STRUCTURE-PROPERTY RELATIONSHIPS IN FUNCTIONAL LAYERED METAL OXIDES AND METAL OXIDE NANOSHEETS

A Dissertation in

Chemistry

by

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Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

May 2020
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Abstract
Layered metal oxides are a class of solid-state materials that are intergrowths of charged layers interleaved with cations or anions. These materials find interesting technological applications such as superconductors, catalyst supports, battery cathodes, ferroelectrics, and fuel cells. Layered perovskite oxides represent a subset of layered oxides containing ABX₃ as their basic building block, where A typically refers to a cation in a cubo-octahedral cavity of twelve X anions (X=O, H, and N) and B refers to the cation within a BX₆ octahedron. Both class of materials are structurally related and are amenable to topochemical ion-exchange reactions that interconvert between structurally related solids without disrupting the parent crystal structure. Furthermore, many of them can readily undergo exfoliation to obtain molecularly thin metal oxide ‘nanosheets’ and can be restacked into three dimensional solids. Exfoliated nanosheets can be stacked with alternating positive charges to make layer-by-layer assemblies with registry or can be restacked by addition of a counterion that typically results in loss of registry between the sheets and results in disordered solids. This dissertation highlights the structure-property correlations of both layered metal oxides as well as metal oxide nanosheets by utilizing chemical principles of solid-state and topochemical reactions (ion-exchange, exfoliation, and reassembly).

The introductory chapter highlights the structural differences of layered metal oxides and briefly overviews the history of topochemical reactions utilized in designing functional materials for diverse applications. Chapter 2 describes the characterization techniques employed to characterize layered metal oxides as well as the mechanisms of strong metal-support interaction (SMSI) in catalysis and perovskite crystallography that are relevant to understanding the material presented in this dissertation.

The diversity of applications exhibited by layered oxides stems from an understanding of the structural chemistry at the atomic level. Layered perovskites have a rich interlayer chemistry and bonding and thus exhibit interesting electronic properties due to rotation of oxygen octahedra. In Chapter 3, a detailed structural and electrical characterization of a bulk Ruddlesden-Popper layered perovskite, Li₂SrNb₂O₇, is presented to probe this structural chemistry in detail as a function of temperature. This layered perovskite, Li₂SrNb₂O₇, undergoes a polar to antipolar (and antiferroelectric) phase transition when cooled from room temperature to 90 K which was found to be a result of the competition of both ferroelectric and antiferroelectric phases. Both experiment
and theory support that the emergent antiferroelectricity is due to a coupling of oxygen octahedral rotations along different crystallographic axes with displacement of A-site cations. The synthesis of the antiferroelectric layered perovskite can have applications as electrostatic capacitors for energy storage.

A fundamental question that has eluded scientists for centuries is the thermochemical quantification of the driving forces for ion-exchange and exfoliation reactions that transforms three-dimensionally bonded layered solids into 2D ‘nanosheets’. The structural transformation to obtain 2D oxide ‘nanosheets’ has been traditionally reported to be driven by the influx of water molecules between the layers that weaken the electrostatic forces between the layers. Additionally, the restacked compounds have been structurally characterized for disorder by X-ray scattering techniques. Chapter 4 reports the first thermochemical quantification of exfoliation-restacking processes in a layered niobate, HCa$_2$Nb$_3$O$_{10}$, by isothermal titration calorimetry. Isothermal titration calorimetry and differential scanning calorimetry measurements on the layered niobate revealed that the overall transformation of an ordered layered oxide to a restacked, disordered solid is driven by a positive entropy change (37.6 ± 7.5 J/mol·K) with a little change in the enthalpy. The positive entropy value was correlated with vibrational sum frequency spectroscopy that showed several layers of oriented water molecules under the charged nanosheet surface. This study addresses a long-standing mechanistic question of the driving forces for exfoliated-restacked solids and opens up avenues to extend this technique to other layered and two-dimensional materials with different types of bonding across the layers.

Chapter 5 discusses the role of metal oxide nanosheets as model catalyst supports to stabilize dinuclear clusters. Metal oxide nanosheets extend laterally and have high surface areas that make them good candidates as catalyst supports. Additionally, they are molecularly thin nanosheets that can be imaged by electron microscopy and can be used to monitor catalytic activity of nanoparticles and low nuclear clusters for heterogeneous catalysis. In this chapter, we report the stability and structure characterization of two dinuclear rhodium and iridium clusters on layered titanate and niobate supports. The stability of dinuclear clusters on both supports could be characterized by aberration-corrected scanning transmission electron microscopy which showed pairs of atoms on several regions of the support. The binding sites of dinuclear rhodium clusters on the layered titanate support were elucidated by a combination of density functional theory,
DRIFTS, and synchrotron X-ray absorption spectroscopy. Overall, this study highlights that nanosheets derived from layered metal oxides can be used as model catalyst supports to stabilize dinuclear clusters which could have implications for heterogeneous catalysis.
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Acknowledgements

The past five years have seen an intense yet exciting phase of my scientific career. There are several people I would like to express my gratitude without whom this thesis would not have been possible. First and foremost, I would like to thank my dissertation advisor, Prof. Tom Mallouk, for giving me the opportunity to grow as a scientist. Tom is an amazing scientist with a good sense of humor who always sticks to fundamental questions. Despite some struggles in the early phase of my career, my frustrations eventually led to experimental breakthroughs. Over the past five years, his mentoring approach enabled me to become an independent researcher and carve out a niche in a diverse group. At the same time, his boundless knowledge and enthusiasm exposed me to several topics of materials research that is well beyond the scope of a graduate student’s career! I would also like to thank the National Science Foundation for providing funding for the work presented in this dissertation.

Over the past five years, I have worked extensively with several collaborators outside our research group. I would like to first thank Dr. Hirofumi Akamatsu and Dr. Arnab Sen Gupta for getting me started on the ferroics project. Arnab walked me through the fundamentals of perovskite crystallography as well as the principles of nonlinear optics and second harmonic generation in Prof. Gopalan’s lab. Hirofumi patiently spent long nights going over the technique of Rietveld refinement and its uses in analyzing synchrotron data. Additionally, Hirofumi and I had numerous e-mail exchanges even after he left to Japan to start his independent career to resolve all the issues that came our way. I would like to thank Sharad Maheshwari for spending several months on doing computational studies on challenging systems and his input is valuable. I would also like to thank the National School on Neutron and X-ray Scattering 2017 for providing me with hands-on experience on several X-ray and neutron characterization techniques that proved to be valuable for my graduate research. Through this 2-week intense summer school, I got an opportunity to meet several graduate students from across the country and was able to expand my professional network. I would like to thank all the staff in Penn State’s Materials Characterization Laboratory for assisting and training us on different equipment. My special mention goes to Jennifer Gray who patiently spent hours on the Titan microscope to image challenging samples as well as Josh Stapleton who always took great interest in my project and helped me out in every possible way.
The MRSEC education and outreach team represents another important component that enabled me to participate in outreach activities.

I would like to thank both the past and present members of the Mallouk Lab, especially Pengtao, Chris Li, Zhifei, Liqiang, Alyssa, Pratibha, Jeremy, Jarrett, and Lanqiu. The Mallouk Lab was indeed like a second family and my conversations with each of them proved to be very valuable in some way. I will always remember the endless conversations I had with Alyssa who was my comrade on the layered materials project for the past 4 years. I am also glad that the lab is bonded over hotpot which has become a tradition in the group.

Additionally, I had some incredible housemates who made me realize that there is a life outside of the laboratory. We generally bonded over Indian food, swing dance, or discussions on bizarre moments from Game of Thrones. The Society for Indian Music and Arts at State College represented another good activity on campus that helped me forget my research struggles. Finally, I would like to thank my family for giving me constant encouragement and always cheering me up whenever I was discouraged! Their role in shaping me as a citizen cannot be appreciated enough. I dedicate this thesis to my parents, teachers, friends, and everyone who influenced me!
Dedicated to my family
Amma, Nanna, and Srushti
Chapter 1

Introduction

1.1 Layered Metal Oxides

A cornerstone of organic chemistry is the synthesis of large, complex molecules from smaller building blocks. These syntheses rely on the preservation of covalent bonds within the precursor molecules as new bonds are formed, an approach that has become increasingly popular over the past few decades in the synthesis of solid state materials with extended lattices. For example, metal organic frameworks with predetermined structures are made in low-temperature reactions that involve coordination of metals by bridging ligands, and extended nanoparticle lattices with programmable structures can be made by exploiting DNA hybridization. Metastable solid state materials synthesized under kinetic rather than thermodynamic control are now being increasingly designed for applications in energy storage, chemical sensing, separations, biomedicine, and other areas.

Layered metal oxides represent a special class of solid-state materials that are amenable to low-temperature chemical transformations without disrupting the covalent bonding within the layers. These compounds can contain stacks of electrically neutral metal-oxide layers, but more commonly they are intergrowths of charged layers that are interleaved with cations or anions, or their metal oxide sheets alternate with covalently bonded interlayers. Examples of layered oxides with uncharged sheets include MoO$_3$.2H$_2$O, which contains distorted MoO$_5$(H$_2$O) octahedral layers with interlayer water molecules, and V$_2$O$_5$ which consists of O atoms in trigonal bipyramidal coordination around V atoms, which are cross-linked in a zig-zag pattern to form sheets. Ionic intergrowths include A$_3$MO$_2$ and A$_2$MO$_3$-type structures that have MO$_6$ edge-sharing octahedra with alkali metal ions inserted between the layers. In addition, they also include alkali metal niobates such as KNb$_5$O$_8$ and K$_4$Nb$_6$O$_{17}$ as well as titanates with the general formulas M$_2$Ti$_n$O$_{2n+1}$ (M = Na, K) and Na$_4$Ti$_n$O$_{2n+2}$. The titanate structures have layer slabs that are sheared in a direction perpendicular to the plane at every n$^{th}$ octahedron. Ternary oxides of other transition metals, such as Mn, V, and W have also been prepared and some of them are anion-exchangers.

* The material presented in this chapter is published in Chem. Soc. Rev. 2018, 47, 2401.
Layered quaternary oxides include mixed-metal oxides, perovskite structures and layered double hydroxides and are discussed in detail below.

Layered perovskites represent a special class of layered materials that contain ABX$_3$ perovskite as their basic building block, where A refers to cations in a cubooctahedral cavity of twelve X anions (where X=O, halogen, N, S, and/or H) and B refers to a cation in a BX$_6$ octahedron. The two most common structural classes of layered oxide perovskites that contain ion-exchangeable cations are Ruddlesden-Popper (RP) phases, $A_2[A_{n-1}B_nO_{3n+1}]$, and Dion-Jacobson (DJ) phases, $A'[A_{n-1}B_nO_{3n+1}]$, where n represents the number of BO$_6$ octahedral layers and comprise the covalent perovskite blocks. The key difference between these structural families is that Dion-Jacobson phases have half the number of interlayer cations as the Ruddlesden-Popper phases, which have a rock salt type AO interlayer (see Figure 1). Aurivillius (AV) phases, Bi$_2$O$_2[A_{n-1}B_nO_{3n+1}]$, represent another class of layered perovskites in which a covalent network of Bi$_2$O$_2^{2+}$ occupies the interlayer galleries. Layered perovskites can have their layers oriented along different crystallographic axes based on the connectivity pattern of BX$_6$ octahedra and the interlayer orientation. These include (110) layered perovskites in which the octahedra are linked at the edges and (111) layered perovskites with the octahedra connected along the faces.

Compared to cation exchangers, which are quite common among layered oxides, layered anion exchangers are relatively rare. Layered double hydroxides (LDHs), which contain positively charged metal hydroxide sheets interleaved with anions, were first discovered in 1940s by Feitknecht while studying the co-precipitation of alkali metal cations with bases. They have a structure analogous to brucite, Mg(OH)$_2$, and contain the general formula $[M^{2+}_{x}\times(1-x)M^{3+}_x(OH)_2]A^{n-}\_{x/n}mH_2O$, where M$^{2+}$ and M$^{3+}$ represent divalent and trivalent cations, x corresponds to the ratio M$^{3+}/(M^{2+} + M^{3+})$, and n represents the anion charge. The choice of M$^{2+}$ and M$^{3+}$ ions used are similar in size to Mg$^{2+}$ ions and can consist of a variety of counter anions such as carbonates, nitrates, and hydroxides. LDHs with the hydrotalcite structure have also been prepared using Li$^+$ and Al$^{3+}$ ions. Layered rare earth hydroxides of general formulas Ln(OH)$_2A^{q+}_{1/q}mH_2O^{25}$ and Ln$_n$(OH)$_{2n}A^{q+}_{4/q}mH_2O^{26}$ represent another class of layered anion exchangers, the properties of which have been recently reviewed.

Layered oxides with cation and anion ordering have been explored for different applications. Brownmillerites are oxygen-deficient layered perovskites of the general formula A$_2$B$_2$O$_5$ having
Figure 1: Structural motifs of selected layered oxides that are amenable to soft chemical
transformations: Binary oxides (a) MoO$_3$.2H$_2$O and (b) V$_2$O$_5$; Ternary oxides (c) ABO$_2$-type LiCoO$_2$ structure, (d) Layered double hydroxide (LDH), (e) Brownmillerite Ca$_2$Fe$_2$O$_5$ structure. Shear structures (f) Knb$_3$O$_8$, (g) K$_4$Nb$_6$O$_{17}$, and (h) Na$_2$Ti$_3$O$_7$; Layered oxide perovskites: (i) Ruddlesden-Popper phase, A$_2$[A$_{n-1}$B$_n$O$_{3n+1}$], (j) Dion-Jacobson phase A'[A$_{n-1}$B$_n$O$_{3n+1}$], and (k) Aurivillius phase Bi$_2$O$_2$[A$_{n-1}$B$_n$O$_{3n+1}$].

alternating layers of oxygen octahedra and tetrahedra and were discovered in the 1920s.$^{28}$ These structures can also have ordered B-site cations that can exhibit tetrahedral and octahedral coordination in the alternating layers. Anion-ordered layered oxides include oxyhydrides, oxychlorides, and oxyfluorides that have been explored for applications as ion conductors and antiferromagnets.$^{29-31}$ The most common families of layered oxide structures are illustrated in Figure 1.

Unlike layered van der Waals solids that have weak intermolecular forces, most layered transition metal oxides consist of charged sheets with charged species intercalated between them. The presence of electrostatic attractive forces make them amenable to ‘host-guest’ chemistry, in which the exchangeable intercalant is the guest species and the metal oxide block is the host. The presence of electrostatic attractive forces can enable layered oxides to be pulled apart into two-dimensional monolayer nanosheets and also stack the monolayers back to form three dimensionally bonded perovskites.$^{32}$

1.2 Solid-State and Topochemical Reactions

Solid state synthesis offers a convenient route to synthesize functional layered oxides but the range of compositions accessible are limited by the competition between thermodynamics and kinetics. The key limiting factor in solid state chemistry is often the requirement for diffusion of individual atoms that necessitates high temperature reaction conditions and thus produces the most thermodynamically stable products.$^{33}$ On the other hand, low temperature syntheses of materials enable one to access kinetic metastable phases, often while retaining some or all of the chemical bonding of precursor molecules. The history of this approach can be traced back to sol-gel synthesis, a molecular approach that uses aqueous and organic phase precursors, which was first demonstrated in the mid 19$^{th}$ century by Ebelman who observed that hydrolysis of
tetraorthoethylsilicate (TEOS) under acidic conditions formed silica. Later, Roy and co-workers expanded the sol-gel method to synthesize several new silicate and ceramic glasses of technological interest. In recent years, sol-gel synthetic techniques have been expanded to include a variety of solid-state structures, including nanostructures. The sol-gel method is also closely related to hydrothermal and solvothermal techniques that have been used to synthesize porous materials such as zeolites and MOFs, as well as shape-controlled nanocrystals of a very broad variety of materials, all from molecular precursors.

**Solid-state synthesis**

The most common route to synthesis of layered oxides is the ceramic method, in which precursor oxides are typically ground and heated to varying temperatures to promote diffusion of atoms. Because refractory intermediates can form at the interfaces between reacting crystal grains, the phase purity of the resulting products often depends on the heating rate, temperature, and pressure. Sol-gel synthetic routes have been utilized to overcome the diffusion barrier in these syntheses by effectively mixing the precursor elements at the molecular level. For example, birnessite $K_xMnO_2$ can be made by reaction of $KMnO_4$ with a sugar such as glucose. Drying followed by calcination at 450°C results in the formation of a layered birnessite structure with interlayer potassium cations. Recently, Ma, *et al.* showed that a new amorphous layered titanate $Ti_{2-x}O_{4-4x}(OH)_{4x}$ could be stabilized en route to making anatase $TiO_2$ by a sol-gel reaction of titanium isopropoxide in ethanol using water as the hydrolysis agent.

A popular sol-gel precursor route to layered oxide perovskites is the polymerizable complex method, also known as *Pechini method*, which is based upon the esterification reaction between a carboxylic acid and an alcohol. This method was originally developed in the 1960s for the synthesis of dielectric films and has now been extended to many layered oxide perovskites. In this method, a chelating carboxylic acid (such as citric acid) solubilizes metal ions such as Nb(V), Ta(V), and Sr(II), and ethylene glycol promotes the esterification process. The Dion-Jacobson phase oxide $KCa_2Nb_3O_{10}$ was synthesized using the *Pechini method* by polymerizing a mixture of $NbCl_5$, $CaCO_3$, and $KCl$ in the presence of ethylene glycol and anhydrous citric acid in methanol followed by calcination in air at 1273 K for 2 h. Pt-loaded $HCa_2Nb_3O_{10}$ nanosheets obtained by this method had improved photocatalytic activity for hydrogen evolution under bandgap irradiation.
when compared with the solid state synthesis approach as a result of higher surface area of the sheets.\textsuperscript{42} The \textit{Pechini method} has also been utilized in the synthesis of A-site and B-site doped layered oxides, such as a new Ruddlesden-Popper phase $K_2CaNaNb_3O_{10}$\textsuperscript{43} and two new Dion-Jacobson phases $KCa_{2-x}Sr_xNb_3O_{10}$ and $KCa_{2}Nb_{3-y}Ta_yO_{10}$\textsuperscript{44} in which the ratio of metal ions was adjusted to tune the band-edge potentials for photocatalysis. Effective strategies of polymerization can expand the choice of layered oxide compositions that are otherwise inaccessible through solid-state synthesis due to diffusion barriers or the volatility of some of their components.

