BL04B2
(High Energy X-ray Diffraction)

1. Abstract

BL04B2 is used in structural studies for disordered materials by pair distribution function (PDF) analysis. PDF analysis using high-energy X-ray diffraction is useful to quantitatively determine the local structure of disordered materials at low scattering angles with a wide *Q* range. BL04B2 is equipped with two Si crystals as a monochromator, providing fixed-energy X-rays of 37.7 keV from Si(111), 61.4 keV from Si(220), and 113.1 keV from Si(333) (third-harmonic generation). The energy at 61.4 keV is mainly used in the PDF analysis. One measurement for PDF analysis at 61.4 keV takes a minimum of 2–3 hours due to the necessity of scanning a point detector with an energy window such as a CdTe- or a Ge-SSDs to eliminate the higher harmonic contamination of X-rays. On the other hand, in FY2017, we developed a new apparatus using a two-dimensional (2D) amorphous silicon (a-Si) digital X-ray flat-panel detector (FPD) to realize the time-resolved PDF analysis at SPring-8.

In FY2018, two improvements were made at BL04B2: (1) the cooling system for a large 2D detector was upgraded to reduce dark noise, and (2) a new sample environment was realized using a microwave reactor. Here, we describe these enhancements.

1. Improvement of the cooling system for a large 2D detector to reduce dark noise

The dedicated setup on beamline BL04B2, in which a large 2D flat-panel detector is used for time-resolved PDF analysis, can collect suitable PDF data in a few seconds [1]. The commissioning of the setup started in December 2017. In FY2018, the related measurements are increasing and occupied about 15% in the user time at both BL04B2 and BL08W beamlines. In addition, we developed *PIXIA* software for data conversion from 2D images into one-dimensional PDF data in collaboration with Dr. Tominaka of NIMS (*PIXIA* software was written in Python and used the *SciPy* and *NumPy* packages, which deal with all the mathematical treatments in a matrix calculation). Because time-resolved PDF measurements provide thousands of 2D diffraction images, rapid and accurate processing of this huge quantity of information is necessary to extract information about structural changes.

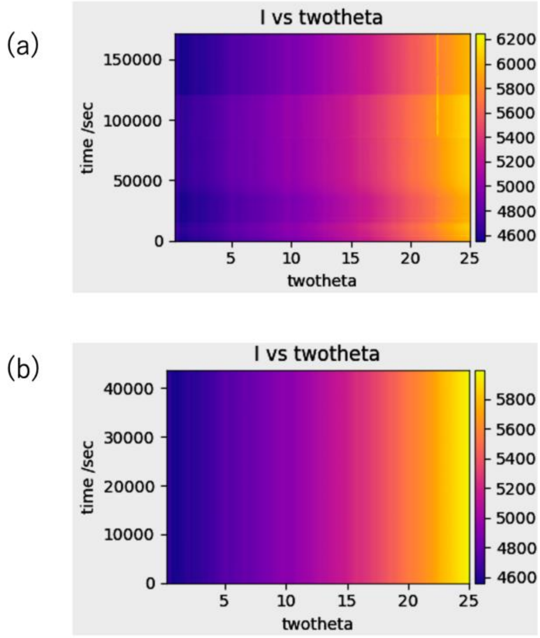

Fig. 1. (a) Time dependence of the background on the flat-panel detector before and (b) after setting the cooling system at BL04B2.

