



# XPS spectra of the U<sup>5+</sup> compounds KUO<sub>3</sub>, NaUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub>

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## ABSTRACT

Valence states of uranium in three ternary uranates KUO<sub>3</sub>, NaUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> were studied using X-ray photoelectron spectroscopy (XPS). The analysis of the U4f photoelectron peak positions, peak widths at half maximum and satellite positions of U4f peaks, shows that the uranium in these compounds is present in a single valence state, namely U<sup>5+</sup>. Since the surface of these compounds is extremely susceptible to oxidation, the XPS spectra were measured after a carefully controlled etching of the surface using an Ar<sup>+</sup> ion beam so that the surface oxidation does not affect the XPS studies.

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## 1. Introduction

The local structure around uranium ions and their exact oxidation states in various uranium ternary oxides have been one of the key topics in actinide solid state research [1–8]. Difficulties with assigning the valences of uranium in NaUO<sub>3</sub> [9], KUO<sub>3</sub> [10] and RbUO<sub>3</sub> [11] have been reported. Formally, these compounds have only one uranium valence, namely U<sup>5+</sup>. Their crystal structures are based on a perovskite structure with only one crystallographic position for U (NaUO<sub>3</sub> [9], KUO<sub>3</sub> [10] and RbUO<sub>3</sub> [11]). Accordingly, there is no objection against classifying these compounds as monovalent compounds. However, reported X-ray photoelectron spectroscopy (XPS) spectra exhibited doublet structures at the U4f peaks, indicating possibility for the existence of mixed valence state [1,12]. The proposed mixed valence was investigated by measuring the UL<sub>3</sub> edge X-ray absorption near edge structure (XANES) spectra of KUO<sub>3</sub>, RbUO<sub>3</sub>, NaUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> [7]. The comparison between measured and calculated XANES spectra, based on self-consistent field full multiple scattering method, showed an excellent agreement by assuming the existence of only U<sup>5+</sup> ions in the structures of these compounds [7].

In this paper, we study the origin of the multiple peak structure in the U4f XPS spectra of KUO<sub>3</sub>, NaUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub>, in order to resolve the inconsistency between the XPS and XANES data. The peak position, peak width at half maximum (FWHM), and satellite peak position of the measured U4f spectra were analyzed to identify the valence states of uranium. The results

clearly show that KUO<sub>3</sub>, NaUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> are monovalent uranates, with a valence state corresponding to U<sup>5+</sup>. However, the intrinsic XPS spectra of U<sup>5+</sup> could be obtained only after removing the surface oxide, which is achieved by carefully controlled Ar<sup>+</sup> ion beam etching.

## 2. Experimental

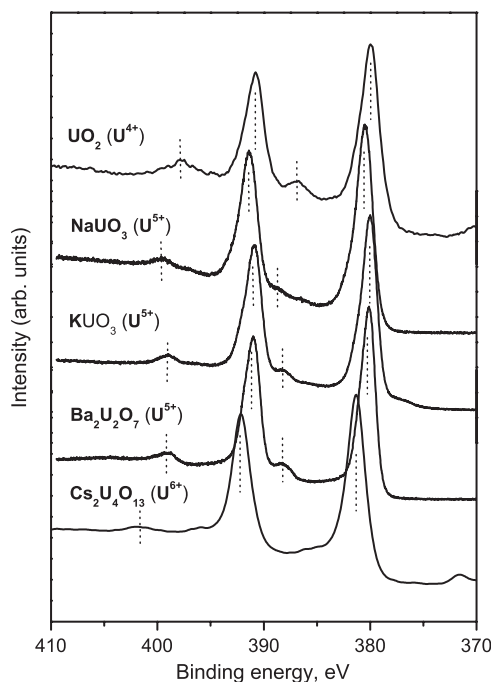
The sample preparation methods for synthesizing KUO<sub>3</sub>, NaUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> compounds are described in [7,13]. The XPS measurements were performed with an upgraded ESCALAB 220i-XL spectrometer, using monochromatic AlK $\alpha$  radiation with a typical spot size of about 500  $\mu$ m. The anode was operated at 15 kV and 150 W. The base pressure is better than  $1 \times 10^{-10}$  mbar. In order to remove the surface oxide, the samples were etched using a 3 kV Ar<sup>+</sup> ion beam. We used a current of 1  $\mu$ A and raster size of 2 mm at a chamber pressure of about  $5 \times 10^{-8}$  mbar during etching. The high resolution spectra were collected with 20 eV pass energy corresponding to an energy resolution of about 0.1 eV. The data acquisition and processing were carried out using the Avantage Data Spectrum Processing Package (Thermo VG Scientific). The C1s peak position of 285.0 eV was used to calibrate the spectra.

