doi:10.1017/S1431927618007912
Microsc. Microanal. 24 (Suppl 1), 2018

Understanding Crystallization Pathways of MnO_x Polymorph Formation via *in-situ* X-ray Scattering

Bor-Rong Chen[1], Wenhao Sun[2,3], Daniil A. Kitchaev[4], John S. Mangum[5], Vivek Thampy[1], Lauren M. Garten[6], David G. Ginley[6], Brian P. Gorman[5], Kevin H. Stone[1], Gerbrand Ceder[2,3], Michael F. Toney[1,7], Laura T. Schelhas[7]

[1.] Stanford Synchrotron Radiation Lightsource, 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.

Presently, ab-initio computation methods have advanced to the point that they are used to design novel compounds with targeted properties and have significantly advanced our understanding of structure-property relationships in inorganic compounds. However, similar quantitative, predictive theories for directing the synthesis of materials do not yet exist, and as a result, the synthesis of many compounds is Edisonian and requires repeated iterations to find the reaction conditions needed to create a particular stable or metastable phase. An understanding of the dynamics of the phase transformations that occur during the synthesis of crystalline materials offers an opportunity for materials discovery, as metastable phases often exhibit superior properties to their stable counterparts.

This challenge of theory-guided synthesis, in particular the targeted synthesis of metastable phases is particularly demanding. To address this challenge, in this work we present on the development of a novel predictive framework for the synthesis of stable and metastable inorganic materials. We demonstrate this framework by investigating the evolution of crystalline intermediate/metastable phases during MnO_2 hydrothermal synthesis through a combination of *in situ* X-ray scattering and ab initio calculations. The hydrothermal reactor used in the work (figure 1, left) was adapted from previously established reactor designs[1], but with both ends of the glass reactor flame sealed to mimic a conventional autoclave (figure 1 right). Additionally, the experimental reaction conditions investigated in this study were guided by thermodynamic calculations that were developed by our theory collaborators, as published in Ref. [2,3].

The influence of $[K^+]$ on the reaction pathway in the MnO_x system was studied, with a fixed $[MnO_4^-]$ and pH value. The study shows the presence of intermediate phases during the transition from MnO_4^- (aq) to MnO_2(s). By varying the $[K^+]$, the polymorphs observed along the reaction pathway can be tuned. The structure of the intermediate phases and overall formation pathways are consistent with our theoretical predictions. These results support the recently proposed theoretical framework that synthesizable metastable phases have nucleated under thermodynamic conditions where they were once the lowest free energy phase, and then grew into conditions where they were metastable.[4] This concept, referred to as remnant metastability, can serve as a general guideline for predicting what metastable materials are synthesizable and under what conditions.

Our approach allows for the prediction of the reaction pathway and shows, remarkably, that even with the same initial precursors and target phases, one can modify that pathway to go through different intermediate phases (which we further show by TEM, can be recovered). We observe a progression of intermediate, metastable phases that are consistent with the predicted phase sequence within our framework. Hence, our work uncovers in a predictive fashion that there is a rich phase landscape that is missed when one just focuses on the end product of a reaction.

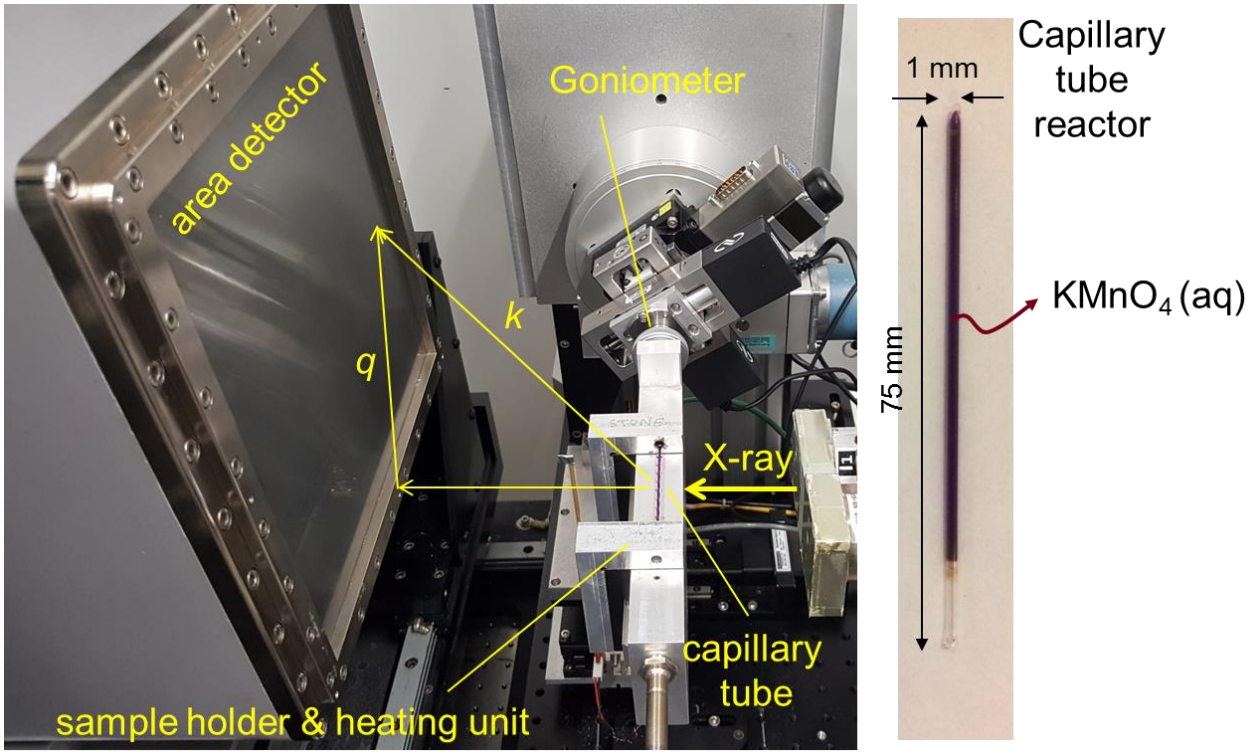

Figure 1. (left) *in situ* hydrothermal reactor setup (right) sealed capillary reaction vessel used for the *in situ* X-ray scattering experiments

References:

[1] K.M.Ø. Jensen, C. Tyrsted, M. Bremholm, B.B. Iversen, (2014) 1594–1611.
[2] D.A. Kitchaev, H. Peng, Y. Liu, J. Sun, J.P. Perdew, G. Ceder, Phys. Rev. B - Condens. Matter Mater. Phys. 93 (2016) 1–5.
[3] D.A. Kitchaev, S.T. Dacek, W. Sun, G. Ceder, J. Am. Chem. Soc. 139 (2017) 2672–2681.
[4] W. Sun, S.T. Dacek, S.P. Ong, G. Hautier, A. Jain, W.D. Richards, A.C. Gamst, K.A. Persson, G. Ceder, Sci. Adv. 2 (2016) e1600225–e1600225.

https://doi.org/10.1017/S1431927618007912