\textit{Topochemical Reactions}

Ion-exchange is one of the most popular soft chemistry routes in designing novel metastable phases of layered oxides and utilizes general chemistry principles of charge density and acid-base chemistry. The higher charge-to-radius ratio of smaller cations (or divalent cations) can drive larger cations out by lowering the electrostatic energy, and thus results in isostructures with smaller cations in the interlayer galleries. Acid-base chemistry is also a powerful tool for exchanging protons reversibly with alkali metal cations or with covalent intergrowth layers. Ion-exchange in layered oxides was first demonstrated in the layered titanate, $Tl_2Ti_4O_9$, by reacting it with molten KNO$_3$-KCl flux to obtain the isostructure $K_2Ti_4O_9$.\textsuperscript{11} Similarly, acid exchange has been demonstrated in the layered titanates $Na_2Ti_3O_7$ and $K_2Ti_4O_9$ to convert them into anhydrous $H_2Ti_3O_7$ and hydrated $H_2Ti_4O_9.H_2O$ respectively. The former could be made to revert to its parent phase by reacting with NaOH.\textsuperscript{45} In recent years, proton exchange has also been demonstrated in layered oxides containing late transition metals such as the layered ruthenic acid $H_{0.22}RuO_2.11$\textsuperscript{46} and the trivalent iridate $K_{0.75}Na_{0.75}IrO_2$, which can be converted to the protonated oxyhydroxide IrOOH.\textsuperscript{47}

Ion-exchange has also been used in layered perovskite oxides to replace alkali metal cations in the interlayer galleries with divalent metal cations\textsuperscript{48,49} and with complex metal halides\textsuperscript{50-52} Wiley and coworkers pioneered topochemical exchange in layered perovskites and also studied the metastability of the ion-exchanged compounds with respect to temperature.\textsuperscript{53} They performed monovalent and divalent ion-exchange in a series of two-layer Dion-Jacobson phase $ALaNb_2O_7$ compounds ($A = H, \text{Li}, \text{Na}, K, \text{NH}_4, \text{and Ag}$) by heating them in molten alkali metal nitrates and
recently extended this to ANdNb$_2$O$_7$.\textsuperscript{51} Ion-exchange has also been reported in oxyfluorides and oxynitrides such as RbLaNb$_2$O$_6$F\textsuperscript{54} and CsCa$_2$Ta$_3$O$_{10-\delta}$N$_y$\textsuperscript{30} respectively upon treatment with acids.

In recent years, ion-exchange in both layered perovskites and non-perovskite oxides has been observed to modify their resulting properties. Mitsuyama, \textit{et al.} reported partial ion-exchange of triple-layered Dion-Jacobson phases KCa$_2$Ta$_3$O$_{10}$ and LiCa$_2$Ta$_3$O$_{10}$ with Na$^+$ using the mixed molten nitrates A$^+$NO$_3$ (A$^+$=K, Na) and NaNO$_3$ to tune the interlayer hydration for photocatalysis. Partially ion-exchanged layers showed the highest photocatalytic activity, resulting from the higher hydration enthalpy of Na$^+$ ions coupled with the optimum interlayer distance for water intercalation.\textsuperscript{55} Similarly, Galven, \textit{et al.} were able to ion-exchange one half of Li$^+$ ions in Li$_2$SrTa$_2$O$_7$ by reacting with NH$_4$Cl in the solid-state to form the acentric compound LiHSrTa$_2$O$_7$.\textsuperscript{56} Another partial ion-exchange route was reported by Cussen who converted HLaTiO$_4$ to the solid-solution H$_{1-x}$Li$_x$LaTiO$_4$.\textsuperscript{57} Recently, Roudebush, \textit{et al.} synthesized two layered iridates Cu$_3$NaIr$_2$O$_6$ and Cu$_3$LiIr$_2$O$_6$ containing the honeycomb lattice from Na$_2$IrO$_3$ and Li$_2$IrO$_3$ by reaction with CuCl below 450$^\circ$C. They found that ion-exchange resulted in vastly different magnetic properties from the parent structure and this difference was attributed to changes in the interlayer spacing of the IrO$_6$ layers.\textsuperscript{58} Controlled ion-exchange of layered oxides can thus be used for fine tuning of the structure to realize useful properties that are difficult to control by direct high temperature synthesis.

\textit{Other Topochemical Reactions}

Topochemical redox reactions have also been demonstrated for Ruddlesden-Popper phase oxides derived from late transition metals, such as Fe, Co, Ni, and Mn, that are not ion-exchangeable but are interesting materials for applications in Li-ion battery anodes, antiferromagnetism, ferroelectrics, and high temperature superconductors. Hayward and co-workers have pioneered rational design principles for topochemical oxidation and reduction by using a combined approach of bond valence sum (BVS) calculations and coordination geometry to deduce the available anion (de-)intercalation sites on reacting with metal fluorides and metal halides, respectively.\textsuperscript{59} The smallest thermodynamic cost for de-intercalation of oxygen atoms was predicted to be the site that results in the largest decrease in BVS of B-site cations (resulting from reduction of B-site cations) but the smallest change in BVS of the A-site cations. The largest difference in the BVS of B-site
and A-site cations was used as a strategy to predict the site of oxygen de-intercalation. This concept was verified experimentally for reduction of a variety of layered oxides such as Ruddlesden-Popper oxide Sr$_2$FeO$_3$ and the layered oxychloride, Sr$_4$Mn$_3$O$_6.5$Cl$_2$, by using CaH$_2$ as the reducing agent at 350°C. Recently, topochemical fluorination has been investigated in a variety of layered oxides by reacting with metal fluorides such as CuF$_2$ or CaF$_2$ in the presence of O$_2$. Topochemical fluorination generally resulted in the intercalation of fluorine atoms into the rocksalt layers with concomitant oxidation of the B-site cations, but it also sometimes resulted in partial ion-exchange with O-atoms at the apical sites. The positions of the inserted F atoms were determined by calculating bond valence sums to determine the local bonding environment. The choice of intercalation vs. ion-exchange was dependent upon the stability of the oxidation state of the B-site cation. The rational design of metastable layered oxides by topochemical oxidation and reduction approaches have been covered in detail in other recent reviews.

1.3 Exfoliation and Reassembly

The exfoliation of layered perovskites was initially reported by Treacy, et al., who intercalated amines into the Dion-Jacobson phase KCa$_2$Nb$_3$O$_{10}$ and observed the formation of individual nanosheets by electron microscopy. Keller, et al. later demonstrated that anionic nanosheets produced by reaction of the acid-exchanged nanosheets with tetrabutylammonium hydroxide (TBA$^+\text{OH}^-$) could be grown layer-by-layer on surfaces by dipping suitably primed substrates alternately in suspensions of the nanosheets and solutions of cationic polymers. In 1996, Sasaki, et al. used TBA$^+\text{OH}^-$ used to swell a layered protonic titanate, H$_{x}$Ti$_{2-x/3}$O$_{4}$·H$_2$O (x ~ 0.7; · , vacancy). In the same report, they coined the single-layer particles in the suspension as “nanosheets” because of the subnanometer thickness and micrometer lateral dimensions of the individual sheets. Since these early reports, TBA$^+\text{OH}^-$ has been widely used to produce stable colloidal suspensions of oxide nanosheets from acidic oxide precursors. However, other exfoliating agents have recently been studied, including tetrabutylphosphonium hydroxide (TBP$^+\text{OH}^-$), which was more effective for completely exfoliating the layered titanate, H$_{0.8}$[Ti$_{1.2}$Fe$_{0.8}$]O$_4$·H$_2$O. The trirutile-like structure of HNbWO$_6$ can be exfoliated using triethanolamine. Well-crystallized layered double hydroxide (LDH) structures can be treated with formamide to achieve the swelling necessary for exfoliation.
The conversion of layered metal oxides into layered hydrated solid acids is achieved by treating the parent compound with an acidic solution. Some examples of these solid acids include HCa$_2$Nb$_3$O$_{10}$·1.5H$_2$O, H$_{0.8}$[Ti$_{1.2}$Fe$_{0.8}$]O$_4$·H$_2$O, and H$_{0.13}$MnO$_2$·0.7H$_2$O. These solid acids react by intercalating organophosphonium ions, organoamines, or organoammonium ions, from basic solutions, but only a fraction of the acid groups can be neutralized because of the large size of these cations.$^{72,74,75}$ The reaction also introduces a large volume of water into the interlayer galleries, which results in gigantic osmotic swelling.

The general mechanism of exfoliation relies upon the osmotic swelling of the layers to produce unilamellar nanosheets; a schematic of the mechanism is shown in Figure 1.2. As the swelling increases, the interlayer spacing increases and the intermolecular forces of neighboring layers are weakened and the structure is prone to delamination, or exfoliation. The difference in osmotic pressure between the interlayer gallery and the surrounding solution determines the degree of osmotic swelling. The osmotic pressure is independent of the exfoliating agent used but depends on its concentration, and the optimal concentration has been found to be 30% - 40% of the cation exchange capacity of the layered solid acid.$^{76}$ Higher concentrations are less effective because excess salt in solution lowers the osmotic pressure difference between the bulk solution and the interlayer galleries.

![Figure 1.2: Schematic representation of the general mechanism of exfoliation. Reproduced with permission from Ref. 76. Copyright 2014 American Chemical Society.](image)

The chemical characteristics of the exfoliating agent affects the stability of the resulting swollen layered oxide. For example, layered titanates intercalated with 2-(dimethylamino)ethanol (DMAE) produced a stable and reversible 100-fold expansion within the interlayer gallery.$^{74}$ Intercalation
of layered oxides with small, polar ions tends to yield stable swollen structures whereas intercalation of larger, less polar ions decreases the stability of the swollen structures, which are more susceptible to complete delamination. The most commonly used cation is the bulky relatively low polarity TBA$^+$ ion, which produces a relatively unstable swollen structure and that can be delaminated by mechanical shaking.

Layered oxide nanosheets are charge-bearing two-dimensional nanomaterials, unlike their electroneutral parent compounds. Colloidal suspensions of negatively charged nanosheets can be restacked, or flocculated, by addition of cations/polycations at high ionic strength where the total charge is in excess of the nanosheets. The flocculation of nanosheets results in micro- and mesoporous randomly restacked lamellar materials in which the crystallinity of the individual two-dimensional oxide layers is preserved. These layers are oriented irregularly and are misaligned in the z-direction in the flocculated materials. Figure 5 illustrates the restacking of charged nanosheets.

![Flocculation](image)

**Figure 1.3**: Flocculation, or restacking, of a colloidal nanosheet suspension through the addition of a counterion to yield a randomly restacked lamellar material. Reproduced with permission from Ref. 80. Copyright 2010 Wiley-VCH.

Anionic nanosheets often restack rapidly upon introduction of cations and can be readily collected through filtration. The flocculated materials have higher porosity than their ordered lamellar parent structures, which can be used to tailor functionality. Flocculation can also be used as a tool to
introduce guest species that may be more difficult to intercalate through typical ion-exchange reactions or other impregnation methods. As an example, Li$^+$ was incorporated into MnO$_2$ by flocculation of the delaminated oxide nanosheets. Electrochemical analysis of the flocculated-LiMnO$_2$ showed smoother charge/discharge of Li$^+$ for lithium-ion battery applications.$^{81}$

While these restacked materials are typically disordered, when flocculation occurs slowly enough and under specific conditions, it can be possible to restack the sheets with registry to recover the structure of the original material. For example, Ca$_2$Nb$_3$O$_{10}^-$ nanosheets can be restacked when dialyzed with KCl; Rietveld refinement of X-ray powder diffraction patterns coupled with microscopic imaging suggested the re-establishment of the parent compound, KCa$_2$Nb$_3$O$_{10}$, with small domains of three-dimensional ordering.$^{82}$

In contrast to flocculation which generally results in randomly oriented aggregates, oxide nanosheets, which bear either negative or positive charge, can be assembled layer-by-layer (LbL) on both planar and high surface area substrates by alternately adsorbing them and oppositely charged polyelectrolytes. The assembly process is similar to the polymer LbL method developed by Decher and coworkers,$^{83}$ but the use of colloidal nanosheets prevents the interpenetration of sequentially grown layers that invariably occurs with linear polyelectrolytes.$^{84}$ This method was originally developed with colloidal and layered silicates$^{85,86}$ and then extended to nanosheet films of exfoliated H$_4$Nb$_6$O$_{17}$ and CsTi$_2$NbO$_7$ by adsorbing positively charged electrolytes such as polyallylamine hydrochloride (PAH). This technique, referred to as ‘molecular beaker epitaxy’, resulted in well-controlled growth of nanosheet multilayers that alternate with polycations as confirmed by ellipsometry.$^{89}$ The LbL assembly method was later extended to assemble other layered oxide nanosheets, such as Ti$_{0.87}$O$_2$$^{87,88}$ and MnO$_2$$^{89}$, onto a variety of substrates. The adsorbed polycations could be decomposed by using UV light, decreasing the inter-nanosheet distance by forming positively-charged NH$_4^+$ cations.$^{88}$ More recently, LbL assembly has been used as a fabrication tool for combining different nanosheets to design photoelectrodes for enhanced light absorption$^{90}$ and channel materials for field-effect transistors.$^{91}$ For example, heteroassemblies of (PDDA/GO/PDDA/Ti$_{0.87}$O$_2$)$_n$ superlattice films have been fabricated on quartz substrates by adsorbing polydiallyldimethylammonium chloride (PDDA) as a cationic layer between the layers of anionic nanosheets (Figure 6). Photocatalytic reduction of graphene oxide
to reduced graphene oxide (rGO) and decomposition of PDDA formed (rGO/Ti$_{0.87}$O$_{2.52}$)$_n$ superlattice films that lowered the nanosheet resistance by six orders of magnitude.$^{91}$

**Figure 1.4:** Fabrication of (PDDA/GO/PDDA/Ti$_{0.87}$O$_{2.52}$)$_n$ superlattice films by layer-by-layer assembly. Adapted with permission from Ref. 91. Copyright 2014 Royal Society of Chemistry.

Langmuir-Blodgett (LB) deposition, originally developed for layer-by-layer transfer of surfactant monolayers to solid surfaces,$^{92}$ is another powerful method for fabricate multilamellar nanosheet films. This technique utilizes the surface tension at the solvent-air interface to create well-packed monolayer films by compression of barriers. This technique has an advantage over layer-by-layer adsorption of colloids from suspensions in that the deposited sheets are well-packed with $>$95% coverage and also show minimal overlaps. Muramatsu, *et al.* first used LB deposition to transfer layered metal oxide nanosheets onto different substrates without the use of amphiphilic additives. Tetrabutylammonium cations used as the exfoliating agent adsorbed onto the nanosheet surface and possibly acted as amphiphiles to enable subsequent depositions.$^{93}$ This method was later extended to perform LB deposition of MnO$_2$ nanosheets exfoliated using tetramethylammonium hydroxide (TBA°OH).$^{94}$ LB deposition of titanate nanosheets (up to 10 layers) was performed at a surface pressure of 10 mN/m by using large nanosheets (10-30 μm) that yielded well-packed monolayers and multilayers. Cross-sectional TEM images of the deposited films on SrRuO$_3$ revealed the homogeneous thickness of the individual sheets thus indicating good coverage and minimal overlap between the sheets.$^{95}$ More recently, Yuan, *et al.* found that densely packed titanate nanosheets could be obtained by using both tetrapropylammonium and
tetrabutylammonium hydroxide as exfoliating agents and that the packing was independent of nanosheet concentration. Shorter exfoliation times (~1 day) and higher TBA+/H+ ratios resulted in a higher concentration of nanosheets at the liquid-air interface, possibly because the adsorbed TBA+ ions conferred hydrophobicity to the nanosheets.

References


Chapter 2†

Rational Design and Functionality

Soft chemical synthesis and assembly of layered oxides can be utilized in a strategic manner to design compositions and structures that exhibit interesting functionalities. These properties impact applications in catalysis and photocatalysis, ferroics, chemical sensing, energy storage, and electronics. In this section, the structure-property relationships will be examined with a focus on two main areas presented in this thesis, namely the stabilization of low nuclear clusters on oxide nanosheet supports, and lifting of inversion symmetry in layer perovskites for ferroelectric applications. This chapter starts with a brief description of the key characterization techniques in the context of characterizing layered metal oxides and metal oxide nanosheets presented in this dissertation. This will be followed by a brief discussion of the metal-metal oxide interface and basics of perovskite crystallography that is useful for understanding Chapters 3 and 5. This section converges on the theme of utilizing solid-state and topochemical synthetic approaches to materials design that can find potential applications as catalytic materials and energy storage applications. These approaches enable a comprehensive understanding of structure, bonding, and reactivity that facilitate the rational design of new materials.

2.1 Characterization Techniques

2.1.1 X-ray and neutron diffraction

X-ray diffraction (XRD) refers to the scattering of monochromatic X-rays by successive planes of atoms within a crystal and is a key analytical tool for determining the crystal structure of a bulk material or thin film. The fundamental principle of X-ray diffraction relies on Bragg’s Law, \( n\lambda = 2d\sin\theta \), where \( \lambda \) represents the wavelength, \( d \) represents the interplanar spacing, and \( \theta \) represents the angle of incidence.

