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Modeling Reaction Pathways in the Solid-State Synthesis of Inorganic Materials

By

Matthew James McDermott

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Engineering - Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Kristin A. Persson, Chair

Professor Gerbrand Ceder

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Modeling Reaction Pathways in the Solid-State Synthesis of Inorganic Materials

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Matthew James McDermott

Abstract

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Doctor of Philosophy in Engineering - Materials Science and Engineering

University of California, Berkeley

Professor Kristin A. Persson, Chair

Synthesis is the major bottleneck in the computational design of new inorganic materials for technological applications, including rechargeable batteries, catalysis, sensing, photovoltaics, and more. Unlike molecular reactions, where individual bond-breaking or formation steps can be explicitly followed, reactions involving solid inorganic materials happen at great spatial scales where atomic control cannot be achieved. This is especially true for solid-state synthesis, which involves the reaction of bulk solid powder precursors at elevated temperatures (i.e., the ceramic method). Solid-state synthesis is an especially attractive approach given its simplicity and scalability to bulk chemical manufacturing. Recent work has focused on the experimental characterization of reaction pathways in solid-state synthesis to elucidate theoretical principles determining the performance of the synthesis reactions. These works have shown that powder reactions often involve a significant number of intermediates, including crystalline phases that sometimes persist as undesirable impurity products. Meanwhile, databases of crystalline materials and their properties have rapidly grown with the development of high-throughput density functional theory calculation workflows. These databases enable the study of phase equilibria, reaction energetics, and predicted products in solid-state reactions.

In this dissertation, we address the current deficit of theoretical models for predicting reaction pathways in solid-state synthesis, taking advantage of the aforementioned breadth of computed thermodynamic data. We focus on the development of both forward and inverse prediction models, with the goal of identifying synthesis reactions that selectively produce desired target phases with minimal competing intermediates. The central contribution of this work is the development of a reaction network model and methodology for predicting reaction pathways and key intermediate phases encountered in solid-state synthesis. The solid-state reaction network is a large graph-based network created from a mixture of computed and experimental free energies, supplemented by a machine-learned descriptor for Gibbs free energy. Using standard graph pathfinding approaches, we perform forward prediction, suggesting a

ranked set of likely reaction pathways in the synthesis of four inorganic materials (YMnO_3 , $\text{Y}_2\text{Mn}_2\text{O}_7$, Fe_2SiS_4 , and $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$). We compare the network-predicted pathways to experimental results characterized in the literature and find that the reaction network model captures key intermediates and reproduces the experimental reaction pathways for several targets.

We then address the current challenge of predicting the selectivity of solid-state reactions. In a detailed study of the synthesis of the $\text{Y}_2\text{Mn}_2\text{O}_7$ pyrochlore, we show that assisted metathesis reactions with precursors $3 A_2\text{CO}_3 + 2 Y\text{Cl}_3 + \text{Mn}_2\text{O}_3$ selectively produce $\text{Y}_2\text{Mn}_2\text{O}_7$, but only when sodium is used as the alkali metal ($A=\text{Na}$). We explain the unique selectivity of the Na-based reaction from observation of the formation of an Na_xMnO_2 intermediate with *in situ* synchrotron X-ray diffraction. It is the stability of this intermediate into high oxygen chemical potential ranges that facilitates direct reaction with YOCl intermediate to produce $\text{Y}_2\text{Mn}_2\text{O}_7$. Using this observation, we develop a selectivity metric related to the change of chemical potentials of the precursors that rationalizes the unique selectivity of the Na_xMnO_2 intermediate due to its direct connection in chemical potential space with $\text{Y}_2\text{Mn}_2\text{O}_7$. We improve upon this idea further and suggest two reaction selectivity metrics (primary and secondary competition) measuring the degree of competitiveness of impurity reactions acquired from the solid-state reaction network. We validate the use of these metrics by applying them to reactions previously documented in the literature, as well as for planning our own experiments synthesizing BaTiO_3 from eleven different precursor combinations spanning a range of chemistries, free energies, and selectivities. Our work culminates in the development of an inorganic synthesis planning workflow that can be used to suggest precursors that optimally yield a desired target.

Along the way, we devise a possible explanation for related experiments that produce two metastable polymorphs: orthorhombic YMnO_3 and layered $\alpha\text{-NaFeO}_2$. Our hypothesis centers around the fact that metastable polymorphs may be stabilized in certain environmental conditions due to differences in defect accommodation between the nominally stable and metastable polymorphs. For both YMnO_3 and NaFeO_2 , we show, with charged point defect density functional theory calculations, that the metastable polymorphs can be targeted in oxygen-rich environments. Altogether, the application of theoretical concepts and predictive models developed herein will greatly enhance both human-led and machine-driven synthesis exploration efforts, reducing the synthesis bottleneck.

Contents

Contents	i
List of Figures	iv
List of Tables	viii
1 Introduction	1
1.1 The synthesis bottleneck	1
1.2 Solid-state synthesis: the ceramic method	2
1.3 Aims of this work	3
1.4 Outline of this dissertation	6
2 Methods	9
2.1 X-ray diffraction (XRD)	9
2.2 Density functional theory (DFT)	13
2.3 Phase equilibria	20
2.4 Reaction thermodynamics	24
3 Solid-state chemical reaction networks	26
3.1 Construction of the solid-state reaction network	26
3.2 Cost functions for edge weighting	29
3.3 Application of graph pathfinding methods	30
3.4 Modeling reaction pathways reported in the experimental literature	33
3.5 Design of synthesis route for novel Mg-ion battery cathode $\text{MgMo}_3(\text{PO}_4)_3\text{O}$.	41
3.6 Ranking candidate pathways	43
3.7 Challenges with the model	44
4 Defect-driven thermodynamic stabilization of metastable polymorphs	46
4.1 The puzzling role of precursor structure in solid-state reactions	47
4.2 Synthesis of orthorhombic yttrium manganese oxide, o-YMnO_3	48
4.3 Discussion of o-YMnO_3 synthesis	61
4.4 Mapping defect-dependent polymorph stability onto the chemical potential diagram	66

4.5	Synthesis of layered sodium iron oxide α -NaFeO ₂	68
5	Rationalizing selective phase formation with chemical potential diagrams	78
5.1	The challenge of designing selective solid-state reactions	79
5.2	Computational methods	79
5.3	Reaction pathway from phase evolution	81
5.4	Thermodynamic stability of Y ₂ Mn ₂ O ₇	83
5.5	Product selectivity via chemical potential distances	84
5.6	Mechanistic facilitation through defect reactions	89
6	Assessing thermodynamic selectivity of solid-state reactions	91
6.1	The interface reaction model	91
6.2	Primary and secondary competition	94
6.3	Synthesis planning workflow	98
6.4	Exploring the selectivity of the solid-state reaction literature	99
6.5	The synthesis of barium titanate (BaTiO ₃)	103
6.6	Recommendations and outlook	111
7	Conclusions	113
7.1	Summary of this work	113
7.2	Future work and outlook	115
	Bibliography	117
A	The <i>reaction-network</i> Python package	134
B	Supplementary Information for Chapter 3	135
C	Supplementary Information for Chapter 4	137
C.1	Experimental methods for YMnO ₃ study	137
C.2	Experimental methods for NaFeO ₂ study	141
D	Supplementary Information for Chapter 5	153
D.1	Experimental methods	153
D.2	Assisted metathesis reaction energetics	155
D.3	<i>Ex situ</i> control experiments	155
D.4	Comparing neighboring ternary oxide structures in chemical potential space .	158
D.5	Pareto frontier of predicted reactions forming Y ₂ Mn ₂ O ₇	160
E	Supplementary Information for Chapter 6	163
E.1	Thermodynamic data	163
E.2	Precursor synthesis	163
E.3	<i>Ex post facto</i> SXRD reactions	164

E.4	Literature reactions	164
E.5	Supplementary figures and tables	166

List of Figures

1.1	The basic procedure for solid-state synthesis.	2
1.2	The aims of this dissertation.	3
2.1	<i>In situ</i> flow-cell/furnace	12
2.2	The gradient heater for <i>in situ</i> variable-temperature measurements	13
2.3	The defect formation energy diagram	18
2.4	Example compositional phase diagrams	22
2.5	Example chemical potential diagrams	23
2.6	Prediction of interface reactions from the ternary phase diagram	25
3.1	Thermodynamic models of chemical reactions in increasing degree of abstraction	27
3.2	Generalized graph architecture of a solid-state chemical reaction network	29
3.3	Example cost functions	31
3.4	Visualizations of several computed reaction networks	34
3.5	Effect of the cost function transformation on reaction energies	45
4.1	Refined weight fractions of crystalline materials at different reaction temperatures	50
4.2	Occupancy of crystallographic sites for LiMnO_2	52
4.3	Diffraction patterns that illustrate the presence of two unique manganese-containing spinel intermediates in the ternary metathesis reactions	53
4.4	Structural relationship between cubic $Fd\bar{3}m$ spinel and tetragonal $I4_1/amd$ spinel	54
4.5	Gibbs free energies and heat capacities as a function of temperature for YMnO_3 polymorphs, and at a pressure of $P = 1$ atm	56
4.6	Y, Mn vacancy formation energies as a function of Fermi energy for YMnO_3 polymorphs for different chemical potentials, μ_Y and μ_{Mn}	58
4.7	DFT-calculated phase diagram of cation-deficient YMnO_3 polymorphs with respect to temperature, T , and a fixed, equal concentration of cation (Y,Mn) vacancies, x in $\text{Y}_{1-x}\text{Mn}_{1-x}\text{O}_3$	59
4.8	Refined fraction of reaction products taken from laboratory PXRD data of <i>ex situ</i> ternary metathesis reactions ($\text{LiMnO}_2 + \text{YOCl}$) at 550 °C	60
4.9	Refined fraction of reaction products taken from laboratory PXRD data of <i>ex situ</i> ternary metathesis reactions ($\text{LiMnO}_2 + \text{YOCl}$) at varied temperatures and reaction times	61

4.10	Structure of reactants, proposed intermediates, and products along the metathesis pathway	64
4.11	Comparison of calculated and experimental heat capacities for h-YMnO ₃ (<i>P</i> 6 ₃ <i>cm</i>)	67
4.12	Defect-dependent polymorph stability of YMnO ₃ visualized on the chemical potential diagram.	69
4.13	Polymorphs of NaFeO ₂	70
4.14	Calculated defect formation energies and charge state transitions as a function of Fermi energy for vacancies in the α , β , and γ phases of NaFeO ₂	74
4.15	Defect-dependent stability phase diagram of NaFeO ₂ polymorphs from density functional theory calculations	75
4.16	Scanning electron micrographs of as-milled and annealed NaFeO ₂ in secondary electron imaging show larger particles present for the annealed samples.	76
4.17	Rietveld refinements of synchrotron XRD data showing the structural differences in as-milled and annealed NaFeO ₂	77
5.1	<i>In situ</i> SPXRD data and calculated weighted scale factors from sequential Rietveld analysis as a function of time for the reaction: $\text{Mn}_2\text{O}_3 + 2 \text{YCl}_3 + 3 \text{Na}_2\text{CO}_3 + \frac{1}{2} \text{O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 6 \text{NaCl} + 3 \text{CO}_2$ under flowing oxygen	82
5.2	Computed phase stabilities in the Y-Mn-O chemical system	83
5.3	Chemical potential diagrams of the Y-Mn-O-Na-Li-K system at 650 °C	85
5.4	Energy and total chemical potential distance distributions for 3,017 predicted chemical reactions forming Y ₂ Mn ₂ O ₇	86
5.5	Compositional variation of the P3-Na _x MnO ₂ intermediate determined by Rietveld analysis.	89
6.1	Modeling chemical reactions at solid-state heterogeneous interfaces in a binary (or quasibinary) chemical system.	92
6.2	Comparison and limiting cases of the cost metrics for primary competition, C_1 , and secondary competition, C_2	95
6.3	Calculated interface reaction hull for BaO TiO ₂ at $T = 600$ °C.	96
6.4	Cartoon model of decomposition pathways in a hull containing n interior vertices.	97
6.5	Synthesis map of 2,110 binary solid-state synthesis reactions reported in the literature.	100
6.6	Synthesis map of 25,905 calculated synthesis reactions producing BaTiO ₃	104
6.7	Interface reaction hulls for selected BaTiO ₃ experiments.	108
6.8	Precursor-target-impurity (PTI) plots summarizing <i>ex post facto</i> SXRD results.	109
6.9	Experimental validation of predicted synthesis performance.	110
B.1	Alternate schematic of reaction network illustrating reaction pathways and simple loops	136

C.1	Quantitative phase analysis calculated from synchrotron X-ray diffraction experiments of reaction $\text{LiMnO}_2 + \text{YOCl} \longrightarrow \text{YMnO}_3 + \text{LiCl}$ when starting from monoclinic ($C2/m$) LiMnO_2	140
C.2	Qualitative data on temperature ranges where phases are forming and reacting, obtained from comparing two SXRD patterns taken 20 minutes apart on a gradient furnace	141
C.3	Weighted scale factor of crystalline materials from neutron refinement at different reaction temperatures reveals the reaction pathway of the ternary metathesis reaction, $\text{LiMnO}_2 + \text{YOCl} \longrightarrow \text{LiCl} + \text{YMnO}_3$	142
C.4	The contributions of the manganese-containing phases LiMnO_2 , t'-spinel, and c'-spinel.	144
C.5	Ratio of the c and a lattice parameters for c'-spinel and t'-spinel from X-ray diffraction patterns.	145
C.6	Calculated phase stability of YMnO_3 polymorphs with respect to temperature and an equal concentration of cation (Y,Mn) vacancies, x	146
C.7	Synthesis graph of synthesis procedure for $\alpha\text{-NaFeO}_2$ including milling (mixing) and annealing (heating) steps.	146
C.8	Resulting X-ray diffraction data and Rietveld refinement of the reaction between $\alpha\text{-Fe}_2\text{O}_3$ and Na_2O_2 that was milled for 5 hours and then annealed at 700 °C for 12 hrs	147
C.9	Resulting X-ray diffraction data and Rietveld refinements of samples milled with 5 g and 2.25 g of starting material ($\gamma\text{-Fe}_2\text{O}_3$ and Na_2O_2)	148
C.10	Collinear antiferromagnetic orderings identified from magnetic ordering workflow for $\alpha\text{-NaFeO}_2$ ($R\bar{3}m$), $\beta\text{-NaFeO}_2$ ($Pna2_1$), and $\gamma\text{-NaFeO}_2$ ($P2_12_12_1$)	149
C.11	Equilibrium concentrations of charged vacancies in NaFeO_2 polymorphs as a function of chemical potentials within the NaFeO_2 stability domain	150
C.12	Defect-dependent Gibbs free energy curves for the three polymorphs of NaFeO_2	151
C.13	Thermogravimetric analysis (TGA) data on the heating of $\alpha\text{-NaFeO}_2$ as-milled powder	151
C.14	XRD of the annealed $\alpha\text{-NaFeO}_2$ plotted with the simulated diffraction pattern of $\beta\text{-NaFeO}_2$ ($Pna2_1$).	152
D.1	Energetics of the assisted metathesis reaction, $\text{Mn}_2\text{O}_3 + 2 \text{YCl}_3 + 3 \text{A}_2\text{CO}_3 + 0.5 \text{O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 6 \text{ACl} + 3 \text{CO}_2$	155
D.2	Bar graphs representing the mole percent amounts of products calculated from <i>ex situ</i> PXRD Rietveld refinements of the binary oxide reactions.	156
D.3	Bar graphs representing the mole percent amounts of products calculated from <i>ex situ</i> PXRD Rietveld refinements of the binary oxide reactions in NaCl.	157
D.4	Bar graphs representing the mole percent amounts of products calculated from <i>ex situ</i> PXRD Rietveld refinements of $\text{Y}_2\text{Mn}_2\text{O}_7$	158
D.5	PXRD results from the reaction: $C2/m \text{ NaMnO}_2 + \text{YOCl} \xrightarrow{\text{O}_2}$	159

D.6	PXRD results from the reaction: $Cmcm$ $\text{Na}_{0.7}\text{MnO}_2 + \text{YOCl} \xrightarrow{\text{O}_2}$	160
D.7	Structures of possible stoichiometric $A\text{-Mn-O}$ ternary oxide intermediates predicted to be stable at $T = 650$ °C.	161
D.8	Energy and total chemical potential distance distribution for 3,017 predicted chemical reactions forming $\text{Y}_2\text{Mn}_2\text{O}_7$	162
E.1	Fitting procedure for formation energy correction of carbonate compounds. . . .	166
E.2	Measured temperature distributions along sample capillary.	167
E.3	Synthesis map of 3,420 open solid-state synthesis reactions reported in the literature. 168	
E.4	Synthesis map of 191,729 calculated open- O_2 synthesis reactions producing BaTiO_3 . 169	
E.5	Full performance of primary and secondary competition scores.	170

List of Tables

3.1	Top five predicted reaction pathways to YMnO_3	36
3.2	Selection of top predicted reaction pathways to $\text{Y}_2\text{Mn}_2\text{O}_7$	37
3.3	Selection of top predicted reaction pathways to Fe_2SiS_4	39
3.4	Selection of top predicted reaction pathways to $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$	40
4.1	Original YMnO_3 structures acquired from the Materials Project database	55
4.2	Re-relaxed YMnO_3 unit cells (AFM ordering) and their lattice parameters . . .	55
4.3	Summary of defect supercells and comparison of the band gaps acquired using the HSE06 and GGA+ U functionals	57
4.4	Calculated properties of NaFeO_2 polymorph structures	72
6.1	Pareto front reactions to BaTiO_3 and their associated Gibbs free energies, ΔG_{rxn} ($T = 650$ °C), primary competition scores, C_1 , and secondary competition scores, C_2	105
6.2	Selected experimental reactions to BaTiO_3 and their associated Gibbs free energies, ΔG_{rxn} ($T = 650$ °C), primary competition scores, C_1 , and secondary competition scores, C_2	107
D.1	Predicted reactions which lie on the Pareto frontier in $\Delta\Phi_{\text{rxn}}$ and $\sum \Delta\mu_{\text{min}}$. .	162
E.1	Selected experimental reactions forming BaTiO_3 and their associated grand potential energies ($\mu_{\text{O}} = -0.2921$ eV), $\Delta\Phi_{\text{rxn}}$ ($T = 650$ °C), primary competition scores, C_1 , and secondary competition scores, C_2	167

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Chapter 1

Introduction

1.1 The synthesis bottleneck

The predictive synthesis of inorganic materials is a grand challenge in modern chemistry and materials science [1]. Unlike organic synthesis, which can often be modeled via discrete reaction steps or mechanisms, inorganic materials synthesis is challenging to model mechanistically [2]. This theoretical shortfall has made synthesizing a predicted material the major bottleneck in high-throughput computational materials design efforts [3]. Even if a new structure is predicted to have groundbreaking state-of-the-art properties, if one cannot devise a synthesis strategy to make the material, it will never be successfully realized or engineered into any product. The scientific community has recognized the importance of this bottleneck in recent years [4], and large research efforts are underway to understand the science of synthesis.

The difficulty in modeling inorganic materials synthesis is primarily due to the incredible spatial scale at which chemical reactions occur in reacting crystalline (periodic) materials, prohibiting the atomic control of individual bond-forming and breaking steps. Even a single spherical microparticle (1 μm diameter) of $\alpha\text{-Fe}_2\text{O}_3$ contains over 8×10^{10} atoms – well beyond what is feasible to model even with state-of-the-art atomistic methods [5]. The inability to deconstruct inorganic reactions into elementary steps has thus far prevented the analogous development of retrosynthetic analysis techniques [6] and computer-aided synthesis planning [7] in the field of inorganic materials chemistry.

The central focus of this dissertation is the development of theoretical modeling approaches for inorganic materials synthesis. In particular, we focus on solid-state synthesis and the modeling of reaction pathways (i.e., reaction steps and the order in which they occur), as well as the application of these models in efforts to reduce the synthesis bottleneck. A reduced synthesis bottleneck would lead to a rapid acceleration in the development of new functional materials for various applications, including energy storage, solar energy genera-

Note: This chapter contains adapted excerpts from a co-authored manuscript of which I am a first author. This work is unpublished as of the time of writing; the main text is available in Chapter 6.

tion, transportation, integrated circuits, sensors, catalysis, and more. The rapid development of materials is not only important for the growth of new desired technologies. It is, in fact, a pressing need for modern society. The successful synthesis of new technological materials may be a deciding factor in whether humanity meets the current suggested greenhouse gas emission guidelines for limiting total global warming to 1.5 °C [8].

1.2 Solid-state synthesis: the ceramic method

While there are numerous inorganic synthesis methods (e.g., hydrothermal, mechanochemical, sol-gel, intercalation, etc.) [9], the primary focus of this dissertation is on bulk solid-state synthesis via the ceramic method (i.e., powder reactions). This choice has been motivated by the straightforward and scalable nature of working with bulk powders, which makes the solid-state approach suitable for any application ranging from one-off laboratory synthesis to industrial mass manufacturing. The only equipment required is basic: tools for grinding (mortar/pestle, mill) and firing (furnace). Solid-state synthesis is also a prime candidate for automated lab experiments, which aim to reduce the time, energy, and material costs of synthesis exploration [10]. The basic steps of solid-state synthesis are summarized in Figure 1.1.



Figure 1.1: The basic procedure for solid-state synthesis. Note that Steps 2-4 are frequently included to increase the total interfacial contact area between differing precursor crystallites but are not explicitly required in all cases.

With the recent rise in frameworks for high-throughput density functional theory calculations [11], we now have massive computational thermodynamic databases that can be used

to characterize the energetics of reactions in solid-state synthesis. Using materials databases such as the Materials Project [12] or Open Quantum Materials Database [13], we can, with sufficient accuracy, predict the thermodynamics of reactions among hundreds of thousands of experimentally known and theoretically hypothesized solids. These developments make it possible to systematically address the challenge of designing predictive models for solid-state synthesis.

1.3 Aims of this work

This dissertation aims to address two complementary challenges in modeling reaction pathways in solid-state synthesis: 1) forward and 2) inverse prediction. These two aims are illustrated in Figure 1.2 and discussed in the following sections.

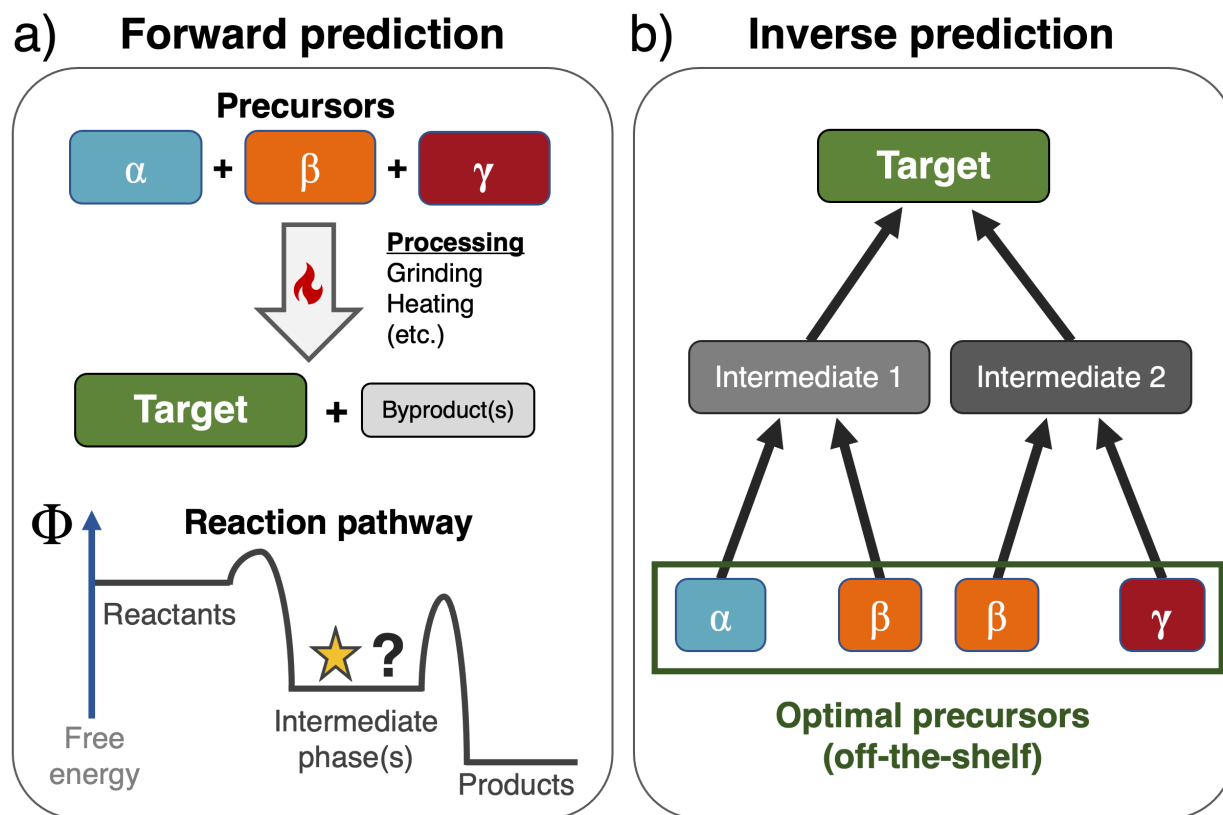


Figure 1.2: The aims of this dissertation. a) Forward prediction: modeling multi-step reaction pathways in solid-state synthesis, with a focus on predicting the intermediate phases that either lead to impurity or final product formation. b) Inverse prediction: identifying the optimal set of precursors/conditions that selectively “control” a reaction pathway towards a desired target (i.e., retrosynthesis).

Forward prediction: modeling reaction pathways in solid-state synthesis

It is often assumed that solid-state reactions are thermodynamically controlled, i.e., they form the phases which minimize the free energy of the system [14]. The rationale for this assumption is that high temperatures ($T > 1000$ °C or even higher) are typically required to achieve the rates of bulk diffusion necessary for the reaction of solids. It is suggested that at these high temperatures, kinetic effects (e.g., differences in diffusivities/reactivity) no longer play a significant role in governing the reaction pathway [15]. Hence, at high temperatures, the global equilibrium state (set of final thermodynamic products) is easily accessible by the reacting system. However, we know that not all solid-state reactions explicitly require high temperatures. For example, metathesis reactions are often quite rapid and even self-sustaining at low synthesis temperatures [16, 17], with reaction onset at temperatures as low as $T = 100$ °C in some systems such as sulfides/chlorides [18]. Even some oxide syntheses, such as that of yttrium barium copper oxide (YBCO) superconductor from barium peroxide (BaO_2), begin at temperatures as low as $T = 600$ °C and complete at 900 °C [19].

The assumption that solid-state reactions purely operate in thermodynamic control, as well as the standard approach of “cook and then look” (*ex situ*) characterization, has historically hindered the study/observation of reaction pathways in solid-state synthesis. Unfortunately, reaction pathways for conventional syntheses from elemental or binary precursors are often not simple. Numerous recent *in situ* studies [19–22] have shown that solid-state reactions may follow complex pathways sometimes composed of several crystalline intermediates that are key to either facilitating or preventing the formation of the global equilibrium products. For example, in the aforementioned $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (YBCO) synthesis using BaO_2 , the formation and low melting temperature of the BaCuO_2 intermediate facilitates the rapid formation of YBCO target [19]. In the assisted metathesis synthesis of yttrium manganese oxides – which will be explored in depth throughout this work – the stability of the A_xMnO_2 intermediate phase determines the selectivity of the reaction in forming YMnO_3 , YMn_2O_5 , or $\text{Y}_2\text{Mn}_2\text{O}_7$.

A central aim of this dissertation is to develop a methodology for *a priori* prediction and ranking of possible reaction pathways in a system, with a focus on predicting which intermediate phases will form. This is crucial for decomposing complex multi-step reaction pathways into their “elementary” steps, which will help determine which phases may be kinetic “sinks” or lead to impurity formation. Accurate forward prediction models will also be a crucial tool for enabling automated or fully autonomous materials synthesis, helping to “close the loop” in laboratory control systems. Altogether, solving the forward prediction problem will enable greater understanding and active control of materials synthesis, allowing for more rapid development and optimization of synthesis procedures.

Inverse prediction: synthesis planning for inorganic materials

To optimize the performance of solid-state reactions and maximize conversion to the target product, the experimentalist often relies on intuition and heuristic rules to choose the 1) precursor compositions, 2) grind time, 3) synthesis annealing temperature, 4) synthesis atmosphere (e.g., vacuum, flowing O_2), 5) synthesis time, and 6) cooling method. Heuristics include well-known rules such as Tammann’s Rule for choosing reaction temperature based on two-thirds of the melting point of the lowest-melting precursor [23], as well as “chemical intuition” and human-biased experimental protocols (e.g., selecting reaction times based on common time increments such as 4h, 8h, etc.) [24]. Unfortunately, these heuristic rules are often insufficient to achieve successful synthesis on the first attempts, and repeated experiments are necessary to optimize the approach, which can be time-intensive and costly. In the worst cases, human-biased heuristics may perform even less successfully than randomly-generated experimental protocols [25].

There is very little theoretical rationale available for the selection of any experimental parameter of solid-state synthesis. Solid-state chemistry has even been dubbed a black box best probed via systematic and extensive iteration [2]. It is hence a goal of this work to develop a theoretical modeling approach for *a priori* prediction of the success of a particular synthesis procedure. In this work, we focus on two problems related to inverse prediction: 1) identifying environmental conditions that stabilize conventionally metastable materials via charged defect accommodation, and 2) choosing reaction precursors that maximize the selectivity of a reaction towards a specific target product with minimal impurity formation. These ideas are discussed further in the following two subsections.

Targeted synthesis of metastable polymorphs via equilibrium defects

Often, a target material is predicted to be metastable, meaning that it is not the phase (or set of phases) predicted to have the lowest total free energy at its specified composition. Despite this, many metastable phases can be successfully synthesized, even when they appear rather high in energy compared to neighboring phases on the compositional phase diagram. A central hypothesis in the synthesis of metastable materials is “remnant metastability,” which states that the formation of a metastable phase occurs because that phase is *truly* stable within the environmental conditions accessed by the synthesis procedure [26]. It is further speculated that 1) all metastable materials that *can* be synthesized must have at least one intensive thermodynamic handle (e.g., pressure, temperature, chemical potential, magnetic field, etc.) that stabilizes them, and 2) metastable phases that cannot be synthesized are *never* stable at any particular set of conditions. This idea is supported by research showing that having a low (i.e., very negative) formation energy and “energy above hull” is a necessary but *not* sufficient condition for synthesizability [27]. If one is to believe this hypothesis, then the approach for the targeted synthesis of metastable phases is to identify which thermodynamic handles can be used to stabilize the phase.

Since solid-state synthesis relies on bulk diffusion of atoms through solids (which we know

occurs through defects such as vacancies, interstitials, grain boundaries, etc.), the ability of a metastable structure to accommodate defects in a particular set of conditions may be an important thermodynamic handle for its stabilization. In this work, we limit the scope of study to charged point defects in semiconductors/insulators, which can be calculated with moderate accuracy through *ab initio* computational approaches, such as density functional theory [28].

This work aims to predict the synthesis conditions and precursors (via the identification of chemical potential ranges) that stabilize one polymorph over another (e.g., layered α -NaFeO₂ over β -NaFeO₂). This approach aims not only to explain why certain metastable polymorphs appear in solid-state synthesis (and why others do not) but also to provide planning guidance for the synthetic chemist to design an experimental procedure with the greatest probability of producing a metastable target.

Identification of selectivity metrics for solid-state reactions

The complex interplay between thermodynamics and kinetics often leads to the formation of secondary, undesired phases [22]. In best cases, these impurity phases can be removed with additional processing; however, sometimes, these impurity phases interfere with the functional ability or safety of the product material for a particular application. This makes non-selective synthesis a major challenge in the optimization and scalability of a synthesis procedure for bulk manufacturing. A classic example of a non-selective synthesis is that of the multiferroic material bismuth ferrite, BiFeO₃, via the standard reaction from binary oxides: $\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \longrightarrow 2 \text{BiFeO}_3$. This synthesis typically leads to the formation of impurity phases Bi₂₅FeO₃₉ and Bi₂Fe₄O₉, which are highly difficult to isolate and remove [29]. The presence of a secondary phase is difficult to predict *a priori* and is often attributed to “kinetic” factors or perhaps to changes in phase equilibria related to precursor purity, morphology, volatility, or processing conditions.

The final major aim of this work is to create and test a solid-state reaction selectivity metric. At the time of writing, no established solid-state reaction selectivity metric exists. Accurate characterization of solid-state reaction selectivity is crucial, as *a priori* calculation of the selectivity of a solid-state reaction would make it feasible to rank synthesis approaches based on their likelihood of success (i.e., the predicted yield of a desired product phase), thereby circumventing the Edisonian approach to synthesis. This would not only reduce the synthesis bottleneck in the computational design of new materials but also significantly decrease the cost of existing synthesis approaches based on suboptimal procedures with high temperatures and/or long reaction times.

1.4 Outline of this dissertation

This dissertation begins with a Methods chapter (Chapter 2) that provides background information, a detailed description of calculations and experiments performed, and the theoretical

models underlying the remainder of the work. The main four chapters (Chapters 3-6) are based on key findings originally presented in published (or soon-to-be-submitted) journal articles by the author. Finally, the dissertation concludes with Chapter 7, which contains a summary of the main findings of the work and a future outlook for the research field.

In Chapter 2, we introduce the background and methods relating to the remainder of this work. We focus on X-ray diffraction (XRD) techniques, explaining the basic principles of XRD, as well as the experimental setups for performing *in situ* and ex post facto diffraction of materials synthesis. We then introduce density functional theory (DFT), discussing the basic theoretical principles of the approach, recent developments in automated DFT workflows, calculation of charged point defects in semiconductors/insulators, and an approximation for Gibbs free energy that is used extensively throughout this work. Methods for calculating phase equilibria are discussed, including their application to the construction of compositional phase diagrams and chemical potential diagrams. Finally, we review how solid-state reaction thermodynamics can be calculated from first principles data and the interface reaction model.

In Chapter 3, we present a chemical reaction network model for solid-state synthesis constructed using data sourced from theoretical and experimental thermochemistry databases. We then propose a computationally tractable approach for suggesting likely reaction pathways via the application of pathfinding algorithms and linear combination of lowest-cost paths in the network. Initial success of the network is shown in predicting complex reaction pathways comparable to those reported in the literature for YMnO_3 , $\text{Y}_2\text{Mn}_2\text{O}_7$, Fe_2SiS_4 , and $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$.

In Chapter 4, we discuss the selective synthesis of two metastable oxide polymorphs: α - YMnO_3 and α - NaFeO_2 . We show, using charged point defect DFT calculations and a chemical potential-based analysis approach, that these metastable polymorphs can become ground-state structures under certain environmental conditions due to their better accommodation of certain defect species (i.e., low defect formation energies).

In Chapter 5, we present a general approach for searching large chemical spaces to identify selective reactions based on the use of chemical potential diagrams. We use the approach to rationalize the selective synthesis of $\text{Y}_2\text{Mn}_2\text{O}_7$ using assisted metathesis with a Na-based precursor. We show that of the three studied $A_x\text{MnO}_2$ intermediates ($A=\text{Li}, \text{Na}, \text{K}$), only NaMnO_2 achieves a minimal near-zero distance in hyperdimensional chemical potential space to $\text{Y}_2\text{Mn}_2\text{O}_7$, thus providing selective access to a phase which was previously thought to be metastable. We further validate this pathway-dependent selectivity mechanism using *in situ* synchrotron-based crystallographic analysis.

In Chapter 6, using the interface reaction model of bulk powder reactions, we propose the idea of two forms of phase competition in solid-state reactions (primary and secondary) and derive equations for measuring selectivity in a high-throughput manner using the enumeration of massive solid-state reaction networks. We review solid-state synthesis reactions in the literature and show that, while many existing literature reactions have favorable selectivity, many other conventional approaches to technologically important materials are suboptimal. Finally, we test our selectivity predictions in a case study system: barium titanate (BaTiO_3).

From a massive chemical system of 17 elements, we compute 25,905 synthesis reactions for BaTiO_3 and select 11 to test experimentally, characterizing their reaction pathways using *ex post facto* synchrotron X-ray diffraction over a wide range of temperatures. We find that two highly-ranked unconventional reactions from BaS/BaCl_2 and Na_2TiO_3 precursors outperform conventional BaTiO_3 synthesis approaches. Furthermore, we find that our proposed secondary phase competition metric correlates strongly with the maximum impurity fraction observed during the reaction pathway for all experiments.

Chapter 2

Methods

This chapter presents an overview of the experimental and computational methods underlying this work. Each section provides a general background suitable for the average scientific reader, as well as details of how the methods are implemented throughout this work.

First, we discuss inorganic synthesis characterization techniques with a focus on X-ray diffraction and experimental setups for observing and resolving intermediate phases within reaction pathways. We then introduce density functional theory as a means for first-principles materials thermodynamic calculations, with a focus on its automated workflow implementations, particularly in the calculation of charged point defects (e.g., vacancies, interstitials). We discuss how to use thermodynamic data for two complementary types of phase equilibria calculations: compositional phase diagrams and chemical potential diagrams. Finally, we introduce the calculation of reactions from thermodynamic data and discuss the use of the compositional phase diagram to predict equilibrium reactions between solids (i.e., the interface reaction model).

2.1 X-ray diffraction (XRD)

For over one hundred years, scientists have utilized the mesmerizing physics of X-ray diffraction (XRD) to characterize crystalline materials. The father-son duo of William and Lawrence Bragg won the Nobel Prize in Physics in 1915 for developing an approach to systematically measure the diffraction of X-rays through materials [30]. Today, XRD is still one most important crystallographic characterization techniques used by solid-state chemists and materials scientists. While XRD is typically used to characterize a crystalline material *after* it has been synthesized, recent work has also shown that it is an optimal approach for observing the synthesis of materials in real-time as it happens (i.e., *in situ*) [2] due to the fact that many reaction pathways involve crystalline intermediates.

In the following sections, we will review the basic principles of XRD and discuss two experimental setups utilized in this work for observing reaction pathways during synthesis.

Basic principles

In 1912, Max von Laue and his coworkers were the first scientists to observe and suggest that X-rays diffract through crystals [31]. Specifically, Laue suggested that X-rays are electromagnetic waves of comparable wavelength to the lattice spacing between atomic planes in a crystal, such that the layers of the crystal would behave just like a diffraction grating. Just one year later, in 1913, Lawrence Bragg formulated a simple equation [32] with his father that provides a geometric explanation of the XRD phenomenon. Their explanation states that diffraction is a result of constructive and destructive interference due to reflections of the x-rays from planes of crystals – as though crystallographic planes behave like mirrors. Bragg’s Law, or the “Bragg condition,” specifies when constructive interference between scattered waves occurs and is written as

$$n\lambda = 2d \sin \theta, \quad (2.1)$$

where n is the diffraction order or wavelength multiple, λ is the wavelength of light, d is the interplanar distance for a specific type of crystallographic plane, and θ is the angle of incidence, defined as the angle between the wave’s direction and the crystallographic plane. When the Bragg condition is reached for a specific plane and angle of incidence, a constructive peak in intensity will be observed. For a single crystal in an X-ray beam, the transmitted X-rays will constructively interfere and produce points on a detector, known as diffraction spots. For a polycrystalline material that is composed of many crystallites of different orientations, diffraction “rings” will be observed instead. The integrated intensity as a function of angle (historically written as 2θ) is known as the diffraction pattern. This pattern serves as a “fingerprint” of the material, allowing one to identify the symmetry, composition, microstructure, and even defects of the measured phase.

Modern crystallography still uses this fundamental scattering principle to characterize crystalline materials. In addition to X-rays, it is also possible to collect diffraction patterns using beams of electrons or neutrons; each approach provides its own advantages/disadvantages. While X-ray beams produced at synchrotron light sources are preferable for their high resolution and intensities, the conventional approach in a solid-state chemistry laboratory setting is to perform XRD analysis on synthesized phase(s) using a laboratory powder diffractometer (e.g., Bruker D8, Panalytical Empyrean). To do this, the powder of interest is placed in a sample holder, which gets placed in the diffractometer. The diffractometer then produces X-rays from an X-ray source. The scattered beam intensity is measured with the detector by rotating it through a range of angles, 2θ , thereby producing a diffraction pattern. Finally, this pattern is fit to a model, often through an optimization approach known as Rietveld refinement. In the Rietveld refinement process, a diffraction pattern of a model system (i.e., a mixture of phases with various crystallite sizes, etc.) is simulated and optimized until it matches the measured pattern within a specified error tolerance [33]. Because of the number of free variables in refinement and possible issues with measurement quality, it tends to be difficult to guarantee that a model for a particular refinement is “correct”. Hence, some amount of chemical intuition must often be incorporated

by the scientist, such that the model is chemically “plausible” for the particular experiment [34].

***In situ* x-ray diffraction**

When used as a characterization technique for solid-state synthesis, XRD has historically been performed almost entirely *ex situ*, i.e., away from the furnace and after an experiment has concluded. While this is still helpful for analyzing the outcome of the reaction and characterizing the final product(s), *ex situ* XRD often does not provide enough information to assess the reaction pathway of a particular experiment. This is because some crystalline intermediates, including metastable phases, may be observed only for short times early in the reaction, well before equilibrium is attained [20]. While one may be able to speculate the individual reaction steps by performing a series of *ex situ* reactions at intermediate times and temperatures, it is most favorable to watch synthesis as it happens in the furnace (*in situ*).

Clausen et al. presented a design for a sample-environment cell enabling *in situ* XRD studies at high temperatures and pressures. Their *in situ* reaction cell was originally designed to capture catalytic activity and structural changes via X-rays from a synchrotron source [35]. Chupas et al. expanded upon this design by creating a more general reaction cell capable of accessing temperatures as high as 1000 °C with static or flowing gas, vapor, or fluid environments [36]. This design is known as the flow-cell/furnace and is conceptually illustrated in Figure 2.1 based on the original drawing by Martinolich & Neilson [14]. The modular design of the flow-cell/furnace allows the experimenter to quickly swap in capillaries holding their different samples. The tube fittings and heating elements allow for precise control of gas flow and temperature within the capillary, respectively. All of this can be performed in the presence of an X-ray beam with minimal scattering from the device. This allows one to observe synthesis as it happens, capturing structural phase changes and the nucleation/growth of new crystalline phases as the sample environment (e.g., temperature) is varied.

The gradient heater

The flow-cell/furnace was modified by O’Nolan et al. for high throughput variable temperature experiments [37]. The “gradient heater” is pictured in Figure 2.2a and features variable-pitch heating wires that have been configured to achieve a spatially-resolved temperature profile that is predominantly linear over the width of the capillary (Figure 2.2b). Like the flow-cell/furnace setup, this device features tube fittings allowing for gas/liquid flow (e.g., O₂, vacuum). In standard operation, the gradient heater approaches a temperature $T = 800$ °C on the hot end. This can be extended to temperatures above 1000 °C by increasing the current flow to the heating elements.

The advantage of the gradient heater is the ability to resolve the kinetic behavior of reactions without multiple experiments: only one single experimental run is required for a

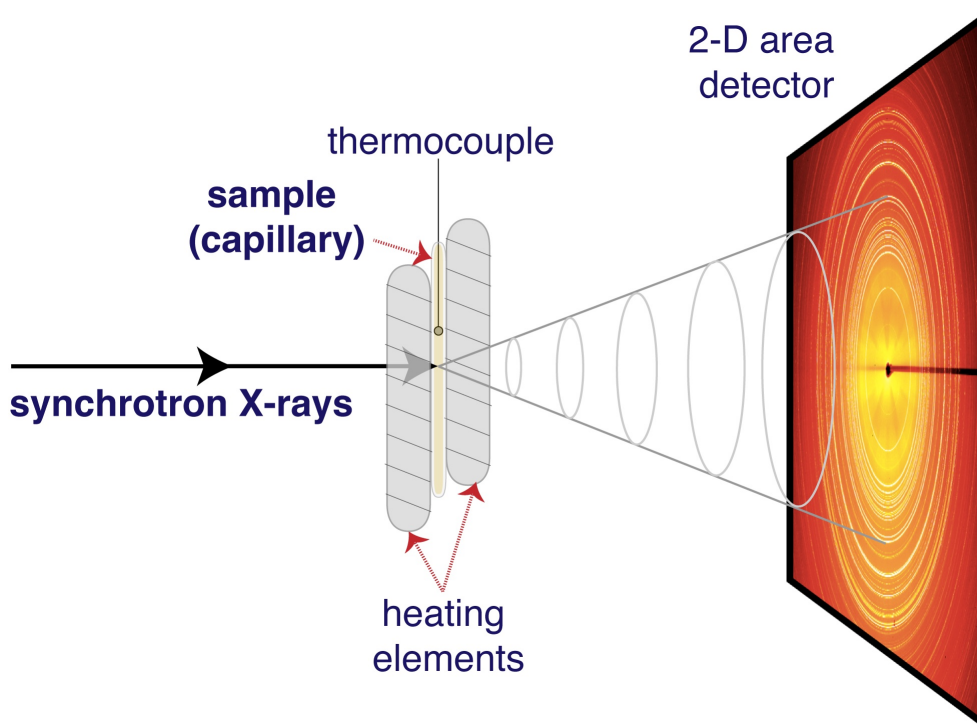


Figure 2.1: *In situ* flow-cell/furnace. This experimental setup permits observation of synthesis as it happens via the use of a synchrotron X-ray beam and two-dimensional area detector measuring scattering from the reacting sample. Heating elements (wound wires) and a thermocouple allow for precise control of the sample environment temperature. This figure has been recreated based on the original drawing by Martinolich & Neilson [14].

particular sample. Time-resolved data is acquired isothermally over a large range of temperatures, where the temperature resolution depends on both the number of spatial points scanned along the length of the capillary and the slope of the temperature curve. This time-resolved data can be used to characterize the reaction pathway of a particular sample at a specific temperature; or alternatively, one can recover an approximation of the reaction pathway by characterizing the final products at ambient temperature for each spatial coordinate along the capillary. The latter approach will be discussed in the following section.

***Ex post facto* x-ray diffraction**

The use of the gradient heater (Figure 2.2) to recover an approximation of the reaction pathway at ambient temperature is known as *ex post facto* (after the fact) X-ray diffraction. This use case of the gradient heater was highlighted in the original work by O’Nolan et al. [37] and will be featured in later chapters.

Ex post facto XRD is advantageous primarily because it allows for the characterization of a reaction pathway solely via measurements completed at ambient temperature, where temperature effects (e.g., lattice expansion) can be ignored in the analysis. This greatly simplifies

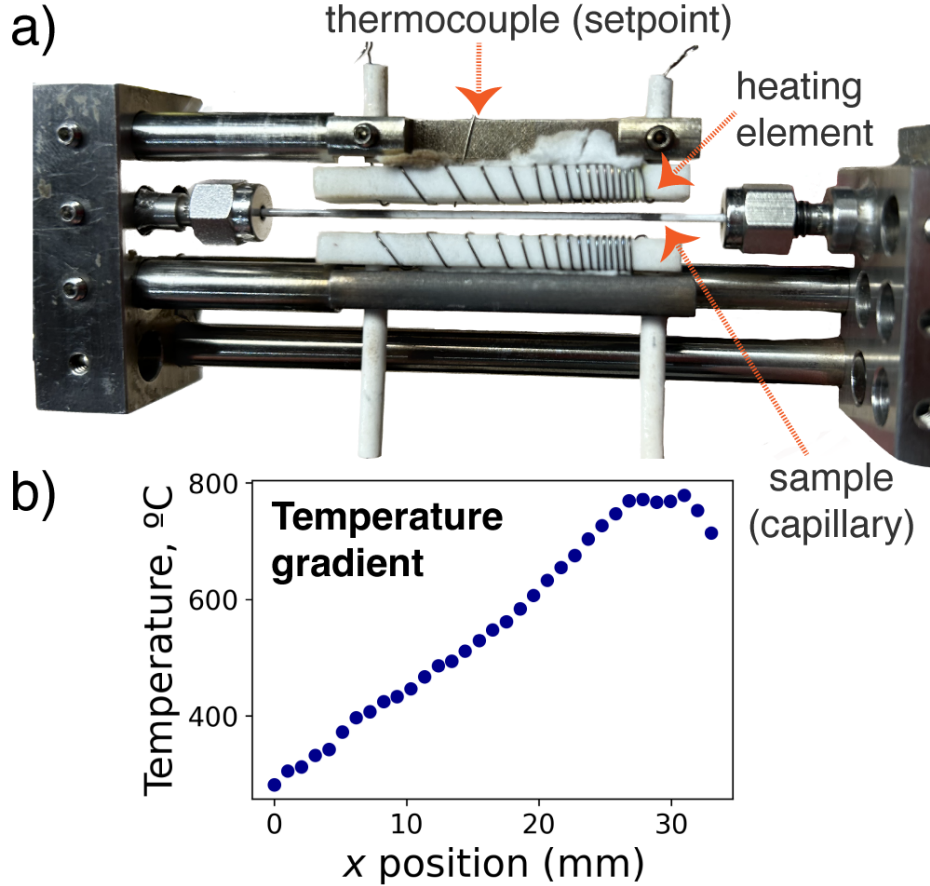


Figure 2.2: The gradient heater for *in situ* variable-temperature measurements. (a) Annotated photograph of the gradient heater setup, (b) the measured temperature gradient over the length of a capillary, as determined from the measured lattice expansion of an NaCl sample.

the post-processing of data, allowing one to perform standard Rietveld refinements. Furthermore, this analysis can be assisted by out-of-the-box dimensionality reduction techniques, such as non-negative matrix factorization (NMF), for more rapid processing.

2.2 Density functional theory (DFT)

Density functional theory is an *ab initio* quantum mechanical approach for modeling the electronic structure of *interacting* many-body systems (e.g., molecules, condensed phases). The approximations made by DFT allow for a quantum mechanical level of accuracy without the need to solve the many-electron Schrödinger equation. For solid-state materials, this enables the accurate calculation of a myriad of key properties, such as ground-state energies and structural configurations, electronic and phonon bandstructures, dielectric constants, and much more [38]. This approach is truly *ab initio* in that it requires no assumptions

beyond the theory itself; the only input needed to calculate these material properties is a starting guess of the atomic positions (and electron density) within the structure.

Most thermodynamic data used in this work and all of the featured calculations are based on DFT, performed either by the author or by the maintainers of the Materials Project database [12]. In the next sections, we will review the basic principles of DFT and discuss its implementation within automated workflows, highlighting the calculation of charged point defects as an important example relevant to this work.

Basic principles

The interactions in an atomic system consisting of N electrons and M nuclei can be modeled by writing the Hamiltonian:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{a=1}^M \frac{1}{m_a} \nabla_a^2 - \sum_{i=1}^N \sum_{a=1}^M \frac{Z_a}{r_{ia}} + \sum_{i=1}^N \sum_{j \neq i} \frac{1}{r_{ij}} + \sum_{a=1}^M \sum_{b \neq a} \frac{Z_a Z_b}{R_{ab}}, \quad (2.2)$$

where we use the system of atomic units for numerical convenience ($\hbar = m_e = e = \frac{1}{4\pi\epsilon_0} = 1$). The first two terms represent the kinetic energies of the electrons and nuclei, respectively. The last three terms represent the potential energies of the electron-nuclei attractions, electron-electron repulsions, and nuclei-nuclei repulsions, respectively. This Hamiltonian can be greatly simplified by the assumption that the nuclei are *stationary*. While this is not explicitly true, the significantly larger size of the nuclei compared to the electrons allows one to model the Hamiltonian of electrons independently; this assumption is common and is known as the Born-Oppenheimer approximation. This has two results: 1) the kinetic energy of the nuclei (second term on the right) is assumed to be exactly zero, and 2) the Coulombic interaction between nuclei (the fifth term on the right) is constant. After these simplifications, we are left with a three-term electronic Hamiltonian,

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{a=1}^M \frac{Z_a}{r_{ia}} + \sum_{i=1}^N \sum_{j \neq i} \frac{1}{r_{ij}}. \quad (2.3)$$

The electronic Hamiltonian can then be used to solve the Schrödinger equation for the many-electron wavefunction. However, this is practically unfeasible, as the electron-electron interaction (the final term on the right in Equation 2.3) makes solving the *interacting* many-body Schrödinger equation extremely challenging.

This difficulty necessitates an alternative approach. One such alternative is known as density functional theory (DFT), which was originally derived by Walter Kohn and Pierre Hohenberg in 1964. In their landmark paper [39], they prove two theorems which have been summarized as follows:

1. The external potential of a many-body interacting system is a unique functional of its ground-state density, or optionally stated: the ground-state energy is a functional of the ground-state density, $E[n(\mathbf{r})]$.

2. Only the ground-state density will minimize the total energy of the system.

Hohenberg and Kohn essentially prove that the electron density, $n(\mathbf{r})$, can be used rigorously in lieu of the many-electron wavefunction. The electron density is defined

$$n(\mathbf{r}) = 2 \sum \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}), \quad (2.4)$$

where the summation occurs over all electronic wavefunctions, $\psi_i(r)$ [40].

The Hohenberg-Kohn theorems are essential because they mathematically prove that in a system of interacting electrons, the electron density captures all important properties of the system. Further, we are guaranteed to find the ground state density of the system if we can guarantee that the calculated density results in the lowest energy possible. This provides us with enough basis to begin formulating an approach to calculate the ground-state electronic structure properties of many-atom systems.

It was Kohn and Lu Jeu Sham who later introduced equations implementing DFT in a practical way for calculations [41]. They formulated the Kohn-Sham (KS) equations based on the simple principle that we can model a system of interacting electrons as a new system of non-interacting particles within a fictitious effective potential, $v_{\text{eff}}^{\text{KS}}(\mathbf{r})$. The KS equations have the form,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}^{\text{KS}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2.5)$$

where $\psi_i(\mathbf{r})$ are solutions to the KS equations and are single-electron wavefunctions (or orbitals). The effective potential is defined as

$$v_{\text{eff}}^{\text{KS}}(\mathbf{r}) = V(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}), \quad (2.6)$$

where $V(\mathbf{r})$ is the “external potential” that includes the Coloumb interaction between the electrons and the nuclei. V_{H} is the Hartree potential, and accounts for Coulombic interactions between an electron and the total electronic density (which does include a self-interaction error). V_{H} is defined as

$$V_{\text{H}}(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'. \quad (2.7)$$

V_{XC} is the exchange-correlation potential and is defined as a derivative of the exchange-correlation energy functional,

$$V_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}(\mathbf{r})}{\delta n(\mathbf{r})}. \quad (2.8)$$

$V(\mathbf{r})$ and $V_{\text{H}}(\mathbf{r})$ can be solved for exactly. However, V_{XC} accounts for the electronic exchange and correlation effects and, therefore, must be approximated. It is not known what the functional form of E_{XC} is exactly; however, there are many common approximations. Modern DFT research has focused on developing more accurate expressions for E_{XC} that are computationally tractable. These exchange-correlation functionals include the local-density

approximation (LDA) or local spin-density approximation (LSDA), generalized gradient approximation (GGA) [42], and meta-GGA functionals such as SCAN [43] or r2SCAN [44]. Further review of exchange-correlation functionals, as well as details concerning the practical implementation of DFT (e.g., pseudopotentials), can be found in Ref. 45.

Finally, we note that the KS equations must be solved self-consistently, beginning first with a guess of the charge density, which is then used as an input to the equations and yields a new charge density. Modern DFT codes, such as the Vienna Ab initio Simulation Package (VASP), have been designed with algorithmic approaches that complete this self-consistent loop efficiently [46, 47].

Automated DFT

Our current Moore’s Law era of computing power growth [48] has made DFT calculations significantly easier, faster, cheaper, and more convenient to run [49]. This has ushered in a modern computational materials science era based on the creation of materials databases from high-throughput DFT calculations (i.e., the Materials Genome Initiative) [50].

To execute on the level required for building a high-throughput database of DFT calculations, one must be able to reliably automate the setup, execution, parsing, and storage of DFT calculation data. To this effect, recent work has focused on the development of standard workflows and input files for various types of DFT calculations, such as interfaces [51], adsorption [52], point defects [53], elastic tensors [54], etc. Many of these workflows have been implemented within the open-source Python package, *atomate* [55].

In this work, we utilize workflows within *atomate*, as well as workflows from the successor package, *atomate2* [56]. We use the workflow management package, *fireworks* [57] to facilitate the launching and storage of DFT calculations. We also use the Python package, *jobflow* [58], to facilitate the writing of custom computational workflows.

Calculation of charged point defect formation energies

One application of density functional theory relevant to solid-state state synthesis is the calculation of formation energies for point defects (i.e., vacancies, substitutions, interstitials). The understanding of point defects is crucial to solid-state reactions, as bulk diffusion through solids is mediated by defects [59]. Due to the associated increase in configurational entropy, there is a significant thermodynamic advantage for point defects to form naturally in crystals. Even though the formation of a single point defect in a perfect crystal always costs some amount of energy (i.e., it has a positive formation enthalpy), the entropy increase associated with increasing the number of configurational states in the crystal will lead to an overall *decrease* in the Gibbs free energy of the system at nonzero temperatures. This simple energy versus entropy counterbalance results in the outcome that all crystals at temperatures above $T = 0$ K have some positive, nonzero equilibrium concentration of point defects, c^{eq} .

For mathematical convenience, and because it is physically relevant for many cases, defect concentrations are often calculated within the *dilute limit*. This means that defects are

assumed to be isolated and defect-defect interactions are negligible. Within the dilute limit, we can derive the equilibrium concentration of defects in a crystal; see Ref. 28 for a detailed step-by-step analysis. The final result of this derivation is that the equilibrium point defect concentration in a crystal can be calculated as

$$c^{\text{eq}} = g \exp \frac{-G^f(P, T)}{k_B T}, \quad (2.9)$$

where g is a degeneracy/multiplicity factor denoting the number of times this defect site repeats per unit cell of the crystal, $G^f(P, T)$ is the Gibbs free energy of formation of the defect, k_B is Boltzmann's constant, and T is temperature. This Arrhenius-like equation captures the limiting behavior: 1) $\lim_{T \rightarrow 0} c^{\text{eq}} = 0$, and 2) $\lim_{\Delta G_f \rightarrow \infty} c^{\text{eq}} = 0$. We note that the first condition evokes the third law of thermodynamics.

DFT calculations can be used to determine $G^f(P, T)$ within reasonable error. While the full calculation of G^f for a point defect requires the explicit calculation of vibrational and electronic contributions to the entropy, a common simplification is to assume that $G^f \approx E^f$ (i.e., disregard entropy and volume effects). This reduces the predictive accuracy of DFT-calculated defect concentrations but may be a reasonable approximation for some analyses, especially those at low temperatures.

The grand canonical approach for point defect formation energy calculations assumes that all point defects X of charge state q interact with the host crystal as though it contains reservoirs of atomic species and electrons at specified chemical potentials. As discussed in Ref. 28, we can formulate the formation energy equation as

$$E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}}, \quad (2.10)$$

where $E_{\text{tot}}[X^q]$ is the calculated energy of the atomic supercell with the defect, $E_{\text{tot}}[\text{bulk}]$ is the calculated energy of the bulk atomic supercell *without* the defect, n_i and μ_i correspond to the number of atoms and chemical potential of an atomic species i required to form the defect, E_F is the Fermi energy (i.e., the chemical potential of electrons), and E_{corr} is a correction energy term which accounts for interaction error between defects in periodic images, or other DFT-based errors. The grand canonical approach differs from the Kröger-Vink (or defect reaction) approach [60] in that charge neutrality is not assumed *a priori* [61]. In the Kröger-Vink approach, it is often assumed that defects must be written as reactions that form charge-neutral pairs or defect combinations. In the grand canonical approach, the condition of charge neutrality is determined after the fact by the self-consistent solution of E_F that leads to an electronically neutral crystal. In other words, E_F is varied until the total charge from all defect species i of N obeys the condition $\sum_i^N q_i c_i^{\text{eq}} = 0$.

When applied to the different charge states, q , of a single defect species (e.g., a sodium vacancy, V_{Na}), this equation allows one to produce the defect formation energy diagram, which is illustrated in Figure 2.3. The defect formation energy diagram in Figure 2.3 corresponds to a defect that can exist in three charge states (+1, 0, -1) in a semiconductor/insulator with a

nonzero bandgap. The slope of each line on the defect formation energy diagram corresponds to the charge state of the defect, and the relative vertical position of the line compared to the other charge states is determined by the relative energetic favorability of forming that defect charge state. The entire set of formation energy lines for a particular defect species can be vertically shifted by changes in the relevant chemical potential(s). It is conventional to plot the transitions (blue stars) between charge states such that the dominant (lowest energy) charge state is known for any value of E_F ; this is illustrated by the shaded yellow region in the figure.

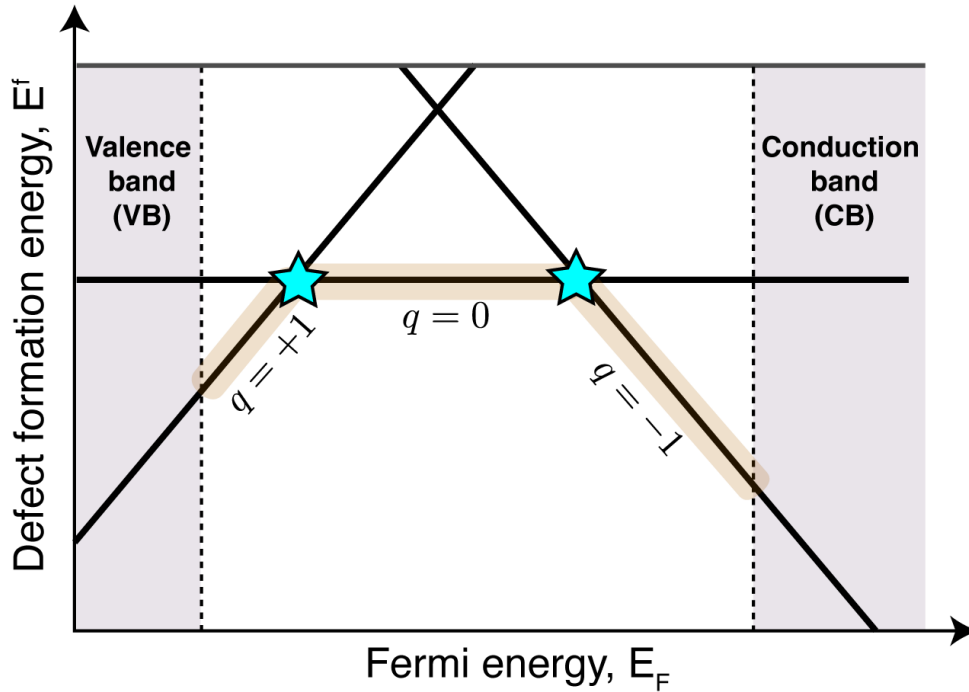


Figure 2.3: The defect formation energy diagram for a hypothetical charged point defect in a semiconductor with three stable charge states. The shaded yellow area indicates the lowest energy charge state(s), as marked by the charge transitions (blue stars). The valence band maximum and conduction band minimum impose bounds for the accessible Fermi energies.

There are at least two popular state-of-the-art schemes for computing the correction energy term (E_{corr}) in Equation 2.10. One is developed by Freysoldt, Neugebauer, and Van de Walle [62] and the other by Kumagai [63]. These correction schemes generally rely on image-charge and potential-alignment corrections. Proper energy correction schemes are important because they allow for approximation of the true dilute limit while maintaining computationally tractable supercell sizes (i.e., on the order of as few as 100 atoms). This is especially crucial when a higher and more expensive level of theory is adopted, such as is common when using hybrid exchange-correlation energy functionals.

High-throughput calculation of defect formation energies with DFT is ongoing, and the scientific community is currently developing workflow tools to enable this, including packages

such as *pyCDT* [53] or *pydefect* [64]. While performing intrinsic defect calculations for even a single phase requires many expensive calculations (100-300 atom supercells for each charge state of every defect species, in addition to the pristine supercell), it is anticipated that current increases in computing power will enable the construction of large (>1000 structures) computed point defect databases in the near future. This development will facilitate significant scientific advances in the use of defect energies for modeling reactive diffusion in solids, phase stability, and more.

Approximations for Gibbs free energy of formation of bulk solids

DFT calculations are performed at $T = 0$ K, which by definition, excludes entropic effects in the calculation of formation energies of materials. Thus, formation energies are reported as ΔE_f instead of the often more-appropriate Gibbs free energy of formation, $\Delta G_f(P, T)$. While the use of $T = 0$ K energies is often assumed to be sufficient for most phase stability analyses performed at lower temperatures, it becomes a greater issue when these calculated energies are used to predict reaction thermodynamics at elevated temperatures. This is especially true when one of the solid structures melts or sublimates at higher temperatures; the entropy of a liquid/gas is significantly higher than that of a solid and may greatly affect the predicted free energy of a reaction, ΔG_{rxn} .

For well-known liquids and gases (e.g., H_2O , molten NaCl , CO_2), it is straightforward to use experimentally-derived Gibbs free energies. For example, in modeling a reaction that produces CO_2 gas at $T = 1000$ K, one may use the experimental Gibbs free energy of formation for CO_2 gas as found in the NIST-JANAF thermochemical tables [65] at that temperature in lieu of the DFT-calculated formation energy of solid crystalline CO_2 at $T = 0$ K. However, for less-known or even hypothetical phases, to predict $\Delta G_f(P, T)$, one must calculate the vibrational/electronic contributions to the entropy of the phase, which is time-intensive. For vibrational contributions, it is common to perform quasiharmonic (and ideally anharmonic) phonon calculations [66] on a solid, using either density functional perturbation theory (DFPT) or the small-displacement method. These calculations are specialized, and the construction of larger phonon databases is ongoing but slow [67, 68].

Recognizing this challenge, Bartel et al. [69] used a recently derived machine learning approach, the sure-independence screening and sparsifying operator (SISSO) [70], to develop a symbolic expression for predicting the elevated temperature contributions to the formation energy of a particular structure. The authors achieved a 43 meV/atom root-mean-square deviation between their predictions and experimentally measured ΔG_f values – an even slightly better performance than achieved using the quasiharmonic approximation (QHA) approach, which is the current standard.

Bartel et al. formulated the problem as the task of machine learning the quantity $G^\delta(T)$, which accounts for 1) the temperature-dependence of the formation enthalpy ΔH_f , and 2)

the temperature-dependent entropic effects. This predicted term appears in the equation

$$\Delta G_{\text{f,pred}}(T) = \Delta H_{\text{f}}(298 \text{ K}) + G^{\delta}(T) - \sum_i^N \alpha_i G_{i,\text{exp}}(T), \quad (2.11)$$

where $\Delta H_{\text{f}}(298 \text{ K})$ is the formation enthalpy calculated by DFT at $T = 0 \text{ K}$, adjusted with corrections to approximate the room temperature phase diagram (as is standard on the Materials Project database, for example), and $\sum_i^N \alpha_i G_{i,\text{exp}}(T)$ includes the temperature effects on the elemental chemical potentials $G_{i,\text{exp}}(T)$ weighted by their relative amounts, α_i in the compound of interest containing N atomic species. This last term can be calculated using an experimental database, such as FactSage [71], which the authors used in their original paper. The SISSO descriptor identified by Bartel et al. is reported in units of eV/atom with the formula

$$G_{\text{SISSO}}^{\delta}(T) = (-2.48 * 10^{-4} * \ln(V) - 8.94 * 10^{-5} \text{mV}^{-1}) T + 0.181 * \ln(T) - 0.882, \quad (2.12)$$

where V is the volume per atom ($\text{\AA}^3/\text{atom}$) of the structure, m is the reduced mass in amu, and T is the temperature in Kelvin. Throughout this work, we utilize this descriptor in conjunction with experimental free energies to improve the accuracy of computed reaction thermodynamics and elevated temperature phase diagrams.

2.3 Phase equilibria

A common application of DFT data is in the thermodynamic calculation of phase equilibria. In this section, we explore two complementary types of phase diagrams that model equilibria/stability: 1) compositional phase diagrams and 2) chemical potential diagrams.

Compositional phase diagrams

The compositional phase diagram is a common construction that determines the stability of different compositions (and their polymorphs) with respect to decomposition. The compositional phase diagram can be used to assess phase stability within a chemical system. Phase stability is determined by calculating the 1) decomposition energy to neighboring compositions or 2) the degree of metastability (often called “energy above hull”) [27]. It can also be used to determine feasible chemical reactions within a system (to be discussed in Section 2.4). For more discussion on the determination of phase stability from the compositional phase diagram, we refer the reader to Ref. 72.

The compositional phase diagram can be constructed, in principle, for any chemical system of size N elements. Figure 2.4 shows two example phase diagrams of size $N = 2$ (binary) and $N = 3$ (ternary). Each of these diagrams is plotted with respect to $N - 1$ composition axes, as the N th compositional axis is linearly dependent on the others. For the ternary phase diagram, a barycentric coordinate system is used. On the binary phase

diagram plot, it is possible to directly observe the energy axis; however, for ternary phase diagrams, their two-dimensional projection is often plotted such that the energy axis goes into/out of the page and must be inferred through a color scale or other means. A phase diagram of size N is generally composed of $(N-1)$ -simplexes; e.g., in ternary phase diagrams ($N = 3$), every phase shares an equilibrium with at least two other phases on one or more 2-simplexes (triangles). Stated more precisely: within the bounds of every simplex, the elemental chemical potentials are constant, and no reaction is predicted to occur between the phases (bounding vertices) of that simplex.

The compositional phase diagram can be determined through an energy minimization approach or more efficiently by calculation of the convex hull [73]. For the latter approach, one first determines the coordinates of all phases within a coordinate system defined by the energy, E , and $N-1$ independent compositional dimensions, x_i . Note that the energies and compositions need to be correctly normalized on a per-atom basis. Finally, the convex hull is computed (e.g., through the Quickhull algorithm [74] or other means). Due to numerical limitations of the Quickhull algorithm, phase diagrams with a large number of elements ($N \geq 10$) may be intractable to calculate. The lower portion of the hull (all phases with energies below the elements) is acquired and often re-plotted in formation energy space, such that the elemental references have energy coordinates $E = 0$. All phases that do not appear “on the hull”, such as the red diamonds in Figure 2.4a, are considered unstable with respect to decomposition. For these phases to be observable (or synthesizable) requires them to be *metastable*, such that they exist in kinetically trapped states (i.e., local energy minima). The synthesizability of metastable phases is an ongoing and debated area of research [27, 75] that is discussed in Chapter 4.

In this work, phase diagrams are computed and plotted using the *pymatgen* package, as originally implemented by Ong et al. [73, 76].

Chemical potential diagrams

Like the compositional phase diagram, the chemical potential diagram is a construction that determines the thermodynamic stability of compositions within a chemical system. However, the chemical potential diagram differs in that it is computed over a coordinate system of N chemical potentials, μ_i . The chemical potential diagram is a more generalized extension of the predominance diagram, which is a plot of one of the two-dimensional projections from a ternary chemical potential diagram. Two example chemical potential diagrams are illustrated in Figure 2.5 for the V-S (binary) and V-S-O (ternary) systems.

