

Experimental report MA-3307

The aim of this experiment was to characterize the electronic states, as well as the local environments of iodine and caesium within a UO_2 matrix, in order to get insights into the chemical interactions between Cs, I, U and O. Cs and I have been implanted separately or co-implanted in sintered UO_2 pellets (8 mm diameter, 0.5 mm thickness) at various concentrations ranging from 2 at.% down to 0.4 at.% (Cs) or 0.02 at.% (I), the lowest concentrations being representative of fission products in a nuclear fuel after 4 irradiation cycles. Two kinds of thermal treatments have been applied: for each sample (i.e. each implantation condition), one third have been annealed 4h at 900°C (H_2 + 300 ppm H_2O environment), and one third 1h at 1200°C (idem). Two reference samples, CsI and Cs_2UO_4 , have also been measured.

XAS measurements have been performed on half pellets confined in Kapton. HERFD XAS spectra have been collected at the L_3 edges of Cs (4.993 keV) and I (4.556 keV) by using 5 Si (311) bent crystals (bending radius 1000 mm) emission spectrometer available on ID26 beamline. The emission spectrometer was tuned to L_3 - M_5 emission line of Iodine (3.938 keV) or Caesium (4.290 keV). Spectra were recorded in a continuous quick scan mode of both monochromator and undulator gap over the requested energy ranges. A helium bag was inserted between the sample, the crystals and the detector to avoid beam absorption by air.

Due to (i) low counting rates related to the low Cs and/or I contents and the huge absorption by the U-rich matrix; (ii) the proximity of Iodine and Caesium L-edges and of U M_1 - and M_2 -edges which reduces the exploitable k -range, even in HERFD, and (iii) normalization problems related to linearity limits on the Si drift detector, we finally decided to focus our measurements on the XANES only and to take full advantage of these first allocated shifts to get very accurate XANES data.

The high brilliance, the very efficient crystal analyzer emission spectrometer and also the great skills and involvement of ID26 staff allowed us to measure Iodine L_3 edge XANES on 12 implanted UO_2 samples, and the Caesium L_3 edge XANES on 9 implanted UO_2 samples.

Iodine L_3 edge

The absorption spectra already exhibit marked differences for as-implanted Iodine samples as a function of the I content (Figure 1). For the most concentrated condition (2 at.% I), a strong modification of the XANES spectrum is observed after annealing at 900°C or 1200°C, with no significant difference between the two annealing conditions, traducing notable changes in the local environment of Iodine atoms above 900°C. However, for the most diluted samples (0.02 at.% I) a continuous evolution of the spectra occurs as a function of the thermal treatment, with two peaks growing at ca. 4562 and 4575 eV (Figure 2), evidencing a very progressive change in the Iodine environment under annealing.

In the co-implanted (Cs and I) samples, Iodine L_3 edge spectra are still different depending on the concentrations. From the comparison of the spectra with the reference spectrum of CsI, it appears that :

- no CsI is present in the as-implanted samples, regardless Cs and I content (Figure 3);
- almost all Iodine reacts with Caesium to form CsI at 900°C for the highest Cs and I content (2 at.% Cs + 1 at.% I), whereas no CsI signature can be observed at 900°C for the lowest Cs and I contents (0.4 at.% Cs + 0.02 at.% I); however the spectrum is very different from the as-implanted one, and the local environment of Iodine remains there to be precised;

- at 1200°C, some characteristic features of CsI can be observed on the XANES spectrum of the most diluted sample, however slight differences remain (Figure 4): this may suggest either a slight deviation from the CsI structure, or that a fraction of iodine may still be in a different chemical form.

