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Coherent X-ray Diffraction for Domain Observation

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Two-dimensional (2D) speckle patterns from the ferroelectric material PZN-9%PT have been observed successfully by coherent x-ray diffraction. The 2D-FFT image of the speckle pattern gives us a spatial autocorrelation function which contains the information of the domain arrangement in the crystal within a few micrometers scale. By the complementary use of an optical microscope and SEM, it has been concluded that there are some scales of higher-order structures (domains) from sub-μm to sub-mm in PZN-9%PT, i.e., a set of domains with a scale forms a higher order of domain. The nature of the pseudo-cubic X-phase is also discussed.

Key words: coherent x-ray diffraction, speckle, PZN-9%PT, X-phase

1. INTRODUCTION

Appearance of the 3rd generation synchrotron radiation source (ESRF, APS and SPring-8) makes it possible to perform the x-ray diffraction experiment using full-coherent x-ray (coherent x-ray diffraction: CXD). Such a CXD technique is expected to be applied to the solid state physics. The large size of the coherent x-ray beam (> 100 μm^2) allows the diffracted x-rays from micrometer-sized domains to interfere each other. The obtained diffracted x-ray pattern is called as speckle. This is a different point from the conventional x-ray diffraction using partial coherent x-ray, where the speckle pattern disappears.

The x-ray speckle pattern well reflects a particle or domain arrangement on the inside of materials. Detection of the arrangement is important for understanding a function of the materials such as ferroelectric and piezoelectric materials, photonic crystals and so on. For this purpose, we have thus constructed the apparatus for CXD at BL22XU of SPring-8. By using the devices, we have succeeded in observing the speckle pattern from the lead-based perovskite ferroelectric material PZN-9%PT ($91\%Pb(Zn_{1/3}Nb_{2/3})O_3$-$9\%PbTiO_3$) at room temperature (RT).

The solid solution of relaxor PZN and ferroelectric PT (PZN-x%PT) gives the colossal piezoelectric response near the MPB (Morphotropic Phase Boundary) region, where $x = 8 \sim 9$ % as $d_{33} = 2500$ pC/N at RT[1]. In PZN-8%PT, it is well known that the zero-field cooled sample transforms into mysterious phase, so called X-phase via a tetragonal (T) phase [2]. In the high temperature cubic (C) phase, the 200 Bragg peak is single. As the C phase transforms into the T phase, many peaks around the 200 position appear, which indicate the appearance of the ferroelectric domain. However the additional peaks are wipes out by the T-to-X phase transition at 340 K. The 200 Bragg peak becomes single again (pseudo-cubic), while the peak is slightly broader than resolution limit [2,3]. By combining the results from the polarized microscope [4] and the AFM (Atomic Force Microscope) measurement [5], the nature of the pseudo-cubic X-phase is now supposed that the rhombohedral (R) ferroelectric domains with a few micrometers scale are systematically arranged. Then the rhombohedral strain in the X-phase is canceled out by the systematic arrangement of the domains, where the pseudo-cubic cell is realized.

If we apply the CXD measurement to PZN-9%PT, the fine structure of the Bragg peak (speckle) at the X-phase will be clarified. The speckle will contain the information of the micro array of the rhombohedral ferroelectric domains.

In this paper, we will show the results of the speckle measurements of the X-phase of *non-poled* PZN-9%PT. All measurements were performed at RT.

2. EXPERIMENTAL

The followings are the experimental setup for CXD constructed at the BL22XU [6] of SPring-8.

2.1 Optical alignment for CXD

The optical alignment at BL22XU [6] of SPring-8 is shown in Fig.1. Incident x-ray energy was tuned to

8.900 keV (wavelength λ = 1.393 Å) with a liquid-nitrogen-cooled Si(111) double-crystal monochromator. For obtaining the coherent region of incident x-ray, we used the 4-jaw slit which blade was well-polished to give a clean plane wave. The obtained coherent x-ray with a size of 10^2 (= $(2a)^2$) μm^2 is applied to the sample. The diffracted x-ray by the sample was closely detected by a high resolution x-ray CCD camera (HRX-CCD camera; Section 2.2). Note that the relationship between the beam size and the two distances (4-jaw slit–to-sample (R_1) and sample-to-HRX-CCD camera (R_2)) is important. We put the 4-jaw slit 0.15 m (= R_1) upstream from the sample, while, the HRX-CCD camera 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 ($R_2 >> a^2/\lambda$) 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.

