

# Understanding Crystallization Pathways in MnO<sub>2</sub> Polymorphs

## Scientific Achievement

Demonstrated predictive synthesis of MnO<sub>2</sub> polymorphs based on principle of remnant metastability—that synthesizable metastable phases nucleate under thermodynamic conditions where they were once the lowest free-energy phase, and then grow into conditions where they are metastable. Using *in-situ* X-ray diffraction measurements, we verify that this framework can predict which phases are more likely to form as well as the progression order of phases.

## Significance and Impact

The successful prediction of phase progression during MnO<sub>2</sub> polymorphs synthesis demonstrates the viability of remnant metastability as a general framework—for predicting synthetically accessible metastable materials and as a practical tool for guiding synthesis.

## Research Details

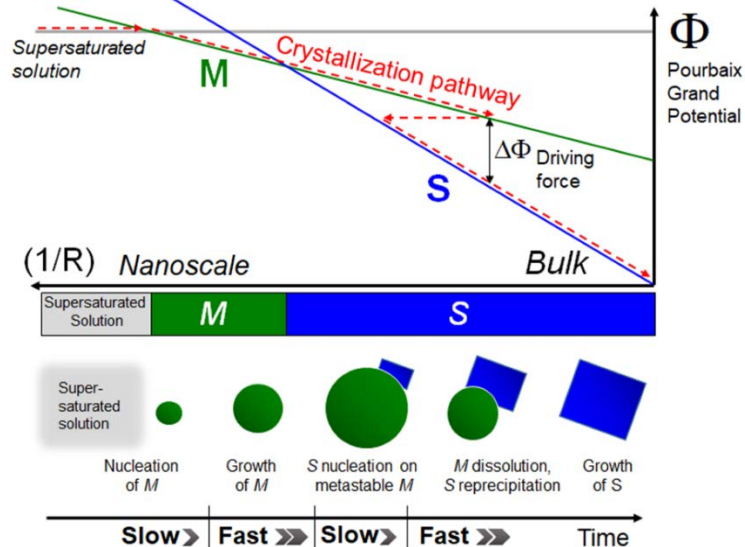
**Theory:** *Ab-initio* predictive framework shows how particle size and solution composition influence polymorph stability during nucleation and growth.

**Synthesis:** Hydrothermal synthesis with varying solution potassium ion concentrations ( $[K^+] = 0, 0.2, \text{ and } 0.33 \text{ M}$ ).

**Characterization:** *In-situ* X-ray diffraction observed predicted progression of crystalline polymorphs during synthesis.

B.-R. Chen, W. Sun, D.A. Kitchaev, J.S. Mangum, V. Thampy, L.M. Garten, D.S. Ginley, B.P. Gorman, K.H. Stone, G. Ceder, M.F. Toney, L.T. Schelhas, *Nature Communications* **9**(1), 2553. DOI: 1038/s41467-018-04917-y

## Schematic Representation of Remnant Metastability in a Crystallization Pathway



## *In-situ* Observation of Predicted Phase Progression

