

Thermodynamic consistency of zircon and Brannerite-type phases for actinide immobilization under repository conditions

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Zircon-type minerals (MTi_2O_6) and brannerite-type minerals (MTi_2O_6) [1,2] are common as accessory phases that occur in a variety of sedimentary, igneous, and metamorphic rocks, as secondary phase of spent nuclear fuel in the nuclear waste deep geological repositories, and as candidate ceramic waste forms for immobilization actinides from defense programs. For instance, $(\text{Zr,U})\text{SiO}_4$ phases has been identified as one of the predominant radioactive phases formed in corium during the Chernobyl nuclear accident as well in the Fukushima Daiichi accident from similar phenomena of melted fuel interaction with structural materials.[3,4] Furthermore, by using these mineral structure “analogues” as a potential ceramic waste form, decades of research has been devoted to the permanent immobilization of actinides and long-lived fission products in zircon and brannerite related ceramic phases.[5] Thus, knowing the chemical and thermodynamic stabilities of these phases is essential for evaluating repositories over geological timescales. Ensuring the consistency of thermodynamic parameters (ΔG , ΔH , and ΔS) is therefore critical for high-fidelity thermodynamic evaluation and modeling. The readiness of such predictions depends on answering two questions: Do we have all thermodynamic parameters for relevant endmember phases in a consistent manner? Can we effectively model the solid solutions that dominate natural mineral and waste forms, and if so, can we accurately account for non-ideal mixing effects in multicomponent systems? In this talk, we will discuss both aspects and present case studies of (1) self-consistent thermodynamic data for coffinite, (2) the impact of non-ideal enthalpic mixing of (U, Th) in zircon and (Ce, U, Th) in brannerite structures, and (3) an on-going calorimetric integrated with thermodynamic modeling study on chernobylite $(\text{Zr,U})\text{SiO}_4$, aiming at determining the mixing thermodynamics with implications for its formation and stability.

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