Direct Observation of the Critical Relaxation of Polarization Clusters in $BaTiO_3$ Using a Pulsed X-Ray Laser Technique

K. Namikawa,[1,2,6] M. Kishimoto,[2,6] K. Nasu,[3,6] E. Matsushita,[4,6] R. Z. Tai,[5,6] K. Sukegawa,[2] H. Yamatani,[2] H. Hasegawa,[2] M. Nishikino,[2] M. Tanaka,[2,6] and K. Nagashima[2]

[1]*Department of Physics, Tokyo Gakugei University, Koganei, Tokyo 184-8501, Japan*
[2]*Quantum Beam Science Directorate, Japan Atomic Energy Agency, Kizugawa, Kyoto 619-0215, Japan*
[3]*IMSS, KEK, Tsukuba, Ibaraki 305-0801, Japan*
[4]*Faculty of Engineering, Gifu University, Gifu, Gifu 501-1193, Japan*
[5]*Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Science, Shanghai 201204, China*
[6]*Japan Science and Technology Agency, CREST, Chiyoda, Tokyo 102-0075, Japan*

(Received 30 September 2008; revised manuscript received 24 June 2009; published 5 November 2009)

We have developed a new method to investigate the relaxation time of the dipole moment in polarization clusters in $BaTiO_3$. Time correlation of speckle intensities was measured by the use of a double pulsed soft x-ray laser. The evolution of the relaxation time of the dipole moment near the Curie temperature (T_C) was investigated. The maximum relaxation time ($\sim$90 ps) is shown to appear at a temperature of 4.5 K above the T_C, being coincident with the one where the maximum polarization takes place. This method is widely applicable to any other critical decay processes at phase transitions.

DOI: 10.1103/PhysRevLett.103.197401 PACS numbers: 78.70.Ck, 61.05.cf, 77.80.Bh, 77.84.Dy

Nanometer scale dipole moments in the polarization clusters in $BaTiO_3$ are supposed to be thermally excited and thermally relaxed within a picoseconds time scale [1]. However, the dynamics of these dipole moments in such a space-time scale has never been observed directly. Observation of the fluctuation in the nanometer regions so far has been investigated by means of speckle intensity correlation measurements by the use of synchrotron radiation (SR). However, intensity correlation measurements so far performed are restricted to the slow phenomena such as macroscopic fluctuation at order-disorder transformation in ordered alloys [2], diffusion process at Brownian motion in colloidal solutions [3], and antiferromagnetic domain fluctuations [4]. Here we show a direct observation of the decay dynamics in polarization clusters in $BaTiO_3$ by means of a speckle intensity correlation measurement in picoseconds order by use of highly coherent plasma based soft x-ray pulse laser (SXRL).

The nature of the phase transition is believed to be manifested in the precursor phenomena. In the case of $BaTiO_3$, this is the appearance of polarization clusters. The existence of the polarization clusters in the paraelectric phase of $BaTiO_3$ has been anticipated from the early days of $BaTiO_3$ research. Burns [5] suggested the emergence of polarization clusters even at temperature 200 K above the T_C by the refractive index measurements of cubic $BaTiO_3$, and this temperature is called Burns temperature, today. Hyper-Raman scattering [6] also hinted the existence of polarization clusters. Recent experiments such as the dielectric relaxation measurement [7], observation of anomalous birefringence [8], and NMR spectroscopy [9,10] indicated polarization clusters exist in the vicinity of the T_C. As shown in our previous Letter [11], we succeeded in the direct observation of the polarization clusters in the paraelectric phase of $BaTiO_3$ near the T_C by means of the SXRL speckles.

