High Resolution Powder X-ray Diffraction

Structural characterization is a principle way to understand the correlation between molecular structure and physical properties. To investigate the crystal structure in non-ambient sample environments, structure determination/refinement from high-resolution powder diffraction has been developed for several years and become more and more mature. A dedicated high-resolution powder X-ray diffraction beamline, **TPS 19A**, was designed not only for studying static structure but also structure dynamics. To fit the purpose, **TPS 19A** was designed to have a high flux X-ray source and high efficiency data acquisition system. Moreover, to reduce the absorption problem caused from Debye-Scheerer geometry, a higher X-ray energy source was taken into consideration. For static structure determination, a new fine-tunable mechanism design for a multi-crystal analyzer was included. This will make alignment of the analyzer crystals more reliable and precise. Three multi-crystal analyzer stages including twenty-seven crystals were installed, the offsets and channel efficiencies were calibrated using a LaB_6 standard material. The design value of peak resolution was ca. 0.005 degree, which is beneficial to obtain accurate diffraction intensity of individual reflection. For structure dynamics, the MYTHEN 24K detector provides fast data acquisition during in-situ experiment. A new refinement strategy, sequential Rietveld refinement, was also introduced.

The source of **TPS 19A** is a 2.0-m long undulator called CU15. Compared with our standard undulator IU 22, CU15 has a shorter magnet period that will benefit the throughput of X-ray powder diffraction at high energy.

Fig. 1: TPS CPMU, CU15.

A PrFeB-based cryogenic permanent magnet undulator (CPMU) with a 15 mm period length has been constructed for TPS Phase-II beamlines to become one of the standard undulators. The minimum magnetic gap is 4 mm to achieve an effective K value of 1.81. The main characteristics of the TPS CU15 are shown in **Table 1**. Compared to a standard undulator (like the in-vacuum undulator with period length of 22 mm at TPS), an increased SR brilliance can be expected at photon energies above 10 keV. Among the main features of the CU15 are the use of (1) a new grade PrFeB permanent magnet material (PM) with high remnant fields; (2) a mechanical frame with force-compensating spring modules; (3) a temperature control system on the permanent magnets; (4) a cryo-cooler to compensate for diverse sources of heat loads (5) compatibility with vacuum regulations of storage rings. **Figure 1** shows the overall structure of the TPS-CPMU.

Table 1: Main characteristics of the TPS CPMU, CU15

Items	Unit	Cryogenic Temperature	Room Temperature
Magnet material		$Pr_2Fe_{14}B$ (NMX-68CU)	
Period	mm	15	
Min. magnetic gap (G_{mag})	mm	4.00	
Effective magnetic field	Tesla	1.30	1.13
Deflection parameter		1.81	1.58
Magnetic force	kN	31.8	23.0
Number of periods		133	
Total cooler capacity	Watt	400	
Operating temperature	K	80	300

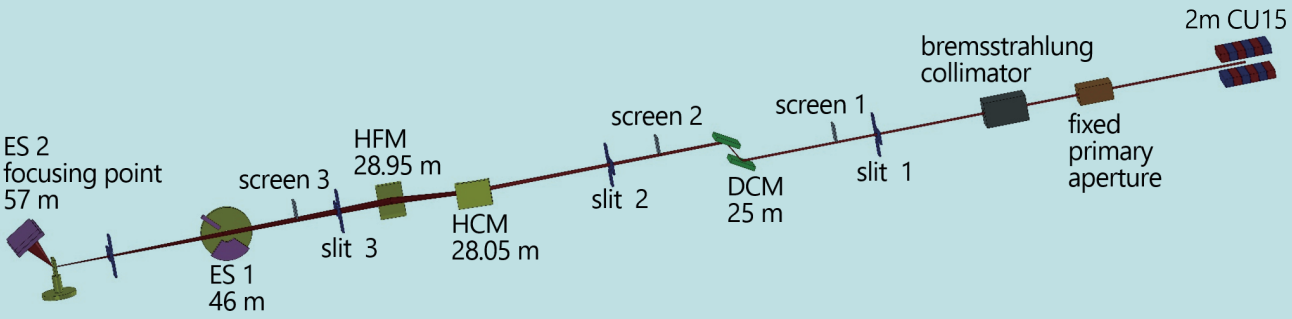

Fig. 2: Beamline layout of **TPS 19A** High Resolution Powder X-ray Diffraction.

