

# ***In-situ* X-ray Characterization of MnOx Polymorphs Formation Pathways via Hydrothermal Synthesis**

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Computational driven design of materials has provided guidelines for precisely synthesizing materials with desired properties. However, the current computational approaches are still limited in predicting intermediate/metastable phases that can be accessed along synthesis pathways. To overcome this bottleneck, we developed a new approach that combines *in-situ* X-ray characterization and thermodynamic calculations to investigate the nature of reaction pathways via hydrothermal synthesis. Our design of hydrothermal reactor was adapted from previously established ones [1], but with both ends of the glass capillary reactor flame sealed to mimic a conventional autoclave. Additionally, the experimental reaction conditions investigated in this study were guided by thermodynamic calculations developed by our theory collaborators, as published in Ref. [2,3].

In our work, the MnOx system is utilized as the chemical space because of its rich polymorphism, which provides many possible reaction pathways to explore. We monitor the hydrothermal synthesis of MnOx in real-time with *in-situ* wide-angle X-ray scattering (WAXS) at 160 °C for 24 hr. Three reaction pathways with different [K<sup>+</sup>] were investigated with controlled [MnO<sub>4</sub><sup>-</sup>] and pH. The results show the evolution of different intermediate phases during the transition from MnO<sub>4</sub><sup>-</sup>(aq) to MnO<sub>2</sub>(s) at different [K<sup>+</sup>]. The crystalline structure of the intermediate phases and overall formation pathways are consistent with our theoretical predictions. In the course of this research, the experimental inputs are used to further refine the theory, which leads to precisely pinpointing the synthesis conditions for specific polymorphs. Overall, this study successfully demonstrates how experiment and theory work together to develop sophisticated modeling for predicting reaction pathways. In particular, the *in-situ* X-ray characterization has irreplaceable significance in monitoring the evolution of intermediates in real-time. The future outlook for this “synthesis by design” approach is promising for other binary and ternary oxides with high polymorphism.

[1] K. M. Ø. Jensen, C. Tyrsted, M. Bremholm, and B. B. Iversen, 1594 (2014).

[2] D. A. Kitchaev, H. Peng, Y. Liu, J. Sun, J. P. Perdew, and G. Ceder, Phys. Rev. B - Condens. Matter Mater. Phys. **93**, 1 (2016).

[3] D. A. Kitchaev, S. T. Dacek, W. Sun, and G. Ceder, J. Am. Chem. Soc. **139**, 2672 (2017).