For the mechanism of paraelectric-ferroelectric phase transition of $BaTiO_3$, the displacive type transition model has been proposed [12] which is due to the softening of the long wavelength component of the transverse optical phonon near the T_C. However, the soft-phonon mode phase transition in $BaTiO_3$ has never been observed because of the over damping of phonons [13,14] in the vicinity of the T_C. On the other hand, such phenomena as x rays diffuse scattering [15], the strong quasielastic neutron scattering [16,17], and relaxation type spectra in hyper-Raman scattering [6] indicated the necessity to incorporate a relaxation type energy dissipative mechanism, coupling with the soft-phonon mode, in the paraelectric phase. From the NMR experiments, Zalar *et al*. [9,10] proposed a model in which the Ti ion fluctuates among some off-center sites and suggested a possibility of coexistence of the displacive type and the order-disorder type at the vicinity of the phase transition. In order to elucidate the nature of this phase transition, it is essential to investigate the behavior of the polarization clusters in the critical region.

The time correlation of the speckle intensities is represented by the fourth order correlation of the scattered electric fields. The intensity correlation $g^{(2)}$ can be written as

$$g^{(2)} = \frac{\langle I(t)I(t+\tau)\rangle_t}{\langle I\rangle_t^2} = \frac{\langle E*(t)E*(t+\tau)E(t+\tau)E(t)\rangle_t}{\langle I\rangle_t^2}, \quad (1)$$

where, t and τ is the time of the speckle measurement that has been tried and the delay time between the x-ray double pulses, respectively. While, $\langle\cdots\rangle_t$ represents the statistical

average over these measurements, each of which is tried at time t. The x-ray source used for the present experiments is a single-shot SXRL, so that $\langle \cdots \rangle_t$ in this Letter represents the ensemble average over the shots of the SXRL. We can write the scattered electric field $E(t)$ and $E(t+\tau)$ for each speckle by the first pulse at time t and by the second pulse at time $t+\tau$, respectively, as follows,

$$E(t) = E_0(t)F(\boldsymbol{k}', \omega')\exp\{i(\boldsymbol{k}' \cdot \boldsymbol{x} - \omega' t)\}, \quad (2)$$

$$E(t+\tau) = E_0{}'(t+\tau)F'(\boldsymbol{k}'', \omega'')\exp\{i[\boldsymbol{k}'' \cdot \boldsymbol{x} - \omega''(t+\tau)]\}, \quad (3)$$

where $E_0(t)$ and $E_0{}'(t+\tau)$ indicate the incident electric field of the first pulse and that of the second, while, $F(\boldsymbol{k}', \omega')$ and $F'(\boldsymbol{k}'', \omega'')$ are the scattering amplitude of the speckle by the first x-ray pulse and that of the second, respectively. Each scattering amplitude $F(\boldsymbol{k}', \omega')$ and $F'(\boldsymbol{k}'', \omega'')$ can be written as follows, respectively,

$$F(\boldsymbol{k}', \omega') = \langle \boldsymbol{k}', \omega' | \langle \varphi' | H_{\text{eff}} | \varphi \rangle | \boldsymbol{k}, \omega \rangle, \quad (4)$$

$$F'(\boldsymbol{k}'', \omega'') = \langle \boldsymbol{k}'', \omega'' | \langle \varphi | H'_{\text{eff}} | \varphi'' \rangle | \boldsymbol{k}, \omega \rangle, \quad (5)$$

where ket $|\varphi\rangle$ etc. represent the spatial distribution of the polarization in clusters. H_{eff} is an effective Hamiltonian that represents the interaction between the first x-ray pulse and the polarization, and it causes the addition of the collective polarization. While, H'_{eff} is the same one in the second x-ray pulse and it causes the subtraction of the collective polarization. Here we include only the subtraction of the collective polarization by the second pulse because the addition by the second pulse is a higher order process. A creation (annihilation) of one polarization causes the addition (subtraction) of the nanometer size collective polarization to (from) the polarization clusters under the condition of critical fluctuation. Once the nanometer size collective polarization has been created in the clusters, then it is subject to a random thermal relaxation with a relaxation time τ_0, and an evolution from φ' to φ'' takes place. After inserting Eqs. (2)–(5) into Eq. (1), taking an average over t under the assumption that an excitation of the polarization is subject to chaotic distribution, we can express the intensity correlation for the delay time τ as follows [18,19],

$$g^{(2)} = 1 + \beta \exp\left(-\frac{2\tau}{\tau_0}\right), \quad (6)$$

wherein, τ is assumed to be much longer compared to the coherence time of the excited state, while the factor β is given by a square of the visibility defined by the absolute value of the first order correlation function of the incident electric fields $E_0(t)$ and $E_0{}'(t+\tau)$. A rigorous theoretical discussion can be found elsewhere [20].

