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Determination of U-oxidation states in the brannerite structure by electron energy-loss (EELS), x-ray photoelectron (XPS) and diffuse reflectance (DRS) spectroscopies.

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Titanate based ceramics (synroc) have received considerable interest as suitable matrices for the immobilisation of high-level nuclear waste (HLW). Actinide-bearing phases, such as zirconolite and pyrochlore, have been extensively studied. Brannerite (ideally UTi_2O_6) is a minor phase in titanate ceramics specifically targeted for the immobilisation of actinide-rich, plutonium-bearing nuclear wastes. As brannerite contains 62.8 wt% UO_2 it can account for a significant fraction of the total amount of actinides in the waste form.

It is anticipated that crystalline waste forms would be stored in geological repositories. The oxidation state of actinides would affect their release rates from waste forms in geologic repositories. Consequently, determining the oxidation states of radionuclides (e.g. uranium and plutonium) in host phases and their alteration products is important for evaluating the probable long-term behaviour of candidate titanate waste forms.

The chemical states of uranium in the brannerite structure have been investigated previously using optical and x-ray absorption spectroscopies. Recently we have used TEM/EELS and XPS to investigate the U oxidation state in these materials. All of these spectroscopic techniques have demonstrated that they are capable of identifying different oxidation states. The main advantage of TEM/EELS over other conventional spectroscopic methods, such as DRS and XPS, is that the electronic density of states in a small volume of material can be probed. Furthermore, because of the high spatial resolution in TEM/EELS, analyses from very fine grained and/or heterogeneous materials can be achieved with confidence. The focus of this study was to ascertain if mixed chemical states of uranium could be consistently determined by these techniques.

The TEM/EELS spectra of UO_2 and $SrCa_2UO_6$, used as U^{4+} and U^{6+} standards, are displayed in Figure 1, showing variations in the $UM_{4,5}$ peak intensities. The M_4 and M_5 peak intensity ratio is sensitive to the formal 5*f*-electron occupancy, and the uranium oxidation state can be derived from the M_4 and M_5 peak ratio and known standards. The intensity of the M_4 and M_5 peaks was derived from a multiple least squares fit routine using four Lorentzian functions. The peak intensity ratio (M_4/M_5) and the derived U valency for all the samples analysed are listed in Table 1.

The binding energy of the U $4f_{7/2}$ XPS peak is directly related to the oxidation state of uranium. Figures 2a and 2b show the U $4f_{7/2}$ XPS spectra of freshly fractured $Th_{0.7}U_{0.3}Ti_2O_6$ and $Th_{0.55}U_{0.3}Ca_{0.15}Ti_2O_6$ surfaces. Each spectrum was fitted with three mixed Gaussian/Lorentzian peaks, corresponding to U^{4+}, U^{5+} and U^{6+}, respectively. Hence XPS results confirm that the U oxidation state in $Th_{0.7}U_{0.3}Ti_2O_6$ and $Th_{0.55}U_{0.3}Ca_{0.15}Ti_2O_6$ is predominantly 4+ and 5+, respectively. This is supported by the DRS results, as shown in Fig. 3. The DR spectrum of $Th_{0.55}U_{0.3}Ca_{0.15}Ti_2O_6$

shows a strong band around 6990 cm^{-1}, which is characteristic of U^{5+}. A number of bands due to U^{4+} are observed in the spectrum of $Th_{0.7}U_{0.3}Ti_2O_6$.

Our preliminary results show that there is a good agreement in the U-oxidation state as determined by the different spectroscopic techniques for all the synthetic samples. The agreement is not as good for the natural samples, presumably due to the inhomogeneity of the samples.

Table 1. A list of samples and techniques (ticks indicate the techniques used for each sample), and the EELS results.

