures $T_c = 106.1(5)$ K and $T_a = 99(2)$ K are obtained. Furthermore, the fast-axis direction changes again below $T \simeq 51$ K. When the minimum value of $\delta_{C543}^{543}(T)$ is defined as $T_F$, $T_F = 51(1)$ K is obtained. Below $T_F$, the value of $\delta_{C543}^{543}$ rapidly increases with decreasing $T$. According to refs. 18 and 19, $\Delta n(T)$ under $E = 0$ V/cm in ferroelectric

![Figure 3](image-url)

**Figure 3.** The corrected and converted retardance ($\delta_{C575}^{575}$ and $\delta_{C543}^{543}$) and fast-axis direction ($\psi_{C575}^{575}$ and $\psi_{C543}^{543}$) as a function of $T$ during cooling in a SrTiO$_3$(110) substrate in the area A shown by the squares in Figs. 1 and 2 at (a) $E = 0$ V/cm and (b) 5.2 kV/cm. The thickness of the substrate is $t = 0.333$ mm.
SrTiO$_3$ (110) in area B

$$E = 5.2 \text{ kV/cm}$$

Poling process

$\lambda = 543 \text{ nm}$

$T_F$

$T_c$

$T_a$

| $E//[001]$ | $T$ (K) | $\Delta n$ (nm) | $\psi_{CE}^{543}$ (deg) |
|------------|---------|-----------------|---------------------|
| 0          | 0       | 0               | -45                 |
| 50         | 50      | 10              | -15                 |
| 100        | 100     | 20              | 0                   |
| 150        | 150     | 30              | 30                  |

$\delta_{CE}^{543}$

Fast-axis direction

SrTiO$_3$ (110)

FD

TP

CP

$E//[001]$

| $E$ (kV/cm) | $T$ (K) |
|------------|---------|
| 0          | 0       |
| 1          | 1       |
| 2          | 2       |
| 3          | 3       |
| 4          | 4       |
| 5          | 5       |

$T_F$

$T_a$

$T_c$

Figure 4. The converted retardance ($\delta_{CE}^{543}$) and the converted fast-axis direction ($\psi_{CE}^{543}$) as a function of $T$ during cooling in a SrTiO$_3$ (110) substrate in the area B shown by the squares in Figs. 1(c) and 2(c) at $E = 5.2$ kV/cm. The transition temperatures are $T_c = 106.1(5)$ K, $T_a = 99(2)$ K, and $T_F = 51(1)$ K. The inset shows the $T$ dependence of the birefringence ($\Delta n$) below $T_F$. The thickness of the substrate is $t = 0.333$ mm.

Figure 5. Phase diagram of $T$ versus $E$. Three phases appear: the cubic paraelectric (CP) phase, the tetragonal paraelectric (TP) phase, and the ferroelectric domain (FD) phase. The intermediate region between $T_a$ and $T_c$ indicates the tetragonal multi-domain state with paraelectricity. The dashed lines are visual guides.

SrTi($^{16}$O$_{1-x}$,$^{18}$O$_x$)$_3$ substrates measured by the rotating analyzer method rapidly increases below 30 K and the maximum value of $\Delta n$ is approximately $1 \times 10^{-3}$ at $x = 0.99$[19]. Furthermore, when $E = 1.40$ kV/cm is applied parallel to [110] in the $x = 1$ substrate, the maximum value of $\Delta n$ is approximately $2.4 \times 10^{-3}$[20]. Because a change in the fast-axis direction cannot be detected by the rotating analyzer method, we do not know how the fast-axis direction changes at the ferroelectric phase transition temperature in SrTi($^{16}$O$_{1-x}$,$^{18}$O$_x$)$_3$. As can be seen in the inset of Fig. 4, the appearance of the electric-field-induced ferroelectric domains in SrTiO$_3$(110) was found to be successfully observed when using the birefringence imaging techniques. The $\delta_{CE}^{543}(T)$ curve at $E = 5.2$ kV/cm bends at $T \approx 39$ K even though there is no anomaly in the $\psi_{CE}^{543}(T)$ curve below $T_F$. We believe that this anomaly below $T_F$ is extrinsic because the huge $\Delta n$ domains in the lower part are spread and moved with decreasing $T$ below $T_F$.

Figure 5 shows the phase diagram of the critical temperatures ($T_c$, $T_a$, and $T_F$). We found that the phase transition between the cubic paraelectric (CP) phase and the tetragonal paraelectric (TP) phase occurs at $T_c \approx 105$ K independent of $E$ and the tetragonal multi-domain state with paraelectricity is realized in the intermediate region between $T_a$ and $T_c$. Furthermore, the electric-field-induced ferroelectric domain (FD) phase appeared above $E \approx 3$ kV/cm and below $T \approx 60$ K. This phase diagram agrees with the data obtained by the dielectric measurements under high electric fields[7-10]. Even though the electric-field-induced ferroelectric domains are successfully observed by the birefringence imaging techniques, we cannot distinguish between
the quantum paraelectric state and the coherent paraelectric state in the TP phase. From the neutron-scattering measurements, the distribution of the tetragonal domains and its electric field dependence were detected[21]. As a result, the orthorhombic ferroelectric phase defined in ref. 21 corresponds to the FD phase. However, there are no anomalies in the δ and ψ images in the intermediate phase between the tetragonal paraelectric phase and the orthorhombic ferroelectric phase. Consequently, we found that the huge ∆n region in the lower part shown in Fig. 1(c) indicated electric-field-induced ferroelectric domains even though the tetragonal paraelectric domains remained in the upper part because the quantum fluctuations were not completely suppressed by the external electric fields up to \( E = 5.2 \, \text{kV/cm} \). When \( T \) decreases below \( T_F \), the direction of \( \psi_{CV}^{543} \) in the ferroelectric domains was found to rotate from \( E \perp \) the fast-axis to \( E \parallel \) the fast-axis; however, that in the paraelectric domains remained at \( E \perp \) the fast-axis. These results are explained by the electrostrictive effect in ferroelectrics.

In conclusion, we successfully observed the electric-field-induced ferroelectric domains in SrTiO\(_3\)(110) at \( E \geq 3 \, \text{kV/cm} \) and \( T \leq 60 \, \text{K} \) even though the tetragonal paraelectric domains cannot be completely suppressed by \( E \). To fully polarize the ferroelectric domains, it is necessary to generate much higher electric fields. Electric-field-induced ferroelectric domains may be influenced by the application of uniaxial stress because SrTiO\(_3\) shows ferroelasticity. As in ref. 21, the electrostrictive deformation at 80 K and under \( E = 4.6 \, \text{kV/cm} \) was found to be reproduced by applying a uniaxial stress of \( \sim 10 \, \text{MPa} \). We expect to observe the stress-assisted ferroelectric state with full polarization if both the electric field and the uniaxial stress are applied along [001] simultaneously. In future studies, we will measure stress-induced birefringence.

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