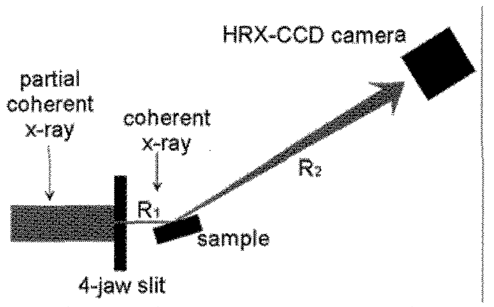

Fig. 1. The optical alignment for CXD at BL22XU of SPring-8. The distances R_1 and R_2 almost satisfy the near-field ($R_1 < a^2/\lambda$) and far-field ($R_2 >> a^2/\lambda$) ranges respectively.

2.2 Installation of HRX-CCD camera [7]

Though a two-dimensional (2D) detector is powerful tool for observing the speckle patterns, a conventional 2D detector has low spatial resolution in other word, visibility and contrast enough for separating each speckle. We have thus developed a HRX-CCD camera for obtaining the well-resolved speckle pattern. We have pursued the resolving power at the cost of sensitivity, and have chosen Lu_2SiO_5 (LSO) for a scintillator, which is made thin down to 10 micrometer. The prepared thin LSO makes it possible to reduce a diffusion of lights as it travels through LSO and provides us a clear image. By coupling a microscope with amplification factor of 10 and a ORCA-HR CCD camera (Hamamatsu Photonics K.K.), we have reached the spatial resolution to 0.5 micrometer at full-width at half maximum.

2.3 Fraunhofer diffraction from the 4-jaw slit

Figure 2 shows a 2D image of the Fraunhofer diffraction from a 8 x 8 μm^2 sized rectangular aperture. The intensity of a valley between peaks reaches to back ground level, which shows the objective visibility is satisfied. It is also confirmed that the serious blurring of the image is not observed. We also performed the 2D -Fast Fourier Transformation (2D-FFT) of the 2D image of the Fraunhofer diffraction. The structural result of the 2D-FFT well represents a spatial autocorrelation function of the rectangular aperture (see Fig. 3). The result means that the quality of the observed 2D image is reliable.

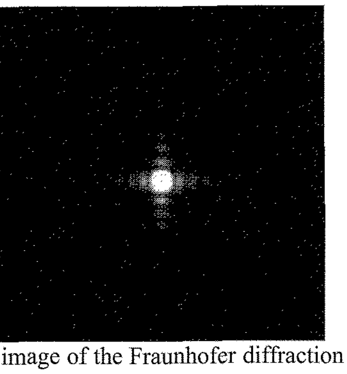

Fig. 2 2D image of the Fraunhofer diffraction from the 8 x 8 μm^2 rectangular aperture.

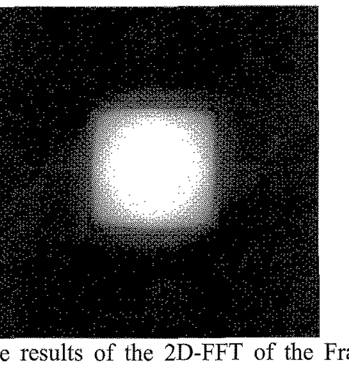

Fig. 3. The results of the 2D-FFT of the Fraunhofer diffraction of Fig. 1. The autocorrelation function of the 8 x 8 μm^2 rectangular aperture is obtained.

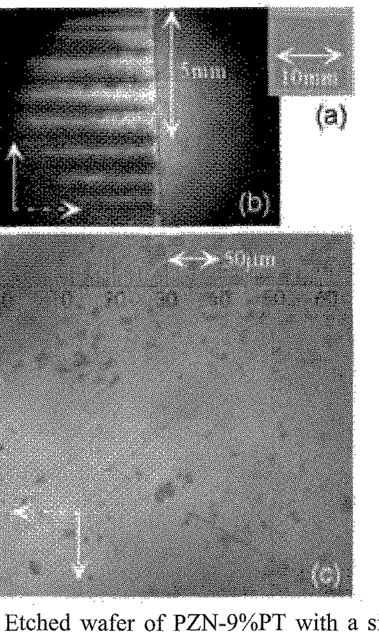

Fig. 4 (a) Etched wafer of PZN-9%PT with a size of 10 mm x 10 mm x 0.25 mm. (b) Microscope image of PZN-9%PT. (c) Polarized microscope image of PZN-9%PT.

