Structural and Energetic Landscapes of Uranothorite Solid Solutions

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Uranothorites ($Th_{1-x}U_xSiO_4$) are important U,Th-containing minerals, which also have potential uses as nuclear waste forms and novel U-Th nuclear fuels. The intermediate phases, also crystallized in the zircon structure type ($I4_1/amd$), bridge the thorite and coffinite endmembers from both structural and thermodynamic aspects. Earlier we performed high temperature oxide melt solution calorimetry to determine the enthalpies of formation of uranothorite solid solutions (x = 0 ~ 1) and reported their non-ideal mixing enthalpies [1]. This non-linear behavior was also seen in variations of their unit cell parameters refined from PXRD data. We have now collected neutron total scattering data and performed Rietveld and pair distribution function (PDF) analyses. Changes in local bonding parameters of U/Th-Si and O-O were observed. Finally, we studied the structural behavior of uranothorites as a function of temperature or pressure. *In situ* heating and pressurizing synchrotron XRD experiments were performed up to 1000 °C and 30 GPa, respectively. Phase decomposition was observed at high temperature. Temperature and pressure dependent unit cell parameters, atomic positions, and atomic displacement parameters were investigated by Rietveld analyses of the XRD data. The results allowed determination of axial and volume thermal expansion coefficients and bulk moduli, and revealed the underlying structural mechanisms. The combined structural and energetic results enhance our understanding of the behavior of uranothorites under various P-T conditions, as encountered in nuclear reactor and geological repository applications.

[1] Guo et al. (2016) Chem. Mater. 28(19) (2016) 7117-7124.