Discovery of New Zirconate Compounds using Speciation Calculations and Hydrothermal Methods

Kameron Johnson and *Maria C. Gelabert
Undergraduate Student, Winthrop University, and Professor, Winthrop University

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This project investigated aqueous modeling coupled with mild hydrothermal methods (200 °C and ≈16 atm) for discovery of new compounds, one specific goal related to development of advanced materials outlined in *SC Vision 2025* and *NSF Big Ideas*. Novel materials for optical applications, such as luminescent scintillators, are desired for improvement of properties, and in this project, we have chosen the K-La-Zr-O quaternary system to combine exploratory hydrothermal synthesis with thermodynamic guidance from aqueous speciation calculations performed with OLI Systems software *(1)*. By altering the composition of the starting materials, it is possible to generate trace amounts of crystals that have either never before been synthesized or have only been hydrothermally synthesized at much higher temperatures. Utilized previously in ceramic engineering applications *(2)*, in the discovery of novel compound $Zn_2EDTA.2H_2O$ *(3)*, it was found that hydrothermal conditions for this compound were just outside of the thermodynamic stability region for ZnO at synthesis temperatures, enabling the hypothesis that new compounds are more likely to be discovered on the edges of those stability regions. Using OLI Studio *Stream Analyzer* aqueous speciation software, yield diagrams were constructed in the quaternary K-La-Zr-O system, with water-soluble metal salts, appropriate chelating agents and acid/base, to aim towards discovery of new rare earth optical compounds. Chemical systems such as this one will readily form highly stable thermodynamic binary compounds, notably zirconia (ZrO_2) and lanthanum hydroxide ($La(OH)_3$). Within the yield diagrams, where metal concentrations are plotted against pH, regions just outside of stability regions for $La(OH)_3$ and ZrO_2 were targeted for Zr:La ratios of 1:1 and 4:1. In hydrothermal autoclaves heated to 200 °C, aqueous mixtures of zirconyl chloride, acetylacetone, lanthanum chloride, ethylenediaminetetraacetate and potassium hydroxide were maintained at 200 °C for 4-7 days, then quenched in cold water. Products were washed and centrifuged, then examined with optical microscopy, scanning electron microscopy (SEM) with energy-dispersive X-ray (EDS) analysis, and powder X-ray diffraction (XRD). X-ray powder patterns show a mixture of products. Scanning electron microscopy (SEM) with energy-dispersive X-ray (EDS) analysis revealed polycrystalline morphology with some single crystals (50 microns) of hexagonal geometry that contain significant amounts of lanthanum, zirconium, oxygen with trace levels of alkali metals, leading us to tentatively conclude that these crystals are of a lanthanum zirconate compound.

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