Thermal behaviour of Tc and Re salts.

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^{99}Tc is a long-lived isotope produced in uranium fission, and it's the largest fraction of the total long-lived radiation emissions in nuclear waste. Tc 7+ compounds are highly mobile in the environment, however relatively little is known regarding their crystal chemistry and thermal behavior. We have studied the structural properties of $(NH_4)TcO_4$ (Tc7+) and confirmed that this is isostructural with $(NH_4)ReO_4$ adopting a tetragonal scheelite type structure in space group $I4_1/a$. The unit cell parameters of $(NH_4)TcO_4$ are strongly temperature dependent and display negative thermal expansion along both the *a*- and *c*-axis over a restricted temperature range. This behavior is similar, but not identical, to the reported highly anisotropic thermal expansion behavior for $(NH_4)ReO_4$. Despite the observed difference it is likely that the origin of the anomalous thermal expansion is the same in both cases, namely it is a consequence of re-orientation of the ammonium ions in the surrounding cage of eight oxygen atoms. To verify this for $(NH_4)TcO_4$ requires we replace the ammonium cation with another small monovalent cation. Therefore we have compared the thermal behavior, via variable temperature synchrotron X-ray diffraction, of some ReO_4 with $ATcO_4$ oxides to determine if Re oxides are suitable surrogates to predict the behavior of Tc oxides and how they may behave in the environment. To then understand the cation dependence of these Tc salts we have taken some of the $ATcO_4$ samples past their melting points and let them solidify again.