Understanding Reaction Pathways Leading to MnO_2 Polymorph Formation

Computational driven design of materials has provided guidelines for designing novel materials with desired properties, especially for metastable materials, which may have superior functionalities than its stable counterparts [1]. However, the synthesis of these metastable materials is usually challenging. The current computational approaches are not able to predict reaction pathways passing through intermediate or metastable phases. As a consequence, the synthesis of many compounds still remains Edisonian, meaning that repeated iteration is usually required to find the reaction conditions needed for synthesizing targeted materials with desired properties. To reduce the amount of cost and effort during this discovery process, a predictive theory for directing the synthesis of materials is necessary.

In the recent article "Understanding Crystallization Pathways Leading to Manganese Oxide Polymorph Formation [2]", researchers from SLAC, LBNL, MIT, Colorado School of Mines, and NREL combined theory and experimental approaches to develop and demonstrate a theoretical framework that guides the synthesis of intermediate/metastable phases. This *ab initio*-computation based framework calculates the influence of particle size and solution composition on the stability of polymorph (substances having the same composition but different crystallographic structures), and predicts the phases that will appear along the different reaction pathways.

To validate this framework, the synthesis of manganese oxide (MnO_2) polymorphs is utilized as a demonstration case. For the theoretical part, a *size-dependent phase diagram* for the MnO_2 system (Figure (a)) is computed. The phase diagram shows stability regions for MnO_2 species as a function of particle size and potassium activity/concentration in the solution. For the experimental part, *in-situ* wide-angle X-ray scattering (WAXS) at SSRL BL11-3 is utilized to track the evolution of intermediate/metastable species occurring during the MnO_2 hydrothermal synthesis. Three synthesis pathways with varying potassium ion concentrations ($[K^+]$ = 0, 0.2, and 0.33 M) were studied.

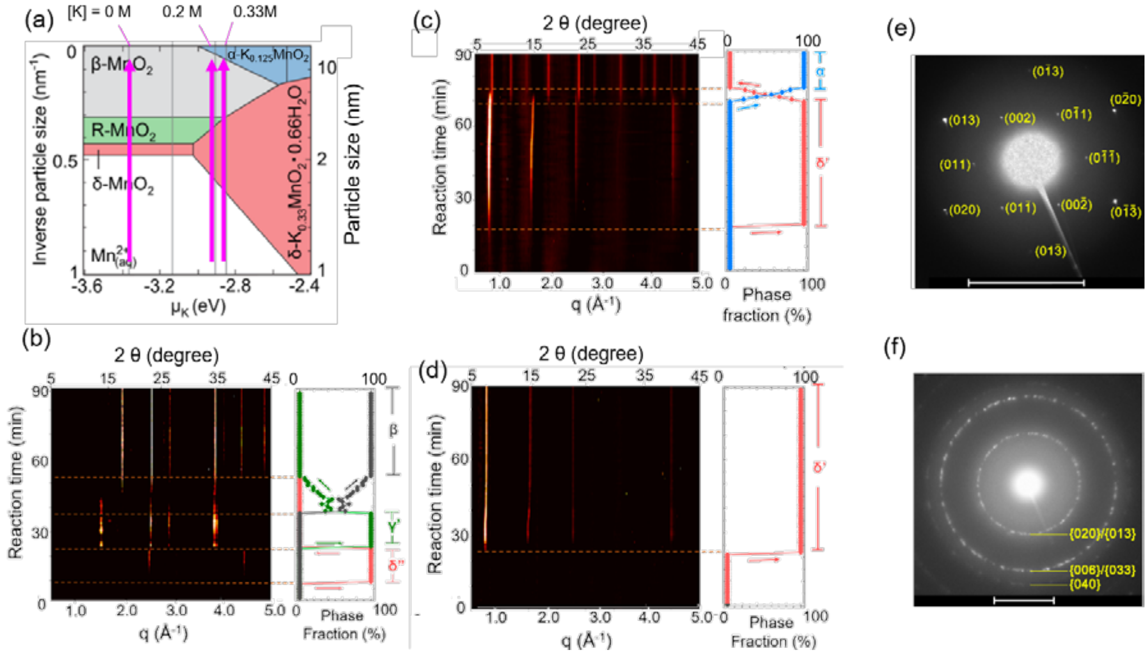

Figure (a) Size-dependent phase diagram of MnO_2 polymorphs. The three arrows mark the reaction progression from nano-size to bulk at different potassium concentrations. (b-d) The evolution of x-ray scattering pattern with time along $[K^+]$ = 0 M (b), 0.2 M (c), and 0.33M (d). The identities and the fractions of the phases are marked in the subfigure to the right. (e-f) Electron beam diffraction patterns of the δ" phase and δ' phase harvested from $[K^+]$ = 0 M and 0.2 M, respectively.

The *in-situ* WAXS successfully captured the evolution of these distinctive reaction pathways, and the phase progression is reflected in the change of diffraction patterns with time. There are four types of MnO_2 polymorph involved in this study: δ, R, β, and α phases. The δ and R phases encompass a large family of structures with varying layer spacing and disorder, respectively. Here, the observed phases in the δ-family are named δ' and δ"; and the observed phase in the R-family is named γ' (Figure (b-d)). In the $[K^+]$ = 0 M pathway, the observed order of phase progression is consistent with that computed in the size-dependent phase diagram (δ → R → β). However, for both $[K^+]$ = 0.2 and 0.33 M, the size-dependent phase predicts a δ → R → β → α transition, but the R and β phases are skipped in the observed progressions. This is because the energy barrier required for the new phase to nucleate is higher than the barrier for crystalline growth; therefore, the initial δ phase is likely to grow beyond its size stability region of the R and β phases. As a consequence, the δ' → α transition was observed instead. For the $[K^+]$ = 0.33 M, not only are the R and β phases are missing, but the reaction pathway were stabilized at the δ' phase without proceeding into the α phase. In this case, the driving force for nucleating the α phase is further reduced by the higher $[K^+]$, thus inhibiting the kinetics for driving the reaction from the δ' to α phases.

These observations illustrate the competing effects of bulk thermodynamics and transformation kinetics in the progression of crystalline phases. More importantly, these results validate a recently proposed concept stating that a synthesizable metastable phase nucleates under thermodynamic conditions where it was once the lowest free energy phase, and then grows into conditions where they becomes metastable [3]. This concept, referred to as *remnant metastability*, can serve as a general guideline for predicting what metastable materials are synthesizable and under what conditions.

Not only showcasing the ability to monitor the reaction pathway in real-time, the research team also showed that the desired metastable/intermediate phases can be harvested. Here, the researchers demonstrated that the δ" phase from $[K^+]$ = 0 M and the δ' phase from $[K^+]$ = 0.2 M can be isolated and stabilized at room temperature by quenching the reaction. The quenched phases were examined by selected area electron beam diffraction (SAED) (Figure (e-f)).

Overall, this combination of computational and experimental methodology offers a rational paradigm for targeted synthesis of metal oxides. This framework not only predicts synthetically-accessible metastable materials, but also serves as a practical tool to guide their synthesis. Ultimately, the researchers believe that the predictive framework can be expanded to other materials systems, such as other binary and ternary oxides, including those with many polymorphs.

References

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Contacts

Bor-Rong Chen and Laura Schelhas, Stanford Synchrotron Radiation Lightsource
Wenhao Sun, Lawrence Berkeley National Laboratory

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