The performance of CPMU has been demonstrated that when the temperature of the PMs are set to about 77 K, an effective field of 1.32 Tesla was measured at a gap of 4 mm. A temperature control system is used to reduce gap errors and temperature variations along the magnet arrays and the PMs are within ±0.4 K. The cooling performance of the CU15 has been demonstrated with two cryo-coolers. The lowest temperature is 60 K that provides a sufficient cooling margin for the CU15 at 80 K.

The main optics composes of a cryo-cooled double crystal monochromator(DCM) and a pair of horizontal focusing mirrors. Because the instrumental equipment including diffractometer, detectors and robots requires large space, the optics is laid out as compact as possible and we try best to reserve a cozy environment for experimental hutch. The total length of beamline is 57 m. The optical hutch is limited to 33 m. The beamline layout is shown in **Fig. 2**.

High resolution powder X-ray diffraction requires a low divergent beam with a small energy bandwidth. In a conventional design, a collimating mirror placed prior to DCM and used to reduce the input beam divergence. However, TPS is a low emittance storage ring. Its vertical divergence reaches the diffraction limit. Any optics will deteriorate the beam divergence due to its manufacturing defects. Thus, the collimating mirror is omitted in our design. Considering the limited space in upstream fan at the beamline, the DCM is plated at 25 m from the source. Considering the working energy range and mechanical feasibility, two switchable crystal sets are installed in the DCM. One is Si(111) and the other is Si(311). In order to optimized the energy bandwidth, a cryo-cooled system is applied to minimize the thermal deformations of the crystals.

After the DCM, a pair of horizontal focusing mirrors (HCM, HFM) are utilized to condition the beam size for the capillaries at the sample position of 46 m. The pair of mirrors is composed of two identical cylindrical mirrors. Their curvature is 22.44 km with a slope error better than 0.5 μrad. According to optical simulations, the two mirrors should be placed at 28.05 m and 28.95 m respectively to produce a spot of 390 μm × 422 μm (H × V) at the sample position. In principle, the contribution of mirror's defects to beam divergence equals the slope error/aberrations multiplied by $\sin(\theta_g)$ in the sagittal direction. For hard X-ray, the grazing angle of θ_g is a small value of few mini-radians. Based on the above principle, the two mirrors are placed horizontally and face-to-face. Therefore, the deterioration of vertical beam divergence can be minimized. Considering the photon flux, the working

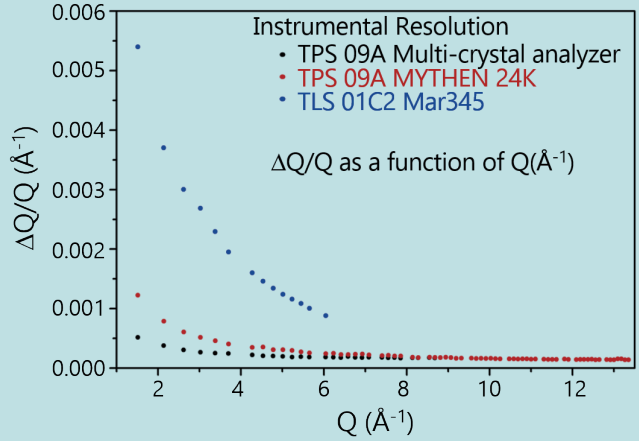

Fig. 3: The instrument resolution function of multi-crystal analyser, MYTHEN 24K and 2D area detector.

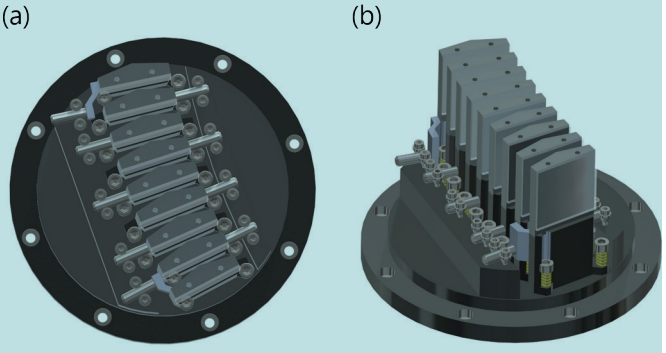

Fig. 4: Fine-tunable multi-crystal analyser stage: (a) top view and (b) side view.