XRD has been used to study the course of ion-exchange, exfoliation and restacking processes in layered materials. Sasaki et al. first reported a detailed in-situ XRD study of exfoliation and re-assembly processes for the layered titanate \( \text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4\cdot\text{H}_2\text{O} \) (\( \square \): vacancy). They found that

† Parts of the material presented in this chapter is published in Chem. Soc. Rev. 2018, 47, 2401.
exfoliation of layered titanates by TBA^+OH^- resulted in the loss of the original Bragg diffraction peaks, and that several sharp reflections appeared in the low angle region, indicative of a spacing >10 nm. They were able to track changes in layer spacing by exposing the powder to varying degrees of relative humidity, thus revealing a stepwise hydration process.\footnote{Restacking of nanosheets by the addition of acid or an alkali metal ions results in the appearance of (hk0) and (00l) reflections in the XRD patterns. The absence of (hkl) reflections was attributed to the loss of three-dimensional structure and orientational disorder when the nanosheets were restacked turbostratically.}\footnote{In recent years, synchrotron powder X-ray diffraction have also emerged as key techniques for probing subtle symmetry differences in bulk layered oxides. Synchrotron X-ray sources have an advantage over laboratory scale X-ray diffractometers as they offer higher beam brightness, a high degree of collimation, and variable monochromatic X-ray wavelengths. These methods have been used to study subtle structural changes in layered materials, including the cooperative tilting and rotation of oxygen octahedra in layer perovskites that break inversion symmetry, leading to piezoelectric and ferroelectric properties.}

Neutron diffraction is a complementary technique that can be used to probe both structure and magnetic properties of different solids. In contrast to X-rays, neutrons scatter off the nucleus of an atom and are dependent upon the absorption cross-section rather than the electron density. This technique can thus be employed to distinguish between lighter elements or different isotopes of the same element that cannot be performed by X-rays alone. In this dissertation, neutron diffraction is utilized to precisely determine the position of O atoms in layered perovskites induced by octahedral distortions.

2.1.2 X-ray absorption spectroscopy

X-ray absorption spectroscopy is a widely used technique to probe the local structural environment of a variety of metal complexes ranging from supported catalysts to protein structures as well as solid-state structures. The physical basis of X-ray absorption spectroscopy involves the excitation of an electron by the absorption of a photon via the well-known photoelectric effect. Excitation of the electron occurs at a particular energy, generally termed as the absorption edge, that is
characteristic to each element. There are two components of X-ray absorption spectroscopy: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). XANES probes the structure at or close to the absorption edge and provides information about the oxidation state whereas EXAFS examines the oscillatory part of the spectrum and can elucidate information about geometry (such as coordination number and bond distances). EXAFS is described by the equation

\[
\chi(k) = \sum_{j} N_j f_j(k) e^{-2k^2 \sigma_j^2} \frac{1}{kR_j} \sin[2kR_j + \delta_j(k)],
\]

where \(k\) is the wavenumber, \(N=\)number of neighboring atoms, \(R=\)nearest neighbor distance, \(\sigma^2=\)disorder in the nearest-neighbor distance.

The oscillatory part of the spectrum, \(\chi(k)\), comprises of sinusoidal waves and occurs due to scattering of the excited electron from the neighboring atom with the scattered wave having a phase shift, \(\delta(k)\). The amplitude, \(f(k)\), and phase shift, \(\delta(k)\), of the scattered wave determines the identity of the scattering atom.

2.1.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a powerful tool for directly imaging individual nanosheets as well as for gaining insights into the nanosheet structure and dimensions at atomic resolution (Figure 2.1). Selected area electron diffraction (SAED) patterns can be used to distinguish between single crystal and polycrystalline samples. The SAED patterns of individual nanosheets show a spot pattern indicating that they are single crystals, whereas restacked layered oxides show concentric rings indicative of polycrystalline structure. Additionally, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) techniques have been utilized to visualize the quality of films obtained by layer-by-layer assembly. This technique collects electrons scattered at high angles and the signal intensity is directly proportional to \(Z^2\), where \(Z\) represents atomic number. Ziegler, et al. characterized the superlattices obtained
Figure 2.1 (a) HAADF-STEM (200 kV) image of Rh ($x = 0.026$)-doped Ti$_{1.86-x}$Rh$_x$O$_4$ nanosheets. (b) Magnified HAADF-STEM image (80 kV) of Rh-doped nanosheets. Reproduced with permission from Ref. Copyright 2015 American Chemical Society.

from alternating assembly of HCa$_2$Nb$_3$O$_{10}$ nanosheets and LDHs by HAADF-STEM at atomic resolution and were able to map out the elemental distribution. This study confirmed that the two kinds of nanosheets alternated in the film, with the bright atoms representing perovskite blocks that contained strongly scattering niobium atoms and the darker regions representing lighter element LDH nanosheets. The authors also noted that the morphology of the nanosheets could be selectively modified by the choice of solvent in which they were dispersed.\textsuperscript{8}

2.2 Interfacial chemistry for catalysis

The metal-metal oxide interface is of great interest in both basic science and in applications that include microelectronics, catalysis, surface chemistry, and fuel cells. The field of heterogeneous catalysis relies on such interfaces for metal-support interactions that modulate the stability, activity, and selectivity of catalytic reactions. The coarsening of nanoparticles at working temperatures limits the lifetime of heterogeneous catalysts used in steam reforming, automotive exhaust treatment, catalytic combustion, selective oxidation reactions, and other applications.\textsuperscript{9}
There are two principal mechanisms of nanoparticle coarsening: particle migration and coalescence (PMC) and Ostwald ripening. PMC results from the diffusion of individual particles on supports, which results in their aggregation and coalescence, whereas Ostwald ripening results from the movement of individual atoms from smaller to larger particles. In both cases, the process minimizes the surface energy. The key to designing a durable catalyst is to inhibit coalescence of nanoparticles under operating conditions; this in turn requires fundamental insights into the interactions that stabilize catalytic nanoparticles on their supports.

Chemical specific interactions between metal nanoparticle catalysts and oxide supports have been shown to prevent particle coarsening, and also to modulate the catalytic activity and selectivity of the supported particles. Plausible explanations for the stabilization of late transition metal such as Pt, Pd Rh, and Co on high surface area oxide support surfaces have been evolving in the surface science literature over the past four decades. The ‘strong metal-support interaction’ (SMSI) was first proposed by Tauster and Fung\textsuperscript{10,11} to explain the suppression of H\textsubscript{2} and CO chemisorption on transition metal nanoparticles supported on reducible oxides, such as TiO\textsubscript{2}, under reducing conditions at high temperatures. They postulated that chemical interactions, possibly metal-metal bonding or formation of intermetallic compounds, between titanium cations and the transition metal suppressed chemisorption.\textsuperscript{10} These earlier models and observations led Fu, \textit{et al.} to propose a physical model based on the difference in work functions ($\phi$) between the TiO\textsubscript{2} oxide support and the more electronegative supported metal ($\phi_{\text{metal}} > \phi_{\text{TiO}_2}$). In that model, the electric field that

\textbf{Figure 2.2:} Schematic illustration of (left) outward migration of Ti$^{3+}$ ions driven by work function differences and (right) encapsulation of metal atoms by TiO$\textsubscript{x}$ to minimize surface energy. Reproduced with permission from Ref. 12. Copyright 2005 American Chemical Society.
develops between the oxide and the supported metal drives the migration of titanium cations and results in encapsulation of the metal to minimize its surface energy (Figure 2.2).

Over the past decade, our group has investigated the chemistry of metal-support interface by studying the chemistry of well-dispersed nanoparticles of late transition metal hydroxide nanoparticles onto layered oxide nanosheets. While studying charge inversion and intercalation of anionic nanosheets by metal and metal oxide nanoparticles, Hata, et al. observed the unusual stability of Rh(OH)$_3$ onto layered Nb oxide nanosheets. The anomalous stability of the Rh(OH)$_3$ nanoparticles was attributed to covalent bonding between the metal and the support. This model was supported by calorimetric measurements that showed that the binding of Rh(OH)$_3$ nanoparticles to the nanosheet surface was an exothermic process. In contrast to field-driven migration model for the SMSI, where the supporting oxide is reduced (Figure 2.2), X-ray absorption measurements showed that Rh(OH)$_3$ nanoparticles were reduced to Rh at high temperatures, whereas the oxidation state of Nb in the nanosheet support remained unchanged. Nanoparticles of other late transition metal oxides were also stabilized by binding to HCa$_2$Nb$_3$O$_{10}$ nanosheets, and their stability against coalescence at high temperature was correlated with the exothermicity of the nanoparticle-support interaction. The exothermicity of the nanoparticle-
support interaction was linearly correlated with metal oxide bond strengths, but the slope of the correlation was different for silicate and niobate nanosheets, with the latter showing much stronger bonding interactions and, experimentally, much greater stabilization of the supported nanoparticles (Figure 2.3a,b). Electronic structure calculations revealed a partial charge transfer from late transition metal to the metal oxide support indicating metal-metal bond formation by the overlap of d-orbitals (Figure 2.3b). The strength of binding interaction could thus be tuned by optimizing the d-band energy level. Charge transfer from the more electronegative transition metal (Pt, Rh, Ir, etc.) to the less electronegative metal (Nb) was found to be consistent with Brewer’s investigations of d-orbital mixing that stabilized early-late transition metal intermetallic alloys such as ZrPt₃,¹⁶ exactly as postulated in the initial 1978 report of the SMSI effect by Tauster et al.¹⁰

In Chapter 5, the stability conferred by layered metal oxide supports to stabilizing dinuclear clusters of Rh and Ir is presented in detail. Both Rh and Ir showed a strong interfacial binding on layered metal oxides and hence were chosen as model systems. The stability was characterized by aberration-corrected HAADF-STEM as well as synchrotron X-ray absorption spectroscopy. Aberration-corrected HAADF-STEM corrects for chromatic aberrations and is a valuable technique to get high resolution images of single atoms and low nuclear clusters in STEM mode. X-ray absorption spectroscopy provides information about the bond distances and the coordination environment of the supported metal clusters and thus complements the structure and stability of metal complexes probed by STEM.

2.3 Ferroelectric Layered Perovskites

Solid-state and topochemical routes have opened up avenues for studying layered perovskites that have exotic symmetry-driven properties such as hybrid improper ferroelectricity.¹⁷-²⁰ The best known ferroelectric perovskites that have been commercialized for piezoelectric applications are lead-based compounds like PZT, PMNPT and PbTiO₃, and the mechanism by which these compounds become ferroelectric is second-order Jahn-Teller effect (SOJT).²¹,²² However, lead is toxic and the use of lead-based products is becoming more tightly controlled worldwide. Secondly, the volatility of Pb results in composition changes at processing temperatures above about 400 °C. Also, until recently, ferroelectricity and piezoelectricity have relied almost exclusively on d⁰ transition metal compounds, which have low electronic
conductivity but are typically diamagnetic.\textsuperscript{22,23} The versatility of layered perovskite chemistry, including soft chemical transformations, has created a paradigm shift as new mechanisms can be explored to lift inversion symmetry and look beyond SOJT transitions for ferroelectric and multiferroic applications.

The convergence of theory and experiments have shown that solid-state and topochemical reactions can be used to drive cooperative oxygen octahedral rotations (OORs)\textsuperscript{24}, a mechanism that can break inversion symmetry in layered perovskites to realize piezoelectric and ferroelectric properties.

\textbf{Figure 2.4}: Schematic drawings of (a) octahedral rotation in an ABO\textsubscript{3} perovskite block seen along the z (or c) axis. (b) Pie chart showing all the possible rotations found in naturally occurring and synthetic perovskites before 2001. (c) Schematic showing oxygen octahedral rotation (ORR) in BO\textsubscript{6} octahedra of an ABO\textsubscript{3} perovskite. Reproduced with permission from Refs. 25 and 26. Copyright 1997 International Union of Crystallography.
Before we further describe the way in which OORs can break inversion symmetry, it is important to note that OORs of various types are already abundantly present in ABO$_3$ perovskites, but that they do not remove the inversion centers from these compounds.\textsuperscript{25,26} Benedek, et al.\textsuperscript{27} have noted that 70\% of all the known natural and synthetic ABO$_3$ perovskites have OORs in their crystal structures in the centric $Pnma$ space group. Moreover, ABO$_3$ compounds that are ferroelectric by virtue of the SOJT do not have OORs.\textsuperscript{27} As shown in Figure 2.4a, the Glazer notation of OORs can be explained by two simple examples. When two adjacent layers undergo OORs in opposite directions, it is called an out-of-phase rotation. If we represent the OOR rotation axes in the three orthogonal directions x, y and z, and the out-of-phase rotation occurs only in the z-direction, then this OOR is represented by $a^0a^0c^-$. Here the superscript of zero denotes no rotation, whereas the negative sign indicates the out-of-phase rotation along that axis. Similarly, $a^0a^0c^+$ denotes an OOR with in-phase rotation along the z-axis only. The pie-chart represents the distribution of OORs present in ABO$_3$ perovskites (Figure 2.4b). The majority of these compounds have OORs represented by $a'a'c^+$, and remain in the centric space group $Pnma$ (orthorhombic).\textsuperscript{25,26}

In order to elucidate how OORs do not lift inversion symmetry in ABO$_3$ perovskites, it is helpful to look at OORs in a single layer of BO$_6$ octahedra. In Figure 2.4c, a two-dimensional representation of the BO$_6$ octahedra in an ABO$_3$ perovskite is shown. If we imagine that the BO$_6$ octahedron at the center of the plane rotates in a clockwise direction about the out-of-plane axis, then the nearest neighbor octahedra rotate in the counter clockwise direction. This leads to the retention of the inversion center at the B site of the BO$_6$ octahedra, which is highlighted by the symbol ‘i’. Now, if this two-dimensional octahedral layer is expanded to infinity along both the x and y axes, then the inversion centers at all the B sites of the individual BO$_6$ octahedra are retained. This makes the entire ABO$_3$ structure centrosymmetric, as shown by the rotated octahedra in Figure 2.4c.
Figure 2.5: Schematic drawings of (a) the ABO$_3$ perovskite structure (also considered as $n = \infty$ layering), and Ruddlesden-Popper structures (b) $n = 1$ RP A$_2$BO$_4$, (c) $n = 2$ RP A$_3$B$_2$O$_7$ and (d) $n = 1$ RP AA’BO$_4$ with red and blue A and A’ cations in alternating layers. The inversion centers are highlighted in the crystal structures by the letter ‘i’. Adapted with permission from Ref. 28. Copyright 2012 Elsevier.

By comparing ABO$_3$ perovskites to the layered perovskites in the Ruddlesden-Popper, Dion-Jacobson and Aurivillius structural families, we observe a key distinction, which is the discontinuity of the BO$_6$ octahedra along the stacking axis. In Figures 2.5a and 2.5b, an ABO$_3$ perovskite is compared with its single-layer Ruddlesden-Popper relative A$_2$BO$_4$. Both the
structures have high symmetry with inversion centers ‘i’ at the B-atom sites that center the BO$_6$ octahedra.\textsuperscript{28} In ABO$_3$, inversion centers also exist at the A sites, but in A$_2$BO$_4$ these exist between the A sites. Interestingly, when these structures are compared with the two-layer A$_3$B$_2$O$_7$ structure shown in Figure 2.5c, we see that the inversion center is absent at the B-site, although inversion centers are retained midway between the A sites, as in the single-layer compound. Furthermore, as seen in Figure 2.5d, when the cations on half the A-sites are replaced by different cations A’ in an ordered fashion (as would occur, e.g., in the compound NaR$TiO_4$, $R =$ rare-earth), the inversion centers are lost at the B-sites but they still exist at the midpoints between the A- and A’-cation sites. This maintains the overall centrosymmetry of this compound, and for AA’BO$_4$, the space group symmetry is $P4/nmm$.

Now, in order to completely remove all the inversion centers in an AA’BO$_4$ compound, OORs need to be introduced, as has been shown by Akamatsu et al.\textsuperscript{17} Introduction of OORs can remove the inversion centers between the A-sites and also between the A’-sites (Figure 2.5a). The appropriate OORs thus render the compounds non-centrosymmetric. DFT calculations performed by Akamatsu et al.\textsuperscript{17} and Sen Gupta et al.\textsuperscript{18} predicted that AA’BO$_4$ compounds such as NaR$TiO_4$ and LiR$TiO_4$ can undergo a phase transition from the centrosymmetric $P4/nmm$ space group to noncentrosymmetric $P-42_1m$. Their calculations predicted centrosymmetric structures with larger rare earth ions La and Nd. With smaller ions (Sm – Ho), the rare earth is underbonded by oxygen and this triggers a rotation of the octahedra such that the coordination environment around the oxygen is satisfied.

In Chapter 3, a detailed structural investigation of a Ruddlesden-Popper niobate, Li$_2$SrNb$_2$O$_7$, is presented which undergoes a structural transformation from a polar structure to an antiferroelectric structure at 90 K resulting from the coupling of oxygen octahedral rotations (OORs) with A-site displacements. The resulting antiferroelectric phase is characterized by a combination of synchrotron X-ray and neutron diffraction as well as electrical characterization techniques.

