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Simulation of thermodynamic mixing properties of actinide-containing zircon solid solutions

E.D.A. Ferriss, R.C. Ewing,* and U. Becker

Department of Geological Sciences, University of Michigan, 2534 C.C. Little, Ann Arbor, Michigan 48109-1005, U.S.A.

Abstract

Solid solutions among zircon ($ZrSiO_4$, $I4_1/amd$) and zircon-structured orthosilicates $ASiO_4$ (A = Hf, Th, U, Pu, or Ce) are important to a wide variety of applications: nuclear materials, geochronology, and even electronic materials. The thermodynamic mixing properties of the following seven binary solid solutions were simulated using density functional theory followed by Monte Carlo modeling and thermodynamic integration: (Zr,Hf)SiO_4, (Zr,Th)SiO_4, (Zr,U)SiO_4, (Zr,Pu)SiO_4, (Zr,Ce)SiO_4, (Hf,Pu)SiO_4, and (Th,U)SiO_4. $ZrSiO_4$ and $HfSiO_4$ were found to form a nearly ideal solid solution, but the miscibility of the other solid solutions was limited to no more than 12 mol% of the substituting cation. The binaries were ranked by extent of miscibility: (Zr,Hf)SiO_4 > (Th,U)SiO_4 > (Zr,Pu)SiO_4 > (Zr,Ce)SiO_4 > (Hf,Pu)SiO_4 > (Zr,U)SiO_4 > (Zr,Th)SiO_4. The extent of solid solution has been estimated for each binary. The end-members $PuSiO_4$, $CeSiO_4$, and $USiO_4$ were determined to be unstable relative to a mixture of $SiO_{2(quartz)}$ and crystalline PuO_2, $CeO_{2(cerianite)}$, or $UO_{2(uraninite)}$. Isostructural thorite ($ThSiO_4$) is calculated to be marginally stable, but its monoclinic polymorph, huttonite, which has the structure of monazite, is marginally unstable relative to $SiO_{2(quartz)}$ and $ThO_{2(thorianite)}$ at 0 K. If thermodynamic equilibrium could be reached at low temperatures, exsolution textures would appear in most zircon solid solutions perpendicular to [001], but perpendicular to a linear combination of [100] and [010] in (Hf,Pu)SiO_4.

Keywords: Solid solution, zircon, coffinite, thorite, hafnon, $PuSiO_4$, $CeSiO_4$, Monte Carlo simulation, quantum mechanics