Time-Resolved Chemical State Analysis By Highly Sensitive High-Resolution PIXE

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ABSTRACT

A high-resolution PIXE system composed of a curved crystal and a position sensitive proportional counter was constructed for rapid chemical state analysis in air. A mechanism to measure the time-variation of PIXE spectra was installed to the system. The system was applied to obtain time-resolved spectra of sulfur Kβ. Time-dependent variation of the fine structure was recognized clearly in the S Kβ spectra obtained from marine sediment samples.

Keywords: chemical state analysis, high-resolution PIXE, time-resolved, S Kβ, v. Hamos

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1. INTRODUCTION

External-beam PIXE with high energy-resolution is an effective tool for direct investigation of the chemical bonding states of atoms in target materials. We have developed a wavelength-dispersive crystal spectrometer system for high-resolution PIXE measurement in air of atmospheric pressure. At the beginning of the development, we constructed a spectrometer composed of a flat analysing crystal and a position-sensitive proportional counter (PSPC) [1]. The utility of the system was well demonstrated by measuring chemical effects reflected in K X-ray spectra from third period elements [2-4]. The detection efficiency of the system has been recently improved by factor of 5~20, adopting two approaches. One is the development of a multistacked PSPC assembly of large sensitive area [5], which is combined with a flat crystal. The second approach is the construction of a focussing-type spectrometer which consists of a cylindrically curved crystal and a single PSPC in v. Hamos geometry. As for the third period elements, rapid chemical state analysis with measuring time of seconds to minutes is now practical. We have installed a mechanism to measure the time variation of PIXE spectra into the data processing software. Time-resolved measurement of Kα1,2 chemical shift was already performed using the spectrometer consisting of a stacked PSPC and a flat crystal [5]. However it was difficult to obtain time-resolved Kβ spectra of minor component elements since the signal to background (S/B) ratio was not high. The S/B ratio is greatly improved when using the focussing spectrometer. We apply the focussing spectrometer to time-resolved measurement of sulfur Kβ spectra.

2. EXPERIMENTAL SETUP

The geometry of focusing is schematically shown in figure 1(a). The radius of curvature of the analyzing crystal is denoted by r. When an X-ray source is located at a point S, X-rays diffracted by the crystal converge to the center axis FA-FB. The practical experimental setup is illustrated in figure 1(b). A target sample is placed in air and bombarded with a 2.1 MeV proton beam of 3 mm diameter. A curved crystal
and a PSPC are set on parallel long-stroke stages ST1 and ST2, respectively. A narrow entrance slit of 0.4 mm width is placed between the target and the crystal, at a position very close (~7 mm) to the proton beam spot on the target. The position of the entrance slit is considered to be the origin of dispersing X-rays in the spectrometer system. The X-ray path length is given by $\sim 2r/\sin \theta$ where $\theta$ is the angle of diffraction.

A cylindrical Ge (111) crystal with $r$ of 150 mm, 50 mm in height and 30 mm in width was used. The interplanar spacing $d = 0.327$ nm of Ge (111) is suitable for sulfur and phosphorus K X-ray measurements. The crystal is mounted on a double-tilt stage (OP1 and OP2). The stage is adjusted by remote control so as to obtain the maximum detection efficiency. A PSPC of 7.4 mm in sensitive height and 30 mm in sensitive width is mounted on stage OP3 and placed perpendicular to the direction of the X-ray path. The PSPC employs a 7-µm-diameter carbon fiber as the anode. Mixed gas of Ar:CH₄ (9:1) or Kr:CO₂ (9:1) is used as the counter gas. The X-ray path from the entrance slit to the PSPC is enclosed within a polyethylene bag filled with helium gas.

3. RESULTS AND DISCUSSION

The detection efficiency of the focusing system is considerably increased compared to that with the previous systems: eleven times of the flat crystal-single PSPC system, and twice of the flat crystal-stacked PSPC system. In addition to the absolute detection efficiency, S/B ratio is greatly improved. The ratio of the Kβ₁ peak ($\theta = 50.4^\circ$) height to background (around $\theta = 49.7^\circ$) obtained with the curved crystal-single PSPC system is 200. This P/B ratio is five times higher than that obtained with the flat crystal-stacked PSPC system.

Like the flat crystal-stacked PSPC systems, the new system is useful for rapid chemical state analysis through Kα₁,₂ chemical shift measurements within a few seconds to one minute. The Kβ spectra reflect the nature of chemical bonding more prominently than the Kα spectra. However for the third period elements, the production cross sections of Kβ are only 1-10 % of those of Kα. Using the new system, measurements of the Kβ spectra can also be carried out in a short time. Figures 2 (a) and (b) show examples of the S Kβ spectra obtained in 5 to 12 minutes of measuring time. Difference in the fine structures of Kβ spectra from elementary sulfur, iron (II) sulfide, Na₂SO₃ and Na₂SO₄ are well recognized.
FIGURE 2. S Kβ spectra of (a) elementary S (FWHM of Kβ₁ peak = 6.7 eV) and Fe (II) sulfide, (b) Na₂SO₃ and Na₂SO₄, and (c) time-resolved S Kβ spectra of a marine sediment sample: proton beam current 30-50 nA; 0.50 eV/channel. The sediment sample was collected from Tokyo Bay in Nov. 2000, kept frozen until PIXE measurement, defrosted and deposited on a Millipore filter. The filter loaded with the sample was taken out of a container charged with N₂ gas immediately before the measurement started.

The improvement of the S/B ratio made it possible to determine the fine structures in Kβ spectra of minor component elements, which had been hidden by the background in the previous systems. We measured time-variations of S Kβ spectra using several marine sediments samples. Along with the Kβ spectra from known targets, time-resolved Kβ spectra from one of the marine sediment samples (S concentration = 2 weight %) are shown in figure 2 (c). The Kβ spectra of the sediment sample from early stage of measurement (0-20 minutes) resemble those of elementary S or sulfide S. After 20 minutes, a low-energy satellite peak Kβ', evidence of S-O bonds, appeared. The intensity ratio of the Kβ'/Kβ₁ in the spectrum obtained after 50 minutes was much smaller than that of sulfate S, and similar to that of sulfite S. However, the high-energy shoulder Kβ'', a characteristic of sulfite S, was not detected in this spectrum. This indicates that a portion of S atoms in the sediment sample was oxidized by air, and once the oxidation had started, the portion quickly reached the highest oxidation state. Time-variation of chemical state of sulfur in practical samples was observed through PIXE analysis for the first time.

REFERENCES