In-Situ studies of phase transformations in Uranium Oxides

Brendan J. Kennedy¹, Gabriel L. Murphy¹,² and Zhaoming Zhang²
¹School of Chemistry, The University of Sydney, Sydney, NSW 2006 Australia
²Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales, Australia
Brendan.Kennedy@Sydney.edu.au

Ternary uranium oxides are of interest in context of both the development of nuclear waste forms and to further understanding the properties of materials containing, or which can access, 5f electrons. SrUO₄ is one such oxide, it is postulated to form from the reaction of spent UO₂ₓ and the fission daughter Sr-90 under oxidising conditions. Diffraction studies have shown that SrUO₄ undergoes an irreversible phase transformation between its rhombohedral, alpha-SrUO₄-d, and orthorhombic, beta-SrUO₄, forms, where the former contains oxygen vacancies and, by extension, reduced uranium valence states whereas beta-SrUO₄ is stoichiometric. The importance of oxygen vacancies in controlling the transformation and precise structure have been studied using a combination of in-situ synchrotron X-ray diffraction and X-ray spectroscopy, supplemented by neutron diffraction and DFT calculations. X-ray absorption near edge structure (XANES) spectra were collected at the U L₃-edge at the Australian Synchrotron. The measurements were performed at in transmission mode using argon-filled ionisation chambers. Temperature control was achieved using a Oxford FMB heater. Data analysis was carried out using the software package ATHENA. These studies reveal the gradual reduction of the oxidation state of the U cations in SrUO₄ as it is heated ultimately leading to a phase transformation. Under reducing conditions reduced SrUO₄ has a superstructure with oxygen-vacancy ordering whereas under oxidising conditions the material is re-oxidised and transforms to the beta phase. The importance of the Sr cation has also been investigated and we demonstrate that whilst it is possible to reduce CaUO₄ there is no experimental evidence for the formation of the high temperature ordered phase