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Author

Shuh, David K.

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SOFT X-RAY SPECTROMICROSCOPY OF ACTINIDE PARTICULATES

Hans J. Nilsson,^{1,2} Tolek Tyliczszak,¹ Richard E. Wilson,^{1,3} Lars Werme,^{2,4}
and David K. Shuh¹

¹Chemical Sciences Division, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720 USA

²SKB, Box 5864, S-102 40, Stockholm, Sweden

³Nuclear Sciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720 USA

⁴Department of Physics, Uppsala University, Box 530, S-751 21, Uppsala, Sweden

1 INTRODUCTION

The Advanced Light Source Molecular Environmental Science (ALS-MES) beamline 11.0.2 scanning transmission x-ray microscope (STXM) has been used to perform soft x-ray spectromicroscopy investigations of solid oxide particulates of uranium, neptunium, and plutonium. The recent progress in the development and application of soft x-ray spectromicroscopy to fundamental scientific studies of actinide materials is described. The motivation for the use of soft x-ray spectromicroscopy is to investigate actinide absorption edges that are not commonly investigated, and to spatially resolve areas within small particles where there are chemically different properties. The K-edges of several important light elements are also located in the soft x-ray region. Of particular relevance for actinide materials is the oxygen K-edge since the actinide oxides are particularly complex and have yet to be fully understood. As soft x-ray STXM spectromicroscopy becomes more fully developed and the actinide spectroscopy understood from a fundamental perspective, this technique will have relevance in several areas of actinide science. A clear area of application will be in the field of actinide environmental chemistry to investigate colloids, interface science, biogeochemical interactions, and transport of actinides that are related to particulates.

2 EXPERIMENTAL

All soft x-ray STXM spectromicroscopy measurements were performed at the ALS-MES beamline at the Lawrence Berkeley National Laboratory (LBNL). The beamline uses an elliptical polarized undulator to produce x-rays from 80 eV to 2160 eV and the ALS-MES STXM resides on a branchline optimized for spectromicroscopy, both of which have been described previously.¹ This results in excellent spatial resolution of 30 nm and an energy resolution of up to 7500 (E/ΔE). Operation of the STXM under ambient atmosphere facilitates experiments using radioactive materials. STXM samples generally consist of solid phase particles in the size range of 50 nm to 2000 nm sandwiched between two Si₃N₄ windows that are attached to an indexed Al holder. To date, several solid state actinide compounds have been investigated using the ALS-MES STXM. The initial actinide particle spectromicroscopy studies have focused on nominal AnO₂ materials obtained from common sources. The Pu material attached to a particle characterized in this investigation

was obtained from an insoluble precipitate isolated following the preparation of a ^{242}Pu stock solution after dissolution and centrifugation.

3 RESULTS

The near edge x-ray absorption fine structure (NEXAFS) spectra of UO_2 , NpO_2 , and PuO_2 are shown in Figure 1. The $4d_{5/2}$ edge spectra from the three actinide dioxides are quite similar in appearance. Previous measurements of U_3O_8 and UO_3 have yielded NEXAFS spectra shifted to higher energies by 0.9 eV and 1.1 eV respectively.² Thus, actinide oxidation states can be determined from the measurements of charge state shifts at the $4d_{5/2}$ edges, although the magnitude of the shifts are small. This also indicates that a mixture of actinide oxidation states could be identified by actinide $4d_{5/2}$ peak broadening.

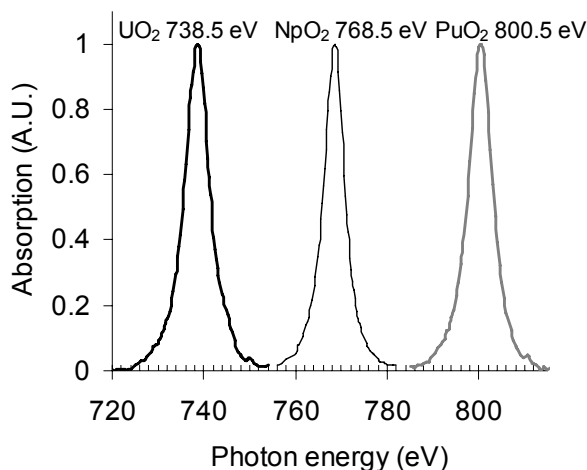


Figure 1 *Spectromicroscopy NEXAFS actinide $4d_{5/2}$ spectra from UO_2 , NpO_2 , and PuO_2 obtained from particles with dimensions of 100 nm to 500 nm. The spectra have been smoothed, background subtracted, and the $4d_{3/2}$ edges have been removed.*

