One-Dimensional Imaging XAFS Measurement Using Photodiode Array Detector

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Abstract

One-dimensional imaging XAFS system was constructed at BL-4 of the SR Center. The transmitted X-ray intensities were detected by the position-sensitive photodiode array detector in the system. The horizontally imaging XAFS spectra were measured for the model sample of Fe compounds in the time scale of 30 min. The S/N ratio was sufficient to distinguish the oxidation state of each compound. The pseudo-two-dimensional measurement was achieved by the vertically linear scan of sample. The two-dimensional map for Co compounds was obtained by the imaging XAFS data.

1. Introduction

Many hard X-ray imaging techniques has been developed at synchrotron facilities [1]. The microbeam generated by the Kirkpatrick-Baez focusing system or zone plate focusing system is effective to focus the prove X-ray on the microscopic region in the sample. The spatial resolution reaches the nanometer order. The advantage of using X-ray is that the distribution of a specific element can be mapped by using the difference of transmittance at the absorption edge. On the other hand, the X-ray absorption fine structure (XAFS) method has been developed to obtain the atomic and electronic structure of the absorption atom. Because the distinction of the different oxidation states is possible, XAFS is one of the most important analytical approach in many fields such as electrochemistry and catalysis chemistry.

The purposes of the imaging XAFS method are to obtain the XAFS spectrum at specific small regions and to map the distribution of the compound distinguished by their XAFS spectra [2]. There are two contradictory demands. One is much higher spatial resolution, that is to obtain the spectra in much smaller region of the sample. The other is to obtain the information in extensive region. A million times of measurements are necessary to examine the sample of 1 cm^2 with the microbeam of $10 \,\mu\text{m} \times 10 \,\mu\text{m}$. There will be a case that the necessary resolution is not clear before the measurement.

We tried to construct the imaging XAFS system of the transmission arrangement with a position-sensitive detector. The similar measurement with fluorescent X-ray has been previously reported [3, 4], however the system is simplified with the transmission mode and is applicable to the tomography technique. This imaging system bases on a concept that a region of the sample and an element of the detector correspond to each other. This implies that the non-parallel X-ray beam is not suitable to the imaging system. A merit of such system is that the large numbers of the XAFS scan is not necessary. The spatial resolution depends on the size of the detector element and the covered view field is determined by the area of the detector and the size of the incident X-ray beam. Although the two-dimensional imaging system is possible by using a 2D detector such as CCD camera, firstly we aimed to establish the one-dimensional imaging XAFS system using the photodiode array (PDA) linear detector to evaluate the validity of the imaging concept.

2. Experimental

Imaging XAFS measurements were performed at BL-4 of the SR Center. Figure 1 shows the photograph of the system in the experimental hutch of BL-4. Transmitted X-ray intensities were measured by the PDA detector (S3904-1024F, Hamamatsu Photonics) with a scintillator

to convert the transmitted X-ray to the visible light. The PDA has the linearly arrayed 1024 elements, and the effective size of an element is $20 \ \mu m \times 2.5 \ mm$. Because there are $5 \ \mu m$ space between each element, total effective area of the detector is 25.6 mm × 2.5 mm. The non-focused X-ray beam at BL-4 (normally 12 mm(H) × 1 mm(V)) is covered by the PDA detector, which is set to be parallel to the X-ray beam. The Tl-doped CsI (50 μm thickness) was used as the scintillator. The detection efficiency and the spatial resolution also depend on the thickness and the kind of the scintillator. The scintillator was mounted on the fiber optical plates which is coupled with the PDA element using the optical grease, and thus the scintillator is changeable to choose the best condition for the X-ray imaging. The scintillator-coupled PDA were put in a case to be shielded from the visible lights. The X-ray beam passed through the window of the aluminum-deposited mylar.



Figure 1 One-dimensional imaging XAFS measurement system with PDA detector.

