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Spontaneous transformations in the solid state: Towards porous and biphasic materials

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by

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by

Eric S. Toberer
for my parents
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Abstract

Spontaneous transformations in the solid state: Towards porous and biphasic materials

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This dissertation describes new routes to macroporous and hierarchically porous monoliths of oxides and metals. The routes are applicable to a broad range of materials, leading to pore walls with functions in energy transduction, catalysis, and photovoltaic materials. While the porous structures formed are random, the average architectural features are well-defined, and the porosity is highly interconnected.

We begin by developing metathetic solid state reactions which yield intimately mixed composites of $\text{K}_2\text{SO}_4$ and functional perovskites (piezoelectric $\text{PbTiO}_3$, catalytic $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) as bulk monoliths. Dissolution of the soluble salt in water leaves behind macroporous monoliths of the desired perovskite phase. We then extend selective leaching to biphasic systems based on $\text{ZnO}$ and a second, immiscible, phase ($\text{NiO}$, $\text{ZnFe}_2\text{O}_4$, $\text{ZnMn}_2\text{O}_4$). Leaching
of the ZnO phase leads to robust oxide monoliths with highly interconnected pores. The porous structures that result are topologically identical to the sacrificial phase, and hence, microstructural control directly leads to control of the resulting pore structure. We also look at how functionality may be layered sequentially by exposing porous monoliths to reactive atmospheres or solutions.

We also develop routes where porosity arises from transformations with an intrinsic volume loss, such as the reduction of $\text{Mn}_3\text{O}_4$ to $\text{MnO}$. The volume loss inherent in this transformation is expressed as rectangular mesopores penetrating through the crystallites. Other systems are described which involve the removal of a sacrificial element from within a phase to induce a volume loss, such as the reduction and evaporation of $\text{Zn}$ from $\text{Zn}_2\text{TiO}_4$ to form porous $\text{TiO}_2$. As these routes are shape-conserving, they may be applied to macroporous materials to form hierarchical macro/mesoporous architectures.

In some of these preparations, the resulting mesopores are aligned locally with certain crystallographic directions. This coupling between morphology and crystallography provides a macroscopic handle on nanoscale structure. Epitaxial thin films of precursor oxide phases were grown on lattice matched single crystal substrates and subsequently rendered porous through reduction. We find that the epitaxy of the pore-forming material results in pores that are crystallographically aligned with the substrate.
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Chapter 1

Introduction

Porous materials are vital in a wide range of applications, including catalytic materials, filters, sensors, batteries, photovoltaics, fuel cells, and optical devices. Many of these applications benefit from the enhanced fluid-solid contact that porous architectures provide. From a preparative standpoint, new routes to form porous materials must control both pore wall *composition* and *morphology*. Pore wall composition dictates the stability, reactivity, and intrinsic material properties such as piezoelectricity, magnetism, or conductivity. Morphology will influence the material’s surface area, strength, and the rate of fluid exchange through the pores. The following will introduce the field of porous materials, both routes to form porous materials and a discussion of applications utilizing porous materials.
1.1 Routes to Porosity

Porous materials are broadly categorized by their size range. IUPAC has chosen the following definitions for porous materials: *microporous* materials with pores sizes less than 2 nm, *mesoporous* materials with pores sizes between 2 and 50 nm, and *macroporous* materials with pore sizes greater than 50 nm. These ranges match the pore diameter ranges characteristic for particular types of porous materials. Zeolitic and open-framework structures typically are microporous, while surfactant-templated materials such as the MCM[1] or SBA[2] materials are mesoporous. In the macroporous regime, there are a variety of ceramic routes such as foaming or templating which give macroporous materials. In Figure 1.1, a partial list of routes to porous materials is shown, along with characteristic size regimes. As the work in the following chapters focuses on porosity in the 30-1,000 nm regime, the following introduction will focus on routes to mesoporous and macroporous materials.

**Mesoporosity** Mesoporous materials can be formed from a bottom-up approach involving the assembly of structure-directing agent or through the removal of an element or phase from a dense material. In the first case, amphiphilic structure-directing agents assemble in solution and spatially control the condensation of metal alkoxides. Unlike in the microporous materials, the
pore walls are initially amorphous, and upon heating form polycrystalline assemblies. Typically, surfactants (MCM materials\cite{1}) or triblock copolymers (SBA materials\cite{2}) are used as structure-directing agents.

A variety of porous metals have been formed via dissolution of a sacrificial element from a binary alloy, most notably the formation of Raney nickel through the dissolution of aluminum from a NiAl alloy.\cite{3, 4, 5, 6, 7, 8} The fine pore size is due to the low temperatures of the partitioning and dissolution, which prevent coarsening of the material. In a similar manner, the spinodal decomposition of a glass followed by selective leaching of one phase is used to obtain porous Vycor™ glass.\cite{9} The controlled dissolution of aluminum in an electric field has been used to form porous alumina with ordered porosity.\cite{10} Nanoparticle compacts may also be considered as mesoporous materials, with
pore diameters on the order of the nanoparticles which form the material.[11]

**Macroporosity**  Macroporous materials may be formed through a variety of spontaneous or templated methods. Many of the traditional ceramic routes to form macroporous materials may be considered template-free, as they rely on the inclusion of volatile pore forming agents which create voids in the material upon firing.[12] Frequently, porous monoliths are formed simply via incomplete densification of a powdered compact. Directional solidification of a liquid-powder mixture followed by freeze-drying and sintering has been used to form materials with oriented pores.[13] Soft chemistry routes involving condensation and evaporation have been used to form a variety of porous structures. One such example is the formation macroporous networks of titania through the controlled evaporation of a titanium sol.[14] Notably, Suzuki has developed a variety of spontaneous routes to form macroporous materials. His group has used gaseous decomposition to induced pores in natural dolomite/zirconia mixtures, leading to porous CaZrO$_3$, a structural ceramic.[15, 16] They have also formed porous zirconia by selective leaching of magnesia from a biphasic mixture formed via a eutectic transformation.[17] Selective leaching has similarly been used to form porous zirconia from the leaching of nickel from nickel/zirconia composites.[18] Porous materials have been formed via deposition from gas or liquid phases (electrodeposition), lead-
Figure 1.2. Monodisperse polystyrene spheres infiltrated into a Millipore™ track-etch membrane for use as a template during crystal growth. Image taken during a collaboration with Fiona Meldrum at the University of Bristol, UK.

Routes which rely on templating agents have recently seen great improvements, particularly in the formation of ordered macroporous materials and in the use of biomaterials as templating structures. Three dimensionally ordered materials (3DOM) with an inverse-fcc structure are quite interesting as they exhibit an optical band gap.\cite{20, 21} Such structures are fabricated by backfilling ordered assemblies of polymer spheres or emulsions.\cite{22} Upon calcination, the infiltrated phase crystallizes and the template burns out. The chemical complexity of the resulting porous bodies has been dramatically extended, with ordered porous structures ranging from battery materials such as LiNiO₂ to
the piezoelectric material PbTiO$_3$.\cite{23, 24} Shown in Figure 1.2 are two different templates used concurrently: a collection of polystyrene spheres infiltrated into a Millipore\textsuperscript{TM} track-etch membrane.

Biotemplating also holds much potential for forming new porous structures with unique morphologies. Diatoms have been converted to other materials in a shape-conserving manner via gas-phase reactions.\cite{25} For example, passing a gas of Mg over diatoms at elevated temperatures converts the initial SiO$_2$ to MgO. Wood and other organic skeletons have natural vessel networks with regularly sized pores and open connectivity. In a similar manner, routes to convert wood to other materials has been quite successful. One example is the reaction of SiO gas with carbonized wood to form monoliths of porous SiC.\cite{26} Sea urchin tests, which are made of single crystals of calcite with ordered pores perforating the crystals, have also been used to template ordered porous structures.\cite{27, 28}

**Hierarchical porosity** Systems involving flow through a porous material represent a fundamental compromise: surface area and diffusivity are inversely related. A material with small pores will have a larger surface area than the analogous material with large pores, but the diffusivity will be hindered and the pressure drop across the material will be much larger.
One remedy is to form hierarchically porous materials which combine the high surface areas of microporous or mesoporous materials with the high diffusivities associated with macroporous materials. Theoretical studies on flow through a bimodal network suggests large gains in fluid-surface contact may be realized through such architectures.[29]

Most of the recent efforts to form hierarchically structured materials have involved soft-chemistry methods involving solutions containing structure directing agents and templates. Much of this work is inspired by work by Yang et al. where thin films were formed with architectural control on three different length scales: pattern stamping to form 1 μm features, latex spheres to give pores 100 nm in diameter, and triblock copolymers to induce 10 nm pores in the macropore walls.[30] Other hierarchically porous structures have been formed through the assembly of mesoporous particles into macroporous structures.[31] Surfactant-templated mesopores have similarly been formed in the walls of macroporous materials formed through sol-gel phase separation[32] or foaming.[33] Macro/mesoporous structures of various compositions have also been formed through casting of other hierarchically porous structures, followed by removal of the template.[34]

Biological structures such as diatoms have served as templates for hierarchically porous structures. For example, diatoms have been converted to or
coated with zeolites through a variety of methods including layer-by-layer film growth, seeding, vapor phase transport, and direct conversion.\textsuperscript{[35, 36]} Similar macro/microporous structures have been formed via the growth of zeolites within opal frameworks.\textsuperscript{[37]}

### 1.2 Applications of porous materials

Pore diameter, connectivity, and wall composition are tailored for particular applications in porous materials. Applications of micro- and mesoporous materials frequently rely on high surface areas and customizable pore wall compositions. Zeolites are well known as catalysts, particularly in the cracking of crude oil to form gasoline. Microporous materials also are finding use in gas sorption and filtration. Similarly, the high surface areas of mesoporous materials leads to their use in catalysis. In contrast to microporous materials, functionality is frequently imparted to mesopore walls through the inclusion of organic or inorganic species such as precious metal catalysts. Mesoporous alumina coated with precious metal nanoparticles plays a primary role in the catalytic conversion of automotive exhaust. Also, mesoporous materials show potential in photovoltaic, battery, and optical applications. Due to their high void space, such materials are also finding use as low-$k$ dielectric materials.
Macroporous materials are used in a wide variety of applications, including catalytic, optical, battery, and structural materials. Macropores in heterogeneous catalysts permit high flow rates of gas through the material without excessive pressure build-up. In fuel cells, macroporous electrodes increase the surface area in contact with the gas stream to allow for the gas-solid oxidation and reduction reactions to occur. Photonic crystals rely on ordered arrays of pores to create a periodic oscillation in the dielectric constant, leading to an optical band gap. 2D photonic structures have been formed through lithographic techniques, while 3D structures have relied on the assembly of colloids or emulsions into periodic structures. Macroporous materials have a variety of structural applications, ranging from biomaterials such as artificial bone to heat exchangers and precursor structures for biphasic composites. Filtration, separation and sensing are all existing applications for porous structures.

**Overview**  Spontaneous routes to porous materials are inherently attractive in that they avoid a pre-formed template. In the work described in this dissertation, we have pursued routes which rely on the thermodynamically driven segregation of phases and elements to induce porosity. Partitioning is achieved by changing temperature or oxygen partial pressure to move from a single phase region to a two phase region in the appropriate phase diagram. When these separations are applied in a sequential manner, materials with unusual
Figure 1.3. Scheme showing how functionality may be layered on porous materials. Starting with a dense composite (a), the selective leaching of one phase leaves behind (b) a macroporous monolith of the other phase. Subsequently, the macroporous material may be (b) reduced to a macroporous metal, (c) decorated with functional groups, or (d) rendered hierarchically porous.
architectures may be formed. Figure 1.3 is a scheme showing how functionality may be layered onto these macroporous materials. Starting from a dense biphasic composite (a), one phase may be removed via dissolution to give (b) a macroporous monolith of the remaining phase. A variety of subsequent reactions may be applied to the resulting porous monolith, ranging from (c) reduction to a porous metal, (d) conformal coating with a second phase, or (e) perforation of the macropore walls with a finer level of porosity.
Chapter 2

Assisted Metathesis

The use of selective leaching of a sacrificial phase or element has a long history in the formation of porous metals and glasses. In contrast, selective leaching has rarely been used to form porous ceramics. We were interested in using the idea of assisted metathesis in the solid state to form dense mixtures of $\text{K}_2\text{SO}_4$ and perovskite oxide phases. By forming bulk pellets and controlling the morphology of the $\text{K}_2\text{SO}_4$ phase, porous perovskite structures with defined morphologies could be obtained through the dissolution of the soluble salt in water. Perovskite chemical compositions were chosen with intrinsic piezoelectric, magnetic, and catalytic properties.
2.1 Prior Work

Metathetic reactions have long been known in chemistry as a means to exchange species between two reactants. Such reactions are of the type:

\[ AX + BY \rightarrow AY + BX \]  \hspace{1cm} (2.1)

Solid state metathetic reactions have been known for over a century. One early example led to mixtures of mixed metal ferrites and LiCl.[38] In the last decade, the Kaner group has extended solid state metathesis to a variety of systems with great success.[39, 40] As the reactions are typically highly exothermic, the reactions are self-propagating and quite rapid. Using such methods, a variety of oxides, nitrides, phosphides, and sulfides have been formed ranging from GaN and ZrN to MoS\(_2\).[39, 41, 42]

The Gopalakrishnan group has pioneered metathetic reactions involving cation exchange in complex oxides. One group of reactions occurs with lithium containing rock salt metal oxides and either lanthanum oxychloride or alkaline earth metal chlorides reacting to form perovskites and LiCl as a second phase.[43] Two examples are shown:

\[ \text{LiMnO}_2 + \text{LaOCl} \rightarrow \text{LaMnO}_3 + \text{LiCl} \]  \hspace{1cm} (2.2)

\[ \text{LiMnO}_2 + \text{SrCl}_2 \rightarrow \text{SrMnO}_3 + 2\text{LiCl} \]  \hspace{1cm} (2.3)
Beyond perovskites, they have used metathetic reactions to alter the composition of complex layered structures, as in the synthesis of Dion-Jacobson phases (equation 2.4) and Aurivillius phases (equation 2.5) from Ruddlesden-Popper precursors:

\[ K_2La_2Ti_3O_{10} + SrCl_2 \rightarrow SrLa_2Ti_3O_{10} + 2KCl \]  
\[ NaLaTiO_4 + BiOCl \rightarrow (BiO)LaTiO_4 + NaCl \]

The Gopalakrishnan group has developed other metathetic reactions which are driven by the formation of a simple binary oxide (Equ. 2.6), instead of a salt. Similar reactions, termed redox metathesis reactions, have been developed which couple ion exchange with a change in oxidation state (Equ. 2.7).

\[ La_2CuO_4 + MoO_3 \rightarrow La_2MoO_6 + CuO \]  
\[ La_2CuO_4 + MoO_2 \rightarrow La_2MoO_6 + Cu \]

The Seshadri group has also previously looked at the formation of perovskite powders through metathetic reactions which are driven forward by the high enthalpy of formation of a sulfate species. For example, powders of PbZrO3 and Ca2SO4 were formed through reaction of alkaline earth perovskite zirconates with lead sulfate:

\[ CaZrO_3 + PbSO_4 \rightarrow CaSO_4 + PbZrO_3 \]
The Seshadri group has previously described a class of reactions which are termed “assisted metathesis”, in that the transfer of the anion from B to C drives the reaction forward.

$$A + BX + CY \rightarrow AB + CX + Y(g) \quad (2.9)$$

For example, powders of PbZrO$_3$ and Ca$_2$SO$_4$ were formed through assisted metathesis according to the reaction:[47]

$$\text{ZrO}_2 + \text{PbSO}_4 + \text{K}_2\text{CO}_3 \rightarrow \text{PbZrO}_3 + \text{K}_2\text{SO}_4 + \text{CO}_2(g) \quad (2.10)$$

This reaction leads to the formation of small (200-400 nm) particles of PbZrO$_3$ with larger particles of K$_2$SO$_4$ interspersed in this matrix.

In a similar manner, powders of polyglycolide and soluble salts have been formed via metathesis.[48] An elimination reaction during polymerization of alkali halogenoacetates leads to an fine dispersion of soluble salts in the polymer matrix. The reaction proceeded according to equation 2.11, with M=monovalent metal and X=halogen.

$$M^{+−}\text{OOC−CH}_2\text{X} \rightarrow MX + \frac{1}{n}[−\text{OOC−CH}_2−]_n \quad (2.11)$$

Pelletization of the resulting powder mixture followed by the selective leaching of the soluble salt leaves a porous pellet of polyglycolide. The pores
so formed were between 0.3 and 1.5 \( \mu \)m in diameter and were replicas of the sharp polyhedral shapes of the salt crystallites.

In this chapter, ceramic analogs to these porous polymers are formed via assisted metathesis followed by selective leaching. Specifically, assisted metathesis routes which yield \( \text{K}_2\text{SO}_4/\text{perovskite powders}^{[47]} \) have been extended to the formation of biphasic monoliths which may be rendered porous through leaching of the \( \text{K}_2\text{SO}_4 \) phase. The most noteworthy result of this preparation has been the formation of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) with a continuous pore network and well-connected grains.\(^{[49]} \) As described in Section 2.3, the mixed electronic and ionic conduction of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) renders it an exceptionally promising material with catalytic properties similar to the precious metals.

Interest in macroporous perovskite materials is fueled by applications in piezoelectric materials\(^{[50]} \) and a variety of catalytic processes ranging from fuel cells to automotive catalytic converters.\(^{[51, 52]} \) In piezoelectric materials, it has been found that there is an enhancement of the piezoelectric response when porous or biphasic materials are used due to an increased deformability of the structure.\(^{[53]} \) In catalytic applications, macroporosity enables high gas flow rates across an active surface which has an enhanced surface area and is structurally and thermally stable.
2.2 PbTiO$_3$/K$_2$SO$_4$

When a strain is applied to a piezoelectric material, a macroscopic voltage is developed. Similarly, an applied voltage induces a mechanical response. The classic piezoelectric materials are BaTiO$_3$ and PbTiO$_3$, which are distorted perovskites with the Ti$^{4+}$ ion off-centered within the oxygen octahedra. Gains in performance have been realized through the introduction of secondary phases or porosity. In the first paper on porous piezoelectrics, a 200-fold increase in the hydrostatic figure of merit was demonstrated.$^{50, 53}$ Hydrophones are underwater sensors which generate a voltage due to isotropic compression. In this early work, porous PbZr$_{0.5}$Ti$_{0.5}$O$_3$ was formed using natural coral as a template which could be removed after infiltration and calcination. Since then, porous piezoelectrics have typically been formed through traditional ceramic processing techniques which rely on volatile species such as BURPS (burned-out plastic spheres), self-raising flour, or polymeric sponges.$^{54, 55}$ Three-dimensionally ordered pore structures have been formed using crystalline assemblies of polystyrene beads as a template. Infiltration of these templates with Pb and Ti precursor solutions followed by gelation and calcination lead to porous perovskite structures.$^{24}$ The following describes our efforts to develop new metathesis chemistry to form PbTiO$_3$ powders and to use the soluble salt byproduct as a sacrificial phase in the for-
mation of porous bulk PbTiO$_3$.

**Preparation**  The assisted metathesis route was envisioned to occur according to:

$$\text{TiO}_2 + \text{PbSO}_4 + \text{K}_2\text{CO}_3 \rightarrow \text{PbTiO}_3 + \text{K}_2\text{SO}_4 + \text{CO}_2$$  \(2.12\)

Accordingly, powders of fine anatase TiO$_2$ (0.005 mol), K$_2$CO$_3$·1.5H$_2$O (0.005 mol), and PbSO$_4$ (0.005 mol) were ground together, cold-pressed at $1.6 \times 10^3$ kg cm$^{-2}$, and heated to 973 K for 12 h to induce the metathesis reaction. The resulting powder was then reground, cold-pressed, and fired at 1048 K for 24 h to form a well-sintered white body. To remove the K$_2$SO$_4$ phase, the monolith was immersed in water for several days. The phase evolution during the firing and dissolution steps was monitored with powder X-ray diffraction (XRD) and thermodiffractometry (TDXRD), with quantitative phase analysis obtained through Rietveld refinement using the XND code. The morphology and grain composition of the dense composite and macroporous material was observed with scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

**Results**  While Equation 2.12 succeeds in describing the net reaction, in-situ XRD (Figure 2.1) indicates that the reaction actually occurs over several well-defined intermediate steps. The first reaction occurs at room temperature and
Figure 2.1. In-situ thermodiffraction patterns obtained during the assisted metathesis reaction to form PbTiO$_3$/K$_2$SO$_4$. PbTiO$_3$ peaks are visible by 875 K. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
Figure 2.2. Powder XRD pattern obtained after grinding together PbSO$_4$ and K$_2$CO$_3$ at room temperature which shows the metathetic exchange of sulfate and carbonate species.

Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
is shown in detail in Figure 2.2. Grinding PbSO₄ and K₂CO₃·1.5H₂O at room temperature initiates one metathetic reaction: the anion exchange between PbSO₄ and K₂CO₃ according to Equation 2.13. This room temperature reaction may be understood by considering the ΔG° of the species involved. We have calculated these values and found a ΔrG of -64.336 kJ mole⁻¹ (Appendix A). The resulting PbCO₃ reacts with K₂CO₃ to form KPb₂CO₃(OH)₂ (seen in Figure 2.2). We observe these reactions are accelerated in a humid environment, suggesting anion exchange occurs through a water-mediated process.

\[
PbSO₄ + K₂CO₃ \rightarrow PbCO₃ + K₂SO₄ \quad (2.13)
\]

and

\[
K₂CO₃ + 4PbCO₃ + 2H₂O \rightarrow 2KPb₂CO₃(OH)₂ + 3CO₂ \quad (2.14)
\]

Heating the resulting combination of TiO₂, K₂SO₄, KPb₂CO₃(OH)₂, and PbCO₃ leads to decomposition of the carbonate species by 600 K (peaks around 20° 2θ). By 875 K, peaks characteristic of PbTiO₃ emerge and by 950 K the pattern can be completely fit to a mixture of PbTiO₃ and K₂SO₄. Rietveld refinement techniques[56] followed by quantitative phase analysis[57] were used to extract a PbTiO₃ to K₂SO₄ mole ratio of 53:47 for the final product. The fit to the tetragonal P4mm phase of PbTiO₃ [58] and the orthorhombic β structure of K₂SO₄ [59] is shown in Figure 2.3a. After washing the product in water, the K₂SO₄ phase has been dissolved, leaving a monolith of PbTiO₃ (Figure 2.3a).
Figure 2.3. X-ray diffraction data, Rietveld fits and difference profiles (from top to bottom) for (a) composite of PbTiO$_3$/K$_2$SO$_4$ (b) PbTiO$_3$ after dissolution of the K$_2$SO$_4$ phase.

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The unit cell volume for the perovskite phase of 63.15(1) Å³ is in good agreement with the reported value of 63.3(3) Å³. This agreement suggests that the samples are quite pure and the presence of a second phase during the sintering process did not lead to significant ion exchange. Close agreement with the literature values for the tetragonal-cubic phase transition (monitored by differential thermal analysis: 758 K reported: 763 K) further suggests these samples are quite pure.

SEM micrographs of cross-sections through the PbTiO₃ and K₂SO₄ composite before and after leaching are shown in Figure 2.4. The composite is a mixture of well-sintered grains with crystallites on the order of 300-500 nm in diameter. Throughout this matrix are larger grains between 15 and 30 µm in size. After leaching, the small PbTiO₃ grains remain as a sponge-like network with voids in the 15-30 µm range. The matrix between the small grains remains quite dense, suggesting that all of the K₂SO₄ grew into larger grains. EDX mapping confirms this distribution of elements (Figure 2.5). While K and S are present throughout, this may be attributed to grains of K₂SO₄ under the surface.
Figure 2.4. SEM micrographs of the sintered composite pellet of PbTiO$_3$ and K$_2$SO$_4$ [(a) and (b)] and macroporous PbTiO$_3$ obtained from removal of the K$_2$SO$_4$ phase [(c) and (d)]. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
Figure 2.5. Elemental mapping reveals the grain morphology of the PbTiO$_3$/K$_2$SO$_4$ composite (a). Regions of K and S are shown in image (b) while Pb is shown in (c). Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
2.3 \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3/\text{K}_2\text{SO}_4 \)

The La\(_{1-x}\text{Sr}_x\text{MnO}_3\) family of perovskites displays a remarkable number of interesting magnetic, conduction, and catalytic phenomena. In particular, the \( x = 0.3 \) compound (La\(_{0.7}\text{Sr}_{0.3}\text{MnO}_3\)) is a half-metallic room temperature ferromagnet which displays colossal magnetoresistance and mixed (e\(^-\) and O\(^{2-}\)) conductivity. These properties all arise from the mixed charge on the perovskite A site (La\(^{3+}\) and Sr\(^{2+}\)) forcing the B site Mn to assume both 3+ and 4+ charges. The mixed conductivity found in this system appears to play a key role in the unusual catalytic activity of this compound. Since the 1970s, it has been known that these perovskites display catalytic activities similar to the precious metals platinum and palladium.[60] Efforts to use these materials in automotive catalytic converters have been promising.[61, 62] These perovskites act as catalysts in other reactions as well, such as methane combustion.[52]

The mixture of La\(^{3+}\) and Sr\(^{2+}\) on the perovskite A site and the associated oxygen vacancies results in the high mixed conductivity of La\(_{0.7}\text{Sr}_{0.3}\text{MnO}_3\). This property, as well as their refractory properties, leads to their use as porous cathodes in solid oxide fuel cells.[51] The role of the cathode in a solid oxide fuel cell is to electro-reduce oxygen from the gas phase to produce O\(^{2-}\) ions which will travel across the electrolyte. As such, the cathode must be a
mixed conductor with high surface area, mechanical stability and a porous architecture which permits rapid gas diffusion through the structure. Typically, porous La$_{0.7}$Sr$_{0.3}$MnO$_3$ cathodes are formed via incomplete densification of powders or inclusion of volatilizing agents (graphite, polymers) which create large spherical voids.[63]

All of these applications involve the exchange of a gaseous reactant over the surface of a solid support. As such, new methods to form these compounds as bulk materials with macroporous architectures in the 1 $\mu$m range have real potential to improve fuel cell and catalytic converter efficiency. In the following, assisted metathesis is employed to form biphasic bulk materials of a soluble salt and lanthanum manganite oxides according to equations 2.15 and 2.16.

$$\text{La}_2\text{O}_3 + \text{MnSO}_4 + \text{K}_2\text{CO}_3 \rightarrow \text{LaMnO}_3 + \text{K}_2\text{SO}_4 + \text{CO}_2 \quad (2.15)$$

$$0.7\text{La}_2\text{O}_3 + 0.3\text{SrCO}_3 + \text{MnSO}_4 + \text{K}_2\text{CO}_3 \rightarrow \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 + \text{K}_2\text{SO}_4 + 1.3\text{CO}_2 \quad (2.16)$$

**Preparation** Composites of La$_{1-x}$Sr$_x$MnO$_3$/K$_2$SO$_4$ were prepared in a manner similar to the PbTiO$_3$/K$_2$SO$_4$ composites of Section 2.2. The intended reactions are shown in Equations 2.15 and 2.16. Powders of La$_2$O$_3$, SrCO$_3$, K$_2$CO$_3$, and MnSO$_4$·5H$_2$O were combined according to a 0.005 mole basis for $x = 0.0$ and 0.3. The powders were ground in a mortar and pestle, cold-pressed,
and calcined at 1228 K in air. The pellets were subsequently ground, pressed, and fired again at 1228 K (x=0.0) or 1473 K (x=0.3) for 24 h. As in the above dissolution of K₂SO₄, the resulting pellets were placed in water for several days. Phase evolution was monitored with powder X-ray diffraction and in-situ TDXRD. Morphology and elemental composition were studied by SEM with an attached energy-dispersive X-ray detector (EDX).

**Results**  The TDXRD data for the LaMnO₃/K₂SO₄ reaction is shown in Figure 2.6. For both the x = 0.0 and 0.3 cases, no immediate metathetic reaction was seen between the sulfate and carbonate systems, unlike in the K₂CO₃/PbSO₄ system. Both show a peak developing at 700 K which corresponds to the main La₁₋ₓSrₓMnO₃ perovskite reflection. Despite these similarities, the phase evolution for the x = 0.0 and 0.3 La₁₋ₓSrₓMnO₃/K₂SO₄ systems was quite distinct. For the x = 0.0 system, the La₂O₃ peak remain present through 1100 K, indicating the perovskite forms directly from the La₂O₃ phase. In contrast, this peak disappears by 450 K for the x = 0.3 system. The intermediate phase (JC-PDF Card 42-0343) is observed above 450 K. The formation of La₂SrOₓ is advantageous, as this ensures good mixing of the A site cations in the final perovskite product.

Rietveld refinement of the XRD powder patterns before and after dissolution of the K₂SO₄ phase was performed with the XND code (Figure 2.7 shows
Figure 2.6. In-situ thermodiffraction patterns obtained during the assisted metathesis reaction to form LaMnO$_3$/K$_2$SO$_4$. The reactant peak patterns are shown at the bottom, suitably scaled with relative heights maintained for each phase. The arrow marks the main LaMnO$_3$ reflection. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
Figure 2.7. X-ray diffraction data, Rietveld fits and difference profiles (from top to bottom) for (a) composite of LaMnO$_3$/K$_2$SO$_4$ and (b) LaMnO$_3$ after dissolution of the K$_2$SO$_4$ phase. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
Figure 2.8. X-ray diffraction data, Rietveld fits and difference profiles (from top to bottom) for (a) composite of La$_{0.7}$Sr$_{0.3}$MnO$_3$/K$_2$SO$_4$ and (b) La$_{0.7}$Sr$_{0.3}$MnO$_3$ after dissolution of the K$_2$SO$_4$ phase. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
LaMnO$_3$, La$_{0.7}$Sr$_{0.3}$MnO$_3$ is in Figure 2.8). The fit to LaMnO$_3$ was improved by using the $R\bar{3}cH$ structure of cation-deficient La$_{0.96}$Mn$_{0.96}$O$_3$ instead of the orthorhombic LaMnO$_3$ structure of the stoichiometric compound\cite{64}. The unit cell volume was found to be 353.03 Å$^3$, close to the value of 352.1 Å$^3$ reported for La$_{0.96}$Mn$_{0.96}$O$_3$\cite{64}. Quantitative phase analysis gave a perovskite:$K_2$SO$_4$ ratio of 54:46, close to the expected 1:1 value. La$_{0.7}$Sr$_{0.3}$MnO$_3$ phase refinement to the $R\bar{3}cH$ structure gave a La:Sr ratio of 0.72:0.28, in good agreement with the expected 7:3 ratio. The perovskite:$K_2$SO$_4$ ratio of 56:44 again matches well with the expected values. The unit cell volume was found to be 351 Å$^3$.

For both samples, $x = 0.0$ and 0.3, the $K_2$SO$_4$ phase is completely removed following washing.

In analogy with our prior results with the PbTiO$_3$/$K_2$SO$_4$ system, firing at 1228 K resulted in La$_{1-x}$Sr$_x$MnO$_3$ grains 300-500 nm in diameter surround large isolated grains of $K_2$SO$_4$ (EDX for the LaMnO$_3$/$K_2$SO$_4$ composite is shown in Figure 2.10). Figure 2.9 shows that on washing, the $K_2$SO$_4$ leave voids 15-30 μm in diameter throughout the pellet. In contrast, sintering at higher temperature (1473 K) resulted in a very different morphology. Figure 2.11 reveals a very dense initial composite composed of 2-5 μm La$_{0.7}$Sr$_{0.3}$MnO$_3$ grains embedded in a continuous second phase of $K_2$SO$_4$. On leaching, the grains remain interconnected and a continuous pore network re-
Figure 2.9. SEM micrographs of (a) the sintered composite pellet of LaMnO$_3$ and K$_2$SO$_4$ and (b) macroporous LaMnO$_3$ obtained from removal of the K$_2$SO$_4$ phase. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
Figure 2.10. Elemental mapping of the LaMnO$_3$/K$_2$SO$_4$ composite shown in (a). Regions of K and S are shown in image (b) while regions of La and Mn are shown in (c). Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
sults. This difference in morphology results from heating above the melting point of K$_2$SO$_4$ (1342 K). The increased temperature and liquid flux lead to coarsening of the La$_{0.7}$Sr$_{0.3}$MnO$_3$. As the grain growth method is mediated through a liquid phase, minimal densification occurs. On cooling, the liquid K$_2$SO$_4$ solidifies in the void spaces between the perovskite grains. As the molar ratio of La$_{0.7}$Sr$_{0.3}$MnO$_3$ to K$_2$SO$_4$ was 1:1, the volume loss associated with the removal of the K$_2$SO$_4$ phase was approximately 54%.

Sintering the resulting macroporous materials improves the grain connectivity but does not eliminate the macroporosity. After firing at 1273 K for 48 h, the porous monoliths remain intact (Figure 2.12). Such high temperature stability is ideal for high temperature catalytic applications.

Impurities in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ will lower the Curie temperature and decrease saturation magnetization. Temperature-dependant dc magnetization measurements were made for a small quantity of macroporous La$_{0.7}$Sr$_{0.3}$MnO$_3$. Figure 2.9 shows magnetization data collected on warming under a 0.1 T field from 5 to 380 K after cooling under the same field. The transition to ferromagnetism is seen around 370 K, in agreement with the known transitions for the $x = 0.3$ composition of the La$_{1-x}$Sr$_x$MnO$_3$ phase diagram[66]. A 5 K magnetization loop is displayed in the inset of this figure. Virtually no hysteresis is present and the saturation magnetization is reduced
Figure 2.11. SEM micrographs of the sintered composite pellet of La$_{0.7}$Sr$_{0.3}$MnO$_3$ and K$_2$SO$_4$ [(a) and (b)] and macroporous La$_{0.7}$Sr$_{0.3}$MnO$_3$ obtained from removal of the K$_2$SO$_4$ phase [(c) and (d)]. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.
Figure 2.12. SEM cross-section showing thermal stability of macroporous LaMnO$_3$ network after firing at 1273 K for 48 h. From ref [65] Reproduced by permission of The Royal Society of Chemistry.
Figure 2.13. Magnetic characterization of the macroporous La$_{0.7}$Sr$_{0.3}$MnO$_3$. Field-cooled magnetization data were acquired in a 100 Oe field on warming after cooling under the same field. The inset is a magnetization loop obtained at 5 K. Reproduced with permission from ref. [49]. © 2004, American Chemical Society.

from the expected spin-only value of 3.7 $\mu_B$ per formula unit to 1.7 $\mu_B$. The sharpness of the ferromagnetic transition and the shape of the hysteresis loop suggests La$_{0.7}$Sr$_{0.3}$MnO$_3$ is the only magnetic phase present.
2.4 Discussion

We have developed a new set of reactions which yield fine powders of important perovskite phases intermingled with a soluble salt (K$_2$SO$_4$ in this case). Anion exchange between the reactants leads to the formation of reactive intermediate species which lowers the temperature of perovskite formation. The phases so formed are quite pure as there is minimal solubility between the salt and perovskite phases. This purity has been determined from magnetic and structural phase transitions and extensive refinement of X-ray diffraction patterns. The reactions described are quite general and may be extended to a variety of other systems. To understand the surprisingly low formation temperature of the perovskites studied, the Gibbs free energies of formation of the relevant species at 1000 K have been compared (Appendix A). These values allow $\Delta_r G$ for the three perovskite compositions to be computed: PbTiO$_3$ = -161.512 kJ mol$^{-1}$; LaMnO$_3$ = -288.31 kJ mol$^{-1}$; La$_{0.7}$Sr$_{0.3}$MnO$_3$ = -347.53 kJ mol$^{-1}$. While these values do not address the intermediate products formed during these reactions, they do show that the net reaction is quite exothermic. In a similar manner, the thermodynamics behind the room temperature metathetic reaction between PbSO$_4$ and K$_2$CO$_3$ also reveals a large $\Delta_r G$ driving the reaction.

By forming the biphasic product as dense pellets, we have used selective
leaching to form porous monoliths of desired perovskite phases. When firing occurred below the melting point of K$_2$SO$_4$, the pores were large and isolated due to the disparity in grain size between the K$_2$SO$_4$ and PbTiO$_3$/LaMnO$_3$ phases. The difference in grain size likely arose due to two factors: first, formation of K$_2$SO$_4$ occurred at room temperature through a water-mediated process, leading to large grains immediately, whereas the perovskite only nucleated above 875 K; second, the sintering temperature of 1048 K is close to the melting point of K$_2$SO$_4$ (1342 K) but too low for rapid densification of the perovskite phases. Other work has shown PbTiO$_3$ does not densify significantly until 1370 K without the aid of a flux.[67] Likewise, rapid densification of LaMnO$_3$ only begins above 1450 K and the addition of Sr actually delays the onset of densification by 200 K.[68] Sintering is rate limited by the diffusion of lanthanum in this system and addition of Sr decreases the number of lanthanum deficiencies. Leaching the soluble salt leaves behind a porous monolith of phase pure perovskite in all cases. The pore architecture obtained by firing the composite above the melting point of K$_2$SO$_4$ was quite open. Instead of isolated large grains of K$_2$SO$_4$, the molten salt formed a continuous network between the perovskite grains. The salt acted as a flux for the growth of the perovskite grains through a transport pathway that did not lead to significant densification. The resulting porosity was much more open and suggests that the extent of porosity could be controlled by adjusting the initial
K$_2$SO$_4$ volume fraction.

Catalytic applications involving porous perovskites are in the 800 K to 1100 K temperature range, which is well within the thermal stability of these materials. Heating LaMnO$_3$ at 1273 K for 48 h caused some grain growth and improved necking, but did not compromise the macropore network. Given the decreased diffusivity of La$_{0.7}$Sr$_{0.3}$MnO$_3$ at these temperatures, this material should display additional improvements in long-term structural stability.

2.5 Conclusion

Assisted metathesis followed by selective leaching has proven to be successful in the formation of porous perovskites with controlled chemistry. The resulting grain and pore morphology can be adjusted through the judicious control of temperature and sintering conditions. The success of selective leaching in the preparation of these macroporous perovskites suggests a wide variety of other macroporous materials can be formed from intimately mixed dense composites. Metathetic routes are particularly appealing, as the resulting phases are well mixed. As described in Section 2.1, a variety of other metathetic routes have been designed which result in powders of a desired phase and a soluble salt. Microstructural control based on heating above or below the
melting point of the soluble second phase has been demonstrated and suggests that the resulting pore architecture is quite tunable. In the following chapter, we describe how selective leaching may be extended to a variety of transition metal oxides. We also investigate how functionality may be layered through subsequent chemical reactions which preserve the macroporous nature of the materials.
Chapter 3

Single-source Precursors

The success of selective leaching in the previous chapter suggests that a variety of other biphasic systems may be rendered porous through differences in solubility. In this chapter, ZnO is exploited as a sacrificial phase as it is readily soluble in both acidic and alkaline conditions. Biphasic composites composed of ZnO and NiO, ZnFe$_2$O$_4$, or ZnMn$_2$O$_4$ are formed and subsequently leached to create macroporous architectures. Subsequently, we demonstrate that these macroporous monoliths can be modified through vapor or liquid phase reactions to give porous metals and conformal coatings of sub-micron particles throughout the inner pore wall surface.
3.1 Prior Work

In the formation of Vycor™ glass, a single phase borosilicate glass undergoes a spinodal decomposition to give regions of borosilicate rich and poor glass on the nanometer scale. Leaching of the borosilicate rich regions leads to a monolith of porous glass. The beauty of this route is that the starting material is single phase and the spinodal decomposition controls the partitioning.[9] In a similar manner, Suzuki has cooled melts through a eutectic point to yield intimately mixed two phase materials. Composites of magnesia and zirconia have been formed in this way, followed by removal of the magnesia phase to yield a monolith of porous zirconia.[17] Similarly, Abe has controlled the crystallization and phase separation of a glass to serve as a precursor biphasic material. Selective leaching in acid leaves behind mesopores (10 nm pores) and walls composed of the catalyst CuTi₂(PO₄)₃.[69] The Gorte group has formed nickel/yttria-stabilized zirconia composites through tape casting and reduction and used the solubility of the nickel phase in acid to form macroporous sheets of yttria-stabilized zirconia.[18] Through this method, pores 1 µm in diameter and porosities in excess of 75% could be obtained without structural collapse.

