Nondestructive visualization of inhomogeneous structure inside 40–500 nm single particles using Bragg coherent X-ray diffraction and phase retrieval analysis

Functional materials often have local inhomogeneities that arise in a macroscopically homogeneous structure and play a leading role in various functions. The nature of local inhomogeneities differs depending on the scale at which they occur. For example, impurities change the electrical conductivity by one order of magnitude at the atomic scale. At the *mesoscale* between atomic and macroscopic scales, i.e., over 1 nm but less than 1 μm atomic plane displacements, such as grain and domain boundary arrangements, significantly affect the dielectric and piezoelectric properties. The correlation between such functionalities and inhomogeneous structures is often better understood by visualizing the structures. Electron microscopy observation techniques have been well established for atomic-scale structures; for the mesoscale, however, visualization remained challenging because of the lack of methods. Visualization techniques in a nondestructive manner are essential to precisely capture the actual image of, for example, electric polarization domains, which are mesoscale structures that largely determine the dielectric constant of multilayer ceramic capacitors and the piezoelectric constant of actuators. This is because the domains originate from the electric polarization that spontaneously arises from head to tail of bound charge pairs at the surfaces and grain boundaries of ferroelectric crystals. Ferroelectric materials are primarily used as fine particles of about 100–500 nm in size and ceramics of about 500 nm in size made from these particles. These crystalline sizes are in the mesoscale. Hence, in a nondestructive visualization method for mesoscale structures was long awaited in order to elucidate ferroelectric's functional mechanisms and help material design.

We reconstructed the real-space images of inhomogeneous mesoscale structures inside fine particles in the 40–500 nm range [1]. Figure 1 shows the cross-sectional images of the atomic plane displacements for the following fine particles: 40-nm-sized Pd and 200-, 300-, and 500-nm-sized $BaTiO_3$ (BTO). The color map represents the degree of displacement of the atomic planes. Whereas the structural inhomogeneity of the metallic Pd was small, about π/6, that of the ferroelectric BTO tended to be significant, about π. The visualization of the non-averaged structures for these single particles in the wide size range was made possible by Bragg coherent X-ray diffraction imaging (Bragg-CDI), to which we applied the improvements of a high signal-to-noise ratio and convergence of analysis [1]. Bragg-CDI is a lensless imaging technique consisting of coherent X-ray diffraction and computer-aided image reconstruction. Since this imaging method was proposed [2], it has attracted much attention as a method of observing inhomogeneous structures inside fine crystalline particles and has been further developed at various synchrotron radiation facilities. In Japan, only National Institutes for Quantum Science and Technology has worked on the Bragg-CDI technique [3] and shared it at SPring-8 **BL22XU**, which is now equipped with an undulator source and a Bragg-CDI system.

Below, we describe the present Bragg-CDI system in BL22XU and how to apply Bragg-CDI to samples. Coherent X-ray diffraction (Fig. 2(a)): The three-dimensional (3D) intensity data of Bragg diffraction are recorded using coherent X-rays as a probe. Coherent X-rays in the hard X-ray range focused down to a μm order fully illuminate an isolated crystalline particle in a powder sample. A two-dimensional detector positioned where the camera length and angle satisfy oversampling and Bragg conditions, respectively, records the scattered X-rays from the particle while scanning the ω angle of the sample so that the Ewald sphere goes across one Bragg spot. The recorded scattering pattern consists of an intense spot (yellow in Fig. 2(a)) and faint fringes (light blue in Fig. 2(a)); such a pattern is called a speckle. A speckle pattern contains information on the particle size and mesoscale non-averaged structure; however, such information cannot be directly extracted from the speckle intensity because the phase of the structural factor has been lost.

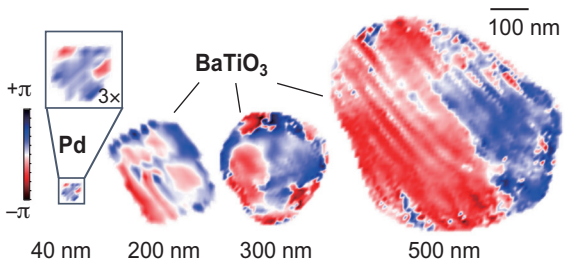


Fig. 1. Color map of atomic plane displacement for a series of samples: 40-nm-sized Pd, and 200-, 300-, and 500-nm-sized BTO. The figure was drawn using VESTA 3 [5].

