Insights into the fabrication and structure of plutonium pyrochlores as nuclear waste form

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Rare earth zirconates ($A_2B_2O_7$) with the pyrochlore crystal structure have been suggested as potential nuclear waste forms for actinide immobilization, e.g for separated plutonium from dismantling of nuclear weapon programs. This study presents a wet-chemical coprecipitation route to fabricate $Nd_2Zr_2O_7$ pyrochlores with 5 and 10 mol% Pu content [1]. $Pu(NO_3)_4$ was dissolved in nitric acid and was mixed with aqoues $Nd(NO_3)_3$ and $ZrOCl_2$ solutions to co-precipitate the metal hydroxides. The washed precipitate was dried and calcined under reducing atmosphere (Ar-5%H_2). Pellets were sintered at 1450 ˚C under reducing atmosphere. SEM analysis indicated a homogeneous uptake of Pu within the pellets and XRD measurements confirmed crystallisation in the pyrochlore crystal structure. X-ray absorption spectroscopy revealed the majority of Pu to be in the tetravalent oxidation state. Pu L_{III}-edge EXAFS measurements showed Pu to occupy the A-site within the pyrochlore crystal structure. The A-site is characterized by eight nearest neighbors with six longer A-O_{48f} and two shorter A-O_{8b} bonds. In order to obtain a reasonable fit of the EXAFS data the degeneracies of the two Pu-O1 paths were inverted to give six short Pu-O and two long Pu-O paths, indicating a significant distortion of the A-site environment in a pyrochlore structure. On average the nearest neighbor Pu-O bond lengths were determined to be 2.35 Å ± 0.03 for $Nd_{1.9}Pu_{0.1}Zr_2O_7$ and 2.33 Å ± 0.03 for $Nd_{1.8}Pu_{0.2}Zr_2O_7$. These findings were supported by the bond valence sum approach. DFT *ab initio* calculations supported the experimental findings. Immobilization of Pu(IV) on the usually trivalent A site with charge compensation via oxygen atoms at former vacant sites resulted in the lowest solution energies of Pu in pyrochlore. Eventhough the incorporation of Pu(IV) at the A-site results in significant distortion of the A-site local geometry, XRD confirmed the long range pyrochlore structure and the structural uptake of Pu(IV) into the pyrochlore structure.

[1] S. Finkeldei, M.C. Stennett, *et al.* (2020) *J. Mater. Chem. A* **8**, 2387-2403.