

Beamline Practice at BL02B2 (Powder diffraction)

Rietveld Refinement using Synchrotron X-ray Powder Diffraction Data

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1. Introduction

The bending magnet beamline BL02B2, which is designed to tune in the x-ray energy range from 12 to 35 keV, is dedicated for the research on accurate structure analysis by powder specimens in the area of materials science. X-ray powder diffraction tell us various information about details of materials, even if during operation. The advantages using synchrotron radiation are mainly mentioned as follows.

- Collect rapidly high angular resolution high counting statistics diffraction data.
- Avoid or exploit absorption edges.
- Small amount of powder specimen (tenths of a milligram).
- High polarized x-ray makes data interpretation relatively straightforward.

We plan to lecture and practice about data collection of powder diffraction (Si, CeO₂, and Al₂O₃) and structure analysis using Rietveld method. In this beamline practice, you try to operate the beamline instruments and perform structure analysis as follows: 1) sample preparation, 2) mounting sample and position alignment on goniometer, 3) Imaging Plate (IP) set in the Debye-Scherrer camera, 4) data collection, 5) data readout of IP, 6) data reduction, 7) whole pattern fitting by LeBail technique, 8) Rietveld refinement. Goal of the practice is to determine lattice parameters, crystal structure and isotropic atomic displacement parameter.

2. Plan of Practice

9:30 (Lecture) Introduction of beamline, alignment of optics, measurement system and major scientific activities at BL02B2/SPring-8.

10:30 (Lecture and Practice) Alignment of the x-ray optics.

11:30 (Lecture and Practice) Sample preparation for Debye-Scherrer method.

12:30 -----Lunch-----

13:30 (Lecture) Introduction of synchrotron powder diffraction experiment.

14:00 (Practice) Measurement of synchrotron powder diffraction.

15:30 (Lecture and Practice) structural analysis based on Rietveld method using JANA2006 software.

17:30 Close.

3. X-ray optics and experimental hutch

Figure 1 shows schematic layout and photographs collimation mirror and double-crystal

monochromator (DMC) in optical hutch of BL02B2 [1]. The beamline optical hutch contains mirror and DMC to tune monochromatic X-ray of energy needed for experiment.

The beamline utilizes a Pt, Ni-coated flat Si mirror to intercepts a photon beam of 1.8mm (V) \times 1.0 mm (H) at a distance of 45 m from a source point. The mirror vertically focuses the beam and for this it dynamically bent by the mirror holder. To accept photon beam with a glancing angle of 2 mrad the mirror is long (about 1 m) and a well polished. The bending radius R_m is adjustable, to focus the beam in the vertical direction. In addition to the bending, the holder provides each end of the mirror with independent horizontal and vertical translations necessary to align the photon beam. Cut-off energy is varied by horizontal translating the mirror perpendicular to the beam axis that the beam will hits either Pt/Si-, Ni/Si-, or non-coated Si surface. The functional diapasons are Si ($y = 0$ mm) 12.4-15.5 keV ($\lambda = 0.8$ -1.0 Å); Ni ($y = 10$ mm) 15.5-28.2 keV ($\lambda = 0.440$ - 0.8 Å) and Pt (-10 mm) 28.3-35.0 keV ($\lambda=0.354$ -0.439 Å). The mirror uses to reject of higher harmonics of the incident beam and within energy area functional is the material (Si or Ni or Pr) with high and non-edge reflectivity. A double-crystal monochromator (DCM) of two Si(111) crystals with a fixed-exit beam geometry provides monochromatic photons. The monochromator is built on goniometer with the surface of the first crystal in the center of rotation. The second crystal can be moved parallel and perpendicular to the crystal surface in order to realize a fixed beam offset during an energy scan. It reduces the motion of the beam position at sample position at 57.5 m. For a given energy range of 12-35 keV, the first crystals rotate within angle range of 9.48° - 3.24° . The photon flux at the sample position is estimated to be about 10^{11} (photons/s) for 25 keV X- rays. For a monochromatic X-ray beamline, a γ -rays stopper is placed downstream the monochromator to stop the γ -rays with direct SR beam. After DCM, the monochromatic beam positioned higher than the direct beam and it passes through a rectangular tube surrounded by the Pb (lead) block.

The large Debye-Scherrer camera with two-axis (ω , 2θ) goniometer having motor-driven x and z stages is equipped in second (experimental) hutch (Figure 2). The station has been designed such that it is capable of accommodating a wide variety of experiments, particularly those utilizing non-standard (low-high temperatures (20 - 1100) K, gas, laser-light) environments. The imaging plate (IP; 200 mm \times 400 mm) and micro-strip MYTHEN are available as a detector. In this practice, we plan to use the IP detector. Data reduction perform using IP reader in front of experimental hatch. All operations of the experimental procedure perform using beamline control software on Windows PC from outside of experimental hatch.

