High-Resolution Powder X-ray Diffraction

Structure and structural transformation are two major topics that involve both attractive and fundamental issues for scientists; they have widespread scientific interest in chemistry, physics, materials science, geoscience, biological and pharmaceutical sciences and industrial applications. The efficient way to obtain a molecular structure normally is by means of X-ray diffraction of a single crystal, but powder diffraction is an alternative approach, for which both the experiment and the preparation of samples are easier. The structure in a non-ambient state might provide direct evidence of molecular motions that correlate with corresponding physical or chemical properties. A proposed dedicated high-resolution powder X-ray diffraction beamline at Taiwan Photon Source (TPS) will be able to offer a rapid data acquisition rate and great angular resolution data.

There are currently several powder-diffraction beamlines and stations in NSRRC, including **TLS 01C2**, **TLS 17A**, **SP 12B2**. These three powder-diffraction stations provide varied ranges of energy as an X-ray source that can serve various scientific projects. The detection systems are an image plate or a charge-coupled device. In phase I of TPS, the powder-diffraction station is located temporarily at **TPS 09A**. A large concentric three-circle diffractometer (**Fig. 1**) equipped with a rapid position-sensitive detector (MYTHEN 24K) and a multi-crystal analyzer system were installed and used for structural characterization and dynamics respectively. During the commissioning period, the most important issue is to integrate a diffractometer with a MYTHEN 24K detector. This detector requires calibrations and corrections of three kinds – angle calibration, intensity correction and off-set calibration. To calibrate the angle, we first collect a series of powder patterns of Si standard to obtain the function of the rotation angles and pixel numbers. For intensity correction, also called flat-field correction, the sensitivity of every pixel is slightly affected by the energy of the radiation. To solve the problem, we must have a correction every 500 eV to improve the response. To obtain a scaling coefficient we can use an attenuated direct beam or a selected diffraction beam to which every pixel is exposed. So far, because of a housing problem of that detector, we cannot perform a detailed measurement. An alternative solution is to simulate an appropriate scaling coefficient using default sensitivity files for varied radiation sources (Ag, Mo, Cu, Cr radiation). For off-center calibration, as the center of the detector is not perfectly the same with the rotation angle on the diffractometer, we must calibrate the off-set effect. The solution is to use software to offset the sample position to the center of the detector. The final cell parameter of NIST standard material 660c, LaB_6, is 4.1568232(4) Å, which is near the result in a NIST report, 4.156826(8) Å. The structure is easily to be solved with a direct method using EXPO 2014 program. In 2016 Q3, powder diffraction opened for user operation; there was 50% user beamtime for powder X-ray diffraction at **TPS 09A**, which served about 20 user groups.

In terms of the performance of the X-ray diffraction instrument, the diffraction pattern measured for a

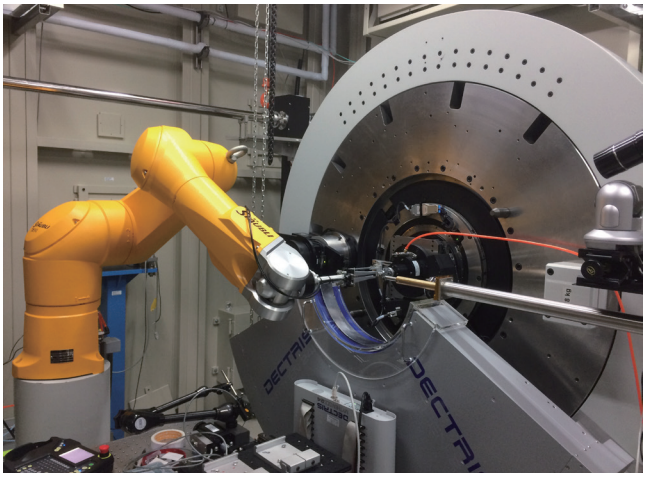

Fig. 1: Schematic of the three-circle powder diffractometer with a detector (MYTHEN 24K), a multi-crystal analyzer system and a robot system.

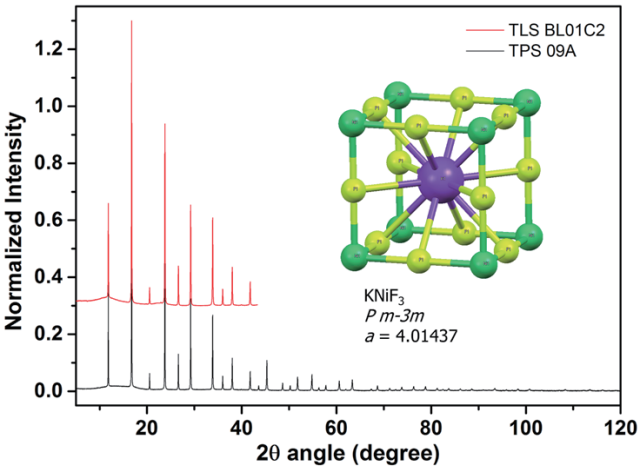

Fig. 2: X-ray diffraction patterns of $KNiF_3$ measured at **TLS 01C2** (MAR345 IP) and **TPS 09A** (MYTHEN 24K); the inset shows a crystal model of $KNiF_3$.

