Development of a Compact XAFS Measurement Chamber under Atmospheric Pressure in the Soft X-ray Region

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Abstract

We have developed a compact experimental set-up for X-ray absorption fine structure (XAFS) measurements in He gas under atmospheric pressure (AP) in the soft X-ray region and used it for Mg and Cl K-edge XAFS measurements of $MgCl_2$ and $MgCl_2 \cdot 6H_2O$. The spectra of $MgCl_2 \cdot 6H_2O$ measured in He under AP were significantly different from those measured in vacuum. This suggests the importance of performing soft X-ray XAFS experiments under AP to obtain reliable spectra from hydrated compounds.

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1. Introduction

X-ray absorption fine structure (XAFS) is a powerful method to probe the local electronic and atomic structures of compounds and a number of spectra have been reported so far. However, it is difficult and challenging to obtain reliable spectra from highly reactive compounds. In the soft X-ray region, spectra are usually measured in vacuum because of the low transmittance of soft X-rays in air. Vacuum environment is also necessary to measure reliable spectra from highly hygroscopic samples. In contrast, some compounds change their structures in vacuum. Typical cases are hydrated compounds, in which hydrated water molecules are easily desorbed in vacuum. To obtain reliable spectra for such compounds, XAFS measurements under atmospheric pressure (AP) is necessary. Although several works have been reported to measure spectra under AP in the soft X-ray region [1, 2, 3], we developed a simple but useful system to measure XAFS spectra in He gas at AP in the soft X-ray region using a thin vacuum-tight Be window and demonstrated the usefulness of the system.

2. Experiment

All the developments and experiments have been performed at the soft X-ray double crystal monochromator beamline (BL-10) of the SR center, Ritsumeikan University [4]. It consists of a 5.1 and 10 μm thick Be foil to cut visible and vacuum-ultra-violet light, a pre-focusing Ni-coated toroidal mirror, a Golovchenko-type double crystal monochromator (DCM), an I_0 monitor made of a Cu mesh, a high vacuum (HV) sample chamber kept in a vacuum below 5×10^{-8} Torr, masks and slits. The available photon energy covers a range from about 1000 to 4000 eV by choosing a pair of monochromatizing crystals, such as beryl(10-10), KTP(011), InSb(111), Ge(111), Si(111) and Si(220). The incident grazing angle of the pre-focusing toroidal mirror is set to 0.7° to filter hard X-rays out and only soft X-rays are monochromatized by the DCM. The beam is focused at the center of the HV sample chamber, whose size is about 2 mm (vertical) × 5 mm (horizontal) at the sample position. The detecting systems prepared in the HV sample chamber are (1) a sample leak current for the total electron yield (TEY) mode, (2) a silicon drift detector (SDD) and a single channel analyzer (SCA) for the partial fluorescence X-ray yield (PFY) mode, and (3) a chevron-type micro channel plate (MCP) attached with a metal anode for the total fluorescence X-ray yield mode. These detecting methods can be used simultaneously [5].

At the downstream of the HV sample chamber, an ICF70 six-way cross nipple was connected and used as a compact AP sample chamber (see Figure 1, 2). A vacuum-tight

15 μm thick Be window separates the HV chamber from the AP chamber. The beam size at the sample position is about 2.5 mm (vertical) × 8 mm (horizontal), since the sample position is out of focus by 500 mm. The same detection systems as at the HV chamber can be use at the AP chamber except for the MCP detector. This experimental set-up makes us possible to measure XAFS spectra both in the HV and AP chambers without any special replacement.