Experiments have been carried out by use of the x-ray speckle intensity correlation measurement system installed at Japan Atomic Energy Agency. The experimental setup is shown in Fig. 1. Characteristics of this SXRL are, one shot per 15 minutes in repetition rate, 7 ps in pulse width, 3.5×10^{10} photons per pulse in photon flux, 13.9 nm in wavelength, $\sim 10^{-4}$ in the band width $\Delta\lambda/\lambda$, and 0.5 mrad in beam divergence. The spatial coherence is estimated to be more than 90% [21,22]. The spot size of the focused x ray at the sample was about 100 μm in diameter. A soft x-ray streak camera was used for the time and the space resolved measurement of the x-ray speckles. Details of this system will be found elsewhere. The sample used in the present experiments was the same one which was used in our previous experiments: a flux-grown $BaTiO_3$ single crystal of 395 K in T_C. The sample temperature has been controlled with an accuracy of ± 0.1 K from the room temperature up to 500 K. The x-ray speckle measurements have been done on (001) surface with 10° grazing angle incidence. This is under the condition of total reflection. However, we can understand that the clusters show the bulk property even under this condition. A macroscopic quantity, the gross polarization density of the clusters over the sample, surely diverges at the bulk T_C, as shown in Fig. 4 of our previous paper [11].

An example of an x-ray streak image of the speckle due to the first and the second SXRL pulse is shown in Fig. 2(a), and the intensity profiles of these streak images in the horizontal direction are shown in Fig. 2(b). The time correlation analysis in this Letter has been done for the specular reflection peak on the right side. We have measured several pairs of x-ray speckle intensities, and normalized each intensity profile by the sum over the relevant profile in order to cancel the shot-by-shot fluctuation of the SXRL pulse intensity. We calculated the $g^{(2)}$ by Eq. (1) from these experimentally measured and normalized speckle intensity profiles. An example of the calculated value of $g^{(2)}$ for the secular reflection from -0.24 μm^{-1} to 0.24 μm^{-1} is illustrated in Fig. 2(c). Outside of this region shown in Fig. 2(c), $g^{(2)}$ heavily fluctuate around 1, because of low signal intensity. Hence, we do not discuss $g^{(2)}$ of this outside region hereafter. As shown in Fig. 2(c), the $g^{(2)}$

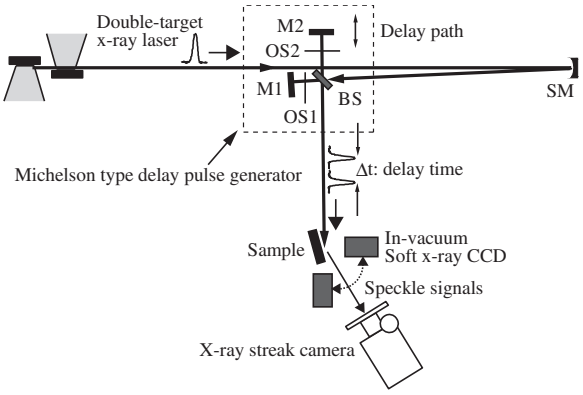

FIG. 1. Schematic set up of x-ray intensity correlation measurements by use of a Michelson type delay pulse generator, and an x-ray streak camera. The delay pulse generator consists of a beam splitter (BS), and two Mo/Si multilayer mirrors $M1$ and $M2$, and two optical shutters OS1 and OS2.

takes a larger value in the center parts of the specular reflection, while the $g^{(2)}$ takes a value of almost 1 in both sides of the center part. This correlation function $g^{(2)}$ for the center part of the specular reflection spatially reflects the autocorrelation among the same points in polarization clusters.

