X-ray photon correlation spectroscopy of structural fluctuations in relaxor ferroelectrics PZN-9%PT

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Abstract. We have performed an x-ray photon correlation spectroscopy measurement of 91%Pb(Zn1/3Nb2/3)O3-9%PbTiO3 and found a slow structural fluctuation in time near TC. The slow fluctuation consists of long-term and short-term fluctuations. We have derived the short-term fluctuation from the intensity fluctuations and found out the relaxation time to be an order of 10 s. It is suggested that the slow fluctuation is owing to the competition between macroscopic tetragonal symmetry and the microscopic orthorhombic symmetry. The competition should be a main reason for the low-frequency dielectric permittivity.

1. Introduction
Recent progress in imaging technology using coherent X-rays has enabled us to obtain spatial or time correlation function of domains. The dynamics — particularly slow dynamics — of mesoscale domains is rarely detectable by the conventional inelastic light-scattering techniques mostly used for measuring phonon-type dynamics with a characteristic time scale of ~ 10^{-12} s, because the slow dynamics is integrated behind a quasi-elastic central peak. In this situation, the detection of the fluctuation is easier in momentum-and-time (q-t) space than in momentum-and-energy (q-\omega) space; the q-\omega space is usually used in conventional inelastic techniques. The slow dynamics of materials is directly related to the low-frequency susceptibilities of materials and is important for understanding the fundamental physics of mesoscopic scale inside materials.

In this paper, we report a result of x-ray photon correlation spectroscopy (XPCS) measurement of the relaxor ferroelectrics 91%Pb(Zn1/3Nb2/3)O3-9%PbTiO3 (PZN-9%PT) [1, 2, 3, 4]. The present target material PZN-9%PT is located near a morphotropic phase boundary (MPB) [5] in the phase diagram and exhibits extremely strong dielectric and piezoelectric responses that are one order of magnitude larger than those of conventional ferroelectric ceramics such as Pb(Zr_xTi_{1-x})O_3 (PZT). PZN-9%PT has a cubic perovskite-type structure at high
temperatures ($T_c = 455$ K on cooling) and shows relaxor-like phenomena. It is generally accepted that such relaxor properties are associated with nanosize (1–100 nm) ferroelectric domains.

2. X-ray Photon Correlation Spectroscopy

We prepared a $10 \times 10 \times 0.25 \text{ mm}^3$ wafer of PZN-9\%PT, which has a PT-concentration gradient as low as $< 0.02 \%$/mm, from a large single crystal grown by JFE Mineral Co., Ltd. [8]. The wafer was cut to provide the (100) plane. Figure 1 shows dielectric constant ($\varepsilon'$) of the sample. It shows relaxor-like phenomena with low frequency relaxation near $T_c$.

XPCS is a novel technique for studying the slow dynamics of various equilibrium and non-equilibrium processes occurring in materials. It is based on the generation of a speckle pattern by the scattered coherent x-ray originating from a material having static or dynamic nano-to-micro meter inhomogeneities.

With coherent x-rays, the coherent sum of scattered x-rays from inhomogeneous materials, i.e., having ordered regions (ORs), results in a speckle pattern. The changes in structure and the arrangement of ORs result in the fine changes to the speckle pattern. A Fourier transformation of the speckle pattern gives the spatial-autocorrelation function (S-ACF), which visualizes the structure and arrangement of ORs through a correlation function. The time evolution of the speckle pattern also gives the time-autocorrelation function (T-ACF) of materials.

The experiment was performed at BL22XU [6] of SPring-8. Incident x-ray energy was tuned to 9.0 keV (wavelength $\lambda = 1.377$ Å) with a liquid-nitrogen-cooled Si(111) double-crystal monochromator. As shown in Fig. 2 (a), the most important point is the relationship among beam size and two distances (aperture-to-sample ($R_1$) and sample-to-detector ($R_2$)) [7]. We put the $10(a_0) \times 10 \mu\text{m}^2$ aperture 0.15 m ($= R_1$) upstream from the sample for selecting coherent area of incident x-ray. The detector was put 1.3 m ($= R_2$) down stream from the sample. $R_1$ and $R_2$ almost satisfy the near-field ($R_1 < a_2/\lambda$) and far-field ($R_2 \gg a_2/\lambda$) ranges respectively. In the former case, the incident x-ray is pseudo-plane wave at the sample position. In the last case, the diffracted x-ray is far-field diffraction, where the speckle patterns show similar shape when the $R_2$ changes.

3. Result and Discussion

Two-dimensional time averaged speckle patterns (static information) were measured by a high-resolution x-ray CCD camera ($4.7 \times 4.7 \mu\text{m}^2$ pixel size) with an exposure time of 60 s. Fig. 2
(b) shows a speckle pattern of 200 reflection measured at 457 K on cooling, 2 K above $T_c$. In this case, the speckle pattern means the fine structure of the 200 Bragg reflection.

In principle, the time evolution of the speckle pattern can be obtained by the continuous measurement, like a “movie”. It is, however, difficult to perform such a measurement due to lack of both coherent photon number and efficiency of the CCD camera, i.e., the minimum exposure time is limited to 60 s for this experiment.

We therefore measured a time evolution of the speckle pattern by a combination of receiving slits and point detector (avalanche photodiode (APD), the maximum count rate is 10 MHz), where some speckles are selected for the measurement. The size of $200 \times 200 \mu m^2$ receiving aperture before the point detector was schematically shown in Fig. 2 (b) by the open square [9]. The positive direction of $2\theta$ angle is also shown.