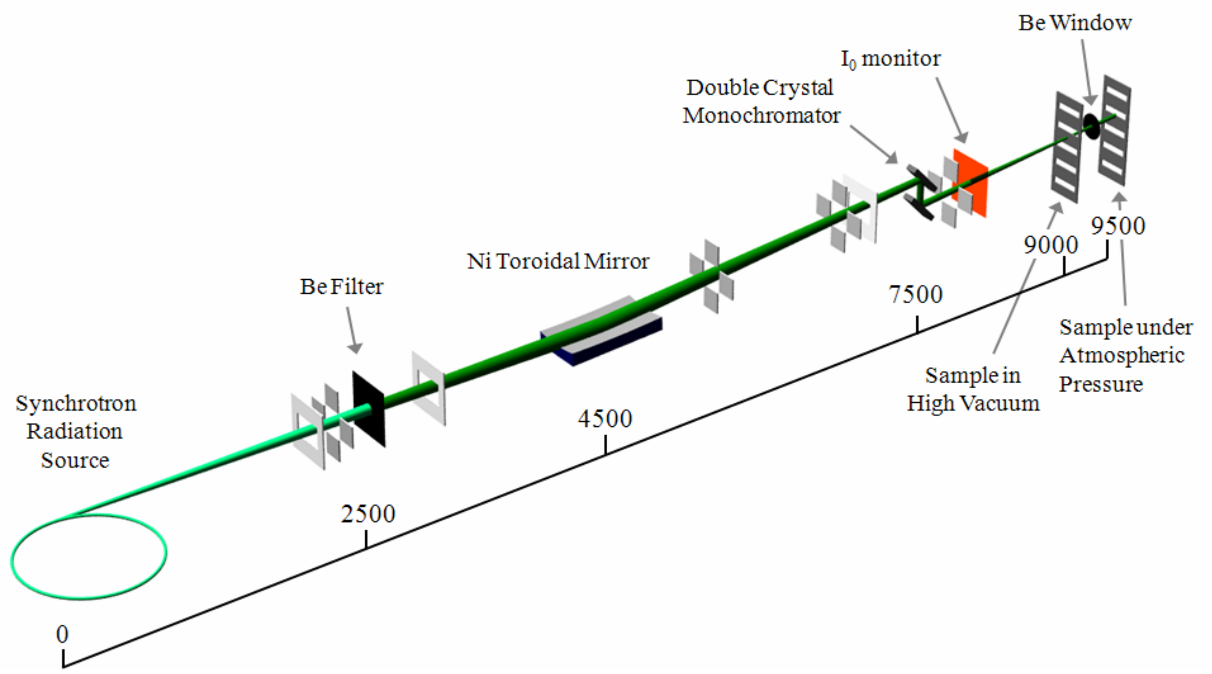

Fig.1. The schematic configuration of the BL-10.

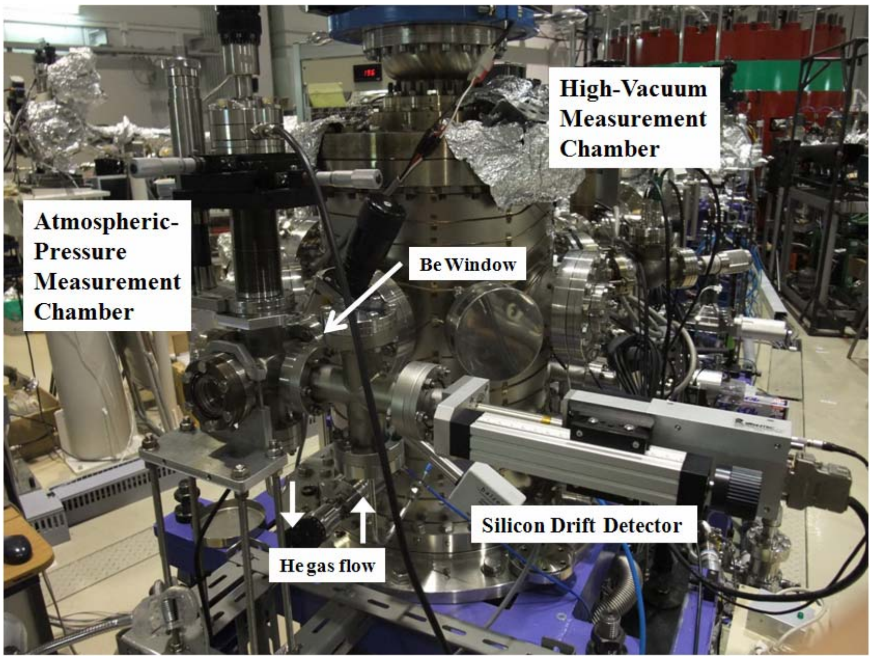

Fig. 2. Photograph of the atmospheric-pressure measurement chamber.

To demonstrate the usefulness of XAFS measurements under AP, Mg and Cl K-edge X-ray absorption near edge structure (K-XANES) measurements were performed for polycrystalline $MgCl_2$ and $MgCl_2 \cdot 6H_2O$, whose grain sizes ranged from about 0.1 to 1.0 mm in diameter, both in HV and under AP. The PFY mode under AP, PFY and TEY mode in HV were used for each sample. All HV measurements were started about 15 minutes after evacuating the HV sample chamber.

3. Results and discussion

(1) Performance test under atmospheric pressure

In the soft X-ray region below 2000 eV, the transmission of Be suddenly drops. Thus, the vacuum-tight Be window to separate the HV chamber from the AP chamber should be as thin as possible. We used a 15 μm thick Be window, which was sealed on a stainless steel mask with a 10 mm ϕ aperture. We found it necessary to keep the HV chamber in vacuum and the AP chamber under an atmospheric pressure to protect the thin Be window. The thin Be window is considerably distorted according to the pressure difference of both the side. However, when maintaining the condition, we found that the danger that the window will be broken can be lessened.