Prior to fitting the data $g^{(2)}$ to the Eq. (2), we averaged the value of $g^{(2)}$ over the 0.08 μm^{-1} region of central part of the specular reflection which corresponds to the size of the speckle $\lambda z/D$, where z is the distance from sample to the streak camera and D is the spot size of the beam at the sample. Then we evaluated τ_0 by the curve fitting of the averaged values $g^{(2)}$ to Eq. (6) as shown in Fig. 3. Results of two independent series of experiments are shown in Fig. 3(a) and in Fig. 3(b). Figure 3(a) shows the results of the first experiment, the relaxation behavior of the intensity correlations is shown for the temperature from 393 K up to 405 K by 2 K, while the Fig. 3(b) shows the results of the second experiment, the relaxation behavior for the temperatures from 401 K up to 405 K by 0.5 K. The averaged values $g^{(2)}$ fit well to the exponential decay curve with single delay time τ_0 for each temperature. The intercept at $\tau = 0$, namely β in Eq. (6), was found to be about 0.6 for all temperatures. The value of $\beta = 0.6$ corresponds to the x-ray visibility 0.8, which is consistent with the estimation. Relaxation times obtained by fitting are an order of several tens of picoseconds. The plots of the relaxation time as a function of the temperature are shown by solid circles and solid triangles in Fig. 4. Open squares in Fig. 4 show the temperature dependence of the cluster polarization $|P|$ obtained in our previous experiment [11]. The solid line and the dotted line is a guide to the eye, respectively. As the temperature decreases, the relaxation becomes rapidly slower from ~20 ps at 6 K above the T_C to the maximum value ~90 ps at 4.5 K above the T_C, then becomes faster again to ~20 ps across the T_C. On the other hand, $|P|$ increases monotonically with decreasing the

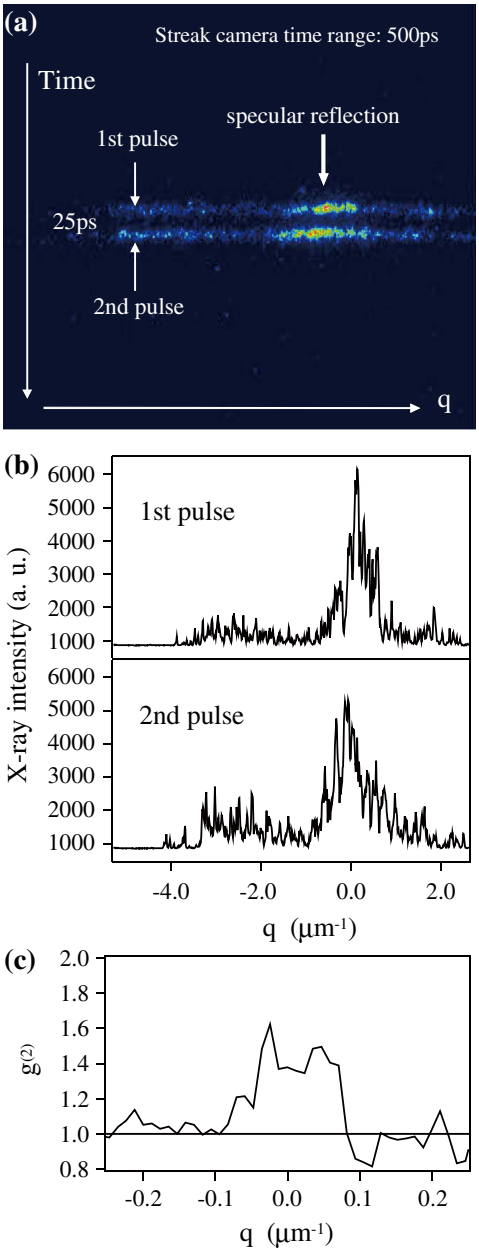

FIG. 2 (color online). (a) A streak camera image of the two speckle intensities separated by a delay time 25 ps, (b) intensity profiles of the speckle images in the horizontal direction, (c) a q dependence of the $g^{(2)}$ in the vicinity of the specular reflection, where q is the value relative to the center of specular reflection.

