Thermodynamics of $CeSiO_4$

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The demonstrated structural and chemical stability of several minerals such as garnet, zircon, and monazite, to house natural actinides such as thorium (Th) and uranium (U) on time scales of hundred million to billion years, has led to the proposal of utilizing mineral motifs as potential ceramic waste forms for permanent immobilization of actinides and long-life fission products. Among the proposed candidates, zircon ($ZrSiO_4$) has received considerable interests due to its very good chemical durability under a multitude of geophysical and geochemical conditions. These factors have led $ZrSiO_4$ as a potential candidate to immoblize plutonium (Pu) coming from decommissioned nuclear weapons. However, the synthesis of the $PuSiO_4$ end-member or even $ZrSiO_4$ loaded with more than 15 wt.% Pu contents has yet to be reported. This is likely attributed to the $\Delta H_{f,ox}$ of $PuSiO_4$ being thermodynamically unfavorable. Thus, the knowledge of the $\Delta H_{f,ox}$ of $PuSiO_4$ is of great importance for assessing the impact of Pu thermodynamic stability when introduced to the zircon matrix. The high radioactivity and chemical toxicity associated with Pu has led to the application of cerium (Ce) as a surrogate, due to their similar crystallographic radii and several chemical properties. The cerium silicate ($CeSiO_4$), stetindite, was discovered in 2009 and later synthesized as a pure phase in 2019. Utilizing high temperature oxide drop solution calorimetry, both $\Delta H_{f,ox}$ and ΔH_f were determined for synthetic stetindite to be 54.71 ± 2.46 and -1944.69 ± 3.05 kJ/mol, respectively. Combining these values with those obtained for coffinite ($USiO_4$) and thorite ($ThSiO_4$), allowed to generate a gerenal energetic trend for actinide orthosilicates, from which the $\Delta H_{f,ox}$ and ΔH_f values were predicted for $PuSiO_4$.