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Picosecond View of Microscopic-Scale Polarization Clusters in Paraelectric $BaTiO_3$

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The polarization clusters existing in both the ferroelectric and the paraelectric phase of $BaTiO_3$ are directly observed and characterized for the first time by a picosecond soft x-ray laser speckle technique. These dynamic clusters appear continuously across the Curie temperature T_c. The clusters' distance increases approximately linearly with temperature, while their mean size does not change significantly. The polarization exhibits a maximum at a temperature about 5 °C above T_c. The clusters' short-range correlation strength diverges as $(T - T_c)^{-0.41\pm0.02}$ as temperature decreases toward T_c.

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The paraelectric-ferroelectric phase transition for the prototype ferroelectric substance $BaTiO_3$ has long been thought as a classic displacive soft-mode type [1,2], whereas anomalies were also known near the phase transition temperature, which was unable to be interpreted simply by a displacive type [3,4]. As measured by Hyper-Raman spectroscopy [5,6], a relaxational dynamics was also observed in the paraelectric $BaTiO_3$ near T_c. NMR experiment [7] has recently shown that Ti ion in the paraelectric phase of $BaTiO_3$ flutters among off-center sites, claiming the coexistence of order-disorder and displacive characters in phase transition of $BaTiO_3$ as that predicted by simulation [8]. However, it is still not clear for this substance how a stable ferroelectric polarization domain turns up from those paraelectric fluctuating dipole moments, in particular, how the dipoles fluctuations correlate spatially each other and evolve into a ferroelectric domain as T_c is approaching.

Molecular dynamic simulations [8] and theory [9], concerning the phase transition mechanism, have shown existence of polarization clusters in paraelectric $BaTiO_3$ near T_c. Although experiments such as neutron scattering [10], x-ray scattering [4,11], and optical birefringence [12,13] showed strongly fluctuating polarizations existing in paraelectric phase of $BaTiO_3$ near T_c, however, such clusters have never been directly observed to date. The reason lies in the fact that the relaxation time of a particular cluster, around an order of nanoseconds [5,7], is too short compared to the general measuring time in practice. Traditional diffuse x-ray scattering or neutron scattering cannot be used to observe the dynamic correlation length, since where the spatial correlation has been averaged by the much longer time for measurement.

In this Letter, we demonstrate the first observation of such clusters fluctuating in the paraelectric phase of a flux-grown $BaTiO_3$, by means of a novel picosecond x-ray laser speckle technique [14,15]. The instantaneously phase-modulated x-rays due to birefringence by those spatial-random-distributed clusters interfere each other to give rise to the speckles. The matter correlation function, related to spatial correlation of those local clusters, was extracted from deconvolution of speckle pattern, from which, the local information, such as the clusters' distance, the cluster size, the cluster polarization, and their temperature evolution, was first successfully characterized and clarified in a microscopic scale within the temperature region ($T_c - 1$ °C $\sim T_c + 20$ °C) experimentally. The present results show a new insight into the phase transition for $BaTiO_3$.

The experiment was conducted with the setup as that described in our previous Letter [14]. Several improvements were made this time to enhance the performance. First, the distance between the charge-coupled device (CCD) camera and the specimen was shortened to 0.2 m, and the slit width was set to be 80 μm (horizontal) $\times$ 50 μm (vertical); Second, the precision of the temperature was improved to be ± 0.1 °C; Finally, a high dc voltage slab electrode was set at the 2.5 mm front of the specimen, which can produce a uniform high electric field (2 KV/cm was selected for the data shown) normal to the specimen surface. The local electric field E_s within the specimen was estimated to be 0.4 V/cm, if we suppose the static dielectric constant ε_s to be 5000 at 123.5 °C. This value is near to that commonly used to measure the ε_s near T_c, and hence believed to be sufficiently large to reverse the clusters' polarizations.

The results are shown in Fig. 1. The strong diffuselike feature of the speckles near T_c as shown in Fig. 1(a) indicates the existence of some microscopic-scale structures in the paraelectric specimen. The sensibility of the

speckles to an electric field, just as shown in the Fig. 1(b), suggests these microscopic-scale structures be of the dipole-related type, as that so-called polarization clusters. Figure 1(c) shows the quantitative vertical intensity distributions of the speckles, which are cross-sectional intensities along q_y direction (q_x averaged) on CCD. The normalization was made with the total photons of each shot. Since the local field E_s at 123.5 °C must be smaller than that at 135.0 °C, the tail for 123.5 °C(E) as shown in Fig. 1(c) still remained compared to that for 135.0 °C(E) due to the incomplete reversing of the relevant polarization clusters. As temperature increases, the diffuselike scattering gradually decreases. There seems no significant difference between the two profiles observed at 140.0 °C and 135.0 °C (E), indicating that both cases approached to the specular pattern, free of the influences of those microscopic-scale polarization clusters.

