Poster Presentation

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High-T, High-P Hydrothermal Synthesis of Uranium Silicates and Germanates

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Most uranium minerals can be classified as oxidized species in which U is fully oxidized to U(VI), and reduced species, in which U occurs primarily as U(IV). Uranyl silicates are an important group of uranium(VI) minerals in the altered zones of many uranium deposits [1]. Uranyl silicates have also received attention because they form when spent nuclear fuel interacts with water containing silicon under oxidizing conditions. One naturally occurring uranium(IV) silicate exists, namely coffinite (USiO4), which is the most important ore mineral for uranium after uraninite. Numerous synthetic uranium(VI) silicates and germanates containing organic amines or alkali metals as countercations have also been reported [2]. In contrast to the uranium(VI) compounds, the chemistry of materials containing uranium(V) is considerably less developed owing to the tendency of U(V) to either oxidize to U(VI) or disproportionate to U(IV) and U(VI). We have synthesized a pentavalent-uranium silicate and a germanate by a high-temperature, high-pressure hydrothermal method in gold ampoules contained in a high-pressure reaction vessel at ca. 600 ºC and 170 MPa [3a,b]. Following the synthesis of the U(V) compounds, a number of mixed-valence uranium silicates and germanates have been synthesized, for example, a mixed-valence uranium(IV,V) silicate, Cs2K(UO)2Si4O12 [3c], a uranium(IV,VI) germanate, Cs8U(UO2)3(Ge3O9)3·3H2O [3d], uranium(V,VI) silicates and germanates, A3(U2O4)Ge2O7 (A = Rb, Cs) and [Na9F2][(UO2)3(Si2O7)2] [3e,f], and a uranium(IV,V,VI) silicate, Na7UO2(UO)2(UO2)2Si4O16 [3g] in which three oxidation states of uranium co-exist in one compound. In addition, tetravalent-uranium compounds, Cs2USi6O15 and Cs4UGe8O20 [3h,i], were also synthesized. All members in the family of uranium silicates and germanates with the oxidation states of uranium from +4 to +6 have been observed. In this presentation the high-temperature, high-pressure hydrothermal synthesis, crystal structures, and XPS spectroscopy of these interesting compounds will be reported.

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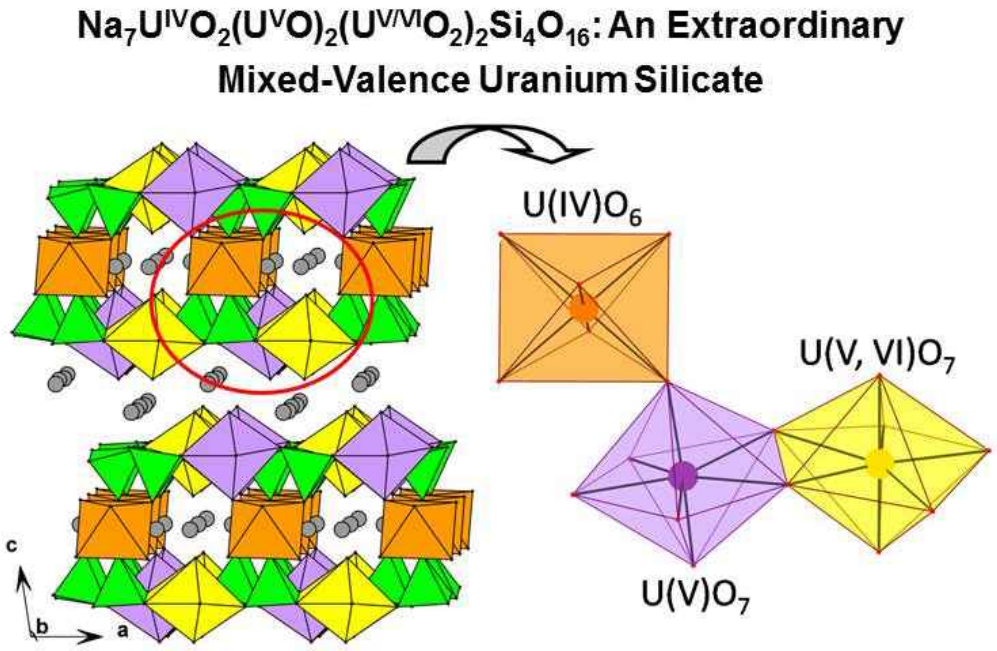

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