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Thermodynamics-Based Discovery of New K-La-Zr-O Compounds via Hydrothermal Synthetic Methods

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Research on Thermodynamic-based Discovery of New K-La-Zr-O Compounds

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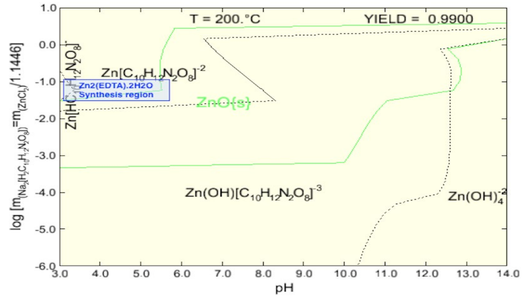
Abstract

This project employs aqueous modeling and solid-state synthetic methods for novel compound discovery under mild hydrothermal conditions (≈ 200 °C, 16 atm.) – one specific goal for advanced material development outlined by *SC Vision 2025* and *NSF's Big Ideas*. Innovative luminescent materials, especially visible-light-emitting scintillators, are desired for improving properties of opto-electronics and other optical material technologies. Guided by aqueous speciation calculations run with OLI Studio, exploratory hydrothermal syntheses are performed in attempt to yield new compounds of the K-La-Zr-O quaternary system, as inspired by several compounds of Na-Y-Si-O and related systems having previously been synthesized by supercritical hydrothermal methods(1). By altering reactant compositions, it is possible to generate trace amounts of crystals that either have never been synthesized or have only been synthesized under extreme conditions as engineered in ceramic applications(2). In the prior discovery of $Zn_2EDTA.2H_2O$, the Gelabert lab showed that conditions necessary to synthesize the compound lie just outside parts of the thermodynamic stability region for ZnO, suggesting that other new compounds are likely to be revealed while working around the edges of such stability regions(3). Through OLI Studio's Stream Analyzer aqueous speciation software, yield diagrams are constructed for the K-La-Zr-O system, with water-soluble metal salts, chelating agent, water, and base as reactants for synthesis of a new rare-earth optical compound(s). Constituents of systems like this are known to readily form stable binary/ternary compounds – in this case, zirconia (ZrO_2) and lanthanum hydroxide ($La(OH)_3$) – under supportive conditions. Within yield diagrams of the Zr and La subsystems, where metal concentration ratios are plotted against base concentrations, locations just outside the ZrO_2 stability region are targeted for 1:1 and 4:1 Zr:La ratios. Use of a scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopic technology (EDS) reveals polycrystalline morphology with some unified crystals (≈ 50 microns) of hexagonal or greater (7+ sides) geometries significantly containing lanthanum, zirconium, oxygen, and carbon (but very limited potassium), leading to the tentative conclusion that these crystals may be of some complex lanthanum zirconate compound.

Introduction

For previously undiscovered $Zn_2EDTA.2H_2O$, conditions necessary to hydrothermally synthesize single crystals of this compound were just outside of the stability region for ZnO (*3*). The region in blue indicates optimal conditions for $Zn_2(EDTA).2H_2O$, and the outlined region in green is where OLI predicts that ZnO would form with over 99% yield.



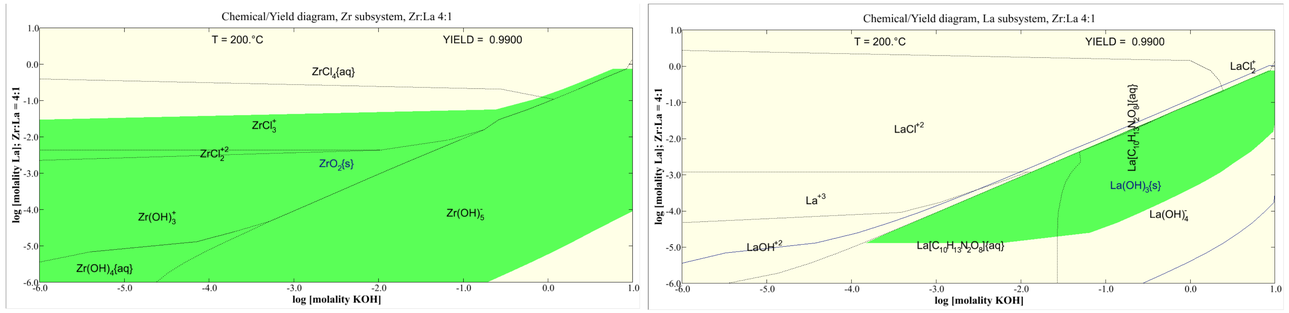
Mild hydrothermal synthetic methods are already used to prepare optically active compounds (*4*), but this process can also enable discovery of compounds with new stoichiometries in new or known systems. By altering the composition of starting materials, it is possible to generate trace amounts of crystals that either have yet to be synthesized or have only been hydrothermally synthesized at much higher temperatures and pressures.

Hydrothermal Synthetic Methods and Materials

Aqueous mixtures of $ZrOCl_2$, $LaCl_3$, EDTA, and KOH were prepared with target amounts corresponding to several locations outside the ZrO_2 stability region. Samples (1E remake, 2A-C .1-.3, 3C, 4A-B, and 5A-B) were sealed in Teflon-lined autoclaves and maintained at 200 °C for 5 days, then quenched in cold water. Products were centrifuged and washed in distilled water (x2) and then ethanol (x2) to prepare for analysis via optical microscopy (Leica DM 2500M), X-ray powder diffraction (XRD, Rigaku Miniflex 600), and scanning electron microscopy (SEM) with energy-dispersive X-ray (EDS) analysis (JEOL 1610 InTouchScope).