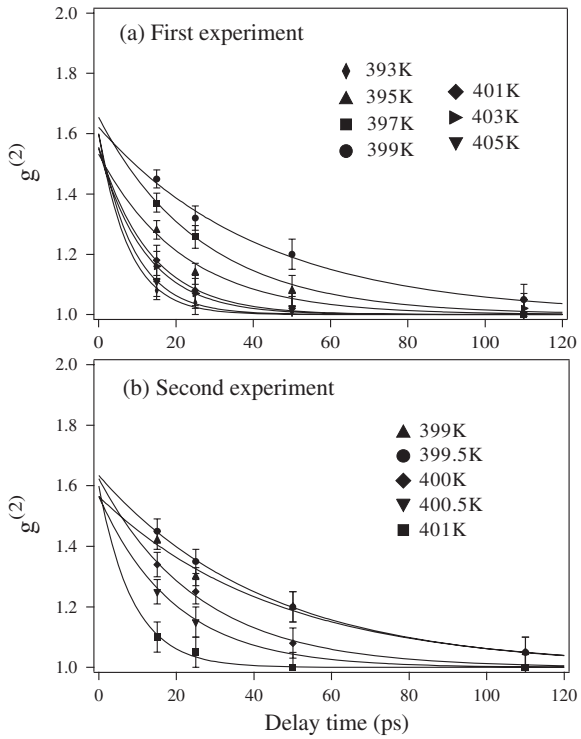

FIG. 3. Decay curves of $g^{(2)}$ as a function of delay time at several sample temperatures (a) from 2 K below the T_C up to 10 K above the T_C by 2 K step: results due to the 1st experiment, and (b) from 4 K above the T_C up to 8 K above the T_C by 0.5 K step: results due to the 2nd experiment.

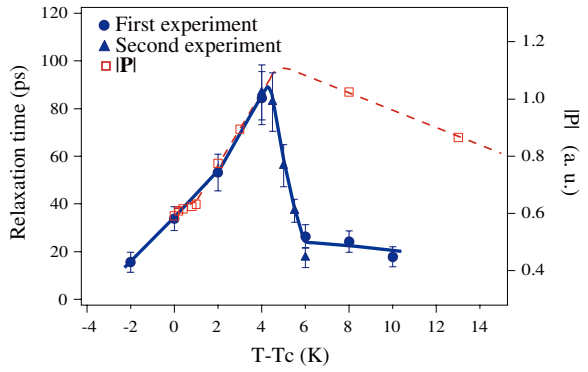

FIG. 4 (color online). Temperature dependence of the relaxation time τ_0 and the polarization of the cluster. A maximum that takes place at 4.5 K above the T_C coincides with the maximum of the polarization of the clusters. Solid and broken lines are just guide to the eye.

temperature and takes a maximum value at around 5 K above the T_C, and then it decreases similarly as the relaxation time. A kind of critical slowing down, increase in fluctuation and increase in relaxation time, seems to takes place in clusters locally at 4.5 K above the T_C.

NMR experiments by Zalar *et al.* suggested two time scale relaxation mode dynamics exist [10]. The slow mode corresponds to the flipping of the polarization of the clusters among $\langle 100 \rangle$ by the time scale less than 10^{-4} s. The structural relaxation of several 10 μs observed by Yan *et al.* in time correlation spectroscopy of optical laser [23] was probably due to this flipping mode. The fast mode is the Ti ion hopping among the $\langle 111 \rangle$ off-center sites which was proposed by Chaves *et al* in their order-disorder model [24]. Mablione *et al.* estimated the relaxation time as 10^{-8} s $\sim 10^{-9}$ s by their dielectric relaxation measurements [25]. This kind of relaxation has been observed as the central peak (CP) in Raman scattering. Sokoloff *et al.* observed two times scale CPs: one is $\sim$5 GHz and another is $\sim$20 cm^{-1} [1]. Our observation of critical slowing down $\sim$90 ps is consistent with CP observations $\sim$5 GHz. The appearance of the CP and critical slowing down near the T_C has been exemplified by the two dimensional model simulation by Stachiotti *et al.* [26] and recently by the quantum Monte Carlo simulation by Kai *et al.* [20]. Why the critical slowing down in our observation does not appear at the T_C but at 4.5 K above the T_C can be explained by the dynamical molecular field due to the polarization in clusters. It is well known that the ferroelectric phase transition occurs at a little bit higher temperature when an external electric field has been applied. The dynamical molecular field in polarization clusters acts to reduce the cluster temperature effectively. On approaching the T_C, the polarization of each cluster decreases again. This decrease in polarization causes the decrease in the relaxation time as shown in Fig. 4.