As the chemical potential is the conjugate variable to the number of particles of a species, the chemical potential diagram can be thought of as a “conjugate” diagram to the compositional phase diagram, conveying equivalent information but plotted within chemical potential space. Indeed, both diagrams require the exact same inputs to construct: a set of compositions and their energies. Despite these diagrams being effectively equivalent in the information they contain, chemical potential diagrams are valuable constructions for observing 1) the relative stability/competition of phases (i.e., via the size of their domains), 2)

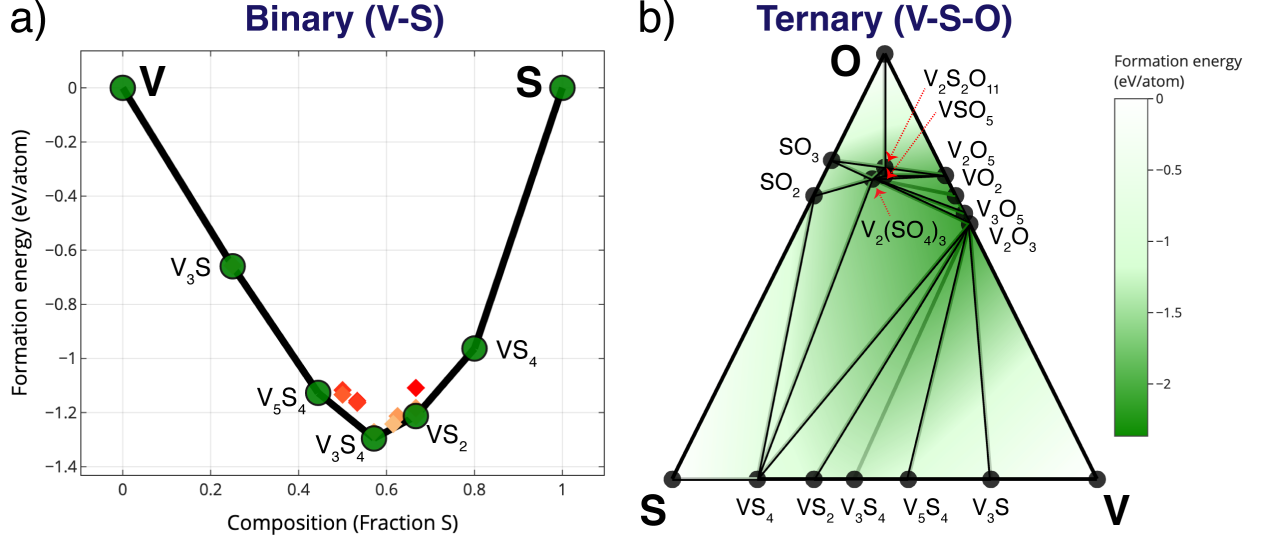


Figure 2.4: Example compositional phase diagrams. (a) Binary compositional phase diagram for the vanadium-sulfur (V-S) chemical system. The green circles correspond to the stable phases, and the yellow/red diamonds correspond to unstable phases. (b) Ternary phase diagram for the vanadium-sulfur-oxygen chemical system. The black circles correspond to stable phases; unstable phases are not labeled. Colored shading indicates the approximate formation energy gradient across the diagram.

interfacial stability, and 3) the valid chemical potential bounds that can be used in grand canonical-like calculations (e.g., point defect energies) [77, 78]. In this work, we develop an algorithmic approach for constructing chemical potential diagrams via the methodology described by Yokokawa [77]. Our algorithmic approach is inspired by a similar method for the construction of Pourbaix diagrams [79], which involves the calculation of the lower envelope of hyperplanes in combined energy vs. chemical potential space.

For a pure substance with n atoms per chemical formula unit, consisting of N unique elements indexed i with normalized concentrations of x_i , its hyperplane in N -dimensional chemical space is defined via the equation

$$\sum_{i=1}^N x_i (\mu_i - \mu_i^0) = \frac{1}{n} \Delta G_f^0(T), \quad (2.13)$$

where the standard Gibbs free energy of formation, $\Delta G_f^0(T)$, has been normalized to an energy-per-atom basis by dividing by the total number of atoms per formula unit, n . Note that all reference chemical potentials μ_i^0 are set to zero, by definition, when working with elements in their standard states. Following the construction of hyperplanes for all phases in the chemical system, the stability domains are acquired by taking the convex hull of all points belonging to that phase in the set of intersections of the lowest energy hyperplanes. In this construction, each stability region is a convex $(N - 1)$ -dimensional polytope in N -dimensional chemical potential space.

Often, it is useful to visualize aspects of high dimensional ($N \geq 4$) chemical potential diagrams, as we will show in Chapter 5. This can be accomplished either by 1) using clever transformations of the axes, 2) setting one or more chemical potentials to fixed values, or 3) taking a slice of the relevant chemical potential polytopes in lower dimensions. In this work, we opt to choose the third option. Phases that do not directly appear on the generalized chemical potential diagram in three dimensions are thus computed first in the full chemical potential space and then sliced to plot in lower-dimensional subspace. For example, three-dimensional polyhedra yielded by slicing a four-dimensional chemical potential diagram make contact with the stability areas of any subset (three-dimensional) chemical potential diagram surface. These contact areas illustrate shared phase equilibria within the higher-dimensional space. This behavior extrapolates to chemical potential diagrams with even higher dimensionality ($N \geq 5$).

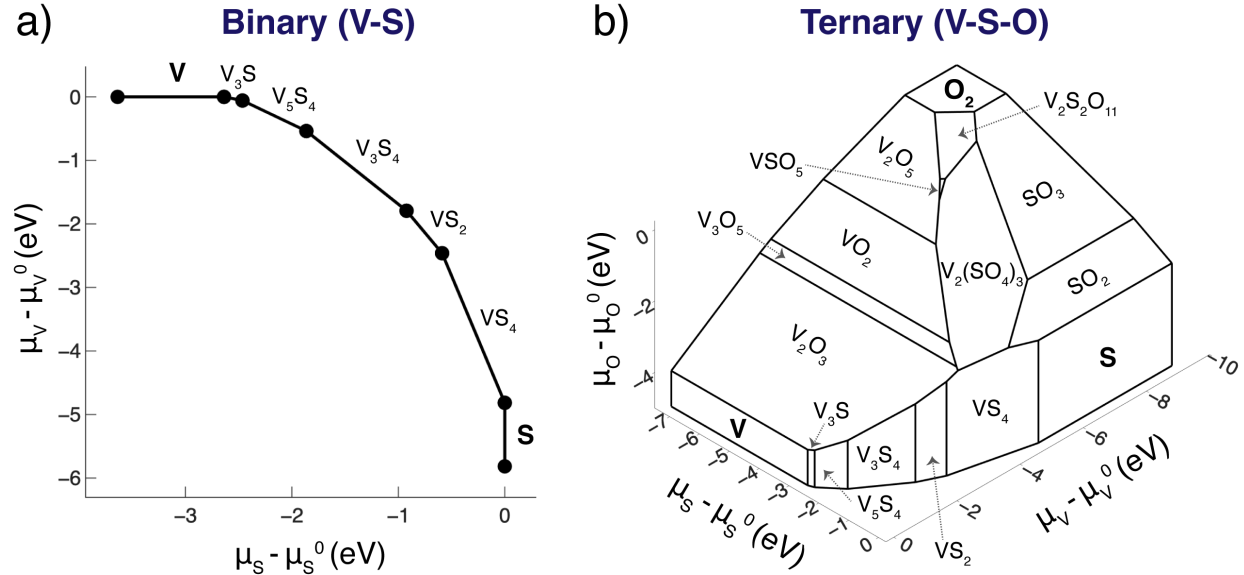


Figure 2.5: Example chemical potential diagrams. (a) Binary chemical potential diagram for the vanadium-sulfur (V-S) chemical system. Lines are stability regions for the annotated composition, and black circles denote transition points (or phase equilibria) between different compositions. (b) Ternary chemical potential diagram for the vanadium-sulfur-oxygen chemical system. The diagram is a three-dimensional surface made of two-dimensional convex polygons. These polygons are the stability domains for the annotated compositions; phase equilibria occur at points and lines of equal chemical potential(s).

The use of chemical potential diagrams will be explored further in Chapter 4 for modeling defect-dependent phase stability and in Chapter 5 for rationalizing solid-state reaction selectivity in the assisted metathesis synthesis of $Y_2Mn_2O_7$.

2.4 Reaction thermodynamics

In this work, we use a combination of computed and experimental thermodynamic data to 1) calculate the free energies of reactions and 2) predict likely interface reactions based on phase equilibria.

Calculation of reaction free energies

Reaction free energies can be calculated by taking the total energy difference between products and reactants,

$$\Delta G_{\text{rxn}} = \sum_j^P n_j G_j - \sum_i^R n_i G_i, \quad (2.14)$$

where ΔG_{rxn} is the Gibbs free energy of the reaction between R reactants indexed i and P products indexed j . The variables n_i and n_j correspond to the stoichiometric coefficient of each reactant and product, respectively, and G_i and G_j correspond to the Gibbs free energy per formula unit of each reactant and product, respectively. The reactant/product energies must be referenced to the same scale; however, this scale can either be in terms of raw energies (such as output from a calculation or software) or formation energies. The normalized energy per atom of the reaction can be obtained by dividing ΔG_{rxn} by the number of atoms in the reaction formula, determined by counting the total number of atoms on one side of the reaction equation (i.e., the number of atoms per composition multiplied by its stoichiometric coefficient).

When using thermodynamic data sourced from DFT, one must be careful to avoid systematic reaction energy errors associated with certain exchange-correlation functionals. For example, the GGA functional tends to result in the overbinding of the O_2 molecule, which leads to a systematic error of around 1.36 eV per O_2 molecule in oxidation reactions [80]. As part of this thesis, the author participated in a study describing a general framework for simultaneous fitting of energy corrections [81]. These energy corrections are currently used on the Materials Project database and throughout the phase diagram and reaction calculations present in Chapters 5 and 6.

Predicting interface reactions

The compositional phase diagram can also be utilized to suggest all equilibrium reactions occurring at the interface between two solids. This approach is detailed thoroughly in Ref. 82 and computationally implemented in the *pymatgen* package. Figure 2.6 illustrates the general concept of predicting equilibrium interface reactions from a compositional phase diagram. In this hypothetical ternary phase diagram, the reaction between phases α and β is indicated by the red dotted tie-line. The 0-simplexes (points) or 1-simplexes (lines) that this tie-line intersects on the ternary phase diagram yield the product(s) resulting from a reaction at that ratio of mixing (i.e., coordinate along the line). This is best observed

by dropping down a binary cross-section (Figure 2.6b) of the full ternary convex hull. In this binary hull, or “interface reaction hull”, the intersections become points on the hull and represent equilibrium reaction products. For example, the pink diamond may represent a reaction such as $0.65 \alpha + 0.35 \beta \longrightarrow 0.75 \delta + 0.25 \epsilon$. Note that the reaction products are predicted with stoichiometric coefficients given by the coordinate at which they intersect along the δ - ϵ simplex, as determined by the lever rule.

The prediction of interface reactions will be more thoroughly explored in Chapter 6.

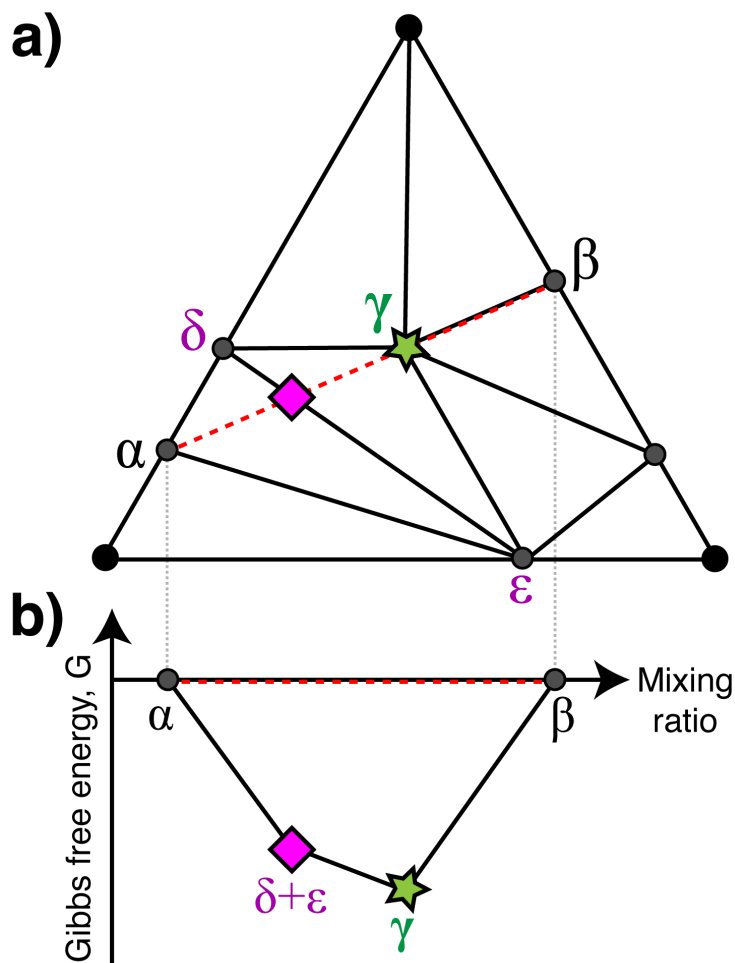


Figure 2.6: Prediction of solid interface reactions from the ternary phase diagram. (a) A ternary phase diagram for a hypothetical system showing the reaction between phases α and β , connected by tie-line. (b) Drop-down binary cross-section of the convex hulls showing intersections of the α - β tie-line with the ternary phase diagram. These intersections yield two reactions that result in a decrease in Gibbs free energy: one forms a mixture of δ and ϵ , and the other produces entirely γ .

Chapter 3

Solid-state chemical reaction networks

In this chapter, we present a chemical reaction network model for predicting and suggesting solid-state inorganic reaction pathways. We propose to leverage recent advances in data-driven methods that have resulted in computational/experimental thermochemistry databases [12, 65, 84, 85] covering hundreds of thousands of materials and millions of associated reaction energies [86]. We employ a reaction network model that blends typical thermodynamic phase diagrams with the connectivity and kinetic heuristics derived from transition state theory. The network model is a convenient data structure for exploring the underlying free energy surface of thermodynamic phase space in solid-state chemistry via existing computational infrastructure for large graph networks.

We outline the methodology used to create the solid-state chemical reaction network from thermochemistry databases and demonstrate its capacity for solid-state reaction pathway prediction by applying it to several reported experimental syntheses for YMnO_3 , $\text{Y}_2\text{Mn}_2\text{O}_7$, Fe_2SiS_4 , and $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, as well as to recommend chemical routes to a novel battery cathode material, $\text{MgMo}_3(\text{PO}_4)_3\text{O}$, that has not been previously synthesized.

3.1 Construction of the solid-state reaction network

The solid-state reaction network is a model for thermodynamic phase space, which is represented by an energy landscape governed by a generalized thermodynamic potential or free energy, Φ . The global minimum in this potential, which depends on the boundary conditions of a particular system, is the thermodynamic equilibrium state of the system. Figure 3.1 depicts three models of chemical reactions in thermodynamic phase space, ordered by increasing level of abstraction. The free energy convex hull construction of Figure 3.1a is a purely thermodynamic model of a chemical reaction between two reactant phases, R_1 and R_2 [82]. This convex hull model, which was discussed extensively in Chapter 2.4, yields the set

Note: This chapter is closely adapted from a prior journal publication of which I am the first author; see Ref. 83: McDermott, M. J. *et al.* A Graph-Based Network for Predicting Chemical Reaction Pathways in Solid-State Materials Synthesis. *Nature Communications* **12**, 3097 (2021).

of products (and thus chemical reactions) that result in the largest decrease in free energy for a given mole ratio of the two reactants. Figure 3.1b abstracts the thermodynamic model further by incorporating the concept of activation energy, E_a , as defined by transition state theory [87]. This enables the inclusion of simple kinetic behavior of reactions, where the height of the activation energy barrier correlates with the rate of reaction.

Abstracting even further, we can consider these reaction coordinate diagrams as weighted directed graphs, like the one shown in the upper portion of Figure 3.1b. In these graphs, the cost/weight of a chemical reaction edge represents an *a priori* unknown function of synthesis parameters such as the thermodynamic driving force, activation energy, etc. Figure 3.1c shows the interlinking of many such graph representations within a set of phases, where each node represents a particular combination of phases (e.g., $R_1 + R_2$) and the edges represent chemical reactions with designated costs. This weighted directed graph, or chemical reaction network, is a densely connected model of thermodynamic phase space where thermodynamic/kinetic features can be combined and transformed into a unique cost representation for each reaction pathway.

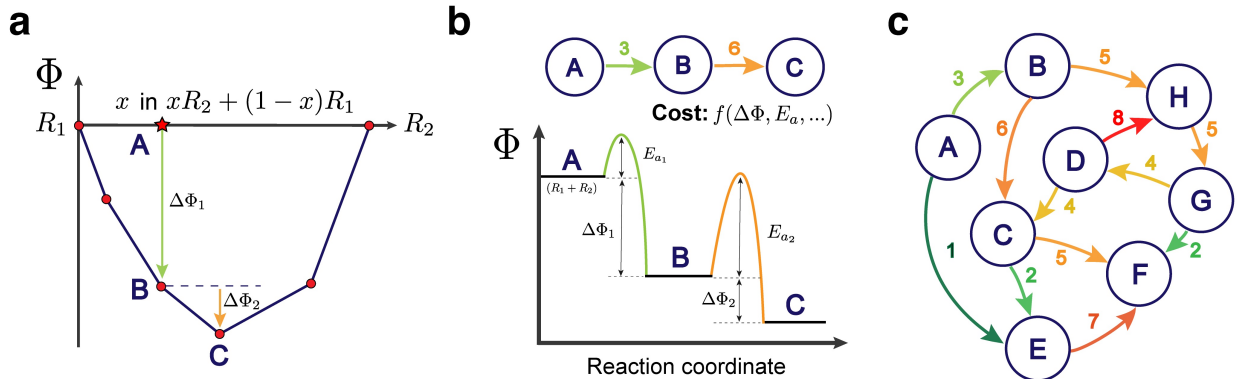


Figure 3.1: Thermodynamic models of chemical reactions in increasing degree of abstraction. The label, A, indicates a combination of arbitrary amounts of phases R_1 and R_2 . Similarly, the other labels (B-F) are combinations of arbitrary amounts of other phases that result from the chemical reactions. (a) The convex hull construction for consecutive reactions between two reactants, R_1 and R_2 . The points drawn indicate sets of chemical reaction products at different stoichiometric mixtures of the reactants, and the lines trace the convex hull indicating the thermodynamic equilibrium (minimum free energy) for all ratios of mixing, x . (b) A traditional reaction coordinate diagram used to represent both the free energies of reaction, $\Delta\Phi$, and activation energies, E_a . This is generalized by a weighted, directed graph connecting the three states (top). The cost/weight of the directed edges, shown as the colored number adjacent to each edge, is some function of the free energy change, activation energy, and other reaction features. (c) A chemical reaction network, which links together many such possible reaction pathways within a given set of phases.

The generalized graph structure of the solid-state reaction network is illustrated in Figure 3.2 for an arbitrary chemical system. Here, “chemical system” refers to the set of all N phases p_i ($i = 1, 2, \dots, N$) that can be produced from a designated set of chemical elements. Each reactant/product node on the graph is created by considering combinations of distinct

phases up to a maximum size, n . This yields the set of all nodes, P , given by

$$\begin{aligned}
 P = & \{p_i | i \leq N\} \\
 & \cup \{p_i + p_j | i, j \leq N; i \neq j\} \\
 & \cup \dots \\
 & \cup \{p_i + p_j + \dots + p_n | i, j, \dots, n \leq N; i \neq j \neq \dots \neq n\}.
 \end{aligned}
 \tag{3.1}$$

In the graph, each of these phase combinations is added twice: first as a reactants node and again as a products node. While higher values of n enable more complex reactions, in general, it suffices to choose $n = 2$ since truly simultaneous reactions among three or more reactants are less likely due to kinetic and steric constraints in a solid composite.

To create the dense set of directed edges at the center of the network, we algorithmically iterate through every possible chemical reaction between all pairs of reactants and product nodes. Using a reaction balancing algorithm, we then solve for the stoichiometric coefficients and add a weighted, directed edge from the reactant node to the corresponding product node for every chemical reaction that is successfully balanced. Note that a vast majority of generated trial reactions cannot be stoichiometrically balanced and hence are excluded from the graph; for example, there are no x , y , or z that satisfy $x\text{Y}_2\text{O}_3 + y\text{MnO}_2 \longrightarrow z\text{YMnO}_3$, so this reaction edge would not appear in the graph. We also exclude trivial identity-like reactions between identical reactants and products, e.g., $\text{Y}_2\text{O}_3 \longrightarrow \text{Y}_2\text{O}_3$. The weight of the reaction edge is determined by a ‘‘cost function’’ that maps features of the chemical reaction (e.g., $\Delta\Phi_{rxn}$) to a single cost value. To facilitate product phases being capable of reacting again, zero-weight edges are added that connect each product node to all reactant nodes that contain, as a subset, at least one of the product phases and/or starting reactant phases (regardless of consideration of stoichiometric coefficients). This creates a large degree of cycles in the network that enable the network to capture multiple-step reaction pathways.

Finally, two more nodes are added: one for the synthesis precursors and one for the selected target. These two external nodes act as single-source and destination nodes linking into and out of the dense network of reactions, defining a net (overall) synthesis reaction. The precursors node connects into the network via zero-weight edges directed towards all reactants nodes that contain, as a subset, at least one of the precursor phases. The target node is connected via a set of zero-weight edges directed from all product nodes which contain the target phase.

Thermodynamic data

While the chemical reaction network can be created from any thermodynamic data – computed, experimental, or a combination of both – in this work, we primarily employ the Materials Project database, which contains well-benchmarked *ab initio* calculated formation enthalpies for over one hundred thousand different materials as calculated with density functional theory (DFT) [11, 12]. To capture the temperature dependence of vibrational degrees of freedom, we employ the machine-learned Gibbs free energy descriptor reported by Bartel

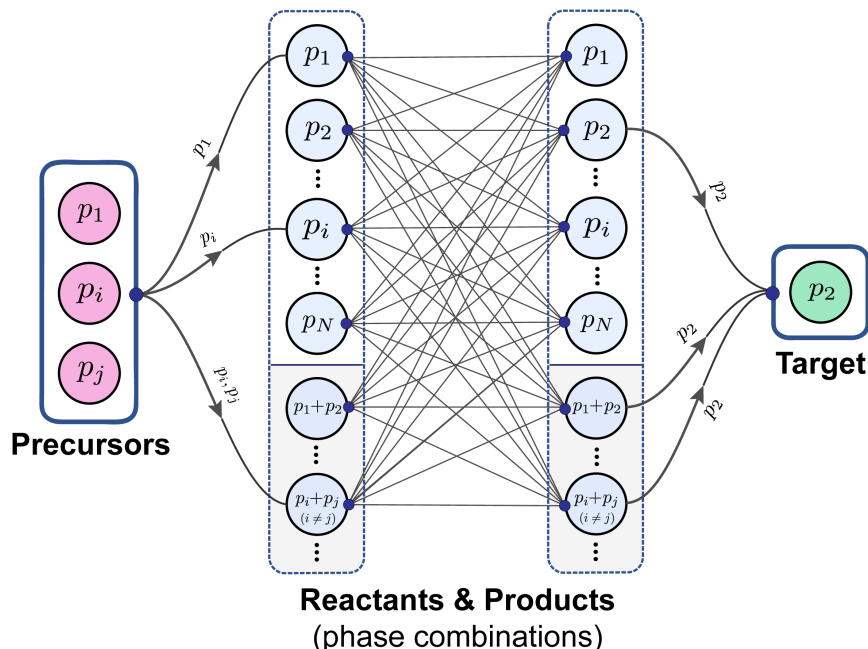


Figure 3.2: Generalized graph architecture of a solid-state chemical reaction network. The reaction network is constructed for a hypothetical chemical system containing N phases p_i ($i = 1, 2, \dots, N$), with nodes made of distinct phase combinations up to maximum size, n . The precursors and target nodes link into and out of the densely connected network of reactions, respectively. The edge directions between the reactant and product nodes have been omitted for clarity; an alternate depiction of the network with edge directions is shown in Figure B.1. These central edges include chemical reactions weighted by their cost value, as well as zero-weight edges which create loops from product nodes back to reactant nodes, so that multiple-step reaction pathways can be captured.

et al. [69] and discussed in Section 2.2, which estimates the finite temperature contribution to the Gibbs free energy of formation of solids, $\Delta G_f(T)$. This contribution incorporates both temperature-dependent enthalpic and entropic effects, although the entropic contribution (TS) typically dominates. The elemental Gibbs free energies used for these formation energy calculations are acquired from FactSage [84]. The Gibbs free energies of formation for non-elemental gases (e.g., CO_2), as well as a small set of solid compounds (A_2O and A_2CO_3 ; $\text{A}=\text{Li}, \text{Na}$) are acquired from NIST-JANAF experimental thermochemical tables [65].

3.2 Cost functions for edge weighting

The cost function determines the weighting of edges in the network, and its mathematical form is critical to the generation of probable reaction pathways. The simplest, and possibly most intuitive, cost function is a one-to-one mapping onto the thermodynamic landscape, such as the measured or calculated Gibbs free energy of reaction, ΔG_{rxn} . However, using unprocessed reaction energies alone poses several problems: 1) negative reaction energies

result in infinite cycles during pathfinding, which precludes the use of Dijkstra’s algorithm and many other pathfinding methods, 2) kinetic effects and other known heuristics about the reaction are necessarily excluded, and 3) reaction costs are affected by stoichiometric scaling. Instead, here we choose a single, positive cost function that maps the Gibbs free energy of reaction, normalized per reactant atom, to a positive value for each reaction. The choice of a functional mapping also provides the opportunity to create different cost functions for chemical reactions where additional information is known, such as experimental data, kinetic factors, and/or other heuristics. One example of a cost function that captures reaction thermodynamics is the *softplus* function, which was originally developed for use as an activation function in neural networks [88]. This function maps the Gibbs free energy of a chemical reaction, ΔG_{rxn} , to a positive cost value, C , via the equation

$$C = \ln\left(1 + \frac{273 \text{ K}}{T} e^{\Delta G_{rxn}}\right), \quad (3.2)$$

where T is the absolute temperature in Kelvin and ΔG_{rxn} is the Gibbs free energy of reaction in units of eV per reactant atom, divided by unity to be dimensionless. Since molar reaction energies scale with the stoichiometric balancing of the reaction, ΔG_{rxn} must be normalized on a per-atom basis independent of the stoichiometric coefficients. The softplus cost function transforms highly exergonic ($\Delta G_{rxn} \ll 0$) reactions into low (near-zero) cost events, whereas endergonic ($\Delta G_{rxn} > 0$) reactions exhibit a finite cost that smoothly approaches a linear scaling as $\Delta G_{rxn} \rightarrow \infty$. Note that different environmental boundary conditions, such as open elements, can be modeled by replacing ΔG_{rxn} with $\Delta \Phi_{rxn}$, where Φ represents a custom thermodynamic potential.

Other monotonically increasing functions, such as those in Figure 3.3, were briefly tested. The Rectified Linear Unit (ReLU) function was not appropriate as it did not discriminate between exergonic reactions, which significantly alters the reaction energy distribution and affects the final ranking of pathways. The piecewise linear function preserved the distribution but requires more unknown parameters, and the discontinuity of the first derivative at zero unnecessarily penalized reactions with marginally positive energies. Hence the softplus function was chosen due to its simplicity, smoothness, and differentiable form.

3.3 Application of graph pathfinding methods

Accommodating parallel pathways

Ideally, predicting a reaction pathway using the network would be fully equivalent to solving the single-source shortest path problem from graph theory using existing algorithms. However, inorganic chemical reactions rarely trace a set of linear steps even in simple syntheses; instead, the precursor phases often undergo reactions concurrently in parallel or react again. Within the network, parallel reactions can be modeled as simultaneous travel along multiple reaction edges. These reactions must obey mass conservation, and phases produced in

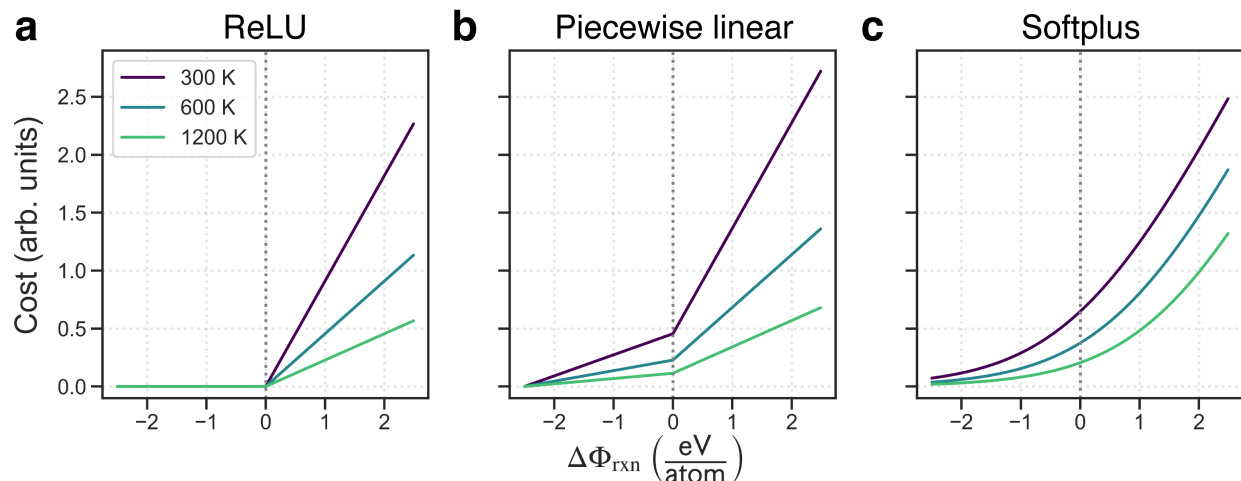


Figure 3.3: Example cost functions. Each cost function is a monotonically increasing function of reaction free energy, $\Delta\Phi_{\text{rxn}}$, and scaled according to temperature, T . The functions include (a) Rectified Linear Unit (ReLU), (b) piecewise linear, and (c) softplus. Each has the result that the thermodynamic free energy of the reaction is rectified to positive values and scaled such that lower reaction temperatures result in higher costs.

one reaction may react with phases in another. These so-called “crossover” reactions, along with the possibility of parallel reactions, prohibit the direct application of shortest path algorithms.

To accommodate parallel paths, we identify not only the single shortest path from precursors to target phase, but a set of k -shortest paths to the target that are present in the network. To computationally generate the k -shortest paths, we utilize Yen’s algorithm [89] which iteratively produces the next $k - 1$ shortest paths via deviations from the first shortest path, as calculated with Dijkstra’s algorithm [90]. The purpose of using Yen’s algorithm is two-fold: 1) to identify a candidate set of reactions that may occur in parallel, and 2) to account for uncertainties in the knowledge of the local synthesis environment, as well as the thermochemistry data used to create the network. For syntheses that involve multiple targets or byproducts (e.g., CO_2), pathfinding is performed towards each target phase separately to ensure that all targets appear in the generated set of shortest paths.

To allow for crossover reactions, we first identify all intermediate phases that appear in the k -shortest paths to each target and then compute all possible reactions between these intermediates that result in the formation of at least one of the targets. These reactions are computed via two approaches: 1) a simple n -combinatorial approach analogous to the one used in the network generation, and 2) a compositional phase diagram approach whereby reaction products are predicted to be the set of phases that yield the minimum thermodynamic potential, Φ_{min} , along a compositional tie-line, as previously developed by Richards et al. [82]. This second approach allows crossover reactions to exceed the constraints of the value of n chosen due to both the inclusion of open elements via a grand potential, as well as the construction of phase diagram simplexes including several product phases in equilibrium.

Since it is recommended to select $n = 2$, this second approach makes it possible to additionally capture the reaction of two solids in a flowing gas (e.g., O_2), which is a commonly encountered experimental scenario in solid-state synthesis.

Combining chemical reactions via mass conservation

When a net reaction is known *a priori*, reaction steps identified during pathfinding can be linearly combined to satisfy the stoichiometric mass constraints of the overall reaction. These constraints correspond to numerically solving the linear system of equations given by

$$A\mathbf{m} = \mathbf{c}, \quad (3.3)$$

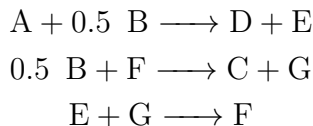
where $\mathbf{m}$ is a vector containing the multiplicity of each reaction (i.e., the factor by which the entire reaction is multiplied), A is the matrix containing the stoichiometric coefficients of all phases present in all reactions where reactants/products have negative/positive coefficients respectively, and $\mathbf{c}$ is a vector containing the stoichiometric coefficients of the net synthesis reaction. We solve this system of equations for the multiplicity vector, $\mathbf{m}$, via application of the Moore-Penrose matrix pseudoinverse as implemented within the SciPy package [91].

The total cost, C_{tot} , for a balanced reaction pathway with l reaction steps is the weighted mean of individual reaction costs, s_i , where the weights are the multiplicities, m_i , for each reaction. The total cost can be calculated as

$$C_{tot} = \frac{\sum_i^l m_i s_i}{\sum_i^l m_i}. \quad (3.4)$$

Identifying interdependent reaction steps

It is often possible to encounter reaction steps in a reaction pathway that are interdependent, which occurs when two or more reactions exclusively share intermediate phases in such a way that no reaction can proceed without the other(s) happening first. To demonstrate this situation, consider a predicted reaction pathway for the hypothetical net reaction $A + B \longrightarrow C + D$:



The net stoichiometry of this pathway indeed balances exactly to $A + B \longrightarrow C + D$, but the second and third reactions are an interdependent pair. In other words, Phase F is a reactant in the second reaction but must be produced by the third reaction, while Phase G is a reactant in the third reaction but must be produced in the second reaction. It is often possible to combine interdependent reactions to form a more simple single reaction; in this case, the second and third reactions are combined as $0.5 B + E \longrightarrow C$.

At the end of the reaction pathway search, we consolidate suggested pathways that contain interdependent reactions. This produces more realistic outputs and tends to greatly reduce the number of predicted pathways.

3.4 Modeling reaction pathways reported in the experimental literature

In the following sections, we apply the reaction network model to solid-state synthesis procedures for YMnO_3 , $\text{Y}_2\text{Mn}_2\text{O}_7$, Fe_2SiS_4 , and $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$. The reaction networks generated for each experimental system are illustrated in Figure 3.4 and constructed primarily using thermochemistry data acquired from the Materials Project (MP) [12]. Via the application of pathfinding algorithms and several post-processing steps, we predict the top-ranked candidate reaction pathways to each of the targets and compare them with previous experimental results. Finally, we apply the network construction to predict synthesis routes towards a novel battery cathode material that has yet to be synthesized, $\text{MgMo}_3(\text{PO}_4)_3\text{O}$, further demonstrating the versatility of the method in advancing inorganic synthesis by design.

Synthesis of YMnO_3 using Li-based assisted metathesis

First, we consider the synthesis of yttrium manganese oxide (YMnO_3) through the solid-state Li-based assisted metathesis reaction first reported by Todd & Neilson [92]. This synthesis route has the advantage of yielding YMnO_3 at temperatures significantly lower than the reaction between binary oxides (500 °C vs. 850 °C), enabling kinetic control and polymorph selectivity. The overall reaction,



proceeds through several steps with distinct intermediate compounds, as determined experimentally through *in situ* temperature-dependent x-ray diffraction performed at a synchrotron beamline [93].

Figure 3.4a shows the chemical reaction network generated for the C-Cl-Li-Mn-O-Y chemical system. The phase diagram for this system includes 853 entries; of these, 53 are predicted by density functional theory (DFT) to be stable at low temperatures. By incorporating vibrational entropic effects through a previously derived machine-learning methodology (see Section 2.2), we find the number of stable species to reduce to 41 at a temperature of 900 K. We include all of these stable entries as well as metastable entries, not including polymorphs, up to a filter of +30 meV/atom above the hull. This cutoff is motivated by DFT calculations and statistics on experimentally available phases [75] showing that – while highly metastable compounds are by no means inaccessible – the distribution of energies above hull for all experimentally synthesized compounds peaks significantly below 30 meV/atom. This process results in a total of 76 phases considered, which yields a reaction network of 5,855 nodes and

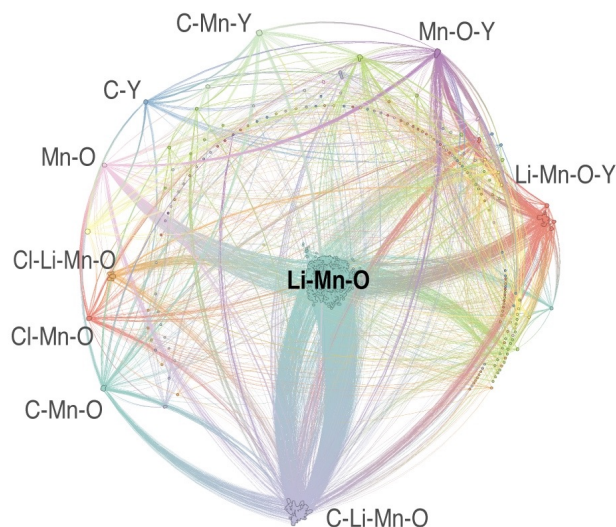
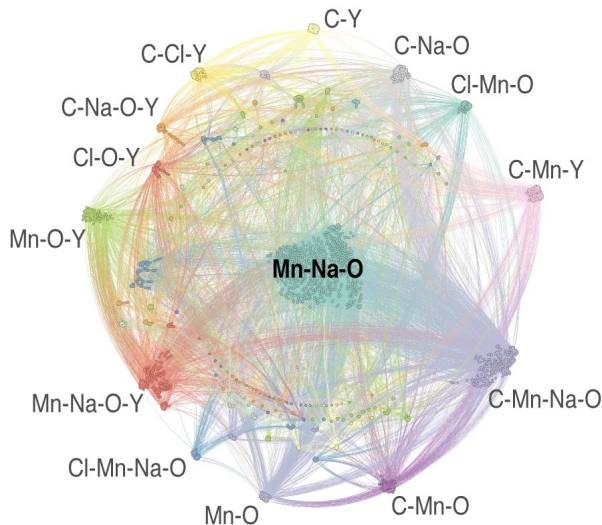
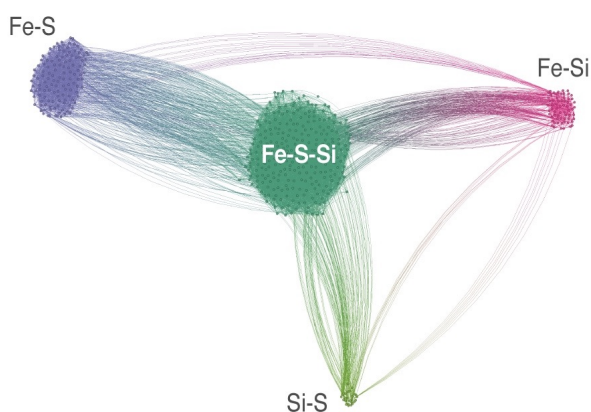
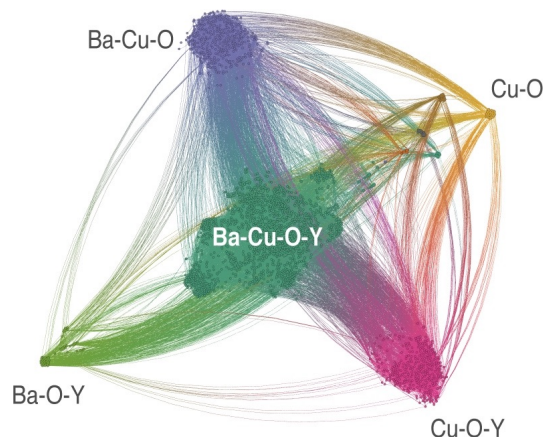
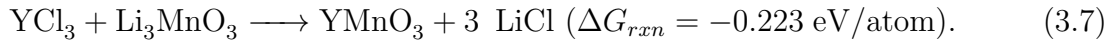
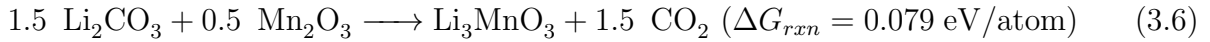
a *C-Cl-Li-Mn-O-Y***b** *C-Cl-Mn-Na-O-Y***c** *Fe-S-Si***d** *Ba-Cu-O-Y*

Figure 3.4: Visualizations of several computed reaction networks. Chemical subsystems are illustrated by color, and prominent subsystems are annotated with labels. Shown are reaction networks for the chemical systems: (a) C-Cl-Li-Mn-O-Y with 5,855 nodes and 121,176 edges, (b) C-Cl-Mn-Na-O-Y with 4,425 nodes and 46,427 edges, (c) Fe-S-Si with 509 nodes and 11,912 edges, and (d) Ba-Cu-O-Y with 2,973 nodes and 33,957 edges.

121,176 edges. Reaction edge costs were calculated using the softplus function applied to reaction free energies normalized by the number of reactant atoms. The 60 shortest paths (20 to each of the products YMnO_3 , LiCl , and CO_2) were identified and crossover reactions were generated considering oxygen as an open element with a chemical potential of $\mu_{\text{O}} = \mu_{\text{O}}^{\text{exp}}(900 \text{ K}, 1 \text{ atm})$ [84]. The final reaction pathways were predicted via this candidate set of reactions by solving for all possible (mass-balanced) linear combinations of reactions up to a maxi-

mum size of five reaction steps. This resulted in 38 pathways, which further reduces to 20 pathways after removing pathways with interdependent reaction steps (see Section 3.3).

Of the 20 remaining total reaction pathways, 11 paths involve reaction steps that produce one or more of the following hypothetical intermediate compounds that, to our best knowledge, have never been experimentally synthesized: Li_3MnO_3 , Li_2MnCO_4 , and Li_2MnCO_5 . Furthermore, each of these phases is predicted to be metastable on the MP database, with energies above the hull of 17, 98, and 35 meV/atom respectively. Interestingly, the lowest cost predicted pathway (before filtering) actually proceeds through the hypothetical Li_3MnO_3 as follows:



This pathway through Li_3MnO_3 , as well as similar ones that rely on the formation of hypothetical compounds, may provide useful insights into understanding the lack of accessibility of certain phases but are deemed less likely to suggest experimentally viable reaction pathways. The five lowest-cost pathways, after removing the pathways which pass through hypothetical intermediates, are summarized in Table 3.1.

Paths 2 and 3 are identical to the experimentally observed low-temperature reaction pathway reported by Todd & Neilson [94], involving the formation and reaction of ternary intermediates $\text{YOCl} + \text{LiMnO}_2 \longrightarrow \text{YMnO}_3 + \text{LiCl}$, with the only difference being that Path 3 first includes the decomposition of Li_2CO_3 to Li_2O before subsequent reaction with YCl_3 . Note that Path 2 includes a reaction with three products (even though the network was restricted to a maximum combination size of $n = 2$) due to the calculation of crossover reactions, which uses the compositional phase diagram to find the most thermodynamically favorable set of products (of any size). Paths 1, 4, and 5 also encompass a plausible reaction pathway and differ primarily in the manner in which Y_2O_3 is formed and subsequently reacted with Mn_2O_3 to produce the final target YMnO_3 . Todd et al. report that the oxidation of $\text{YCl}_3 \longrightarrow \text{YOCl} \longrightarrow \text{Y}_2\text{O}_3$ and reaction of binary oxides $\text{Y}_2\text{O}_3 + \text{Mn}_2\text{O}_3 \longrightarrow 2 \text{YMnO}_3$ is also a plausible reaction pathway that may simultaneously occur, although *ex situ* control reactions showed that it is much slower and only feasible at higher temperatures. While Li_2O (Paths 1, 3-5) and LiYO_2 (Paths 1, 4, 5) were not directly observed in the diffraction results, all of the other intermediate phases suggested by the top predicted paths (YOCl , $\text{Y}_3\text{O}_4\text{Cl}$, Y_2O_3 , LiMnO_2) were indeed observed in experimental data. Hence the reaction network predictions here seem to capture the form of both experimentally observed reaction pathways, suggesting that the model performs quite well with this particular system.

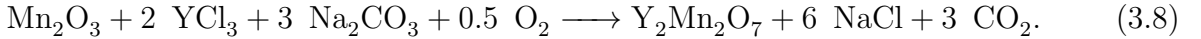
Synthesis of $\text{Y}_2\text{Mn}_2\text{O}_7$ using Na-based assisted metathesis

According to the original report by Todd & Neilson, substituting Na for Li in the aforementioned assisted metathesis synthesis of YMnO_3 changes the main product to the pyrochlore

Path	Total Cost	Reactions	ΔG_{rxn} (eV/atom)	Cost
1	0.246	$0.6667 \text{ Li}_2\text{O} + 0.3333 \text{ YCl}_3 \longrightarrow \text{LiCl} + 0.3333 \text{ LiYO}_2$	-0.260	0.210
		$0.5 \text{ YCl}_3 + 1.5 \text{ LiYO}_2 \longrightarrow \text{Y}_2\text{O}_3 + 1.5 \text{ LiCl}$	-0.164	0.229
		$0.5 \text{ Y}_2\text{O}_3 + 0.5 \text{ Mn}_2\text{O}_3 \longrightarrow \text{YMnO}_3$	-0.048	0.254
		$\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$	0.145	0.300
2	0.249	$\text{Li}_2\text{CO}_3 + \text{YCl}_3 \longrightarrow \text{YOCl} + 2 \text{ LiCl} + \text{CO}_2$	-0.110	0.240
		$\text{YOCl} + \text{LiMnO}_2 \longrightarrow \text{LiCl} + \text{YMnO}_3$	-0.069	0.249
		$\text{Li}_2\text{CO}_3 + \text{Mn}_2\text{O}_3 \longrightarrow \text{CO}_2 + 2 \text{ LiMnO}_2$	0.007	0.266
3	0.254	$\text{Li}_2\text{O} + \text{YCl}_3 \longrightarrow \text{YOCl} + 2 \text{ LiCl}$	-0.281	0.206
		$\text{YOCl} + \text{LiMnO}_2 \longrightarrow \text{LiCl} + \text{YMnO}_3$	-0.069	0.249
		$\text{Li}_2\text{CO}_3 + \text{Mn}_2\text{O}_3 \longrightarrow \text{CO}_2 + 2 \text{ LiMnO}_2$	0.007	0.266
		$\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$	0.145	0.300
4	0.260	$4 \text{ Li}_2\text{O} + 3 \text{ YCl}_3 \longrightarrow \text{Y}_3\text{O}_4\text{Cl} + 8 \text{ LiCl}$	-0.297	0.203
		$0.6667 \text{ Li}_2\text{O} + 0.3333 \text{ YCl}_3 \longrightarrow \text{LiCl} + 0.3333 \text{ LiYO}_2$	-0.260	0.210
		$0.5 \text{ Y}_3\text{O}_4\text{Cl} + 0.5 \text{ LiYO}_2 \longrightarrow \text{Y}_2\text{O}_3 + 0.5 \text{ LiCl}$	-0.057	0.252
		$0.5 \text{ Y}_2\text{O}_3 + 0.5 \text{ Mn}_2\text{O}_3 \longrightarrow \text{YMnO}_3$	-0.048	0.254
		$\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$	0.145	0.300
5	0.267	$3 \text{ Li}_2\text{O} + 2 \text{ YCl}_3 \longrightarrow \text{Y}_2\text{O}_3 + 6 \text{ LiCl}$	-0.306	0.202
		$0.6667 \text{ Li}_2\text{O} + 0.3333 \text{ YCl}_3 \longrightarrow \text{LiCl} + 0.3333 \text{ LiYO}_2$	-0.260	0.210
		$0.5 \text{ YCl}_3 + 1.5 \text{ LiYO}_2 \longrightarrow \text{Y}_2\text{O}_3 + 1.5 \text{ LiCl}$	-0.164	0.229
		$0.5 \text{ Y}_2\text{O}_3 + 0.5 \text{ Mn}_2\text{O}_3 \longrightarrow \text{YMnO}_3$	-0.048	0.254
		$\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$	0.145	0.300

Table 3.1: Top five predicted reaction pathways to YMnO_3 . These are the lowest total cost reaction pathways after filtering for interdependent reaction steps and previously unsynthesized compounds. Paths 2 and 3 match the experimentally reported pathway most closely, however the oxidation of $\text{YCl}_3 \longrightarrow \text{YOCl} \longrightarrow \text{Y}_2\text{O}_3$ and subsequent reaction with Mn_2O_3 in Paths 1, 4, and 5 were experimentally suggested as a possible route, albeit much slower and only kinetically accessible at higher temperatures.

$\text{Y}_2\text{Mn}_2\text{O}_7$ [92], represented by the net reaction:



It was shown via *in situ* x-ray diffraction that, similar to the Li-based reaction, the Na-based reaction pathway similarly depends on the formation of an intermediate alkali manganese oxide phase – in this case Na_xMnO_2 [95]. This reaction is discussed in more depth in Chapter 5. Through a cascade of defect reactions, Na_xMnO_2 reacts with Y_2O_3 , as formed through the previously described oxidation of $\text{YCl}_3 \longrightarrow \text{YOCl} \longrightarrow \text{Y}_2\text{O}_3$.

The reaction network for the C-Cl-Mn-Na-O-Y chemical system was constructed with the same parameters as the Li-based network: a temperature of $T = 900$ K and a 30 meV/atom filter, resulting in 66 entries mapped to 4,425 nodes and 46,427 edges. Figure 3.4b illustrates the network for this system, which is similar in shape to the Li-based system, but with a higher number of prominent chemical subsystems. Pathfinding was also performed with identical parameters as the Li system, including $k = 20$ paths to each target, a maximum reaction combination size of 5, and an open oxygen chemical potential of $\mu_{\text{O}} = \mu_{\text{O}}^{\text{exp}}(900 \text{ K}, 1 \text{ atm})$ [84]. The pathfinding process resulted in 44 potential reaction pathways, 35 of

Path	Total Cost	Reactions	ΔG_{rxn} (eV/atom)	Cost
1	0.238	$\text{Na}_2\text{CO}_3 + \text{YCl}_3 \longrightarrow \text{CO}_2 + \text{YOCl} + 2 \text{NaCl}$	-0.178	0.226
		$0.5 \text{ O}_2 + 2 \text{ YOCl} + 2 \text{ NaMnO}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 2 \text{ NaCl}$	-0.164	0.229
		$\text{Mn}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CO}_2 + 2 \text{ NaMnO}_2$	0.024	0.271
2	0.246	$2.125 \text{ O}_2 + 0.1667 \text{ YMn}_{12} + 0.9167 \text{ Y}_2\text{O}_3 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7$	-0.926	0.113
		$0.5 \text{ O}_2 + \text{Na}_4\text{Mn}_2\text{O}_5 + 4 \text{ YOCl} \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + \text{Y}_2\text{O}_3 + 4 \text{ NaCl}$	-0.222	0.217
		$\text{Na}_2\text{CO}_3 + \text{YCl}_3 \longrightarrow \text{CO}_2 + \text{YOCl} + 2\text{NaCl}$	-0.178	0.226
		$0.5 \text{ Mn}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CO}_2 + 0.5 \text{ Na}_4\text{Mn}_2\text{O}_5$	0.120	0.294
		$1.308 \text{ Mn}_2\text{O}_3 + 1.026 \text{ Y}_2\text{O}_3 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 0.05128 \text{ YMn}_{12}$	0.144	0.300
3	0.246	$0.5 \text{ O}_2 + \text{Na}_4\text{Mn}_2\text{O}_5 + 4 \text{ YOCl} \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + \text{Y}_2\text{O}_3 + 4 \text{ NaCl}$	-0.222	0.217
		$\text{Na}_2\text{CO}_3 + \text{YCl}_3 \longrightarrow \text{CO}_2 + \text{YOCl} + 2 \text{ NaCl}$	-0.178	0.226
		$2 \text{ MnO}_2 + \text{Y}_2\text{O}_3 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7$	-0.070	0.249
		$0.25 \text{ O}_2 + 0.5 \text{ Mn}_2\text{O}_3 \longrightarrow \text{MnO}_2$	-0.058	0.252
		$0.5 \text{ Mn}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CO}_2 + 0.5 \text{ Na}_4\text{Mn}_2\text{O}_5$	0.120	0.294
4	0.248	$4 \text{ Na}_2\text{CO}_3 + \text{YCl}_3 \longrightarrow \text{Na}_5\text{Y}(\text{CO}_3)_4 + 3 \text{ NaCl}$	-0.193	0.223
		$0.5 \text{ O}_2 + 2 \text{ YOCl} + 2 \text{ NaMnO}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 2 \text{ NaCl}$	-0.164	0.229
		$0.25 \text{ Na}_5\text{Y}(\text{CO}_3)_4 + 0.75 \text{ YCl}_3 \longrightarrow \text{CO}_2 + \text{YOCl} + 1.25 \text{ NaCl}$	-0.050	0.254
		$\text{Mn}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CO}_2 + 2 \text{ NaMnO}_2$	0.024	0.271
11	0.259	$\text{Na}_2\text{O} + \text{YCl}_3 \longrightarrow \text{YOCl} + 2 \text{ NaCl}$	-0.535	0.164
		$2 \text{ YOCl} + \text{Na}_2\text{O} \longrightarrow \text{Y}_2\text{O}_3 + 2 \text{ NaCl}$	-0.339	0.196
		$2 \text{ MnO}_2 + \text{Y}_2\text{O}_3 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7$	-0.070	0.249
		$0.25 \text{ O}_2 + 0.5 \text{ Mn}_2\text{O}_3 \longrightarrow \text{MnO}_2$	-0.058	0.252
		$\text{Na}_2\text{CO}_3 \longrightarrow \text{CO}_2 + \text{Na}_2\text{O}$	0.328	0.351

Table 3.2: Selection of top predicted reaction pathways to $\text{Y}_2\text{Mn}_2\text{O}_7$. The complex defect cascade observed in the experiment is not directly present in the predicted pathways, although the reaction of $2\text{MnO}_2 + \text{Y}_2\text{O}_3 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7$ present in Paths 3 and 11 represents the net effect of the defect cascade reaction, and Path 11 is overall the closest to the experimentally observed pathway.

which do not contain interdependent reaction steps, and 24 of which further do not contain any reaction steps with the hypothetical phases Na_3MnO_3 , $\text{Mn}_8\text{Cl}_3\text{O}_{10}$, and Na_2MnO_3 . A selection of the top predicted pathways is shown in Table 3.2.

The top predicted pathway (Path 1) is directly analogous to the observed kinetically favorable pathway in the Li-based synthesis, although this was not observed experimentally for the Na-based synthesis. Instead, Paths 3 and 11, which contain the final reaction step $2\text{MnO}_2 + \text{Y}_2\text{O}_3 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7$, more closely resemble the experimentally observed pathway, which involves a cascade of defect reactions where MnO_2 sub-units (anchored within Na_xMnO_2) react with Y_2O_3 , resulting in a steady increase of the effective Na concentration, x , as $\text{Y}_2\text{Mn}_2\text{O}_7$ forms.

Interestingly, $\text{Na}_4\text{Mn}_2\text{O}_5$, $\text{Na}_5\text{Y}(\text{CO}_3)_4$, and YMn_{12} appear as intermediate phases in several of the top predicted pathways but were not observed experimentally. While each of these phases is experimentally synthesizable and predicted by DFT as stable, their synthesis in the literature is reportedly difficult and involves long heating times [96], hydrothermal methods [97], or the use of a levitation furnace [98], respectively. Hence these phases may be kinetically inaccessible using ceramic methods, including the assisted metathesis synthesis method discussed here.

Synthesis of Fe_2SiS_4 using iron silicide precursors

Jiang et al. previously showed that Fe_2SiS_4 can be synthesized at significantly lower temperatures by avoiding the kinetically limiting steps encountered when using elemental Fe and Si precursors [21]. They showed that pre-reacting iron with silicon to create iron silicide precursors greatly expedited the formation of Fe_2SiS_4 at temperatures as low as 550 °C, via the net reaction,



The reaction network for the Fe-S-Si chemical system was constructed at a temperature of $T = 900$ K with a much less stringent energy above hull filter of 0.5 eV/atom. This higher energy cutoff was chosen due to the relatively small size of the chemical system (3 elements), which allowed for consideration of a wider range of metastability. The constructed network includes 22 entries mapped to 509 nodes and 11,912 edges and its illustration is shown in Figure 3.4c. Since there is only one target in the net reaction (Fe_2SiS_4), higher cutoffs were also chosen for the pathfinding process: $k = 75$ shortest paths and a maximum reaction combination size of 6. The pathfinding process resulted in 340 suggested reaction pathways. However, as before, we demote pathways that include hypothetical compounds or compounds that only exist under conditions far from those considered here. While silicon monosulfide (SiS) has been experimentally synthesized, it primarily appears as a molecular gas and only exists naturally under astrophysical conditions, such as in massive star-forming [99]. Additionally, the SiS_4 structure was experimentally reported [100] as a delithiated version of Li_4SiS_4 , but does not appear to have been synthesized on its own. Excluding these two compounds, as well as interdependent reactions steps, yields 49 possible pathways. A selection of the top predicted pathways after filtering is shown in Table 3.3.

The predicted pathways for this synthesis capture many of the intermediates that were experimentally observed. In the experiment, Jiang et al. observed the initial production of FeS_2 , which was quickly consumed to yield FeSi , Fe_{1-x}S , and SiS_2 ; the reaction of these phases yields the target Fe_2SiS_4 , but not all intermediates were fully consumed in the process. Nearly every predicted path successfully identifies the experimentally observed reaction between SiS_2 and FeS , but only 4 of the 49 paths also include the formation of FeS_2 and FeSi with this final step. Path 14 is the lowest cost of such paths and involves elemental Si as an additional intermediate phase that reacts with FeS_2 . While Path 14 is the closest to the experimentally observed pathway, it differs slightly in two regards. In the predicted pathway, FeS_2 is consumed by reaction with elemental Si to produce Fe_2SiS_4 , and SiS_2 is formed from sulfidation of FeSi . In the experiment, FeSi actually appears after SiS_2 is formed, suggesting that there is a more complicated missing step (or several steps) involving the reaction of FeS_2 with precursors to form a mixture of Fe_{1-x}S , FeSi , and SiS_2 intermediates.

Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (YBCO) using barium peroxide

Miura et al. recently investigated a significant improvement in the solid-state powder synthesis of the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (YBCO) by substituting barium carbonate, BaCO_3 ,

Path	Total Cost	Reactions	ΔG_{rxn} (eV/atom)	Cost
1	0.177	$0.6667 \text{ FeSi}_2 + 3.333 \text{ S} \longrightarrow \text{SiS}_2 + 0.3333 \text{ Fe}_2\text{SiS}_4$	-0.787	0.129
		$5 \text{ S} + \text{Fe}_3\text{Si} \longrightarrow \text{Fe}_2\text{SiS}_4 + \text{FeS}$	-0.586	0.156
		$0.4286 \text{ Fe}_5\text{Si}_3 + 4 \text{ S} \longrightarrow \text{Fe}_2\text{SiS}_4 + 0.1429 \text{ FeSi}_2$	-0.543	0.162
		$\text{SiS}_2 + 2 \text{ FeS} \longrightarrow \text{Fe}_2\text{SiS}_4$	0.270	0.335
2	0.177	$0.6667 \text{ FeSi}_2 + 3.333 \text{ S} \longrightarrow \text{SiS}_2 + 0.3333 \text{ Fe}_2\text{SiS}_4$	-0.787	0.129
		$5 \text{ S} + \text{Fe}_3\text{Si} \longrightarrow \text{Fe}_2\text{SiS}_4 + \text{FeS}$	-0.586	0.156
		$\text{S} + 0.4 \text{ Fe}_3\text{Si} \longrightarrow \text{FeS} + 0.2 \text{ FeSi}_2$	-0.545	0.162
		$0.4286 \text{ Fe}_5\text{Si}_3 + 4 \text{ S} \longrightarrow \text{Fe}_2\text{SiS}_4 + 0.1429 \text{ FeSi}_2$	-0.543	0.162
		$\text{SiS}_2 + 2 \text{ FeS} \longrightarrow \text{Fe}_2\text{SiS}_4$	0.270	0.335
3	0.179	$0.6667 \text{ FeSi}_2 + 3.333 \text{ S} \longrightarrow \text{SiS}_2 + 0.3333 \text{ Fe}_2\text{SiS}_4$	-0.787	0.129
		$2 \text{ FeSi} + 6 \text{ S} \longrightarrow \text{SiS}_2 + \text{Fe}_2\text{SiS}_4$	-0.632	0.149
		$5 \text{ S} + \text{Fe}_3\text{Si} \longrightarrow \text{Fe}_2\text{SiS}_4 + \text{FeS}$	-0.586	0.156
		$0.4286 \text{ Fe}_5\text{Si}_3 + 4 \text{ S} \longrightarrow \text{Fe}_2\text{SiS}_4 + 0.1429 \text{ FeSi}_2$	-0.543	0.162
		$\text{S} + 0.5 \text{ Fe}_3\text{Si} \longrightarrow \text{FeS} + 0.5 \text{ FeSi}$	-0.509	0.167
		$\text{SiS}_2 + 2 \text{ FeS} \longrightarrow \text{Fe}_2\text{SiS}_4$	0.270	0.335
4	0.180	$0.6667 \text{ FeSi}_2 + 3.333 \text{ S} \longrightarrow \text{SiS}_2 + 0.3333 \text{ Fe}_2\text{SiS}_4$	-0.787	0.129
		$2 \text{ FeSi} + 6 \text{ S} \longrightarrow \text{SiS}_2 + \text{Fe}_2\text{SiS}_4$	-0.632	0.149
		$5 \text{ S} + \text{Fe}_3\text{Si} \longrightarrow \text{Fe}_2\text{SiS}_4 + \text{FeS}$	-0.586	0.156
		$0.4286 \text{ Fe}_5\text{Si}_3 + 4 \text{ S} \longrightarrow \text{Fe}_2\text{SiS}_4 + 0.1429 \text{ FeSi}_2$	-0.543	0.162
		$0.5 \text{ Fe}_5\text{Si}_3 + 4 \text{ S} \longrightarrow \text{Fe}_2\text{SiS}_4 + 0.5 \text{ FeSi}$	-0.521	0.166
		$\text{SiS}_2 + 2 \text{ FeS} \longrightarrow \text{Fe}_2\text{SiS}_4$	0.270	0.335
14	0.189	$2 \text{ S} + 0.5 \text{ Fe}_3\text{Si} \longrightarrow \text{FeS}_2 + 0.5 \text{ FeSi}$	-0.635	0.149
		$2 \text{ FeSi} + 6 \text{ S} \longrightarrow \text{SiS}_2 + \text{Fe}_2\text{SiS}_4$	-0.632	0.149
		$5 \text{ S} + \text{Fe}_3\text{Si} \longrightarrow \text{Fe}_2\text{SiS}_4 + \text{FeS}$	-0.586	0.156
		$2 \text{ Fe}_5\text{Si}_3 + 20 \text{ S} \longrightarrow \text{Si} + 5 \text{ Fe}_2\text{SiS}_4$	-0.541	0.163
		$\text{Si} + 2 \text{ FeS}_2 \longrightarrow \text{Fe}_2\text{SiS}_4$	0.055	0.278
		$\text{SiS}_2 + 2 \text{ FeS} \longrightarrow \text{Fe}_2\text{SiS}_4$	0.270	0.335

Table 3.3: Selection of top predicted reaction pathways to Fe_2SiS_4 . Each pathway successfully includes the experimentally observed reaction between intermediates SiS_2 and FeS . The observed FeSi intermediate only appears together with the other two intermediates in 4 of the 49 predicted paths. Path 14 is the lowest cost path which captures all experimentally observed intermediate phases.

Path	Total Cost	Reactions	ΔG_{rxn} (eV/atom)	Cost
1	0.180	$\text{BaO}_2 + \text{CuO} \longrightarrow \text{BaCuO}_2 + 0.5 \text{ O}_2$	-0.160	0.177
		$\text{Y}_2\text{Ba}_4\text{O}_7 + 6 \text{ CuO} \longrightarrow \text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.137	0.181
		$3 \text{ Y}_2\text{O}_3 + 12 \text{ BaCuO}_2 \longrightarrow \text{Y}_2\text{Ba}_4\text{O}_7 + 2 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	0.039	0.212
2	0.182	$2 \text{ BaO}_2 + 2 \text{ CuO} \longrightarrow \text{Ba}_2\text{Cu}_2\text{O}_5 + 0.5 \text{ O}_2$	-0.225	0.167
		$\text{BaO}_2 + \text{CuO} \longrightarrow \text{BaCuO}_2 + 0.5 \text{ O}_2$	-0.160	0.177
		$0.8 \text{ Y}_4\text{Ba}_3\text{O}_9 + 5.6 \text{ CuO} \longrightarrow \text{Y}_2\text{Cu}_2\text{O}_5 + 0.6 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.053	0.195
		$3.5 \text{ Y}_2\text{O}_3 + 9 \text{ BaCuO}_2 \longrightarrow \text{Y}_4\text{Ba}_3\text{O}_9 + 1.5 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	0.014	0.208
		$2 \text{ Ba}_2\text{Cu}_2\text{O}_5 + \text{Y}_2\text{Cu}_2\text{O}_5 \longrightarrow \text{O}_2 + \text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	0.039	0.212
3	0.182	$\text{BaO}_2 + \text{CuO} \longrightarrow \text{BaCuO}_2 + 0.5 \text{ O}_2$	-0.160	0.177
		$0.8 \text{ Y}_4\text{Ba}_3\text{O}_9 + 5.6 \text{ CuO} \longrightarrow \text{Y}_2\text{Cu}_2\text{O}_5 + 0.6 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.053	0.195
		$\text{Y}_2\text{Cu}_2\text{O}_5 + 4 \text{ BaCuO}_2 \longrightarrow \text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.010	0.203
		$3.5 \text{ Y}_2\text{O}_3 + 9 \text{ BaCuO}_2 \longrightarrow \text{Y}_4\text{Ba}_3\text{O}_9 + 1.5 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	0.014	0.208
4	0.185	$\text{BaO}_2 + \text{CuO} \longrightarrow \text{BaCuO}_2 + 0.5 \text{ O}_2$	-0.160	0.177
		$0.8 \text{ Y}_4\text{Ba}_3\text{O}_9 + 5.6 \text{ CuO} \longrightarrow \text{Y}_2\text{Cu}_2\text{O}_5 + 0.6 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.053	0.195
		$\text{Y}_2\text{Cu}_2\text{O}_5 + 4 \text{ BaCuO}_2 \longrightarrow \text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.010	0.203
		$2.25 \text{ Ba}_2\text{CuO}_3 + 2.375 \text{ Y}_2\text{O}_3 \longrightarrow \text{Y}_4\text{Ba}_3\text{O}_9 + 0.375 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.007	0.204
		$0.5 \text{ Y}_2\text{O}_3 + 4 \text{ BaCuO}_2 \longrightarrow \text{Ba}_2\text{CuO}_3 + 0.5 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	0.022	0.209
10	0.190	$4 \text{ BaO}_2 + 6 \text{ CuO} \longrightarrow \text{O}_2 + 2 \text{ Ba}_2\text{Cu}_3\text{O}_6$	-0.231	0.166
		$\text{BaO}_2 + \text{CuO} \longrightarrow \text{BaCuO}_2 + 0.5 \text{ O}_2$	-0.160	0.177
		$\text{Y}_2\text{Ba}_4\text{O}_7 + 6 \text{ CuO} \longrightarrow \text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	-0.137	0.181
		$3 \text{ Y}_2\text{O}_3 + 12 \text{ BaCuO}_2 \longrightarrow \text{Y}_2\text{Ba}_4\text{O}_7 + 2 \text{ Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	0.039	0.212
		$\text{Y}_2\text{O}_3 + 2 \text{ Ba}_2\text{Cu}_3\text{O}_6 \longrightarrow \text{O}_2 + \text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$	0.075	0.219

Table 3.4: Selection of top predicted reaction pathways to $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (shown here as $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$). Seven of the top ten pathways capture the BaCuO_2 intermediate, but $\text{Ba}_2\text{Cu}_3\text{O}_6$ only appears in Path 10 and beyond. Path 10 represents the closest match to the experimentally observed pathway, in which the predicted $\text{Y}_2\text{Ba}_4\text{O}_7$ composition appears to facilitate representation of the observed reaction of Y_2O_3 with Ba-Cu-O melt, which cannot be captured by the reaction network model.

with barium peroxide, BaO_2 , resulting in the following net reaction [19],



The reaction network for the Ba-Cu-O-Y chemical system was constructed using a temperature of $T = 1200$ K and 0.1 eV/atom filter. We again selected a less restrictive energy cutoff due to the smaller size of the system, resulting in a network of 54 entries mapped to 2,973 nodes and 33,957 edges. The network is illustrated in Figure 3.4d. Similar to the assisted metathesis systems, the pathfinding was conducted with $k = 20$ paths to each target, a maximum reaction combination size of 5, and an open oxygen chemical potential of $\mu_{\text{O}} = \mu_{\text{O}}^{\text{exp}}(1200 \text{ K}, 1 \text{ atm})$ [84]. The pathfinding process yielded 52 potential reaction pathways, 22 of which do not contain interdependent reaction steps or reaction steps with the hypothetical phases Cu_8O_7 , $\text{Ba}_8\text{Cu}_8\text{O}_{19}$, and $\text{Y}_2\text{Ba}_3\text{O}_6$. A selection of the top predicted pathways is shown in Table 3.4.

The predicted reaction pathways to YBCO capture many key aspects of the experimentally observed reaction pathway, but with some slight differences that can be attributed to the inability of the network to capture thermal decomposition/melting. In the experimental pathway, Miura et al. observed that $\text{Ba}_2\text{Cu}_3\text{O}_6$ was the first intermediate phase to form due to its high thermodynamic driving force reacting from the $\text{BaO}_2|\text{CuO}_2$ interface,

followed by peritectic decomposition of $\text{Ba}_2\text{Cu}_3\text{O}_6$ into BaCuO_2 , subsequent eutectic melting of the $\text{BaCuO}_2|\text{CuO}$ interface, and finally rapid reaction of the Ba-Cu-O melt to form oxygen-deficient YBCO with a final O_2 uptake step. In the predicted pathways, we see the formation of BaCuO_2 in 7 of the top 10 predicted paths, although $\text{Ba}_2\text{Cu}_3\text{O}_6$ only appears as an intermediate phase beginning with Path 10. Path 10 is the closest to the experimentally observed pathway, passing through both $\text{Ba}_2\text{Cu}_3\text{O}_6$ and BaCuO_2 intermediate phases. However, similar to Paths 1-4, the formation of YBCO from BaCuO_2 involves the formation of a Y-Ba-O phase ($\text{Y}_2\text{Ba}_4\text{O}_7$ or $\text{Y}_4\text{Ba}_3\text{O}_9$) to balance the reaction; in each case, this intermediate is consumed by CuO to yield more of the YBCO product. Hence the Y-Ba-O intermediate effectively serves as an intermediate composition that allows the network to capture a more complex reaction appearing to involve three components, i.e., the reaction of Y_2O_3 with a eutectic mixture of BaCuO_2 -CuO. So while the Y-Ba-O intermediates were not observed in the experiment, their presence in the predicted pathways clearly serves as a convenient mechanism for splitting the $\text{Y}_2\text{O}_3|\text{Ba-Cu-O(liquid)}$ reaction into two smaller steps that can be captured by the network. Interestingly, two other routes to form YBCO also appear in Paths 2-4, involving the reaction of $\text{Ba}_2\text{Cu}_2\text{O}_5$ (or BaCuO_2) with $\text{Y}_2\text{Cu}_2\text{O}_5$ to yield YBCO directly. These may serve as alternative routes towards YBCO, which should be explored in future studies.