Prior to the measurement, the AP chamber was filled with He gas whose the transmittance of soft X-rays is high. It takes about 10 minutes to completely replace the air inside with He gas with the flow of 500 sccm. During measurements, the He gas flow was kept constant, typically at 20 sccm, which is the optimum flow rate to obtain a PFY spectrum with the highest S/N ratio. We also found it difficult to obtain a TEY spectrum under AP, because ionized He gas disturbs the sample current. Photon fluxes for energies between 1000 and 4500 eV were monitored with a Si PIN photodiode (AXUV-SP2, IRD Co.) at the sample position both in the HV and AP sample chambers (see figure 2). The difference of photon fluxes is larger in the lower region of photon energy because of the lower transmittance of the Be window. The difference of photon fluxes for the KTP crystal was smaller than predicted. This might be due to the radiation damage of the crystal; the measurement was carried out first under AP and later in HV.

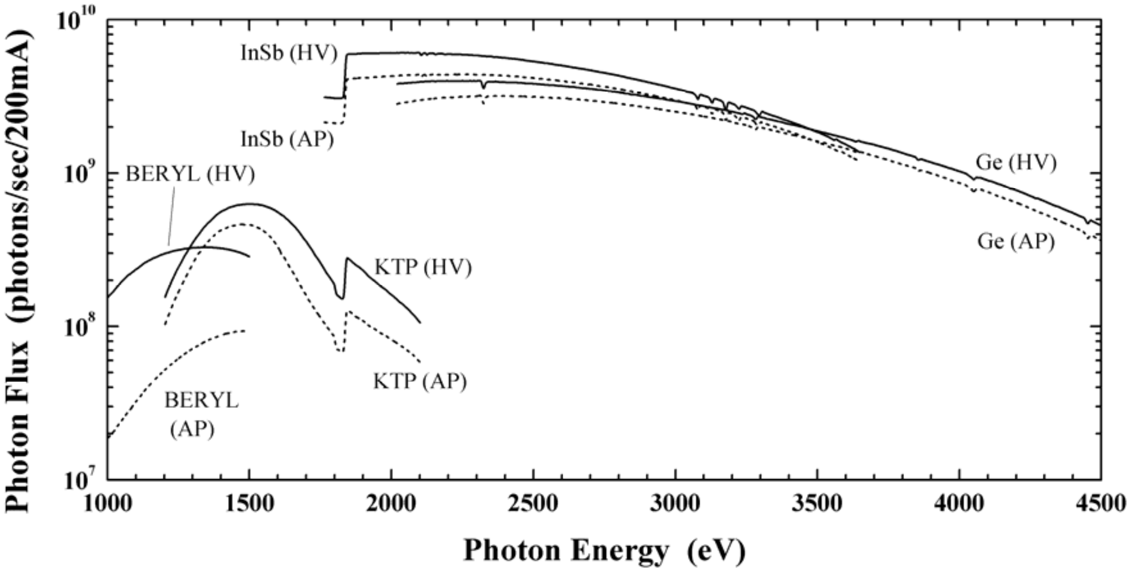

Fig.3. Observed photon fluxes on the sample position in HV (solid line) and under AP (dashed line).

(2) XAFS spectra in vacuum and under atmospheric pressure

The observed Mg and Cl K-XANES spectra of $MgCl_2$ and $MgCl_2 \cdot 6H_2O$ are shown in figure 4. The XANES spectra were compared with theoretical XANES spectra simulated with FEFF-8.4 based on the real-space full multiple-scattering theory [6].

For Mg K-XANES spectra of $MgCl_2$ (figure 4 (a)), spectral shapes of PFY (HV), TEY (HV) are similar to that of PFY (AP). Note that the white line of PFY is heavily suppressed compared with that of TEY. This is due to the self-absorption effect in the PFY spectrum. The characteristic peaks are observed a white line at 1309.5 eV and a shoulder peak at 1311.5 eV. The spectral shape of $MgCl_2$ are well-reproduced by the FEFF simulation. However, it should be noted that another feature at 1313.5 eV appears in the spectrum of PFY (AP).

In contrast, Mg K-XANES spectrum from $MgCl_2 \cdot 6H_2O$ under AP is distinctly different from those in HV as shown figure 4 (b). The simulated spectrum is very similar to that of PFY (AP). This clearly indicates that the sample in vacuum is not $MgCl_2 \cdot 6H_2O$, any more, but changed to anhydrous $MgCl_2$, desorbing crystalline water molecules. In fact, the spectra from $MgCl_2 \cdot 6H_2O$ in HV (both PFY and TEY) are close to those of $MgCl_2$ in figure 4 (a). Careful examination revealed that the spectra from $MgCl_2 \cdot 6H_2O$ in HV (PFY) is a superposition of the spectra from $MgCl_2$ and $MgCl_2 \cdot 6H_2O$. This is because the spectrum was quickly measured in HV after evacuation, and a part of $MgCl_2 \cdot 6H_2O$ remained in bulk, detected with the bulk-sensitive FY method.