Inspired by the Vycor™ glass process, the Seshadri group has used soft-chemistry methods to form intimately mixed precursors for selective leach-
ing. By precipitating hydroxy double salts of nickel and zinc, followed by decomposition of this single phase precursor, fine mixtures of NiO and ZnO could be obtained.[70] In a similar manner, combustion synthesis starting from ions mixed in solution can be used to give mixtures of NiO and ZnO.[71] As the starting precursor has the ions mixed on an atomic level, the material so formed has a random mixture of the two phases, thereby avoiding inhomogeneities that would arise due to powder mixing. The decomposed powder is quite fine, as the resulting biphasic materials have grains less than a micron in diameter. The pore networks that develop upon removal of the sacrificial phase are thus also of this length scale.

3.2 Biphasic Composites with Sacrificial ZnO

Wurtzite ZnO is one of the few amphoteric transition metal oxides, which makes ZnO an ideal sacrificial phase for sacrificial leaching. Additionally, ZnO does not display complete miscibility with most other transition metal oxides. By working in two phase regions, composites of sacrificial ZnO and a second, desired, phase may be prepared. The following describes our efforts to produce macroporous NiO, ZnFe$_2$O$_4$, and ZnMn$_2$O$_4$. 
**Preparation**  Dense bulk composites of ZnO and a desired phase (NiO, ZnFe$_2$O$_4$, or ZnMn$_2$O$_4$) were prepared via the decomposition of oxalate precursors followed by pelletization and firing. Oxalates were prepared by coprecipitation of dissolved metal salts with oxalic acid. For the NiO and ZnFe$_2$O$_4$ oxalate precursors, Ni or Fe salts [Ni(CH$_3$CO$_2$)$_2$·4H$_2$O (0.08 mol) or FeCl$_2$·4H$_2$O (0.08 mol)] and Zn acetate [Zn(CH$_3$CO$_2$)$_2$·H$_2$O (0.08 mol)] were dissolved in 200 cm$^3$ water and combined with 200 cm$^3$ of 1 M oxalic acid. The solution immediately became cloudy with the crystalline precipitate of [M$_{0.5}$Zn$_{0.5}$(C$_2$O$_4$)·2H$_2$O; M = Ni or Fe]. The precipitate was allowed to settle and was repeatedly washed. For the ZnMn$_2$O$_4$ oxalate precursor, the starting Zn:Mn metal ion ratio was 2.5:1 [Zn(CH$_3$CO$_2$)$_2$·2H$_2$O (0.1 mol) and Mn(CH$_3$CO$_2$)$_2$·4H$_2$O (0.04 mol)]. For all three oxalates, the precipitate was dried and calcined as a powder in air at 873 K for 1 h. The resulting powders were then ground by hand, cold-pressed at 1.6×10$^3$ kg cm$^{-2}$, and fired again in air at 1273 K to 1473 K. Following firing, the pellets were leached in stirring 4 M NaOH at 337 K for 3 days with periodic replacement of the solution. The dense and porous pellets were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray analysis. Mass loss during leaching was monitored for comparison with XRD phase analysis.
Firing and leaching conditions were determined empirically. Initially, the pellets were fired at too low a temperature (<1200 K) for sufficient connectivity, leading to crumbling of the pellets during leaching. To increase the porosity, the volume percent of the sacrificial phase was increased. This had a secondary effect of increasing the leaching rates, as the increased porosity improved pore connectivity. Likewise, stirring and the increase in leaching temperature were used to increase leaching rates.

**Results** Powder X-ray diffraction patterns for the dense biphasic pellets are shown across the top of Figure 3.1. Rietveld refinement of the pattern shown in (a) to the cubic $Fm\bar{3}m$ phase of NiO and the hexagonal $P6_3mc$ phase of ZnO indicates the sample is phase pure. Quantitative phase analysis using Rietveld scale factors give a NiO:ZnO mole ratio of 72:28. This ratio is quite different than the 1:1 ratio of the starting metal acetates. No loss of mass is observed during the sintering process, indicating that the starting ratio is preserved. Instead, the discrepancy may be explained by the high levels of Zn substitution allowed onto the Ni site in rock salt NiO. This hypothesis is supported by the unusually large unit cell volume obtained from the powder diffraction data (fit: 74.51 Å$^3$, literature: 72.88 Å$^3$). The unit cell should expand, as the ionic radii of Zn$^{2+}$ and Ni$^{2+}$ are respectively 0.74 and 0.69 Å. From the Ni$_{1-x}$Zn$_x$O:ZnO ratio and assuming the Ni:Zn mole ratio remains 1:1, a value
Figure 3.1. X-ray diffraction data is shown for composites of ZnO and (a) NiO, (c) ZnFe$_2$O$_4$, and (e) ZnMn$_2$O$_4$ along with Rietveld fits to the phases present and difference profiles. Leaching in alkali removes the ZnO phase, leaving phase pure (b) NiO, (d) ZnFe$_2$O$_4$, and (f) ZnMn$_2$O$_4$. The data, Rietveld fits, and difference profiles are shown from top to bottom.
Figure 3.2. SEM cross-sections of (a) the dense NiO/ZnO composite and (b) the resulting macroporous NiO obtained after leaching. From ref [65]. Reproduced by permission of The Royal Society of Chemistry.
Figure 3.3. SEM cross-sections of (a) the dense ZnMn$_2$O$_4$/ZnO composite and (b) the resulting macroporous ZnMn$_2$O$_4$ obtained after leaching Reproduced with permission from ref. [72]. © 2005, Wiley-VCH.

of $x = 0.3$ is obtained. Similar levels of Zn$^{2+}$ substitution have been found in prior NiO/ZnO studies[71]. Leaching out the wurtzite phase in base leaves behind the rock salt phase (Figure 3.1b) with no remnant wurtzite. The mass loss due to leaching was 34%, which corresponds to an $x$ of 0.26 for the rock salt Ni$_{1-x}$Zn$_x$O phase. The wurtzite phase occupied 35% of the composite volume and removal of this phase should induce a corresponding porosity. From the mass and physical dimensions, a porosity of 45% is observed, suggesting the material was not entirely dense before leaching.

In Figure 3.2, micrographs are shown of cross-sections of NiO/ZnO before
and after the leaching processes. The initial monolith is quite dense, with grains 500 nm in diameter. Following leaching, the grains are quite faceted and well-connected with robust grain boundaries. The grains and pore network are both 500 nm in diameter. As the pore morphology is simply a function of the grain size, adjusting the sintering conditions enables the control of the resulting pore morphology. In this manner, pores ranging from 0.5 μm to 5 μm have been formed.

Decomposition and firing of the 4Zn:Mn oxalate leads to a mixture of spinel ZnMn$_2$O$_4$ and wurtzite ZnO (Figure 3.1e). Rietveld refinement suggests a substitution of Mn into the wurtzite lattice (Zn$_{0.9}$Mn$_{0.1}$O) and a ZnO:ZnMn$_2$O$_4$ mole ratio of 9:1. Substitution of Mn into the wurtzite lattice results in this shifting of the phase ratio from 4:1 to 9:1. This level of substitution is consistent with prior work on this system.[73] The unit cell volume was found to increase as a function of Mn substitution through 8% and then flatten out at higher concentrations as ZnMn$_2$O$_4$ was formed as a second phase. The mass loss observed during the leaching process (65% loss) gives a ZnO:ZnMn$_2$O$_4$ mole ratio of 5:1. Powder XRD following leaching (Figure 3.1f) confirms the complete removal of the wurtzite phase, suggesting a porosity of 60-70% (Appendix B)

Cross-sections of the ZnMn$_2$O$_4$/ZnO monolith reveal a very dense interior
Figure 3.4. EDX mapping of a dense ZnMn$_2$O$_4$/ZnO composite (a). The distribution of (b) Zn and (c) Mn is shown, with regions of lower Zn concentration corresponding to regions of high Mn concentration.
Figure 3.5. SEM micrographs during the leaching process, showing (a) a partially leached pellet of ZnO/ZnMn$_2$O$_4$ and (b) across the whole pellet when the leaching is finished.
(Figure 3.3a). EDX imaging of the interior is shown in Figure 3.4, showing a distribution of zinc throughout the cross-section. The regions of lower zinc concentration (the darker regions in Figure 3.3b) map to regions of high manganese concentration (the lighter regions in Figure 3.3c). The spinel grains are 1-2 µm in diameter and appear randomly distributed throughout the pellet. SEM observations of the leaching process reveal that dissolution occurs as a front which moves towards the center of the pellet. Figure 3.5a shows a cross-section of a partially leached pellet of ZnMn$_2$O$_4$ and ZnO, which is macroporous on both sides, and dense in the middle. The smoothness of the dissolution front suggests that all pores are equally accessible and that there are not serious bottlenecks in the pore network. As shown in Figures 3.5 and 3.3b, after the leaching process is complete the pellet remains robust and is composed of 1-2 µm grains. As the ZnO phase occupied 70 volume percent, the porosity is extensive and the material appears very open. Despite the low ZnMn$_2$O$_4$ volume fraction, the grains are still well connected. EDX elemental analysis indicates the relative amounts of zinc, manganese, and oxygen (15:27:58) correspond to Zn$_{1.0}$Mn$_{1.8}$O$_4$.

For the Zn/Fe system, the powder pattern in Figure 3.1c refines to a 58:42 ratio of ZnO:ZnFe$_2$O$_4$. This difference from the expected 1:1 ratio may be due to substitution of Fe into the wurtzite phase or differences in X-ray absorp-
Figure 3.6. SEM cross-sections of (a) the dense ZnFe$_2$O$_4$/ZnO composite and (b) the resulting macroporous ZnFe$_2$O$_4$ obtained after leaching. Reproduced with permission from ref. [74]. © 2005, American Chemical Society.
tion cross sections of ZnO and ZnFe$_2$O$_4$. The ZnO is completely removed during the leaching process (d), and induces an additional porosity of 24% (Appendix B).

Figure 3.6 shows the ZnO/ZnFe$_2$O$_4$ pellet before and after alkali leaching. The initial monolith is reasonably dense and composed of 1-3 µm grains. Following leaching of the ZnO phase, the monolith has been rendered porous on this length scale. As the ZnO phase was only 24% volume percent, the resulting porosity is not dramatic. The grains which form the pore walls remain well-connected and the monolith is robust. This grain connectivity is vital for the conversion to macroporous Fe metal, described in Section 3.3.

### 3.3 Subsequent Chemistry - Reduction

Following our work on macroporous oxides, we were interesting in using these materials as templates for further chemistry. In particular, we sought to reduce the oxides to macroporous metals while retaining the macropore network. Such structures would be useful as structural materials, heat-exchangers, and as electrodes in fuel cells. In particular, the nature of the leaching process ensures pore connectivity, providing an optimal architecture for fluid flow through the materials. In this work, we have formed
Porous nickel and iron from $\text{ZnFe}_2\text{O}_4$ and NiO. Porous metals may be formed through a variety of methods: dissolution,[3] reduction,[21] foaming,[75], organic templating,[76] and electrodeposition,[19] all of which result in different structures with different uses. There has been over a century of study on the kinetics and modeling of the reduction of metal oxides to metals in a reducing atmosphere.[77, 78, 79, 80] The Stein group has recently shown the formation of three-dimensionally ordered porous nickel oxide via infiltration of assemblies of latex spheres. Reduction of the macroporous nickel oxide to nickel metal conserved the shape of the pore network.[21]

**Preparation** Conversion of the NiO and ZnFe$_2$O$_4$ macroporous monoliths to porous metals was carried out in a tube furnace with a flowing 5%-H$_2$/N$_2$ atmosphere at 723-973 K for 3-12 hrs. The effects of varying flow rate, ramp rate, temperature, and reduction time on the resulting morphology were all investigated. The materials so formed were metallic in color and were quite ductile. In the reduction of ZnFe$_2$O$_4$ above 873 K, deposition of zinc at the end of the tube furnace hot zone was observed. Between reductions, the tube was rinsed with hydrochloric acid to remove accumulated zinc.

**Results** Beginning with a macroporous monolith of rock salt Ni$_{0.7}$Zn$_{0.3}$O, firing in a reducing atmosphere at 723 K resulted in a macroporous monolith
Figure 3.7. Reduction in a 5%-H$_2$ atmosphere of (a) Zn$_{0.3}$Ni$_{0.7}$O to ZnO and Ni; (b) ZnFe$_2$O$_4$ to ZnO and Fe. From top to bottom, XRD traces, Rietveld fits to the respective metals and ZnO, and difference profile. (a) reproduced with permission from ref. [74]. © 2005, American Chemical Society.
of Ni metal and ZnO. The resulting material was metallic in color and quite strong. The powder pattern and Rietveld refinement of the resulting pellet is shown in Figure 3.7a. Quantitative phase analysis using Rietveld scale factors gives a Ni:ZnO mole ratio of 78:22, in rough agreement with the high levels of substitution found in the initial macroporous oxide. The Ni peaks are quite broad, possibly due to difficulties in preparing these samples for diffraction, or due to the fine size of the grains (Scherrer broadening suggests 50 nm grains). Leaching the remaining ZnO in alkali leaves a porous Ni monolith.

Reduction of the macroporous ZnFe₂O₄ monolith at the same temperature (723 K) likewise produced a robust monolith of Fe metal and ZnO. Figure 3.7b shows this mixture of phases and the corresponding Rietveld refinements. Quantitative phase analysis gives a Fe:ZnO mole ratio of 64:36, in agreement with the 66:33 ratio we would expect from the stoichiometry of the spinel. As in the NiO system, the remnant ZnO may be removed by leaching in alkali.

When the macroporous ZnFe₂O₄ was reduced at higher temperatures (973 K), the resulting XRD pattern showed phase pure Fe metal and the mass loss corresponded to the removal of zinc and its oxygen counterion. At these temperatures, ZnO is reduced to Zn (mp 692.5 K[81]). The liquid Zn is then transported out of the hot zone of the furnace through the vapor phase, where it deposits as long whiskers of Zn metal on the inside of the tube. The high
Figure 3.8. The stability of ZnO depends on the $\text{H}_2/\text{H}_2\text{O}$ ratio and temperature. Above the line, ZnO is unstable and transforms to Zn metal.
level of volatility of ZnO is well known in air at temperatures above 1500 K.\[82\]

The Zn\(^{2+}\) reduction occurs in a flowing H\(_2\) atmosphere, which is vital to remove oxygen released during reduction of the oxide. Before passing over the sample, the gas passes through a desiccant which reduces the H\(_2\)O levels to less than 1 ppm. Thus the gas stream in contact with the sample should have a minimum composition of 10\(^6\) \(P_{H_2}/P_{H_2O}\). Figure 3.8 shows how the \(P_{H_2}/P_{H_2O}\) ratio affects equilibrium phase stability, with ZnO being reduced for values above the curve. The vaporization process for ZnO has been studied by mass spectroscopy and reveals that elemental Zn gas is the only Zn species present.\[83\] Knudsen weight-loss measurements have been used to determine the rate of sublimation under neutral conditions.\[84\] The high-temperature vaporization behavior of ZnO has been reviewed at O\(_2\) pressures of 10\(^{-15}\) and 0.2 atm.\[85\] The reaction to describe this reduction and deposition at the cold end of the tube is:

\[
\text{ZnO}(s) + H_2 \rightleftharpoons Zn(g) + H_2O \rightarrow Zn(s) + H_2O
\]  

(3.1)

\[
P_{Zn} = \frac{KP_{H_2}}{P_{H_2O}}
\]  

(3.2)

The interplay between zinc vapor pressure \((P_{Zn})\), water partial pressure \((P_{H_2O})\), and hydrogen partial pressure pressure \((P_{H_2O})\) is clear. The flowing atmosphere drives the reaction forward through transport of Zn and H\(_2\)O out of the furnace hot zone while maintaining the \(P_{H_2}\) at 0.05 atm.
The morphology of the resulting metals was probed by scanning electron microscopy. In Figure 3.9, a fracture surface through a Ni pellet interior is shown. The macropore network remains intact and the pore walls have undergone significant morphological changes during the transformation from oxide to metal. The walls are smooth and no longer appear to be a collection of discrete, connected polyhedra. Such restructuring reduces the surface energy, resulting in a material which is reminiscent of the periodic minimal surfaces found in a variety of tethered biphasic systems such as block copolymers. The fracture has clearly occurred through a ductile process, leaving a surface far rougher than the brittle fracture surfaces seen in cross-sections of macroporous oxides. In Figure 3.10, the top surface of the macroporous iron monolith is shown after reduction of ZnFe$_2$O$_4$ at 973 K. The material has a similar morphology to the reduced nickel, with smooth pore walls which are well-connected. For the reduction and vapor phase leaching of zinc, a mass loss of 53% is expected, in comparison this sampled showed a 46% mass loss and a 15% linear contraction, corresponding to a volume loss of 40% (see Appendix B).
Figure 3.9. SEM micrograph showing a cross-section of macroporous nickel obtained from the macroporous oxide. From ref [65] Reproduced by permission of The Royal Society of Chemistry.
Figure 3.10. SEM of top surface of macroporous Fe metal after reduction and vapor phase leaching of Zn at 973 K. Reproduced with permission from ref. [74]. © 2005, American Chemical Society.
3.4 Subsequent Chemistry - Conformal Coating

When macroporous materials are coated with a second phase, it is typically to serve one of two roles: to cover the walls with catalytic particles or to densify the material without shrinkage via repeated infiltrations.[86] In the catalysis case, a coating of nanoparticles is applied as a wash-coat to an inert monolith which ideally does not interact with the nanoparticles. Deactivation of the catalytic particles can occur via reaction with the backbone, leading to an undesired ternary phase.

As the selective leaching route described in Section 3.2 is applicable to the formation of many different oxides as macroporous monoliths, we were interested in exploring reactive dip-coating. In this, the macroporous support reacts with the coating to form a desired oxide phase through co-diffusion of cations. The material so formed should show enhanced thermal stability, as it has already reached an equilibrium state with the macroporous backbone. As described in the previous chapter, one class of materials which would benefit from reactive dip-coating are the lanthanum-based ternary and quaternary oxides. Materials such as La$_{0.7}$Sr$_{0.3}$MnO$_3$ have shown increasing promise as substitutes for precious metal catalysts.

Conformal coatings with partial surface coverage are particularly interesting in catalysis, as the three-phase boundary between the backbone, coating,
and vapor phase is frequently the active site in the catalyst. Reactive dip-coating should be able to control the chemistry and morphology of these triple point boundaries as the amount of material deposited is a function of solution concentration and number of dipping cycles.

**Preparation** Macroporous NiO pellets were prepared according to Section 3.2 and immersed in a solution of lanthanum acetate (10 g lanthanum acetate in 20 cm$^3$ of diluted nitric acid). Trapped bubbles were removed by centrifuging the pellets while in solution. After drying, the lanthanum acetate coating was decomposed at 1273 K for 1 h in air. To build up a thicker coating which would be quite visible by SEM, 5 dip coatings were performed. A series of dippings in nitric acid solution which did not contain lanthanum were performed as a control.

A variety of alternate approaches were employed to improve the solution penetration into the pellets and to obtain a more consistent coverage of the inner surface. Bubbles were also removed by boiling the solution and letting the pellets remain in solution for 24 h. To obtain a more consistent coverage, the pellets were dried in a vacuum oven and in air below and above 373 K. Concentration gradients which arise during evaporation were reduced by gelling the solution by addition of ammonium hydroxide.
Figure 3.11. Powder XRD pattern of La₄Ni₃O₁₀ conformal coating on NiO. From top to bottom: data, Rietveld refinements for NiO and La₄Ni₃O₁₀, and difference pattern.