## 3. Results and discussion

The XPS spectra of the compounds KUO<sub>3</sub>, NaUO<sub>3</sub>, Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> and reference compounds UO<sub>2</sub> (U<sup>4+</sup>) and Cs<sub>2</sub>U<sub>4</sub>O<sub>13</sub> (U<sup>6+</sup>) are shown in Fig. 1.

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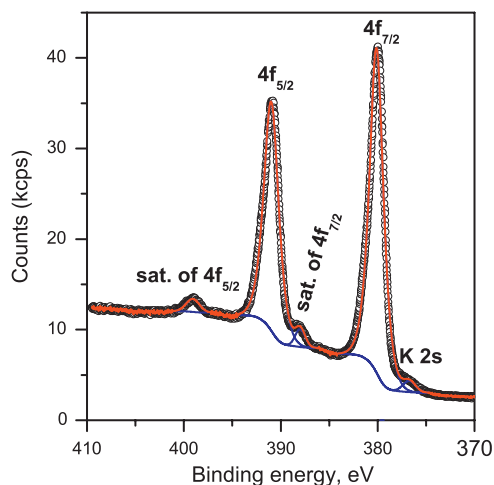
E-mail address: [junhu.liu@sckcen.be](mailto:junhu.liu@sckcen.be) (J.-H. Liu).



**Fig. 1.** The U4f XPS spectra of NaUO<sub>3</sub>, KUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> measured after 10, 20 and 15 s etching times, respectively. The XPS data of UO<sub>2</sub> and Cs<sub>2</sub>U<sub>4</sub>O<sub>13</sub> [14] are also shown for a comparison. No etching for UO<sub>2</sub> and Cs<sub>2</sub>U<sub>4</sub>O<sub>13</sub> was carried out before measuring spectra.

The spectra of NaUO<sub>3</sub>, KUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> were collected in the 370–410 eV energy range after about 10–20 s etching with an Ar<sup>+</sup> ion beam. The UO<sub>2</sub> and Cs<sub>2</sub>U<sub>4</sub>O<sub>13</sub> have been used as reference compounds for U<sup>4+</sup> and U<sup>6+</sup> [14] oxidation states, respectively. The XPS data on UO<sub>2</sub> were obtained with same instrument as used in present study. In all spectra, we observed four peaks which originate from U4f excitations. The most intense peaks at about 380 and 392 eV correspond to the spin–orbit (L–S) split U4f<sub>7/2</sub> and U4f<sub>5/2</sub> states, respectively. The low intensity peaks at about 388 and 400 eV exhibit a drastic energy dependence on the uranium valence states, see Fig. 1. These low-intensity excitations are shake-up satellites [5], which occur as a consequence of the change in electrostatic potential during the photoelectron excitation process. Namely, the XPS process can modify the energy of the valence electrons in such a way that the core level electrons experience an increase in the energy barrier which they need to overcome. This will cause a decrease in the core level electron kinetic energy and the appearance of an additional/satellite peak at the high binding energy (BE) side of the main peak. This is applicable for both U4f<sub>7/2</sub> and U4f<sub>5/2</sub> states. The BE of the U4f satellite peak is much more sensitive to the valence state than the BE of the main U4f peak, so that they can be used as a nice probe to identify the U chemical state. In UO<sub>2</sub> (U<sup>4+</sup>) the satellite peaks appear at energy of about 6.8 eV than main U4f<sub>7/2</sub> and U4f<sub>5/2</sub> peaks. In the case of NaUO<sub>3</sub>, KUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> the satellite peaks occur at about 7.9–8.1 eV from the main U4f<sub>7/2</sub> and U4f<sub>5/2</sub> peaks. In Cs<sub>2</sub>U<sub>4</sub>O<sub>13</sub> (U<sup>6+</sup>) the energy separation is about 10 eV, so that the satellite peak of U4f<sub>7/2</sub> overlaps with the U4f<sub>5/2</sub> peak and cannot be observed separately [14].

