ESRF	**Experiment title:** **Determination of charge distribution and local structure in uranium-americium mixed oxides using XAS**	**Experiment number**: MA-2723
Beamline: BM20	**Date of experiment**: from: 10/12/2015 to: 15/12/2015	**Date of report**: 30/03/2016 *Received at ESRF:*
Shifts: 14	**Local contact(s)**: HENNIGH Christoph	
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1. Introduction

Mixed uranium-americium oxides represent possiblez transmutation targets for GEN IV reactores. For this reason, these materials have recently been the focus of several studies. The initial experiments were principally dedicated on samples characterized by Am/(U+Am) ratios inferior to 20% [1]–[4]. Thanks to XAS measurements on samples with Am/(Am+U) ratios up to 20%, a peculiar behavior of these compounds was highlighted: the Am is purely trivalent, while the U is partially oxidized to the pentavalent state, with very close Am(+III) and U(+V) contents, suggesting a charge compensation mechanism. A recent XAS experiment was performed on an $U_{0.5}Am_{0.5}O_2$ sample [5]. The measure pointed out that the compound was hypo-stoichiometric, with an O/M (oxygen/metal) ratio equal to 1.92(2). Also in this case, the americium was purely trivalent, whereas the uranium had an average oxidation state equal to 4.65(3). Moreover, EXAFS spectra showed that the increase of americium content is responsible for modifications of the local fluorite structure; in particular, the oxygen seems to form clusters around the uranium.

In this study, we extended the structural investigation of $(U,Am)O_{2\pm x}$ samples to higher Am content, up to Am/(Am+U) equal to 70%, by combining XRD and XAS.

2. Experiment

$(U,Am)O_{2\pm x}$ pellets with Am/(Am+U) equal to 0.15, 0.3, 0.6 and 0.7 were manufactured using the UMACS process [6]. The XRD and XAS samples were obtained by grinding the pellets.

XRD analysis was performed using a Bruker D8 Advance diffractometer in θ-θ Bragg-Brentano geometry. XAS measurements were performed at the BM20 beamline, both in transmissions and fluorescence modes at various temperatures: 15 K, 100 K, 150 K and room temperature. XANES and EXAFS spectra were recorded at Am LIII, U LIII and U LII edges.

3. Results

The X-ray diffraction performed on the manufactured samples confirmed the presence of one single phase with fluorite structure, confirming the achievement of the solid solution.

The results of the XAS measurements performed at 15 K are here presented.

In Figure 1-(a) we show the XANES spectra recorded at the Am LIII edge of our samples, compared to two reference materials: an oxalate, in which the Am is purely trivalent, and $Am^{+IV}O_2$. In Figure 1-(b), we have reported the white line positions of the spectra (the maxima of the curves). A slight shift toward higher energies is observed for the samples with highest Am content, indicating the presence of tetravalent Am.

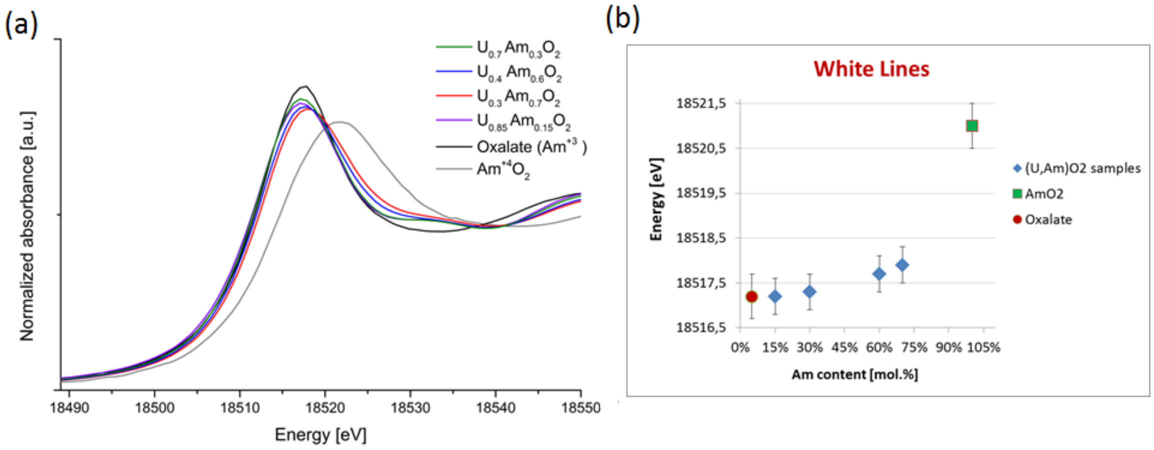

Figure 1. (a) XANES spectra recorded at the Am LIII edge. (b) White line positions.