Reproduced with permission from ref. [74]. © 2005, American Chemical Society.
Results  Following dip coating and firing, powder XRD reveals the presence of two phases: the original NiO monolith and the Ruddlesden-Popper $m = 3$ phase $\text{La}_4\text{Ni}_3\text{O}_{10}$\[^{[87]}\] (Figure 3.11). A NiO:La$_4$Ni$_3$O$_{10}$ mole ratio of 90:10 is obtained from quantitative phase analysis using Rietveld scale factors. From the broadening of the $\text{La}_4\text{Ni}_3\text{O}_{10}$ peaks, an average grain size of 40 nm is calculated from the Scherrer formula. While it is initially surprising that such a complicated phase was formed as a conformal coating, rather than the $m = 1 \text{La}_2\text{NiO}_4$ or $m = \infty \text{LaNiO}_3$, the $m = 3 \text{La}_4\text{Ni}_3\text{O}_{10}$ phase is known to be the stable phase in air.$^{[88]}$

The inner surface is shown in Figure 3.12, and reveals a collection of sub-micron particles (30-400 nm) coating the pore walls. In contrast, the pore walls of the control sample, which underwent the same dipping and firing process but without La, remained quite smooth did not show any evidence of these particles. Given the agreement between the XRD line broadening and the SEM analysis, we believe the dipping process forms a conformal coating of sub-micron particles $\text{La}_4\text{Ni}_3\text{O}_{10}$ through a processes of reactive dip coating. As the dipping process is additive, the coverage of the conformal coating may be adjusted via the solution concentration or number of dipping cycles.
Figure 3.12. SEM micrograph displaying \( \text{La}_4\text{Ni}_3\text{O}_{10} \) sub-micron particles coating a monolith of macroporous NiO. Reproduced with permission from ref. [74]. © 2005, American Chemical Society.
3.5 Discussion

Selective leaching has proven to be quite successful in the formation of porous monoliths. In the previous chapter, metathetic reactions were used to generate an intimate mixture of two phases. In a similar fashion, such mixtures may be developed through the decomposition of single-source precursors. The selective leaching of a soluble oxide (ZnO) from a variety of biphasic materials has yielded robust macroporous materials with three dimensionally interconnected pores.

Selective leaching of oxides is a promising technique for forming materials with well-defined porosity and high levels of pore connectivity. Extension of this technique to other systems is aided by phase diagrams, which act as road maps for finding two-phase regions of temperature and composition to work within. As long as there is some difference in stability in solution between the two phases bounding this region, it is simply a matter of controlling the microstructure to match the desired pore architecture.

Several factors are important to obtain a continuous pore network penetrating through a robust material. The initial monolith must be dense enough that upon removal of the sacrificial phase, there remains sufficient connectivity between the grains of the desired phase that the monolith does not crumble to powder. The volume fraction of the sacrificial phase must be high enough
to ensure complete leaching, but not to the degree that the desired phase is simply a collection of isolate grains. Intimate mixing of the two phases is vital to form robust monoliths. As the fracture strength of a ceramic material is governed by the size of its largest crack/void, agglomeration of the sacrificial phase leading to large voids must be avoided (see Section 5.3). We have found single source precursors to be a satisfactory way to avoid this issue. Another crucial factor is the rate of grain growth. As seen in the previous chapter, highly dissimilar materials (PbTiO$_3$ and K$_2$SO$_4$, for example) with different melting points and constituent ions exhibited very different rates of grain growth. This lead to a ‘bricks in sand’ morphology, with large grains of K$_2$SO$_4$ (the bricks) embedded in a matrix of small perovskite grains (the sand). Upon washing, isolated pores were formed and pore walls composed of grains much smaller than the pores themselves. If the ‘sand’ had instead been removed, we would be left with a powder of large isolated grains (the ‘bricks’). In this chapter, both the desired and sacrificial phases have been zinc-containing oxides with similar rates of grain growth. As the grain sizes between the phases are comparable, each phase was continuous throughout the composite. Excessive heating can also cause problems by encouraging abnormal grain growth, leading to a non-uniform microstructure. Formation of these large grains may affect the composition, and thus the porosity, in nearby regions (see Section 5.3 for an example of this phenomena).
The modification of macroporous materials through subsequent chemistry remains a rich, and largely unexplored field. We have studied how robust macroporous metals may be formed through shape-conserving reduction reactions and how conformal coatings may be applied through reactive dip coating. The Stein group has used ordered macroporous structures for applications in optics, catalysis, and energy storage. Ordered macroporous TiO$_2$ has been formed through pseudomorphic transformations of macroporous SiO$_2$.\cite{89} Catalytically active transition metal-substituted polyoxometalates have been attached to macro- and mesoporous supports.\cite{90} A final example is the impregnation of tin salts into macroporous supports followed by calcining to form SnO$_2$ conformal coating for battery applications.\cite{91}

### 3.6 Conclusion

Macroporous oxides have been formed through the selective leaching of a phase from a dense composite. The route permits control of chemical composition, pore dimensions/porosity, and is quite general. The pore connectivity of the resulting materials is quite high as the pores were formed via selective leaching. We have developed new methods to modify the pore wall composition, either through high temperature reduction or through reactive conformal coatings. These extensions lead to the formation of robust macroporous met-
als and coatings of sub-micron particles of a ternary phase on a macroporous support.

So far, we have focused on temperature as the independent variable to induce phase separation. In the reduction of oxides to metals, we have also begun to exploit oxygen partial pressure as a means to induce phase separation. Through the judicious control of both these variables, we have separated mixed metal oxides into two immiscible phases (Ni metal and ZnO in one case), one of which can be removed through leaching. In these systems, the volume loss inherent in these transformations resulted in a macroscopic shrinkage of the pellets and also in the formation of transient pores. This work sets the stage for the following chapters, in which reductive phase transformations will be explored which do not result in a macroscopic shrinkage and the volume loss is instead expressed as stable pores. At higher temperatures, Zn volatilization was observed from the lattice, with Zn metal deposited at the edge of the furnace hot-zone. In Chapter 5, the volume loss inherent in this removal of Zn and its oxygen counterion will be exploited in pore formation.
Chapter 4

Porosity through Solid State Reactions

In the previous chapter, we found that the transformation from oxides to metals conserved the macropore architecture. In this chapter, we show how unusual mesoporous architectures can be obtained when Mn$_3$O$_4$ is reduced to MnO. Such mesopores are similar to the transient pores seen with the reduced metals, but more thermally stable. As the transformation preserves the initial macroporous structure, we obtain hierarchical macro/mesoporous monoliths. This process proves to be very robust, as the pores may be closed and reformed upon redox cycling. Such regenerative pore structures open up a new field of applications in catalysis, where loss of surface area with time may be remedied.
through a simple redox cycling process.

### 4.1 Prior work

The use of oxygen partial pressure as an independent variable to control phase stability is emphasized in this chapter. In particular, we focus on morphological changes induced by reductive phase transformations and regeneration of high surface area structures through redox cycling.

Other work on the control of oxygen partial pressure in titanium-based systems has led to the development of several unusual structures. The Chen group has shown that oxidizing titanium metal can form nanorods of TiO$_2$ as aligned arrays from the surface.$^{[92]}$ A similar coating of aligned TiO$_2$ nanorods has been observed by the Sandhage group. In this case, reduction of bulk rutile TiO$_2$ in flowing H$_2$ ‘carves’ the surface, leaving a similar coating of aligned TiO$_2$ nanorods.$^{[93]}$ The reduction of oxide nanowires has been used to pattern arrays of sub-micron particles of NiAs, akin to the formation of droplets due to a Rayleigh instability.$^{[94]}$

Oxygen partial pressure has also been used to induce phase separation in a regenerative manner. The reduction of LaFe$_{0.57}$Co$_{0.38}$Pd$_{0.05}$O$_3$ leads to the expulsion of Pd from the oxide. The resulting decoration of Pd nanoparticles
is catalytically active and may be regenerated by reabsorbing the Pd into the oxide in an oxidizing environment and then regenerating the particles upon reduction.[95] In a similar manner, differences in oxide stability have been used to precipitate nanoparticles of nickel on the surface of magnesia following reduction of a nickel/magnesium oxide. [96]

4.2 Mn$_3$O$_4$ to MnO

Microporous manganese oxides have been found in nature with structures composed of one-dimensional pores with precise diameters corresponding to an integer number of MnO$_6$ octahedra in width and height. The todorokite structure, shown in Figure 4.1 has pore walls composed of three octahedra per side, giving a pore diameter of 0.69 nm. Much like zeolites, the local environment inside the pores may be tuned by controlling pore diameter and chemical constituents. As such, these materials have found use in catalytic processes. The Suib group has done much involving the synthesis, characterization, and catalytic applications of these materials. [97, 98] Industrially, manganese oxides (layered MnO$_2$ phases) are used predominantly in batteries as hosts for the intercalation of lithium ions.
Preparation  Porous monoliths of Mn$_3$O$_4$ were prepared by cold-pressed (1.6 × 10$^3$ kg cm$^{-2}$) and heating commercially available Mn$_3$O$_4$ powder. Heating conditions were chosen so that some necking of the grains occurred, but grain growth and densification were minimized. A typical run would involve heating at 1125 K for 12 to 24 h.

Reduction of Mn$_2$O$_3$ to MnO was achieved by firing in a tube furnace in a flowing 5%-H$_2$/N$_2$ atmosphere between 723 K and 923 K for 1 to 5 h. The mass before and after the reduction was monitored to ensure complete transformation. Redox cycling of the macroporous Mn$_3$O$_4$ pellets was repeated up to three times to investigate the morphological evolution upon redox cycling. As above, flowing 5%-H$_2$/N$_2$ was used to reduce the spinel to the rock
salt at 723 K for 6 h. Reoxidation to Mn$_2$O$_3$ was performed in a box furnace with an air atmosphere at 923 K for 18 h. In determining the conditions required to transform Mn$^{3+}$ to Mn$^{2+}$ and the reverse reaction, we benefited from the published phase diagrams for the Mn$_3$O$_4$-MnO and Mn$_3$O$_4$-Mn$_2$O$_3$ systems.$^{[99, 100]}$

Powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and N$_2$ sorption measurements were used to monitor the phase and morphology evolution during the redox cycling.

**Results**  Figure 4.2 shows SEM micrographs of a macroporous Mn$_3$O$_4$ pellet and the hierarchically porous MnO that is formed upon reduction. A cross-section of the macroporous Mn$_3$O$_4$ is shown Figure 4.2(a), revealing a network of pores ranging from 1-3 $\mu$m in diameter. The grains are well connected, so much so that the fracture surface is intragranular and not at the grain boundaries. When reduced, the macropore network remains intact (Figure 4.2(b)) and mesopores are found penetrating through the macropore walls. Figure 4.2(c,d) shows that the pores are 50 nm in diameter, rectangular in cross-section, and aligned across 1-2 $\mu$m. The rectangular shape and co-alignment suggests the pores are within single grains of MnO instead of being formed at the union between several grains. In Chapter 5, TEM analysis shows that the pore walls are composed of the $\{100\}$ rock salt faces. This would agree with
Figure 4.2. (a) SEM micrograph of cross-section through macroporous Mn$_3$O$_4$ formed by powder sintering. (b) After reduction to MnO, the macropore network remains intact. The phase transformation results in mesopores penetrating through the macropore walls, as shown in the fracture surface in (c). At higher magnification (d), it is revealed that the mesopores in (c) have a rectangular, aligned morphology. From ref[65]. Reproduced by permission of The Royal Society of Chemistry.
the ‘broken-bond’ model for surface energy: the \{100\} faces are the lowest energy faces for the rock salt crystal structure.

Deactivation of catalysts typically occurs due to poisoning of the active surface or sintering due to the high temperatures required for the catalytic process. With this in mind, we thought to regenerate the hierarchically porous MnO through redox cycling. In Figure 4.3, the phase evolution is traced during a series of redox cycles. XRD powder patterns and corresponding Rietveld refinements are shown for two redox cycles. The initial monolith of Mn$_3$O$_4$ is heated in air to form Mn$_2$O$_3$ (volume change: 0.3\% expansion), and then reduced to MnO (volume change: 15.7\% contraction, see Appendix B). This cycle of heating in oxidizing and reducing atmospheres is then repeated several times. Morphologically, these phase changes were monitored via SEM (Figure 4.4). The first panel (a) shows the sample after one redox cycle has closed the mesopores while leaving the macropores intact. A second round of reduction reforms the mesopores shown in (b). The bottom images show the sample after three redox cycles, with the macropore network still intact and mesopores continuing to be reformed.

The morphological changes that occur during redox cycling were followed with N$_2$ sorption measurements. Table 4.1 shows surface area and cumulative pore volume between 10-175 nm during the redox cycling process. The
Figure 4.3. The phase evolution during redox cycling starting from macroporous Mn$_3$O$_4$ (a). The monolith may be reduced to MnO (b), reoxidized to Mn$_2$O$_3$ (c), and reduced again to MnO (d). Not shown is the intermediate transition through Mn$_3$O$_4$ when going from MnO to Mn$_2$O$_3$. 
### BET and BJH pore measurements

<table>
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<th>cum. vol. (cm³/g)</th>
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</tr>
</thead>
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<td>0.001</td>
<td>0.5% 0%</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.9</td>
<td>0.000</td>
<td>0% 0%</td>
</tr>
<tr>
<td>MnO (RI)</td>
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<td>0.041</td>
<td>18% 15.7%</td>
</tr>
<tr>
<td>Mn₂O₃ (OI)</td>
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<td>0.004</td>
<td>2% 0%</td>
</tr>
<tr>
<td>MnO (RIII)</td>
<td>3.7</td>
<td>0.038</td>
<td>17% 15.7%</td>
</tr>
</tbody>
</table>

Table 4.1. Summary of N₂ sorption measurements during vapor phase leaching of Mn₃O₄.

BET surface area (SA) and cumulative volume between 10-175 nm is reported. The volume at this length scale may be converted to a porosity, and compared with that expected from the unit cell change from Mn₂O₃ to MnO.

Initial macroporous Mn₃O₄ has a fairly high surface area arising from pores less than 5 nm in diameter but minimal porosity in the 10 - 175 nm range is present. Firing this macroporous monolith in air and converting to Mn₂O₃ closes these small pores, with a corresponding decrease in surface area. Surface area values near 1 m²/g are typical for macroporous materials. Reduction to MnO increases the surface area and induces porosity which agrees well with the volume loss associated with the conversion of Mn₂O₃ to MnO. The cumulative pore volume is integrated between 10-175 nm to avoid including the smaller macropores. The surface area increase is fairly small due to the density of MnO, large pore size (30 nm), and the relatively low porosity induced. Reoxidation closes the mesopores and reduces the surface area back.
to a ‘macroporous’ level. Likewise, the porosity in the 10-175 nm regime has dropped to almost zero. After three redox cycles, the surface area and porosity are remarkably similar to that obtained after just one reduction, highlighting the robustness of this process. The N$_2$ sorption isotherms which were used to calculated these values are shown in Figure 4.5. For the macroporous precursor, minimal gas volume is adsorbed until bulk condensation at $p/p_0$ in excess of 0.98. Hysteresis is observed at high $p/p_0$ for the samples with mesopores (b,d), as gas preferentially condenses within these pores due to their high surface curvature. Reoxidation eliminates most of the mesopores, but as seen in panel (c), some slight hysteresis is still observed. BJH pore size distributions are shown in Figure 4.6, with peaks around 50 nm for the hierarchically porous MnO samples and no evidence of mesoporosity in the oxidized samples.

4.3 Discussion

Solid state reactions which have an intrinsic volume loss were used to induce mesopores in dense and macroporous bulk monoliths. In this chapter, the focus has been on reduction reactions which liberate oxygen to induce a volume loss. SEM observations of the mesopore formation reveals that immediately following reduction of the Mn$_3$O$_4$ (723 K), the resulting pores are cylindrical in shape and point from the outside of the grains inward. The ra-
Figure 4.4. SEM micrographs showing the morphology during various stages of redox cycling. The mesopores close upon reoxidation to Mn$_2$O$_3$ (a), and reform upon reduction to MnO (b). After three redox cycles, the hierarchical porosity remains intact (c, d). (a,b) reproduced with permission from ref. [101]. © 2006, American Chemical Society. (c) from ref [65] Reproduced by permission of The Royal Society of Chemistry.
Figure 4.5. N₂ sorption measurements of the (a) initial pellet of Mn₃O₄, (b) first reduction to hierarchically porous MnO, (c) first reoxidation to Mn₂O₃, and (d) after three reductions to MnO.
Figure 4.6. BJH pore size distribution for the initial $\text{Mn}_3\text{O}_4$ macroporous monolith, after the first reduction to MnO, after the first reoxidation to $\text{Mn}_2\text{O}_3$, and after the second reduction to MnO. Reproduced with permission from ref. [101]. © 2006, American Chemical Society.
Figure 4.7. The spinel (a-d) and rock salt (e,f) structures have similar oxygen sublattices.

Spinel sublattices: (a) oxygen, (b) oxygen and tetrahedral sites, (c) oxygen and octahedral sites, (d) complete structure. Rock salt oxygen sublattice (e), and the complete structure (f).
dial orientation of the pores agrees with the prevailing understanding of oxide reduction as a core-shell process, with reduction occurring first on the outer layer. Minimal shrinkage is observed during the reduction processes, indicating that morphology is pinned by the inner spinel structure. With increasing heating (923 K), the pores adopt a rectangular morphology, presumably to reduce the surface energy.

The transformation from Mn$_3$O$_4$ spinel to rock salt MnO involves a loss of oxygen and restructuring of the Mn ions in the fcc-oxygen lattice. The unit cells for the spinel and rock salt structures are built up from their sublattices in Figure 4.7. The oxygen sublattices for spinel and rock salt are shown in (a) and (e) respectively. Partial occupancy of the tetrahedral sites in Mn$_3$O$_4$ by Mn$^{2+}$ is shown in (b). The octahedral sites are partially filled in (c) with the Mn$^{3+}$ atoms. In the rock salt structure, the cation (Mn$^{2+}$) completely occupies these octahedral sites (f). The emphasis here is that the sublattice shown in (c) is a vacancy-rich version of the rock salt structure (f), enabling a topotactic conversion during the reduction of Mn$_3$O$_4$ to MnO. The presence of aligned rectangular pores instead of a bulk contraction suggests that the transformation is topotactic, an issue that will be extensively addressed in Chapter 5. The volume loss associated with the spinel to rock salt transformation is 15.8% (See Appendix B). The results of two other systems, V$_2$O$_5$ and Co$_3$O$_4$, are described
in Appendix C. With these systems, reduction again induces a large volume change which is expressed as porosity.

These reductions are found to be particularly robust reactions, with the possibility to cycle the reduction and reoxidation repeatedly to regenerate the mesopores. Beyond gas-phase reductions, there are a variety of intercalation reactions which result in large volume changes. One could imagine a battery structure that generates mesopores during the de-intercalation process, creating a high surface area material to increase electrolyte contact during the recharging processes. This new route to mesoporous solids may be included in the wide variety of spontaneous events which lead to unusual patterning such as the self-organizing structures found in breath figures and Bénard-Marangoni convection.[102, 14].

4.4 Conclusion

Solid state reactions which cause volumetric contractions may be expressed not as a bulk shrinkage, but as pores penetrating throughout the resulting material. In the case of Mn$_3$O$_4$, the transformation occurs in a temperature regime where solid state diffusion is quite slow. The pore forming process is robust, and the mesopores may be closed and reopened repeatedly through redox cy-
cling. In the following chapter, new solid state transformations will be developed which lead to porous materials due to volume losses at diffusion-limiting temperatures.
Chapter 5

Porosity Through Vapor Phase Leaching

The reduction reactions and associated morphological changes explored in the previous chapters suggest that volume changes in the solid state can be harnessed to give rise to unusual architectures, such as bimodal porosity. As described in Chapter 1, many applications benefit from hierarchically porous structure, as such morphologies enable the usually contraindicative properties of high diffusivity and large surface areas.

In this chapter, we further explore the vapor phase leaching of Zn, observed with the Zn/Fe alloys in Chapter 3. The volume loss inherent in the reduction and evaporation of Zn from ternary oxides leads to the formation of unusual
architectures in the resulting oxide. In particular, the reduction and leaching of $\text{ZnMn}_2\text{O}_4$ to $\text{MnO}$ and $\text{Zn}_2\text{TiO}_4$ to $\text{TiO}_2$ is studied. This volume loss may be coupled with reductive phase transformations akin to those seen in Chapter 4.

\section*{5.1 Prior Work}

The selective removal of one element from within a phase dates back to pre-Columbian American craftsmanship, in which the luster of gold-copper alloys was improved by leaching in alkali solution to remove the outer layer of copper, leaving an layer of mesoporous pure gold. The modern analog to this process is the formation of Raney nickel, a high surface area catalyst developed in the 1920s. Raney nickel is formed through the selective dissolution of aluminum from a Ni-Al alloy, leaving a porous network of nickel.\cite{3}

The volatility of certain elements such as zinc and lead at high temperature has long been the bane of ceramicists. Methods have been developed to reduce compositional change during firing when volatile elements are present, but this volatility has largely been viewed as the unfortunate reality of working with such elements.\cite{82} In the following, we harness this volatility as a way to induce porosity, and as such, have develop methods to increase the rate of volatilization. These methods are thus the high-temperature vapor phase
analogs to the dissolution during the formation of Raney nickel.

