

# Redox Response of Actinide Materials to Highly Ionizing Radiation\*

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Actinide materials are often exposed to high-energy heavy ion irradiation in the form of fission fragments. These high specific energy particles deposit energy in a material primarily through ionization of electrons along their paths. Subsequent electron relaxation causes atomic displacements, forming a damaged ion track. Actinide dioxides with the fluorite structure are highly radiation tolerant, exhibiting neither phase transformations nor amorphization within tracks. However, the precise nature of their radiation response is not known. It was recently shown that swift heavy ion irradiation reduced the Ce<sup>4+</sup> in fluorite-structured CeO<sub>2</sub> to Ce<sup>3+</sup> [1]. This process has important implications for actinide oxides, as their accessible cation electronic configurations vary across the actinide series due to the effects of *f*-electron itinerancy.

To study the radiation response of actinide oxides, powders of ThO<sub>2</sub>, UO<sub>3</sub>, and the uranium oxide hydration products UO<sub>2</sub>(OH)<sub>2</sub> (uranyl hydroxide) and [(UO<sub>2</sub>)<sub>8</sub>O<sub>2</sub>(OH)<sub>12</sub>](H<sub>2</sub>O)<sub>10</sub> (metaschoepite), along with micro- and nanocrystalline CeO<sub>2</sub>, were irradiated with 167 MeV Xe and 950 MeV Au ions to fluences of up to 1 × 10<sup>14</sup> [2]. Irradiation-induced structural modifications were characterized using x-ray diffraction (XRD), while valence changes were tracked using x-ray absorption spectroscopy (XAS).

ThO<sub>2</sub>, for which thorium is stable only in a tetravalent state, exhibited unit cell expansion and the accumulation of heterogeneous microstrain under irradiation. These saturated, as a function of fluence, at higher values when the ion energy was increased. This is consistent with the “velocity effect” wherein the radial distance from the ion path within which energy is deposited increases with ion velocity, producing larger tracks, but lower energy densities and less energy available to displace atoms. No valence changes were observed. CeO<sub>2</sub> exhibited the same structural changes, but with a lack of dependence on ion energy, suggesting that they were not caused directly by defect formation but rather by valence reduction. XAS results confirmed the partial reduction of Ce to the trivalent state, with concomitant changes to ionic radii and electrostatic forces driving expansion and microstrain accumulation. No dependence of valence reduction on ion energy was observed, as was also the case for the structural modifications. These results indicate coupling between changes to electronic and atomic structures.

\* This work was supported by the Energy Frontier Research Center *Materials Science of Actinides* funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-SC0001089).

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Similar study of CeO<sub>2</sub> nanospheres showed enhanced reduction to Ce<sup>3+</sup>. To maintain charge neutrality, this reduction requires the segregation of oxygen from ion tracks. The presence of surfaces allows for efficient loss of anions to the environment, promoting radiation-induced reduction of nanocrystalline material. Its unit cell expansion was an order of magnitude larger than that of the microcrystalline material.

Because hexavalent uranium phases are generally based on uranyl coordination polyhedra, radiation-induced valence reduction has a strong effect on their structure. The three such materials tested all transformed under irradiation to fluorite structured UO<sub>2+x</sub> phases as their U<sup>6+</sup> was reduced to U<sup>4+</sup>.

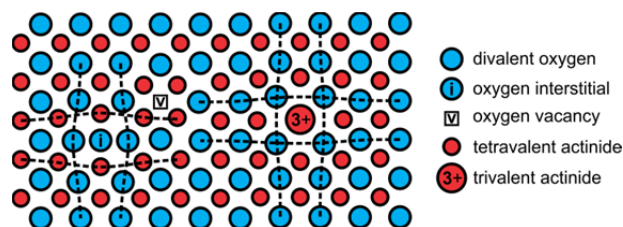


Figure 1: Illustration of the effects of irradiation on fluorite-structured materials. Both Frenkel defects (left) and valence reduction (right) distort the structure.

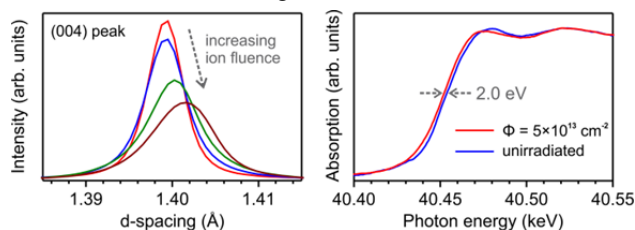


Figure 2: XRD (left) and XAS (right) results for irradiated CeO<sub>2</sub>, indicating expansion, microstrain, and reduction.

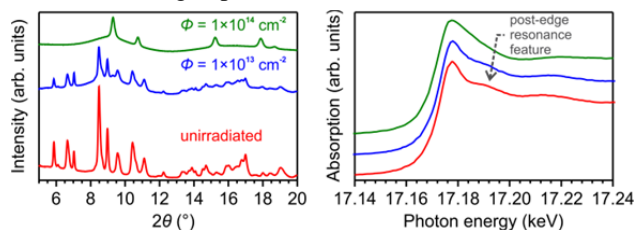


Figure 3: XRD (left) and XAS (right) results for irradiated UO<sub>3</sub>, showing production of U<sup>4+</sup> and a fluorite structure.

## References

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- [2] C.L Tracy *et al.*, *Nature Commun.* **6** (2015) 6133.