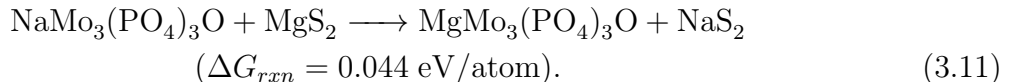
3.5 Design of synthesis route for novel Mg-ion battery cathode $\text{MgMo}_3(\text{PO}_4)_3\text{O}$

Finally, we apply the same reaction network code to demonstrate a different use case: designing synthesis routes to a desired target material. Previously, Rong et al. identified a novel Mg battery cathode material, $\text{MgMo}_3(\text{PO}_4)_3\text{O}$, which was predicted by DFT calculations to possess an unprecedented, fast Mg^{2+} mobility in the dilute Mg concentration limit [101]. To our best knowledge, since the publishing of their report in 2017, no experimental studies on the synthesis of $\text{MgMo}_3(\text{PO}_4)_3\text{O}$ have been published. According to MP, this material is metastable with a significantly large energy above hull of 0.103 eV/atom. Since approximately 20% of all known oxides exhibit an energy above hull higher than 100 meV/atom, [75] this metric does not directly imply that $\text{MgMo}_3(\text{PO}_4)_3\text{O}$ is impossible to synthesize, but an energy above hull of this magnitude is typically a sign that the material is at least challenging to synthesize.

To assist in the development of solid-state synthesis routes, we search for possible reactions within a very large reaction network encompassing both the Mg-Mo-P-O system and 39 additional elements that frequently appear in solid-state syntheses, including nearly all the major anions, alkali and alkaline earth cations, and several transition metals. The total chemical system includes 43 elements: Ag, Al, B, Ba, Be, Bi, Br, C, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, F, Fe, I, K, La, Li, Mg, Mn, Mo, N, Na, Ni, O, P, Pb, Rb, S, Sc, Se, Si, Sr, Te, Ti, V, Y, Zn, and Zr. We calculated the thermodynamic stability of all phases in this system

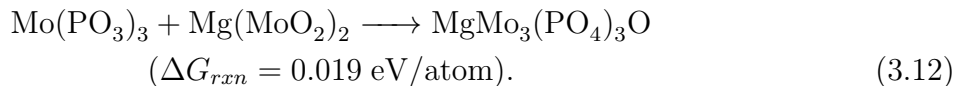
at $T = 800$ K (a relatively low synthesis temperature) and used an energy above hull filter of 0.11 eV/atom, as this cutoff is just large enough to include the target phase. The final reaction network, which includes only reaction edges that can be successfully balanced to form the target phase, contains 21,564 entries mapped to 660,909 nodes and 663,176 edges. We found a total of 2,270 unique reactions yielding $\text{MgMo}_3(\text{PO}_4)_3\text{O}$ as a product.

The full list of 2,270 discovered reactions includes many reactions that would be challenging to achieve in an experiment for reasons other than the metastability of the target phase, such as reactions that also yield side products that are metastable or highly reactive (e.g., Li metal). One method for distilling down the list of candidate reactions is to use a “metathesis-like” approach and search for reactions that involve the formation of a byproduct that does not include any of the elements in the target, i.e., a second product that does not contain Mg, Mo, P, or O. This is a similar principle as that of metathesis reactions in the sense that it includes the formation of an easily separable compound or highly stable phase which acts as a thermodynamic “sink” that may increase the driving force of the reaction. Filtering by this constraint reduces the list of candidate reactions down to a more manageable set of 186. Interestingly, nearly every reaction in this candidate set has a similar form: ion exchange from a closely related phase, such as $\text{NaMo}_3\text{P}_3\text{O}_{13}$, $\text{MgFe}_3\text{P}_3\text{O}_{13}$, or $\text{MgV}_3\text{P}_3\text{O}_{13}$, as demonstrated by the example:



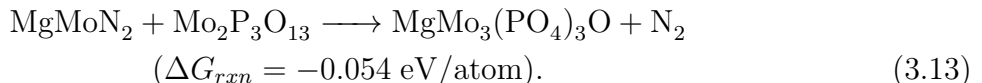
While this reaction may be feasible, it still requires first developing a synthesis route to make the $\text{NaMo}_3(\text{PO}_4)_3\text{O}$ precursor, which is also significantly metastable and not known to be experimentally synthesizable.

Besides ion exchange routes, there are only two other reactions that emerge. The first is direct formation of $\text{MgMo}_3(\text{PO}_4)_3\text{O}$ (with no byproduct) from simple ternary phases:



While both of these reactants are predicted to be stable by DFT, $\text{Mg}(\text{MoO}_2)_2$ does not appear to have been previously synthesized in the literature. Assuming this phase is synthesizable (which is likely considering its predicted stability), it is still possible that this reaction might not be spontaneous due to its predicted positive ΔG_{rxn} . However the small magnitude of this reaction energy is close enough to zero that it may truly be negative, considering both the uncertainties of DFT and the applied Gibbs free energy descriptor.

Finally, the second reaction is an interesting pathway using the ternary nitride, MgMoN_2 , and $\text{Mo}_2\text{P}_3\text{O}_{13}$:



Both precursors of this reaction are predicted to be stable via DFT calculations on the MP database, but we could not find any literature discussing the synthesis of $\text{Mo}_2\text{P}_3\text{O}_{13}$. MgMoN_2 , on the other hand, has been reported to be synthesized via solid-state reaction [102]. This reaction between ternary nitrides may be a promising synthesis route to $\text{MgMo}_3(\text{PO}_4)_3\text{O}$, assuming that $\text{Mo}_2\text{P}_3\text{O}_{13}$ can first be synthesized – which is a strong possibility given its predicted stability in DFT calculations.

3.6 Ranking candidate pathways

The cost function approach that is central to our model is a necessary transformation for applying pathfinding methods that not only allows for the combination of various reaction metrics (e.g., ΔG_{rxn} , E_a), but also serves as a particularly powerful way to navigate uncertainties in thermochemistry data. By transforming reaction free energies to positive costs, we no longer restrict possible reactions to only those with negative free energies (Figure 3.5). This seems to be a crucial reason for the model’s success since reaction steps that occur experimentally are not always predicted to be thermodynamically favorable using computed – or even experimental – data. For example, the well-studied thermal decomposition of $\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$, which appears frequently throughout Table 3.1, is highly endergonic ($\Delta G_{\text{rxn}} > 0$) when modeled with MP data (+0.333 eV/atom at $T = 0$ K). This is somewhat expected, as MP often reports much more negative formation energies for carbonate compounds due to the elemental energy corrections used, which are not always applicable to polyatomic ions. However, this reaction is still highly endergonic using NIST-JANAF experimental data (+0.145 eV/atom at $T = 900$ K), even though the decomposition of lithium carbonate has been observed to occur spontaneously just above temperatures in this range ($T \sim 900$ K) [103]. We hypothesize that the specific local environment conditions during synthesis, which can differ from the average or global conditions, play a major role in governing the extent of decomposition. Hence it is desirable to retain some degree of flexibility in deciding what is thermodynamically feasible.

It is worth noting that the final ranking of the candidate set of predicted reaction pathways is very sensitive to the choice and form of the cost function. Here, we apply the softplus function to approximate reaction Gibbs free energies derived via a machine-learned model of the vibrational energy that does not explicitly include configurational degrees of freedom. Indeed, in the examples presented, it is not always the lowest total cost path that corresponds to the experimentally observed reaction sequence. The set of suggested pathways also typically includes one or more predictions that are very close to the observed pathways. Since the differences between the highest-ranked (lowest-cost) pathways are small, we strongly recommend users of the model consider several highly ranked pathways. The candidate sets are limited enough in size (often fewer than 100 paths) such that they can be manually inspected by the user.

3.7 Challenges with the model

Combinatorial expansion

The primary challenge that is addressed by our work is the high degree of complexity inherent to thermodynamic phase space, which ordinarily leads to combinatorial explosion during both the creation of the network and subsequent pathfinding steps. For example, consider a reaction network with N phases and a maximum phase combination size, n . If, during the graph generation, every possible chemical reaction between any two nodes is considered, the number of reactions calculated, R , would be

$$R = \left[\sum_{i=1}^n \binom{N}{i} \right]^2 = \left[\binom{N}{1} + \binom{N}{2} + \dots + \binom{N}{n} \right]^2. \quad (3.14)$$

In the C-Cl-Li-Mn-O-Y reaction network shown in Figure 3.4a, which contains $N = 76$ distinct phases, the maximum number of possible reactions described by equation (3.14) is $R \approx 5.78 \times 10^3$ ($n = 1$), 8.56×10^6 ($n = 2$), and 5.36×10^9 ($n = 3$). This equation scales quickly as constraints are relaxed, often leading to the consideration of millions – or even billions – of possible reactions.

Our implementation reduces the complexity and degrees of freedom of the phase space by introducing a series of filters, including 1) restricting the number of phases considered via thermodynamic stability arguments (energy above the hull), 2) limiting the maximum number of phases present on each side of the reaction to a small number ($n = 2$), 3) using a cost function to prioritize reactions which are more likely to occur, 4) enforcing mass conservation via stoichiometric constraints, and 5) removing interdependent reaction steps. The first two filters work together during graph generation to limit the combinatorial size/complexity of the network. This number can be reduced by decreasing either N , n , or both. Since it is typically optimal to consider as many phases as possible, and because we see that the complexity scales especially quickly with increasing n , it is more favorable to maintain a large N and enforce a constraint of $n = 2$. This choice greatly minimizes the combinatorics of the network but does not inherently sacrifice the complexity of reaction pathways that can occur. In fact, the choice of $n = 2$ may more realistically capture the behavior of reacting solids by dividing reaction pathways into pseudo-elementary steps that more closely follow the free energy surface. This decision is further justified by recent work suggesting that the most thermodynamically favorable pairwise reactions direct the reaction pathway in typical solid-state synthesis procedures [19].

Incorporating kinetics into the cost function

Addressing the combinatorial challenges associated with reaction pathway prediction in large chemical spaces can result in approximations of complex behavior that do not always capture specifics. This complex behavior includes: 1) changes in reaction kinetics due to melting, 2)

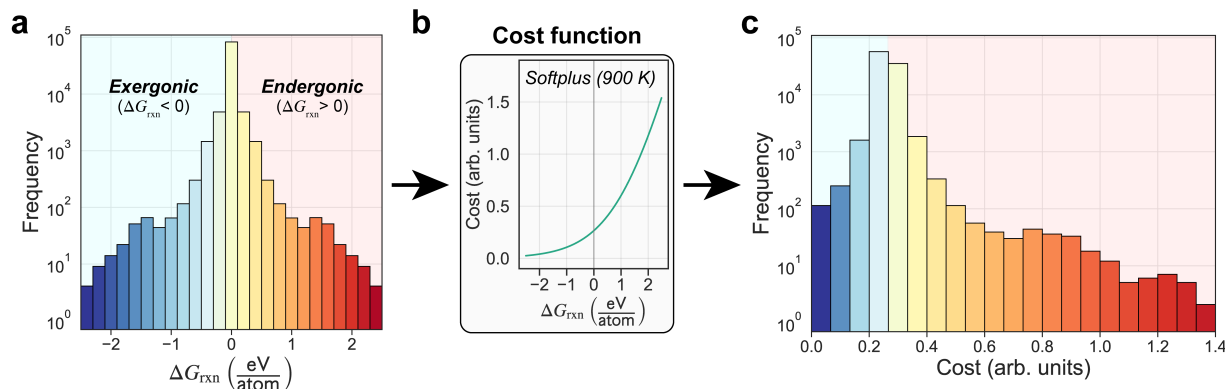


Figure 3.5: Effect of the cost function transformation on reaction energies. (a) Distribution of reaction Gibbs free energies (normalized per reactant atom) in the C-Cl-Li-Mn-O-Y chemical system. (b) The softplus cost function, described in Equation (3.2), which is used to monotonically transform reaction energies. (c) Final distribution of reaction costs (in arbitrary units) after transformation. A reaction free energy of zero corresponds to a cost of ~ 0.265 .

amorphous intermediates, and 3) defect reactions involving non-stoichiometric compounds. Each of these challenges massively expands the configurational degrees of freedom and necessitates the collection of significantly more thermodynamic data. However, a complete predictive understanding of solid-state synthesis can not be attained without first developing models that incorporate these effects. In future investigations, we expect to address some aspects of these challenges, for example, by including kinetic features leading to more complex reaction pathway selection. While we did not include any kinetic features in this work, we anticipate that several metrics from recent data-oriented studies in chemistry and materials science may be included as extra parameters in the cost function. Such parameters may include the structural (dis)similarity between phases [104, 105], the average number of bonds broken/created in a reaction, the change in the information entropy description of atomic configurations, the change in atomic density, etc. The exact weighting of these parameters within the cost function model is unknown as of now, however, and would best be investigated via high-throughput, automated experiments and detailed studies that systematically probe the impact of precursor composition/morphology, reaction conditions, etc., on the resulting reaction pathways.

Chapter 4

Defect-driven thermodynamic stabilization of metastable polymorphs

This chapter discusses the selective synthesis of two metastable oxide polymorphs, o-YMnO₃ and α-NaFeO₂, and presents a theoretical argument for their experimentally-observed synthesizability. While challenging, if not impossible, to predict the synthesizability of a metastable polymorph *a priori*, here we show that for some materials, density functional theory calculations suggest that structural differences in charged defect accommodation may stabilize one polymorph over another within a specific range of chemical potentials. Furthermore, these chemical potential ranges can be targeted by the synthesis environment (e.g., high oxygen partial pressures) or precursor composition/structure.

For YMnO₃, we focus on the ternary metathesis synthesis reaction $\text{LiMnO}_2 + \text{YOC}l \longrightarrow \text{YMnO}_3 + \text{LiCl}$ and discuss its formation of two yttrium manganese oxide products (hexagonal and orthorhombic YMnO₃) when starting from three different LiMnO₂ precursor structures. Using *in situ* and *ex post facto* temperature-dependent synchrotron X-ray diffraction (SXRD), along with neutron powder diffraction (NPD) data, we identify reaction intermediates and compare the temperature ranges at which they react to form YMnO₃ products. We discover that each reaction pathway, when starting with different LiMnO₂ phases, proceeds through a series of defect-accommodating intermediates: r-YOCl, Y₃O₄Cl, and two lithium manganese oxide spinels. The spinel intermediates form from a disproportionation reaction resulting in a reduced Mn(II,III) spinel resembling Mn₃O₄ and an oxidized Mn(III,IV) spinel resembling LiMn₂O₄. The relative amount of these two spinels changes as a function of reaction progress (e.g., how much LiCl had formed) and influences the amount of h-YMnO₃ and o-YMnO₃ that is observed after heating at ~600 °C for one hour. DFT calculations reveal that o-YMnO₃ is stabilized through small concentrations of cation defects

Note: This chapter is closely adapted from two prior co-authored journal publications, the first of which I contributed to as a co-first author; see Ref. 94: Todd, P. K. *et al.* Defect-Accommodating Intermediates Yield Selective Low-Temperature Synthesis of YMnO₃ Polymorphs. *Inorganic Chemistry* **59**, 13639–13650 (2020), and Ref. 106: McAuliffe, R. D. *et al.* Direct Mechanochemical Synthesis, Phase Stability, and Electrochemical Performance of α-NaFeO₂. *Inorganic Chemistry* **62**, 3358–3367 (2023).

on the order of $\sim 2.2\%$ in our observed products, which we correlate to the amount of oxidized Mn(III,IV) spinel present at the temperature when YMnO_3 forms. After two weeks of heating, these ternary metathesis reactions yield the slightly cation deficient o- YMnO_3 . Controlling the composition and subsequent oxidation state of manganese in these spinel intermediates affords opportunities for increased kinetic control in synthesizing complex oxides at low temperatures.

For NaFeO_2 , we explore the mechanochemical synthesis of the layered α - NaFeO_2 phase. We show that the α phase can be directly synthesized by milling of Na_2O_2 and γ - Fe_2O_3 for 5 hours without any additional high-temperature annealing. In investigating the mechanochemical synthesis, it was observed that the precursor compositions and mass amounts affect the resulting NaFeO_2 structure. DFT calculations on the phase stability of NaFeO_2 phases show that the α phase is stabilized over the β phase in more oxidizing environments, which is provided by the oxygen-rich reaction between Na_2O_2 and Fe_2O_3 . Furthermore, a third polymorph, γ - NaFeO_2 , is not predicted to be stable at any set of chemical potentials. This prediction is supported by the lack of observation of the γ phase in mechanochemical synthesis.

While presented retrospectively as a theoretical rationale for the experimental observations of these two case study systems, the defect accommodation hypothesis offers *a priori* predictive power, promising a novel approach for selective synthesis of some metastable phases. We show that the chemical potential diagram further serves as a planning tool for the materials chemist to “design” the reaction pathway, providing a rationale for selecting optimal precursors and synthesis environments leading to the direct formation of metastable materials.

4.1 The puzzling role of precursor structure in solid-state reactions

In molecular chemistry, it is well known that proper selection of precursor structure and composition permits product selectivity under mild reaction conditions. In comparison, product selectivity in inorganic materials synthesis is often limited to the product at a global (or deep local) minimum on a potential energy landscape due to the significant thermal energy barrier of diffusion [107]. For more kinetic variables to influence the pathway, such as the effect of precursor *structure* on product selectivity, the reaction must proceed to completion at low temperatures [108].

A good starting point when synthesizing extended crystalline solids at low temperatures is to use a structural framework that retains geometric motifs from precursor to product. A specific example is the intercalation/deintercalation of cations or anions from a rigid inorganic framework [109, 110]. This supports the high capacity achieved when cycling battery electrodes [111], or selective replacement of interstitial cations in layered polymorphs of LiAlO_2 [112]. These topotactic examples are limited to removing labile ions from a

rigid host structure. In contrast, most inorganic materials synthesis involves more complex reaction pathways where the structural similarities between precursor and product are less clear.

In the two systems studied here, the structure of the precursors plays a significant role in deciding the outcome of the reaction. For example, the monoclinic structure of LiMnO_2 promotes the formation of o-YMnO_3 at long times, but the tetragonal structure promotes o-YMnO_3 at short time scales due to the nature of its reaction intermediates. Similarly, in the sodium iron oxide system, the gamma phase of Fe_2O_3 is required to achieve the selective synthesis of $\alpha\text{-NaFeO}_2$. We will show in the following sections how the precursor structure influences the reaction pathway, in this case, promoting the formation of charged defects that result in the stabilization of one product polymorph over another.

4.2 Synthesis of orthorhombic yttrium manganese oxide, o-YMnO_3

Solid-state metathesis reactions, often performed at low temperatures, offer the conditions necessary to observe the effects of precursor structure on product selectivity [113, 114]. In the preparation of complex oxides, collaborators showed that assisted metathesis reactions of the form $3 A_2\text{CO}_3 + 2 Y\text{Cl}_3 + \text{Mn}_2\text{O}_3 \xrightarrow{\text{O}_2} 2 Y\text{MnO}_3 + 6 A\text{Cl} + 3 \text{CO}_2$ ($A = \text{Li, Na, K}$) selectively synthesize three unique yttrium manganese oxide products depending on the identity of the alkali carbonate precursor [92]. When using lithium, they identified LiMnO_2 and YOCl as key intermediates that kinetically yield the metastable orthorhombic polymorph of YMnO_3 at temperatures below 850°C . In contrast, the stable phase, hexagonal YMnO_3 , is produced from reactions of the binary oxides (Y_2O_3 , Mn_2O_3) at temperatures above 900°C . By starting directly with these ternary materials as precursors, a metathesis reaction can be written as



which yields o-YMnO_3 at temperatures as low as 500°C .

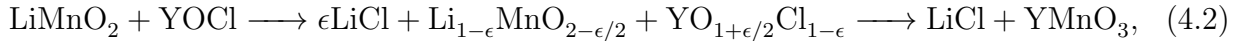
The three structures of LiMnO_2

Here, we focus on the role that the LiMnO_2 precursor structure plays in determining the reaction pathway towards YMnO_3 . The three polymorphs of LiMnO_2 crystallize as derivatives of the rock salt structure with octahedrally-coordinated cation sites (Figure 4.1); however, the transition metal polyhedral connectivity varies between the structures. The monoclinic polymorph ($C2/m$, m-LiMnO_2) forms as a slightly distorted analog to $R\bar{3}m$ LiCoO_2 , where the Jahn-Teller active Mn(III) induces a slight shift in the manganese oxide layering. m-LiMnO_2 is the most disordered of the three, with 10% of lithium sitting on manganese sites and vice versa [115]. The orthorhombic polymorph ($Pmnm$, o-LiMnO_2) is also a layered

structure where the manganese oxide layers adopt a corrugated rock salt layering as compared to m-LiMnO₂. o-LiMnO₂ also has somewhat less site mixing, with only 5% cation inversion [116]. The tetragonal polymorph (*I*4₁/*amd*, t-LiMnO₂) orders with manganese sites forming the octahedral framework of a spinel and lithium occupying the remainder of the octahedral sites [117]. As this phase is formed by the chemical insertion of Li into LiMn₂O₄ under mild conditions, it does not exhibit any notable site mixing in its pristine form.

The reaction pathway

The reaction of LiMnO₂ and YOCl to form YMnO₃ and LiCl through defect accommodating intermediates can be generally described as



where ϵ describes the amount of lithium chloride that has formed at a particular temperature or time and $\text{Li}_{1-\epsilon} \text{MnO}_{2-\epsilon/2}$ and $\text{YO}_{1+\epsilon/2} \text{Cl}_{1-\epsilon}$ describe the average composition of two disproportionated lithium manganese oxide spinels and two oxygen-rich yttrium oxychloride intermediates (r-YOCl, Y₃O₄Cl), respectively. As the value of ϵ changes over the progress of the reaction, we observe different crystalline intermediates that describe these average compositions. The composition of these intermediates defines the reaction pathway and thus the distribution of the final YMnO₃ products.

Thermodiffraction using synchrotron and neutron radiation reveals the influences of precursor polymorph on this reaction. Synchrotron X-ray diffraction (SXRD) experiments were performed on the gradient furnace [37], heating a single capillary to a range of temperatures along the length of the sample, with the coolest part of the sample at 300 °C and the hottest part at 750 °C. After being heated for 40 min, the sample was cooled. Diffraction patterns were then taken at room temperature after heating, which we refer to as *ex post facto* or “after the fact” SXRD. This technique allows one to directly compare lattice parameters between phases formed at different dwell temperatures without the need to include thermal expansion effects. Using the gradient furnace also permits the collection of isothermal *in situ* kinetic data. The quantitative analysis of crystalline phases from *ex post facto* SXRD experiments is shown in Figure 4.1 with temperature ranges of each phase illustrated in Figure C.2. Complementary temperature-dependent neutron powder diffraction (NPD) experiments were also performed to confirm the identity of observed intermediates and to better analyze the composition of lithium-containing intermediates. The quantitative phase analysis from NPD experiments is shown in Figure C.3.

Regardless of LiMnO₂ precursor, the first observed reaction forms lithium chloride, two manganese-containing spinel phases, and oxygen-rich yttrium oxide chloride (Figures 4.1 and C.3). The two spinel intermediates form as lithium and oxygen are removed from LiMnO₂ to form LiCl and Y₃O₄Cl, respectively. Here, a disproportionation of LiMnO₂ into two distinct spinel phases is observed: a cubic spinel phase resembling *Fd* $\bar{3}$ *m* LiMn₂O₄ (*c'*-spinel) and

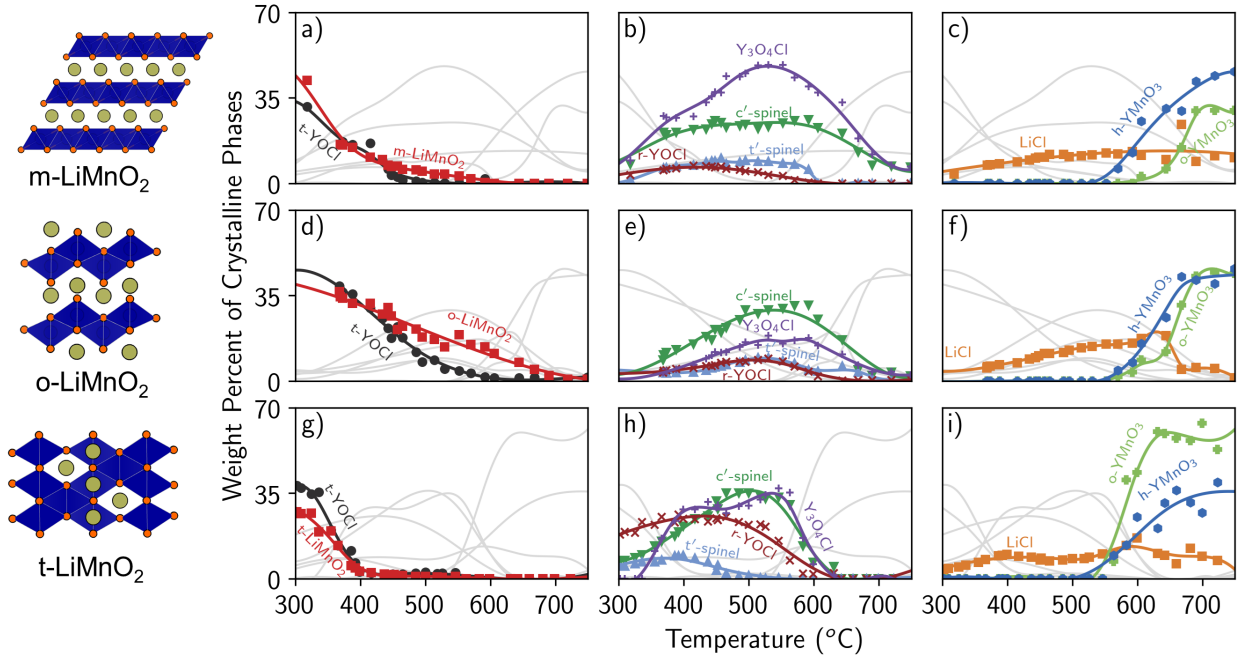


Figure 4.1: Refined weight fractions of crystalline materials at different reaction temperatures. These data reveal the reaction pathway of the ternary metathesis reaction, $\text{LiMnO}_2 + \text{YOCl} \rightarrow \text{LiCl} + \text{YMnO}_3$ when changing the LiMnO_2 precursor. Samples were heated for 40 min at the given temperature before being cooled to room temperature over the course of 30 minutes for a *ex post facto* measurement. Slow cooling was required to preserve the integrity of the LiCl-weakened capillaries. Each row highlights the structure of LiMnO_2 precursor and the reaction pathway as a function of temperature: (a-c) $m\text{-LiMnO}_2$ ($C2/m$), (d-f) $o\text{-LiMnO}_2$ ($Pmnm$) and (g-i) $t\text{-LiMnO}_2$ ($I4_1/amd$). Each column shows the phase fractions (weight percent) of crystalline phases along the pathway. For clarity, the presented phases are separated into the reactants, LiMnO_2 (red square) and $t\text{-YOCl}$ (black circle) (a,d,g); the intermediates, $\text{Y}_3\text{O}_4\text{Cl}$ (purple cross), $r\text{-YOCl}$ (rose x), $t'\text{-spinel}$ (green triangle) and $c'\text{-spinel}$ (sky blue triangle) (b,e,h); and the products LiCl (orange square), $h\text{-YMnO}_3$ (blue hexagon) and $o\text{-YMnO}_3$ (light green cross) (c,f,i).

a tetragonal spinel phase resembling $I4_1/amd$ Mn_3O_4 ($t'\text{-spinel}$). In SXR experiments collected *ex post facto* (Figure 4.1), the relative weight percent of the $c'\text{-spinel}$ is at least double that of the $t'\text{-spinel}$ for all reaction pathways, yet *in situ* SXR and NPD experiments yield more $t'\text{-spinel}$ over similar temperature ranges (Figure C.1 and C.3). Concomitantly, $Cmcm$ $\text{Y}_3\text{O}_4\text{Cl}$ forms through the oxygenation of the $t\text{-YOCl}$ precursor. This reaction proceeds through a disordered rhombohedral form of YOCl ($R\bar{3}m$) that is poorly resolved in the diffraction data but has been previously observed in assisted metathesis reactions with lithium [93]. The results in Figure 4.1b,e,h confirm the presence of each intermediate, yet subtle differences are observed in the precursor reactivity, the relative amounts of each intermediate, and the temperature range over which the intermediates form and react.

The reaction pathway starting with $m\text{-LiMnO}_2$ (Figure 4.1a-c) yields intermediates at the lowest temperatures when compared to the other polymorphs of LiMnO_2 , yet the intermediates do not react fully until temperatures reach 600 °C. In Figure 4.1b, significant

amounts of r-YOCl, Y_3O_4Cl , the two manganese-containing spinel phases, and LiCl form by 300 °C. *In situ* SXRD experiments in Figure C.1 confirm that the relative amounts of each precursor begin decreasing at temperatures as low as 150 °C to yield c' -spinel and r-YOCl. Furthermore, calculated site occupancies from the *in situ* NPD experiments reveal the occupancy of the (2d) lithium site of m-LiMnO₂ in Figure 4.2 decreases by ~24% by 300 °C, whereas the oxygen occupancy remains constant. The m-LiMnO₂ and YOCl precursors continue to react until depleted at 570 °C and 443 °C, respectively. Near 500 °C, the relative amount of the reaction intermediates is the highest, with Y_3O_4Cl representing the largest fraction at 48 wt%. Here, the intermediates react to yield different polymorphs of YMnO₃. First, r-YOCl and t' -spinel react at lower temperatures (r-YOCl: 465 °C; t' -spinel: 570 °C) followed by Y_3O_4Cl and c' -spinel (Y_3O_4Cl : 592 °C; c' -spinel: 644 °C). As all intermediates start to decrease, the h-YMnO₃ phase forms at 570 °C followed by the formation of o-YMnO₃ at 644 °C. More h-YMnO₃ is formed as a result of this reaction with 50% more h-YMnO₃ present at 750 °C. LiCl intensity in the SXRD *ex post facto* data decreases rapidly at 600 °C when starting with o-LiMnO₂. In its place, the capillary began to crystallize into a trigonal silicate phase, indicating that LiCl reacted with the reaction vessel. The silicate phase is modeled using the LeBail method and is not accounted for in the wt % of the final product presented in Figure 4.1.

The reaction starting from o-LiMnO₂ (Figure 4.1d-f) yields a pathway where the precursors begin to react near 300 °C and persist to the highest observed temperatures (o-LiMnO₂: 668 °C; YOCl: 495 °C). Compared to m-LiMnO₂, o-LiMnO₂ begins reacting at higher temperatures, as supported in the calculated lithium site occupancies in Figure 4.2 and *in situ* NPD results in Figure C.3. As precursors react, the same intermediates are formed; however, there is significantly less Y_3O_4Cl formed at a maximum of 18 wt% at 530 °C as compared to 48 wt% at the same temperature for reactions starting with m-LiMnO₂. Also, the t' -spinel intermediate is observed up to 606 °C. Here, a concomitant decrease of phase fraction for all intermediate phases is observed, resulting in equal amounts of h-YMnO₃ and o-YMnO₃ form at 570 °C and 606 °C, respectively.

For reactions starting with the t-LiMnO₂ polymorph, the precursors react over a narrower temperature range, where t-LiMnO₂ and YOCl are completely depleted by 392 °C in Figure 4.1g, and m-LiMnO₂ and o-LiMnO₂ persist to higher temperatures of 570 °C and 668 °C, respectively. This is evident in the calculated site occupancies in Figure 4.2, where the (4a) lithium site occupancy appears to decrease below 300 °C, yet is completely reacted by 300 °C. Contrary to the other LiMnO₂ polymorphs, there is a significant fraction of t' -spinel compared to c' -spinel at 300 °C. This t' -spinel reacts at 400 °C to yield more c' -spinel in Figure 4.1h. Also, r-YOCl forms in a relatively large amount reaching 26 wt% as opposed to a maximum of 7 wt% and 9 wt% for reactions with m-LiMnO₂ and o-LiMnO₂ respectively. Near 500 °C, Y_3O_4Cl , r-YOCl, and c' -spinel react completely by 560 °C to yield o-YMnO₃ and h-YMnO₃. Here, 25% more o-YMnO₃ was observed than h-YMnO₃ at 725 °C.

Central to understanding the reaction pathway in these ternary metathesis reactions is the disproportionation of spinel intermediates into a c' -spinel and t' -spinel (Figure 4.1b,e,h). To properly identify the two phases, both SXRD and NPD are needed. In the SXRD results,

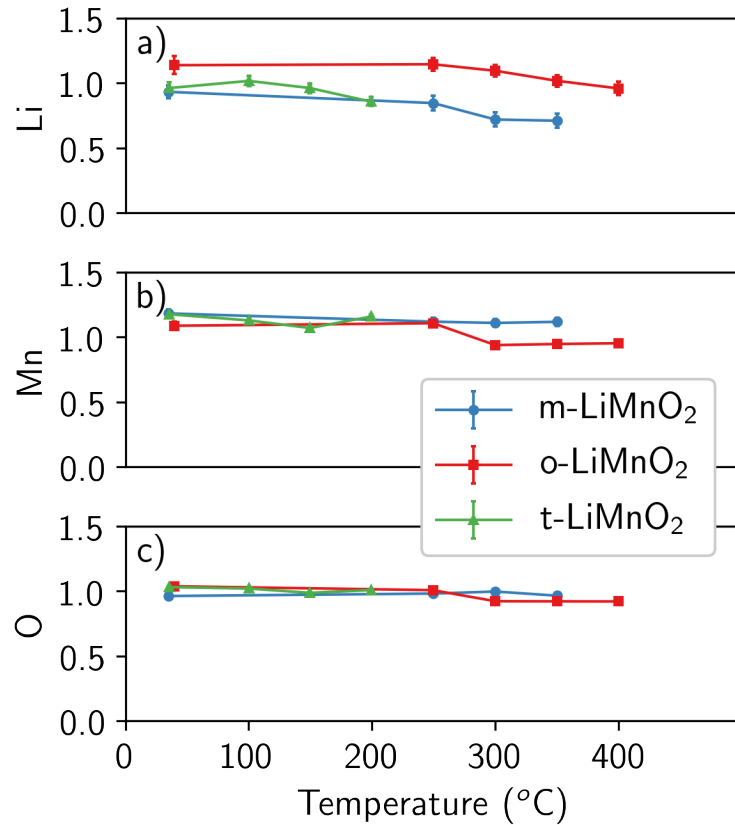


Figure 4.2: Occupancy of crystallographic sites that correspond to lithium-rich (left), manganese-rich (center), and oxygen (right) sites within the crystal lattice for o-LiMnO₂ (red), m-LiMnO₂ (blue), and t-LiMnO₂ (green). As all occupancies were refined together with the scale factor for the phase, values should be considered relative rather than absolute.

this spinel disproportionation is most easily observed in diffraction patterns taken from the reaction o-LiMnO₂ + YOCl (Figure 4.3), as Bragg peaks from both the monoclinic and tetragonal polymorphs of LiMnO₂ overlap with those of the t'-spinel phase (Figure C.4). The c'-spinel is most evident in the X-ray diffraction patterns (Figure 4.3a, Figure C.4) by the strong (111) reflection at $Q = 1.33 \text{ \AA}^{-1}$. The t'-spinel is harder to distinguish with X-rays, as evidenced by the small (112)_t peak at $Q = 2.04 \text{ \AA}^{-1}$, or by a small shoulder on the (111)_c peak of c'-spinel corresponding to the (101)_t peak at $Q = 1.28 \text{ \AA}^{-1}$. In the neutron diffraction pattern (t-LiMnO₂ + YOCl) presented in Figure 4.3b the t'-spinel is easily identifiable by a strong (202) reflection at $2.55 \text{ \AA}^{-1}$ and the c'-spinel is identified by the (202) reflection at $2.64 \text{ \AA}^{-1}$. The site occupancies of the t'-spinel phase were refined from the neutron data and indicated the presence of lithium on the tetrahedral (4c) manganese site of Mn₃O₄, with a refined Li occupancy of 0.43 ± 0.15 at 450 °C. The intensity of Bragg peaks from the c'-spinel in the NPD results is not high enough to successfully refine occupancies of this phase. While

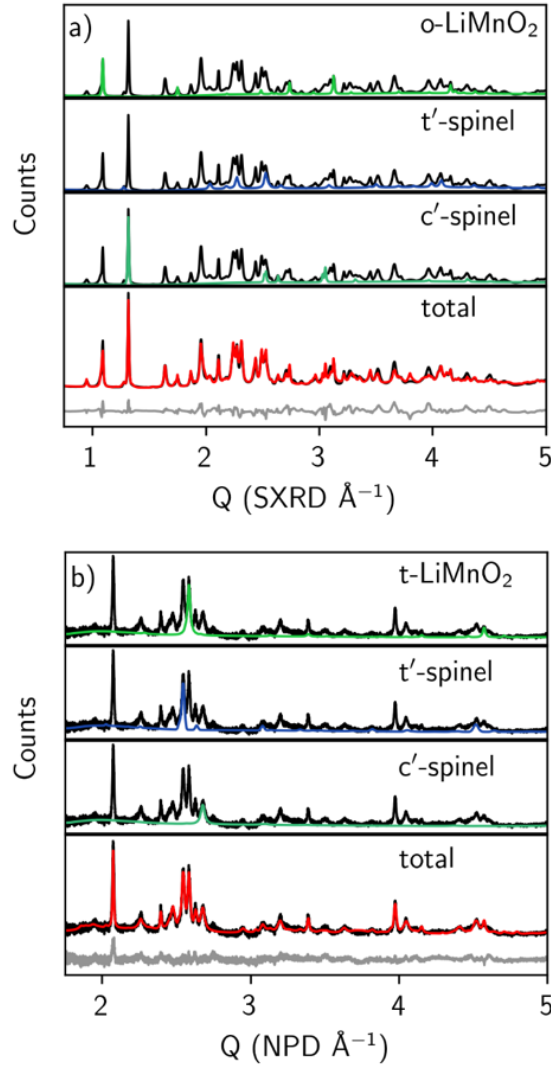


Figure 4.3: Diffraction patterns that illustrate the presence of two unique manganese-containing spinel intermediates in the ternary metathesis reactions. a) SXRD patterns of o-LiMnO₂ + YOCl at 500 °C and b) NPD pattern of t-LiMnO₂ + YOCl at 400°C. The contributions of each lithium manganese oxide phase are highlighted: LiMnO₂ precursor (top), t'-spinel (second from top), and c'-spinel (third from top). The overall fit from Rietveld refinement (bottom) also contains t-YOCl, r-YOCl, Y₃O₄Cl and LiCl (red) along with a difference pattern (gray).

we are unable to refine the occupancies of all observed spinel intermediates and achieve a unique result, we simply note that site mixing on this tetrahedral site can occur.

Simultaneous formation of the cubic and tetragonal spinel phases (Figure 4.4) suggests a charge disproportionation of manganese during the reaction. The tetragonal spinel unit cell is distinguishable crystallographically by a contraction of the a_t axis due to a Jahn-Teller

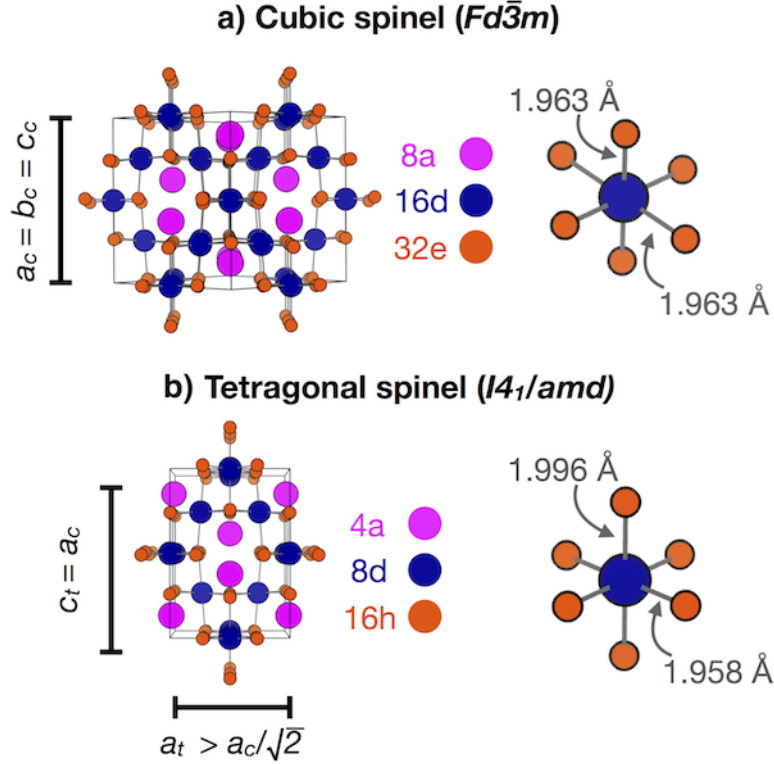


Figure 4.4: Structural relationship between a) cubic $Fd\bar{3}m$ spinel and b) tetragonal $I4_1/amd$ spinel. The geometric relationship between unit cells is shown in the Wyckoff positions highlighted. The tetrahedral cation sites $((8c)_c$ and $(4c)_t$), octahedral cation sites $((16d)_c$ and $(8c)_t$), and oxygen site $((32e)_c$ and $(16h)_t$) are highlighted. Finally, the local $[MnO_6]$ octahedra are shown for each structure with the axial and equatorial bond distances labeled to highlight the Jahn-Teller distortion in tetragonal spinels.

distortion of Mn(III) containing $[MnO_6]$ octahedra. To ensure the validity of refining both cubic and tetragonal spinel phases, the c' -spinel was fit using a formally tetragonal setting ($I4_1/amd$ $LiMn_2O_4$) which refined to a metrically cubic unit cell when $a_t = b_t = \sqrt{2} \times c_t$ (e.g., the c_t/a_t ratio remained close to the expected value of 1.41 for a cubic spinel in Figure C.5 a)). For comparison, the t' -spinel c_t/a_t ratio yielded a tetragonal ($I4_1/amd$) cell with a c_t/a_t ratio of 1.63 (Figure C.5b). The suppression of a Jahn-Teller distortion in c' -spinel and the simultaneous presence of the distortion in t' -spinel suggests a charge disproportionation between the two intermediates.

Density functional theory calculations of $YMnO_3$

To evaluate the defect- and temperature-dependent thermodynamic stability of $YMnO_3$ polymorphs, we performed DFT calculations using the Vienna *Ab initio* Simulation Package (VASP) [46]. We used the Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [118] plus Hubbard- U extension (GGA +

Table 4.1: Original YMnO₃ structures acquired from the Materials Project database

Name	Spacegroup	<i>mpid</i>	Energy above hull (eV/atom)	Num. atoms
h-YMnO ₃	$P6_3cm$	mp-19385	0	30
h-YMnO ₃	$P6_3/mmc$	mp-19227	0.021	10
o-YMnO ₃	$Pnma$	mp-20699	0.023	20

Table 4.2: Re-relaxed YMnO₃ unit cells (AFM ordering) and their lattice parameters

Structure	a (Å)	b (Å)	c (Å)	Volume (Å ³)
h-YMnO ₃ ($P6_3cm$)	6.215	6.215	11.58	387.5
h-YMnO ₃ ($P6_3/mmc$)	3.618	3.618	11.41	129.8
o-YMnO ₃ ($Pnma$)	5.343	5.888	7.477	235.2

U) with $U = 3.9$ eV for Mn [119, 120]. The Projector Augmented Wave (PAW) method [121, 122] was used for modeling core states with a plane wave basis and a minimum energy cutoff of ≥ 520 eV.

The original structures for the hexagonal and orthorhombic YMnO₃ polymorphs were acquired from the Materials Project (MP) database [12]; their properties are shown in Table 4.1. Our early DFT calculations showed that the calculated material properties are particularly sensitive to the initialized magnetic ordering of the structures. For example, all structural relaxations performed using the GGA+ U scheme with a ferromagnetic (FM) ordering yield an incorrect zero band gap for both the centrosymmetric (high-temperature) and noncentrosymmetric (low-temperature) h-YMnO₃ structures. Previous studies suggest that below their Néel temperatures, the hexagonal and orthorhombic phases acquire triangular and sinusoidally-modulated antiferromagnetic (AFM) orderings, respectively [123, 124]. To initialize an appropriate magnetic ordering in our calculations, we enumerated many possible collinear magnetic orderings for each structure using the high-throughput DFT workflow developed by Horton et al. [125]. We found several orderings which opened the GGA-calculated band gap to 1-2 eV for both the hexagonal and orthorhombic phases. Each of these collinear orderings was of AFM type and slightly higher in energy (< 2 meV/atom) than any of the FM orderings. For each structure, we selected the lowest energy AFM ordering which also resulted in a substantial non-zero band gap. The original MP structures were then re-relaxed with these AFM orderings in 2x2x2 supercells with a k -point grid density of 5000 per atom until forces on the atoms were 1×10^{-4} eV/Å or less. Table 4.2 contains the lattice parameters and volume for each re-relaxed structure.

Density functional perturbation theory (DFPT) was then used to calculate force constants for 11 equally spaced deformations spanning $\pm 4\%$ lattice strain of the re-relaxed (primitive) cells. We used a k -point grid density of 5000/atom, plane wave energy cutoff

of 620 eV, and energy convergence criterion of 1×10^{-8} eV for the self-consistent electronic loop. Force constants were mass-weighted and symmetrized to acquire phonon modes used to approximate the Helmholtz free energy, $F(V, T)$, as a function of the volume of the deformed cells. Using the *phonopy* package, the Vinet equation of state [126] was fit to these free energy curves for each structure at temperatures ranging from $T = 0$ to 1400 K (in 100 K steps) and minimized at a pressure of $P = 1$ atm, yielding the Gibbs free energy curves, $G(P, T)$, of each structure. Figure 4.5 shows Gibbs free energies, $G(P, T)$, and heat capacities, $c_p(T)$ calculated with quasiharmonic approximation (QHA) for each of the YMnO_3 structures.

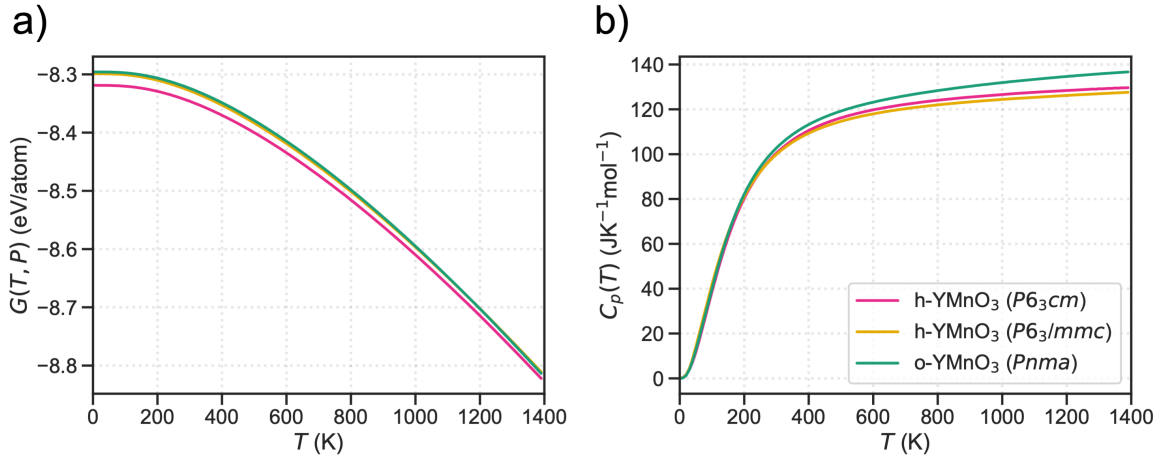


Figure 4.5: Gibbs free energies and heat capacities as a function of temperature for YMnO_3 polymorphs, and at a pressure of $P = 1$ atm.

Vacancy formation energies for yttrium and manganese cations, $E^f[V_Y]$ and $E^f[V_{Mn}]$, were calculated for each YMnO_3 structure via the charged-defect supercell approach with finite-size corrections developed by Freysoldt et al. [28, 62] and implemented by Broberg et al. [53] in the *atomate* workflow interface [55]. We used a k -point grid density of 100/atom and supercell dimensions outlined in Table 4.3. Using computed defect formation energies, the thermodynamic stability of the polymorphs was modeled using a defect concentration-dependent thermodynamic potential, Φ , defined as

$$\Phi(P, T, x) = G^{QHA}(P, T) + (E^f[V_Y] + E^f[V_{Mn}]) x, \quad (4.3)$$

where T is the temperature, P is the pressure, $G^{QHA}(P, T)$ is the Gibbs free energy calculated using QHA, $E^f[V_Y]$ and $E^f[V_{Mn}]$ are the defect formation energies of yttrium and manganese vacancies respectively, and x is the concentration of cation vacancies in $\text{Y}_{1-x}\text{Mn}_{1-x}\text{O}_3$. A paired cation vacancy concentration was used as an equivalent representation of oxygen hyper-stoichiometry $\text{YMnO}_{3+\delta}$, where $x = \delta/(3 + \delta)$. This aligns with previous observations that rare-earth perovskite manganites RMnO_3 accommodate excess oxygen via cation (R, Mn) vacancies (instead of oxygen interstitials) due to their close-packed structure [127–130].

Structure	Magnetic Ordering	Supercell	Number of atoms	HSE06 band gap (eV)	GGA+ <i>U</i> band gap (eV)
h-YMnO ₃ (<i>P6₃cm</i>)	AFM	2x2x1	120	2.38	1.15
h-YMnO ₃ (<i>P6₃/mmc</i>)	AFM	4x2x1	160	2.1	1.21
o-YMnO ₃ (<i>Pnma</i>)	AFM	2x2x2	160	2.57	1.34

Table 4.3: Summary of defect supercells and comparison of the band gaps acquired using the HSE06 and GGA+*U* functionals

It was noted that in LaMnO₃, cation vacancies were found in equal proportions for small values of δ [128], although this is not necessarily true for more oxidizing conditions [129].

Entropic contributions to vacancy formation were not included in the calculation of vacancy formation energies. Thus the calculated vacancy formation energies, $E^f[V_Y] + E^f[V_{Mn}]$, are independent of temperature. The Fermi energy of electrons, E_F , typically solved for self-consistently via charge balance of defect concentrations at equilibrium, was left as a free variable in phase diagram construction.

The resulting defect formation energy diagrams, which show vacancy formation energy as a function of Fermi energy for each polymorph, are displayed in Figure 4.6. Figure 4.6a is constructed using chemical potentials from the YMnO₃-MnO-Y₂O₃ equilibrium on the Y-Mn-O phase diagram, and Figure 4.6b using chemical potentials from the YMnO₃-YMn₂O₅-Y₂O₃ equilibrium. The change in chemical potentials simply shifts the vertical position of the defect formation energy curves and hence has no impact on the phase diagrams created in Figures 4.7 and C.6. Finally, the YMnO₃ phase diagram is re-plotted in Figure C.6 to show the spread of the phase boundary with different values of Fermi energy, E_F . All Fermi energies lie within the GGA+*U* band gaps of all structures considered. Note that the phase boundary shifts rightward (towards higher values of vacancy concentration) as E_F decreases.

Our DFT calculations show that small changes in the manganese oxidation state can change the relative stability of the two YMnO₃ polymorphs. A previous study [131] showed that the orthorhombic polymorph o-YMnO₃ is readily produced and stabilized in oxygen-rich environments. As with other perovskite manganites, excess oxygen, δ , in o-YMnO_{3+ δ} , has been shown to manifest as the formation of nearly-equivalent amount cation (yttrium and manganese) vacancies, x , in Y_{1-x}Mn_{1-x}O₃. It was hypothesized by Bergum, et al. that excess oxygen stabilizes the orthorhombic phase via an increase in perovskite geometric stability resulting from the decrease in ionic radius that occurs with partial oxidation of Mn(III) to Mn(IV) [132]. To computationally test this hypothesis, we first calculated the defect-free Gibbs free energies, $G(P, T)$, for the hexagonal and orthorhombic polymorphs using the QHA approach for considering phonon vibrational entropy contributions. We also considered the centrosymmetric hexagonal structure (*P6₃/mmc*), which through a ferroelectric phase transition, is stable at temperatures above $T \sim 1250$ K [133]. Our calculations show that the typical ground-state hexagonal (*P6₃cm*) structure is thermodynamically stable at all temperatures studied ($T \leq 1400$ K) and with a pressure of $P = 1$ atm. The orthorhombic (*Pnma*) polymorph and centrosymmetric hexagonal polymorph (*P6₃/mmc*) Gibbs free energies were approximately +23.0 and +19.9 meV/atom higher than that of the hexagonal

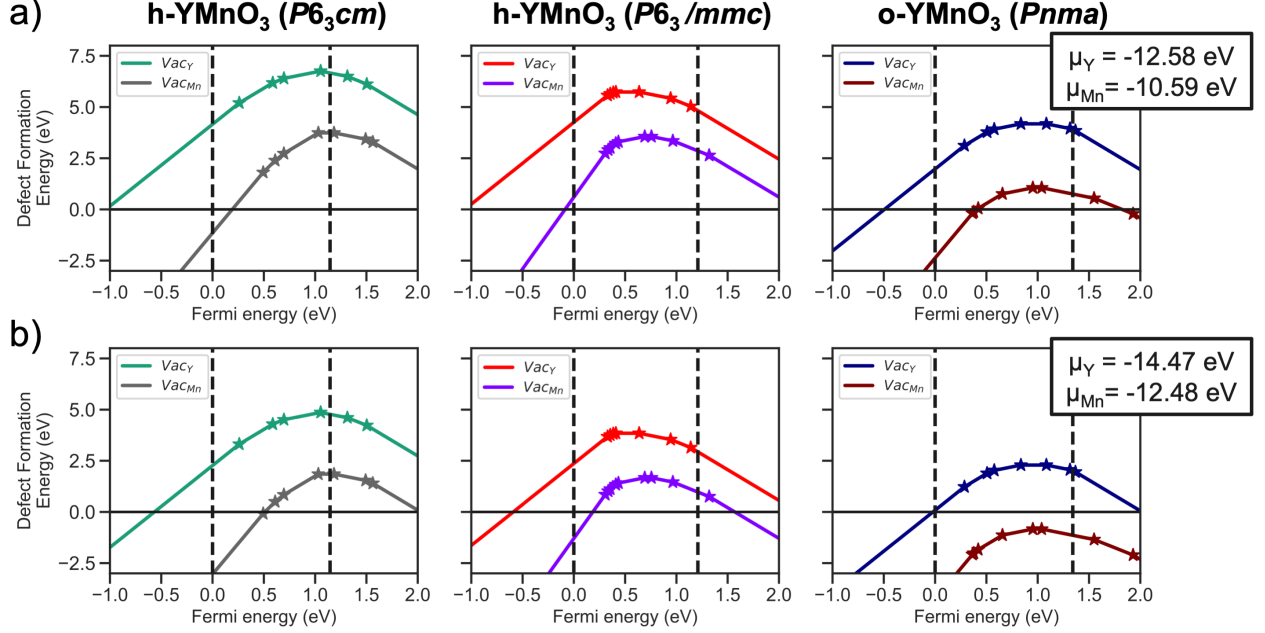


Figure 4.6: Y, Mn vacancy formation energies as a function of Fermi energy for YMnO_3 polymorphs for different chemical potentials, μ_Y and μ_{Mn} . The dashed lines represent the valence band maximum (VBM) and conduction band minimum (CBM). (a) The upper bounds, and (b) the lower bounds of the window of chemical potential stability of YMnO_3 as determined by simplexes in the Y-Mn-O phase diagram (0 K) constructed from the MP database.

phase at $T = 0$ K, decreasing to +7 and +11 meV/atom at $T = 1400$ K, respectively. The Gibbs free energies and heat capacities, $c_p(T)$, are shown as a function of temperature in Figure 4.5.

Using these calculation results, we can determine the cutoff threshold for o- YMnO_3 stability with respect to cation vacancies. The defect-dependent thermodynamic potential, $\Phi(P, T, x)$ (Equation 4.3) was minimized at $P = 1$ atm resulting in the phase diagram in Figure 4.7. The cation-deficient orthorhombic polymorph, o- $\text{Y}_{1-x}\text{Mn}_{1-x}\text{O}_3$, is predicted to be stable above a defect concentration threshold of approximately $x \simeq 0.022$ (2.2%) at $T = 0$ K, which appears to decrease with temperature. The centrosymmetric hexagonal structure h- YMnO_3 ($P6_3/mmc$) was not found to be the minimum energy phase of the three structures at any values of T or x and hence does not appear in the diagram. Figure C.6 shows the sensitivity of this phase boundary to the value of Fermi energy, E_F . Lower values of E_F merely shift the location of the phase boundary towards slightly higher cutoff values, near $x \sim 0.034$ at $T = 0$ K. Furthermore, changes in the values of chemical potentials do not affect the phase diagram (with the caveat that negative defect formation energies are unphysical) since the polymorphs are compared with *identical* compositions at all points on the diagram.

Importantly, and in agreement with the hypothesis by Bergum, et al., the significantly

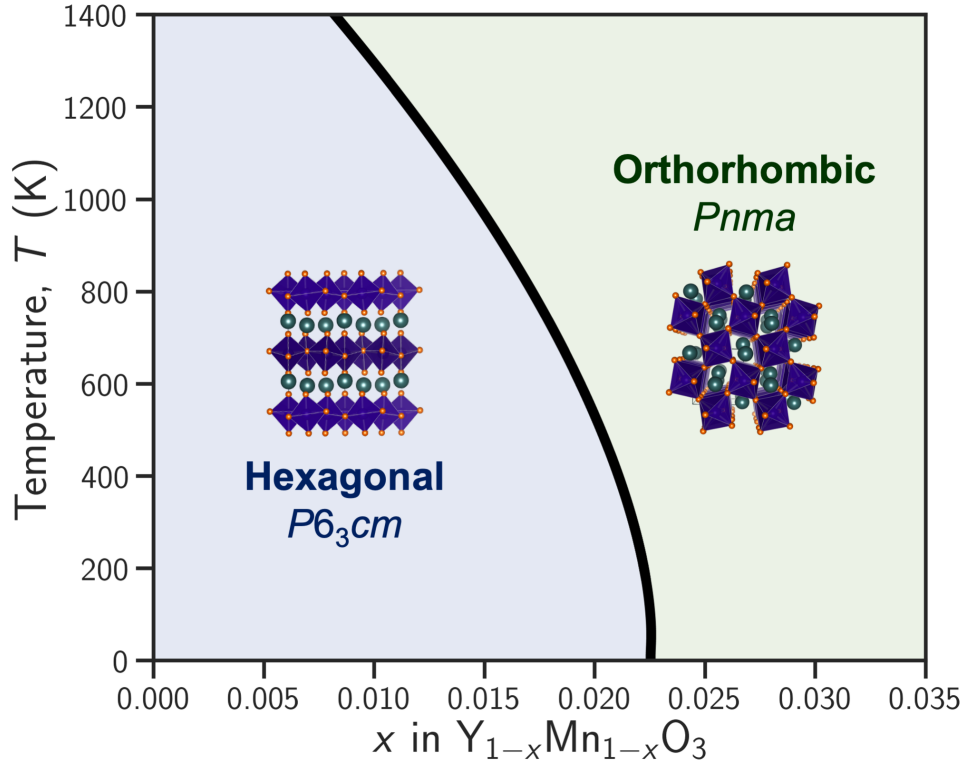


Figure 4.7: DFT-calculated phase diagram of cation-deficient YMnO_3 polymorphs with respect to temperature, T , and a fixed, equal concentration of cation (Y,Mn) vacancies, x in $\text{Y}_{1-x}\text{Mn}_{1-x}\text{O}_3$. All structures are initialized with AFM magnetic orderings, and the Fermi energy of electrons is fixed at $E_F = 1.0$ eV.

lower cation vacancy formation energies in the orthorhombic phase offset the difference in energies due to polymorphism (~ 20 meV) between the hexagonal ($P6_3cm$) and orthorhombic structures. According to the defect formation energy curves, which are shown in Figure 4.6, o- YMnO_3 exhibits significantly lower cation vacancy formation energies than h- YMnO_3 ($P6_3cm$). This difference, of 2.5 eV and 2.6 eV for Y and Mn vacancies, respectively, at $E_F = 1.0$ eV, appears to stabilize the orthorhombic phase even at minimal cation vacancy concentrations on the order of $\sim 2\text{-}3\%$. These vacancies correspond to an increased oxidation state of manganese in order to maintain charge neutrality in the structure.

While the reaction pathway can control the initial polymorph selectivity of YMnO_3 , over long periods of time the defects can equilibrate to lead to a single YMnO_3 product. Control reactions were performed at 550°C , for each LiMnO_2 precursor, to determine product selectivity in these ternary metathesis reactions. Figure 4.8 depicts the phase fractions from PXRD results after short (1 h) and long (168 or 336 h) duration reactions. After dwelling for 1 h at 550°C , reactions starting with m- LiMnO_2 yield the highest conversion to products, which supports the lower onset temperature for YMnO_3 in Figure 4.1c. Interestingly, o- YMnO_3 is observed as the majority phase over h- YMnO_3 after 1 h (Figure 4.8a). Both

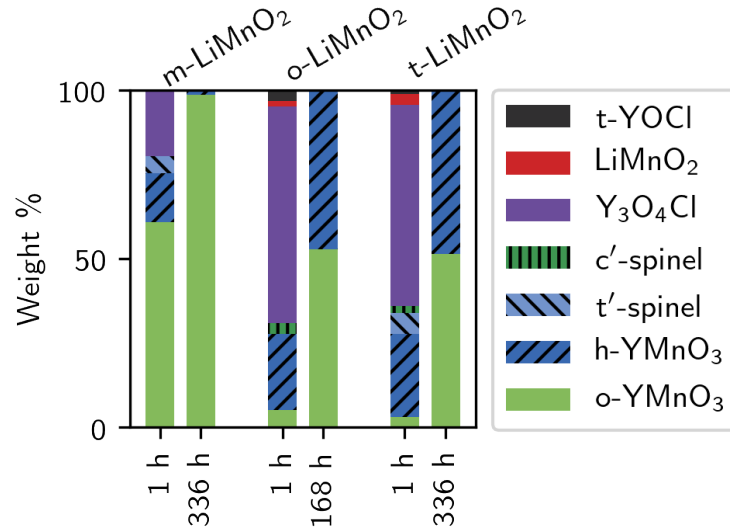


Figure 4.8: Refined fraction of reaction products taken from laboratory PXRD data of *ex situ* ternary metathesis reactions ($\text{LiMnO}_2 + \text{YOCl}$) at 550 °C comparing short and long duration reactions. The results are separated by LiMnO_2 precursor: a) monoclinic ($C2/m$), b) orthorhombic ($Pmnm$) and c) tetragonal ($I4_1/amd$).

t-LiMnO_2 and o-LiMnO_2 reactions yield little conversion to YMnO_3 after one hour, which also supports the results in Figure 4.1f,i, where 550 °C was near the onset temperature of YMnO_3 for both reactions. After long-duration reactions with m-LiMnO_2 , o-YMnO_3 is the only product observed, whereas o-LiMnO_2 and t-LiMnO_2 yield mixtures of hexagonal and orthorhombic YMnO_3 after one week at 550 °C suggesting these reactions are not at equilibrium after one week.

As reactions starting with m-LiMnO_2 yield YMnO_3 products at the lowest temperatures and reaction times, control reactions performed at varied reaction temperatures yield a better understanding of how YMnO_3 phase selectivity changes with reaction temperature. Figure 4.9a-c shows the product distribution calculated from Rietveld refinements of laboratory PXRD data at different reaction temperatures (500 - 600 °C) as a function of time of reaction (without re-mixing). Taken together, the results from these *ex situ* reactions reveal a change in phase selectivity of YMnO_3 products as a function of temperature. Below 600 °C, the orthorhombic phase dominates for long-duration reactions. At 600 °C or above, the product fraction shifts to favor h-YMnO_3 at longer time point reactions, but a mixture of polymorphs still exists after *two* weeks at 600 °C.

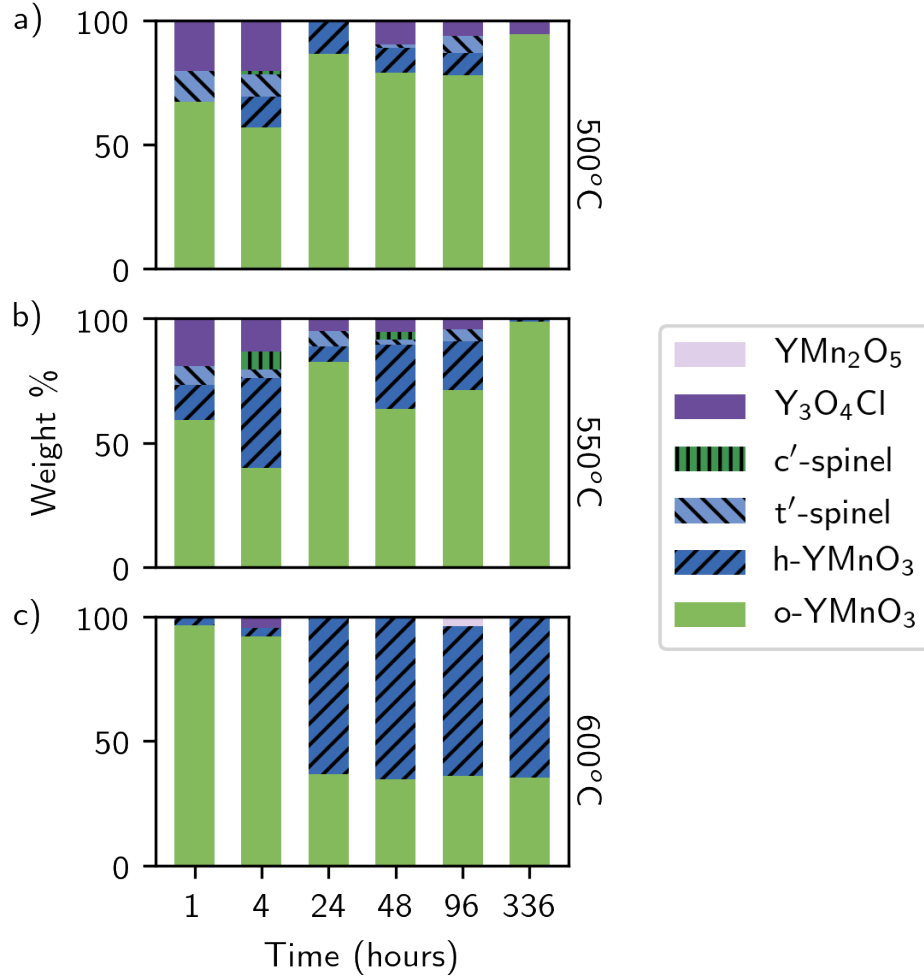


Figure 4.9: Refined fraction of reaction products taken from laboratory PXRD data of *ex situ* ternary metathesis reactions ($\text{LiMnO}_2 + \text{YOCl}$) at varied temperatures and reaction times. Subplots (a-c) show the progression of reaction products when starting with monoclinic ($C2/m$) m - LiMnO_2 at (a) 500 °C, (b) 550 °C, and (c) 600 °C. As the temperature increases, the hexagonal YMnO_3 product selectivity increases over the orthorhombic product.

4.3 Discussion of o - YMnO_3 synthesis

Reaction Pathway

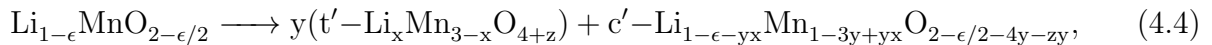
The reaction of LiMnO_2 and YOCl to form LiCl and YMnO_3 proceeds through several crystalline intermediates that can be observed in diffraction experiments. The two yttrium-containing intermediates (r - YOCl and $\text{Y}_3\text{O}_4\text{Cl}$) show to what extent the reaction has progressed (ϵ in Equation 4.2), while the two manganese-containing intermediates (c' -spinel and

t'-spinel) control the ratio of hexagonal and orthorhombic YMnO_3 formed in the final product. By understanding the pathway, insight and control over the reaction can be obtained.

As the reaction progresses, the yttrium oxychloride precursor loses chlorine to LiCl and replaces it with oxygen obtained from lithium manganese oxide species in the reaction. The intermediate $\text{YO}_{1+\epsilon/2}\text{Cl}_{1-\epsilon}$ crystallizes into two distinct phases. At low values of ϵ the more chlorine-rich rhombohedral r-YOCl forms. As more chlorine in the structure is replaced with oxygen, an orthorhombic $\text{Y}_3\text{O}_4\text{Cl}$ type phase forms with the composition $\text{YO}_{1+\epsilon/2}\text{Cl}_{1-\epsilon}$ with a maximum ϵ of $2/3$. Beyond $\epsilon = 2/3$, we hypothesize Y_2O_3 will form, yet we do not observe this phase as an intermediate. Previous studies have observed the transition $\text{Y}_3\text{O}_4\text{Cl} \longrightarrow \text{Y}_2\text{O}_3$ in related metathesis reactions [93], as well as in thermogravimetric studies of rare-earth halides [134, 135]. In those studies, oxygenation occurred when performing the reactions in air or under flowing oxygen. In a sealed environment, as studied here, oxygen must come from the reaction to yield lithium manganese oxide spinels. Further chlorine loss and oxygen abstraction from lithium manganese oxide phases past the point of $\epsilon=2/3$ requires conversion to an oxide.

In Equation 4.2, the Li-Mn-O intermediates are represented generally as $\text{Li}_{1-\epsilon}\text{MnO}_{2-\epsilon/2}$, yet we observe two distinct spinel intermediates: a c'-spinel resembling cubic $Fd\bar{3}m$ LiMn_2O_4 and a t'-spinel resembling tetragonal $I4_1/amd$ Mn_3O_4 . Here, the two spinel intermediates form from a disproportionation reaction as lithium and oxygen leave the phase to form LiCl and oxygenated $\text{YO}_{1+\epsilon/2}\text{Cl}_{1-\epsilon}$. The observation of two spinels can be attributed to the well-known propensity of Jahn-Teller active Mn(III) to distort the $[\text{MnO}_6]$ octahedra in these spinels, as presented in Figure 4.4. This disproportionation can manifest in different ways in these Li-Mn-O spinels as a function of composition and oxidation state of manganese. The effect of losing either oxygen or lithium from LiMnO_2 has been previously investigated in the context of lithium-ion batteries. With all Mn(III) , $\text{Li}_2\text{Mn}_2\text{O}_4$ adopts the tetragonal $I4_1/amd$ spinel structure, where all $[\text{MnO}_6]$ are distorted. Upon delithiation, a phase transition to the cubic spinel, $Fd\bar{3}m$ LiMn_2O_4 , is observed. This cubic spinel is observed electrochemically over the range $0.24 < \text{Li}_x\text{Mn}_2\text{O}_4 < 1$, or when the manganese oxidation state is greater than 3.5 [136]. When $x = 0.24$, a disproportionation reaction occurs, resulting in a Mn(IV) cubic spinel ($\text{Li}_4\text{Mn}_5\text{O}_{12}$), and a mixed Mn(II,III) tetragonal spinel (Mn_3O_4) [137]. Alternatively, the presence of oxygen vacancies in the cubic spinel $\text{LiMn}_2\text{O}_{4-\delta}$ also results in a similar disproportionation. Here, the cubic spinel is observed when $(4-\delta) > 3.833$. Then, a disproportionation reaction occurs to yield tetragonal Mn_3O_4 , cubic $\text{LiMn}_2\text{O}_{4-\delta}$, and tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ over the range $3.33 < (4-\delta) < 3.833$ [138].

