



	Experiment title: EXAFS/XANES investigation of plutonium and americium pyrochlores considered as targets for transmutation	Experiment number: HS-3178
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Report:

Management of long-lived nuclear wastes is, after safety, the main issue of nuclear industry, both in terms of scientific challenge as well as public acceptance. Among the different options that have been envisioned and explored for minor actinides over the past thirty years, two alternatives currently remain: long term disposal in a safe repository or nuclear wastes “burning” in a so-called transmutation process. Materials selected for such applications have to meet the following criteria: high incorporation amount of actinides, good structural and chemical stability, low thermal dilatation and resistance to radiation.

Among the various ceramics envisaged, zirconia based pyrochlore oxides of composition $An_2Zr_2O_7$ (An=actinide) appear to be a very good candidate. Results obtained with lanthanide pyrochlores submitted to ion-beam irradiation show that Zr based pyrochlores, unlike Ti based, remain crystalline with a transition from pyrochlore structure to a defect fluorite structure [1]. The ordered pyrochlore belongs to the Fd-3m space group and is a superstructure of the ideal defect fluorite structure (Fm-3m) with exactly twice the lattice constant. In the pyrochlore structure, Am and Zr cations have first coordination shells clearly different: 8 (2+6) oxygen atoms and 6 oxygen atoms respectively. Whereas second coordination shell (cation-cation) is the same for both cations (6xAm+6xZr at the same distance). The structural phase transition from pyrochlore to defective fluorite involves the randomization of the oxygen atoms into the anionic and vacant positions of the pyrochlore structure. In the ideal fluorine defect structure, the Am and Zr cations share the same position and thus have the same local environment: a first coordination shell consisting of 7 oxygen atoms at the same distance and the same second coordination shell observed in the pyrochlore structure.

However, this strong radiation tolerance still has to be confirmed on alpha emitter materials (e.g. americium). In that prospect, $^{241}Am_2Zr_2O_7$ sample was synthesized [2] and its evolution under the effect of alpha self-irradiation as a function of time was followed by XRD. A transition from the pyrochlore phase to a defect-fluorite phase was observed after ~200 days as the superstructure peaks slowly vanish and completely disappear after about 200 days [3]. However, the fluorite structure is surprisingly resistant to self-irradiation induced amorphization as compared to other materials considered for transmutation or long-term storage [4]. In order to better understand the underlying phenomena involved in this phase transition as well as the significant resistance to amorphization of the defect fluorite phase, characterization of Am and Zr local environments by XAS have been undertaken.

Results

XANES and EXAFS spectra on 2 $\text{Am}_2\text{Zr}_2\text{O}_7$ samples have been collected at Zr K edge and Am L_{II} edges at a temperature of 15 K. The first sample (called “fresh”) has been synthesized a few weeks before the experiment whereas the second sample (called “old”) was a year old. X-ray diffraction measurements performed prior to XAS measurements attested for a pyrochlore structure (Fd-3m $a=10.667\text{\AA}$) for the “fresh” sample and for a defect-fluorite (Fm-3m $a=5.323\text{\AA}$) for the “old” one. The Fourier transforms at both edges are compared in Figures 1 and 2.

