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Role of water and hydroxyl groups in the structures of stetindite and coffinite, $MSiO_4$ (M = Ce, U)

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Orthosilicates adopt the zircon structure-types ($I4_1/amd$), consisting of isolated SiO_4 tetrahedra joined by A-site metal cations, such as Ce and U. They are of significant interest in the fields of geochemistry, mineralogy, nuclear waste form development and material science. Stetindite ($CeSiO_4$) and coffinite ($USiO_4$) can be formed under hydrothermal conditions despite both being recently found to be thermodynamically metastable by high temperature oxide melt calorimetry. Water has been hypothesized to play a significant role in stabilizing and forming these orthosilicate phases, though little experimental evidence exists. To understand the effects of hydration or hydroxylation on these orthosilicates, *in situ* high temperature synchrotron X-ray diffraction (HT-XRD) and laboratory-based vibrational spectroscopy was conducted from 25 °C to ~1000°C. From the HT-XRD it was found that, stetindite maintains its $I4_1/amd$ symmetry with increasing temperature but exhibits a discontinuous expansion along the *a*-axis during heating, presumably due to the removal of water confined in the [001] channels, which shrink against thermal expansion along the *a*-axis. Coffinite was also found to expand nonlinearly up to 600 °C, and then thermally decompose into a mixture of UO_2 and SiO_2. A combination of dehydration and dehydroxylation is proposed for explaining the thermal behavior of coffinite synthesized hydrothermally. The additional *in situ* high temperature Raman and FTIR spectroscopy further confirm the presence of the confined water in stetindite and combination of each for coffinite.