The BEs and the FWHMs of the peaks were obtained by a fit which includes four peaks on a Shirley background. Fig. 2 shows the measured spectrum and the fit for KUO<sub>3</sub>. The fit parameters for NaUO<sub>3</sub>, KUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> compounds, together with XPS data on UO<sub>2</sub> and Cs<sub>2</sub>U<sub>4</sub>O<sub>13</sub> [14] are collected in Table 1.



**Fig. 2.** The XPS spectrum of U4f core level electrons in KUO<sub>3</sub>, after 20 s etching. The open circles are the experimental data and the fits are represented with solid lines.

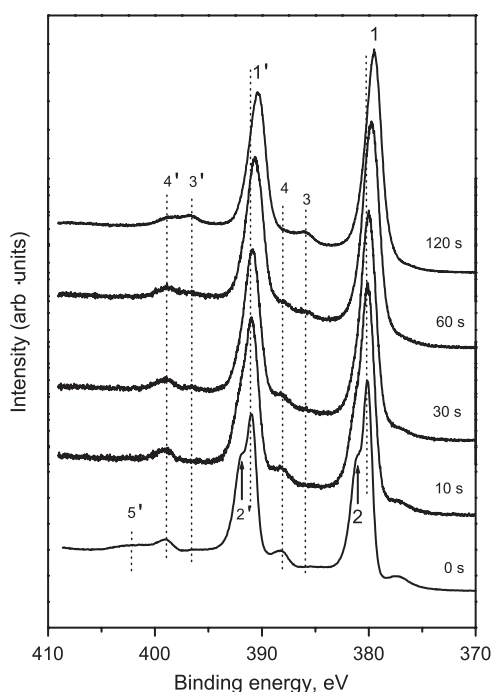
The goodness of the fit, and the fact that FWHMs agree with those in U<sup>4+</sup> and U<sup>6+</sup> compounds indicate that we can interpret the U4f spectra as single peaks and therefore consider a single valence in all measured U<sup>5+</sup> materials. Second, the BEs and the satellite positions of the U4f peaks in U<sup>5+</sup> compounds are higher/lower in energy than those in U<sup>4+</sup>/U<sup>6+</sup>, as expected for such a difference in the oxidation state. However, the BEs of the satellite peaks exhibit larger variations as a function of the uranium valence with respect to the BEs of the main peaks, see Fig. 1. Because of that, and due to the fact that BEs might be influenced by the charging effect, we use relative position of the satellite peaks with respect to the main peak to determine the uranium valence. In NaUO<sub>3</sub>, KUO<sub>3</sub> and Ba<sub>2</sub>U<sub>2</sub>O<sub>7</sub> (U<sup>5+</sup>), the distance of the U4f<sub>5/2</sub> satellite peak from the main peak is about 7.9–8.1 eV, see Table 1. This value when compared with 6.8 and 10 eV for UO<sub>2</sub> (U<sup>4+</sup>) and Cs<sub>2</sub>U<sub>4</sub>O<sub>13</sub> (U<sup>6+</sup>), respectively, indicates the presence of uranium valence in these compounds between U<sup>4+</sup> and U<sup>6+</sup>.

As already mentioned, the intrinsic spectra for U<sup>5+</sup> samples could not be obtained without Ar<sup>+</sup> ion beam etching, so the etching time was found to be a critical parameter. Short etching time did not completely remove the surface oxide, whereas too long etching time introduced a reduction of the surface (U<sup>5+</sup> to U<sup>4+</sup>). This is demonstrated in Fig. 3, which shows the evolution of U4f XPS spectra of KUO<sub>3</sub> with the etching time.

