



	Experiment title: Homogeneity at molecular scale of mixed (U,Am) and (Np,Pu) compounds probed by XAS	Experiment number: 20-01-700
Beamline: BM20	Date of experiment: from: 26/02/2011 to: 01/03/2011	Date of report: 12/2011
Shifts: 9	Local contact(s): Christoph Hennig	<i>Received at ESRF:</i>
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Report:

Innovative fuel cycles are currently studied within the framework of the fourth generation (GEN-IV) nuclear reactors development. The two main objectives of these fuel cycles are an efficient use of energetic resources by recycling together the major and valuable actinides such as uranium and plutonium, and a drastic decrease of the radiotoxicity of the ultimate wastes by partitioning and transmutating the minor ones such as americium, curium or neptunium. Indeed, the challenge is to be able to incorporate a large amount (up to ~20 at.%) of highly radioactive minor actinide into the mixed (U,Pu) nuclear fuel. Moreover, only a fluorite type solid solution, as in case of pure (U,Pu)O₂, has to be obtained for the final product.

Rather than a mechanical mixing of pulverulent compounds, as in the actual MOX manufacturing process, innovative synthesis methods based on co-precipitation are currently developed [1]. In particular, the oxalic co-precipitation of U(IV) and Pu(III) followed by the thermal conversion of the co-precipitate into oxide, was recently optimized in the CEA Atalante facility at Marcoule. Characterization on mixed U(IV)-An/Ln(III) oxalate structures [2] indicated that a solid solution with the generic formula M_{2+x}U(IV)_{2-x}An(III)_x(C₂O₄)₅.nH₂O (M = monocharged cation) can be expected. The originality of this mixed oxalate is based on a mixed crystallographic site which can accept either a tetravalent actinide or a trivalent one. Monovalent cations equilibrate the charge in the structure depending on the molar ratio of An(III) to An(IV). Thermal conversion of the co-precipitates should lead to an ideal (U,An)O₂ fluorite-type solid solution.

As observed during our last XAS experiment on ROBL [3], the oxalic coprecipitation developed for (U,Am) system has been validated with the observation of an ideal solution for a (U_{0.9},Am_{0.1}) mixed oxalate and the two actinide ions are tenfold coordinated by five bidentate oxalate ligands.

Results

The main goal of this new experiment was to determine if new optimized calcination conditions would lead to the formation of an (U,Am)O₂ solid solution. Results obtained for a 10% Am, 90% U sample are summarized in Figure 1-4. XANES spectrum collected at Am L₃ (Cf Figure 1) shows that valence of Am cations is +III as observed in our recent results obtained on a (U_{0.9},Am_{0.1})O₂ sample synthesized by conventional powder metallurgy process and sintered for 4 hours at 1700°C [4]. The two samples exhibit very similar EXAFS spectra at both U and Am edges as illustrated by Figure 3 and 4. Main differences are the reduced amplitudes of EXAFS oscillations observed for both cations in the case of the sample obtained with the wet route. These features suggest that a solid solution is now effectively obtained with the oxalic coprecipitation route.

Furthermore, based on comparison of U-L₃ XANES spectra (Cf figure 2) a similar charge compensation mechanism (U⁺⁵-Am⁺³), as previously observed [4], is also taking place using mixed oxalate wet method.