5.2 ZnMn$_2$O$_4$ to MnO

In the reduction of macroporous Ni$_{0.7}$Zn$_{0.3}$O and ZnFe$_2$O$_4$ to give Ni and Fe metals, there was a significant volume loss during both the reduction of Ni and Fe, and during the leaching of the remaining ZnO (see Chapter 3.3 and Appendix B). While this volume loss resulted in transient pores, the temperatures required to leach out the Zn were too high to maintain the pore network. As shown in the previous chapter, working at diffusion-limiting temperatures can result in this volume loss being expressed as mesopores instead of a bulk contraction. These ideas are combined in this section with the reduction and vapor phase leaching of ZnMn$_2$O$_4$ in a 5%-H$_2$/N$_2$ atmosphere. A discussion of the reduction and vaporization of Zn is found in Section 3.3.

Preparation  The volume loss associated with the reduction and vapor phase leaching of spinel ZnMn$_2$O$_4$ to rock salt MnO was used to induce mesopores into the walls of dense and macroporous pellets. Dense ZnMn$_2$O$_4$ was formed by the decomposition of a mixed metal oxalate followed by high temperature firing. A mixed metal oxalate of Zn and Mn was precipitated by addition of an excess of oxalic acid to a solution of Zn and Mn acetate in a manner simi-
lar to Section 3.2. The oxalate precipitate was then dried and decomposed at 873 K for 1 h. Dense pellets of ZnMn$_2$O$_4$ were then prepared by cold-pressed (1.6×10$^3$ kg cm$^{-2}$) the powder into pellets and firing at 1273 K for 48 h. Biphasic pellets of ZnO/ZnMn$_2$O$_4$ were similarly formed by coprecipitation, decomposition and sintering as described in Section 3.2. Removal of the ZnO phase through alkali leaching leaves behind a macroporous monolith of ZnMn$_2$O$_4$

For both the dense and macroporous pellets of ZnMn$_2$O$_4$, transformation to mesoporous MnO occurred through vapor phase leaching. The pellets were placed in the hot zone of a tube furnace under flowing 5%-H$_2$/N$_2$ and heated for sufficiently hot and long enough to reduce the Mn$^{3+}$ to Mn$^{2+}$ and evaporate the Zn from the lattice (3 K/min ramp to 925 K with a hold of 6 h is a representative set of conditions). When larger samples were reduced and leached, it was necessary to do two runs, with an intermediate removal of the Zn metal from the alumina tube. Crucial to the leaching process is a flowing atmosphere, as this facilitates removal of Zn vapor from over the substrate. A second benefit of the flowing atmosphere is it keeps the oxygen partial pressures to a minimum. Obtaining a suitable flow rate was determined experimentally; if the flow rate is insufficient, Zn metal will be deposited on both the downstream and upstream ends of the tube. High flow rates were avoided to keep the sample temperature accurate.
To understand the vapor phase leaching process, thermogravimetric analysis (TGA) and *ex-situ* thermodiffraction were employed. The resulting mesoporous materials were characterized by X-ray diffraction, N$_2$ sorption measurements, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Samples were prepared for TEM analysis by impregnating with M-Bond 610 epoxy while under vacuum and then polishing with diamond lapping films (6 µm down to 1 µm films). Repeating this impregnation and polishing process resulted in dense composites of MnO and epoxy which were quite smooth. By polishing, the pellets were thinned such that the exposed surfaces were from well within the original pellets. A focused ion beam (FIB) was used to cut lamella out from the composites for TEM analysis.

**Results**  Reduction and vapor phase leaching of dense ZnMn$_2$O$_4$ induces mesopores, as shown in Figure 5.1. The pores are 50 nm in diameter and rectangular in shape. In cross-section, the pore network appears random and the rectangular pores are only aligned over short (<2 µm) distances. The morphology is very reminiscent of that observed for dense Mn$_3$O$_4$ transformed to MnO, as described in Chapter 3.

Reduction and leaching of macroporous ZnMn$_2$O$_4$ to rock salt MnO maintains the macropore network and does not alter the basic geometry of the grains forming the macropore walls (Figure 5.2a,b). Like the dense ZnMn$_2$O$_4$
Figure 5.1. SEM image of mesoporous MnO cross-section formed through vapor phase leaching of dense ZnMn$_2$O$_4$ in 5%-H$_2$/N$_2$. Reproduced with permission from ref. [103]. © 2006, American Chemical Society.
pellet, vapor phase leaching has induced mesopores into the walls of the macroporous monolith. The fracture surface on the upper right of Figure 5.2c is enlarged in (d), revealing the mesopores are 20-80 nm in diameter and rectangular in shape. Unusually, the rectangular mesopore walls are aligned across each grain.

In an effort to determine the relationship between reduction conditions and resulting morphology, a large section of parameter-space was explored. Flow rate, pressure, ramp rate, and leaching time and temperature were all varied. Surprisingly, no effect on the resulting morphology was observed. If the time, temperature, or flow rate was too low, the leaching of the zinc would not be complete, but the fundamental morphology would be basically unchanged. The pores are always rectangular in shape and average 50 nm in diameter. This is in contrast to the Zn$_2$TiO$_4$ system discussed in Section 5.3. A discussion of the similarities and differences between these two systems occurs in Section 5.4.

In order to understand the phase evolution during the vapor phase leaching process, TGA and TDXRD techniques were employed. Figure 5.3 reveals that the transformation from ZnMn$_2$O$_4$ to rock salt MnO occurs over two clearly defined steps: a low temperature loss at 670 K and a much larger loss at 900 K. As in the reduction of Mn$_3$O$_4$ to MnO in a reducing atmosphere de-
Figure 5.2. SEM micrographs showing inner fracture surfaces of hierarchically porous MnO formed through vapor phase leaching of macroporous ZnMn$_2$O$_4$. The fracture surface in the upper right part of (c) is shown at higher magnification in (d), revealing aligned rectangular pores. (b) Reproduced by permission of The Royal Society of Chemistry, ref [65]. (c) Reproduced by permission from ref. [103]. © 2006, American Chemical Society. (d) Reproduced by permission from ref. [72]. © 2005, Wiley-VCH.
Figure 5.3. Thermogravimetric measurement of spinel $\text{ZnMn}_2\text{O}_4$ (S) in 5%-H$_2$/N$_2$ shows a small step at 700 K due to the transformation to the metastable rock salt $\text{Zn}_{0.33}\text{Mn}_{0.67}\text{O}$ (MR). The large step at 900 K is due to the removal of Zn and its O counterion from the rock salt lattice, leaving rock salt MnO (R). Reproduced with permission from ref. [103].

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scribed in Chapter 4, reduction occurred by 700 K. Here the observed mass loss of 6.3% at 670 K corresponds to the expected mass loss of 6.6% for the reduction of ZnMn$_2$O$_4$ to ZnMn$_2$O$_3$ (Zn$_{0.33}$Mn$_{0.67}$O). The reduction and removal of Zn and its oxygen counterion causes the larger observed mass loss beginning at 850 K (experimental, 28.3%; calculated, 36.4%). The discrepancy between the two mass losses may be due to the incomplete removal of the Zn from the lattice. The resulting Zn:Mn ratio would be 1:9, suggesting 80% of the Zn was removed. Zn$_{0.1}$Mn$_{0.9}$O is approximately the solubility limit for Zn in rock salt at these temperatures.[104]

*Ex-situ* X-ray diffraction is shown in Figure 5.4 for a series of samples heated to the indicated temperatures for 30 min. Starting with the initial macroporous ZnMn$_2$O$_4$, rock salt MnO peaks appear by 700 K. Initially, the rock salt peaks are quite off-set from the expected MnO peak positions (unit cell volume: 84.9 Å$^3$, pure MnO: 87.9 Å$^3$). By 725 K all of the spinel has converted to rock salt, and ZnO has begun to partition out of the metastable Zn$_{0.33}$Mn$_{0.67}$O rock salt lattice. Quantitative phase analysis from Rietveld scale factors indicates that the wurtzite ZnO phase is never more than 8 mol %. After leaching at 925 K for 12 hr, the MnO pattern agrees with the literature values for the pure MnO peak positions.

The leaching of Zn from the metastable rock salt may be described qual-
Table 5.1. Elemental analysis of the initial macroporous spinel ZnMn$_2$O$_4$ and the resulting rock salt material after three different reductions.

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<thead>
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<th>Composition</th>
<th>Zn%</th>
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<td>macroporous spinel</td>
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<td>58</td>
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<tr>
<td>reduced, 925 K 1 h</td>
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<td>42</td>
<td>51</td>
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<tr>
<td>reduced, 925 K 4 h</td>
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<td>45</td>
<td>50</td>
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</table>

Figure 5.4. Ex-situ powder XRD measurements to understand the phase evolution during the reduction and leaching of ZnMn$_2$O$_4$. Note the large initial shift in MnO lattice parameters from the marked expected values. Reproduced with permission from ref. [103]. © 2006, American Chemical Society.
tatively in a ZnO-MnO free-energy diagram (Figure 5.5).[105] From TGA measurement, the Mn$^{3+}$ has transformed to Mn$^{2+}$ with a characteristic loss of oxygen at 670 K. The oxygen deficient spinel ZnMn$_2$O$_3$ is not stable, and XRD patterns show the concurrent transformation to rock salt. This transformation from ZnMn$_2$O$_3$ (A) to rock salt (B) is shown as a large energy drop in Figure 5.5. If the system were closed, partitioning of ZnO out of the metastable rock salt would then occur. In this case the system is open, with a flowing atmosphere to aid in the transport of Zn out of the hot zone. Instead of partitioning, direct evaporation of Zn from the lattice can occur, moving the composition from (B) to (C). From the high-temperature XRD studies we find that both processes do occur, with the direct leaching of Zn from the rock salt lattice dominating. Wurtzite is not stable above 875 K in flowing 5%-H$_2$/N$_2$, suggesting that the free energy schematic does not apply above these temperatures and instead would be between Zn (l)-MnO.

Elemental analysis of the rock salt during the leaching process was determined with EDX analysis. Table 5.1 shows how the Zn:Mn ratio decreases with increasing leaching temperature and time. After 12 h at 750 K, minimal Zn has been removed from the lattice; higher temperatures are required. More than half the Zn is removed after just 1 h at 925 K and with increasing time, the Zn level continues to decrease.
Nitrogen sorption measurements were used to characterize the initial macroporous monolith and the resulting hierarchical pore structures. Table 5.2 shows that the surface area for macroporous ZnMn$_2$O$_4$ is low, as expected for a collection of 1 µm grains, and there is no porosity in the 10-200 nm regime. Reducing the sample at 725 K for 2 h induces the phase transformation to rock salt and the surface area increases by an order of magnitude. The BJH pore size distribution has a peak at 30 nm. Integrating the pore volume between 10-200 nm gives a volume which can be converted to a porosity of 17.5% in that size regime. If the spinel to rock salt transformation resulted in no contraction and all volume loss was expressed as mesopores, a porosity of 13.0% would be expected.

Leaching the rock salt at 925 K increases the surface area and porosity due to the loss of Zn and O. The expected surface area for the resulting material may be calculated by assuming square one dimensional pores 50 nm in diameter and a porosity of 35%, giving a surface area of 11 m$^2$/g. The macropore contribution to this surface area additionally contributes 1 m$^2$/g for a collection of 1 µm cubes. The sum of the mesopore and macropore surface areas compares favorably with the 13.5 m$^2$/g obtained from nitrogen sorption measurements. As well, the cumulative pore volume in the 10-200 nm range matches the volume change expected for the spinel to leached rock salt conver-
Figure 5.5. For the ZnO-MnO system, only two thermodynamically stable phases are present: wurtzite ZnO and rock salt MnO. The 'spinel' ZnMn$_2$O$_3$ (a) is unstable and transforms to the rock salt (b). Evaporation of Zn from the lattice reduces the free energy of the system and drives the composition towards (c). Reproduced with permission from ref. [103]. © 2006, American Chemical Society.
BET and BJH pore measurements

<table>
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<th></th>
<th>SA (m²/g)</th>
<th>pore diameter (nm)</th>
<th>cum. vol. cm³/g</th>
<th>Porosity (10 - 200 nm)</th>
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</table>

Table 5.2. Summary of N₂ sorption measurements during vapor phase leaching of ZnMn₂O₄. The initial macroporous ZnMn₂O₄, Zn₀.₃₃Mn₀.₆₇O formed through reduction at 725 K, and Zn₀.₁Mn₀.₉O after reduction/leaching at 925 K are presented. For each sample, the surface area (SA), average pore diameter (d), and cumulative pore volume in the 10-200 nm are given, as well as the measured porosity and what is expected given changes in structure and composition.

The agreement between these results suggests that all volume loss due to phase transformations and loss of ions is expressed through the formation of mesopores rather than a net contraction of the bulk material. The sorption isotherms for the Zn₀.₁Mn₀.₉O sample shown in Figure 5.6a are characteristic for a porous material with only large (>20 nm) pores; at low partial pressures there is minimal volume of N₂ adsorbed and hysteresis behavior at high partial pressures. The BJH pore size distribution is shown in Figure 5.6b and confirms the presence of mesopores with an average pore diameter of 50 nm. As well, the tail of the macroporous regime is seen as a spike at 250 nm, but the rest of this peak is out of the range for N₂ sorption measurements.
Figure 5.6. Nitrogen sorption measurements of hierarchically porous MnO formed through vapor phase leaching of macroporous ZnMn$_2$O$_4$. (a) Characteristic of a mesoporous material, the sorption isotherms exhibit hysteresis at high partial pressure. (b) BJH pore size distribution shows a peak at 50 nm due to the mesopores, and the beginning of the macropore peak beginning at 250 nm. From ref [65] Reproduced by permission of The Royal Society of Chemistry.
The rectangular mesopores were observed to be aligned over short ranges (<2 µm) in the SEM. The occurrence of rectangular pores is unusual, as well as alignment between the pores, and suggests that crystallography is playing a role in the pore formation process. To understand this relationship between crystallography and morphology, samples were prepared for TEM. Both the final sample (vapor phase leaching at 925 K, Zn_{0.1}Mn_{0.9}O) and an intermediate sample were considered (reduction at 725 K, Zn_{0.33}Mn_{0.67}O). Electron transparent lamella were prepared from each of these samples using a FIB, one of which is shown in Figure 5.7a. The lamella were approximately 14 µm by 4 µm by 50 nm and successfully bisected the rock salt grains in the sample. The gray regions between the grains is epoxy.

Figure 5.8 shows regions from the two different samples. Both the samples show contrast variations due to the presence of pores and these contrast variations appear as aligned striations across local regions 300 - 1000 nm in width. Leaching of the Zn at higher temperature has clearly coarsened the pores, in agreement with the BJH[106] pore size distribution measurements. As well, the pores of the high temperature Zn_{0.1}Mn_{0.9}O sample are more clearly rectangular in shape and the domains of alignment more clearly defined.

With transmission electron microscopy, imaging and diffraction are intrinsically linked. In particular, diffraction patterns may be obtained for specific
Figure 5.7. TEM images of MnO-epoxy lamella prepared with a focused ion beam. (a) At low magnification, cross-sections through individual grains are visible, as are the necks between grains. (b) At higher magnification, contrast variations are present due to aligned mesopores. The region of pores on the left have been tilted into the [100] zone axis (inset).

Reproduced with permission from ref. [103]. © 2006, American Chemical Society.
Figure 5.8. TEM images showing cross sections through two samples. (a) was reduced to rock salt $\text{Zn}_{0.33}\text{Mn}_{0.67}\text{O}$ at 723 K for 2 h and (b) was leached at 925 K for 12 h to form $\text{Zn}_{0.1}\text{Mn}_{0.9}\text{O}$. Reproduced with permission from ref. [103]. © 2006, American Chemical Society.

regions of the sample and the sample may be translated and tilted. By inserting a selected area aperture and tilting into a zone axis, the crystallographic orientation of a particular region of the sample could be determined. For example, in Figure 5.7b, the inset diffraction pattern is obtained for the region of the center left part of the $\text{Zn}_{0.1}\text{Mn}_{0.9}\text{O}$ lamella. To determine grain size, the stage was translated and the displacement at which the zone axis was lost was noted. In the case of the inset in Figure 5.7b, the diffraction pattern is for the [100] zone axis. By overlaying the diffraction pattern on the image and accounting for rotation between the diffraction pattern and image, the pore wall orientation can be determined. We find that the pore walls are composed of $\{100\}$ faces. As well, the [100] zone axis looks directly down the pore channel.
These results are consistent with the \{100\} faces of rock salt being the lowest energy faces.

After tilting into a zone axis with the selected area aperture inserted, the average grain size may also be determined by translating the stage. For the final sample (925 K, Zn$_{0.1}$Mn$_{0.9}$O), the grain diameter ranged between 300-1,000 nm. As the focused ion beam cuts randomly through the grains, most cross-sections will not be through the center of each grain. Thus the average grain size is more towards the higher end of this range. In contrast, the sample which was only heated to 725 K had grains which were markedly smaller in size (200-400 nm).

Diffraction patterns for the final sample are shown in Figure 5.9. The [211] pattern is shown in (a) and the [110] pattern is shown in (b), with expected reflections marked ([211] zone axis: \{02\} and \{11\}; [110] zone axis: \{002\} and \{22\}). As well, superlattice peaks at twice the lattice spacings are present ([211]: \{01\} and \{11\}; [110]: \{001\} and \{10\}). These super lattice reflections were present for both samples and for all zone axes studied. Like rock salt, the superlattice was face centered and not primitive. Other rock salt structures with face centered super-lattice ordering have been observed, such as the MnMg$_6$O$_8$ structure.[107] These superlattice peaks may instead be artifacts from the TEM, such as double diffraction. A reduced sample was studied with
Figure 5.9. TEM diffraction patterns of Zn$_{0.1}$Mn$_{0.9}$O leached at 925 K. (a) [211] zone axis pattern with \{02\overline{2}\} and \{1\overline{1}\overline{1}\} reflections indicated. Superlattice reflections of \{01\overline{1}\} and \{\overline{1}\overline{1}\overline{1}\} are present. (b) [110] zone axis pattern with \{002\} and \{\overline{2}20\} reflections indicated. Superlattice reflections of \{001\} and \{\overline{1}10\} are also present. Reproduced with permission from ref. [103]. © 2006, American Chemical Society.

synchrotron X-ray diffraction and did not show any evidence of superlattice reflections.

5.3 Zn$_2$TiO$_4$ to TiO$_2$

Following our work on the reduction and leaching of manganese oxides, we turn our attention to the ZnO-TiO$_2$ system. Zn$_2$TiO$_4$ is amenable to vapor phase leaching to TiO$_2$ as the titanium ion is difficult to reduce to its metallic state and TiO$_2$ does not sinter rapidly at the temperatures involved. Titania is particularly appealing for vapor phase leaching as there are a variety of
applications involving nanostructured titania. In particular, titania displays interesting photoelectrochemical properties due to its large band gap and the positions on its band edges. Fujishima and Honda demonstrated in 1972 the electrochemical photolysis of water using titania.[108] Since then, titania has been used in dye-sensitized solar cells, water purification, and self-cleaning structures.[109] For solar cells, high surface areas are needed for contact between the dye and the titania, leading to the use of thin films of colloidal TiO$_2$ nanoparticles. The following describes our efforts to form porous titania through vapor phase leaching Zn$_2$TiO$_4$.

**Preparation**  Selective leaching was chosen to form a macroporous monolith of Zn$_2$TiO$_4$. Dense composites of Zn$_2$TiO$_4$ and ZnO were formed from powders of anatase TiO$_2$ (0.02 mol) and wurtzite ZnO (0.1 mol) by mixing and pressing into pellets. Dense biphasic pellets were formed after firing in air at 1473 K for 12 h in a covered alumina crucible. ZnO powder was added around the pellets to maintain a Zn-rich atmosphere during firing. Dilute acid was used to remove the ZnO phase while leaving the Zn$_2$TiO$_4$ unaffected. Initial work on this system used alkali leaching, but Zn$_2$TiO$_4$ is somewhat soluble in concentrated base.