[Exercise 1: In this practice, wavelength is $\lambda = 0.5$ Å ($E=24.8$ keV). When crystal plane uses Si (111), what is degree of θ_M in monochromator?] (Hint: $\lambda = 2d(111)\sin \theta_M$ and d -value = 3.136 Å). Write the answer in last page.

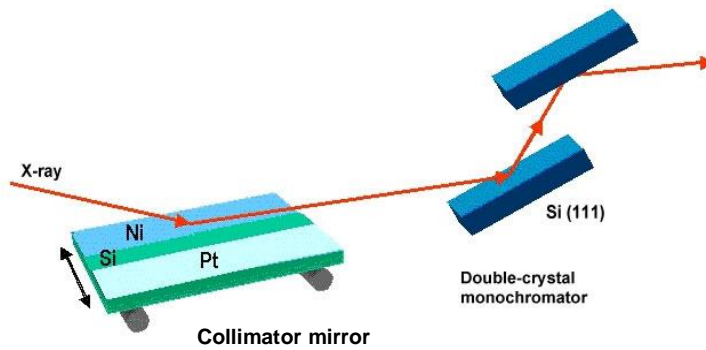
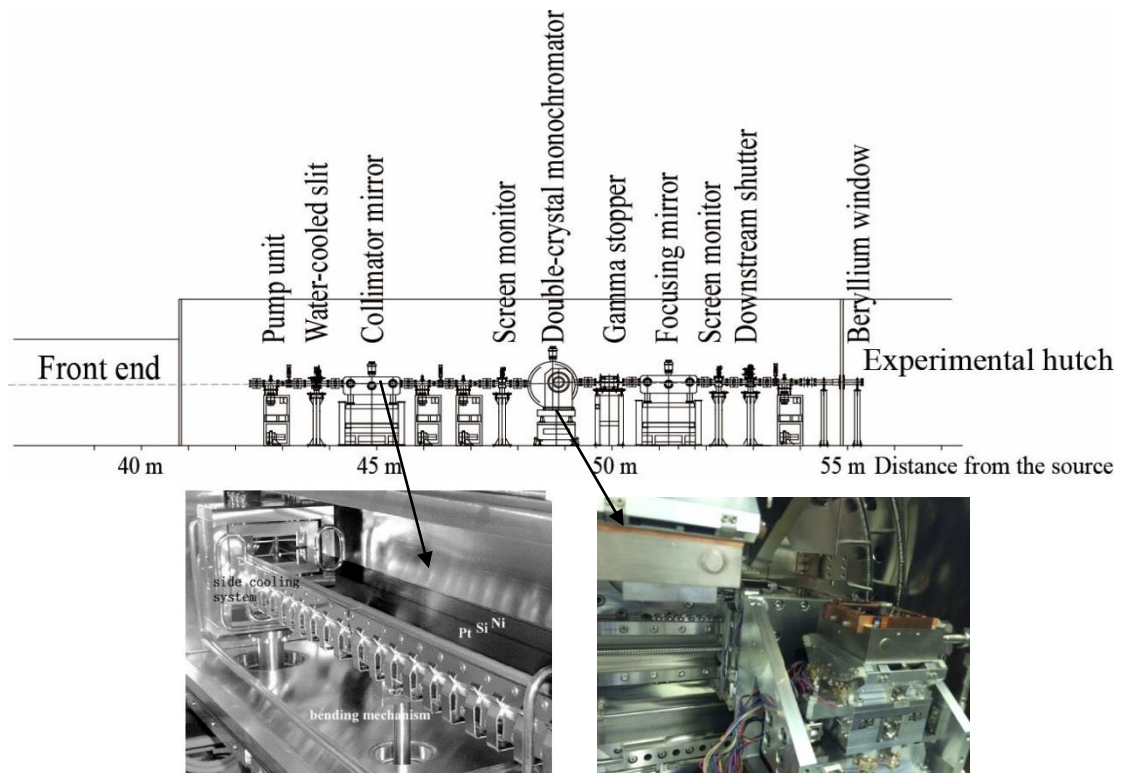
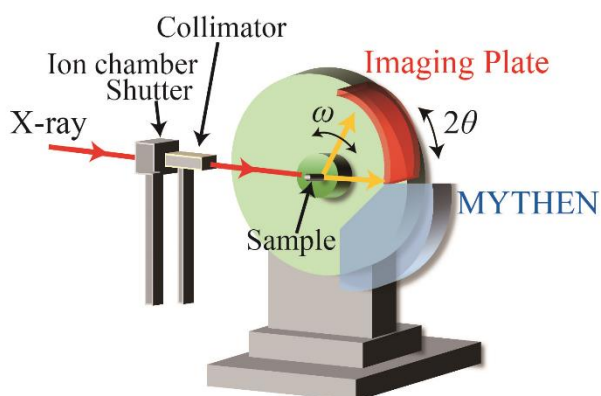
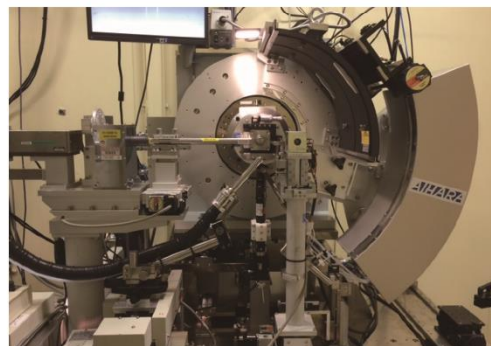


