Ferroelectric Domain Formation in BaTiO₃ Observed by Speckle Techniques

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A scenario of ferroelectric domain formation in BaTiO₃ is proposed based on our previous observation of temperature evolution of polarization clusters in paraelectric phase, ferroelectric domains, and relaxation dynamics of the polarizations. How the temporal polarization clusters observed at high temperature phase corrugate into static polarization domains in ferroelectric phase is discussed. Temporal polarization clusters turn out to static ones at 4.5°C above Currie temperature due to a kind of critical slowing down which take place in polarization clusters. Static polarization clusters work like as super paraelectric dipole moments and dipole interaction among static polarization clusters increase according as power low when the temperature decrease toward Currie temperature. These static polarization clusters order at Currie temperature due to a mean field working among them. Bunches of ordered static polarization clusters evolve into relevant complete ferroelectric domains 6°C bellow the Currie temperature.

Key words: BaTiO₃, phase transition, relaxation time, polarization clusters, ferroelectric domain.

1. INTRODUCTION

Ferroelectric phase transition in prototype ferroelectrics BaTiO₃ has long been a problem in debate. Soft phonon mode is a probable candidate to explain how the transition takes place [1]. Approaching to the phase transition temperature, a long range transverse optical phonon face to slow down, and finally a static displacement of Ti ion takes place. This mode of phase transition is a so called displacive type phase transition. However, in case of BaTiO₃, this mode becomes hardly to observe in the vicinity of the transition temperature because of over dumping [2,3]. Meanwhile, such phenomena as X-ray diffuse scattering [4], the strong quasielastic neutron scattering [5], relaxation type hyper-Raman scattering [6], and anomalous birefringence has been observed [7]. These experimental facts suggested existence of microscopic dipole moments and the ferroelectric phase transition take place through the ordering of these dipole moments. This mode of phase transition is a so called order-disorder type phase transition. Existence of the polarization clusters in the paraelectric phase of BaTiO₃ has been anticipated by the refractive index measurement from the early days of research [8]. Comes et al. proposed a model in which the Ti ion fluctuates among eight off-center sites [4]. Zalar et al. suggested a possibility of coexistence of displacive type and order-disorder type phase transition [9,10]. At any rate, we need to incorporate a relaxation type energy dissipative mechanism, coupling with soft phonon mode. Necessity of investigation of the dynamics of the polarization clusters is inevitable.

An advent of plasma based soft X-Ray pulse laser [11] enabled us to investigate the behavior of temporal polarization clusters in the vicinity of the Currie temperature. Advantages of the plasma based soft X-Ray laser pulse are their spatial coherence; more than 80%, short pulse width; 7ps, and strong peak intensity; more than 10⁸ photons per pulse[12]. Owing to these characteristics of the plasma based soft X-Ray laser, we developed speckle techniques [13,14], and we determined the temperature dependence of the mean size of the temporal polarization clusters, mean distance among polarization clusters, and polarization density of the polarization clusters. Recently, we developed a creation-annihilation type intensity correlation spectroscopy by means of soft X-Ray laser [15,16]. We determined the temperature dependence of the relaxation time of the polarization in the clusters. We found a critical slowing down take place in the polarization clusters at about 4.5K above Currie temperature.

Based on above mentioned our previous observations and related experimental and theoretical results by others, here we propose and discuss a scenario how the temporal polarization clusters observed in the paraelectric phase corrugate into the permanent ferroelectric domains in the ferroelectric phase.
2. FERROELECTRIC DOMAINS

Our BaTiO₃ sample was a flux-grown so-called butterfly type single crystal with alternative a/c domains aligned in parallel. The Curie temperature (Tₑ) was 122°C. We observed speckle patterns from these alternative a/c domains by use of coherent soft X-ray pulse laser. Experimental set up is illustrated in Fig.1. Here, the X-ray source is a coherent single shot pulse laser, 13.9nm in wave length, 7ps in pulse duration, 10⁻⁴ in band width; ∆λ/λ. A molybdenum silicon multi layered mirror was used to make a vertically polarized pulse beam. An incident slit set just in front of the sample, 80µm (horizontal) × 200µm (vertical), makes almost coherent beam. Sample is mounted as a/c domains boundary aligned parallel vertically. The X-ray beam incidents onto the sample surface with 10° grazing angle. Speckle patterns reflected from the sample are recorded on CCD camera set at 500mm from the sample.