Figure 2 shows a Pu elemental map (left) and NEXAFS spectra (middle, right) obtained from the precipitated solid described in the experimental section. The Pu elemental map is generated from the on-resonance absorption at 800 eV contrasted to the absorption below the threshold, at 792 eV (left). A comparison of the Pu $4d_{5/2}$ NEXAFS spectra collected from a 40 nm diameter Pu-rich region of the particle located by the elemental map, to that of PuO_2 , shows that the Pu material associated with the particles is not PuO_2 (middle). There is a distinct energy shift compared to the PuO_2 spectrum, indicating that there is a clear difference in Pu oxidation state.

The composition of the particles was identified by NEXAFS spectromicroscopy. The right panel of Figure 2 shows the Si K-edge spectra obtained from a bulk-like region of the particle compared to the absorption background obtained from a Si-mirror in the beamline. The Si K-edge spectrum obtained from the particles is characteristic of the signature of a well-known Si material, SiO_2 .³

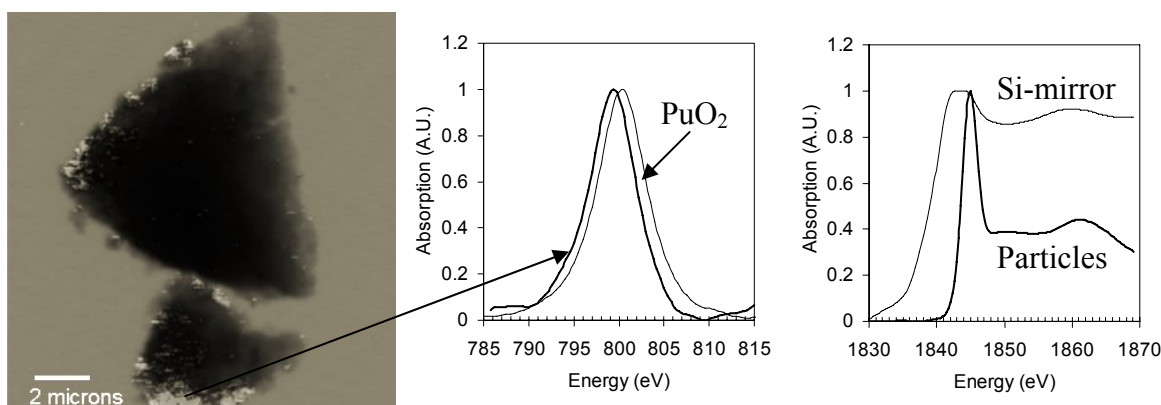


Figure 2 *Pu elemental map (left) showing Pu (light) on the particles (dark) generated from a precipitate obtained during the preparation of a Pu stock solution. The middle and right plots are the NEXAFS spectra collected from the particles at the Pu 4d_{5/2} edge and the Si K-edge, respectively. The spectra are compared to a reference PuO₂ spectrum and the Si absorption from beamline mirrors.*

4 CONCLUSIONS

Soft x-ray STXM spectromicroscopy is beginning to develop into a useful tool for investigating actinide particulates. The spectroscopy at the actinide 4d_{5/2} edges can provide chemical information about the oxidation states of actinides, although work remains to more fully elucidate the fundamental charge state shifts with reference materials. The absorption at the actinide 4d_{5/2} edges provides a suitable response to image the morphologies of sub-micron actinide particles down to the 30 nm spatial resolution level and can derive actinide elemental maps with the same dimensions. Spectromicroscopy has successfully characterized actinide particles of unknown composition and has shown that the Pu associated with the SiO₂ particles in this investigation is not primarily PuO₂.

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