

**AOFSRR 2015**

Asia Oceania Forum for Synchrotron  
Radiation Research



ANSTO

Australian  
Synchrotron



in conjunction with

**USER  
MEETING  
2015**

National Centre for Synchrotron Science

25-27 NOVEMBER 2015

Contribution ID : 211

Type : Poster

## Comparing and Contrasting the Anomalous Structural Phase Transformations Between the Isostructural Orthorhombic and Rhombohedral Forms of $\text{CdUO}_4$ and $\text{SrUO}_4$

*Friday, 27 November 2015 13:30 (45)*

The resurgence of interest that is currently enveloping the nuclear power industry has reinvigorated research attempts into optimising current  $\text{UO}_2$  based fuel. However, little progress has been made regarding the understanding of the solid state chemistry of  $\text{UO}_2$  fuels matrices, the interaction they have with fission daughters such as Sr-90/Cs-137 and the solid-phases that form during fission. This has resulted in significant challenges for nuclear waste treatment methods, with no viable long term solutions for nuclear waste.

We have investigated the ternary uranium oxide systems of  $\text{CdUO}_4$  and  $\text{SrUO}_4$  using in situ synchrotron X-ray powder diffraction and absorption spectroscopy (XAS). We have found that both oxides can form iso-morphous rhombohedral and orthorhombic structures. Despite these structural similarities, we found that the structural phase transformation that occurs between the rhombohedral and orthorhombic forms is anomalous and considerably contrasting. In  $\text{SrUO}_4$ , we found the rhombohedral form is a metastable structure that seeks to transform to the orthorhombic form, but is impeded by a large thermodynamic barrier. This barrier can be reduced by formation of vacancies in the oxygen sub-lattice allowing the rhombohedral structure to transform to the stable orthorhombic form with subsequent oxygen reabsorption. In  $\text{CdUO}_4$ , we see opposite, the orthorhombic form is metastable and the rhombohedral is the preferred low energy configuration. However in both instances the transformation does proceed with the generation of vacancies in the oxygen sub-lattice with in situ XAS measurements revealing the reduction of U(VI) to U(V).

### Keywords

Uranium Oxide Structural Chemistry Phase Transformation XAS SXRDPD diffraction

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**Session Classification :** Poster Session 2

**Track Classification :** Energy Materials