- Lanthanum chloride heptahydrate, $LaCl_3.7H_2O$
- Zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$
- Disodium dihydrogen ethylenediaminetetraacetate dihydrate, $Na_2H_2EDTA.2H_2O$, a.k.a. "EDTA"
- Potassium hydroxide, KOH
- ≈ 10g distilled, deionized H_2O per sample
- Acetylacetone, a.k.a. "acac" (Sample 1E remake only)
- pH measurement with Accumet probe
- Teflon liners, Parr acid digestion vessels
- 200 °C, Heratherm mechanical convection oven

Yield Diagrams

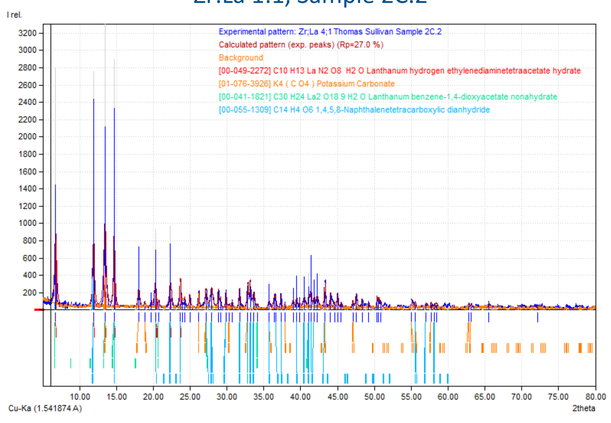


Chemical/yield diagrams are shown for Zr:La 4:1, (left): zirconium subsystem, (right): lanthanum subsystem; these diagrams illustrate log molalities of La vs. log molalities of KOH; 99% yield regions for zirconia (ZrO_2) (left) and lanthanum hydroxide {$La(OH)_3$} (right) are highlighted in green.

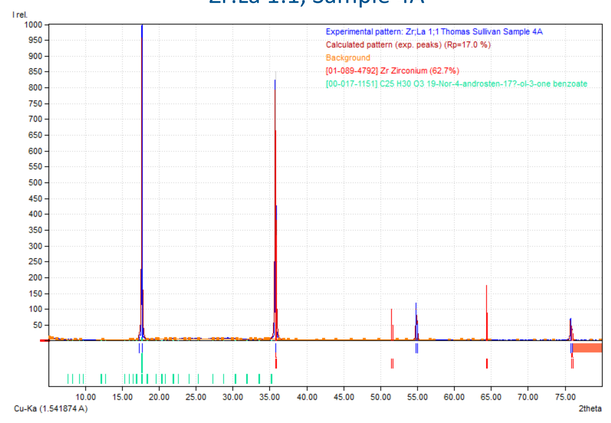
X-ray Powder Diffraction

Analyses on XRD patterns for samples, such as 4A (XRD patterns shown below), reveal a mixture of mostly binary and ternary phase components. Crystalline products consisting of any new phases (ternary and/or quaternary) will likely be in small yield, and thus not readily, if at all, identifiable with X-ray powder diffraction. Having high figures of merit for patterns of only pure elemental (single-component) phases may suggest that a significant portion of the synthesized material is some compound(s) for which XRD patterns and/or .CIF files have not yet been published.

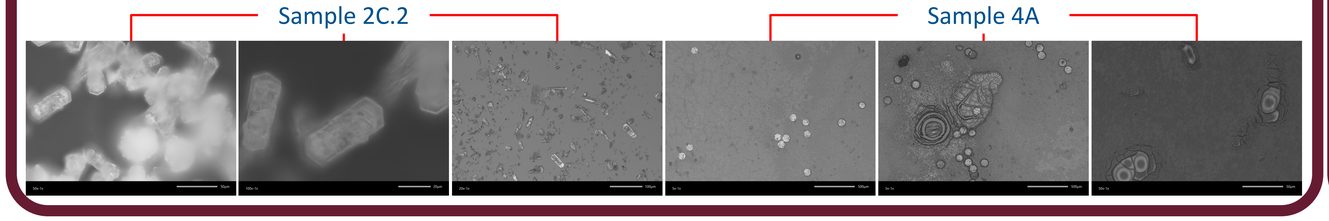
Zr:La 1:1, Sample 2C.2



Zr:La 1:1, Sample 4A

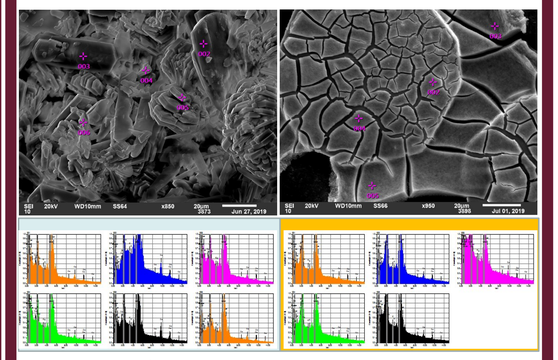


Optical Scope Microscopy



Scanning Electron Microscopy/EDS

Scanning Electron Microscopy with Energy-Dispersive Spectroscopy X-ray analysis was used for imaging, element identification and analysis.



Sample 2C.2 Sample 4A

Future Work

- Continue SEM/EDS analyses of samples (5A-B,3C)
- Continue exploration of this and related systems with different compositions of starting materials
- Inclusion of high-temperature solid state investigation of phase diagram(s)

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Acknowledgments

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