References


Chapter 3

Competing polar and antipolar structures in the Ruddlesden-Popper layered perovskite Li$_2$SrNb$_2$O$_7$* 

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*This work is published in Chem. Mater. 2019, 31, 4418.
3.1 Introduction

Noncentrosymmetric materials are interesting to investigate because of their properties of technological relevance, which include as piezoelectrics, ferroelectrics, and multiferroics. Ferroelectric oxides are widely used in ultrasonics, electronics, sensors, capacitors, and actuators and are dominated by ABO$_3$ perovskites, where polarization is induced by off-centering of 3$d^0$ cations by second-order Jahn Teller (SOJT) active effects.\(^1\) This mechanism limits the range of available compositions of acentric perovskites to those that incorporate 3$d^0$ cations that can hybridize with O 2$p$ states.\(^2\) Over the past few years, a series of non-centrosymmetric layered oxides have been predicted by theory and confirmed by experiment, in which inversion symmetry is lifted by a combination of oxygen octahedral rotations (OORs) and A-site cation ordering.\(^3\)-\(^7\) Benedek and Fennie first proposed a ‘hybrid improper ferroelectricity’ (HIF) mechanism\(^8\), where inversion symmetry is lifted by condensation of two distinct symmetry-breaking modes (rotation and tilting of oxygen octahedra) in the n=2 Ruddlesden-Popper (RP) compound Ca$_3$Mn$_2$O$_7$. This mechanism has since been realized experimentally in several n=2 RP and Dion-Jacobson (DJ) phase layer perovskites\(^7,9\)-\(^17\) as well as in perovskite superlattices\(^18,19\) and molecular perovskites\(^20\). In related work, Rondinelli and co-workers employed group theoretical methods to elucidate the crystal chemical principles that govern the design of acentric n=1 RP AA’BO$_4$ layer perovskites.\(^21\) Over the past few years, a number of layered oxides with polar space group symmetry have been reported experimentally and noncentrosymmetricity has been attained by the trilinear coupling of A-site cation displacements and OORs.\(^7,10,22\)

More recently, the HIF mechanism has been extended to include antiferroelectric displacements of A-site cations driven by a reversal in the direction of OORs. Antiferroelectrics are materials that contain electric dipoles oriented antiparallel within individual domains. They are known to have low dielectric loss and are gaining attention as energy storage materials, but they cannot be readily distinguished from other centrosymmetric materials by symmetry.\(^23\) Another limitation is that most known antiferroelectrics are lead-based compounds that are toxic. One approach to overcome these limitations is to search for centrosymmetric materials that have polar metastable phases. Lu et al. predicted a polar-to-nonpolar phase transition in a series of n=2 RP A$_3$B$_2$O$_7$ thin films resulting from compressive and/or axial strain, which could be used to tune weak ferromagnetism in antiferromagnetic compounds by varying the applied electric field at the
boundary of the phase transition.\textsuperscript{24,25} Similarly, Nowadnick \textit{et al.} identified the antipolar $Pnam$ phase as one of the ferroelectric switching pathways in the $n=2$ RP $Ca_3Ti_2O_7$ using group theory, where the polar and antipolar phases differ merely in the octahedral rotation sense ($a^0a^0b^+$) across the interlayers.\textsuperscript{26} Recently, Yoshida \textit{et al.} observed a structural transformation from a polar $A2_1am$ phase to a non-polar $Pnab$ phase by an in-phase to out-of-phase change in the OOR sense in $n=2$ RP $Sr_3Zr_2O_7$.\textsuperscript{11} This kind of polar-to-antipolar phase transition could be very interesting for realizing new antiferroelectric materials for energy storage applications.

In this study, we report another polar-to-antipolar phase transition in a polycrystalline $n=2$ RP phase layered niobate $Li_2SrNb_2O_7$, which contains intergrowths of two perovskite $SrNb_2O_6$ layers with Li-O interlayers when cooled from room temperature to 90 K. The structure of $Li_2SrNb_2O_7$ was previously assigned to the centrosymmetric $Amam$ space group\textsuperscript{27} but this study reveals that the polar $A2_1am$ and antipolar $Pnam$ structures are energetically more stable by both theory and experiment. The two structures result from the coupling of two octahedral rotations and tilts (denoted by irreducible representations (irreps) $X_3^-$ and $X_2^+$) along different crystallographic axes and differ merely in the phase of their rotation across the interlayers, i.e., order parameter directions of the irreps (\textbf{Figure 3.1}). In contrast to studies on $A_3B_2O_7$ systems that mentioned that the nonpolar $Pbcn$ phase ($a^a(c^-)$) competes with the polar $A2_1am$ phase, this study reveals that there is a competition between the polar $A2_1am$ and antipolar $Pnam$ phases, both of which have OORs denoted by $a^a(c^+).$ In the former structure, the combination of the $X_3^-(a, -a)X_3^- (a, -a)$ and $X_2^+ (a, -a)X_2^+ (a, -a)$ distortion modes lifts inversion symmetry and induces a polar $\Gamma_5^-$ ($a$, $a$) distortion mode, while in the latter structure, the combination of the $X_3^- (a, -a)X_3^- (a, -a)$ and the $X_2^+ (a, a)X_2^+ (a, -a)$ distortion modes keeps inversion symmetry and induces an antipolar $M_5^-(a, 0)$ distortion mode. A phase diagram of $Li_2SrNb_2O_7$ was determined by combining optical second harmonic generation, temperature-dependent synchrotron X-ray and neutron diffraction, and electrical characterization.
Figure 3.1: (a) Calculated crystal structure and (b) layer resolved polarization of n=2 RP Li$_2$SrNb$_2$O$_7$ in the polar $A2i$ am space group. (c) Calculated crystal structure and (d) layer resolved polarization of n=2 RP Li$_2$SrNb$_2$O$_7$ in the antipolar $Pnam$ space group. (e) Schematic of octahedral rotation patterns from which the $A2i$ am and $Pnam$ structures are constructed with fixed tilt. The blue and orange octahedra represent alternating layers and are corner-shared but their connectivity is omitted to clearly show the rotation patterns.$^{28}$
Table 3.1: Calculated energies of Li$_2$SrNb$_2$O$_7$ with different oxygen octahedral rotations (in meV/formula unit).

<table>
<thead>
<tr>
<th>Space Group</th>
<th>OOR pattern$^a$</th>
<th>Total energy$^b$ (meV/f.u.)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Amam$</td>
<td>($\Phi\Phi0$)</td>
<td>$-81$</td>
<td>Previously reported$^{27}$</td>
</tr>
<tr>
<td>$A2_{1}am$</td>
<td>($\Phi\Psi_{z}$)</td>
<td>$-89$</td>
<td>Polar structure</td>
</tr>
<tr>
<td>$Pnam$</td>
<td>($\Phi\Psi_{z}$)</td>
<td>$-90$</td>
<td>Antipolar structure</td>
</tr>
<tr>
<td>$Cmca$</td>
<td>($00\Psi_{z}$)</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Octahedral rotation patterns are in Aleksandrov notation.

$^b$Total energies are with respect to the parent $I4/mmm$ structure.

3.2 Experimental Section

3.2.1 First principles calculations: First-principles calculations based on density functional theory (DFT) were carried out using the projector augmented-wave (PAW) method$^{29,30}$ and the GGA-PBEsol functional$^{31-33}$ as implemented in the Vienna Ab initio Simulation Package (VASP)* code$^{34-37}$. PAW data sets with radial cutoffs of 1.4 Å, 2.1 Å, 1.5 Å, and 0.8 Å were employed for Li, Sr, Nb, and O, respectively. Li 1s, Sr 4s, 4p, and 5s, Nb 4p, 4d, and 5s, and O 2s and 2p orbitals are treated as valence electrons. A plane-wave cutoff energy of 550 eV and 700 eV was used when structural optimization and density functional perturbation theory (DFPT) calculations were performed, respectively. Γ-centered k-point mesh sampling of $4 \times 4 \times 1$ was used for the $\sqrt{2} \times \sqrt{2} \times 1$ supercells of the conventional $I4/mmm$ unit cell with 24 atoms, except for the DFPT calculations, where an $8 \times 8 \times 2$ mesh was used for the accuracy. Lattice constants and internal atomic coordinates were optimized until residual forces and stresses become less than 0.01 eV/Å and 0.08 GPa, respectively. The Born effective charge tensors were calculated by using DFPT calculations implemented in the VASP code.

* Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the products identified are necessarily the best available for the purpose.
Figure 3.2 Energy band structures of Li$_2$SrNb$_2$O$_7$ from aristotype $I4/mmm$ structure.

Phonon frequencies were derived from the calculated force constants using the PHONOPY code$^{38}$. The phonon dispersion curves were displayed for a standard primitive cell$^{39,40}$ along a $q$-space path based on crystallography$^{41}$. Ground-state structures for Li$_2$SrNb$_2$O$_7$ were explored via a method described by Togo and Tanaka$^{42}$ as follows: zone-center phonon frequencies were calculated for the $\sqrt{2} \times \sqrt{2} \times 1$ supercell of the conventional cell of the aristotype $I4/mmm$ phase. After perturbing the structure according to the eigenvectors of the obtained imaginary-frequency unstable phonon modes, structure optimizations were performed under symmetry constraints to obtain new stable structures with lower symmetry. Subsequently, we calculated phonon frequencies for the fully-relaxed structures to see if unstable modes were still found. If not found, the structure was proven to be dynamically stable. If found, structural perturbations and subsequent optimization were done. This process was repeated until no unstable phonon modes were observed. The cell size was fixed during the structure exploration. We note that zone-boundary phonon modes at the X and M points, which are $(1/2 \ 1/2 \ 0)$ and $(0 \ 0 \ 1)$ in the conventional basis ($(0, 0, 1/2)$ and $(1/2, 1/2, -1/2)$ in the primitive basis)$^{43}$ respectively, are folded into the $\Gamma$ point for the $\sqrt{2} \times \sqrt{2} \times 1$ supercell. Therefore, we explored stable structures within a subspace spanned with linear combinations of atomic displacement modes at the $\Gamma$, X, and M points. This method has been applied to ground-
state structure explorations for other layer perovskite systems, resulting in a good agreement with the results of experimental structural identifications. Symmetry mode analysis was performed to decompose distortions into symmetry-allowed modes with relevant irreps using the AMPLIMODES tool.

3.2.2 Synthesis: Polycrystalline Li$_2$SrNb$_2$O$_7$ was synthesized by grinding the precursors Li$_2$CO$_3$ (>99%, Aldrich), SrCO$_3$ (>99.9%, Aldrich), and Nb$_2$O$_5$ (>99.5%, Alfa Aesar) and heating them at 600 °C for 12 h followed by re-grinding, pelletizing and heating the pellet at 1050 °C for 6 h. The second heating step was repeated until the phase-pure compound was obtained.

3.2.3 Materials Characterization: Phase purity was confirmed by laboratory X-ray diffraction using a Malvern Panalytical theta-theta X-ray diffractometer (monochromatized Cu Kα radiation). Temperature-dependent synchrotron X-ray diffraction patterns (SXRD) were obtained at the 11-BM-B beamline of Argonne National Laboratory (λ = 0.412632 Å) using 12 Si (111) crystal analyzers and LaCl$_3$ scintillation detectors.

Neutron powder diffraction (NPD) was performed at the BT-1 powder diffractometer at NIST using Ge(311) and Ge(733) monochromators with wavelengths of 2.079 Å and 1.197 Å respectively. Measurements were performed at 90 K and 300 K after loading the sample in a vanadium can. Rietveld refinement of synchrotron x-ray and neutron diffraction patterns were performed by using GSAS-EXPGUI programs. Temperature-dependent optical SHG measurements were performed in reflection geometry using a Ti-sapphire laser of incident wavelength 800 ± 20 nm, 80 fs pulses at a frequency of 2 kHz. Polarization-field hysteresis and current versus field measurements were performed by first depositing 200 nm Pt electrodes on a dense pellet for electrical contact and then applying a DC field of 1 kV-10 kV using a Sawyer-Tower circuit at a measurement frequency of 10 Hz. Low temperature dielectric measurements
were obtained using a Precision LCR Meter (HP4284A, Agilent Technologies, Santa Clara, CA) at a frequency range of $10^3$-$10^6$ Hz from 300 K down to 100 K at 10 K intervals.

3.3 Results and Discussion

3.3.1 First Principles Calculations

To check dynamical stability, phonon dispersion curves were calculated for the aristotype $I4/mmm$ phase (Figure 3.2). Phonon dispersion curves showed structural instabilities at the $\Gamma$, $X$, and $M$ points that were frequently observed to generate lower symmetry structures in other RP

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**Figure 3.3:** (a) Temperature-dependent SHG measurement of polycrystalline Li$_2$SrNb$_2$O$_7$. (b) Tracking the disappearance of the 021 and 221 superlattice reflections with increasing temperature using synchrotron X-ray diffraction.
To thoroughly search for the most stable structural phase by unstable phonon modes based on the calculations, a “family-tree” diagram was constructed that lists the total energies of all the structures with respect to the parent $I4/mmm$ structure. First-principles calculations by DFT revealed that among the several metastable phases, the polar $A2_{\text{IAM}}$ phase was energetically similar to the antipolar $Pnam$ phase and both had the lowest energy with respect to the parent $I4/mmm$ phase. The two most stable structures of $\text{Li}_2\text{SrNb}_2\text{O}_7$ are the antipolar $Pnam$ structure whose net polarizations in alternating double perovskite layers are cancelled and the polar $A2_{\text{ IAM}}$ structure which has net polarization (Figure 3.1). One of the common maximum supergroups of the two phases is $Amam$ space group. The corresponding $Amam$ structure has an $a' a' c^0$ OOR pattern. Symmetry mode analysis for the two structures with respect to the $Amam$ phase revealed that the polar $A2_{\text{IAM}}$ and $Pnam$ phases are derived by $\Gamma_2 \Gamma_2$ and $Y_2^2 Y_2$ distortion modes from the $Amam$ phase, respectively. Symmetry mode analysis with respect to the parent $I4/mmm$ structure provides us with more insight into the symmetry aspects of the structural features. Both structures have the same OORs represented by the irreps, $X_2^-$ and $X_3^+$ (Table A1). The difference is in the direction of the order parameter of the irreps. Depending on the relative direction of the $X_2^-$ and $X_3^+$ modes, induced modes can be polar ($\Gamma_5^-$) or antipolar ($M_5^-$). In the $A2_{\text{IAM}}$ structure, the combination of the $X_2^- (a, -a)$ and $X_3^+ (a, -a)$ distortion modes breaks inversion symmetry and induces a polar $\Gamma_5^-(a, a)$ distortion mode. As in hybrid improper ferroelectrics, the freezing of two types of OORs drives the polar distortion. On the other hand, in the $Pnam$ structure, the combination of the $X_2^- (a, -a)$ and $X_3^+ (a, a)$ distortion modes induces an antipolar $M_5^- (a, 0)$ distortion mode, retaining inversion symmetry. The freezing of two types of OORs leads to the antipolar distortion. Thus, the $Pnam$ phase could be a hybrid improper antiferroelectric.\cite{13,14} When the direction of tilts are fixed and rotations are varied (Figure 3.1e), the two structures have the same rotation direction for the two layers within a perovskite block, but the direction is in-phase across neighboring double perovskite layers. The condensation of the $X_3^- (a, -a)X_3^- (a, -a)$ distortion mode leads to the common supergroup $Amam$ phase. The $\Gamma_2^2 \Gamma_2^2$ and $Y_2^2 Y_2$ distortion modes with respect to the $Amam$ phase mainly consist of the combination of the $X_2^+ (a, -a)X_2^+ (a, -a)$ and $\Gamma_5^-(a, a)\Gamma_5^-(a, a)$ distortions and that of the $X_2^+ (a, a)X_2^+ (a, a)$ and $M_5^- (a, 0)M_5^- (a, 0)$ distortions, respectively (Figure A1). The difference in the rotation patterns for $A2_{\text{IAM}}$ and $Pnam$ structures can be represented by the Glazer notation $a' a' c^+/a' a' c^+$ and $a' a' c^+/a' a' -(c^+)$ as described before\cite{48} and can be more easily distinguished using Aleksandrov notation (Table 3.1).
3.3.2 Structural Characterization

Optical second harmonic generation (SHG) showed a finite signal at 300 K, consistent with the polar $A_{21}am$ structure. The gradual disappearance of the SHG signal at 550 K indicates a transition to a centrosymmetric structure, which was found to be reversible upon cooling (Figure 3.3a). At low temperatures, SHG shows a thermal hysteresis behavior where the signal peaks at 150 K but doesn’t recover until 200 K during the heating cycle, thus indicating a first-order phase transition (Figure A2). Room temperature synchrotron X-ray diffraction patterns revealed the presence of two weak (021) and (221) superlattice reflections (i.e. $\frac{1}{2} \frac{3}{2} 0$ and $\frac{1}{2} \frac{3}{2} 2$ with respect to the $I4/mmm$ structure) that correspond to $\sqrt{2}a_p \times \sqrt{2}a_p \times c_p$ enlargement of the unit cell with respect to the aristotype tetragonal $I4/mmm$.
The room temperature scan matched well with both the $A_{21}am$ and $Amam$ structures, but they could not be readily distinguished using X-rays (Figure A3). On the other hand, powder neutron diffraction at 300 K indicated that the room temperature phase could be fitted to the polar $A_{21}am$ structure (Figure 3.4a), which gave a slightly better fit than the $Amam$ structure (Figure A4). Thus, the structure was found to be polar at room temperature, in good agreement with the SHG result. The refinement of both synchrotron X-ray and neutron diffraction data were complicated by the presence of stacking faults, which cause largely asymmetric peak profiles (the inset of Figure 3.4a). The stacking fault could also be imaged by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging along [101] axis which showed a triple layered perovskite block as highlighted (Figure 3.4b). Both HRTEM and HAADF-STEM images indicated multiple kinds of stacking faults but did not accurately reveal all the different types of stacking faults present (Figure A5). Tables 3.2 and 3.3 list the refined atomic coordinates for $Li_2SrNb_2O_7$ using SXRD and NPD data, respectively. The structure (Figure 3.2b).
refined structure for A2\textit{am} phase showed a small structural distortion as indicated by small OOR (Figure A6).

At high temperatures, SXRD showed the disappearance of the (021) and (221) superlattice reflections at 650 K and revealed a phase transition to the tetragonal \textit{I4/mmm} structure. The disappearance of the (221) reflection at 550 K likely corresponds to a centrosymmetric structure as it correlated well with the disappearance of SHG signal, but the space group could not be determined unambiguously. The disappearance of the (221) reflection did not match the \textit{Amam} model (that is expected from first principles calculations) as it has the same reflection conditions as A2\textit{am} structure. With decreasing temperature, several new reflections appeared at 200 K that matched well with the antipolar \textit{Pnam} structure. These include reflections such as (141), (270), (290), (341), (490), (690), and many more that are forbidden in the A2\textit{am} space group as they do not obey the reflection condition \(k + l = 2n\) for \textit{A}-centered lattices. Figure 3.5a and 3.5b track the thermal evolution of the (141) and (341) reflections with temperature and reveal that there is a marked increase in the intensity of these reflections at around 200 K. However, in these temperature ranges, there seems to be a coexistence of both polar and antipolar phases, thus indicating a diffuse phase transition between the A2\textit{am} and \textit{Pnam} phases. Powder neutron diffraction collected at 90 K could be fitted with the \textit{Pnam} model (Figure A7 and Table A2).