Figure 1. Schematic view in the optical an experimental hutches of the BL02B2 beamline. Distance from light source (m).



(a) Schematic View



(b) Photograph

Figure 2. Large Debye-Scherrer camera (a):Schematic view and (b) Photograph installed at the experimental hutch. The camera radius of IP is 286.48 mm.

4. Sample preparation

The samples used for practice should be finely and uniformly ground and loaded in capillaries. In this practice, all samples average bulk compositions and structures are known. In general, sample preparation required the material, an instrument for grinding, and a sample holder (grass capillary). You should use $\phi 0.2$ mm low X-ray absorption glass capillary. The capillary substrate is amorphous to avoid any diffraction interference. The transmission method using grass capillary has one of advantage of which the X-ray diffraction position and intensity exactly can collect on detector. The main steps for sample preparation:

- 1) Obtain a few tenths of a milligram (or more) of the material, as pure as possible.
- 2) (Optional) Grind gently the sample to homogenize powder. Fine powder can minimize displacement of peak profile by preferred orientation in capillary.
- 3) Set sample holder to goniometer head and fix capillary to holder by Cray.

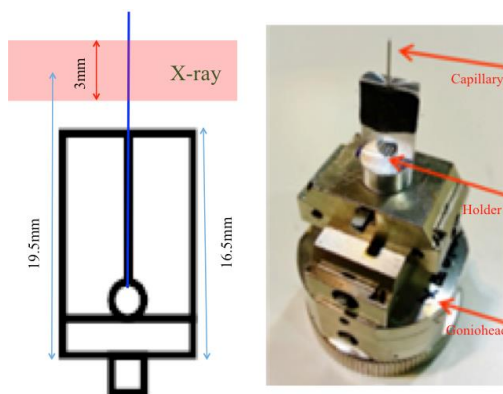


Figure 3. Mounting sample on goniometer head

[Exercise 2: Calculate 2θ of 111 Bragg reflection in CeO_2 ($\lambda = 0.5 \text{ \AA}$)] Write the answer in last page. Hint: Cubic cell parameter $a = 5.4111 \text{ \AA}$, $d(hkl) = (1/a^2(h^2+k^2+l^2))^{-1/2}$, $\lambda = 2d\sin\theta$

5. Practice

5.1 Experiment

- Sample mount to Debye-Scherrer camera
 - ✓ Set the sample Debye-Scherrer camera, and adjust the center of rotation.

- Erase Imaging plate (IP) data and IP set up
 - ✓ Put into the erase box with white side of facing upward
 - ✓ Push the START button.
 - ✓ Clean the IP surface using alcohol.
 - ✓ Put the IP into cassette of Debye-Scherrer camera (Put the white surfacing toward the sample.).
 - ✓ Close the leak screw and then open the vacuum pump valve
 - ✓ Exit from the hutch

- Data Collection: X-ray exposure
 - ✓ Data collection perform using the Labview software (Scan3_Spinner; Figure 4), and set “exposure time” for 5 min. and “shift of IP” to 12 mm in the Debye-Scherrer camera dialog.
 - ✓ In “IP_move” dialog, select “initial position”, and then run the program.
 - ✓ Run the “Scan3_Spinner” software.

- Reading IP data
 - ✓ Open the experimental hutch.
 - ✓ Close the vacuum pump valve, and then open the leak valve.
 - ✓ Pick up the IP from the cassette.
 - ✓ Put IP into the envelope, and bring IP to the IP reader (BAS-2500) in front of hatch.
 - ✓ Set IP into the IP reader in the darkroom.
 - ✓ In IP read software on the computer BL02B2-3, input file name (no extension) and comment (not mandatory) and click the “Read” button. Reading takes ~5 min.
 - ✓ The recorded 2D image data can see using “Image Gauge” program.

