



	<b>Experiment title:</b> XAS study of dense $U_{1-y}Am_yO_{2-x}$ ( $y=0.10 ; 0.15; 0.20$ ) obtained by conventional powder metallurgy	<b>Experiment number:</b> 20-01-705
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 03/09/10 to: 07/09/10	<b>Date of report:</b> 05/01/11
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## Report:

Partitioning and Transmutation of MA is the key issue for reducing nuclear waste radiotoxicity.  $U_{1-y}Am_yO_{2-x}$  blankets are promising fuels for the transmutation of Minor Actinides (MA) in Fast Neutron Reactors. The  $U_{1-y}Am_yO_{2-x}$  fabrication is challenging due to the high oxygen potential of the  $AmO_{2-x}$ . These oxides exhibit a significantly higher equilibrium oxygen potential in comparison to other actinide oxides such as  $UO_2$  [1]. An accurate control of the sintering atmosphere is necessary to achieve the targeted O/M value. As a consequence, a thermodynamical modelling is currently developed to determine optimum sintering conditions for given O/M ratios and MA content. Due to the lack of experimental data in the U-Am-O system [2] to refine the modelling, an experimental determination of the O/M ratio is mandatory as also its eventual consequences on the homogeneity of the solid solution. The present work focuses on the XAS characterization of  $U_{1-y}Am_yO_{2-x}$ .

For this experiment,  $U_{1-y}Am_yO_{2-x}$  ( $y=0.10; 0.15; 0.20$ ) compounds were fabricated using conventional powder metallurgy process [3]. To study Am and U chemistry as a function of oxygen potential, samples were sintered in various moisture-added Ar containing 5% of  $H_2$  atmospheres. For each sample, fluorescence and transmission signals were collected at the uranium  $L_{II}$ , uranium  $L_{III}$  and the americium  $L_{III}$  edges. Energy calibrations were achieved using Y, Mo and Zr foil located after the second ionization chamber. All measurements were performed at 20K using the closed-cycle a helium cryostat. At both uranium  $L_{III}$  and americium  $L_{III}$  edges, EXAFS spectra were collected up to  $18 \text{ \AA}^{-1}$  but only up to  $13.2 \text{ \AA}^{-1}$  for uranium  $L_{II}$  edge. This limitation is due to the presence of a small amount of neptunium resulting from the  $^{241}Am$  decay.

In a first part, we investigated the effect of the oxygen potential studying three  $U_{0.85}Am_{0.15}O_{2\pm x}$  samples sintered in different atmospheres. The Am  $L_{III}$  edge XANES spectra of both  $U_{0.85}Am_{0.15}O_{2\pm x}$  compounds and references ( $Am^{+IV}O_2$  and mixed ( $U^{+IV}, Am^{+III}$ ) oxalate) are presented in Figure 1. It shows that the XANES spectra remain identical to the signal collected for the  $Am^{+III}$  reference compound. Thus, the oxidation state of americium is  $Am^{+III}$  whatever the sintering atmosphere. As already observed in [4],  $Am^{+IV}$  is easily reduced in  $Am^{+III}$ . The U  $L_{III}$  edge XANES spectra, presented in Figure 2, point out the difference of the white line position for each spectrum. This shift is due to the decreasing of the  $U^{4+}/U^{5+}$  ratio while the oxygen potential increases. It indicates that, during the sintering, a total reduction of  $Am^{+IV}$  to  $Am^{+III}$  and a partial oxidation of  $U^{+IV}$  to  $U^{+V}$  are occurring. The oxidation of  $U^{+IV}$  to  $U^{+V}$  is enhanced as the oxygen potential increasing. The O/M ratios were calculated for each compounds using the determined oxidation state of U and Am. The results show that the O/M increase with the oxygen potential; which is in agreement with the expected results. These additional experimental data are currently used to refine the thermodynamical modelling