The disproportionation reaction in the ternary metathesis reactions studied here differs from those cases, as both lithium and oxygen vacancies are introduced simultaneously. Therefore, we define a range in manganese oxidation states for cubic spinels, $+3.33 < \text{Mn} < +3.88$, where the endpoints represent $\text{LiMn}_2\text{O}_{3.833}$ and $\text{Li}_{0.24}\text{Mn}_2\text{O}_4$, respectively. Then, we apply these constraints to describe the observed disproportionation reaction into c'-spinel and t'-spinel intermediates:



where x is the degree of site mixing on the tetrahedral site of the t' spinel and y represents the amount of t' spinel relative to c' spinel upon disproportionation. The variable z determines the amount of cation vacancies in t' -spinel, which is related to the extent of charge disproportionation of Mn(III) to Mn(II) and Mn (IV). In Equation 4.4, we assume some concentration of lithium on the tetrahedral site of the t' spinel, as evidenced from neutron diffraction data; yet, the disproportionation reaction could plausibly yield Mn_3O_4 when $x = 0$. As constructed, the composition of these spinels can exist up to $x = 0.5$. At $x = 0.5$, the t' -spinel would formally be $Li_{0.5}Mn_{0.5}Mn_2O_4$ where the oxidation state of manganese would remain Mn(III), thus making disproportionation redundant. The value of y in Equation 4.4 then becomes directly influenced by the amount of lithium on the tetrahedral site of the t' -spinel. Lower values of x will result in more t' -spinel Mn_3O_4 with Mn(II,III), whereas higher values of x will result in a more equal phase fraction of each spinel intermediate. The varying degree of spinel disproportionation may explain why we observe different ratios of t' -spinel to c' -spinel in the presented experiments. For example, experiments collected *ex post facto* after 40 minutes at each temperature observe more c' -spinel (Figure 4.1), whereas for *in situ* NPD and SXRD experiments, the samples experience a longer aggregated time at elevated temperatures which results in more conversion to the t' -spinel (Figure C.1 and C.3). This supports control reactions performed with longer dwell times, in which the t' -spinel is often always the observed spinel in XRD results.

The progress of the reaction (ϵ) and the degree of disproportionation (y) determine which $YMnO_3$ polymorph is observed. Figure 4.7 shows that the stability of $YMnO_3$ is directly influenced by cation defects, specifically the oxidation state of manganese. This observation is supported in previous studies on assisted metathesis reactions to yield $YMnO_{3+\delta}$, where Mn(IV) defects result in the orthorhombic product over h- $YMnO_3$ at temperatures below 850 °C. The value of ϵ in Equation 4.4 influences the composition of the spinel intermediates, specifically, the ratio of lithium to manganese. As more lithium chloride and Y_3O_4Cl forms, the value of y in Equation 4.4 should increase, resulting in a higher relative fraction of *reduced* Mn(II,III) t' -spinel. If less LiCl and Y_3O_4Cl have formed, a greater fraction of *oxidized* Mn(III,IV) c' -spinel will be observed relative to t' -spinel. The observed results suggest that the spinel intermediates react individually with the yttrium oxychloride intermediates to yield different $YMnO_3$ product. Here, Mn(II,III) t' -spinel will yield a product resembling h- $YMnO_{3-\delta}$ [139] and the Mn(III,IV) c' -spinel will result in o- $YMnO_{3+\delta}$, as supported by the calculated phase diagram in Figure 4.7. While SXRD experiments show more c' -spinel formation than t' -spinel for all three starting polymorphs, a larger weight percent of c' -spinel corresponds to a larger final concentration of o- $YMnO_3$ in the final product. The varying weight percentage of Y_3O_4Cl in the intermediate compositions is indicative of the presence of amorphous intermediates, which likely play a role in reaction pathways, but they are not studied in this work due to the technical challenges of such data analysis. Analysis of *in situ* SXRD data (Figure C.2) shows that h- $YMnO_3$ forms as t' -spinel is consumed, providing further evidence to a link between the two phases.

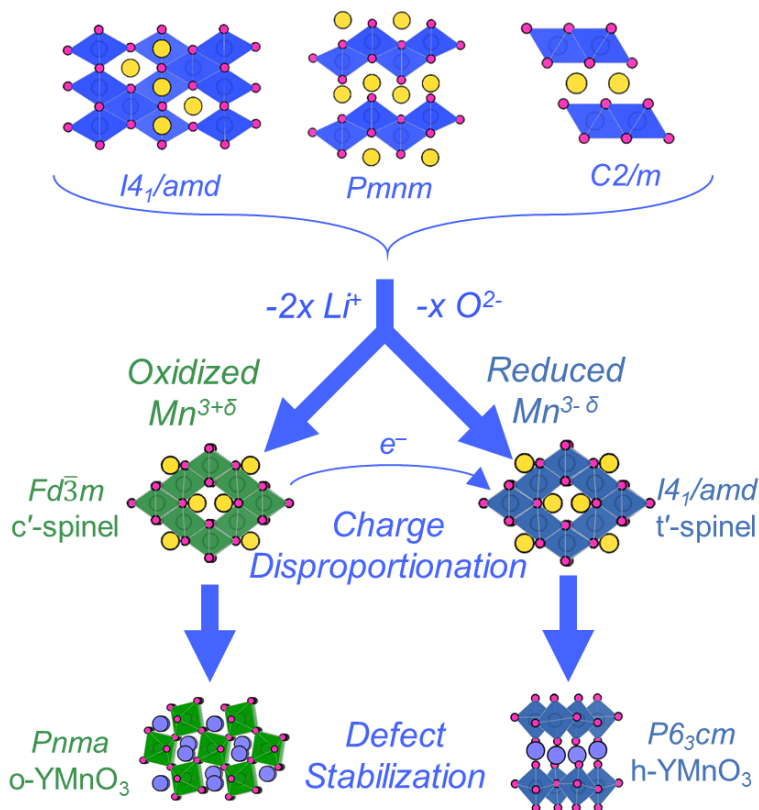


Figure 4.10: Structure of reactants, proposed intermediates, and products along the metathesis pathway. The charge disproportionation to form c' -spinel and t' -spinel stabilizes $o\text{-YMnO}_3$ and $h\text{-YMnO}_3$ respectively.

LiMnO_2 Polymorph Effects

The identity of the LiMnO_2 precursor kinetically controls the composition and relative amount of each intermediate when they react to form YMnO_3 . The results collectively support a relatively slow reaction pathway to spinel intermediates when starting with the layered $m\text{-LiMnO}_2$ or $o\text{-LiMnO}_2$ as opposed to starting with the spinel $t\text{-LiMnO}_2$. Previous electrochemical studies have identified the mechanism of the layered-to-spinel transition as proceeding slowly to the cubic spinel LiMn_2O_4 through a disordered “splayed” intermediate ($R\bar{3}m$ LiMnO_2) where manganese moves from manganese oxide layers into the octahedral spinel sites vacated by lithium [140–142]. The presented results proceed through a similar kinetic pathway where the layered precursors react over a broad temperature range to yield the spinel intermediates, although we do not observe the “splayed” intermediate in our diffraction data as this level of resolution is limited within a multi-phased sample. Both $m\text{-LiMnO}_2$ and $o\text{-LiMnO}_2$ are slow to transition to the spinel intermediates, yet the $m\text{-LiMnO}_2$ precursor reacts at a lower temperature. The reason for the differences in reactivity between

o-LiMnO₂ and m-LiMnO₂ is due to the degree of structural rearrangement necessary to adopt the spinel structure. As lithium is removed from o-LiMnO₂ and m-LiMnO₂, manganese must move to fill the octahedral (16d) site in the spinel intermediates. The o-LiMnO₂ structure adopts a corrugated rocksalt ordering of manganese oxide layers which requires 50% of the manganese atoms to migrate into the octahedral spinel site, whereas in the monoclinic $C2/m$ structure, only 25% of the manganese must move to accommodate the reaction to the spinel intermediate. Thus, starting with m-LiMnO₂ results in higher values of ϵ at lower temperatures, or a greater value of Y₃O₄Cl and Mn(II,III) t'-spinel at 450 °C when h-YMnO₃ forms. As there is more reduced spinel intermediate, the fraction of h-YMnO₃ to o-YMnO₃ is greatest. In comparison, the value of ϵ is lower when starting with o-LiMnO₂, or less Y₃O₄Cl and Mn(II,III) t'-spinel have formed at 500 °C. Then, the amounts of c'-spinel, t'-spinel, r-YOCl, and Y₃O₄Cl all decreased, which results in equal amounts of o-YMnO₃ and h-YMnO₃.

The reaction pathway starting with t-LiMnO₂ yields a different reaction to spinel intermediates. The results in Figure 4.1g,h denote the same t'-spinel, yet the temperature at which the t'-spinel reacts corresponds to an increase in c'-spinel and not h-YMnO₃, which was observed when starting with m-LiMnO₂. We hypothesize that the observed t'-spinel resembles a tetragonal spinel closer to Li_{2- ϵ} Mn₂O_{4- $\epsilon/2$} , where $1 < \epsilon < 2$, and not a t'-spinel resembling Mn₃O₄. Thus, we are observing a disproportionation regime that was not present in the diffraction patterns starting from the layered LiMnO₂ precursors where a spinel is observed only when $\epsilon \geq 1$. Instead, more o-LiMnO₂ and m-LiMnO₂ precursor persisted over this $1 < \epsilon < 2$ range when starting with the layered phases whereas the transition from t-LiMnO₂ to spinel intermediates was discrete, supporting the formation of a unique spinel intermediate over this region. This observation results in a pathway where the amount of Mn(III,IV) c'-spinel is greatest; or the value of ϵ is lowest when YMnO₃ is observed resulting in more o-YMnO₃ relative to h-YMnO₃.

YMnO₃ Polymorph Selectivity

The DFT-calculated phase diagram in Figure 4.7 suggests that the phase stability is correlated to the overall concentration of cation defects in the YMnO₃ lattice. Specifically, cation vacancies paired with partial oxidation of Mn(III) to Mn(IV) appear to stabilize the orthorhombic phase due to its significantly lower cation vacancy formation energies. This form of cation vacancy-driven stabilization was similarly shown for CsPbI₃ [143] and Sc_{1-x}S [144]. In YMnO₃, we predict the critical vacancy concentration which stabilizes the orthorhombic polymorph to be on the order of 2-3%, which is rather low, but it is justified by the very small energy difference between the hexagonal and orthorhombic polymorphs. The calculated concentration is also sensitive to limitations and approximations in our approach, which include: 1) the assumption that the defect formation energy does not change with temperature, 2) the assumption of a fixed value of Fermi energy, 3) the prerequisite that structural selectivity in YMnO₃ can be modeled assuming an *equal* concentration of cation vacancies, 4) the lack of consideration of anharmonic phonon effects, and 5) the small (uncorrectable) errors inherent to the finite size defect supercell approach. It is also important to note that

Figure 4.7 must be considered from a fixed composition viewpoint; i.e., the phase diagram shows the predicted phase stability as a function of vacancy composition rather than oxygen partial pressure. This is important in distinguishing the defect mechanisms between the two structures. For example, it is known that hexagonal rare earth manganites $\text{RMnO}_{3+\delta}$ synthesized under high oxygen pressure can accommodate excess oxygen via interstitials due to their more open structure [145]. Hence the constructed phase diagram provides a route to understanding thermodynamic stability when approached from a synthesis route in which cation vacancies exist or are likely to form, such as from an intermediate structure containing Mn(IV).

We anticipate that the inclusion of anharmonic effects could change the calculated Gibbs free energies of the YMnO_3 phases considerably at high temperatures. This is likely the explanation of the unexpected negative slope of the phase boundary in Figure 4.7, which is due to the decrease in the free energy difference of the orthorhombic $G(P, T)$ curve with respect to the hexagonal $G(P, T)$ curve at high temperature. Indeed, the heat capacity of h- YMnO_3 ($P6_3cm$), which indicates the second derivative of $G(P, T)$ with temperature, underestimates the experimental heat capacity by $\sim 10\%$ at $T = 1400$ K, as seen in Figure 4.11. Therefore anharmonic effects are likely required to explain the proposed entropic stabilization of the hexagonal phase at high temperature that has been experimentally observed [131, 132, 146]. Nevertheless, we believe that the location of the phase boundary at lower temperature is still a reasonable estimate of the order of magnitude of the critical concentration of cation vacancies which switch the stability between the hexagonal and orthorhombic YMnO_3 phases. Even with differing values of Fermi energy within the band gap (Figure C.6) we predict this phase boundary to be located in the range $x \simeq 0.022\text{--}0.034$ at $T = 0$ K.

In all of the presented ternary metathesis reactions, long-duration reactions yield greater amounts of o- YMnO_3 (Figure 4.8). While the amount of h- YMnO_3 and o- YMnO_3 depends on the oxidation state of manganese in the spinel intermediates at *short* reaction times, the overall phase stability will reflect the concentration of defects closer to equilibrium, where the overall YMnO_3 phase stability will be dependent on the number of defects that are *initially* present in the LiMnO_2 precursors. The calculated concentration of cation defects needed to yield o- YMnO_3 is small ($\sim 2.2\%$), which supports that even small amounts of impurities or site defects in the bulk LiMnO_2 precursors will result in o- $\text{YMnO}_{3+\delta}$ at temperatures below 600°C , if allowed to equilibrate. At 600°C , h- YMnO_3 begins to dominate, which supports previous phase diagrams above 800°C [148].

4.4 Mapping defect-dependent polymorph stability onto the chemical potential diagram

In the previous section, we showed that $\Phi(P, T, x)$ can be written as a function of pressure, temperature, and a fixed concentration, x , of a defect species (Equation 4.3). While this thermodynamic potential can be used to successfully build a phase diagram for various

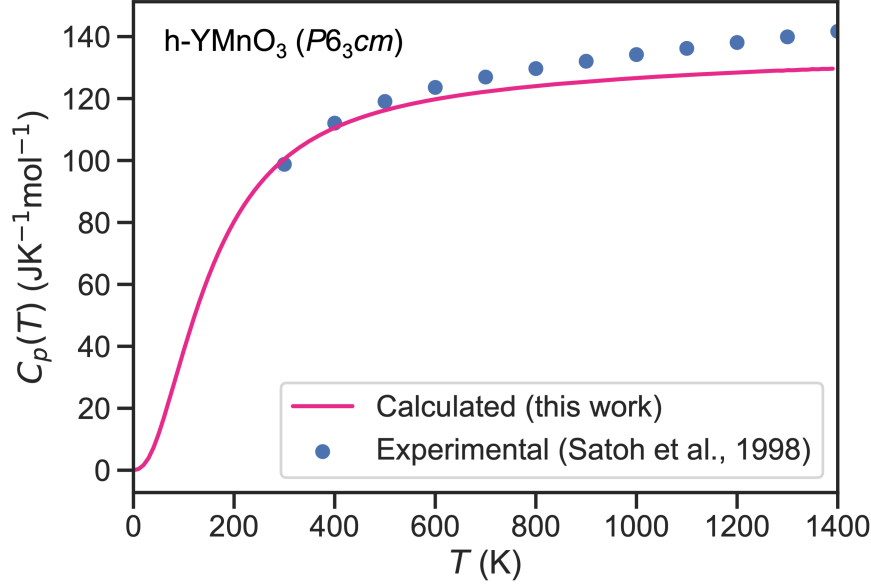


Figure 4.11: Comparison of calculated and experimental heat capacities for h-YMnO₃ ($P6_3cm$). Experimental heat capacity data is acquired from Satoh et al. [147].

polymorphs of a single composition, it is limited by the fact that one of its parameters is an extensive variable that is challenging to control: the defect concentration, x . In reality, the synthesis environment often controls the conjugate variable: the chemical potential, μ . The specific values of chemical potentials “seen” by the forming product during synthesis determine the various defect “costs”. For example, an oxygen vacancy will have a higher formation energy (higher cost) in an oxygen-rich environment due to the larger μ_{O} term appearing in Equation 2.10.

Rather than assuming a fixed concentration of defects and then identifying the polymorph with the lowest Φ , it is possible to solve for the defect formation energies at a particular set of chemical potentials, use these to determine the equilibrium defect concentrations, and then include the *total* energetic cost of all the equilibrium defects within the Gibbs free energy equation for the phase. We model this as

$$G(P, T) = G_{\text{bulk}}(P, T) - k_B T \sum_i c_i^{\text{eq}}(P, T), \quad (4.5)$$

where G_{bulk} is the Gibbs free energy of the bulk phase, P is pressure, T is temperature, k_B is Boltzmann’s constant, and c_i^{eq} is the equilibrium defect molar concentration for a defect indexed i . Equation 4.5 accounts for the total free energy decrease from all point defects at their equilibrium concentrations, i.e., where $\frac{\partial G}{\partial c_i} = 0$ [28]. Note that it is possible to approximate the Gibbs free energy of the bulk phase as $G_{\text{bulk}} \approx E_{\text{bulk}}$. This assumes that the bulk mechanical (PV) term is small (which is conventionally assumed) and that the bulk entropic (TS) term is minimal.

The polymorph with the minimum G (Equation 4.5) at a particular set of chemical potentials is predicted to be the equilibrium (stable) structure, regardless of whether its pristine bulk structure is nominally the ground-state polymorph. Put simply, if a metastable polymorph can accommodate charged defects of a certain type much more easily than the ground-state structure, its higher bulk energy may be offset by its lower defect formation energies. This suggests that the metastable may be synthesizable because it is *actually* the stable phase during synthesis, i.e., synthesizability via the principle of remnant metastability, as proposed by Sun et al. [26].

Using the chemical potential diagram, it is possible to visualize phase boundaries from Equation 4.5. To do this, one superimposes the stability regions of all polymorphs for a particular bulk composition on that composition’s stability domain on the chemical potential diagram. For example, consider the synthesis of YMnO_3 , as previously discussed in Sections 4.2 and 4.3. If we use the same DFT-calculated defect thermodynamics as shown in Figure 4.6, we can generate a defect-dependent chemical potential diagram for this system and target, as shown in Figure 4.12.

Figure 4.12 reaffirms both the conclusions from the previously calculated phase diagram (Figure 4.7) and the literature: $\alpha\text{-YMnO}_3$ is stabilized at high oxygen chemical potentials (i.e., oxygen-rich environments).

4.5 Synthesis of layered sodium iron oxide $\alpha\text{-NaFeO}_2$

In this section, we turn to another system: sodium iron oxide (NaFeO_2), and perform a case study of the selective synthesis of the layered α phase. The controlled synthesis of layered transition metal oxides (AMO_2 , where A is an alkali metal, and M is a transition metal) is one of the most critical aspects of the development of battery materials. Candidate compounds include LiCoO_2 and related compounds containing Ni, Mn, Fe, Al, and other transition metals [149–156], as well as their sodium analogs [157–166] are numerous methods reported to fabricate these layered metal oxides, including direct solid-state synthesis [154, 155, 164–170], hydrothermal [171], molten salts [158, 172–174], precipitation [149, 150, 175–178], and vapor deposition among other methods [151–153, 179–181]. Each of these synthesis techniques imparts unique morphologies, sizes, as well as transition-metal ordering within the crystal lattice that mediate electrode fabrication and electrochemical performance [174, 177, 178, 181–184].

One such cathode material is $\alpha\text{-NaFeO}_2$, also known as $O3$ -type NaFeO_2 due to its stacking, which has a layered rock-salt structure (Figure 4.13a) that provides routes for Na-ion mobility [185]. With an operating voltage of 3.3 V vs. Na/Na^+ and its high earth abundance, $\alpha\text{-NaFeO}_2$ is a promising cathode material for sodium-ion batteries [186]. $\alpha\text{-NaFeO}_2$ is commonly synthesized by mixing a Na-containing precursor (Na_2CO_3 , NaOH , Na_2O_2) with iron oxide ($\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4) and heating the sample between 400 and 700 °C [186–193]. However, care must be taken to select the correct precursors and synthesis

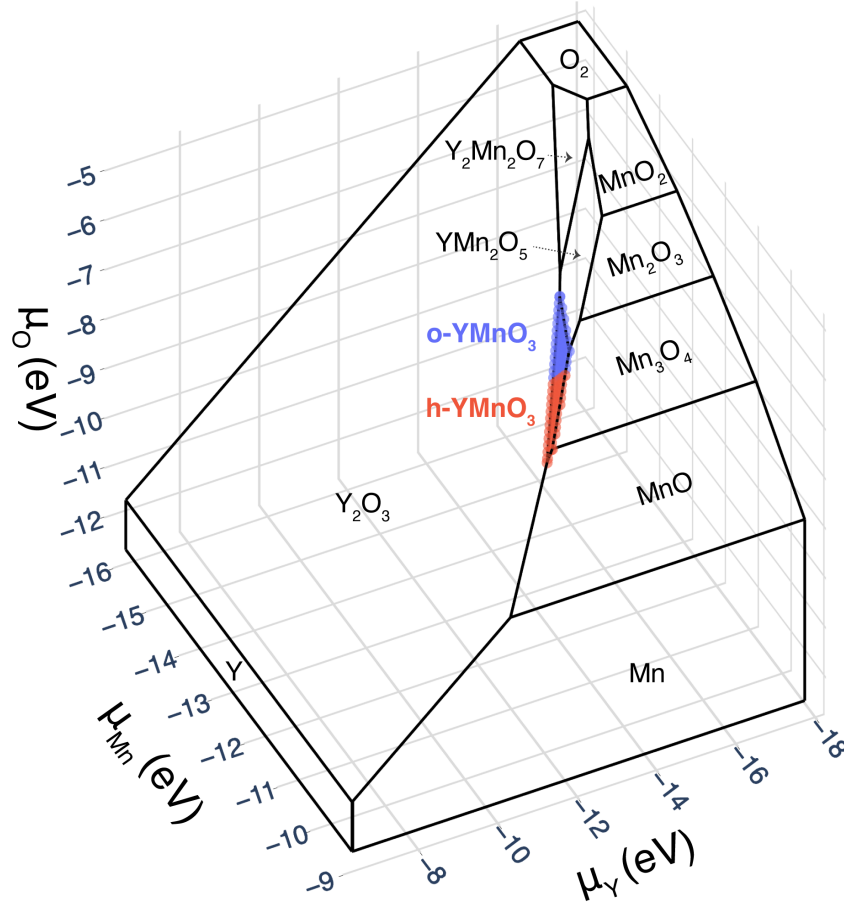


Figure 4.12: Defect-dependent polymorph stability of YMnO_3 visualized on the chemical potential diagram. $\alpha\text{-YMnO}_3$ (blue) appears to be stabilized over the ground-state structure (h-YMnO_3 , red) at higher oxygen chemical potentials, as extensively confirmed in the literature.

conditions; several different polymorphs of NaFeO_2 exist (Figure 4.13) and, often, a mixture of both α - and β - NaFeO_2 (wurtzite-like structure) is formed during synthesis [190].

Here, we report the direct synthesis of $\alpha\text{-NaFeO}_2$ by mechanochemical milling of Na_2O_2 and $\gamma\text{-Fe}_2\text{O}_3$. In our procedure, $\alpha\text{-NaFeO}_2$ is synthesized without any additional heat treatments. While many cathode materials have been synthesized by mechanochemical methods, in this study, we performed density functional theory (DFT) calculations to understand the stability of α - and β - NaFeO_2 and discuss the role of charged point defects (especially vacancies) in preferentially stabilizing the α phase over the other known NaFeO_2 polymorphs in oxygen-rich environments. Upon annealing the as-milled material, we obtained a sample with larger particle sizes, higher crystallinity, and improved electrochemical properties.

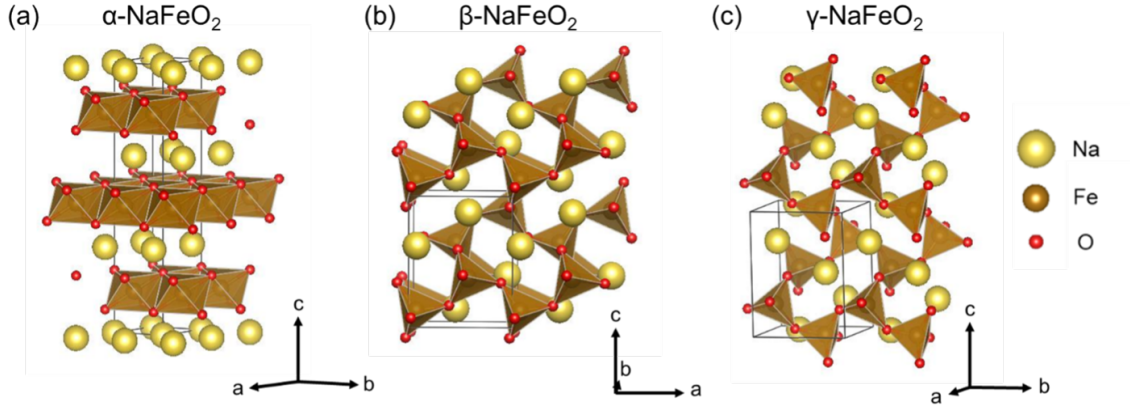


Figure 4.13: Polymorphs of NaFeO_2 . (a) $\alpha\text{-NaFeO}_2$ ($R\bar{3}m$) has a layered structure with Na ions between FeO_2 layers. (b) $\beta\text{-NaFeO}_2$ ($Pna2_1$) has a wurtzite-like structure with corner-shared Fe tetrahedra, and (c) $\gamma\text{-NaFeO}_2$ ($P2_12_12_1$) is a high-temperature phase similar to $\beta\text{-NaFeO}_2$, with orthorhombic symmetry. The black outline represents the unit cell of each structure.

DFT calculations

Density functional theory calculations were performed using the Vienna Ab initio Simulation Package (VASP, v6.2.1) with Projector Augmented Wave (PAW) pseudopotentials [46, 122]. All relaxation calculations were performed with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [118] within the Generalized Gradient Approximation with Hubbard U (GGA+ U) using a plane wave cutoff energy of 520 eV. A value of $U = 5.3$ eV was used for Fe, as determined via the approach from Wang et al. [80] and implemented in *pymatgen* [194]. The HSE06 exchange-correlation functional [195] was used for the calculation of band structures used in point defect corrections.

The α -, β -, and γ - NaFeO_2 structures were originally acquired from the Materials Project database [12] with identifiers *mp-19359*, *mp-21060*, and *mp-21880*, respectively. Collinear magnetic orderings were determined for each structure via the magnetic orderings workflow developed by Horton et al. [125] and implemented in the *atomate* package [55].

Point defect formation energies were calculated using the charged defect supercell approach with finite-size corrections developed by Freysoldt et al. [62] and implemented by Broberg et al. [53]. Only charged vacancies were considered in our analysis. We included all integer charge states in the ranges Na: [-1, 1], Fe: [-4, 4], and O: [-2, 2]. Vacancy sites were identified using *pymatgen*, and all supercell structures were constructed with a scaling of 3x2x2, resulting in a total size of 192 atoms for each calculation. Each defected structure was initialized with its corresponding magnetic ordering, as identified via the aforementioned workflow.

The Na-Fe-O chemical potential diagram was constructed using thermodynamic data acquired from the Materials Project (v2021.11.10) via the approach described by Todd et al. [95] and in Section 2.3 of this dissertation. The relative stability of the bulk phases and

their regions of stability on the chemical potential diagram were calculated at $T = 0$ K (i.e., without finite temperature effects). The chemical potentials have not been re-referenced and are plotted with respect to the energy output from the VASP calculations.

The thermodynamic stability of NaFeO_2 polymorphs as a function of environmental chemical potentials was determined by identifying the polymorph with the minimum Gibbs free energy (including the contribution from equilibrium defect concentrations) following the approach described in Section 4.4. We approximated the Gibbs free energy of the bulk phase as $G_{\text{bulk}} \approx E_{\text{bulk}}$; i.e., assuming minimal contributions from the bulk mechanical (PV) and bulk entropic (TS) terms. A temperature of $T = 1000$ K (slightly above the annealing temperature of 700 °C) was used in Equation 4.5 and in the self-consistent solution of the Fermi energy, E_F , that enters in the calculation of equilibrium defect concentrations. The Fermi energy was solved for in a self-consistent fashion at each set of chemical potentials within the bounds of the NaFeO_2 stability region on the Na-Fe-O chemical potential diagram. This resulted in changes in the vacancy formation energies and, thus, equilibrium concentrations as a function of chemical potentials.

Mechanochemical Synthesis of $\alpha\text{-NaFeO}_2$

$\alpha\text{-NaFeO}_2$ was synthesized through a mechanochemical process without external heating. The selection of Fe_2O_3 precursor polymorph and the amount of milled material were critical to polymorphic control.

The Fe_2O_3 precursor selected played a role in the resulting NaFeO_2 product that was synthesized. Reactions between Na_2O_2 and $\alpha\text{-Fe}_2\text{O}_3$ resulted in a mixture of α - and β - NaFeO_2 , while for the same conditions, reactions between Na_2O_2 and $\gamma\text{-Fe}_2\text{O}_3$ resulted in pure $\alpha\text{-NaFeO}_2$. The XRD results from these mechanochemical reactions are shown in Figure C.8. As previously reported by Takeda et al., the formation of $\beta\text{-NaFeO}_2$ from $\alpha\text{-Fe}_2\text{O}_3$, and $\alpha\text{-NaFeO}_2$ from $\gamma\text{-Fe}_2\text{O}_3$, is likely due to the similarity in the oxygen packing in the structure of the starting materials as both $\beta\text{-NaFeO}_2$ and $\alpha\text{-Fe}_2\text{O}_3$ have hexagonal closest packing (*hcp*) of oxygen and $\alpha\text{-NaFeO}_2$ and $\gamma\text{-Fe}_2\text{O}_3$ have cubic closest packing (*ccp*) of oxygen [190]. However, the results obtained from this mechanochemical synthesis differ from the solid-state reactions that have been previously reported. In the solid-state reactions, both $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ will form $\alpha\text{-NaFeO}_2$ when reacted with Na_2O_2 above 400 °C. It is shown that in solid-state reactions with $\alpha\text{-Fe}_2\text{O}_3$, $\beta\text{-NaFeO}_2$ forms as an intermediate phase which proceeds to transform into $\alpha\text{-NaFeO}_2$ at 400 °C [190]. However, even with heating the sample to 700 °C for 12 hours, pure $\alpha\text{-NaFeO}_2$ is not obtained via the mechanochemical synthesis using $\alpha\text{-Fe}_2\text{O}_3$. Mechanochemical reactions with $\gamma\text{-Fe}_2\text{O}_3$, however, form $\alpha\text{-NaFeO}_2$ without any additional heating required. In solid-state reactions between $\gamma\text{-Fe}_2\text{O}_3$ and Na-containing precursors, $\gamma\text{-Fe}_2\text{O}_3$ is known to form a Na-doped $\gamma\text{-Fe}_2\text{O}_3$ structure before reacting fully to form $\alpha\text{-NaFeO}_2$ [190]. This intermediate Na-doped $\gamma\text{-Fe}_2\text{O}_3$ structure was not observed in this study, but the formation of this intermediate may be present at shorter milling times that were not investigated here.

Structure	Spacegroup	Magnetic Ordering	Bandgap (eV)	Stability (meV/atom)
Alpha (α)	$R\bar{3}m$	AFM	2.65	+8.7
Beta (β)	$Pna2_1$	AFM	3.32	+0 (stable)
Gamma (γ)	$P2_12_12_1$	AFM	3.21	+7.6

Table 4.4: Calculated properties of NaFeO₂ polymorph structures

The amount of material being milled at the same milling conditions is also important. When milling up to 2.25 g of the combined precursors (γ -Fe₂O₃ and Na₂O₂), the synthesis proceeded as predicted forming pure α -NaFeO₂; however, when the amount of precursor being milled was increased to 5 g, the synthesis forms a mixture of α - and β -NaFeO₂. The refinements of X-ray diffraction data for these experiments are shown in Figure C.8 in the Appendix.

The change in polymorph formation as a function of initial precursor mass could be due to several different possibilities. First, during the synthesis of α -NaFeO₂, a Na-doped γ -Fe₂O₃ phase forms which stabilizes γ -Fe₂O₃ [190]. Without this sodiation step, γ -Fe₂O₃ will transform to α -Fe₂O₃ at 400 °C. It is possible that with the additional material present, either less mixing occurs or the sample heating is altered, leading to less doping into γ -Fe₂O₃. Therefore, upon local heating during milling, α -Fe₂O₃ is formed which will react with Na₂O₂ to form β -NaFeO₂. Second, it is also possible that the formation of O₂ is limiting the sodiation of γ -Fe₂O₃. As the mass of precursors is increased, the amount of gas evolved from the precursors increases as well. Indeed, the sodiation of γ -Fe₂O₃ is slower when reacting NaNO₃ and γ -Fe₂O₃ in an atmosphere of O₂ rather than N₂ [189]. These results show that reaction environment and defect formation could play a large role in directing the synthesis of a specific polymorph. Understanding the role of defects and environmental conditions is critical to understanding how to direct synthesis in this system and for other layered transition metal oxides.

Phase stability of NaFeO₂ polymorphs

To better understand how synthesis conditions influence polymorph selection in NaFeO₂, charged point defect calculations were performed with density functional theory (DFT) on the three known NaFeO₂ structures: alpha (α), beta (β), and gamma (γ). To acquire the input structures, we first performed collinear magnetic ordering analysis and re-optimized the three NaFeO₂ polymorph structures initially obtained from the Materials Project. The ground-state magnetic orderings are illustrated in Figure 4.13. The calculated properties of these re-relaxed structures are shown in Table 4.4

With the acquired antiferromagnetic (AFM) orderings, β -NaFeO₂ is predicted to be stable from the DFT calculations using the GGA+U level of theory. The gamma phase is predicted to be the next most stable with an energy of 7.6 meV/atom above that of the ground state

(β) phase, followed by the α phase with an energy difference of +8.7 meV/atom above the ground state. The lowest energy AFM magnetic ordering was necessary for both correctly identifying this polymorph ordering and for converging the defect calculations, similar to what was found for YMnO_3 in Section 4.2 of this chapter.

The defect calculations reveal that the α - NaFeO_2 phase, which is nominally metastable, may be stabilized in oxygen-rich environments, i.e., where the oxygen chemical potential, μ_{O} , is high. The calculated vacancy formation energy diagrams for each of the NaFeO_2 polymorphs are plotted in Figure 4.14. Note that the defect formation energy diagram for β - NaFeO_2 (Figure 4.14b) contains two unique oxygen vacancy curves, as there are two symmetrically distinct oxygen vacancy sites in this polymorph.

While β - and γ - NaFeO_2 have very similar formation energy curves, it is apparent that α - NaFeO_2 has noticeably lower stability of the neutral oxygen vacancy charge state and consistently lower formation energies for cation vacancies (both Fe and Na). Indeed, as one varies the applied chemical potentials towards regions of higher μ_{O} (and correspondingly lower μ_{Fe} and μ_{Na}), the self-consistent solution of the Fermi energy for the α phase leads to low values ($E_F \rightarrow 0$), where Fe vacancies have a charge state of zero. When this is coupled with the low values of μ_{Fe} in this region, the result is a significant decrease in the formation energy of Fe vacancies ($\Delta E^f \rightarrow 0$), and thus a corresponding increase in the predicted equilibrium concentration of these defects. Hence, we find a defect-dependent phase transition where α - NaFeO_2 is stabilized by defect accommodation, as illustrated in the chemical potential diagram in Figure 4.15. This phase transition is predicted to become favorable near the three-phase point where NaFeO_2 is in thermodynamic equilibrium with the Na_4FeO_4 and Na_3FeO_3 . The α phase remains stable over the competing β and γ phases throughout the high oxygen chemical potential region.

We have noted via changes in color shading in Figure 4.15 where the predicted equilibrium molar defect concentrations rapidly increase to high concentrations ($> 10\%$), well above the typical “dilute limit” assumed in point defect calculations. Plots of equilibrium defect concentrations as a function of chemical potentials are shown in Figure C.11. It should be expected that defect-defect interactions will begin to occur before a 10% molar concentration is reached, the effects of which are not captured by our computational approach. However, the presence of a predicted transition from β - to α - NaFeO_2 should not be affected.

Interestingly, the γ - NaFeO_2 phase is not predicted to be stable over any set of chemical potentials. While the energy of the gamma phase is predicted to be lower than that of the α phase, it has very similar defect formation energy curves to β - NaFeO_2 , which means that it follows the same trends in Gibbs free energy as a function of chemical potentials (see Figure C.12). Even when β - NaFeO_2 is predicted to further stabilize at the low oxygen chemical potentials (near the Fe/ NaFeO_2 boundary in Figure 4.15), the free energy of the γ phase remains consistently higher.

The exact set of chemical potentials at which the $\beta \rightarrow \alpha$ phase transition is expected to occur is likely sensitive to small errors in calculations, including our assumption that differences in finite-temperature effects are negligible for both the free energies of each bulk phase as well as individual defect energies. We also did not model other intrinsic point defects

(e.g., interstitials and substitutions), which may contribute to defect-dependent stabilization. However, the presence of a phase transition dependent on oxygen chemical potential is meaningful and supported by experimental observations of NaFeO_2 synthesis. For example, Na_2O_2 is often used as a precursor (instead of Na_2O) for solid-state synthesis of NaFeO_2 , despite having a much less favorable reaction energy ($\Delta E_{\text{rxn}} = -0.073$ eV/atom for Na_2O_2 vs. -0.196 eV/atom for Na_2O) [154, 190]. Furthermore, the use of Na_2O_2 will result in the production of O_2 gas via the balanced reaction $\text{Na}_2\text{O}_2 + \text{Fe}_2\text{O}_3 \longrightarrow 2 \text{NaFeO}_2 + 0.5 \text{O}_2$, which may produce a locally oxidizing environment during synthesis, especially when performed in a sealed container. Finally, it has been suggested that the phase transition from $\alpha\text{-NaFeO}_2 \rightarrow \beta\text{-NaFeO}_2$ occurs at 760°C [196]. Since higher temperatures result in more reducing (i.e., lower μ_{O}) environments, this observation supports the predicted stability of the β phase at lower oxygen chemical potentials in Figure 4.15.

Defect-dependent stability phase diagrams, such as Figure 4.15, can be used to both rationalize the appearance of a metastable phase under certain synthesis conditions and as a tool for designing synthesis routes that target a specific phase. In this case, the proximity of the $\alpha\text{-NaFeO}_2$ region (red) to the binary phases Na_2O_2 (or NaO_2) and Fe_2O_3 suggests that these phases would be optimal precursors for targeting the α phase. The shared phase boundary between $\alpha\text{-NaFeO}_2$ and O_2 also suggests that an oxygen-rich environment would be most suitable for the synthesis of the α phase. These predictions are supported by our mechanochemical synthesis approach, which directly uses or involves Na_2O_2 , Fe_2O_3 , and O_2 gas.

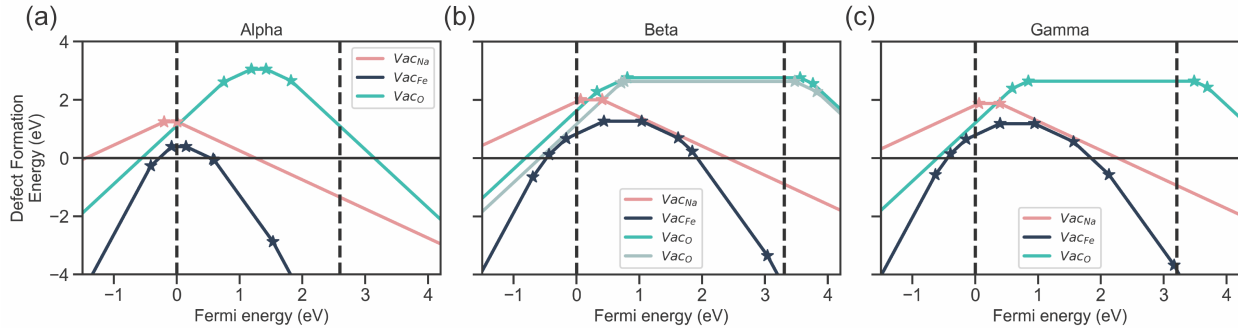


Figure 4.14: Calculated defect formation energies and charge state transitions as a function of Fermi energy for vacancies in the (a) α , (b) β , and (c) γ phases of NaFeO_2 . The defect formation energy curves shown are calculated at chemical potentials corresponding to where NaFeO_2 is thermodynamically stable with Na_4FeO_4 and Na_3FeO_3 , near where $\alpha\text{-NaFeO}_2$ is predicted to be stabilized over the β phase (i.e., $\mu_{\text{Na}} = -3.28$ eV, $\mu_{\text{Fe}} = -12.10$ eV, and $\mu_{\text{O}} = -5.76$ eV).

Comparison of as-milled and annealed samples

The as-milled samples were annealed to increase crystallinity, to further react any remaining $\gamma\text{-Fe}_2\text{O}_3$ and Na_2O_2 , and to study changes in material performance because of heat treatment.

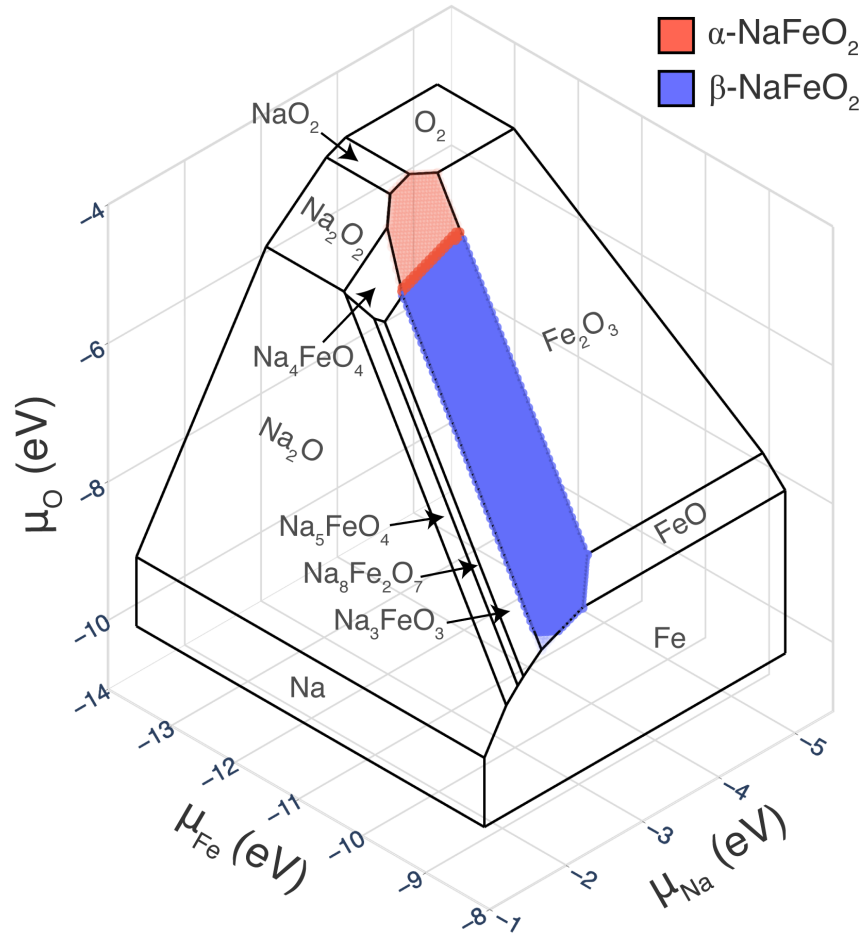


Figure 4.15: Defect-dependent stability phase diagram of NaFeO_2 polymorphs from density functional theory calculations. The stability of the α , β , and γ polymorphs is compared as a function of elemental chemical potentials on the Na-Fe-O chemical potential diagram. Color shading indicates the stable polymorph at each point on the chemical potential diagram surface, bounded by the stability of the NaFeO_2 bulk composition. The gamma (γ) phase is not predicted to be stable at any set of chemical potentials and hence does not appear on the diagram. Lighter shading denotes regions where at least one defect exceeds 10% molar concentration (i.e., well above the dilute limit assumed in point defect calculation methodology).

Upon annealing at 700 °C for 12 hours, an increase in the particle size of the samples was observed using scanning electron microscopy (SEM). The as-milled sample, Figure 4.16a,c contains both small particles ($< 5 \mu\text{m}$) and larger faceted particles ($\sim 30 \mu\text{m}$), while the annealed sample, Figure 4.16b,d contains larger consolidated particles ($> 50 \mu\text{m}$) and fewer small particles. Images obtained in backscattering mode, Figures 4.16c,d show that the particles are relatively uniform in composition throughout the sample.

The sample stoichiometry was investigated using inductively coupled plasma-optical emission spectroscopy (ICP-OES) ICP-OES measurements showed that the annealed sample has

a lower Na:Fe ratio. The observed Na:Fe ratio for the as-milled sample was 1.03:1, while the annealed sample was 0.94:1, with an error of ± 0.006 for the Na measurement and ± 0.01 for the Fe measurement. TGA measurements of as-milled sample shown in Figure C.13 indicate that there is a mass loss upon heating which most likely corresponds to a removal of a Na carbonate-terminated particle surface rather than a loss of Na within the bulk of the particles. Therefore, the overall Na:Fe ratio of the samples remains consistent during the annealing process.

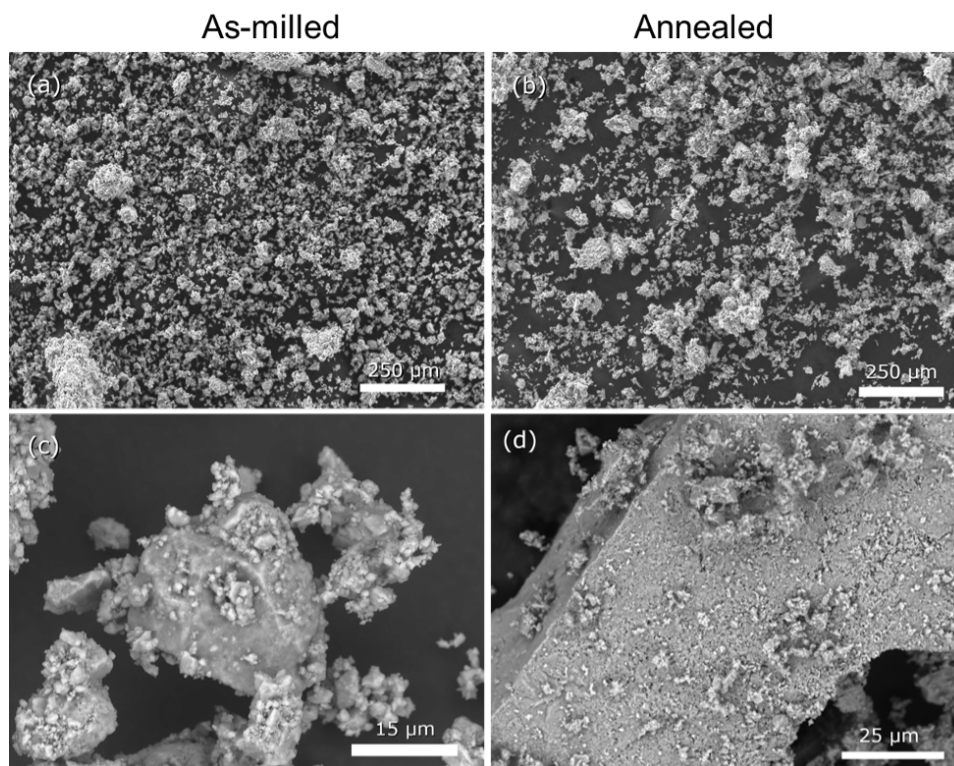


Figure 4.16: Scanning electron micrographs of as-milled (a) and annealed (b) NaFeO_2 in secondary electron imaging show larger particles present for the annealed samples. Backscattered electron images of as-milled (c) and annealed (d) NaFeO_2 indicate that the particles within each sample have the same composition.

The X-ray powder diffraction data for the as-milled and annealed samples showed diffraction peaks that were largely consistent with the reported $R\bar{3}m$ model for $\alpha\text{-NaFeO}_2$ [197] from a Rietveld refinement of the structural model. The peaks for the annealed sample were sharper than for the as-milled sample, indicating an increase in long-range ordering. Some additional peaks were observed at 2.1 , 2.2 , 2.7 , 3.1 , and 3.6° that are consistent with $\beta\text{-NaFeO}_2$.

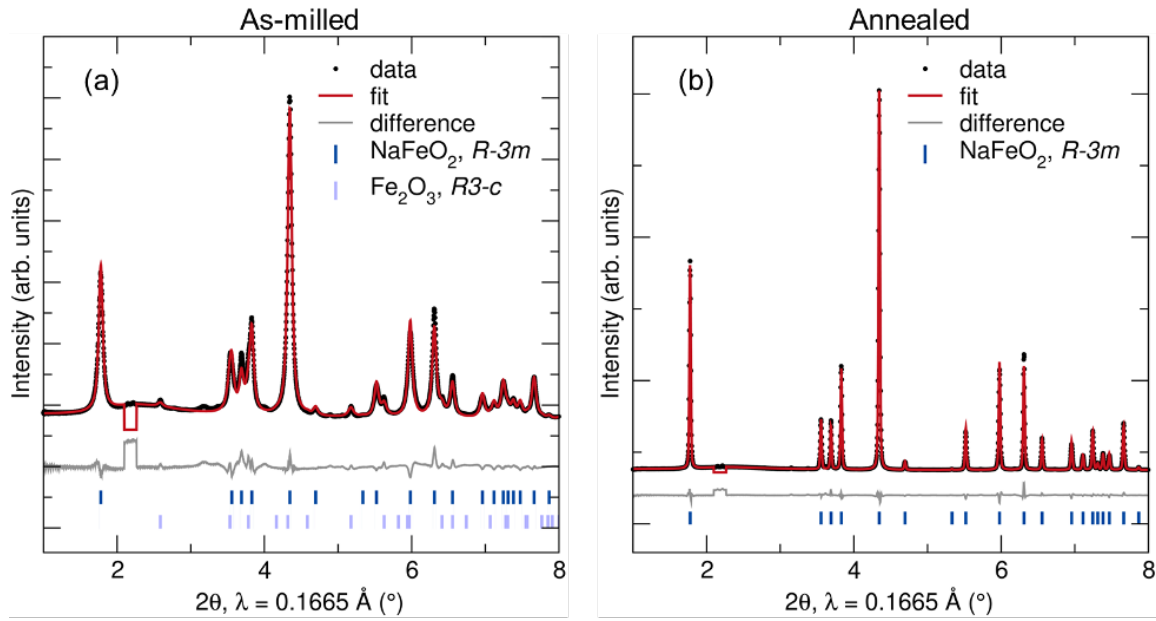


Figure 4.17: Rietveld refinements of synchrotron XRD data showing the structural differences in (a) as-milled and (b) annealed NaFeO_2 . The XRD pattern for the as-milled sample has more impurity peaks and broader peaks, indicating a lower crystallinity than observed in the annealed sample.

Chapter 5

Rationalizing selective phase formation with chemical potential diagrams

In this chapter, we describe an approach for searching large chemical spaces to identify selective reactions based on differences in chemical potentials at interfaces. Using the assisted metathesis of yttrium manganese oxides as a case study, we use our approach to explain why the nominally “innocent” Na_2CO_3 precursor enables the synthesis of single-phase $\text{Y}_2\text{Mn}_2\text{O}_7$ – an outcome that was previously only accomplished at extreme pressures and which cannot be achieved with closely related precursors of Li_2CO_3 and K_2CO_3 under identical conditions. Using the previously described solid-state reaction network model, we enumerate all possible reactions to $\text{Y}_2\text{Mn}_2\text{O}_7$ in an expanded chemical space including Y, Mn, O, alkali metals, and halogens, using thermodynamic parameters obtained from density functional theory calculations. From this, we identify reactions that minimize the thermodynamic competition from intermediates, using the sum of differences in chemical potential across all possible reactant-product interfaces as a competition cost metric. We show that only the Na-based intermediates minimize the distance in the hyperdimensional chemical potential space to $\text{Y}_2\text{Mn}_2\text{O}_7$, thus providing selective access to a phase that was previously thought to be metastable. Experimental evidence validating this mechanism for pathway-dependent selectivity is provided by intermediates identified from *in situ* synchrotron-based crystallographic analysis.

The approach of calculating chemical potential distances in hyperdimensional compositional spaces provides a general method for designing selective solid-state syntheses that will be useful for gaining access to metastable phases and for identifying reaction pathways that can reduce the synthesis temperature, and cost, of technological materials.

Note: This chapter is closely adapted from a prior journal publication of which I am a co-first author; see Ref. 95: Todd, P. K. *et al.* Selectivity in Yttrium Manganese Oxide Synthesis via Local Chemical Potentials in Hyperdimensional Phase Space. *Journal of the American Chemical Society* **143**, 15185–15194 (2021).

5.1 The challenge of designing selective solid-state reactions

To address the challenge of designing selective reactions in solid-state chemistry, one must have an understanding of how the reaction proceeds. Pairwise reactions at interfaces between solids dominate selection of a reaction pathway [19, 22]. With the inclusion of additional elements, as in metathesis reactions [16, 198], one can avoid highly stable and thus unreactive intermediates, as demonstrated in the formation of MgCr_2S_4 while avoiding the inert reactant Cr_2S_3 [199, 200]. As we have discussed extensively in this work, “assisted” metathesis reactions reach quantitative yields at lower temperatures than conventional ceramic reactions [201], and they can even exhibit product selectivity depending on which alkali ($A = \text{Li}, \text{Na}, \text{K}$) carbonate precursor is used. This was seen for the reactions of $3 A_2\text{CO}_3 + 2 \text{YCl}_3 + \text{Mn}_2\text{O}_3$, where in the case of Li_2CO_3 the reaction selectively forms orthorhombic YMnO_3 , Na_2CO_3 yields $\text{Y}_2\text{Mn}_2\text{O}_7$, and K_2CO_3 does not yield selectivity [92].

Using the yttrium manganese oxide system once again as a case study system, a central challenge addressed by this work is to understand the origin of the different product outcomes that result from changing an ancillary precursor that is not directly involved in any elementary reaction producing a yttrium manganese oxide. In conventional stoichiometric reactions using binary yttrium oxide and manganese oxide precursors, hexagonal YMnO_3 , denoted h- YMnO_3 , forms at temperatures greater than 950 °C [202, 203]. Previous reports have described the synthesis of $\text{Y}_2\text{Mn}_2\text{O}_7$ under high temperatures and highly oxidizing conditions (1100 °C and 4 GPa with $\text{KIO}_4 \longrightarrow \text{KIO}_3 + \frac{1}{2}\text{O}_2$) [204] or hydrothermally under oxidizing conditions ($\text{NaOH}, \text{NaClO}_3$ in H_2O at 500 °C and 3 GPa) [205], leading to its previous characterization as a metastable phase [206]. Interestingly, thermogravimetric analysis shows the $\text{Y}_2\text{Mn}_2\text{O}_7$ pyrochlore to be stable up to 800 °C, above which it decomposes to the perovskite YMnO_3 [205]. Therefore, if $\text{Y}_2\text{Mn}_2\text{O}_7$ is stable at the lower temperatures, its stability cannot solely explain why only the sodium-based assisted metathesis precursors are selective for its formation given the low reaction temperatures for all of the alkali metathesis reactions.

5.2 Computational methods

Calculating thermodynamic free energies

DFT-based atomic structures and formation enthalpies for material phases in the Y-Mn-O-Na-Li-K chemical systems were acquired from the Materials Project (MP) database, version 2021.05.13 [12]. Gibbs free energies of formation, $\Delta_f G^0(T)$, of solid DFT compounds were estimated using the machine-learned Gibbs free energy descriptor approach implemented by Bartel, et al. [69] and applied to MP data (see Chapter 2.2). The *pymatgen* package was used to perform convex hull phase stability analysis [76].

To model the energetics of reactions occurring in flowing O_2 gas, the grand potential energy, Φ , was used as the relevant thermodynamic potential defined as

$$\Phi = G(P, T) - \mu_{\text{O}} N_{\text{O}}, \quad (5.1)$$

where Φ is normalized to the number of non-oxygen atoms. Since in place of $G(P, T)$ we used standard Gibbs free energies of formation, $\Delta G_f^0(T=650^\circ\text{C})$, the chemical potential of oxygen was assigned a value of zero, i.e., $\mu_{\text{O}} = \mu_{\text{O}}^0$ ($p = 0.1$ MPa, $T = 650$ °C). While this did not result in a shift in the total grand potential energy of any particular phase, it did change the number of atoms used for normalization and hence affected the magnitude of the normalized reaction energies, $\Delta\Phi_{\text{rxn}}$.

Calculation of chemical potential “distance”

The “chemical potential distance”, $\Delta\mu_{\min}(P_a, P_b)$, between any two phases P_a and P_b was calculated geometrically by finding the minimum Euclidean distance between the domains (i.e., the convex stability polytopes) of each phase on the chemical potential diagram. This was accomplished practically by computing the minimum Euclidean distance between all pairs of vertices ($\boldsymbol{\mu}_{a_i}$, $\boldsymbol{\mu}_{b_j}$) defining each of the two convex polytopes of phases P_a and P_b :

$$\Delta\mu_{\min}(P_a, P_b) = \min_{i,j} \left\{ \|\boldsymbol{\mu}_{a_i} - \boldsymbol{\mu}_{b_j}\| \right\} \quad (5.2)$$

While the minimum distance between vertices is not necessarily equivalent to the minimum distance between any facet of the polytopes, the implementation of the more accurate distance calculation is nontrivial. We thus found the vertex-based k-d tree method, as implemented in SciPy, to be an appropriate trade-off between computational complexity and accuracy.

Enumerating reactions with $\text{Y}_2\text{Mn}_2\text{O}_7$ as a product

Chemical reactions with $\text{Y}_2\text{Mn}_2\text{O}_7$ as a product were enumerated via the network-based approach described in Chapter 3, and implemented in the *reaction-network* Python package (Appendix A). In this work, reactions up to a size $n = 2$ are enumerated from the set of 2,878 phases predicted to be stable at $T = 650^\circ\text{C}$ within the alkali metal (Li, Na, K, Rb, Cs), halogen (F, Cl, Br, I), carbon (C), and target (Y, Mn, O) chemical system. To account for the system being open to oxygen gas, we also consider reaction equations with oxygen as an optional reactant or product beyond the $n = 2$ limitation.

The enumerated reactions were compared against each other by using both the normalized reaction free energy and a “total” chemical potential distance for the reaction as “cost” variables. For the purposes of ranking reactions, the total cost of a reaction, C , was calculated using the softplus function with an equally weighted mean between the two cost variables

$$C = \ln \left(1 + \frac{273}{T} \exp \left(\frac{\Delta\Phi_{\text{rxn}} + \sum \Delta\mu_{\min}}{2} \right) \right), \quad (5.3)$$

where T corresponds to a temperature of $T = 923$ K, the reaction energy, $\Delta\Phi_{\text{rxn}}$, corresponds to the normalized change in grand potential energy, and $\sum \Delta\mu_{\text{min}}$ represents the total chemical potential distance for a reaction, which is calculated as the sum of the (minimum) chemical potential distances between all possible pairwise interfaces in the reaction, excluding the interface(s) between the reactants. For example, in the hypothetical reaction $A+B \rightarrow C+D$, the total chemical potential distance is calculated by taking the summation of $\Delta\mu_{\text{min}}(A, C)$, $\Delta\mu_{\text{min}}(A, D)$, $\Delta\mu_{\text{min}}(B, C)$, $\Delta\mu_{\text{min}}(B, D)$, and $\Delta\mu_{\text{min}}(C, D)$.

The full set of enumerated chemical reactions, as well as all experimental raw data, processed data, data processing scripts, and figure plotting scripts, are available at <https://github.com/GENESIS-EFRC/y2mn2o7-selectivity>. The entire reaction enumeration and ranking approach has also been implemented within the aforementioned reaction-network Python package and can be applied in a similar fashion to recommend precursors for synthesizing other target materials. The applicability of this approach beyond the Y-Mn-O system is the subject of future work(s).

5.3 Reaction pathway from phase evolution

In situ synchrotron powder X-ray diffraction (SPXRD) studies were used to identify the intermediate phases and reaction pathways that permit the selective formation of $\text{Y}_2\text{Mn}_2\text{O}_7$ through assisted metathesis reactions with Na_2CO_3 . Figure 5.1 shows the integrated SPXRD diffraction patterns collected during a reaction using precursor phases of $\text{Mn}_2\text{O}_3 + 2\text{YCl}_3 + 3\text{Na}_2\text{CO}_3$. Data were collected during heating to 650°C at $10^\circ\text{C}/\text{min}$ then dwelling at 650°C for 60 min, performed under flowing oxygen. Quantitative phase analysis using the Rietveld method reveals the identities and phase fractions of intermediates of $\text{P3-Na}_x\text{MnO}_2$, $\text{P2}'\text{-Na}_x\text{MnO}_2$, YOCl , $\text{Y}_3\text{O}_4\text{Cl}$, Y_2O_3 ; products of NaCl and $\text{Y}_2\text{Mn}_2\text{O}_7$; and a small amount of Na_3MnO_4 impurity, as summarized in Figure 5.1. No other yttrium manganese oxide phases were observed.

The relevant intermediates that exist at the onset of formation of $\text{Y}_2\text{Mn}_2\text{O}_7$ are Y_2O_3 , $\text{P3-Na}_x\text{MnO}_2$, and a small amount of Mn_2O_3 . Y_2O_3 forms with a very small particle size (less than ~ 35 nm), and its production yields a large fraction of the expected NaCl product (Figure 5.1). $\text{P3-Na}_x\text{MnO}_2$ forms directly from the reaction of Na_2CO_3 and Mn_2O_3 , in agreement with a previous *in situ* and computational study [22]. Once both of these key intermediates are present, $\text{P3-Na}_x\text{MnO}_2$ then reacts with Y_2O_3 to form pyrochlore $\text{Y}_2\text{Mn}_2\text{O}_7$, also triggering the formation of $\text{P2}'\text{-Na}_x\text{MnO}_2$ ($Cmcm$ structure, with a slight shear of the ideal $\text{P2-P6}_3/mmc$ structure) [207–209]. Thereafter, selective formation of $\text{Y}_2\text{Mn}_2\text{O}_7$ is sustained through the reaction of $\text{P2}'\text{-Na}_x\text{MnO}_2$ with Y_2O_3 . After $\text{P3-Na}_x\text{MnO}_2$ is fully consumed, the rate of $\text{Y}_2\text{Mn}_2\text{O}_7$ production slows dramatically, as Na_3MnO_4 gradually forms (Figure 5.1). Na_3MnO_4 does not appear in reaction products of *ex situ* studies of these assisted metathesis reactions performed on bulk scales, although it may be present as a trace quantity [92].

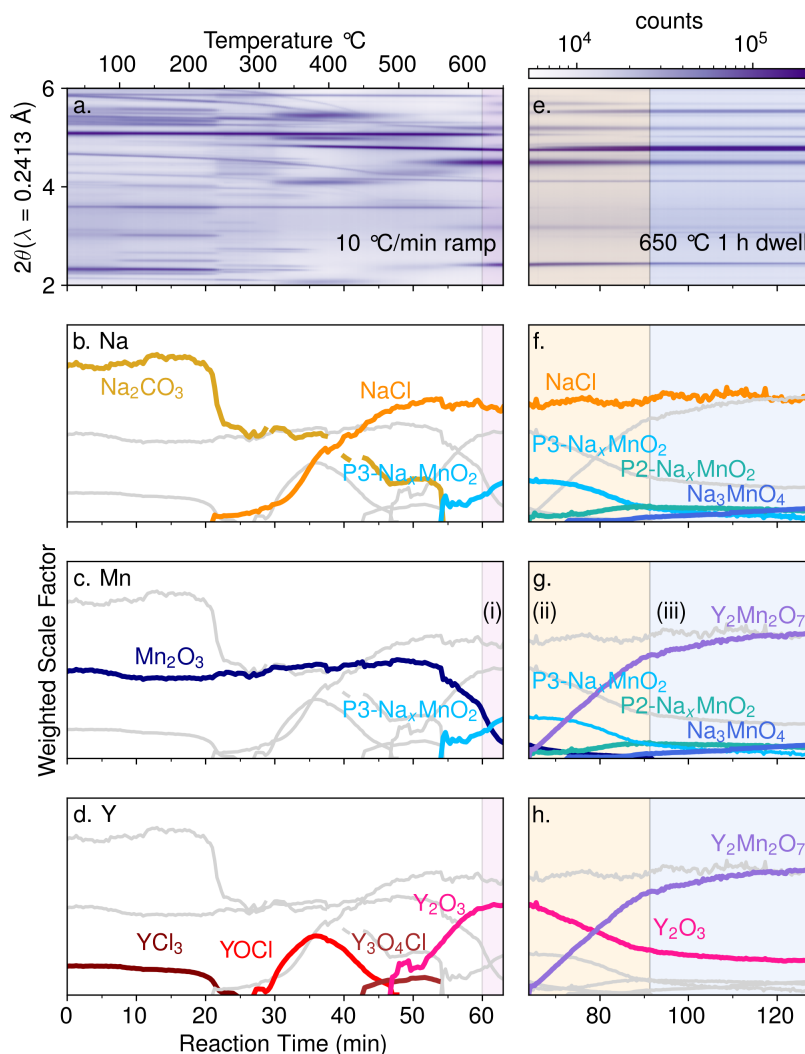


Figure 5.1: *In situ* SPXRD data and calculated weighted scale factors from sequential Rietveld analysis as a function of time for the reaction: $\text{Mn}_2\text{O}_3 + 2 \text{YCl}_3 + 3 \text{Na}_2\text{CO}_3 + \frac{1}{2} \text{O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 6 \text{NaCl} + 3 \text{CO}_2$ under flowing oxygen. The reaction is separated into two main vertical panels: (a-d) heating at 10 °C/min to 650°C and (e-h) dwelling at 650 °C for 60 min. (a,e) The *in situ* diffraction data plotted using a false color representation of the diffraction counts. Calculated weighted scale factors of phases over the course of the reaction are plotted and separated into horizontal panels by cation element: (b,f) sodium, (c,g) manganese, and (d,h) yttrium. The gray lines in each horizontal panel show the observed phases containing the other cations. The shaded regions (i), (ii), and (iii) correspond to trajectories highlighted in Figure 5.5.

5.4 Thermodynamic stability of $\text{Y}_2\text{Mn}_2\text{O}_7$

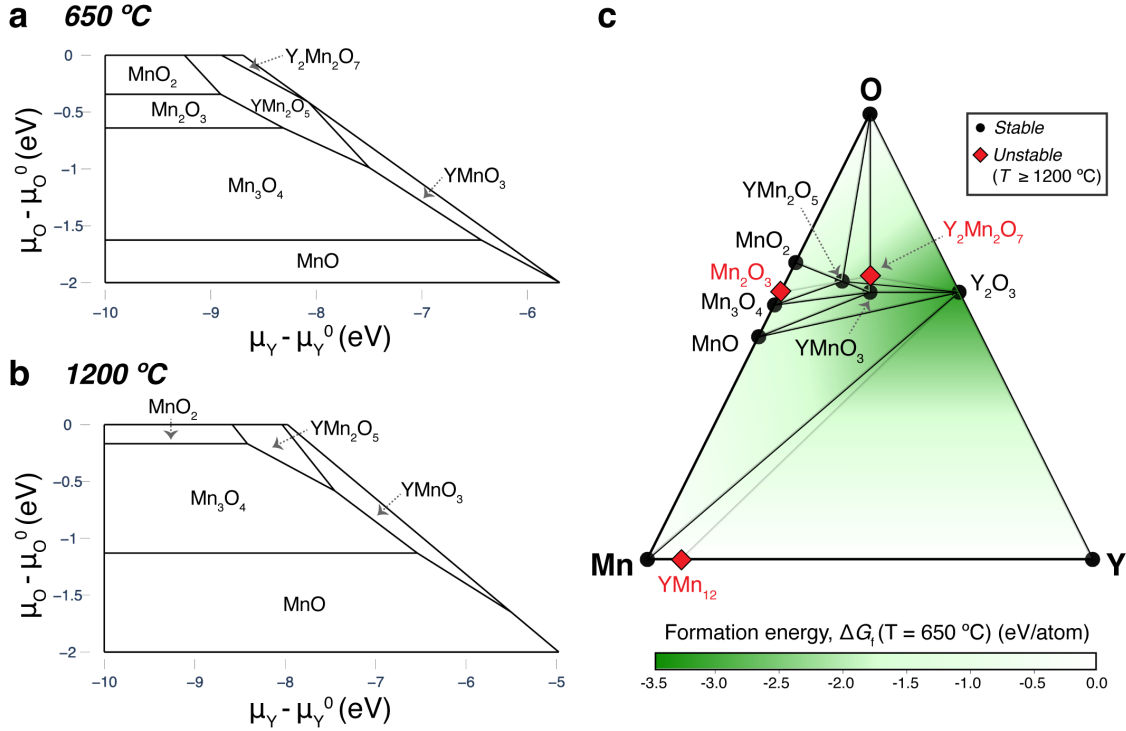


Figure 5.2: Computed phase stabilities in the Y-Mn-O chemical system. Predominance diagrams are shown as a function of oxygen and yttrium chemical potentials, μ_{O} and μ_{Y} , at temperatures of (a) 650 °C and (b) 1200 °C, referenced to their standard elemental state. (c) Predicted ternary compositional phase diagram for the Y-Mn-O system at 1200 °C (black lines/circles) overlaid on the phase diagram at 650 °C, where red squares and gray lines mark phases and facets that are destabilized at $T \geq 1200 \text{ °C}$, respectively. $\text{Y}_2\text{Mn}_2\text{O}_7$ is predicted to be stable at low temperatures ($T \leq 1100 \text{ °C}$).

Evaluation of the Y-Mn-O phase diagram reveals that $\text{Y}_2\text{Mn}_2\text{O}_7$ is thermodynamically stable (i.e., it is on the convex hull) at low temperatures ($T \leq 1100 \text{ °C}$). Using error-corrected formation energies derived from DFT calculations [11] and a previous Gibbs free energy model for solids [69], the phase diagram of the Y-Mn-O system has been calculated at finite temperatures relevant to the synthesis reactions being investigated, with results of calculations at 650 °C and 1200 °C shown in Figure 5.2. Figure 5.2a depicts that the predominance area of $\text{Y}_2\text{Mn}_2\text{O}_7$ is quite small, indicating its low relative stability with respect to thermodynamic decomposition to neighboring phases. For a 1:1 Y:Mn composition ratio in an environment open to oxygen, h- YMnO_3 is thermodynamically stable at all temperatures and under a wide range of oxygen chemical potentials, while $\text{Y}_2\text{Mn}_2\text{O}_7$ is thermodynamically stable only below $\sim 1100 \text{ °C}$ and at higher oxygen chemical potentials (i.e., oxygen-rich conditions). While the predicted temperature below which $\text{Y}_2\text{Mn}_2\text{O}_7$ is stable is overestimated by these calculations since only h- YMnO_3 was observed to form at 950 °C in experiments

[203], the low-temperature thermodynamic stability of $\text{Y}_2\text{Mn}_2\text{O}_7$ is assessed experimentally here by heating $\text{Y}_2\text{Mn}_2\text{O}_7$ in flowing oxygen at 650 °C for two weeks (Figure D.4 in Appendix), a result that is in agreement with previous thermogravimetric analysis [205]. The fact that the Li_2CO_3 and K_2CO_3 precursors do not produce the thermodynamically favored phase of $\text{Y}_2\text{Mn}_2\text{O}_7$ at temperatures below 950 °C and $p(\text{O}_2) = 1$ atm (i.e., $\mu_{\text{O}} - \mu_{\text{O}}^0 \approx 0$) indicates that the metathesis reaction temperatures are sufficiently low to yield kinetic control in the formation of $\alpha\text{-YMnO}_3$ or h-YMnO_3 [18]. Finally, it indicates the need for a deeper understanding of the specific factors that determine which reaction pathway is followed for a given alkali carbonate precursor.