The macroporous Zn$_2$TiO$_4$ was subject to vapor phase leaching in flowing 5%-H$_2$/N$_2$ for 2-12 h at 923-1123 K. See Section 5.2 for a further discussion.
of experimental set-up for the leaching of Zn from transition metal oxides. The resulting monoliths of TiO$_2$ were characterized by X-ray diffraction, N$_2$ sorption measurements, and scanning electron microscopy (SEM). To understand the phase evolution during the vapor phase leaching process, thermogravimetric analysis (TGA), ex-situ thermodiffraction, and solid state $^{67}$Zn and $^{47,49}$Ti NMR were employed. The NMR measurements were performed at the National High Magnetic Field Laboratory, Tallahassee, FL through a collaboration with the Chmelka group and are described in Appendix D.

**Results** The material formed by high temperature firing was characterized by powder XRD before and after acid leaching (Figure 5.10). Before leaching, Rietveld refinement using the XND code reveals two phases: Zn$_2$TiO$_4$ (cubic inverse spinel, Fd$ar{3}$m) and ZnO (wurtzite, P6$_3$mc). Quantitative phase analysis of the initial composite suggests a ZnO:Zn$_2$TiO$_4$ mole ratio of 74:26, in good agreement with the 75:25 expected from the initial mole ratio. After leaching, Zn$_2$TiO$_4$ is the only phase present in the powder pattern. The removal of the ZnO phase results in a significant mass loss, and concurrently a significant increase in porosity of the remaining macroporous Zn$_2$TiO$_4$ (mass loss: 52.7%, expected: 52.4%; porosity: 50%). The agreement between the expected and obtained values can be attributed to the low solubility of titanium into ZnO and the minimal loss of Zn during the original high temperature firing. The
Figure 5.10. X-ray diffraction data, Rietveld fits and difference profiles (from top to bottom) for (a) ZnO/Zn$_2$TiO$_4$ and (b) macroporous Zn$_2$TiO$_4$ after leaching.
morphology evolution during the leaching process is shown in Figure 5.11. The fracture surface shows that the initial composite shown in (a) has minimal porosity with grains 2-5 \( \mu m \) in diameter. Leaching in dilute acid removes the ZnO, leaving a well-connected monolith of Zn\(_2\)TiO\(_4\). As the porosity is due to leaching, the pores are interconnected throughout.

EDX analysis of the elemental composition of the pellet before and after acid leaching is in agreement with the XRD refinements. The initial composite gives a Zn:Ti ratio of 6.5:1 (expected: 6:1) for cross-sections through the material. The outer surface is decorated with the occasional large (20-50 \( \mu m \)) grain which has an elemental composition of 2:1, suggesting it is the inverse spinel. The regions between these large grains are more rich in Zn (9Zn:Ti), possibly to compensate for the migration of Ti to these large grains. After leaching, the material reflects the composition of the inverse spinel with a 2Zn:Ti ratio.

Reduction and leaching of the Zn leaves does not compromise the macro-pore network shown in panel (c) of Figure 5.11. As we have seen in the other cases for vapor phase leaching, the volume loss inherent in this transformation has been expressed through the formation of porosity (d), not a bulk contraction of the monolith. In other systems, such as ZnMn\(_2\)O\(_4\), this volume loss has not affected the grain boundary connectivity. In this case, the connectivity has been reduced and the porous grains are not well-connected. This will be
Figure 5.11. SEM micrographs showing (a) dense composite of Zn$_2$TiO$_4$ and ZnO and (b) the macroporous monolith of Zn$_2$TiO$_4$ that remains after leaching. Reduction and vapor phase leaching of Zn leaves (c,d) hierarchically porous TiO$_2$. 
Figure 5.12. \( \text{N}_2 \) sorption isotherm for a hierarchically porous monolith of TiO\(_2\). No hysteresis is evident until high partial pressures, indicative of the filling of large pores.

\( \text{N}_2 \) sorption isotherms confirm the porosity observed and suggest the average pore diameter is 150 nm. Figure 5.12 shows the isotherm for a leached pellet, showing minimal volume adsorbed until very high partial pressures. This hysteresis behavior is characteristic of the filling of macropores right before bulk condensation. In contrast to the porous MnO of the previous section, with hysteresis behavior starting at 0.80 \( p/p_0 \), the TiO\(_2\) hysteresis does not begin until 0.97 \( p/p_0 \).
Figure 5.13. Thermogravimetric measurement of Zn$_2$TiO$_4$ in 5%-$\text{H}_2$/N$_2$ shows a large step corresponding to the reduction and removal of Zn from the lattice.
The phase evolution during the vapor phase leaching of Zn$_2$TiO$_4$ was studied with thermogravimetric measurements (TGA) and ex-situ thermodiffraction (TDXRD). The TGA trace for Zn$_2$TiO$_4$ in flowing 5%-H$_2$/N$_2$ is shown in Figure 5.13. One large step is observed beginning at 950 K and finishing by 1130 K. The dotted line indicates the expected mass retained for the conversion of Zn$_2$TiO$_4$ to TiO$_2$. The mass continues a slight decline after removal of the Zn, possibly due to reduction of the Ti$^{4+}$. From this single step TGA, it is clear that the removal of Zn occurs at noticeably higher temperatures than the ZnMn$_2$O$_4$ system and without a major reduction in Ti oxidation state.

TDXRD patterns in Figure 5.14 show that the phase pathway is also quite different from the spinel ZnMn$_2$O$_4$ to rock salt MnO conversion. Starting with the inverse spinel Zn$_2$TiO$_4$, a significant mass loss (12%) and color change to blue occurs by 925 K. Despite these changes, the powder pattern remains single phase. By 975 K, a mixture of Zn$_2$TiO$_4$ and the defect spinel Zn$_2$Ti$_3$O$_8$ are present. This new phase is actually Zn[Ti$_{1.5}$$\square$$_{0.5}$]O$_4$ which is a metastable structure in the space group $P4_322$.\[110] The polymorphs of TiO$_2$ (anatase and rutile) appear by 1025 K, and after 12 h at this temperature, rutile is the only phase present. Multiple polymorphs of titania frequently are seen in nanostructured systems where there is competition between surface and volume free energies.\[111] There are several additional low angle peaks present during this
Figure 5.14. *Ex-situ* XRD patterns for Zn$_2$TiO$_4$ heated briefly in 5%-H$_2$/N$_2$ at subsequently higher temperatures. Starting with the inverse spinel Zn$_2$TiO$_4$, the defect spinel Zn$_2$Ti$_3$O$_8$ appears as an intermediate phase. Rutile and anatase polymorphs of TiO$_2$ begin to appear by 1025 K and after sufficient heat treatment, rutile TiO$_2$ is the only phase present.
Figure 5.15. (a) During the early stages of leaching, the surface is covered in a forest of rods, shown in cross-section. (b) Surface curvature creates unusual patterns in this forest. 

transformation to rutile and are attributed to shear phases of slightly reduced titania.[112] Corresponding solid state $^{67}$Zn and $^{47,49}$Ti Nuclear Magnetic Resonance (NMR) measurements were taken of the initial Zn$_2$TiO$_4$ material and the intermediate samples during the leaching processes and are described in Appendix D.

The transformation from inverse spinel through defect spinel to rutile TiO$_2$ requires significant rearrangement of the cations and anions involved. The reduction and leaching of Zn$^{2+}$ from the inverse spinel can be imagined in the following manner: First, the nucleation of Zn$_2$Ti$_3$O$_8$ particles on the surface of Zn$_2$TiO$_4$, presumably in an epitaxial manner. Second, Zn removal from the underlying Zn$_2$TiO$_4$, leading to growth of the intermediate spinel into the grain as rods. Third, conversion of Zn$_2$Ti$_3$O$_8$ to TiO$_2$. In reality, the second and third
Figure 5.16. The volume loss during the Zn leaching of Zn$_2$TiO$_4$ is tracked in a series of micrographs. (a)-(d) show top and cross-sectional views during the leaching processes and (e) and (f) show the final TiO$_2$ rods obtained.
steps happen simultaneously across the sample. Both of these processes rely on diffusion of Zn to the surface for evaporation, which will be hindered by the formation of a passivation layer of TiO$_2$ on the surface. Mass transport appears to happen particularly rapidly at the grain boundaries, leading to loss of grain connectivity. This description of leaching is supported by the formation of aligned rods. The nucleation of grains on the Zn$_2$TiO$_4$ surface after a brief reduction is shown in Figure 5.15. The first micrograph shows a cross-section through the initial dendrites that form, while the second image shows both top-down and a cross-section of the material. Surface curvature leads to unusual patterning of the rods. Figure 5.16 shows SEM images for aligned rods of intermediate Zn$_2$Ti$_3$O$_8$ and the final TiO$_2$. Micrographs (a-c) are different views of the same sample which was leached at 923 K for 12 h. In panel (a), two grains are shown with a coating of TiO$_2$ dendrites, which can be seen clearly as aligned rods in panel (b). The underlying dense spinel material is visible as well, and shown in cross-section in panel (c). These aligned dendrites are found under other leaching conditions. A sample leached at 973 K for 8 h is shown in panel (d), again with highly aligned rods radiating away from the center of the grain. Panels (e) and (f) shows that the rod structure is preserved with increasing temperature, although the average diameter begins to increase. The sample shown in (e) was reduced at 998 K for 12 h and the sample in (f) was formed at 1023 K for 4 h.
5.4 Discussion

As described in this chapter’s introduction, selective leaching appears to be the ceramic analog to Raney nickel formation. In both cases, a sacrificial element is removed from an atomically mixed binary or ternary material, creating a volume loss. In the Zn$_2$TiO$_4$ situation, this analogy is apt as the pores in both routes form on the surface and grow inwards as dendrites. Crystallography plays some role, as the transformation of Zn$_2$TiO$_4$ to Zn[Ti$_{1.5}$□$_{0.5}$]O$_4$ is topotactic. The leaching of zinc from the reduced ZnMn$_2$O$_4$ spinel is a two step process where mesopores nucleate and penetrate through the grains during the low temperature reduction. At higher temperatures, the leaching of zinc occurs within a mesopore template to control this additional volume loss. Thus, the Raney nickel analogy is a good comparison, but is not complete. In the two systems studied here, crystallography, defects, and other microstructural issues frequently arise that make the leaching process much more complicated than for Raney nickel. Predicting morphologies may not be possible, but intelligent design can point towards other likely systems.

Starting with the sacrificial element, zinc has a variety of properties which lend it to vapor phase leaching at moderate temperatures. Zinc is inexpensive, easily reduced to its metallic state, has a low melting point, and a high vapor pressure. Of the other elements, the few others that do possess these properties
Properties of potential sacrificial elements

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta G^\circ_f$ (kJ/mole O$_2$)</th>
<th>mp (K)</th>
<th>vp at mp (atm)</th>
<th>vp at 800 K (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>-640</td>
<td>419.6</td>
<td>$2 \times 10^{-4}$</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>Tin</td>
<td>-530</td>
<td>231.9</td>
<td>$8 \times 10^{-26}$</td>
<td>$1 \times 10^{-14}$</td>
</tr>
<tr>
<td>Lead</td>
<td>-385</td>
<td>327.4</td>
<td>$6 \times 10^{-12}$</td>
<td>$6 \times 10^{-8}$</td>
</tr>
<tr>
<td>Sodium</td>
<td>-770</td>
<td>98</td>
<td>$1 \times 10^{-10}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Magnesium*</td>
<td>-1145</td>
<td>650</td>
<td>$4 \times 10^{-3}$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 5.3. Free energies of formation of the oxide species, elemental melting points (mp) and vapor pressures of the liquids at the melting points and at 800 K. Values calculated from CRC Handbook.[81] * Vapor pressure for solid species.

are too hazardous or expensive to be considered for applications. In Table 5.3, various relevant properties are given for a few select elements. The free energy of formation of the oxides ($\Delta G^\circ_f$) at room temperature is given, as well as the melting points, vapor pressure of the liquid at the melting point temperature, and the vapor pressure at 800 K. Comparing zinc and tin, both are easily reduced and exhibit low melting points. Unfortunately for vapor phase leaching, tin shows virtually no volatility, suggesting that a better strategy would be to partition tin out as a liquid followed by solution leaching upon cooling (see Appendix C). Lead and sodium may both be reduced and are low melting, but are not amenable to applications. Magnesium is almost identical to zinc, except is much harder to reduce.

While zinc is the most suitable elemental species for vapor phase leach-
ing, a variety of other reactions may be conceived that achieve similar results through the use of binary gaseous species. Halogenated species are frequently quite volatile and a variety of oxides show some volatility in air as well. Flowing environments would be necessary to remove the volatile species so that coarsening does not occur (as gas-phase grain growth can be quite rapid). One such example is the formation of high-surface area ceria formed through sublimation of tin dioxide.[113]

Having considered the sacrificial element, the other half of vapor phase leaching is the material that remains. Several clear trends have appeared from our work with the transition metal oxides (routes involving reduction have included $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{O}$, $\text{ZnFe}_2\text{O}_4$, $\text{Mn}_3\text{O}_4$, $\text{ZnMn}_2\text{O}_4$, and $\text{Zn}_2\text{TiO}_4$; $\text{Co}_3\text{O}_4$ and $\text{V}_2\text{O}_5$ are found in Appendix C). First, the volume loss must occur at temperatures where solid state diffusion will not close the resulting pores. In cases where the product has been a metal, such as nickel, cobalt, or iron, transient pores may occur, but the temperatures are high enough that they are rapidly smoothed out. Second, large grains help induce pore formation by pinning the second phase on top of the first. The necessary grain size is a function of the temperature and the corresponding solid state diffusion rate. This observation was particularly clear in the reduction of $\text{Zn}_2\text{TiO}_4$, where the dendrite formation on large grains was pinned to the underlying unleached material. In con-
trast, small grains adopted a more worm-like pore morphology. For Zn$_2$TiO$_4$, aligned pores were seen for grains greater than $>2\mu$m in diameter, while for ZnMn$_2$O$_4$, grains as small as 200 nm ended up perforated. Strong necking between the grains may also encourage pore formation, as this helps to prevent a contraction of the grain during the volume loss. Third, the morphology obtained is surprisingly independent of leaching parameters. For Zn$_2$TiO$_4$ and ZnMn$_2$O$_4$, a variety of heating rates, leaching temperatures, and times were tried, including multistep reductions, but the resulting morphology was largely controlled by the phase transformations and ion mobility in the system. With that said, for systems where solid state diffusion is more rapid, as in the V$_2$O$_5$ to V$_2$O$_3$ conversion, care must be taken not to allow excessive sintering after the pores form.

5.5 Conclusion

In this chapter, selective leaching of a sacrificial element have been used to induce mesopores in dense materials. In the leaching of Zn$_2$TiO$_4$, the sacrificial zinc may be entirely removed, leaving behind titania. Zinc appears to be an ideal sacrificial element, as it is readily reduced and as a metal has a high vapor pressure. We find that selective leaching may be applied sequentially after a transformation which induces mesopores. In the reduction and leaching
of ZnMn$_2$O$_4$, mesopores are initially nucleated at low temperature during the spinel to rock salt phase transformation and at higher temperatures the zinc is removed, leaving a highly mesoporous material. To reduce the surface free energy of the mesopores, the pores adopt low energy faces and run parallel to these planes. In the following chapter, the crystallographic control of pore orientation is verified through the growth and reduction of spinel films. The resulting thin films show aligned pores running in crystallographically determined directions.
Chapter 6

Hydrothermal Growth and Conversion of Thin Films

In the previous chapter, the formation of pores during the spinel to rock salt conversion was dictated by the topochemical nature of the transformation. To minimize surface energy, rectangular pores formed which were aligned the \(<100>\) MnO crystallographic directions. As such, controlling the initial orientation of the spinel grains could lead to control of the resulting pore orientation. In this chapter, a new method to form epitaxially oriented films of \(\text{Mn}_3\text{O}_4\) and \(\text{ZnMn}_2\text{O}_4\) is developed. Reduction and vapor phase leaching of these films to MnO occurs in a topochemical manner, and the resulting pore network is explored.
6.1 Prior work

The Lange group has grown a variety of epitaxial thin films via heterogeneous nucleation on single crystal substrates. These routes have been used to form thin films of BaTiO$_3$,[114] PbTiO$_3$,[115] KTaO$_3$,[116] and ZnO.[117, 118] The success of this method relies on starting with ions dissolved in solution, and then changing the conditions to favor the nucleation of the desired phase. By providing a substrate with a similar surface chemistry in the solution, one can lower the barrier to nucleation and obtain preferential oriented nucleation on the substrate surface. To form oxides, hydrothermal conditions are frequently employed.

The percent yield of a phase as a function of temperature and $p$H describes the free energy of formation of the desired phase. For example, at 423 K, ZnO precipitation occurs between $p$H 7 and 10.5, and outside of this $p$H range there is insufficient driving force for nucleation.[117] Knowing the shape of the free energy curve is useful in determining optimal growth conditions. If the driving force to nucleation is too great, all of the ions will precipitate simultaneously, resulting in minimal secondary growth of the crystallites. In contrast, if the driving force to nucleation is low, nucleation will be rare and the particles which do form will be in a solution still containing a high concentration of ions, leading to significant secondary growth. Insertion of a lattice-matched
substrate will decrease the barrier to heterogeneous nucleation, but will not affect the homogeneous nucleation rate. Ideally, a pH and temperature are selected which barely favor nucleation, thereby biasing nucleation so that heterogeneous nucleation dominates and the film can grow from the remaining ions in solution.

6.2 Mn$_3$O$_4$ on MgAl$_2$O$_4$

Thin films of Mn$_3$O$_4$ were grown by the Roy group in 1970 using vapor phase transport of MnCl$_2$ onto (100) MgO substrates.[119] Epitaxial (001) oriented Mn$_3$O$_4$ films were formed on (100) MgO surfaces. Reduction of these films at 1273 K converted the spinel structure to MnO, which began to diffuse into the substrate. XRD patterns show that the structural relationship between the Mn$_3$O$_4$ and MnO phases was conserved, with the $<100>$ MnO direction normal to the substrate surface. Oxidation to Mn$_2$O$_3$ resulted in a polycrystalline film.

In the following, a new hydrothermal method to form Mn$_3$O$_4$ films is developed. At room temperature and pressure, the Pourbaix diagram suggests that the spinel phase is stable from a pH of 6 to 15.[120] Hydrothermal conditions like those employed here typically shift these boundaries down in pH but
do not radically distort the diagram. Prior work involving the hydrothermal growth of Mn\(^{3+}\) oxides has focused on the formation of manganese zinc ferrite powders for their magnetic properties.[121]

**Preparation**  Hydrothermally grown thin films of Mn\(_3\)O\(_4\) were grown on single crystal substrates of MgAl\(_2\)O\(_4\). Substrates from MTI with (100) and (111) orientations were cleaned by sonicating with acetone, ethanol, and firing in air at 973 K for 2 h. Solutions of 0.1 M manganese acetate were prepared using Millipore water (18.2 M\(\Omega\)), and the pH was adjusted to the desired level with glacial acetic acid or NaOH. Parr bombs (24 ml capacity) were filled with 10 ml of the acetate solution, and then a substrate held in a Teflon holder was placed in the solution. The holder suspended the substrate half way down from the top of the water level. Films were then grown on the substrates by heating in an oven at 423 K from 4 h to 7 days. Following growth, the substrates were removed and rinsed with ethanol and water to remove excess powder from the surface. To coalesce the islands, films were heated at 1073 K for 2 h in air. Films were regrown up to four times to build up a thicker layer of precipitated material. Hydrothermal reactions were also conducted without substrates present to quantify percent yield as a function of pH, temperature, concentration, and reaction time.

