A Next Generation Synthesis Center (GENESIS)
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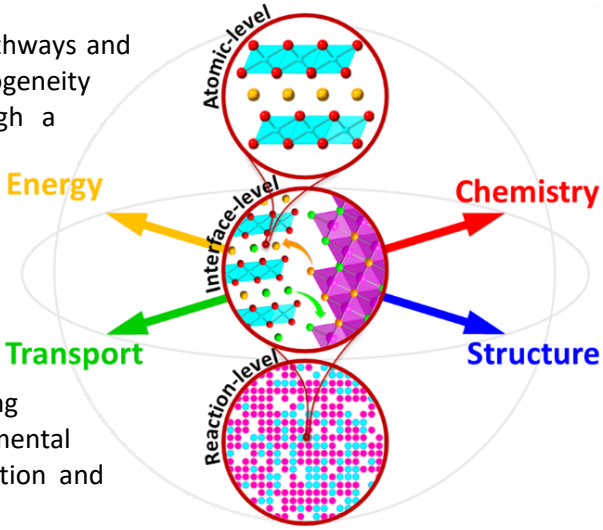
Mission Statement: *"To elucidates how key structural and chemical transformations are governed by the flow of energy and atoms across multiple length scales by integrating advanced in situ diagnostics and data science tools to interrogate and predict the pathways that govern synthesis and lead to new materials.*

We will further develop and integrate the computational and *in situ* experimental infrastructure to address precision synthesis of bulk materials systems. For polycrystalline inorganic solids, our aim is to produce materials that have homogeneous local and long-range crystalline structures. At the *atomic scale*, this requires control of atomic configurations that are desired, along with control of composition, structural defects and impurities. At the *mesoscale* (interfacial, particle- and reaction-scales), precision synthesis involves the ability to control chemical microenvironments, relative kinetics, heterogeneity, compositional gradients, and microstructure.

We will study model systems to resolve synthesis pathways and interrogate how the composition, structure, and heterogeneity of multi-component reactive system evolve through a thermodynamic landscape. Developments of *in situ* diagnostics that span Å-to-mm length scales will be leveraged to build a fundamental understanding of the interplay between thermodynamic driving forces, reaction pathways and kinetics, and transport kinetics, which are all affected by the synthesis conditions as well as the choice of precursors and the properties of resulting product. The understanding gained, through both computational and experimental investigations, will ultimately enable *de novo* prediction and adaptive control of synthesis routes.



In GENESIS, we aim to unravel this complexity by emphasizing understanding and control on the atomic-scale and mesoscale phenomena, as well as how they impact the reaction outcome. In the picture of synthesis as the flow of atoms and energy from reagents to products, we focus on making and breaking bonds, along with the redistribution of atoms and energy between these. GENESIS see the need to develop new tools to drive new understanding in synthesis and will continue these efforts, where next generation computational and experimental tools will be developed, benchmarked, and integrated with the previous successful developments and current ongoing efforts.

For Atomic-Level Control. The preparation of many bulk inorganic solids is carried out by either reacting mixtures of precursor powders at high temperature or through precipitation from solution. High temperatures facilitate diffusion in the solid state and drives reactions towards a thermodynamic minimum. However, a wider range of metastable material products exist at local minima in the reaction landscape. Accessing these metastable products (intermediates with respect to the global minimum) requires kinetic control, achieved for example, through defect engineering, precursors design, or solution routes. This thrust will focus on kinetically

controlled reactions in metastable phases and phases incorporating metastable defects within a thermodynamically stable product. The key questions being addresses in studies of atomic scale phenomena: *What defines the point of differentiation between forming structure A vs structure B? How does this "tipping point" differ for different pathways leading to the same product? What is the relative importance of precursor vs conditions? What governs the range of different compositions that can be achieved for the same structure? Do reactions from isomorphic precursors to isomorphic products follow parallel pathways?*

For Mesoscale Control. The synthesis of solid inorganic materials is intrinsically non-uniform, involving heterogeneous mixtures of particles of different material phases. Reagents with one set of structures and compositional distributions evolve to form products with a different set of structures and compositional distributions. This evolution involves correlated parameters, across multiple length scales, from atoms to interfaces to reactive particle aggregates. Progress will require new tools capable of interrogating systems at multiple length scales to 1) evaluate native morphological features and how these evolve, and 2) manipulate morphology and evaluate difference in reaction evolution. These capabilities are critical to controlling syntheses and ultimately for the eventual scale-up of bulk materials. The key questions: *How does a reaction evolve from an interface and between particles? What heterogeneity exists and on what scale, and can it be controlled through, eg. reagent architecture? Can we control transport and reaction outcomes by designing pairwise reactions or with tailored architecture? Do preferential transport directions and lowest surface energies impact outcomes? Is the reaction enhanced at the higher energy faces? What are the effects on nucleation? Can we harness surface effects such as mobility and melting?*

Advancing Tools. GENESIS will develop and integrate new tools across the spectrum of theory, simulation, data analytics, and experimentation to elucidate the role of defects, heterogeneity, and microstructure in synthesis to address the science questions above. We focus on tool development and their integration to provide understanding from data, and to develop active control of reactions. The new characterization tools will complement the suite of capabilities GENESIS has already developed and utilized. While we have begun to examine the effects of architecture in how reactions proceed, incorporating the role of defects into such models requires theory and atomistic calculations of energetics and kinetic properties of defects and amorphous materials.

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