2 Dimensional Position Sensitive XAFS by Using In-house X-ray Spectrometer

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Abstract. Position sensitive XAFS measurements by using the in-house X-ray spectrometer and the position sensitive X-ray detector were attempted. The in-house spectrometer produces monochromized divergent X-ray beam. Therefore, an extended direct-beam image projected on the detector can be taken, and its extension rate is depending on the arrangement of the sample and the detector. A position sensitive XAFS measurement was demonstrated by using Ni metal foil and NiO powder as a model sample. Ge(220) or Si(400) Johansson-type bent single-crystal was used as monochromator, and Mo and LaB₆ were used as the target and filament, respectively. Tube voltage and current were operated at 16 kV and 100 mA (1.6 kW). XAFS spectra were measured by transmission-mode with sample set/reset method and required time of each experiment is about 6 hours in total. It was confirmed that metal and oxide spectra with enough quality for structural analysis were clearly separated by each position in the sample.

1. Introduction

X-ray absorption spectroscopy (XAS) was applied for analyzing the local structure in various material systems by using the Fourier calculation method in the early 70’s and plays an important role in structural chemistry and physics. Since synchrotron radiation facilities were provided for XAS experiments, this technique has been applied to various field of engineering, material science, environmental science, catalytic science, and so on. In-house x-ray absorption spectrometers have been developed since 80’s [1].

In the early 00’s, a new in-house spectrometer apparatus of which size is smaller due to using a compact x-ray source was developed [2]. This spectrometer, Rigaku R-XAS looper, showed good performance at experimental energy range of 5 to 25 keV, and was available to apply to measurements at S K absorption edge (~2.5 keV) [3]. On the other hand, the pixel-array type position sensitive area detector namely D/teX-25 has recently developed for high-speed and high-sensitivity x-ray diffractometry by Rigaku corporation, and its detecting window size is 12.8 mm x 12.8 mm including 512 pixel x 512 pixel with about 24 micrometer of pixel size [4]. The in-house spectrometer is employed a focused optical system with Johansson-type bent monochromator and the output beam is divergent in vertical direction within 4 degree in divergence angle as shown in figure 1.
The window size of the position sensitive detector is suitable to detect the direct beam radiated and monochromized by the in-house spectrometer. Achievement of a position sensitive XAS is expected by using the in-house spectrometer with the 2-dimensional detector.

2. Experimental
In this study, all experiments were carried out at around Ni K absorption edge (8332 eV) using Ge(220) and Si(400) monochromator for the measurements with standard and high energy resolution, respectively. Mo and LaB₆ was respectively used as x-ray source target and anode filament, and operating tube voltage and current were 16 kV and 100 mA (1.6 kW).

To evaluate the quality of monochromized x-ray radiation, the image of the direct incident beam was detected at the x-ray beam energy of 8400 eV corresponding to just above the Ni K absorption edge. The spectrometer has two slits of beam-width limiting slit placed just before the focusing point and divergence slit placed at 60 mm from beam source point. A model sample of a tape stuck metal nickel foil and pasted NiO powder was used for the experiments of the position sensitive XAS.

3. Results

3.1. Direct image of incident beam
Spectrometer was positioned at the energy of 8400 eV using Ge(220) or Si(400) monochromator, and direct beam images were obtained by the detector D/teX-25 located at 220 mm behind the focus point F in figure 1. Figure 2 shows the direct beam images with various condition of divergence slit (DS) using Si(400) as monochromator. The vertical divergence of direct beam is 4 degree when the DS size is 8 mm. Figure 3 shows the direct beam images with different size of the beam width slit and fixed size of DS. The output beam from the spectrometer has divergence vertically by Bragg reflection from bent monochromator and horizontally due to beam width. Therefore, the vertical width of beam in the window of the detector is same irrespective of the kind of monochromator crystal. On the other hand, the

![Figure 1. Schematic diagram of the in-house spectrometer and its optical system. S : x-ray source, M : monochromator, F : focus point, O : center of Rowland circle, DS : divergence slit.](image1)

![Figure 2. Direct beam images with different DS size using Si(400) monochromator at 8400 eV.](image2)

![Figure 3. Direct beam images with different size of the beam width slit using Ge(220) (left) and Si(400) (right).](image3)
horizontal width depends on monochromator crystal at the same energy of x-ray because of difference of the path length between x-ray source point S and focus point F. The value of lengths are shown in the inset figures.

3.2. Position sensitive XAFS measurement
When an analysis of local structure or chemical state is applied to a multiphase material with position dependence, there are two way of approach; one is a method with scanning the irradiating position using microsized beam, the other is the method in this study. The position sensitive XAS was demonstrated by using a model sample of Ni metal foil and NiO powder were put on a adhesive paper tape. The photograph of the sample is shown in figure 4.

The image of direct beam transmitted through the model sample is shown in figure 5. The intensity map images were measured using Ge(220) monochromator at 231 points of the energy around Ni K absorption edge. The required time for the measurements of the intensity of transmitted through the sample and of blank was totally for 6 hours. The resultant XAFS spectra of areas 1 and 2 in figure 5 are shown in figure 6. The pattern profile of these spectra shows the features of each Ni metal and NiO. In case of using Si(400) as monochromator, measured spectra have an applicable quality to analysis of the chemical state of absorbing element by using the profile of XANES (x-ray absorption near-edge structure).

4. Summary
The results of demonstration in this study indicated that the combination of the in-house x-ray spectrometer and the position sensitive array detector is effective in the measurements and analysis of the position sensitive XAS.

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