The coherent scattering mechanism is shown in Fig. 2 from the view of polarization clusters. Experiments have shown evidence that the clusters polarize preferably along the crystallographic axis (x, y, or z in Fig. 2) [2,10]. By a picosecond y-polarized x-ray illumination, these clusters with polarizations along the y or $-y$ are spatially recorded on the phase of the scattered beam due to the birefringence. The x- or z-polarized clusters would be indistinguishable from the nonclusters region (cubic),

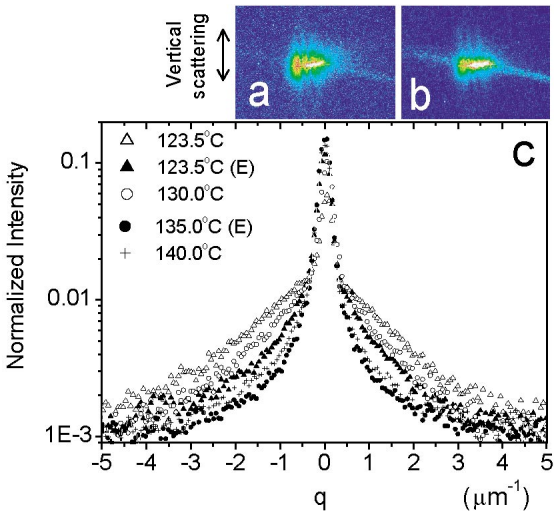

FIG. 1 (color online). Experimental results. (a) and (b) are examples of the instantaneous speckles patterns for $T = 123.5$ °C recorded on a soft x-ray CCD, without and with undergoing an external electric field, respectively. The dc electric field was set to be 2 KV/cm normal to the $BaTiO_3$ surface. The vertical fringes are the Fresnel diffraction pattern of the slit. The approximately horizontal comet's tail in both figures is due to the surface roughness of the specimen, free from the influences such as the temperature and the external electric field. (c) shows the quantitative vertical intensity distribution. The normalization was made with the total photons of each shot. q is scattering vector.

since they all exhibit an ordinary refraction index for the grazing incident x-ray beam. The additional phase from the ith y-polarized cluster is estimated to be $\Delta\phi_i = 2\pi l \mathrm{Re}(\varepsilon_{33}^{1/2} - \varepsilon_{11}^{1/2})_i/\lambda$, where l is the average x-ray path length within the specimen, ε_{ii} is the dielectric tensor. The experiment was carried out with a 89 eV coherent photon beam and the scattering angle off the sample surface was 10 °. This angle, being less than the critical angle (14 °), implies that our experiment is sensitive to correlations at surface of the sample alone. The photon energy is 89 eV, near to the binding energy of the $N_5 4d_{5/2}$ electrons in Ba [16]. Therefore, it can be anticipated that the anomalous dispersion would contribute a nontrivial value to the $\Delta\phi_i$. The x-rays due to spatial phase modulation interfere each other to give rise to the speckles patterns.

For phase modulation, the matter correlation function [14,15] is simplified to be $\gamma(\Delta y) = \langle \exp\{i[\phi(y + \Delta y) - \phi(y)]\}\rangle_y / D_y$, where D_y is the vertical illumination size at the specimen, $\phi(y)$ is the phase function as shown in Fig. 2. This matter correlation function can be directly extracted from the speckle pattern as $|\gamma(\Delta y)| = \mathcal{F}[I(q)]/\mathcal{F}[I_{Sp}(q)]$, where the $\mathcal{F}$ denotes the operation of Fourier transform, the $I(q)$ and the $I_{Sp}(q)$ denote the intensity distributions along the y-direction for the speckle pattern and the specular pattern, respectively. The transferred momentum q in the y-direction was parallel to the specimen surface and well defined due to the near-surface clusters structure, while that perpendicular to the specimen surface, q in the x-direction, was undefined due to total reflection.

