 ROBL-CRG	Experiment title: Impact of synthesis process on homogeneity at atomic scale of (U,Am)O _{2-x} samples	Experiment number: 20-01-738
Beamline: BM 20	Date of experiment: from: 01/02/2014 to: 04/02/2014	Date of report: 02/2014
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1. Introduction

In the framework of minor actinide transmutation in fast neutron reactors, U_{1-y}Am_yO_{2±x} compounds are promising targets. At both *Commissariat à l'Energie Atomique et aux Energies Alternatives* (CEA) and Joint Research Center - Institute for Transuranium Elements (JRC-ITU), processes are being developed to synthesize such compounds, with an emphasis on dense U_{0.85}Am_{0.15}O_{2±x} samples. At CEA, these processes were up to now mainly based on powder metallurgy and solid-state reactions from UO₂ and AmO₂ precursors [1,2], whereas a combination of external gelation sol-gel and infiltration methods was developed at ITU [3,4]. Recently, X-ray absorption spectroscopy (XAS) studies performed both by CEA and ITU on their respective compounds show discrepancies. The major one was the presence in CEA samples of Am^{+III} and mixed U^{+IV/+V} [5–7], but of Am^{+III/+IV} and U^{+IV} for ITU ones [4]. However, the samples being sintered in different conditions and the XAS data acquired on different beamlines, only highly speculative explanations could be proposed [7]. To understand this discrepancy, a joint ITU-CEA XAS experiment was performed in the framework of a Talisman joint research project.

2. Samples and experimental conditions

The composition of the samples studied was U_{0.85}Am_{0.15}O_{2±δ}. They were prepared either by solid state route at CEA (Samples A and B) or sol-gel/infiltration at ITU (Samples C, D and E). Samples A and C are non-sintered precursors, Samples B and E were sintered at CEA and Sample C was sintered at ITU. XANES and EXFAS spectra were recorded at Am L_{III} edge, whereas only XANES was collected at U L_{III} edge. For EXAFS, U L_{II} edge was preferred due to the presence of Np (from ²⁴¹Am

α -decay) in the samples. Spectra were recorded at room temperature in both transmission and fluorescence modes. For each edge, at least two spectra were recorded.

3. XANES Results

The XANES spectra of the five samples are presented in **Figure 1**, together with those of several reference compounds: U^{+IV}O_2 , $(\text{U}^{+IV}_{0.5}, \text{U}^{+V}_{0.5})_4\text{O}_9$ and $\text{U}^{+V/+VI}_3\text{O}_8$ to determine the oxidation states of uranium, as well as $\text{Am}^{+IV}\text{O}_2$ and a mixed $(\text{U}, \text{Am}^{+III})$ oxalate for those of americium.

At both U and Am L_{III} edges, the spectra corresponding to the sintered samples are identical. At the Am L_{III} edge, the positions of white line and inflexion points are equal to those corresponding to the (U,Am) oxalate, indicating the sole presence of Am^{+III} in the samples. At the U L_{III} edge, the spectra are shifted towards higher energies compared to that of UO_2 and thus located between those of UO_2 and U_4O_9 , suggesting a mixed +IV/+V oxidation state of uranium. For the precursors (Sample A and C), the spectra however present some discrepancies compared to those of the sintered samples. Uranium is notably present at higher oxidation states in both these samples, and americium is even found to be +III/+IV in Sample C, which also seems to be less crystallized than the four other samples, based on a preliminary comparison of EXAFS spectra obtained.

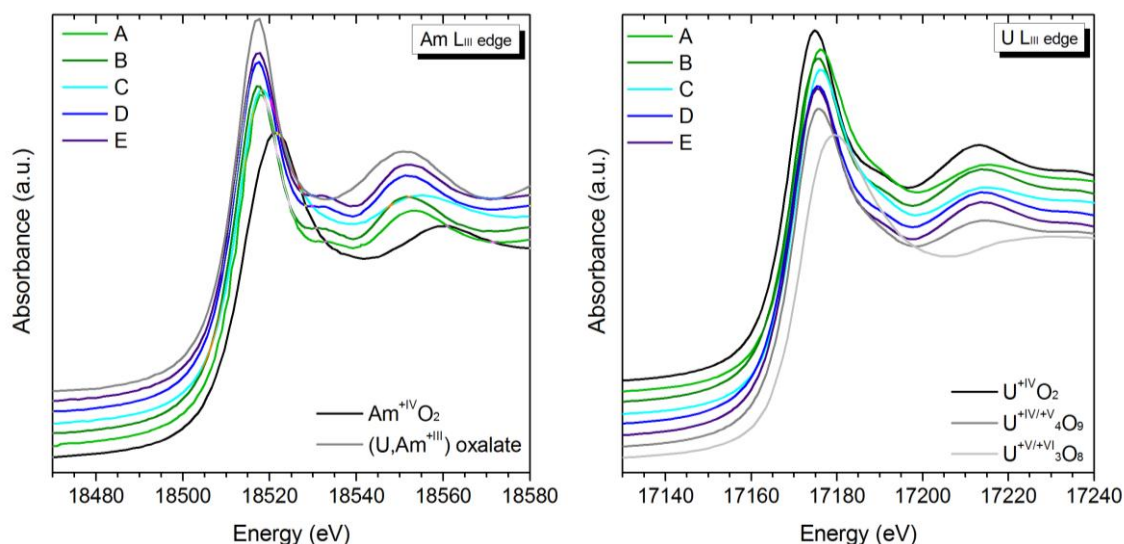


Figure 1. XANES spectra recorded at (left) U L_{III} and (right) Am L_{III} edges.

4. Conclusion

Based on the preliminary analysis of the XANES spectra, the synthesis process does not seem to be the reason for the discrepancy previously reported for XAS studies of $\text{U}_{1-y}\text{Am}_y\text{O}_{2\pm\delta}$ samples [4–7]. The ongoing analysis of the EXAFS spectra is now being performed and will bring further information for the comparison of the samples and the synthesis routes.

5. References

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