Progress on the Bent Laue Analyzer for Actinide Fluorescence XAFS

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Introduction

Previous work reported on in APS activity reports has demonstrated the potential of using a bent silicon crystal in the Laue geometry as an x-ray wavelength dispersive analyzer [1]. This report updates that work. We have designed and built a prototype analyzer with three separate motions (θ, focus, slit angle) for use between 12 and 18 keV. This device has been described recently by Kropf et. al. [2]. Previous work had demonstrated only a limited background rejection capability, primarily due to the Soller slit design. However, the complete instrument, with an adjustable, fine array of Soller slits, has achieved a background rejection of nearly 1000:1. We have demonstrated the effectiveness of this instrument in resolving neighboring actinide $L\alpha$ lines and in measuring the x-ray absorption fine structure (XAFS) spectra of as low as 0.6 ± 0.2 milligram of neptunium per gram of uranium (mg Np/g U) [3].

Methods and Materials

Measuring the L-edge fluorescence XAFS in mixed actinide samples is a challenging problem. For the samples we report on here, excellent energy resolution is required, since the $L\alpha_1$ fluorescence lines for U, Np, and plutonium (Pu) are separated only by about 350 eV; the $L\alpha_2$ lines are separated by less than 150 eV from neighboring $L\alpha_1$ lines. We have used the bent Laue analyzer (BLA) to study an approved testing material (ATM) of spent uranium oxide nuclear fuel that is primarily uranium (IV) oxide. This sample also contains small quantities of fission products [4-7]. We have also studied oxidized alteration phases that formed on the surface of this ATM during aqueous corrosion testing [4]. Since the matrix in the alteration phases is predominantly uranium (VI) oxide [6], these particles are easily distinguished from the unaltered spent fuel. We did not observe Np incorporated into the alteration phases, with an estimated sensitivity of better than 0.3 mg Np/g U [6].

The 140-μm Si wafer used for the BLA had a <100> surface normal, and the <111> planes were used as the diffracting planes, resulting in a 35.3° asymmetry angle. The active area was a 30×120 mm rectangular window cut into the bender form to allow the x-rays to pass through to the detector. Direct x-rays were absorbed by 70-mm-long stainless-steel Soller slits, spaced at 1° intervals (about 3.6 mm apart at the analyzer center).

Two NaI scintillation detectors were used to detect x-rays. The highest energy resolutions achieved for the analyzer were 71 eV and 79 eV full width at half-maximum (FWHM) at the positions of the two detectors for the uranium $L\alpha_1$ fluorescence line (13,615 eV). All measurements reported on here were made at MR-CAT undulator beamline 10-ID at the APS, with a focused beam (spot of about 10 μm).

Results

Figure 1 shows a scan of intensity versus energy for the ATM sample as the incident energy is held fixed both below and above the Pu L_3 edge while the analyzer angle is scanned. Strontium Kα fluorescence is visible in both scans. The Np $L\alpha$ fluorescence is not visible on this scan because of the noise level (count time).
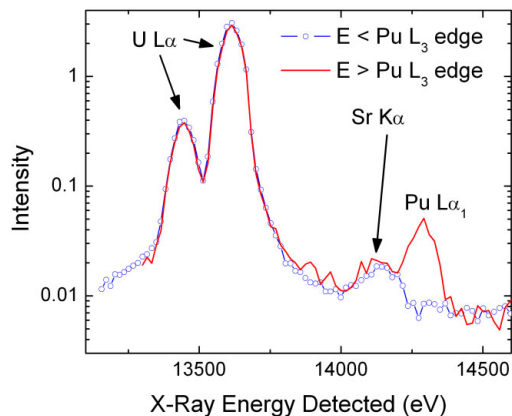

FIG. 1. Bent Laue analyzer angle scans with ATM sample (incident x-ray energy above and below the Pu L_3 edge, optimal tune for Pu $L\alpha_1$).

Figure 2 shows the absorption spectra for Pu, Np, and molybdenum (Mo) in the ATM sample. Plutonium, with the highest concentration (8.3 mg Pu/g U [7]), gives the best signal. The extended x-ray absorption fine structure (EXAFS) data clearly identify the Pu in a PuO_2-like phase [8]. The Pu is likely incorporated in the UO_2 matrix. The Mo is present at a lower concentration (3.0 mg Mo/g U [7]), and the Fourier transform reveals some Mo-O nearest neighbors but a larger number of Mo-metal nearest neighbors, indicating that the Mo is present in
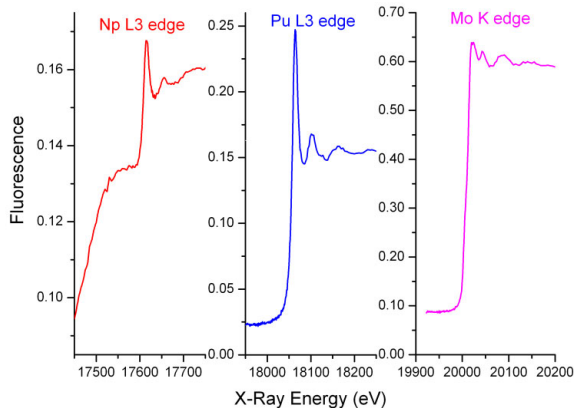
FIG. 2. X-ray absorption spectra of unaltered ATM sample using the BLA.

both oxide and metallic forms. The Np is present in an even smaller amount: 0.4 mg Np/g U calculated by Guenther et al. [7], or 0.6(2) mg Np/g U as measured from the fluorescence spectra. The background on which the Np L_3-edge spectrum rides is composed of the uranium fluorescence that makes it through to the detector and an unexpected contribution from inelastic scattering attributable to the uranium. At 1 part in 1700, the Np signal-to-background ratio is 0.15, barely large enough to measure a usable EXAFS signal. The data shown are summed from 24 hours of data acquisition. By comparing the Np XANES to published spectra [9], it seems reasonable to assign to the Np an oxidation state of +4. The EXAFS data also suggest an NpO_2-like phase, given the similarity to the PuO_2 spectrum.

Discussion

The BLA has exhibited promising results for a very difficult system. In fact, the high background rejection observed could recommend this type of detector for other applications. A BLA with a peak-to-valley ratio of better than 500:1 extends useful spectroscopic limits by as much as 50 when compared with current, state-of-the-art germanium detectors, when used for mixed actinides. If a higher-resolution analyzer (thinner crystal) and slightly more efficient Soller slits are used, it is likely that additional sensitivity (factor of 3 in increase) could be achieved. However, given the interference of inelastic scattering from the uranium M edges, it is difficult to envision making useful EXAFS measurements at concentrations lower than 0.05 mg Np/g U, which is 10 times lower than the current samples.

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