To further elucidate the electrical properties of the emergent phase at low temperatures, polarization-field hysteresis loops, \(P(E)\), were measured under liquid nitrogen. The \(P(E)\) measurements suggested antiferroelectric behavior at 77 K as shown by the double hysteresis loops with polarization values of \(\approx 1.0 \ \mu\text{C/cm}^2\), although the loops could not be saturated (Figure 3.5c). The measured polarization was much lower than the calculated value by DFT (25 \(\mu\text{C/cm}^2\)). The low polarization value was attributed to the polycrystalline nature of the sample which had random orientations and was consistent with previous polarization values obtained on polycrystalline samples. Additionally, the current (\(I\)) vs voltage (\(V\)) curve showed a peak in the current at high electric fields resulting from polarization that is suggestive of antiferroelectric behavior (Figure A8). Room temperature \(P(E)\) measurements showed a high loss in capacitance values due to conductivity of lithium ions (Figure A9).
Figure 3.6: Temperature-dependent dielectric permittivity measurements of Li$_2$SrNb$_2$O$_7$ plotted as (a) $\varepsilon'$ vs $T$ and (b) inverse dielectric permittivity vs $T$ at 1 MHz.

Temperature-dependent dielectric permittivity values were measured in the frequency ranges of $10^3$-$10^6$ Hz in the temperature range of 100-300 K and are plotted as dielectric constant $\varepsilon'$ vs $T$ as well as $1/\varepsilon'$ vs $T$ in Figure 3.6a and 3.6b. An increase in the measured relative permittivity values was observed at all frequencies upon decreasing the temperature to 200 K. The dielectric anomaly correlated well with antiferroelectric behavior that emerges starting at 200 K as antiferroelectric materials are known to have large dielectric constants (Figure 3.6a). A plot of inverse dielectric permittivity vs $T$ ($1/\varepsilon'$ vs $T$) indicated that it follows the Curie-Weiss law, $\varepsilon' = C/(T-\theta)$ for $T >$
Figure 3.7 (a) Total energy as a function of mode amplitude showing the stability of in-phase rotation ($X_2^+$) and out-of-phase tilts ($X_3^-$). (b) Total energy as a function of the amplitude of $\Gamma_5^-$ mode resulting from the condensation of $X_2^+$ (a, -a) and $X_3^-$ (a, -a) to induce a polar phase ($A2_1am$). (c) Total energy as a function of the amplitude of $M_5^-$ mode resulting from the condensation of $X_2^+$ (a, a) and $X_3^-$ (a, -a) to induce an antipolar phase ($Pnam$).

Table 3.2: Refined atomic positions and thermal parameters for Li$_2$SrNb$_2$O$_7$ against the $A2_1am$ model using SXRD data at 300 K. Values in parentheses indicate one standard deviation.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>8b</td>
<td>-0.5100(0)</td>
<td>-0.0038(3)</td>
<td>0.7598(6)</td>
<td>0.0000(5)</td>
</tr>
<tr>
<td>Nb1</td>
<td>8b</td>
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<td>8b</td>
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<td>0.0037(3)</td>
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<td>8b</td>
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<td>0.4934(7)</td>
<td>0.3835(7)</td>
<td>0.0054(0)</td>
</tr>
<tr>
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<td>8b</td>
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<td>0.2202(2)</td>
<td>0.2823(7)</td>
<td>0.0045(0)</td>
</tr>
<tr>
<td>O4</td>
<td>4a</td>
<td>-0.7412(5)</td>
<td>0.7874(1)</td>
<td>0.00000</td>
<td>0.0055(5)</td>
</tr>
<tr>
<td>Sr1</td>
<td>4a</td>
<td>-0.7369(9)</td>
<td>0.2452(6)</td>
<td>0.00000</td>
<td>0.0046(9)</td>
</tr>
</tbody>
</table>
Lattice parameters: $a = 5.5918(5) \, \text{Å}$, $b = 5.5987(0) \, \text{Å}$, and $c = 18.0102(6) \, \text{Å}$, $R_{wp} = 31.88\%$, $R_p = 7.75\%$.

Table 3.3: Refined atomic positions and thermal parameters for Li$_2$SrNb$_2$O$_7$ against the $A2_{1}am$ model using NPD data at 300 K. Values in parentheses indicate one standard deviation.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
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<td>0.0259(9)</td>
<td>0.7615(9)</td>
<td>-0.0171(9)</td>
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<tr>
<td>Nb1</td>
<td>8b</td>
<td>$-0.7385(2)$</td>
<td>0.2462(2)</td>
<td>0.3844(9)</td>
<td>0.0046(9)</td>
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<tr>
<td>O1</td>
<td>8b</td>
<td>$-0.4950(2)$</td>
<td>0.0032(3)</td>
<td>0.5981(5)</td>
<td>0.0002(8)</td>
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<tr>
<td>O2</td>
<td>8b</td>
<td>0.0224(3)</td>
<td>0.5030(8)</td>
<td>0.3838(9)</td>
<td>0.0064(5)</td>
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<td>8b</td>
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<td>0.0052(4)</td>
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<tr>
<td>O4</td>
<td>4a</td>
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<td>0.0058(0)</td>
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<tr>
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<td>0.2562(2)</td>
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<td>0.0050(1)</td>
</tr>
</tbody>
</table>

Lattice parameters: $a = 5.5932(0) \, \text{Å}$, $b = 5.5910(8) \, \text{Å}$, and $c = 18.0001(9) \, \text{Å}$, $R_{wp} = 10.08\%$, $R_p = 7.84\%$.

206 K, where $C$ is a Curie constant and $\theta$ is a Curie-Weiss temperature. Based on the Curie-Weiss fit, $C = 1.1 \times 10^4 \, \text{K}$, and $\theta = -0.33 \, \text{K}$. The extremely low $\theta$ value was attributed to a series addition of capacitance values from both polar and nonpolar domains possibly due to the presence of grain boundaries thus making the resulting capacitance values much lower.

3.3.3 Origin of Ferroelectricity/Antiferroelectricity

The polar-to-antipolar phase transition shown upon cooling down to 90 K is the result of a change in the OOR direction across the interlayers and the two phases compete, thus resulting in a diffuse phase transition in the SXRD data. In this system, both the SOJT mechanism, where $d$(Nb)-p(O) charge transfer induces a polarization in the NbO$_2$ layer, and the trilinear coupling of OOR and OOT distortions with A-site cation displacement, played an important role in stabilizing the polar
and antipolar phases. From Figure 3.1, the calculated layer-resolved polarization values indicated that for both $A2_1am$ and $Pnam$ phases, the polarization in the NbO$_2$ layers enhances the polarization in the SrO layers. This is in contrast to Sr$_3$Zr$_2$O$_7$, where polarization is merely contributed to by A-site cation displacements induced by OOR and OOT distortions$^{13}$. Considering each distortion mode individually, calculations revealed that the out-of-phase OOT mode resulted in a net energy gain but the in-phase OOR mode did not result in energy minimization (Figure 3.7a). This observation is in sharp contrast to previous studies on hybrid improper ferroelectrics, where each of and modes resulted in significant energy gains. Calculations were also performed to determine the energetics of the coupling of OOR and OOT modes with the displacement of A-site cations (Figure 3.7b and c). Both polar and antipolar phases were found to be energetically most stable when they had a finite amplitude of OOR and OOT modes coupled with A-site displacements. This observation was corroborated with calculations on the energetic contributions of the different distortion modes which revealed that the trilinear coupling of $X_2^+$ and $X_3^-$ modes with the polar (or antipolar) modes resulted in the lowest energy structure (Figure A10). Hence, the hybrid improper
ferroelectricity/antiferroelectricity mechanism plays an equally important role in stabilizing the polar phase for Li$_2$SrNb$_2$O$_7$.

3.4 Conclusion

In summary, this study has revealed a new polar layered oxide, Li$_2$SrNb$_2$O$_7$, with an $A2_1am$ structure at room temperature that shows a phase transition to an antipolar $Pnam$ phase upon cooling to 200 K. On heating to high temperatures, it undergoes a phase transition to an unknown centrosymmetric phase at 550 K and a tetragonal $I4/mmm$ structure at 650 K. Figure 3.8 shows the phase diagram of Li$_2$SrNb$_2$O$_7$ as a function of temperature. Temperature-dependent second harmonic generation revealed a noncentrosymmetric-to-centrosymmetric phase transition upon cooling from room temperature to 90 K. The polar-to-antipolar phase transition was also confirmed by polarization-hysteresis loop measurements which showed double hysteresis behavior at 90 K and an increase in the dielectric susceptibility at 200 K. The phase transition was attributed to a competition between hybrid improper ferroelectric/antiferroelectric mechanisms, where the polar/antipolar phases were stabilized by a trilinear coupling with oxygen octahedral distortions. Additionally, the SOJT mechanism also plays an important role in stabilizing the polar/antipolar phases in this system. The polar-to-antipolar phase transition offers a novel path to realize antiferroelectric materials in compounds that have energetically similar polar and antipolar structural phases. New materials discovered by this method can be interesting for applications in energy storage devices.

3.5 References


Chapter 4

Thermochemical Measurements of Exfoliation and Restacking Processes in a Layered Calcium Niobate by Isothermal Titration Calorimetry*

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*This work is taken from the final draft of a manuscript in preparation.
4.1 Introduction

Lamellar compounds are materials that are covalently bonded laterally but stacked vertically by electrostatic or weak van der Waals forces. Layered oxides represent a special class of materials containing intergrowths of charged layers interleaved with cations or anions making them amenable to low temperature topochemical ion-exchange and exfoliation reactions.\(^1\) In the past few decades, topochemical ion-exchange and exfoliation reactions have been extensively utilized in layered metal oxides for realizing many interesting properties ranging from photocatalysts, battery electrodes, catalyst supports, high-\(k\) dielectrics, and ferroelectrics.\(^2\) With a growing interest in nanomaterials, liquid-phase exfoliation has been demonstrated in a variety of layered solids to form 2D sheets, such as clays\(^3\), layered birnessites\(^4\), graphene\(^5\), chalcogenides\(^6\), and layered perovskites\(^7\). A key principle that drives exfoliation in systems containing charged layers with a counterion is through osmotic swelling which causes an influx of solvent molecules that weakens the interlayer interactions.\(^8\) On the other hand, layered materials bonded via weak van der Waals forces are exfoliated by shear in the presence of different intercalating reagents\(^9,10\). In addition to exfoliation, nanosheets can also be flocculated into three-dimensional solids that typically results in the formation of precipitates (turbostratic restacking) with loss of registry between layers\(^11\) but occasionally can re-form the bulk layered solid with the layers oriented.\(^12\)

Over the past few decades, a variety of models have been proposed to understand the driving forces for exfoliated/restacked phases in different layered solids. For instance, Sasaki \textit{et al.} followed the reassembly of titanate nanosheets upon drying by in-situ X-ray diffraction to obtain the TBA-intercalated compound.\(^13\) Their study established a pairwise association of nanosheets with varying humidity that resulted in a gradual increase in the number of layers. Similarly, Petkov \textit{et al.} investigated exfoliated-restacked phases of layered WS\(_2\) by pair distribution function and found that they possess a significant three-dimensional order thus indicating that it is not turbostratic restacking.\(^14\) More recently, Geng \textit{et al.} found that swelling of layered materials is driven by osmotic pressure difference between the interlayer galleries and the surrounding environment and established a threshold concentration for maximum swelling for different amines and ammonium hydroxides.\(^15,16\)

Despite some progress in mechanistic understanding of exfoliation and restacking processes, a quantitative understanding of the thermochemistry that converts a three-dimensionally ordered
layered solid to two-dimensional nanosheets and back to a bulk solid is lacking. Isothermal titration calorimetry (ITC) is a technique that can directly quantify the thermochemistry (enthalpy and entropy) of a chemical process under wet chemical conditions. This instrument has traditionally been utilized to study biomolecular interactions, such as protein-protein interactions,\textsuperscript{17-19} where a high-affinity ligand binds to macromolecules. In recent years, however, this technique has been utilized to quantify the enthalpy of binding of metal nanoparticles onto catalyst supports\textsuperscript{20,21} and more recently, cation exchange in nanocrystals\textsuperscript{22}. In this study, we report the first quantification of the thermochemistry of exfoliation/restacking processes in a layered calcium niobate using ITC by constructing a Born-Haber cycle for the different chemical processes. Layered calcium niobate has been extensively investigated for ion-exchange, exfoliation, restacking, and assembly processes\textsuperscript{23-25} and was thus chosen as the model system for this study. The thermochemical values quantified by ITC were correlated with vibrational sum frequency spectroscopy (VSFS) measurements on a well-packed monolayer of calcium niobate nanosheets at the air-water interface of a Langmuir trough which indicated a high degree of oriented water molecules under the nanosheets. This study revealed that restacking of calcium niobate is entropically driven due to oriented water dipoles under the charged nanosheet surface that cause a significant disorder upon restacking.

4.2 Materials and Methods

4.2.1 Synthesis and Exfoliation

KCa$_2$Nb$_3$O$_{10}$ was prepared by solid state reaction as previously reported with a few modifications.\textsuperscript{20} Briefly, K$_2$CO$_3$ (5\% excess), CaCO$_3$ (Sigma Aldrich), and Nb$_2$O$_5$ (Sigma Aldrich) were ground and calcined at 1200 °C for 24 hours. The parent solid (0.5 g) was acid-exchanged for 3 days using hydrochloric acid (50 mL, 1 M) with the acid being replaced every 24 hours. The proton-exchanged solid, HCa$_2$Nb$_3$O$_{10}$, was exfoliated by stirring 0.1 g compound in 50 mL tetra-$n$-butylammonium hydroxide (TBAOH) (TBA$^+$/H$^+$ = 0.25) overnight and the resulting suspension was allowed to settle before collecting the sheets by decantation. (In this study, the protonated solid was exfoliated using 0.24 mol eq. TBAOH to prevent excess TBAOH interfering with the measurement of thermochemical parameters. The choice of molar ratio of TBA$^+$/H$^+$ used for exfoliation is consistent with the optimal concentration of 30-40\% of cation-exchange capacity used to exfoliate other layered metal oxides, such as layered titanates, that results in maximum
swelling.\textsuperscript{15}) Partial exchange of H\textsuperscript{+} with Na\textsuperscript{+} was performed to obtain the ordered layered niobate, Na\textsubscript{0.24}H\textsubscript{0.76}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}, by stirring HCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} with 0.24 mol eq. NaOH (1 M) for 1 day. The restacked niobate phase was obtained by dropwise addition of NaCl solution to the nanosheets.

4.2.2 Characterization

X-ray diffraction patterns were collected using the PAnalytical Empyrean diffractometer with a monochromatized Cu-K\textalpha radiation (1.54059 Å) in Bragg-Brentano geometry. Isothermal titration calorimetry experiments were performed in triplicate using a standard volume NanoITC (TA instruments) equipped with a hastelloy cell. Injections were performed using a 250 μL syringe by titrating 10 μL every 25 minutes with a stirring rate of 250 rpm at 298 K. The concentrations of all titrations were optimized such that the saturation occurred at 12\textsuperscript{th}-15\textsuperscript{th} injection in order to obtain the inflection point at the midpoint of the isotherm. Differential thermal analysis (DTA) was performed by heating the ordered layered niobate and restacked layered niobate from 298 K to 773 K using SDT Q600 V20.9 at 10 °C/min in air to measure the heat of dehydration. Vibrational sum frequency spectroscopy was performed using a Nd:YAG laser (1068 nm) with a 30 ps pulse duration, 40 mJ pulse energy, and 50 Hz maximum repetition rate. The fundamental beam is directed into the harmonic unit (H500) where the second harmonic visible beam (532 nm) is generated. The fundamental and second harmonic enter the optical parametric generator/difference frequency generator unit (PG501/DFG series).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{X-ray diffraction pattern of (a) HCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}, (b) ordered Na\textsubscript{0.24}H\textsubscript{0.76}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} (o-Na\textsubscript{0.24}H\textsubscript{0.76}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}) in the wet state, and (c) restacked Na\textsubscript{0.24}H\textsubscript{0.76}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} (r-Na\textsubscript{0.24}H\textsubscript{0.76}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}) in the wet state. Note that the intensities are in logarithmic scale. The intensities for the restacked phase are multiplied by 2.}
\end{figure}
which allows tuning of the IR frequency between 1000 and 4000 cm\(^{-1}\), with a spectral resolution of < 6 cm\(^{-1}\). The incident angles of the IR and visible beams at the sample interface were 55° and 60° with respect to the surface normal, and the VSFS signal was collected at 59°. The IR frequency was scanned in 3 cm\(^{-1}\) increments between 2800 and 3000 cm\(^{-1}\), and 5 cm\(^{-1}\) increments between 3000 and 3800 cm\(^{-1}\). Calcium niobate nanosheets (3.8 mM) were dropcasted onto a PTFE Langmuir trough (NIMA Technology, England) and the solution was allowed to equilibriate for 20 minutes, after which the surface pressure, measured by the Wilhelmy Plate method, was maintained at 17 mN/m to obtain a well-packed monolayer at the air-water interface. Three individual trial spectra were collected and normalized by dividing the raw VSFS intensity by the product of the visible and IR intensities at the sample stage for every data point.