The thin films were characterized with thin film XRD using a Philips
Hydrothermal reactions were conducted on aqueous solutions containing manganese acetate to determine the solubility boundaries of manganese under hydrothermal conditions. Following a hydrothermal reaction, a large quantity of precipitated brown powder is observed, and under some conditions a brown film forms on the surface. XRD patterns of the precipitated powder reveals that at low temperatures (363 K), the intermediate phase MnO(OH) is observed and with increasing temperature, the powder is phase
Figure 6.2. SEM micrograph of Mn$_3$O$_4$ powder precipitated from 0.1 M Mn acetate after 18 h at 423 K and a starting pH of 5.1.

pure Mn$_3$O$_4$. Rietveld refinement of the powder to the $I4_1/amd$ phase of Mn$_3$O$_4$ is shown in Figure 6.1 and gives a unit cell value of 314.50 Å$^3$, in agreement with the known value of 313.82 Å$^3$. Trace amounts of MnOOH in the sample were also refined and shown in Figure 6.1. Percent yield of Mn$_3$O$_4$ was found to vary greatly with pH, with no powders forming below pH 4.5, and by pH 5.5 the percent yield is 30%. A SEM micrograph of these powders is shown in Figure 6.2, with sharply faceted polyhedra grains 0.5-2 µm in diameter. The diameter of the grains was found to vary with pH, with fewer grains nucleating at low pH and showing extensive coarsening, while at higher pH, the nucleation rate was more rapid, and less secondary growth led to smaller
crystallites. The nucleation rate was also found to vary vertically in solution, with minimal precipitation near the bottom of the vessel and high levels of growth occurring near the liquid surface. In some cases, the precipitation near the surface was so extensive that macroscopic films would form on the surface which were thick enough to be handled. By immersing a clean glass slide at an angle throughout the solution, it was found that heterogeneous nucleation of Mn$_3$O$_4$ primarily occurred in the upper half of the solution, and within a few millimeters of the liquid-gas interface, growth was significantly accelerated. The pH after these reactions typically drops by 0.5, which may be explained by the net reaction:

$$3\text{Mn}^{2+} + 4\text{OH}^- \rightarrow \text{Mn}_3\text{O}_4 + 4\text{H}^+ + 2\text{e}^- \quad (6.1)$$

Precipitation of the Mn$_3$O$_4$ from manganese acetate requires an oxidation of some of the Mn$^{2+}$ to Mn$^{3+}$, as indicated by the $2\text{e}^-$ in the above equation. As precipitation is greatest at the liquid-air interface, the oxidation appears to occur through an oxygen gas mediated reaction (Equation 6.2). The role of oxygen in forming Mn$_3$O$_4$ hydrothermally from Mn$^{2+}$ has previously been shown.[121]

$$3\text{Mn}^{2+} + 3\text{OH}^- + \frac{1}{2}\text{O}_2 \rightarrow \text{Mn}_3\text{O}_4 + 3\text{H}^+ \quad (6.2)$$

Thin films of Mn$_3$O$_4$ were grown on (100) and (111) substrates of MgAl$_2$O$_4$. 

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Figure 6.3. SEM micrographs of (100) MgAl\(_2\)O\(_4\) single crystal surfaces after growth of Mn\(_3\)O\(_4\) at \(p\text{H}\) values of (a) 4.5, (b) 5.0, and (c) 5.5. The films were grown with a 0.1 M acetate solution at 423 K for 18 h.

Figure 6.4. SEM of Mn\(_3\)O\(_4\) grown on (111) MgAl\(_2\)O\(_4\) at pH 5.0 and 423 K.
under identical hydrothermal conditions to the powder samples. The substrates were suspended polished side down in solution to prevent precipitation of crystallites onto the film surface. As found in the powder precipitation studies, $pH$ had the largest effect on precipitation. SEM micrographs are shown in Figure 6.3 for three different $pH$ values for films grown on (100) MgAl$_2$O$_4$. Starting with $pH$ 4.5, the substrate is largely unaltered, with isolated square pyramidal islands formed on the surface. Across an entire substrate, the islands are aligned, and have in-plane edges running in the substrate $<110>$ directions. With increased $pH$ the islands shrink in size and are more numerous on the substrate and by $pH$ 5.5 the islands have begun to coalesce. Along with $pH$, film growth also depended on solution concentration and reaction time. Lower concentrations produced cleaner films with fewer mis-aligned grains, while higher concentrations led to more material which had nucleated in solution and subsequently attached to the film. Growth on a (111) MgAl$_2$O$_4$ substrate is shown in Figure 6.4, with triangular islands beginning to coalesce.

From the SEM micrographs, the films appear to be oriented both in-and out-of-plane with the substrate. Thin film XRD was used to characterize the films through a combination of on-axis $\theta$-$2\theta$ and off-axis $\phi$-scans and $\omega$-rocking curves. Figure 6.5a shows thin film XRD patterns collected for a film grown on
Figure 6.5. XRD scans of Mn$_3$O$_4$ grown on (100) oriented spinel. a) Out-of-plane orientation characterized by $2\theta$-$\theta$ and b) In-plane orientation of the film determined by $\phi$ scans of off-axis $\{112\}$ reflections of Mn$_3$O$_4$ and the $\{202\}$ substrate reflections.
(100) MgAl$_2$O$_4$. Only the (004) Mn$_3$O$_4$ peak is present with the substrate peaks. Off axis $\phi$-scans of the substrate 202} and film {112} reflections are shown in Figure 6.5b. On-axis $\omega$-rocking curves give a FWHM of 0.2° [(004) reflection], and off-axis $\omega$-rocking curves also give a FWHM of 0.2° [(112) reflection]. For the (111) substrates, the (101) Mn$_3$O$_4$ reflections are present. In-plane orientation of the film was studied with off-axis $\phi$-scans of the film {103} reflections and substrate {113} reflections.

To further increase the smoothness of the films, some were heat treated to 1173-1223 K. Above 1273 K, Mn$_3$O$_4$ will rapidly form a solid solution with MgAl$_2$O$_4$. As the film and substrate are essentially isostructural, the thermal expansion coefficients track each other on heating (expansion at 1273 K: substrate 0.7%, film 0.6%).

**Epitaxial relationship** The substrates are MgAl$_2$O$_4$ single crystals, which has a cubic spinel structure with $a = 8.0831$ Å. The films of Mn$_3$O$_4$ and ZnMn$_2$O$_4$ (described in the following section) are isostructural; both have structures based on the spinel with octahedrally coordinated Mn$^{3+}$. These cations undergo Jahn-Teller distortions and elongate the octahedra along the $c$-axis. As such, the resulting structures are tetragonal with longer $c$-axes than comparable spinel phases. To further complicate the comparison between the films and substrate, the unit cells are rotated by 45° about the $c$-axis and the lengths of a
Figure 6.6. The (a) Mn₃O₄ and (b) MgAl₂O₄ unit cells, with the Mn₃O₄ cell rotated by 45° so as to continue the structure of the underlying MgAl₂O₄. This unit cell orientation is preserved in (c-f). Approximately coplanar reflections are shown for this orientation of the film unit cell with the substrate: (c) (001)ᵥ and (001)ᵣ, (d) (112)ᵥ and (202)ᵣ, (e) (101)ᵥ and (111)ᵣ, (f) (103)ᵥ and (113)ᵣ.
<table>
<thead>
<tr>
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</tr>
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<tr>
<td>a, c (Å)</td>
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<td>Mn_3O_4</td>
</tr>
<tr>
<td>ZnMn_2O_4</td>
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<td>MgAl_2O_4</td>
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<table>
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<th>Lattice Mismatch</th>
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<td>orientation:</td>
</tr>
<tr>
<td>Mn_3O_4</td>
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<td>ZnMn_2O_4</td>
</tr>
</tbody>
</table>

Table 6.1. Summary of lattice parameters for the relevant phases, and the lattice mismatch is calculated for epitaxial growth on (100) and (111) substrates. The pseudocubic cell parameters (a_{pc}) were calculated by averaging the lengths and b are divided by \sqrt{2}. Unit cell parameters are found in Table 6.1, as well as the pseudocubic dimensions for Mn_3O_4 and ZnMn_2O_4.

In Figure 6.6a,b, the Mn_3O_4 unit cell is shown above the MgAl_2O_4 structure with the c-axes parallel. For the structures to be continuous across the interface, the Mn_3O_4 has been rotated by 45° about the c-axis. For films grown on the (100) substrates, the presence of only the (004) reflection indicates the c-axis of the film is normal to the substrate (Figure 6.6c). In-plane orientation may be determined from the \phi-scans. The superposition of the \{112\} film and \{202\} substrate reflections indicates the in-plane component of the planes are
parallel, as shown in Figure 6.6d. From these measurements, the film growth is thus determined to be an epitaxial continuation of the underlying spinel crystal structure. The narrow FWHM (0.2°) of the ω-rocking curves is a reflection of the low lattice mismatch when the Mn$_3$O$_4$ c-axis is normal to the substrate (Table 6.1).

Films grown on the (111) substrates had the (101) vector normal to the substrate. This reflection is the (111) reflection in the pseudocubic cell, and drawn schematically in Figure 6.6e. Off-axis scans show \{103\} film and \{113\} substrate reflections occur at the same in-plane angles. These reflections are drawn schematically in Figure 6.6f. Through a combination of on- and off-axis scans, the film orientation is shown to be a continuation of the underlying spinel lattice.

6.3 ZnMn$_2$O$_4$ on MgAl$_2$O$_4$

The hydrothermal synthesis described in the previous section was also extended to the formation of ZnMn$_2$O$_4$ powders and films. ZnMn$_2$O$_4$ is a stable phase in water and will precipitate even at room temperature with sufficient time.[122] To accelerate this precipitation, we used hydrothermal conditions.
Preparation  Thin films of ZnMn$_2$O$_4$ were prepared in a similar manner to the Mn$_3$O$_4$ films prepared in Section 6.2. Solutions containing 0.1 or 0.05 M acetate species (with a 1:2 Zn:Mn acetate ratio) were prepared and heated with a suspended MgAl$_2$O$_4$ substrate at 423 K for 2-72 h. Unlike in the previous section, optimal thin film growth appeared when the pH was not adjusted with acid or base addition. The roles of pH, time, and concentration were all studied. Reactions without substrates were also used to determine which phases were present and to calculate percent yield.

Epitaxial orientation of the films was studied with thin film X-ray diffraction. Elemental analysis was performed with energy dispersive X-ray analysis (EDX) of the deposited ZnMn$_2$O$_4$ films and through EDX and Rietveld refinement of the precipitated powders.

Results  Hydrothermal reaction of the acetate species precipitated ZnMn$_2$O$_4$ powders. Figure 6.7 shows the XRD powder pattern and corresponding Rietveld fit to the $I4_1$/amd structure of ZnMn$_2$O$_4$. No other phase is present and the unit cell volume of 301.40 Å$^3$ matches well with the literature value of 302.44 Å$^3$. The refined occupancies maintain the Zn:2Mn ratio, indicating that the precipitated powder is of the expected composition. Elemental analysis of the precipitated powders was measured with EDX and gave an approximate stoichiometry of Zn$_{0.96}$Mn$_{2.04}$O$_4$. The corresponding powder is shown in Fig-
Figure 6.7. XRD pattern of precipitated ZnMn$_2$O$_4$ powder with Rietveld fit super-imposed and the difference profile shown below.

Figure 6.8 with faceted octahedral grains. The kinetics of grain growth were studied as a function of time, with 0.05 M solutions held at 423 K for 4, 8, and 64 h. After 4 h, faceted crystallites are formed 50-200 nm in diameter. Coarsening of these particles with time leads to larger grains 0.1-1 µm in diameter by 64 h. As with Mn$_3$O$_4$, excessive acidity (pH less than 4.9) prevented the precipitation of the oxide species. As the stability regime for ZnO is between 7 and 10.5 under identical hydrothermal conditions, the precipitation of zinc from solution must be driven by the manganese.[117]

Films were prepared hydrothermally on (100) and (111) MgAl$_2$O$_4$ in a similar manner to the Mn$_3$O$_4$ films. The resulting morphology was similar to the epitaxial islands of Mn$_3$O$_4$, with a square pyramidal or triangular shape, de-
Figure 6.8. ZnMn$_2$O$_4$ powder precipitated after 64 h at 423 K and a starting pH of 6.5.

Figure 6.9. SEM micrograph of ZnMn$_2$O$_4$ thin film in plan view. The film was grown in a 0.05 M acetate solution with a pH of 6.5 (natural) for 3 days at 423 K.
pending on the substrate orientation. The nucleation and growth rates were
found to be slower for the ZnMn$_2$O$_4$ phase, making time a key parameter in
the growth of continuous films. A film grown at a pH of 6.5 and concentration
of 0.05M for 3 d is shown in Figure 6.9. Cross-sectioning the film reveals it is
750 nm thick and dense. Heating for 4 hours or less produced films less than
300 nm and the faceted morphology is not fully developed. Elemental compo-
sition of the films was determined with EDX measurements and gave a Zn:Mn
ratio of 37:63, corresponding to Zn$_{1.1}$Mn$_{1.9}$O$_4$.

As ZnMn$_2$O$_4$ is isostructural with Mn$_3$O$_4$ and appeared to grow with the
same morphology and orientation as the Mn$_3$O$_4$ films, we can expect similar
growth orientations. Thin film XRD of the films grown on (100) substrates
only shows (004) peaks for $\theta$-2$\theta$ scans (Figure 6.10a). The (111) substrates have
ZnMn$_2$O$_4$ reflections at multiples of (101) (Figure 6.10b).

For the (100) substrate, off-axis $\phi$-scans of the substrate \{220\} and film \{112\}
reflections are shown in Figure 6.10c. Similar scans are shown in Figure 6.10d
for the (111) substrate with film \{103\} reflections and substrate \{113\} reflec-
tions. As in the Mn$_3$O$_4$ films, the long c-axis points out of plane for the (100)
substrate, but is forced into plane for the (111) substrates, creating a large lat-
tice mismatch.

On-axis and off-axis $\omega$-rocking curves for the films grown on the (100)
Figure 6.10. Thin film XRD scans of ZnMn$_2$O$_4$ films on (a) (100) and (b) (111) MgAl$_2$O$_4$ substrates. Off-axis $\phi$-scans show the (c) (100) and (d) (111) substrates and films, with the reflections indicated.
substrate have are quite narrow (FWHM on-axis (004): 0.05°; FWHM off-axis (112): 0.15°). In contrast, the films grown on (111) substrates exhibit broader $\omega$-rocking curves (FWHM on-axis (202): 0.75°; FWHM off-axis (103): 1.15°).

**Epitaxial relationship**  Thin film diffraction of the ZnMn$_2$O$_4$ films grown on (100) and (111) substrates reveals identical crystallographic relationships as found for the Mn$_3$O$_4$ films. In both orientations, the films are an epitaxial continuation of the underlying spinel lattice. The lattice mismatch for ZnMn$_2$O$_4$ grown on these two orientations of MgAl$_2$O$_4$ is listed in Table 6.1. The mismatch on the (100) substrates is extremely low, leading to narrow $\omega$-rocking curves. In contrast, films grown on the (111) substrate had much broader $\omega$-rocking curves due to the large lattice mismatch between the tetragonal and cubic cells in this orientation.

### 6.4 Topochemical reduction

Reduction in the bulk of Mn$_3$O$_4$ and ZnMn$_2$O$_4$ to MnO induced mesopores 30-50 nm in diameter due to the volume losses intrinsic in this transformation. Prior work suggests that the transformations are topochemical and conserve the oxygen sublattice (Section 5.2). In this section, the epitaxial films which have been grown hydrothermally are reduced and the corresponding crystal-
lographic and morphological changes are characterized.

**Preparation**  Thin films of Mn$_3$O$_4$ and ZnMn$_2$O$_4$ were reduced in a tube furnace under flowing 5% H$_2$ at 723-923 K for 1-4 h. Following reduction, the films were studied with thin film XRD and SEM. Samples were prepared for the SEM by fracturing with a diamond scribe and mounting with top-down and cross-section orientations. Elemental composition of the films following reduction was determined using a FEI Sirion SEM with EDX capabilities.

**Results**  Reduction of the Mn$_3$O$_4$ and ZnMn$_2$O$_4$ resulted in a 16% and 42% volume loss, respectively. SEM imaging of the resulting films shows that for the MnO films formed from Mn$_3$O$_4$, the resulting films have cracks 30-100 nm in diameter covering the surface and no clear mesoporosity in cross-section. MnO films formed from ZnMn$_2$O$_4$ films also did not appear ordered from above, but in cross-section, aligned rectangular pores were observed through the sample. Figure 6.11 shows a representative set of pores for a (100) film. The walls of the pores are composed of \{100\} faces and the pores appear to run in the <100> direction. The average pore diameter is approximately 30-50 nm, which is similar to the dimensions found in bulk samples. Unlike in the bulk polycrystalline samples, the average pore direction is not isotropic; instead the pores are aligned across the entire substrate. Cross-sections of the (111) films
Figure 6.11. (100) ZnMn$_2$O$_4$ thin film after reduction and vapor phase leaching to MnO, shown in cross-section.
revealed a similar morphology, but with the pores rotated by approximately 45° (Figure 6.12). Heat treatment of the films at higher temperatures (1100 K) preserves the pore morphology, but some coarsening does occur, with pores ranging from 50-70 nm.

The difference between the MnO films from Mn₃O₄ and ZnMn₂O₄ films likely arises out of the difference in volume loss and how it was expressed. In both samples, the initial spinel to rock salt transformation likely nucleates pores throughout the film. The leaching of zinc at higher temperature enlarges these pores, making them more visible in the SEM. The appearance of random porosity on the outer surface is similar to that observed in bulk samples; fre-
Figure 6.13. $\theta$-2$\theta$ scan of (100) MnO film formed upon reduction of ZnMn$_2$O$_4$ film on (100) MgAl$_2$O$_4$.

Consequently the rectangular, aligned nature of the porosity is only visible in cross-section. The complete leaching of Zn from the rock salt lattice is confirmed by EDX: only Mn, O, and the substrates elements were observed after reduction at 923 K for 4 h.

MnO films formed from ZnMn$_2$O$_4$ were studied with thin film XRD to correlate crystallography and morphology. Thin film XRD reveals the transformation to MnO occurred in a topochemical manner, with the resulting crystallographic relationships: $(100)_{film}||(100)_{sub}$, $(111)_{film}||(111)_{sub}$. Figure 6.13 shows a $\theta$-2$\theta$ scan of a (100) MnO film on a (100) MgAl$_2$O$_4$ substrate. While there is out of plane alignment, $\omega$-rocking curves indicate that the resulting film is not highly epitaxial [on axis (200) scan: 5° FWHM].
Figure 6.14. (111) MnO film formed upon reduction of ZnMn$_2$O$_4$ film on (111) MgAl$_2$O$_4$.

(a) $\theta$-$2\theta$ scan and (b) $\phi$-scans of the 200$_f$ and 400$_{sub}$ reflections.
Figure 6.15. A delaminating section of (001) ZnMn$_2$O$_4$ film, 500 nm in thickness. (b) After reduction the film remains intact, and (c) aligned square pores perforate the delaminated region.
Similarly, reduction of films grown on (111) substrates lead to poorly aligned epitaxial films. Figure 6.14 shows a $\theta$-2$\theta$ scan of a (111) MnO film on a (111) substrate and the corresponding off-axis $\phi$-scans for the (200)$_f$ and (400)$_{sub}$ reflections. The $\phi$-scans are quite broad, as are the $\omega$-rocking curves [on axis (111): $7^\circ$ FWHM; off axis (200): $5^\circ$ FWHM]. The curve width is likely due to the poor lattice matching (10%) between the resulting MnO films and the substrate and the low temperatures of the reduction.

A partially delaminated sample gave insight into the reduction process. Starting with a ZnMn$_2$O$_4$ film which had some delamination, Figure 6.15a, the sample was reduced, leached, and cross-sectioned. Figure 6.15b,c shows that even in regions where there is no contact with the substrate, the resulting pores are still aligned with the substrate. This indicates that the transformation is intrinsically topochemical and not due to nucleation of the MnO phase off of the substrate.

### 6.5 Discussion

Hydrothermal growth of thin films continues to expand as a low-cost method to form epitaxial structures. Here we have extended the technique to two spinel systems, Mn$_3$O$_4$ and ZnMn$_2$O$_4$. Hydrothermal growth of films is an
amazingly robust method; for both compositions epitaxial films were formed on the first attempt. Film growth was optimized by varying pH, concentration, temperature, and reaction time for the two compounds. The thickest, smoothest Mn₃O₄ were formed with a starting solution of 0.1 M manganese acetate at pH 5.0 which was heated to 423 K for at least 8 h. The most continuous ZnMn₂O₄ films were grown in 0.05 M acetate solution without pH adjustment at 423 Kf for at least 24 h. In all cases, the films grew epitaxially as a continuation of the underlying spinel lattice.

Once prepared, the epitaxial spinel films were reduced in 5%-H₂ to study the topochemical nature of the transformation and to further correlate crystallography with the resulting morphology. From thin film XRD patterns of the reduced samples, the transformation is clearly topotactic in nature. Studying a delaminated sample removed the role of the substrate in the reduction, and suggested that the topotactic transformation was intrinsic to the film and not nucleated by the substrate.

