

Crystallographic relationships and intermediate oxides in the oxidation of UO_2

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The oxidation of uranium dioxide, UO_2 , is of major interest to the nuclear industry. As UO_2 is oxidised to U_4O_9 , U_3O_7 , and U_3O_8 , often during short- or long-term storage, the physical and chemical properties of the fuel are altered. The crystal structure of these higher oxide phases is somewhat uncertain. Crystallographic relations during an oxidation process can have significant effects on the rate, mechanism, and properties of the product. Allen and Holmes theorized a transformation of (111) UO_2 into (100), however, recent lab-based work has shown that the UO_2 (001) surfaces oxidise to form U_3O_8 (130) in a topotactic transformation [2].

We present work from experiments at the ID11 and ROBL (BM20) beamlines at ESRF, where x-ray diffraction and HERFD-XANES data was obtained during in-situ oxidation of a (001) UO_2 thin film as it topotactically oxidised to U_3O_8 . With this data, we show new insight into the mechanisms of this topotactic transformation, revealing that the intermediate oxide phases (UO_{2+x} , $\beta\text{-U}_4\text{O}_9$, U_3O_7) form during this process. This provides a novel route for obtaining single crystal (multi-domain) samples of these intermediate oxides, allowing single crystal x-ray diffraction analysis of their crystallographic structures, which we will compare with published structures. Furthermore, investigation of diffuse scattering in the UO_{2+x} , $\beta\text{-U}_4\text{O}_9$ range, along with the coupling of these results to XANES spectra gives unprecedented insight into the relationship between oxidation states and structural ordering in the UO_{2+x} phase range.

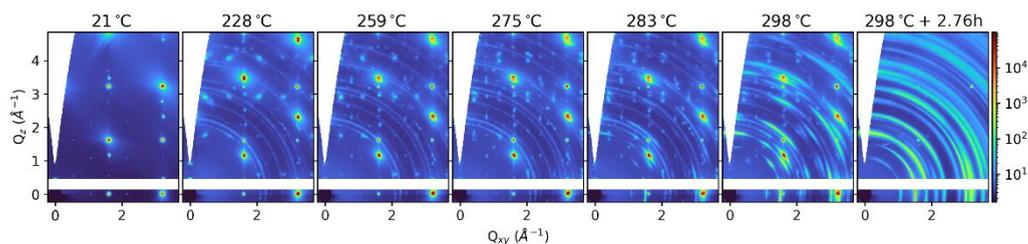


Figure 1: Reciprocal space maps taken from a single crystal UO_2 thin film at exposed to air at increasing temperatures (given above each plot) showing the formation of U_4O_9 , U_3O_7 , and finally U_3O_8 .

[1] G. C. Allen, N. R. Holmes, J. Nucl. Mater. 231-237, 223 (1995).

[2] J. M. Wasik (2009) "Oxidation of Uranium Dioxide" (Doctoral thesis, University of Bristol, Bristol, UK)