Phase retrieval analysis (Fig. 2(b)): To reconstruct the real image, one uses Fourier iterative phase retrieval algorithms of hybrid input–output (HIO) and error reduction (ER). Both algorithms have two constraints: speckle intensity data in reciprocal space and support in real space. While the series of HIO–ER is repeated several hundreds of times until the structural factor satisfies the constraints, the support is updated several times by fitting to the reconstructed image in progress; this is called the shrink-wrap (SW) algorithm and increases the oversampling ratio and consequently refines the phase. The image reconstruction in the 40–500-nm-size range, which electron beams and visible light could not achieve, has thus been performed [1].

The advanced Bragg-CDI technique not only reveals the inhomogeneity of structures but also provides more clues to reveal its origin. Recently, the paraelectric (PE) – ferroelectric (FE) phase transition and dislocation at the PE phase for a BTO single particle have been successfully observed with coherent X-ray diffraction and Bragg-CDI, respectively, where a micro-electromechanical system (MEMS) heater chip was used [4]. MEMS devices are easily installed in Bragg-CDI systems because a geometrical change for Bragg-CDI is no more than about 3°, which is 1/100th more minor than that of other imaging techniques e.g., 180° of computer tomography. As shown in Fig. 3(a), the speckle from the BTO splits from 200 reflections (PE phase) to the pair of 200–002 reflections (FE phase) at ~400 K, which corresponds to T_C. The reconstructed 3D image (Fig. 3(b)) exhibits an outer shape with a many-curved surface. The 2D image (Fig. 3(c)) is the cross-section of the 3D image cut by the blue plane, showing an uneven electron density. Focusing on the high crystallinity region surrounded by the dashed line, the phase showed a steep gradient, indicating a dislocation perpendicular to the direction of the black arrow (Fig. 3(d)). Bragg-CDI can thus be used in combination with MEMS devices and other measurement techniques; consequently, one can identify domains and dislocations.

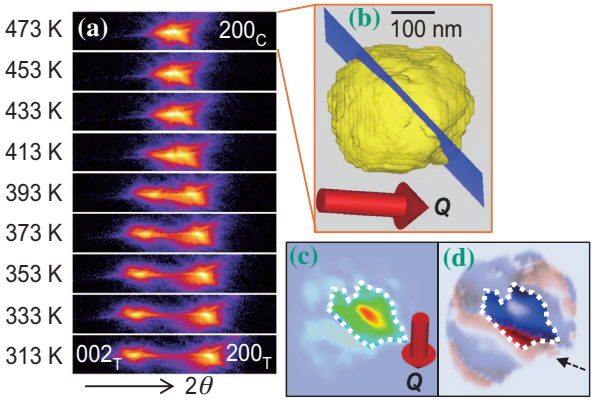
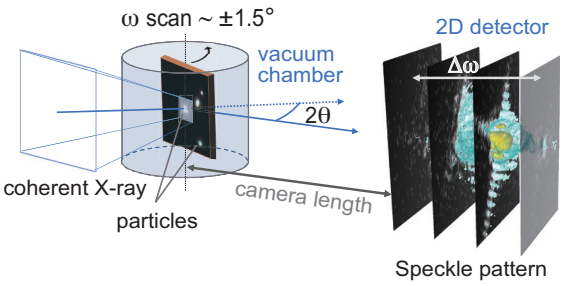


Fig. 3. **(a)** 3D image obtained by applying Bragg-CDI to the speckle at 473 K. **(b)** The cross-sectional view cut by the blue plane in the 3D image. **(c)** Electron density. **(d)** Phase image. The figures were drawn using VESTA 3 [5].

(a) Coherent X-ray diffraction



(b) Phase retrieval analysis

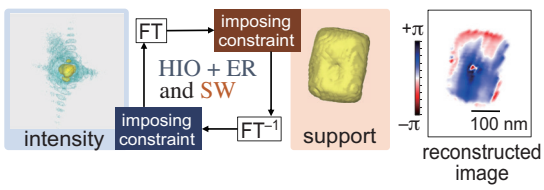


Fig. 2. Schematic diagram of the present Bragg-CDI system. **(a)** Coherent X-ray diffraction. **(b)** Phase retrieval analysis. Part of the figures was drawn using VESTA 3 [5].

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