2.4 Sample preparation and microscopy

PZN-9%PT single crystal was grown by the supported solution Bridgman method using PbO as a self-flux at the JFE Mineral Co., Ltd [8]. Figure 4(a) shows a picture of a chemically etched wafer of *non-poled* PZN-9%PT with the size of 10 mm x 10 mm x 0.25 mm. The sub-mm sized lateral stripe pattern is easily seen by naked eyes. Figure 4(b) shows the low resolution microscope image of the same sample. The lateral stripe pattern is clearly seen. Figure 4(c) shows the image by the polarized microscope with the crossed Nicols. The slanted stripe pattern can be seen. The distance between the domains is about 5 ~ 10 μm. The crystal orientation is shown by the solid and dotted arrows in Figs. 4(b) and 4(c), where the arrows are perpendicular to the {100} plane. Note that the field of vision is reversed in Fig. 4(c).

We used the same type of PZN-9%PT wafer in the present CXD measurement.

3. RESULTS AND DISCUSSIONS

3.1 Speckle pattern from PZN-9%PT

Figure 5 shows the speckle pattern of the 200 Bragg diffraction of the X-phase in PZN-9%PT. The conventional x-ray diffraction measurement shows that the peak is single shape (data not shown), which is consistent with the previous reports [2-3]. There is no additional peak from the rhombohedral macro domain around the 200 Bragg spot.

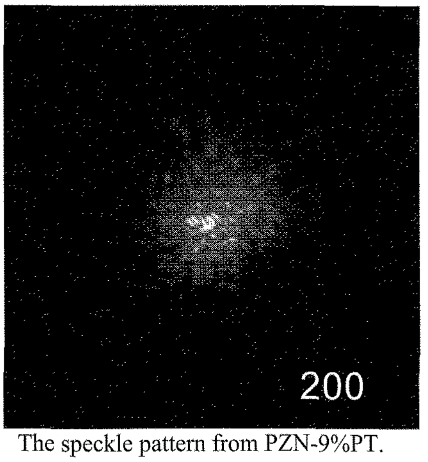

Fig. 5 The speckle pattern from PZN-9%PT.

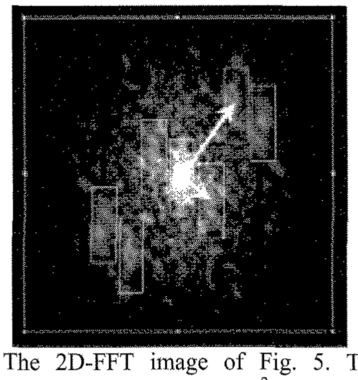

Fig. 6 The 2D-FFT image of Fig. 5. The flame surrounding the image is 20 x 20 μm^2 rectangular.

The speckle pattern shown in Fig. 5 is the fine structure of the 200 Bragg peak. There is a characteristic stripe-like structure around the center. The shape includes the information of the micrometer sized domain in PZN-9%PT. We performed the FFT of the 2D image of the speckle pattern of Fig. 5 as shown in Fig. 6. The 2D-FFT image represents a spatial autocorrelation function of the illuminated area of PZN-9%PT.

Generally, the autocorrelation function is even-function and takes maximum value at the center. In Fig. 6, we can see the bright areas except for the central area, which are marked by the white boxes for a guide to the eyes. There are two characteristic distance of the bright area from the central position. The directions are shown by white arrows for a guide to the eyes. The long and short arrows correspond to about 6 and 2 μm, respectively. Thus, the 2D-FFT image indicates that there are similar structures at the position directed by the arrows. We can conclude that the domain with the size of a few micrometers is observable by the CXD.

The observed scale of domain corresponds to the one obtained from the polarized microscope.