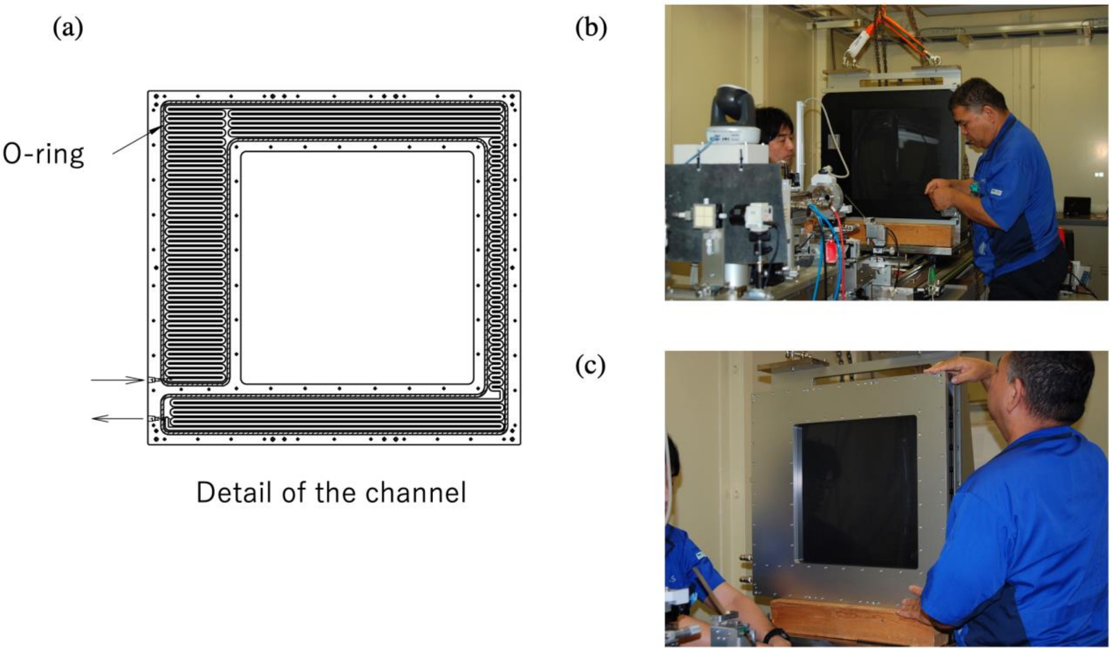

Fig. 2. (a) Detail of channels in the cooling system for FPD. (b) Before and (c) after setting for the cooling system by flowing water through the channel at BL04B2.

After realizing rapid and accurate processing of a huge amount of data using *PIXIA* software, we set to tackle the dark noise of the 2D detector in the time-resolved PDF analysis. Figure 1(a) shows the time dependence of the background on the 2D detector before working the cooling system. We initially collected the dark noise data for 10,000 s without cooling. Then the detector was cooled by a fan after 10,000 s. Turning on the fan initially decreases the dark noise, but it gradually increases due to the fever of the 2D detector around 40,000 s. The increase is almost equal to the scattering intensity from disordered materials. Therefore, it is necessary to completely remove the heat for the 2D detector.

Figure 2 shows a cooling system for the FPD. Cooling is attempted by flowing water through a channel. Figure 1(b) shows the resultant background reduction. We confirmed that the dark noise is a constant regardless of whether the detector and/or the fan are working. The improved cooling system prevents the instability of the dark noise from the heat by the FPD itself.

3. New sample environment using a microwave reactor

The dedicated setup used for time-resolved PDF analysis is compatible with existing instruments for different sample environments such as an aerodynamic levitation furnace, acoustic levitation furnace, or diamond anvil cell. In addition, we installed a microwave heating system using a Biotage Initiator microwave reactor in FY2018. The microwave reactor realized solvothermal and hydrothermal conditions in a temperature range from room temperature to 573 K at a pressure of less than 20 bar (1 bar = 0.1 MPa). To observe structural changes in disordered materials for the chemical condition in real time, we modified the reactor by forming holes in the metallic compartment and removing the Teflon inner walls to allow X-rays to pass through the glass vial with the minimum background intensity associated with the reactor.

Figure 3 shows the time-dependence PDF analysis under hydrothermal conditions in a lepidocrocite-type layered titanate from the precursor solution [2]. Tominaka and coworkers confirmed using time-resolved PDF analysis that the formation of the lepidocrocite-like prestructure is key to form the layered titanate under hydrothermal conditions. Hence, it is now possible to observe structural changes in disordered materials, which were previously unknown. We expect that additional improvements will contribute to direct observations of structural changes in disordered materials at SPring-8.

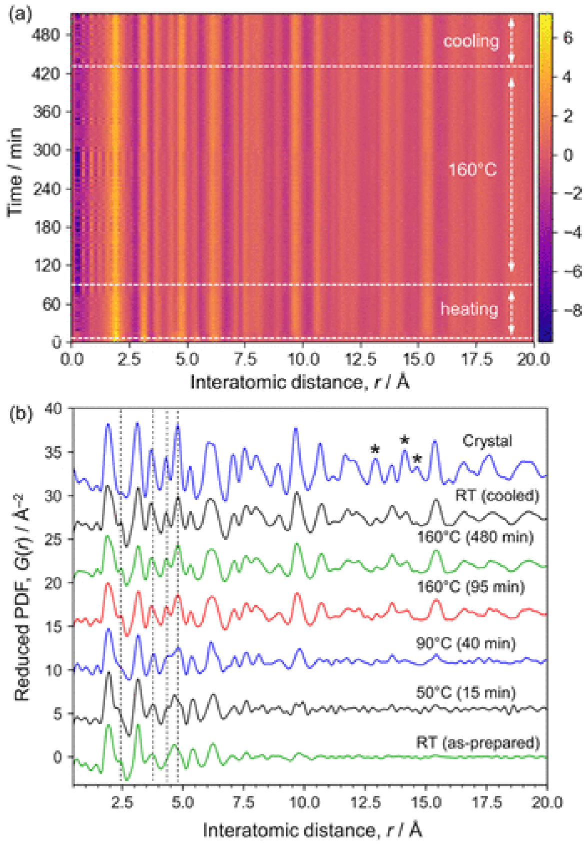

Fig. 3. Time dependence of the PDF data. (a) Two-dimensional plot of time dependence *in situ* PDFs. (b) Selected one-dimensional plots shown with the *ex situ* PDF for the crystalline product [2].

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References:

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[2] S. Tominaka et al., *ACS Omega* **3**, 8874-8881 (2018).