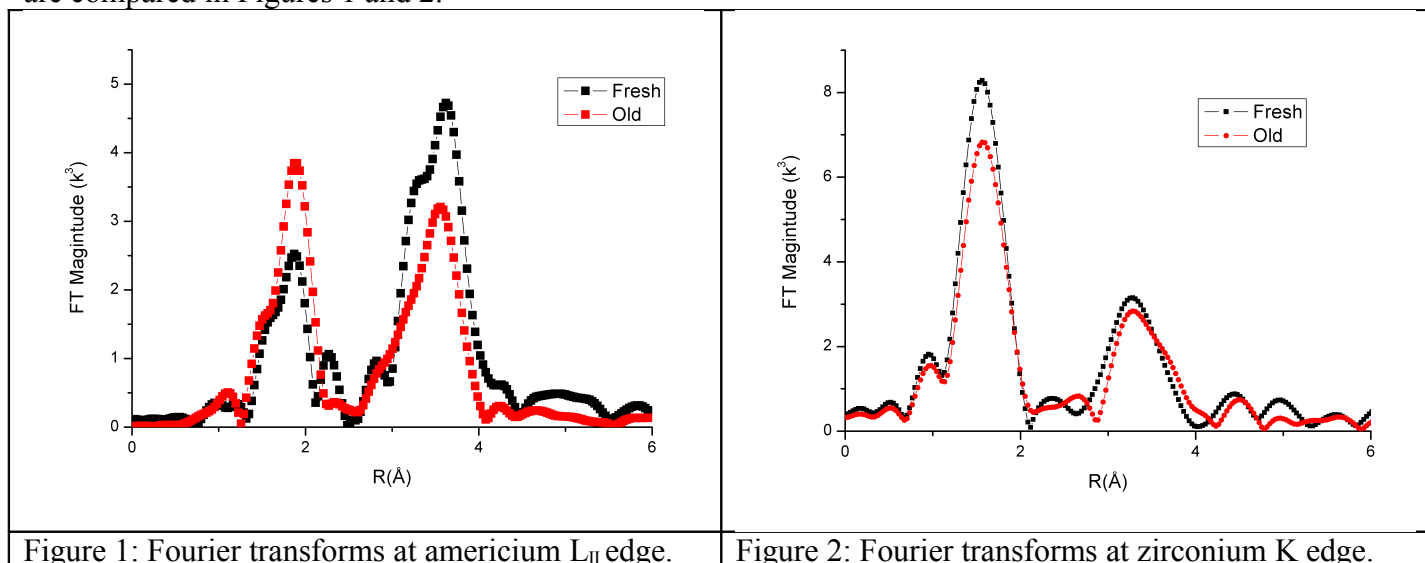


Figure 1: Fourier transforms at americium L_{II} edge.

Figure 2: Fourier transforms at zirconium K edge.

In the case of americium, a clear modification of radial distribution around Am ions can be observed. For the fresh sample, the fit gives the expected pyrochlore local environment with: 2.8 ± 0.5 O at 2.31 ± 0.02 Å, 4.8 ± 0.5 O at 2.53 ± 0.02 Å, 6 ± 0.5 Am at 3.76 ± 0.02 Å and 6 ± 0.5 Zr at 3.74 ± 0.02 Å. For the one year old sample, the fit confirms the fluorite structure with a first coordination shell consisting of only one shell of 6.6 ± 0.5 O at 2.35 ± 0.02 Å (peak at ~ 1.9 Å in Figure 1). The cation-cation shells included in the second (peak at ~ 3.8 Å in Figure 1) are clearly distorted with 5.2 ± 0.5 Am at 3.75 ± 0.02 Å and 6.3 ± 0.5 Zr at 3.65 ± 0.02 Å. The Am-Am distance is coherent with the fluorite structure but the Am-Zr distance is shorter than expected. Such observations seem to indicate that Zr local environment does not follow the evolution observed around Am ions.

Results obtained at Zr K edge validate that hypothesis as the Zr-O polyhedra, with only coordination shell of 6.6 ± 0.5 O at 2.14 ± 0.02 Å (peak at ~ 1.8 Å in Figure 2) for both samples, appear to be stable in regard to alpha self-irradiation. Moreover, the cation-cation coordination sphere (peak at ~ 3.3 Å in Figure 2) follows the same evolution observed for Am with a distortion due to Zr-Zr and Zr-Am distances clearly different.

Unlike picture given by XRD measurement, Am and Zr cations local environments after self-alpha irradiation are clearly non equivalent. Modifications appear to be mainly localized around Am cations whereas the ZrO_7 polyhedra seem to be very robust against irradiation. Same conclusions have been obtained on $\text{Gd}_2(\text{Ti,Zr})_2\text{O}_7$ pyrochlore samples submitted to ion irradiation [5]. Thus, the structural phase transition from the pyrochlore structure to the fluorite defect structure appears to be rather a disruption of the long-range order probed by XRD due to cation disorder and interpolyhedral (ZrO_7 and AmO_7) rotations along edges and corners leading to the change in Am environment and the disorder in second coordination shells [6]. To definitively conclude on the mechanism induced by self-alpha irradiation, XAS measurements on two years aged sample is proposed.

References

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