The increasing of the U oxidation state as a function of Am content the analyzed samples is evident. In fact, for the $U_{0.85}Am_{0.15}O_{2\pm x}$ and $U_{0.7}Am_{0.3}O_{2\pm x}$ compounds, the spectra are between those of the $U^{+IV}O_2$ and $(U_{0.5}^{+IV},U_{0.5}^{+V})_4O_9$ reference materials (Figure 2-(a)), whereas the $U_{0.4}Am_{0.6}O_{2\pm x}$ and $U_{0.3}Am_{0.7}O_{2\pm x}$ spectra are between the $(U_{0.5}^{+IV},U_{0.5}^{+V})_4O_9$ and $(U_{2/3}^{+V},U_{1/3}^{+VI})_3O_8$ (Figure 2-(b)).

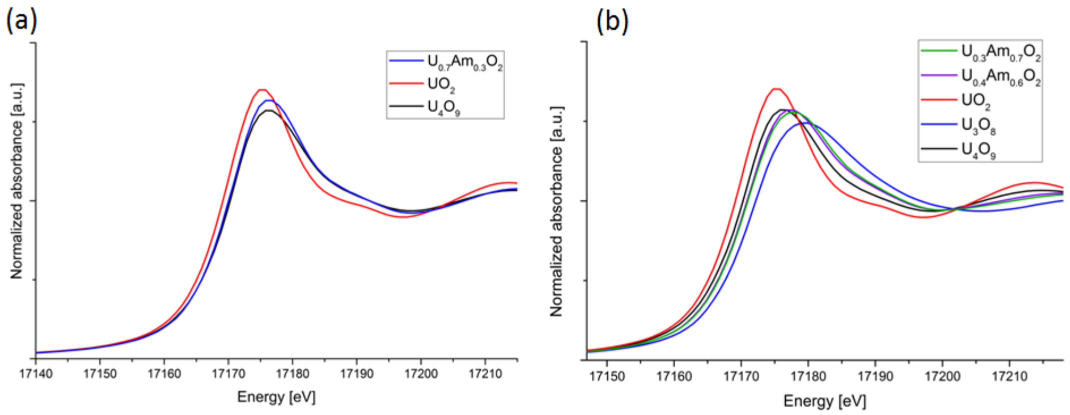

Figure 2. XANES spectra recorded a the U LIII edge for the $U_{0.7}Am_{0.3}O_2$ (a) and the $U_{0.4}Am_{0.6}O_2$, $U_{0.3}Am_{0.7}O_2$ (b).

The XANES spectra have been fitted by linear combination with the reference materials, in order to estimate the Am and U oxidation states and therefore to find the O/M ration of the samples. The result is shown in Table 1. The Am is purely trivalent for Am/(Am+U)<50%, whereas for the $U_{0.4}Am_{0.6}O_2$ and $U_{0.7}Am_{0.3}O_2$ samples the Am^{+3} purcentage is fixed at around 50%, and the Am^{+4} content increases. The U average oxidation state increases as a function of Am content, but it is still lower than 5. The global O/M decreases with the Am increasing, till the 1.87 value in the $U_{0.7}Am_{0.3}O_2$.

Table 1. Results of the linear combination fit on XANES spectra.

