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Particle Size vs. Local Environment Relationship for ThO₂ and PuO₂

Laura Bonato,¹ Matthieu Virot,¹ Elodie Dalodière,¹ Thomas Dumas,² Adel Mesbah,¹ Oliver Dieste Blanco,³ Thierry Wiss,³ Damien Prieur,⁴ André Rossberg,⁴ Laurent Venault,² Philippe Moisy,² Sergey I. Nikitenko¹

¹ Université de Montpellier, Institut de Chimie Séparative de Marcoule (ICSM), UMR 5257, CEA-CNRS-UM-ENSCM, Site de Marcoule BP17171, 30207 Bagnols sur Cèze, France. e-mail: matthieu.virot@cea.fr.² French Nuclear and Alternative Energies Commission (CEA) Nuclear Energy Division, Department of Mining and Fuel Recycling Processes (DMRC), Site de Marcoule BP17171, 30207 Bagnols sur Cèze, France.³ European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements (ITU), Postfach 2340, 76125 Karlsruhe, Germany.⁴ Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany

Nanomaterials have attracted considerable interest in recent interdisciplinary research for their technological applications related to the nanometric size of the building blocks composing the solids (ex: crystallite or atomic and molecular groups).[1,2] Nanostructured materials can be defined as solid samples exhibiting a microstructure the characteristic length scale of which is roughly ranging between 1 and 10 nm.[1] The controlled microstructure of materials at the atomic level offers new physical and chemical properties in comparison to similar bulk materials already applied, for instance, in catalysis, synthesis of luminescent materials, preparation of cosmetic and solar creams, preparation of solar cells, etc.[3,4] Such paradigm has been attributed to the increased surface-to-volume ratio of the shrinking particle size which increase the number of surface and interface atoms generating stress, strain, and structural perturbations.[2] In actinide chemistry, the synthesis and characterization of nanomaterials is very scarce but is of growing interest due to the contribution of actinide nanomaterials in environment (ex: migration of actinides) and industry (ex: high burn up structures). Recently, we observed the nanostructuring of PuO₂ and noticed its outstanding reactivity under ultrasound irradiation which stirred up our curiosity concerning the local environment of this oxide at the nanoscale.[5]

In this work, we investigate the synthesis and relevant characterization of nanostructured PuO₂ and ThO₂. Th can be considered as a good surrogate for Pu because both elements exist at the (+IV) oxidation state, their oxide crystallize in the fluorite Fm-3m structure, and they both exhibit close ionic radii. More precisely, Th only exists at the +IV oxidation state thus avoiding misinterpretations related to the potential contribution of other oxidation states in the crystalline structure. The synthesis studies allowed us to select the nanostructuring conditions for the various oxides and a careful characterization and correlation with AFM, HR-TEM, Raman spectroscopy, XRD and XAS techniques allowed us to probe the local disorder for the various oxides as a function of the particle size. Particularly, EXAFS investigations clearly show a linear decrease of the coordination number for An-O and An-An spheres with the shrinking particle sizes. The crystalline nature of the particles (HR-TEM, XRD) suggest that these observation are correlated to the increasing surface contribution of these particles. These new results raise the question of the physico-chemical properties of oxide nanomaterials crystallizing in the fluorite structure which are materials of paramount importance for engineering applications such as nuclear energy, solid oxide fuel cells, catalysis, or sensors.

References

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