4.3 Results and Discussion

4.3.1 Synthesis and Exfoliation: SEM images of both parent and the protonated layered oxides (KCa\(_2\)Nb\(_3\)O\(_{10}\) and HCa\(_2\)Nb\(_3\)O\(_{10}\)) as well as the ordered layered oxide, Na\(_{0.24}\)H\(_{0.76}\)Ca\(_2\)Nb\(_3\)O\(_{10}\), showed highly ordered layered planes whereas the restacked phase showed aggregates thus confirming that addition of NaCl resulted in turobstratically restacked phases (Figure B1). HCa\(_2\)Nb\(_3\)O\(_{10}\) nanosheets exfoliated by using 0.25 molar equivalent TBAOH solution showed the presence of nanosheets that extend laterally to a few hundred nanometers as with excess TBAOH but showed a few overlapped regions (Figure B2). The presence of nanosheets was also verified by noting an absorbance band at 275 nm by UV-visible spectroscopy (Figure B3). The ordered layered oxide Na\(_{0.24}\)H\(_{0.76}\)Ca\(_2\)Nb\(_3\)O\(_{10}\) and the restacked layered oxide were characterized by X-ray diffraction in the wet state by equilibrating both solids with water. Both solids displayed an increase in the \(d\)-spacing from 14.42 Å (2\(\theta\) = 6.15°) in HCa\(_2\)Nb\(_3\)O\(_{10}\) to 16.69 Å (2\(\theta\) = 5.73°) and 17.14 Å (2\(\theta\) = 5.18°) in the ordered and restacked layered oxides, respectively (Figure 4.1). In addition, the loss of registry upon restacking was confirmed by the loss of crystallinity as reflected by the suppressed peak intensity and asymmetry.
4.3.2 Isothermal Titration Calorimetry

In this work, ITC was used to quantify the enthalpy and entropy of ion-exchange, exfoliation, and restacking processes under wet chemical conditions. This technique functions on the basis of an incoming cation (L) that binds to the metal (M) with great affinity as follows:}

\[
\text{M} + n\text{L} \rightarrow \text{ML}_n, \quad (1)
\]

where \( K_a = \frac{[\text{ML}_n]}{[\text{M}][\text{L}]} \).

In this work, the ligand (L) corresponds to the reagent that causes exfoliation or restacking processes and the metal oxide is the receptor (M). When both the reactant and product are in equilibrium as shown in Eq. (1), the binding stoichiometry \( n \) and the equilibrium constant \( K_{eq} \) can be extracted from the slope of the isotherm at the inflection point. The slope of the isotherm, \( K_{eq} \), can be used to calculate \( \Delta G \) and \( \Delta S \) using the following relations:

\[
\Delta G = -RT\ln K_{eq} \quad (2)
\]

\[
\Delta G = \Delta H - T\Delta S \quad (3)
\]
In the ITC experiments, the concentrations of both the titrant and the sample cell solutions are optimized such that the saturation of the signal occurred at the midpoint of the isotherm. The isotherm for the restacking process ($\Delta H_1$) in this study showed a very small value of enthalpy that was independent of the concentration of NaCl solution used thus indicating a minimal contribution from acid-base neutralization. However, the isotherm showed a large positive entropy value that is consistent with what is expected from Eq. (3) for a spontaneous process (i.e. $\Delta G < 0$). The blank titration of NaCl solution into water (Figure 4.3b) did not show an isotherm indicating that no chemistry occurred.

The thermochemistry of exfoliation and restacking processes in the layered niobate HCa$_2$Nb$_3$O$_{10}$ was quantified by constructing a Born-Haber cycle that involved three interactions: titration of TBA$^+$OH$^-$ into the layered oxide, HCa$_2$Nb$_3$O$_{10}$ to obtain the turbostratically restacked Na$_{0.24}$H$_{0.76}$Ca$_2$Nb$_3$O$_{10}$ phase ($\Delta H_1$), titration of the layered oxide, HCa$_2$Nb$_3$O$_{10}$ with TBAOH to obtain the exfoliated nanosheets ($\Delta H_2$), and titration of the layered oxide, HCa$_2$Nb$_3$O$_{10}$ with NaOH to obtain the ordered phase ($\Delta H_3$). Additionally, dehydration of restacked ($\Delta H_{d, \text{restacked}}$) and ordered niobate phases ($\Delta H_{d, \text{ordered}}$) were included to obtain the enthalpy change in the anhydrous state (Scheme 4.1). Thus, the effective thermochemical process in transforming an ordered solid to restacked layered solid can be quantified as $\Delta H = \Delta H_1 + \Delta H_2 - \Delta H_3 + \Delta H_{d, \text{restacked}} - \Delta H_{d, \text{ordered}}$. The concentration of NaCl solution used in the first step had a minimal effect on the measured thermochemical values as there is no contribution from acid-base neutralization. Benchtop titrations that mimicked ITC titrations to restack HCa$_2$Nb$_3$O$_{10}$ nanosheets using identical molar ratios of NaCl further showed that the process involved minimal pH change even past saturation thus indicating that the contribution of acid-base neutralization can be ignored (Figure B4). In the latter two steps, a 0.25 molar

![Figure 4.2: (a) Representative ITC thermogram and (b) integrated heat data with independent binding model for the titration of TBA$^+$OH$^-$ into the layered oxide, HCa$_2$Nb$_3$O$_{10}$.](image)
equivalent OH$^-$ was titrated at the inflection point to minimize the contribution from acid-base neutralization.

A representative isotherm along with the integrated heat data fitted using an independent-binding model is shown in Figure 4.2 and the thermochemical data ($\Delta H$, $\Delta G$, and $\Delta S$) for all three processes described above are summarized in Table 4.1. The restacking process was found to be entropically driven with $\Delta H = -2.7 \pm 0.5$ kJ/mol and $\Delta S = 37.6 \pm 7.5$ J/mol K. Figure 4.3a shows the representative isotherm for the restacking process. The enthalpies of exfoliated ($\Delta H_2$) and ordered phases ($\Delta H_3$) were found to be $-22.9 \pm 0.7$ kJ/mol and $-49.9 \pm 1.0$ kJ/mol, respectively.

4.3.3 Differential Thermal Analysis

Differential scanning calorimetry/thermogravimetric analysis (DTA) was utilized to quantify the enthalpy of dehydration in both ordered and restacked Na$_{0.24}$H$_{0.76}$Ca$_2$Nb$_3$O$_{10}$ (Figure 4.4). The enthalpies of dehydration were calculated by integrating the curve between 35 ℃ and 185 ℃. The dehydration enthalpies of the ordered ($\Delta H_d$, ordered) and restacked ($\Delta H_d$, restacked) phases for the reaction Na$_{0.24}$H$_{0.76}$Ca$_2$Nb$_3$O$_{10}$ - 0.5H$_2$O → Na$_{0.24}$H$_{0.76}$Ca$_2$Nb$_3$O$_{10}$ + 0.5 H$_2$O were found to be $-9.74$ kJ/mol and $-29.3$ kJ/mol respectively. The weight loss measured by DTA corresponded to a loss of approximately 0.5 mol H$_2$O/mol HCa$_2$Nb$_3$O$_{10}$ (see Appendix B for details). Both solids also showed an exothermic signal at around 310 ℃ which probably represented the

![Graphs showing isothermal titration calorimetry](image)

**Figure 4.3:** Isothermal titration calorimetry of (a) NaCl solution (291 mM) into HCa$_2$Nb$_3$O$_{10}$ nanosheets and (b) blank titration of NaCl into water.
topochemical condensation of the layered solids to Ca$_4$Nb$_6$O$_{19}$ that is consistent with literature on the protonated layered niobate HCa$_2$Nb$_3$O$_{10}$.$^{27}$ On accounting for the dehydration enthalpy, the overall process for transforming

**Table 4.1:** Thermochemical parameters for exfoliation and restacking processes from isothermal titration calorimetry.

<table>
<thead>
<tr>
<th>Process</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol·K)</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>K ($\times 10^3$ M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_1$</td>
<td>$-2.7 \pm 0.5$</td>
<td>$37.6 \pm 7.5$</td>
<td>$-13.9 \pm 2.4$</td>
<td>$0.4 \pm 0.4$</td>
</tr>
<tr>
<td>$\Delta H_2$</td>
<td>$-22.9 \pm 0.7$</td>
<td>$-4.0 \pm 5.0$</td>
<td>$-21.7 \pm 1.4$</td>
<td>$7.4 \pm 3.8$</td>
</tr>
<tr>
<td>$\Delta H_3$</td>
<td>$-49.9 \pm 1.0$</td>
<td>$-94.4 \pm 3.7$</td>
<td>$-21.7 \pm 0.9$</td>
<td>$6.8 \pm 2.2$</td>
</tr>
</tbody>
</table>

Figure 4.4: Differential scanning calorimetry and Thermogravimetric analysis of (a) ordered and (b) restacked Na$_{0.24}$H$_{0.76}$Ca$_2$Nb$_3$O$_{10}$.

an ordered layered solid to a restacked layered solid was found to be $\Delta H = 4.74 \pm 0.20$ kJ/mol and $\Delta S = 128.0 \pm 8.8$ J/mol K.

**4.3.4 Vibrational sum frequency spectroscopy**

Vibrational sum frequency spectroscopy (VSFS) was used to probe the oriented water molecules under well-packed monolayers of nanosheets at the air-water interface in a Langmuir trough. VSFS spectra showed $-\text{OH}$ stretches at $\sim 3200$ cm$^{-1}$ and $3400$ cm$^{-1}$, respectively. The stretching frequency between $3200$ cm$^{-1}$ and $3450$ cm$^{-1}$ was assigned to the oriented water molecules under the nanosheets. The $-\text{OH}$ stretches were found to be significantly more intense than the uncharged octadecanol at the air-water interface thus indicating several layers of oriented water molecules (Figure 4.5). Both VSFS and ITC measurements suggest the possibility that a large number of ordered water molecules under the nanosheets were expelled upon restacking.

The relationship between surface charge density and thermochemical quantities have been investigated for the mercury-solution interface by performing temperature-dependent
electrocapillary measurements at different potentials. They correlated an increase in the surface excess volume/entropy at negative potentials with a decrease in the oriented water dipoles adsorbed to the inner layer of the electrochemical double layer through the negative oxygen end. At positive potentials, a lower surface excess entropy was observed resulting from the orientation of water molecules. HCa$_2$Nb$_3$O$_{10}$ nanosheets have a surface zeta-potential value in the range of about -35 to -50 mV. Our experimental results for the restacking process of calcium niobate nanosheets qualitatively agree with the electrocapillary measurements performed on mercury electrodes, where the water dipoles oriented at the surface for several layers under the highly charged nanosheet surface are displaced upon restacking with sodium chloride.

### 4.4 Conclusion

In summary, we report the first quantification of the thermochemistry of exfoliation and restacking processes in a layered niobate by isothermal titration calorimetry. The overall process was found to occur with $\Delta H = 4.74 \pm 0.20$ kJ mol$^{-1}$ and $\Delta S = 128.0 \pm 8.8$ J/mol$\cdot$K. The change in orientation from a three-dimensional ordered phase to a turbostratically disordered phase was found to be driven by a positive entropy change with little change in enthalpy. The positive entropy value for restacking process could be correlated with a high degree of oriented water molecules under the charged nanosheet surface by vibrational sum frequency spectroscopy that were expelled when the nanosheets were restacked. The insights gained from this study open an avenue to understanding the driving forces for exfoliation and restacking in a wide variety of layered solids, including layered van der Waals solids such as graphene and layered dichalcogenides.
4.5 References


Chapter 5*

Stabilization of Dinuclear Rhodium and Iridium Clusters on Layered Titanate and Niobate Supports

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*This work is taken from the final version of a manuscript in preparation.
5.1 Introduction

Atomically dispersed catalysts comprising single atoms and low nuclear clusters are gaining increasing attention as heterogeneous catalysts as they are structurally different from bulk metal and metal nanoparticles. The different catalytic activity stems from both surface effects, where the number of unsaturated bonds increase with decreasing size, and electronic effects that result in discrete energy levels of electrons and greater orbital overlap with substrate molecules.\(^1,2,3,4,5,6,7\) For instance, Fu et al. first reported that atomically dispersed gold and platinum species are responsible for the catalytic activity of water-gas shift reaction.\(^7\) Similarly, Qiao et al. reported that single-atom Pt on FeO\(_x\) support showed an enhanced catalytic performance for CO oxidation when compared to platinum clusters.\(^3\) Atomically dispersed single atom and cluster catalysts represent a unique platform to attain enhanced catalytic activity at low loadings and simultaneously maximizes the utilization of the metal thus reducing cost.\(^5\)

In recent years, the structure and catalytic activity of single atom catalysts has been extended to clusters of low nuclearity, such as dimers, and even trimers, on different supports by wet chemical deposition. The stability of dinuclear clusters has been characterized on different supports by aberration-corrected transmission electron microscopy and has been tested for catalytic performance for reactions such as CO oxidation, hydrogenation, and water gas-shift reaction.\(^8,9,10,11,12,13\) For instance, dinuclear clusters of iridium stabilized on Fe\(_2\)O\(_3\)\(^8\) and WO\(_3\)\(^9\) substrates showed an enhanced photocatalytic activity for water oxidation. In contrast to single atom catalysts that are solely dependent upon the coordination environment of the ligands, clusters containing more than a single atom are also affected by \(d\)-orbital overlap of the metal atoms that results in different catalytic activity.\(^2\) Surface science studies on metal clusters have shown a nonlinear trend in their catalytic activity at the sub-nanometer regime when compared to bulk metal or nanoparticles due to their different affinity to substrate molecules.\(^14,15\) Thus, metal clusters of well-defined nuclearity is an emerging direction to investigate structure-property correlations in heterogeneous catalysis at the atomic level.

Nanosheets exfoliated from layered metal oxides could be potential candidates as catalyst supports as they have high surface areas and are well-ordered crystalline surfaces (Figure 5.1) that extend laterally and can be imaged by electron microscopy. Exfoliated nanosheets have previously been
found to stabilize metal and metal hydroxide nanoparticles whose thermal stability was investigated by transmission electron microscopy.\textsuperscript{16,17} The resistance to sintering of metal oxide nanoparticles was attributed to an interfacial bond resulting from $d$-electron charge transfer to the support.\textsuperscript{17} Metal clusters containing pairs of atoms supported on transition metal oxide nanosheet supports could present a novel class of catalytic materials and extend the previously known SMSI effect on metal nanoparticles to low nuclear clusters. This could also aid in understanding the effect of nuclearity on the strength of the interfacial bond and its implications to heterogeneous catalysis.

In this paper, we report that dimeric rhodium and iridium clusters could be stabilized onto layered titanate ($\text{H}_{0.13}\text{Ti}_{0.87}\text{O}_2$) and layered niobate ($\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}$) supports and their stability was investigated by a combination of aberration-corrected transmission electron microscopy (HAADF-STEM), DRIFT spectroscopy, X-ray absorption spectroscopy (EXAFS and XANES), and electronic structure calculations. HAADF-STEM images revealed well dispersed clusters of both rhodium and iridium dimers that had mean nearest-neighbor distances similar or slightly smaller than a Poisson distribution for a random distribution of atoms suggesting the absence of aggregation. DRIFT spectroscopy further revealed that the carboxylate ligands bound to the dirhodium core remained intact upon binding to the support. X-ray absorption spectroscopy and electronic structure calculations showed that the dinuclear rhodium cluster was possibly bound to the titanate support through an end-on binding mode at room temperature. Dinuclear rhodium clusters were found to be stable on the titanate support up to 100 $^\circ$C beyond which they were partially reduced to metallic clusters.

**5.2 Materials and Methods**

*Synthesis of Rh(II) Dimer:* Rhodium (II) dimer, [$\text{Rh}_2(\text{OAc})_2(\text{bpy})_2(\text{H}_2\text{O})(\text{OAc})]^{2+}$, was synthesized as reported in the literature previously.\textsuperscript{18} Briefly, rhodium (II) acetate (Acros Organics) (0.239 g, 0.54 mmol) was refluxed with excess 2,2’ bipyridine (Sigma Aldrich) (0.156 g, 1 mmol) in ethanol for 3 hours upon which the solution turned from green to reddish brown and then cooled to room temperature using an ice-bath. The dimeric complex was isolated by slow evaporation of diethylether and then filtered off to obtain dark red crystals. The crystals could be re-dispersed
Figure 5.1: Crystal structures of (a) layered titanate, $\text{K}_{0.8}\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$ and (b) layered niobate, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ supports. Red spheres represent O atoms, purple spheres represent K atoms, white spheres represent Li spheres atoms, and blue represent Ca atoms.

in tetra-$n$-butylammonium hydroxide solution and retain its dimeric structure (Figures C1 and C2). $^1$H NMR (500 MHz, Deuterium Oxide) $\delta$ 8.19 (d, $J = 6.2$ Hz, 1H), 7.82 (t, $J = 8.1$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 3.13 – 3.06 (m, 3H), 2.45 (s, 1H), 1.81 (s, 1H), 1.60 – 1.50 (m, 3H), 1.26 (h, $J = 7.1$ Hz, 3H), 0.85 (t, $J = 7.7$ Hz, 5H).

*Synthesis of Ir(IV) Dimer:* Ir$^{\text{IV}}$ homo-dimer was synthesized by following previously established methods.$^{19}$ Briefly, $\text{C}_p\text{Ir(pyalc)}\text{Cl}$ precursor (2 mM) was treated with excess NaIO$_4$ (100 mM) to form the blue Ir$^{\text{IV}}$ dimer, $[\text{Ir(pyalc)}(\text{H}_2\text{O})_2(\mu-\text{O})]_2$. The Ir homodimer complex had an absorbance band at 580 nm consistent with the literature in basic conditions.

*Synthesis of Layered Titanate and Niobate Supports:* $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was prepared by heating stoichiometric amounts of K$_2$CO$_3$ (5% excess) (Sigma Aldrich), CaCO$_3$ (Sigma Aldrich), and Nb$_2$O$_5$ (Sigma Aldrich) up to 1473K for 24 h. $\text{K}_{0.8}\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$ was prepared as reported in the literature.$^{20}$ Proton-exchange of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was performed by reacting 0.1 g compound with nitric acid for 3 days with the acid being replaced every 24 h. Acid-exchange of $\text{K}_{0.8}\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$ was performed by stirring the compound in HCl (1 M) for 3 days. The proton-exchanged $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ and $\text{H}_{0.13}\text{Ti}_{0.87}\text{O}_2$ were exfoliated by stirring both compounds in excess tetra-$n$-
butylammonium hydroxide (TBA⁺OH⁻) solution (25 mM) overnight. The suspensions were allowed to settle for several hours after which the sheets were collected by decantation.

Figure 5.2: A. Representative HAADF-STEM image of Rh^{II} dimer/H_{0.13}Ti_{0.87}O_2 support. B-D. HAADF-STEM image and EDS maps of Rh and Ti K-edges indicating the homogeneous distribution of Rh on H_{0.13}Ti_{0.87}O_2 support. E. Line intensity profile of Rh^{II} dimer complex supported on H_{0.13}Ti_{0.87}O_2 nanosheets.

