X-ray absorption spectroscopy using BL11 at SAGA-LS, and its applications for materials science

T Okajima1,2, K Sumitani1, M Kawamoto1 and E Kobayashi1
1 Kyushu Synchrotron Light Research Center, 8-7 Yayoigaoka, Tosu Saga 841-0005, JAPAN
2 Research Center for Synchrotron Light Applications, Kyushu University, 6-1 Kasugakohen, Kasuga, Fukuoka 816-8505, JAPAN
E-mail: okajima@saga-ls.jp

Abstract. Beamline BL11 at the Saga Light Source (SAGA-LS) is designed for X-ray absorption fine structure (XAFS) experiments in the energy range 2.1–23 keV using a Si(111) double crystal monochromator. For XAFS experiments, the sample temperature can be controlled in the range of 15–1073 K using a cryostat and furnaces. Besides the transmission measurement mode, we can obtain XAFS spectra in fluorescence measurement mode and conversion electron yield modes. An XAFS measurement system under atmospheric pressure for soft X-rays with energies under 3.5 keV was also installed on this beamline. In addition, we can perform in situ XAFS measurements under toxic and harmful gas atmospheres by using a quick XAFS measurement system.

1. Introduction

The Saga Light Source (SAGA-LS) is a compact synchrotron light source with a storage electron energy of 1.4 GeV [1]. The purpose of this facility is to play a pivotal role in the promotion of industrial development through the collaboration between universities and industry in Kyushu. The SAGA-LS has been operated since February 17, 2006. Six prefectural (BL07, BL09A, BL10, BL11, BL12, and BL15) and three other agency beamlines (BL06, BL13, and BL18) are now in operation at SAGA-LS. The prefectural beamlines are open to the public and are available for multiple users such as universities, institutes, and industries. The light sources of these beamlines consist of four bending magnets for BL09A, BL11, BL12 [2], and BL15 [3], an undulator for BL10 [4], and a superconducting wiggler for BL07 [5]. Summaries of these beamlines are listed in Table 1.

The BL11 beamline is mainly designed for X-ray absorption fine structure (XAFS) experiments. This beamline was constructed in the winter of 2010 as the fourth public beamline. In this paper, we introduce beamline BL11 and review some interesting experimental results that have been undertaken with BL11 at SAGA-LS.
Table 1. Beamlines at SAGA-LS

| Beamline | Source | Monochrometer | Photon energy | Main experiments | Category |
|----------|--------|---------------|---------------|-----------------|----------|
| BL06     | BM     | Double crystal | 2.1keV - 23keV | XAFS, SAXS      | Kyushu U. |
| BL07     | W      | Double crystal | 5keV - 35keV   | PXD, XAFS, Imaging | Pref.    |
| BL09A    | BM     | None           | White beam     | Irradiation, Topography | Pref.    |
| BL10     | U      | VLS-PGM        | 40eV - 90eV    | PEEM, ARPES     | Pref.    |
| BL11     | BM     | Double crystal | 2.1keV - 23keV | XAFS, SAXS      | Pref.    |
| BL12     | BM     | VLS-PGM        | 40eV - 1500eV  | XPS, NEXAFS     | Pref.    |
| BL13     | U      | VLS-PGM        | 15eV - 600eV   | ARPES           | Saga U.  |
| BL15     | BM     | Double crystal | 3.5keV - 23keV | XRD             | Pref.    |
| BL18     | BM     | Multi layered mirror | ca. 92eV | Irradiation | Nikon Ltd. |

Source: W, wiggler; BM, bending magnet; U, undulator.

Category: Pref., public beamline by Saga Prefecture Government; Kyushu U., Saga U. and Nikon, contract beamline by Kyushu University, Saga University and Nikon Corporation, respectively.

VLS-PGM: Varied-line-spacing plane grating monochrometer.