The parameters extracted from $\gamma(\Delta y)$ as follows are pure one-dimensional parameters of the clusters

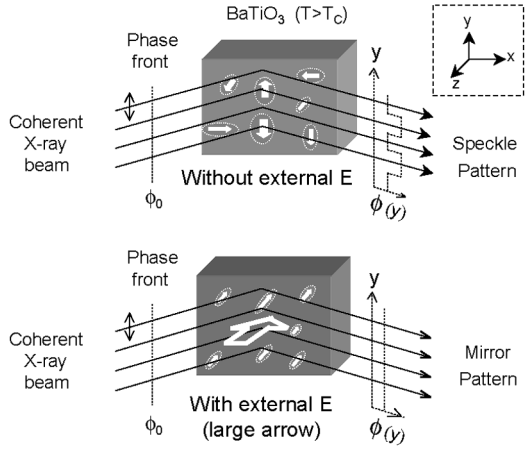

FIG. 2. Schematic diagram of the coherent scattering mechanism due to polarization clusters. x, y, and z correspond to the crystallographic axes (a, b, and c; $a = b = c$ for paraelectric phase). The ellipses stand for the regions of the clusters each with an instantaneous polarization directed along the arrow. The double arrow indicates the x-ray polarization.

(y-directional distribution). The mean size σ_s of clusters can be naturally considered to be the half width of the autocorrelation part of $\gamma(\Delta y)$. If we denote the mean distance of the clusters as d, then $\gamma(d/2)$ must be the first minimum from the origin of the profile of $\gamma(\Delta y)$. The correlation depth is defined as $\Delta\gamma_m = \gamma(0) - \gamma(d/2)$, where the $\gamma(0)$ is 1, indicating the maximum autocorrelation. Suppose the additional phase given by the ith cluster to be $\Delta\phi_i = 2\pi l\Delta n_i/\lambda$, the correlation depth can be expressed as $\Delta\gamma_m = (\sigma_s/4d)(l/\lambda)^2\langle(\Delta n)^2\rangle$. The random distribution of the polarizations' magnitudes in the clusters suggests $\langle(\Delta n)^2\rangle = 2\langle\Delta n\rangle^2$ from a statistic viewpoint. Therefore, the average refractive index difference $\langle(\Delta n)\rangle$ can be extracted from such parameters as the cluster size, the cluster distance, and the correlation depth, which can be directly estimated from the matter correlation function. The polarization in the cluster relates the refractive index difference by the quadratic Kerr effect, so we can estimate the mean polarization magnitude within the clusters as $|P| \propto \langle\Delta n\rangle^{1/2}$.

Figure 3 shows the extracted physical parameters of the clusters. Figure 3(a) shows the evolutions of the mean size σ_s and the mean distance d of those y-polarized clusters with respect to the temperature. There seems no significant change of the cluster size observed in the experiment. However, the distance increases versus temperature approximately linearly with a fitting slope of 0.33 μm/°C. By extrapolating the two dashed lines (linear fitting) in Fig. 3(a), one may find a crossover at a lower temperature T_D (estimated to be 6 °C below T_c, not drawn in the figure). The T_D might be understood as a temperature where dynamic clusters have completely condensated into a ferroelectric domain. Figure 3(b) shows the mean magnitude $|P|^2$ of the polarizations within clusters, where a peak was observed at temperature about 5 °C above T_c. Molecular dynamic simulations [8] have shown that a crossover from displacive to order-disorder transition exists in the vicinity of T_c. The temperature for this crossover might be estimated from that of the peak of the $|P|^2$. As shown in the figure, as temperature approaches T_c, the $|P|^2$ behaves monotonically increasing at relatively higher temperatures, indicating the increase of the cooperative motions among Ti ions within the cluster. However, this increase was observed to stop at a temperature very close to T_c, implying the breaking of the cooperative motions of particles near phase transition due to the increase of fluctuation of dipole moment among off-center sites.

The macroscopically averaged polarization within the specimen may be defined as $(\sigma_s/d)^3|P|$ from a three-dimensional viewpoint. We show the temperature dependence of this physical quantity in Fig. 4. The quasilinear behavior at higher temperatures in Fig. 4 is completely consistent with that measured by Burns [12] and Ishidate[13] with the use of birefringence of visible laser.