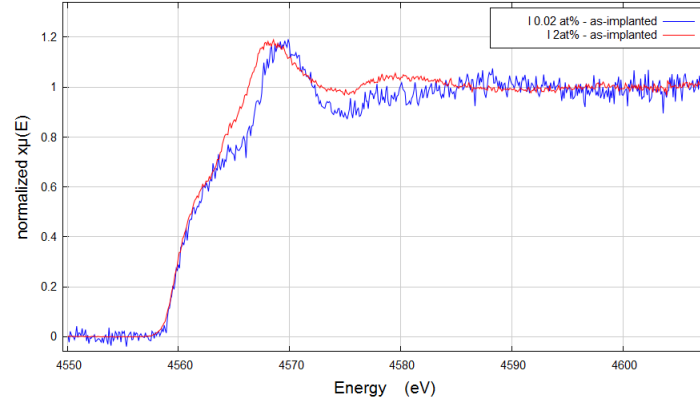


Figure 1: Iodine L₃ edge XANES, as-implanted samples

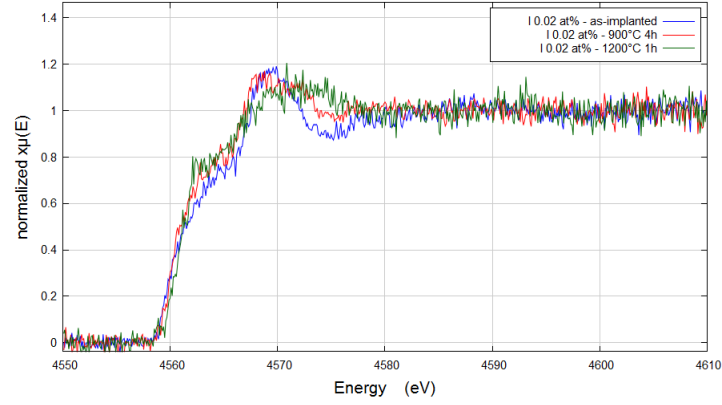


Figure 2: Iodine L₃ edge XANES as a function of the thermal treatment in the most diluted Iodine implanted material

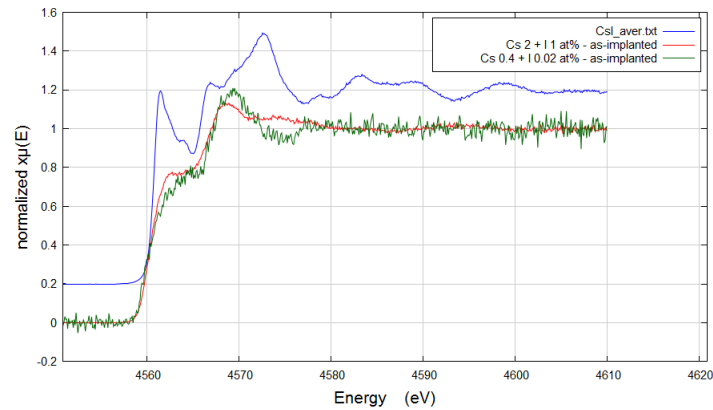


Figure 3: Iodine L₃ edge XANES, as-implanted samples. CsI reference spectrum is shown for comparison.

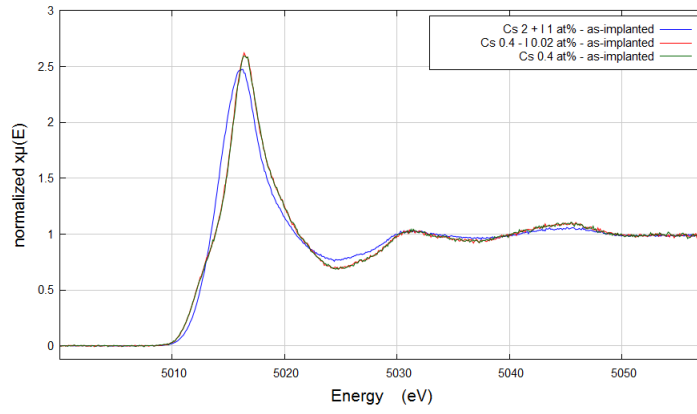


Figure 5: Cs L₃ edge XANES, as-implanted samples

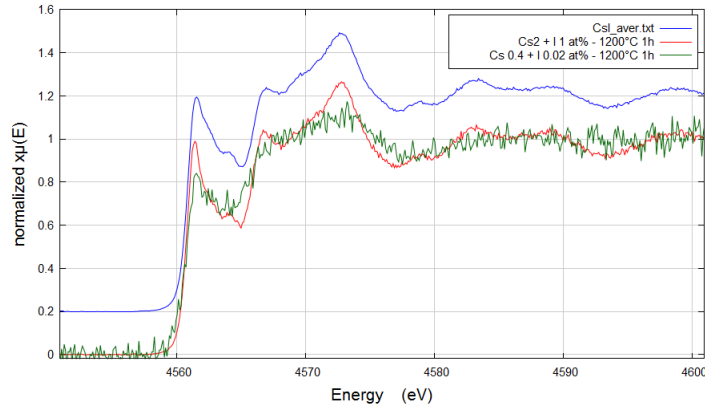


Figure 4: Iodine L₃ edge XANES, samples annealed 1h at 1200°C. CsI reference spectrum is shown for comparison.