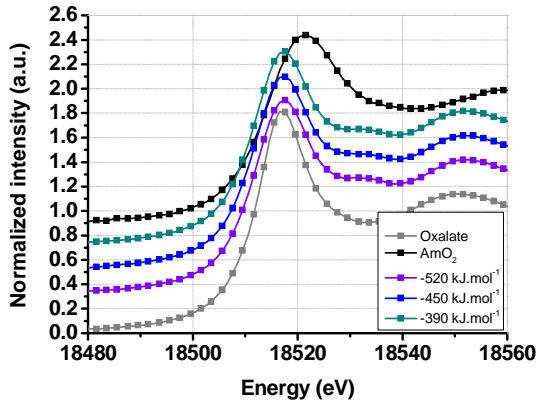


Figure 1: Am L<sub>III</sub> edge XANES spectra

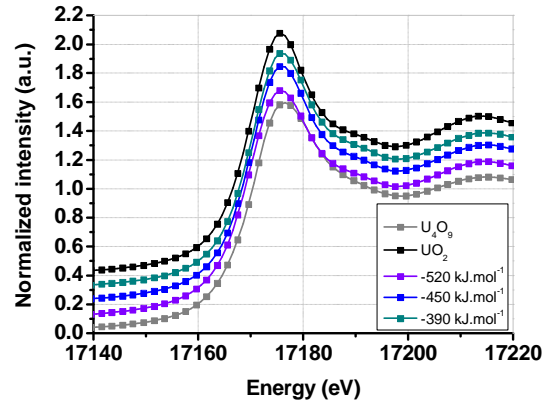


Figure 2: U L<sub>III</sub> edge XANES spectra

In a second part, the effect of the Am was investigated studying  $U_{1-y}Am_yO_{2-x}$  compounds with different Am contents ( $y=0.10; 0.15; 0.20$ ). These materials were sintered in the same sintering conditions, i.e. reducing conditions. The collected Am L<sub>III</sub> edge and U L<sub>III</sub> edge XANES, presented in Figure 3, indicates that the Am oxidation state remains unchanged at +III while there is a  $U^{+IV}/U^{+V}$  mixed valence depending on Am content.

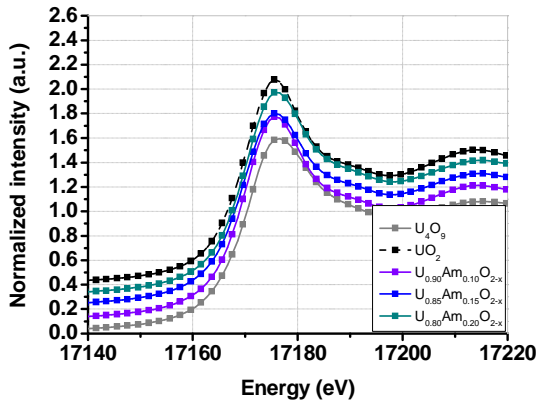


Figure 3: U L<sub>III</sub> edge XANES spectra

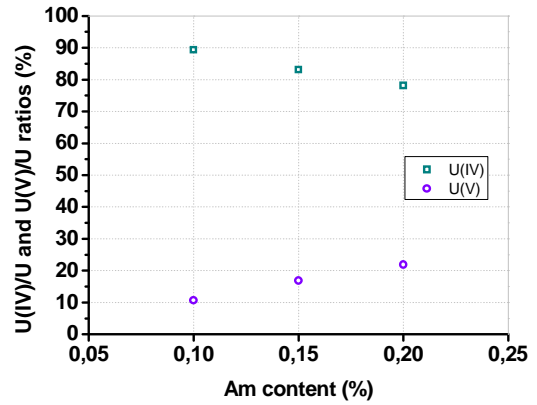


Figure 4:  $U^{+IV}/U$  and  $U^{+V}/U$  ratios as a function of Am content

The Figure 4 presents both  $U^{+IV}/U$  and  $U^{+V}/U$  ratios as a function of the Am content. According to linear fit, the  $U(V)$  molar fraction  $y'$  can be expressed by the equation (1).

$$y' = \alpha y(1 - y) \quad (1)$$

Therefore, the solid solution can be described by  $U_{(1-\alpha y)(1-y)}^{4+} U_{\alpha y(1-y)}^{5+} Am_y^{3+} O_{2-x}$  for these sintering conditions.

The EXAFS analyses are still in progress.

- [1] T. M. Besmann et T. B. Lindemer, "Chemical thermodynamic representations of  $\langle PuO_{2-x} \rangle$  and  $\langle U_{1-z}Pu_zO_w \rangle$ ", Journal of Nuclear Materials, vol. 130, 489-504 (1985)
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- [3] D. Prieur et al., "Fabrication and characterization of minor actinides bearing fuels obtained by conventional powder metallurgy process", Powder Technology (2010)
- [4] P.M. Martin et al., "XAS investigation of  $(U,Am)O_2$  and  $(U,Pu)O_2$  solid solutions obtained by oxalic co-precipitation", ESRF, experimental report form CH-2738, (2009)