

Homework 6
Advanced Materials Thermodynamics
Due Monday October 7, 2024

The formation of complex multicomponent oxides for catalysts, battery electrodes, solid state electrolytes for fuel cells and hydrogen generation, and high temperature super conductors are an important area of active research. These oxides are formed by solid state reactions starting from oxide powders that are mixed and fired in a furnace. Problems include unintended byproduct phases, and incomplete solid-state reactions due to poor kinetics. This is a multidimensional phase space, and the simplest approach is a three-dimensional ternary phase diagram with a vertical axis of chemical potential or of reaction energy. Reaction energy can be calculated using density functional theory simulations (DFT) but this ignores the entropic and kinetic features. So experimental verification of DFT predictions is necessary. Experimentation in this complex space requires hundreds of synthesis reactions making automation desirable. Chen J, Cross SR, Miara LJ, Cho JJ, Wang Y, Sun W *Navigating phase diagram complexity to guide robotic inorganic materials synthesis* Nat. Syn. **3** 606-614 (2024) describe an approach using DFT ternary reaction energy plots and an automated robotic laboratory to determine the best synthetic route to several complex multicomponent oxides of lithium like the materials studied last week. All of Chen's reactions begin with a ternary mixture of three oxides.

- a) Explain how you would determine the composition in a ternary phase diagram. What do the three axis represent?
- b) Figure 1 shows the DFT results for mixtures of B_2O_3 , BaO , and Li_2O . Four slices through the ternary phase diagram are shown. Explain what each of these slices pertains to and why the plots c, e, and h were made. What is the vertical axis in Figures b, d, and g?
- c) Where would Ba_3BO_3 and $Ba_3(BO_3)_2$ be on these ternary plots? Why is $LiBaBO_3$ unlikely to form? What is an isopleth? What does barycentric mean?
- d) Explain the logic behind the synthesis principles listed on page 607 second column. Do you agree with this approach?
- e) Explain why robotic processing is better than people. Look at the videos in the supplemental material and give a critique of this approach, that is, does it seem reasonable to you?