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Electron energy loss spectroscopy investigations through nano-ablated actinide dioxide samples

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ABSTRACT

Lamellas of actinide (Th, Np) dioxides ($\sim$10 μm × $\sim$10 μm × $\sim$0.02–0.20 μm) were produced by focused ion beam for transmission electron microscopy and electron energy loss (EEL) spectroscopy examinations. These samples allow quantitative analysis of the EEL spectra recorded for ThO_2, and NpO_2 as a function of the thickness. The O and P edges were recorded over zero loss to 400 eV loss. ThO_2 and NpO_2 EEL spectra are compared with those reported earlier for UO_2. The energy lost was studied through a range of thicknesses going from $\sim$20 to $\sim$200 nm. It was observed that the O and P edges are not thickness dependant as expected confirming the core loss nature of these edges. The edges allow reconstruction of the electronic transitions, the lowest energy loss edges for P transitions corresponds to P_3 electron transitions (from 15 to 17 eV) from the 6p(2/3) level. Two next P_1 and P_2 edges are partially overlapping. The followed O edges are suggested to be a pre-peak and the $O_{4,5}$ transitions. The edge analysis allows also better interpretation of the loss spectrum with identification of the plasmon peak of the core electron transition edges. The technique may be applied for identification of the actinide in fuels or waste forms.

1. Introduction

Transmission electron microscopy (TEM) has been used since decades for the characterization of actinide materials (Moore, 2010) pointing out the potential of electron energy loss (EEL) spectroscopy for their analysis. Several EEL spectroscopy studies may be found about thorium or neptunium phases in the literature.

Electron and X-ray interactions with matter were used as probes to characterize the structure and chemistry of zirconia–thoria–urania ceramics (Curran et al., 2003) prepared by co-precipitation of Zr, Th and U salts. These investigations revealed the phase structure and chemistry of these materials.

For neptunium, Buck and Fortner (1997) detected low levels of transuranics with EEL spectroscopy on the transmission electron microscope. More recently Buck et al. (2010) examined the problems associated with analysis of low levels of neptunium in a uranium matrix with EEL spectroscopy. The detection of neptunium in a matrix of uranium can be impeded by the occurrence of a plural scattering event from uranium (U-M_5 + U-$O_{4,5}$) that results in severe overlap on the Np-M_5 edge at 3665 eV. Low levels of Np (1600–6300 ppm) can be detected in uranophane [$Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$], by confirming that the energy gap between the Np-M_5 and Np-M_4 edges is at 184 eV and showing that the M_4/M_5 ratio for the neptunium is smaller than that for uranium.

The low energy EEL investigations of actinide compound samples in the TEM require careful preparation such as that provided by focus ion beam (FIB). In the present work, actinide dioxide specimens were extracted by FIB and were investigated by EEL spectroscopy in order to determine the electronic structure of tetravalent actinides and to contribute to the analysis of these actinides in fuel and waste form materials.

2. Experimental and data treatment

2.1. Actinide dioxide sample

The thorium dioxide (ThO_2) sample was obtained by gelation. The material was calcined. The powder was then sintered under inert atmosphere at $\sim$1000 °C.

Similarly NpO_2 was obtained by gelation under reducing conditions (iodide) followed by calcination. The powder was further sintered under reducing conditions.

The sample preparation by FIB, the TEM observations and EELS measurements were carried out at the electron microscopy facility at PSI following the protocol used for UO_2 in a recent study

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(Degueldre et al., 2013). The facility is adapted for the handling of alpha isotope material with an activity below 100 LA (limite d'autorisation) allowing the work on small actinide sources.

2.2. Focused ion beam

The FIB work was carried out with a Zeiss Nvision 40 Crossbeam workstation. It includes both a focus ion beam and a scanning electron microscope. The FIB unit operates with a source of Ga^+ ions that can be accelerated from 1 to 30 kV; the SEM unit operates from 0.5 to 30 kV. The FIB resolution reaches 4 nm for 30 kV and 1.6 nm for the SEM at 30 kV. The minimum usable Ga^+ ion beam size is 4 nm.

2.3. Transmission electron microscopy and electron energy loss spectroscopy

The transmission electron microscope is a JEOL 2010 type TEM unit equipped with a LaB_6 electron gun and operated at 200 keV. The TEM unit is equipped with a Gatan Enfina electron energy loss spectrometer. The EELS energy resolution was 0.5–1.0 eV in the studied domain. EEL spectra images were taken by Gatan Orius 11Mpixels CCD camera. The EELS data were acquired and worked out using Gatan's EELS analysis tools included in Gatan DigitalMicrograph software. The analysis routines follow a similar approach to that adopted in EL/P. Once a spectrum from 0 to about 500 eV, including the zero loss peak (ZLP) has been acquired, the menu 'thickness measurement' in DigitalMicrograph® may be used to evaluate the local sample thickness with a precision of 10%. The conditions for the EEL spectra records were: energy of incident electron 200 keV, electron energy calibration at zero loss, β: 5 mrad, θ: 5 mrad, aperture 3 mm and a current density 30 pA cm^{-2} for an electron spot of $\sim$15 nm.