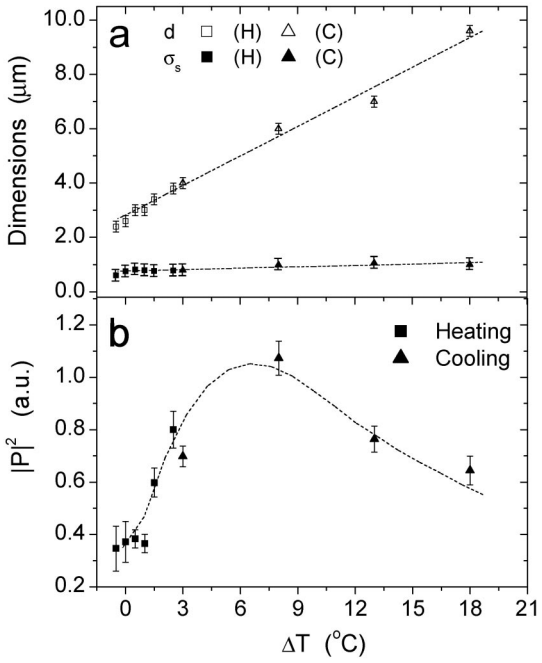

FIG. 3. The temperature evolution of the characteristic parameters of the clusters. d: the mean distance of the adjacent two clusters; σ_s: the mean size of the clusters; H: heating; C: Cooling. The error bars were estimated from the spatial resolution (about 0.2 μm) of the present setup. The dashed lines in Fig. 3(a) were linearly fitting results. The dashed line in Fig. 3(b) was drawn as a guide to the eyes.

Nevertheless, the picosecond x-ray speckles measurement provides a new feature as shown in the lower temperature region near to T_c in Fig. 4. The macroscopically averaged polarization diverges as temperature approaches T_c. We can give an alternative expression for this quantity as $G = (1/d)^3(\sigma_s^3|P|)$, which is in fact the dipole potential that the adjacent clusters feel each other, and hereafter called the short-range correlation strength of the local clusters. From the inset of Fig. 4, one can clearly see that the clusters' short-range correlation strength G increases in a form of power law $\mu^{-\kappa}$ as temperature approaches T_c. The critical exponent κ is determined to be 0.41 ± 0.02 by a least square fitting.

We stress that the speckle is a coherent scattering from the polarization clusters. The cluster is a dynamic correlated region where unit cells polarize coherently. NMR experiment [7] showed a relaxation time of Ti ion at each off-center site to be about 10 ns at a temperature of 5 °C. On the other hand, hyper-Raman experiment [5] showed the relaxation time of the overdamped phonon to be an order of several hundreds of picoseconds in the same temperature region. Thus, an order of nanoseconds might be a measure of the relaxation time of cluster. The 7 ps of x-ray laser pulse make the present observation of such clusters essentially in an instantaneous way. A simple analysis is given to explain why the structures of dynamic

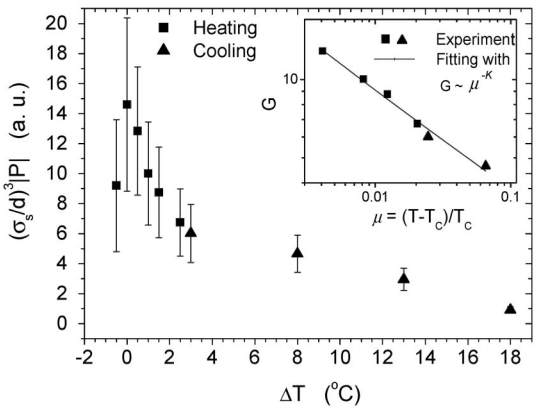

FIG. 4. The temperature evolution of the macroscopically averaged polarizations fluctuations within the paraelectric $BaTiO_3$. The error bars were estimated from that shown in Fig. 3. The inset shows the data near the T_c, which has been reorganized into a logarithmic scale, with its x axis replaced by a reduced temperature μ, and its y-axis name replaced by the G, the short-range correlation strength of the local clusters as explained in the text. The solid line is the least-square fitting with $G \propto \mu^{-\kappa}$, which give the critical exponent $\kappa = 0.41 \pm 0.02$.

clusters cannot be obtained from intensity integration measurement. We use the one-dimensional complex transmittance $\mathcal{T}(y, t)$ to describe the dynamic clusters distribution. The relaxation time of cluster is t_0. If we suppose the integration time on detector to be t_m, then the Fourier transform of the time-integral speckles would be $\gamma_{t_m}(\Delta y) \propto \langle \int_0^{t_m} \mathcal{T}^*(y + \Delta y, t)\mathcal{T}(y, t)dt \rangle$, where t is time and is the spatial average along y. Obviously, if t_m is much larger than t_0, the clusters' structure will be severely smoothed by the time-integration process within the bracket and consequently the $\gamma_{t_m}(\Delta y)$ will no more reflect the true correlation of those dynamic clusters.