Caesium L₃ edge

In the as-implanted state, Cs L₃ edge spectra are quite similar, regardless the presence of Iodine or not (Figure 5). This is especially true for the lowest concentrations: spectra with or without Iodine are identical, suggesting no (or very rare) Cs - I interactions in the most diluted co-implanted material before annealing. This is consistent the higher [Cs] / [I] in the latter (20, against 2 for the highest Cs and I concentrations). More generally, the absence of CsI in the as-implanted samples is confirmed whatsoever.

Spectra of the Cs 0.4 at.% samples (w/o Iodine) reveal a slight evolution of the local environment of Cs at 900°C, the so-called white line being slightly shifted toward low energy. This might traduce the partial formation of Caesium Uranate Cs₂UO₄, as it can be deduced from the comparison with the Cs₂UO₄ reference spectrum (Figure 6).

Spectra recorded with the co-implanted concentrated sample confirm the formation of CsI at high temperature, as already deduced from the Iodine spectra (Figure 7). At low concentrations, spectra obtained with or without Iodine remain almost identical after thermal treatments at 900°C and 1200°C, suggesting very few Cs - I interactions. Further analysis are still required to determine the speciation of the Cs introduced in strong excess with respect to Iodine.

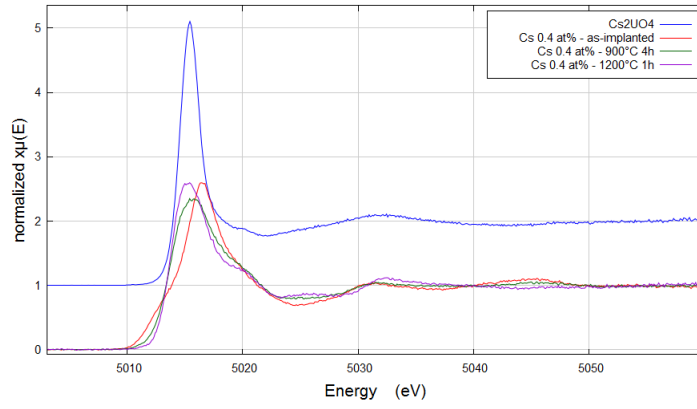


Figure 6: Cs L_3 edge XANES, Cs implanted material only. Cs_2UO_4 spectrum is shown for comparison.

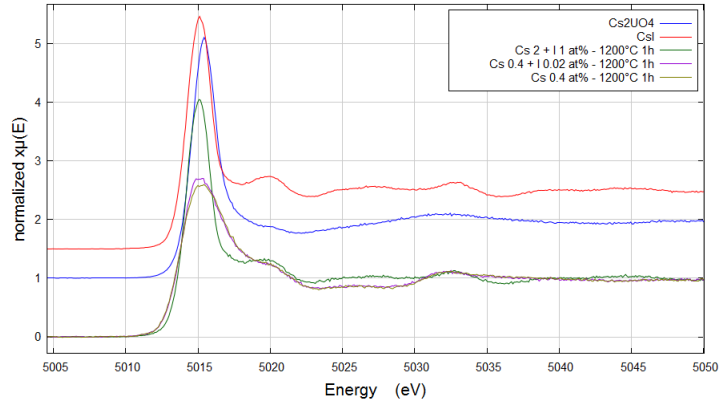


Figure 7: Cs L_3 edge XANES, samples annealed 1h at 1200°C. CsI and Cs_2UO_4 spectra are shown for comparison.

Conclusions, prospects

We managed to obtain very accurate XANES data on Cs and/or I implanted in UO_2 , with reasonable counting times, even for, e.g., Iodine concentrations as low as 0.02 at.% for which an acceptable signal / noise ratio could be reached in ca. 6 hours. Some very interesting differences have been observed as a function of Cs and/or I concentrations and as a function of the thermal treatment, revealing more complex chemical behaviours of these elements, when implanted in UO_2 , as expected.

Analysis of the numerous XANES data obtained during the 18 shifts allocated on ID26 beamline is still in progress, mainly by means of *ab initio* electronic structure calculations and XANES simulations with the FDMNES code.

Unfortunately, we did not manage to get “clean” EXAFS data despite the highly efficient 5 crystals analyzer spectrometer of ID26. Since such data would be highly precious, a very important task will thus consist in finding a way to measure EXAFS on Cs and I within UO_2 . This might lead us to rather consider the K edges. But higher X-ray energy would mean higher X-ray penetration depth, and the latter would become larger than the Cs and/or I implantation depths: a novel approach for homogeneously incorporating Cs and/or I within UO_2 would then become unavoidable and should be implemented first.