Structural Transition and Electron Transfer in Coffinite, USiO₄, at High Pressure

D.M. Reaman, W.R. Panero Ohio State University 
Z.X. Liu Geophysical Laboratory, Carnegie Institution of Washington 
J.Z. Hu Stony Brook University 
C. Poinssot Commissariat à l’Energie Atomique

Coffinite, USiO₄, forms as an alteration product of uraninite (UO₂) under reducing conditions in the presence of silica-rich solutions occurring in nature as microscopic intergrowths with other minerals. Coffinite and thorite (ThSiO₄) are the only actinide minerals that have the zircon structure. The high-pressure behavior of synthetic coffinite was, for the first time, studied in a diamond-anvil cell up to 45 GPa. In situ synchrotron X-ray diffraction and infrared (IR) spectroscopy at the COMPRES beamlines X17C and U2A of the NSLS consistently evidenced a pressure-induced phase transition to a scheelite-structured polymorph at 14 – 17 GPa. This irreversible transformation, which occurs similarly in zircon (ZrSiO₄), was independently confirmed by quantum-mechanical calculations using density functional theory. Interestingly, the IR measurements suggest that water is partially covalently bonded within the coffinite structure in correlation with a possible pressure-induced increase in the oxidation state from U⁴⁺ to U⁵⁺.

Figures: (a) Selected XRD patterns show a pressure-induced phase transition in coffinite starting at ~16.6 GPa and a partial amorphization at significantly higher pressures. The dot symbols indicate the diffraction maxima from the scheelite-structured USiO₄ high-pressure phase. (b) Lattice of zircon-structured coffinite at ambient conditions and (c) scheelite-structured high-pressure phase. Blue spheres are U, green spheres are Si and red spheres are O.


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