In-Situ studies of phase transformations in Uranium Oxides

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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, 5*f* electrons. $SrUO_4$ is one such oxide, it is postulated to form from the reaction of spent UO_{2+x} and the fission daughter Sr-90 under oxidising conditions. Diffraction studies have shown that $SrUO_4$ undergoes an irreversible phase transformation between its rhombohedral, alpha-$SrUO_{4-d}$, and orthorhombic, beta-$SrUO_4$, forms, where the former contains oxygen vacancies and, by extension, reduced uranium valence states whereas beta-$SrUO_4$ 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 L_3-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 $SrUO_4$ as it is heated ultimately leading to a phase transformation. Under reducing conditions reduced $SrUO_4$ 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 $CaUO_4$ there is no experimental evidence for the formation of the high temperature ordered phase