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Comparison of thermal expansion of Tc and Re salts.

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^{99}Tc is the most significant long-lived product of uranium fission, producing the largest fraction of the total long-lived radiation emissions of nuclear waste. Tc^{7+} compounds are highly mobile in the environment. Relatively little is known regarding the solid state chemistry of Tc. Recently we studied the structural properties of $(\text{NH}_4)\text{TcO}_4$ (Tc^{7+}) and confirmed that this is isostructural with $(\text{NH}_4)\text{ReO}_4$ adopting a tetragonal scheelite type structure in space group $I4_1/a$. The unit cell parameters of $(\text{NH}_4)\text{TcO}_4$ are strongly temperature dependent with the structure showing negative thermal expansion along both the a - and c -axis, albeit at different temperatures. This behavior is significantly different to that previously reported for the isostructural oxide $(\text{NH}_4)\text{ReO}_4$, although we note that the data for $(\text{NH}_4)\text{ReO}_4$ was collected at much lower resolution. Nevertheless it is clear in the literature that the thermal expansion behavior of $(\text{NH}_4)\text{ReO}_4$ is highly anisotropic. Despite the difference in the thermal expansion between what we have observed for $(\text{NH}_4)\text{TcO}_4$ and that described by others for $(\text{NH}_4)\text{ReO}_4$ it is likely that the origin of the anomalous thermal expansion in 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 $(\text{NH}_4)\text{TcO}_4$ requires we replace the ammonium cation with another small cation. Therefore we have compared the thermal behavior of AReO_4 with ATcO_4 to determine if Re oxides are suitable surrogates to predict the behavior of Tc oxides and how they may behave in the environment.

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