Structural-chemical elucidation of low dimensional ternary uranium oxide systems is considered an essential aspect of the nuclear fuel cycle since understanding of their physicochemical properties may guide the storage and disposal of spent nuclear fuel [1]. The study of these systems allows for further exploration of the peculiar, exotic and poorly known properties of materials containing, or which can access, 5f electrons. SrUO₄ exemplifies this, a potential waste form resulting from reaction between spent UO₂+x fuel and the fission daughter Sr-90. We have found, through a combination of in situ synchrotron X-ray powder diffraction and X-ray absorption spectroscopy, that during its first order rhombohedral-orthorhombic transition under oxidising conditions, the rhombohedral form of SrUO₄, α, undergoes a spontaneous reduction of the uranium valence state through oxygen vacancy formation [2]. The process is synergetic, as the triality of oxygen vacancy formation, subsequent ion diffusion and uranium reduction, seemingly reduces the activation energy barrier for the transformation to the thermodynamically favoured stoichiometric orthorhombic form, β-SrUO₄. However formation of the orthorhombic form is only possible if a source of oxygen is present, without this, the oxygen deficient α-SrUO₄-x remains rhombohedral as shown by in situ neutron powder diffraction measurements. These experimental observations are further supported by ab initio DFT+U calculations using the self consistently calculated Hubbard U parameter values and bond valence sums calculations [2-3]. These methods indicate the affinity for α-SrUO₄-x to retain oxygen vacancies as opposed to β-SrUO₄, a consequence of the crystal lattice's ability to stabilise the coordination environment of the Sr²⁺ cation via the flexibility of uranium to undergo reduction through vacancy formation.

CaUO₄, isostructural to α-SrUO₄, but unlike α-SrUO₄ does not have a stable orthorhombic polymorph as shown by both in situ synchrotron X-ray powder diffraction measurements and ab initio calculations. Introducing Sr ions into the CaUO₄ lattice in the form of a solid solution, α-Sr₁-xCaxUO₄ (0 < x < 0.4), provides a means to atomically engineer the lattice to promote oxygen vacancy formation, and presumably diffusion, at high temperatures. When CaUO₄ or α-SrUO₄ is treated under highly reducing conditions, both materials undergo unusual reconstructive phase transformations at high temperatures to a monoclinic structure. These phase transformations are reversible, and cooling the sample yields the corresponding rhombohedral structure again. It is remarkable that the ordered monoclinic structure is favoured at high temperatures and the disordered rhombohedral structure at low temperatures. This investigation in SrUO₄ highlights the rich and remarkable structural chemistry and crystallography that may be found within poorly understood actinide systems whilst demonstrating the successful marriage of experimental and theoretical approaches towards elucidating their chemical and physical phenomena.