5.5 Product selectivity via chemical potential distances

We hypothesize that the generalized chemical potential diagram, which was previously devised as a three-dimensional extension of predominance diagrams with application to modeling interface stability and reactivity [77], clarifies the large differences in product selectivity that arise by changing the identity of the alkali precursor. As the mathematical dual to the convex hull of the extensive energy-composition space, the generalized chemical potential diagram explicitly defines phase stability regions as bounded convex $n - 1$ dimensional polytopes within the full n -dimensional, intensive chemical potential space. Although in principle the chemical potential diagram conveys identical information as the traditional compositional phase diagram, it has the unique advantage of directly revealing the *relative* stability of phases. In fact, the volume of each phase’s stability polytope increases with its energy “below” the convex hull, i.e., the energy that would be released forming this phase via decomposition from the neighboring phases within a facet of the hull. The chemical potential diagram also directly links thermodynamic phase construction with atomic diffusion, and its construction even permits the visualization of diffusion paths in solid-state reactions [77]. Hence the chemical potential diagram is well-suited for application to understanding and predicting the local behavior of reactions at solid interfaces.

Selective reactions in solid-state chemistry need to minimize the probability of forming an undesired product phase at any point in time during the reaction pathway. As has been previously proposed [59], a reaction at the interface between two solid phases can proceed through either interface control or diffusion control, the latter resulting in local thermodynamic equilibrium and the corresponding requirement that elemental chemical potentials be continuous across the interfaces between reactants and product phase(s). All solid-state reactions eventually tend towards diffusion control as the product layer thickness grows. For this reason, predicted reactions which pose synthetic challenges are those in which it is impossible to achieve local equilibrium without decomposition to other phases before formation of the equilibrium product. On the chemical potential diagram, such reactions involve reactant-product pairs which do not share a phase boundary. Considering the reaction $\text{Y}_2\text{O}_3 + \text{Mn}_2\text{O}_3 \longrightarrow 2 \text{YMnO}_3$, if local equilibrium is achieved during the reaction, then according to Figure 5.3a, one expects YMn_2O_5 and/or Mn_3O_4 to form before formation

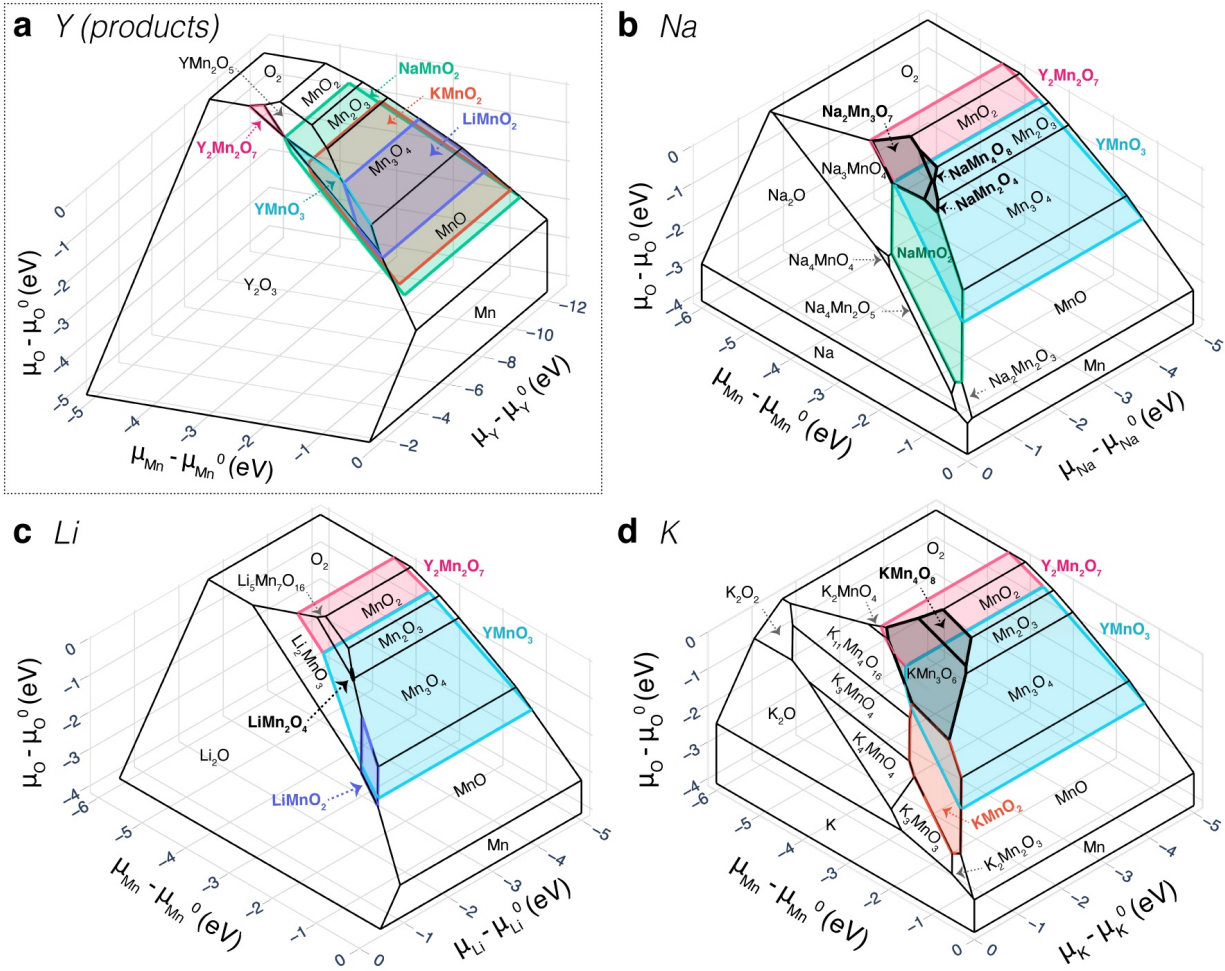


Figure 5.3: Chemical potential diagrams of the Y-Mn-O-Na-Li-K system at 650 °C, plotted in product (boxed) and reactant subspaces. (a) Y-Mn-O product subspace where the stability polytopes of stoichiometric NaMnO_2 (green), LiMnO_2 (purple), and KMnO_2 (orange) have been plotted as lower-dimensional slices, appearing as thin polyhedra due to the added degree of freedom (μ_Y). The NaMnO_2 polyhedron extends to high enough μ_O and low enough μ_{Mn} to reach $\text{Y}_2\text{Mn}_2\text{O}_7$, while the LiMnO_2 and KMnO_2 polyhedra do not. As such, LiMnO_2 and KMnO_2 suggest the formation of YMnO_3 and/or YMn_2O_5 depending on the value of μ_Y , as previously observed [92–94]. (b–d) A-Mn-O reactant subspaces with visualized slices of the YMnO_3 (cyan) and $\text{Y}_2\text{Mn}_2\text{O}_7$ (magenta) polytopes. The other shaded areas (gray) highlight A_xMnO_2 intermediates (and structurally-related neighbors) that lead directly to the formation of yttrium manganese oxide products.

of the final YMnO_3 product, consistent with the results of control reactions presented in Figure D.2 (Appendix) and the previously-reported phase diagram [203].

Therefore, selective reactions are those which can be balanced, produce the desired product, and minimize the distance in chemical potential space between pairwise reactant-product

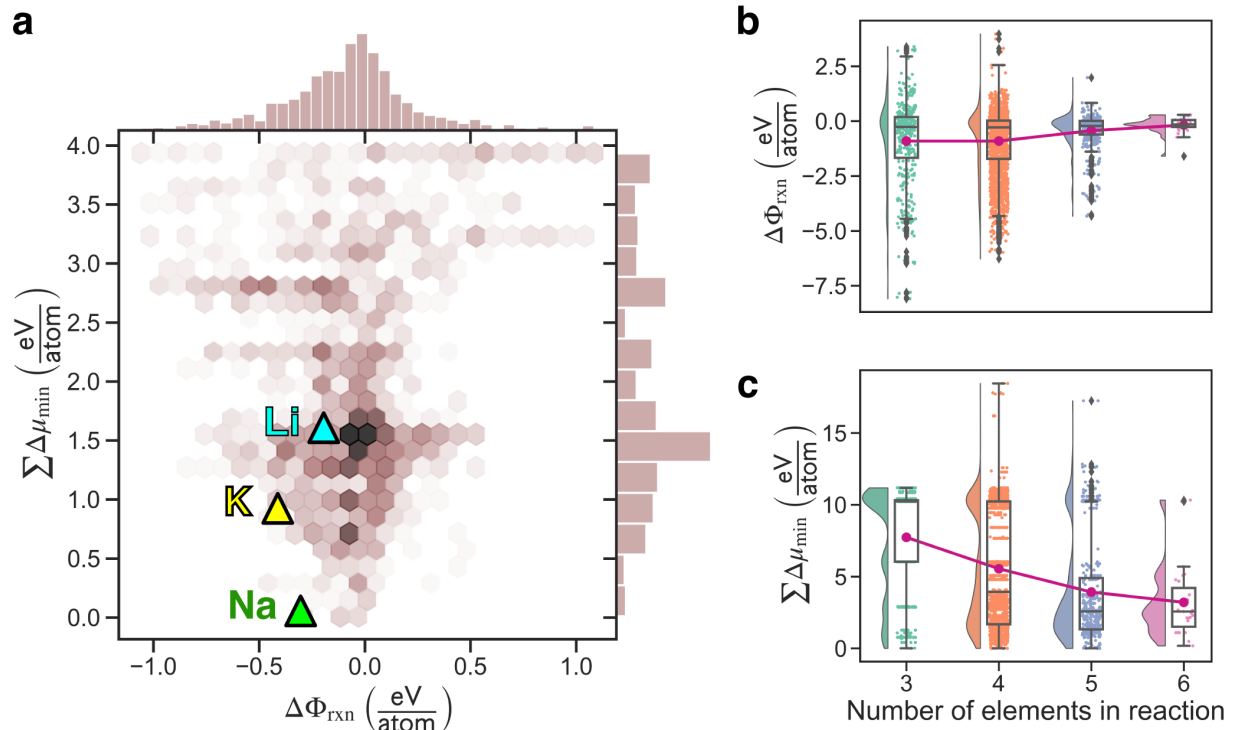


Figure 5.4: Energy and total chemical potential distance distributions for 3,017 predicted chemical reactions forming $\text{Y}_2\text{Mn}_2\text{O}_7$. The reactions were predicted from a chemical space consisting of all alkali metals (Li, Na, K, Rb, Cs), halogens (F, Cl, Br, I), carbon (C), and the target elements (Y, Mn, O). Oxygen was treated as an open element with a chemical potential corresponding to μ_{O}^0 ($p = 0.1$ MPa, $T = 650$ °C). (a) A hexbin plot showing the distribution of reaction energies (in grand potential), $\Delta\Phi_{\text{rxn}}$, and calculated total chemical potential distance values, $\Sigma\Delta\mu_{\text{min}}$ for each reaction. The three colored triangles indicate the specific reactions $2 \text{AMnO}_2 + 2 \text{YOCl} + \frac{1}{2} \text{O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 2 \text{ACl}$ for $A=\text{Li, Na, K}$. (b,c) Distributions of reaction energies and total chemical potential distances as a function of the number of elements in the reaction. All reactions include at least the three elements of the target phase (Y, Mn, O). The mean values for each distribution are connected by a magenta line.

interfaces. On the chemical potential diagram, this manifests as determining whether each reactant-product pair shares a boundary (i.e., zero distance) or is separated by the polytope(s) of one or more additional phases (i.e., non-zero distance). This also applies to product-product pairs, which may further react if they do not share a boundary on the chemical potential diagram. Plotting trial reactants in the three-dimensional chemical potential subspace of the product (Figure 5.3a), or plotting products in the reactant subspace (Figure 5.3b-d), permits direct visualization of the pairwise interfaces that control reactivity [19, 22]. The primary advantage of calculating a distance value rather than a Boolean variable for whether or not two phases share a boundary is that the distance is more robust against inaccuracies in thermochemical data. Furthermore, it conveys the degree to which the competing phases may interfere with the selectivity of the reaction.

Visualizing three-dimensional slices of the full Y-Mn-O-Na-Li-K chemical potential space reveals why only the sodium-based intermediates lead to the formation of $\text{Y}_2\text{Mn}_2\text{O}_7$. Figure 5.3a illustrates slices of the stoichiometric AMnO_2 intermediates in the Y-Mn-O product chemical potential space. The NaMnO_2 stability polyhedron extends well beyond the range of both the LiMnO_2 and KMnO_2 phases. In fact, this Na-containing phase extends into high enough μ_{O} values to reach the stability area for $\text{Y}_2\text{Mn}_2\text{O}_7$. This enhanced stability of the NaMnO_2 phase into higher oxygen (and lower manganese) chemical potentials suggests that it may be uniquely capable of forming a stable interface with $\text{Y}_2\text{Mn}_2\text{O}_7$ and facilitating direct reaction to this pyrochlore phase. Specifically, the nearly shared boundary between the NaMnO_2 intermediate and $\text{Y}_2\text{Mn}_2\text{O}_7$ means that the reaction kinetics should be facile since the local chemical potentials of Mn and O do not need to change as the intermediate converts to the product. Furthermore, even though the *global* oxygen chemical potential is controlled through partial pressure of O_2 , the reaction of NaMnO_2 provides *locally* available oxygen at the chemical potential required to form $\text{Y}_2\text{Mn}_2\text{O}_7$. In the case of the $\text{A} = \text{Li}, \text{K}$ precursors, the lack of available oxygen with an appropriately high chemical potential necessitates the reaction to proceed through other intermediates before it is even possible to reach $\text{Y}_2\text{Mn}_2\text{O}_7$.

The complementary inverse slices of the Y-Mn-O ternaries within the reactant A-Mn-O spaces (Figure 5.3b-d), along with the study of the atomic structures of the AMnO_2 phases, provide further explanation as to why the sodium-based intermediates facilitate reaction to $\text{Y}_2\text{Mn}_2\text{O}_7$ even for Na-deficient phases, Na_xMnO_2 (where $x < 1$). In agreement with prior work [210], the sodium-based phases show a strong preference for the layered $\alpha\text{-NaFeO}_2$ -type structures relative to tunnel-like (e.g., Ramsdellite-derived) or spinel-derived structures. $\text{Na}_2\text{Mn}_3\text{O}_7$, NaMn_2O_4 , and NaMn_4O_8 , illustrated as gray shaded areas in Figure 5.3b, are all predicted to share the structurally analogous layered framework with stoichiometric NaMnO_2 (Figure D.7a in the Appendix). Together these structures create an interconnected pathway along the Na-Mn-O chemical potential surface towards higher oxygen chemical potentials where the surface touches the $\text{Y}_2\text{Mn}_2\text{O}_7$ product (e.g., oxidation states ranging from +3 to +5 depending on the nature of the vacancies and whether the composition is Na-poor or Mn-poor). In contrast, LiMnO_2 has a narrower range of stability than its neighboring Li-Mn-O phases, which each prefer distinct non-layered structures (Figure D.7b in the Appendix). In both the Li_2CO_3 assisted metathesis reactions [93] and the direct reaction between LiMnO_2 and YOCl [94], we observed formation of YMnO_3 and YMn_2O_5 , suggesting that the decreased range of chemical potentials over which layered LiMnO_2 is stable and lack of structural homology between the Li_xMnO_2 phases inhibits the accessibility of $\text{Y}_2\text{Mn}_2\text{O}_7$ (e.g., due to rearrangement of the phases into spinel-derived structures). Finally, in the K_2CO_3 assisted metathesis reactions, no product selectivity was observed as the reaction produced a mixture of YMnO_3 , YMn_2O_5 , and $\text{Y}_2\text{Mn}_2\text{O}_7$ products [93]. While the K_xMnO_2 phases indeed exhibit a similar extension into high oxygen chemical potentials akin to Na_xMnO_2 (Figure 5.3d), the stoichiometric KMnO_2 ground-state structure does not follow the layered (nor even another common) MnO_2 framework [210] (Figure D.7c in Appendix), although the layered phase is predicted to be about 44 meV/atom higher in energy than the ground state. We

thus conclude that similar to Li, the K-based system lacks the structural connectivity for interconversion between different $K_x\text{MnO}_2$ intermediates, although direct formation of K-deficient phases may promote formation of $\text{Y}_2\text{Mn}_2\text{O}_7$. In both the Li and K systems, the initial formation of YMnO_3 or YMn_2O_5 hence imposes significant kinetic barriers to the formation of $\text{Y}_2\text{Mn}_2\text{O}_7$. According to the chemical potential diagrams, YMnO_3 would have to decompose into YMn_2O_5 and Y_2O_3 en route to forming $\text{Y}_2\text{Mn}_2\text{O}_7$, which is consistent with myriad control experiments between binary yttrium and manganese oxides, with or without the presence of sodium (see Figures D.2 and D.3 in the Appendix). Based on these observations, we argue that the minimized chemical potential distance presented in Figures 5.3 and 5.4 and ability of sodium-based intermediate to interconvert across a wide range of stoichiometries and oxidation states explain why sodium provides selectivity of $\text{Y}_2\text{Mn}_2\text{O}_7$ via a kinetically-viable pathway at lower temperatures.

Analysis of 3,017 unique chemical reactions predicted to form $\text{Y}_2\text{Mn}_2\text{O}_7$ within the full alkali metal (Li, Na, K, Rb, Cs), halogen (F, Cl, Br, I), carbon (C), and target (Y, Mn, O) chemical system show that the Na-based ternary metathesis reaction, $2 \text{NaMnO}_2 + 2 \text{YOCl} + \frac{1}{2} \text{O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 2 \text{NaCl}$ is the most optimal reaction for both minimizing the total chemical potential distance and maximizing the (negative) grand potential energy of reaction, $\Delta\Phi_{\text{rxn}}$, when these two parameters are weighted equally. This result suggests that the Na-based pathway is not only a good pathway for producing $\text{Y}_2\text{Mn}_2\text{O}_7$ but that it may also be the most suitable metathesis reaction for making this product. The energy and total chemical potential distributions for these reactions illustrate that the Na-based reaction (green triangle in Figure 5.4a) optimizes both total chemical potential distance and overall reaction energy. The Na-based reaction has a near-zero total chemical potential distance (0.055 eV/atom) that is significantly smaller than those of the Li and K reactions (1.608 and 0.924 eV/atom, respectively) and has a more negative reaction energy than any other reaction pathway with a near-zero total chemical potential distance. Figure 5.4 also reveals a major design principle behind using an expanded chemical space with metathesis reactions – the addition of other elements beyond those of the target phase (Y, Mn, O) can decrease the mean total chemical potential distance of the reaction without significantly changing the mean reaction energy. This hence provides many more opportunities for finding selective reactions beyond those that exclusively contain the target chemical species, i.e., 3,017 reactions in the full 13-element chemical system vs. 362 potential reactions in the Y-Mn-O chemical system.

Direct ternary metathesis reactions carried out between Na_xMnO_2 and YOCl do indeed form $\text{Y}_2\text{Mn}_2\text{O}_7$ as predicted, but they also reveal important mechanistic details missing from the presented thermodynamic analysis that impacts product selectivity. For example, available density functional theory data is highly focused on stoichiometric compounds but tends to be lacking for solid solution and defect-containing phases. The reaction $\text{NaMnO}_2 + \text{YOCl} \xrightarrow{\text{O}_2}$ results in some $\text{Y}_2\text{Mn}_2\text{O}_7$ formation, but also the formation of YMnO_3 and YMn_2O_5 (Figure D.5 in Appendix), suggesting that the evolution of the Na_xMnO_2 precursor during the reaction is important to consider, as illustrated in Figure 5.3b. A partially-oxidized precursor in the reaction, $\text{P2}'\text{-Na}_{0.7}\text{MnO}_2 + \text{YOCl}$ selectively yields $\text{Y}_2\text{Mn}_2\text{O}_7$, but

the reaction is incomplete after 24 h (Figure D.6 in Appendix). Together, these control reactions suggest that the reaction rates also depend on the specific nature of defects present in the reactants and intermediates.

5.6 Mechanistic facilitation through defect reactions

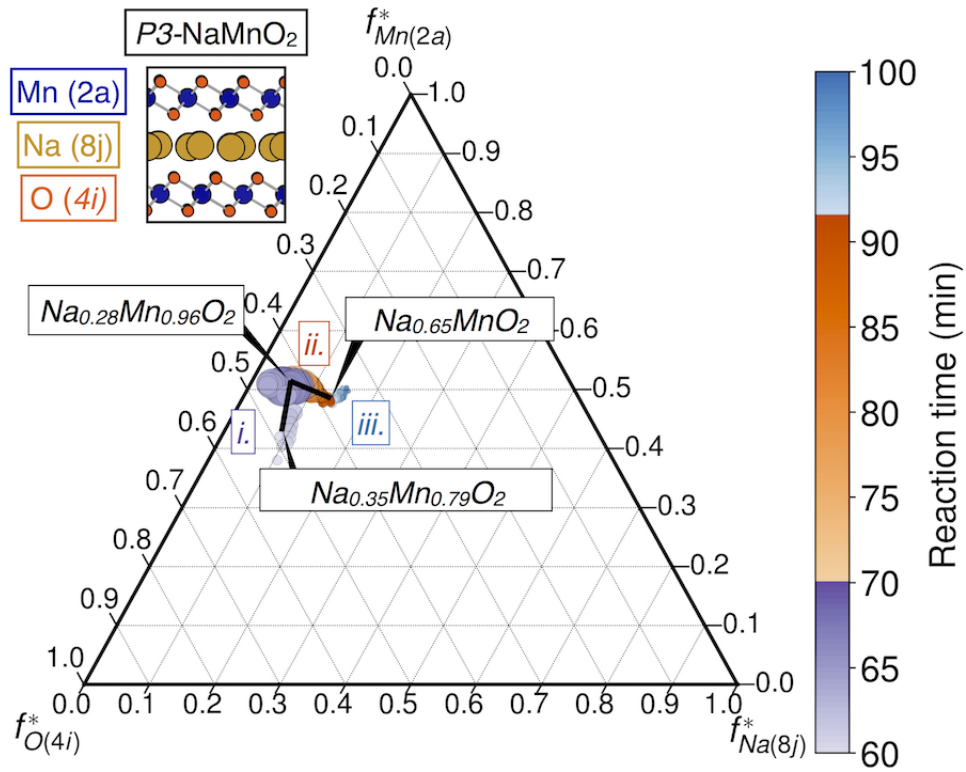
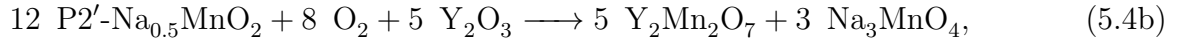
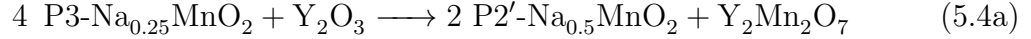


Figure 5.5: Compositional variation of the $P3\text{-Na}_x\text{MnO}_2$ intermediate determined by Rietveld analysis. In the f^* diagram, each axis denotes the X-ray scattering power from a crystallographic Wyckoff site within the lattice. For reference, calculated trajectories that correspond to the different stoichiometries of $P3\text{-Na}_x\text{MnO}_2$ are provided as black lines. The color bar in the figure follows the evolution of the $P3\text{-Na}_x\text{MnO}_2$ intermediate in the assisted metathesis reaction presented in Figure 5.1 with highlighted trajectories (i-iii) reflecting shaded regions in Figure 5.1i-iii. The diameter of each circle mirrors the calculated weighted scale factor (WSF) in Figure 5.1 for $P3\text{-Na}_x\text{MnO}_2$ and thus corresponds to the amount of this layered phase. The structure of $P3\text{-Na}_x\text{MnO}_2$ is shown with Wyckoff atom sites labeled. The figure contains compositions for which the WSF is greater than 20% of the maximum WSF for the phase shown in Figure 5.1. Detailed analysis of individual site occupancies is provided in the SI.

Analysis of the *in situ* diffraction data reveals that selective formation of $\text{Y}_2\text{Mn}_2\text{O}_7$ occurs

through two parallel reactions that start during trajectory (ii) in Figure 5.5:



consistent with the predicted thermodynamic connectivity in Figure 5.3. In contrast, Li-based assisted metathesis reactions performed at temperatures between 500 °C and 850 °C proceed via LiMnO_2 -based intermediates that result in the direct formation of YMnO_3 phase [93, 94], which is also predicted from the thermodynamic connectivity (Figure 5.3a,c).

Based on the stoichiometry of the residual Na-Mn-O phases in each step, there is a loss of $\text{Mn}^{4+} + 2 \text{ O}^{2-}$ along with the consumption of Y_2O_3 . Thermodynamically, we expect that stoichiometric NaMnO_2 reacts with Y_2O_3 at a relatively high μ_{O} and low μ_{Mn} (see Figure 5.3b), as suggested by the average stoichiometry of the transferred species in the parallel cascade of defect reactions (Equations. 5.4a and 5.4b). Curiously, the $\text{Y}_2\text{Mn}_2\text{O}_7$ -forming reaction does not proceed via a typically labile topochemical deintercalation of the alkali cation [211] or oxygen anion [212–214], but instead the chemical potential boundaries shown in Figure 5.3 guide the reaction to direct formation of the $\text{Y}_2\text{Mn}_2\text{O}_7$ product from the Na-Mn-O intermediates by avoiding the formation of other Y-Mn-O phases.

Chapter 6

Assessing thermodynamic selectivity of solid-state reactions

In this chapter, we propose the idea of two forms of phase competition in solid-state reactions (primary and secondary) and derive equations for measuring selectivity in a high-throughput manner using the enumeration of massive solid-state reaction networks. We review solid-state synthesis reactions in the literature and show that, while many existing literature reactions are predicted to be selective, many other conventional approaches to technologically important materials are suboptimal. Finally, we test our selectivity predictions in a case study system: barium titanate (BaTiO_3). From a massive chemical system of 17 elements, we compute 25,905 synthesis reactions for BaTiO_3 and select 11 to test experimentally, characterizing their reaction pathways using *ex post facto* synchrotron X-ray diffraction over a wide range of temperatures. We find that two highly-ranked unconventional reactions from BaS/BaCl_2 and Na_2TiO_3 precursors outperform conventional BaTiO_3 synthesis approaches. Furthermore, we find that our proposed secondary phase competition metric correlates strongly with the maximum impurity fraction observed during the reaction pathway for all experiments. Our synthesis planning workflow promises to enable the predictive synthesis of inorganic materials, facilitating the optimization of existing synthesis approaches and the design of synthesis approaches to never-before-synthesized materials, including those that cannot be easily made from conventional “off-the-shelf” precursors.

6.1 The interface reaction model

In this section, we continue discussing the interface reaction model for bulk solid-state powder reactions and use it to derive two solid-state reaction selectivity cost metrics that predict the degree of phase competition in solid-state synthesis.

Note: This chapter is closely adapted from a draft of a co-authored manuscript of which I am the first author. This work is unpublished at the time of writing and will be later submitted for publication in a scientific journal.

A cartoon model of the initial stages of a powder reaction in solid-state synthesis is shown in Figure 6.1a. The precursor powder mixture is composed of solid crystallites of various shapes, sizes, and orientations. As the precursor mixture is heated, atoms gain enough kinetic energy to interdiffuse among the precursors, particularly at contact areas of different precursor crystallites, where there is a thermodynamic driving force to form one or more new phases. The formation of this new product phase proceeds via nucleation and growth at the interface, happening throughout interfacial contact areas in the precursor powder mixture until the precursors are fully consumed and thermodynamic equilibrium is attained [59].

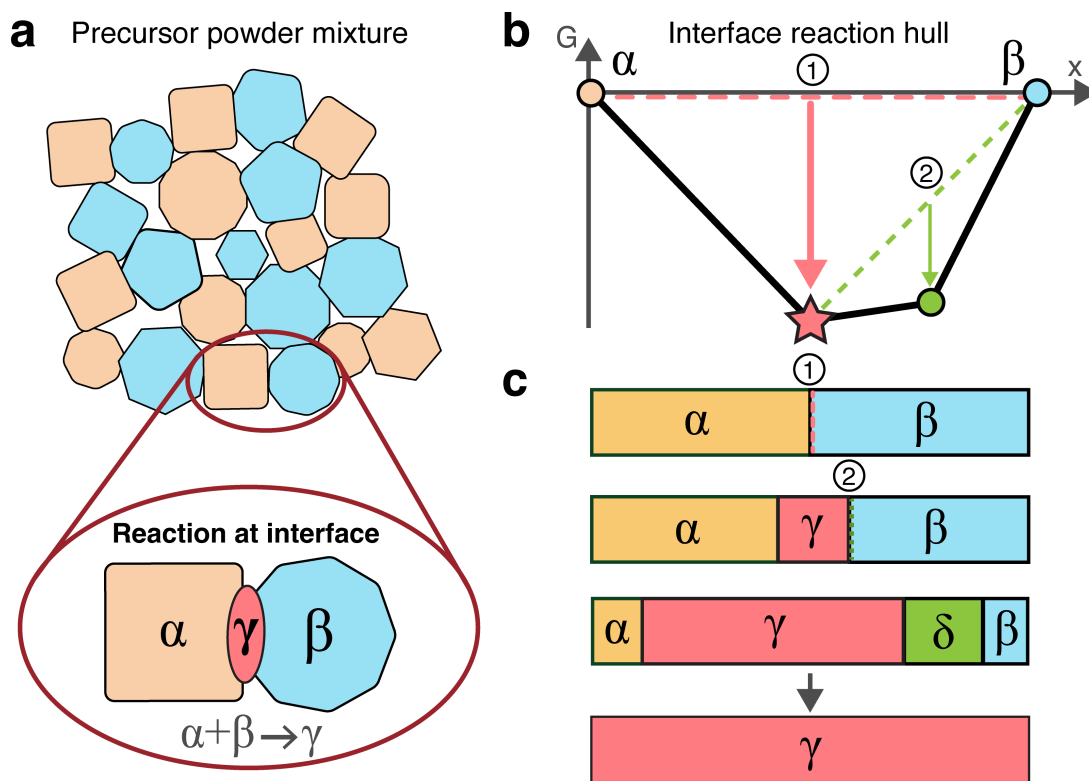


Figure 6.1: Modeling chemical reactions at solid-state heterogeneous interfaces in a binary (or quasibinary) chemical system. (a) Cartoon model of a powder reaction depicting a mixture of powder particles for hypothetical precursor phases, α (orange), and β (blue). The zoomed-in section highlights the nucleation of a new phase, γ (red), at the interface between precursor particles according to the reaction $\alpha + \beta \rightarrow \gamma$ (b) Interface reaction hull model of possible reactions at the interface between α and β forming γ (Reaction 1) or δ (Reaction 2). (c) Cartoon model of steps in one possible reaction pathway of a 1-dimensional interface reaction of an equal mixture of α and β . The system may react towards a local equilibrium state in which all phases on the interface reaction hull are present; however, with infinite time, the system should approach the global equilibrium state composed entirely of γ .

The predicted equilibrium phase(s) are determined via the construction of a convex hull in free energy and composition space, where the composition axis is a normalized (atomic)

mixing ratio between the two precursor phases [82]. For binary chemical systems (two elements), this “interface reaction hull” (Figure 6.1b) is simply a subsection of the typical energy-composition phase diagram. For ternary (or higher) chemical systems, however, the interface reaction hull is considered *quasibinary*. It is formed by taking a cross-section of the higher-dimensional phase diagram and plotting all points where the tie-line intersects a phase or set of phases, depending on the number of elements in the system. This results in a convex hull where the vertices can be either phases or *combinations* of phases with defined mixing ratios. In this construction, “metastable” reaction products are those which appear above the convex hull lines, as these phases do not yield the minimum free energy at their given composition. These reaction products are not captured with convex hull slices [82], as they can only be identified through combinatorial reaction enumeration instead of energy minimization approaches. Note that it is possible to construct the interface reaction hull with other thermodynamic potentials, such as the grand potential energy, $\Phi = G - \sum_i^N \mu_i n_i$, where one or more elements are considered open to the system. This construction allows for the reaction of two solid precursors within the presence of a gaseous environment (e.g., flowing O_2), as commonly occurs in solid-state synthesis.

Which phases appear as reaction products (and in what sequence they appear) cannot be predicted with thermodynamics alone; to do so requires intimate knowledge of the kinetic rates of all physically feasible reactions. However, a commonly adopted theoretical simplification is to assume that as a powder mixture is heated, the reaction product(s) with the largest reaction energy ($\Delta G_{rxn,1}$ in Figure 6.1b) will nucleate and grow first [19, 22]. This hypothesis is based on the fact that the activation energy barrier to nucleation scales as $\Delta G^\ddagger \propto \frac{\gamma^3}{\Delta G_{rxn}^2}$. However, one must not discount the surface energy cost, γ , especially when comparing the feasibility of reactions of similar energies [215]. As previously mentioned, one must also remember that interfacial reactions are often transport-limited due to the relatively slow nature of solid-state diffusion; hence, the activation energy of nucleation may not play a significant role in deciding the outcome of the reaction pathway.

A combinatorial complex situation arises in solid-state reactions following the nucleation of a new phase. This new phase (e.g., γ in Figure 6.1) yields two new interfaces with the remaining precursors, allowing for subsequent reaction(s) between the new product phase and one or more of the precursors. One possible reaction pathway for the cartoon model is shown in Figure 6.1c. In this reaction pathway, the first step is $\alpha + \beta \rightarrow \delta$, followed by the reaction of $\beta + \delta \rightarrow \gamma$. In a truly 1-dimensional solid-state reaction, local thermodynamic equilibrium may be achieved when the system reaches a state in which all stable product phases on the interface reaction hull have formed, and the growth of the product layer(s) slows down until it ceases entirely. This situation has been experimentally observed in many previous works on diffusion couples [59, 216]. While this configuration may be stable, it is not the “global” equilibrium state, which for the cartoon system of Figure 6.1 is entirely δ when reacted from an equal 1:1 mixture of α and β . In experiments with powder reactions, the accessibility of the global equilibrium state is often encouraged by re-grinding steps in which new interfaces are exposed and mixed to facilitate complete conversion to the equilibrium products. In

systems with significant phase competition and slow atomic diffusivities, this can require high temperatures and long heating times, which may make synthesis difficult when the desired thermodynamic products are no longer stable at the required high temperatures. It is ideal to avoid this situation entirely by choosing precursors and a synthesis environment that produces minimal phase competition; this is the motivation for assessing thermodynamic selectivity in synthesis planning involving solid-state reactions.

6.2 Primary and secondary competition

The selectivity of a solid-state reaction can be assessed via two metrics which we refer to herein as “primary” and “secondary” competition. The primary competition score, C_1 , is a measure of the degree of competition in the formation of the first phase in the reaction between the precursors, and the secondary competition score, C_2 , is a measure of the likelihood that subsequent reactions will occur after the initial formation of the target phase(s). Like reaction energies, C_1 and C_2 have been formulated such that their minimization is favorable; i.e., lower values suggest *more* selective reactions.

The difference between primary and secondary competition for an interface reaction hull with a single competing phase is illustrated in the cartoon model in Figure 6.2a. The primary competition (yellow arrow) effectively measures the energetic favorability and multitude of available reactions forming competing phases from the precursors. In contrast, the secondary competition (smaller green arrow) is a measure of the remaining reaction energy to form a competing phase from the reaction of the target phase with one or more of the remaining precursors. Secondary competition relates closely to the concept of decomposition free energy [72]. In the simple model system in Figure 6.2a, the length of the secondary arrow is indeed exactly equal to the decomposition free energy of the competing phase (i.e., how much the competing phase “pulls down” the convex hull).

The primary and secondary competition are *partially* correlated due to the geometric constraints of the convex hull. Figure 6.2b-e illustrates the extreme limiting cases for combinations of high/low primary and secondary competition for a symmetric interface reaction hull with two competing phases. The geometric correlation between the two metrics is most apparent when C_2 is high (Figure 6.2d-e); it is impossible to construct a hull where C_2 is high and $C_1 \approx 0$. At best, it is possible to achieve the situation illustrated in Figure 6.2d, where a competing phase is high in energy but similar enough in composition to a precursor, such that it results in non-negligible secondary reaction energies.

Thus far, we have only considered simple interface reaction hulls with 1-2 competing phases/reactions. However, in real systems, there is often significantly more competition. Figure 6.3 shows the interface reaction hull at $T = 600$ °C for the reaction between BaO and TiO_2 , which is a common reaction step in the synthesis of BaTiO_3 (BTO). In BTO synthesis, there have been experimental observations (blue squares) of secondary phases Ba_2TiO_4 , BaTi_2O_5 , as well as other phases such as $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$, BaTi_4O_9 , etc. [217]. This system will be explored extensively later throughout this work.

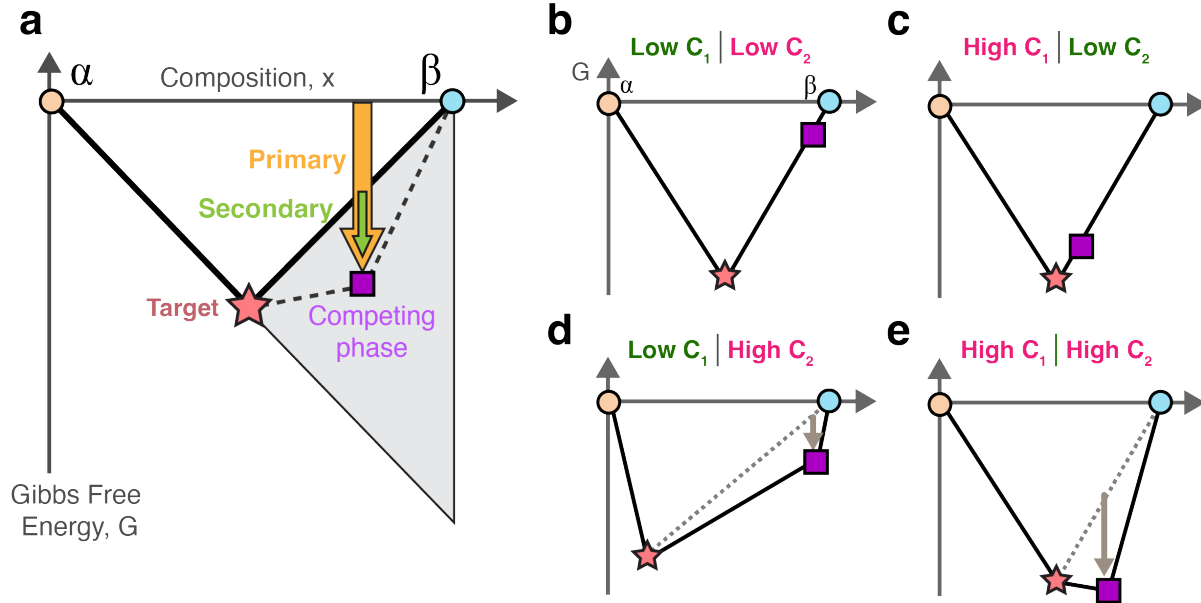


Figure 6.2: Comparison and limiting cases of the cost metrics for primary competition, C_1 , and secondary competition, C_2 . (a) Illustration of primary and secondary reaction energies to form a competing phase (green circle). The primary reaction is between the original α and β precursors, whereas the secondary reaction has a smaller reaction energy and occurs between the target phase, T (pink triangle), and remaining β precursor. (b-e) Examples of limiting cases with different combinations of low or high C_1 and C_2 , showing that these metrics can be varied independently despite their inherent geometric correlation.

To measure selectivity in real, complex systems like BTO, which have significantly more than one competing reaction, it becomes necessary to derive formulas that account for multiple competing reaction energies with a single cost metric. For the primary competition score, C_1 , this means identifying a functional form that assesses the relative competitiveness of the target reaction of interest versus all other competing reaction energies. It is helpful to frame this problem statistically as calculating the probability of achieving a state with a specific energy within a set of accessible states. A familiar functional form that accomplishes this is that of the Boltzmann distribution, which considers each reaction as an accessible state with a probability that is determined by its free energy. To formulate this as a positive cost metric which can vary between 0 and ∞ , we monotonically transform the probability using the negative of a natural logarithm

$$C_1 = -\ln P = -\ln \frac{e^{-\frac{\Delta G_{\text{rxn}}}{k_b T}}}{Q}, \quad (6.1)$$

where k_b is the Boltzmann constant, T is the temperature of the synthesis, and Q behaves like a canonical partition function, $Q = \sum_i e^{-\frac{\Delta G_{\text{rxn},i}}{k_b T}}$. The Boltzmann distribution form is useful because it 1) implicitly yields a higher competition score for spaces with a larger number of reactions, 2) includes a temperature term for “smearing” the probability distribution, and

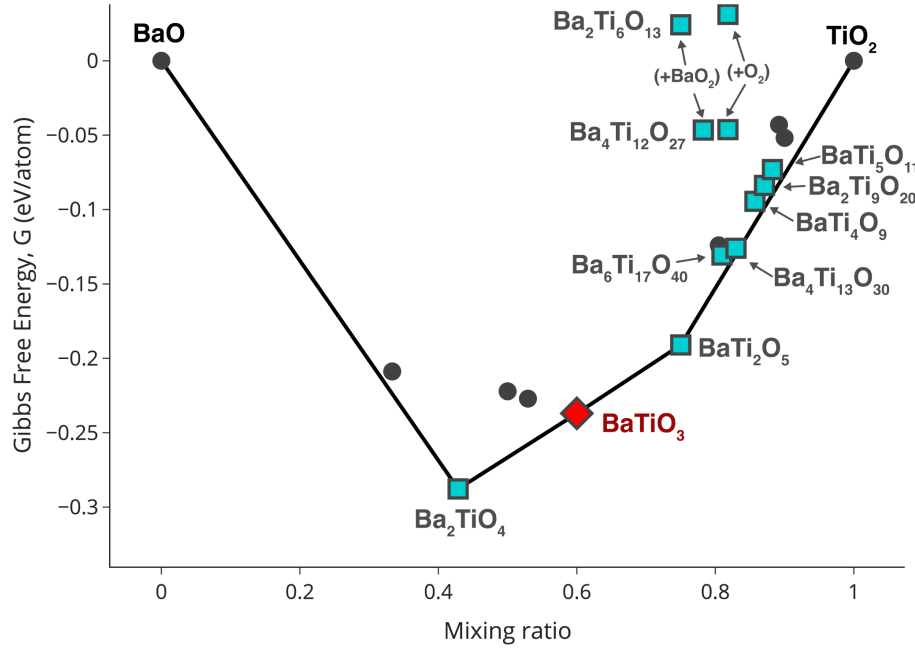


Figure 6.3: Calculated interface reaction hull for BaO|TiO₂ at $T = 600\text{ }^{\circ}\text{C}$. Blue squares denote experimentally known barium titanate phases. Ba₂TiO₄ is the most commonly observed intermediate/impurity in standard syntheses of BaTiO₃ from BaO (or BaCO₃) and TiO₂; it is also predicted to be the phase with the greatest driving force to form.

3) allows for equal comparison across different systems at identical temperatures due to its consistent scaling.

For the secondary competition, C_2 , one must also consider the situation in which there is more than one possible secondary reaction. Because the available secondary reactions depend on the phases already formed and available to (re-)react in the system, the secondary competition score will depend on the exact sequence of phase formation. Predicting this sequence requires information about the reaction kinetics of the system, which is currently prohibitive. It is feasible, however, to develop a secondary competition metric based on all mathematically possible sequences and their reaction energies as determined through geometric interpretation of the interface reaction hull.

A full secondary reaction sequence is a series of decomposition-like reactions by which secondary phases are produced from compositional neighbors on the interface reaction hull. Figure 6.4 illustrates all possible reaction sequences for an interface reaction hull (or a subset of the hull) consisting of a various number of interior vertices (stable reactions), n . The total reaction energy, $\Delta G_{d,i}$, of a single secondary reaction sequence, i , is a summation of all the reaction energies, $\Delta G_{rxn,j}$, along the series, and is calculated as

$$\Delta G_{d,i} = \sum_{j=1}^n \Delta G_{rxn,j} = \Delta G_{rxn,1} + \Delta G_{rxn,2} + \Delta G_{rxn,3} + \dots, \quad (6.2)$$

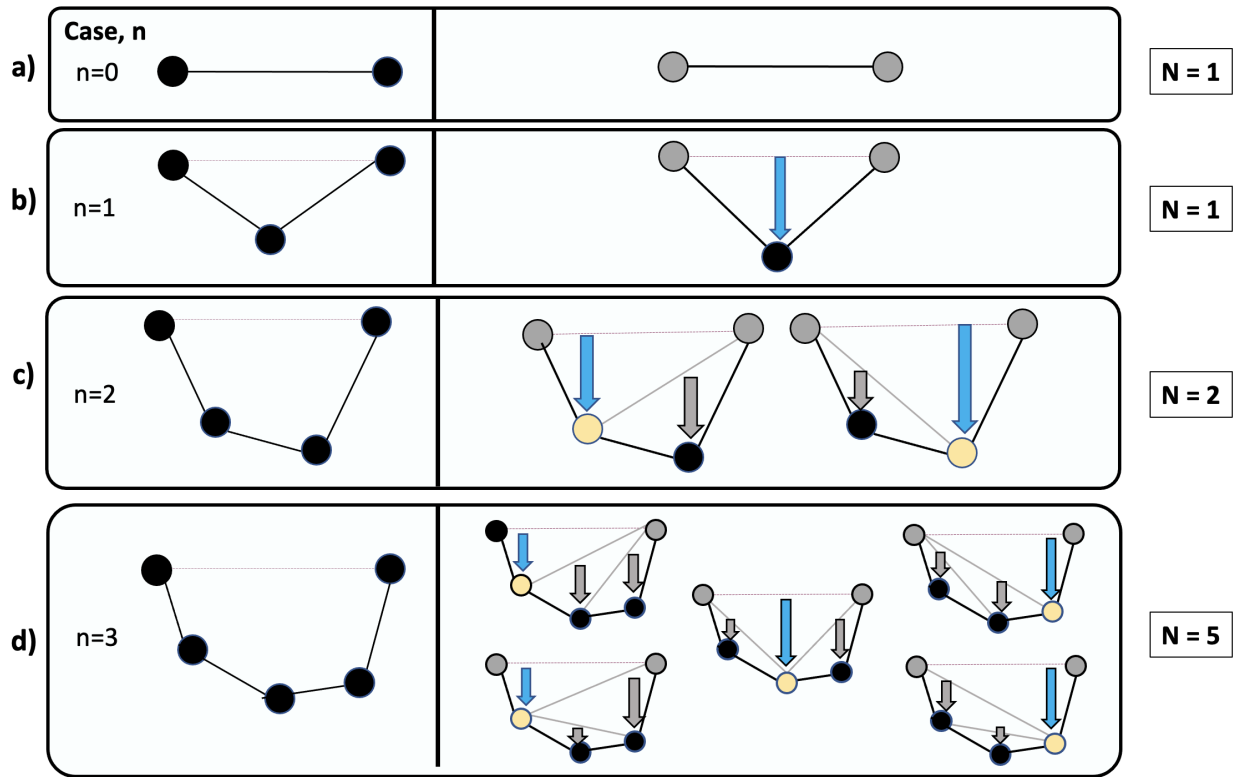


Figure 6.4: Cartoon model of decomposition pathways in a hull containing n interior vertices. (a-d) Decomposition pathways are illustrated for cases $n = 0, 1, 2, 3$ respectively. The blue arrow indicates the first reaction in the decomposition pathway, and the gray arrows indicate secondary, tertiary, etc. reactions. The number of unique decomposition pathways, N , follows the Catalan number sequence.

Here, we assume that secondary reactions do not “cross” on the interface hull; i.e., once a vertex has been reached, the phase(s) at this vertex can only participate in subsequent reactions with the nearest vertices previously reached. This assumption ensures that all possible secondary reaction sequences have the same number of steps, which equals the number of interior vertices, n .

The calculation of the number of unique secondary reaction sequences, N , can be solved recursively and is mathematically identical to the problem of determining the number of full binary trees with n interior nodes [218]. The solution is

$$N(n) = \frac{(2n)!}{(n+1)!n!}, \quad (6.3)$$

where $n \geq 0$. Equation 6.3 produces the famous Catalan numbers sequence (1, 1, 2, 5, 14, 42, 132, 429, ...).

The reaction energy for each secondary reaction is calculated by computing the altitude of the triangle, h , formed by the product vertex and two reactant vertices. The total number

of times the energy of a reaction indexed j appears in the set of all possible secondary reaction sequences is referred to as the altitude multiplicity, $k_{h,j}$, which can be calculated as the product of three Catalan numbers

$$k_{h,j} = N(n_l) \cdot N(n_r) \cdot N(n - n_l - n_r - 1), \quad (6.4)$$

where n_l and n_r refer to the number of interior vertices to the left and right of the vertex of interest, respectively. This multiplicity formula allows one to calculate the mean free energy of all possible secondary reaction sequences

$$\overline{\Delta G_d} = \frac{1}{N} \sum_i^N \Delta G_{d,i}, \quad (6.5)$$

without using a computationally-intensive recursive approach.

Finally, we can derive a formula for the secondary competition score, C_2 , for a particular reaction in an interface reaction hull of arbitrary size as a summation of three free energy terms:

$$C_2 = - \left(\Delta G_{hull} + \overline{\Delta G_{d,l}} + \overline{\Delta G_{d,r}} \right). \quad (6.6)$$

Here, ΔG_{hull} is the energy above hull of the reaction of interest, and $\overline{\Delta G_{d,l}}$ and $\overline{\Delta G_{d,r}}$ are the mean free energies of secondary reaction sequences to the left and right of the reaction of interest, respectively, as calculated by Equation 6.5. The energy above hull term is included as a penalty to account for reactions that do not produce the ground-state phases at their composition, as well as reactions that have a net positive free energy ($\Delta G_{rxn} > 0$); without this metric, most endergonic reactions would appear to be perfectly selective. We take the negative of the free energy summation so that C_2 behaves as a ‘‘cost’’ metric, where higher values denote less selective reactions (i.e., more likely to produce secondary phases).

6.3 Synthesis planning workflow

The synthesis reaction calculation procedure was implemented as a Python-based workflow in the existing *reaction-network* package (see Appendix A). The workflow was constructed using the *jobflow* package [58]. All calculations were launched using the FireWorks workflow library [57].

The workflow consists of three sequential steps. First, phases and their formation energies for the chemical system of interest are acquired from the Materials Project [12] and NIST-JANAF [65] databases, using the aforementioned Gibbs free energy descriptor to acquire $\Delta G_f(T)$ at the selected synthesis temperature, as necessary. The total number of phases can be optionally reduced by setting a threshold for the maximum energy above hull (ΔG_{hull}). In this work, we used a moderately large threshold of $\Delta G_{hull} \leq 0.050$ eV/atom, evaluated at $T = 300$ K. Second, reaction enumeration is performed for this chemical system using both the combinatorial and free energy minimization approaches based on our previous

work on solid-state reaction networks (see Chapter 3 or Ref. 83). For systems with an open element, such as O_2 gas, this reaction enumeration step is performed again using the grand potential energies, where the open element has been assigned a user-defined value for the chemical potential (often its standard state, $\mu = \mu^0$ eV). Finally, reaction competition scores are calculated for all reactions that form the desired target composition (i.e., target reactions). The competition scores are calculated for each target reaction by first acquiring the subset of all enumerated reactions that involve the target reaction’s precursors. Then, these reactions are used to compute the interface reaction hull, from which C_1 (Equation 6.1) and C_2 (Equation 6.6) are derived. For open systems, this is performed once again, this time including any additional open reactions (e.g., with open O_2 on either side of the equation). In the open case, all reactions are modeled using grand potential energies with the corresponding elemental chemical potential.

When ranking synthesis reactions, we use the cost function approach explored in Chapter 3, where a reaction’s “cost”, C , is defined over the range $C \in [0, \text{inf})$ and is some weighted function of relevant reaction parameters. As in our previous work, we use the *softplus* functional form with reaction energy and competition scores as inputs,

$$C = \ln \left(1 + \frac{273}{T} \exp(x_0 \Delta \Phi_{\text{rxn}} + x_1 C_1 + x_2 C_2) \right), \quad (6.7)$$

where T is the absolute temperature of synthesis in Kelvin, Φ_{rxn} is the reaction energy (Gibbs free energy or grand potential energy), and x_0 , x_1 , and x_2 are user-defined weights for each parameter of the function. We find that for the BaTiO_3 system, a weighting of $x_0 = 0.10$, $x_1 = 0.10$, and $x_2 = 0.80$ often produces reasonably diverse results that do not significantly favor one parameter over another.

6.4 Exploring the selectivity of the solid-state reaction literature

The conventional approach in synthesis planning for bulk solid-state reactions is to select precursor compositions and reaction conditions based on heuristics (e.g., Tamman’s Rule) and chemical intuition. Our computational synthesis planning workflow allows us to explore, using quantitative predictions, whether solid-state reactions previously reported in the literature are predicted to be favorable based on their reaction energies and competition scores.

Reaction energies and competition scores were calculated for 5,530 unique reactions reported in the text-mined solid-state reaction literature dataset by Kononova et al. [219], including both binary (i.e., two-precursor) reactions and reactions in an open environment with an optional third gaseous reactant (e.g., O_2 gas). The calculation results for the 2,110 binary (closed environment) reactions are visualized in Figure 6.5.

The literature reactions span a wide range of reaction energies and competition scores. The mean reaction energy is $\Delta G_{\text{rxn}} = -0.030$ eV/atom; however, 837 reactions (39.7%)

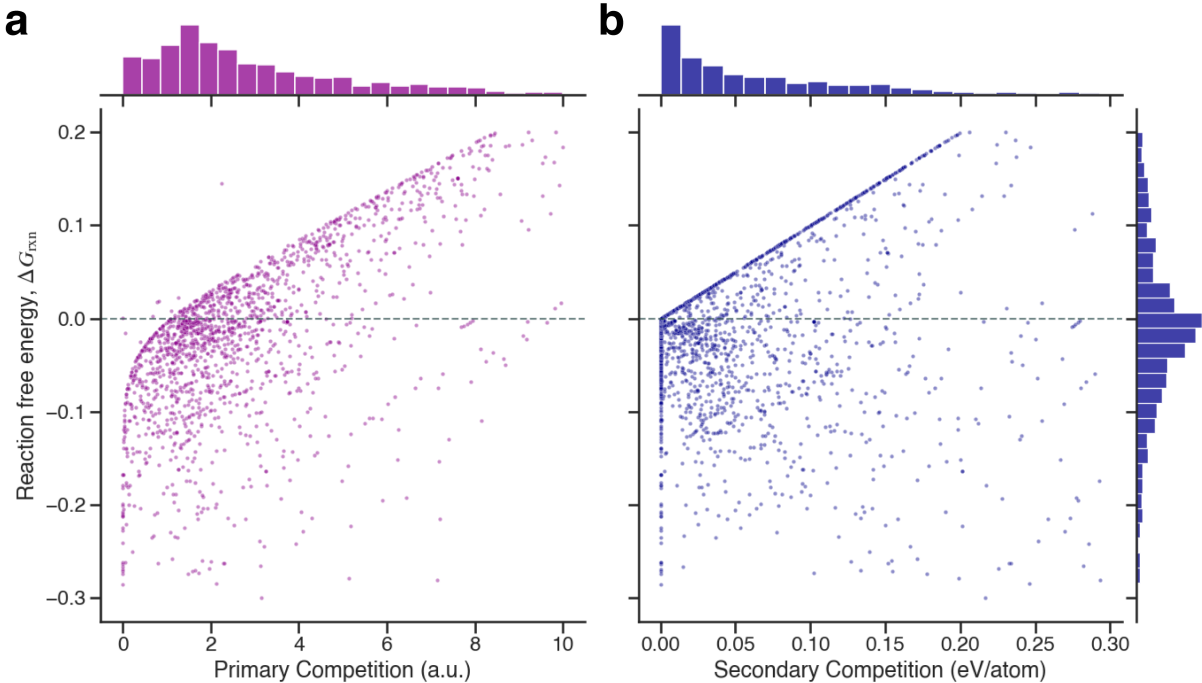


Figure 6.5: Synthesis map of 2,110 binary solid-state synthesis reactions reported in the literature. Reactions are plotted on a shared axis of reaction energy, ΔG_{rxn} , and on independent axes of (a) primary competition, C_1 , and (b) secondary competition, C_2 . Histograms showing the distribution of these values are shown on the margins.

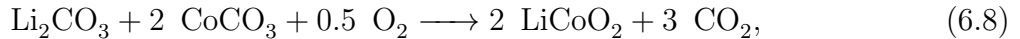
are predicted to have positive (free energies $G_{\text{rxn}} > 0$) and 18.2% have energies $G_{\text{rxn}} > 0.1$ eV/atom. Close to half (48%) of these positive energy reactions involve a carbonate precursor, even after applying our carbonate correction and the experimental formation energy for CO_2 gas. We also computed reaction energies and competition scores for 3,420 literature reactions containing an optional open element (e.g., O_2 gas), modeled using grand potential energies. These results are visualized in Figure E.4 (Appendix). The trends for the open-environment reactions are similar to those seen in the non-open reactions; however, the distribution of reaction energies is wider, and a relatively higher number of reactions are associated with low (near-zero) competition scores.

Many reactions reported in the literature are ranked quite favorably by our proposed competition metrics. Notable selective and energetically favorable reactions include the conventional syntheses of prototypical spinel $\text{MgO} + \text{Al}_2\text{O}_3 \longrightarrow \text{MgAl}_2\text{O}_4$ ($\Delta G_{\text{rxn}} = -0.0596$ eV/atom, $C_1 = 0.567$ a.u., $C_2 = 0.000$ eV/atom) [220], yttrium aluminum garnet (YAG) $1.5 \text{ Y}_2\text{O}_3 + 2.5 \text{ Al}_2\text{O}_3 \longrightarrow \text{Y}_3\text{Al}_5\text{O}_{12}$ ($\Delta G_{\text{rxn}} = -0.0578$ eV/atom, $C_1 = 0.616$ a.u., $C_2 = 0.000$ eV/atom), and the negative thermal expansion material $3 \text{ WO}_3 + \text{Sc}_2\text{O}_3 \longrightarrow \text{Sc}_2(\text{WO}_4)_3$ ($\Delta G_{\text{rxn}} = -0.010$ eV/atom, $C_1 = 0.897$ a.u., $C_2 = 0.000$ eV/atom). Interestingly, one class of reactions frequently associated with a low secondary competition score

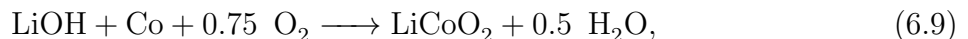
($C_2 = 0$) involve the production of ABO_4 compositions from binary oxides, including that of prototypical zircon $\text{SiO}_2 + \text{ZrO}_2 \longrightarrow \text{ZrSiO}_4$ ($\Delta G_{\text{rxn}} = -0.005$ eV/atom, $C_1 = 0.979$ a.u., $C_2 = 0.000$ eV/atom).

Many other reported literature reactions, however, are predicted to be extremely unfavorable in their selectivity. In fact, 39% of closed reactions and 43.9% of open reactions have C_2 values greater than 0.1 eV/atom, indicating significant phase competition. Unsurprisingly, many of these reactions include elemental precursors, such as the synthesis of iron silicide via $\text{Fe} + 2 \text{ Si} \longrightarrow \text{FeSi}_2$ ($\Delta G_{\text{rxn}} = -0.4065$ eV/atom, $C_1 = 2.861$ a.u., $C_2 = 0.248$ eV/atom). Note, however, that not all elemental reactions are predicted to be unselective: for example, the synthesis of cadmium telluride via $\text{Cd} + \text{Te} \longrightarrow \text{CdTe}$ is quite favorable ($\Delta G_{\text{rxn}} = -0.673$ eV/atom, $C_1 = 0.0$ a.u., $C_2 = 0.0$ eV/atom) [221]. Interestingly, of the 141 closed reactions with extremely high values of $C_2 \geq 0.5$ eV/atom, 58% of the reactions involve the production of O_2 gas as a byproduct, which may indicate incorrect modeling of the environmental conditions of synthesis (i.e., actual conditions that are more reducing than assumed). Many of these reactions have substantially high reaction energies and yield target phases that are not in our database. Often, these target phase compositions are incorrectly assumed from our method for discretizing doped/alloyed products. For example, the least favorable (highest cost) reaction in the database involves production of a non-existent phase: $\text{CaO} + 3 \text{ CeO}_2 \longrightarrow \text{CaCe}_3\text{O} + 3 \text{ O}_2$ ($\Delta G_{\text{rxn}} = 3.041$ eV/atom, $C_1 = 118.658$ a.u., $C_2 = 3.041$ eV/atom). In the original work from which this reaction was extracted, the authors synthesized $\text{CaO}:x\text{Ce}^{3+},x\text{Na}^+$ with only small concentrations ($x=0.02$). Hence, the presence of some seemingly impossible reactions may be due to errors in the literature extraction process. Other nonselective reactions include the synthesis of CsPbBr_3 from bromide precursors $\text{CsBr} + 2 \text{ PbBr}_2 \longrightarrow \text{CsPbBr}_3$ ($\Delta G_{\text{rxn}} = -0.271$ eV/atom, $C_1 = 1.589$ a.u., $C_2 = 0.1555$ eV/atom) [222] and synthesis of NaMO_2 ($M=\text{Co},\text{Mn}$) from carbonates via $M\text{CO}_3 + 0.5 \text{ Na}_2\text{CO}_3 + 0.25 \text{ O}_2 \longrightarrow \text{NaMO}_2 + 1.5 \text{ CO}_2$ ($\Delta\Phi_{\text{rxn}} = 0.112$ and 0.073 eV/atom, $C_1 = 36.543$ and 21.651 a.u., $C_2 = 1.123$ and 0.664 eV/atom, respectively).

While reactions can still be successful despite unfavorable (high) C_1 and C_2 scores, these reactions are suboptimal and likely require the fine-tuning of reaction conditions to avoid impurity phase formation or follow-up regrinding steps and long heating times to reach thermodynamic equilibrium. The optimization of synthesis reactions is especially important for key technological materials, such as Li-ion battery cathodes. For example, the synthesis of LiCoO_2 from carbonate precursors,



has a reaction energy $\Delta\Phi_{\text{rxn}} = 0.030$ eV/atom and competition scores $C_1 = 4.557$ a.u. and $C_2 = 0.111$ eV/atom. In the literature, it is often reported that synthesis via these precursors involves very long heating times, with up to three separate heat treatments of 24h each [223], owing to the predicted lack of selectivity of this approach. Surprisingly, the highest-ranked synthesis procedure from our calculations begins with Co metal,



which has a reaction energy $\Delta\Phi_{\text{rxn}} = -1.046$ eV/atom and competition scores of $C_1 = 0.000$ a.u. and $C_2 = 0.011$ eV/atom. While this reaction is highly favorable from a thermodynamic standpoint, it may be impractical due to its extremely negative reaction energy. Instead, we recommend another highly ranked reaction using LiOH and Co_3O_4 :



which has a reaction energy $\Delta\Phi_{\text{rxn}} = -0.210$ eV/atom and competition scores $C_1 = 0.002$ a.u. and $C_2 = 0.011$ eV/atom. The use of a LiOH precursor is significantly more favorable than Li_2CO_3 or lithium peroxide, Li_2O_2 . Notably, this recommendation was not captured in a previous solid-state synthesis planning work [215] due to their restriction of searching for precursors only within the Li-Co-O-C system. The favorable use of precursors containing elements beyond those found in the target product is in agreement with our previous works [92–95], which highlight the benefit of considering high-dimensional chemical spaces when devising selective synthesis reactions [224].

Similarly, for the Li-ion battery cathode LiFePO_4 , the highest-ranked reaction in the literature, according to our synthesis planning workflow, is via direct reaction of lithium and iron(II) phosphate [225]:



which was calculated to have $\Delta G_{\text{rxn}} = -0.008$ eV/atom, $C_1 = 1.933$ a.u., and $C_2 = 0.000$ eV/atom. This reaction was ranked significantly higher than reactions using precursors Li_2CO_3 , Fe_2O_3 , $\text{LiP}(\text{HO}_2)_2$, or $\text{FeP}(\text{H}_2\text{O}_3)_2$.

While not included in the original literature reaction dataset, our recent observations [95] of selectivity in the synthesis of the pyrochlore $\text{Y}_2\text{Mn}_2\text{O}_7$ are also validated by the new competition score metrics. The synthesis from binary oxides, $\text{Y}_2\text{O}_3 + 2 \text{ MnO}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7$ ($\Delta\Phi_{\text{rxn}} = -0.190$ eV/atom, $C_1 = 2.012$ a.u., $C_2 = 0.071$ eV/atom), is outperformed by the Na-based metathesis reaction $2 \text{ NaMnO}_2 + 2 \text{ YOCl} + 0.5 \text{ O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 2 \text{ NaCl}$ ($\Delta\Phi_{\text{rxn}} = -0.262$ eV/atom, $C_1 = 0.876$ a.u., $C_2 = 0.100$ eV/atom). While the metathesis reaction appears to have a higher C_2 score, this score is due entirely to the predicted decomposition of NaMnO_2 precursor in air via $3.5 \text{ NaMnO}_2 + \text{O}_2 \longrightarrow \text{Na}_2\text{Mn}_3\text{O}_7 + 0.5 \text{ Na}_3\text{MnO}_4$ ($\Delta\Phi_{\text{rxn}} = -0.100$ eV/atom); no other product phases are predicted to form. We saw in Chapter 5 that the predicted decomposition of NaMnO_2 did not impede the reaction progress, instead following a sequence of formation of Na_xMnO_2 intermediates. Contrast that with the Li-based metathesis reaction, $2 \text{ LiMnO}_2 + 2 \text{ YOCl} + 0.5 \text{ O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 2 \text{ LiCl}$ ($\Delta\Phi_{\text{rxn}} = -0.187$ eV/atom, $C_1 = 2.189$ a.u., $C_2 = 0.216$ eV/atom), which has significantly higher competition scores due in part to the predicted formation of YMn_2O_5 and even more negative decomposition energy (-0.161 eV/atom) to produce Li_2MnO_3 and $\text{Li}_5\text{Mn}_7\text{O}_{16}$. Hence, like our previously proposed “chemical potential distance” metric, the competition score metrics can be used to distinguish which species (and thus byproduct salts) are optimal for use in metathesis reactions.

In this section, we saw that our free energy and competition score metrics could be used to rationalize the performance of existing synthesis approaches in the literature. We showed

that for many target materials, syntheses from conventional precursors are actually quite selective, including for CdTe, MgAl_2O_4 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Sc}_2(\text{WO}_4)_3$, ZrSiO_4 , and others. However, many other target materials are frequently made with nonselective synthesis approaches. In particular, elemental precursors often have quite poor selectivities, as do certain conventional precursors; this was demonstrated in particular for the use of carbonate precursors in the reaction to produce Li-ion battery cathodes LiCoO_2 and LiFePO_4 , as well as the Na-ion battery cathodes NaCoO_2 and NaMnO_2 .

6.5 The synthesis of barium titanate (BaTiO_3)

To more rigorously investigate the performance of our reaction selectivity metrics, we completed experiments characterizing the reaction pathways for several reactions spanning a range of reaction energies and competition scores. We selected the ferroelectric barium titanate, BaTiO_3 (BTO), as a case study system. As originally discussed in Figure 6.3, BaTiO_3 is an ideal target for studying the thermodynamic selectivity of solid-state reactions due to the high number of competing phases in the Ba-Ti-O chemical system and the fact that conventional routes from binary oxides are well-known to proceed through intermediates (especially Ba_2TiO_4) [217]. At least 12 unique barium titanate compositions have been experimentally observed, including the compositional neighbors of BTO (which are some of the main impurities during BTO synthesis): Ba_2TiO_4 and BaTi_2O_5 . Other commonly observed minor impurities include $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$, BaTi_4O_9 , and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$. Other compositions in this space, such as $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, $\text{BaTi}_5\text{O}_{11}$, $\text{Ba}_4\text{Ti}_{12}\text{O}_{27}$, and $\text{Ba}_2\text{Ti}_6\text{O}_{13}$, have been previously synthesized but are less commonly observed as intermediates or impurity phases in BTO synthesis [217]. Another motivation for choosing BTO as a target system, besides its technological importance and popularity in the literature, is the kinetic accessibility of its chemical system: even with the high number of competing Ba-Ti-O phases, BaTiO_3 is generally regarded as quite straightforward to synthesize. The ease with which Ba-Ti-O phases can be synthesized removes some dependency of reaction outcomes on kinetic factors and provides a greater justification for our attempts at measuring intermediate/impurity formation through a purely thermodynamic lens.

Using our synthesis planning workflow, we computed reactions and competition scores for 25,905 closed reactions and 191,729 open- O_2 synthesis reactions producing BaTiO_3 , selected from a massive 17-element reaction network composed of reactions among 1943 phases (≤ 0.050 meV/atom above the hull) within a chemical system consisting of the target metals (Ba, Ti), alkali/alkaline earth metals (Li, Na, K, Mg, Ca, Sr), halogens (F, Cl, Br), chalcogens (O, S) pnictogens (N, P), and additional elements (C, H). The free energies, C_1 , and C_2 scores for the closed/open reactions are shown in the synthesis maps illustrated in Figure 6.6 and Figure E.4 (Appendix), respectively.

The synthesis maps for BaTiO_3 (Figure 6.6) provide a visual guide for solid-state synthesis planning and can be examined interactively or exported to downsized tables via various filters and ranking approaches. The shapes of the synthesis map distributions (especially

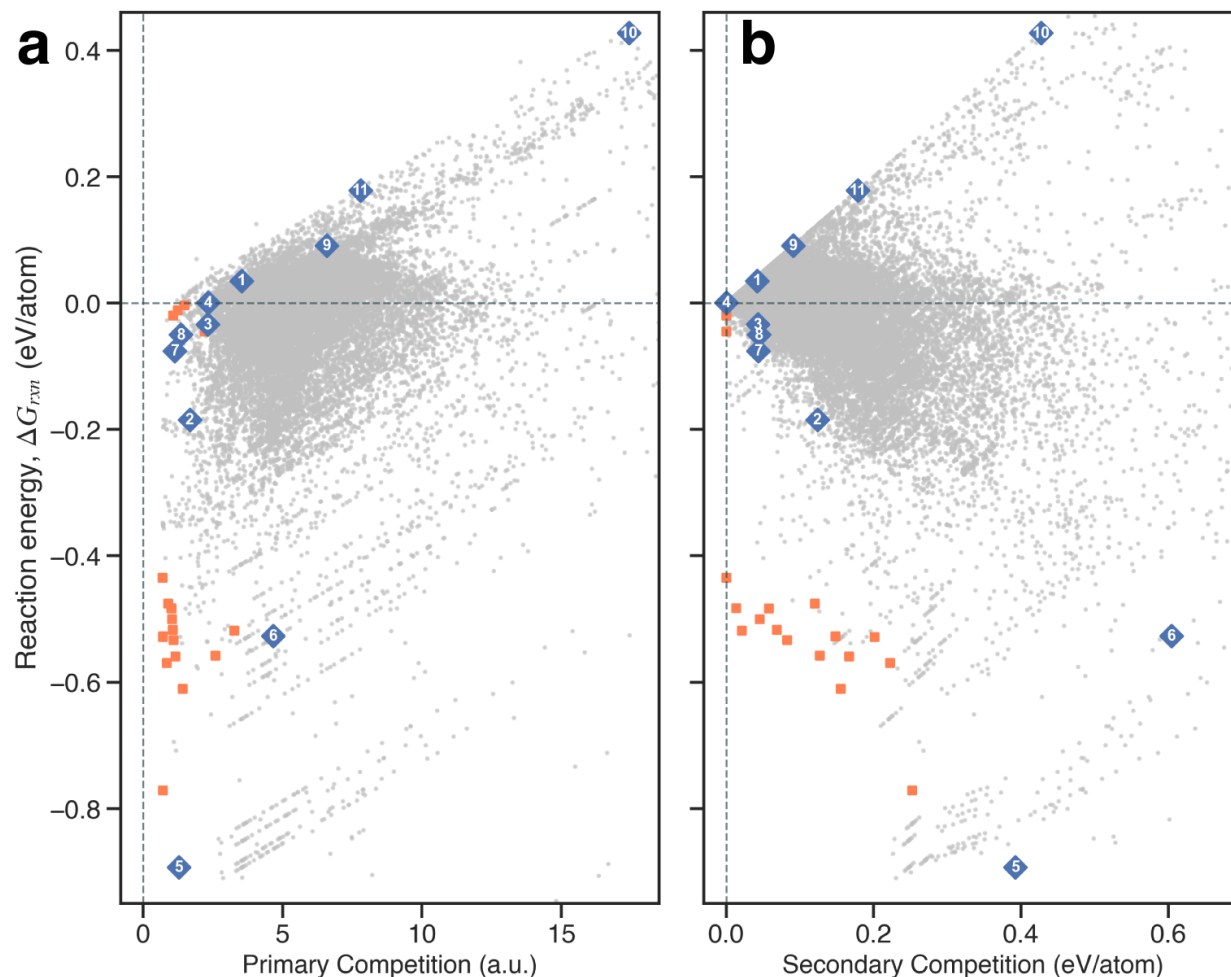


Figure 6.6: Synthesis map of 25,905 calculated synthesis reactions producing BaTiO_3 . Reaction energies and competition scores are calculated assuming a temperature of $T = 650^\circ\text{C}$. Reactions are plotted on a shared axis of reaction energy, ΔG_{rxn} , and on independent axes of (a) primary competition, C_1 , and (b) secondary competition, C_2 . Orange squares represent reactions on the three-dimensional Pareto frontier of ΔG_{rxn} , C_1 , and C_2 . Blue diamonds indicate selected reactions experimentally tested in this work.

