Understanding Crystallization Pathways of Manganese Oxide Polymorphs
Formation by using in-situ X-ray Scattering

Bor-Rong Chen¹, Wenhao Sun², Daniil A. Kitchaev⁴, John S. Mangum⁵, Vivek Thampy¹, Lauren M. Garten⁶, David G. Ginley⁶, Brian P. Gorman⁵, Kevin H. Stone¹, Gerbrand Ceder²,³, Michael F. Toney¹,⁷, Laura T. Schelhas⁷.

¹ Stanford Synchrotron Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, 94025, USA.
² Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA.
³ Department of Materials Science and Engineering, UC Berkeley, Berkeley, CA, 94720, USA.
⁴ Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA.
⁵ Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO, 80401, USA.
⁶ National Renewable Energy Laboratory, Golden, CO, 80401, USA.
⁷ Applied Energy Programs, SLAC National Accelerator Laboratory, Menlo Park, CA, 94025, USA.

Hydrothermal synthesis is challenging in metal oxide systems with diverse polymorphism, as subtle variations in synthesis parameters significantly change the reaction products. This sensitivity is rooted in the non-equilibrium nature of low-temperature crystallization, during which the competition between different metastable phases can lead to complex multistage crystallization pathways. Here, we propose a theoretical framework to predict how particle size and solution composition influence polymorph stability during nucleation and growth. To validate this framework experimentally, we use the hydrothermal synthesis of MnO₂ as a demonstration case. We investigate the nature of synthesis pathways by using in-situ X-ray techniques, including scattering and spectroscopy, to monitor how the species in the solution evolves during the reaction in real-time. In the experiment, three synthesis pathways with varying potassium ion concentrations ([K⁺] = 0, 0.2, and 0.33 M) in the solution were studied. We find that our computed size-dependent phase diagrams qualitatively capture which metastable/intermediate polymorphs appear, the order of their appearance, and their relative lifetimes, under these three [K⁺] conditions. This combination of computational and experimental approach offers a more rational and systematic paradigm for the aqueous synthesis of target metal oxides.