Composition	Nominal U valency	EELS M_4/M_5 (derived valency)	EELS	XPS	DRS
UO_2 (U^{4+} standard)	4+	0.431 ± 0.005 (4.0)	√	-	-
$SrCa_2UO_6$ (U^{6+} standard)	6+	0.581 ± 0.019 (6.0)	√	-	-
UTi_2O_6	4+	0.392 ± 0.025 (3.5)	√	√	√
$Y_{0.5}U_{0.5}Ti_2O_6$	5+	0.515 ± 0.035 (5.1)	√	√	√
$U_{0.8}Ca_{0.2}Ti_2O_6$	4.5+	0.441 ± 0.017 (4.2)	√	√	√
$Th_{0.7}U_{0.3}Ti_2O_6$	4+	0.425 ± 0.019 (3.9)	√	√	√
$Th_{0.55}U_{0.3}Ca_{0.15}Ti_2O_6$	5+	0.532 ± 0.034 (5.3)	√	√	√
$*(U_{0.65}Ca_{0.22}Y_{0.06}Pb_{0.05}Th_{0.04}Ln_{0.03})_{1.05}$ $(Ti_{1.93}Si_{0.11}Al_{0.06}Fe_{0.05})_{2.09}O_6$	4+ - 5+	0.464 ± 0.029 (4.5)	√	√	√
$*(U_{0.80}Ca_{0.30}Pb_{0.06}Th_{0.02}Y_{0.02}Ln_{0.01})_{1.21}$ $Ti_{1.94}Fe_{0.06}Al_{0.02})_{2.02}O_6$	4+ - 5+	0.518 ± 0.034 (5.2)	√	√	√
$*(U_{0.86}Y_{0.04}Th_{0.03})_{0.93}(Ti_{2.06}Fe_{0.04})_{2.10}O_6$	4+ - 5+	0.503 ± 0.021 (5.0)	√	√	√

* Denotes natural brannerite, composition determined by SEM-EDX analysis.

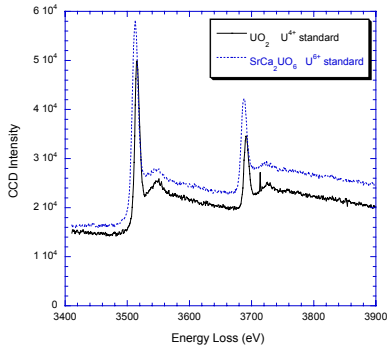

Figure 1. U $M_{4,5}$ EELS spectra of U valence standards, UO_2 and $SrCa_2UO_6$.

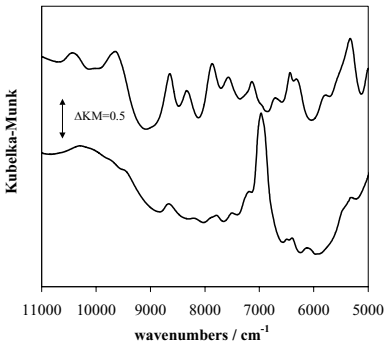

Figure 3. DR spectra of $Th_{0.7}U_{0.3}Ti_2O_6$ (bottom) and $Th_{0.55}U_{0.3}Ca_{0.15}Ti_2O_6$ (top).

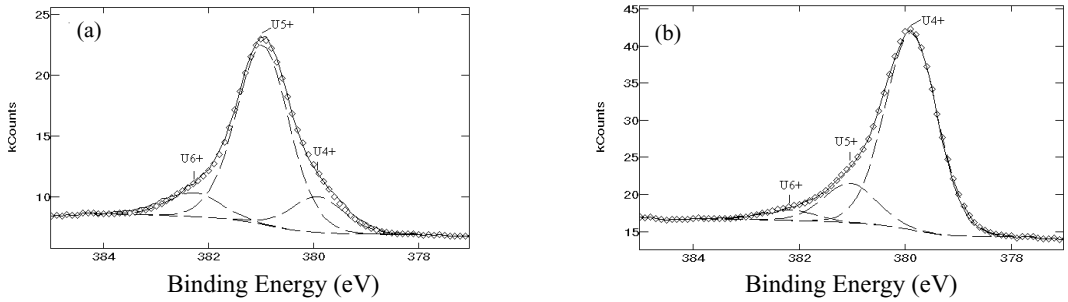

Figure 2. XPS spectra for freshly fractured (a) $Th_{0.7}U_{0.3}Ti_2O_6$, and (b) $Th_{0.55}U_{0.3}Ca_{0.15}Ti_2O_6$ surfaces.

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