Fig.1. Experimental layout of speckle observation by use of soft X-ray pulse laser.

Fig.2 illustrates temperature dependence of speckle patterns. Fig.2 (a) is a direct image of slit observed at CCD. We can recognize the diffraction pattern of slit in inserted enlarged image. At room temperature, we recognize two groups of diffraction patterns in Fig.2 (b). As the temperature increases these two groups of diffraction patterns begin to merge as recognized in Fig.2 (c). At 118°C, two groups of diffraction patterns merge into one group in Fig.2 (d). Then as the temperature increase more and more approaching to the Tₑ, interference patterns begin to diverge as recognized in Figs. 2(e) ~2(g). Half width of the autocorrelation function of the spatial power spectrum of the speckle patterns in Figs. 2(d) ~2(g). Half width of the autocorrelation function of the spatial power spectrum of the speckle patterns can be estimated from the width of autocorrelation part of the spatial power spectrum of the speckle patterns. Fig.3 shows temperature evolution of size of the polarized microscopic region that corresponds to the width of bunch of microscopically polarized regions. Fig.3 shows temperature dependence of size of the polarized microscopic region. The size of the microscopic polarized region varies from 6µm at 118°C to 2µm at 121°C. It will be clarified later that this microscopic polarized region is a bunch of aligned polarized clusters.

Fig.2. Speckle patterns observed by single exposure of 7ps soft X-ray laser pulse at various temperatures

We define a matter correlation function by a normalized convolution of complex beam transmittance function over the sample. This matter correlation function can be extracted from Fourier transforms of speckle pattern and that of diffraction pattern of the slit. The spatial power spectrum of the matter correlation function calculated from the Fourier transform of the matter correlation function gives a static domain distribution in wave number space. Size of the bunch of polarized microscopic region can be estimated from the width of autocorrelation part of the spatial power spectrum of the speckle patterns. Fig.3 shows temperature evolution of size of the polarized microscopic region. The size of the microscopic polarized region varies from 6µm at 118°C to 2µm at 121°C. It will be clarified later that this microscopic polarized region is a bunch of aligned polarized clusters.
3. POLARIZATION CLUSTERS

When we observe an enlarged mirror reflection pattern shown in Fig. 2 (h), we recognize a diffuse like tail structures around the central peak. These diffuse like patterns means that any microstructures exist in the sample. In order to investigate these diffuse like patterns more in detail, we conducted observations of these diffuse scattering using a similar experimental set up as described in Fig. 1. An example of the speckle pattern observed at 130°C is illustrated by CCD image in the inserted picture in Fig. 4. Intensity profiles shown in Fig. 4 are the vertical intensity distribution of the speckle patterns obtained under various conditions, which are the cross sectional intensities along vertical direction.

Fig. 4. Normalized speckle intensity profiles of specular reflections obtained under various temperature conditions. The character (E) means with electric field applied.

The tails of the specular reflection become more distinguished at near the Currie temperature. When an electric field is applied perpendicular to the sample surface, the tails are shrinks down. This electric field dependence of the speckle patterns imply that these microscopic structure which giving the speckle patterns is polarization clusters distributed within the sample.

By use of de-convolution techniques, we calculated autocorrelation function of the polarization clusters distribution from the intensity profiles in Fig. 4. Half width at the half maximum of the autocorrelation function $\sigma_s$ gives the size of the polarization clusters. First minimum of the auto-correlation function appears at the distance $d$ corresponding to the separation distance among clusters. Depth of the first minimum of the auto-correlation functions is proportional to the magnitude of $\Delta n$, where $\Delta n$ means additional refraction coefficient due to the birefringence. Polarization density of the cluster, $P$, is the origin of the additional refraction coefficient, $\Delta n$, connected by the quadratic Kerr effect, as $\sqrt{\Delta n} \propto |P|$.

