

HR-XANES/RIXS structural studies of actinide materials

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The actinide (An) $M_{4,5}$ edge high energy resolution X-ray absorption near edge structure (HR-XANES) and core-to-core 3d4f resonant inelastic X-ray scattering (3d4f RIXS) are becoming increasingly important for electronic structure and speciation studies of actinide materials. The methods will be outlined and recent results for U, Np and Pu containing materials will be discussed.^[1] The experiments were performed at the CAT-ACT beamline at the Karlsruhe Research Accelerator (KARA), Karlsruhe Germany.^[2]

One of the long standing debates in actinide chemistry is the level of localization and participation of the An 5f valence orbitals in covalent bonds across the actinide series. The role of the 5f valence orbitals of uranium (U), neptunium (Np) and plutonium (Pu) in chemical bonding will be illuminated. An $M_{4,5}$ HR-XANES and 3d4f RIXS results reveal that the 5f orbitals are active in the chemical bonding for U and Np, shown by significant variations in the level of their localization evidenced in the spectra. In contrast, the 5f orbitals of Pu appear localized and surprisingly insensitive to different bonding environments. The relative energy differences between the $5f\phi/\delta$ and $5f\pi^*/5f\sigma^*$ orbitals are used as a qualitative measure of overlap-driven $An(VI)O_2^{2+}$ (actinyl) bond covalency.^[1a]

It will be also demonstrated that the Pu M_5 edge HR-XANES method can be very efficiently used to determine Pu oxidation states, which control the solubility limit of Pu in a glass matrix. HR-XANES results show that the addition of excess Si_3N_4 is not sufficient for complete reduction of Pu to Pu(III), which has a relatively high solubility limit (9–22 wt % Pu) due to its network-modifying behavior in glasses. Evidences will be provided that the initially added Pu(VI) might be partly preserved during vitrification at 1200/1400 °C in Ar atmosphere. Pu(VI) could be very advantageous for vitrification of Pu-rich wastes, since it might reach solubility limits of 40 wt % comparable to U(VI).^[1c]

Finally, the Pu M_5 edge HR-XANES spectra of Pu(IV), $Pu(V)O_2^{1+}$, $Pu(VI)O_2^{2+}$ in aqueous solution and PuO_2 will be reported and the potential presence of Pu(V) in colloidal Pu(IV) under given experimental conditions will be discussed. Based on those reference systems, a comprehensive model for formation and growing mechanisms of colloidal Pu(IV) triggered upon X-ray irradiation will be proposed.

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