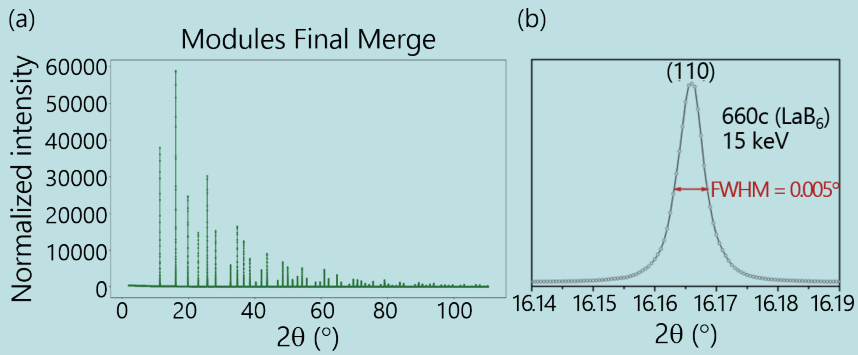

Fig. 5: (a) Powder diffraction pattern for NIST standard material LaB_6 (660c) measured with multi-crystal analyser; (b) peak resolution of (110) reflection.

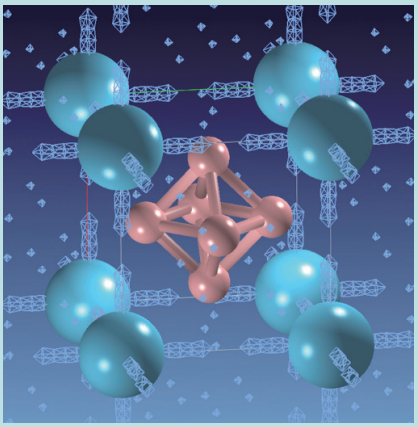

Fig. 6: Difference Fourier map of LaB_6, blue ball = La; brown ball = B.

energy and realistic mirror length, the grazing angle of the mirror is set at 2.5 mrad. Additionally, both mirrors have three reflection coatings, Pt, Rh and Si, to minimize high harmonics contamination. From optical simulations, the expected flux is 2.98×10^{12} photons/s with energy bandwidth of 2.34 eV at 30 keV when the above optical parameters are taken into account.

In the endstation, three different detection systems will be installed at **TPS 19A**: (1) multi-crystal analyzer (MCA); (2) 1D position sensitive detector, MYTHEN 24K; (3) 2D area detector. The full peak at half maximum (FWHM) of LaB_6 standard from MCA, MYTHEN 24K, 2D area detector are 0.005, 0.02 and 0.06 degree respectively using 15 keV and 0.2 mm capillary. The instrument resolution function is shown in **Fig. 3.** Obviously, MCA has the best resolution. However, MYTHEN 24K can also provide great data quality within minutes. Although the resolution of the area detector is not as good as others, but when anisotropic information from materials like thin film or fiber diffraction, is needed it will be a great tool. For unknown or electron density study, MCA is undoubtedly the best choice. However, in most of the global powder diffraction beamlines, to simplify the design of the MCA no alignment mechanism for the crystals is provided. We try to introduce a fine-tunable mechanism to make the alignment of every crystal more precise and faster, as shown in **Fig. 4**. The final powder pattern of the standard material LaB_6 is shown in **Fig. 5**. An extremely narrow peak width, high S/N ratio and low background data was obtained. The d-spacing resolution is up to 0.5 Å, after detail structure analysis, a difference Fourier map shows clear bonding density distribution. It proves the high quality data required not only for structure determination but also electron density distribution studies. (Reported by Yu-Chun Chuang, Chi-Yi Huang, and Jui-Che Huang)

Soft X-ray Tomography at TPS

Soft X-ray tomography (SXT) is constructed at **TPS 24A**, which is an emerging technique to image an ultrastructure of 3D frozen-hydrated cells and tissue. Particularly, SXT images present a natural contrast of individual organelles inside the cells in a nearly native state without the need of staining and sectioning. This technique can visualize an entire 3D cell, which makes some bio-medical studies possible and sometimes easy, such as the cellular reaction with antifungal peptoids,[1] immune T cells communication with bacteria,[2] degranulation of granule-containing vesicles in mast cell,[3] and virus-induced endoplasmic reticulum alterations.[4] In addition, SXT can be correlated with fluorescence 3D-structured illumination microscopy (3D-SIM) to provide the bio-sample with structural and functional information.

SXT beamline is a transmission full-fill microscopy, it covers the energy range of 260–2,600 eV at the Taiwan Photon Source (TPS) and is shown in **Fig. 1**. The photon beam from bending magnet source is collected by a pair of Kirkpatrick-Baez (KB) mirror and a refocusing vertical mirror. The beam is focused to the exit slit position, or secondary source position. This is the source for a condenser in microscopy. The optic of the plane-grating