3.3 Plural order structure in PZN-9%PT

We have also taken the SEM (Scanning Electron Microscope) image of another wafer of PZN-9%PT as shown in Fig. 7 with the amplification factor of 2000. The slanted stripe pattern is consistent with the one which is observed by the polarized microscope shown in Fig. 3(c) and present CXD.

The SEM image shows that there are two length scales of domain wall in the field of vision. The large one is about 2 ~ 3 μm, while the smaller one is about 0.5 μm. The domain walls are running alternately as shown in the Fig. 7 by white solid (larger domain) and dotted (smaller domain) arrows.

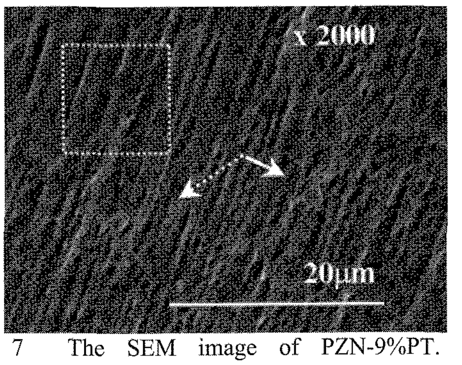

Fig. 7 The SEM image of PZN-9%PT. The amplification factor is 2000. The square drawn by the dotted line is 10 x 10 μm^2 area.

We can confirm that there are arranged sub-micrometer sized domains (SMSD) in the non-poled PZN-9%PT, at present. However the FFT image of the present CXD measurement does not show the trace of the SMSDs. This is due to the distribution of the size of the SMSD. As seen in the Fig. 7, there are many SMSDs in the 10 x 10 μm^2 area and the size of SMSD is distributed around 0.5 μm. Therefore, the distribution of the bright area surrounded by the white boxes in Fig. 6 may include the information of the SMSD. If we could use an x-ray with a size of about 1 x 1 μm^2, SMSD could be clearly seen in the FFT image. On the other hand, the few-micrometer sized domain could be clearly observed by the present CXD. This is due to the small number of domains in the 10 x 10 μm^2 illuminated area.

It is interesting to know the inside of the SMSD. Since a butterfly shaped diffuse scattering [9] is observed around the Bragg spot by the normal x-ray diffraction experiment, a polar cluster (Polar Nano Region: PNR [9]) may randomly exist in SMDS, which is smaller than thousands Å.

In summary, SMSDs are arranged without external field in PZN-9%PT like an engineered domain. The set of SMSDs forms larger domain with a few micrometers scale. Furthermore, the domain forms larger domain with hundreds micrometers scale. While, there might be a PNR in the SMSD. There are some scales of higher-order structures from sub-μm to sub-mm in PZN-9%PT. The phenomena may be generally seen at a PT concentration near MPB.

3.4 Nature of the X-phase

The present speckle measurement and related experiments show the existence of systematic arrangement of domains in each order in the PZN-9%PT crystal. Such a systematic arrangement of the domains will cancel out the rhombohedral strain and provide the pseudo-cubic cell. This is the reason why only the single peak is observed for the X-phase by the conventional x-ray and neutron diffractions. The scenario of the X-phase supposed in the introduction is supported by the present measurements.

4. CONCLUSIONS

We have succeeded in observing the 2D speckle pattern from the ferroelectric material PZN-9%PT by using the 10 x 10 μm^2 coherent x-ray. The 2D-FFT image of the speckle pattern gives us a spatial autocorrelation function which includes the information of the arrangement of the domains in the crystal within micrometers scale. By the complementary use of the optical microscope and SEM, we have concluded that there are some scales of higher-order structures (domains) from sub-μm to sub-mm in PZN-9%PT, i.e., a set of domains with a scale forms a higher order of domain. By taking into account these results, the nature of the X-phase is clearly understood. The systematic arrangement of the domains will cancel out the rhombohedral strain and provide the pseudo-cubic cell with a rhombohedral symmetry.

The present CXD technique is not the finally established technique for micro-domain observation. We used the thick wafer for this study. However, the situation loses the longitudinal coherence (about 0.7 μm for $\Delta E/E \sim 10^{-4}$). The thin wafer with micrometer thickness is needed to make the most of the longitudinal coherence. The driving device of the beam size is also required for the advanced measurement. It is shown that the easily detectable scale is the same order as that of the incident coherent beam.

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