X-Ray Diffractometry for the Structure Determination of a Submicrometer-Scale Single Powder Grain

So far, the structure identification and characterization of various new materials have been carried out by powder diffraction experiments since newly synthesized materials are obtained in powder and/or in polycrystalline forms in most cases. This research technical trend is accelerated by the high-photon flux monochromatic X-rays of synchrotron radiation (SR) in addition to the progress of computers and software for structure determination. Consequently, the development of an *ab initio* structure analysis technique, which denotes unknown structure determination, is now one of the most topical research subjects in powder crystallography. On the other hand, an X-ray SR beam with high brilliance and small divergence allows us to suggest an alternative method by which we can determine the crystal structure of a micrometer- or submicrometer-scale single crystal corresponding to a single grain of powder sample. In fact, some structure determinations of a few micrometer-sized single crystals have recently been reported using an SR focusing technique [1].

However, the structure determination of a submicrometer-scale single crystal has not been carried out yet. This is mainly caused by three technical difficulties that need to be overcome: the accurate intensity data collection of very weak diffraction spots, the precise centering of the invisible sample and the infallible manipulation of a submicron-scale single crystal. The combination of the SR focusing technique and the precise-axis control of the diffractometer is one of the solutions for the first and second difficulties. The latest focusing technique for an SR diffraction experiment can firmly produce the micrometer-scale high-flux SR beam. The precise-axis control enables to move and keep the submicrometer-scale sample within the micrometer-scale focused SR beam. We have therefore developed and optimized a high-precision diffractometer, which combined an SR focusing technique and a low eccentric sample rotation at the undulator beamline **BL40XU**, to enable the structure analysis of a submicrometer-scale single powder grain [2]. As for the third difficulty, since the development of systematic manipulation techniques to select and capture one single grain of powder sample is still in progress, several submicrometer-scale single powder grains have been presently attached to a fine glass fiber by the conventional sample manipulation technique.

We designed the phase zone plate for the structure analysis of a submicrometer-scale single powder grain. The diameter and focal length of the phase zone plate are 100 μm and 300 mm for the 15 keV SR beam, respectively.

The schematic diagram of the developed system and the experimental setup around the phase zone plate focusing system are shown in Fig. 1. The beam size and photon flux density at the focal position (= sample position) were 1.4×2.9 μm^2 (vertical × horizontal) and 3.1×10^9 photons/sec/μm^2,

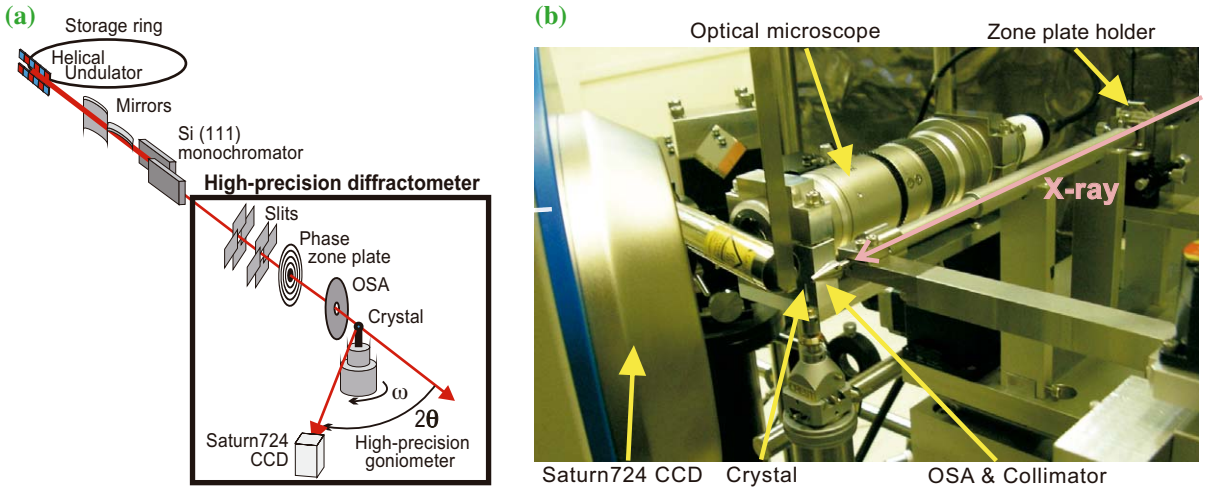

Fig. 1. **(a)** Schematic of the experimental setup. **(b)** Experimental setup around the phase zone plate focusing system.

respectively. The corresponding gain factor, therefore, is nearly 400.