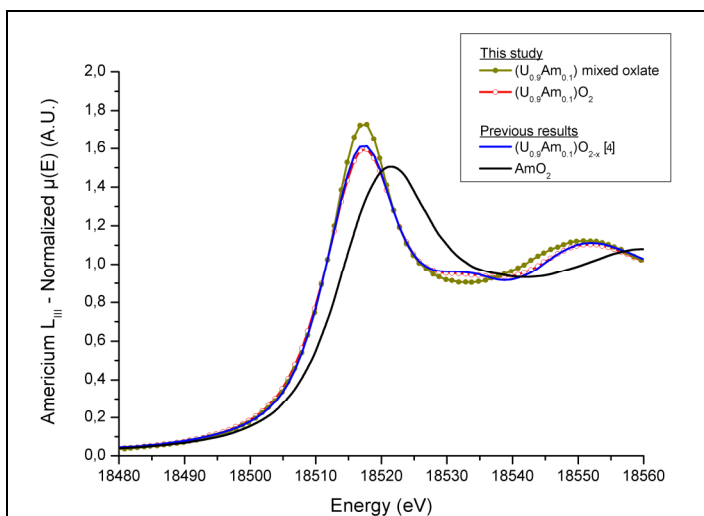


Figure 1: (U,Am) samples Am L₃ XANES spectra

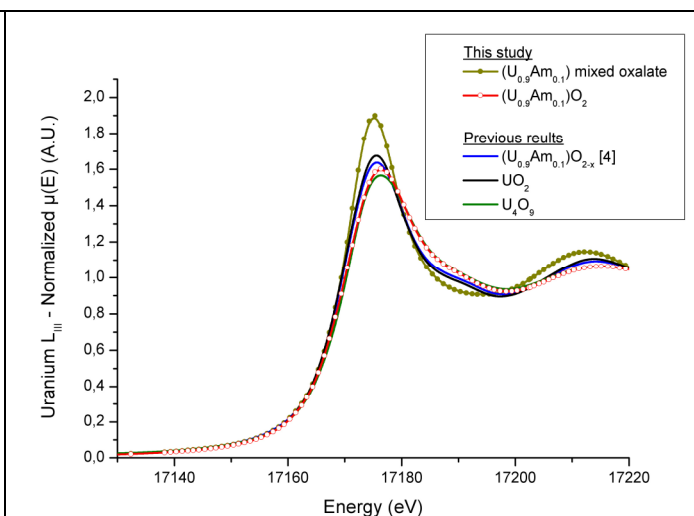


Figure 2: (U,Am) samples U L₃ XANES spectra

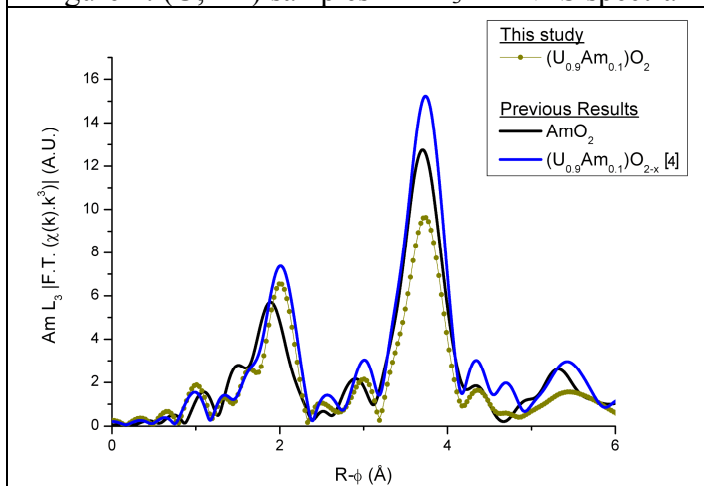


Figure 3: (U,Am) samples – Am L₃

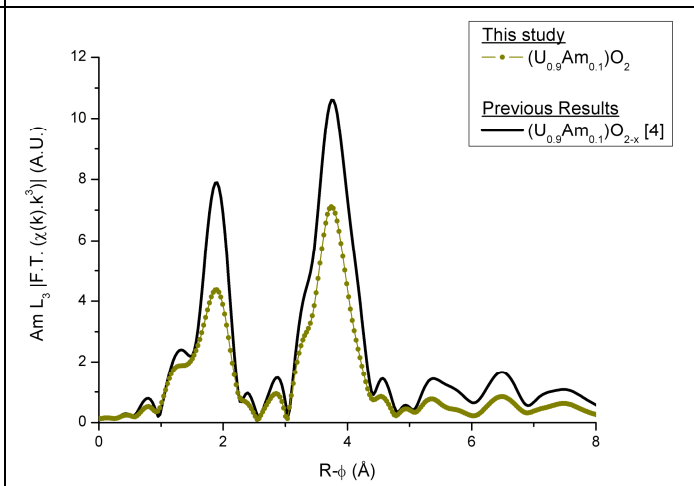


Figure 4: (U,Am) samples – U L₃

References

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