The shot-by-shot fluctuations were also observed in speckles at 123.5 °C, and a ten-shot-averaged speckles profile at this temperature was found to coincide with the single-shot profile with a high E applied normally or with temperature heated to be 140 °C, although such data are not shown here. This means that such strong shot-by-shot fluctuations in the speckles are due to the dynamic nature of those clusters, and that no significant change of the static surface structure, such as surface corrugation, takes place within our observation temperatures. Since we have used the profile at 140 °C as the specular pattern in extracting the matter correlation function, the undesirable effects of the static surface structure are compensated to a negligible level.

It should be pointed out that the diffuselike feature of the speckles as shown in Fig. 1(a) mainly originated from the finite pixel size (25 μm) of our CCD camera, corresponding to a resolution of 0.056 μm^{-1} in q-space for the present setup. This implies that the correlation of those clusters separated beyond 100 μm in r-space will be averaged as a statistical ensemble. However, this value of 100 μm is larger than the slit width of the experiment, and its influence falls well beyond the correlation region as discussed in text.

In conclusion, the dynamic polarization clusters in the paraelectric $BaTiO_3$ near T_c have been observed at surface for the first time by means of a picosecond x-ray speckles technique. This dynamic polarization cluster provides a direct information of the spatial correlation of those fluctuating dipole moments in surface during phase transition. The knowledge of such spatial correlation of fluctuating dipole moments plays also an essential role in understanding the nature of the relaxor ferroelectrics [17] or the quantum paraelectrics [18]. In this context, the relaxation time of the clusters would be another important parameter. This might be observed from time correlation of two photons scattered at a certain q position of the speckles. Such a study is still in progress at present.

[1] W. Cochran, Adv. Phys. **9**, 387 (1960); **10**, 401 (1961).
[2] J. Harada, J. D. Axe, and G. Shirane, Phys. Rev. B **4**, 155 (1971).
[3] Y. Luspin, J. L. Servoin, and F. Gervais, J. Phys. C **13**, 3761 (1980).
[4] R. Comes, M. Lambert, and A. Guinier, Solid State Commun. **6**, 715 (1968).
[5] H. Vogt, J. A. Sanjurjo, and G. Rossbroich, Phys. Rev. B **26**, 5904 (1982).
[6] K. Inoue, Ferroelectrics **52**, 253 (1983).
[7] B. Zalar, V. V. Laguta, and R. Blinc, Phys. Rev. Lett. **90**, 037601 (2003).
[8] M. Stachiotti, A. Dobry, R. Migoni, and A. Bussmann-Holder, Phys. Rev. B **47**, 2473 (1993).
[9] H. Takahasi, J. Phys. Soc. Jpn. **16**, 1685 (1961).
[10] Y. Yamada, G. Shirane, and A. Linz, Phys. Rev. **177**, 848 (1969).
[11] H. Motegi and T. Mitsui, J. Phys. Chem. Solids **25**, 253 (1964).
[12] G. Burns and F. H. Dacol, Solid State Commun. **42**, 9 (1982).
[13] M. Takagi and T. Ishidate, Solid State Commun. **113**, 423 (2000).
[14] R. Z. Tai, K. Namikawa *et al.*, Phys. Rev. Lett. **89**, 257602 (2002).
[15] R. Z. Tai *et al.*, in *Eighth International Conference on Synchrotron Radiation Instrumentation, San Francisco, California, 2003*, edited by Tony Warwick *et al.*, AIP Conf. Proc. No. 705 AIP, New York, 2004) 1122.
[16] A. C. Thompson *et al.*, *X-ray data Booklet* (Berkeley, California, 2001), p. 1-5.
[17] P. M. Gehring, S. Wakimoto, Z. G. Ye, and G. Shirane, Phys. Rev. Lett. **87**, 277601 (2001).
[18] C. Ang, Z. Yu, and Z. Jing, Phys. Rev. B **61**, 957 (2000).