These results are illustrated in Figs. 5(a) and 5(b) as functions of the temperature difference from Currie temperature, $\Delta T$. The average size of the polarization clusters shows no significant change with temperature, ~800nm. Mean separation distance among polarization clusters decreases with the temperature approaching to the Currie temperature, ~2.3$\mu$m at Currie Temperature. While the maximum value of the polarization appears near 5°C above the Currie temperature, not at just the Currie temperature. At this temperature, we could find no significant anomalous behavior in temperature dependences of size of polarization clusters and distance of separation among the polarization clusters. It is notable that all these quantities are continuous even we cross the Curie temperature. Instantaneous behaviors of the microscopic polarization clusters looks like nothing to do with the macroscopic thermo dynamical quantity such as Currie temperature. Average size of the polarization clusters and the mean separation distance among polarization clusters show almost linear temperature dependence. Extrapolations of these linear lines accidentally merge at $T_p$, 6°C below the Currie temperature, 118°C. This merging means separation of the two clusters become twice of the half of the cluster size. Whole volume of the sample filled with the polarization.

Fig. 5. Temperature dependence of the size of the polarization clusters and separation distance among polarization clusters (a), squared values of the polarization density of the clusters. Dashed lines in Figs. 5(a) and 5(b) are drawn as a guide to the eye.
4. RELAXATION TIME

Nanometer scale dipole moments in the polarization clusters in BaTiO$_3$ are supposed to be thermally excited and thermally relaxed with in a picoseconds time scale. In order to elucidate the nature of the phase transition, it is essential to investigate these thermal behaviors of the polarization clusters in critical region. Intensity correlation spectroscopy is known a powerful technique to investigate the dynamic fluctuation of the material. This is a method to recognize how the similarity exists between two speckle intensity obtained by two successive observations. Here we describe a new intensity correlation spectroscopy developed to measure the relaxation dynamics of the polarization clusters in critical region of phase transition. Principle of the creation-annihilation type two pulses intensity correlation spectroscopy is illustrated in Fig.6. Here, the first pulse increases the polarization then the second pulse subtracts the residual excess polarization. Intensity correlation between the first Storks like scattered pulse and the second scattered anti-Storks like pulse is examined [17].

We developed a new intensity correlation measurement system by use of soft X-ray coherent pulse laser as shown in Fig.7. This instrumentation is composed of plasma based soft X-ray pulse laser as a coherent soft X-ray source, Mo-Si multilayered beam splitter, Michelson type delay generator, and streak camera. Streak camera resolves the two successively scattered X-ray pulses. The time resolution of the streak camera is 1ps the sufficient to resolve the scattered pulses of 7ps pulse width. We calculated intensity correlation from the specular reflection parts of intensities profile of the speckle recorded in streak camera. This part of scattered intensity reflects relevant phenomenon which has been took place at any polarization clusters within the irradiated sample area.

Fig.6. Principle of creation-annihilation type intensity correlation spectroscopy. First X-ray pulse creates additional polarization in polarization clusters and the second X-ray pulse annihilates the residual excess polarization survived until by the delayed time $t + \tau$.

Fig.7. Schematic layout of X-ray intensity correlation measurement system. Delayed double pulses are created.

An example of the intensity correlation $g^{(2)}$ is illustrated in the inserted figure in Fig.8. Relaxation time $\tau_0$ is obtained from an average over the central part of the profile $g^{(2)}$ corresponding to the speckle size. The results of measurements are shown in independently obtained Figs. 8(a) and 8(b). Here we plot the relaxation time as a function via delay time. Relaxation time varies with the temperature of the sample. Most of the curve intercept at $\tau_0=0$ around 1.6. This value means the visibility of the incident soft X-ray is 0.8. Temperature step is 2°C in Fig.8 (a), while 0.5°C in Fig.8 (b).

Fig.8. Decay curve of the intensity correlation as a function of delay time at several sample temperatures.
5. DISCUSSION

As we can recognize from the data in Fig.8, relaxation time $\tau_0$ varies with temperature. Temperature dependence of relaxation time $\tau_0$ is shown in Fig.9 by solid blue marks. Blue line in Fig.9 is a guide to profile of variation of relaxation time. Temperature dependence of cluster polarization is shown by red open marks in Fig.9 obtained from the data shown in Fig. 5(b). Red line in Fig.9 is a guide to profile of variation of polarization density of the clusters.