The present experiments so far performed are the direct measurement of the thermal decay process in the polarization clusters in $BaTiO_3$; however, the present method can be applied widely to the relaxation phenomena of nanostructures appearing in other materials such as CDW in TTF-TCNQ, SDW in antiferromagnetic Chromium, and dynamical stripes in cuprate high T_C superconductors. By use of a much shorter x-ray pulse such as the x-ray free electron laser (XFEL), we can directly observe that the relaxation process turns over from the dynamical to the dissipative in the nanostructure of condensed matters.

The sample investigated in this work has been furnished by Professor A. Sawada, Okayama University. We thank him for his courtesy.

[1] J. P. Sokoloff, L. L. Chase, and D. Rytz, Phys. Rev. B **38**, 597 (1988).
[2] S. Brauer *et al.*, Phys. Rev. Lett. **74**, 2010 (1995).
[3] S. B. Dierker, R. Pindak, R. M. Fleming, I. K. Robinson, and L. Berman, Phys. Rev. Lett. **75**, 449 (1995).
[4] O. G. Shpyrko *et al.*, Nature (London) **447**, 68 (2007).
[5] G. Burns and F. H. Dacol, Solid State Commun. **42**, 9 (1982).
[6] K. Inoue, Ferroelectrics **52**, 253 (1983).
[7] T. Mitsui, *Springer Handbook Condensed Matters*, edited by W. Martienssen and H. Warlimont (Springer, Berlin, 2002).
[8] Takagi and T. Ishidate, Solid State Commun. **113**, 423 (2000).
[9] B. Zalar, V. V. Laguta, and R. Blinc, Phys. Rev. Lett. **90**, 037601 (2003).
[10] B. Zalar, A. Lebar, J. Seliger, R. Blinc, V. V. Laguta, and M. Itoh, Phys. Rev. B **71**, 064107 (2005).
[11] R. Z. Tai *et al.*, Phys. Rev. Lett. **93**, 087601 (2004).
[12] W. Cochran, Adv. Phys. **9**, 387 (1960); **10**, 401 (1961).
[13] G. Shirane, J. D. Axe, and J. Harada, Phys. Rev. B **2**, 3651 (1970).
[14] J. D. Axe and G. Shirane, Phys. Rev. B **4**, 155 (1971).
[15] Comes, M. Lambert, and A. Guiner, Solid State Commun. **6**, 715 (1968).
[16] J. Harada, J. D. Axe, and G. Shirane, Phys. Rev. B **4**, 155 (1971).
[17] Y. Yamada, G. Shirane, and A. Linz, Phys. Rev. **177**, 848 (1969).
[18] R. Loudon, *The Quantum Theory of Light* (Oxford Science Publications, Oxford, 1983).
[19] J. W. Goodman, *Speckle Phenomena in Optics* (Roberts and Company Publishers, Greenwood Village, 2006).
[20] K. Ji, K. Namikawa, H. Zheng, and K. Nasu, Phys. Rev. B **79**, 144304 (2009).
[21] M. Tanaka *et al.*, Opt. Lett. **28**, 1680 (2003).
[22] M. Nishikino *et al.*, Phys. Rev. A **68**, 061802(R) (2003).
[23] R. Yan *et al.*, Appl. Phys. Lett. **93**, 192908 (2008).
[24] A. S. Chaves, F. C. S. Barreto, R. A. Nogueira, and B. Zeks, Phys. Rev. B **13**, 207 (1976).
[25] M. Maglione, R. Bohmer, A. Loidl, and U. T. Hochli, Phys. Rev. B **40**, 11 441 (1989).
[26] M. Stachiotti, A. Dobry, R. Migoni, and A. Bussmann-Holder, Phys. Rev. B **47**, 2473 (1993).