Deposition of Dimeric Rhodium and Iridium:

Rhodium (II) dimer was deposited onto titanate nanosheets (H_{0.13}Ti_{0.87}O_2) at different weight loadings by stirring the suspension at 45°C for 48 hours in accordance with previous studies that reported a relatively slow ligand-exchange kinetics of acetate ligands. At 1 wt%, the suspension turned pale yellow whereas at higher weight loadings, the suspension turned light green. The dimeric Rh-supported titanate nanosheets were subjected to UV-ozone treatment for 20 minutes to remove the bound bipyridyl ligands.

Iridium (IV) dimer was deposited onto a layered niobate support by stirring the suspension at room temperature overnight followed by photochemical treatment for 25 minutes as has been reported previously to remove the pyalc ligand.
5.3 Characterization

5.3.1 X-ray Crystallography: Single crystals suitable for X-ray crystallography studies were obtained by slow evaporation of diethylether onto the Rh$^{II}$ dimer complex suspended in ethanol. A suitable crystal was selected and mounted using the nylon loop using a little paratone oil, on the Bruker SMART APEX CCD area-detector diffractometer. The crystal was at room temperature [298(2) K] during data collection. Using Olex2$^{22}$, the structure was solved with the XS$^{23}$ structure solution program using Direct Methods and refined with the XH$^{23}$ refinement package using Least
Squares minimization. No restraints/constraints were used. The hydrogen atoms were placed geometrically and rode the parent atoms during the refinement.

5.3.2 HAADF-STEM: Suspensions of titanate and niobate nanosheets with adsorbed rhodium and iridium dimers were dropcasted onto lacey carbon gold-coated grids. HAADF-STEM images were obtained using an aberration corrected FEI-Titan³ G2+ operating at 300 kV (and at 80 kV). All samples were subjected to beam shower for 20 min to get rid of carbon contamination. The semi-angle of the probe-forming aperture was 21.4 mrad. A probe current of 0.1 nA and a dwell time of 5 µs was used to acquire the images. EDS analysis was performed using the SuperX EDS detector. The nearest-neighbor distances were experimentally determined on a large area of HAADF-STEM images by first filtering the images using a bandpass filter to resolve the atoms better and then applying a Gaussian blur (with a pixel setting of 4) to enhance the Z-contrast between the bound atoms and the underlying support. The measured nearest neighbor distances were correlated with a Poisson distribution that is expected for a random distribution of dimers without preferential aggregation. The probability distribution function (PDF) of the nearest neighbor distribution of dimers is given as PDF(r) = 2πλr*exp(−πλr^2), where r = 1/2√λ; λ is the areal density of atoms obtained by summing the number of atoms in a region of interest divided by the corresponding area.24

5.3.3 DRIFTS: DRIFT spectra were collected on a Vertex V70 spectrometer (Bruker optics, Billerica, MA) equipped with deuterated triglycerine sulfate (DTGS) detector (10 kHz scan velocity) by dropcasting the supported rhodium complex onto a 100 nm gold-coated micro cover glass. Spectra were collected by averaging 100 scans at a resolution of 6 cm⁻¹ using a Praying mantis diffuse reflectance accessory (Harrick scientific, Pleasantville NY) with a gold substrate used as the reference.

5.3.4 X-ray absorption spectroscopy: Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Spectroscopy (XANES) data were collected at Rh-K edge (23220 eV) in fluorescence mode at 10-BM-B beamline at Argonne National Laboratory using the vortex detector. Rh foil and RhII Dimer were used as standards for the measurement. Samples were
heated ex-situ in 3% H\textsubscript{2}/He (flow rate of 100 cm\textsuperscript{3}/min) from 373 K-673 K (at 50 K intervals) for 30 min and cooled to room temperature prior to acquiring a scan. Each temperature scan was measured in triplicate. Data were background subtracted and normalized using Athena and fitted using Artemis software.

5.3.5 Electronic Structure Calculations:
Electronic structure calculations were performed using Vienna Ab initio Simulation Package (VASP).\textsuperscript{25-27} The projector augmented wave (PAW)\textsuperscript{27} method was used for core-valence treatment. The exchange and correlation energies were calculated using the Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{28} functional described within the generalized gradient approximation (GGA).\textsuperscript{29} A plane-wave basis set cutoff energy of 550 eV was used. All calculations allowed for spin polarization.

The ionic convergence limit was set to 0.05 eV Å\textsuperscript{-1} while the electronic convergence limit was set to 10\textsuperscript{-5} eV. Hubbard-U corrections were included for the Ti cation \textit{d}-electrons with the value of \textit{U}-\textit{J} = 4.0 eV for Ti \textit{d}-electrons based on the literature values reported for other layered titanate.\textsuperscript{30}

The structure model of potassium titanate K\textsubscript{0.8x}Ti\textsubscript{1.73x}Li\textsubscript{0.27x}O\textsubscript{4x} (KLTO) was used as a precursor to construct the model of layered titanate nanosheet support. KLTO contains interlayer K\textsuperscript{+} ions with corrugated host layers of edge sharing TiO\textsubscript{6}\textsuperscript{2-} octahedra. Li\textsuperscript{+} ions occupy 13.5% of Ti octahedral sites. Figure C7 shows the DFT optimized bulk KLTO lattice along with the computationally obtained lattice constants. The lattice parameters obtained through DFT matches well with the experimentally reported values for KLTO.\textsuperscript{20}

The model of single layer titanate sheet is modeled in their proton exchanged form (H\textsubscript{4}Ti\textsubscript{7}O\textsubscript{16}), i.e. by ‘leaching’ out the alkali cations, including the exchangeable Li ions in the host framework, and
balancing the residual charge with 4 protons. Two of those protons in the unit cell are bound to the unsaturated oxygen atom (due to vacancy left from the leaching of Li$^+$ ions) in the host layer while the binding of the other two protons was tested with different possibilities as shown in Figure C8. A 2 x 1 supercell model of the layered titanate with residual protons were optimized using the lattice constants obtained for KLTO. A vacuum region of ~10 Å was inserted to exclude the periodic interaction between the titanate layers. Dipole corrections were also added in the direction perpendicular to the titanate layer. The sampling of the Brillouin zone for the supercell was conducted with a k-point mesh of 5 x 5 x 1 generated automatically using the Monkhorst-Pack method.$^{31,32}$

5.4 Results and Discussion

5.4.1 X-ray Crystallography: Figure C3 and Table C1 give the crystal structure data and refinement for the Rh$^{II}$ complex which was different from the previously predicted structure from elemental analysis.$^{18}$ Crystal Data for C$_{28}$H$_{34}$N$_{4}$O$_{11}$Rh$_{2}$ ($M$ = 808.41 g/mol): triclinic, space group P-1 (no. 2), $a = 9.6725(7)$ Å, $b = 11.7545(9)$ Å, $c = 15.4619(12)$ Å, $\alpha = 68.7540(10)^\circ$, $\beta = 86.0520(10)^\circ$, $\gamma = 68.8980(10)^\circ$, $V = 1524.7(2)$ Å$^3$, $Z = 2$, $T = 298(2)$ K, $\mu$(MoK$\alpha$) = 1.149 mm$^{-1}$, $D_{calc} = 1.761$ g/cm$^3$, 13832 reflections measured (2.84° ≤ 2Θ ≤ 56.56°), 7065 unique ($R_{int} = 0.0174$, $R_{sigma} = 0.0325$) which were used in all calculations. The final $R_1$ was 0.0362 (>2sigma(I)) and $wR_2$ was 0.0963 (all data).

5.4.2 Deposition of Rhodium and Iridium Dimers: Both iridium and rhodium dimers adsorbed onto layered niobate and titanate supports were found to have weight loadings of 0.579 % and 0.488 % respectively by ICP-AES. The binding of rhodium dimer onto layered niobate support was also reflected by a drop in the UV-vis absorbance of the supernatant collected by centrifuging the nanosheets (Figure C4a). The measured absorbance indicated that 1.67% Rh bound to the support. EDS maps indicated that Rh$^{II}$ dimer and Ir$^{IV}$ dimer bound to titanate and niobate supports had a homogeneous distribution without formation of nanoparticles thus suggesting the absence of aggregation (Figure 5.2 b-d and Figure C6). X-ray photoelectron spectroscopy on the Rh$^{II}$ complex showed that the oxidation state of the complex was maintained upon binding to the support with a binding energy of 308.15 eV (Figure C4b). This binding energy is consistent with what is expected for Rh$^{II}$ carboxylates$^{33}$. 
5.4.3 HAADF-STEM: HAADF-STEM images of both Rh\textsuperscript{II} dimer/titanate (Figure 5.2) showed the presence of both single atoms and pairs of bright spots that represent rhodium atoms supported on titanate nanosheets. Rhodium atoms appear brighter under STEM mode when compared to Ti atoms due to the Z-contrast (Z=45 for Rh vs Z=22 for Ti). This is reflected by a higher intensity for the rhodium atoms in the line profile scan when compared to titanium atoms. However, the crystalline lattice of the H\textsubscript{0.13}Ti\textsubscript{0.87}O\textsubscript{2} could not be imaged possibly due to beam damage at 300 kV. Similarly, pairs of iridium atoms could also be observed as bright spots on the niobate lattice (Z = 77 for Ir vs Z = 41 for Nb) (Figure C5). Line intensity scan showed a higher intensity for Ir in comparison to Nb atoms (Figure C6).

Both systems indicated the presence of single atoms as well as pairs of atoms on several regions of the support. Single atoms were formed possibly as a result of beam damage upon prolonged exposure. In order to quantify the stability of dimers on niobate and titanate supports, a statistical averaging technique was employed similar to previous literature on single atoms and clusters supported on metal oxide supports to determine the nearest neighbor distances.\textsuperscript{12,13,24} Based on the statistical analysis, rhodium dimers had a mean nearest-neighbor distance ($d_{NN}$) of about 0.95 ± 0.57 nm compared to a distance of 1.02 nm that is expected from a random distribution of atoms (Figure 5.3). Similarly, iridium dimers on the niobate support had a $d_{NN}$ of 0.89 ± 0.60 nm compared to an expected distance of about 0.94 nm for a random distribution. Statistical analysis for both rhodium and iridium dimers indicated that the mean distribution of atoms was similar to a random distribution expected from the Poisson function thus suggesting the absence of preferential aggregation.

5.4.4 DRIFTS: DRIFT spectra of Rh\textsuperscript{II} dimer and Rh\textsuperscript{II} dimer/Titanate support looked very similar revealing the presence of C—H (2966 cm\textsuperscript{-1}), –COO\textsubscript{as} (1445 cm\textsuperscript{-1}) and –COO\textsubscript{s} (1578 cm\textsuperscript{-1}) stretches in both systems (Figure 5.4). The retention of carboxylate stretches in the vibrational spectrum upon binding indicates that the complex binds to the titanate support by the retention of at least one acetate ligand (and possibly by the displacement of axial water ligand).
5.4.5 X-ray Absorption Spectroscopy: X-ray absorption spectroscopy (EXAFS and XANES) was performed to probe the structure and stability of the dimer on titanate support at room temperature and also after reduction at high temperatures. First, Rh K-edge XANES spectrum on Rh$^{II}$ dimer/Titanate indicated that the oxidation state was maintained upon binding to the titanate support. Figure 5.5A shows that the edge position of both Rh$^{II}$ dimer and Rh$^{II}$ dimer/Titanate were quite similar thus indicating that the oxidation state was maintained. The Fourier Transform (FT) data showed a peak at 1.5 Å corresponding to the Rh—O scattering path and another peak at 2.2 Å corresponding to the Rh—Rh scattering path (Figure 5.5B). Additionally, the fitting of the

**Figure 5.5:** (A) Normalized XANES and (B) FT-EXAFS spectrum of Rh$^{II}$ Dimer and Rh$^{II}$ Dimer/Titanate support. (C) Feff Fit and (D) DFT-optimized structure of Rh$^{II}$ Dimer on H$_{0.15}$Ti$_{0.87}$O$_2$ support with a single-site binding mode.
first coordination shell using DFT-optimized structures with a single-site binding mode (see below) indicated that the system had a bond length of 2.654 Å which was close to the bond length of 2.627 Å for the dimer complex (Figure 5.5C and D). Attempts to fit the first coordination shell of EXAFS data using other DFT-optimized structures with a dual-site binding mode were unsuccessful due to longer Rh-Rh scattering paths (Figure C10) thus indicating that the end-on binding mode is a plausible structure model.

Temperature-dependent EXAFS measurements under reducing conditions revealed that the oxidation state and Rh-Rh CN were maintained until 100 °C beyond which it transforms into partially reduced metallic rhodium clusters (Figure C11). The coordination numbers of the complex at high temperatures are listed in Table C2. The particle size of the clusters at high temperatures under reducing conditions is consistent with previous studies on Rh(OH)$_3$ nanoparticles which had a CN of ~6 at 400 °C (particle size ~1 nm) under reducing conditions.

**5.4.6 Electronic Structure Calculations:** The binding interaction of the Rh dimer on the layered titanate support is not well understood in the current literature. Both monodentate and bidentate binding modes through side-on and end-on binding of Rh atoms respectively, are possible. Under the constraints that both Rh atoms in the dimer retain their +2 oxidation state (and thus, its octahedral geometry), we use DFT calculations to identify the binding mode of the dimer. To model the monodentate or end-on binding of the dimer on layered titanate, we open the axial coordination of the dimer by removing axially bound water. The binding site on the layered titanate is created by consuming the proton bound to unsaturated oxygen atom to protonate the free acetate in the dimer lattice. In order to optimize the structural model with the bidentate or side-on binding configuration of the dimer, it was essential to open up the equatorial coordination. In order to do that, we manipulated the bidentate acetates on the equatorial coordination of the dimer. Of the two bidentate acetates, one consumes a proton on the titanate surface while the other acetate moves to occupy the axial position left vacated by removal of axially bound water. The free acetate also takes up another proton from the layered titanate and thus opens up the binding site on the titanate support for bidentate binding. The structure models for the monodentate and bidentate binding modes are given in Figure 5.5D and Figure C9, respectively.

The Rh-Rh bond distance in the DFT optimized structure with a monodentate binding is 2.649 Å which is in reasonable agreement with the value obtained from the EXAFS fit of 2.654 Å (Table
5.1. The Rh-Rh bond distance in all the bidentate models were severely elongated. The Rh-O bond distance between Rh atom and one of the axial acetates is also elongated which indicates the loss of the octahedral geometry of the dimer. All the optimized structures along with their EXAFS fits are shown in Figure C9. These results suggest that the end-on binding mode by the displacement of water ligand through the axial position is likely preferred (Scheme 5.1).

Table 5.1: EXAFS fitting parameters for Rh\textsuperscript{II} dimer/Titanate support ($S_0^2 = 1.00$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å(^2))</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh\textsuperscript{II} Dimer</td>
<td>1</td>
<td>2.6267</td>
<td>0.00237 ± 0.00416</td>
<td>0.0213</td>
</tr>
<tr>
<td>Rh\textsuperscript{II} Dimer/Titanate</td>
<td>1</td>
<td>2.6543</td>
<td>0.00224 ± 0.00390</td>
<td>0.0106</td>
</tr>
</tbody>
</table>

\textbf{Scheme 5.1.} Synthesis and Deposition of Rh\textsuperscript{II} dimer/Titanate support with possible binding mode.

5.5 Conclusion

In this study, we report that layered metal oxides can be used as model supports to stabilize dinuclear transition metal clusters and their stability was characterized by a combination of electron microscopy, X-ray absorption spectroscopy, and first principles calculations. HAADF-STEM images revealed the absence of high nuclear clusters in both rhodium and iridium dimers and had several regions with well-resolved dimers. Statistical analysis of STEM images of both rhodium and iridium dimers revealed a mean nearest neighbor distance similar to what is expected from a Poisson distribution thus suggesting the absence of high nuclear clusters. Further, both DFT modeling and EXAFS fitting of rhodium dimers on layered titanate support showed that the dimer was bound end-on through a single Rh atom. Rhodium dimers were stable upto 100 °C
under reducing conditions and then transformed to partially reduced metallic clusters with a coordination number of $5.39 \pm 2.95$ at 400 °C. The stability of dinuclear clusters supported on layered oxide supports thus provide insights into their role as novel catalytic systems.

5.6 References


Chapter 6

Conclusions and Future Work

In this dissertation, the structure-property relationships of both layered metal oxides and metal oxide nanosheets have been elucidated by designing them using solid-state reactions followed by topochemical ion-exchange and exfoliation reactions. The structural transformations of bulk oxides and oxide nanosheets were investigated using X-ray and neutron techniques (i.e. synchrotron powder X-ray diffraction, neutron diffraction, and X-ray absorption spectroscopy), isothermal titration calorimetry, and transmission electron microscopy. The structural insights gained from this dissertation can have far-reaching implications in fields such as heterogeneous catalysis as well as energy storage.

The chemistry of layered metal oxides and metal oxide nanosheets have been studied for several decades. However, there are several fundamental questions that need to be addressed to make strides in both mechanistic understanding as well as for designing novel materials for catalytic and energy applications, including fuel cells, batteries, and capacitors. Specifically, these include exploration of thermochemical factors that govern the exfoliation and restacking processes of different layered solids as well as using nanosheets as supports to stabilize atomically precise clusters comprising different metals and nuclearity. This section seeks to highlight some of the future challenges that stem from the work presented in this dissertation.

