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Thorite: An oddity in phase stability among the zircon-structured orthosilicates at high pressures

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Abstract

Synthetic thorite and huttonite, two polymorphs of $ThSiO_4$, were investigated by a combination of in situ high-pressure synchrotron X-ray powder diffraction and in situ high-pressure Raman spectroscopy. The average onset pressure of the thorite-to-huttonite transition was determined to be 6.6 ± 0.2 GPa, using both techniques. The bulk moduli of thorite and huttonite were determined to be 139(9) and 246(11) GPa, respectively, by fitting their unit-cell volume data to a second-order Birch-Murnaghan equation of state (EOS). Based on its bulk modulus, thorite is the most compressible zircon-structured orthosilicate, as it has the largest unit-cell volume among tetravalent metal orthosilicates. The pressure derivatives of the vibrational modes of thorite were found to be consistent with those previously reported for other orthosilicates (e.g., zircon, hafnon, stetindite, and coffinite), while having the smallest Grüneisen parameter. A new *P-T* phase diagram for $ThSiO_4$ is proposed, where the boundary of the thorite → huttonite transition is: $P(T) = (7.8 \pm 0.9\ \text{GPa}) - (0.006 \pm 0.002\ \text{GPa/K})T$. Based on the new *P-T* phase diagram, we further estimated the enthalpy of formation of huttonite, $\Delta H_{f,ox}$, to be 0.6 ± 6.0 kJ/mol, suggesting its metastability and rare locality in nature.

Keywords: Thorite, huttonite, X-ray diffraction, high pressure, equation of state, phase diagram, metastability