2. Beamline BL11 at SAGA-LS and the XAFS measurement system

X-rays from a bending magnet with a 1.46-tesla magnetic field and critical energy of 1.9 keV are used. A fixed-exit double-crystal monochrometer with Si(111) crystals was installed and X-rays with photon energies from 2.1 keV to around 23 keV generated by the beamline were used. This beamline has two experimental huts along its length, as shown in Figure 1, located at 12 m and 20 m from the light source, respectively. After the 1st experimental hutch, a 1 m long rhodium-coated fused silica bent cylindrical mirror is installed. A 0.125 mm thick beryllium window is placed at the end of the front end section. Monochromatic X-rays are guided to the experimental stations through a 0.05 mm thick Kapton® window placed at the end of transport section. The Kapton® window separates the vacuum in the transport channel from the experimental station but lets the X-rays pass. When experiments in the 2nd experimental hutch are performed, the vacuum pass is set in the 1st experimental hutch. Figure 2 shows the observed photon flux at the 2nd experimental hutch with and without the mirror. We can use X-rays of almost $1 \times 10^{10}$ photons per second at a keV energy range by using a focusing mirror. The photon fluxes are suddenly decreased at the energy range above 10 keV by the cut-off energy determined by the grazing incident angle to the mirror.

The XAFS spectrometer allows X-ray absorption measurements in transmission mode, fluorescence mode, and conversion electron yield mode. Three lengths of the ionization chamber (65, 170, and 310 mm) were prepared for the transmission mode measurements. The current in the ionization chamber was amplified to a voltage, converted to frequency, and then counted. Different gases, namely, helium, nitrogen, argon, and mixtures of these gases, can be injected. For the fluorescence mode measurements, a Lytle-type detector, a germanium 19-element solid-state detector (19-Ge SSD), and a silicon drift-chamber detector (SDD) can be used. The Lytle-type detector contains an aluminium solar slit and a 20-mm long ionization chamber. The elements of the 19-Ge SSD have an effective area of 100 mm² × 19 elements and a thickness of 10 mm, enabling detection of more than 95% of the incident X-rays. The element of the SDD has an effective area of 50 mm² and a thickness of 0.35 mm. The SDD can be operated without liquid nitrogen. In addition to the detectors, a cryostat and furnaces can be used in the beamline. Using these apparatuses, the sample temperature can be controlled in the range 15–1073 K. The research areas that require this XAFS station include the following examples: the local structure analysis of catalysts for fuel cells and electrode materials...
for rechargeable lithium-ion batteries, and chemical species analysis of environmental materials.

![Figure 1. Schematic layout of beamline BL11 at SAGA-LS. MBS is the main beam shutter which contains the photon absorber (ABS) and beam shutter (BS) made of tungsten. DSS is the downstream shutter.](image1)

**Figure 1.** Schematic layout of beamline BL11 at SAGA-LS. MBS is the main beam shutter which contains the photon absorber (ABS) and beam shutter (BS) made of tungsten. DSS is the downstream shutter.

**Figure 2.** Observed typical photon flux at the XAFS sample position in the 2nd experimental hutch. The photos pass through a slit located just before the sample with a size of 5 mm (horizontal) × 1 mm (vertical). The sample was positioned 22 m from the source point.

### 3. Experimental results at BL11

#### 3.1 XANES spectroscopy for materials science

With the development of synchrotron light sources, X-ray absorption fine structure (XANES) spectroscopy has become an important branch of X-ray spectroscopy. The XANES spectrum is sensitive to the chemical environment of a specific element, such as chemical bonding, charge state, and magnetic state. XANES is not only an analytical tool for characterization, but a uniquely useful technique for deeply investigating the local environment of selected elements [6–8].

Many investigations have been performed recently using XANES spectroscopy at BL11 [9]. Han et al. discovered tetravalent dysprosium (Dy) in the perovskite-type oxide BaZr$_{0.8}$Dy$_{0.2}$O$_3$ after heat-treating in pure O$_2$ gas at 1 atm by using XANES spectroscopy [10]. They prepared two types of BaZr$_{0.8}$Dy$_{0.2}$O$_3$ materials, one treated at 1600 °C in pure O$_2$ gas at 1 atm and the other in H$_2$ gas at 1 atm. Figure 3 shows the Dy L$_{3}$-edge XANES spectra of these materials and the reference samples of Dy$_2$O$_3$. The perovskite-type oxide BaZrO$_3$, in which 20% of Zr was replaced by Dy, was prepared by a conventional solid state reaction method. After sintering at 1600 °C in pure O$_2$ at 1 atm pressure for 24 h, they obtained a black pellet as shown in Figure 3(a). The pellet changed color to white after
subsequent heat-treating in H₂ for 120 h at 600 °C. The Dy L₃-edge XANES spectrum of the black pellet shows triple peaks (Figure 3(a)), in contrast to the single peak spectra of the white pellet (Figure 3(b)) and trivalent dysprosium in Dy₂O₃ (Figure 3(c)), which were similar. That is to say, Dy in the black pellet heat-treated at pure O₂ at 1 atm is multivalent and that in the white pellet heat-treated in H₂ is trivalent. These features are also observed for Dy⁴⁺-containing fluorides which are reported to exhibit double-peak spectra [11]. In addition to this result, XRD analysis with Rietveld refinement, thermogravimetry experiments, and hydroxide ion measurements at several temperatures led them to conclude that tetravalent dysprosium exists in perovskite-type oxide barium zirconate.