Structure analysis was performed for the submicron-scale $BaTiO_3$ single powder grain. The grains of $BaTiO_3$ were attached to the tip of a fine glass fiber with epoxy adhesive using an optical microscope and a micromanipulator. Figures 2(a) and 2(b) show the optical microscope and SEM images of the tip of a fine glass fiber, respectively. Several $BaTiO_3$ grains were attached to the glass fiber. The maximum grain size was about 600 × 600 × 300 nm^3.

The diffraction data were collected using the ω-oscillation mode at room temperature. The exposure time and the ω-axis scan step, Δω, were 15 s and 1°, respectively. With this setup, the 360 diffraction images were collected in 180 min. The overlapped diffraction pattern of the 360 images is shown in Fig. 2(c). The accidentally diffracted spots of the other $BaTiO_3$ grains sometimes interfered with the diffraction pattern during ω-oscillation. These extra spots can be discriminated systematically, because the diffraction pattern no longer shows the Debye-Scherrer pattern but the superposition of several single-crystal diffraction patterns. At present, however, it is very difficult to directly identify the sample grain corresponding to the diffraction spots among several sample grains (Fig. 2(b)). The solved crystal structure is shown in Fig. 2(c). Only the thermal vibration of the Barium atoms was refined anisotropically. The reliability factor of the refinement finally became R_1 = 5.24%.

The crystal structure of a submicron-scale $BaTiO_3$ single powder grain was successfully determined with several single powder grains. This success proves that the diffraction measurement of a single powder grain has a sufficient advantage in the determination of an unknown crystal structure for any powder-formed crystalline sample.

We have also developed a laser-pump and SR-probe diffraction technique using the same diffractometer system. Now, we are ready to apply the structure analysis of a single powder grain for the research of the photo-induced phase transition combined with the pump and probe technique [3-5].

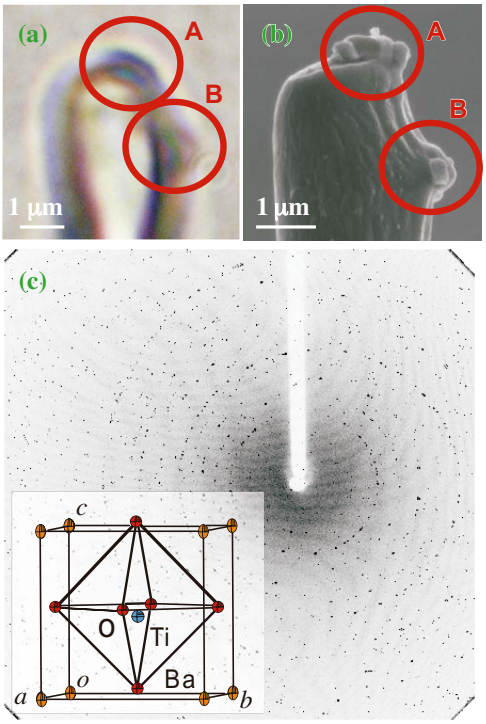

Fig. 2. Photographs of $BaTiO_3$ powder grains attached to the tip of a fine glass fiber: **(a)** optical microscope image. **(b)** SEM image of the same sample. The size of the large grain is about 600 × 600 × 300 nm^3. A and B in each figure indicate the positions of existing $BaTiO_3$ grains. **(c)** Measured diffraction image of $BaTiO_3$ grains. All the measured images are overlapped on one image to show the Bragg diffraction spots clearly.

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