- Powder data transformation from 2D to 1D data
 - ✓ Copy IPV32.exe, GRFONT.dat, and GRWND.EXE to the folder of image data file. IPV32.exe is transformation software from 2D to 1D.

- ✓ Double click “IPV32.exe” IP type 100micro(0)/50mic(1) : 1
- ✓ Input image file name (*.img), and then appear operating menu.
- ✓ Next operation is referred in beamline manuals.

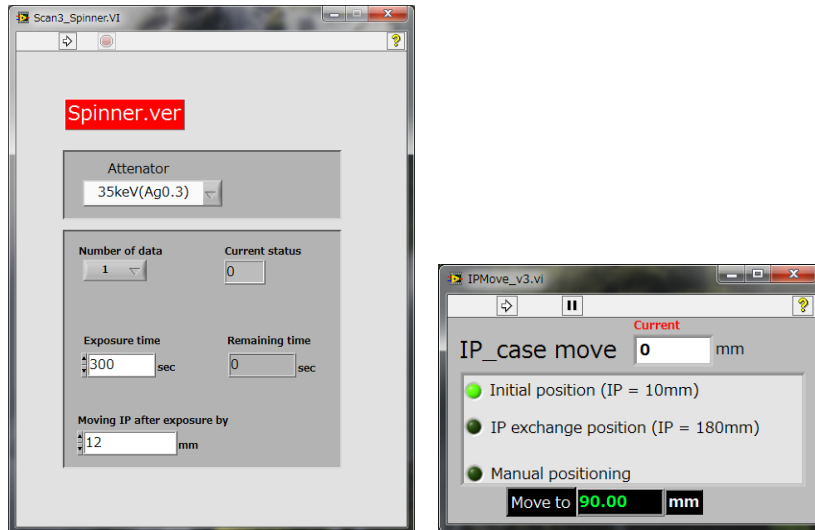


Figure 4. Interface of measurement software.

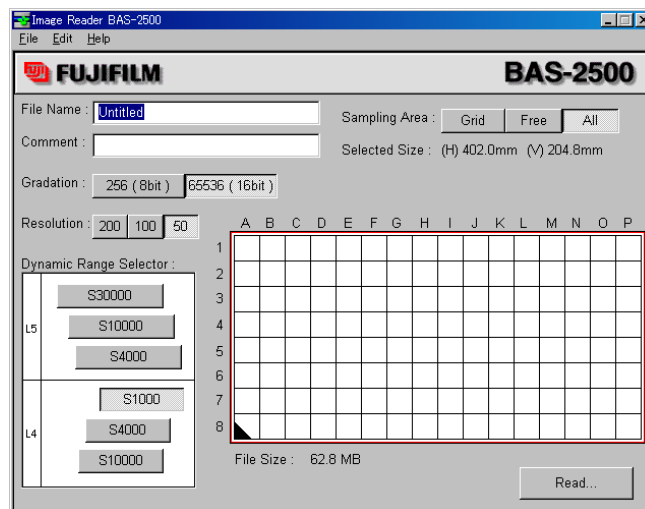


Figure 5. Interface of IP reader (BAS-2500).

5.2 Data analysis

Profile fitting:

Profile fitting is the most precise way to determine diffraction peak position, intensity, and width for calculating lattice parameters and crystallite size. To practice we will use the powder diffraction option (LeBail technique and Rietveld analysis) implemented in Jana2006 (Petricek and Dusek [3]). The software can be downloaded from <http://jana.fzu.cz> web site.

The Le Bail algorithm involves refining the unit cell, the profile parameters, and the peak intensities to match the measured powder diffraction pattern. For computing, the unit cell and space group of the sample must be predetermined because they are included as a part of the fitting technique. It is not necessary to know the structural factor and associated structural parameters, since they are not considered in this type of analysis. In the practice, LeBail powder characteristics for test samples will be analyzed using pseudo-Voigt profile function, Legendre background corrections and a shift of the peaks due to the sample being slightly shifted from the center of the diffraction circle (details see SPring-8/BL02B2 Jana2006 guidance). The pseudo-Voigt function can be considered as combination of the Gaussian and Lorentzian (longer tail) terms. The profile fitting allows determine exact values of unit cell parameters together each reflection indexing to a specific hkl usable for structure refinement.

