Decoding kinetic selectivity in diffusion-limited solid state synthesis reactions through machine-learning accelerated molecular dynamics

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1. Introduction

In the past decade, the demand for new inorganic materials to improve energy technologies has led to the emergence of powerful, data-driven materials design. However, processes for realizing materials designed *in silico* through inorganic synthesis remain in their infancy and lag behind organic synthesis due to the absence of a general mechanistic model for solid-state reactions[1, 2]. Current state-of-the-art atomistic modeling of solid state synthesis describes reaction behavior in terms of bulk thermodynamic properties from high-throughput databases of density functional theory (DFT) calculations such as the Materials Project (MP) [3]. Prominent examples include reaction networks [4] which produce thermodynamically favorable reaction pathways linking products and reactants and active learning algorithms [5] which propose recipes based on thermodynamics and then update the recipes according to experimental results. While thermodynamics defines the possible reaction products, predictions based solely on reaction energetics can be inaccurate — especially for systems with competing product phases that have similar formation energies [6]. In such cases, limited transport of essential constituents may prevent the formation of globally stable products, hindering attainment of thermodynamic equilibrium. Prior attempts to understand such effects in solid-state reactions have led to the use of empirical rate expressions [7, 8], which fit an effective rate constant from the degree of conversion of the reactants. Although useful, such models cannot be applied to predict solid-state reaction products *a priori*. A truly predictive synthesis framework necessitates developing a mechanistic understanding of solid-state reaction kinetics.

2. Our Approach

We hypothesize that the phase evolution of products in powder synthesis reactions can be described as an optimization of the *local* energy under the time-dependent constraint of available ionic fluxes through a defective, liquid-like interphase with the same stoichiometry as candidate product phases. To showcase our approach and specifically, the effects of diffusive fluxes on product selectivity, we study product selectivity in the Ba-Ti-O chemical space, which is particularly challenging due to the sheer number of ternary phases which are on or very close to the convex hull of stability. Prior work has shown transport of ionic constituents through such amorphous interphases is highly correlated [9], leading us to compute the full ionic transport tensor as per the Onsager transport framework from molecular dynamics (MD) trajectories [10, 11].

3. Why has no one attempted this?

Computing reliable estimates of atomistic transport coefficients, especially the cross-ion transport coefficients, requires long nanosecond scale MD trajectories, which are out of reach for ab initio molecular dynamics (AIMD). Using machine learning interatomic potentials (MLIP) alleviates some of the computational cost of such simulations, however, MLIPs often lack information of atomic configurations far from equilibrium, and hence perform poorly when simulating the evolution of amorphous interphases through MD [12]. In addition, no framework exists for linking the atomistic transport of ions to the complex spatio-temporal evolution of product phases seen in a solid-state reaction.

4. Our Solution

To address the computational cost associated with long AIMD simulations, we train an Atomic Cluster Expansion (ACE) [13] based MLIP for the Ba-Ti-O system. We chose this potential due to its simplicity, and because it has shown success in recent literature on modeling a wide range of tasks in a variety of material systems [14, 15]. We train the MLIP through the framework shown in Figure 1. Initially, we ran AIMD on both crystalline and amorphous configurations of compositions found on the thermodynamic hull of stability of the Ba-Ti-O system to generate data to train a baseline ACE-based MLIP. We then perform several rounds of high temperature machine-learning driven MD as a sampling strategy to active learn the far from equilibrium configurations typically encountered when simulating the evolution of amorphous interphases. This approach encour-
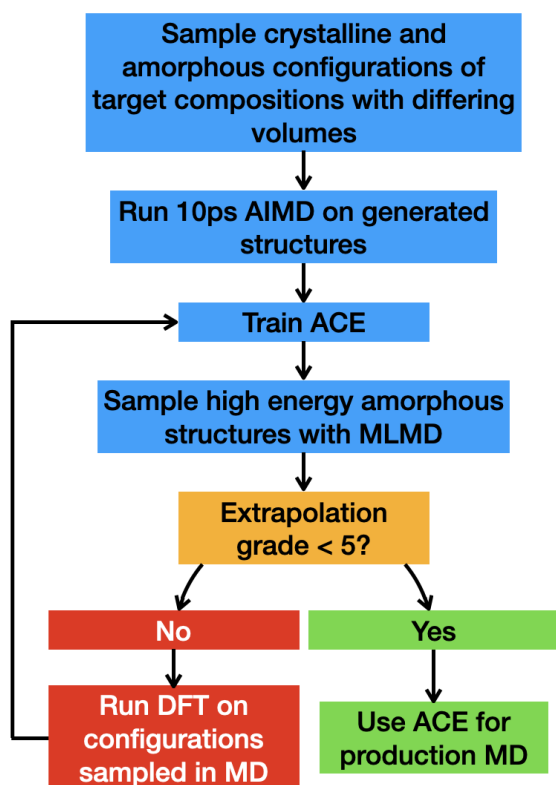
Fig. 1: Our strategy to train an ACE potential capable of performing MD on amorphous interphases: we explicitly provide amorphous configurations of target compositions in the initial training data and active learn amorphous configurations that are out of distribution (OOD) for the model, which are sampled through high temperature MLMD. We quantify the degree of OOD of a configuration by the extrapolation grade of the ACE potential [12].

ages the MLIP to accurately capture both equilibrium and out-of-equilibrium interactions between ions, thereby producing a potential suitable for the task at hand. We implemented the workflow using the `atomate2`[16], `Jobflow`[17], `FireWorks`[18] and `pacemaker`[14] python packages to allow for probing atomistic transport during solid-state reactions in a high-throughput manner on high-performance computing resources. To address the second challenge, we recently developed a discrete cellular automaton model (ReactCA) [19] capable of simulating the evolution of precursor powders placed in cells through pairwise reactions, mimicking a powder synthesis reaction. This approach allows us to link first-principles thermodynamics and atomistic transport coefficients to macroscopic reaction rates, thereby providing a comprehensive framework for understanding diffusion-limited solid-state reactions.

5. Our Findings

Our approach produces fitted cross-ion transport coefficients that explain the selectivity towards specific phases when reactions are diffusion-limited. In particular, our results explain the absence of the Ba_2TiO_4 phase from experiments performed at elevated temperatures. Additionally, we simulate phase evolution over the course of a series of solid-state reactions using ReactCA and a fixed set of precursors to study the changes in reaction outcome as a function of varying precursor ratios and the heating profiles. We find that our simulation outcomes accurately map onto prior experimental results for these reactions, and we capture the correct order and quantities of elusive intermediates phases which are crucial in determining the final phase distribution of reaction products. Through these simulations, we observe that an interplay between diffusion and thermodynamics dictates the compositions of phases that are allowed to grow over time. This is the first work that presents a general predictive framework for solid-state synthesis outcomes that integrates rigorously computed ionic transport coefficients (enabled by machine-learning molecular dynamics), first-principles thermodynamics and a cellular automaton model to predict the spatio-temporal evolution of phases over the course of the synthesis reaction. We anticipate that this work will serve as a stepping stone towards a full mechanistic model of solid-state reaction kinetics, with immediate applications in the context of digital twins and autonomous synthesis labs.

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