The spectrum of as-received sample (0 s in Fig. 3) shows a doublet structure of U4f main peaks (peaks 1, 2, 1' and 2'), in agreement with previously reported spectra [1]. After 10–30 s etching, the doublet structure has completely disappeared, and the spectra revealed the four-peak structure (peaks 1, 4, 1' and 4'), which is previously discussed to be the fingerprint of a single U<sup>5+</sup> chemical state. At higher etching times, at 60 and 120 s, the new peaks denoted as 3 and 3', appear in the spectra. Their intensities increase by increasing the etching time which indicates the progressing reduction of the surface of the material. Since the very minor etching removes the higher BE peaks from the doublets (peaks 2 and 2'), and the satellite peak of peak 2' (namely, peak 5'), it seems that the doublet structure in the XPS spectra of as-received samples originates from the surface oxidation of the material, which transforms some of the U<sup>5+</sup> to U<sup>6+</sup> state. Therefore, the intrinsic U<sup>5+</sup> spectrum could only be obtained by carefully controlled etching process which removes the surface U<sup>6+</sup> containing oxide without introducing the reduction of the surface.

**Table 1**  
Fitting parameters for  $\text{K}_2\text{U}_2\text{O}_7$ ,  $\text{Na}_2\text{U}_2\text{O}_7$  and  $\text{Ba}_2\text{U}_2\text{O}_7$  and XPS data of  $\text{UO}_2$  and  $\text{Cs}_2\text{U}_4\text{O}_{13}$ .

Fitting parameters		$\text{UO}_2$	$\text{K}_2\text{U}_2\text{O}_7$	$\text{Ba}_2\text{U}_2\text{O}_7$	$\text{Na}_2\text{U}_2\text{O}_7$	$\text{Cs}_2\text{U}_4\text{O}_{13}$ [14]
$\text{U}4f_{7/2}$ (eV)	BE	380.0	380.1	380.2	380.6	381.3
	FWHM	1.9	1.8	1.7	1.9	1.9
$\text{U}4f_{5/2}$ (eV)	BE	390.9	391.0	391.1	391.4	392.1
	FWHM	2.0	1.9	1.8	1.9	1.9
4f peak separation (eV)		10.9	10.9	10.9	10.8	10.8
Satellite of $\text{U}4f_{7/2}$ (eV)	BE	386.8	388.0	388.1	388.5	
	FWHM	1.4	1.2	1.6	1.0	
Satellite of $\text{U}4f_{5/2}$	BE	397.7	399.1	399.0	399.5	402.2
	FWHM	2.2	1.6	1.9	1.6	2.5
Satellite from main peak (eV)	$\text{U}4f_{7/2}$	6.8	7.9	7.9	7.9	
	$\text{U}4f_{5/2}$	6.8	8.1	7.9	8.1	10.1

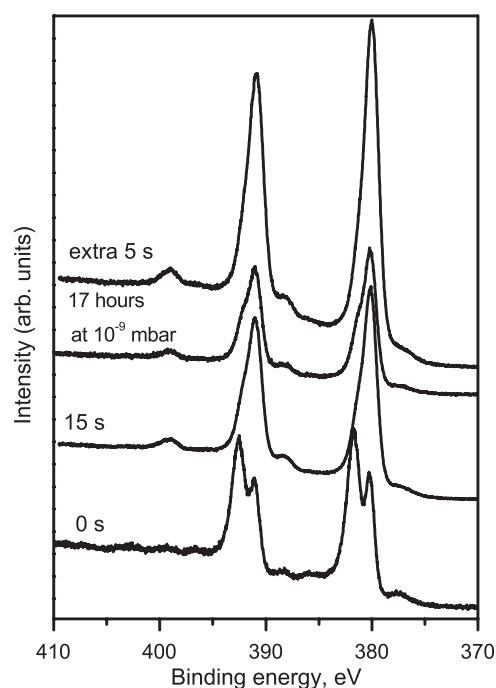


**Fig. 3.** Evolution of  $\text{U}4f$  XPS spectra of  $\text{K}_2\text{U}_2\text{O}_7$  with the etching time. The peaks denoted as 1–5 are discussed in the text.