3. Results

3.1. Sample preparation by focused ion beam

The powder samples of actinide dioxides (AnO_2) were glued with C pasta on a typical SEM Al stub. The powder sample was first examined using the SEM instrument of the FIB unit. The grains form large particle aggregates with sizes about several ten of μm. The thickness of the particle aggregates was about 20 μm. Trapezoidal digging across and aside the sample was necessary for the extraction of a thin lamella. This digging was carried out using 30 kV accelerated Ga^+ ions. For a current of 30 nA, 10 μm were eroded. The coarse lamella, about 1 μm thick, now liberated on 3 sides was subsequently freed from below using lateral-diagonal ion milling. Once the coarse sample prepared, the transfer needle was approached and attached using carbon strip produced by deposition of carbon from a precursor gas decomposed by the ion beam. This allowed fixing the sample in order to proceed to its complete liberation by ablation of the 4th side. The coarse lamella was subsequently lifted and approached to the TEM sample carrier made of a 3 mm half moon holding a comb like structure, the so-called 'omniprobe grid'. The specimen was fixed by carbon coating to one of the comb teeth. It was then freed from the transfer needle by sputtering away the carbon strip on the needle side.

The attached TEM sample was then shaped to an edge with variable thickness, allowing for the study of the thickness dependence of the EELS signal. For the fine milling to the final polishing, the ablation was carried out with a 2 kV Ga^+ ion current of 80 pA and with an incident angle from 30° to 1°. The TEM samples were about $10 \times 10 \times (0.020–0.200)$ μm surrounded by thicker edges for mechanical support. It should be noted that during preparation the abrasion is made using diagonal incidence that reduces the impact of gallium from the point of view of damage and contamination. Both implantation and damage data described in the following were estimated insignificant for an orthogonal implantation, which corresponds to a conservative Ga FIB treatment. Because of its higher porosity the ThO_2 sample morphology was more uneven.

3.2. Electron-microscopy and energy loss spectroscopy

The FIB produced samples were examined by TEM (see Fig. 1) prior to EEL analysis. The locations of the various domains for EEL analysis with respective thicknesses ranging from 20 to 200 nm are located on line drawn on the lamellas (see Fig. 1).

The EEL spectrum shown in Figs. 2 and 3 is plotted on a log scale. They reveal the following features:

- the zero loss energy peak (intensity used to normalize the spectra)
- the plasmon part of the spectrum, and
- the core loss electron edges.

The plasmon part develops below the core (P & O transitions as quoted) parts of the spectra. The thickness of the specimen at the recorded EEL spectra location was calculated as performed earlier (Degueldre et al., 2013).

Interestingly, the EELS spectrum shows in the low energy part above the plasmon the P_3 edge of the tetravalent actinide that peaks at 15–17 eV. The plasmon hump partially superposes on the 2 other P edges, namely P_2 and P_1 edges around 27 and 35 eV respectively, as well as the O L edge at 42 eV. This statement on the P_3 edge is carefully assessed in the discussion section, as these actinide P peaks were never reported in the EELS literature. Table 1 presents the characteristics of the EELS peaks recorded.

The O_4 and O_5 edges of Th and Np are known and are to be found between 95–102 and 109–115 eV respectively. As reported by Moore and van der Laan (2007) (Veal and Lam, 1974) the edges are in fact the O_5(pp) edges with pp standing for pre-peak and the $O_{4,5}$ respectively.

The results gained for the core edges and on the plasmon peak are discussed in Section 4.

4. Discussion

The spectra were further analysed to extract the relevant spectroscopic data.

The external electronic configuration of An^{4+} is $5f^n$ e.g. (Ippolito et al., 2005). The f electrons are however not detected in EEL spectra because their transitions (around 2 eV e.g. (Veal and Lam, 1974)) are masked in the zero loss peak.

The full electron configuration of An^{4+} is:

$$\underset{K}{1s^2}\ ,\underset{L}{2s^2p^6}\ ,\underset{M}{3s^2p^6d^{10}}\ ,\underset{N}{4s^2p^6d^{10}f^{14}}\ ,\underset{O}{\mathbf{5s^2p^6d^{10}f^{n}}}\ ,\underset{P}{\mathbf{6s^2p^6d^0}}\ ,\mathbf{7s^0} \qquad \text{corresponding to the transitions}$$

with $n = 0, 2, 3$ for Th^{4+}, U^{4+} and Np^{4+} respectively.

However, the ion electronic configuration has to be completed for the molecular orbitals. The study of small actinide molecules presents a challenge for experimental and theoretical chemists. The nearly degenerated 5f, 6d, 7s, and 7p orbitals give rise to a multitude of possible configuration interactions and a dense manifold of low-lying states, which complicates computations and renders assignment of experimental spectra difficult. (Infante et al., 2007; Zhou and Ozolins, 2011). However, any energy changes due to degeneration, hybrid or molecular orbital formation are rather small.