



Figure 1. Crystallite size along *a* axis (red circles, left ordinate) and micro-strain (blue triangles, right ordinate) of various molar types. Crystallite size along the direction of *c* axis shows analogous behavior.

Keywords: crystallite size, micro-strain, enamel development

MS14-P11 High-temperature, high-pressure 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 U⁶⁺, and reduced species, in which U occurs primarily as U⁴⁺. Uranyl silicates are an important group of U(VI) minerals in the altered zones of many uranium deposits.¹ One naturally occurring U(IV) silicate exists, namely coffinite (USiO₄), which is an important ore mineral for uranium. Numerous synthetic U(VI) silicates and germanates containing organic amines or alkali metals as countercations have also been reported.² In contrast to the U(VI) compounds, the chemistry of materials containing U(V) is considerably less developed owing to the tendency of U⁵⁺ to either oxidize to U⁶⁺ or disproportionate to U⁴⁺ and U⁶⁺. We have synthesized a U(V) silicate and a germanate by a high-T, high-P hydrothermal method in gold ampoules contained in a high-pressure reaction vessel at ca. 600 °C and 170 MPa.^{3a,3b} Following the synthesis of the U(V) compound, a number of mixed-valence uranium silicates and germanates have been synthesized, for example, a mixed-valence U(IV,V) silicate, Cs₃K(UO)₂Si₃O₁₀,^{3c} U(IV,VI) germanate, Cs₈U(UO₂)₃(Ge₃O₉)₃·3H₂O,^{3d} U(V,VI) germanates, A₃(U₂O)₂Ge₂O₇ (A³⁺ = Rb, Cs),^{3e} and a U(IV,V,VI) silicate, Na₇U^{IV}O₂(U^VO)₂(U^{V/VI}O₂)₂Si₄O₁₆,^{3f} in which three oxidation states of uranium co-exist in one compound. In addition, tetravalent-uranium compounds, Cs₃USi₆O₁₅ and Cs₃UGe₈O₂₀,^{3g,3h} 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.

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