



Contribution ID: 31

Type: Poster

In-situ high temperature XAS experiments on oxide nuclear fuels and precursors

Tuesday 20 May 2014 17:30 (4h 30m)

Over the last decades, the application of XAS (X-ray Absorption Spectroscopy) to actinide-bearing materials has proven to be a very reliable method to obtain valuable information on these oxides, through a coupled insight into oxidation states and local structure. Experiments were notably performed on UO_{2+x} , $U_1-yPu_yO_{2+x}$ and $U_{1-y}Am_yO_{2+x}$ compounds [1-4]. Concerning the latter for instance, an unexpected charge distribution was identified over a large range of composition ($0.05 \leq x \leq 0.50$), with the complete reduction of Am to the trivalent state whereas uranium is partially oxidized to pentavalent state, a result which was not available via other characterization methods [3,4]. Such data remain however limited to measurements performed after fabrication (i.e. ex-situ) at RT (room temperature) or below (15 or 77 K). Even if they are very valuable, the same information must be obtained under thermodynamic conditions where elemental mechanisms are taking place.

To perform the in-situ XAS experiment a new experimental set-up dedicated to actinide-based materials has been developed. It consists of a furnace based on the heating wire technology [5] embedded in a dedicated second confinement barrier. The aim of this experimental set-up is to cover thermodynamic conditions encountered during fuel fabrication (precursor calcination, sintering), irradiation in reactor (LWR, Na-FNR...) or severe nuclear accidents. The existing version can heat the sample up to 2000 K under various atmospheres by flushing any gases around the heating wire: air, neutral (Ar, N₂) and reductive (Ar+H₂+O₂). During the thermal sequence, the oxygen potential can be dynamically modified by mixing the gases and is measured at the furnace entrance.

The first in-situ high temperature measurements on U-bearing samples were performed at INE-ANKA beam-line. They were focused on U/Ln oxide behaviours and on the conversion into oxides of several U/Ln precursors for nuclear fuel fabrications. The results obtained notably showed, through XANES spectra, the successive variations of oxidation states of the cations occurring during these conversions, as well as some changes in local symmetry and crystallinity. Concerning the experimental setup, the experiment confirmed the feasibility of the measurements in a double-sealed environment under controlled conditions. It thus represents the first step of a bigger project, which aims at performing in-situ XAS measurements on transuranium (i.e., Pu, Am, Np)-bearing samples.

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Primary author: Dr MARTIN, Philippe (CEA Cadarache - Nuclear Fuel department)

Co-authors: Dr NEUVILLE, Daniel (CNRS-IPGP, Géochimie & Cosmochimie); Mr LEBRETON, Florent (CEA Marcoule); Dr ROTHE, Joerg (Karlsruhe Institute of Technology - Institute for Nuclear Waste Disposal); Dr DARDENNE, Kathy (Institut für Nukleare Entsorgung (INE), Karlsruhe Institute of Technologie (KIT)); Mr BATAILLE, Marc (CEA Marcoule DEN/DTEC); CAISSO, Marie (CEA Marcoule DEN/MAR/DTEC/SDTC/LEMA); Dr BES, René (CEA Cadarache - Nuclear Fuel Department); Dr DELAHAYE, Thibaud (CEA Marcoule DEN/DTEC)

Presenter: Mr LEBRETON, Florent (CEA Marcoule)

Session Classification: Poster

Track Classification: Solid State Chemistry and Physics of the Actinides