Structure refinement using Rietveld method:

The Rietveld method is similar to the full pattern decomposition using LeBail algorithm, except that the values of the integrated intensities are no longer treated as variables. The profile intensities compose information about the electron density inside the unit cell, namely where the atoms are located. In Rietveld the intensities are included into all calculations as functions of relevant geometrical, specimen and structural parameters. Full profile refinement is computationally intense and employs the non-linear least squares method which requires a reasonable initial approximation of many parameters. Therefore, usually LeBail technique used to perform a full pattern decomposition prior to Rietveld refinement which use suitably determined relevant parameters (background, peak shape, zero shift or sample displacement, and unit cell dimensions) as the initial approximation. For Rietveld calculations the structural factor and associated structural parameters needed and therefore structural information imported for calculations using known or isomorphs structures (for the practice samples this information presented in the subsequent paragraph). Complementing atomic positions in the unit cell affect the profile peak intensities but not the positions.

Rietveld refinement fits the whole pattern at once and refines: atomic positions (Al_2O_3), lattice parameters, profile parameters (the peak shape), background parameters, and atomic displacement parameters.

There are several advantages of the beamline experiment making data calculation and interpretation relatively straightforward:

- Utilizing linearly polarized synchrotron X-ray ($P=1$) and high beam energy (short wavelengths of 0.5 \AA , high penetration) make equal to 1 the polarization correction and absorption factors which are involved in converting diffracted radiation intensities to structure factors during the process of structure determination for the experiments.
- Using a small quantity of well-ground powder sample avoids extinction effect, which is destructive interference from re-reflections within the crystals.

Cerium oxide

Stoichiometry = CeO_2

Space Group = $Fm-3m$ (225)

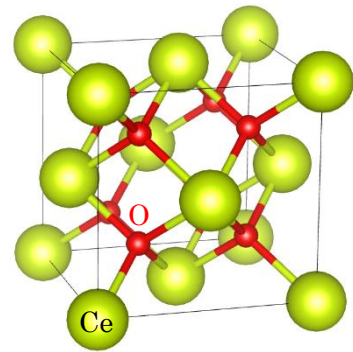
$a = 5.4111 \text{ \AA}$

Atomic Positions

Ce	$4a$	$0, 0, 0$
O	$8c$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$

Coordination Numbers/Geometry

Ce	CN=4 atoms of O	Tetrahedral coordination
O	CN=4 atoms of Ce	Tetrahedral coordination



Silicon

Stoichiometry = Si

Space Group = $Fd-3m$ (227)

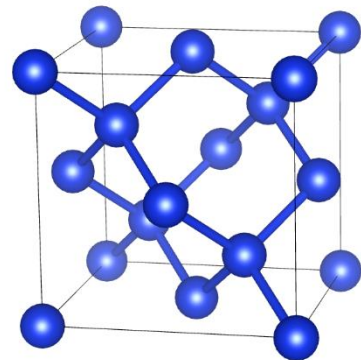
$a = 5.43118 \text{ \AA}$

Atomic Positions

Si	$4a$	$0, 0, 0$
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Coordination Numbers/Geometry

Si	CN=4	Tetrahedral coordination
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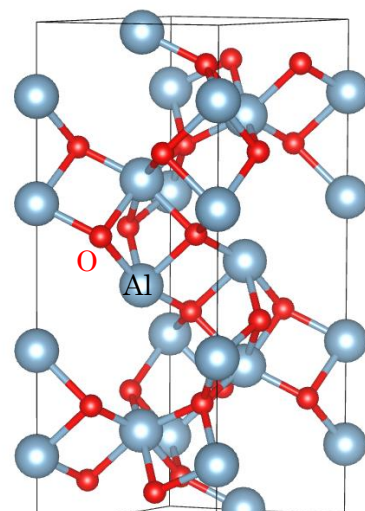
α -Aluminium oxide

Stoichiometry = Al_2O_3

Space Group = $R-3c$ (167)

$a = 4.7591 \text{ \AA}$ $c = 12.9918 \text{ \AA}$

Atomic Positions



Al 12c 0, 0, 0.355

O 18e 0.303, 0, 1/4

Coordination Numbers/Geometry

Al CN= 6 Octahedral coordination

O CN= 4 Tetrahedral coordination

References

- [1] M. Yamakata et al., *Nucl. Instrum. Methods Phys. Res.* **A467/468**, (2001) 667
- [2] E. Nishibori et al., *Nucl. Instrum. Methods Phys. Res.* **A467/468**, (2001) 1045
- [3] V. Petricek et al., *Z. Kristallogr.* **229(5)**, (2014) 345.

Excise Answer

1: $\theta_M = 4.5724^\circ$

2: $2\theta = 9.1798^\circ$