	Americium				**Uranium**				
Am%	**Oxalate O/Am = 1.5**	**AmO_2 O/Am = 2**	**Am^{+3}**	**Am^{+4}**	**UO_2 O/U = 2**	**U_4O_9 O/U = 2.25**	**U_3O_8 O/U = 2.67**	**Av Oxid state**	**O/M**
15%	1	0	**0.15**	**0**	0.52	0.48		**4.24**	**2.03**
30%	1	0	**0.30**	**0**	0.14	0.86		**4.43**	**2.00**
60%	0.86	0.14	**0.51**	**0.09**		0.64	0.36	**4.80**	**1.90**
70%	0.74	0.26	**0.51**	**0.19**		0.55	0.45	**4.88**	**1.87**

The $U_{0.7}Am_{0.3}O_2$ and $U_{0.3}Am_{0.7}O_2$ EXAFS spectra collected at the Am-LIII and U-LII edges and their Fourier transforms (FT) are shown in Figure 3. The Am spectra present the typical features of the fluorite structure, with two main peaks in the FT corresponding to the first O shell and the first cationic shell. The only evident effect of the Am increase is a drop of the spectrum intensity, indicating increasing disorder. On the contrary, the U spectrum shows also a deformation of the first oxygen shell, similar to that one of U_4O_9, which coul indicate O clusters around U. In order to have more detailed information, the EXAFS spectra analysis is currently underway.

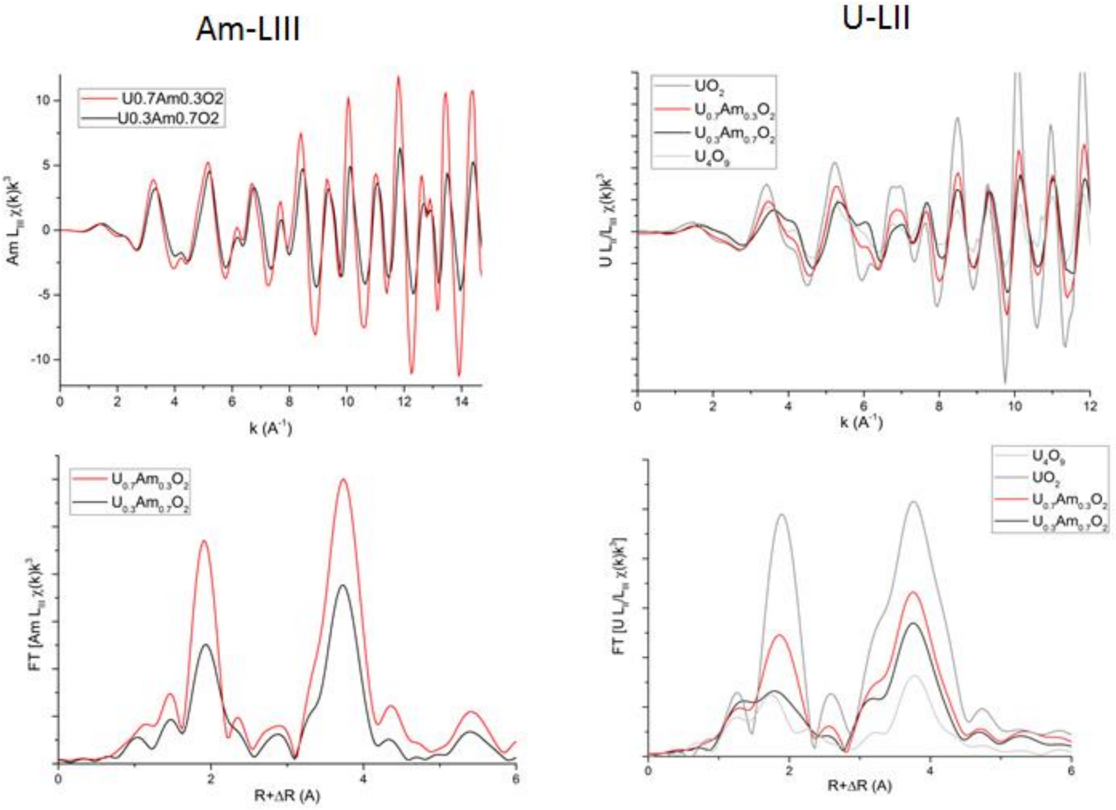

Figure 3. EXAFS spectra and their Fourier transform collected at the Am-LIII edge (left) and the U-LII edge (right)

4. Conclusions

In this work, we have investigated for the first time the local structure of $(U,Am)O_2$ compounds with Am contents higher than 50 mol.%. These samples are stable in a hypo-stoichiometric form (O/M <2), in which the Am^{+3} content is fixed at around 50 mol.% and the remaining Am is tetravalent, whereas the U oxidation state furtherly increases with the Am content.

5. References

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