As described above, additional peak appears at 1313.5 eV, in the spectrum from

$MgCl_2$ of PFY (AP) (see figure 4 (a)). This feature can be interpreted as the contribution from $MgCl_2 \cdot 6H_2O$, since highly deliquescent $MgCl_2$ adsorbed water during the sample preparation in air. This ‘surface layer’ can be estimated to be about several μm orders.

On the other hand, in Cl K-XANES spectra from $MgCl_2$ and $MgCl_2 \cdot 6H_2O$, no significant spectral changes were observed between the spectra measured under AP and in HV, as shown in Figure 4 (c), (d). This shows that hydration occurs exclusively around the Mg ions.

These results demonstrate the necessity and the importance of XAFS measurements both in AP and HV in the soft X-ray region to obtain reliable spectra from hygroscopic and hydrated compounds.

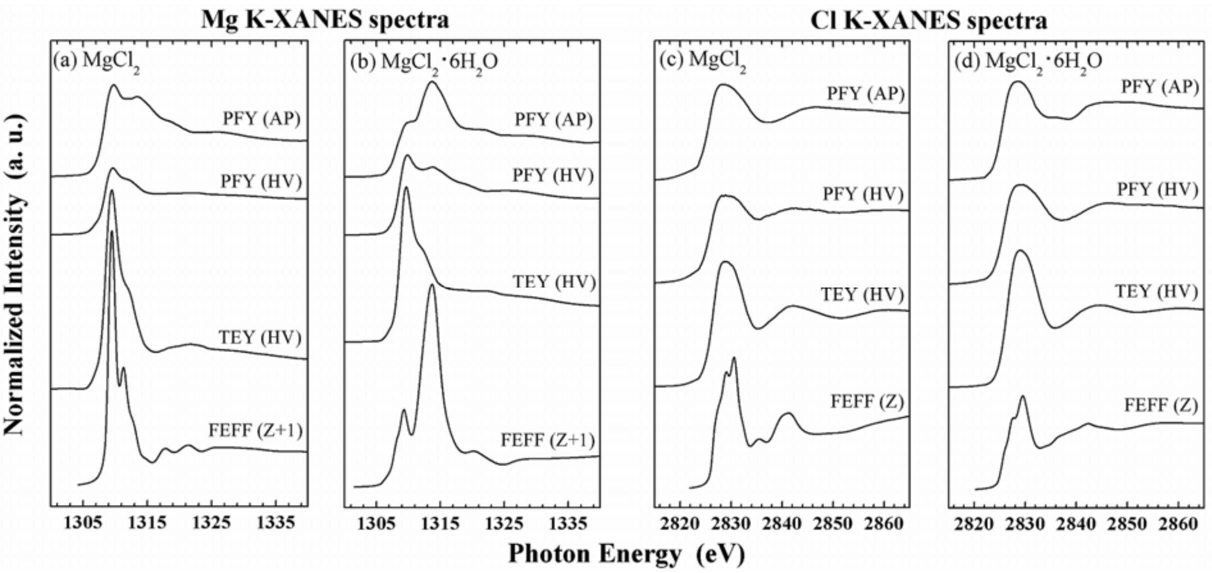

Fig.4. Observed and simulated Mg and Cl K-XANES spectra. (a) Mg K-XANES spectra of $MgCl_2$, (b) Mg K-XANES spectra of $MgCl_2 \cdot 6H_2O$, (c) Cl K-XANES spectra of $MgCl_2$, (d) Cl K-XANES spectra of $MgCl_2 \cdot 6H_2O$. Simulated XANES spectra by FEFF of (a) and (b) used the Z+1 approach to obtain a better agreement with the observed spectra [7].

5. Summary

An experimental set-up for XAFS measurements under AP in the soft X-ray region was developed at BL-10 of the SR center, Ritsumeikan University, and was used for Mg and Cl K-XANES measurements of $MgCl_2$ and $MgCl_2 \cdot 6H_2O$. The reliable XANES spectrum of $MgCl_2 \cdot 6H_2O$ could be obtained under AP, but not in vacuum. These results indicate the necessity and the importance of XAFS measurements under AP in the soft X-ray region.

In addition, we will develop the new AP chamber for a developed transfer vessel.

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