Figure 6.6b) highlight the inherent tradeoff between driving force and reaction selectivity. Not all reactions must sacrifice good driving force or selectivity, however; several reactions occupy the lower left corner of the synthesis map, where both competition scores and reaction energies are low/negative. Due to the cost-oriented nature of our selectivity metrics, the task of selecting an optimal synthesis reaction can be transformed into an optimization problem of simultaneous minimization of all three reaction metrics: $\Delta\Phi_{\text{rxn}}$, C_1 , and C_2 . One such approach to simultaneous minimization of cost metrics that was explored in Chapters 3 and 5 is to define a “cost function” weighting the various reaction metrics. This approach assumes an optimal weighting scheme exists; however, currently, these must be assigned based on

desired behavior by the user. A more unrestricted approach is to consider reactions lying on the Pareto front [215]. Here, we calculate a 3-dimensional Pareto front along the axes of ΔG_{rxn} , C_1 , and C_2 . The Pareto-optimal reactions for BaTiO_3 are marked as orange squares in Figure 6.6 and summarized in Table 6.1.

Table 6.1: Pareto front reactions to BaTiO_3 and their associated Gibbs free energies, ΔG_{rxn} ($T = 650$ °C), primary competition scores, C_1 , and secondary competition scores, C_2 .

Rank	Reaction	ΔG_{rxn}	C_1	C_2	Cost	Theoretical
0	$8 \text{ O}_2 + \text{Ba}_4\text{TiP}_4 \rightarrow \text{Ba}_3\text{P}_4\text{O}_{13} + \text{BaTiO}_3$	-2.305	4.947	0.211	0.175	
1	$\text{BaO}_2 + 0.09091 \text{ Ti}_6\text{O} \rightarrow 0.09091 \text{ BaTiO}_3 + 0.4545 \text{ Ba}_2\text{TiO}_4$	-1.486	3.496	0.055	0.196	
2	$\text{BaO}_2 + 0.2 \text{ Ti}_3\text{O} \rightarrow 0.2 \text{ BaTiO}_3 + 0.4 \text{ Ba}_2\text{TiO}_4$	-1.405	3.199	0.049	0.198	
3	$\text{BaO}_2 + 0.5 \text{ Ti} \rightarrow 0.25 \text{ BaTiO}_3 + 0.25 \text{ Ba}_3\text{TiO}_5$	-1.489	3.318	0.104	0.199	
4	$\text{BaO}_2 + 0.3333 \text{ Ti}_2\text{O} \rightarrow 0.3333 \text{ BaTiO}_3 + 0.3333 \text{ Ba}_2\text{TiO}_4$	-1.326	2.895	0.062	0.201	
5	$\text{BaO}_2 + 0.25 \text{ Ti}_3\text{O}_2 \rightarrow 0.5 \text{ BaTiO}_3 + 0.25 \text{ Ba}_2\text{TiO}_4$	-1.254	2.887	0.119	0.212	Ti_3O_2
6	$\text{TiO} + \text{BaO}_2 \rightarrow \text{BaTiO}_3$	-1.045	2.627	0.106	0.223	
13	$\text{TiC} + \text{BaCO}_3 \rightarrow \text{BaTiO}_3 + 2 \text{ C}$	-0.435	0.699	0.000	0.234	
14	$\text{BaH}_4\text{O}_3 + 0.25 \text{ Ti}_4\text{H}_7 \rightarrow \text{BaTiO}_3 + 2.875 \text{ H}_2$	-0.483	1.009	0.014	0.235	Ti_4H_7
15	$\text{BaO}_2 + 0.3333 \text{ Ti}_2\text{S} \rightarrow 0.3333 \text{ BaS} + 0.6667 \text{ BaTiO}_3$	-1.367	0.841	0.563	0.237	
16	$\text{BaH}_4\text{O}_3 + 0.5 \text{ Ti}_2\text{H}_3 \rightarrow \text{BaTiO}_3 + 2.75 \text{ H}_2$	-0.500	1.034	0.045	0.238	Ti_2H_3
17	$\text{BaH}_4\text{O}_3 + 0.25 \text{ Ti}_4\text{H}_5 \rightarrow \text{BaTiO}_3 + 2.625 \text{ H}_2$	-0.517	1.062	0.069	0.240	Ti_4H_5
18	$\text{BaH}_4\text{O}_3 + \text{TiH}_2 \rightarrow \text{BaTiO}_3 + 3 \text{ H}_2$	-0.483	1.016	0.058	0.241	
19	$\text{BaO}_2 + 0.3333 \text{ Ti}_3\text{N}_2\text{O}_3 \rightarrow \text{BaTiO}_3 + 0.3333 \text{ N}_2$	-0.771	0.704	0.252	0.241	$\text{Ti}_3\text{N}_2\text{O}_3$
20	$\text{BaH}_4\text{O}_3 + \text{TiH} \rightarrow \text{BaTiO}_3 + 2.5 \text{ H}_2$	-0.533	1.093	0.083	0.241	
24	$\text{Ti}_8\text{C}_5 + 8 \text{ BaCO}_3 \rightarrow 8 \text{ BaTiO}_3 + 13 \text{ C}$	-0.528	0.708	0.148	0.246	
25	$\text{BaH}_4\text{O}_3 + \text{Ti} \rightarrow \text{BaTiO}_3 + 2 \text{ H}_2$	-0.611	1.414	0.156	0.248	
26	$\text{BaO}_2 + 2 \text{ LiTiO}_2 \rightarrow \text{Li}_2\text{TiO}_3 + \text{BaTiO}_3$	-0.475	0.894	0.121	0.248	
27	$6 \text{ Na}_3\text{P} + \text{BaTi}(\text{S}_2\text{O}_7)_3 \rightarrow \text{BaTiO}_3 + 6 \text{ Na}_3\text{PSO}_3$	-0.980	1.940	0.337	0.249	Na_3PSO_3
28	$\text{BaH}_4\text{O}_3 + 0.25 \text{ Ti}_4\text{H}_3 \rightarrow \text{BaTiO}_3 + 2.375 \text{ H}_2$	-0.559	1.157	0.167	0.251	Ti_4H_3
34	$\text{Ti}_3\text{C}_2 + 3 \text{ BaCO}_3 \rightarrow 3 \text{ BaTiO}_3 + 5 \text{ C}$	-0.528	0.706	0.201	0.253	
38	$0.5 \text{ Ti}_2\text{C} + \text{BaCO}_3 \rightarrow \text{BaTiO}_3 + 1.5 \text{ C}$	-0.569	0.847	0.222	0.254	
40	$\text{BaCO}_3 + 2 \text{ Ti} \rightarrow \text{TiC} + \text{BaTiO}_3$	-0.893	1.275	0.392	0.256	
43	$\text{O}_2 + 0.3333 \text{ Ba}_2\text{Ti}_{13}\text{O}_{22} \rightarrow 0.6667 \text{ BaTiO}_3 + 3.667 \text{ TiO}_2$	-0.519	3.268	0.021	0.258	
55	$\text{Ba}_2\text{Ti}_{13}\text{O}_{22} + 6 \text{ BaO}_2 \rightarrow 5 \text{ BaTi}_2\text{O}_5 + 3 \text{ BaTiO}_3$	-0.558	2.593	0.127	0.262	
65	$\text{BaTiS}_3 + 6 \text{ KO}_2 \rightarrow 3 \text{ K}_2\text{SO}_3 + \text{BaTiO}_3$	-1.060	1.967	0.482	0.263	
110	$0.5 \text{ BaF}_2 + 0.5 \text{ Li}_2\text{TiO}_3 \rightarrow \text{LiF} + 0.5 \text{ BaTiO}_3$	-0.020	1.079	0.000	0.270	
130	$\text{Ba}_3(\text{PO}_4)_2 + 3 \text{ Li}_2\text{TiO}_3 \rightarrow 2 \text{ Li}_3\text{PO}_4 + 3 \text{ BaTiO}_3$	-0.011	1.239	0.000	0.273	
160	$\text{Ti} + 0.25 \text{ Ba}(\text{NO}_3)_2 \rightarrow 0.25 \text{ BaTiO}_3 + 0.25 \text{ Ti}_3\text{N}_2\text{O}_3$	-1.836	3.307	0.915	0.276	$\text{Ti}_3\text{N}_2\text{O}_3$
166	$\text{CaTiO}_3 + \text{K}_3\text{BaPCO}_7 \rightarrow \text{BaTiO}_3 + \text{K}_3\text{CaPCO}_7$	-0.004	1.490	0.000	0.276	$\text{K}_3\text{BaPCO}_7, \text{K}_3\text{CaPCO}_7$
235	$\text{Ba}_3\text{Ti}_2\text{O}_7 \rightarrow \text{BaTiO}_3 + \text{Ba}_2\text{TiO}_4$	-0.045	2.213	0.000	0.282	$\text{Ba}_3\text{Ti}_2\text{O}_7$

Interestingly, many Pareto-optimal reactions involve extremely unconventional reactants or byproducts, including some hypothetical phases that have not yet been synthesized. For example, the reaction $3 \text{ BaO}_2 + \text{Ti}_3\text{N}_2\text{O}_3 \rightarrow 3 \text{ BaTiO}_3 + \text{N}_2$ ($\Delta G_{\text{rxn}} = -0.771$ eV/atom, $C_1 = 0.704$ a.u., $C_2 = 0.252$ eV/atom) uses a $\text{Ti}_3\text{N}_2\text{O}_3$ precursor that has not been reported in the literature. Many of the Pareto front reactions have quite negative reaction energies, including several reactions of the form $\text{BaO}_2 + \text{Ti}_x\text{O}$ ($x \in \{0, 0.6, 1, 2, 3, 6\}$), which have reaction energies $\Delta G_{\text{rxn}} < -1.0$ eV/atom but also suboptimal competition scores and produce unwanted ternary Ba-Ti-O byproducts. Another unique synthesis reaction identified from the Pareto reactions is $\text{BaCO}_3 + \text{TiC} \rightarrow \text{BaTiO}_3 + 2 \text{ C}$ ($\Delta G_{\text{rxn}} = -0.435$ eV/atom, $C_1 = 0.699$ a.u., $C_2 = 0.0$ eV/atom), which has a favorable reaction energy and

very low competition scores. However, this reaction involves the use of a titanium carbide precursor. TiC is extremely refractory and unlikely to react even at very high temperatures; it is also difficult to grind and process for solid-state synthesis. Finally, two of the most promising reactions with optimal selectivity and more moderate driving forces are metathesis reactions: $\text{BaF}_2 + \text{Li}_2\text{TiO}_3 \longrightarrow \text{BaTiO}_3 + 2 \text{LiF}$ ($\Delta G_{\text{rxn}} = -0.020$ eV/atom, $C_1 = 1.079$ a.u., $C_2 = 0.0002$ eV/atom), and $\text{Ba}_3(\text{PO}_4)_2 + 3 \text{Li}_2\text{TiO}_3 \longrightarrow 2 \text{Li}_3\text{PO}_4 + 3 \text{BaTiO}_3$ ($\Delta G_{\text{rxn}} = -0.011$ eV/atom, $C_1 = 1.239$ a.u., $C_2 = 0.0002$ eV/atom). These results yet again highlight the thermodynamic advantage of solid-state metathesis in providing selective thermodynamic “shortcuts” to desired target products [224].

To test the accuracy of our reaction selectivity predictions, we selected 11 reactions from Figure 6.6 spanning a wide range of chemistries, free energies, and competition scores. The selected experimental reactions are shown in Table 6.2 and highlighted as blue diamonds in Figure 6.6. We choose to include the conventional synthesis approach (Expt. 1, $\text{BaCO}_3 + \text{TiO}_2 \longrightarrow \text{BaTiO}_3 + \text{CO}_2$) as a baseline reference. We did not experimentally test the analogous reaction with BaO precursor (Figure 6.3) due to its hygroscopic nature and the fact that the reaction of BaO is likely accounted for by the thermal decomposition of BaCO_3 ; however, we did test the alternative reaction from barium peroxide, BaO_2 (Expt. 2). We included two reactions that form BaTiO_3 directly with no byproducts (Expts. 3, 4). Two reactions involving elemental titanium precursor (Expts. 5, 6) were selected to probe the performance of elemental reactions that sacrifice selectivity for higher driving forces. Two metathesis-like reactions (Expts. 7, 8) were selected due to their predicted high performance, including the very unconventional use of a sulfide precursor (BaS) in making an oxide. Finally, three of the selected reactions (Expts. 9-11) were intentionally selected for being endergonic ($\Delta G_{\text{rxn}} > 0$) reactions to validate the accuracy of our free energy predictions. We note that only one reaction (Expt. 5) is explicitly a Pareto-optimal reaction. However, several of the selected reactions are near the Pareto front or similar to Pareto-optimal reactions; we often elected to test reactions that were easier to handle experimentally or involved more readily available precursors. For example, Expt. 7 follows the Pareto-optimal metathesis structure previously described ($\text{BaX}_2 + \text{A}_2\text{TiO}_3 \longrightarrow \text{BaTiO}_3 + 2 \text{AX}$) but yields NaCl instead of LiF.

Plotting the interface reaction hulls (Figure 6.7) of the selected experiments helps to rationalize their predicted competition scores and reaction energies. Immediately, we see from the interface reaction hulls that most precursor combinations involve a large number of competing reactions (blue dots) that may interfere with the selected reaction (red diamond). Seven of the eleven reactions (all but Expts. 4, 5, 7, 8) are *not* the minimum points of their respective hulls, suggesting that a more favorable reaction is possible from the same precursors. However, being the minimum of the reaction hull is not a sufficient selectivity metric alone. In Expt. 5 (Figure 6.7e), many competing reactions exist on or just slightly above the hull, which leads to a high C_2 value (Table 6.2). Finally, having a positive ΔG_{rxn} does not guarantee that zero reaction between the precursors will occur; the hulls for Expts. 9-11 (Figure 6.7i-k) indicate significant competition, including several reactions close to the hull.

Table 6.2: Selected experimental reactions to BaTiO₃ and their associated Gibbs free energies, ΔG_{rxn} ($T = 650$ °C), primary competition scores, C_1 , and secondary competition scores, C_2 .

Expt.	Reaction	ΔG_{rxn}	C_1	C_2
1	$\text{BaCO}_3 + \text{TiO}_2 \longrightarrow \text{BaTiO}_3 + \text{CO}_2$	0.035	3.535	0.042
2	$\text{BaO}_2 + \text{TiO}_2 \longrightarrow \text{BaTiO}_3 + 0.5 \text{ O}_2$	-0.185	1.671	0.124
3	$\text{Ba}_2\text{TiO}_4 + \text{TiO}_2 \longrightarrow 2 \text{ BaTiO}_3$	-0.034	2.317	0.043
4	$\text{Ba}_2\text{TiO}_4 + \text{BaTi}_2\text{O}_5 \longrightarrow 3 \text{ BaTiO}_3$	0.000	2.327	0.000
5	$\text{BaCO}_3 + 2 \text{ Ti} \longrightarrow \text{BaTiO}_3 + \text{TiC}$	-0.893	1.275	0.392
6	$\text{Ba(OH)}_2 \cdot \text{H}_2\text{O} + 3.666 \text{ Ti} \longrightarrow \text{BaTiO}_3 + 1.333 \text{ Ti}_2\text{H}_3$	-0.527	4.656	0.604
7	$\text{BaCl}_2 + \text{Na}_2\text{TiO}_3 \longrightarrow \text{BaTiO}_3 + 2 \text{ NaCl}$	-0.076	1.138	0.044
8	$\text{BaS} + \text{Na}_2\text{TiO}_3 \longrightarrow \text{BaTiO}_3 + \text{Na}_2\text{S}$	-0.050	1.356	0.045
9	$2 \text{ BaS} + 3 \text{ TiO}_2 \longrightarrow 2 \text{ BaTiO}_3 + \text{TiS}_2$	0.091	6.584	0.091
10	$\text{BaSO}_4 + \text{TiO}_2 \longrightarrow \text{BaTiO}_3 + \text{SO}_3$	0.427	17.427	0.427
11	$\text{BaSO}_4 + 2 \text{ TiO}_2 \longrightarrow \text{BaTiO}_3 + \text{TiSO}_5$	0.178	7.802	0.178

The 11 synthesis experiments were performed using the gradient furnace [37], allowing us to study reaction products at a wide range of temperatures ($\sim 300 - 1000$ °C) with *ex post facto* synchrotron X-ray diffraction (SXRD). Phase fractions (mol %) were determined via semi-quantitative phase analysis of SXRD patterns acquired at various positions (temperatures) along the length of the sample. *Ex post facto* phase fraction plots are similar to those often plotted for *in situ* data, in that they illustrate the reaction pathway of precursors upon heating. However, one must recognize that each point is pseudo-independent from those around it and is best interpreted as the result of an isothermal (*ex situ*) reaction.

To compare the performance and selectivity of reactions from *ex post facto* data, we propose the use of Precursor-Target-Impurity (PTI) plots, which capture key aspects of the reaction pathway independent of the kinetics of that reaction. This is necessary given the range of different chemistries explored in our reactions. The PTI plots for all experimental reactions are shown in Figure 6.8. Each plot is composed of three quantities, each of which is a phase fraction (Mol %) measured at any point within the *ex post facto* data. These quantities include: 1) the minimum precursor remaining, 2) the maximum target formed, and 3) the maximum impurity formed. The first quantity (gray bar, minimum precursor remaining) gives insight into the reactivity and kinetics of the reaction: high values indicate reactions that did not complete at any temperature within the ~ 60 mins. The second quantity (green bar, maximum target formed) provides a measure of the success of the reaction in producing the target product(s); a phase fraction of 100% indicates that the entire sample was composed of expected reaction product(s) at one or more temperature points. Finally, the third quantity (pink bar, maximum impurity formed) provides a measure of the selectivity of the reaction pathway, indicating the maximum percentage of intermediates or secondary phases remaining at any point in the reaction pathway. We note that the design of

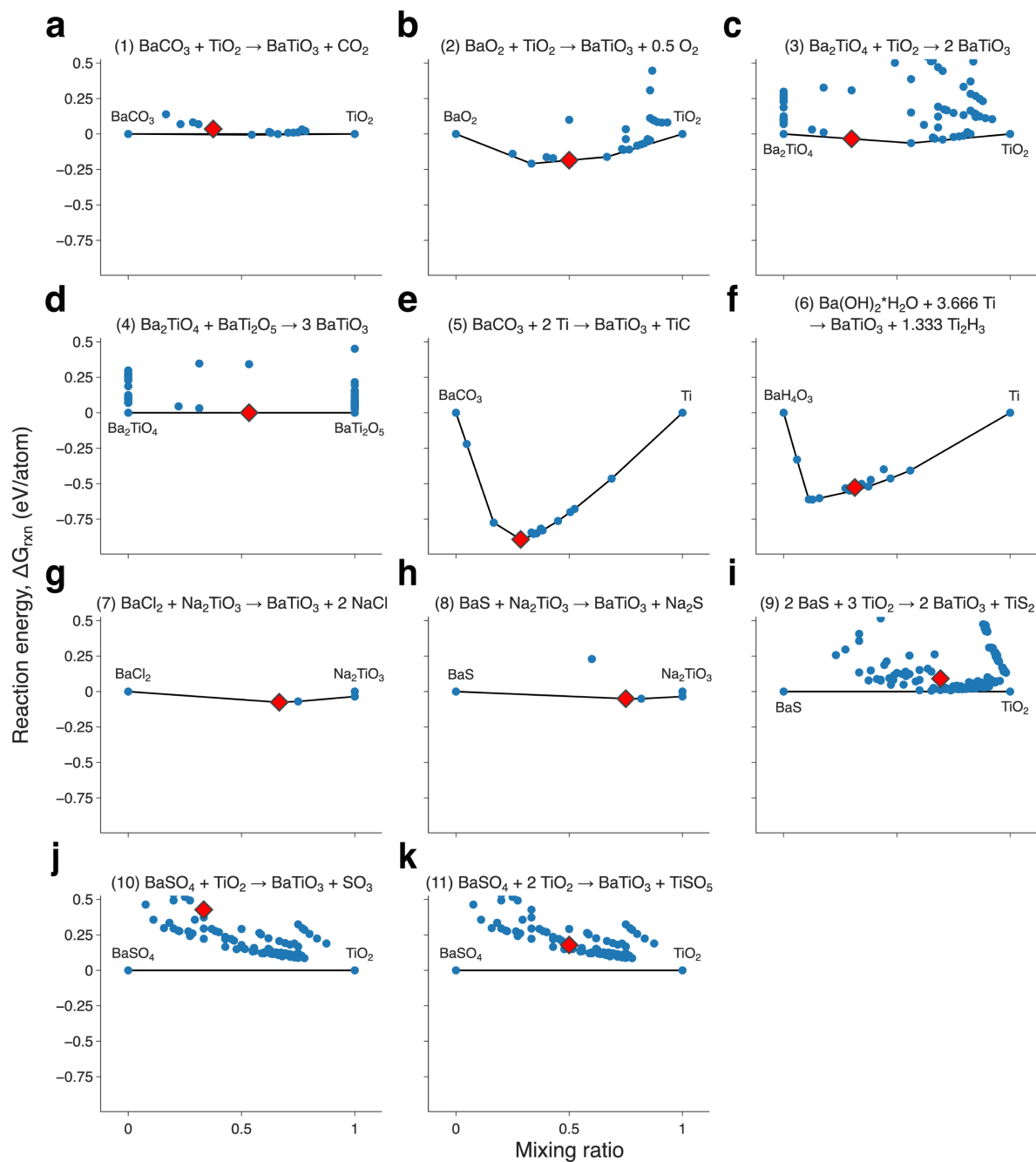


Figure 6.7: Interface reaction hulls for selected BaTiO_3 experiments. (a-k) hulls for Experiments 1-11 from Table 6.2, respectively, extracted from the full reaction network calculated during the synthesis planning workflow. Red diamonds mark the selected reactions of interest. All hulls are plotted on a uniform energy scale to facilitate comparison.

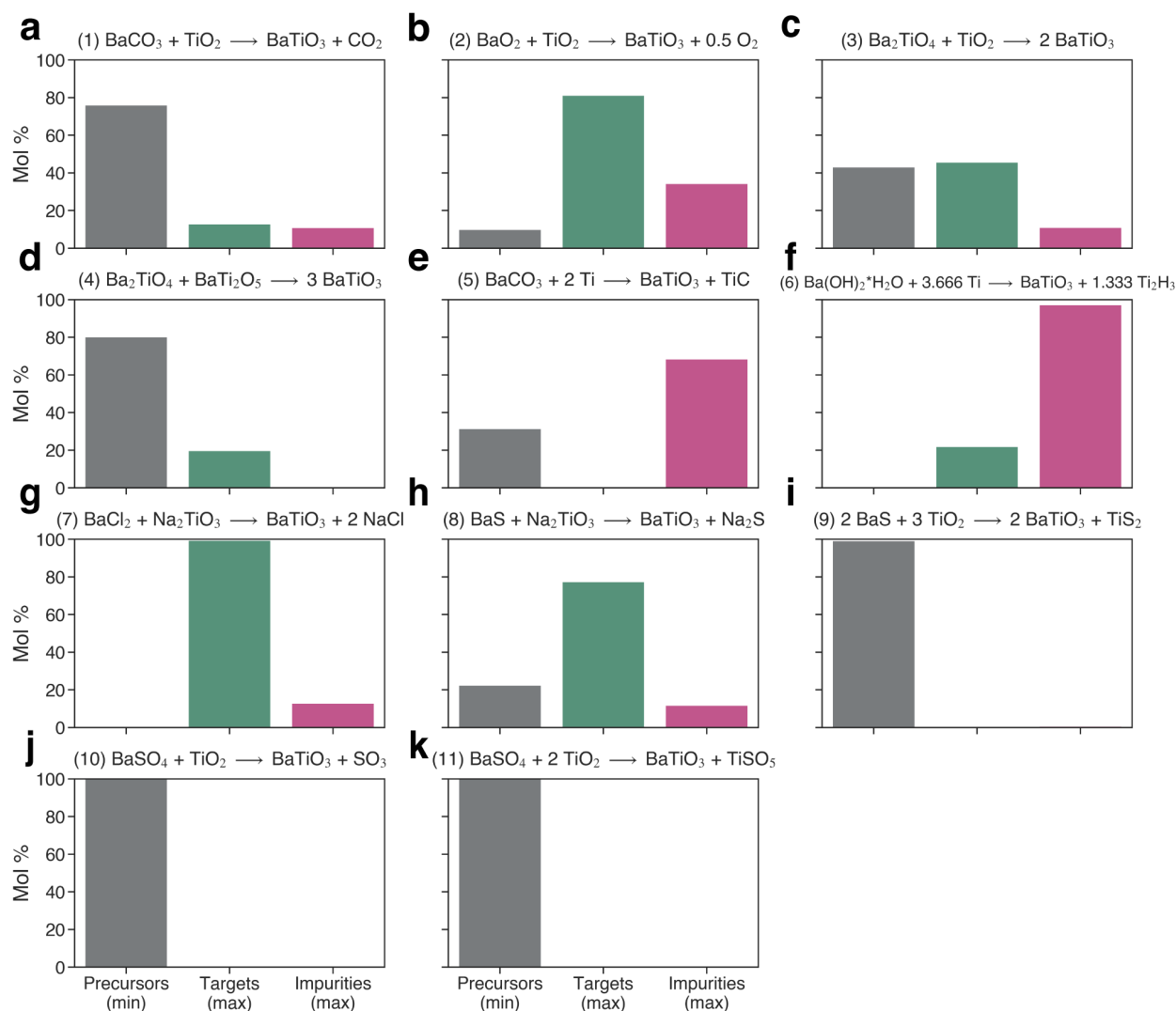


Figure 6.8: Precursor-target-impurity (PTI) plots summarizing *ex post facto* SXRD results. (a-k) Categorized phase amounts for Experiments 1-11, respectively. Gray bars indicate the minimum mole percent of precursors remaining at any position (i.e., temperature) along the length of the sample, after the conclusion of the experiment (~ 60 min). Likewise, the green and pink bars indicate the maximum mole percent of target phases and impurity phases, respectively, as observed at any position after heating and cooling.

the PTI plot permits the measurement of poor selectivity in even nominally well-performing reactions, as both the target and impurity phase fractions can theoretically reach 100% within the same reaction.

The experimental SXRD results are plotted as a function of reaction energy and secondary competition in Figure 6.9. Our experiments show that the computed reaction energy is a strong predictor for the reactivity of a given set of precursors, as measured by the mini-

precursor remaining. In Figure E.5a (Appendix), we see that the remaining precursor amounts yield a sigmoid-like shape centered around a reaction energy of zero. This trend is partially broken for the most exergonic reaction, Expt. 5, which did not fully react within the timeframe of the experiment. We attribute this exception to the use of Ti metal as a precursor, as the Ti likely experienced surface oxidation during the preparation of the sample leading to a decrease in the total driving force of the reaction. The recovery of a sigmoid-like shape validates the use of DFT-computed data for modeling reaction thermodynamics, especially when paired with correction schemes and experimental data, as completed here.

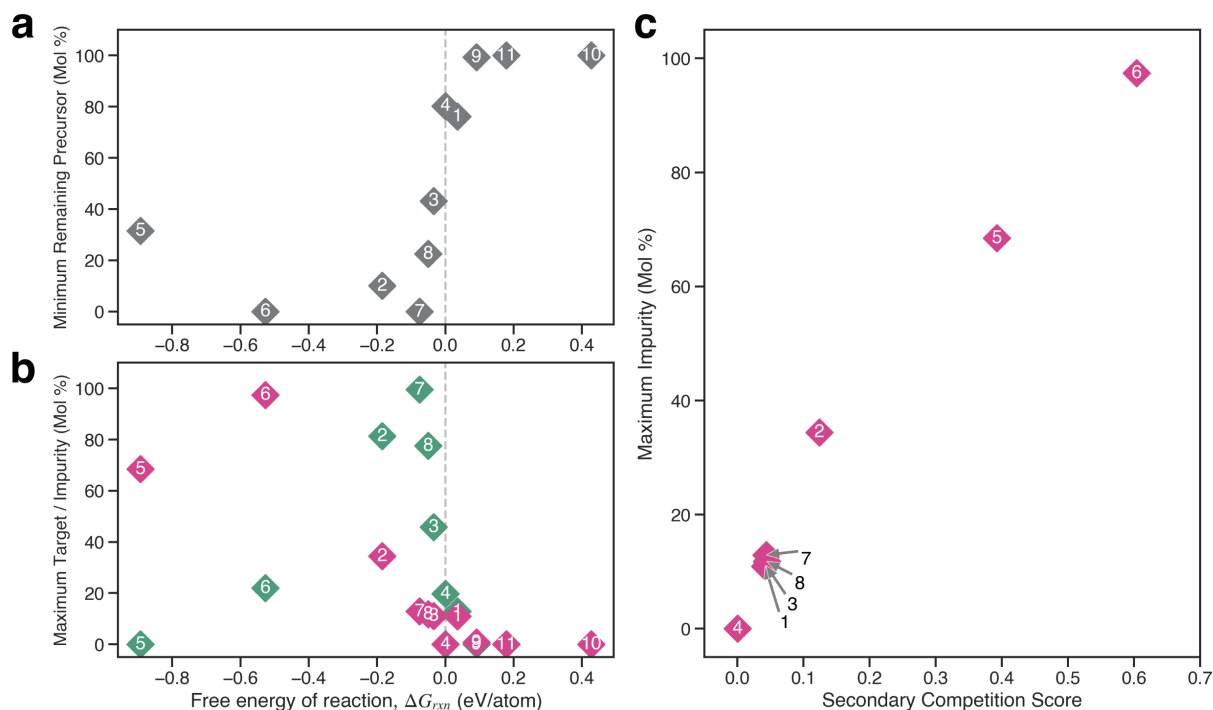


Figure 6.9: Experimental validation of predicted synthesis performance. (a) Minimum remaining precursor (gray) as a function of each reaction’s free energy. (b) Maximum target (green) and impurity (pink) formed during the reaction as a function of each reaction’s energy. (c) Maximum impurity formed in Expts. 1-8 as a function of the secondary competition score, showing a strong performance of C_2 for predicting impurity formation in the synthesis of BaTiO₃. Experiments 9, 10, and 11 are not shown (see Figure E.5 in Appendix), as they did not react to produce any phases.

Interestingly, the reaction energy also correlates with the target and impurity phases formed during the experiments (Figure 6.9b). The maximum target formed peaks not with the highest driving force reactions but rather with Expts. 2, 7, and 8, which have reaction energies of -0.185, -0.076, and -0.050 eV/atom, respectively. While this may be related to the fact that Expts. 7 and 8 are selective (low competition scores), we note that Expt. 2 has a quite high C_2 score of 0.124 eV/atom. Hence there seems to be some rationale for choosing reactions that have only moderately large driving forces, as highly exergonic reactions appear

to produce significant amounts of impurity phases. Whether this is explicitly due to the inherent tradeoff between driving force and selectivity cannot be confirmed.

The experimental results indicate that our metric for secondary competition, C_2 (Equation 6.6), appears to be a strong predictor for impurity formation. According to Figure 6.9c, the maximum measured impurity formation uniformly increases with predicted C_2 value. Interestingly, however, the primary competition metric, C_1 , does not seem to correlate strongly with impurity formation (Figure E.5 in Appendix). This is best observed in Expt. 5, which resulted in significant impurity formation (primarily Ba_2TiO_4), despite having a very low C_1 score (the second lowest, 1.275 a.u.). Because the formula for C_1 involves the use of a normalization factor that depends on the sum of all possible reactions, it is likely significantly biased by how well a particular compositional space has been explored in the thermodynamic data. This bias limits the use of C_1 in a similar manner to the “selectivity” metric used by Aykol et al. [215], which in their study was a count of the number of alternative phases that the reaction of the precursors could form.

6.6 Recommendations and outlook

The strong performance of C_2 in predicting impurity formation in our experiments suggests that the decomposition free energy of competing phases appears to be the critical factor in determining the selectivity of a solid-state reaction. However, as we show here, it is not explicitly the decomposition energy of a competing phase that matters, but rather the *reaction energy* to produce competing phase(s) as measured from the reaction of precursors with the target phase(s) of interest. One can imagine a situation, for example, in which there are a great number of competing reactions on the hull that *individually* have low decomposition reaction energies from their neighbors but collectively lead to a high C_2 value in their summation. In a sense, C_2 measures how much the interface reaction hull is ‘stretched outwards’ from the target product by the full spectrum of competing reactions, thereby providing a measure of the relative driving force to form impurity phases. One may ask if it is necessary to consider all decomposition pathways described by Equation 6.2 and illustrated in Figure 6.4, or if it is sufficient to consider only the secondary reaction on either side of the target with the maximum reaction energy. Considering only the maximum energy secondary reactions *does* account for much of the value of C_2 ; however, because C_2 considers both the maximum energy secondary reactions and further subsequent reactions, its value will always be higher than the maximum reaction energies alone. Since C_2 is a more conservative metric (always higher), we recommend its use.

In Chapter 5, we suggested a possible solid-state reaction selectivity metric (“total chemical potential distance”) based on the difference in elemental chemical potentials between precursors and targets, as measured by distance along the chemical potential diagram. This metric was used to rationalize the unique selectivity of the Na-based precursor in synthesizing pyrochlore $\text{Y}_2\text{Mn}_2\text{O}_7$ from YOCl and AMnO_2 ($A=\text{Li,Na,K}$). While straightforward to compute using just the chemical potential diagram (which relies on phase equilibria alone),

this metric operates in the space of chemical potentials rather than reaction energies, rendering it less intuitive and making it difficult to discern precisely what the specific competing reactions are. We generally recommend the use of C_2 over the “total chemical potential distance”. Both selectivity metrics can be described as summations of the decomposition energies of competing phases – and are even correlated – however, because of how chemical potential relates to slopes of the hull, the total chemical potential distance is biased in particular by competing phases that are close in composition to elemental precursors. This is especially apparent with defect compositions, such as Mg_{149}Cl . Chemical potential diagrams featuring these compositions may lead to very high (unfavorable) total chemical potential distance values for synthesis reactions, even when these phases are not associated with high competing reaction energies.

The major limitation of our current synthesis planning workflow is the assumption that optimal synthesis reactions can be predicted with thermodynamics alone. While this is certainly not true for all chemistries, we show that at least for chemical systems that have favorable solid-state reaction kinetics (e.g., the Ba-Ti-O system studied here), thermodynamics alone can provide much of the rationalization for the observation of impurity phases. To say that impurity/secondary phases are inherently “kinetic” products is a misnomer. While impurity phases are indeed not the “thermodynamic” products (i.e., phases expected at global thermodynamic equilibrium), the interface reaction model explored in Figure 6.1c shows that the secondary phases may indeed be “locally” stable. In other words, these impurity products form stable interfaces with other phases in the mixture. They cannot be easily converted to the global thermodynamic products of the system without being kinetically provoked (e.g., through re-grinding or subsequent heating). This becomes a problem for chemical systems with lower driving forces and/or slower kinetics, where impurity phases may be nearly impossible to remove once formed (e.g., as in the synthesis of BiFeO_3).

We note that many unconventional synthesis routes suggested by our synthesis planning workflow involve the formation of byproducts that are not always easy to remove from the product mixture. For example, this includes reactions that selectively produce BaTiO_3 and another Ba-Ti-O phase, like several of the reactions in the Pareto optimal set (Table 6.1) that produce Ba_2TiO_4 . It is thus practical to filter recommended synthesis reactions by whether or not byproducts can be easily separated, i.e., if they are gaseous species (e.g., O_2 or CO_2) or contain only extraneous elements not found in the target product (e.g., NaCl) that a solvent can selectively wash away. Other reactions involve metastable or even hypothetical precursors/byproducts that may not be acquirable. It is thus also practical to filter recommended synthesis reactions by whether precursors can easily be purchased or synthesized. We note that, while not explicitly demonstrated here, the synthesis planning workflow can be used for multi-step syntheses; i.e., to recommend optimal synthesis routes to a difficult-to-acquire precursor that can be used to selectively synthesize the target of interest. Finally, as mentioned previously, some suggested synthesis reactions involve precursors that are refractory, hard, or otherwise difficult to react, except for at extremely high temperatures. Future work should focus on incorporating models for estimating reaction kinetics, perhaps, for example, using machine-learned solid-state diffusivities or melting points.

Chapter 7

Conclusions

7.1 Summary of this work

In Chapter 3, we discussed the design of a solid-state chemical reaction network model constructed from available thermochemistry data and demonstrated the model as a predictor of reaction pathways in solid-state materials synthesis. The framework effectively reduces the large, complex thermodynamic landscape to a computationally tractable structure through i) creation of a weighted directed graph representation of the available thermodynamic phase space, ii) mapping of rigorous thermodynamic data and possible heuristics into a versatile cost function, and iii) application of graph pathfinding algorithms to identify probable reaction routes. While the framework explores reaction trajectories in the most general way possible, allowing for parallel combined pathways, the combinatorial complexity is reduced by chemically motivated filters such as: 1) restricting the number of phases considered via thermodynamic stability arguments, 2) limiting the maximum number of simultaneously reacting phases, and 3) enforcing mass conservation via stoichiometric constraints. As a demonstration, the framework was shown to identify complex reaction pathways comparable to those observed in several experimental solid-state synthesis studies. We envision our methodology to be used to suggest possible synthesis precursors/routes that create efficient thermodynamic conditions for targeting desired phases, as well as the identification of byproducts and possible intermediates along synthesis routes. Future work will benefit tremendously by combining the framework “live” with automated data collection, *in situ* phase identification, rapid analysis techniques, and automated feedback loops, moving towards active control of solid-state synthesis.

In Chapter 4, we studied reactions of three polymorphs of LiMnO_2 with YOCl to form LiCl and YMnO_3 using X-ray and neutron diffraction and density functional theory calculations. The reactions form several crystalline intermediates, including r-YOCl , $\text{Y}_3\text{O}_4\text{Cl}$ and two lithium manganese oxide spinel intermediates. The two spinel intermediates, reduced t' -spinel and oxidized c' -spinel, are the result of manganese disproportionation as lithium and oxygen are removed from LiMnO_2 over the course of the reaction. DFT-calculated ther-

mochemistry reveals that small changes in the manganese oxidation state change the relative stability of the two polymorphs of YMnO_3 , suggesting that t' -spinel leads to formation of h - YMnO_3 while c' -spinel leads to the formation of o - YMnO_3 . By changing the LiMnO_2 precursor, the ratio of reduced to oxidized spinel intermediates changes, which results in different ratios of the observed products. By tuning the composition of these spinel intermediates, the concentration of defects can be synthetically controlled in the resulting YMnO_3 products. Paired with additional post-synthesis treatment, these defects can be influenced or removed, which provides increased selectivity in the synthesis of complex oxides. By understanding the role defect-accommodating intermediates play in determining the structure of the final product, routes to new metastable complex solids can be discovered. We also studied the synthesis of α - NaFeO_2 directly via a mechanochemical approach without any required additional heating of the sample (which is required by other synthesis methods). The synthesis of the α - NaFeO_2 is shown to be sensitive to the Fe_2O_3 polymorph as well as the mass of the precursor being milled, indicating that defect concentration and synthesis environment may be critical parameters to control gain polymorph control in this system. While the α phase is predicted by density functional theory calculations to be metastable (even at $T=0$ K), we show via charged point defect calculations that at high oxygen chemical potentials, α - NaFeO_2 is thermodynamically stabilized over the β - and γ - polymorphs due to its greater ability to accommodate equilibrium cation vacancy concentrations at the annealing temperature. Upon annealing the sample, the α - NaFeO_2 has higher crystallinity, larger particle size, and is less disordered. Understanding the synthesis process provides important information that may guide further polymorph control in layered transition metal oxides.

In Chapter 5, we showed that in the reaction of $3\text{Na}_2\text{CO}_3 + 2\text{YCl}_3 + \text{Mn}_2\text{O}_3$, the $\text{Y}_2\text{Mn}_2\text{O}_7$ pyrochlore forms selectively via the direct reaction of Na_xMnO_2 and Y_2O_3 intermediates, as revealed by *in situ* temperature- and time-dependent SPXRD experiments. However, this pyrochlore selectivity is not achieved with the analogous Li_2CO_3 or K_2CO_3 precursors. Mapping the reaction species in chemical potential space illustrates that NaMnO_2 , and structurally-related compositional variants permit a small difference in local chemical potentials between the $\text{Na}_x\text{Mn}_y\text{O}_2$ intermediates and $\text{Y}_2\text{Mn}_2\text{O}_7$, as the chemical stability windows of structurally homologous $\text{Na}_x\text{Mn}_y\text{O}_2$ phases connect directly with that of $\text{Y}_2\text{Mn}_2\text{O}_7$. The short distance in chemical potential space illustrates why the reaction to form $\text{Y}_2\text{Mn}_2\text{O}_7$ is selective. In contrast, the other alkali-based (Li, K) intermediate phases lack the same degree of structural homology and share different boundaries, thus resulting in the formation of different products. The mechanistic details obtained from crystallographic analysis highlight that the thermodynamic boundaries dictate the reactivity rather than the mobility of an alkali cation within the oxide framework. This analysis illustrates how local thermodynamic equilibrium principles provide a direct connection to reaction kinetics in guiding the mechanistic pathway of solid-state reactions, thus providing a notion of a protecting group in materials synthesis. The thermodynamic underpinnings permit high-throughput prediction of precursors in higher dimensional chemical spaces that can impart selectivity, kinetic viability, and reversibility.

In Chapter 6, we proposed two thermodynamic selectivity metrics for solid-state reac-

tions: primary (C_1) and secondary (C_2) competition. We show that, while both metrics are theoretically necessary to quantify phase competition in a reacting system of solid particles, the proposed secondary competition score metric, C_2 , correlates most strongly with measured impurity formation in 11 synthesis experiments for the ferroelectric, barium titanate (BaTiO_3). The primary competition score, C_1 , as well as the previously proposed “total chemical potential distance” selectivity metric [95], generally correlate with C_2 but are somewhat biased in their current formulation by the quantity of phase data available and the presence of phases which have compositions close to elemental references. Hence, we recommend the use of C_2 in particular for synthesis planning. We anticipate that the selectivity metrics presented here and our computational synthesis planning workflow will lead to great reductions in the synthesis bottleneck, providing more rapid development of synthesis approaches for new, predicted materials. Our workflow also promises to optimize existing suboptimal synthesis procedures for existing technologically important materials and provide a theoretical rationale for the use of certain precursors over others. The key strength of our approach and computational method is the ability to consider extremely wide ranges of chemistries, which allows us to bypass commonly encountered intermediates in target systems with a large number of competing phases. We envision this approach to be useful both to the synthetic chemist as well as robotic/automated laboratory efforts. Our predictions can be used to determine and order the synthesis reactions tested in the laboratory, reducing the cost and current trial-and-error approach to inorganic materials synthesis. The future inclusion of models for the kinetic behavior of reactions, such as estimates of the reactivity of precursors based on solid-state diffusivities, will further enhance predictions.

7.2 Future work and outlook

Synthesis science is a rapidly growing and exciting current area of research. This dissertation has addressed significant challenges related to reaction pathway prediction in solid-state synthesis, but the practical implementation of these concepts has only just begun. Future work should aim to incorporate the models presented here into a broader and more diverse set of synthesis experiments, with a special focus on incorporating these models both *a priori* and *in situ*. Further theoretical developments are needed to address current limitations; most importantly, we must face the looming challenge of modeling kinetic effects related to particle sizes, defects, differences in atomic diffusivities, high-temperature behavior, phase changes (e.g., melting), differences in reactivity, etc.

In addition to addressing kinetic effects, future work should further explore the role of point defects in the thermodynamic stabilization of metastable polymorphs (see Chapter 4). It is still unclear to what degree this hypothesis can explain the synthesizability of metastable compounds. To address this, as well as other key scientific problems involving point defects, the community should come together to develop and maintain a database of calculated point defect formation energies. While these calculations are extremely costly to perform, recent advances in computing (e.g., integration of GPUs in supercomputers) have made the creation

of such a database a now tractable challenge. If this were to be accomplished, one could not only explore the defect stabilization hypothesis presented here but also perform studies to develop/train models for predicting diffusion in reacting solids. Such models would allow for rapid, on-the-fly prediction of kinetic behavior in solid-state reactions.

In this work, we presented models for both forward (pathfinding) and inverse (synthesis planning) reaction pathway prediction. We still have yet to fully unite these efforts in a bidirectional manner, and future work should explore agreement between the forward and inverse models. In other words, when we design an “optimal” synthesis protocol for a target material, do our forward models predict that we will successfully make that material? Testing this idea will allow for more rapid iteration and development of new synthesis models, which has been an extremely slow process due to the unguided and exploratory nature of synthesis experiments. In doing so, we will also be able to better address possible limitations of our models beyond the case study systems (oxides in particular) presented here. Is it possible, for example, to adapt our models to other synthesis approaches, such as hydrothermal synthesis? How can we better model compositionally undefined phases (e.g., melts, amorphous solids, alloys)? There are still many lingering questions yet to be addressed.

Finally, we expect that the synthesis modeling tools presented in this work will be valuable not only to the experimental solid-state chemist but also to future automated synthesis laboratory developments. It is these automated materials synthesis laboratories that will provide the high throughput experimentation necessary to refine predictive models. In turn, we expect that the resulting enhanced predictive models will enable truly autonomous control systems for computer-driven materials synthesis. Once that point is reached, and synthesis laboratories become self-driving fully closed-loop systems, we will enter a new era of materials design where the synthesis bottleneck no longer hinders chemists and materials scientists from fully realizing a material designed *in silico*. It will be possible, then, to move directly from *ab initio* predictions to a fully synthesized material ready for implementation in technological devices. The importance of this scientific milestone cannot be overstated; this new materials- and synthesis-by-design paradigm will serve as the foundation for humanity’s next great technological revolutions.

Bibliography

1. Kovnir, K. Predictive Synthesis. *Chemistry of Materials* **33**, 4835–4841 (2021).
2. Kohlmann, H. Looking into the Black Box of Solid-State Synthesis. *European Journal of Inorganic Chemistry* **2019**, 4174–4180 (2019).
3. Kim, E. *et al.* Materials Synthesis Insights from Scientific Literature via Text Extraction and Machine Learning. *Chemistry of Materials* **29**, 9436–9444 (2017).
4. De Yoreo, J. *et al.* *Basic Research Needs Workshop on Synthesis Science for Energy Relevant Technology* (United States, 2016).
5. Schade, R. *et al.* Towards Electronic Structure-Based Ab-Initio Molecular Dynamics Simulations with Hundreds of Millions of Atoms. *Parallel Computing* **111**, 102920 (2022).
6. Corey, E. & Cheng, X.-M. *The Logic of Chemical Synthesis* (John Wiley & Sons, Inc., 1989).
7. Coley, C. W., Green, W. H. & Jensen, K. F. Machine Learning in Computer-Aided Synthesis Planning. *Accounts of Chemical Research* **51**, 1281–1289 (2018).
8. IPCC. *Global Warming of 1.5°C: IPCC Special Report on Impacts of Global Warming of 1.5°C above Pre-industrial Levels in Context of Strengthening Response to Climate Change, Sustainable Development, and Efforts to Eradicate Poverty* 1st ed. (Cambridge University Press, 2018).
9. West, A. R. *Solid State Chemistry and Its Applications* Second edition, student edition (Wiley, Chichester, West Sussex, UK, 2014).
10. Szymanski, N. J. *et al.* Toward Autonomous Design and Synthesis of Novel Inorganic Materials. *Materials Horizons* **8**, 2169–2198 (2021).
11. Jain, A. *et al.* Formation Enthalpies by Mixing GGA and GGA + U Calculations. *Physical Review B* **84**, 045115 (2011).
12. Jain, A. *et al.* Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Materials* **1**, 011002 (2013).
13. Kirklin, S. *et al.* The Open Quantum Materials Database (OQMD): Assessing the Accuracy of DFT Formation Energies. *npj Computational Materials* **1**, 15010 (2015).

14. Martinolich, A. J. & Neilson, J. R. Toward Reaction-by-Design: Achieving Kinetic Control of Solid State Chemistry with Metathesis. *Chemistry of Materials* **29**, 479–489 (2017).
15. Kamm, G. E. *et al.* Relative Kinetics of Solid-State Reactions: The Role of Architecture in Controlling Reactivity. *Journal of the American Chemical Society* **144**, 11975–11979 (2022).
16. Wiley, J. B. & Kaner, R. B. Rapid Solid-State Precursor Synthesis of Materials. *Science*, 1093–1097 (1992).
17. Martinolich, A. J. & Neilson, J. R. Pyrite Formation via Kinetic Intermediates through Low-Temperature Solid-State Metathesis. *Journal of the American Chemical Society* **136**, 15654–15659 (2014).
18. Martinolich, A. J., Kurzman, J. A. & Neilson, J. R. Circumventing Diffusion in Kinetically Controlled Solid-State Metathesis Reactions. *Journal of the American Chemical Society* **138**, 11031–11037 (2016).
19. Miura, A. *et al.* Observing and Modeling the Sequential Pairwise Reactions That Drive Solid-State Ceramic Synthesis. *Advanced Materials* **33**, 2100312 (2021).
20. Shoemaker, D. P. *et al.* In Situ Studies of a Platform for Metastable Inorganic Crystal Growth and Materials Discovery. *Proceedings of the National Academy of Sciences* **111**, 10922–10927 (2014).
21. Jiang, Z., Ramanathan, A. & Shoemaker, D. P. In Situ Identification of Kinetic Factors That Expedite Inorganic Crystal Formation and Discovery. *Journal of Materials Chemistry C* **5**, 5709–5717 (2017).
22. Bianchini, M. *et al.* The Interplay between Thermodynamics and Kinetics in the Solid-State Synthesis of Layered Oxides. *Nature Materials* **19**, 1088–1095 (2020).
23. Merkle, R. & Maier, J. On the Tammann–Rule. *Zeitschrift für anorganische und allgemeine Chemie* **631**, 1163–1166 (2005).
24. Huo, H. *et al.* Machine-Learning Rationalization and Prediction of Solid-State Synthesis Conditions. *Chemistry of Materials* **34**, 7323–7336 (2022).
25. Jia, X. *et al.* Anthropogenic Biases in Chemical Reaction Data Hinder Exploratory Inorganic Synthesis. *Nature* **573**, 251–255 (2019).
26. Sun, W. *et al.* The Thermodynamic Scale of Inorganic Crystalline Metastability. *Science Advances* **2**, e1600225 (2016).
27. Aykol, M., Dwaraknath, S. S., Sun, W. & Persson, K. A. Thermodynamic Limit for Synthesis of Metastable Inorganic Materials. *Science Advances* **4**, eaaq0148 (2018).
28. Freysoldt, C. *et al.* First-Principles Calculations for Point Defects in Solids. *Reviews of Modern Physics* **86**, 253–305 (2014).

29. Bernardo, M., Jardiel, T., Peiteado, M., Caballero, A. & Villegas, M. Reaction Pathways in the Solid State Synthesis of Multiferroic BiFeO₃. *Journal of the European Ceramic Society* **31**, 3047–3053 (2011).
30. Bragg, L. *Nobel Lecture: The Diffraction of X-Rays by Crystals*. Technical University of Stockholm. 1922.
31. Eckert, M. Max von Laue and the Discovery of X-ray Diffraction in 1912. *Annalen der Physik* **524**, A83–A85 (2012).
32. Bragg, W. H. The Reflection of X-Rays by Crystals. *Nature* **91**, 477–477 (1913).
33. McCusker, L. B., Von Dreele, R. B., Cox, D. E., Louër, D. & Scardi, P. Rietveld Refinement Guidelines. *Journal of Applied Crystallography* **32**, 36–50 (1999).
34. Toby, B. H. *R* Factors in Rietveld Analysis: How Good Is Good Enough? *Powder Diffraction* **21**, 67–70 (2006).
35. Clausen, B. S. *et al.* In Situ Cell for Combined XRD and On-Line Catalysis Tests: Studies of Cu-based Water Gas Shift and Methanol Catalysts. *Journal of Catalysis* **132**, 524–535 (1991).
36. Chupas, P. J. *et al.* A Versatile Sample-environment Cell for Non-ambient X-ray Scattering Experiments. *Journal of Applied Crystallography* **41**, 822–824 (2008).
37. O’Nolan, D. *et al.* A Thermal-Gradient Approach to Variable-Temperature Measurements Resolved in Space. *Journal of Applied Crystallography* **53**, 662–670 (Pt 3 2020).
38. Hasnip, P. J. *et al.* Density Functional Theory in the Solid State. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **372**, 20130270 (2014).
39. Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. *Physical Review* **136**, B864–B871 (3B 1964).
40. Bai, J., Hong, J., Chen, H., Graetz, J. & Wang, F. Solvothermal Synthesis of LiMn_{1-x}FexPO₄ Cathode Materials: A Study of Reaction Mechanisms by Time-Resolved in Situ Synchrotron X-ray Diffraction. *The Journal of Physical Chemistry C* **119**, 2266–2276 (2015).
41. Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review* **140**, A1133–A1138 (4A 1965).
42. Perdew, J. P. & Yue, W. Accurate and Simple Density Functional for the Electronic Exchange Energy: Generalized Gradient Approximation. *Physical Review B* **33**, 8800–8802 (1986).
43. Sun, J., Ruzsinszky, A. & Perdew, J. P. Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Physical Review Letters* **115**, 036402 (2015).
44. Furness, J. W., Kaplan, A. D., Ning, J., Perdew, J. P. & Sun, J. Accurate and Numerically Efficient r2SCAN Meta-Generalized Gradient Approximation. *The Journal of Physical Chemistry Letters* **11**, 8208–8215 (2020).

45. Sholl, D. S. & Steckel, J. A. *Density Functional Theory* (John Wiley & Sons, Inc., Hoboken, NJ, USA, 2009).
46. Kresse, G. & Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Physical Review B* **54**, 11169–11186 (1996).
47. Kühne, T. D. *et al.* CP2K: An Electronic Structure and Molecular Dynamics Software Package - Quickstep: Efficient and Accurate Electronic Structure Calculations. *The Journal of Chemical Physics* **152**, 194103 (2020).
48. Shalf, J. The Future of Computing beyond Moore’s Law. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **378**, 20190061 (2020).
49. Rogl, P., Podlucky, R. & Wolf, W. DFT Calculations: A Powerful Tool for Materials Design. *Journal of Phase Equilibria and Diffusion* **35**, 221–222 (2014).
50. De Pablo, J. J. *et al.* New Frontiers for the Materials Genome Initiative. *npj Computational Materials* **5**, 1–23 (2019).
51. Mathew, K. *et al.* MPInterfaces: A Materials Project Based Python Tool for High-Throughput Computational Screening of Interfacial Systems. *Computational Materials Science* **122**, 183–190 (2016).
52. Montoya, J. H. & Persson, K. A. A High-Throughput Framework for Determining Adsorption Energies on Solid Surfaces. *npj Computational Materials* **3**, 1–4 (2017).
53. Broberg, D. *et al.* PyCDT: A Python Toolkit for Modeling Point Defects in Semiconductors and Insulators. *Computer Physics Communications* **226**, 165–179 (2018).
54. De Jong, M. *et al.* Charting the Complete Elastic Properties of Inorganic Crystalline Compounds. *Scientific Data* **2**, 150009 (2015).
55. Mathew, K. *et al.* Atomate: A High-Level Interface to Generate, Execute, and Analyze Computational Materials Science Workflows. *Computational Materials Science* **139**, 140–152 (2017).
56. Ganose, A. *The Atomate2 Package* The Materials Project, 2023.
57. Jain, A. *et al.* FireWorks: A Dynamic Workflow System Designed for High-throughput Applications. *Concurrency and Computation: Practice and Experience* **27**, 5037–5059 (2015).
58. Ganose, A. *The Jobflow Package* The Materials Project, 2023.
59. Schmalzried, H. *Solid State Reactions* 2nd ed. (Verlag Chemie, Weinheim, Germany, 1981).
60. Kröger, F. A. & Vink, H. J. in *Solid State Physics* (eds Seitz, F. & Turnbull, D.) 307–435 (Academic Press, 1956).

61. Anand, S., Toriyama, M. Y., Wolverton, C., Haile, S. M. & Snyder, G. J. A Convergent Understanding of Charged Defects. *Accounts of Materials Research* **3**, 685–696 (2022).
62. Freysoldt, C., Neugebauer, J. & Walle, C. G. V. de. Fully Ab Initio Finite-Size Corrections for Charged-Defect Supercell Calculations. *Physical Review Letters* **102**, 016402 (2009).
63. Kumagai, Y. & Oba, F. Electrostatics-Based Finite-Size Corrections for First-Principles Point Defect Calculations. *Physical Review B* **89**, 195205 (2014).
64. Kumagai, Y., Tsunoda, N., Takahashi, A. & Oba, F. Insights into Oxygen Vacancies from High-Throughput First-Principles Calculations. *Physical Review Materials* **5**, 123803 (2021).
65. Chase, J. M. W. *NIST-JANAF Thermochemical Tables* 4th ed. (American Institute of Physics for the National Institute of Standards and Technology, Washington D.C., 1998).
66. Togo, A. & Tanaka, I. First Principles Phonon Calculations in Materials Science. *Scripta Materialia* **108**, 1–5 (2015).
67. Petretto, G., Gonze, X., Hautier, G. & Rignanese, G.-M. Convergence and Pitfalls of Density Functional Perturbation Theory Phonons Calculations from a High-Throughput Perspective. *Computational Materials Science* **144**, 331–337 (2018).
68. Petretto, G. *et al.* High-Throughput Density-Functional Perturbation Theory Phonons for Inorganic Materials. *Scientific Data* **5**, 180065 (2018).
69. Bartel, C. J. *et al.* Physical Descriptor for the Gibbs Energy of Inorganic Crystalline Solids and Temperature-Dependent Materials Chemistry. *Nature Communications* **9**, 4168 (2018).
70. Ouyang, R., Curtarolo, S., Ahmetcik, E., Scheffler, M. & Ghiringhelli, L. M. SISSO: A Compressed-Sensing Method for Identifying the Best Low-Dimensional Descriptor in an Immensity of Offered Candidates. *Physical Review Materials* **2**, 083802 (2018).
71. Bale, C. *et al.* FactSage Thermochemical Software and Databases. *CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry)* **26**, 189–228 (2002).
72. Bartel, C. J. Review of Computational Approaches to Predict the Thermodynamic Stability of Inorganic Solids. *Journal of Materials Science* **57**, 10475–10498 (2022).
73. Ong, S. P., Wang, L., Kang, B. & Ceder, G. Li-Fe-P-O₂ Phase Diagram from First Principles Calculations. *Chemistry of Materials* **20**, 1798–1807 (2008).
74. Barber, C. B., Dobkin, D. P. & Huhdanpaa, H. The Quickhull Algorithm for Convex Hulls. *ACM Transactions on Mathematical Software (TOMS)* **22**, 469–483 (1996).
75. Sun, J. *et al.* Accurate First-Principles Structures and Energies of Diversely Bonded Systems from an Efficient Density Functional. *Nature Chemistry* **8**, 831–836 (2016).

76. Ong, S. P., Jain, A., Hautier, G., Kang, B. & Ceder, G. Thermal Stabilities of Delithiated Olivine MPO₄ (M=Fe, Mn) Cathodes Investigated Using First Principles Calculations. *Electrochemistry Communications* **12**, 427–430 (2010).
77. Yokokawa, H. Generalized Chemical Potential Diagram and Its Applications to Chemical Reactions at Interfaces between Dissimilar Materials. *Journal of Phase Equilibria* **20**, 258 (1999).
78. Yokokawa, H., Yamaji, K., Horita, T., Sakai, N. & Brito, M. E. Utilization of Generalized Chemical Potential Diagrams for Multi-Component Systems in Understanding Interface Stability. *Materials Science Forum* **502**, 111–116 (2005).
79. Patel, A. M., Nørskov, J. K., Persson, K. A. & Montoya, J. H. Efficient Pourbaix Diagrams of Many-Element Compounds. *Physical Chemistry Chemical Physics* **21**, 25323–25327 (2019).
80. Wang, L., Maxisch, T. & Ceder, G. Oxidation Energies of Transition Metal Oxides within the GGA+U Framework. *Physical Review B* **73**, 195107 (2006).
81. Wang, A. *et al.* A Framework for Quantifying Uncertainty in DFT Energy Corrections. *Scientific Reports* **11**, 15496 (2021).
82. Richards, W. D., Miara, L. J., Wang, Y., Kim, J. C. & Ceder, G. Interface Stability in Solid-State Batteries. *Chemistry of Materials* **28**, 266–273 (2015).
83. McDermott, M. J., Dwaraknath, S. S. & Persson, K. A. A Graph-Based Network for Predicting Chemical Reaction Pathways in Solid-State Materials Synthesis. *Nature Communications* **12**, 3097 (2021).
84. Bale, C. *et al.* FactSage Thermochemical Software and Databases, 2010-2016. *CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry)* **54**, 35–53 (2016).
85. Bale, C. W. & Eriksson, G. Metallurgical Thermochemical Databases—A Review. *Canadian Metallurgical Quarterly* **29**, 105–132 (1990).
86. Jain, A., Shin, Y. & Persson, K. A. Computational Predictions of Energy Materials Using Density Functional Theory. *Nature Reviews Materials* **1**, 15004 (2016).
87. Eyring, H. The Activated Complex in Chemical Reactions. *The Journal of Chemical Physics* **3**, 107–115 (1935).
88. Dugas, C., Bengio, Y., Bélisle, F., Nadeau, C. & Garcia, R. *Incorporating Second-Order Functional Knowledge for Better Option Pricing in Advances in Neural Information Processing Systems* (eds Leen, T., Dietterich, T. & Tresp, V.) **13** (MIT Press, 2000).
89. Yen, J. Y. Finding the K Shortest Loopless Paths in a Network. *Management Science* **17**, 712–716 (1971).
90. Dijkstra, E. W. A Note on Two Problems in Connexion with Graphs. *Numerische Mathematik* **1**, 269–271 (1959).

91. Virtanen, P. *et al.* SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nature Methods* **17**, 261–272 (2020).
92. Todd, P. K. & Neilson, J. R. Selective Formation of Yttrium Manganese Oxides through Kinetically Competent Assisted Metathesis Reactions. *Journal of the American Chemical Society* **141**, 1191–1195 (2019).
93. Todd, P. K., Smith, A. M. M. & Neilson, J. R. Yttrium Manganese Oxide Phase Stability and Selectivity Using Lithium Carbonate Assisted Metathesis Reactions. *Inorganic Chemistry* **58**, 15166–15174 (2019).
94. Todd, P. K. *et al.* Defect-Accommodating Intermediates Yield Selective Low-Temperature Synthesis of YMnO₃ Polymorphs. *Inorganic Chemistry* **59**, 13639–13650 (2020).
95. Todd, P. K. *et al.* Selectivity in Yttrium Manganese Oxide Synthesis via Local Chemical Potentials in Hyperdimensional Phase Space. *Journal of the American Chemical Society* **143**, 15185–15194 (2021).
96. Brachtel, G. & Hoppe, R. Die Koordinationszahl 5 Bei Mn III: Na₄Mn₂O₅. *Zeitschrift für anorganische und allgemeine Chemie* **468**, 130–136 (1980).
97. Awaleh, M., Ali, A. B., Maisonneuve, V. & Leblanc, M. Microwave-Assisted Synthesis, Crystal Structures and Thermal Behaviour of Na₅Y(CO₃)₄ and Na₅Yb(CO₃)₄·2H₂O. *Journal of Alloys and Compounds* **349**, 114–120 (2003).
98. Deportes, J. & Givord, D. Magnetic Structure of YMn₁₂. *Solid State Communications* **19**, 845–851 (1976).
99. Morris, M., Gilmore, W., Palmer, P., Turner, B. E. & Zuckerman, B. Detection of Interstellar SiS and a Study of the IRC +10216 Molecular Envelope. *The Astrophysical Journal* **199**, L47 (1975).
100. Murayama, M. *et al.* Synthesis of New Lithium Ionic Conductor Thio-LISICON—Lithium Silicon Sulfides System. *Journal of Solid State Chemistry* **168**, 140–148 (2002).
101. Rong, Z. *et al.* Fast Mg²⁺ Diffusion in Mo₃(PO₄)₃O for Mg Batteries. *Chemical Communications* **53**, 7998–8001 (2017).
102. Wang, L. *et al.* Solid State Synthesis of a New Ternary Nitride MgMoN₂ Nanosheets and Micromeshes. *Journal of Materials Chemistry* **22**, 14559–14564 (2012).
103. Timoshevskii, A. N., Ktarkherman, M. G., Emel'kin, V. A., Pozdnyakov, B. A. & Zamyatin, A. P. High-Temperature Decomposition of Lithium Carbonate at Atmospheric Pressure. *High Temperature* **46**, 414–421 (2008).
104. Zimmermann, N. E. R. & Jain, A. Local Structure Order Parameters and Site Fingerprints for Quantification of Coordination Environment and Crystal Structure Similarity. *RSC Advances* **10**, 6063–6081 (2020).

105. De, S., Bartók, A. P., Csányi, G. & Ceriotti, M. Comparing Molecules and Solids across Structural and Alchemical Space. *Physical Chemistry Chemical Physics* **18**, 13754–13769 (2016).
106. McAuliffe, R. D. *et al.* Direct Mechanochemical Synthesis, Phase Stability, and Electrochemical Performance of α -NaFeO₂. *Inorganic Chemistry* **62**, 3358–3367 (2023).
107. Stein, A., Keller, S. W. & Mallouk, T. E. Turning down the Heat: Design and Mechanism in Solid-State Synthesis. *Science (New York, N.Y.)* **259**, 1558–1564 (1993).
108. Soderholm, L. & Mitchell, J. F. Perspective: Toward “Synthesis by Design”: Exploring Atomic Correlations during Inorganic Materials Synthesis. *APL Materials* **4**, 053212 (2016).
109. Rouxel, J. & Tournoux, M. Chimie Douce with Solid Precursors, Past and Present. *Solid State Ionics* **84**, 141–149 (1996).
110. Gopalakrishnan, J. Chimie Douce Approaches to the Synthesis of Metastable Oxide Materials. *Chemistry of Materials* **7**, 1265–1275 (1995).
111. Vitoux, L. *et al.* The Na_xMoO₂ Phase Diagram ($1/2 \leq x \leq 1$): An Electrochemical Devil’s Staircase. *Chemistry of Materials* **29**, 7243–7254 (2017).
112. Poeppelmeier, K. R. & Kipp, D. O. Cation Replacement in α -LiAlO₂. *Inorganic Chemistry* **27**, 766–767 (1988).
113. Gillan, E. G. & Kaner, R. B. Synthesis of Refractory Ceramics via Rapid Metathesis Reactions between Solid-State Precursors. *Chemistry of Materials* **8**, 333–343 (1996).
114. Martinolich, A. J., Higgins, R. F., Shores, M. P. & Neilson, J. R. Lewis Base Mediated Polymorph Selectivity of Pyrite CuSe₂ through Atom Transfer in Solid-State Metathesis. *Chemistry of Materials* **28**, 1854–1860 (2016).
115. Armstrong, A. R. & Bruce, P. G. Synthesis of Layered LiMnO₂ as an Electrode for Rechargeable Lithium Batteries. *Nature* **381**, 499–500 (1996).
116. Croguennec, L., Deniard, P., Brec, R. & Lecerf, A. Preparation, Physical and Structural Characterization of LiMnO₂ Samples with Variable Cationic Disorder. *Journal of Materials Chemistry* **5**, 1919–1925 (1995).
117. Mosbah, A., Verbaere, A. & Tournoux, M. Phases Li_xMnO₂ λ rattachees au type spinelle. *Materials Research Bulletin* **18**, 1375–1381 (1983).
118. Perdew, J. P., Burke, K. & Ernzerhof, M. *Generalized Gradient Approximation Made Simple* (1996).
119. Wang, Y., Fu, Z.-W., Yue, X.-L. & Qin, Q.-Z. Electrochemical Reactivity Mechanism of Ni₃N with Lithium. *Journal of The Electrochemical Society* **151**, E162–E167 (2004).
120. Hautier, G., Ong, S. P., Jain, A., Moore, C. J. & Ceder, G. Accuracy of Density Functional Theory in Predicting Formation Energies of Ternary Oxides from Binary Oxides and Its Implication on Phase Stability. *Physical Review B* **85**, 155208 (2012).