X-Ray absorption spectra were measured by moving stepwise the monochromator, and the observed intensities were transferred to a computer through the PDA controller (Unisoku) at each X-ray energy. All components were controlled by a newly-developed computer program modified from the normal XAFS measurement (Figure 2). Because BL-4 has no focusing system, the intensity distribution in the X-ray beam is almost flat. The incident X-ray intensity (I_0) was thus measured with the same PDA detector by using a part of the beam passed through the region without sample. The XAFS spectra at the selected detector elements can be shown in the program window during the measurement in real time. The shortest exposure time of

the detector is 2 ms, however the time of several seconds per point is necessary to obtain the analyzable XAFS spectra in BL-4.



Figure 2 Main window of imaging XAFS measurement program with PDA detector.

3. Results and Discussion

The experimental results are summarized in Figure 3 for a model sample of the onedimensionally arranged Fe compounds. The powders of Fe, FeO, Fe₃O₄, and Fe₂O₃ were held in narrow slits in the Al plate. Figure 3(a) shows the distribution of the transmitted X-ray intensities at the X-ray energy of 7117 eV, and the XAFS spectra of Figure 3(b) were constructed using the data at 301 points of X-ray energies. The required time was ~30 min to obtain this imaging XAFS spectra. The patterns of the XAFS spectra are clearly different for each compound and the absorption edge energies are correctly shifted corresponded to the valence state of the Fe atom.



Figure 3 Imaging XAFS spectra of Fe model sample observed with PDA detector. (a) Transmitted X-Ray intensities at 7117 eV. (b) Normalized XAFS spectra at each compound.

The two-dimensional imaging XAFS map can be obtain by the scan of the sample in the perpendicular (vertical) direction to the X-ray beam. Figure 4 shows an observed result for a model Co sample. Small lumps of powdery cobalt oxide and lithium cobaltate are 2-dimensionally arranged on the tape in this sample (Figure 4(a)). The vertical spatial resolution in the onedimensional imaging system is decided by the vertical width of the X-ray beam. When the vertical width of X-ray beam is set to 1 mm, the sample is moved by 0.5 mm step in the vertical direction. Total fifteen lines were corrected by the scan of the sample. The result based on the analysis of each XAFS spectrum is mapped to Figure 4(b), and the XAFS spectra of three selected pixels are plotted in Figure 4(c). The energy of the absorption edge (E_0) differs for the component species depending on the valence state of the Co atom. The painted colors in Figure 4(b) correspond to the value of E_0 . The red regions have the higher E_0 value than that of the blue regions. The brightness of the colors reflects the absorbance jump ($\Delta \mu t$) at the absorption edge, which is proportional to the density of the absorption atom and the thickness of the sample. The E_0 values were evaluated by the first differential curves of the observed spectra. Cobalt oxide and lithium cobaltate were successfully separated by color at almost all region of the sample. Some pixels in the lump of lithium cobaltate were misjudged to be cobalt oxide

(blue color). It was found that the absorption edge jump is too large in these misjudged region according to the analysis of XAFS spectra at each pixel. The apparent energy of the absorption edge becomes low when the absorbance in the post edge region are underestimated by the too low transmitted X-ray intensity due to the too large thickness of the sample. This limitation is mainly due to the low dynamic range of the PDA detector. For the current X-ray imaging system detecting the transmitted X-rays, the sample thickness and density are important to obtain the correct assignment of the sample species.



Figure 4 Line-scanning imaging XAFS spectra observed with PDA detector. (a) Photograph of sample. (b) X-Ray imaging map generated using the values of E_0 and $\Delta \mu t$. (c) XAFS spectra at selected positions.

4. Conclution

The one-dimensional X-ray imaging system has been successfully constructed and the analysis of the imaging XAFS data brings out the limitation for the imaging XAFS system in the transmission mode. Because the dynamic range is limited to be about five orders for the PDA detector, the requirement of the sample thickness is stricter than that of the conventional transmission mode. The map of the chemical species was almost correctly generated using the values of E_0 and $\Delta \mu t$ obtained from the XAFS spectra. The imaging XAFS data including the spectra and information on their position are extremely useful to analyze the atomic and electronic structure of the absorption atom in heterogeneous samples.

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