Applications of Aqueous Stability Diagrams to Hydrothermal Synthesis

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Abstract: Hydrothermal methods have been successful in polycrystalline and single-crystal synthetic schemes. This method's most beneficial advantages are mild working temperatures compared to the high temperatures required for solid state reaction or melt crystal growth. Mild hydrothermal methods (<230 °C) for synthesis of ceramic powders have used thermodynamic calculations to optimize yields for chemical systems such as lead titanate and hydroxyapatite. These calculations are accomplished with OLI Stream Analyzer 9.5, with a large databank of thermodynamic information for solids and aqueous species and calculation limits of 300 °C, 1500 bar and 30 *m* ionic strength. This software can simulate reactions under different conditions based on reactant input, and stability diagrams show the boundaries of thermodynamic phase stability. As an extension to yield-optimizing applications, this project investigates OLI applicability towards the discovery of new quaternary solid state compounds. For previously discovered $Zn_2EDTA.2H_2O$ single crystals, it was found that hydrothermal conditions for this compound were just outside of the stability region for ZnO. For this project, the methodology has focused on alkali metal-rare earth silicates and zirconates [(Na,K)-(Y,La)-(Si,Zr)-O], with variable concentration and pH in the search for new phases. The process is aided by the use of stability diagrams showing the boundaries of thermodynamic phase stability, pointing to specific compositions that could yield new compounds, and therefore which specific point in phase space to be explored. Experimental conditions include reactants of rare earth chlorides, sodium metasilicate, zirconyl chloride, and alkali metal hydroxide base, enclosed in Teflon-lined digestion vessels and heated at 200 °C for one week. After products are collected, washed, and centrifuged, they are examined by optical microscopy, powder X-ray diffraction and scanning electron microscopy. Experiments performed using lanthanum or yttrium chloride and sodium metasilicate yielded no new or existing phases in the explored regions of phase space. The analogous procedures with zirconyl salt are under current exploration.