![Figure 3. Dy L₃-edge XANES spectra of (a) BaZr₀.₈Dy₀.₂O₃₋δ heat-treated in O₂ at 1600 °C for 24 h, (b) BaZr₀.₈Dy₀.₂O₃₋δ subsequently heat-treated in H₂ at 600 °C for 120 h, after the heat-treatment in O₂ at 1600 °C, and (c) Dy₂O₃.](image)

3.2 In situ XAFS measurement of NiO reduction
Quick-XAFS (QXAFS) measurements have been widely used at many synchrotron radiation facilities. In an QXAFS measurement system, XAFS spectra are obtained by moving a monochrometer with a constant velocity. Scanning times of a few minutes can be routinely achieved, with some special systems measuring even below one second.

Metal oxides are used as catalysts for the reforming of hydrocarbons [12, 13]. Among the transition-metal oxides, the reduction of nickel monoxide (NiO) by hydrogen has been the subject of the most extensive fundamental studies, becoming an important reference system [13, 14]. We demonstrated the in situ XAFS observation of the reduction of NiO using a QXAFS system. The in situ XAFS measurements were carried out in a reaction cell in transmission mode. The cell was made of fused quartz with Kapton® windows. Powders of NiO were mixed with boron nitride powder and packed inside the cell. The specimen was heated to about 1073 K in a 2% H₂/98% N₂ gas with a flow rate of 50 ml/min. The temperature of the specimen was raised continuously at a rate of 10 K/min. The spectra were registered once every minute, and it took about 30 seconds to measure one spectrum. Figure 4 shows the Ni K-edge in situ XANES spectra and the Fourier transform of the EXAFS \(\langle k^2\chi(k)\rangle\) spectra for NiO powder. The insets of Figure 4(a) show the XANES spectra obtained at temperatures of 310 and 1073 K, and the XANES spectrum of Ni foil at the upper right side. At around 8355 eV, the typical strong white line for NiO in the 310 K spectrum is clearly observed. The intensity of the white line exhibits a monotonic decrease above about 773 K (red solid line) with increasing temperature, while the pre-edge feature at around 8340 eV for metallic Ni appears. A comparison of the spectrum at 1073 K and the spectrum of Ni foil shows that the reductions of Ni in NiO are insufficient. Linear combination analysis of the XANES spectra also showed about 90% of the Ni in NiO was present as Ni in metal after reduction at 1073 K. In Figure 4(b), the peaks at 1.5 Å and 2.5 Å become consistent with the presence of Ni-O (in NiO) and Ni-Ni (in NiO) bonds, respectively. The inset at the upper right side also shows the \(k^2\chi(k)\) spectra for Ni metal. This figure indicates that the peak corresponding to the Ni-Ni bond (in Ni metal) appears at 2.0 Å, shown as a dotted line in Figure 4.
4(b). The spectrum also shows the reductions of Ni in NiO are insufficient. These spectra clearly show the reduction from Ni in NiO to Ni metal occurs according to the increase of the temperature in a reduction atmosphere.

**Figure 4.** (a) Ni K-edge in situ XANES spectra and (b) Fourier transform of EXAFS ($k^3\chi(k)$) spectra for NiO powder.