Fig.9. Temperature dependence of relaxation time $\tau_0$ and the polarization density of the polarization clusters.

As the temperature decreases the relaxation time suddenly increases at $6^\circ$C above the $T_c$, and rise up to maximum around 90ps at 4.5$^\circ$C above the $T_c$. At the same temperature, the polarization of the polarization clusters takes the maximum value. It looks like a kind of critical slowing down takes place in polarization clusters at this temperature. This phenomenon means that temporal polarization clusters turn out to static one at this temperature. This static polarization clusters act like as super paraelectric dipole moment, which order at Curie temperature $T_c$ due to the mean field working among them. The quantity $\sigma_s^2 |P|/d^3$ is a dipole potential working between two polarization clusters. Fig.10 shows this dipole potential increases according as the critical exponent near the Curie temperature. The mean field works to order the polarization clusters at Currie temperature. Order-disorder type phase transition takes place at Curie temperature by way of alignment of these polarization clusters. These polarization clusters merge completely at $6^\circ$C below the Curie temperature.

An image of scenario for the domain formation from temporal polarization clusters to complete ferroelectric domains is illustrated in Fig.11.

Here, $T_p$ indicates the temperature where the static polarization clusters take place, and $T_d$ indicates the temperature where the complete domains are formed. In the temperature region, $T_p > T > T_c$, polarization clusters are static, however, average value of macroscopic polarization $<P>_1 = 0$. In the temperature region, $T_c > T > T_d$, static polarization clusters align, however, the polarization clusters merges not completely. In this region, bunching size of polarization clusters increases gradually probably toward the size of domain size at $T_d$ as we mentioned as in describing the result of Fig.3.

Fig.10. Temperature dependence of the dipole interaction among polarization clusters. Insertion figure shows the increase of the dipole interaction subjects to an exponent low.

Fig.11. Images of ferroelectric domain formation begin with temporal polarization clusters and arrive at complete domains. For the simplicity one directional polarization is drawn pictorially.
Similar polar microscopic regions are anticipated on the isotope doped sample, SrTi (18O,16O)x3. Yagi et al. [18] proposed a model in which microscopic ferroelectric regions takes place within symmetry breaking regions even in cubic phase by the results of Raman scattering and TEM observations. On the relaxer ferroelectrics Pb(Mg1/3Nb2/3)O3, Fu et al. [19] reported that static polarized nanostructures appear from sufficiently higher temperature than Currie temperature. They proposed an image where the polar nano-regions corrugate into domains in which polarization of each polar nanoregion aligns into one direction. Crossover temperature similar to Tp situates in much higher temperature region, however, ferroelectric domain takes place at just Tc. From general point of view, Matsushita et al. discussed this kind of precursor phenomenon of phase transition in Perovskite type ferroelectrics [20]. They developed a theory applicable to the morphotropic phase boundary (MPB) region of mixed Perovskite oxide. They calculated the free energy as a function of the reduced temperature. They discussed the critical relaxation of polarization clusters for the first order phase transition. They succeeded to define the Tp and Td on the basis of reduced temperature.

6. CONCLUDING REMARKS

By use of soft X-ray pulse laser speckle techniques, we can draw a thorough image of ferroelectric domain evolution in prototype ferroelectrics BaTiO3. Temporal polarization clusters appear at sufficiently higher temperature. Approaching to critical region of phase transition, critical slowing down takes place in these temporal polarization clusters at 4.5°C above Currie temperature and results in a crossover from temporal polarization to static polarization. These static polarization clusters behave as super paraelectric dipole moments and order at Currie temperature. Each bunch of these ordered static polarization clusters corrugate into domain completely at 6°C below the Currie temperature. This kind of behavior is fund in other Perovskite type ferroelectrics, such as isotope doped SrTi (18O,16O)x3, and Pb(Mg1/3Nb2/3)O3. Behavior of these materials can be understood on a unified point of view. On the same frame work, we could discuss phase transition behavior in PMN-PT near MPB.

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