6.1 Thermochemical Quantification of Exfoliation and Restacking Processes

Despite the advances made in topochemical ion-exchange and exfoliation reactions to interconvert between different structural families of layered oxide compounds, there is very little known about the thermochemistry of exfoliation and restacking reactions in layered materials. In this dissertation, we reported that the restacking process in a layered perovskite system, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, using $\text{NaCl}$ is driven by a significantly positive entropy change accompanied with almost no change in enthalpy. It would be interesting to do a follow-up study comparing the effects of cation size on the enthalpy and entropy values quantified by ITC by restacking the nanosheets using $\text{NaCl}$, $\text{KCl}$, and $\text{RbCl}$. The thermochemical quantities measured by restacking using different cation sizes are affected by the free energy of hydration as well as the electrostatic interaction between the leaving ion and the counterion. Based on this thermochemical understanding of ion-
exchange reactions, and given the fact that smaller cations have larger enthalpies of formation, we expect that exchange of smaller cations would have a more favorable electrostatic energy and thus result in a more favorable free energy value. This study would establish a thermochemical trend for the effect of cation size on the replacement of TBA$^+$ ions upon restacking. Similarly, it would be interesting to measure the thermochemistry of intercalation and swelling of layered compounds, such as titanates, by using aliphatic ligands of different chain lengths.

The thermochemical quantification of exfoliated-restacked phases in layered oxide compounds opens up avenues to studying a variety of layered materials that are amenable to chemical exfoliation, such as layered dichalcogenides, MXenes, graphene, etc. There is a growing body of literature on different chemical routes to produce single layers, bilayers, and multilayers of nanosheets. For instance, layered dichalcogenides such as MoS$_2$ and WS$_2$ were found to exfoliate as trilayers when treated with sub-stoichiometric amounts of $n$-butyllithium followed by horn sonication. ITC could be an effective technique to gain a mechanistic understanding of the forces that drive the formation of bilayers and trilayers vs single sheets. The ion-exchange, exfoliation, and pillaring/intercalation reactions that have been established in layered materials can be quantified using ITC by careful considerations of thermochemical cycles that minimize heats from acid-base neutralization or other side reactions that can complicate quantification of thermochemical quantities.

### 6.2 Layered metal oxides as catalyst support materials

In Chapter 5, nanosheets obtained by exfoliation of layered niobate and titanate compounds were used as model supports to stabilize dinuclear clusters of rhodium and iridium. Both metals were previously found to have a strong interfacial bond with the layered niobate support resulting from a partial charge transfer to the niobate compound that was also quantified by isothermal titration calorimetry. The stability and structure of rhodium dimers bound to titanate nanosheets could be characterized by using a combination of DRIFTS, X-ray absorption spectroscopy and density functional theory. Although the direct structural characterization of these systems by electron microscopy proved to be challenging, they were both found to be stable as dimers on oxide supports.

The stability of dimeric complexes onto layered oxide supports can be extended to heterobimetallic complexes comprising two different transition metals. Lately, heterobimetallic clusters
comprising early-late transition metals and late-late transition metals are gaining a lot of interest for heterogeneous catalysis given the fact that they comprise two different metals of varying electronic structures. The Lewis base transition metal functions as a nucleophile and can donate electrons whereas the Lewis acid early transition metal can accept electrons into its vacant d-orbitals. The varying roles played by the two different metal centers have a synergistic effect that activates different steps in a catalytic reaction with one metal getting reduced whereas the other one getting oxidized. This phenomenon can have a significant impact on various multi-step catalytic processes such as alkene hydrogenation and C—H bond activation as well as electrocatalysts.\(^4\)

Although heterobimetallic complexes comprising a variety of transition metals have been synthesized for several decades, there are only few reports of stabilizing them onto oxide supports for heterogeneous catalysis. For instance, Thompson et al. were able to install a heterobimetallic Al-Co complex onto the Zr\(_6\)-oxide node of MOF NU-1000 that catalyzed the oxidation of benzyl alcohol to benzoic acid.\(^5\) More recently, Desai et al. installed a heterobimetallic Rh—Ga cluster onto the Zr\(_6\)-oxide nodes of MOF NU-1000 which showed selectivity for hydrogenation of alkynes to E-alkenes.\(^6\) Thus, stabilizing heterobimetallic clusters onto layered metal oxides would be the ultimate goal in realizing these systems as supports for a variety of heterogeneous catalytic processes.

The immobilization of heterobimetallic clusters onto metal oxide nanosheets would provide both a fundamental understanding of how they bind to oxide supports and would also enable them to be used for heterogeneous catalytic processes that rely on the presence of two different metals. However, there are a few challenges that need to be addressed in realizing these systems. First, it is important to design heterobimetallic systems that can be dispersed in aqueous conditions with kinetically labile ligands. Second, the structural characterization of the binding sites onto metal oxide nanosheets could be challenging as direct imaging requires two metals that have a high Z-number compared to the support. Recently, a few water-soluble Ni(II)-Cu(II) heterobimetallic complexes with labile aquo- and hydroxo ligands have been reported whose structures have been investigated by single crystal X-ray diffraction.\(^7,8\) Although these complexes comprise 3d transition metals, the synthesis of heterobimetallic clusters comprising a heavier metal, such as a lanthanide, and a catalytically interesting 5d transition metal (such as Pt or Ir) could be attempted.
using similar approaches. The resulting heterobimetallic clusters could then be dispersed onto metal-oxide nanosheets comprising a 3d transition metal whose lattices are well-characterized at the atomic resolution. The stability of these systems could then be characterized using X-ray absorption spectroscopy (EXAFS and XANES) as a function of temperature and their role for catalysis could be tested using thermally programmed desorption with CO as the probe molecule.

References

Appendix A

Supporting Information for Chapter 3

Figure A1: Group-subgroup relationship between space groups and irreps that transform $I4/mmm$ space group to the lowest symmetry $Pnam$ and $A2_1am$ space groups.

Table A1: Results of symmetry-mode analysis of $\text{Li}_2\text{SrNb}_2\text{O}_7$ with respect to parent $I4/mmm$ phase.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\text{Irrep}^a$</th>
<th>$\text{Irrep}^a$</th>
<th>$\text{Irrep}^a$</th>
<th>$\text{Irrep}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M^-$</td>
<td>$\Gamma^-$</td>
<td>$X^+$</td>
<td>$X^-$</td>
</tr>
<tr>
<td>$A2_1am$</td>
<td>-</td>
<td>0.18</td>
<td>0.18</td>
<td>0.69</td>
</tr>
<tr>
<td>$Amam$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.69</td>
</tr>
<tr>
<td>$Pnam$</td>
<td>0.24</td>
<td>-</td>
<td>0.17</td>
<td>0.69</td>
</tr>
</tbody>
</table>

$^a$Amplitudes of $\Gamma^-_5$, $X_2^+$, and $X_3^-$ modes are shown in units of Å. The $\Gamma^-_5$ mode is a polar mode whereas $M^-_5$ is an antipolar mode. The $X_2^+$ and $X_3^-$ modes correspond to octahedral rotations represented by (00ψz) and (ϕφ0), respectively.
**Figure A2:** Low temperature SHG measurement of Li$_2$SrNb$_2$O$_7$.

**Figure A3:** Attempts to refine (a) room temperature synchrotron XRD data against $A2_{1}am$ structure ($R_{wp} = 31.88\%$) and (b) 200K synchrotron XRD data against $Pnam$ structure ($R_{wp} = 32.07\%$). Large intensity mismatch and peak asymmetry are due to the presence of stacking faults.
$R_{wp} = 10.11\%, \ R_p = 7.75\%, \ \chi^2 = 4.65$

(a)

$R_{wp} = 10.66\%, \ R_p = 8.49\%, \ \chi^2 = 5.14$

(b)

**Figure A4:** Comparison of neutron diffraction fits at 300 K against (a) $A_2\text{iam}$ and (b) Amam models.

**Figure A5:** (a) HRTEM, (b) HAADF-STEM, and (c) SAED pattern of Li$_2$SrNb$_2$O$_7$ indicating the presence of stacking faults.
Figure A6: Refined structures from NPD data for Li$_2$SrNb$_2$O$_7$ at 300 K using (a) $A_2am$ and (b) $Amam$ models.

Figure A7: Structural refinement of Li$_2$SrNb$_2$O$_7$ NPD data using the $Pnam$ model at 90 K.
Table A2: Refined atomic positions and thermal parameters for Li$_2$SrNb$_2$O$_7$ against the $Pnam$ model at 90 K using NPD data. Values in parenthesis indicate one standard deviation.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
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<tr>
<td>Li1</td>
<td>8b</td>
<td>-0.02600(0)</td>
<td>-0.72771(9)</td>
<td>0.51229(9)</td>
<td>-0.0225(4)</td>
</tr>
<tr>
<td>Nb1</td>
<td>8b</td>
<td>0.24674(6)</td>
<td>-0.50068(3)</td>
<td>0.36535(1)</td>
<td>0.0045(4)</td>
</tr>
<tr>
<td>O1</td>
<td>8b</td>
<td>-0.01587(3)</td>
<td>-0.75185(2)</td>
<td>0.63372(8)</td>
<td>0.0023(5)</td>
</tr>
<tr>
<td>O2</td>
<td>8b</td>
<td>0.00783(6)</td>
<td>-0.74550(9)</td>
<td>0.34704(9)</td>
<td>-0.0076(8)</td>
</tr>
<tr>
<td>O3</td>
<td>8b</td>
<td>0.25906(6)</td>
<td>-0.53466(9)</td>
<td>0.47000(6)</td>
<td>0.0045(0)</td>
</tr>
<tr>
<td>O4</td>
<td>4a</td>
<td>0.22861(7)</td>
<td>-0.45750(6)</td>
<td>0.25000(0)</td>
<td>0.0055(5)</td>
</tr>
<tr>
<td>Sr1</td>
<td>4a</td>
<td>0.76145(2)</td>
<td>-0.49849(6)</td>
<td>0.25000(0)</td>
<td>0.0046(9)</td>
</tr>
</tbody>
</table>

Lattice parameters: a=5.58902(2) Å, b=5.59422(8) Å, c=17.93307(3) Å, $R_{wp} = 10.31\%$, $R_p = 7.99\%$, $\chi^2 = 4.71$.

Figure A8: Current ($I$) versus voltage ($V$) curve for Li$_2$SrNb$_2$O$_7$ at 170 K.
Figure A9: Attempts to measure P-E hysteresis for Li$_2$SrNb$_2$O$_7$ at room temperature.

Figure A10: Energetic contributions of OOR ($X_2^+$), OOT ($X_3^-$), and (anti-)polar ($\Gamma_5^-, M_5^-$) modes to layer resolved polarizations in Pnam (transparent) and A2$_1$am phases (orange).
Appendix B

Supporting Information for Chapter 4

**Figure B1:** Scanning Electron Microscopy images of (A) KCa$_2$Nb$_3$O$_{10}$, (B) HCa$_2$Nb$_3$O$_{10}$, (C) ordered-Na$_{0.24}$H$_{0.76}$Ca$_2$Nb$_3$O$_{10}$, and (D) restacked- Na$_{0.24}$H$_{0.76}$Ca$_2$Nb$_3$O$_{10}$.

**Figure B2:** Atomic Force Microscopy image of HCa$_2$Nb$_3$O$_{10}$ nanosheets obtained using 0.95 mM (0.25 mol eq.) TBA$^+$OH$^-$ solution.
**Figure B3:** UV-visible spectroscopy of HCa$_2$Nb$_3$O$_{10}$ nanosheets exfoliated using 0.95 mM TBAOH in the ITC.

**Figure B4:** Benchtop titration of 3.8 mM HCa$_2$Nb$_3$O$_{10}$ nanosheets (1.3 mL) with NaCl solution (29.1 mM) to monitor pH changes.
Calculation for Dehydration Enthalpy

The dehydration enthalpy of both ordered and restacked layered niobate was determined from the weight loss by integrating the area under the DTA curve from 35 °C to 185 °C which represents the heat released upon dehydration (47.043 mW·K for the restacked compound). A heating rate of 10 K/min (or 0.167 K/s) was used for the measurement in both cases.

Weight change of restacked layered niobate at 185 °C = (9.082272-8.908794) mg = 0.173 mg

\[ \text{H}_2\text{O} = 9.61 \times 10^{-6} \text{ mol H}_2\text{O} \]

\[ \text{Enthalpy of dehydration} = \frac{47.043 \text{ mW} \cdot \text{K}}{0.167 \text{ K/s}} \times \frac{1}{9.61 \times 10^{-6} \text{ mol H}_2\text{O}} = -29.3 \text{ kJ/mol} \]

The molar ratio of water to the niobate compound in the solid was calculated as follows:

Moles of restacked niobate solid after dehydration = 0.000017 mol

\[ \frac{\text{Moles of H}_2\text{O}}{\text{Moles of dehydrated niobate}} = \frac{9.61 \times 10^{-6} \text{ mol H}_2\text{O}}{0.000017 \text{ mol niobate}} = 0.565 \sim 0.5 \text{ mol H}_2\text{O/mol niobate} \]
Figure C1: UV-vis spectrum of dimeric Rhodium (II) complex in TBAOH solution.
Figure C2: $^1$H NMR spectrum of Rh$^{II}$ dimer complex in TBA$^+$OH$^-$ solution.
**Figure C3:** Crystal structure of Rh(II) dimer complex.

**Table C1:** Crystal data and structure refinement for Rh(II) dimer.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Empirical formula</td>
<td>C$<em>{28}$H$</em>{34}$N$<em>4$O$</em>{11}$Rh$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>808.41</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>298(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
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<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>9.6725(7)</td>
</tr>
<tr>
<td>b/Å</td>
<td>11.7545(9)</td>
</tr>
<tr>
<td>c/Å</td>
<td>15.4619(12)</td>
</tr>
<tr>
<td>α/°</td>
<td>68.7540(10)</td>
</tr>
<tr>
<td>β/°</td>
<td>86.0520(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>68.8980(10)</td>
</tr>
<tr>
<td>Volume/Å$^3$</td>
<td>1524.7(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ$_{calc}$/g/cm$^3$</td>
<td>1.761</td>
</tr>
<tr>
<td>μ/mm$^1$</td>
<td>1.149</td>
</tr>
<tr>
<td>F(000)</td>
<td>816.0</td>
</tr>
<tr>
<td>Crystal size/mm$^3$</td>
<td>0.23 × 0.07 × 0.04</td>
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<tr>
<td>Radiation</td>
<td>MoKα ($λ = 0.71073$)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>2.84 to 56.56</td>
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<tr>
<td></td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11 ≤ h ≤ 12, -15 ≤ k ≤ 15, -19 ≤ l ≤ 20</td>
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<tr>
<td>Reflections collected</td>
<td>13832</td>
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<tr>
<td>Independent reflections</td>
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<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.020</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0362, wR₂ = 0.0909</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0441, wR₂ = 0.0963</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.96/-0.42</td>
</tr>
</tbody>
</table>
Figure C4: (a) UV-vis spectrum of Rh\textsuperscript{II} dimer complex on a layered niobate support and the supernatant Rh\textsuperscript{II} dimer solution. (b) XPS on Rh\textsuperscript{II} dimer complex and Rh\textsuperscript{II} dimer/Titanate support.
Figure C5: (A) HAADF-STEM image, (B)-(D) EDS maps, and (E) EDS spectrum of Ir\textsuperscript{IV} Dimer/ HCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} nanosheets.
Figure C6: (a) HAADF-STEM image and (b) line intensity profile of Ir(IV) dimer supported on HCa$_2$Nb$_3$O$_{10}$ nanosheets.
Figure C7: Optimized $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ structure with computationally obtained lattice constants. Experimental lattice constants are shown in the parentheses.
Figure C8: DFT optimized structures of layered titanate support. Energy values are in eV.
EXAFS Fitting Details

EXAFS data were processed using Athena software by aligning each data set against the reference Rh foil and merging the triplicate scans to get an averaged scan. The averaged scan was background subtracted and the pre-edge and post-edge regions were normalized. In Artemis, the Fourier transformed data for each temperature scan was fitted using a $k^2$-weighting using a $k$-space range of $2.0 \text{ Å}^{-1} < k < 9.0 \text{ Å}^{-1}$ and an $R$-space range of $1.0 \text{ Å} < R < 2.8 \text{ Å}$. The backscattering amplitude was set to 1.0 throughout the refinement. A Debye-Waller factor of 0.003 was used as the starting point to fit the Rh—N, Rh—O and Rh—Rh scattering paths. For the high temperature measurements, the backscattering amplitude was set to the value obtained from the data collected from the unsupported rhodium dimer and the coordination number was varied.

Figure C9: EXAFS Fitting of Rh$^{11}$ Dimer ($S_0^2 = 1$).
Figure C10: Attempts to fit Rh\textsuperscript{II} Dimer on H_{0.13}Ti_{0.87}O\textsubscript{2} support with DFT-optimized structure models for dual-site binding modes.
**Figure C11:** Temperature-dependent FT-EXAFS data under reducing conditions to track the Rh-Rh coordination number.

**Table C2:** Coordination number and Rh-Rh bond lengths on H_{0.13}Ti_{0.87}O_2 nanosheets from EXAFS analysis.

<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>CN</th>
<th>σ²</th>
<th>Rh—Rh (Å)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.21 ± 0.78</td>
<td>0.0054 ± 0.0065</td>
<td>2.6432</td>
<td>0.0305</td>
</tr>
<tr>
<td>200</td>
<td>4.27 ± 1.10</td>
<td>0.0041 ± 0.0021</td>
<td>2.6940</td>
<td>0.0132</td>
</tr>
<tr>
<td>300</td>
<td>4.94 ± 1.31</td>
<td>0.0039 ± 0.0022</td>
<td>2.6831</td>
<td>0.0152</td>
</tr>
<tr>
<td>400</td>
<td>5.39 ± 2.95</td>
<td>0.0039 ± 0.0027</td>
<td>2.6759</td>
<td>0.0171</td>
</tr>
</tbody>
</table>
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Ph.D. in Chemistry, The Pennsylvania State University, University Park, PA 2020
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Publications:

Presentations:
1. “Stabilization of Dinuclear Rhodium Clusters on a Layered Titanate Support” MRS Fall Meeting, Boston, MA. December 2019. (Talk)
3. “Competing polar and anti-polar structural phases in n=2 RP layered perovskite Li$_2$SrNb$_2$O$_7$” Penn State Materials Research Science and Engineering Center Seminar. November 2018. (Talk)
4. “Layered oxide nanosheets as model supports for investigating nanoparticle-support interactions by isothermal titration calorimetry and UHV calorimetry” 252nd ACS National Meeting, Philadelphia, PA. August 2016. (Poster)