121. Blöchl, P. E. Projector Augmented-Wave Method. *Physical Review B* **50**, 17953–17979 (1994).
122. Kresse, G. & Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Physical Review B* **59**, 1758–1775 (1999).
123. Muñoz, A. *et al.* Magnetic Structure of Hexagonal RMnO₃ (R=Y, Sc): Thermal Evolution from Neutron Powder Diffraction Data. *Physical Review B* **62**, 9498–9510 (2000).
124. Muñoz, A. *et al.* The Magnetic Structure of YMnO₃ Perovskite Revisited. *Journal of Physics: Condensed Matter* **14**, 3285 (2002).
125. Horton, M. K., Montoya, J. H., Liu, M. & Persson, K. A. High-Throughput Prediction of the Ground-State Collinear Magnetic Order of Inorganic Materials Using Density Functional Theory. *npj Computational Materials* **5**, 64 (2019).
126. Vinet, P., Ferrante, J., Smith, J. R. & Rose, J. H. A Universal Equation of State for Solids. *Journal of Physics C: Solid State Physics* **19**, L467 (1986).
127. Tofield, B. & Scott, W. Oxidative Nonstoichiometry in Perovskites, an Experimental Survey; the Defect Structure of an Oxidized Lanthanum Manganite by Powder Neutron Diffraction. *Journal of Solid State Chemistry* **10**, 183–194 (1974).
128. Roosmalen, J. van & Cordfunke, E. The Defect Chemistry of LaMnO₃± δ 4. Defect Model for LaMnO₃+ δ . *Journal of Solid State Chemistry* **110**, 109–112 (1994).
129. Alonso, J. A. *et al.* Non-Stoichiometry, Structural Defects and Properties of LaMnO₃+ δ with High δ Values ($0.11 \leq \delta \leq 0.29$). *Journal of Materials Chemistry* **7**, 2139–2144 (1997).
130. Dabrowski, B. *et al.* Tolerance Factor Rules for Sr_{1-x-y}CaxBayMnO₃ Perovskites. *Journal of Solid State Chemistry* **170**, 154–164 (2003).
131. Brinks, H., Fjellvåg, H. & Kjekshus, A. Synthesis of Metastable Perovskite-Type YMnO₃ and HoMnO₃. *Journal of Solid State Chemistry* **129**, 334–340 (1997).
132. Bergum, K. *et al.* Synthesis, Structure and Magnetic Properties of Nanocrystalline YMnO₃. *Dalton Transactions* **40**, 7583–7589 (2011).
133. Gibbs, A. S., Knight, K. S. & Lightfoot, P. High-Temperature Phase Transitions of Hexagonal YMnO₃. *Physical Review B* **83**, 094111 (2011).
134. Wendlandt, W. W. The Thermal Decomposition of Yttrium, Scandium, and Some Rare-Earth Chloride Hydrates. *Journal of Inorganic and Nuclear Chemistry* **5**, 118–122 (1957).
135. Garcia, E., Corbett, J. D., Ford, J. E. & Vary, W. J. Low-Temperature Routes to New Structures for Yttrium, Holmium, Erbium, and Thulium Oxychlorides. *Inorganic Chemistry* **24**, 494–498 (1985).

136. Ohzuku, T., Kitagawa, M. & Hirai, T. Electrochemistry of Manganese Dioxide in Lithium Nonaqueous Cell: III . X-Ray Diffractational Study on the Reduction of Spinel-Related Manganese Dioxide. *Journal of The Electrochemical Society* **137**, 769–775 (1990).
137. Liu, T. *et al.* Correlation between Manganese Dissolution and Dynamic Phase Stability in Spinel-Based Lithium-Ion Battery. *Nature Communications* **10**, 4721 (2019).
138. Sugiyama, J., Atsumi, T., Hioki, T., Noda, S. & Kamegashira, N. Nonstoichiometry and Defect Structure of Spinel $\text{LiMn}_2\text{O}_4\text{-}\delta$. *Journal of Power Sources* **68**, 641–645 (1997).
139. Atsumi, T., Ohgushi, T., Namikata, H. & Kamegashira, N. Oxygen Nonstoichiometry of $\text{LnMnO}_3\text{-}\delta$ (Ln=La, Pr, Nd, Sm and Y). *Journal of Alloys and Compounds* **252**, 67–70 (1997).
140. Reed, J., Ceder, G. & Ven, A. V. D. Layered-to-Spinel Phase Transition in Li_xMnO_2 . *Electrochemical and Solid-State Letters* **4**, A78 (2001).
141. Armstrong, A. R., Dupre, N., Paterson, A. J., Grey, C. P. & Bruce, P. G. Combined Neutron Diffraction, NMR, and Electrochemical Investigation of the Layered-to-Spinel Transformation in LiMnO_2 . *Chemistry of Materials* **16**, 3106–3118 (2004).
142. Armstrong, A. R., Paterson, A. J., Dupré, N., Grey, C. P. & Bruce, P. G. Structural Evolution of Layered $\text{Li}_x\text{Mn}_y\text{O}_2$: Combined Neutron, NMR, and Electrochemical Study. *Chemistry of Materials* **19**, 1016–1023 (2007).
143. Kye, Y.-H. *et al.* Vacancy-Driven Stabilization of the Cubic Perovskite Polymorph of CsPbI_3 . *The Journal of Physical Chemistry C* **123**, 9735–9744 (2019).
144. Burdett, J. K. Electronic Structure and Properties of Solids. *The Journal of Physical Chemistry* **100**, 13263–13274 (1996).
145. Skjærvø, S. L. *et al.* Formation Mechanism and Growth of MNbO_3 , M=K, Na by in Situ X-ray Diffraction. *Journal of the American Ceramic Society* **100**, 3835–3842 (2017).
146. Chen, X.-J. *et al.* Hard Superconducting Nitrides. *Proceedings of the National Academy of Sciences* **102**, 3198–3201 (2005).
147. Satoh, H., Iwasaki, J.-i., Kawase, K. & Kamegashira, N. High Temperature Enthalpies and Heat Capacities of YbMnO_3 and YMnO_3 . *Journal of Alloys and Compounds* **268**, 42–46 (1998).
148. Balakirev, V. F., Vedmid', L. B., Yankin, A. M., Fedorova, O. M. & Golikov, Yu. V. Heterogeneous Phase Equilibria in the Tb-Mn-O System. *Inorganic Materials* **42**, 1230–1235 (2006).
149. Guilmard, M., Pouillier, C., Croguennec, L. & Delmas, C. Structural and Electrochemical Properties of $\text{LiNi}_{0.70}\text{Co}_{0.15}\text{Al}_{0.15}\text{O}_2$. *Solid State Ionics* **160**, 39–50 (2003).

150. Thomas, M., David, W., Goodenough, J. & Groves, P. Synthesis and Structural Characterization of the Normal Spinel $\text{Li}[\text{Ni}_2]\text{O}_4$. *Materials Research Bulletin* **20**, 1137–1146 (1985).
151. Gwon, H. *et al.* Ion-Exchange Mechanism of Layered Transition-Metal Oxides: Case Study of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. *Inorganic Chemistry* **53**, 8083–8087 (2014).
152. Kalyani, P., Kalaiselvi, N., Renganathan, N. & Raghavan, M. Studies on $\text{LiNi}_{0.7}\text{Al}_{0.3-x}\text{Co}_x\text{O}_2$ Solid Solutions as Alternative Cathode Materials for Lithium Batteries. *Materials Research Bulletin* **39**, 41–54 (2004).
153. Obrovac, M., Mao, O. & Dahn, J. Structure and Electrochemistry of LiMO_2 (M=Ti, Mn, Fe, Co, Ni) Prepared by Mechanochemical Synthesis. *Solid State Ionics* **112**, 9–19 (1998).
154. Broussely, M., Pertion, F., Labat, J., Staniewicz, R. & Romero, A. Li/LixNiO₂ and Li/LixCoO₂ Rechargeable Systems: Comparative Study and Performance of Practical Cells. *Journal of Power Sources* **43**, 209–216 (1993).
155. Broussely, M. *et al.* LixNiO₂, a Promising Cathode for Rechargeable Lithium Batteries. *Journal of Power Sources* **54**, 109–114 (1995).
156. Mizushima, K., Jones, P., Wiseman, P. & Goodenough, J. LixCoO₂ (0. *Materials Research Bulletin* **15**, 783–789 (1980).
157. Xiang, X., Zhang, K. & Chen, J. Recent Advances and Prospects of Cathode Materials for Sodium-Ion Batteries. *Advanced Materials* **27**, 5343–5364 (2015).
158. Lamb, J., Jarvis, K. & Manthiram, A. Molten-Salt Synthesis of O₃-Type Layered Oxide Single Crystal Cathodes with Controlled Morphology towards Long-Life Sodium-Ion Batteries. *Small (Weinheim an der Bergstrasse, Germany)* **18**, 2106927 (2022).
159. Hasa, I., Buchholz, D., Passerini, S. & Hassoun, J. A Comparative Study of Layered Transition Metal Oxide Cathodes for Application in Sodium-Ion Battery. *ACS Applied Materials & Interfaces* **7**, 5206–5212 (2015).
160. Cabana, J. *et al.* Study of the Transition Metal Ordering in Layered $\text{Na}_x\text{Ni}_{1-x}/2\text{Mn}_{1-x}/2\text{O}_2$ ($2/3 \leq x \leq 1$) and Consequences of Na/Li Exchange. *Inorganic Chemistry* **52**, 8540–8550 (2013).
161. Huang, Q. *et al.* Improving the Electrochemical Properties of the Manganese-Based P3 Phase by Multiphasic Intergrowth. *Inorganic Chemistry* **57**, 15584–15591 (2018).
162. Komaba, S. *et al.* Study on the Reversible Electrode Reaction of $\text{Na}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ for a Rechargeable Sodium-Ion Battery. *Inorganic Chemistry* **51**, 6211–6220 (2012).
163. Xiao, B., Omenya, F., Reed, D. & Li, X. A Glance of the Layered Transition Metal Oxide Cathodes in Sodium and Lithium-Ion Batteries: Difference and Similarities. *Nanotechnology* **32**, 422501 (2021).
164. Vassilaras, P., Ma, X., Li, X. & Ceder, G. Electrochemical Properties of Monoclinic NaNiO_2 . *Journal of The Electrochemical Society* **160**, A207–A211 (2013).

165. Rai, A. K., Anh, L. T., Gim, J., Mathew, V. & Kim, J. Electrochemical Properties of Na_xCoO_2 ($x \approx 0.71$) Cathode for Rechargeable Sodium-Ion Batteries. *Ceramics International* **40**, 2411–2417 (2014).
166. Han, M. H., Gonzalo, E., Casas-Cabanas, M. & Rojo, T. Structural Evolution and Electrochemistry of Monoclinic NaNiO_2 upon the First Cycling Process. *Journal of Power Sources* **258**, 266–271 (2014).
167. Komaba, S., Takei, C., Nakayama, T., Ogata, A. & Yabuuchi, N. Electrochemical Intercalation Activity of Layered NaCrO_2 vs. LiCrO_2 . *Electrochemistry Communications* **12**, 355–358 (2010).
168. Rougier, A., Gravereau, P. & Delmas, C. Optimization of the Composition of the $\text{Li}_{1-z}\text{Ni}_1+z\text{O}_2$ Electrode Materials: Structural, Magnetic, and Electrochemical Studies. *Journal of The Electrochemical Society* **143**, 1168–1175 (1996).
169. Ohzuku, T., Ueda, A. & Nagayama, M. Electrochemistry and Structural Chemistry of LiNiO_2 (R3m) for 4 Volt Secondary Lithium Cells. *Journal of The Electrochemical Society* **140**, 1862–1870 (1993).
170. Qiu, Z., Zhang, Y., Dong, P., Wang, D. & Xia, S. A Ternary Oxide Precursor with Trigonal Structure for Synthesis of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Cathode Material. *Journal of Solid State Electrochemistry* **21**, 3037–3046 (2017).
171. Su, D., Wang, C., Ahn, H.-j. & Wang, G. Single Crystalline $\text{Na}_{0.7}\text{MnO}_2$ Nanoplates as Cathode Materials for Sodium-Ion Batteries with Enhanced Performance. *Chemistry – A European Journal* **19**, 10884–10889 (2013).
172. Kim, Y. Lithium Nickel Cobalt Manganese Oxide Synthesized Using Alkali Chloride Flux: Morphology and Performance as a Cathode Material for Lithium Ion Batteries. *ACS Applied Materials & Interfaces* **4**, 2329–2333 (2012).
173. Chen, H. & Grey, C. P. Molten Salt Synthesis and High Rate Performance of the “Desert-Rose” Form of LiCoO_2 . *Advanced Materials* **20**, 2206–2210 (2008).
174. Liu, J. *et al.* Improving the Electrochemical Performance of Layered Lithium-Rich Transition-Metal Oxides by Controlling the Structural Defects. *Energy & Environmental Science* **7**, 705–714 (2013).
175. Spahr, M. E., Novák, P., Schnyder, B., Haas, O. & Nesper, R. Characterization of Layered Lithium Nickel Manganese Oxides Synthesized by a Novel Oxidative Coprecipitation Method and Their Electrochemical Performance as Lithium Insertion Electrode Materials. *Journal of The Electrochemical Society* **145**, 1113–1121 (1998).
176. Xie, H. *et al.* Synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with 5-Sulfosalicylic Acid as a Chelating Agent and Its Electrochemical Properties. *Journal of Materials Chemistry A* **3**, 20236–20243 (2015).

177. He, K., Ruan, Z., Teng, X. & Zhu, Y. Facile Synthesis and Electrochemical Properties of Spherical $\text{LiNi}_{0.85-x}\text{Co}_{0.15}\text{Al}_x\text{O}_2$ with Sodium Aluminate via Co-Precipitation. *Materials Research Bulletin* **90**, 131–137 (2017).
178. Seo, J.-S. & Lee, J.-w. Fast Growth of the Precursor Particles of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.16}\text{Al}_{0.04})\text{O}_2$ via a Carbonate Co-Precipitation Route and Its Electrochemical Performance. *Journal of Alloys and Compounds* **694**, 703–709 (2017).
179. Rao, M. M. *et al.* Electrochemical Behaviour of Solid Lithium Nickellate (LiNiO_2) in an Aqueous Electrolyte System. *Journal of Solid State Electrochemistry* **4**, 17–23 (1999).
180. Kalyani, P., Kalaiselvi, N. & Muniyandi, N. A New Solution Combustion Route to Synthesize LiCoO_2 and LiMn_2O_4 . *Journal of Power Sources* **111**, 232–238 (2002).
181. Kwon, S. N., Song, J. & Mumm, D. R. Effects of Cathode Fabrication Conditions and Cycling on the Electrochemical Performance of LiNiO_2 Synthesized by Combustion and Calcination. *Ceramics International* **37**, 1543–1548 (2011).
182. Purwanto, A. *et al.* NCA Cathode Material: Synthesis Methods and Performance Enhancement Efforts. *Materials Research Express* **5**, 122001 (2018).
183. Mao, F., Guo, W. & Ma, J. Research Progress on Design Strategies, Synthesis and Performance of LiMn_2O_4 -based Cathodes. *RSC Advances* **5**, 105248–105258 (2015).
184. Fergus, J. W. Recent Developments in Cathode Materials for Lithium Ion Batteries. *Journal of Power Sources* **195**, 939–954 (2010).
185. Okada, S. *et al.* Layered Transition Metal Oxides as Cathodes for Sodium Secondary Battery. *Electrochemical Society Meeting Abstracts* **MA2006-02**, 201–201 (2006).
186. Yabuuchi, N., Yoshida, H. & Komaba, S. Crystal Structures and Electrode Performance of $\alpha\text{-NaFeO}_2$ for Rechargeable Sodium Batteries. *Electrochemistry* **80**, 716–719 (2012).
187. Kubota, K. *et al.* Understanding the Structural Evolution and Redox Mechanism of a $\text{NaFeO}_2\text{-NaCoO}_2$ Solid Solution for Sodium-Ion Batteries. *Advanced Functional Materials* **26**, 6047–6059 (2016).
188. Yoshida, H., Yabuuchi, N. & Komaba, S. Na Insertion Mechanism in $\alpha\text{-NaFeO}_2$ as Positive Electrode Materials for Na-Ion Batteries. *Electrochemical Society Meeting Abstracts* **MA2012-02**, 1850–1850 (2012).
189. Kugai, J. *et al.* Effects of Sodium Nitrate and Heat Treatment Atmosphere on the Synthesis of $\alpha\text{-NaFeO}_2$ Layered Oxide. *Materials Chemistry and Physics* **249**, 122948 (2020).
190. Takeda, Y., Akagi, J., Edagawa, A., Inagaki, M. & Naka, S. A Preparation and Polymorphic Relations of Sodium Iron Oxide (NaFeO_2). *Materials Research Bulletin* **15**, 1167–1172 (1980).

191. Monyoncho, E. & Bissessur, R. Unique Properties of α -NaFeO₂: De-intercalation of Sodium via Hydrolysis and the Intercalation of Guest Molecules into the Extract Solution. *Materials Research Bulletin* **48**, 2678–2686 (2013).
192. Zhao, J., Zhao, L., Dimov, N., Okada, S. & Nishida, T. Electrochemical and Thermal Properties of α -NaFeO₂ Cathode for Na-Ion Batteries. *Journal of The Electrochemical Society* **160**, A3077–A3081 (2013).
193. Susanto, D. *et al.* Anionic Redox Activity as a Key Factor in the Performance Degradation of NaFeO₂ Cathodes for Sodium Ion Batteries. *Chemistry of Materials* **31**, 3644–3651 (2019).
194. Ong, S. P. *et al.* Python Materials Genomics (Pymatgen): A Robust, Open-Source Python Library for Materials Analysis. *Computational Materials Science* **68**, 314–319 (2013).
195. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *The Journal of Chemical Physics* **118**, 8207–8215 (2003).
196. West, A. R. NaAlO₂ and NaFeO₂ Polymorphism. *Nature* **249**, 245–246 (1974).
197. Seibel, E. M. *et al.* Structure and Magnetic Properties of the α -NaFeO₂-Type Honeycomb Compound Na₃Ni₂BiO₆. *Inorganic Chemistry* **52**, 13605–13611 (2013).
198. Bonneau, P. R., Jarvis, R. F. & Kaner, R. B. Rapid Solid-State Synthesis of Materials from Molybdenum Disulphide to Refractories. *Nature* **349**, 510–512 (1991).
199. Miura, A. *et al.* Selective Metathesis Synthesis of MgCr₂S₄ by Control of Thermodynamic Driving Forces. *Materials Horizons* **7**, 1310–1316 (2020).
200. Wustrow, A. *et al.* Synthesis and Characterization of MgCr₂S₄ Thiospinel as a Potential Magnesium Cathode. *Inorganic Chemistry* **57**, 8634–8638 (2018).
201. Seshadri, R., Brock, S. L., Ramirez, A., Subramanian, M. A. & Thompson, M. E. Advances in the Development and Growth of Functional Materials: Toward the Paradigm of Materials by Design. *MRS Bulletin* **37**, 682–690 (2012).
202. Kamata, K., Nakajima, T. & Nakamura, T. Thermogravimetric Study of Rare Earth Manganites AMnO₃ (A=Sm,Dy,Y,Er,Yb) at 1200°C. *Materials Research Bulletin* **14**, 1007–1012 (1979).
203. Balakirev, V. F. & Golikov, Yu. V. Heterogeneous Phase Equilibria in Rare Earth–Mn–O Systems in Air. *Inorganic Materials* **39**, S1–S10 (Suppl 1 2003).
204. Fujinaka, H., Kinomura, N., Koizumi, M., Miyamoto, Y. & Kume, S. Syntheses and Physical Properties of Pyrochlore-Type A₂B₂O₇ (A=Tl,Y; B=Cr,Mn). *Materials Research Bulletin* **14**, 1133–1137 (1979).
205. Subramanian, M., Torardi, C., Johnson, D., Pannetier, J. & Sleight, A. Ferromagnetic R₂Mn₂O₇ Pyrochlores (R = Dy–Lu, Y). *Journal of Solid State Chemistry* **72**, 24–30 (1988).

206. Gardner, J. S., Gingras, M. J. P. & Greedan, J. E. Magnetic Pyrochlore Oxides. *Reviews of Modern Physics* **82**, 53–107 (2010).
207. Caballero, A. *et al.* Synthesis and Characterization of High-Temperature Hexagonal P2-Na_{0.6}MnO₂ and Its Electrochemical Behaviour as Cathode in Sodium Cells. *Journal of Materials Chemistry* **12**, 1142–1147 (2002).
208. Paulsen, J. & Dahn, J. Studies of the Layered Manganese Bronzes, Na_{2/3}[Mn_{1-x}Mx]O₂ with M=Co, Ni, Li, and Li_{2/3}[Mn_{1-x}Mx]O₂ Prepared by Ion-Exchange. *Solid State Ionics* **126**, 3–24 (1999).
209. Clément, R. J., Bruce, P. G. & Grey, C. P. Review—Manganese-Based P2-type Transition Metal Oxides as Sodium-Ion Battery Cathode Materials. *Journal of The Electrochemical Society* **162**, A2589–A2604 (2015).
210. Kitchaev, D. A., Dacek, S. T., Sun, W. & Ceder, G. Thermodynamics of Phase Selection in MnO₂ Framework Structures through Alkali Intercalation and Hydration. *Journal of the American Chemical Society* **139**, 2672–2681 (2017).
211. Neilson, J. R. & McQueen, T. M. Bonding, Ion Mobility, and Rate-Limiting Steps in Deintercalation Reactions with ThCr₂Si₂-type KNi₂Se₂. *Journal of the American Chemical Society* **134**, 7750–7757 (2012).
212. Hayward, M. A., Green, M. A., Rosseinsky, M. J. & Sloan, J. Sodium Hydride as a Powerful Reducing Agent for Topotactic Oxide Deintercalation: Synthesis and Characterization of the Nickel(I) Oxide LaNiO₂. *Journal of the American Chemical Society* **121**, 8843–8854 (1999).
213. Tsujimoto, Y. *et al.* Infinite-Layer Iron Oxide with a Square-Planar Coordination. *Nature* **450**, 1062–1065 (2007).
214. Yajima, T. *et al.* A Labile Hydride Strategy for the Synthesis of Heavily Nitridized BaTiO₃. *Nature Chemistry* **7**, 1017–1023 (2015).
215. Aykol, M., Montoya, J. H. & Hummelshøj, J. Rational Solid-State Synthesis Routes for Inorganic Materials. *Journal of the American Chemical Society* **143**, 9244–9259 (2021).
216. Van Loo, F. J. J. Multiphase Diffusion in Binary and Ternary Solid-State Systems. *Progress in Solid State Chemistry* **20**, 47–99 (1990).
217. Bierach, J. W. *The Formation of Barium Titanate Ceramics by Solid State Reaction*. PhD thesis (Lawrence Berkeley National Laboratory, 1988).
218. Stanley, R. P. & Fomin, S. Enumerative Combinatorics, 159–285 (1999).
219. Kononova, O. *et al.* Text-Mined Dataset of Inorganic Materials Synthesis Recipes. *Scientific Data* **6**, 203 (2019).
220. Agrafiotis, C. C., Pagkoura, C., Lorentzou, S., Kostoglou, M. & Konstandopoulos, A. G. Hydrogen Production in Solar Reactors. *Catalysis Today. I.A. Vasalos Festschrift* **127**, 265–277 (2007).

221. Tan, G. L., Yang, Q., Hömmerich, U., Seo, J. T. & Temple, D. Linear and Non-Linear Optical Properties of Capped CdTe Nanocrystals Prepared by Mechanical Alloying. *Optical Materials* **27**, 579–584 (2004).
222. Posudievsky, O. Yu. *et al.* Structural and Spectral Characteristics of Mechanochemically Prepared CsPbBr₃. *Theoretical and Experimental Chemistry* **53**, 235–243 (2017).
223. Kumta, P. N., Gallet, D., Waghray, A., Blomgren, G. E. & Setter, M. P. Synthesis of LiCoO₂ Powders for Lithium-Ion Batteries from Precursors Derived by Rotary Evaporation. *Journal of Power Sources* **72**, 91–98 (1998).
224. Neilson, J. R., McDermott, M. J. & Persson, K. A. *Modernist Materials Synthesis: Finding Thermodynamic Shortcuts with Hyperdimensional Chemistry* <http://arxiv.org/abs/2303.11915> (04/05/2023). preprint.
225. Herstedt, M. *et al.* Surface Chemistry of Carbon-Treated LiFePO₄ Particles for Li-Ion Battery Cathodes Studied by PES. *Electrochemical and Solid-State Letters* **6**, A202 (2003).
226. Peixoto, T. P. The Graph-Tool Python Library. *figshare* (2014).
227. Graphistry, I. *Graphistry Hub* Graphistry Hub. <https://hub.graphistry.com/>.
228. Tarascon, J. M. & Guyomard, D. Li Metal-Free Rechargeable Batteries Based on Li_{1+x}Mn₂O₄ Cathodes (0 ≤ x ≤ 1) and Carbon Anodes. *Journal of The Electrochemical Society* **138**, 2864 (1991).
229. Wang, Y. *et al.* Hydrothermal Synthesis of Two Perovskite Rare-Earth Manganites, HoMnO₃ and DyMnO₃. *Journal of Solid State Chemistry* **178**, 1317–1320 (2005).
230. Fuchs, B. & Kemmler-Sack, S. Synthesis of LiMnO₂ and LiFeO₂ in Molten Li Halides. *Solid State Ionics* **68**, 279–285 (1994).
231. Ashiotis, G. *et al.* The Fast Azimuthal Integration Python Library: pyFAI. *Journal of Applied Crystallography* **48**, 510–519 (2015).
232. Pathak, P. D. & Vasavada, N. G. Thermal Expansion of NaCl, KCl and CsBr by X-ray Diffraction and the Law of Corresponding States. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **26**, 655–658 (1970).
233. Kirkham, M., Heroux, L., Ruiz-Rodriguez, M. & Huq, A. AGES: Automated Gas Environment System for in Situ Neutron Powder Diffraction. *Review of Scientific Instruments* **89**, 092904 (2018).
234. Toby, B. & Dreele, R. V. GSAS-II: The Genesis of a Modern Open-Source All Purpose Crystallography Software Package. *Journal of Applied Crystallography* **46**, 544–549 (2013).
235. Yang, X., Juhas, P., Farrow, C. L. & Billinge, S. J. L. *xPDFsuite: An End-to-End Software Solution for High Throughput Pair Distribution Function Transformation, Visualization and Analysis* <http://arxiv.org/abs/1402.3163> (04/14/2023). preprint.

- 236. Farrow, C. L. *et al.* PDFfit2 and PDFgui: Computer Programs for Studying Nanostructure in Crystals. *Journal of Physics: Condensed Matter* **19**, 335219 (2007).
- 237. Wojdyr, M. Fityk: A General-Purpose Peak Fitting Program. *Journal of Applied Crystallography* **43**, 1126–1128 (2010).
- 238. Momma, K. & Izumi, F. VESTA 3 for Three-dimensional Visualization of Crystal, Volumetric and Morphology Data. *Journal of Applied Crystallography* **44**, 1272–1276 (2011).
- 239. Yin, L. *et al.* Extending the Limits of Powder Diffraction Analysis: Diffraction Parameter Space, Occupancy Defects, and Atomic Form Factors. *Review of Scientific Instruments* **89**, 093002 (2018).
- 240. Yin, L. *et al.* Thermodynamics of Antisite Defects in Layered NMC Cathodes: Systematic Insights from High-Precision Powder Diffraction Analyses. *Chemistry of Materials* **32**, 1002–1010 (2020).
- 241. Barin, I. *Thermochemical Data of Pure Substances* (VCH, Weinheim; New York, 2008).

Appendix A

The *reaction-network* Python package

As part of this work, a Python package for solid-state reaction network analysis and synthesis planning was created and used in Chapters 3, 5, and 6. The *reaction-network* package is available on Github at the following address:

<https://github.com/GENESIS-EFRC/reaction-network>.

Appendix B

Supplementary Information for Chapter 3

Thermodynamic phase diagram calculations and reaction balancing procedures are performed using algorithms implemented in the *pymatgen* package [194]. Graphs are implemented using the *graph-tool* package [226] and visualized in Figure 3.4 using Graphistry Hub [227].

Ab initio thermochemistry data used in this work are available via the open-access Materials Project database [12] (version 2020.09.08). Supplemental experimental data were acquired from the open-access NIST-JANAF database [65].

An alternative schematic of the reaction network graph architecture is illustrated in Figure B.1.

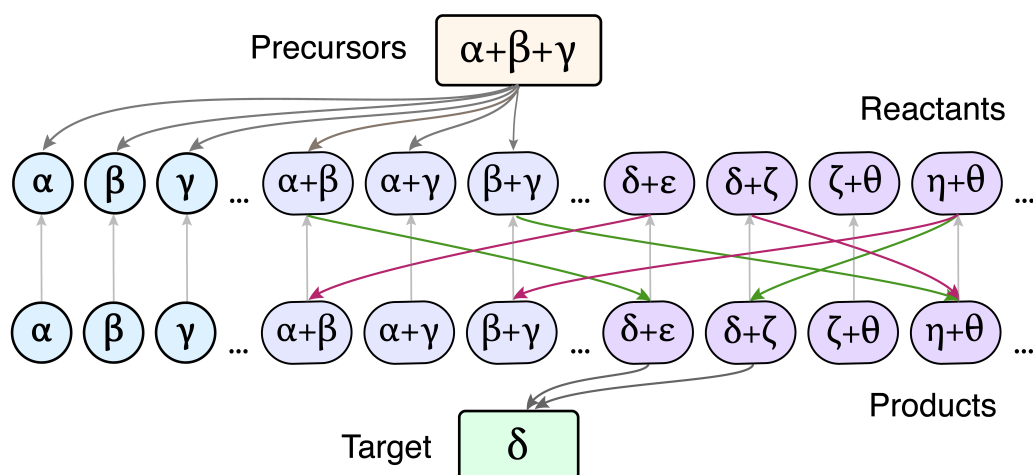


Figure B.1: Alternate schematic of reaction network illustrating reaction pathways and simple loops. The weights of edges are shaded red (high-cost), green (low-cost), and gray (zero-cost). The network depicts a hypothetical chemical system containing eight phases, labeled by Greek letters. Only two reaction pathways exist to the target, δ , starting from the precursors α , β , and γ . The first pathway is the simple one-step reaction: $\alpha + \beta \longrightarrow \delta + \epsilon$. The second pathway contains two steps: $\beta + \gamma \longrightarrow \eta + \theta \longrightarrow \delta + \zeta$. Only simple loops are illustrated here; however, the network features many more zero-cost looping edges between a product node and any reactant node which contains a subset of the product or precursor phases.

Appendix C

Supplementary Information for Chapter 4

C.1 Experimental methods for YMnO_3 study

Precursor Synthesis

YOC was synthesized by heating yttrium chloride hexahydrate (Acros Organics, 99.9%) in an alumina crucible in air at 400 °C for 4 h with heating and cooling rates of 5 °C/min [134].

LiMn_2O_4 was synthesized by reacting stoichiometric amounts of Li_2CO_3 (Baker, 99.3%) and Mn_2O_3 . Mn_2O_3 was synthesized by heating MnCO_3 (Sigma Aldrich, 99.9%) in an alumina crucible in air at 850 °C for 12 h with heating and cooling rates of 10 °C/min. The Li_2CO_3 and Mn_2O_3 powders were mixed using a mortar and pestle and heated in an alumina crucible at 800 °C for 24 h with heating and cooling rates of 10 °C/min. To prepare t- LiMnO_2 , LiMn_2O_4 powder was refluxed under nitrogen in a 4 M acetonitrile solution with LiI (Alfa Aesar, 99.9%) where the overall Li:Mn ratio was 6:1 [228, 229]. The reflux was performed at 82 °C using an oil bath to maintain the correct temperature. After refluxing, the powder was filtered and washed with acetonitrile to remove LiI and I_2 and dried under vacuum at 80 °C.

m- LiMnO_2 was synthesized by ion exchange from NaMnO_2 [230]. NaMnO_2 was synthesized by reacting stoichiometric amounts of Na_2CO_3 (Macron Chemicals, 99.5%) and MnO_2 (Trinox 95%). The powders were mixed using a mortar and pestle and heated in an alumina crucible to 700 °C for 24 h with heating and cooling rates of 5 °C/min. The resulting black powder was moved into a glovebox antechamber while hot to prevent corrosion due to ambient humidity. NaMnO_2 was mixed with 3 times the stoichiometric amount of LiI using a mortar and pestle inside an Ar-filled glovebox. The mixture was heated to 460 °C for 4 h in an alumina crucible inside a sealed quartz ampule. The reaction was cooled for 9 h (1 °C/min). Excess LiI and NaI were removed by washing with water.

o- LiMnO_2 was synthesized by reacting Li_2CO_3 (Baker, 99.3%) and MnO_2 (Alfa Aesar, 99.9%) with 15 mol% excess Li_2CO_3 . The powders were milled using an 8000M Spex Mix-

erMill within a 30 mL polypropylene bottle placed inside the steel Spex jar. The powders were milled for 90 min with 5 mm spherical yttria-stabilized zirconia milling media in a 2:1 weight ratio of media to sample. The resulting gray powder was pelleted using ~ 1 short ton of force. The pellets were placed inside beds of sacrificial powder in an alumina boat and heated under flowing argon. The samples were heated at 600 °C for 4 h and 900 °C for 48 h with heating and cooling rates of 10 °C/min.

***Ex situ* reactions**

Ex situ control reactions were prepared by mixing LiMnO_2 and YOCl in a mortar and pestle for 15 min under argon. This homogenized mixture was pelleted using ~ 1 short ton of force, placed in a cylindrical alumina crucible, and sealed in an evacuated quartz ampule (≤ 15 mTorr). Reactions were heated at 10 °C/min to the dwell temperature (500-600 °C). To avoid exposure to ambient oxygen due to the propensity for lithium chloride to chemically react with quartz at temperatures above 600 °C, long duration reaction ampules were placed into a larger diameter evacuated quartz ampule (e.g., double-sealed). Sample purity and product identification was verified by laboratory powder X-ray diffraction (PXRD) data collected on a Bruker D8 Discover diffractometer using $\text{Cu K}\alpha$ radiation and a Lynxeye XE-T position-sensitive detector.

***Ex post facto* SXRD reactions**

Synchrotron X-ray diffraction (SXRD) data were collected at beamline 28-ID-2 at the National Synchrotron Light Source II at Brookhaven National Laboratory. Data for all reactions were obtained using a gradient furnace, where the calibrated horizontal beam position defines the sample temperature [37]. In the gradient furnace, varying density of heating elements along the device allow for a single capillary to be simultaneously heated to a range of temperatures as a function of position along the capillary. Samples were loaded into a 1.1 mm OD quartz capillary and sealed with epoxy (Aremco-BondTM 570). Calibration of detector curvature was performed using CeO_2 at all points along the gradient furnace using pyFAI [231]. A single characteristic position was set to 450 °C (using a PID-controlled power source) which created a reproducible temperature range from 300 °C to 750 °C along the capillary. Position was related to temperature with a calibration run based on the thermal expansion of NaCl [232]. Samples were held at temperature for 40 min before being cooled over the course of 35 minutes to room temperature. Slow cooling was necessary to prevent the capillary from breaking after it had been exposed to LiCl at high temperatures. *Ex post facto* diffraction patterns were then taken along the length of the capillary with a wavelength of 0.1949 Å for m- LiMnO_2 and o- LiMnO_2 and 0.19319 Å for t- LiMnO_2 . SXRD data were collected on a Perkin Elmer plate detector at a distance of 1400 mm. The experimental data was reduced in real-time using analysis software xpdAn and xpdTools, which are open-source projects in the xpdAcq organization on GitHub (<https://github.com/xpdAcq>).

***In situ* NPD reactions**

Neutron powder diffraction (NPD) experiments were performed at beamline BL-11A POW-GEN at the Spallation Neutron Source at Oak Ridge National Laboratory. The samples were measured using the MICAS vacuum furnace with the AGES gas handling insert [233]. Stoichiometric mixtures of LiMnO_2 and YOCl were mixed with an agate mortar and pestle in an argon-filled glovebox. Then, the homogenized powder was loaded into quartz baskets lined with Al_2O_3 cloth (Zircar Zirconia, Tricon Knit Cloth). The Al_2O_3 cloth was used to minimize Li-containing compounds from reacting with the quartz holder. For *in situ* measurements, the samples were heated in argon at a rate of $1\text{ }^\circ\text{C}/\text{min}$ and 1 h dwell scans were collected every $50\text{ }^\circ\text{C}$ starting at $100\text{ }^\circ\text{C}$ for the t- LiMnO_2 mixture and $250\text{ }^\circ\text{C}$ for the o- LiMnO_2 and m- LiMnO_2 mixtures. The t- LiMnO_2 mixture was kept below the melting point of LiCl , reaching a maximum temperature of $500\text{ }^\circ\text{C}$ to prevent leakage of molten LiCl through the glass frit holding up the sample. The glass baskets were redesigned with a closed bottom for subsequent experiments with m- LiMnO_2 and o- LiMnO_2 to access higher temperature and observe the formation of YMnO_3 . NPD patterns of empty quartz baskets lined with Al_2O_3 cloth were collected every $100\text{ }^\circ\text{C}$ and were subtracted from the *in situ* diffraction patterns.

***In situ* SXRD reactions**

In situ SXRD experiments were performed at beamline 17-BM-B ($\lambda = 0.2415\text{ \AA}$) at the Advanced Photon Source (APS) at Argonne National Laboratory using a Perkin Elmer plate detector at a distance of 700 mm. Homogenized metathesis precursors were packed into a quartz capillary (1.1 mm OD, 0.9 mm ID) at Colorado State University in an argon-filled glovebox. Then, capillaries were sealed under vacuum ($< 20\text{ mTorr}$) using a methane-oxygen torch. All capillaries were loaded into a flow-cell apparatus [36] equipped with resistive heating elements and heated at $10\text{ }^\circ\text{C}/\text{min}$ to $600\text{ }^\circ\text{C}$. While heating, the samples were continuously rocked at $\pm 5^\circ$ around the axis of the capillary. Diffraction patterns were collected every two seconds and summed every 20 seconds. Images collected from the plate detector were integrated using GSAS-II and calibrated using a LaB_6 standard.

Rietveld refinements

Quantitative phase analysis of X-ray and neutron data diffraction data was performed using the Rietveld method as implemented in TOPAS v6. To consistently analyze powder patterns which could contain upwards of five distinct crystallographic phases, the following assumptions were made for analyzing X-ray diffraction data: atomic displacement parameters (ADPs) were fixed using a B_{iso} value of $2.5\text{ \AA}^2$ for all atoms, peak broadening was assumed to be a result of crystal size using a Lorentzian function, and site occupancies were fixed at one. Lattice parameters were held constant when the calculated weight percents was less than 5% due to the large amount of overlap between intermediate phases in the

diffraction data. For analyzing weight percents in neutron diffraction data, the ADPs were refined, and peak broadening was fit as a function of Lorentzian and Gaussian functions, and all site occupancies were fixed at full occupancy of 1. To obtain occupancies from neutron diffraction data, the ADPs were fixed at $1.5 \text{ \AA}^2$ and the occupancies were refined. Data from post ex facto SXRd runs is plotted as weight percent to account for inconsistent packing densities along the length of the capillary. The data should be considered qualitative as a result.

Density functional theory calculations

The Python Materials Genomics package (*pymatgen*) [194] was used to create and process all VASP input/output files. The *phonopy* [66] package was used to process force constants, apply the quasiharmonic approximation (QHA), and produce the Gibbs free energy, $G(P, T)$, of each structure.

Diffraction and occupancies data

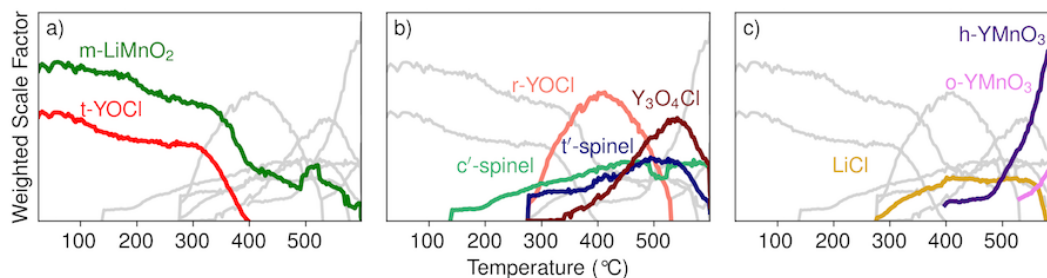


Figure C.1: Quantitative phase analysis of crystalline materials calculated from synchrotron X-ray diffraction experiments of the ternary metathesis reaction $\text{LiMnO}_2 + \text{YOCl} \longrightarrow \text{YMnO}_3 + \text{LiCl}$ when starting from monoclinic ($C2/m$) LiMnO_2 . Reactions were heated at $10 \text{ }^\circ\text{C/min}$ to $600 \text{ }^\circ\text{C}$. Each row of subpanels presents a) precursors, b) intermediates, and c) products as calculated from Rietveld analysis.

The relative amount of the two spinel intermediates provides a metric to analyze the progress of the reaction pathway in this intermediate temperature regime (e.g., how much lithium chloride had formed). In the SXRd results in Figure 4.1, the weight percent of c' -spinel was greater than t' -spinel for all polymorphs, whereas in the neutron diffraction experiments (Figure C.3), the fraction of t' -spinel was higher. As the NPD was collected *in situ*, the reaction had progressed for approximately 14 hours upon reaching $500 \text{ }^\circ\text{C}$, whereas the SXRd results reflect a one hour reaction for each temperature due to collection across a temperature gradient *ex post facto*. Thus, the greater weight fraction of t' -spinel in the NPD patterns supports a reaction pathway where more lithium has been removed from the spinel intermediates and thus, the weight percent of Mn_3O_4 increases.

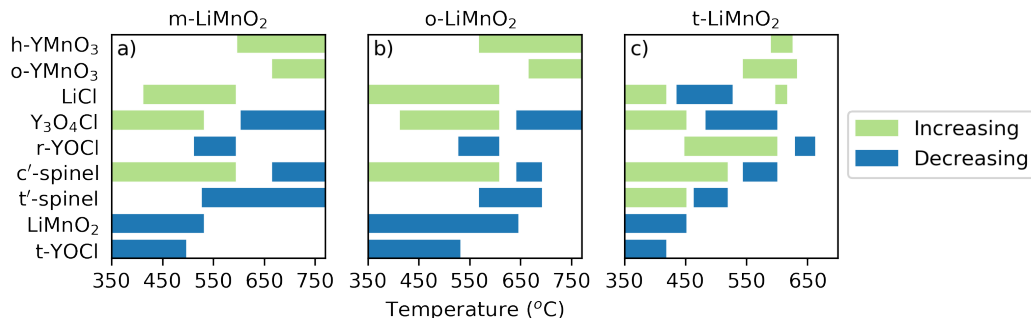


Figure C.2: Qualitative data on temperature ranges where phases are forming and reacting, obtained from comparing two SXRD patterns taken 20 minutes apart on a gradient furnace. Green indicates a phase with increasing intensity, while blue indicates a phase with decreasing intensity. o-YMnO₃ forms in temperature ranges where c'-spinel is reacting, while h-YMnO₃ forms in temperature ranges where t'-spinel is reacting when starting from the monoclinic and orthorhombic LiMnO₂ phases.

C.2 Experimental methods for NaFeO₂ study

α -NaFeO₂ was synthesized by first combining Na₂O₂ (Sigma Aldrich) and γ -Fe₂O₃ (Inframat Advanced Materials) into a 65 mL stainless-steel SPEX jar with six (6) 5-mm and three (3) 1/2-inch stainless steel milling media in an Ar-filled glovebox. The Na₂O₂ and γ -Fe₂O₃ (1:1 mol ratio) were milled under Ar for 5 hours using a SPEX 8000M Mixer/Mill. The resulting powder was then heated in air to 700 °C for 12 hours with a 10 °C/min heating rate. After heating for 12 hours, the sample was furnace cooled by turning off the heating of the furnace with no specific cooling rate set. A synthesis graph of this synthesis process generated using SynCheck [219] is shown in Figure C.7.

Na₂O₂ is a reactive chemical. It is a strong oxidizer, an explosion hazard, and water-reactive. All preparation and reactions were performed under Ar, ensuring that no water, metal powders, or organic compounds were present in the milling jar during the reaction.

Data suitable for X-ray diffraction and PDF analyses were collected at 28-ID-1, at the National Synchrotron Light Source II, Brookhaven National Laboratory ($\lambda=0.1665$ Å). The distance between the sample and detector was calibrated using a CeO₂ standard (NIST SRM 674b) and GSAS II [234]. Rietveld refinements were carried out in TOPAS-Academic v6 [235]. Extraction of PDF data was done in xPDF Suite and modeling of the PDF data was done in PDFgui [236]. Details of the refinements can be found in the Supporting Information in the Appendix. Bond length of interest were quantified fitting Gaussian functions to the peaks in the PDF data within fity [237]. Crystal structures were visualized using VESTA [238].

Scanning electron microscopy (SEM) was performed using a Hitachi TM3030 Plus.

For inductively coupled plasma-optical emission spectroscopy (ICP-OES) chemical analysis, 18 MW ultrapure deionized water, HCl acid (Aristar Plus, VWR Chemicals), HNO₃ acid (Aristar Plus, VWR Chemicals), were used as reagents. A mixture of HCl:HNO₃ was

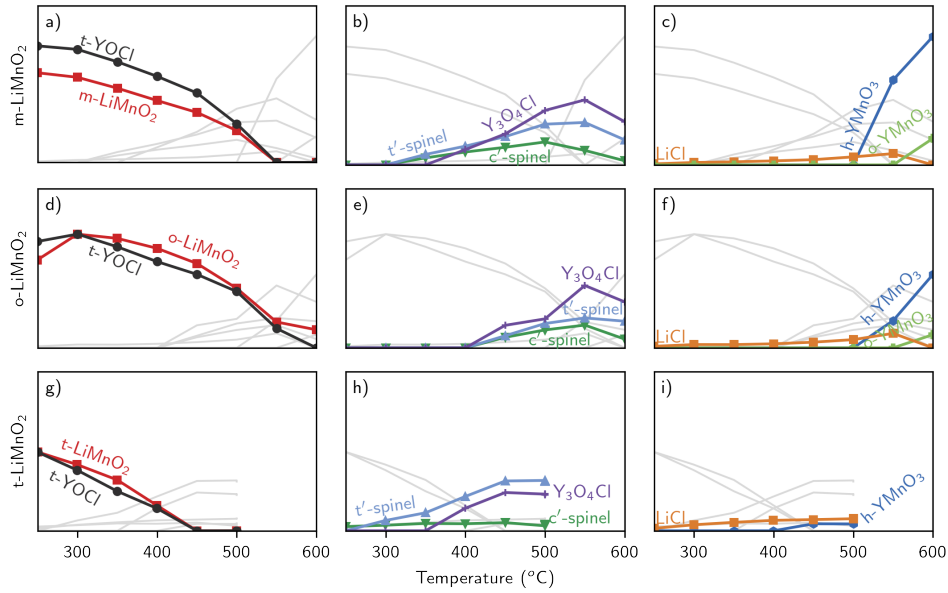


Figure C.3: Weighted scale factor of crystalline materials from neutron refinement at different reaction temperatures reveals the reaction pathway of the ternary metathesis reaction, $\text{LiMnO}_2 + \text{YOCl} \longrightarrow \text{LiCl} + \text{YMnO}_3$. Each row of subpanels is from a single precursor: (a-c) monoclinic ($C2/m$), (d-f) orthorhombic ($Pmnm$) and (g-i) tetragonal [$(I4_1/amd)$]. Each column highlights phase fractions containing a specific cation to provide clarity with many overlapping phases: (a,d,g) Lithium, (b,e,h) Manganese, (c,f,i) Yttrium.

prepared in a 3:1 volume ratio to dissolve the NaFeO_2 . 1,000 mg/L ICP standards were purchased from Sigma Aldrich (TraceCERT grade) and diluted to prepare standards. ICP-OES measurements were carried out on a Thermo Scientific iCAP 7400 ICP-OES Duo and iCAP 7600 (Thermo Fisher Scientific).

The synthesis graph, shown in Figure C.7, was generated using SynCheck to ensure that the synthesis description contained in the experimental methods can be interpreted using natural language processing methodologies [219].

Laboratory X-ray diffraction data were collected on a Rigaku SmartLab diffractometer in reflection geometry using $\text{Cu-K}\alpha$ radiation. The samples synthesized with 5 grams of precursor material were measured using a Scintag XDS 2000 diffractometer with $\text{Cu-K}\alpha$ radiation. Rietveld refinements were performed using Topas V6 software.

Samples were synthesized by combining Na_2O_2 and $\gamma\text{-Fe}_2\text{O}_3$ into a stainless-steel SPEX jar with 6 5-mm and 3 1/2-inch stainless steel milling media in an Ar-filled glovebox. The Na_2O_2 and $\gamma\text{-Fe}_2\text{O}_3$ (1:1 mol ratio) were milled under Ar for 5 hours using a SPEX 8000M Mixer/Mill, as stated in the Methods section. Synthesis was also attempted using $\alpha\text{-Fe}_2\text{O}_3$, however even after annealing at 700 °C for 12 hours, the sample was still a mixture of α - and β - NaFeO_2 , as shown in Figure C.8.

Samples with different starting precursor masses were also tested. For the sample that

used 2.25 g of total starting material (γ -Fe₂O₃ and Na₂O₂), the resulting X-ray diffraction data (Figure C.9c/d shows only the presence of α -NaFeO₂ both before and after annealing. X-ray diffraction measurements of the sample the used 5 g of total starting material shows a mixture of phases after milling (Figure C.9a) which results in a mixture of α - and β - NaFeO₂ phases after annealing at 700 °C for 12 hours (Figure C.9b).

Thermogravimetric analysis (TGA) measurements were performed using a TA Instruments Q500. The as-milled NaFeO₂ sample was heated with a ramp rate of 10 °C/min under a 50/50 mixture of dry air and N₂ with a 12-hour hold at 700 °C to mimic the annealing heat treatment. TGA data is shown in Figure C.13.

Upon heating the sample, mass loss occurs until it reaches a plateau of 2.2% mass loss at 310 °C. This initial mass loss is likely due to the removal of bonded water on the surfaces of the particles. The rate of mass loss increases again at 400 °C and continues as the sample is heated to 700 °C. By 700 °C, the mass loss reaches 7.3%. This second region of mass loss is also seen in previous studies during the synthesis of NaFeO₂ and is thought to be due to the continued residual water loss and the loss of O₂ during the synthesis process. However, for this sample NaFeO₂ is already formed, and the mass loss is likely due to the removal of a sodium carbonate layer on the surface. In calculating the difference in Na content from ICP between the as-milled and annealed sample, if all of the excess Na was in the form of a surface carbonate and all of the carbonate was removed upon heating, one would expect a total mass loss of 4.0% which corresponds well to the 5% mass loss during this second region. Additional water is most likely also lost in this region. The mass loss at 700 °C is slow and after 12 hours at 700 °C the mass loss is at a maximum of 7.6%.

Rietveld refinements of structural models against the diffraction data were carried out in TOPAS-Academic V6 software. Refined parameters included lattice parameter, isotropic displacement parameters (B_{iso}) for Fe and O sites, pseudo-Voigt type peak profile parameters, and scale factor. The background was fit using an eight-term Chebyshev polynomial function. The scattering from the borosilicate capillary was accounted for by fitting a pseudo-Voigt function to the baseline. Occupancy factors were fixed to the normal composition.

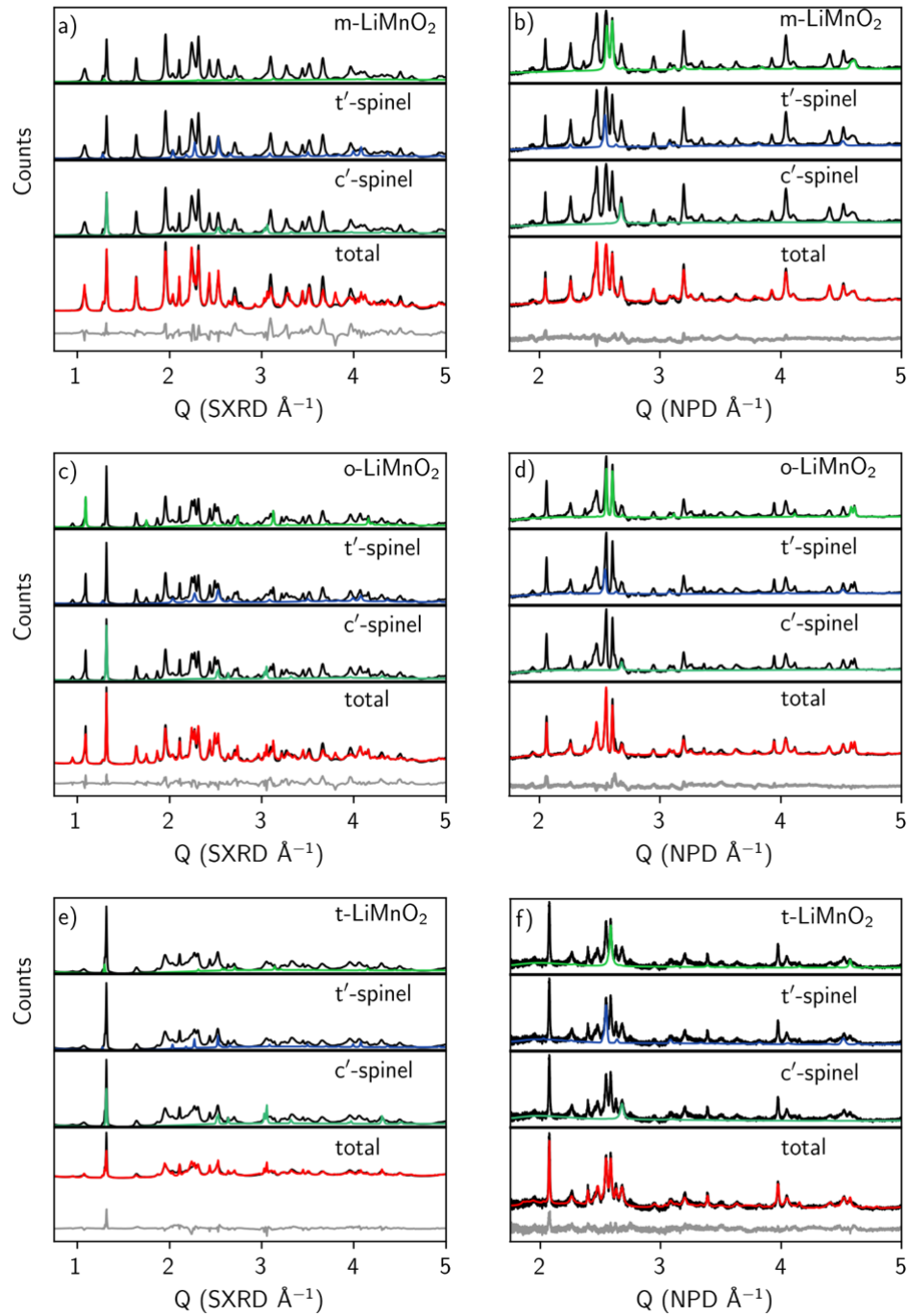


Figure C.4: The contributions of the manganese-containing phases LiMnO₂(top), t'-spinel (second from top), and c'-spinel (third from top) are overlaid on the pattern. The overall fit (bottom) also contains t-YOCl, r-YOCl, Y₃O₄Cl and LiCl (red) along with a difference pattern (gray) for reactions of o-LiMnO₂ (SXR (a), NPD (b)), m-LiMnO₂ (SXR (c), NPD (d)), and t-LiMnO₂ (SXR (e), NPD (f)).

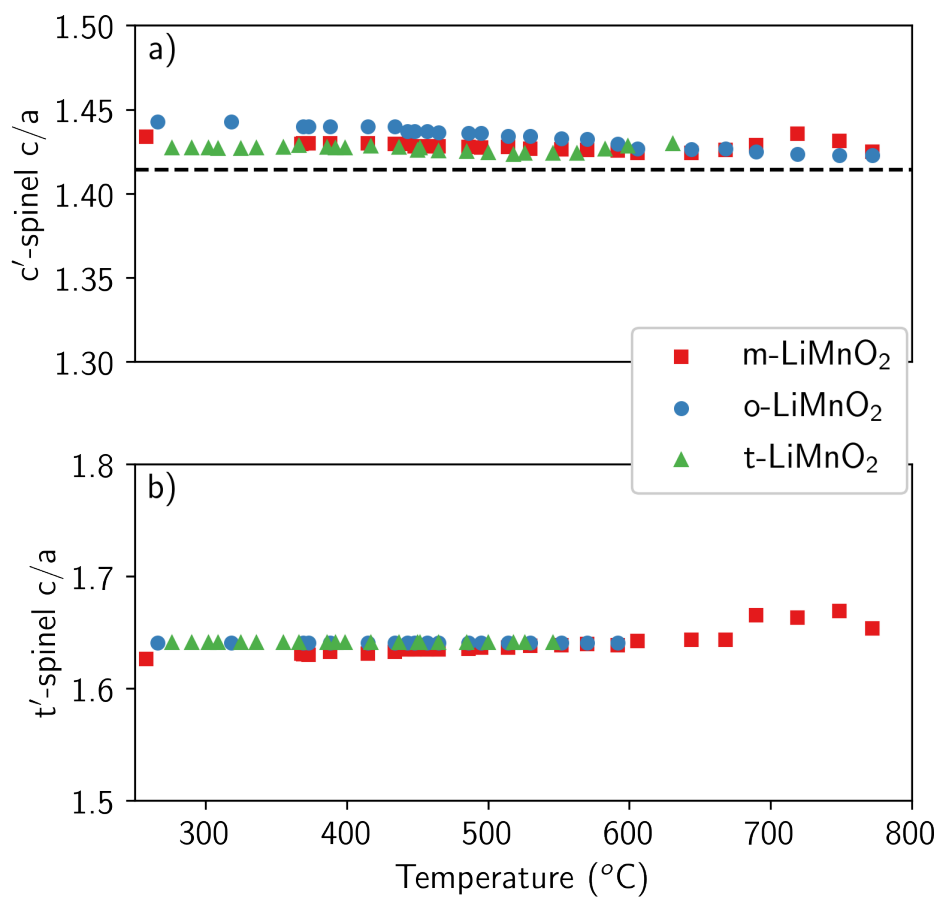


Figure C.5: Ratio of the c and a lattice parameters for (a) c' -spinel and (b) t' -spinel from X-ray diffraction patterns used in Figure 4.1. Data points are separated by LiMnO₂ precursor: o-LiMnO₂ (red squares), m-LiMnO₂ (blue circles) and t-LiMnO₂ (green triangles).

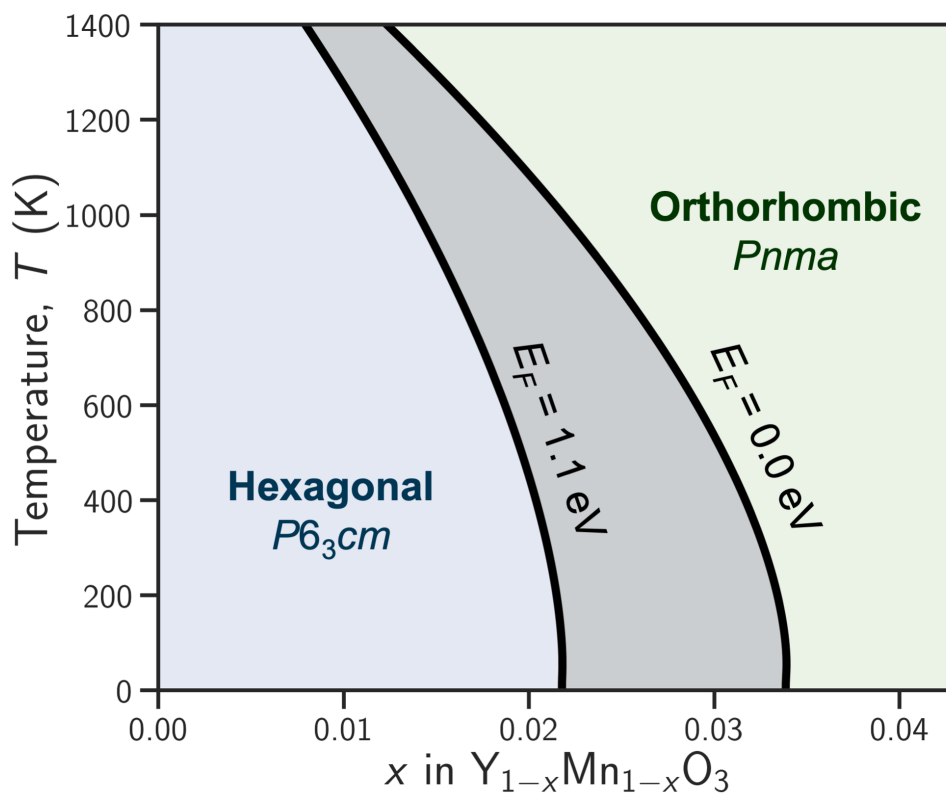


Figure C.6: Calculated phase stability of $YMnO_3$ polymorphs with respect to temperature and an equal concentration of cation (Y,Mn) vacancies, x . The phase diagram is constructed for all values of Fermi energy, E_F , within the band gap to show the phase boundary shifts with changing E_F .

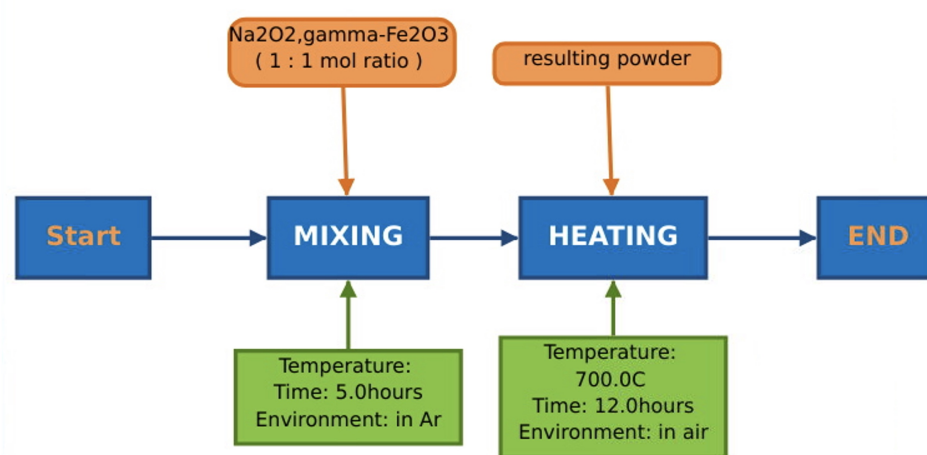


Figure C.7: Synthesis graph of synthesis procedure for α - $NaFeO_2$ including milling (mixing) and annealing (heating) steps.

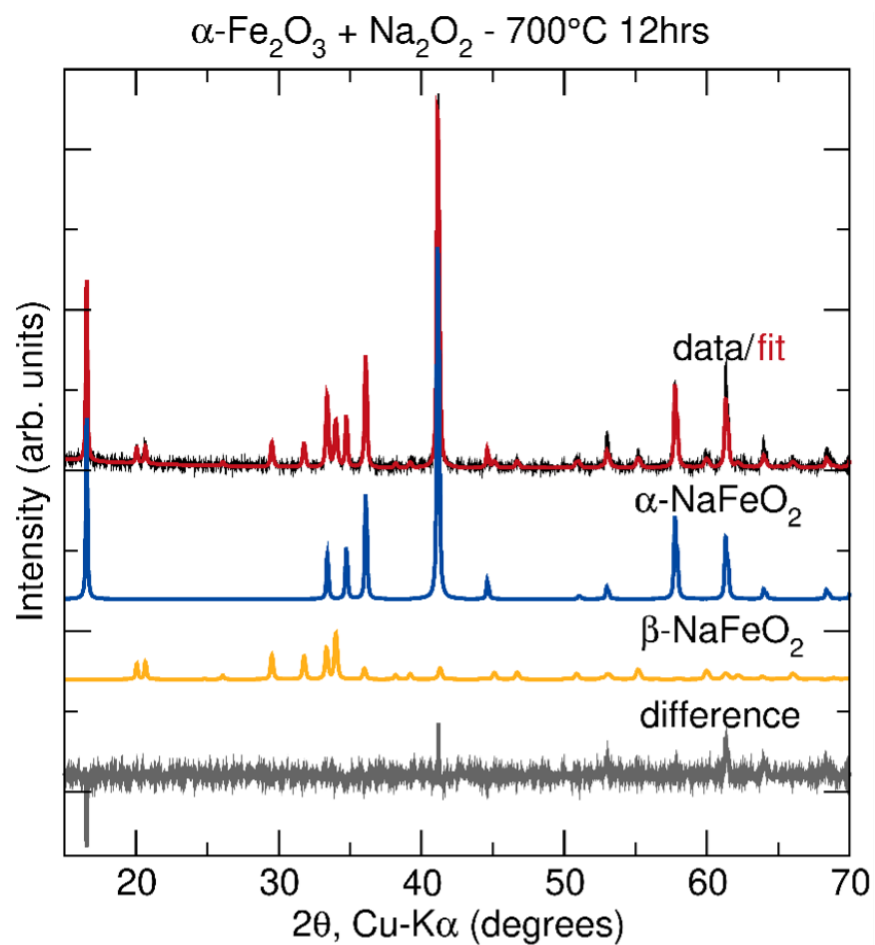


Figure C.8: Resulting X-ray diffraction data and Rietveld refinement of the reaction between $\alpha\text{-Fe}_2\text{O}_3$ and Na_2O_2 that was milled for 5 hours and then annealed at 700°C for 12 hrs. The sample resulted in a mixture of α - and β - NaFeO_2 phases.

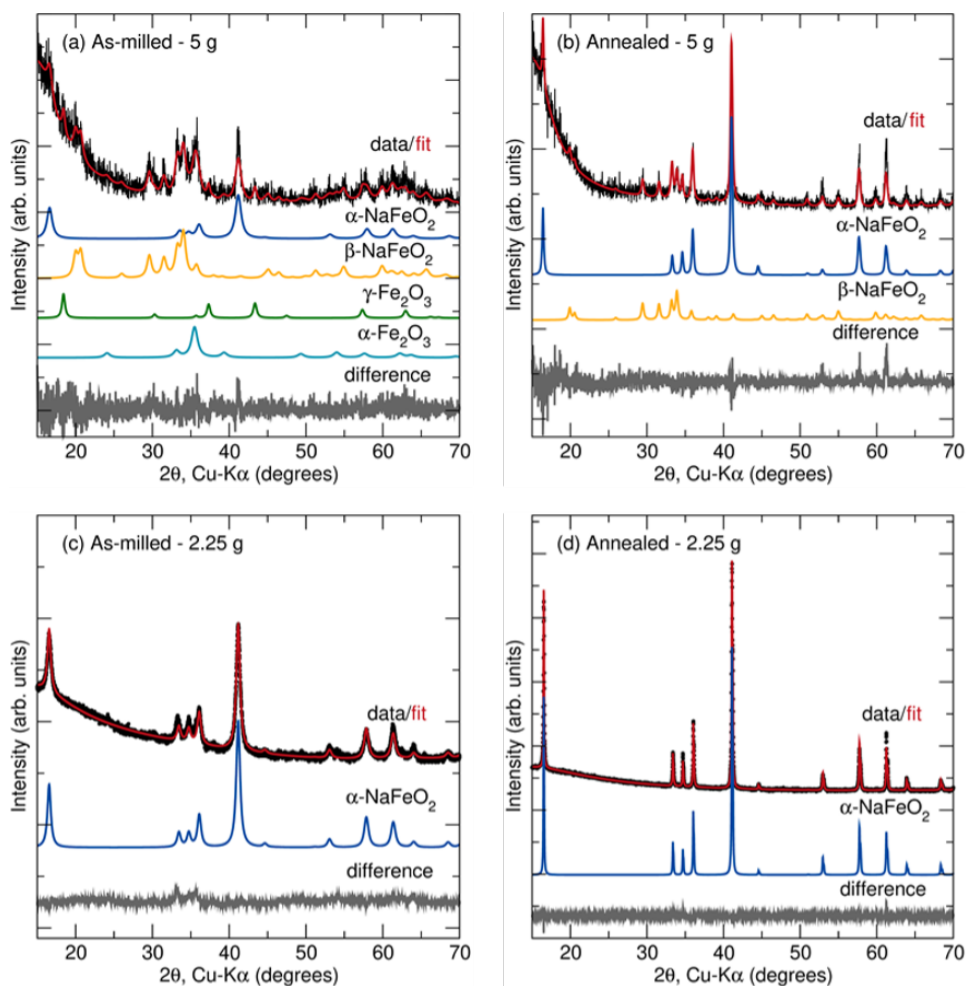


Figure C.9: Resulting X-ray diffraction data and Rietveld refinements of samples milled with (a) 5 g of starting material ($\gamma\text{-Fe}_2\text{O}_3$ and Na_2O_2) and (c) 2.25 g of starting material showing that as-milled samples are significantly different based on the mass of precursor used. The XRD of the annealed samples show that the mass makes a difference on the resulting polymorphs with (b) 5 g of precursor resulting in a mixture of α - and β - NaFeO_2 phases, while (d) 2.25 g of precursor results in pure α - NaFeO_2 .

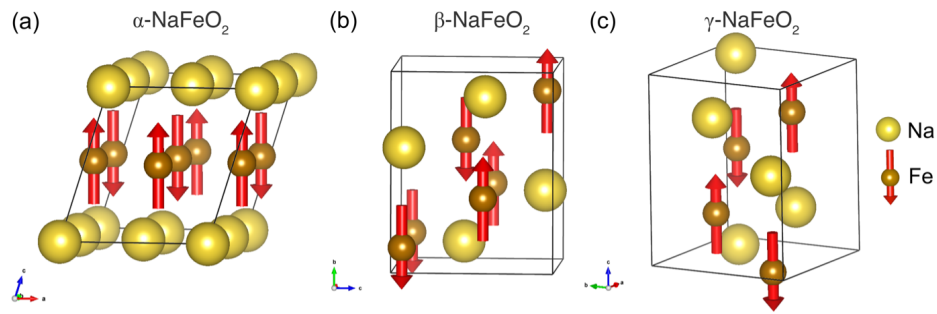


Figure C.10: Collinear antiferromagnetic orderings identified from magnetic ordering workflow for (a) $\alpha\text{-NaFeO}_2$ ($R\bar{3}m$), (b) $\beta\text{-NaFeO}_2$ ($Pna2_1$), and (c) $\gamma\text{-NaFeO}_2$ ($P2_12_12_1$). These magnetic orderings were used in all charged point defect calculations.

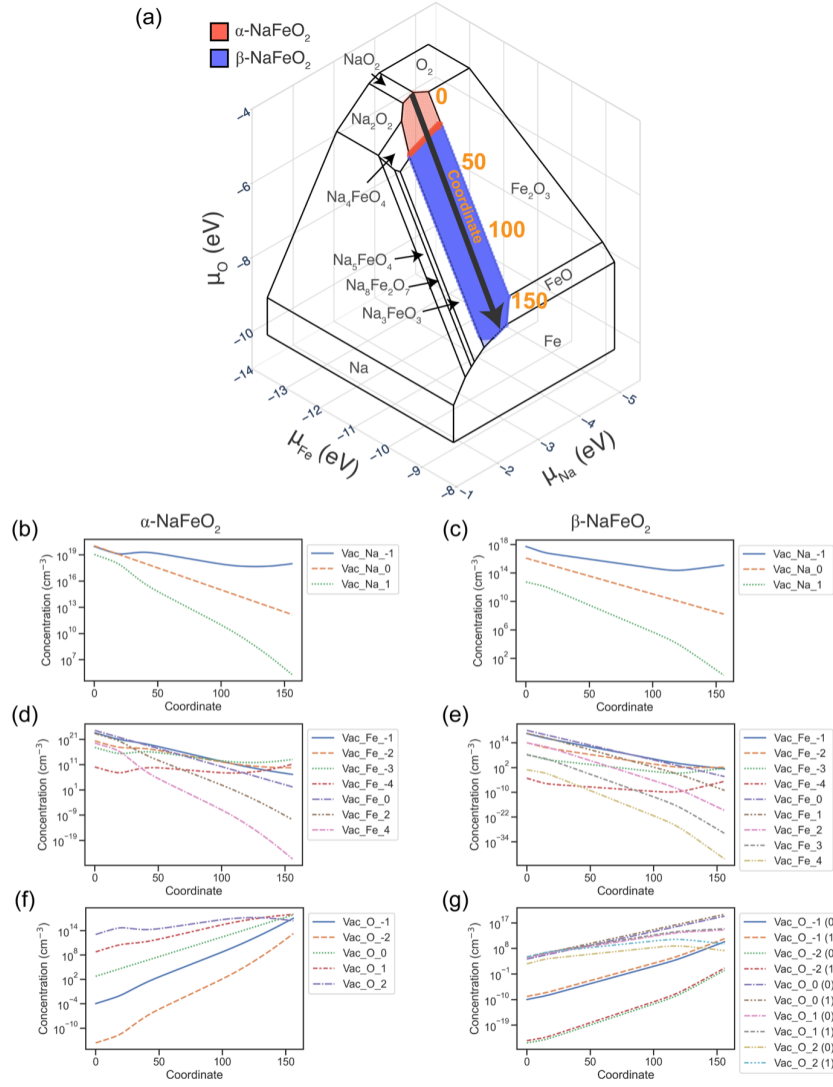


Figure C.11: Equilibrium concentrations of charged vacancies in NaFeO_2 polymorphs as a function of chemical potentials within the NaFeO_2 stability domain. (a) Chemical potential diagram for Na-Fe-O chemical system with overlaid coordinate axis (black) and coordinate step numbers labeled (orange). Vacancy concentrations are plotted as a function of the chemical potential coordinate for (b,c) Na vacancies spanning $[-1,1]$ charge states, (d, e) Fe vacancies spanning $[-4,4]$ charge states, and (f, g) O vacancies spanning $[-2, 2]$ charge states, for $\alpha\text{-NaFeO}_2$ and $\beta\text{-NaFeO}_2$, respectively. Concentration lines are labeled by element and charge state. O vacancies in $\beta\text{-NaFeO}_2$ are distinguished between their two unique sites using parenthetical labels (indexed 0 or 1). As expected, the vacancy concentrations follow the opposite trend of their corresponding chemical potentials, e.g., the O vacancy concentration increases as μ_{O} decreases (coordinate increases). Concentration magnitudes are similar between the polymorphs except with Fe vacancies. $\alpha\text{-NaFeO}_2$ exhibits significantly higher Fe vacancy concentrations due to its smaller Fe vacancy formation energies, helping to stabilize the phase in the higher μ_{O} region.

