Contribution ID: **47** Type: **Oral**

Influence of high americium contents in the local structure and charge distribution of mixed uranium-americium oxides

Tuesday 20 May 2014 16:15 (25 minutes)

Mixed uranium-americium oxides are regarded as promising compounds for transmutation in order to reduce americium contribution to radiotoxicity and heat load of ultimate nuclear waste [1]. These materials are thus currently studied, not only in terms of fabrication processes [2–5] or during experimental irradiations [3,6,7] but also through more fundamental research to understand their thermodynamic and physical properties [8–11]. In this context, XAS experiments reported by Prieur et al. on samples with americium content of 10 to 20 at.% evidenced a peculiar behaviour. Americium was present as Am(+III) state whereas uranium was oxidized to a mixed valence, U(+IV/+V), with similar Am(+III) and U(+V) mole fractions hence O/M (oxygen to metal) ratios close to 2.00 [8,11]. Despite the presence of cations at three different oxidation states, these compounds remain monophasic, presenting the expected fluorite-type structure without any major structural distortions or disorder. These results remain however limited to relatively low americium contents.

In this work, we combine XRD and XAS at U and Am LII/LIII edges to study the influence of such cationic charge distribution in mixed uranium-americium oxides presenting higher americium contents: 40 and 50 at.%. These compounds exhibit a single fluorite-type structure [12,13]. XANES results show that the same behaviour is observed for these samples, i.e., americium remain Am(+III) while uranium is oxidized even though this oxidation does not compensate for Am(+III) in the 50%-Am sample which thus presents an O/M ratio close to 1.93. Based on linear combination of reference compound spectra (U(+IV)O2, U(+IV/+V)4O9, U(+V+VI)3O8), the average oxidation state of uranium is estimated around 4.67, which corresponds to the upper limit of existence of a fluorite-type-derived cubic structure in the U-O system (U3O7). EXAFS spectrum analyses show that the local structure around americium remains fairly close to that found for lower americium contents, with only a limited increase of structural disorder and the possible presence of vacancies in the oxygen sublattice. Around uranium, EXAFS spectra reveal significant distortions of the first coordination shell that consists of several U-O distances whereas only one U-(U/Am) distance is present in the second coordination shell. The presentation will focus on the relationship between the charge distribution and the local structure, with an emphasis on the apparent limitation of uranium oxidation states similar to that observed in the U-O system.

References:

[1] D. Warin, J. Nucl. Sci. Technol. 44 (2007) 410.
[2] D. Prieur, F. Lebreton, P.M. Martin, et al., J. Eur. Ceram. Soc. 32 (2012) 1585.
[3] T. Delahaye, F. Lebreton, D. Horlait, et al., J. Nucl. Mater. 432 (2013) 305.
[4] D. Horlait, A. Feledziak, F. Lebreton, et al., J. Nucl. Mater. 441 (2013) 40.
[5] D. Horlait, F. Lebreton, A. Gauthé, et al., J. Nucl. Mater. 444 (2014) 181.
[6] E. D'Agata, P.R. Hania, S. Bejaoui, et al., Nucl. Eng. Des. 242 (2012) 413.
[7] D. Prieur, A. Jankowiah, T. Delahaye, et al., J. Nucl. Mater. 414 (2011) 503.
[8] D. Prieur, P.M. Martin, A. Jankowiak, et al., Inorg. Chem. 50 (2011) 12437.
[9] D. Prieur, P.M. Martin, F. Lebreton, et al., J. Solid State Chem. 194 (2012) 206.
[10] F. Lebreton, R.C. Belin, D. Prieur, et al., Inorg. Chem. 51 (2012) 9369.
[11] D. Prieur, P. Martin, F. Lebreton, et al., J. Nucl. Mater. 434 (2013) 7.
[12] F. Lebreton, D. Horlait, T. Delahaye, P. Blanchart, J. Nucl. Mater. 439 (2013) 99.
[13] D. Horlait, F. Lebreton, P. Roussel, T. Delahaye, Inorg. Chem. 52 (2013) 14196.

Primary author: Mr LEBRETON, Florent (CEA, DEN, DTEC/SDTC/LEMA –30207 Bagnols-sur-Cèze, France)

Co-authors: Dr SCHEINOST, Andreas (Helmholtz Zentrum Dresden Rossendorf (HZDR), Institute of Radiochemistry –P.O. Box 10119, 01314 Dresden, Germany); Dr HORLAIT, Denis (CEA, DEN, DTEC/SDTC/LEMA - 30207 Bagnols-sur-Cèze, France); CAISSO, Marie (CEA Marcoule DEN/MAR/DTEC/SDTC/LEMA); Dr BLANCHART, Philippe (GEMH/ENSCI –87065 Limoges, France); Dr MARTIN, Philippe (CEA Cadarache - Nuclear Fuel department); Dr DELAHAYE, Thibaud (CEA, DEN, DTEC/SDTC/LEMA - 30207 Bagnols-sur-Cèze cedex)

Presenter: Mr LEBRETON, Florent (CEA, DEN, DTEC/SDTC/LEMA –30207 Bagnols-sur-Cèze, France)

Session Classification: Solid State Chemistry and Physics of the Actinides

Track Classification: Solid State Chemistry and Physics of the Actinides