$KNiF_3$ powder with X-rays (15.0 keV) demonstrates the high- quality data (rapid, wide *Q*-range and small background) that can be recorded. The PXRD pattern was obtained using a MYTHEN 24K detector of radius 761.5 mm of curvature, in an exposure of typical duration 30 s. For comparison, the XRD pattern for the same sample measured with an imaging plate and exposure duration 120 s and 108 s for readout at **TLS 01C2** is shown in **Fig. 2**. The MYTHEN 24K detector obviously provides superior data, not only the collection speed but also the ratio of signal to noise, data range and peak resolution. For peak resolution, **Fig. 3** presents a high-resolution powder diffraction pattern of a quartz sample collected with 15-keV X-rays and the same set-up as for the preceding sample. The packed fingerprint pattern of (122), (203) and (031) signals of the quartz sample are well resolved from the wide-*Q*-range XRD pattern. Several projects benefiting from the advantages of the high-resolution and non-ambient sample environments are currently under way, including measurement of Li-ion battery electrodes in situ during charging and discharging cycles, measurements at high (up to 1000 °C) and low temperature (100 K with a LN_2 cryostream, 10 K with a cryostat) and a gas-loading experiment.

The intrinsic problem in powder diffraction is overlapping of diffraction signals. To improve the refinement and accurate structure determination, a multi-crystal analyzer was designed and commissioned. Our design used nine Si(111) crystals in which every crystal is 2° apart from any other.[1] In data shown in **Fig. 4**, the recording was taken from 5° to 50° with step 0.005°. The total duration of measurement was 12.5 h. The maximum angular resolution is about 0.007°, but we are still optimizing the multi-crystal analyzer system. Comparing the peak resolution at the present detector system at various endstations, the maximum resolution from the image-plate detector (MAR345) is about 0.08-0.1°. The MYTHEN 24 K detectors has a small pixel size, a large dynamic range and a rapid readout. The eventual maximum resolution from the NIST 660c standard (LaB_6, capillary 0.2 mm) is 0.015°. The ultra-high resolution from the Si(111) crystal analyzer is 0.007°. A convenient system for data collection and processing is in development. The output data from a MYTHEN 24K detector and a multi-crystal analyzer will be normalized, merged and gridded automatically. An automatic robotic sample changer will also be installed to increase beamline performance.

A dedicated high-resolution powder X-ray diffraction beamline, **TPS 19A**, has been under planning. The previous optics and endstation design and conceptual design report had been reviewed by Science Advisory Committee (SAC) members and synchrotron powder-diffraction experts. The procurement will begin in early 2018; the beamline components will be installed and commissioned in 2019. Once the beamline is complete, the endstation will be moved from **TPS 09A** to **TPS 19A**. Our goal of **TPS 19A** is to have it open for user operation in 2020 Q2. (Reported by Yu-Chun Chuang)

| Reference |

1. J. L. Hodeau, P. Bordet, M. Anne, A. Prat, A. N. Fitch, E. Dooryhe, G. Vaughan, and A. Freund, Proc. SPIE **3448**, 353 (1998).

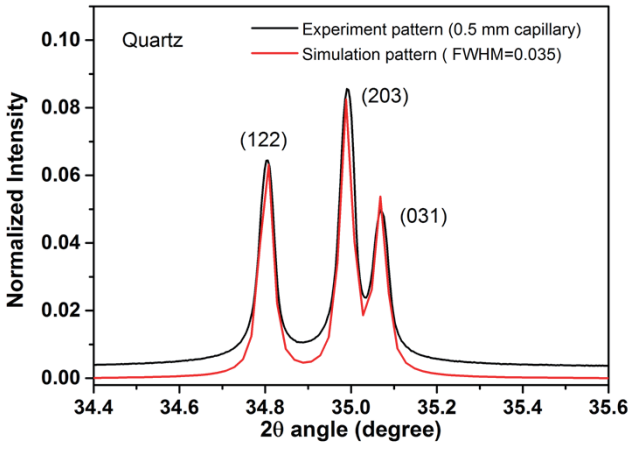

Fig. 3: Powder diffraction pattern for a quartz sample; the inset shows an expanded view of the well resolved fingerprint pattern (122), (203) and (031) of quartz.

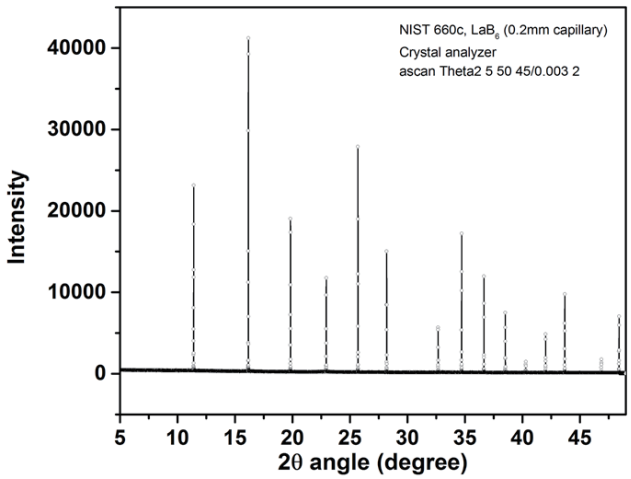

Fig. 4: Powder-diffraction pattern for NIST standard material LaB_6 (660c) measured with a crystal analyzer.