Time-resolved scattered intensity was measured around $(2, 0, 0)$. The temperature was set at a certain temperature and controlled within 0.04 K. Since the present measurement is sensitive to an extrinsic effect as the stage drift just after the temperature set, the measurement was started after the stabilization of the whole measurement system. Figure 3(a) shows a measurement result of 455 K. The intensities ($I$) are normalized by the monitor counts of the incident x-ray ($I_0$) as $I/I_0$. The count rate was $\sim$200 kHz for $I$ and $\sim$20 kHz for $I_0$. The estimated fluctuation of the present normalized count rate is $\Delta I/I_0 \sim 0.07$. We also show the data of 454 K in Fig. 3 (a), where the fluctuation is no longer observable. The higher noise level compared to that of 455 K is due to the lower count rate compared to that of 455 K. Note that the intensity of 454 K is multiplied by a factor of 8.5. It is clear that the intensity exhibits large thermal fluctuations in time and the fluctuation consists of multiple time scale, i.e., long term fluctuation with about 1000 s and short-term fluctuation with tens of s. Such a multiple-time-scale fluctuation should strongly be correlated with the low-frequency dielectric permittivity as shown in Fig. 1. The existence of the large thermal fluctuation indicates an easy responsibility to the AC-electric field, which will give large dielectric permittivity.

As shown in Fig. 3 (b), we calculated T-ACF defined as $C(\tau) = \langle I(t)I(t+\tau) \rangle / \langle I \rangle^2$, where $\tau$ is the lag time. Short-term relaxation with 10-s-order can be seen in the total T-ACF. It also contains non-trivial long-and-middle-term relaxation over 100 s and hinders the estimation of the short-term component. In this paper, we have tried to obtain a typical relaxation time of the short-term fluctuation. As seen in the data of 455 K in Fig. 3 (c), we firstly eliminate the components of the long-and-middle-term fluctuations, which are estimated by the data...
Figure 3. (a) Time dependence of the intensity measured around (2, 0, 0) at 455 K ($T_c$) and 454 K ($< T_c$). (b) Calculated total T-ACF of 455 K from (a). (c) Time dependence of the intensity and estimated long-and-middle-term fluctuations at 455 K. (d) Calculated T-ACF from (c).

smoothing over 100 s range (see solid line in Fig. 3 (c)). The difference between the data and the solid line approximately gives a component of the short-term fluctuation. By using the difference, we calculated the T-ACF as shown in Fig. 3 (d). $C(\tau)$ was roughly analyzed by the function $\propto e^{-\tau/\tau}$ (see solid line in Fig. 3 (d)) and the typical relaxation time of the short-term fluctuation was obtained as $\tau = 19$ s. The order is consistent with the result previously obtained by intensity fluctuation spectroscopy using nano-focused x-ray [10]. T-ACF of 454 K is also shown in Fig. 3 (d), which represents that the error level of the present T-ACF measurement is low and the data taken at 455 K is reliable.

As mentioned above, the measurement was done around (2, 0, 0) with the receiving aperture of $200 \times 200 \mu m^2$. The corresponding length scale inside the area is from hundreds of nm to tens of $\mu m$ [11]. Thus the observed intensity fluctuation in that region mainly reflects the structural fluctuation with the length scale. The time scale is related to the size scale, i.e., the long-term fluctuation comes from the tens-of-$\mu m$ region (whole region of the x-ray irradiated area), while the short-term fluctuation comes from the hundreds-nm regions.

We speculate that the slow fluctuation comes from the competition between macroscopic tetragonal symmetry and the microscopic orthorhombic symmetry. As is well known, the cubic phase macroscopically transforms into the tetragonal phase. On the other hand, there are local polarized regions with [110]-polarization (so-called polar nano region (PNR)) during the macroscopic cubic-to-tetragonal transition. This is suggested by diffuse scattering [12, 13] and

International Conference on Frustration in Condensed Matter (ICFCM) IOP Publishing
Journal of Physics: Conference Series 320 (2011) 012086 doi:10.1088/1742-6596/320/1/012086

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thermal [14] measurement. We also mention the precise properties of the dielectric permittivity as shown in Fig. 1. The dielectric permittivity reaches maximum at 459 K, 4 K above $T_c$. The downturn before the phase transition should be caused by the competition between PNRs and macroscopic tetragonal symmetry that starts appearing. Note that the summation of the $(110)$ and $(001)$ polarization can give rhombohedral and monoclinic symmetries as observed in the MPB region [15].

4. Summary

We have performed an x-ray photon correlation spectroscopy measurement of PZN-9%PT and found a slow structural fluctuation in time near $T_c$. The slow fluctuation consists of long-term and short-term fluctuations. We have derived the short-term fluctuation from the intensity fluctuations and found out the relaxation time to be an order of 10 s. It is suggested that the slow fluctuation is owing to the competition between macroscopic tetragonal symmetry and the microscopic orthorhombic symmetry. The competition should be a main reason for the low-frequency dielectric permittivity.

We finally mention here that the data acquisition and analysis methods shown in this paper are not sophisticated yet. After the improvement of the methods, we will take the temperature and momentum dependence of the intensity fluctuation and derive the real multiple scales of time and space in relaxor ferroelectrics.

Acknowledgments

This work was partly supported by the following projects. Grant-in-Aid for Scientific Research on Priority Areas “Novel States of Matter Induced by Frustration” (19052002) and Grants-in-Aid for Scientific Research for Young Scientists B (16740177, 21710099) by MEXT and CREST “Novel Measuring and Analytical Technology Contributions to the Elucidation and Application of Material” by JST.

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