### XAFS Measurement at Sulfur K-edge Region

Materials containing sulfur and phosphor play important roles in various research fields, especially in environmental and biochemical sciences, as well as in many industrial applications in the fields of rubber, cosmetics, pharmaceuticals, pesticides, and fertilizers. XAFS is one of the most suitable methods for observing the many functions and transformations of these species. However, because X-rays with energies between 2 and 4 keV barely penetrate the atmosphere, XAFS spectra are usually measured in vacuum, and for this reason, XAFS measurements of these species have been restricted.

We installed a new XAFS measurement system using helium paths that is easy to operate and allows the collection of XAFS spectra in the soft X-ray region around the sulfur and phosphor K-edges under atmospheric pressure [15]. XAFS spectra can be obtained simultaneously in partial fluorescence yield (PFY) mode using an SDD and in convergent electron yield (CEY) mode. Figure 5(a) shows sulfur K-edge XANES spectra of amino acids obtained by the CEY mode. These acids have sulfur with different chemical bonding states. The XANES structures clearly show the chemical shift according to the chemical bonding states. Figure 5(b) also shows the sulfur K-edge XANES spectrum of residual fuel oil obtained by the PFY mode. The oil specimen was packed in a polyethylene bag and was only attached to the sample holder as shown in the inset. These results clearly show that the newly installed XAFS measurement system using a helium pass is useful for XAFS measurement in the soft X-ray region for the measurement of both solid- and liquid-state specimens.
4. Conclusion
In this paper, we introduced the beamline optics and XAFS measurement system in the BL11 beamline. We also presented results of XAFS applications carried out at BL11. These results indicated that BL11 has a performance as good as that of the other XAFS beamlines. An aim of third generation synchrotron radiation facilities is to realize measurements at extreme conditions of time, space, quantity, and so on. The effort to extend the capabilities of XAFS measurement systems is also expanding the range of XAFS applications. As a consequence, stable and versatile XAFS beamlines are becoming more important. It is our aim that the BL11 beamline will become a pioneering facility.

5. References
[1] Yoshida K, Iwasaki Y, Takabayashi Y, Koda S, Okajima T, Setoyama H, Yoshimura D, Tomimasu T and Ohgaki H 2007 AIP Conf. Proc., 879, 179-183
[2] Kamada M, Kondo Y, Azuma J, Takahashi K, Miyata H, Tsuji J, Hashimoto H, Yamashige H, Matsuo S, Kurisaki S, Wakita H, Furuya K, Harata A, Tochihara H, Watanabe T, Inaba M, Okajima T, Setoyama H, Yoshimura D and Fujimoto S 2007 AIP Conf. Proc., 879, 623-626
[3] Okajima T, Chikaura Y, Suzuki Y, Tabata M, Soejima Y, Haru K, Haruki R, Nagata K, Hiramatsu N, Khono A, Takumi M, Setoyama H and Yoshimura D 2007 AIP Conf. Proc., 879, 820-823
[4] Yoshimura D, Setoyama H and Okajima T 2010 AIP Conf. Proc., 1234, 423-426
[5] Kawamoto M, Sumitani K and Okajima T 2010 AIP Conf. Proc., 1234, 355-358
[6] Koningberger DC and Prince R 1998 X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES in Chemical Analysis (New York: John Wiley & Sons)
[7] Stöhr J 1996 NEXAFS Spectroscopy (Berlin: Springer-Verlag)
[8] Tanaka I, Mizoguchi T and Yamamoto T 2005 J. Am. Ceram. Soc., 88, 2013
[9] SAGA-LS Users report, http://www.saga-ls.jp/?page=43 (in Japanese)
[10] Han D, Uda T, Nose Y, Okajima T, Murata H, Tanaka I 2012 Adv. Mater., 24, 2051-2053
[11] Hu Z, Kaindl G, Vandré D, Hoppe R and Wortmann G 1994 J. Alloys Compd., 205, 263
[12] Thomas J M and Thomas E J 1997 Principles and Practice of Heterogeneous Catalysis (New York: VCH)
[13] Kung H H 1989 Transition Metal Oxides: Surface Chemistry and Catalysis (New York: Elsevier)
[14] Delmon B 1997 Handbook of Heterogeneous Catalysts, ed G Ertl, H Knözinger and J Weikamp (New York: Wiley-VCH) pp 264-277
[15] Okajima T and Ohtani R 2011 Diamond Light Source Proc., 1, e141