Low temperature oxidation of uranium dioxide: an X-ray and electron diffraction study

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Oxidation of UO₂ has been intensively studied since many decades. A lot of work focused on low temperature oxidation (< 400 °C) related to long term dry storage of spent nuclear fuel.[1] Interpretation was based mainly on conventional X-ray techniques and more recently, synchrotron X-ray and neutron diffraction have contributed to the understanding of the complex reaction mechanisms.[2,3] Similar electron diffraction studies remain scarce.

Upon oxidation of UO₂ to U₃O₈ intermediate uranium oxides are formed: cubic β-U₄O₉, tetragonal β-U₃O₇ and various non-cubic, metastable compounds with generalized formula U₃O₇, the structure of which remain incompletely described today. To investigate the course of oxidation, UO₂ powders were oxidized at various temperatures in dry air, for a limited amount of time. The samples present an increasing degree of oxidation. X-ray diffraction analysis shows that β-U₃O₇ forms when UO₂ is oxidized at 250 °C (Figure 1, sample S5). A broad phase field forms upon oxidation at lower temperatures (S1-S4) Full pattern analysis assigns this to U₄O₉ formation with low degree of oxidation (S1, S2) and both U₄O₉ and U₃O₇ formation with extended amounts of oxidation (S3, S4).

Electron diffraction investigations on the S5 sample powder, the XRD pattern of which could readily be indexed according to a fluorite-derived structure, shows additional superlattice reflections (Figure 2), apparently incommensurate with the parent structure and also different from the structure recently refined by Desgranges et al.[3] It remains to be investigated whether the observed modulated structure is to be assigned to a novel (stable or metastable) phase or whether a continuous phase field forms near β-U₃O₇.

References


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