Transformations in dimensionally confined materials in 2D (thin films) or 1D (materials infiltrated into pores) frequently exhibit different morphologies due to geometric or surface effects. For example, diblock copolymers which assemble into ordered domains as thin films will likely be isotropic in the bulk. Here, we found that the Mn₃O₄ system, with a 16% volume loss, did
not exhibit the bulk behavior upon reduction and no oriented mesopores were observed. The volume loss instead appeared as random cracks throughout the material. In contrast, reduction and vapor phase leaching of ZnMn$_2$O$_4$ thin films mimicked the bulk behavior, leading to rectangular, aligned pores.

Similar transformations can be imagined in other epitaxial thin films. Zn$_2$TiO$_4$ promises to be particularly successful, as the surfaces of the bulk samples typically showed more aligned porosity than the internal surfaces. In the titania system, the leaching temperature was quite high and some coarsening occurs in the bulk. For thin film, the temperatures required for vapor phase leaching remain the same as with the bulk samples, but much shorter times are required due to the short diffusion path length and the smaller amount of material required to volatilize ($10^{-4}$ g instead of 0.1 g Zn). Preliminary results of spin coating zinc and titanium precursors onto MgO single crystals was promising, with epitaxial growth of Zn$_2$TiO$_4$. Attempts to grow Zn$_2$TiO$_4$ hydrothermally were not successful. A variety of compounds of type Zn$_x$V$_{2.5}$O$_{2x+1}$ exist and should be amenable to thin film growth. Reduction of zinc vanadates in the bulk is quite promising (50 nm aligned pores) and would likewise benefit from the shorter reduction times found in thin film reductions to prevent coarsening (Appendix C).
6.6 Conclusion

In this chapter, the hydrothermal growth of Mn$_3$O$_4$ and ZnMn$_2$O$_4$ spinel films has been developed. The films grow epitaxially on MgAl$_2$O$_4$ substrates as a continuation of the substrate crystal structure. Through the choice of appropriate growth conditions, nucleation of isolated islands or dense films up to 2µm thick may be formed. Reduction and vapor phase leaching of these films to MnO occurred topochemically with [001]$_{MnO}$||[001]$_{sub}$. For the ZnMn$_2$O$_4$ films, the large volume loss was expressed as rectangular pores oriented along $<100>$ with walls composed of {100} planes. As the films are single-crystalline, the resulting pore network is macroscopically aligned across the entire substrate. Such macroscopic control of mesopore orientation is quite unusual, particularly given that the pore walls remain single crystalline across the substrate.
Appendix A

Thermodynamics of Perovskite Metathesis

Here we calculate the thermodynamics of formation for the assisted metathesis reactions found in Chapter 2. Starting with the known values of $\Delta G_f$ for the various species involved, the $\Delta_r G$ may be calculated as the difference between the summation of the reactant and product $\Delta G_f$ values. In Table A.1, the observed reaction between PbSO$_4$ and K$_2$CO$_3$ at room temperature is explained by the $\Delta_r G$ of -64.336 kJ mol$^{-1}$. The assisted metathesis reactions which yield perovskites are shown in Table A.2. By summing the $\Delta G_f$ at 1000 K for the species involved, $\Delta_r G$ values for the formation of PbTiO$_3$, LaMnO$_3$, La$_{0.7}$Sr$_{0.3}$MnO$_3$ are obtained. The reactions are quite exothermic,
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<th>Metathetic exchange thermodynamics</th>
<th>$\Delta G_f$ (300 K) (kJ mol$^{-1}$)</th>
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<tr>
<td>Reactants:</td>
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<tr>
<td>$\Delta G_f$</td>
<td>PbSO$_4$</td>
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<tr>
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<tr>
<td></td>
<td>-815.544</td>
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<td>-1063.998</td>
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<td>-1943.88</td>
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$\Delta_r G$ (300 K) = -64.336

Table A.1. Room temperature $\Delta G_f$ values for species involved in the metathesis reactions between PbSO$_4$ and K$_2$CO$_3$. The net $\Delta_r G$ at 300 K is calculated from the individual $\Delta G_f$ values.

with $\Delta_r G$ values of -161.512, -288.31, and -347.53 kJ mol$^{-1}$, respectively.
### Assisted metathesis thermodynamics

**$\Delta G_f (1000 \text{ K}) (\text{kJ mol}^{-1})$**

<table>
<thead>
<tr>
<th>PbTiO$_3$:</th>
<th>Reactants: [PbSO$_4$, TiO$_2$, K$_2$CO$_3$]</th>
<th>$\Delta G_f$</th>
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<td>2172.984</td>
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<table>
<thead>
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<td></td>
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<td>2334.496</td>
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</table>

$\Delta r G = -161.512$

<table>
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<tr>
<th>La$_{1-x}$Sr$_x$MnO$_3$:</th>
<th>Reactants: [MnSO$_4$, SrCO$_3$, La$_2$O$_3$, K$_2$CO$_3$]</th>
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<td>2726.77</td>
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$\Delta r G$ for $x = 0.0$ | -288.31 |
| $x = 0.3$ | -347.53 |

### Table A.2.

The assisted metathesis reactions of Chapter 2 are considered in terms of the Gibbs free energies of formation of the relevant species. $\Delta r G$ for K$_2$SO$_4$/PbTiO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0, 0.3$) at 1000 K are calculated from $\Delta G_f$ values. All data from reference [123] except $^*$ $\Delta G_f$ calculated for LaMnO$_3$ using data provided in reference [124].

We assume that Sr substitution ($x = 0.3$) leaves $\Delta G_f$ unchanged.
Appendix B

Volume Changes Associated with the Creation of Pores

The following two tables may be used to determine the expected volume loss from selective leaching of phases and elements. Relevant phases are introduced in the first table, with crystal structures, unit cell volumes, $Z$, masses, and densities. These values are used in the second table to calculate the volume loss for various leaching steps. When several leaching steps were applied sequentially, a net volume loss is given for the total process. The volume losses are calculations only, and do not reflect initial porosity (the starting material is assumed to be 100% dense) or sintering effects. These assumptions are supported by SEM cross-sections of the original dense monoliths and $N_2$ sorp-
tion measurements. Perovskites formed below the K$_2$SO$_4$ melting point and ZnFe$_2$O$_4$ are the exceptions, and did not display complete densification.
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<th>Mass (amu)</th>
<th>Density (g cm⁻³)</th>
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<td>Zn₂TiO₄ inverse spinel</td>
<td>605.538</td>
<td>8</td>
<td>242.66</td>
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<td>MgAl₂O₄ spinel</td>
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Table B.1. Unit cell parameters.
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<th>product</th>
<th>pore diameter</th>
<th>vol. loss (calc.)</th>
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<tbody>
<tr>
<td>PbTiO$_3$ / K$_2$SO$_4$</td>
<td>water</td>
<td>PbTiO$_3$</td>
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<td>63.3%</td>
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<tr>
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<tr>
<td>Ni$<em>{0.7}$Zn$</em>{0.3}$O</td>
<td>H$_2$</td>
<td>0.7 Ni / 0.3 ZnO</td>
<td>0.5-5 µm</td>
<td>18.6%</td>
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<tr>
<td>0.7 Ni / 0.3 ZnO</td>
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<tr>
<td>ZnFe$_2$O$_4$ / ZnO</td>
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<tr>
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</tr>
<tr>
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<tr>
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<td>58.8%</td>
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<td>hierarch.</td>
<td>78.9%</td>
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<td>H$_2$</td>
<td>2 MnO</td>
<td>30-100 nm</td>
<td>49.8%</td>
</tr>
</tbody>
</table>

Table B.2. Reactions and associated volume losses.
Appendix C

Other Systems Studied Here

The following describes several routes which are extensions of the work described in this thesis. First, the $\text{Mn}_3\text{O}_4$ reduction transformation of Chapter 4 is extended to other systems where there are large volume losses present, namely $\text{V}_2\text{O}_5$ and $\text{Co}_3\text{O}_4$. Second, the vapor phase leaching of Sn from $\text{SnO}_2$-$\text{Mn}_2\text{O}_3$ compounds is studied. Third, reduction reactions are explored which simultaneously induce a phase separation. In this way, ferromagnetic-antiferromagnetic composites are formed which exhibit exchange biasing.

$\text{V}_2\text{O}_5$ to $\text{V}_2\text{O}_3$ Reductive phase transitions were briefly explored in the $\text{V}_2\text{O}_5$ system. Conversion to $\text{V}_2\text{O}_3$ occurs in a flowing 5%-H$_2$ atmosphere and yields a 43% volume loss. To observe this volume loss with bulk monoliths, pellets
Figure C.1. (a) SEM micrograph of sintered V$_2$O$_5$ which was reduced to V$_2$O$_3$ (b) with a corresponding perforation of the grains (c).

were formed by cold pressing V$_2$O$_5$ powders and firing at 853 K for 50 h (Figure C.1a). Reduction was carried out under flowing 5%-H$_2$ at 923 K for 1-4 h, with a corresponding mass loss (observed: 16%, expected: 17%). The resulting SEM microstructure is shown in Figure C.1b,c, with pores 50-100 nm in diameter penetrating through the material. The expression of porosity was found to depend on grain size, with smaller grains simply contracting while larger grains ended up perforated with pores. This may be the result of pinning from the interior structure coupled with fairly high solid state diffusion rates. Particularly large grains showed pores with perpendicular walls, as seen in Figure C.2.

The phase behavior of vanadium oxides is quite rich; as a function of temperature and oxygen partial pressure a multitude of phases exist between V$_2$O$_5$ and V$_2$O$_3$.\cite{125} By working at a lower oxygen partial pressure, one could
lower the \( \text{V}_2\text{O}_5 \) to \( \text{V}_2\text{O}_3 \) transition and thereby reduce diffusion and pore collapse. The redox behavior of \( \text{V}_2\text{O}_5 \) powders has been studied and correlated with grain morphology.\[126\] As well, the \( \text{ZnO-\text{V}_2\text{O}_5} \) system has a number of intermediate phases which could be exploited to give volume losses through zinc evaporation (\( \text{ZnV}_2\text{O}_6, \text{Zn}_2\text{V}_2\text{O}_7, \text{Zn}_3(\text{VO}_4)_2 \)).\[127\]

\textbf{Co}_3\text{O}_4 \textbf{to Co} \quad \text{Co}_3\text{O}_4 \) heated in a flowing 5%-H\(_2\) atmosphere will reduce to Co metal. To study the morphological effect of this transformation, commercially available \( \text{Co}_3\text{O}_4 \) powders were cold pressed and fired in \( \text{O}_2 \) at 1223 K for 4 h. Reduction was carried out at 873 K for 6 h The resulting morphology is similar to the reduction of other oxides to metals (Section 3.3), with macropores penetrating throughout the structure and smooth pore walls 0.5-2 \( \mu \text{m} \) in diameter.
Vapor phase leaching of tin  An analogous system to ZnMn$_2$O$_4$ is SnMn$_2$O$_4$, as the reduction of zinc and tin occur at fairly similar temperature and both elements display low melting points (Zn: 692.9 K Sn: 505.2 K). Pellets of both SnMn$_2$O$_4$ and SnMnO$_3$ were formed and reduced in flowing 5%-H$_2$/N$_2$. SnMn$_2$O$_4$ was prepared by heating equimolar amounts of SnO$_2$ and Mn$_2$O$_3$ at 1673 K for 12 h under a N$_2$ atmosphere. SnMnO$_3$ was prepared according to Equation C.1. The precursor Li$_2$SnO$_3$ was prepared from powders of Li$_2$CO$_3$ and SnO$_2$ at 973 K in air for 24 h, followed by heating at 1273 K for 16 h and 1673 K for 3 h. The resulting Li$_2$SnO$_3$ was ground with MnCl$_2$·4H$_2$O and KCl in a 1:1:2 molar ratio. A molten salt reaction was conducted in a tungsten crucible at 873 K for 2 h under N$_2$ to give SnMnO$_3$ and soluble salts. [128]

\[
\text{Li}_2\text{SnO}_3 + \text{MnCl}_2 \xrightarrow{\text{KCl}} \text{SnMnO}_3 + \text{LiCl} \quad \text{(C.1)}
\]

Reduction of SnMn$_2$O$_4$ in 5-%H$_2$ at 923 K reduction for 12 h induced a mass loss of 10.7%, in close agreement to the 10.9% mass loss expected for the reduction to Sn metal and MnO. The resulting microstructure is shown in Figure C.3, with large droplets of Sn metal and a porous MnO structure. The droplets are found at all length scales, from 1 mm to 0.1 μm. Reductive transformations where the removal of tin creates a volume loss is promising, but we have focused on zinc as its high volatility lends itself to *in-situ* removal through vapor phase leaching.
**Biphasic materials**  Exchange-biased materials physically couple a ferromagnetic phase with an antiferromagnetic phase. When the volume of the ferromagnetic particles is small, surface interactions with the neighboring antiferromagnetic particles can act to pin orientation of the ferromagnetic phase. Application of an external magnetic field creates a bulk orientational preference of the magnetic moments, which appears as a shifting of the hysteresis loop. Exchange-biased materials are found in a variety of different memory devices, including the giant-magnetoresistive (GMR) read heads in hard drives and to pin the orientation of magnetic particles which would otherwise be superparamagnetic.

We have begun exploring how spontaneous processes can create biphasic composites. By starting with single phase Mn$_{3-x}$Co$_x$O$_4$ and heating in a reducing atmosphere, intimately mixed composites of MnO and Co are formed. In a flowing 5%-H$_2$ atmosphere, the manganese reduction occurs by 723 K, and
the cobalt gradually partitions out of the lattice at higher temperatures. The phase evolution has been studied using synchrotron X-ray and neutron diffraction methods. Shown in Figure C.4 are the synchrotron diffraction patterns and corresponding Rietveld refinement for the original Co$_{0.3}$Mn$_{2.7}$O$_4$ spinel, the resulting rock salt Co$_{0.1}$Mn$_{0.9}$O after reduction at 723 K, and the fcc-Co/MnO composite formed after reduction at 923 K. Quantitative phase analysis of the biphasic mixture indicates the Co reduction and partitioning is not complete, with only 3% Co instead of 10% Co present as a second phase, and a prominent decrease in the MnO lattice parameter from the expected pure phase remains.

MnO is a classic antiferromagnet below its Néel temperature of 118 K, and Co is ferromagnetic below 1388 K. The magnetic coupling of the Co may thus be probed by looking at the hysteresis magnetization behavior above and below the MnO Néel temperature. Hysteresis loops are shown in Figure C.6 for the composite at 5 K and 150 K. A clear shift in the hysteresis loop is observed at 5 K, indicating exchange-biasing due to the antiferromagnetic MnO. Zero-field cooling/field cooling magnetization measurements are shown in Figure C.5 for Mn$_3$O$_4$, MnO, and the biphasic composites with 10% and 20% substitution of Co in the initial material. The magnetization has clearly increased with the increase in Co.
Figure C.4. Synchrotron diffraction patterns and corresponding Rietveld fits are shown for the original 10%-Co Mn$_3$O$_4$ material, after reduction at 723 K to MnO, and after further reduction at 923 K to Co/MnO. From top to bottom: data, Rietveld fits, difference profile.
Figure C.5. Zero-field cooling/field cooling magnetization measurements for Mn$_3$O$_4$, MnO, 10% and 20% Co/MnO.
Figure C.6. Hysteresis measurements for 10\% Co/MnO at 5 K and 150 K, showing a clear shift at 5 K.
Appendix D

Solid-state NMR studies of Zn$_2$TiO$_4$

Chapter 5 describes the sequential leaching of ZnO and elemental Zn from Zn$_2$TiO$_4$ to form hierarchically porous TiO$_2$. The leaching process was monitored by thermodiffractometry (Figure 5.14), and with solid-state Nuclear Magnetic Resonance (NMR) through a collaboration with the Chmelka group. As solid-state NMR probes the local environment around the target nuclei, the information is complementary to the longer-range structural ordering described by powder X-ray diffraction. *Ex-situ* solid-state $^{67}$Zn and $^{47,49}$Ti measurements monitored the local environments around these elements during the leaching process.

The quadrupolar character, low gyromagnetic ratio, and low natural abundances of $^{67}$Zn and $^{47,49}$Ti nuclei makes solid-state NMR measurements ex-
Table D.1. Solid-state NMR properties of the isotopes of Zn and Ti. The sensitivity is a relative value scaled to $^1$H.

tremely difficult. Second-order quadrupolar effects lead to peak broadening which may be reduced through the use of high magnetic fields. For $^{47,49}$Ti nuclei, the situation is further complicated by the similar resonance frequencies between the two nuclei. The resulting spectra consist of overlapping signals from both isotopes, further complicating deconvolution.

To obtain the high magnetic fields required to suppress the second-order quadrupolar effects, all NMR measurements were conducted on a Bruker DRX-830 spectrometer at the National High Magnetic Field Laboratory in Tallahassee, FL. Measurements were conducted with a 19.6 T field at 51.92 MHz for $^{67}$Zn and 46.80 MHz for $^{47,49}$Ti using a standard Hahn-Echo pulse sequence. The $^{67}$Zn spectra were recorded under conditions of magic angle spinning (MAS) at 10 kHz speeds, while the $^{47,49}$Ti spectra were obtained under static conditions. The large quadrupole moments of $^{47,49}$Ti give rise to broad resonances which prevent the separation of their center-band signals from spin-
ning side-bands under MAS conditions.

Figure D.1 shows the $^{67}$Zn spectra obtained ZnO/Zn$_2$TiO$_4$ samples during the leaching process. In panel (a), two peaks are present at 231 ppm and 75 ppm, corresponding to the ZnO and Zn$_2$TiO$_4$ respectively. After acid leaching, only the resonance of Zn$_2$TiO$_4$ at 79 ppm remains (Figure D.1b). The complete removal of the ZnO phase is in agreement with the XRD data shown in Figure 5.10.

The reductive leaching of Zn from Zn$_2$TiO$_4$ was also monitored with solid-state NMR. The spectra shown in Figure D.1c shows a sample during an intermediate state of reduction (1 h at 1023 K with a 9% mass loss and a color change from white to blue). The spectra shows that the main Zn$_2$TiO$_4$ resonance has shifted to 91 ppm. Further reduction maintains this peak position. We attribute this shift to the reduced titanium oxidation state which is clear from the color change. Reduction does not significantly broaden the peak, indicating that the zinc sites are quite uniform across the sample. The corresponding XRD patterns are shown in Figure D.1d,e for the Zn$_2$TiO$_4$ sample before (b) and during (c) reduction. Rietveld refinement reveals virtually no difference in the crystalline nature of the two samples. The unit cell of the reduced sample contracts slightly, as expected during the transition from the inverse spinel to the intermediate defect spinel. As the intermediate material
is structurally quite similar, the shift is likely due to the changing electronic environment arising from reduction of the titanium.

Figure D.2 shows $^{47,49}$Ti spectra at three points in the leaching process. The initial macroporous $\text{Zn}_2\text{TiO}_4$ is shown in panel (a), with a peak at 95 ppm and shoulders at -175 and 320 ppm. Reductive leaching at 1023 K for 1 h shrinks the shoulder at -175 ppm while the shoulder at 320 ppm grows. This trend continues with increasing reduction times: the spectrum shown in panel (c) was obtained after reducing for 12 h. The growth of the peak at 320 ppm is due to the decreased electronic shielding of the nuclei as the sample is reduced and some of the Ti$^{4+}$ becomes Ti$^{3+}$. As the $^{47}$Ti and $^{49}$Ti peaks are superimposed and broadened from anisotropic interactions, the powder patterns may not be uniquely deconvoluted.
Figure D.1. (a-c) Solid-state NMR spectra of $^{67}$Zn during the leaching process. (a) Biphasic mixture of ZnO/Zn$_2$TiO$_4$ and (b) the resulting macroporous Zn$_2$TiO$_4$ obtained after acid leaching. (c) Zn$_2$TiO$_4$ after reduction in 5% H$_2$/N$_2$ at 1023 K for 1 h. (d,e) XRD powder patterns and corresponding Rietveld fits for the samples studied in (b) and (c) respectively.
Figure D.2. Static $^{47,49}\text{Ti}$ solid-state NMR spectra obtained during the reductive leaching of Zn$_2$TiO$_4$. The spectrum in (a) corresponds to the initial macroporous monolith of Zn$_2$TiO$_4$. $^{47,49}\text{Ti}$ NMR measurements were obtained following reduction in 5% H$_2$/N$_2$ at 1023 K for (b) 1 h and (c) 12 h.
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