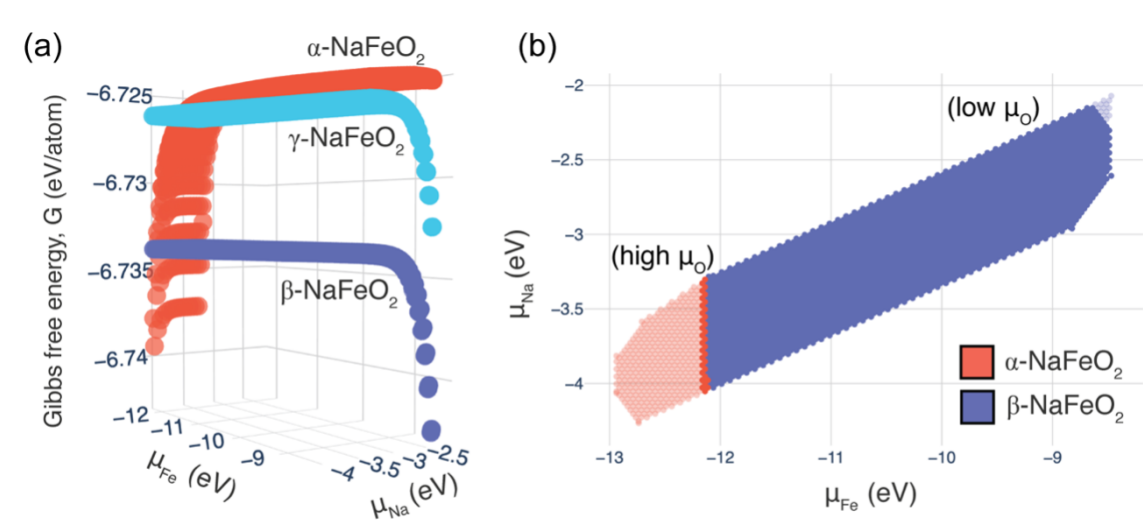


Figure C.12: (a) Calculated Gibbs free energy curves for the α -, β -, and γ - NaFeO_2 as determined by Equation 4.5. The free energies rapidly diverge towards negative infinity at high oxygen chemical potentials for α - NaFeO_2 , and at low oxygen chemical potentials for β - and γ - NaFeO_2 . (b) A two-dimensional view of the NaFeO_2 stability domain with shading indicating which polymorph is stable as a function of Na and Fe chemical potentials. Lighter shading indicates where at least one molar defect concentration exceeds 10%.

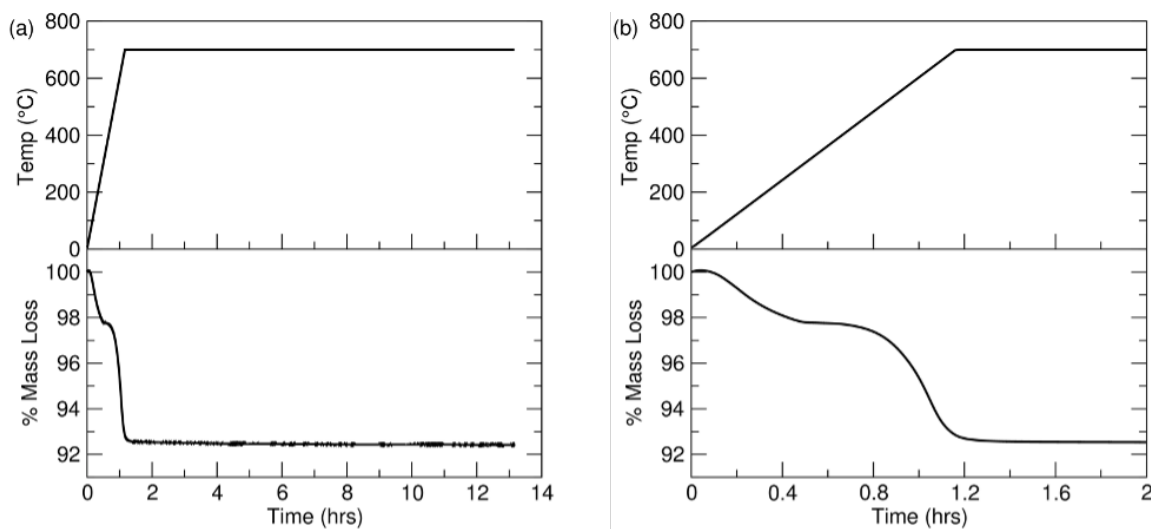


Figure C.13: Thermogravimetric analysis (TGA) data on the heating of α - NaFeO_2 as-milled powder over (a) the entire annealing time and (b) a zoomed-in section highlighting the first 2 hours of the annealing process showing the two-part mass loss on heating.

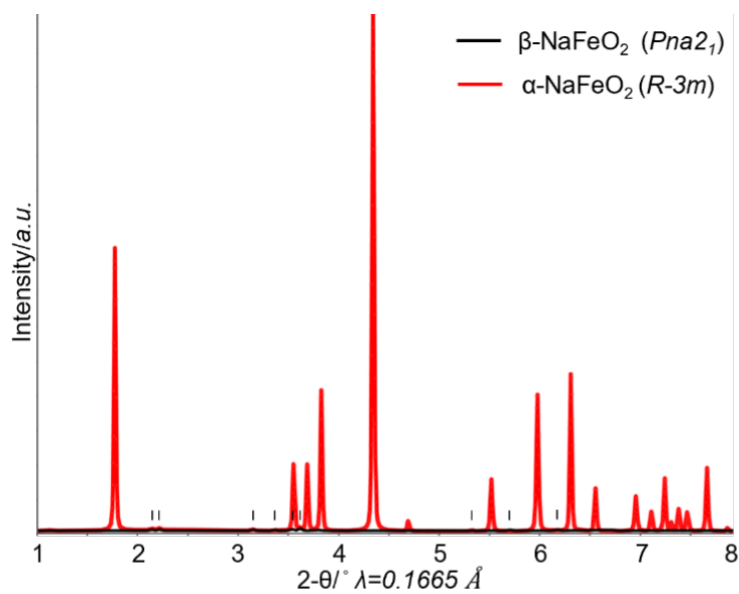


Figure C.14: XRD of the annealed $\alpha\text{-NaFeO}_2$ plotted with the simulated diffraction pattern of $\beta\text{-NaFeO}_2$ ($Pna2_1$).

Appendix D

Supplementary Information for Chapter 5

D.1 Experimental methods

All reagents were prepared, stored, and weighed in an argon-filled glovebox with O_2 and H_2O levels $\leq 0.1\text{ppm}$. Manganese(III) oxide (Sigma Aldrich 99%) was purified by heating Mn_2O_3 in an alumina boat at $1\text{ }^\circ\text{C}/\text{min}$ to $700\text{ }^\circ\text{C}$ for 16 h in air and quenched into the glovebox; purity was verified by powder X-ray diffraction (PXRD). Manganese (IV) oxide (Sigma Aldrich $\geq 99\%$), YCl_3 (Alfa Aesar 99.9%), sodium carbonate (ACROS Organics 99.5%), and manganese (II) carbonate (Sigma Aldrich $\geq 99.99\%$) were purchased and stored under argon. All gases (O_2 , Ar, He) were purchased through Airgas at the Ultra High Purity grade (99.999%). NaMnO_2 ($C2/m$) was prepared by mixing manganese (III) oxide and sodium carbonate in a 1:1 molar ratio, grinding for 15 minutes in an agate mortar and pestle, and pelleting using a $1/4$ in die under ~ 1 tn of force. The pellet was placed upon a sacrificial layer of powder in an alumina crucible and heated in a muffle furnace at $1\text{ }^\circ\text{C}/\text{min}$ to $700\text{ }^\circ\text{C}$ for 10 h. The reaction was subsequently quenched into the antechamber of the glovebox and stored under argon. Similarly, $\text{Na}_{0.7}\text{MnO}_2$ ($Cmcm$) was prepared by mixing manganese (II) carbonate and sodium carbonate in a 0.70:1 Na:Mn ratio following the same pellet preparation as NaMnO_2 . The reaction was performed by heating at $5\text{ }^\circ\text{C}/\text{min}$ to $1050\text{ }^\circ\text{C}$ for 15 h and then quenching into the antechamber of a glovebox and stored under argon. Y_2O_3 was purified of hydroxide in an alumina boat at $1\text{ }^\circ\text{C}/\text{min}$ to $900\text{ }^\circ\text{C}$ for 4 h in air, cooled to $200\text{ }^\circ\text{C}$ at $1\text{ }^\circ\text{C}/\text{min}$ for 12 h, and quenching into the glovebox. YOCl was prepared by heating $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ in an alumina boat to $350\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$ for 4 h in air. The YOCl product formed as the $P4/nmn$ PbClF structure-type. All prepared reactants were confirmed using laboratory PXRD. Preparations for *ex situ* assisted metathesis reactions have been described in detail previously where reaction yields match the expected $\text{Y}_2\text{Mn}_2\text{O}_7\cdot 6\text{NaCl}$ by PXRD (14.2(3) mol% $\text{Y}_2\text{Mn}_2\text{O}_7$) [92]. Laboratory PXRD data were collected on a Bruker D8 Discover diffractometer using $\text{Cu K}\alpha$ radiation and a Lynxeye XE-T position-sensitive

detector.

For temperature-dependent *in situ* assisted metathesis reactions that produce carbon dioxide as a by-product, open-ended quartz capillaries (1.1 mm OD) were packed in a glove-bag under argon using glass wool as a plug. Synchrotron X-ray diffraction experiments were performed at beamline 17-BM-B ($\lambda = 0.2415 \text{ \AA}$) at the Advanced Photon Source (APS) at Argonne National Laboratory using a Perkin Elmer plate detector at a distance of 700 mm. All capillaries were loaded into a flow-cell apparatus equipped with resistive heating elements and heated at $10 \text{ }^\circ\text{C/min}$ [36]. Gas flow (O_2 , He) was controlled through mass flow controllers at a rate of 0.2 cc/min . Assisted-metathesis reactions were heated to a maximum temperature of $850 \text{ }^\circ\text{C}$ while the sample continuously rocked at $\pm 5^\circ$ around the axis of the capillary. Diffraction patterns were collected every two seconds and summed every 20 seconds for powder averaging. Plate detector images were integrated using GSAS-II and calibrated using a LaB_6 standard.

All Rietveld refinements were performed using TOPAS v6. Due to the number and positional overlap of intermediates during the sequential refinements, thermal displacement parameters were fixed at $5\text{\AA}^2$ and the full-width-half-max using a Lorentzian polynomial was fixed at 178 nm to better account for changes in peak intensity during the reaction. In order to compare the relative fractions of phases determined from Rietveld calculations, a weighted scale factor (WSF) is defined as: $Q_p = S_p \cdot V_p \cdot M_p$ where Q_p = weighted scale factor of phase p, S_p = Scale factor calculated from Rietveld for phase p, V_p is the volume of the unit cell for phase p, and M_p is the atomic mass of the unit cell for phase p. It should be noted that we omit the Brindley coefficient for microabsorption correction in our calculation of weighted scale factor due to the unreliable refinement of particle sizes for individual phases. Amorphous material and product lost as vapor are not accounted for in the sequential refinement. We reference all phases by their nominal stoichiometric formula; however, the actual chemical formula may be distinct from the written formula as XRD data alone cannot typically resolve non-stoichiometric compounds.

It has been recently demonstrated by some of us that f^* diagrams are a powerful tool for understanding defects in chemical systems with three different crystallographic sites, allowing a diffraction analog of a ternary phase diagram to be calculated in which each axis represents the relative scattering power of each crystallographic site (at $2\theta = 0$) rather than the chemical composition [239, 240]. The f^* diagram method is applied here with a slight modification to understand the evolution of defects within the Na_xMnO_2 intermediates. The $C2/m$ P3 structure has three distinct crystallographic sites (one for each element), whereas the $Cmcm$ Birnessite P2 phase has four distinct crystallographic sites (2 Na, 1 Mn, 1 O) rather than three. Therefore, the scattering powers of the two Na sites were summed together in the construction of the f^* diagram.

D.2 Assisted metathesis reaction energetics

The assisted metathesis net reaction $\text{Mn}_2\text{O}_3 + 2 \text{YCl}_3 + 3 \text{A}_2\text{CO}_3 + 0.5 \text{O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 6 \text{A}\text{Cl} + 3 \text{CO}_2$ ($\text{A} = \text{Li, Na, K}$) is predicted to be exergonic ($\Delta G < 0$) for all temperatures (Figure D.1). The least negative reaction energy occurs for lithium, followed by sodium, and then potassium.

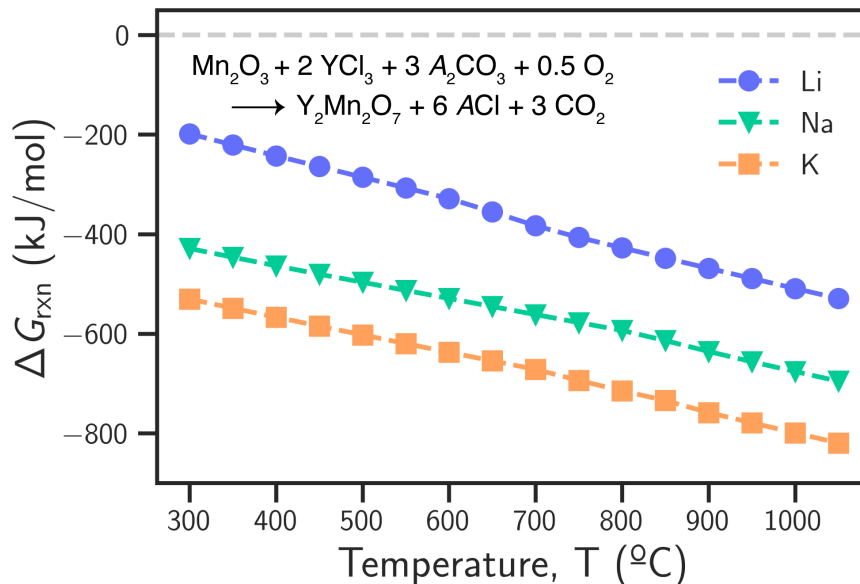


Figure D.1: Reaction energetics of the assisted metathesis reaction, $\text{Mn}_2\text{O}_3 + 2 \text{YCl}_3 + 3 \text{A}_2\text{CO}_3 + 0.5 \text{O}_2 \longrightarrow \text{Y}_2\text{Mn}_2\text{O}_7 + 6 \text{A}\text{Cl} + 3 \text{CO}_2$ for alkali metals $\text{A} = \text{Li, Na, and K}$ as predicted by Materials Project data and machine-learned descriptor for solids [69]. Thermochemical data for A_2CO_3 and ACl were acquired from experimental tables [241] and CO_2 from the NIST-JANAF database [65]; changes in slope are due to the melting of A_2CO_3 and/or ACl .

D.3 *Ex situ* control experiments

Control reactions of binary yttrium and manganese oxides reveal that the sodium carbonate assisted metathesis reaction pathway is selective for $\text{Y}_2\text{Mn}_2\text{O}_7$. Analysis of *ex situ* control reactions, $2 \text{MnO}_2 + \text{Y}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3 + \text{Y}_2\text{O}_3$, performed at 650 °C under flowing O_2 at ambient pressure (Figure D.2) reveal that the reactions contain a finite fraction of $\text{Y}_2\text{Mn}_2\text{O}_7$ at initial time points (i.e., no selectivity), and the phase fraction of $\text{Y}_2\text{Mn}_2\text{O}_7$ decreases at longer times in favor of YMn_2O_5 . Based on Figure 5.2 this suggests that the true μ_{O} is near the border between YMn_2O_5 and $\text{Y}_2\text{Mn}_2\text{O}_7$.

Additionally, the presence of a six molar equivalent of sodium chloride does increase the initial yield of $\text{Y}_2\text{Mn}_2\text{O}_7$, but YMn_2O_5 increases in phase fraction at long reaction times

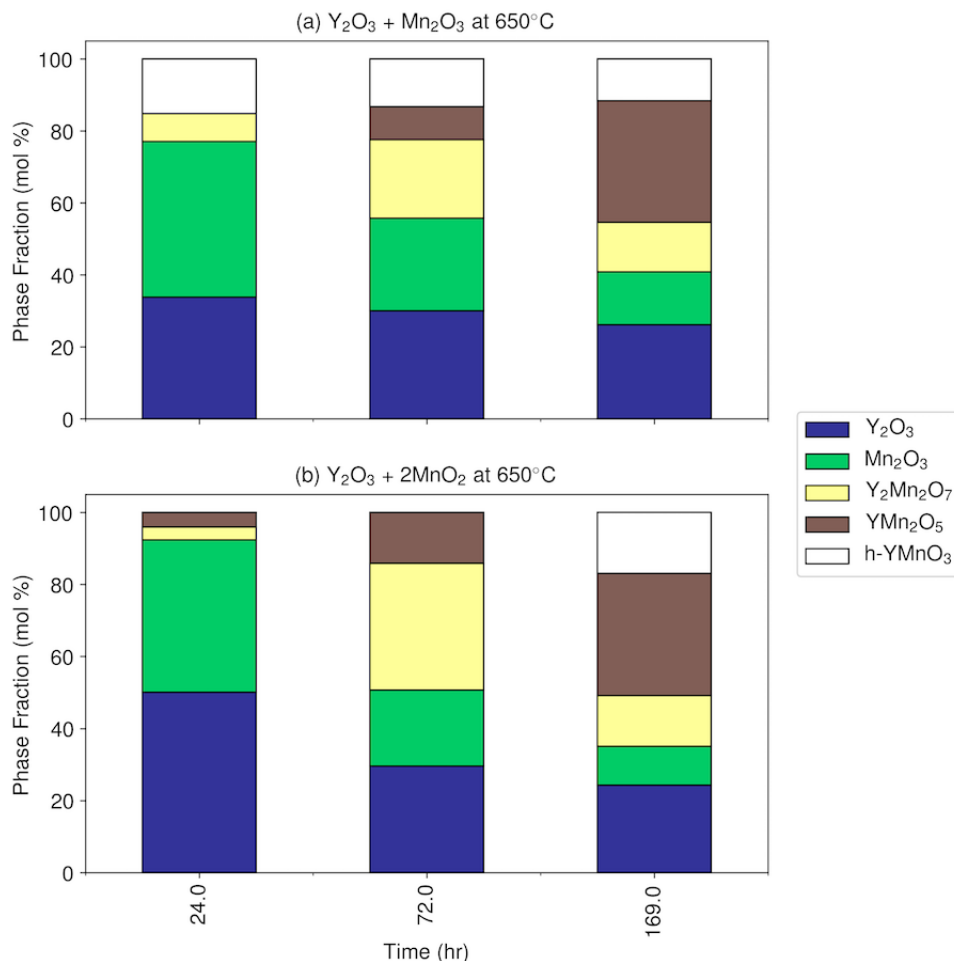


Figure D.2: Bar graphs representing the mole percent amounts of products calculated from *ex situ* PXRD Rietveld refinements of the reaction: (a) $\text{Mn}_2\text{O}_3 + \text{Y}_2\text{O}_3 \xrightarrow{\text{O}_2}$ and (b) $2 \text{MnO}_2 + \text{Y}_2\text{O}_3 \xrightarrow{\text{O}_2}$. The reactions were heated at 10 °C/min to 650 °C for 24, 72, and 128 hours under flowing oxygen. Each color bar is represented in the legend as a different product phase.

(Figure D.3). In order to assess the stability of pyrochlore, washed $\text{Y}_2\text{Mn}_2\text{O}_7$ was heated at 650 °C under flowing oxygen for long-duration reactions. Only partial decomposition occurs to the binary oxides, $\text{Mn}_2\text{O}_3 + \text{Y}_2\text{O}_3$, after 24 h; the composition remains constant even after heating for 2 weeks (Figure D.4).

Control ternary metathesis reactions performed using nominally stoichiometric, ideal sodium manganese oxide precursors do not yield selectivity for $\text{Y}_2\text{Mn}_2\text{O}_7$. In the case of Li_2CO_3 -based assisted metathesis reactions [92], we previously identified that the ternary metathesis reaction, $\text{LiMnO}_2 + \text{YOCl} \longrightarrow \text{YMnO}_3 + \text{LiCl}$ yielded improved selectivity for orthorhombic YMnO_3 over the analogous assisted metathesis reactions [93]. However, the reaction, $2 \text{NaMnO}_2 + 2 \text{YOCl} \xrightarrow{\text{O}_2}$, results in a mixture of Y-Mn-O products (Figure D.5).

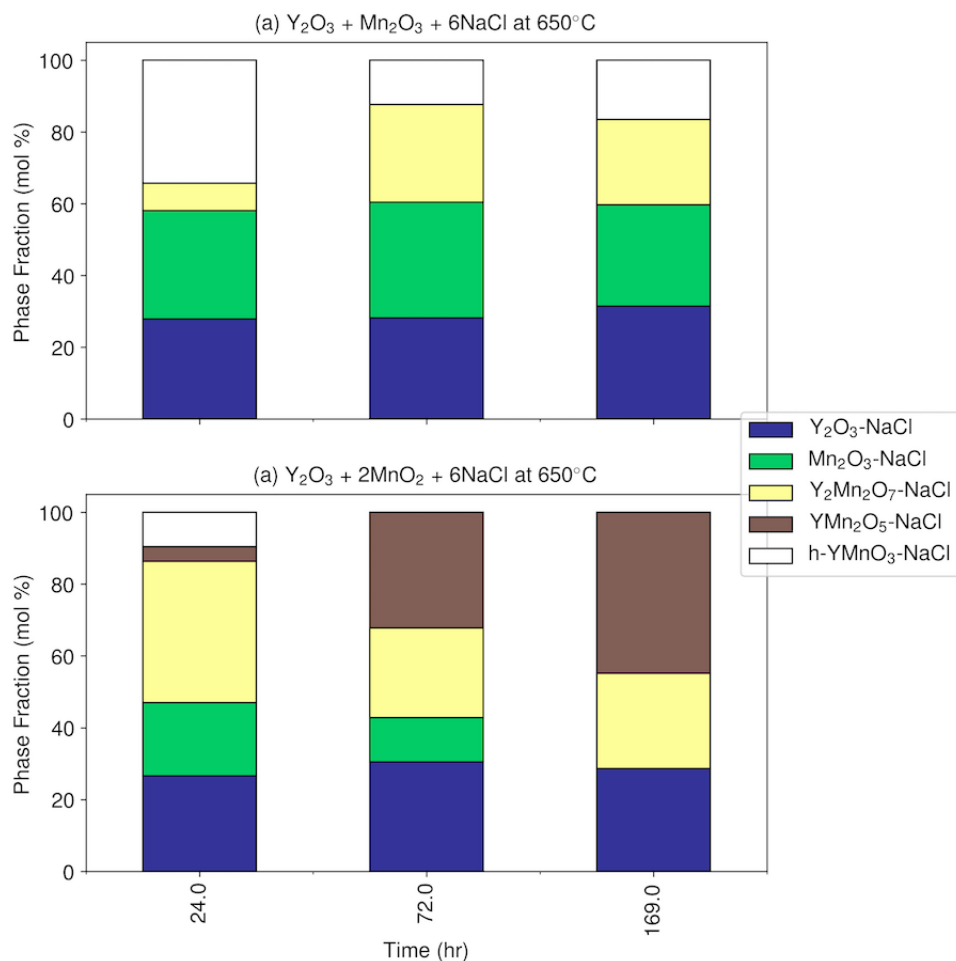


Figure D.3: Bar graphs representing the mole percent amounts of products calculated from *ex situ* PXRD Rietveld refinements of the reaction: (a) $\text{Mn}_2\text{O}_3 + \text{Y}_2\text{O}_3 \xrightarrow{6\text{NaCl}, \text{O}_2}$ and (b) $2\text{MnO}_2 + \text{Y}_2\text{O}_3 \xrightarrow{6\text{NaCl}, \text{O}_2}$. The reactions were heated at $10^\circ\text{C}/\text{min}$ to 650°C for 24, 72, and 128 hours under flowing oxygen. Each color bar is represented in the legend as a different product phase. Mole fractions are presented after subtracting the contribution from NaCl for comparison.

Furthermore, using a partially-oxidized precursor in the reaction, $\text{P2-2Na}_{0.7}\text{MnO}_2$ with 2 YOCl selectively yields $\text{Y}_2\text{Mn}_2\text{O}_7$, but it is incomplete after 24 h (Figure D.6). Together, these control reactions lend support to the sodium-based reaction pathway in selectively yielding $\text{Y}_2\text{Mn}_2\text{O}_7$.

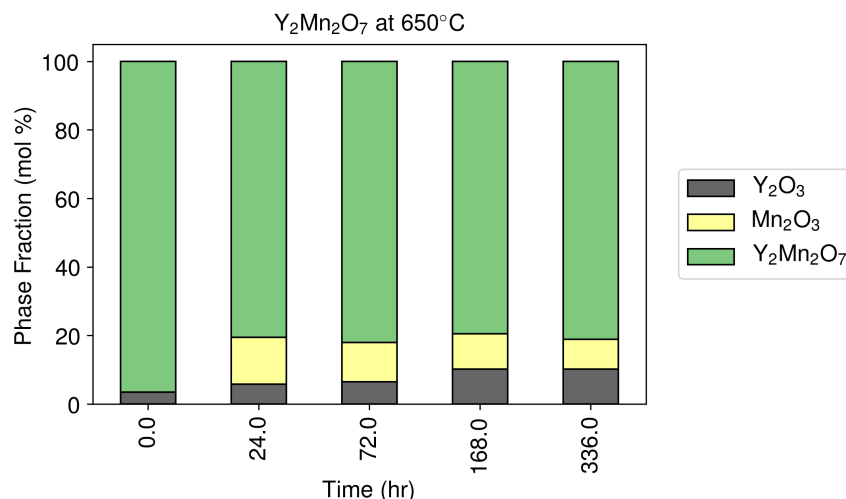


Figure D.4: Bar graphs representing the mole percent amounts of products calculated from *ex situ* PXRD Rietveld refinements of $\text{Y}_2\text{Mn}_2\text{O}_7$. The reactions were heated at $10\text{ }^\circ\text{C}/\text{min}$ to $650\text{ }^\circ\text{C}$ for 24, 72, 128, and 336 hours under flowing oxygen. Each color bar is represented in the legend as a different calculated phase.

D.4 Comparing neighboring ternary oxide structures in chemical potential space

Comparing the accessibility and similarity of ternary oxide structures offers insight into why the assisted metathesis reaction proceeds differently across the different alkali species. The structures of the possible stoichiometric $A\text{-Mn-O}$ ternary oxide intermediates are illustrated in Figure D.7. The sodium-based phases (Figure D.7a) show a strong preference for the layered Birnessite, $\delta\text{-MnO}_2$, framework. As illustrated by the gray shaded areas in Figure 5.3b, the compositions of neighbors to NaMnO_2 (mp-18957) that move towards higher μ_{O} include NaMn_2O_4 (mp-1002571), NaMn_4O_8 (mp-1016155) and $\text{Na}_2\text{Mn}_3\text{O}_7$ (mp-19080). Note that the $\text{Na}_2\text{Mn}_3\text{O}_7$ phase has a layered crystal structure akin to NaMnO_2 , but with regularly ordered Mn vacancies; this phase is experimentally observed in trace quantities in 24 h reactions at $650\text{ }^\circ\text{C}$ [92]. For values of $x \leq 0.25$ in Na_xMnO_2 (e.g., NaMn_4O_8), the Hollandite $\alpha\text{-MnO}_2$ framework was previously shown to be thermodynamically favorable [210]; however, the layered NaMn_4O_8 (mp-1016155) phase is predicted to be stable at $T = 650\text{ }^\circ\text{C}$.

In contrast, in the Li-Mn-O system (Figure D.7b), as one looks at phases towards higher μ_{O} starting from the layered LiMnO_2 (mp-754656), all neighboring phases would require a structural rearrangement (and thus kinetic barrier) as they become deficient in lithium. Nearly all of the subsequent phases prefer a spinel-like connectivity, which consists of three-dimensionally interconnected layers of edge-connected manganese-oxygen octahe-

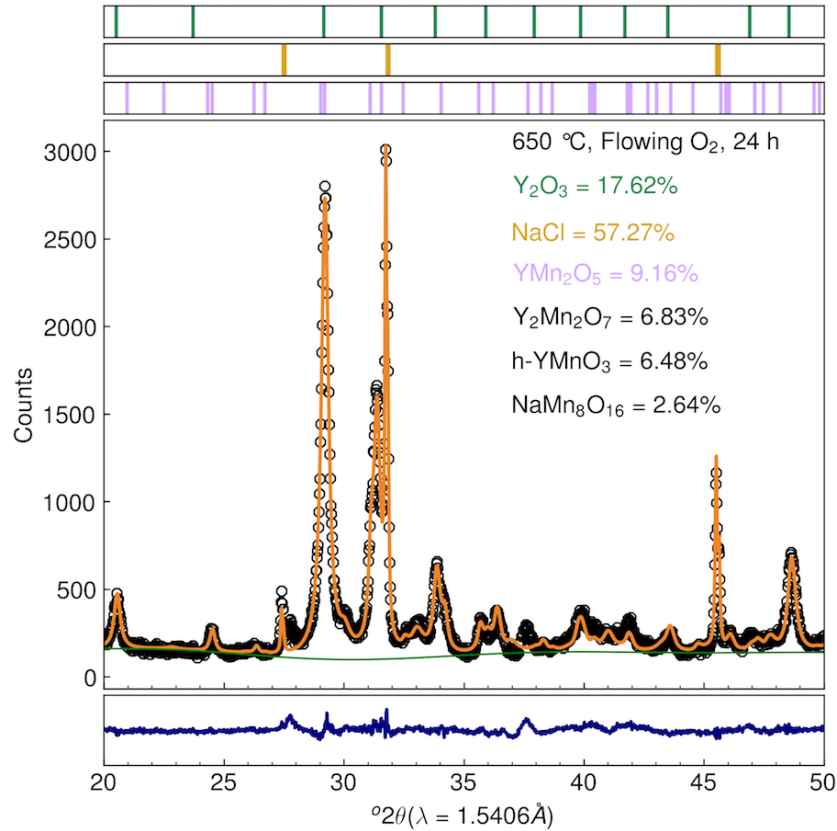


Figure D.5: PXRD results from the reaction: $C2/m \text{ NaMnO}_2 + \text{YOCl} \xrightarrow{\text{O}_2}$. The reaction was performed by heating at 10 °C/min to 650 °C and dwelling for 24 h. Raw data: black circles, Rietveld refinement: orange, background: green, difference: navy. Tick marks denote the majority phases and are highlighted by color and mole percent as calculated from Rietveld refinements. All other product mole percents are highlighted in black without tick marks.

dra, including LiMn_2O_4 (mp-1097867, pictured), $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (mp-691115), and $\text{Li}_{11}\text{Mn}_{13}\text{O}_{32}$ (mp-531021). A closer look at LiMn_2O_4 reveals that a polymorph with a layered structure is predicted (mp-1176656); however, it is 0.046 eV/atom above the hull (at $T = 650$ °C).

Finally, in the K-Mn-O system (Figure D.7c), the predicted ground state KMnO_2 (mp-554900) phase is not of a layered MnO_2 framework; although, the layered phase (mp-1002570) is about 0.044 eV/atom above the hull at $T = 650$ °C. In the K-deficient regime, the layered phase dominates, but KMn_2O_4 (mp-1003314) is predicted to be metastable (0.007 eV/atom above hull). The layered structures KMn_3O_6 (mp-1016190) and KMn_4O_8 (mp-1003312) are both predicted to be stable, however. As in the Li-Mn-O system, accessing these K-deficient phases from the ground-state stoichiometric KMnO_2 phase would require structural rearrangement, posing a significant kinetic barrier. Experimentally, K_2CO_3 -based assisted metathesis reactions do yield some $\text{Y}_2\text{Mn}_2\text{O}_7$ product at 650 °C; however, the reaction is not selective for $\text{Y}_2\text{Mn}_2\text{O}_7$ [92], which is consistent with this analysis.

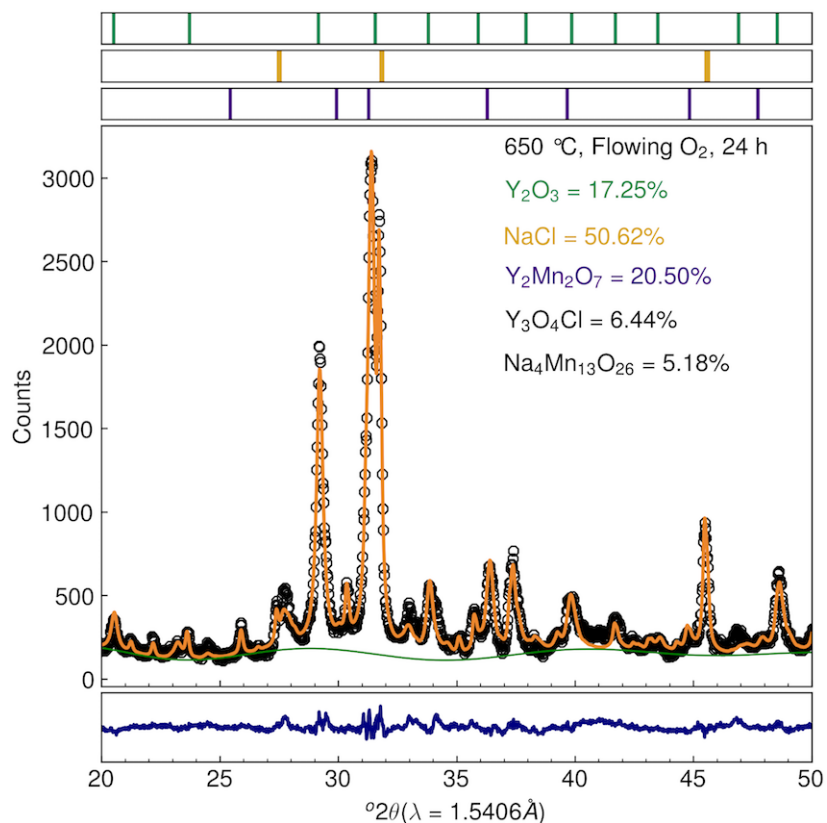
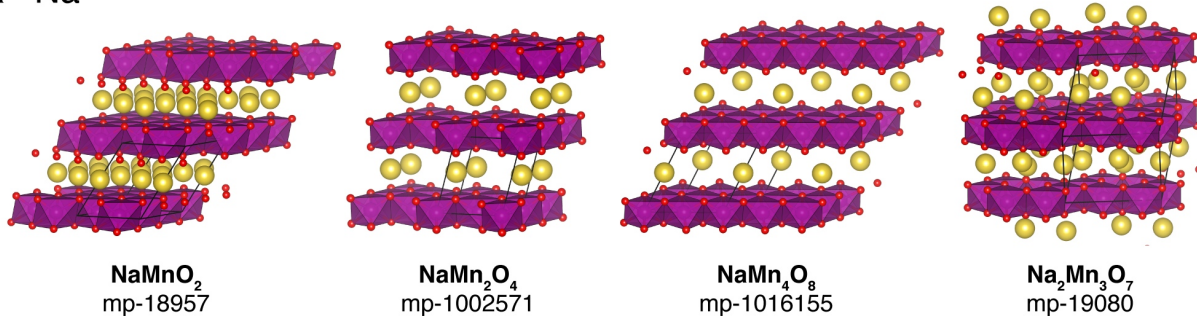


Figure D.6: PXRD results from the reaction: $Cmcm \text{ Na}_{0.7}\text{MnO}_2 + \text{YOCl} \xrightarrow{\text{O}_2}$. The reaction was performed by heating at 10 °C/min to 650 °C and dwelling for 24 h. Raw data: black circles, Rietveld refinement: orange, background: green, difference: navy. Tick marks denote the majority phases and are highlighted by color and mole percent as calculated from Rietveld refinements. All other product mole percents are highlighted in black without tick marks.

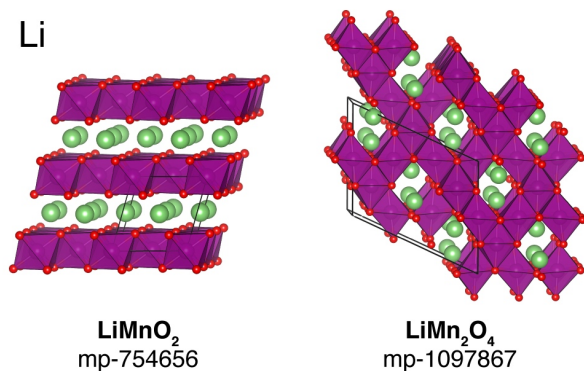
D.5 Pareto frontier of predicted reactions forming $\text{Y}_2\text{Mn}_2\text{O}_7$

As was demonstrated in a recent work on predicting solid-state synthesis routes [215], a candidate set of several recommended reactions can be generated by calculating the Pareto frontier along the reaction distribution shown in Figure 5.4. This is shown in Figure D.8, and the corresponding reactions are shown in Table D.1. In particular, the reaction $\text{O}_2 + 4 \text{ Y}_3\text{BrO}_4 + 4 \text{ KMn}_3\text{O}_6 \longrightarrow 4 \text{ KBr} + 6 \text{ Y}_2\text{Mn}_2\text{O}_7$ stands out as a promising alternative reaction with a zero total chemical potential distance and moderately negative reaction energy. However, it requires KMn_3O_6 as a precursor, which to our knowledge, has not been previously experimentally synthesized.

a Na



b Li



c K

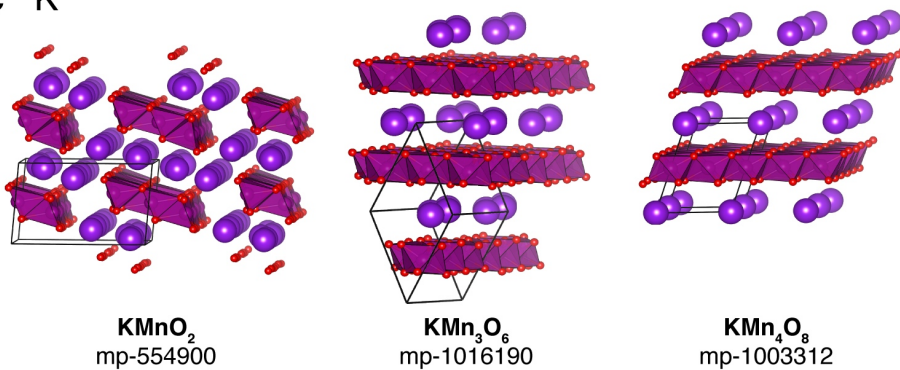


Figure D.7: Structures of possible stoichiometric *A*-Mn-O ternary oxide intermediates predicted to be stable at $T = 650$ °C for *A* equal to **a**, Na, **b**, Li, **c**, K. Unit cells are drawn and each structure's Materials Project ID (mp-id) is provided.

Reaction	$\Delta\Phi_{\text{rxn}}$ (eV/at.)	$\sum \Delta\mu_{\text{min}}$ (eV/at.)
$4 \text{ YCl}_3 + 4 \text{ Na}_3\text{MnO}_4 \longrightarrow \text{O}_2 + 12 \text{ NaCl} + 2 \text{ Y}_2\text{Mn}_2\text{O}_7$	-0.444	0.219
$\text{O}_2 + 4 \text{ YOCl} + 4 \text{ NaMnO}_2 \longrightarrow 4 \text{ NaCl} + 2 \text{ Y}_2\text{Mn}_2\text{O}_7$	-0.303	0.055
$\text{O}_2 + \text{YMnO}_3 + 0.5 \text{ RbI} \longrightarrow 0.5 \text{ Y}_2\text{Mn}_2\text{O}_7 + 0.5 \text{ RbIO}_3$	-0.258	0.035
$\text{O}_2 + 4 \text{ Y}_3\text{BrO}_4 + 4 \text{ KMn}_3\text{O}_6 \longrightarrow 4 \text{ KBr} + 6 \text{ Y}_2\text{Mn}_2\text{O}_7$	-0.159	0.000
$3.667 \text{ K}_2\text{MnO}_4 + 0.5 \text{ Y}_2\text{O}_3 \longrightarrow \text{O}_2 + 0.667 \text{ K}_{11}\text{Mn}_4\text{O}_{16} + 0.5 \text{ Y}_2\text{Mn}_2\text{O}_7$	0.016	0.000
$0.2667 \text{ Y}(\text{IO}_3)_3 + 0.2667 \text{ MnO}_2 \longrightarrow \text{O}_2 + 0.1333 \text{ Y}_2\text{Mn}_2\text{O}_7 + 0.8 \text{ I}$	0.439	0.409

Table D.1: Predicted reactions which lie on the Pareto frontier in $\Delta\Phi_{\text{rxn}}$ and $\sum \Delta\mu_{\text{min}}$

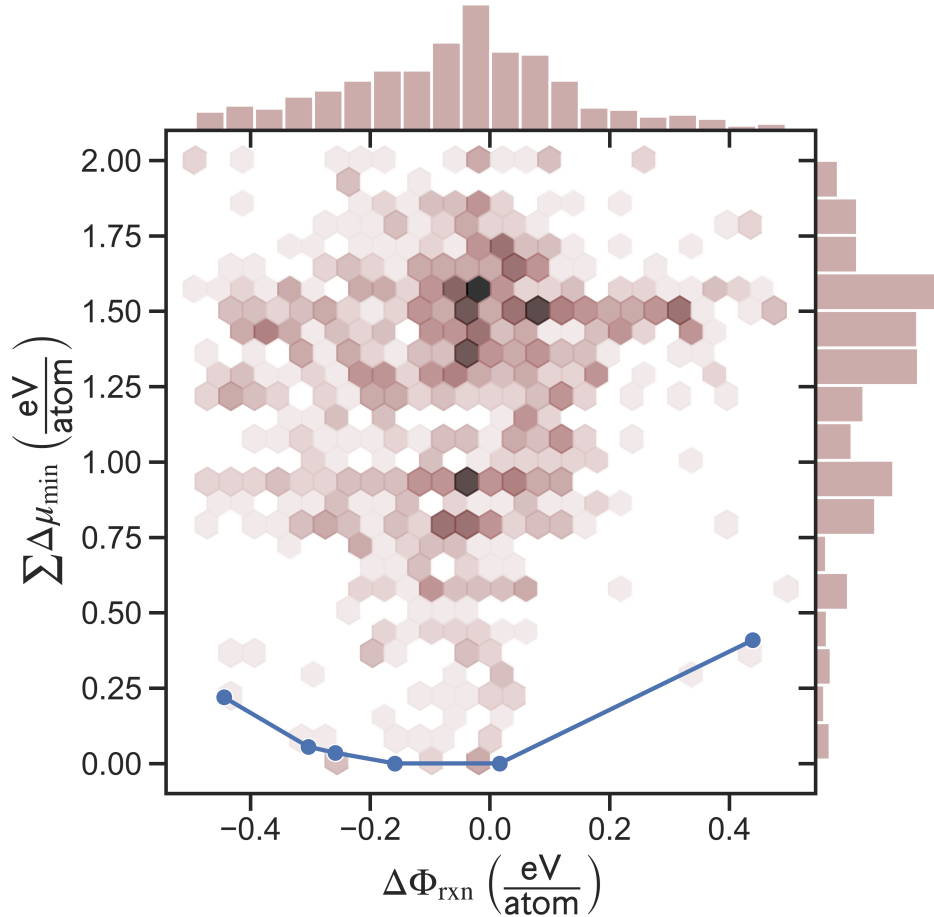


Figure D.8: Energy and total chemical potential distance distribution for 3,017 predicted chemical reactions forming $\text{Y}_2\text{Mn}_2\text{O}_7$. The Pareto frontier is given by the blue line. Reactions along this frontier, shown as blue dots, are reproduced in Table D.1.

Appendix E

Supplementary Information for Chapter 6

E.1 Thermodynamic data

Gibbs free energies of formation, $\Delta G_f(T)$, were acquired or approximated in an approach similar to previous works [83, 95]. To summarize again here, we acquired experimental $\Delta G_f(T)$ values from the NIST-JANAF thermochemical tables [65] where available. Experimental values were limited primarily to compounds with low melting points ($T_m < 1500$ °C). For solid compounds with melting points above this threshold, as well as for all other phases not available in the NIST-JANAF thermochemical tables, we estimated $\Delta G_f(T)$ using the machine-learned Gibbs free energy descriptor identified by Bartel et al. [69]. This descriptor was applied using formation enthalpies $\Delta H_f(T = 298\text{K})$ acquired from the Materials Project (MP) database [12], version 2022.10.28.

Because of systematic errors associated with using GGA exchange-correlation functions for estimating formation energies of carbonate compounds [24, 215], we fit and applied an energy correction of 0.828 eV per CO_3^{2-} anion. This was determined by calculating the mean error between computed and experimental $\Delta G_f(T=300\text{ K})$ values for 15 metal carbonate compounds (Figure E.1).

E.2 Precursor synthesis

Precursors for all experiments were either purchased from chemical providers or produced via a solid-state synthesis approach, as necessary. The synthesis procedures for all custom-made precursors were based on documented methods in the literature.

Barium sulfide was synthesized with stoichiometric amounts of activated carbon (J.T Baker 99.9%) and barium sulfate (J.T Baker 99.9%). The chemicals were mixed and ground in a mortar and pestle. The mixture was then placed in an alumina boat to heat in air at 1100°C for 7 min with heating and cooling rates of 10°C/min. BaTi_2O_5 was synthesized with

stoichiometric amounts of BaCO_3 (J.T Baker 99.9%) and TiO_2 (Acros Organics 99.9%). The chemicals were mixed and ground in a mortar and pestle. The mixture was then heated in an alumina boat at 900°C for 5 h. The powder was then reground and reheated at 1225°C for 24 h at a heating and cooling rate of $3^\circ\text{C}/\text{h}$ each. Ba_2TiO_4 was synthesized with stoichiometric amounts of BaCO_3 (J.T Baker 99.9%) and TiO_2 (Acros Organics 99.9%). The chemicals were mixed and ground in a mortar and pestle. The mixture was then heated in an alumina boat at 950°C for 16 h under Ar flow. The powder was then reground and reheated at 1100°C for another 16 h at a heating rate of $10^\circ\text{C}/\text{min}$. Na_2TiO_3 was synthesized with stoichiometric amounts of NaOH (Fisher Scientific 99.9%) and TiO_2 (Acros Organics 99.9%). The chemicals were mixed and ground in a mortar and pestle. The mixture was then heated in an alumina boat at 500°C for 90 min.

E.3 *Ex post facto* SXRD reactions

Synchrotron X-ray diffraction (SXRD) experiments were performed at beamline 28ID-2 (XPD) at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. Data was collected using the gradient furnace setup described by O’Nolan et al. [37] and pictured in Figure 2.2. Samples were packed into 1mm OD glass capillaries and loaded into the gradient furnace, which heated the sample to different temperatures across different positions on the capillary. We performed experiments in two temperature ranges: one spanning 282°C to 779°C , and a hotter setting spanning 403°C to 1064°C . The temperature calibration curves were determined using measured *in situ* lattice expansion from NaCl and Al_2O_3 standards and are shown in Figure E.2. Most experiments were reacted for ~ 60 min and cooled down to 30°C over a time of ~ 15 min.

The variable heating of the gradient furnace facilitated the capture of x-ray diffraction patterns of 30-35 temperature points along the length of the capillary. Patterns from these temperatures were collected *in situ* and *ex post facto* (after the experiment, at ambient temperature). For this work, we chose only to study the *ex post facto* data, as it allows for recovery of the approximate reaction pathway of each experiment without the explicit modeling of thermal expansion effects.

E.4 Literature reactions

Solid-state literature reactions studied in this work were acquired from the text-mined dataset of inorganic materials synthesis recipes originally extracted from the literature by Kononova et al. [219]. We used the set of 31,782 synthesis reactions available at https://github.com/CederGroupHub/text-mined-synthesis_public (version 2020-07-13). The original dataset was filtered down to 8,530 total reactions satisfying the following criteria: 1) two or fewer solid precursors with at most one open gaseous element (i.e., O_2 , H_2 , and N_2), 2) no elements for which the Gibbs free energy descriptor does not apply (e.g., Ne,

Ar, Pm, Ra) or with an atomic number greater than 94, 3) fewer than 11 elements total (due to limitations in the convex hull algorithm), 4) no ions, and 5) stoichiometrically balanceable after adjusting compositions for hydrates and fractional formulas. For reactions containing variable compositions with one open variable (e.g., $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$), we attempted to substitute all extracted values of x and kept all successfully balanced reactions.

For each of these filtered reactions, we performed the reaction calculation workflow described in the main text. Metastable phases were considered up to a maximum threshold of $\Delta G_{\text{hull}} = 0.050$ eV/atom, evaluated at $T = 300$ K. Reaction energies and phase competition values were computed at the maximum temperature, T_{syn} reported during synthesis (i.e., taken from any of the heating steps). If a maximum heating temperature was not provided, a synthesis temperature of 800°C was assumed. Formation energies, $\Delta G_{\text{f}}(T_{\text{syn}})$, were assigned based on the ground-state energy for a given composition; i.e., we selected the lowest available formation energy of all possible polymorphs with the composition of interest. For compositions that did not appear in our thermodynamic data (e.g., missing phases like CsInF_4 , or substituted variable compositions such as $\text{Pb}_{0.4}\text{Si}_{0.6}\text{O}_{1.6}$), we assumed these phases to be on the hull and interpolated their energy from neighboring phases on the compositional phase diagram. For reactions with an open gas (i.e., O_2 , H_2 , N_2), we assigned a chemical potential of $\mu_{\text{gas}} = 0$ eV (i.e., standard state at T_{syn}) for that element. For reactions completed in air, we assigned a chemical potential of $\mu_{\text{O}} = \frac{1}{2}k_{\text{b}}T_{\text{syn}} \ln(0.21)$ eV.

Duplicate reactions with the same reaction equation (and completed at the same temperature and chemical potential) were removed, as well as identity reactions (e.g., $A \rightarrow A$). Reactions with two or more interpolated entries were also removed. Finally, we removed reactions with $\Delta G_{\text{rxn}} \in [-0.001, 0.001]$ eV/atom if they contained at least one interpolated entry, as these reactions provided no information due to the interpolation (i.e., the near-zero reaction energy was artificially imposed). Altogether, this process resulted in a total of 2,110 “closed” reactions and 3,420 “open” (i.e., open element) reactions. We used a constant temperature parameter of $T = 300$ K in the formula for primary competition (Equation 6.1) so that literature reactions could be compared on the same scale.

E.5 Supplementary figures and tables

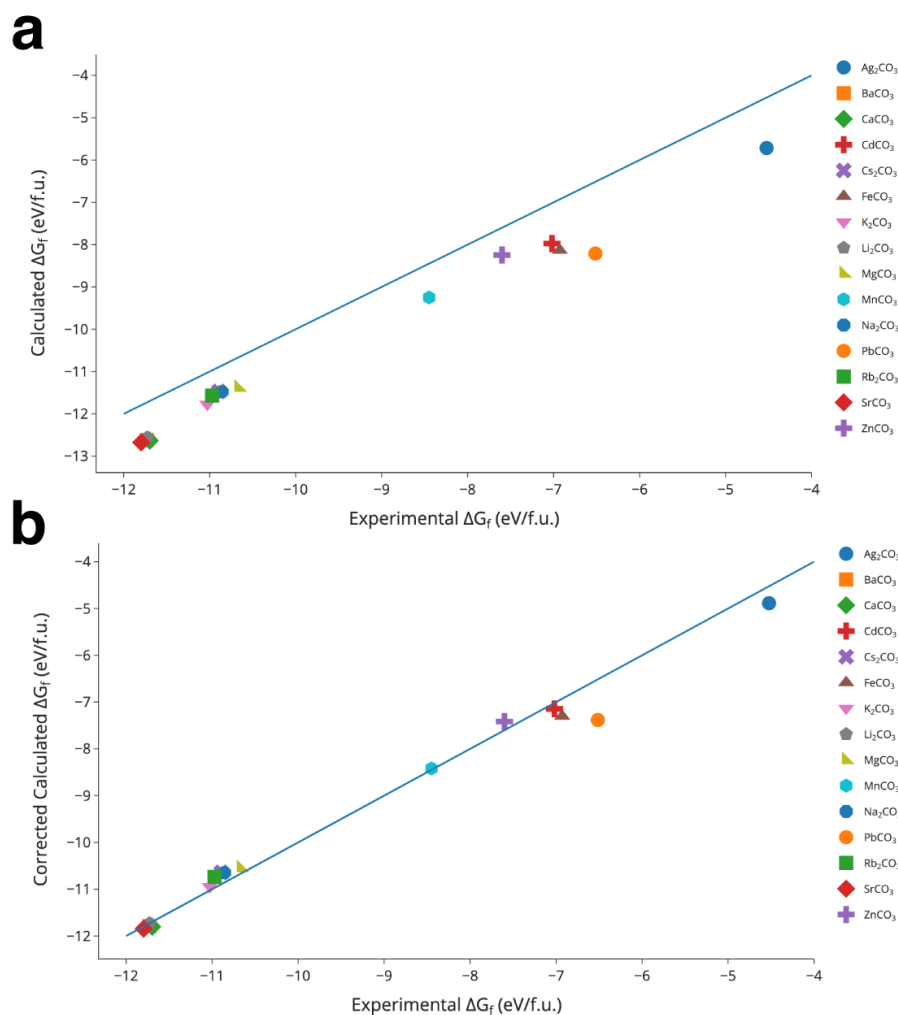


Figure E.1: Fitting procedure for formation energy correction of carbonate compounds. (a) Carbonates exhibit a systematic negative shift in predicted Gibbs free energy of formation, ΔG_f ($T = 300$ K) compared to the experimental values. (b) Energies of the same carbonate compounds after applying a fit energy correction of $0.830 \text{ eV}/\text{CO}_3^{2-}$.

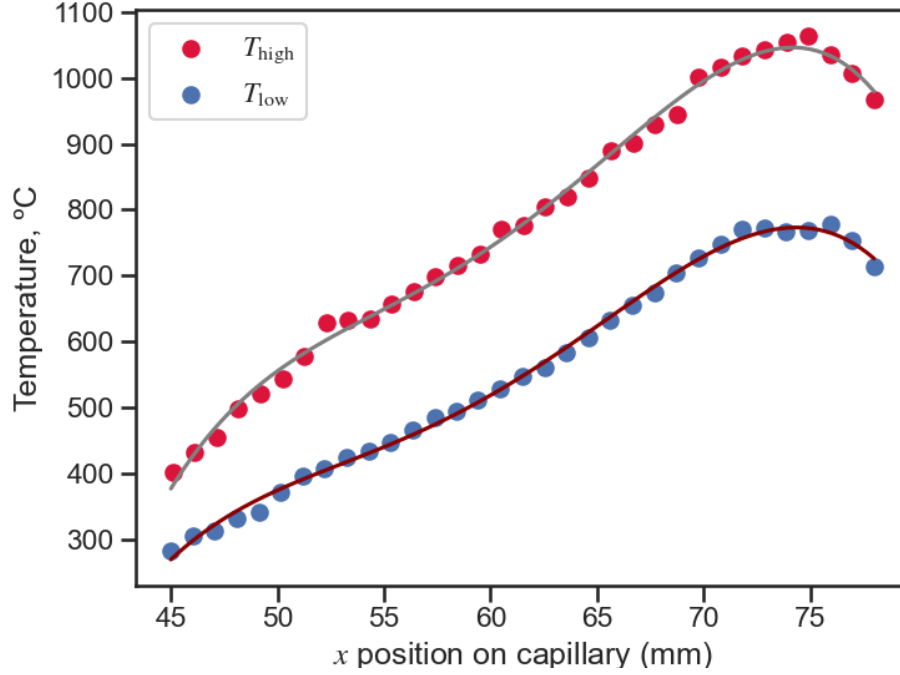


Figure E.2: Measured temperature distributions along sample capillary. Temperatures were determined by refinement of lattice parameters from NaCl (T_{low}) or Al_2O_3 (T_{high}) standards. Most experiments were performed with the high-temperature (red) setup to maximize reaction completion.

Table E.1: Selected experimental reactions forming BaTiO_3 and their associated grand potential energies ($\mu_{\text{O}} = -0.2921$ eV), $\Delta\Phi_{\text{rxn}}$ ($T = 650$ °C), primary competition scores, C_1 , and secondary competition scores, C_2 .

Expt.	Reaction	$\Delta\Phi_{\text{rxn}}$	C_1	C_2
1	$\text{BaCO}_3 + \text{TiO}_2 \longrightarrow \text{BaTiO}_3 + \text{CO}_2$	0.107	3.785	0.043
2	$\text{BaO}_2 + \text{TiO}_2 \longrightarrow \text{BaTiO}_3 + 0.5 \text{ O}_2$	-0.661	2.779	0.124
3	$\text{Ba}_2\text{TiO}_4 + \text{TiO}_2 \longrightarrow 2 \text{ BaTiO}_3$	-0.085	3.208	0.043
4	$\text{Ba}_2\text{TiO}_4 + \text{BaTi}_2\text{O}_5 \longrightarrow 3 \text{ BaTiO}_3$	0.001	4.129	0.000
5	$\text{BaCO}_3 + 2 \text{ Ti} \longrightarrow \text{BaTiO}_3 + \text{TiC}$	-1.562	27.823	5.342
6	$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O} + 3.666 \text{ Ti} \longrightarrow \text{BaTiO}_3 + 1.333 \text{ Ti}_2\text{H}_3$	-0.709	32.423	5.559
7	$\text{BaCl}_2 + \text{Na}_2\text{TiO}_3 \longrightarrow \text{BaTiO}_3 + 2 \text{ NaCl}$	-0.105	2.879	0.044
8	$\text{BaS} + \text{Na}_2\text{TiO}_3 \longrightarrow \text{BaTiO}_3 + \text{Na}_2\text{S}$	-0.052	17.706	2.199
9	$2 \text{ BaS} + 3 \text{ TiO}_2 \longrightarrow 2 \text{ BaTiO}_3 + \text{TiS}_2$	0.169	19.265	2.252
10	$\text{BaSO}_4 + \text{TiO}_2 \longrightarrow \text{BaTiO}_3 + \text{SO}_3$	0.990	7.065	0.330
11	$\text{BaSO}_4 + 2 \text{ TiO}_2 \longrightarrow \text{BaTiO}_3 + \text{TiSO}_5$	0.535	5.159	0.178

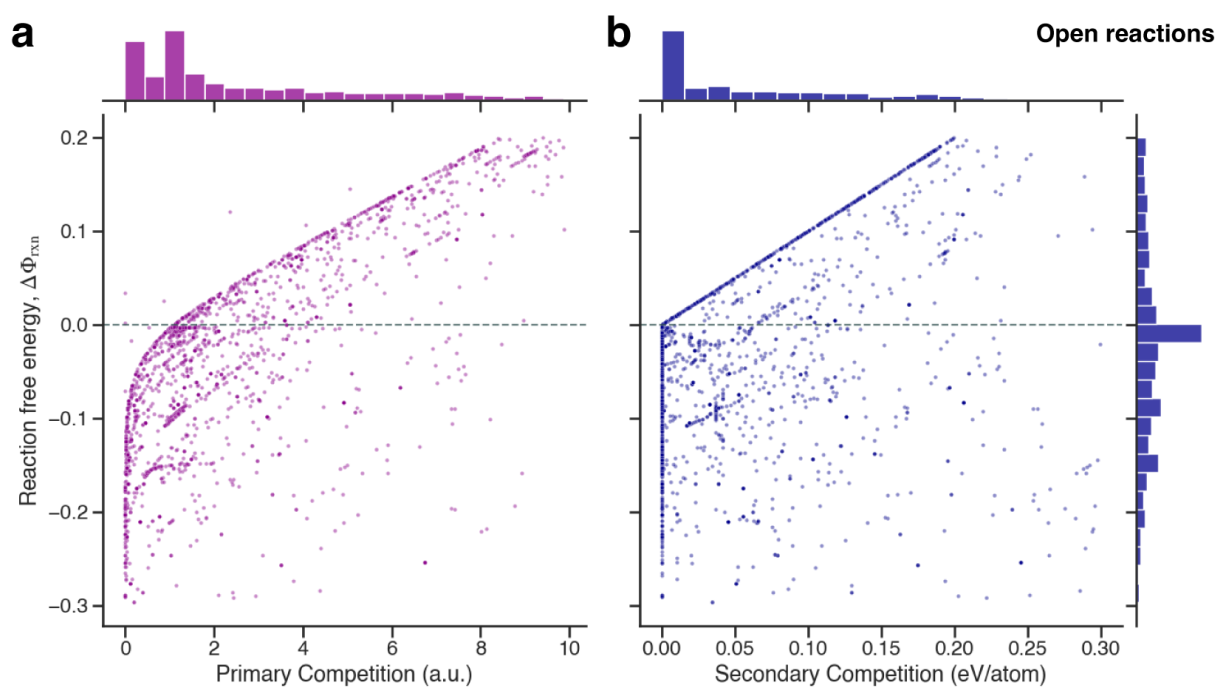


Figure E.3: Synthesis map of 3,420 open solid-state synthesis reactions reported in the literature. Reactions are plotted on a shared axis of reaction energy, $\Delta\Phi_{\text{rxn}}$, and on independent axes of (a) primary competition, C_1 , and (b) secondary competition, C_2 . Histograms showing the distribution of these values are shown on the margins.

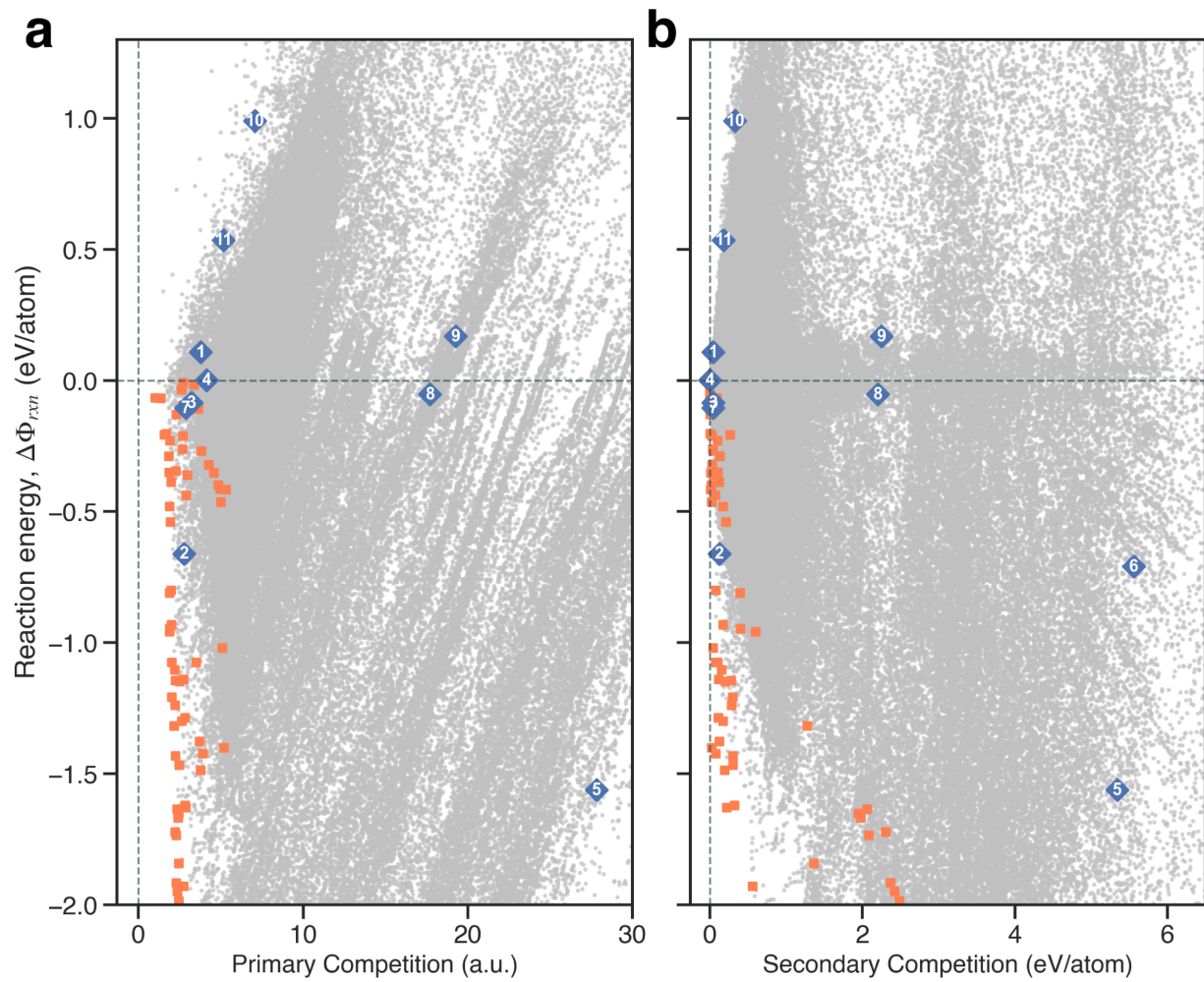


Figure E.4: Synthesis map of 191,729 calculated open-O₂ synthesis reactions producing BaTiO₃. Reaction energies and competition scores are calculated assuming a temperature of $T = 650$ °C and oxygen chemical potential $\mu_{\text{O}} = -0.2921$ eV. As in Figure 6.6, reactions are plotted on a shared axis of energy, $\Delta\Phi_{\text{rxn}}$, and on independent axes of (a) primary competition, C_1 , and (b) secondary competition, C_2 . Orange squares represent reactions on the three-dimensional Pareto frontier of $\Delta\Phi_{\text{rxn}}$, C_1 , and C_2 . Blue diamonds indicate selected reactions experimentally tested in this work.

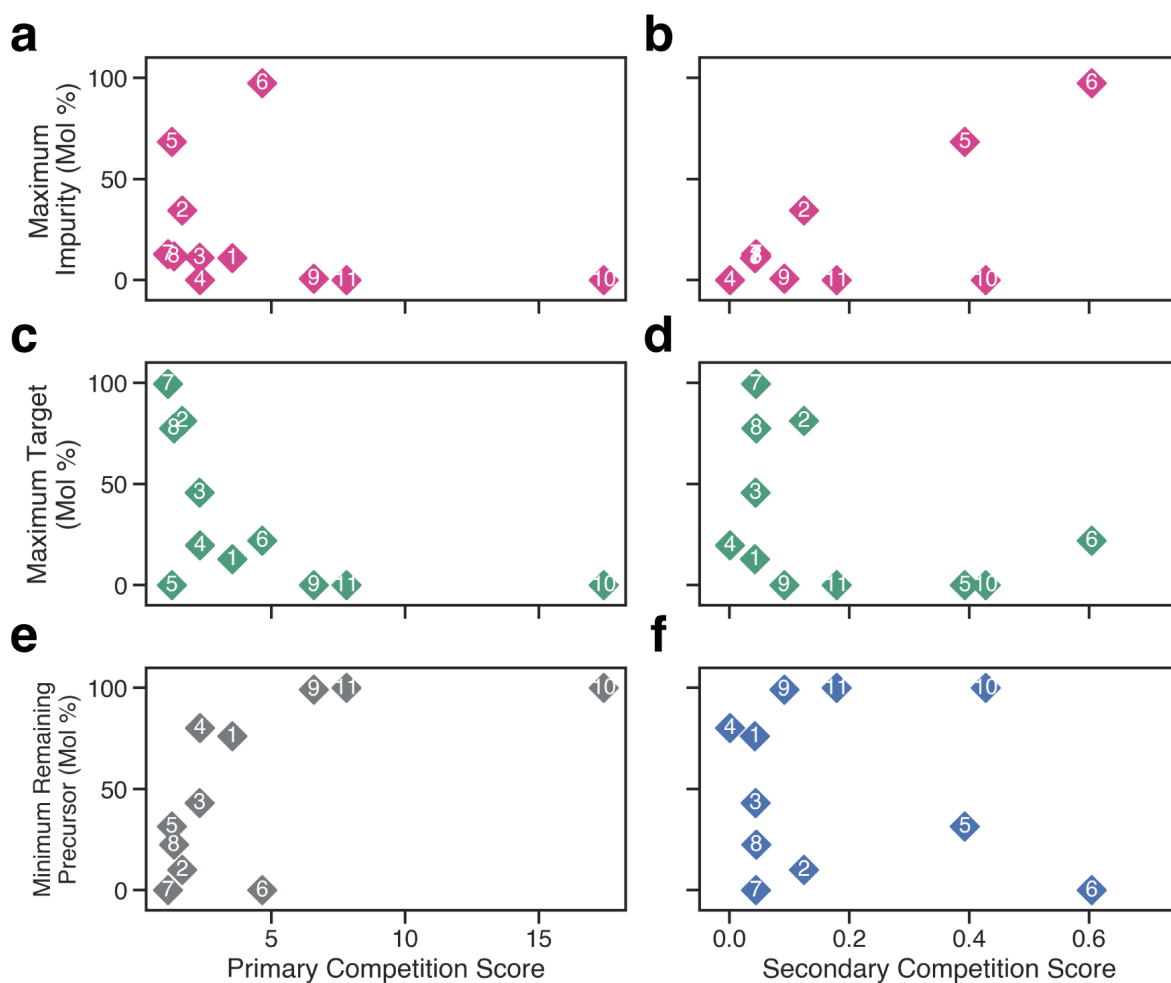


Figure E.5: Full performance of primary and secondary competition scores. (a,c,e) Plots of primary maximum impurity, maximum target, and minimum remaining precursor (molar percent) as a function of primary competition score, respectively. (b,d,f) Similar plots for secondary competition score. Secondary competition score shows the greatest correlation with experimental results for maximum impurity observed, when the non-reacting experiments (Expts. 9-11) are excluded.