Experimental Report

Proposal: **6-06-453** **Council:** 4/2014

Title: Characterisation of cuboctahedra in UO2+x as function of temperature

This proposal is resubmission of: 6-06-450

Researh Area: Materials

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Samples: UO2
U4O9
UO2 depleted U

Instrument	Req. Days	All. Days	From	To
D4	5	5	15/12/2014	20/12/2014

Abstract:

We aim at characterising the local order associated to oxygen incorporation in UO2+x with 0 < x < 0.25 at different temperatures in order to better describe UO2 behaviour under irradiation. The UO2+x diffraction patterns will be measured experimentally on several samples with different x at several temperatures in order to explore the UO phase diagram. The corresponding PDFs will be compared to UO2 and U4O9 reference PDFs obtained at the same temperature. Either the sample is a mixture of this two phases(as expected at low temperature) or new local defects are to be tested using pdfgui software.

Report on D4 experiment 6-06-453

This report summarises the results of the experiment No. 6-06-453 carried out in 2014 relative to the study of uranium oxides fuel. In this experiment, we continued studying oxygen defect aggregates in hyper-stoichiometric uranium oxide UO_{2+x} and in particular the cuboctahedral structures as a function of temperature in UO_{2+x} with x roughly equal to 0.03 .

We performed previously several neutron diffraction experiments on U_4O_9 compound at ILL, [1] [2], that gave a comprehensive understanding of the long-range ordering of cuboctahedral defects that can be viewed as clusters of 5 interstitial oxygen atoms and their induced relaxation in the regular UO_2 crystalline lattice. In this experiment, we focused on UO_{2+x} compounds, that are a mixture of UO_2 and U_4O_9 at room temperature, according U-O phase diagram, to determine how the cuboctahedral defects behave when the UO_2-U_4O_9 mixture is transformed in UO_{2+x} by increasing temperature. This result is expected to shed light on the defects existing in UO_{2+x} that have to be known for an accurate prediction of nuclear fuel modelling.

We first manufactured and further oxidized UO_2 samples using a specially conceived annealing device at CEA Cadarache. Our UO_2 samples consisted of two sets of disks either 1mm or three mm thick and a third set of three fuel pellets of identical cumulated length (see Table 1). All the samples were of identical cross-sections and were mirror polished with silicon carbide and a diamond paste with a 1 μm grain size. Samples were then oxidized at 1280°C under controlled oxygen partial pressure maintained using a humidified mixture of argon and Hydrogen or carbon monoxide and dioxide for the lower and higher oxygen partial pressures respectively .

Table 1 General description of sample oxidation conditions Group

	Constitutions	Gas phase	pO2/atm
A	2 pellets (l=27mm)	H2/H2O	$10-19$
B	2 pellets (l=27mm)	CO/CO2	$10-18$
C	9 3mm-disks	H2/H2O	$10-19$
D	28 1mm-disks	CO/CO2	$10-18$
E	2 pellets (l=27mm)	As fabricated	Stoichiometric UO2

The five samples were sealed under vacuum in silica tubes by the glass blower at ILL. This new procedure for UO_2 samples is standard for D4 furnace experiments and worked very well for our experiment, and will therefore be adopted for our future D4 furnace experiments because it overcomes the difficulties encountered before with the helicoflex-sealed vanadium containers used in the furnace.

Sample B, D and E were measured as function of temperature up to 900°C for the highest temperature. Samples A and C should have had the same stoichiometry as sample B and D respectively, but the measurement performed at room temperature showed that it was actually less. So it was decided not to measure these samples as a function of temperature. Moreover the U_4O_9 sample that was used for previous experiments was also measured at room temperature to check whether its PDF changes over time or time. For this last measurement, an additional authorisation was obtained.

A first data treatment was performed during the experiment to calculate the PDF of sample B, D and E as a function of temperature. A first analysis of these data showed several positive points:

- The samples were of good quality. For deviations from stoichiometry below roughly 0.25, UO_{2+x} is known to be a two-phase mixture at room temperature. In Fig 1(a) the

subtraction of the neutron diffraction pattern obtained on our UO_{2+x} sample D at room temperature with that of our reference UO_2 sample, sample. The result compares favourably with a U_4O_9 spectrum suggesting 1) that the UO_{2+x} data may be obtained from a linear combination of UO_2 and U_4O_9 data and 2) the coexistence of two distinct phases at room temperature.

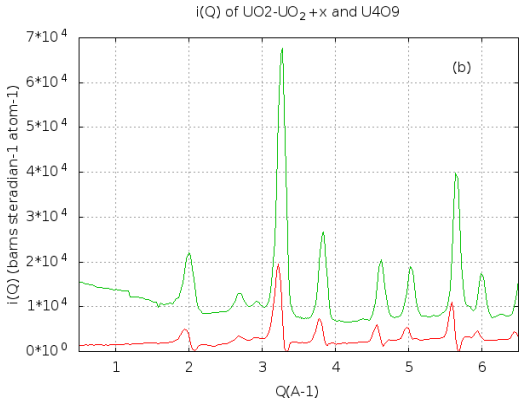

Fig 1 RED line: difference between UO2+x and UO2 diffraction patterns at room temperature; Green line: the $i(Q)$ of U_4O_9

- The phase transition from UO_2-U_4O_9 mixture to UO_{2+x} phase was observed as a function of temperature. Although we are still in the process of refining the structural model for our UO_{2+x} samples, a preliminary analysis of our data indicates a deviation-from-stoichiometry of roughly 0.03. This estimated deviation from stoichiometry is entirely consistent with the observed transition temperature on the two-phase diagram (estimated above 400°C) as may be seen.
- Furthermore, a novel result of this experiment concerns the fact that in the single phase region (i.e. above 400°C) the basic cuboctahedral defect structure appears to remain, although the long-range ordering of these defects breaks down.

Moreover the results obtained on sample E, the UO_2 reference sample, can be compared to recent literature data [3].

After several test with different sample holders, we can now say that we reached a safe and efficient procedure for handling and measuring UO_2 based samples on D4. The obtained results are promising and many new original experiments now become feasible in an easy way.

Many thanks to the ILL glass blower Christian Lazzarotto, as well as the radioprotection and safety teams of the ILL.

[1] L. Desgranges, G. Baldinozzi, G. Rousseau, J. -C. Niepce et G. Calvarin, «Neutron diffracton study of the in situ oxidation of UO2,» Inorganic Chemistry, vol. 48, pp. 7585-7592, 2009.
[2] L. Desgranges, G. Baldinozzi, D. Simeone et H. E. Fischer, «Refinemen of the a-U4O9 crystalline structure: new insight into the U4O9 to U3O8 transformation,» Inorganic Chemistry, vol. 50, pp. 6146-6151, 2011.

[3]L. Skinner, C. Benmore, J. Weber, M. Williamson, A. Tamalonis, A. Hebden, T. Wiencek, O. Alderman, M. Guthrie, L. Leibowitz et J. Parise, «Molten Uranium dioxide structure and dynamics» 2014 November 21. [En ligne]. Available: www.sciencemag.org.