

Revisit the thermodynamics of orthosilicates for actinide waste form

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Zircon ($ZrSiO_4$; $I4_1/amd$) can accommodate actinides, such as thorium, uranium, and plutonium. The zircon structure has been determined for several of the end member compositions of other actinides, such as plutonium and neptunium. In this talk, we will discuss two thermodynamic discoveries of these orthosilicate compounds related to waste application. First is the recent experimentally determined enthalpy of formation of stetindite ($CeSiO_4$), a surrogate of $PuSiO_4$, along with those of coffinite and thortite, from which we developed an empirical energetic relation for actinide orthosilicates. The predicted enthalpies of formation of $AnSiO_4$ are important for evaluating the thermodynamic stability of immobilizing Pu or minor actinides in the zircon structure. Second, we report the thermodynamic non-ideality when multiple cations (e.g. U, Th, Pu, Ce) mix in the cation sublattice, and its benefits in stabilizing the metastable matrix when actinides are incorporated. This non-ideality could be primarily an electronic effect from the removal of An 5f-O 2p covalent interaction. The implication of combining the two thermodynamic studies is that one may increase the loading of Pu and minor actinides in the zircon matrix and stabilize them by the electron-driven enthalpic and configuration-driven entropic effects. Future thermodynamic studies on the mixed $AnSiO_4$ is needed for validating our hypothesis.