Finally, the high susceptibility of  $\text{U}^{5+}$  to oxidation is illustrated in Fig. 4. We first measured the  $\text{U}4f$  spectrum of as received  $\text{K}_2\text{U}_2\text{O}_7$ . Then we measured the  $\text{U}4f$  spectrum after 15 s  $\text{Ar}^+$  etching. After that, the sample was left overnight in the analysis chamber for 17 h at the pressure of about  $\sim 10^{-9}$  mbar. Subsequently, the  $\text{U}4f$  spectrum was acquired at the same measurement spot. Although the sample was kept under high vacuum, the acquired spectrum showed the intensity increase in the high BE peak in the doublet, indicating the oxidation of  $\text{U}^{5+}$  to  $\text{U}^{6+}$ .

#### 4. Conclusions

We investigated the valence states of uranium in  $\text{K}_2\text{U}_2\text{O}_7$ ,  $\text{Na}_2\text{U}_2\text{O}_7$  and  $\text{Ba}_2\text{U}_2\text{O}_7$  using XPS. Based on the positions and FWHMs of  $\text{U}4f$  peaks, and the satellite peak positions of  $\text{U}4f_{5/2}$  peaks observed in



**Fig. 4.** Evolution of  $\text{U}4f$  XPS spectra of  $\text{K}_2\text{U}_2\text{O}_7$  showing in situ oxidation of  $\text{U}^{5+}$  to  $\text{U}^{6+}$  in the XPS analysis chamber.

present study, we conclude that  $\text{Na}_2\text{U}_2\text{O}_7$ ,  $\text{K}_2\text{U}_2\text{O}_7$  and  $\text{Ba}_2\text{U}_2\text{O}_7$  are monovalent  $\text{U}^{5+}$  uranates. Moreover, we found that the  $\text{U}^{5+}$  state is susceptible to further oxidation by exposure to air as well as reduction by exposure to the  $\text{Ar}^+$  ion beam, which both result in the formation of doublet structure at the  $\text{U}4f$  peaks. The acquisition of the intrinsic XPS spectra of  $\text{U}^{5+}$  was possible only through carefully controlled etching.

#### References

- [1] G.C. Allen, J.A. Crofts, M.T. Curtis, P.M. Tucker, *J. Chem. Soc. Dalton Trans.* 1974 (1974) 1296.
- [2] B.W. Veal, D.J. Lam, W.T. Carnall, H.R. Hoekstra, *Phys. Rev. B* 12 (1975) 5651.
- [3] C. Keller, U.K. Jorgensen, *Chem. Phys. Lett.* 32 (1975) 397.
- [4] G.C. Allen, A.J. Griffiths, B.J. Lee, *Trans. Met. Chem.* 3 (1978) 229.
- [5] S. Bera, S.K. Sali, S. Sampath, S.V. Narasimhan, V. Venugopal, *J. Nucl. Mater.* 255 (1998) 26–33.

- [6] M.A. Denecke, *Coord. Chem. Rev.* 250 (2006) 730–754.
- [7] A.V. Soldatov, D. Lamoen, M.J. Konstantinović, S. Van den Berghe, A.C. Scheinost, M. Verwerft, *J. Solid State Chem.* 180 (2007) 54–61.
- [8] N.L. Misra, D. Lahiri, K.D. Singh Mudher, L. Olivi, S.M. Sharma, *X-ray Spectrom.* 37 (2008) 215–218.
- [9] A.M. Chippindale, P.G. Dickens, W.T.A. Harrison, *J. Solid State Chem.* 78 (1989) 256–261.
- [10] P.G. Dickens, A.V. Powell, *J. Mater. Chem.* 1 (1991) 137–138.
- [11] W. Ruedorff, S. Kemmler, H. Leutner, *Angew. Chem.* 74 (1962) 429–430.
- [12] S. Van den Berghe, M. Verwerft, J.-P. Laval, B. Gaudreau, P.G. Allen, A. Van Wyngarden, *J. Solid State Chem.* 166 (2002) 320–329.
- [13] S. Van den Berghe, A. Leenaers, C. Ritter, *J. Solid State Chem.* 177 (2004) 2231–2236.
- [14] S. Van den Berghe, J.-P. Laval, B. Gaudreau, H. Terryn, M. Verwerft, *J. Nucl. Mater.* 277 (2000) 28–36.