

Observation and modeling of multicomponent ceramics synthesis: A case study of $YBa_2Cu_3O_{6+x}$

Solid-state synthesis from powder precursors is the primary processing route to advanced multicomponent ceramic materials. While precursors and products of the synthesis have been characterized intensively, the reaction in the furnace is still a "black box" [1]. In order to peel off this black box, *in situ* characterization studies are essential. These analyses have revealed that solid-state reactions often evolve through a variety of nonequilibrium intermediates, some of which are recognized as new phases, prior to the formation of the equilibrium phase [2].

From the end of the 18th century to the beginning of the 19th century, Gibbs and Ostwald built the fundamental of thermodynamics and kinetics, and solid-phase reactions were also understood using these theories. The Gibbs free energy can distinguish whether reactions can proceed in infinite time, and kinetic requirements for diffusion, nucleation, and crystal growth are utilized for the explanation of how fast thermodynamically favorable reaction can proceed. Reactions in organic chemistry, which normally involve small molecules, are generally predicted well by computational approaches and depicted as "an energy landscape" with thermodynamic states joined with kinetic barriers. On the other hand, a similar computational analysis of solid-phase reactions, which handle particles of submicron to tens of microns, are not as straightforward. As a result, understanding the solid-phase reaction mechanism continues to be a challenging issue.

Recent advances in density functional theory provide the structure-property relationships of countless experimental and hypothetical compounds. Theory and computation can also help guide synthesis planning by evaluating thermodynamic stability or overall reaction energies [3]. Nonetheless, they do not provide mechanistic insights into which nonequilibrium intermediates will appear during phase evolution. Indeed, solid-state reactions have too many parameters: composition, starting materials, heating temperature, heating rate, atmosphere, etc. For example, Martin Jansen shows the thought experiment that investigates how many samples need to be synthesized and tested to definitely include YBCO in the output of a high-throughput method [4]. Using a throughput rate of 105 samples per day, a systematic and unbiased, one might even say "mechanical", search through the parameter space would take about 27000 years. Thus, one needs to find reasonable criteria to restrict the parameter space under investigation.

The complexity of phase evolution in solid-state synthesis arises from the various pathways by which an initially heterogeneous mixture of precursor particles can transform to a homogeneous target phase. At the microscopic level, solid-state reactions initiate in the interfacial regions between precursors as the system is heated. Because interfacial reactions can only occur between two solid phases at a time, we hypothesize that by determining which pair of precursors exhibits the most reactive interface, we can anticipate which interfacial reaction initiates the overall solid-state reaction, as illustrated schematically in Fig. 1. Once two precursors react to form a new phase, this nonequilibrium intermediate will then react through its interface with other precursors and intermediate phases. By decomposing the overall phase evolution into a sequence of pairwise reactions, we can calculate the thermodynamics and analyze the kinetics of each reaction step separately, providing a simplified theoretical picture to conceptualize and navigate ceramic synthesis [5].

We demonstrate how this concept of sequential pairwise reactions enables us to model phase evolution in the ceramic synthesis of the classic high-temperature superconductor, $YBa_2Cu_3O_{6+x}$ (YBCO).



Fig. 1. Schematic of sequential pairwise interfacial reactions. [5]

Figure 2 shows *in situ* synchrotron X-ray diffraction patterns measured at SPring-8 **BL02B2** for phase evolution in YBCO synthesis in air from the mixture of Y_2O_3 , BaO_2 and CuO in 30 minutes. The fast formation of YBCO when starting from BaO_2 originates from the large thermodynamic driving force at the $BaO_2|CuO$ interface, which is larger than other $Y_2O_3|CuO$ and $Y_2O_3|BaO_2$ interfaces. SEM/DF-STEM provides direct observation of the microstructural evolution during the solid-state reaction. In a later stage, liquidus Ba-Cu-O react with Y_2O_3 solid to form YBCO, suggesting the fast diffusion is the key for this quick formation of YBCO.

In situ X-ray diffraction and microscopy observation were essential to prove the framework of subsequent interfacial reactions and inform our understanding of the interplay between thermodynamic and kinetics during the synthesis of multi-component ceramics. DFT calculations can be used in concert to predict which intermediate phases form by comparison of thermodynamic driving forces. This work enables solidstate and materials chemists to design crystallization pathways that target (or avoid) specific intermediates, which will accelerate the design of time- and energyefficient ceramic synthesis recipes for new materials.



Fig. 2. In situ synchrotron XRD pattern for heating of the $Y_2O_3 + BaO_2 + CuO$ precursor mixture and Gibbs reaction energies for the lowest energy reactions at each interface in the $Y_2O_3 + BaO_2 + CuO$ precursor mixture. [5]



Fig. 3. In situ microscopy of YBCO formation from Y_2O_3 , BaO₂, and CuO particles. A video of the reaction is provided as video S1 (https://onlinelibrary.wiley.com/doi/full/10.1002/adma.202100312#support-information-section) in Supporting Information. [5]

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